# Drainage basin nutrient inputs and eutrophication: an integrated approach

Edited by — Paul Wassmann and Kalle Olli
—*—
Norwegian College of Fishery Sciences,
University of Tromsø, Tromsø, Norway
—*—
Tartu University, Department of Botany and Ecology,
Lai st. 40, 51005, Tartu, Estonia

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# Contents

# Integrated approaches to drainage basin nutrient inputs and coastal eutrophication: an introduction

Paul Wassmann
Norwegian College of Fishery Science
University of Tromsø
N-9037 Tromsø, NORWAY
paulw@nfh.uit.no

Kalle Olli
Institute of Botany and Ecology
Tartu University
Lai 40, 51005, Tartu
Estonia
kalle.olli@ut.ee

## Ingress

Eutrophication is an increase in primary production due to increased nutrient supply and its consequences. In its widest sense *eutrophication means any increase of nutrient availability that increases primary production*. Frequently, however, eutrophication is understood exclusively as the consequence of nutrient input by anthropogenic activities. The primary consequence of eutrophication in aquatic environments is an enhancement of algal productivity and accumulation of algal biomass. Secondary consequences are changes in community structure of plankton and benthos.

Man-induced eutrophication or changes in biodiversity are nothing new: they are a well-known consequence of human culture. Eutrophication phenomena accompanied all human settlements. Even in the early days of mankind human activities resulted in ecosystem changes. Several large animals such as the mammoth survived the glacial periods, but not the last one. It has been suggested that Neolithic hunters decimated this species to extinction. Similar suggestions have also been made regarding other large mammals that did not continue to exist after the last glacial. The main sewage canal in the city of Rome, 'cloaca', has given rise to a number of expression regarding sewage pathways in numerous languages. Since classical and medieval times there have been 'clean-ups' of unsanitary, plague-ridden cities. Eutrophication is thus the oldest environmental problem of human civilization and not a recent phenomenon. However, with the significant increase of human population over recent decades, eutrophication has developed from a more or less local to a global issue. Due to changes in human living conditions and the declining number of people employed in agriculture, the population in the coastal zone increases steadily. The nutrient concentration increases continually from small streams over rivers and larger lakes to the estuaries. The consequences of this, such as discoloured waters, 'rotten' bottom water, odour and reduced fishing yields are obvious to even a casual observer. The combined effect of increasing human population and movement to the coastal zone, the environmental pressure on rivers, estuaries and shelf regions results in an ever-increasing pressure on the entire coastal zone (Figure 1). Consequently, eutrophication turns into an escalating global phenomenon as long as the human population increases. *Homo sapiens* has thus a vital impact on nature that is part of its culture. As a consequence of that we have to distinguish between natural and cultural eutrophication. In most of this text the term eutrophication stands for cultural eutrophication.

## Causes of eutrophication

In general, the nutrient elements limiting the primary production in freshwater is phosphorus (mainly phosphate) while that in the marine environments is nitrogen (mainly nitrate). In the marine environment, exceptions have been reported to this general rule. Thus the eastern Mediterranean Sea and many eutrophied estuaries are P rather than N limited, while the equatorial Pacific and extensive regions around Antarctica appear to be Fe-limited. What are the sources of nutrients to aquatic ecosystems? There is nutrient supply from

- agriculture and husbandry,
- aquaculture and factories,
- sewage from towns, river run-off and erosion,
- atmospheric deposition,
- nitrogen fixation.

28% of the annual N fixation of the global biosphere is caused by nitrogen fertilizer production, which is energetically expensive and largely based on fossil fuel consumption. A three-fold increase in N utilization by agriculture in Western Europe and USA has been recorded between 1950 and 1970 on agricultural land that actually declines because increased efficiency or over-exploitation (Figure 2). Animal waste from intensive husbandry is of particular significance for nutrient point sources: considerable amounts are directly supplied to freshwater and fields. There are also significant losses by $NH_3$ emission and denitrification on fields, rivers or shallow estuaries, connecting the agricultural lands directly to the atmosphere. Agricultural run-off has given rise to significant eutrophication in most estuaries, but also in entire coastal seas such as the southern North Sea, Baltic Sea, Kattegat, northern Adriatic Sea, Chesapeake Bay and Seto Inland Sea in Japan.

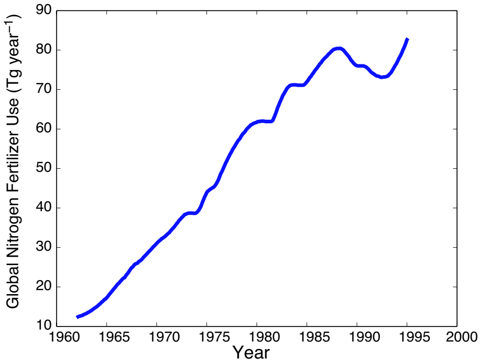

Figure 2: Annual global nitrogen fertilizer consumption for 1960–1995 (1 Tg = $10^{12}$ g; data from FAO 1999). The rate of increase was relatively steady until the late 1980s, when the collapse of the Soviet Union reduced fertilizer use in Russia and former Soviet republics. Fertilizer use is growing again, driven in large part by use in China (modified from Matson et al. 1997 and Anonymous 2000).

Aquaculture techniques are applied to restricted areas such as straights, fjords and rias where it, in the worst case, may induce anoxia (if hydrodynamic energy supply is insufficient). C and N supply is normally regulated by environmental control, but can be detrimental in some areas. It has been reported that accumulation rates of fat- and N-rich food and faeces at the bottom below caged fish production sites could make up to 10 cm per month! As much as 30 and 40% of the annual discharge of P and N, respectively, is caused by aquaculture in some fjords. Unless an entire region is used for aquaculture, it has 'local' consequences for both plankton and benthos. However, large factories of the food industry can discharge significant amount of dissolved and particulate organic matter as well as nutrients into the recipient that can represent important point sources.

Close to cities and dense populated areas sewage is of utmost significance, but compared to run-off from agricultural drainage basins, point sources are of less significance; see also Chapter 2. The emphasis given to sewage treatment in many re-

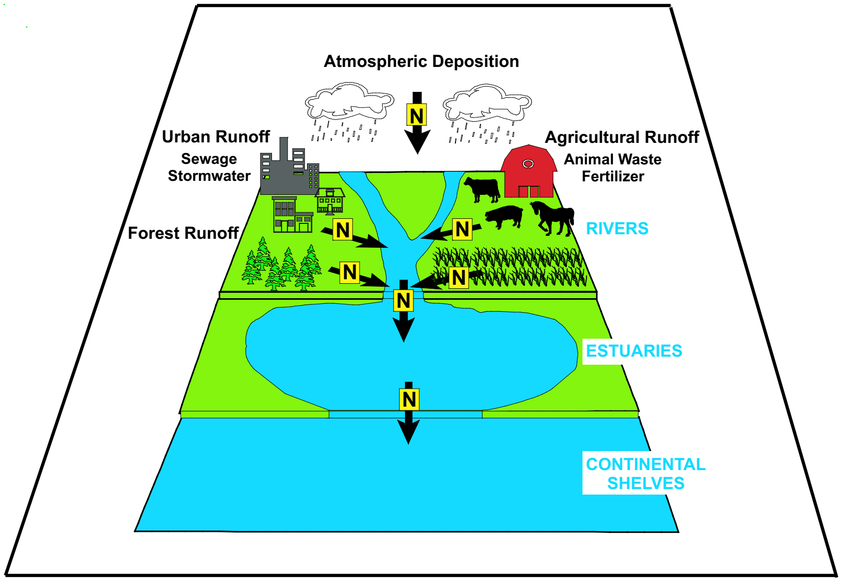

Figure 1: N and P associated with the production of food and energy enter coastal ecosystems (S. Seitzinger, pers. com.)

gions is in contrast to the inefficient and at time completely lacking emphasis on the largest nutrient source for aquatic recipients, i.e. the agriculture. Sewage discharge has 'local' consequences, although local could mean entire estuaries, river mouths and fjords. The frequent removal of P by sewage plants and the decline of utilization of P fertilizers (in contradiction to N, Figure 3) results often in an excess supply of N. Consequently, marine recipients are forced into P rather than N limitation. Far more emphasis has been given to sewage treatment than manipulations of effluents from agriculture, and this can be partly explained by the relative simplicity of removing nutrients from point sources.

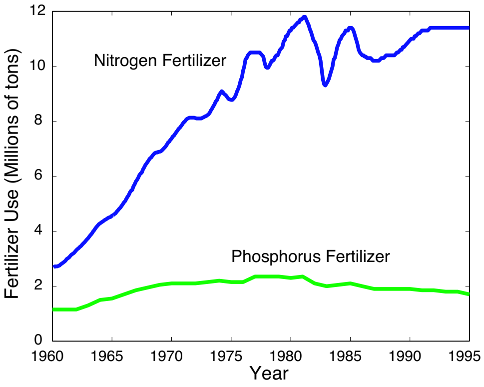

Figure 3: U.S. commercial fertilizer use (modified from Evans et al. 1996 and Anonymous 2000).

River-run off has changed significantly over the last 200 years in many region of the world. Large-scale manipulation of lower reaches of river has resulted in greater river speeds. The residence times of water in the Rhine river water shed was far greater before 1850 when it was so shallow and meandering south of the town of Strasbourg that one could walk through it even during flood times! Extensive wetlands have been removed in favour of shipping and straightforward navigation. Both agriculture and logging result in increased erosion as trees, bushes and vegetation is reduced. Removal of wetlands for agricultural purposes results in decreasing self-purification as denitrification decreases. As a consequence, we experience an increased contribution of particulate matter and nutrients to estuaries. Due to various practices, N supply to marine waters does still increase in Western Europe, while P supply decreases (Figure 3). As a consequence P limitation in eutrophicated coastal regions increases.

Lately, more focus has been given to the role of the atmosphere affecting the availability of nutrients in aquatic ecosystems (see Chapter 1). Generally, nutrient supply from the atmosphere is in the form of N. Only in case dust is deposited particulate P is deposited atmospherically. Atmospheric deposition of nutrients is partly due to fossil energy application, leading to the emission of $NO_x$ gasses to the atmosphere. Here these gasses are transformed to nutrients such as $NO_3$ that can be deposited as wet or dry deposition. However, much of the atmospheric nutrient deposition comes from the emission of $NH_4$ by intensive husbandry and meat production. The annual atmospheric supply of N to open Skagerrak is more than 30% of N the budget! It is relatively lower in the winter months when run-off from land is prominent, but can be the dominating N source during summer. Atmospheric N deposition is closely reflected to source regions, the movements of air masses and the low-pressure pathways. Atmospheric deposition of N gives rise to a wide spread eutrophication of freshwater and terrestrial environments as well as the sea. Eutrophication due to use of fossil energy depends on emission and precipitation pattern.

During nutrient limiting conditions N fixation can be an important source of N in fresh water and brackish water bodies such as the Baltic Sea. The significance of N fixation is still a matter of discussion in marine environments. However, the global $N_2$ cycle has changed greatly due to the production of fertilizers as human $N_2$ fixation is now in the same order of magnitude than the calculated global fixation.

## State of the art of research regarding river and drainage basin pollution of nutrients

The drainage basin with all ongoing human activities (such as waste production, leaching of agricultural chemicals etc.) and the coastal waters into which they drain, constitute large-scale ecosystems, that has to be protected from deterioration. Interactions between land activities, fresh water and coastal seas receive increasingly attention. International conferences, (e.g. the 'Stockholm Water Symposia' in 1997 and the 'Man and River System' conference in Paris in 1998) have been organised within the scope of these issues. The understanding of the dynamics and causes of the large-scale and long-term changes of riverine loads has been regarded as particularly important. The problems of river basin pollution of nutrients that have been addressed include:

- observed water quality changes and their relation to anthropogenic and natural variability (i.e. trend analysis)
- links between land-use, point sources and physiographic factors
- quantification of nutrient retention in rivers and lakes by empirical relationships
- modelling of biogeochemical processes
- assessment of future scenarios.

Recent research indicates that the main uncertainty is the lack of knowledge of nutrient transformation processes between the root-zone and the rivers (see Chapter 3). Attempts to integrate detailed process-oriented models with more simple large-scale approaches are in progress in Scandinavia. Another interesting topic is related to large-scale experiments in Eastern Europe with its dramatic decline in industrial and agricultural production, which has created an unique opportunity to study the river response on such changes (e.g. the Mantra-East project http://www.mantraeast.org; Chapter 3).

## State of the art of research regarding atmospheric deposition of nutrients

The processes governing the atmospheric transport, transformation and deposition of nutrients to coastal ecosystems is an important area of research within the atmospheric, marine and terrestrial sciences (see also Chapter 1). The combustion of fossil fuels and the emissions from agriculture into the atmosphere constitutes a highly significant and growing percentage of total N-loading into estuarine and coastal waters (Duce, 1986). In fact, rainfall associated deposition events are known to stimulate primary production in N-limited coastal and offshore waters (Paerl, 1995). Estimates of atmospheric inputs to the Baltic Sea (HELCOM, 1996), based on studies of the Group of Experts on Airborne Pollution of the Baltic Sea Area (EGAP), constitutes a considerable fraction of the total nutrient load, although much uncertainty surrounds these estimates (Asman & al., 1995). However, only little effort has been put into experimental investigations of the atmospheric load of nitrogen in the coastal zone.

The processes controlling the atmospheric deposition loads are not well understood. For the dry deposition of the gaseous species the horizontal gradients are of major importance. This is in particular true for $NH_3$, which can also be emitted from the water since, unlike $HNO_3$, it does not fully dissociate. Emission and deposition of $NH_3$ is influenced by chemical and biological gradients in the water and fluxes of both $HNO_3$ and $NH_3$ are influenced by the physical gradients caused by change in the wave field. Also horizontal changes due to atmospheric internal boundary layers influence the deposition of both gases. The nitrogen gases $HNO_3$ and $NH_3$ are both chemically reactive and soluble. Therefore it has been hypothesised that uptake of the gases by sea spray can influence the deposition of the gases. This has been tested in a series of field experiments and the results supported the hypothesis (Geernaert *et al.*, 1998).

In order to develop models, which can calculate the nitrogen load to the coastal waters with sufficiently high accuracy (time resolution equal to or smaller than a week and grid size capturing the horizontal inhomogeneity) the air-sea gas fluxes dependencies of the horizontal and vertical inhomogeneity have to be well known. This knowledge is rather limited to non-existent in Scandinavia for the time being.

## State of the art of research regarding marine eutrophication

The response of coastal ecosystems to nutrient loading is a central theme in estuarine research (Nixon & al., 1996), especially the role of nutrients (N, P, and Si) in limiting the growth of phytoplankton. Substantial changes in nutrient loading have occurred, especially during the last century. Large increases in nutrient loading associated with increases in population growth, changes in agricultural practices including the increased use of inorganic fertilisers, changes in collection and treatment of sewage, and increases in nitrate deposition from the atmosphere have occurred. In the last decade, major reductions in P loading through better sewage treatment, with a more or less maintained N loading have occurred. These changes in nutrient loadings and ratios have affected the productivity of coastal and marine waters and have changed the potential limiting nutrients in governing system production (Conley, 1999). These questions are also important in Scandinavia where the assessment of nutrient loadings and their effects on the Baltic Sea ecosystem are co-ordinated at high international levels (HELCOM, 1996). Scientists from the Nordic countries are at the forefront of determining the role of nutrient loading in governing ecosystem functioning (e.g. Kivi *et al.*, 1993; Borum, 1996; Elmgren & Larsson, 1997).

## Scope of the present text

This electronic book contains some of the information gathered by the Nordic network for research and education ‘Integrated approaches to drainage basin nutrient inputs and coastal eutrophication’. This network attempted to co-ordinate the relevant, but scattered expertise regarding nutrient inputs and eutrophication in the Nordic and some non-Nordic countries. It was financed by the Nordic Academy of Advanced education (NorFA; http://www.norfa.no). As a continuation of the education activities during the time of the net-

What are the goals of this book? The present text attempts to improve the understanding of traditionally separated fields of science, all contributing and determining the eutrophication of rivers and coastal ecosystems: (a) atmospheric deposition, (b) agriculture and land use, (c) point source emissions, i.e. sewage discharge from urban areas and industry (Figure 4). Despite the fact that points a–c determine the state of aquatic ecosystems and have been intensively investigated *per se*, no strong endeavours have been undertaken to couple these processes in an integrated manner. Much of the details are present, but the grand view is missing. This text attempts to make a contribution to achieve this ambitious, but never-the-less crucial goal: to view the eutrophication of streams and coastal areas and human activities in the catchment areas and beyond (atmospheric deposition) in a balanced and concurrent manner.

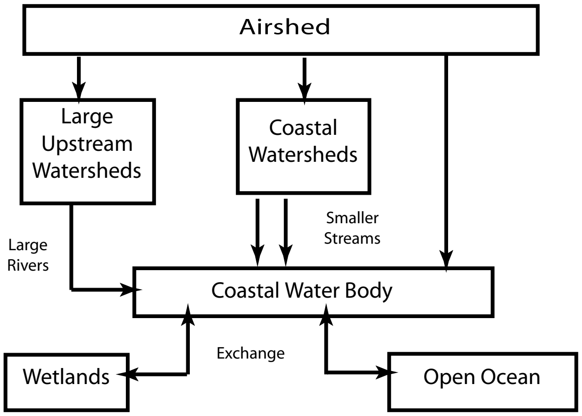

Figure 4: Schematic drawing showing general sources of nutrients and main routes of transport to coastal waters. Notice how strongly coastal waters are exposed for increases of nutrient discharge, integrating effects from the entire watershed, the atmosphere and the open ocean. From Anonymous 2000.

work, the senior scientists made an effort to make the networks joint experience and expertise available to students, young scientists, administrative personnel and interested individuals through this electronic book.

Genuine education is basically dependent on the quality of the research it is based upon and by and large most of the evidence presented here derives from recent and ongoing research projects. We believe that the basis for integrated approaches to drainage basin nutrient inputs and coastal eutrophication is still in its infancy and that far more emphasis has to be given to basic, integrated research. This research will become crucial for a forthcoming generation of scientist dealing with nutrient discharge and eutrophication. The complex questions regarding drainage basin nutrient inputs and coastal eutrophication cannot be adequately addressed at agricultural high schools, freshwater institutes, oceanographic faculties or organizations that deal with atmospheric chemistry. The problems of drainage basin nutrient inputs and coastal eutrophication are entangled and can only be tackled in concerted action. A forthcoming generation of scientists dealing with these questions need fora where they can develop their scientific specialities in an integrated context. Our educational structures separate the scientists that have to co-operate in the future to solve immanent environmental questions. This text is thus also meant to serve as a base for improved education by pointing at relevant sides of drainage basin nutrient inputs and coastal eutrophication that are not dealt with at agricultural high schools, freshwater institutes, oceanographic faculties or organizations that deal with atmospheric chemistry.

The network aimed at an improvement of the educational standard in the Nordic countries and after its completion we hope that this freely available text will continue to serve this purpose. The network became aware about the difficulty to obtain appropriate education in integrated eutrophication as the various research fields that contribute to a holistic view on eutrophication are spread over several unconnected institutions, often even over several countries. Here we attempt to summarise the expertise of the network and make it available to institutions and interested groups of scientists inside the Nordic countries and beyond. We make the Nordic expertise more comprehensive with contributions from scientists from other countries.

The text follows basically the schematic drawing in Figure 4 and is separated into 7 different parts. First, we start with an atmospheric section (Part I) that deals in detail with the transport, transformation and deposition of nutrients; (Chapter 1). A description and evaluation of the most important technique to assess nutrient deposition. i.e. numerical modelling, is a cornerstone of Part I. A run-off section (Part II) follows focusing on the impact of agriculture on freshwater run-off and water quality (Chapter 2), river supply to lakes and the coastal zone (Chapter 3), and the supply of nutrients through ground waters (Chapter 4). Part II is finalized through an extensive manuscript focussing upon nutrient supply in the Seine River drainage basin (Chapter 5). Here the linkages between human activity, water quality and consequences for nutrient discharge into the coastal zone are the focus. Chapter 5 is also a good example how numerical models can be applied in assessment of drainage basin nutrient dynamics.

After this we switch over to eutrophication processes in pelagic ecosystems (Part III) and deal with eutrophication effects on phytoplankton (Chapter 6), nutrient cycling and vertical export (Chapter 9), harmful algae (Chapter 7) and the interaction of natural perturbations and human activities on coastal ecosystems (Chapter 8). Both harmful algae chapter (Chapter 7) and human activities and natural perturbations chapter (Chapter 8) include important information about the effect of eutrophication of recipients that also could be presented in case studies (Part VI). Part III is finalized by by an evaluation of the dose-response relationship and eutrophication in European waters (Chapter 10). The chapter contains important information in the context of Part V. Part IV is dedicated the benthic environment where the basic features of marine eutrophication, as reflected by benthic nutrient release (Chapter 12), benthic metabolic pathways (Chapter 11) and benthic-pelagic coupling (Chapter 13), are presented.

Part V is dedicated to the background of mariculture (Chapter 15) and its effect on the evironments, cultural eutrophication (Chapter 17), ecological quality assessment (Chapter 16), and the cultural eutrophication (Chapter 17). Chapter 17 an attempt is made to summarise previous chapters and to put our knowledge of drainage basin nutrient inputs and eutrophication into an overbranching perspective. We finish this text by presenting a number of case studies (Part VI). The number of case studies is still limited. In order to wide the scope of the text, we hope that we can expand this section in years to come to comprise a majority of eutrophicated, coastal regions in Europe and beyond. Also an overview over eutrophication related web sites and an key-term index will be presented at the end.

Although a balanced presentation of the various aspects of drainage basin nutrient inputs and eutrophication has been the main ambition, this text is not complete. It is open for changes, amendments and additional contributions. The editors welcome comments and suggestions for improvements. Also, additional chapters are welcome (e.g. in the case study section or for an entirely missing section on the socio-economic aspects of eutrophication).

The text is kept in an electronic format, made available on a server at the University of Tartu in Estonia www.ut.ee/˜olli/eutr. Each author is responsible for the particular text and the figures submitted to the web site. The editors have streamlined the text, formatted the text and compiled it. Needles to say that the editors take full responsibility for for editorial mistakes.

## Acknowledgements

The editors thank NorFA for the financial support over 5 years that made it possible to gather the various Nordic experts in drainage basin nutrient inputs and coastal eutrophication annually around one table. To the best of our knowledge, these traditionally separated fields of science were gathered for the first time in the Nordic countries. Exiting views developed that changed our opinions on the subject. Everyones perspective on eutrophication changed for good during this process. The editors wish to thank the Nordic network participants for their contributions and the steering committee of the network for enthusiasm, ideas and good leadership. In particular we wish to thank the many compassionate foreign colleagues for their contributions which significantly balanced and improved this text.

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# Part I

# Atmospheric block

# Chapter 1

# Atmospheric deposition of nutrients

Lise Marie Frohn and Ole Hertel
Ministry of the Environment
National Environmental Research Institute
Department of Atmospheric Environment
Frederiksborgvej 399
DK-4000 Roskilde, Denmark
http://www.dmu.dk

## 1.1 Introduction

Deposition is the ultimate path by which trace gases and particles are removed from the atmosphere. Among these deposited pollutants are compounds which act as nutrients in marine as well as terrestrial ecosystems (or environments). In order to quantify the amount of nutrients deposited in this way it is necessary to understand the governing processes taking place prior to the deposition as well as the deposition process itself. To promote this understanding it is necessary to investigate measurements as well as modelling of atmospheric deposition.

In this chapter the main pathway of nutrients through the atmosphere is described. It ranges from emissions of chemical components over wind-driven transport and chemical transformation in the air to deposition to the surface. This pathway is described in Sections 1.2 to 1.5. How the deposition is quantified is covered in Sections 1.6 and 1.7.

## 1.2 Sources

Nutrients deposited from the atmosphere include phosphorus and nitrogen. The atmospheric input of phosphorus to the marine environment is insignificant compared to the other sources of this nutrient. Input of nitrogen from the atmosphere is, however, potentially significant. An example taken from an international research project shows that on yearly average approximately 24% of the external nitrogen input to the Kattegat Sea (located between Denmark and Sweden) is from the atmosphere (Spokes *et al.*, 2004). Furthermore if only the summer period is considered, the contribution from the atmosphere can be as high as 40% on average over the entire sea area. This indicates that the atmospheric load may be even higher in areas close to nitrogen sources and thus can contribute a substantial amount of external nitrogen into e.g. coastal systems.

The most important groups of atmospheric nitrogen compounds in terms of nutrient deposition are

- The $NH_x$ group: gaseous ammonia ($NH_3$) and ammonium in particles ($NH_4^+$ aerosol).

- The $NO_y$ group: the gaseous compounds nitric oxide (NO), nitrogen dioxide ($NO_2$), dinitrogen pentoxide ($N_2O_5$), peroxy nitric acid ($HNO_4$), nitric acid ($HNO_3$) and nitrous acid ($HNO_2$) as well as peroxy acetyl nitrate (PAN), nitrate in particles ($NO_3^-$ aerosol) and nitrate radicals.

- Organic nitrogen compounds, e.g. organic nitrate.

The sum of NO and $NO_2$ is denoted $NO_x$ and the sources of all the atmospheric nitrogen compounds are the emissions of $NH_3$ and $NO_x$. $NH_3$ is primarily emitted from processes related to agriculture such as livestock production (including the spread of manure) and fertilizer application and production. $NH_3$ emissions are therefore quite high in countries with widespread intense agricultural activities. An example of the $NH_3$ emission density for the European area is presented in Figure 1.1.

The high emission density in Denmark, The Netherlands and Belgium is caused, in part, by the high density of pig farms in these countries. There is a strong seasonal variation in $NH_3$ emissions, typically related to the spread of manure and fertilizer on fields. The rate of emission is in general higher during the day than during the night, due to the typically higher temperature and wind speed during daytime.

$NO_x$ is primarily emitted from combustion processes involving fossil fuels. The dominating component in the release is NO (estimated to contribute around 90–95% of the total emission). The combustion processes include power plants, industrial furnaces as well as road traffic. An example of the $NO_x$ emission density for the European area is presented in Figure 1.2.

The emission density is highest in densely populated areas and the emissions over sea areas arise from ship traffic and oil rigs. Highest emission rate over land is obtained during rush hours, and for the emissions related to heating and power

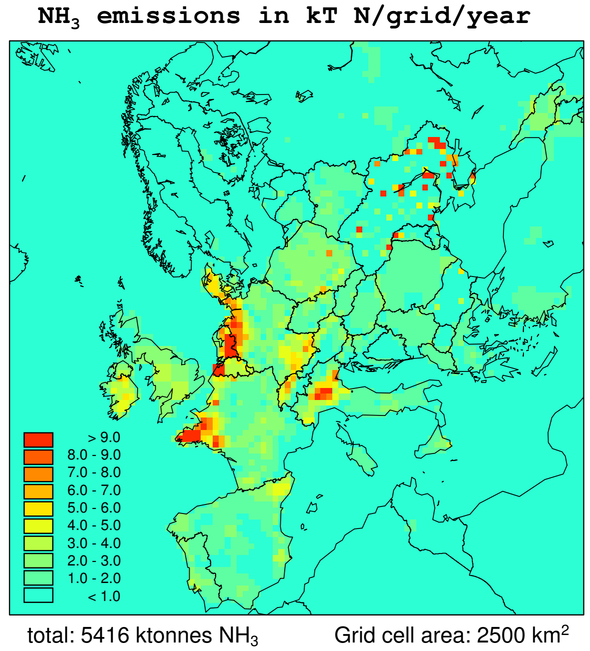

Figure 1.1: The emission density of ammonia for the European area. The emission inventory is based on data obtained from the European Monitoring and Evaluation Programme (EMEP)

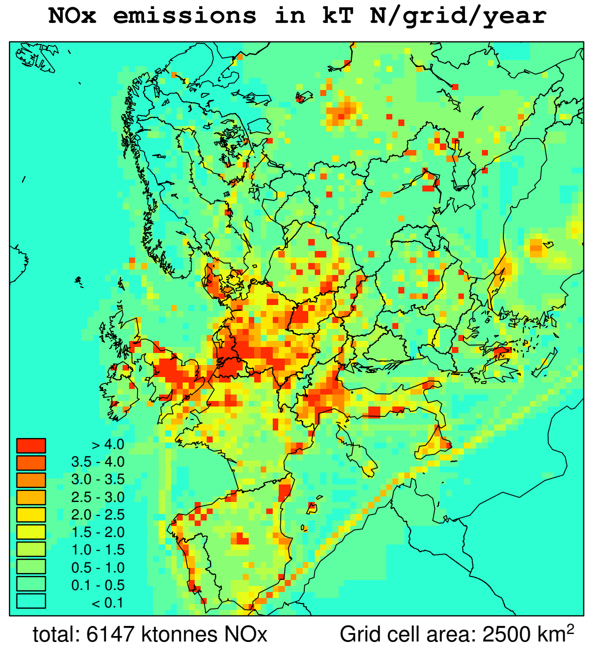

Figure 1.2: The emission density of nitrogen oxides for the European area. The emission inventory is based on data obtained from the European Monitoring and Evaluation Programme (EMEP)

production there is also a seasonal variation with higher emission rates during wintertime.

There are several institutions that gather emission data and transform them into emission inventories describing the spatial distribution of emissions over large areas. Concerning $NH_3$ and $NO_x$ important data providers are:

- The Global Emissions Inventory Activity (GEIA, Graedel *et al.*, 1993). This inventory covers the globe with a resolution of 1°and is available at http://geiacenter.org
- The Emission Database for Global Atmospheric Research (EDGAR, Oliver *et al.*, 1999). This inventory also covers the globe with a resolution of 1°and is available at http://arch.rivm.nl
- The United Nations Economic Commission for Europe/Co-operative programme for monitoring and evaluation of long range transmission of air pollutants in Europe (UNECE/EMEP, Vestreng, 2001). This inventory covers the majority of the European area with a resolution of 50 km ×50 km and is available at http://www.emep.int/index_data.html.
- The Generation and Evaluation of Emission data (GENEMIS, Schwarz *et al.*, 2000; Wickert *et al.*, 2001). This inventory covers a large part of the European area with a resolution of 16.67 km ×16.67 km. It is developed at the University of Stuttgart.

If the emitted nitrogen compounds were to deposit at the location where they are emitted, it would be easy to determine which of the ecosystems are likely to receive high amounts of nutrients from the atmosphere. Unfortunately the processes are more complex than this. $NH_3$ and $NO_x$ transforms into other chemical species that have very long lifetimes in the atmosphere and therefore can be transported across rather long distances, in some cases up to several thousand kilometers.

## 1.3 Transport

The driving force of the atmosphere described by the meteorology is responsible for the transport of nutrients (and pollutants) in the troposphere. Pressure and temperature gradients make the air masses move and the result is that the nutrients (in gaseous and particulate form) are moved along with the air.

The region of the atmosphere governing transport and dispersion of the majority of the pollutants is the planetary boundary layer. This layer is defined as the layer where the wind structure is influenced by the surface of the Earth.

### 1.3.1 Turbulence

The wind transports the air masses around, however, the wind is, through the mechanical formation of turbulence, also responsible for a significant part of the mixing of the pollutants in the air.

There are two types of turbulence; mechanical and convective. Mechanical turbulence, characterised by small eddies close to the surface, is thus a result of the wind dragging over the surface. Smooth surfaces like fields of grass or calm water surfaces produce little mechanical turbulence, whereas rough surfaces like forests or buildings can result in the production of large amounts of mechanical turbulence. Convective turbulence, characterised by large eddies with a long lifetime, is the result of the sun heating the surface, which then in turn heats the air mass just above the surface. This heated air mass then rises because of its temperature being higher than the temperature of the surrounding air — so-called bouyancy — and the result is turbulence.

Several other meteorological factors may affect the concentration of pollutants in the air:

- Direction and speed of the horizontal wind, generated by the geostrophic wind at the top of the planetary boundary layer and affected by terrain friction forces, and local meteorological winds (land-sea breezes, mountain-valley winds and city-countryside circulation.

- The flow of air masses around obstacles, e.g. buildings.

- Atmospheric stability which affects the dilution of the pollutants.

- Height above the surface.

- The strength of the temperature inversion, which affects the height of the planetary boundary layer.

- Vertical atmospheric movements due to high and low pressure systems or complex terrain effects.

- Internal boundary layers which are formed within the planetary boundary layer due to changes in surface roughness.

### 1.3.2 Atmospheric stability

The atmospheric conditions may be divided into three classes in terms of stability: neutral, stable and unstable conditions. These three categories are characterised by the following:

- *Neutral* conditions where the temperature is homogeneous throughout the boundary layer. This situation typically occurs in the transition from day to night and is characterised by strong winds and clouds and large amounts of mechanical turbulence.

- *Stable* conditions where the temperature is lowest close to the surface and increases towards the top of the boundary layer. This situation typically occurs during nighttime or in winter situations and is characterised by little turbulence and a strong stratification of the planetary boundary layer which is quite shallow.

- *Unstable* conditions where the temperature of the air closest to the surface is higher than the temperature of the air above it. This situation typically occurs during daytime at summer when the sun is shining and it is characterised by large amounts of convective turbulence usually resulting in the formation of cumulus clouds during the day.

Examples of the behaviour of a plume from a chimney under stable and unstable conditions are shown in Figure 1.3.

### 1.3.3 The Planetary Boundary Layer

The height of the planetary boundary layer varies with the atmospheric stability and this is important for the concentrations of pollutants in the air because the majority of the pollutant mass typically is confined within this layer. During nighttime when conditions in most cases are stable, the planetary boundary layer is shallow, down to 20–50 meters and the surface concentration of pollutants can therefore be quite high, especially close to emission sources that are active during the night. Under unstable conditions the planetary boundary layer can be as high as 2 kilometers and pollutants are in this case distributed in the air column mainly by convective turbulence. In the vicinity of the top of the boundary layer, the horizontal winds are typically stronger and the pollutants that end up at these higher levels may be transported far away from the emission sources. In neutral conditions emitted pollutants are quickly mixed in the air by mechanical turbulence and the surface concentration is not particularly high. During neutral conditions the strong horizontal wind speeds can transport pollutants across large distances.

### 1.3.4 Atmospheric trajectories

It is important to realise that pollutants emitted at the surface at one point may travel to a completely different location before they are deposited. A typical method to study the movement of air masses is to calculate so-called trajectories based on the wind speed and direction. Trajectories can be calculated forward as well as backward in time. Forward trajectories are typically used in connection with the calculation of pollutant distribution from accidental releases where the emission source is single and strong, whereas

Figure 1.3: Left: The behaviour of a chimney plume under stable atmospheric conditions (nighttime), characterised by little turbulence. Right: Same type of chimney plume, under unstable (daytime) atmospheric conditions, characterised by a high amount of conventive turbulence. (The pictures have kindly been provided by Dr. Torben Mikkelsen, Risø National Laboratory and Dr. Thomas Ellermann, National Environmental Research Institute)

the backward trajectories are typically used for modelling air pollution from multiple distributed emission sources.

The procedure for calculating backward trajectories is to choose a starting point and then calculate back in time according to the direction and speed of the wind. In order to study the sensitivity of the trajectories to the choice of starting point several trajectories can be calculated with pertubed starting points. An example of a such a sensitivity investigation is given in Figure 1.4. In the left and center part of the figures it is seen that even though the wind may come from one direction at the surface, this does not necessarily mean that it is the direction the air mass is coming from originally. In the right hand part of the figure is given an example where 150 km difference in starting points for the trajectories results in a completely different origin of the air mass.

Another method for testing the accuracy of calculated trajectories is to release large numbers of balloons with tracking equipment and then evaluate the calculated trajectories with the observations. An example of such an evaluation can be found in Stohl (1998): a review of trajectory application.

## 1.4 Transformation

All chemical components which constitute nutrients in the ecosystem are reactive in one way or the other in the atmosphere. The chemistry is taking place on very different time scales and is highly complex. It is crucial to include the most imporant chemical transformations in the pathway description if the contributions of nutrients are to be described as accurately as possible.

In the chemistry of air pollution one distinguishes between *primary* and *secondary* air pollutants. Roughly it can be said that primary pollutants are directly emitted from the sources and in the air they transform by chemical reactions into secondary pollutants which are subsequently deposited. In the case of nitrogen, the primary pollutants are $NH_3$, NO and $NO_2$ and the secondary pollutants are $NO_2$ and all the other nitrogen containing components that are produced from the primary pollutants in the air. Most important reaction products for the nutrient deposition are components containing nitrate ($NO_3^-$) or ammonium ($NH_4^+$) in particulate phase.

In Figure 1.5 the pathways for emission and deposition of $NH_3$ and $NH_4^+$ are shown. $NH_3$ is emitted in agricultural processes and is then present in the atmosphere in gaseous form. $NH_3$ quickly dry deposits close to the source, however some of it is also transformed to $NH_4^+$ in par-

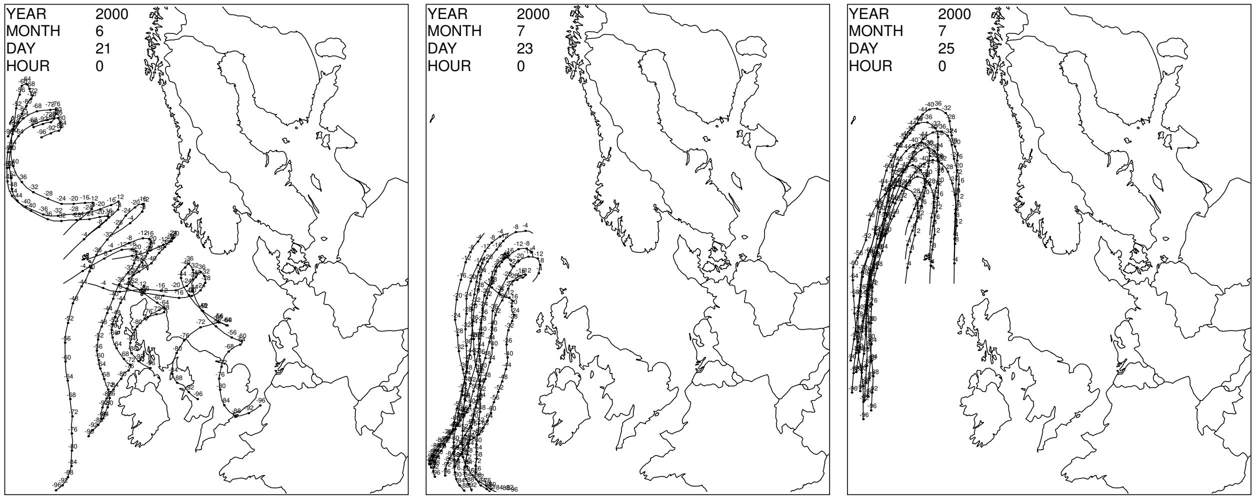

Figure 1.4: Trajectories calculated on the basis of wind speed and direction. There are 9 trajectories in each plot and the distance between the starting points is 150 km.

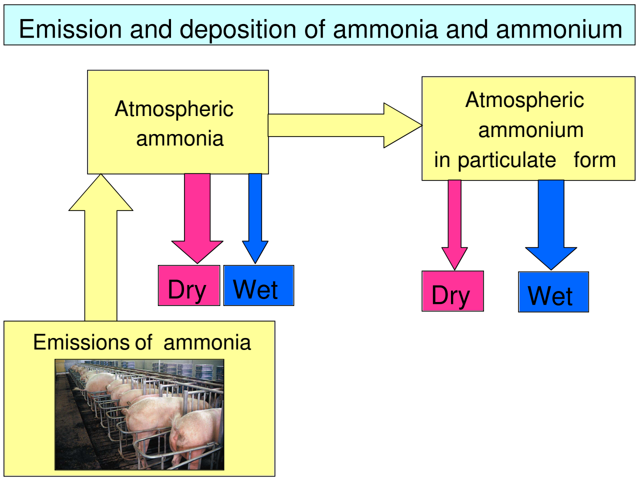

Figure 1.5: Pathway for ammonia and ammonium in the atmosphere from emission sources to final deposition. Ammonia is deposited close to the source, whereas ammonium can be transported across long distances before subsequent deposition occurs.

ticulate form. Particulates have a long lifetime in the atmosphere ($\simeq$one week) and can therefore be transported across long distances. The most important removal pathway for $NH_4^+$ is wet deposition.

In Figure 1.6 the corresponding pathways for emission and deposition of $NO_x$ and $NO_3^-$ are shown. $NO_x$ is emitted in combustion processes and is then present in the atmosphere in the form of gaseous NO and $NO_2$. NO is slowly transforming into $NO_2$ by reacting with oxygen in the atmosphere (this is why $NO_2$ is both a primary and a secondary component), and some of the $NO_2$ dry deposits close to the source. Some of the $NO_2$ and NO transforms into nitric acid ($HNO_3$) which subsequently transforms into $NO_3^-$ in particulate form. As for ammonium the lifetime of particulate nitrate can be quite long and the most important removal pathway is also wet deposition.

There are many chemical components in the atmosphere, the total number has been estimated to be around 3000. The majority is reactive and the approximate number of different reactions taking place between these approximately 3000 species is *ca* 20,000. Reaction rates typically depend on temperature, pressure, sun angle and concentration of the chemical components. Due to this complexity of the chemical atmosphere, it is not straightforward to predict what will happen in terms of chemical reactions with the emitted nitrogen before it deposits again somewhere else.

## 1.5 Deposition pathways

There are two pathways for the atmospheric deposition, wet and dry. The two processes are com-

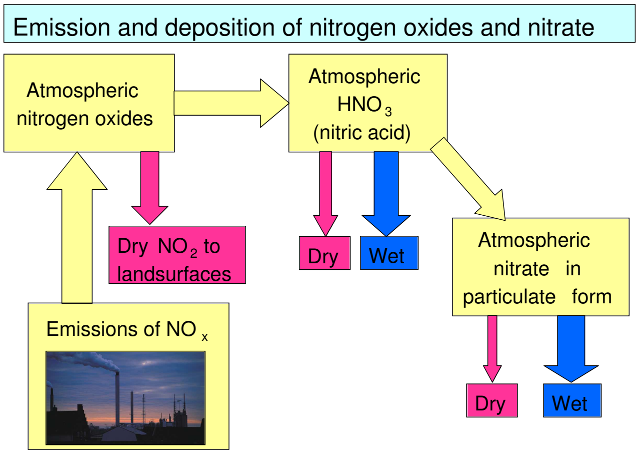

Figure 1.6: Pathway for nitrogen oxides and nitrate in the atmopshere from emission sources to final deposition. Nitrogen dioxide and nitric acid are deposited close to the source, whereas nitrate can be transported across long distances before subsequent deposition occurs.

pletely different in their nature, one depends on solubility and whether it rains or not, the other depends on a whole number of physical, chemical and biological properties of the surface. In this section the processes of wet and dry deposition will be described. How to quantify the deposition is the subject of Sections 1.6 and 1.7.

### 1.5.1 Wet deposition

Wet deposition is the process where gaseous and particulate components are scavenged (taken up) by the means of cloud, fog and rain droplets or snowflakes and subsequently transferred to the ground. Four different processes can be distinguished (Seinfeld & Pandis, 1998):

- Precipitation scavenging, i.e. the removal of species by a raining cloud.
- Cloud interception, i.e. the impaction of cloud droplets on the terrain usually at the top of tall mountains.
- Fog deposition, i.e. the removal of material by settling fog droplets.
- Snow deposition, i.e. the removal of material during a snowstorm.

In this text we will focus on the most common of these processes, namely the precipitation scavenging.

Three steps are necessary for wet deposition to take place. Firstly the pollutants need to come into contact with condensed water in the atmosphere, secondly the pollutants must be scavenged by the droplets and thirdly it then has to start raining before the condensed water evaporates back into water vapor, thereby releasing the pollutants back into the air.

Concerning the wet scavenging, two different processes can be distinguished: *below-cloud* scavenging and *in-cloud* scavenging. The first refers to the process where pollutants are taken up in falling raindrops. This is also denoted *rainout*. The second refers to the process where pollutants are taken up in droplets inside the cloud. These pollutants will only wet deposit if it starts raining from the cloud in which case the process is denoted *washout*.

Most of the pollutants in the air are deposited in the beginning of a rain event, i.e. the air is left more or less clean afterwards. The result is that wet deposition is a very episodic phenomenon where the day to day variation can cover several orders of magnitude.

### 1.5.2 Dry deposition

Dry deposition is the process of transferring gaseous and particulate components to the ground in the absence of precipitation. Turbulence in the air is responsible for this process together with a number of other factors. Turbulence in air can best be described as a movement of the air in eddies and whirls which twine in and out of themselves. As the air in this way describes a circle-like motion, some of the pollutants in the air ends up sticking to the surface, and this process is denoted dry deposition. It depends on a number of factors, some of which include:

- The level of turbulence in the air.
- The roughness of the surface.

- The vegetation on the surface.
- The time of day and year (due to seasonal and diurnal differences in vegetation cover, turbulent conditions, atmospheric stability and planetary boundary height).
- The physical and chemical properties of the component being deposited.
- The moisture content on the surface.

*In general the deposition follows the turbulence level, i.e. the higher the level of turbulence, the more material is transported to the surface and subsequently deposited.* The deposition also follows the roughness of the surface as a consequence of the greater production of turbulens over a rough surface. The deposition to a surface covered by vegetation is furthermore enhanced by the uptake of components through the stomatal openings, which again has a diurnal as well as a seasonal variation. The result is that the deposition is higher to surfaces covered by forest (particularly in the growth season) or buildings than to smooth surfaces like calm water surfaces or fields with low vegetation.

The vegetation itself influences the dry deposition through the process of capture of gases. This process depends on the ability of the plant to take up the pollutant in question. Uptake will e.g. not take place if the leaf pores (stomata) are closed as is the case during night and winter time. For gaseous compounds it is the chemical properties such as reactivity and solubility that are important, whereas for particulate materiale it is the physical properties such as hygroscopisity, size, density and shape that influence the dry deposition process. Finally some chemical species are insoluble in water and will therefore not deposit to water surfaces or wet (e.g. dew-covered) land surfaces.

In the most widely used formulation for dry deposition it is assumed that the dry deposition flux is directly proportional to the concentration $C$ of the chemical component being deposited:

$$F = -v_d C \tag{1.1}$$

where $F$ is the vertical dry deposition flux, i.e. the amount of material depositing to a unit surface per unit time. The constant of proportionality between flux and concentration, i.e. $-v_d$ is denoted the *deposition velocity* and has the units of length per unit time. The advantages of this formulation of dry deposition is that all of the complexities of the process are represented in one single parameter, the deposition velocity. The disadvantage is that $v_d$ depends on many different physical and chemical properties and therefore can be quite difficult to quantify. An example of a $v_d$ parameterisation is given in Box 1.5.2.

## 1.6 Measurements of deposition

How is the amount of nutrients deposited from the atmosphere quantified? Why is it necessary to quantify it and how can it be done? Basically there are two ways; measurements and modelling. Although these ways may also be combined.

### 1.6.1 Measurements of deposition

Many different measurement techniques exist, some very complex, resource demanding and expensive in terms of equipment, some much more simple and likewise inexpensive. In general it is less difficult to measure wet deposition than dry deposition due to the nature of the deposition process; the chemical components are confined to the liquid of the rain drops, also after the deposition has taken place, whereas the dry depositing gases are not confined and can undergo physical transformations (e.g. re-emission). In both processes, however, the components can undergo chemical transformations after deposition.

#### Measurements of wet deposition

The basics of measuring wet deposition is to first collect the precipitation, then analyse it for content of different pollutants. There are two

In order to determine the deposition velocity $v_d$ several different descriptions have been constructed, the most popular being the resistance model for dry deposition (see e.g. Seinfeld & Pandis, 1998). In this description the deposition is represented by three steps: (1) aerodynamic transport down through the atmospheric surface layer to a very thin layer of stagnant air just adjacent to the surface; (2) molecular (for gases) or Brownian (for particles) transport across this thin stagnant layer of air called the *quasi-laminar sublayer*, to the surface it self; and (3) uptake at the surface. Each of these steps contributes to the value of the deposition velocity $v_d$.

In order to actually calculate a value of $v_d$ it has proven useful to think of the three steps of the deposition process mentioned above as a series of resistances to deposition (the analogue is to electrical resistances in series and the calculation method when electrical resistances are combined). For dry deposition the resistances are determined:

- The aerodynamic resistance $r_a$ depending on the turbulence intensity, which in turn depends on the stability of the lower atmosphere and the surface roughness.
- The quasi-laminar layer resistance $r_b$ depending on the molecular properties of the depositing component and the characteristics of the surface.
- The surface or canopy resistance $r_c$ depending on the accessibility of the gas to reaction sites within the plant, for vegetation, and on the reactivity and solubility of the depositing component as well as the moisture level and pH of the surface for soil, building materials, water and snow surfaces.

When the values of the resistances have been determined the deposition velocity can be calculated as:

$$v_d = \frac{1}{r_a + r_b + r_c} \tag{1.2}$$

Several different mathematical expressions are proposed for the three different resistances, however many of these are quite complicated and the interested reader is referred to (Seinfeld & Pandis, 1998) for further investigations.

methods for collecting precipitation and numerous techniques for the subsequent analysis. The two collection methods are:

- Bulk sampling: The precipitation is collected in a bucket, which is open all the time. In most cases a net prevents leaves etc from falling into the bucket. This sampling method has a slight tendency to cause an overestimation of the wet deposition, because some material is also deposited when it is not raining (dry deposition). Due to the complexity of the dry deposition process, the amount of material dry deposited in the bulk sampler is however much smaller than the dry deposited material in the vicinity of the sampler. An example of a bulk sampler is presented in Figure 1.7.
- Wet-only sampling: The precipitation is collected in a bucket, which is only open when it rains. A sensor registers whether it is raining and the lid is automatically opened at the beginning of a rain event and closed at the end. Again some kind of net is built into the system to prevent contamination of the samples with organic material. This sampling method may cause underestimation of the wet deposition depending on the sensitivity of the sensor which determines the status of the lid (open or closed). An example of a wet-only sampler is presented in Figure 1.8.

Once the samples are collected there are many different ways of determining what chemical components they contain. A commonly applied technique is ion chromatography, other examples are atomic absorption methods, spectrophotometric methods or atomic emission methods.

### Measurements of dry deposition

Measurement techniques for dry deposition can be divided into two categories: direct and indirect. When applying one of the direct methods the flux of the chemical component is determined explic-

Figure 1.7: An example of a bulk sampler applied in the Danish Background Monitoring Programme. The bottle collecting the precipitation is located inside the grey tube beneath the funnel (black). (Picture kindly provided by Dr. Thomas Ellermann, National Environmental Research Institute).

Figure 1.8: An example of a wet-only sampler applied in the Danish Background Monitoring Programme. The black bucket contains the bottle where the precipitation is sampled. A motor is located inside the top of the white table and this is used to move the lid (positioned on top of the sampling bucket in the picture). The white bucket acts as a rest for the lid when it is raining. To the left of the table is seen the sensor that controls the position of the lid. (Picture kindly provided by Dr. Thomas Ellermann, National Environmental Research Institute).

itly. This is done either through a collection of the material at the surface or through a measurement of the vertical flux in the air just above the surface. When applying an indirect method the flux is not measured directly, instead the concentration or the vertical gradient of the concentraion is measured. Some examples of direct and indirect measuring techniques are listed below (Seinfeld & Pandis, 1998):

- Surrogate surfaces (direct method): a surrogate surface, such as a filter substrate, is used to collect depositing material. This method is best for particles where the nature of the surface is less important.

- Natural surfaces (direct method): analysis of material deposited on natural surfaces by e.g. leaf washing or snow analysis. This approach is ineffective for gases due to the chemical binding of gases to the surface.

- Chamber method (direct method): deposition to surfaces in a chamber (soil or vegetation) can be calculated by measuring the fluxes in and out of the chamber over a given time interval. This method is suitable for gaseous species, however establishing the chamber is resource consuming both in terms of time and money.

- Eddy Correlation (direct method): statistical correlations of the fluctuations in wind and concentration fields are measured to directly obtain values of the associated vertical fluxes. If the fluctuations correlate, high-speed measurements of vertical velocity and concentration are used to derive the vertical turbulent flux. Assuming theat the turbulent transport is dominating and that chemical reactions are absent, this is a direct measure of the local vertical flux at the measurement point, and the deposition velocity can be obtained by dividing the flux with the mean concentration. This method is suitable for gaseous species, however very fast-response equipment is required.

- Eddy Accumulation (direct method): In this method air is collected in two separate containers with the vertical velocity determining which container receives the sampled air. One container is used for positive vertical velocities and the second is used for negative vertical velocities the instantaneous sampling rate for each container is proportional to the magnitude of the velocity. The collected air is then analyzed for the species of interest and the results are used to calculated the net flux.

- Gradient Method (indirect method): In this method the deposition velocity is determined by measuring the vertical concentration gradient of the depositing chemical component and then the theory of gradient-transport is used to determine the associated deposition flux. An example of a gradient method measuring system is presented in Figure 1.9.

- Inferential Method (indirect method): Measured ambient concentrations at a particular reference height are multiplied by a deposition velocity assumed to be representative of the local surface to compute the dry deposition rate. This method is dependent on the availability of (routine) measurements of air concentrations and the derived values for the deposition flux are clearly dependent on the validity of the estimated deposition velocity.

Generally the measurement methods related to micrometeorology (e.g. the fluctuations in the wind or the direction of the vertical wind speed) are dependent on the turbulent characteristics of the area where the measurements are performed. In most cases the deposition fluxes derived using these methods are representative for a larger area than just the local area where the measurement was made. In contrast, the methods related to the properties of the surface provide dry deposition fluxes that are representative of the spatial scale of the piece of surface that is analysed. Therefore if the surface characteristics are inhomogeneous the measured deposition flux is not representative of a very large area. In most cases the micrometeorological measuring techniques produce results that are representative for a larger area compared to the surface measuring techniques.

Figure 1.9: Measurements of concentrations of e.g. $NH_3$ in several heights can provide the basis for calculating the deposition using the Gradient method. This particular tower with measurements in 5 heights (the small grey tubes contain denuders for sampling concentrations) was operated at the island of Gotland in 1998. (Picture kindly provided by Bjarne Jensen, National Environmental Research Institute).

## 1.7 Modelling of deposition

Measurements of atmospheric deposition are generally expensive and time consuming and therefore sparse. In order to complement the monitoring and for other purposes as well atmospheric concentrations and depositions of nutrients are frequently calculated with the aid of atmospheric models.

*What is the contribution from a source located at point A to the deposition of nutrients at point B?*

*What is the most feasible strategy in terms of economy for reducing the pollution e.g. with the goal of keeping the pollution and deposition below agreed limit values?*

*What will be the effect on local deposition of* *nutrients if a source is removed or added at a specific site?*

Questions like these cannot be answered by measurements only. Full scale experiments are too expensive and involve a large risk of investing in the wrong solutions. Sensible use of suitable models provide the best answer in cases like these.

Procedure for construction of a model:

- Decide on the size of the domain; is this a local, regional or maybe global study?
- Discretize the domain into areas which comply with the resolution of the results that you are interested in.
- Describe the physical and chemical processes that you want to include in the model in mathematical terms (parameterise processes that you have no accurate description for).
- Construct a way to solve the equations (usually numerical).

When the last step is completed the model is ready to be described in a programming language and run on a computer.

### 1.7.1 Model domain

In order to construct a model describing transport and chemistry of certain species in the atmosphere, the ideal model domain would be the entire globe. However this is not very practical as the globe is spherical (see Figure 1.10) and the equations describing the physics are quite complicated in spherical co-ordinates.

The alternative is to select an area (a model domain) and make it flat, at least for the purpose of modelling it. This is illustrated in Figure 1.11 where the domain of a hemispheric air pollution model is presented. In this domain the surface of the majority of the Northern Hemisphere is projected on to a plane with the North Pole in the centre. This is called a polar stereographic projection, and for this particular example the projection is true at 60°north.

Independent of the projection, the domain of the model has to be discretized, horizontally as well as vertically. One way to carry out this discretisation is to divide the (3-D) model domain into boxes. How many boxes depends on what features the model should be able to describe. If — for example — the study is trying to quantify the nitrogen input into a coastal ecosystem, then the resolution has to reflect the size of this particular area as well as having a resolution that resolves the emission sources sufficiently to provide a realistic concentration and deposition distribution for the area.

In the case of the model domain presented in Figure 1.11 the horizontal domain is divided into 96×96 grid points, each with a size of 150 km×150 km. This resolution is not high enough for studying nitrogen input to small water bodies, and the resolution is therefore increased over certain areas of the model domain. For this particular model an area over Europe is discretised with a 50 km×50 km resolution and furthermore an area over Denmark and important surroundings is discretised with a resolution of 16.67 km×16.67 km.

Other models have similar features in which the resolution is gradually increased over certain areas, thereby giving the possibility of ‘zooming’ in on areas of interest. Due to the large amount of computer power needed for these kinds of models it is not possible just to increase the model resolution over the entire model domain. Due to the fast happening processes in the atmosphere it is necessary to have a quite large model domain in order to account for all the sources of nitrogen. If one imagines the concept of an airshed (similar to the concept of a watershed) then the airshed for a typical coastal area is many times larger than the watershed for the same area (Paerl *et al.*, 2002).

### 1.7.2 Model equations

In order to model the processes in the atmosphere it is necessary to have a mathematical description of them. Considering chemical compounds in the atmosphere, the pathway to be described starts with the *emission* of the compounds, subsequent

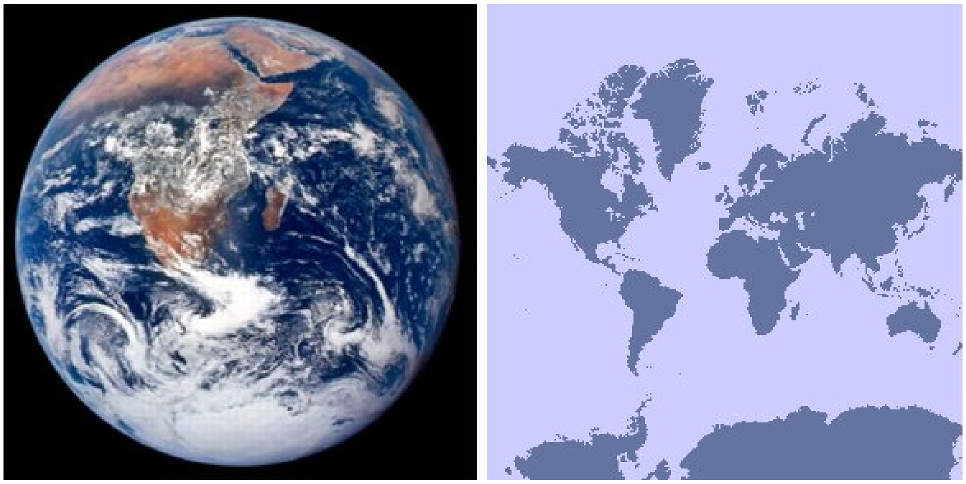

Figure 1.10: Left: The Earth as viewed from space. Right: The earth unfolded, thus giving rise to distortions (e.g. of Antarctica and Greenland).

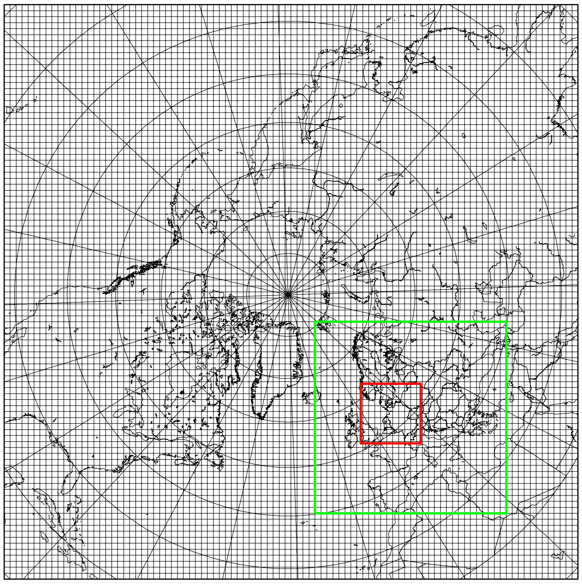

Figure 1.11: An example of a model domain of an air pollution model. The projection is polar stereographic and true at 60°north.

*transport* and *dispersion* by the wind, *chemical transformation* due to the influence of sunlight as well as mixing with other chemical components, and finally the *deposition* of the compound to the surface.

In mathematical terms this can be expressed as a set of partial differential equations (an example is given in Box 1.7.2), which in most cases (except for a few rather uninteresting ones) cannot be solved analytically. Instead the equations are solved numerically.

The set of equations depicted in Box 1.7.2 has to be solved for every grid box in the model domain, for every time step of the model run. Taken the model with the domain in Figure 1.11 as an example there are 96 by 96 by 20 grid boxes in the model. Furthermore there are 60 chemical species in the model giving a total of 11,059,200 equations with the same amount of unknowns to be solved at each time step. A time step in an atmospheric transport chemistry model typically has a value around 500 seconds depending on the time of the day (many chemical reactions depend on the amount of sunlight available) and this gives approximately 5400 time steps to be carried out to complete calculations for one month. In total that means that 59,241,922,560 equations have to be solved, each involving many floating points op-

The mathematical description of the *emission-transport-dispersion-chemistry-deposition* pathway is in the Danish model DEHM-REGINA (Christensen, 1997; Frohn *et al.*, 2001, 2002) given by the following set of differential equations:

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\left(u\frac{\partial c_i}{\partial x}+v\frac{\partial c_i}{\partial y}+w\frac{\partial c_i}{\partial z}\right) \\ &+ K_x\frac{\partial^2 c_i}{\partial x^2}+K_y\frac{\partial^2 c_i}{\partial y^2}+\frac{\partial}{\partial z}\left(K_z\frac{\partial c_i}{\partial z}\right) \\ &+ E_i\left(x,y,z,t\right)-\Lambda_i c_i \\ &+ Q_i\left(c_1,c_2,\ldots,x_q\right) \quad (i=1,2,\ldots,q) \end{aligned} \tag{1.3}$$

where $c_i$ is the concentration of chemical component $i$, $u$, $v$ and $w$ are the wind velocities in the $x$, $y$ and $z$ directions respectively, $K_x$, $K_y$ and $K_z$ are dispersion coefficients, $E_i$ is the emission of chemical component $i$, $\Lambda$ is the scavenging coefficient for chemical component $i$ and $Q$ denotes the mathematical treatment of the chemical reactions. At first the set of equations looks linear, however this is not the case. The chemical reactions are highly non-linear and this complicates the solution of the equation.

For one specific location (grid point), the left hand side of the equation gives the change in concentration of chemical component $i$ as a function of time. The first three terms on the right hand side of the equation describe the change in concentration due to transport by the wind (advection), the next three terms describe the change in concentration due to dispersion and the last three terms describe the change due to emissions, wet deposition and chemical reactions respectively. The process of dry deposition is described by the vertical dispersion term, where dry deposition is the lower boundary condition.

In order to solve the set of equations it is customary to perform a so-called splitting and divide the equation into submodels, i.e. first calculate the change in concentration due to advection, then the change in concentration due to dispersion and finally the change in concentration due to chemistry, emissions and wet deposition. Each of these so-called sub-models have different mathematical and numerical properties. In order to optimize the accuracy and stability of the solution it is therefore custom to apply different numerical solution techniques for the different parts of the equation (the different sub-models). However, such a procedure needs a careful analysis in order to avoid numerical errors especially when a splitting is performed for processes taking place on similar timescales.

erations (flops). Atmospheric transport-chemistry models are therefore typically operated on large workstations or computer clusters, rather than on ordinary personal computers.

### 1.7.3 Model input

Once the solution technique for the equations is in place, several kinds of input data are required for the model calculations:

- Meteorology: wind speed, wind direction, temperature, pressure, humidity, solar radiation etc, preferably in 3-D.
- Surface emissions of the primary air pollutants
- Land use and roughness maps
- Initial and boundary concentrations

#### Meteorology

Meteorological data may be obtained from many different sources, however the use of output from numerical weather prediction (NWP) models is becoming more and more frequent. This type of data should be 3-D in order to describe the three-dimensional transport in the atmosphere. The temporal resolution of data sets like these are typically a couple of hours and the meteorological variables are then interpolated in the air pollution model in order to get meteorological fields for every time step. It is possible to save data from the NWP model with a higher frequency, however the disc space needed for storage usually sets the limit. A way to work around this problem is to run the NWP coupled together with the air pollution model, thereby calculating the meteorological variables everytime the air pollution model is run. This in turn gives rise to a problem concerning computation time, especially if the model has to be applied for various scenarios.

In the DEHM-REGINA model mentioned previously, the meteorological input consists of results from the NWP MM5 (Mesoscale Meteorological Model, Version 5, Graedel *et al.*, 1993). An example of output for the hemispheric model domain (presented in Figure 1.11) is given in Figure 1.12.

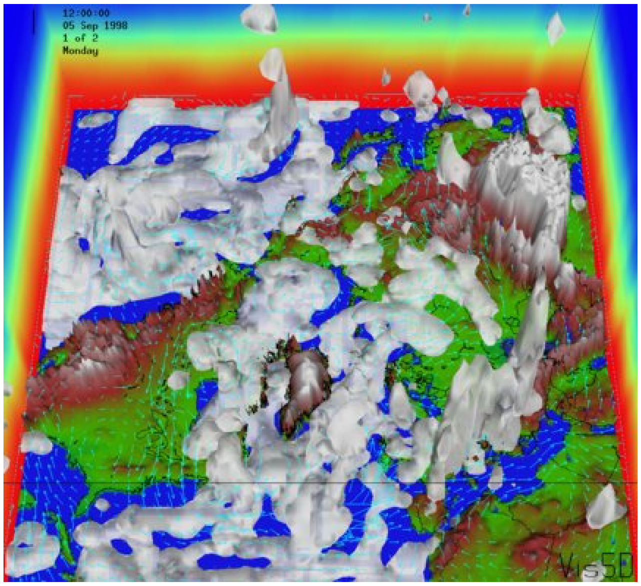

Figure 1.12: Graphic representation of some of the meteorological variables applied in the air pollution model DEHM-REGINA. The horizontal streamlines and the cloud water content are shown.

#### Emissions

Emission data for all the primary components included in the model are also necessary. The data should be gridded and as many of the sources as possible should be included. Emission data are typically obtained as yearly totals, or in some cases as monthly totals. The seasonal as well as the day to day variation can however be quite strong, and if possible data sets with (at least) a seasonal variation should be applied.

Alternatively parameterisations of the temporal variations can be used. An example of a parameterisation of the temporal variation in $NH_3$ emissions is presented in Figure 1.13. The day to day changes in emission are in this case based on information concerning agricultural practise and the variations within the day are parameterised according to meteorological factors such as temperature and wind speed (Ambelas Skjørth *et al.*,

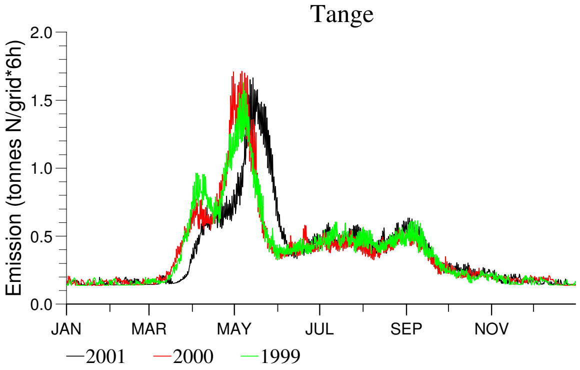

Figure 1.13: Emission data for the years 1999 (green line), 2000 (red line) and 2001 (black line). The emission data include a parameterisation of the seasonal variations based on agricultural practise as well as a parameterisation of the variations within the day based on meteorological factors. (The plot has kindly been provided by Carsten Ambelas Skjøth, National Environmental Research Institute).

2004). The result is a significant spring peak in the emissions.

Figure 1.13 presents the emissions calculated for the years 1999, 2000 and 2001 for a specific site in Denmark (the measurement station Tange). The emission peaks are slightly shifted from year to year as a result of temperature distribution differences between the years (in a cold spring the emission peak will be located later than in a relatively warm spring period).

In Figure 1.14 are shown to sets of time series of concentrations. Each set consists of one curve presenting measured concentrations at Tange and one curve presenting concentrations for Tange calculated with an air pollution model. The emission data input for the model results presented to the left in the Figure contain no information considering the temporal variation, whereas the emission data input for the time series presented in the right part of the Figure includes the parameterisation of the temporal variation presented in Figure 1.14. It is clear from the figures that for the component $NH_3$ it is very important to describe the temporal variations of the emissions in the model in order to be able to reproduce measured concentrations (Ambelas Skjørth *et al.*, 2004).

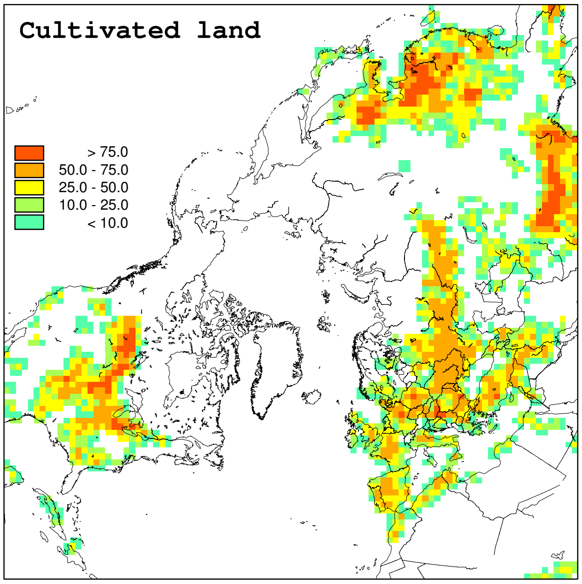

Figure 1.16: An example of one of the categories in the land use data set applied in the DEHM-REGINA model: a map of the percentage of cultivated land over the Northern Hemisphere

Considering again the DEHM-REGINA model as an example, there are 16 different chemical components which are primary. Emission data sets for these components are derived from a combination of hemispheric and European data sets and an example of the ammonia ($NH_3$) emissions for different horizontal resolutions are given in Figure 1.15.

### Land use

The dry deposition of pollutants and nutrients is dependent on the composition of the surface and therefore it is necessary also to include data describing the surface characteristics. In this kind of data sets the surface is classified into a number of different categories like e.g. forest, crop land, water areas etc. An example of a land use data set for one specific category is presented in Figure 1.16.

### Initial and boundary conditions

The atmosphere is a chemically dynamical environment and starting a model run with concentra-

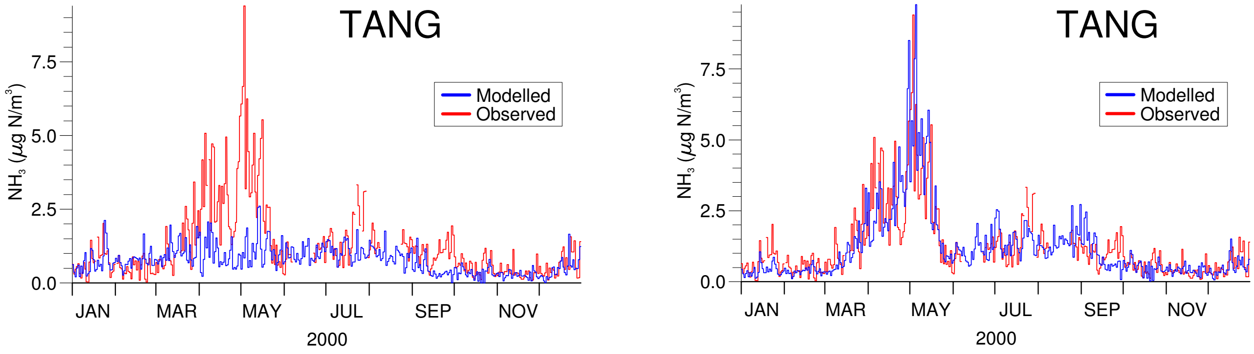

Figure 1.14: Modelled and measured concentrations of $NH_3$ at the Danish measurement station Tange. Model calculations are performed with emission data without temporal variations (left) as well as with emission data where the temporal variations are described using a parameterisation based on agricultural practise and meteorological conditions (right). (The plot has kindly been provided by Carsten Ambelas Skjøth, National Environmental Research Institute).

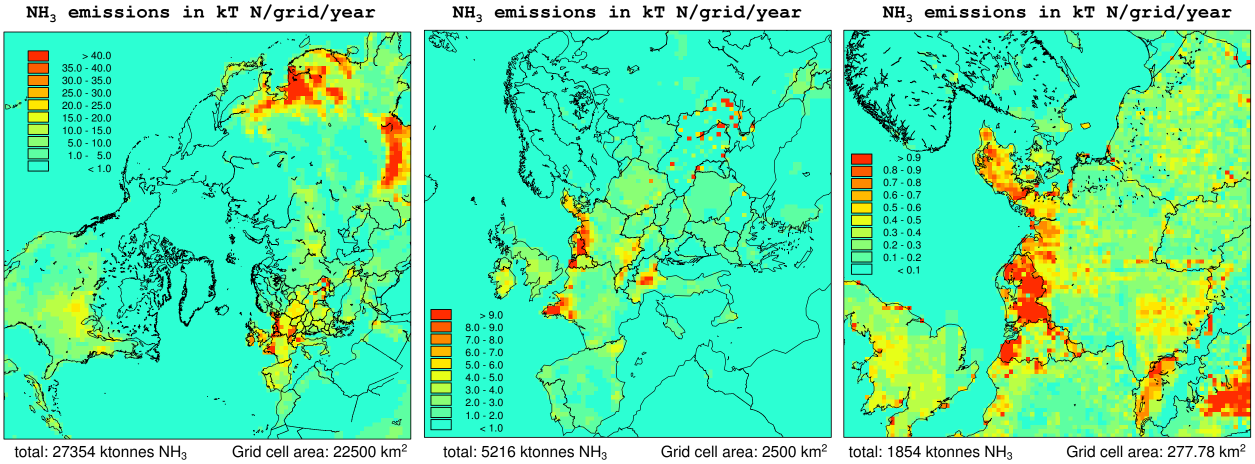

Figure 1.15: Left: emissions of $NH_3$ for the northern hemisphere, derived from a global emission inventory (the GEIA emission inventory mentioned earlier in this chapter) and a European inventory (the EMEP emission inventory). The resolution is 150 km ×150 km. Centre: emissions of $NH_3$ for the European area (the EMEP emission inventory). The resolution is 50 km ×50 km and it is seen that more features are visible in this resolution. Right: emissions of $NH_3$ for Denmark, Germany and surroundings. The resolution is now 16.67 km ×16.67 km (using the GENEMIS emission inventory) and it is clear that there is a strong spatial dependency of the emissions.

tions of the different chemical components equal to zero will result in a system which requires a very long spin-up time in terms of the modelled time period to become balanced (several years). If instead the initial conditions consist of a set of background concentrations for the different chemical components, the spin-up time can be reduced to a couple of months calculated (again in terms of modelled time period). During the model run boundary conditions are needed in order to describe what is the concentration of the air flowing in from outside the model domain at the lateral boundaries as well as at the top of the domain.

It is very important that the resolution in the input data is at least as high as the resolution of the model domain. If the resolution in the input data is coarser than the resolution of the model, then the amount of information needed for fully exploiting the capacity of the model with its given resolution is too small.

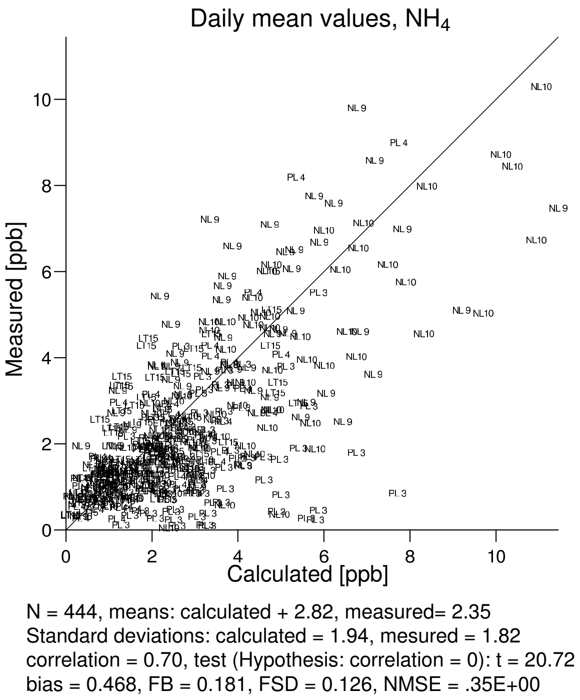

Figure 1.17: Scatter plot for ammonium ($NH_4$) for daily mean concentrations calculated with the DEHM-REGINA model (Frohn, 2004). Several statistical parameters are evaluated from the data set, e.g. the correlation, the bias, the fractional bias (FB), the fractional standard deviation (FSD) and the normalised mean square error (NMSE).

### 1.7.4 Model validation

Model results are obviously only useful if the models are capable of representing the actual situation. That is, if the model results comply with the results obtained from measurements. In order to evaluate the performance of an air pollution model it is therefore common to carry out a validation with measurements of air pollutant concentrations and depositions. This is done by comparing e.g. calculated and measured mean concentrations or accumulated depositions on monthly (mainly depositions), daily or hourly basis for as many measurement stations as possible.

To determine how the model is performing in general the concentrations from all available measurement stations can be compared with calculated values in a so-called scatter plot (see Figure 1.17). If the model is perfect for all the different areas represented by different measurement stations, then all the points in the scatter plot will lie on the 1:1 line. Deviations from this line is an indication of the concentrations being either over- or underestimated by the model. In order to determine how well the performance of the model is, several statistical parameters are calculated on the basis of the data set. These parameters are also used in e.g. sensitivity analyses of different model configurations.

In order to determine when and where the over- or underestimated values are obtained the calculated and measured values can be compared in time series (see Figure 1.18). The time series can be investigated for just one measurement station in order to understand the behaviour of the model in the particular region where the station is located, or it can be investigated for the mean value of all the measurements obtained at the different stations.

### 1.7.5 Model result examples

One of the advantages of applying a model is that the deposition to e.g. an entire area can be assessed, even for areas that are not accessible for performing measurements. An example of an atmospheric transport-chemistry model that has been extensively used in this context is the Atmospheric Chemistry and Deposition model (ACDEP; Hertel *et al.*, 2002). This model is applied in the Danish Background Monitoring Programme for calculating surface concentrations and depositions of nitrogen and sulphur to Danish land and sea areas. The irregular model domain covers the Danish national territory and the horizontal resolution of the model is 30 km. An example of calculated nitrogen depositions for the year 2002 is presented in Figure 1.19. It is important to note that the dry deposition velocity is different for land and sea surfaces and therefore there are two different deposition maps, one for land, and one for the marine areas, lakes and streams.

The ACDEP model has also been utilised in other research projects where larger water bodies have been the focal point. Examples are calculations for the Baltic Sea area (Hertel *et al.*, 2002) and the North Sea area (Hertel *et al.*, 2003).

Considering the calculations for the Baltic Sea, the nitrogen deposition was calculated with a horizontal model resolution of 30 km to the entire Baltic Sea area, and furthermore surface concentrations at 16 measurement stations located in Denmark, Sweden, Germany, Finland, Poland, Estonia, Latvia and Lithuania were calculated in order to compare the calculated concentrations with measurements in the vicinity of the Baltic Sea.

An example of the computed total atmospheric nitrogen deposition for the year 1999 is presented in Figure 1.20. The deposition has a pronounced south-north gradient with depositions in the range from 1000 kg N km$^{-2}$ in the south to 200 kg N km$^{-2}$ in the north. This gradient is due to transport from the areas with high emission densities in the northern part of the European continent. These results are consistent with results from other air pollution models (Hertel *et al.*, 2003).

The results from the ACDEP model studies on the deposition to the Baltic Sea region, supports the generally accepted fact that episodes of high atmospheric nitrogen deposition are the result of

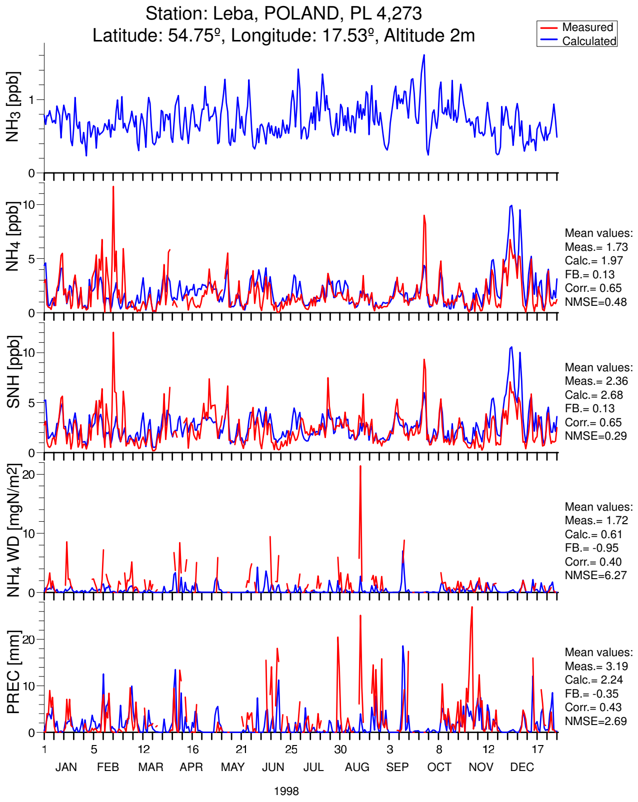

Figure 1.18: Time series of ammonium ($NH_4$, second panel), sum of ammonia ($NH_3$) and ammonium (SNH, third panel), Wet deposition of ammonium (fourth panel) and precipitation (fifth panel). The time series are obtained for the measurement station Leba located in Poland. Red is measurements and blue is model calculations. There are no measurements of ammonia concentrations at this measurement station.).

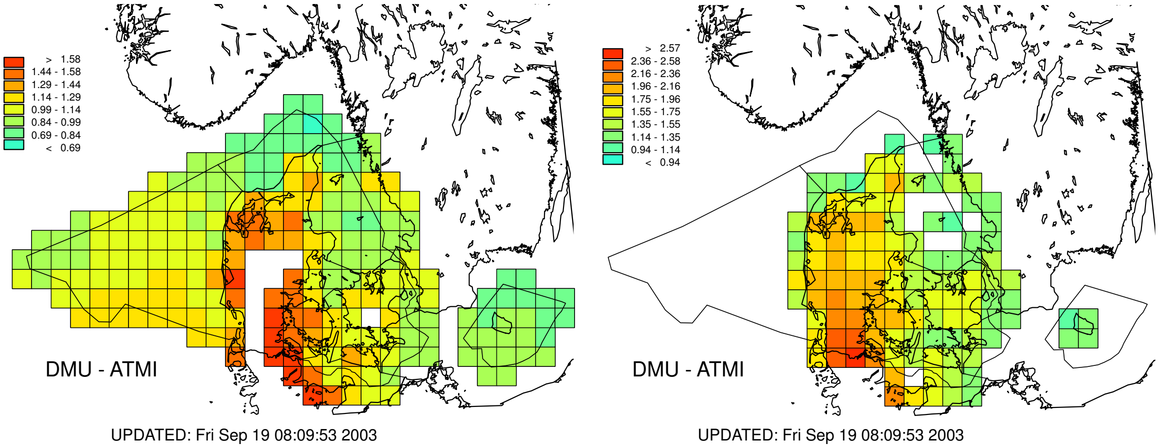

Figure 1.19: Nitrogen deposition in Tonnes N per km$^2$ for the year 2002 calculated with the ACDEP model. Left: deposition to water surfaces, right: deposition to land surfaces.

precipitation events. Depositions may be somewhat elevated close to the coast when transport from nearby agricultural activities lead to high ammonia concentrations. However, the resulting dry deposition is considerably smaller than what is observed from rain out of ammonium and nitrate in particulate form.

In Figure 1.21 is shown a simulation of an event with high local wet deposition of atmospheric nitrogen in a belt from the coast of Poland and out to Gotland in the Baltic Sea. The simulation is performed with the ACDEP model. The episode took place on July 26, 2002 and the results in the figure are given in the form of daily mean values (for the concentrations) and daily total values (for the precipitation and deposition). In Figure 1.21 is shown the precipitation in mm (*upper left*), the concentration of ammonia in $\mu$g N m$^{-3}$ (*upper right*), the concentration of particulate ammonium in $\mu$g N m$^{-3}$ (*lower left*) and the total nitrogen deposition in Tonnes N km$^{-2}$ (*lower right*).

As described in Section 1.4 the dry deposition is related to the atmospheric concentrations of gas-phase ammonia, whereas the wet deposition is related to the concentrations of particulate-phase ammonium. When the precipitation plot (the upper left part of the figure) is compared with the ammonium concentration plot (lower left part of

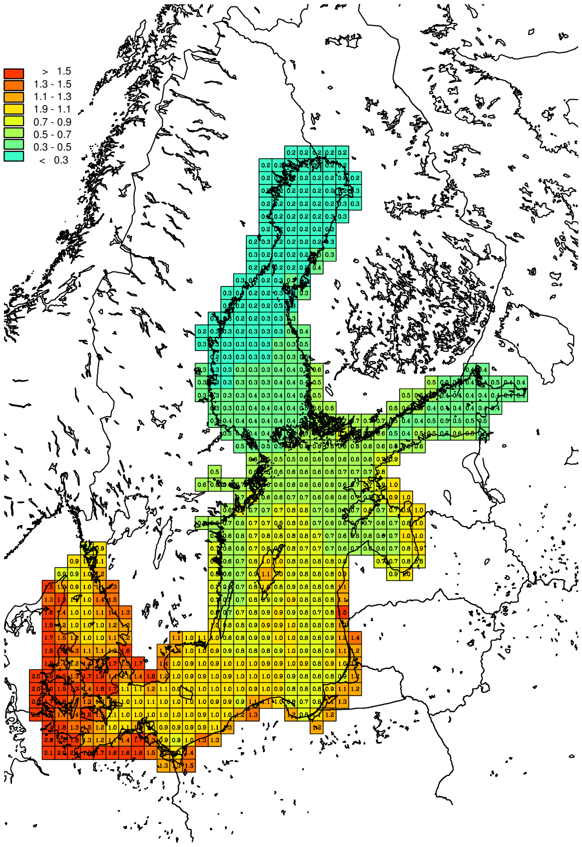

Figure 1.20: Atmospheric deposition of nitrogen in Tonnes N km$^{-2}$ to the entire Baltic Sea for the year 1999. The calculations have been performed with the ACDEP model.

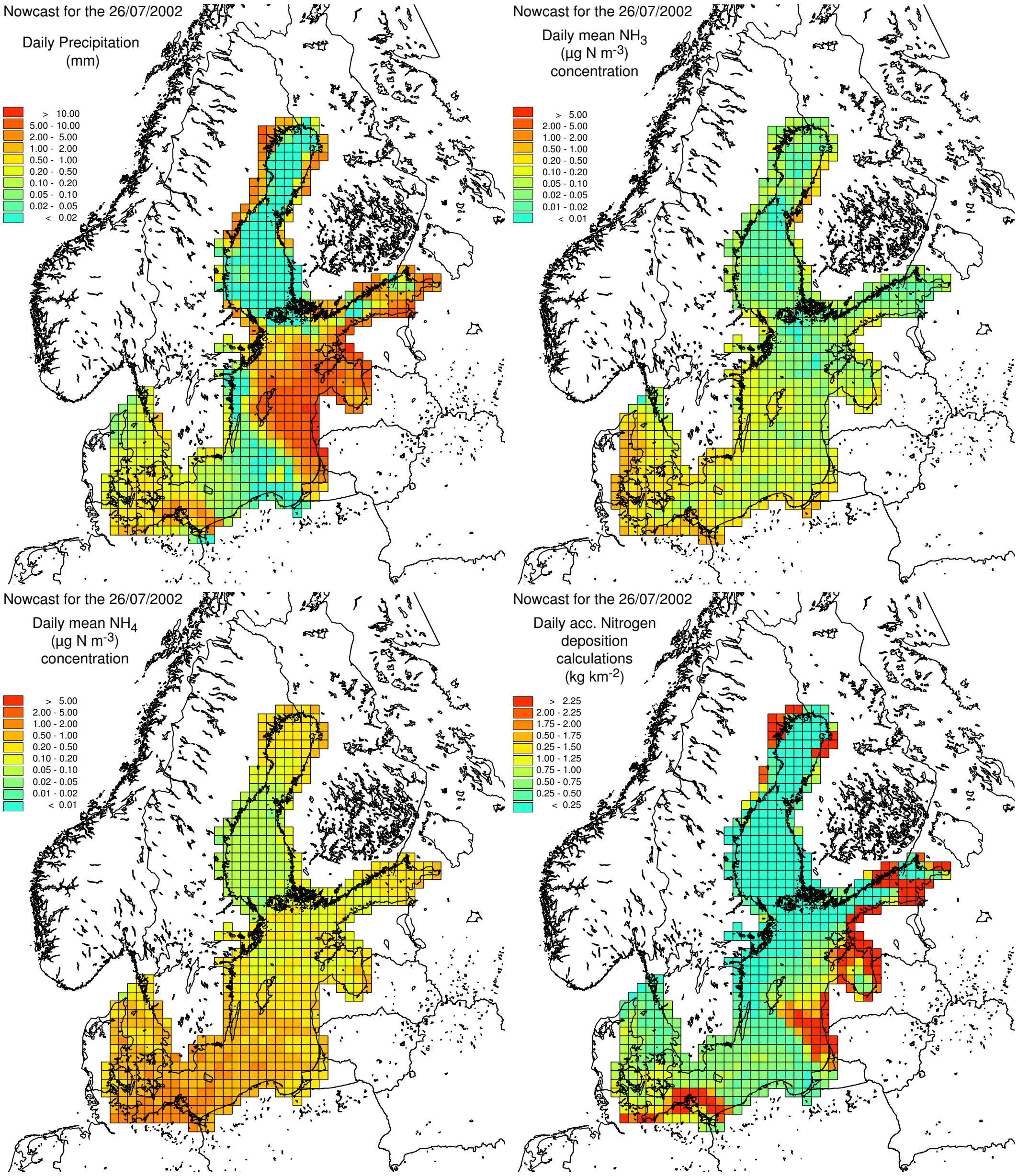

Figure 1.21: Episode of high nitrogen deposition on July 26, 2002. The upper left figure shows the precipitation in mm, the upper right figure the concentration of ammonia in $\mu$g N m$^{-3}$. The lower left figure shows the concentration of ammonium in $\mu$g N m$^{-3}$, and the lower right figure shows the total nitrogen deposition in Tonnes N km$^{-2}$.

the figure) and the total deposition plot (lower right part of the figure) it can be seen that high concentrations of ammonium in the southwestern part of the Baltic combined with moderate precipitation amounts in the same region produce high amounts of deposition. Likewise moderate concentrations of ammonium in the Gulf of Riga, the Gulf of Finland and the northern part of the Gulf of Bothnia as well as off the coast of Latvia and Lithuania combined with high amounts of precipitation in these areas also produce peaks in the atmospheric deposition of nitrogen.

Another example of atmospheric deposition calculated with an air pollution model is presented in Figure 1.22 showing the atmospheric deposition to the North Sea calculated with the ACDEP model (Hertel *et al.*, 2002). The depositions are seen to vary between 0.3 to more than 3 tonnes N km$^{-2}$. Smallest values are found in the northern part of the North Sea, that is far from the large source areas in the northern part of the European continent. Largest deposition densities are found in the southern part and especially at the coastline of France, Germany, Belgium and the Netherlands.

## Acknowlegdements

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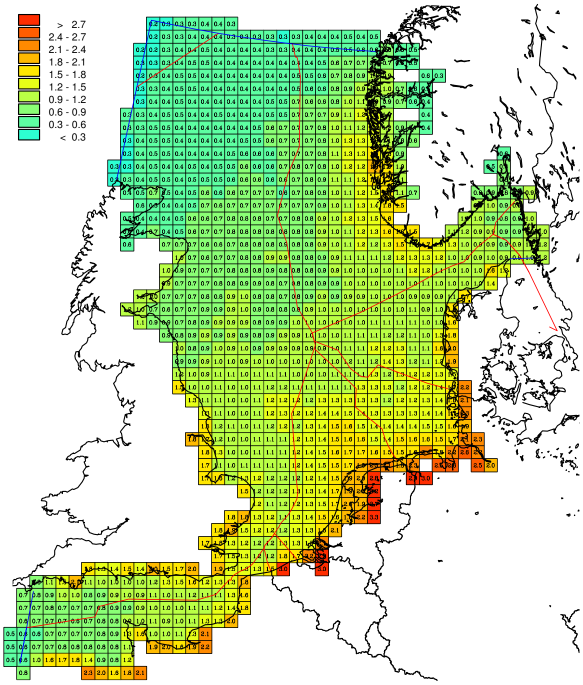

Figure 1.22: The total atmospheric nitrogen deposition to the North Sea in 1999. Depositions are given in tonnes N km$^{-2}$. The results reflect to a large degree the distribution of the source areas around the North Sea, but also the distribution of precipitation is important. For example the large depositions at the Norwegian coast reflect the high precipitation amounts due to the mountains in this region.

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# Part II

# Runoff block

# Chapter 2

# Agriculture and the Water Quality Impacts. Challenges in terms of Quantification, Control and Management

Nils Vagstad and Johannes Deelstra
Jordforsk
The Norwegian Centre for Soil and Environmental Research

## 2.1 Introduction

### 2.1.1 Short-term historical perspective

During the first two to three decades after the second world war, most countries encouraged their agricultural sector to increase the production quantities and to decrease the production costs so that the consumers could benefit from lower prices on agricultural produces. However, this could only be achieved by more intensive production, e.g. by tremendous increases in nutrient inputs through fertilisers (crop production) and concentrated feedstuff (livestock production), higher livestock densities and substantial mechanisation of the sector as such.

The adverse impacts of agriculture on the quality of surface and ground waters were more or less neglected throughout Europe for many decades, but became gradually a priority issue on the political agenda during the 1980s. For example, the EC launched their Nitrates Directive in 1991 (91/676/EC) to control or reduce nitrate losses and eutrophication caused by agricultural activities. Several international conventions were established for the protection of marine and freshwater bodies. They include for example the Oslo-Paris Commission (OSPAR), dealing with the North Sea, and the Helsinki Commission for the protection of the marine environment of the Baltic Sea (HELCOM). The nutrient reduction targets that had been accepted were rather ambitious. The nutrient load to the marine environments for example should be reduced by 50% within 1995. Eventually it became clear that these targets were difficult, if not impossible to achieve. But maybe the most striking issue was the difficulty to quantify and verify the actual achievements in terms of reduced nutrient loads. This was enhanced by the lack of comparability and transparency in the quantification tools and methods used by the different countries to report on nutrient loads. It became clear that the general understanding of the processes leading to nutrient runoff from agriculture were poorly understood or to put it in other words, the complexity of the processes in the soil-water-biosphere system and its interactions with the socio-economic processes were severely underestimated when the reduction goals were established.

### 2.1.2 The agricultural contribution to decreased water quality

Agriculture represents a major source of nutrient inputs to surface and ground waters throughout Europe as well as in the Baltic Sea Region. Soil loss due to erosion processes on agricultural land and pesticide leaching from intensive crop production are also major issues of concern.

The agricultural pollution sources are usually divided in two groups;

- point sources, e.g. storage of animal manure
- non-point sources, or diffuse sources, i.e. leaching and runoff from agricultural land

The diffuse sources are of main concern with regard to impacts and control. They are, contrary to most point sources, usually very difficult to quantify accurately while the possible control mechanisms and management options are not necessarily straightforward. This is due to their 'diffuse' character with a spatial as well as temporal variability in terms of loads and cause-effect relationships.

This paper outlines in brief some aspects related to the loss processes of nitrogen (N) and phosphorus (P), the potentials for controlling or reducing these losses, and the overall management including monitoring of diffuse agricultural pollution sources.

## 2.2 Loss processes and governing factors

The efficient management and control of N and P losses from diffuse agricultural sources requires understanding of the fundamental loss processes. The loss processes and mechanisms are slightly different for N and P. Basically, however, the processes can be divided in three main categories

- The mobilisation processes, e.g. the mineralisation of organic N and the detachment of P-containing soil particles.
- The transport processes, e.g. leaching though the soil profile to groundwater systems, subsurface runoff, surface runoff.
- The retention processes, e.g. the potentials for denitrification, immobilisation and sedimentation along the hydrological pathways by which the nutrients are transported.

Generally, climate, topography and soil types in addition to farming systems and practices are the most important governing factors influencing the magnitude and the variability in losses, and to a large degree determining the hydrological pathways by which nutrients are transported.

N losses are mainly the result of leaching processes with surface runoff rarely being a significant pathway. The prerequisites for leaching of N are:

1. Leachable N in the root zone, which mainly will be in the form of $NO_3$-N.
2. Surplus water for downward transport of N.

How much of the N that finally reaches the surface water depends to a large degree on the fate of the N after it is leached from the root zone of the soil. At intensively drained soils a large part of the leached N will presumably be transported directly to the surface water through the subsurface drainage system. However, on more coarse textured soils, a large part of N may also be transported downwards to the ground water and reach the surface water at a later stage, depending on the residence time. In the latter case, significant reduction of nitrate due to denitrification processes may occur. Investigations in Denmark indicated that only around 10% of the nitrate lost from the root zone on some sandy soil catchments reached the surface water, whereas more than 50% in clay soil catchments (Grant *et al.*, 1997).

Often a close link is suggested to exist between fertiliser application levels and N losses, and consequently also that reduction in losses thereby can be obtained by a reduction in the N applications. An overall impression exists that the major cause of N-losses from agricultural is the fertiliser use. However, several studies have indicated that N losses first of all depend on transformation processes related to soil organic matter, and that N application levels when being within the limits of yield response, only moderately affects the losses. Norwegian studies (Lyngstad, 1990) using labelled N ($^{15}$N) revealed that roughly 2–10% of the leached N derived from pre-season applied fertiliser, whereas the main part originated from mineralization of soil organic N. These findings are in agreement with results from studies in other countries. On the other hand, it is a well known fact that N applications, when exceeding crop nutrient requirements may result in substantial leaching losses. Figure 2.1, based on field lysimeter experiments in Norway, illustrates clearly the relations between yield response and leaching of N. One dry year (1976) with minor yield response to applied N resulted in much larger leaching losses compared to a year with normal yield response (1981).

Poorly drained soils, long residence times for water in catchment areas, and high soil pH will contribute to increased gaseous losses, and thereby reducing N losses to the open water courses. The hydrological properties of soils and catchments are, indirectly, of great importance for the potential buffering of N leaching.

The phosphorus loss processes are in principle quite different from the N processes, and depend less on biological soil processes. The P adsorption capacity of most soils is very high, usually resulting in moderate leaching of P. The exceptions are coarse textured sandy soils or peat soils with low contents of Al, Fe or Ca. Soil erosion is usually a major source of P losses from agricultural land. P containing soil particles may be transported both by surface runoff, and by percolating water through macro-pores, cracks and finally through the tile drain systems reach the open water courses. In regions with a cold winter climate, P containing plant residues at the soil surface may also pose a risk for substantial P losses by surface runoff during melting periods. Also manure or slurry applications may result in direct losses either as surface runoff or through the soil matrix, cracks and/or macro-pores. As for the plant residue losses, this will be P forms with rather high bio-availability. Very high P losses have, for example, been measured in areas with long-term applications of large amounts of pig manure in Latvia (Vagstad *et al.*, 1999)

## 2.3 Monitoring of nutrient losses — methodological aspects

Within the context of the water protection work (e.g. the EU Water Framework Directive) it is necessary to know the sources contributing to reduced water quality in addition to their relative contribution within the watersheds. In the selection and implementation of optimal and cost-efficient measures, a proper understanding of the underlying processes resulting in e.g. nutrient losses is paramount. This understanding should form the basis for policy decisions in relation to water protection and land use issues.

Quantification of diffuse nutrient losses can either be done by direct measurements (monitoring) or by modelling. However, modelling can only be considered a tool which can supplement, and not replace monitoring. Measuring nutrient losses at catchment scale is not necessarily a straightforward task. The choice of methodology regarding the accuracy and precision of the collected data has to be a compromise between costs (e.g. equipment and operation and maintenance costs) and

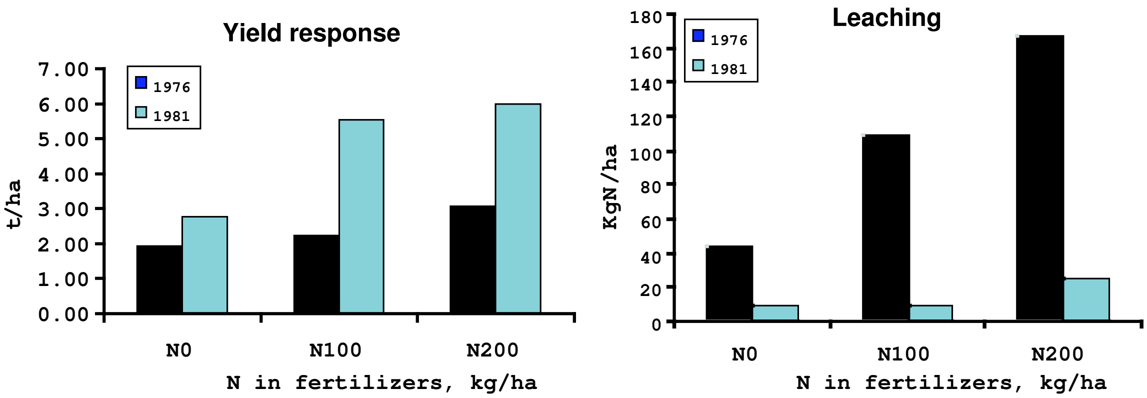

Figure 2.1: Yield response (left) and the corresponding leaching losses of N (right) at different N application levels in two meteorologically contrasting years. Based on Norwegian field lysimeter experiments (Uhlen, 1989).

end-users demand (e.g. researchers, managers, public authorities). There is no specific method which can be recommended, except that each case has to be considered separately on the basis of the site specific conditions like catchment size, topography, channel characteristics, climatological conditions and the geo-hydrological settings.

Correct measurements of N and P losses (loads in surface waters at catchment scale) require reliable and precise data on nutrient concentrations as well as on water discharge. The reliability of the data may be affected by both field procedures as well as analytical procedures. The difficulties in obtaining correct water discharge data may often be underestimated. Different methods can be used to obtain information about stream discharge but they are often based on the combination of direct measurement of the water level and a known head-discharge relation for the measurement location, representing the relation between the water level and the discharge (Deelstra *et al.*, 1998). The measurement location can be a natural profile or fixed structure. In case natural profiles are used for discharge measurement, a head-discharge function has to be established though calibration measurements. However, a problem often associated with natural profiles is the changing flow conditions due to variations in roughness conditions in the channel bed because of vegetative growth. This can lead to large uncertainties in the head-discharge relation. In case a long term monitoring programme is to be initiated, it is an advantage to use fixed devices for discharge measurement. The main advantage of a such structure is the availability of a known head-discharge relation while in addition much higher accuracies can be obtained when they are build according to the specifications. It goes beyond doubt that a good discharge measurement program only can be obtained when sufficient attention is paid to the operation and maintenance of the measurement location and systems involved in the data collection and processing.

The selection of the appropriate water sampling strategy is an important issue in catchment monitoring programs (Deelstra *et al.*, 1998). In many cases the sampling strategy has to be adjusted to the dynamics involved in the loss processes thereby to avoid erroneous results. The losses of P, and to a lesser extend N, are typically event based, and depend on a combination of the prevailing geo-hydrological settings, climatological conditions and agricultural practices. The losses may vary greatly over relatively short time periods. In general one can differentiate between two sampling strategies being 1) grab or ‘point’ sampling and 2) volume proportional composite sampling. A combination of these two sampling techniques can occur, for instance point sampling during stable, low flow periods and volume proportional composite sampling during certain storm events.

Comparative studies of different sampling strategies in the Nordic countries revealed substantial differences in calculated loads depending on the method used (e.g. Rekolainen et al., 1991, Kronvang and Bruhn, 1996; Deelstra, 1996b; Deelstra, 1996a; Haraldsen, 2002). The general conclusion is that point sampling strategies tend to lead to erroneous estimates, particularly for the P losses. A Norwegian study (Eggestad *et al.*, 1994) compared weekly point sampling during one year with flow proportional sampling in five small catchments. Weekly or forth-nightly sampling resulted in severely underestimated loads (<10% of the 'true' figures for P as defined by the flow proportional sampling) as well as severe overestimates (more than twice the 'true' figure). The deviations of N were generally less than for P. One should, however, bear in mind the prevailing geohydrological conditions in the Norwegian catchments, with a low base flow component in the total runoff volume in addition to many event flow situations of rather short duration.

## 2.4 Measurements of diffuse nutrient losses in the Nordic/Baltic region

National programmes for monitoring nutrient losses from agricultural soils have a relatively short history in the Nordic-Baltic region. For example, such programmes were established in 1988 in Sweden, in 1989 in Denmark, and as late as 1992 in Norway. Finland has the longest tradition of monitoring agricultural losses, which was begun in 1962 in four agricultural streams. In Estonia, Latvia and Lithuania such programs were established in 1994/1995 through co-operation with Swedish and Norwegian research institutes. This has created scientific networks with mutual benefits concerning the understanding of the diffuse nutrient loss processes. Methodological aspects have played an important role in this co-operation. The emphasis on the harmonisation of methods concerning the measurement of nutrient loads from agriculture will be further strengthened through the implementation of the GEF/Baltic Sea Regional Project, and will apply to all Baltic States. A comparison of results from the Latvian and Estonian catchments with some of the results obtained in Norwegian catchments might be of interest. Figures 2.2 and 2.3 present the measured N losses (Total-N) and P losses (Total-P) in three Norwegian catchments, two Latvian catchments and one Estonian catchment, all characterised by cereal production and low-moderate animal densities. Weather conditions are rather similar, in terms of temperatures and mean annual precipitation (550–750 mm). Data cover the time period from 1994–1997.

Results show that both N and P losses are relatively high in the Norwegian catchments compared to the Estonian and Latvian catchments. This is also the case when compared with other Nordic countries. Annual mean N losses (Tot. N) in the Norwegian catchments ranged from around 20–45 kg ha$^{-1}$, whereas the P losses (Tot. P) ranged from around 0.4–1.5 kg ha$^{-1}$. N surpluses, defined as the difference between inputs (fertilisers, manure, atmospheric depositions) and outputs (yield withdrawals) showed only moderate variations between the Norwegian catchments (50–70 kg N ha$^{-1}$). There were no particularly good correlations between the measured losses and the N surpluses, although some tendencies (increased losses by increased surpluses) may be observed for time records of individual catchments (Bechmann *et al.*, 1998). Previous investigations indicated correlations only at very high surpluses, e.g. due to severe crop failures (Vagstad *et al.*, 1997).

It should be noticed that much higher losses were measured in two other Norwegian catchments, 70–80 kg N ha$^{-1}$ and 2.0–2.5 kg P ha$^{-1}$. However, these catchments were characterised by more complex crop rotation systems, whereas the annual precipitation was around 1000 mm yr$^{-1}$.

In contrast, N losses in the Baltic catchments were 6–15 kg ha$^{-1}$, whereas the P losses ranged from 0.07–0.4 kg ha$^{-1}$. These losses are substantially lower than the observed losses in Norway, and even lower than most of the observations in

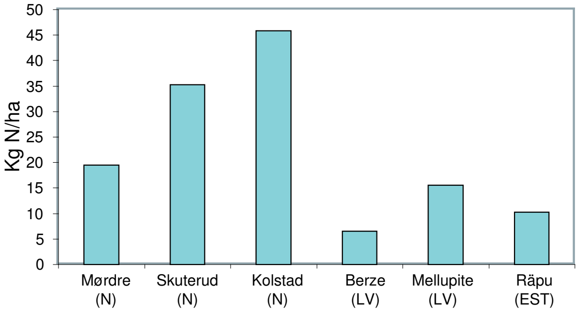

Figure 2.2: Measured N load in surface water from a few small agricultural catchments in Norway, Latvia and Estonia. Kg Tot.N $ha^{-1}$ agricultural land during 1994–1997.

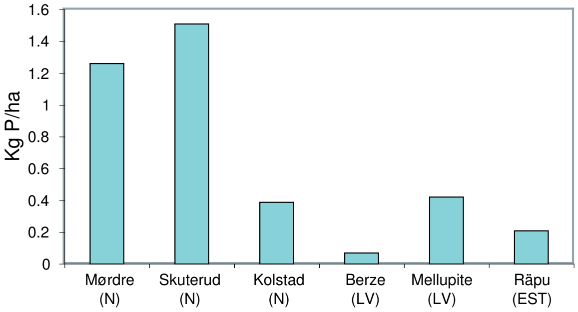

Figure 2.3: Measured P load in surface water from a few small agricultural catchments in Norway, Latvia and Estonia. Kg Tot.P $ha^{-1}$ agricultural land during 1994–1997.

other Nordic countries. At the same time, 10–20 times higher losses of both N and P were observed in some areas that belonged to industrialised, state-run pig farms during the Soviet era in Latvia.

The differences in N and P losses between the Norwegian catchments and the Estonian and Latvian catchments are too large to be explained simply by different management practices (generally larger fertiliser applications in the Norwegian catchments). Much higher soil erosion in the Norwegian catchments (Mørdre and Skuterud) is the main explanation for the differences in P losses. For N, however, the causes for the observed differences are probably much more complex. In short, it is suggested that a thorough look into the hydrological processes may be of great help in explaining these differences. The relation between fast flow processes and slow flow processes may be of particular interest. For N, the general conditions will be that the longer the water remains in the soil, the higher the potentials for e.g. denitrification. Denitrification and more or less temporal immobilisation of N may also occur in surface water channels, depending on e.g. flow velocity, easily available organic matter, vegetative growth, etc. Hydrograph recession analysis may give indications of water residence times in various catchments. The steeper the descending part of the hydrograph is (expressed by the recession coefficient), the faster the runoff response to a rainfall event. A comparative study of the Norwegian catchment on one side, and the Estonian and Latvian catchments on the other side, indicated significant differences with regard to recession coefficients (Deelstra *et al.*, 1998). There also appeared to be a rather good correlation between measured N losses and recession coefficients (Table 2.1).

One major cause of different recession coefficients may be different drainage intensities, being a result of different drain spacing with higher densities leading to higher discharge intensities during runoff events compared to lower intensities. The drain spacing in Norwegian clay soils is normally 6–10 meters whereas 18–32 meters is the normal range in the Baltic States. Another reason for the slower response in the Baltic catchments might be a larger contribution of groundwater flow in the runoff processes. It is obvious that denitrification processes as well as other N transformation processes in soil may be affected by these differences. It is a well known fact that significant nitrogen retention can occur in groundwater systems due to denitrification processes (Potsma *et al.*, 1991; Grant *et al.*, 1997). Moreover, measurements in sub-catchments, fields and tile drain collectors also indicate that nitrogen may be retained or immobilised in channels and streams in typical low-land areas in Latvia and Estonia. Nitrate concentrations at such sites were usually less than 60% as compared to the concentrations at the catchment outlet (Vagstad *et al.*, 1999). By having a system that is mainly characterised by fast flow processes (like most Norwegian catchments), relatively large

Table 2.1: Average N losses in kg ha$^{-1}$ in two Norwegian and in one Latvian and one Estonian catchment, and average hydrograph recession coefficients for the same period of measurements.

| Catchment | Average N losses, kg ha$^{-1}$ | Average recession coefficient |
|---|---|---|
| Skuterud (N) | 33 | 3.10 |
| Mørdre (N) | 20 | 1.54 |
| Berze (LV) | 12 | 0.77 |
| Rapu (EST) | 7 | 0.34 |

parts of the nutrients lost from the root zone will enter directly into the surface water. Under otherwise similar conditions may a system, mainly characterised by slow flow processes result in smaller inputs or loads to the receiving surface waters due to increased denitrification losses.

## 2.5 The management of diffuse agricultural pollution sources

The EC Directive 2000/60/EC (The Water Framework Directive) sets the scene for the future management of water resources at watershed level in Europe. It is basically action oriented, in terms of maintaining or, if necessary, improving the ecological status of the water resources. When dealing with diffuse agricultural sources, it is also necessary to consider the sustainability aspects related to agricultural production. One should bear in mind that the present agriculture to a large extent mirrors the market conditions for agricultural produces, and that socio-economic implications often are integrated effects of changes in the agricultural structures.

The management of the diffuse agricultural pollution sources must be based on the best possible knowledge being:

1. the documentation of the magnitude and variation in the 'true' nutrient losses obtained through appropriate monitoring techniques,
2. the understanding of the loss processes and how they are influenced by natural conditions (non-manageable factors) and farm practices (manageable factors), and finally
3. how farm practices can be adjusted to reduce these losses and at which costs.

In many cases the question of interest is not only reducing the losses, but also how to avoid increased losses. Especially the last aspect might well be the case in some areas of the Baltic States, provided increased agricultural activities occur due to increased activities in the Baltic economies.

One typical characteristic of the Baltic agriculture during the Soviet time was the rather low efficiency in crop production. The fertiliser use was at a typical Nordic level with N-applications varying from 100–120 kg N ha$^{-1}$ while crop yields were only about half (see Figure 2.4).

The plant nutrient management is of particular importance for the nutrient loss potentials, especially on animal farms. Balanced fertilisation, according to crop nutrient requirement, is an important measure to control the nutrient losses. But all measures that increase the efficiency in crop uptake of applied nutrients may also contribute to reduced losses (e.g. irrigation, corrections for micro-nutrient deficiencies, weed control). *In many cases, however, it is the handling of animal manure that represent the most critical issue in terms of nutrient management.* The animal manure is a valuable nutrient sources with high contents of N, P and K. It is therefore important

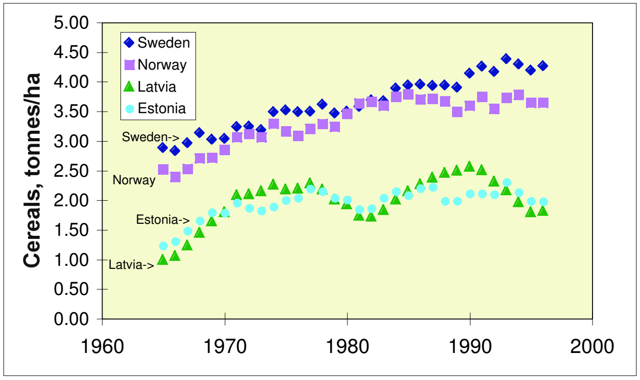

Figure 2.4: Crop yield development (total cereals in t ha$^{-1}$) in Estonia, Latvia, Sweden and Norway, 1960–1996. Sequential 5-year averages.

to enhance the recycling of these nutrients and to optimise its utilisation in agricultural production through proper collection and storage routines and through proper application methods. Inappropriate storage and application methods (e.g. winter application, too high amounts on a limited land area) may cause high losses of highly bio-available nitrogen and phosphorus, whereas the high contents of digestible organic matter may cause oxygen deficiencies in local recipients. A nutrient accounting system on field and farm level may be an important instrument in order to avoid excessive use of plant nutrients and resulting high nutrient losses. This system would need to take account of all available nutrients, in particular the animal manure, and adjust the application of commercial fertilisers in order to balance the total application to the crop nutrient requirements.

Another possible strategy for the reduction of the environmental effects of agriculture may be to modify the hydrology in transforming nutrients. Controlled drainage (Gillam & Skaggs, 1986) has proven to be an efficient measure in reducing nitrogen losses under certain conditions in the US. Low-land areas of the Baltic States may be well suited for this measure, in which ground water level during off-season periods is raised by blocking the subsurface drainage systems and thereby enhancing denitrification process. Ponds, constructed wetlands and buffer strips may also be useful measures that may significantly reduce the inputs of both N and P to surface waters.

In general, the management of diffuse nutrient losses has to take into account the complexity in the cause-effect relationships between the loss processes and the ameliorating factors. Measures must be site-specific, i.e. adjusted to the local conditions regarding soils, agricultural practices and the geo-hydrological setting. A clear understanding of the field and catchment hydrology especially concerning the pathways of nutrients from the soil profile to the receiving waters is needed. Bearing in mind the reduction targets as defined by e.g. HELCOM and OSPAR (50% reduction of nutrient inputs to the sea), the implications can be different under different hydrological situations. When having a system, mainly characterised by fast flow processes, a reduction in root zone losses can result in an immediate reduction of the nutrient input to the surface water. On the other hand, with a system mainly characterised by slow flow processes, even significant reductions in root zone losses may pass unnoticed by the time the water reaches the outlet stream of the catchment.

Considering the time scale involved in the transport processes, this also suggests that a long-term perspective has to be applied in the management of the diffuse agricultural pollution sources.

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# Chapter 3

# Supply of nutrients by rivers and point sources to the coastal zone

Per Stålnacke
Norwegian Institute for Water Research (NIVA)
Brekkeveien 19
P.O.Box 173, Kjelsaas
N-0411 Oslo, Norway
www.niva.no
per.stalnacke@niva.no

## 3.1 Introduction

The management of inland landscapes and freshwater resources is a key determinant of coastal zone water quality. Observations of water quality in many parts of the world indicate that river loadings of biotically active elements have increased several fold since the beginning of the Industrial Era. Water monitoring in numerous individual river basins and coastal zone areas have connected these excessive levels of river borne nutrients and associated shifts in nutrient ratios to shifts in nutrient limitations, coastal and freshwater eutrophication, toxic phytoplankton blooms, and bottom-water hypoxia. Nitrogen and phosphorus transported with rivers from land to sea have been reported to be the major sources contributing to the eutrophication of e.g. the Baltic Sea. Nutrient loadings associated with human population growth and economic development are now important contributors to riverine fluxes of nutrients to the coastal zone. In order to gain a clear understanding of the impact of these changes in nutrient loading, a thorough survey of the point source (i.e. industrial waste water and sewage waste water) and non-point source (i.e. inputs from agriculture, logging, construction, and atmospheric deposition) inputs must be available. Despite the importance of land-coastal zone interactions, we currently lack a consistent system for monitoring and assessing the dimensions of such change at anything but the local scale.

Agricultural and urban land use has increased the fluxes of nutrients and sediments into surface waters and ground waters. To promote the long-term sustainability of natural and managed watersheds, fundamental processes that control water quality on a watershed scale need to be investigated. Scientific results clearly indicate that monitoring programs that try to determine long term trends of basin scale nutrient fluxes require high resolution data sets.

Control of the emissions and fluxes of nutrients has for many decades been regarded as one of the most urgent environmental protection issues in e.g. the Baltic Sea Region. *Phosphorus (P) and nitrogen (N) are key elements of many biogeochemical processes and are regarded as limiting elements of aquatic and terrestrial ecosystem processes and are one of the basic chemical constituents in surface waters.* Excessive emissions of nutrients to water bodies have been found to significantly accelerate the otherwise natural process of eutrophication, e.g., development of blue-green algae and oxygen depletion.

It is well known that the dynamics of nutrient emissions and fluxes in catchments is complicated and entails great temporal and spatial variability, and which makes it difficult to empirically derive simple cause and effect relationships. In addition, it is widely accepted that nutrient concentrations also depend on factors such as the following: flow conditions; hydrological pathways; the occurrence of other nutrients or micronutrients; bioavialability; processes such as mineralisation, immobilisation and denitrification; and the ratio between N and P. However, little is known about the relative importance of, and the interactions between, these factors in time and space.

In this chapter, I describe typical characeristics and features of the waterborne fluxes of nutrients in river basins. More precisey, the following issues are covered:

- an overview on our scientific knowledge about long-term trends of riverine nutrient loads;
- the impact of different sources on and retention of the transport of nutrients at the mouths of the rivers;
- the controllability of riverine loads of nutrients.

Examples from Baltic Sea rivers are used for illustrative purposes. The annex 3.A in the end of the chapter gives further details regarding the Baltic Sea rivers and its drainage basin.

## 3.2 Long-term changes in nutrient loads

It has already been pointed out in several articles that prevailing weather conditions often cause natural fluctuations in time series of nutrient concentration values, and this may impede the detection of existing trends. Furthermore, a number of studies have shown that the level of nitrogen losses in individual years is influenced primarily by *variations in precipitation and water discharge*. Nutrient losses are also affected by changes in *crop yields*, which, in turn, are largely influenced by the weather conditions. Current hydrometeorological conditions other than water discharge can have an impact on phosphorus losses. For example, a study in Estonia and found that 20 times more phosphate phosphorus was released from frozen soils than in thawed soils. Accordingly, during periods including several mild winters, it could be expected that losses will either be increased due to an elevated risk of soil erosion, or be lowered due to less freezing out of plant residues, especially on grassland. In both cases, a detected trend might be falsely interpreted as being the result of changes in agricultural practices.

In a frequently cited study, Larsson and coworkers (1985) reported that the total input of phosphorus to the Baltic Sea may have increased as much as ten times from the turn of the century to the 1980s, and they also claimed that the input of nitrogen may have increased about four times during the same period of time. Unfortunately, it is difficult to determine the exact size of the rise in nutrient loads due to uncertainty regarding the natural background concentrations and the impact of old agricultural practices. Nevertheless, it is indisputable that the present input of nutrients to the Baltic Sea by far exceeds the natural loading, and a more detailed discussion is needed to clarify the matter of when the major increases began.

Let us first consider the past few decades, during which time the national water quality monitoring programs have covered a substantial part

Figure 3.1: The Narva River, a typical Baltic Sea river. Photo: Per Stålnacke, Jordforsk.

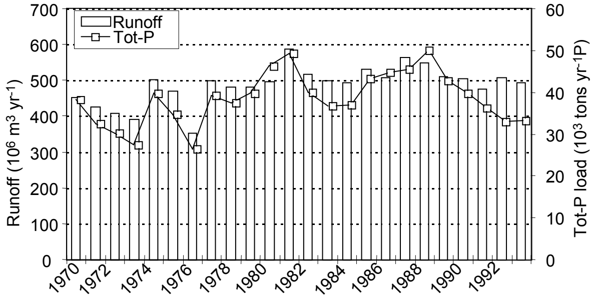

Figure 3.2: Annual riverine input of water, nitrogen and phophorus to the Baltic Sea. Source Grimvall & Stålnacke 2001.

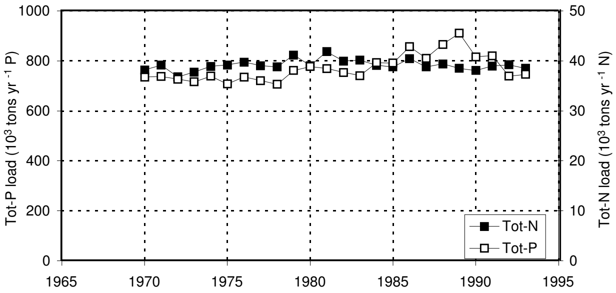

Figure 3.3: Flow-normalised input of nitrogen and phosphorus from rivers to the Baltic Sea. Source Grimvall & Stålnacke 2001.

of the Baltic Sea drainage basin. The graphs in Figure 3.2 include the period 1970 to 1993 and show our estimates of the annual riverine input of nutrients to the Baltic Sea as well as the in the area. As can be seen, the average input of both nutrients and water was slightly higher in the 1980s than in the 1970s. In addition, it is obvious that there is a strong correlation between the interannual variation in the nutrient loads and the runoff. Closer examination of the data showed that the *input of nitrogen became practically constant* when we normalized the estimated values to represent an average input of water to each of the main basins of the Baltic Sea (see Figure 3.3). Flow normalization of *phosphorus had a similar effect*, and the only temporal changes worth mentioning are a small increase in the 1980s and a minor decrease in the early 1990s.

The longest time series with consistent water quality data for periods up to half a century exist in only a couple of rivers. The graphs in Figure 3.4 show annual flow-weighted mean values of nitrate and phosphate at Lobith on the Rhine River, near the border between Germany and the Netherlands. As can be seen, *the nitrate concentration approximately tripled from the early 1950s to 1980.* The phosphate concentration at

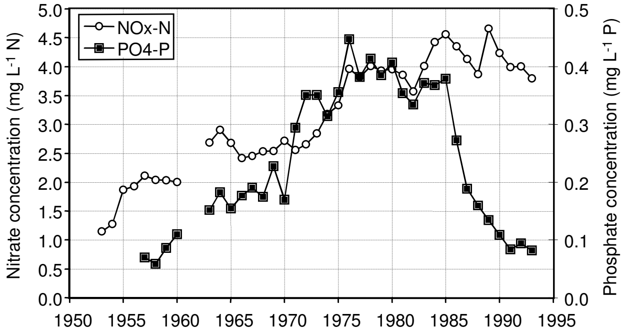

Figure 3.4: Annual flow-weighted mean concentrations of $NO_3$-N and $PO_4$-P at Lobith on the Rhine. Sources: van Dijk, G.M., Stålnacke, P., Grimvall, A., Tonderski, A., Sundblad, K., Schäfer, K. 1996, and Netherlands Institute for Inland Water Management and Wastewater Treatment (RIZA).

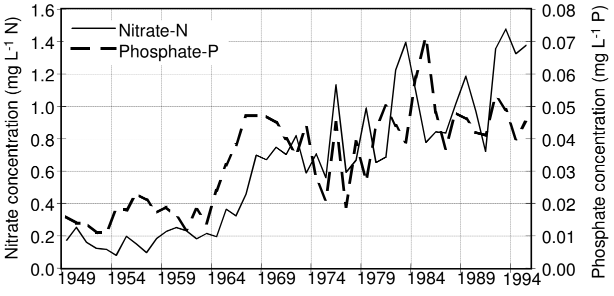

Figure 3.5: Flow-weighted annual concentrations of nitrate-N and phosphate-P at Daugavpils on the Daugava river 1949–1995. Source: Latvian Hydrometeorolgical Agency.

the same site increased about fivefold from the late 1950s to 1980, when a massive action programme curbed the upward trend and turned it into a decrease. The time series of phosphate data from the Rhine RiverFigure 3.4 shows a very dramatic decrease in the mid 1980s, when *several major point emissions of phosphorus were practically eliminated and phosphorus-containing detergents were phased out.* Over less than a decade, the phosphate concentration in the river dropped from a very high level to the values that had prevailed in the 1950s. The measurements in the Daugava River appear to represent the longest series of nutrient concentrations data available for the Baltic Sea drainage basins. As can be seen in Figure 3.5, the nitrate concentration in this river increased during the post-war period, and the critical decade was the 1960s. This is a decade later than in the Lower Rhine, for example.

Extending the time scale to a century or more provides mainly indirect information regarding nutrient trends in the rivers. Some of this information indicates that *considerable changes in water quality may already have occurred in the 19th century*, because, during that period in history, sewage emissions increased due to *urbanization, and expanded tilling and ditching favored erosion and leaching processes.* Studies of lake sediments have demonstrated that the loss of phosphorus increased long before commercial fertilizers became widely used.

Furthermore, both model calculations and the classical Rothamsted experiments show that older agricultural practices also resulted in substantial export of nitrogen to water. *Notwithstanding, it is completely clear that the turnover of nutrients in the environment has accelerated since World War II, in particular due to increased use of commercial fertilizers, changes in the agricultural landscape and the formation of $NO_x$ in combustion processes.*

## 3.3 Nutrient sources and retention

Since, loads in rivers normally are well documented, accurate and precise estimations of emissions from various sources (i.e. source apportionment) are a prerequiste for our understanding and our ability to control nutrient fluxes. Source apportionment has normally been performed through inventories of point and diffuse sources. Point source emissions are normally easy to obtain directly from monitoring data from municipal wastewater treatment plants (WWTP) or indirectly from *per-capita emission coefficients.* For example, by assumptions that humans excrete 4.4 kg N $yr^{-1}$ per person combined with information of the purification in WWTP, e.g. by assuming a per capita nitrogen load in wastewater of 3.3 kg N yr$^{-1}$ per person. Areal nutrient leakage from diffuse sources is normally more problematic but can be estimated from emission coefficients for different land use categories obtained from plot or field experiments or through modelling of the upper soil layer. Geographical Information Systems (GIS) are often used to perform regional assessments. Alternatively, source apportionment may be based on *statistical analysis* of observed river nutrient loads (i.e., transport) and explanatory variables (i.e., factors explaining variability in loads between sites or in time). This methodology can be divided into two categories: *regression analysis* between observed concentration and water discharge, and regression analysis between observed load and watershed characteristics (see e.g Alexander et al., 2000). Recently another alternative of source apportionment has become available because dynamic process based models have been successfully applied in large watersheds. *Dynamic models,* which conceptually describe all physical, chemical and biological processes, aim to simulate time series of nutrient transport at the root-zone or in first-order or second-order streams. Source apportionment is a parallel result even if the main purpose of these models is usually prediction or better understanding of processes. For large-scale water management, all the above mentioned methods are potential tools that give results of different temporal and spatial scales. The different methods, however, also have a large variety of input demands in the form of data and work. For decision makers and scientists faced with a specific water management problem, it is therefore essential to choose methods that meet the often limited available input data, gives the wanted results, and is economically feasible. Unfortunately, comparable studies of different methods and models for nitrogen source apportionment are scarce. Model applications are often performed and described for specific watersheds, where other models have not been applied. Continuous changes in land use and agricultural practices also prevent fair comparison, even if models are applied in the same watersheds but on different occasions.

*Monitoring of nutrients* is important for the identification of emissions sources, e.g. from various land use categories, municipal wastewater and septic systems. Therefore, planning of actions for water protection measures require an understanding of the forces that drive different nutrient transformation processes in soils, ground waters, streams and rivers. However, the efficiency of source control measures in rivers depends not only on the quantification of the load, sources and loss of nutrients in the soils, groundwater and river network. This is due to the fact that the total sum of emissions of nutrients to surface waters in a river basin is normally larger than the nutrient load at the river mouth. *Retention is a collective and lumped expression for a large number of biogeochemical and hydrological processes that temporarily decrease, decay, degrade, transform, or permanently retard or remove the substance from a river basin.* Nutrient retention capacity in the subbasin is dependent from various factors: trophic status, depth of the waterbody, water residence time, ratio of lake area to the catchment area, nitrogen loading, loading of organic matter, denitrification activity (primarily dependent on sufficient amounts of reducable organic substrates, low oxygen concentrations and high temperature). Nutrient retention processes in rivers and in their drainage basins could therefore be of significance against increased nutrient loads to the maritime waters. Consequently *retention processes/potentials and buffering capacities in river basins should also be considered and be an integrated part when planning water protection measures and strategies.* In practise, policy implementation and remediation have been hampered by a substantial uncertainty involved in assessment of the contribution different sources made to the riverine transport of N and P. This has for example been observed in the Baltic Sea region. The importance of taking retention into account when estimating the contribution of nutrients from non-point and point sources have been emphasises in numerous studies. However, many studies on a global, regional and national scale are marred by defectives about the relative importance of retention when estimating the quantity reaching the sea from different sources: see e.g. the classical work by Howarth (1996). *Nutrient retention is normally defined as the amount of nutrients that is biogeochemically transformed or retarded* (temporarily or permanently). It is traditionally divided into:

- sedimentation or settling of particle-bound nutrients (N and P);
- uptake and storage of nutrients by plankton, macrophytes and fish (N and P);
- biochemical cycling between different forms that finally may lead to disappearance from the river system via denitrification (N).

Retention in river basins, and in particular retention in streams, rivers and lakes, are of great importance when using a mass balance approach to assess nutrient sources and retention on regional or national level. Estimates of nutrient delivery from various sources will obviously be affected by permanent or temporary retention. The retention potential at a river and drainage basin scale has in literature been given considerable attention. *Nitrate and phosphorus in particular is usually subject to substantial retention.* However, N and P-retention are highly variable in time and space and could range between 0% and 100% depending on the flow paths and water course character (e.g. presence of lakes in a drainage basin). *In Sweden, the N-retention from the root-zone to the coastal sea has been estimated to 48%.* In Vistula and Oder, nitrogen retention has been estimated to ˜ 50% and 30%, respectively, while the corresponding estimates for phosphorus were in the range 25–30%. These examples clearly illustrate the great range in various retention estimates.

Besides retention in the main stream of a river, in smaller channels and streams, in lakes and reservoirs there can be retention in the terrestrial part of the river basin: in the topsoil, in the root-zone, and in deeper soil layers and groundwater. For instance, may N be lost from the soils via denitrification in the case of anaerobic conditions, an organic carbon source and high temperature. In addition, wet soils in combination with high pH may cause significant gaseous losses of N through ammonia volatilisation (and thereby reduced leaching losses). Even though the biogeochemical and physical processes have been extensively studied on an experimental scale and even on the scale of small catchments, there are yet very few studies that have attempted to examine the significance of these processes on a large river-basin scale (Billen *et al.*, 1994). *Retention processes could also be one reason for the rather weak water quality response to the dramatic decline in industrial and agricultural production in the Baltic States after the independence (Grimvall & Stålnacke, 2001).* Another aspect of retention is related to the balance between various substances. For example, may reduced emissions of phosphorus and organic matter (e.g. due to installation of sewage treatment plants), under certain conditions, reduce the denitrification capacity in rivers and thus increase the load of nitrogen on maritime areas.

To conclude: even though detailed knowledge about processes and mechanisms related to self-purification and retention of nutrients are relatively well-known, still a lot of research on the governing factors for retention of nutrients at catchment/river basin scale are needed. The quantification of retention is regarded of particular challenge.

## 3.4 Controllability of riverine loads of nutrients

There is a widespread conception that it is relatively easy to control riverine loads of phosphorus. Point emissions often play a major role in the most severe cases of river pollution, and efficient techniques for removal of phosphorus can be introduced in existing wastewater treatment systems. The rehabilitation of the Rhine River Figure 3.4 provides a striking example of how successful such measures can be. When several major point emissions of phosphorus to this river were practically eliminated and phosphorus-containing detergents were phased out in the 1980s, *it took* *less than a decade for the phosphate concentration in the Lower Rhine to reach the much lower level that had prevailed in the 1950s.* The results of almost daily measurements in the Odense River in Denmark illustrate more moderate decreases in phosphorus that have been observed in some rivers leading to the Baltic Sea. As can be seen in Figure 3.6, a downward trend prevailed in 1987–1991, and thereafter the phosphate concentration leveled out. Furthermore, the decrease was accompanied by a significant shift in the relationship between concentration and flow: the concentration peaks that previously appeared during low-flow conditions have been practically absent since 1992, which indicates that the present riverine loads are dominated by non-point sources. It is also noteworthy that the amounts of phosphate leveled out at values exceeding 0.05 mg L$^{-1}$, which is much higher than the natural background concentration. Hence, it seems to be comparatively easy to reduce phosphorus from high to moderate concentrations, whereas further reduction is a more difficult and time-consuming task.

Observations in the lake-rich Motala River Basin in Sweden (Figure 3.7) provide a thought-provoking example of the inertia of the systems that control the transport of phosphorus with rivers. In the mid 1970s, tertiary treatment was introduced at all major wastewater treatment plants in this basin, and the total point emissions of phosphorus in the study area dropped by almost 200 tons yr$^{-1}$ to less than 10% of the previous level. In spite of that, the flow-normalized transport of phosphorus at the river mouth has remained at about 100 tons yr$^{-1}$ for at least 20 years.

*The recent dramatic decrease in the use of mineral fertilizers in Eastern Europe has created new possibilities to test hypotheses regarding large-scale fluxes of nitrogen in the Baltic Sea drainage basin.* Thus far, studies of small catchments in Estonia have provided clear evidence of downward trends in the output of nitrate with water. In contrast, it is remarkable that no trends have appeared in several major rivers entering the Baltic Sea. Statistical trend assessments of nutrient loads carried by the Daugava and other Latvian rivers showed that most of the interannual variation could be attributed to natural changes in runoff (Laznik *et al.*, 1999). Moreover, a similar study of the Oder and Vistula Rivers in Poland revealed that the flow-normalized loads remained practically constant from 1989 to 1995.

There are several possible resons for the lack of downward trends in the mentioned rivers. Organic nitrogen accumulated in soil during periods of more extensive use of fertilizers may continue to be an important source of nitrate in agricultural runoff for quite some time. Another plausible explanation is the retention of nitrogen in large groundwater aquifers.

## 3.5 Other abatement measures and future perspectives

Up to 90% of the total flow in a river, is derived from the first and second order streams, also termed headwaters. The control of river-water quality and subsequent retention in these headwaters could therefore be seen as a priority. In addition, once the river water is 'contaminated' there is very little possibility of the in-stream nutrient retention processes operating to control river-water quality further downstream, at least when lakes and other impoundments are absent. *When it comes to possible abatement strategies one must distinguish between measures at source and measures at transport.* Wetlands and buffer zones, e.g., riparian strips along agricultural fields or streams, may be regarded as an intermediate between measure at source and measure at transport.

*Wetlands is a lumped concept that includes bogs, mires, marshes, floating meadows, and ponds.* There has been a great interest in constructed wetlands for wastewater treatment and for reduction of non-point-source pollution. However, the influence of wetlands on natural North European condition has been questioned, as high hydraulic loads result in short residence time and most of the transport occur in late autumn and early spring when biochemical activity is low. In

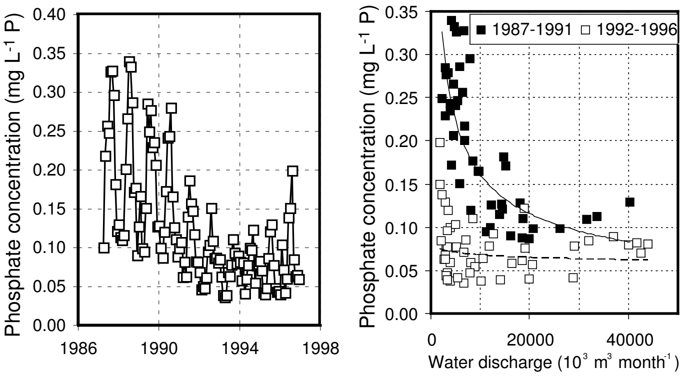

Figure 3.6: Monthly flow-weighted mean concentrations of $PO_4$-P at Kratholm on the Odense River: a) time series plot; b) scatter chart of concentration vs discharge. Source of raw data: County Board of Funen, Denmark.

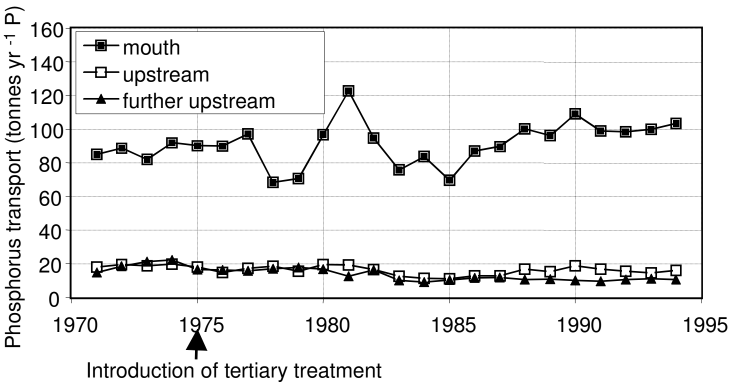

Figure 3.7: Annual phosphorus transports at three sites in the Motala River Basin in Sweden. Tertiary treatment was introduced around 1975 at all major municipal treatment plants located between the sampling sites at Motala and Norrköping. Source: Grimvall & Stålnacke (2001).

Figure 3.8: A constructed wetland in the agricultural landscape. Photo: Bent Braskerud, Jordforsk.

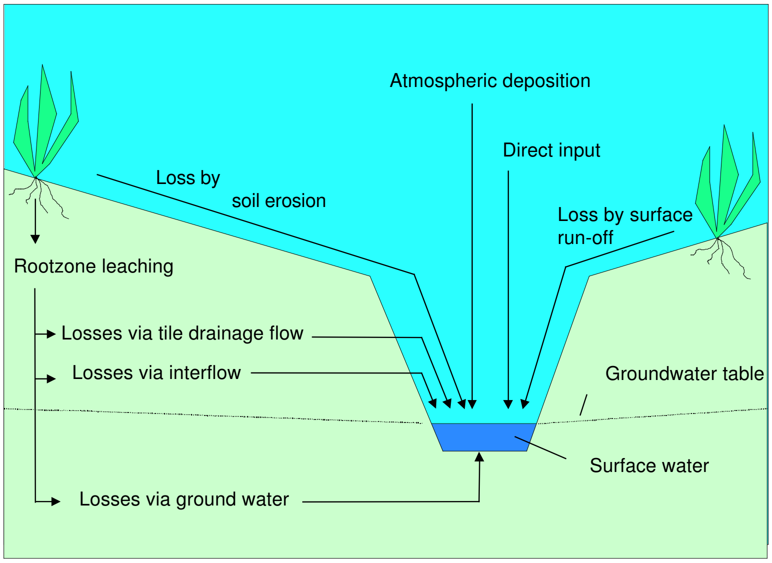

Figure 3.9: The most important "hydrological" processes/pathways as regards nitrogen and phosphorus losses from diffuse sources to surface waters (e.g. first-order streams. Source: Borgvang, S-A. and Selvik, J.R. (Eds.). 2000. Development of HARP Guidelines — Harmonised Quantification and Reporting Procedure for Nutrients. SFT Report 1759/2000. ISBN 82-7655-401-6. 179 pp.).

one river basin in southeastern Sweden, it was estimated by model calculations that conversion of 1% of the basin into wetlands would reduce the nitrogen transport by 10–16% and that more than 5% conversion to wetlands is required to reduce the transport by 50% (Arheimer, 1998). It is generally accepted that small wetlands remove less nitrogen than lakes due to the lower water residence times. Small constructed wetlands (CWs) in first and second order are widely used in Sweden and Denmark to mitigate fluxes of soil particles and nutrients from agricultural watersheds. In Norway, Braskerud (2001) found a N and P-retention of 3–15% and 20–44% in four CWs. The high hydraulic loads and low temperatures explained the low N-removal. In natural wetlands in the landscape, studies have shown that they may be a source rather than a sink. Grimvall & Stålnacke (1996) and Arheimer (1998) showed that wetlands (i.e. mires and peat bogs, respectively) in S Sweden delivered N, and Lidén et al (1999) showed similar results for the wetlands in the Kasari River in Estonia.

*It is generally accepted and uncontroversial that buffer zones has large potential to control water pollutants due to sedimentation, plant uptake, and retention in soil and microbial processes.* On the other hand, the heterogeneity in terms of soils, biogeochemistry and water pathways are complicated and the understanding of the mechanisms controlling buffer zones are less known. Moreover, results on actual retention potential are controversial since both low and high retention is reported in literature.

Snowmelt runoff can also hamper the retention effect in buffer zones and wetlands, due to its considerable amount combined with low soil and water temperature leading to increased risk of low uptake by vegetation or algae and low denitrification. Information regarding the fate of N in buffer zones during such circumstances are limited, even though recent studies has shown that retention can be high in wetlands and in buffer strips exposed to surface runoff.

Furthermore, retention in buffer strips and wetlands may also be limited by (i) the organic carbon availability, (ii) soil moisture content, (iii) the residence time for groundwater or surface water and (iv) hydrological routing and pathways hydrological routing and pathways (Figure 3.9). The latter is one of the key issues to determine, e.g. the hydrological flow-path through the buffer zone, since surface water always take the shortest and easiest route even in flat landscapes. And in case lateral flow dominate, i.e passage via tile drains, groundwater or interflow (Figure 3.9) wetlands and buffer strips may be less effective. It is also important to distinguish between retention due to vegetation uptake (storage) and denitrification (bacterial transport and gaseous loss processes). Haycock et al., (1997) indicated that denitrification is the dominant retention process in buffer zones during the dormant season when soil moisture content is high, while N uptake by vegetation dominates during the summer and growing season.

*To conclude, the establishment of wetlands and buffer zones next to or in streams and rivers does not guarantee high nutrient removal.* Construction of riparian buffer zones is primarily a question of setting aside land which in turn is a political and economical issue, e.g. in terms of political demand for food production, and less an ecological issue. It is generally accepted that *changes in management practices rarely lead to rapid large-scale changes in nutrient losses to water recipients.* One important reason is the buffering capacity of agricultural soils and the retention capacity of the agricultural landscape. Another reason is that management practices usually do not change very fast, although they did in the Baltic states. *After all, nutrient losses are unavoidable processes, and can be influenced by field operations only to a certain extent.* When the feasibility of reducing the input of nutrients to seas is discussed, the retention of nitrogen and phosphorus in the drainage area must also be taken into account. For example, considerable retention may - besides the surface waters itself- aslo take place in the soil column and in groundwater aquifers (see Section 4). A short-term measure might be to establish grassland/pasture or plant marketable industrial crops to reduce the nutrient losses by leaching of mineralised N or P in surface runoff from unprotected soils. A long-term measure might be to plant forest (or energy forest).

## 3.6 Concluding remarks

Together, the examples used to illustrate the controllability of riverine loads of nutrients have drawn attention to the role of long-term processes and hydrological pathways. Although it is often easy to reduce very high concentrations and loads to more moderate levels, it may take decades to achieve further reduction. In addition, successful abatement of riverine nutrient pollution of the Baltic Sea will probably require coordinated control of both phosphorus and nitrogen emissions.

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# Appendix 3.A

## The Baltic Sea drainage basin and rivers

The total area of the Baltic Sea drainage basin (Fig. 3.10) is 1,745,136 km$^2$, and the annual inflow of freshwater with the rivers is 475 km$^3$ yr$^{-1}$, which corresponds to 15,130 m$^3$ s$^{-1}$. In Sweden and Finland, there are several medium-sized rivers, whereas a few large rivers dominate in the southern and eastern parts of the Baltic Sea drainage basin. Together, the ten largest river basins (Neva, Vistula, Daugava, Neman, Oder, Kemijoki, Göta, Ångermanälven, Lule, Indalsälven) cover 56% of the total drainage area and contribute 52% of the total freshwater input to the Baltic Sea (Table 3.B). It is also noteworthy that the five largest lakes in Europe (Ladoga, Onega, Vänern, Peipus and Vättern) are all located in the drainage basin of the Baltic Sea.

There is a large spatial variation in specific runoff: the highest values (i.e. up to 15 L s$^{-1}$ km$^2$) have been recorded in the mountain regions of northwestern Sweden and the lowest values (approximately 5 L s$^{-1}$ km$^2$) in the Polish and German parts of the drainage basin. A majority of the rivers normally have a pronounced flow peak during snowmelt in spring. This is particularly true for the rivers in northern Sweden and Finland and the major rivers in the eastern parts of the drainage basin. Dams constructed to level out seasonal variation in riverflow are primarily found in northern and central Sweden, and the lowest level in regualtion capacity is found in four of the ten largest rivers in the area, i.e. the Daugava, Neman, Vistula and Oder Rivers. Further details regarding hydrology can be found in an article by Bergström and Carlsson (1994).

Considered in its entirety, the Baltic Sea drainage area is dominated mainly by forests and to a somewhat lesser extent by arable land (Fig. 3.11), although there are substantial differences among sub-basins. In the drainage basin of the Gulf of Bothnia, for example, arable land and pasture accounts for about 5% of the area, whereas the same land-cover categories make up about 50% of the drainage basin of the Baltic proper. *Poland alone accounts for about 40% of the arable land in the whole Baltic Sea drainage basin.* The bedrock in the Nordic countries consists primarily of species of granites and gneisses, whereas sedimentary bedrocks dominate in the southern and eastern part of the drainage basin. The Baltic Sea drainage basin has about 85 million inhabitants; the highest population density is found in the southern parts of the basin, and Poland alone accounts for about 45% of the total population. Most of the largest cities are located on the coast, and the largest inland cities are located in the Neman, Vistula and Oder Basins.

Rivers play a crucial role in the total input of nutrients to the Baltic Sea. Several studies have indicated that nutrient delivery along this route may exceed the combined contribution from atmospheric deposition on the sea, point emissions along the coast, and nitrogen fixation by marine organisms. There are also strong indications that the riverine loads of nutrients have increased dramatically over the past century. However, data regarding the historical development of nutrient loading of the Baltic Sea are uncertain, and even loading during the past few years has been a matter of controversy.

## Appendix 3.B

Time-averaged runoff and riverine export of $NO_3$-N, total-N, $PO_4$-P and total-P to the major sub-basins of the Baltic Sea. The selected rivers are the ten largest in the Baltic Sea drainage basin. Study period: 1980-1993. Source: Stålnacke, P., Grimvall, A., Sundblad, K. and Tonderski, A. 1999. Estimation of riverine loads of nitrogen and phosphorus to the Baltic Sea, 1970-1993. Environmental Monitoring and Assessment 58: 173-200.

| Baltic Sea sub-basin/river | Runoff $10^9$ m$^3$ yr$^{-1}$ | $NO_3$-N tonnes yr$^{-1}$ | total-N tonnes yr$^{-1}$ | $PO_4$-P t yr$^{-1}$ | total-P tonnes yr$^{-1}$ |
|---|---|---|---|---|---|
| Gulf of Bothnia | | | | | |
| Kemijoki | 18.9 | 1 100 | 6 900 | 140 | 420 |
| Lule R. | 16.7 | 560 | 3 300 | 40 | 180 |
| Ångermanälven R. | 17.1 | 890 | 4 650 | 35 | 200 |
| Indalsälven R. | 15.3 | 1 390 | 4 540 | 25 | 140 |
| Other monitored rivers | 11.5 | 15 980 | 60 250 | 1020 | 3250 |
| Non-monitored rivers | 24.3 | 7 960 | 20 750 | 610 | 1 220 |
| Subtotal | 103.8 | 27 880 | 100 390 | 1870 | 5 400 |
| Gulf of Finland | | | | | |
| Neva R. | 81.7 | 21 260 | 55 590 | 1 200 | 3 210 |
| Narva R. | 14.3 | 4 010 | 26 400 | 290 | 750 |
| Other monitored rivers | 18.5 | 11 830 | 17 110 | 550 | 660 |
| Non-monitored rivers | 7.7 | 8 620 | 26 870 | 560 | 1 510 |
| Subtotal | 122.2 | 45 720 | 125 970 | 2 600 | 6 130 |
| Gulf of Riga | | | | | |
| Daugava R. | 23.3 | 28 680 | 70 130 | 970 | 1 330 |
| Other monitored rivers | 9.7 | 21 480 | 35 940 | 450 | 670 |
| Non-monitored rivers | 3.3 | 4 120 | 7 160 | 90 | 240 |
| Subtotal | 36.3 | 54 280 | 113 230 | 1 510 | 2 240 |
| Baltic proper | | | | | |
| Neman R. | 20.5 | 31 650 | 58 3401 | 4 140 | 5 410 |
| Vistula R. | 32.4 | 59 280 | 119 080 | 3 570 | 5 510 |
| Oder R. | 16.3 | 41 900 | 71 430 | 2 510 | 6 630 |
| Other monitored rivers | 19.9 | 18 760 | 36 430 | 900 | 1 340 |
| Non-monitored rivers | 23.9 | 41 410 | 77 740 | 2 100 | 4 300 |
| Subtotal | 113.0 | 193 000 | 363 020 | 13 220 | 23 190 |
| Western Baltic | | | | | |
| Göta R. | 18.0 | 10 080 | 16 250 | 60 | 300 |
| Other monitored rivers | 11.4 | 47 620 | 57 210 | 880 | 1 860 |
| Non-monitored rivers | 8.0 | 38 980 | 49 830 | 1 110 | 2 040 |
| Subtotal | 37.4 | 96 680 | 123 290 | 2 050 | 4 200 |
| Total Baltic Sea | 412.7 | 417 560 | 825 900 | 21 250 | 41 160 |

# Appendix 3.C

Figure 3.10: The Baltic Sea drainage basin and its major sub-basins and rivers. Source: http://maps.grida.no/baltic/

## Appendix 3.D

Figure 3.11: Landcover of the Baltic Sea drainage basin. Source: Sweitzer, J., Langaas, S. and Folke, C. 1996. Land cover and population density in the Baltic Sea drainage basin: a GIS database. Ambio 25:191-198.

# Chapter 4

# Coastal Nutrient Inputs from Groundwater: Case Studies from the East Coast of the United States

Matthew Schwartz
University of Edinburgh
School of Geosciences
The Kings Buildings
West Mains Road
Edinburgh EH9 3JW, UK
Matt.Schwartz@ed.ac.uk

## 4.1 Introduction

Non-point source nutrient fluxes are a growing issue in the assessment of coastal ocean and estuarine biogeochemistry. Surface water discharge has long been recognized as an important source of dissolved compounds, including nutrients, to the coastal zone and the transport of river-borne dissolved constituents continues to be a well-studied realm of environmental science (Maybeck, 1982; Berner & Berner, 1987). River discharge has been gauged for centuries and long-term studies have been performed to assess the chemistry of fluvial discharge and its biogeochemical impact on estuarine and coastal ocean waters (e.g., Maybeck, 1982; Sharp *et al.*, 1986; Pennock, 1987; Cifuentes *et al.*, 1990; Lebo *et al.*, 1994). More recently, environmental regulators and researchers have come to recognize the importance of non-point source discharges, including land surface runoff and atmospheric deposition of dissolved and aerosol compounds (Paerl, 1997). As has been discussed elsewhere in this text, both fluvial dischargeChapter 3 and non-point source discharges from atmosphereChapter 1 and play an agricultureChapter 2 important role in nutrient fluxes to the coastal zone.

In recent decades, researchers have begun to turn attention to an underground path to the coastal oceans: *submarine groundwater discharge*. Submarine freshwater springs in the coastal ocean were used as sources of potable water for sailors and coastal residents alike for at least 2,000 years Kohout (1966). Originally considered a novel process, limited to the existence of occasional springs, it has taken some time for the true extent of coastal groundwater discharge to be recognized. *In research initiated over the past 25 years, we are becoming aware of the fact that groundwater inputs account for a significant portion of the water and chemical flux to the coastal zone.*

The role of groundwater transport has gained increasing attention in both marine (Dahm *et al.*, 1998) and freshwater (Church, 1996) aquatic research, particularly in light of research showing considerable groundwater fluxes directly to estuaries and the coastal ocean (e.g., Cable *et al.*, 1996; Moore, 1996). The use of new groundwater tracers and the expansion of the scope of submarine groundwater discharge research has led to the still-growing realization that the direct discharge of groundwater to coastal zones is not a novel process, but, does indeed occur "anywhere that an aquifer . . . is connected hydraulically with the sea through permeable bottom sediments and the [potentiometric] head is above sea level" (Johannes, 1980).

## 4.2 Submarine Groundwater Discharge: Processes

### 4.2.1 Water transport via SGD

The term 'submarine groundwater discharge' (SGD) commonly refers to the exchange of terrestrially-derived groundwater with fresh, estuarine, and coastal waters (though Burnett *et al.*, 2003 correctly point out that SGD can also include wave pumping and other processes that involve the flushing of sediments that are saturated with surface water). *Groundwater will flow within an aquifer if there is a potentiometric head between the aquifer recharge zone and the discharge zone; that is, water will flow 'downhill' even when present in the pores of sedimentary material.*

When an aquifer's discharge zone intersects with porous bottom sediments in the coastal zone, groundwater will flow into the coastal ocean (or estuary) as SGD (Figure 4.1). Unconfined aquifers will interact with the seawater-saturated sediments and create a restricted, and often diffuse, *zone of SGD that is typically within 100–200 m from the coast* (Taniguchi *et al.*, 2002). As illustrated in Figure 4.1, groundwater discharge from confined aquifers can occur as springs or diffuse discharge at distances of several to hundreds of kilometers from shore.

### 4.2.2 Nutrient transport via SGD

The environmental quality of groundwater is a near-universal concern. Groundwater quality is affected by anthropogenic activities ranging from the application of agricultural pesticides and fertilizers to leaking petroleum underground storage tanks. While the immediate effect of groundwater contamination is the pollution of potable drinking water sources in the vicinity of the contamination source, groundwater flow transports dissolved constituents away from the source area. Where groundwater flow is toward the coastline, SGD can discharge these nutrients and contaminants to the coastal zone and, along with surface runoff and atmospheric deposition, provides an important non-point source discharge to estuarine and coastal ocean receiving waters.

In the eastern United States, the land bordering estuaries and the coastal zone is the site of both agricultural and industrial activities, as well as the site of large urban population centers, including Washington, D.C.; Philadelphia, PA; New York, NY; and Boston, MA (Figure 4.2). Industrial activities and ubiquitous petroleum underground storage tanks are a continuing threat to groundwater quality. Compounds such as polycyclic aromatic hydrocarbons (PAHs), chlorinated aliphatics (e.g., trichloroethylene), and petroleum constituents (benzene, toluene, ethylbenzene, and xylenes) and additives (e.g., MTBE) have affected both surface and confined aquifers in urban and suburban regions throughout the world.

Even rural areas experience risks to groundwater quality. Nitrate contamination of aquifers is common in agricultural areas that border estuaries (Hamilton *et al.*, 1993). Reclaimed marshland and undeveloped coastal plain areas are also widely utilized as cropland and for animal husbandry. *Groundwater chemistry in aquifers underlying agricultural regions is affected by the infiltration of pesticides, fertilizers, and animal waste products from industrial farming centers.*

In addition to the transport of allochthonous chemical compounds to the coastal zone, SGD also has local effects due to groundwater-surface water

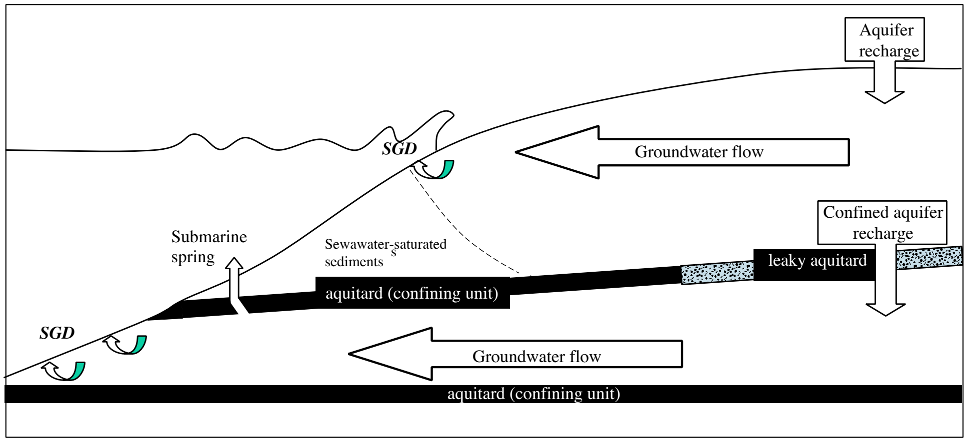

Figure 4.1: Submarine groundwater discharge schematic. Submarine groundwater discharge can occur from confined and unconfined aquifers. Discharge from confined aquifers can take the form of submarine springs and can occur at some distance from the shoreline, even at the shelf break. Potentiometric head can be visualized as the difference in elevation between the recharge and discharge zones of the source aquifer.

Figure 4.2: Eastern United States, showing selected urban areas.

interactions. This 'subterranean estuary' (Moore, 1999) is a particularly dynamic area where the interaction of water masses with different alkalinity and chemical composition precipitate and liberate both dissolved and solid phases. Strong redox gradients in this zone will enhance chemical reactions and can liberate both organic and inorganic compounds and stimulate biogeochemical processes that further affect groundwater chemistry (Dahm *et al.*, 1998). Organic matter degradation can take place through a variety of pathways in the groundwater, including aerobic oxidation, sulfate reduction, and methanogenesis, further altering groundwater chemistry prior to discharge.

The interaction between seawater-saturated sediments and freshwater aquifers is not a one-way exchange. Groundwater withdrawal in the coastal zone has increased to satisfy the growing demand for drinking water and agriculture as the coastal population increases (Paerl, 1997). This has led to saltwater intrusion into coastal aquifers. In addition to rendering the groundwater non-potable, salt water intrusion into these aquifers causes ion exchange and other reactions to occur, which chemically alter the intruding seawater and enrich the fluids in metals and nutrients (Burnett *et al.*, 2003). Subterranean interactions between seawater and fresh water can induce the liberation of ions adsorbed to sediment particles, including radium (Ku *et al.*, 1992; Moore, 1999). Researchers can make use of these geochemical processes to identify SGD tracers and quantify groundwater fluxes.

## 4.3 Locating and Measuring Submarine Groundwater Discharge

Identifying where SGD occurs and the rates of groundwater flux is no trivial matter. *The most obvious SGD tracer in the coastal zone is salinity*. Terrestrial aquifers contain freshwater while the salinity of coastal zone receiving waters will be higher, up to full oceanic salinity of 35 psu (or even higher in tropical lagoons). Through careful assessment of salinity signals, Johannes (1980) identified groundwater discharge as an important source of water and dissolved compounds to a western Australian coastal lagoons, while, in the process, proposing the theoretical ubiquity of SGD.

Although the first ancient evidence of SGD was via the observation of active submarine springs in the coastal ocean, most groundwater discharge to the coastal zone (especially that from unconfined aquifers; Figure 4.2) is not accompanied by a marked freshening of surface receiving waters. Often SGD occurs with no discernible salinity signal at all. Other tracers may be helpful in cases where SGD is suspected due to coastal aquifer geometry (i.e., strike and dip) or biogeochemical observations in the absence of salinity anomalies.

*Seasonally, temperature anomalies may be useful SGD tracers.* Because groundwater temperatures remain relatively constant throughout the year, the temperature difference between surface water and groundwater will increase when surface water is warmed or cooled. Miller and Ullman (2004) identified localized groundwater discharge to the Delaware coastal zone using remote thermal imaging to locate warm water plumes in cold winter surface waters. Similar techniques were used by Banks and colleagues (1996) and Portnoy and colleagues (1998) in separate studies of groundwater-surface water interactions. Moore and colleagues (2002) inferred groundwater-surface water interactions from annual temperature excursions in a submarine confined aquifer located on the South Carolina continental shelf. Finally, Taniguchi and colleagues (2003) calculated groundwater flux rates using subsurface temperature trends in Cockburn Sound, Western Australia.

An increasingly common, and powerful, tool for identifying SGD in the coastal zone is via chemical tracers, both natural and introduced. *Natural radioactive elements*, including radon-222 and a suite of radium isotopes ($^{223}$Ra, $^{224}$Ra, $^{226}$Ra, and $^{228}$Ra) have been used as valuable tracers of SGD to estuarine and coastal zones (e.g., Moore, 1996; Cable *et al.*, 1996; Krest *et al.*, 2000; Schwartz, 2003; Charette *et al.*, 2003). *Artificial chemical tracers* can be introduced into aquifer recharge zones to assess groundwater flow where flow lines are short (i.e., rapid discharge). In coastal zone receiving areas with restricted surface water exchange, *dissolved nutrients* may serve as an indicator of SGD, though it has proved difficult to use nutrients as a primary groundwater tracer. *Stable isotope signatures* of dissolved nutrients (e.g., $^{15}NO_3$) hold some promise for utility as SGD tracers (Schwartz, 2001)

Groundwater radium concentrations are altered by seawater-fresh water interactions in coastal aquifers. As noted above, surface water-groundwater interactions in submarine aquifers can release ions adsorbed to charged particles, such as clay minerals and glauconite sands. This is particularly common in aquifers that are subjected to saltwater intrusion or regular saltwater flushing. Radium is one such ion that can be liberated by gradients in groundwater conductivity. Dissolved radium concentrations can, therefore, be much higher in the discharged groundwater than in the receiving surface waters (oceanic or salt marsh). Rama and Moore (1996), Krest and colleagues (2000), and Charette and colleagues (2000) utilized the differences in half-life of the

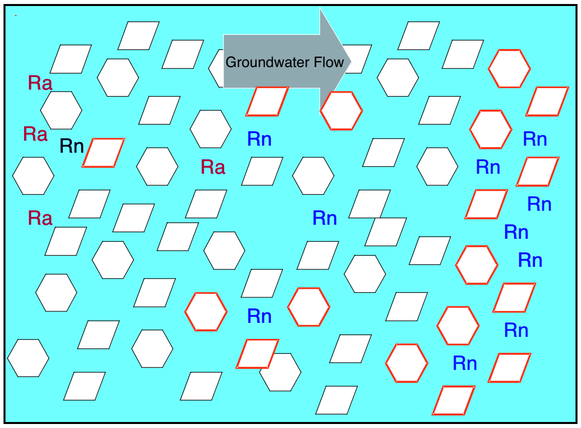

Figure 4.3: Illustration of radon enrichment in aquifers. As groundwater flows through the aquifer, $^{226}$Ra decays to form $^{222}$Rn, a noble gas that does not react with dissolved or particulate material in the aquifer. Radium is very particle reactive and will bind to charged mineral surfaces (depicted by red coatings of some mineral grains.

radium isotope quartet (ranging from 3.7 days to 1600 years) to simultaneously quantify SGD fluxes (and differentiate groundwater input) from surficial and confined aquifers.

Radon-222 is enriched in groundwater because its geochemical properties differ significantly from $^{226}$Ra, its parent nuclide. Radon is a noble gas and does not react with other ions, while radium is highly particle reactive and will adsorb onto particles in the water column or in aquifers. Even in saline water, much radium will be adsorbed to particle surfaces. As groundwater flows through an aquifer, radium will be adsorbed onto charged surfaces of mineral grains. The radon formed by the decay of dissolved and particle-bound radium is transported as a dissolved gas within the groundwater (Figure 4.3). This process leads to a progressive enrichment in groundwater radon prior to discharge.

By measuring excess $^{222}$Rn (i.e., the amount of dissolved radon that is not supported by water column and benthic $^{226}$Ra), Cable and colleagues (1996) and Hussain and colleagues (1999) identified significant groundwater flow to the northeastern Gulf of Mexico and Chesapeake Bay, respectively.

In areas where groundwater flow is rapid and discharge occurs quickly, artificial tracers can also be used to identify the location and rate of groundwater discharge. Working in the Florida Keys, Dillon et al. (1999) injected sulfur hexafluoride ($SF_6$) into the surficial aquifer to trace the flow of wastewater effluent through the carbonate platform.

While dissolved nutrients, including nitrate and silicate, are difficult to use as primary tracers of SGD, they may have a value as a secondary tracer in studies that pair thorough investigations of nutrient dynamics with the use of a primary tracer such as those mentioned above. Methane ($CH_4$) has been combined with $^{222}$Rn to assess SGD in the Gulf of Mexico and Florida Bay (Cable *et al.*, 1996; Corbett *et al.*, 1999).

## 4.4 Nutrient Fluxes from Submarine Groundwater Discharge

The nature of chemical tracers of groundwater discharge underscores the fundamental issue of SGD vis--vis nutrient fluxes: groundwater chemistry differs from surface water chemistry. Therefore, groundwater discharge to surface waters can alter the chemistry (and, by extension, the biogeochemistry) of the receiving waters in the coastal zone.

Surface water discharge to the coastal zone undergoes physical and biogeochemical processing via the estuarine filter (Kennedy, 1984), within which particle precipitation, geochemical transformation, and biological uptake alter the water chemistry such that the water that leaves the estuary is different from that which enters the estuary as fluvial discharge. Submarine groundwater discharge bypasses the estuarine filter, though there is evidence that the groundwater discharge is geochemically altered via passage through a 'subterranean estuary' (Paerl, 1997; Charette & Sholkovitz, 2002). Where aquifer chemistry has been affected by anthropogenic activities (e.g., infiltration of fertilizers and agricultural runoff), inorganic nutrients may be transported with groundwater, bypassing the estuarine

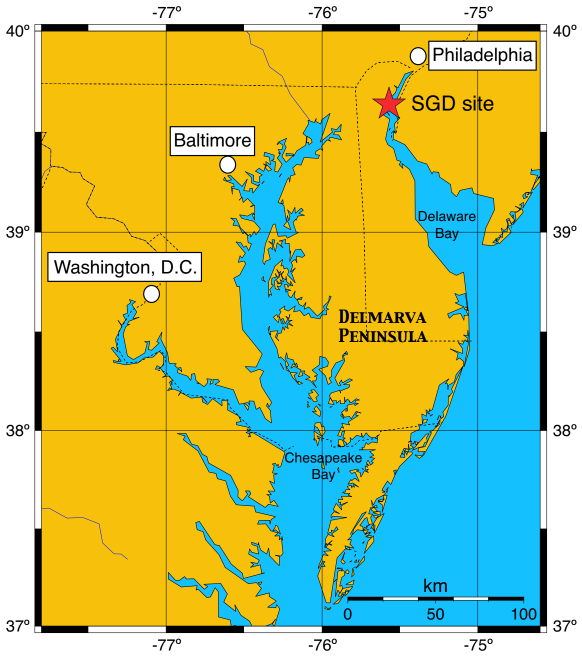

Figure 4.4: Delmarva Peninsula. The peninsula is located on the mid-Atlantic bight of the eastern United States and contains portions of the states of Delaware, Maryland, and Virginia. Star indicates location of SGD study site in Schwartz (2003).

filter to be transported (more or less) directly into receiving waters.

### 4.4.1 Case study: Nitrate and SGD in the Delaware River and Bay Estuary

Using excess $^{222}$Rn as a groundwater tracer in the Delaware Estuary, Schwartz (2003) calculated a groundwater flux of 14.5–29.3 m$^3$ s$^{-1}$, equivalent to the discharge of the Schuylkill and Brandywine Rivers, the second and third largest tributaries to the Delaware River and Bay. This discharge occurred along 12 km of the estuary and is equal to an upward flow velocity of 5–10 cm d$^{-1}$.

Agriculture, including crop and chicken farming, is a major industry on the Delmarva Peninsula, a broad coastal plain peninsula located near several major urban centers and separating the Chesapeake Bay and the Delaware Bay (Figure 4.4).

Two aquifers are hydraulically connected to the surficial aquifer in the vicinity of the Delaware SGD site. These units were identified by reviewing stratigraphic maps of the underlying geology of the Delmarva Peninsula and appear to be the source of the groundwater discharge (Schwartz, 2003). The geochemistry of these source aquifers has been affected by agricultural activities and groundwater nitrate concentrations are as high as 1,000 µM (Bachman & Ferrari, 1995). Nitrate is a potential nutrient for both heterotrophic and autotrophic organisms in the estuary.

The groundwater-mediated nitrate flux to the Delaware SGD zone was calculated by multiplying the groundwater flux rate by the average nitrate concentrations in the two source aquifers (175 µM); this resulted in a groundwater nitrate flux of 2.5–5.1 moles s$^{-1}$. The groundwater nitrate flux compares favorably to non-point source and fluvial nitrate sources to the Delaware Estuary (Table 4.1).

It must be noted that this groundwater nitrate flux refers only to the 12-km long site studied by Schwartz (2003); additional SGD sites in the Delaware estuary have been indicated by excess radon data (Schwartz, 2001) and subcropping stratigraphy (Krantz, personal communication). Therefore, the groundwater nitrate flux calculated above should be considered to be the minimum groundwater contribution to the estuarine receiving waters.

### 4.4.2 Other SGD nutrient flux investigations

While assessing global new-nitrogen fluxes to the coastal ocean, Paerl (1997) observed that "parallel estimates for groundwater-nitrogen inputs into these [coastal] waters . . . indicate a growing budgetary role for this nitrogen source, ranging from <10 to 30% of the new nitrogen inputs." This same study estimated that SGD to the coastal ocean accounts for 5–10 Tg N y$^{-1}$; this value is up to one-third that of the coastal ocean new-nitrogen loading by both atmospheric deposition (ca. 35 Tg N y$^{-1}$) and the combined effect of flu-

Table 4.1: Delaware River and Bay nitrate fluxes.

| Delaware Estuary Nitrate Source | Nitrate flux [moles $s^{-1}$] | SGD Nitrate Flux as Percentage of Cited Flux | Citation |
|---|---|---|---|
| SGD | 2.5–5.1 | N/A | Schwartz, 2001 |
| Wet atmospheric deposition | 7 | 36–73% | Scudlark & Church, 1993 |
| Municipal industrial effluent | 16 | 16–32% | Scudlark & Church, 1993 |
| 14 Major municipal and sewage effluents, combined | 7.1 | 35–72% | Frake *et al.*, 1983 |
| Delaware R. at Trenton | 18 | 14–28% | Scudlark & Church, 1993 |
| Delaware R. at Trenton | 20.7 | 12–25% | Frake *et al.*, 1983 |
| Delaware River at S=0 | 55 | 5–9% | Scudlark & Church, 1993 |
| Schuylkill River | 14.7 | 17–35% | Frake *et al.*, 1983 |
| Lower Delaware Bay tributaries, combined | 8 | 31–64% | Scudlark & Church, 1993 |

vial discharge and surface runoff (30 Tg N $y^{-1}$). Both the aforementioned case study and the results summarized above certainly suggest that the 'growing budgetary role' ascribed to groundwater nutrient fluxes by Paerl (1997) may yet increase as additional studies are undertaken.

Several SGD assessments were performed throughout the eastern USA over the past 25 years. Though this SGD research constitutes only a fraction of the studies on surface water impacts on estuarine and coastal biogeochemistry, many studies have revealed that the biogeochemical impact of SGD can be important both locally and regionally. These studies have determined the flux of dissolved nutrients, including nitrate, phosphate, the dissolved inorganic nitrogen (DIN), and dissolved inorganic phosphate (DIP). Some notable research into SGD nutrient fluxes to the coastal zone include:

- Great South Bay, New York: Capone and Bautista (1985)
  - SGD flux of 3.6–18.3 $m^3$ $m^{-2}$ $y^{-1}$
  - SGD nitrate concentration at discharge: 10 µM (average)
  - SGD nitrate loading accounts for ≥ 20% of the new nitrogen inputs via surface runoff
- Waquoit Bay, Massachusetts: Valiela et al. (1992)
  - SGD nitrate loading in three subtributaries: 61 mmol $m^{-2}$ $y^{-1}$
- Eastern Florida Bay, Florida: Corbett et al. (1999)
  - SGD DIN: 110 ±60 mmol $m^{-2}$ $y^{-1}$
  - SGD PO4: 0.21 ±0.11 mmol $m^{-2}$ $y^{-1}$
  - SGD DIN flux is 3.7 times higher than area-normalized Everglades surface water flux, while SGD DIP flux is 2.1 times higher than area-normalized Everglades surface water flux
- Coastal Ocean of the South Atlantic Bight, South Carolina: Krest et al. (2000)
  - SGD-derived marsh input to coastal ocean:
    - ∗ 6.6 ×108 mol N $y^{-1}$

        - 3.2 ×107 mol P $y^{-1}$
    - Fluvial input to coastal ocean:
        - 6.0 ×108 mol N $y^{-1}$
        - 2.6 ×107 mol P $y^{-1}$
    - Estimated that half of the terrestrially-derived nutrient flux to the coastal ocean originates from salt marshes, with groundwater being the primary source of marsh nutrients

- Pettaquamscutt River, Rhode Island: Kelly and Moran (2002)
    - SGD DIN: 61–180 mmol $m^{-2}$ $y^{-1}$
    - SGD DIP: 4.4–13 mmol $m^{-2}$ $y^{-1}$

- Elizabeth River, Virginia: Charette and Buessler (2004)
    - SGD DIN: 1644 ±1680 mmol $m^{-2}$ $y^{-1}$
    - SGD DIP: 58 ±62 mmol $m^{-2}$ $y^{-1}$
    - SGD DIN flux is 1.7 times the Chesapeake Bay areal average for DIN loading, while the SGD DIP flux is 2.7 times greater than areal-avergaged Chesapeake Bay DIP loading

As a comparison, the Delaware SGD nitrate flux, above, is equivalent to 3300–6700 mmol N $m^{-2}$ $y^{-1}$ throughout the groundwater discharge zone.

## 4.5 The Future

According to a recent summary, estimates of the global magnitude of SGD based on hydrological and water balance calculations range from 0.3–16% of river discharge, with most estimates in the range of 6–10% (Burnett *et al.*, 2003). These values refer only to the discharge of fresh, terrestrially-derived water via SGD and, therefore, ignore the contribution of seawater discharged to the coastal zone following mixing with fresh groundwater. As this mixing of fresh water and seawater within the aquifer has important ramifications for the chemistry of the discharged groundwater, these freshwater-only estimates must be considered the lower boundary.

The increased use of radioisotope tracers over the past ten years has allowed researchers to more accurately constrain groundwater discharge fluxes. By pairing multiple tracers and improved seepage meter technologies, groundwater flux estimates can be made more accurate yet (Burnett *et al.*, 2003). Improved accuracy in groundwater flux calculations will yield better nutrient flux data. Furthermore, as multiple tracers, including dissolved nutrients and stable isotope signatures, are added to the existing radioisotope tracers, we can increase our understanding of how SGD transports dissolved nutrients to the coastal zone.

The number of investigations into the transport of nutrients to the coastal zone via SGD is growing, but this remains a relatively new field of research. Most of the existing research has been performed in the eastern United States and in limited regions of Europe, Japan, and Oceania (Taniguchi *et al.*, 2002). There is a conspicuous lack of SGD studies in Asia, India, Africa, South America, and the western United States. An expansion of SGD studies, including assessments of SGD-nutrient fluxes to estuaries and the coastal ocean, will provide insight into anthropogenic impacts on, and non-point source nutrient fluxes to, the coastal zone.

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# Chapter 5

# Drainage basin use and nutrient supply by rivers to the coastal zone. A modelling approach to the Seine river.

Josette Garnier
Gilels Billen
UMR 7619 Sisyphe
CNRS et Universite Pierre & Marie Curie
Boite 105, 4 place Jussieu
7505 Paris
Josette.Garnier@ccr.jussieu.fr

Philippe Cugier
IFREMER, Direction de l'Environment Littoral
Department d'Ecologie Cotriere
B.P. 70, 29280 Plouzane

## 5.1 Abstract

A modelling approach has been developed with special emphasis on the understanding of the nutrient dynamics and fate of the phytoplankton, often leading to eutrophication problems. The stream-order concept used by geomorphologists has proved very useful for modelling — the ecological and biogeochemical functioning of hydrosystems at the basin scale. A basic hypothesis to the approach is that related ecological processes are the same throughout the whole hydrographic network.

The RIVERSTRAHLER model, validated on several European rivers, can be used to determine the temporal variations of the equilibrium between phytoplankton production and heterotrophic respiration which controls the oxygen levels at the scale of the hydrographic network. P/R diagrams are good indicators of the ecological functioning of an aquatic systems. In addition, the model leads to the calculation of the Redfield ratios, that describe the respective role of nitrogen, phosphorus and silica in nutrient limitation of algal growth.

The RIVERSTRAHLER model can be also used to test management scenarios aimed at reducing eutrophication problems at the scale of large river basins. In addition, it has been recently coupled to a model of the marine systems. Application of these coupled models to the case of the Seine river and Seine Bight system shows that domestic reduction of phosphates inputs is only efficient if it is carried out at the basin scale: such a reduction should banish phosphates detergents and should be accompanied by a program of reduction of diffuse phosphorus sources. The scenarios also showed that only a drastic program of nitrogen reduction by tertiary treatment in wastewater treatment plants (at least 70% reduction) would be efficient in preventing marine eutrophication.

## 5.2 Introduction

The functioning of aquatic ecosystems is strongly conditioned by the levels and proportions of nitrogen, phosphorous and silica in surface waters. They are themselves determined by the lithology and the land use of the watershed. The problem of eutrophication resulting from nutrient excess is wide-spread throughout the north-western Europe and the northern Gulf of Mexico where the population density is especially high and the agriculture intensive (CCMCE, 2000; Turner *et al.*, 2003). In north-western Europe, most of the large rivers suffer from eutrophication (Rousseau *et al.*, 2002): the Elbe, the Rhine, the Scheldt, the Seine, the Loire, the Garonne, etc. Since the 1960s, the role of nutrients as factors controlling the trophic state of aquatic systems has given rise to numerous discussions and research efforts; however, the research has often been focused mainly on lake environments. The interest in river nutrient supply to eutrophication is more recent because rivers have been seen as systems capable of transporting, purifying and eventually, evacuating downstream all the pollutants discharged into them. Similarly, the link between the eutrophication of coastal zones and the fluxes from the watershed basins is a relatively new line of research (Billen *et al.*, 2001; Cugier *et al.*, 2004a; Officer & Ryther, 1980; Smayda, 1990). Eutrophication of large river is linked to the development of microscopic planktonic algae, as opposed to eutrophication by macrophytes in small ones. Because they have a high growth rate, phytoplankton organisms respond immediately to environmental constraints and are therefore an excellent reference indicator of water quality, both by their biomass and their composition. In critical eutrophication conditions, algal bloom is often a great nuisance to river and coastal zones, preventing normal water use particularly for drinking purposes, recreation, shell fish production, etc. (UNESCO, 2003).

All along the hydrographic network and in its stagnant annexes such as ponds or reservoirs, mechanisms of retention or elimination of nutrients are at work, greatly modifying the fluxes that are transferred downstream. The riparian zones that form the interface between the soil of the watershed basin and the surface water act as very efficient filters for nitrates of agricultural origin (Howarth *et al.*, 1996; Tilman *et al.*, 2001). Since nitrogen, phosphorus and silica have different origin and circulate in different ways, the ratios between these elements change considerably from the upstream to the downstream sectors of the hydrographical network. These ratios should be compared to the average composition of the algal biomass which determines the proportions of nutrients taken up by phytoplankton. The mean N:P ratio of aquatic plants is on the order of 7 (in N and P weight) (Redfield *et al.*, 1963); the mean Si:N ratio of diatom populations in freshwater is 5.5 (in Si and N weight) whereas it is about 2 for marine diatoms (Conley & Kilham, 1989). Whereas phytoplankton bloom intensity and duration is mainly driven by the nutrient loading, the composition of the phytoplankton blooms depends more on their ratios. In strongly human impacted systems, silica issued of diffuse natural origin, from weathering of the rocks, may be limiting compared to the phosphorus and nitrogen leading to a shift from diatom blooms to undesirable non-diatom blooms (often mucilaginous *Phaeocystis* and/or toxic *Dinophysis* at the coastal zone (Rousseau *et al.*, 2002; Flynn, 2002; Cugier *et al.*, 2004b).

Although a great number of lake systems have been successfully restored by reducing point discharges of nutrients (domestic discharges), rehabilitating rivers is more complicated. On the basis of the river continuum concept or RCC (Vannote *et al.*, 1980), the river, from the headwaters to the estuary, can be represented as a succession of interdependent systems, which means that to quantify the nutrient load and understand eutrophication phenomena at any point in the river, one must take into account the processes occurring upstream.

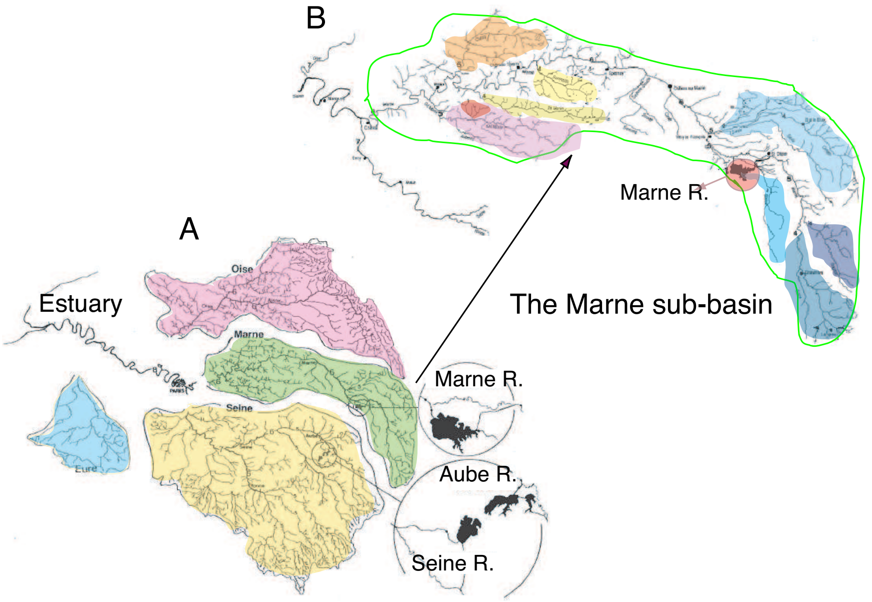

Figure 5.1: Hydrographic network and modelling strategy. Example of the Seine River: a) at the scale of the whole watershed, 4 sub-basins and one branch are considered, whereas b) one of the sub-basin can (the Marne here) can be divided into 8 sub-basins and one branch. The reservoirs are taken into account as mixed reactors.

## 5.3 Generic modelling approach

As it is clearly impossible to study the thousands of kilometres of rivers in the largest hydrographic networks, a way around the complexity had to be found. This is why we constructed a mathematical model (RIVERSTRAHLER, Billen *et al.*, 1994; Garnier *et al.*, 1995) based on a geomorphological analysis by stream-order (Strahler, 1957); it takes into account the river network as a regular confluence pattern of tributaries of increasing order with mean characteristics (from orders 1 to 8 in the case of the Seine). The RIVERSTRAHLER model combines a model of the ecological processes (RIVE) and a simplified hydrological model (HYDROSTRAHLER) which takes into account the basin-scale hydromorphological, meteorological and input constraints from point sources (domestic and industrial discharges) and diffuse sources (leaching of rocks and soils). All these constraints are important controlling factors in phytoplankton development.

According to the heterogeneity within any watershed on the point of view of the geomorphology, the human activity, etc., the watershed under study can be split into several homogeneous sub-basins, providing that data are available. Here, the Seine was divided into 4 sub-basins (Upstream Seine, Marne, Oise and Eure) whereas two sub-basins were considered for the Scheldt (Upstream Scheldt and Rupel) and the Mosel (Upstream Mosel and Meurthe) and one for the Loire. Note however that for the scenarios of phosphorus reduction explored below, the Marne was divided into 9 sub-basins (Figure 5.2). The results obtained for each sub-basins are then taken by a model of a main branch, for which the hydromorphology is described every km.

The HYDROSTRAHLER module calculates the hydrology of the whole drainage network, from the morphological characteristics by stream order. Discharge in order n tributaries is calculated as the sum of the discharges of their two n-1 order tributaries, the discharges of lateral tributaries of order 1 to n-1, and the flow from its direct watershed, i.e. the part of the watershed that does not belong to the catchment of the tributaries (see Billen et al. 1994). The latter is calculated from precipitation and potential evapotranspiration data with a classical rain-discharge conceptual model, taking into account the role of a soil and an aquifer reservoir (see e.g. Bultot & Dupriez 1976). This model, which involves 4 parameters (soil saturation, infiltration rate, internal flow rate, aquifer flow rate), can distinguish between three compo-

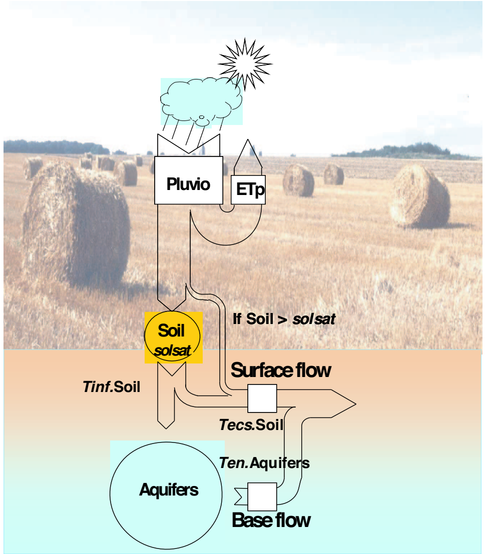

Figure 5.2: Schematic representation of the HYDROSTRAHLER model and its parameters: *solsat* – water saturation level of the soil (mm); *tinf* – rate of infiltration (decade-1); *tecs* – rate of superficial runoff (decade-1); *ten* – water table runoff (decade-1). Soil and Aquifers are the water reservoirs.

nents of the discharge from the watershed: the base flow supplied by the water table, the internal (or hypodermic) flow supplied by the soil reservoir, and the surface runoff supplied in periods of soil saturation (Figure 5.2). For some applications of the model, a module describing snow melting can be added (Hannon *et al.*, 1996; described also in Garnier *et al.*, 2002).

From the value of the discharge (Q, $m^3\ s^{-1}$) calculated by stream order, width (w, m), slope (s, $m\ m^{-1}$), mean depth (d, m) and flow velocity (v, $m\ s^{-1}$) are calculated by rearranging of the Manning's empirical formula (Billen *et al.*, 1994). The flow from the direct catchment area of the river, or from its lateral tributaries of lower stream orders, 'dilutes' the water masses flowing through the main channel. The corresponding dilution factor and its variations with the stream order and the season are very important for controlling the ecological functioning of rivers.

In the main branch of the river, the calculation is similar, taking into account the contribution to the flow of both the direct watershed and the considered sub-basins. In regulated sectors, the values of the depth and the wetted section are taken into account.

Besides data of rainfall, potential evapotranspiration and air temperature, which are required for the HYDROSTRAHLER model, additional constraints act on the ecological model (Figure 5.3). Besides inputs (points and diffuse, see above), meteorological constraints such as water temperature, photoperiod and light intensity seasonal variations are represented by sine functions (During the photoperiod, the hourly irradiance is also calculated as a sine function (Billen *et al.*, 1994).

The model of ecological functioning (RIVE model, Billen *et al.*, 1994; Garnier *et al.*, 1995) constitutes the common module for the calculation of water quality in the sub-basins and the main branch of the studied river. It consists of 22 variables, including nutrients (nitrate and ammonium, phosphate, dissolved silica), dissolved and particulate organic matter (as two classes of biodegradability), two taxonomic groups of phytoplankton (diatoms and non-diatoms), two groups of zooplankton (rotifers and micro-crustaceans) and bacteria (Figure 5.4). The description of the phytoplankton dynamics is based on the Aquaphy module by Lancelot et al. (1991) which distinguishes between photosynthesis, controlled by light intensity, and algal growth controlled by nutrient availability. The module has been adapted to two groups of algae (diatoms and non diatoms) and a formulation for loss processes by excretion and grazing has been added (Garnier & Billen, 1993; Garnier *et al.*, 1998). The impact of invasive molluscs such as *Dreissena* as well as that by viruses is represented by constant rates, modulated by temperature. The degradation of organic matter and bacterioplankton dynamics are described according to the HSB module (Garnier *et al.*, 1992; Billen & Servais, 1989; Barillier & Garnier, 1993). The RIVE model also includes a calculation of nutrient exchanges across the sediment-water interface (Venice) as a result of a given sedimentation flux of organic material, taking into account organic matter degradation, associated ammonium and phosphate release and

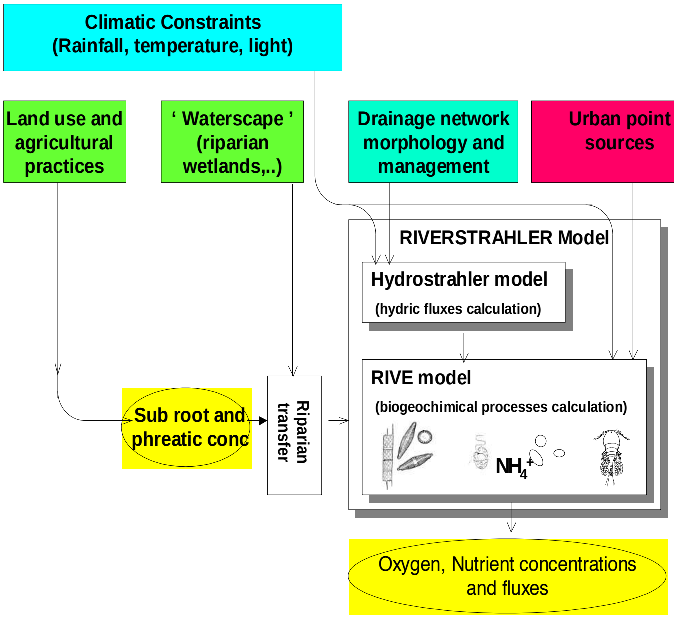

Figure 5.3: Data requirement for the construction of the Riverstrahler model. From the top to bottom: climatic constraint data controlling the hydrology and the ecological processes via the Rive model, geo-morphology driving the hydrology, diffuse and point sources acting on the ecological processes. Riparian retention is taken into account according to Billen & Garnier (1999). The output of the model are the seasonal variations of the water quality variables and fluxes.

oxygen consumption, nitrification and denitrification, phosphate and ammonium adsorption onto inorganic material, mixing processes in the interstitial and solid phases and accretion of the sedimentary column by inorganic matter sedimentation (Billen *et al.*, 1989; Billen & Servais, 1989). Sedimented biogenic silica is redissolved (Garnier *et al.*, 2004b). Water column nitrification Brion & Billen (1998) and phosphate adsorption on suspended inorganic particles (and their subsequent sedimentation) are also taken into account in the model.

The kinetics of the major processes involved in the ecological functioning and the corresponding parameters are mostly derived from experimental field work. Essentially, the same kinetic formulations are used in the model applied to any of the rivers. Only the parameter values are occasionally modified within the narrow range of experimental determinations (Table 5.1). Contrarily to the HYDROSTRAHLER hydrological modelling, the ecological modelling approach is deterministic as the kinetics formulations and parameter determinations are independent from the validation of the model, based on field observations.

A basic assumption behind the RIVERSTRAHLER model is that of the unicity of control processes in the functioning of aquatic ecosystems throughout the entire aquatic continuum. We found that the kinetics of the microscopic processes are identical from upstream to downstream and that the way in which these processes are expressed in situ is entirely conditioned by the constraints (meteorological, hydrological, point and diffuse sources of nutrients, cf. Figure 5.3).

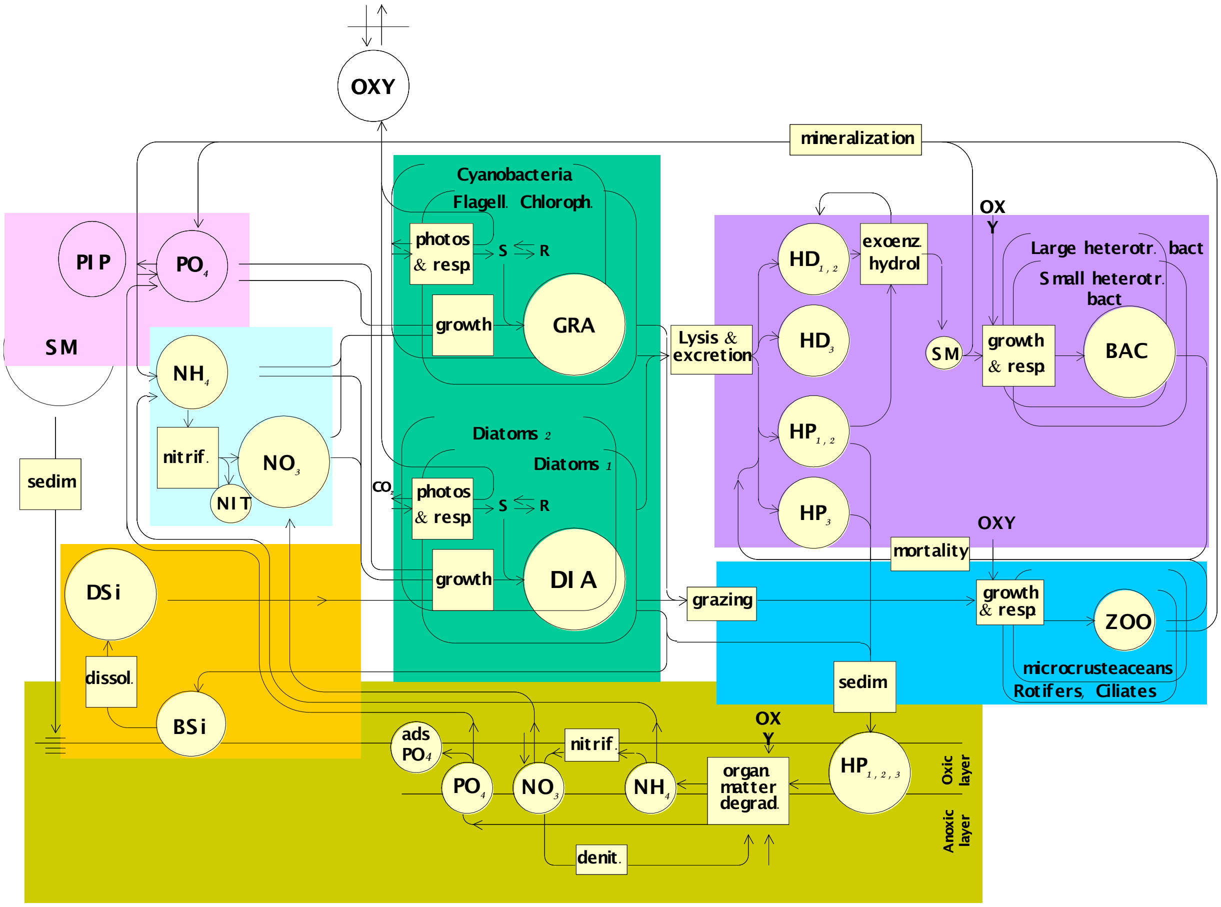

Figure 5.4: Representation of the RIVE model showing the complex interactions between the main biological compartments in the water column, at the water-interface sediment and the stocks of nutrients and organic matter.

In literature, whereas most of the nutrient flux modelling approaches are based on a statistical approach at basin scale (Behrendt, 1988; Behrendt & Böhme, 1993; Stålnacke *et al.*, 1999, 2003), models of phytoplankton development usually only describe one river sector (on the Rhine: Admiraal et al., 1993; on the Loire: the POLUPA model by the Agence de lEau Loire-Bretagne; on the Lot: Capblancq & Dauta, 1978; Qotbi, 1996; on the Mosel: Schöl et al., 1999; on the Rhine: Schöl et al., 2002). The RIVERSTRAHLER approach describes the ecological and microbial transformation of nutrients with a multiscaling spatial approach of the hydrographic network and main branch. It differs from the POTAMON model designed for simulating potamoplankton from source to mouth of the main river (Everbeck *et al.*, 2001).

## 5.4 Origin and processes of nutrient transformation in the river continuum

### 5.4.1 Diffuse and point inputs of nutrients in the drainage networks

Starting from the levels in the streams at the head of the basins, whose water is a mixture of surface runoff and groundwater, the nutrient content evolves from upstream to downstream of the hydrographic network partly because of point discharges of nutrients and partly because of the processes that transform, immobilise or eliminate them during their transfer downstream. In order to build a model it is therefore necessary to estimate the input of nutrients.

Dissolved inorganic forms of nutrients (Si, N, P) control algae growth. In water affected by agricultural soils leaching (already in the headwaters), heavily loaded with nitrates, phosphorus is the limiting element. In zones with large domestic and industrial discharges (e.g. in order 5 of the Seine basin), phosphorus is, on the contrary, in excess (Table 5.2). The silica produced by rock weathering is relatively constant in time, and is in excess compared to the phosphorus (Table 5.2). However, the large input of nitrogen and phosphorus can modify the ratio to a point where silica becomes limiting, in particular when the uptake by phytoplankton greatly lowers the concentrations (Garnier *et al.*, 1995).

Diffuse sources are taken into account through mean nutrient concentrations in each of the the two components of runoff (surface- and groundwater flow) as calculated by the HYDROSTRAHLER model. Regarding surface water, these concentrations are calculated from the land use in the watershed and from a coefficient of transfer through the riparian zones (Billen & Garnier, 1999). The composition of the water from phreatic aquifers is obtained by an inventory of the concentrations in the aquifers (Billen & Garnier, 1999).

The point sources for each sub-basin and the main axis are calculated from data on wastewater discharges from wastewater treatment plants and from industries not connected to a sewage network. In the sub-basins, they are attributed by stream order; on the main axes, they are represented by kilometre points at the sites of the discharges into the river.

Table 5.2: Inputs of nitrogen, phosphorus and silica to the hydrographic network of the Seine River. Redfield ratio (RR: g/g). Situation in 1991.

| 1991 | *RR* | Seine | Marne | Oise | Eure | Main axis |
|---|---|---|---|---|---|---|
| Diffuse sources, kT,y$^{-1}$ | | 25.3 | 13.9 | 16.6 | 14.3 | |
| N | | 25.3 | 13.9 | 16.6 | 14.3 | |
| P | | 0.3 | 0.2 | 0.2 | 0.1 | |
| Si | | 24.5 | 14.7 | 19.8 | 8.5 | |
| N/P | 7.2 | 84 | 69 | 83 | 143 | |
| Si/P | 40.2 | 82 | 73 | 99 | 85 | |
| Si/N | 5.6 | 0.96 | 1.01 | 1.19 | 0.59 | |
| Point sources, kT, y$^{-1}$ | | | | | | |
| N | | 5.1 | 2.6 | 4.7 | 1.4 | 40.3 |
| P | | 1.6 | 0.9 | 1.4 | 0.4 | 7.1 |
| N/P | 7.2 | 3.2 | 2.9 | 3.4 | 3.5 | 5.7 |

A study carried out on the treated and untreated wastewater in the Paris urban area (Servais *et al.*, 1999; Garnier *et al.*, sumbitted) made it possible to convert the variables provided by sewage networks and treatment plants into state variables in the RIVE model. Biological oxygen demand (BOD) is for example converted into different fractions of organic carbon and a relationship between BOD and heterotrophic bacteria is used.

### 5.4.2 Transformation of nutrients in the drainage networks

In any aquatic continuum, from head waters to the coastal zone, the nutrient load can be reduced by a variety of processes related to the biology (uptake, retention in the biomass, elimination), the hydrology (dilution), the geo-morphology (retention) (Figure 5.5).

#### Flow rate and retention

Ecological processes can strongly modify the dynamics of nutrients along a river continuum but the nutrients issued from point source discharges generally have a relatively constant flux, independent of the flow rate in the receiving river, whereas the diffuse inputs are closely linked to its flow rate.

It has therefore often been proposed that the flux-flow rate or the concentration-flow rate relationship be used to define what shares of the load have a diffuse or a point origin at a given station. The limitations of this method are due to the need for simplifying assumptions which are not always verified. Thus, to consider the base flow as constant is the same as saying that any increase in the flow rate is due to an inflow of surface water whereas a distinction should be made between floods containing a large component of surface water and those that are mainly due to aquifer recharge since the two might have very different effects in terms of nitrogen and phosphorous transport.

Contrarily to dissolved inorganic silica and nitrogen mostly immobilized or eliminated through biological processes, inorganic phosphorus, although kept low by the algae throughout the vegetative period in the upstream rivers, is largely transported as particulate inorganic phosphorus (44%) at the outlet of the Seine, of which 20 to

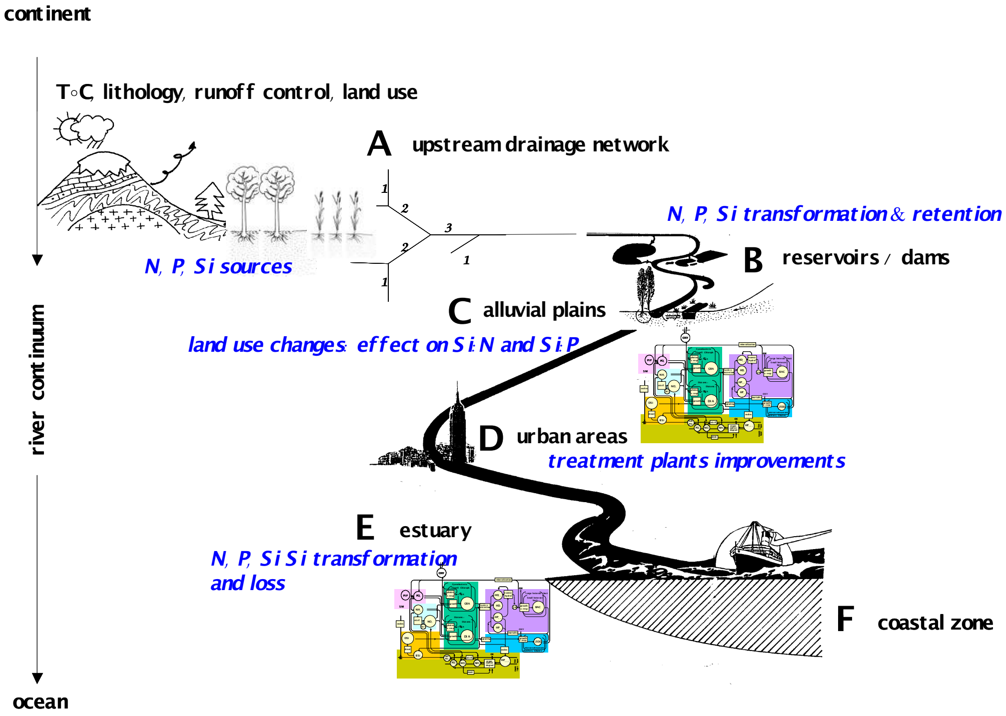

Figure 5.5: Schematic representation of an aquatic continuum and the fate of nutrients.

35% is deposited in the flood zones but probably re-suspended during floods and transported downstream (Némery, 2003; Némery *et al.*, 2004). In this case, the retention of the phosphorous is temporary and only delays its transport. Note that in periods of strong floods, deposits in the flood zones of particulate phosphorus were estimated to be around 10 g P $m^{-2}y^{-1}$ in the alluvial plain of the Seine (average over the last 40 years, Fustec *et al.*, 1998).

### Elimination by denitrification

Regarding nitrogen, largely is excess compared to the algal requirement in river networks devoted to agriculture due to fertilization (from 50 to 250 kg $ha^{-1}$ in Eastern and Western European countries respectively), elimination mechanism in the watersheds is mainly due to denitrification process. Denitrification transforms nitrate into gaseous nitrogen that escapes into the atmosphere, this process definitely eliminates the nitrogen from the aquatic medium. Because denitrification is an anaerobic process, it occurs mostly in the riparian zones of the hydrosystems (Watts & Seitzinger, 2000; Maître *et al.*, 2003), or in the water column of rivers or lakes when they are deep and anoxic and enriched in organic matter (Garnier *et al.*, 1999b; Tomaszek & Czerwieniec, 2000). Such conditions are frequent at low flow in the rivers strongly impacted by waste water treatment plant, rich in organic matter as it used to be in the Seine downstream of Achères WWTP (end of the 70'ies) or in the Scheldt estuary before domestic wastewater effluents, those of Brussels city especially, were treated (end of the 90'ies). A great deal of the nitrates arriving from the upstream basin, as well as those produced by the nitrification of ammonia, were actually eliminated in this way but, fortunately, wastewater treatments have been widely implemented and improved due to successive European Directives for rehabilitation of surface water quality, so that the denitrification process in rivers themselves is, at present, essentially benthic. Its power to eliminate nitrates depends on the level of organic matter in the sediments, on the depth of the water column and on the residence time of the water masses in contact with the sediments. This dependence can be quantified with the model by Kelly et al. (1987) (Figure 5.3). *In stagnant systems, e.g. lakes, reservoirs and ponds, benthic denitrification can easily eliminate 80% of the incoming nitrate load as observed in the large reservoirs of the Seine* (Molot & Dillon, 1993; Garnier *et al.*, 1999b). Therefore, the stagnant annexes can be efficient denitrification sites in the whole hydrographical network, but their role at the outlet of the river is often limited due to the upstream situation of these hydraulic annexes.

### Phytoplankton nutrient uptake and release

In most large Western Europe rivers, around 200 species of phytoplankton can be inventoried of which half belong to the diatom family (chromophyte algae with a siliceous shell), and half to the Chlorophyceae (green algae) and the others are distributed between Cyanobacteria (blue-green algae), Dinophyceae, Chrysophyceae, Euglenophyceae (Seine: Garnier et al., 1995; Meuse and Mosel: Descy, 1987, Everbecq et al., 2001, Schöl et al., 1999; Lot : Capblancq & Dauta, 1978; Qotbi, 1996; Loire: Leitao & Lepretre, 1998; Rhine: Schöl et al., 2002). The centric diatoms generally dominate the communities in the spring, sometimes accompanied by pennated diatoms, the Chlorophyceae being characteristic to summer. The Cyanobacteria, typical of eutrophic systems, but known to be unable to form large populations in turbulent systems (Reynolds *et al.*, 1983; Steinberg & Hartmann, 1988; Mischke, 2003), are however found in significant numbers in rivers during periods of pronounced low flow but equally in eutrophicated stagnant systems connected to the river from which they originate (Köhler, 1993; Bonnet, 1995; Bonnet & Poulin, 2002).

As it is not possible to routinely determine the specific composition and the biovolume of phytoplankton through the microscope at the scale of a watershed basin, it is often easier to use other biomass estimators; the amount of chlorophyll being the basic variable generally determined from a

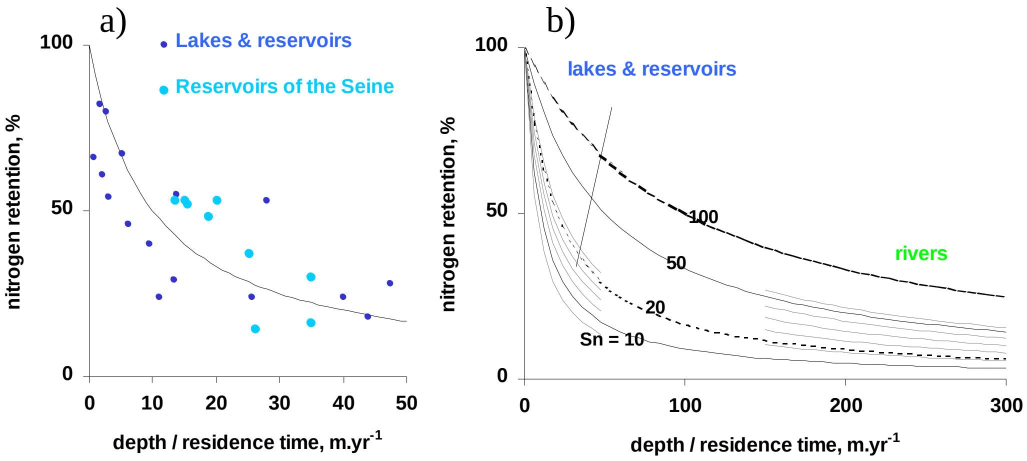

Figure 5.6: The model by Kelly et al. (1987) relies the nitrogen retention (R%) in a non stratified aquatic and well oxygenated system to the ratio of the depth (Z) divided by the residence time (T). Retention % = Sn/(Z/T + n), where Sn is a mass transfer parameter that express the ratio of the denitrifying activity at the sediment interface and the nitrate mean concentration within the water column. a) The relationship is shown for the different reservoir dams in the Seine basin (cyano blue circles) and for various stagnant media described in the literature (dark blue circles, Andersen, 1977; Calderoni *et al.*, 1978; Dillon & Mollot, 1990; Schelske, 1985). b) The panel on the right shows the magnitude of the expected nitrogen retention by benthic denitrification in stagnant annex media in the Seine system and of its actual hydrographical network as a function of the Sn value.

carbon:chlorophyll a ratio. In the Seine, this ratio is on the order of 35–40 (Garnier *et al.*, 1998).

The Redfield ratio (1958) C/N/P (106/16/1 in moles, i.e., C/N = 5.68 g $g^{-1}$, N/P = 7.2 g $g^{-1}$, C/P = 41 g $g^{-1}$) establishes the average phosphorus and nitrogen needs of algae. For the silica needed by diatoms, one must also take into account the molar ratio of Si/C = 0.4 (0.98 in g $g^{-1}$) (Redfield *et al.*, 1963; Conley & Kilham, 1989). Thus, the N:P:Si ratios in the water are compared with those of the organisms to define nutrient limitations. Moreover, the seasonal evolution of these ratios determines the ecological succession of the species (Tilman *et al.*, 1982). In the model, these ratios are used to take into account the limitation of the phytoplankton by nutrients but also to calculate the seasonal and spatial dynamics of these elements.

The process of synthetising biomass is considered to follow Michaelis-Menten kinetics in relation to the external concentration of nutrients (N, P, Si): $\mu = \mu_{max} C_{N,P,Si}/C_{N,P,Si} + k_{N,P,Si}$ where C is the N, P, Si concentration and k is the half-saturation constant, the concentration for which $\mu = \mu_{max}/2$. This constant characterises the affinity of algae for nutrients. Below this value, one considers that there is limitation. This approach does not take into account the decoupling of nutrient uptake from the algae growth which, if the algae have stored reserves, may continue in conditions that are *a priori* limiting (Droop, 1969, 1973; Di Toro, 1980; Dauta, 1982). Phytoplankton species and/or communities can be identified by their $\mu_{max}$ and k, $\mu_{max}$ being also dependant on the temperature (Figure 5.7; Table 5.3; Dauta, 1982; Ahlgren, 1987; Belkoura & Dauta, 1992 and other references in Garnier et al., 1998).

Contrarily to nitrogen concentrations, greatly in excess of the algae needs as soon as the head waters, phosphorus concentrations in the upstream basins are close to the value of the half-saturation constant of phosphorus, and is the limiting nutrients as generally admitted for freshwater systems (Wetzel, 1983).

Silica may become limiting when diatoms build up a high biomass, in the spring, due to excess

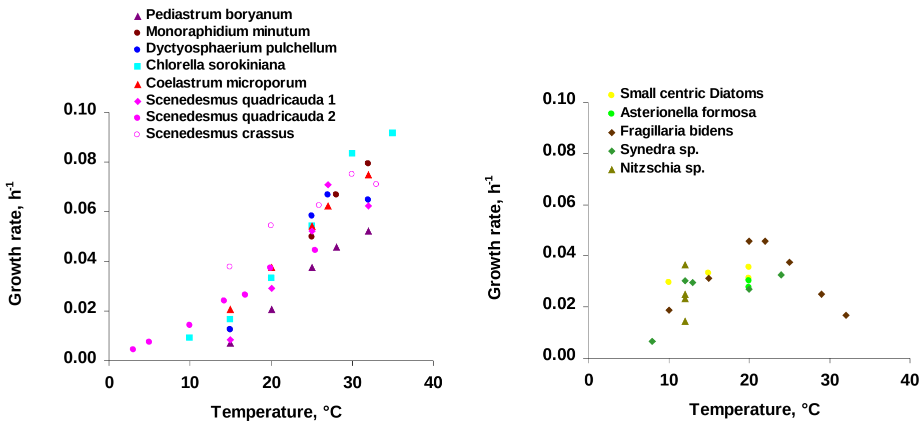

Figure 5.7: Relationship between phytoplankton growth rate (µ) and temperature for green algae and diatoms for species in pure culture (see Garnier et al., 1995)

Table 5.3: Temperature dependence (Topt, dti) of the specific photosynthesis rate (PBm) and growth rate (µ) of Chlorophyceae and diatoms in the Seine. Half-saturation constants (Ks) of the two groups for Si, N, P.

| | Diatoms | Chlorophyceae |
|---|---|---|
| Topt (°C) | 19-23 (21) | 33 (37) |
| dti (°C) | 12-16 (13) | 21 (17) |
| Growth rate at Topt, $h^{-1}$ | 0.04 (0.03-0.05) | 0.08 (0.09-0.06) |
| PBm at Topt, µg C µg Chl $a^{-1}$ $h^{-1}$ | 5 | 1.4 |
| kpSi ($mgSiO_2L^{-1}$) | 0,13–0,17 | |
| | 0.25 (SD=0.26, n=37) | – |
| KsP (µg P $L^{-1}$) | 4.3–5.9 | 1.1 |
| | 7.1 (SD =15.8, n =32) | 46.1 (SD= 55.2, n=20) |
| KsN (µg N $L^{-1}$) | 14 independantly from the species | |

in phosphorus, causing dissolved-silica depletion (Garnier *et al.*, 1995). The sedimentation of their frustules may cause significant silica retention at that time, especially in the sectors of the hydrographical network where algae growth is the strongest or in reservoirs, when their residence time is long enough and strongly stratified (Officer & Ryther, 1980; Trifu *et al.*, 2000; Garnier *et al.*, 1999a).

Besides a bottom-up control by nutrients, phytoplankton is submitted to a top-down control by animal filtration. In rivers, zooplankton is actually dominated by small organisms that have a short generation time and do not exceed 1000 ind $l^{-1}$ in the Seine (Testard, 1990; Akopian *et al.*, 2001). These organisms are weak feeders (2.3 to 5.9 µL.ind$^{-1}$ h$^{-1}$) in contrast to benthic organisms (e.g., the fresh-water mussel *Dreissena polymorpha*) that have a mean abundance reaching 200 to $500\times10^6$ individuals within the 160 km of the canalised sector and a high filtration rate, 16.5 µL ind$^{-1}$ h$^{-1}$ for the veliger and veliconcha larvae (Testard, 1990; Akopian *et al.*, 2001, 2002). Similar density of *Dreissena* are found on the other canalised river (the Mosel: Bachmann & Usseglio-Polatera, 1999; the Rhine: Schöl *et al.*, 2002). Taken into account the *Dreissena* in the model clearly showed their role to sudden declines of phytoplankton.

Apart from *Dreissena* filtration, the assumption of massive phytoplankton death by viral, bacterial or fungal infection cannot be excluded; many studies show that a phytoplankton biomass consisting of single-species populations is particularly vulnerable to viral lysis (Suttle & Chan, 1993; Bratbak *et al.*, 1993; Wommack & Colwell, 2000).

## 5.5 Modelling phytoplankton and nutrients in drainage networks

### 5.5.1 Seasonal and geographical variations of phytoplankton development and nutrients

By coupling the hydrological and ecological models, it is possible to calculate the mean phytoplankton growth rate, integrated over the water column, at any point in the hydrographic network. Phytoplankton only develops when its growth rate is higher than the rate of dilution by lateral inflows. Therefore, phytoplankton can only grow significantly in rivers from order 5 upward (Figure 5.8). As the depth increases with the order, the mean phytoplankton growth rate decreases in the higher orders under light limitation. The low growth rates upstream are the result of nutrient limitation.

As described above, the model is able to adequately simulate the seasonal variations of phytoplankton in the main sub-basins as well as in the main axis of the Seine River (Figure 5.9). As predicted by the comparison between the dilution rate and the phytoplankton growth rate, the phytoplankton biomass is only significant from order 5 upward and therefore increases from upstream to downstream. In accordance with the observations, the model predicts a spring peak dominated by diatoms and a summer peak dominated by Chlorophyceae. In the downstream part of the sub-basins, the model reproduces the sudden declines in spring bloom. In the summer, phytoplankton biomass again increases downstream of Paris and reaches its maximum in the estuary, downstream of Poses (Garnier *et al.*, 2001).

Simulations of the seasonal variations in phytoplankton biomass are also shown for 10 different years with various hydrological conditions at the outlet of the Marne sub-basin, taken as 9 subbasins (Figure 5.10). The control of the spring bloom of phytoplankton by the flow rates is confirmed. As soon as the flow rates have decreased

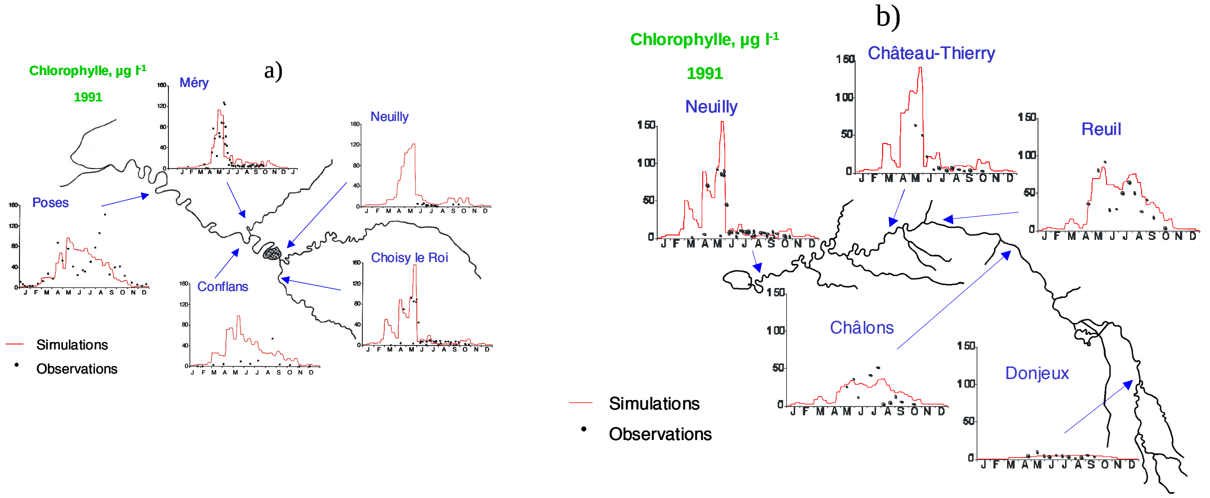

Figure 5.9: Seasonal and geographical variations of phytoplankton development in the Seine (1991). a) outlet of the major sub-basins and mouth of the river; b) Marne from order 4 (Donjeux) to order 6 (mid 6: Reuil, outlet: Neuilly).

in late winter or early spring, the phytoplankton builds up a large biomass that remains high if the water flow stays low (in 1991, 1993, 1997). The early spring bloom can be disrupted by a late rainy event (in April 1998), whereas when high flow rates are maintained until spring, the bloom may be delayed and reduced in intensity (in 1995 and 1999).

The model was used to investigate in what conditions the different nutrients might become limiting for the phytoplankton and what would be the impact on its mean summer and spring levels (Table 5.4).

This simulation confirms that nitrogen is far from being limiting: only a very strong reduction in the fluxes (99%) would cause any effect on the spring averages of the phytoplankton biomass. A phosphorus reduction scenario is more realistic given its point sources, but it would still have to be considerable (90% reduction) to affect the spring bloom of phytoplankton. The phytoplankton is also very sensitive to dissolved silica variations since a 50% reduction in the input significantly decreases its biomass. Although such a reduction is not feasible, because of the diffuse origin of silica due to rock weathering, its retention in stagnant systems (large reservoirs) could nevertheless influence its concentration downstream and subse-

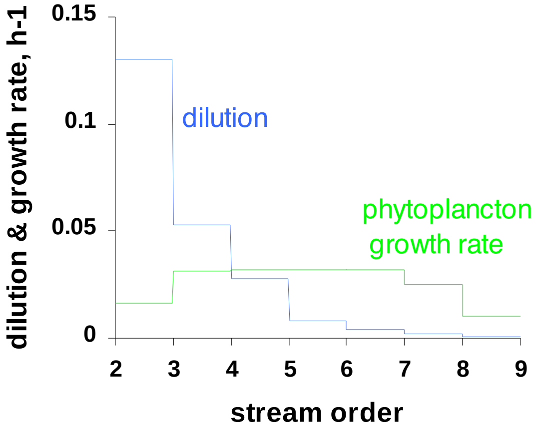

Figure 5.8: Comparison of the variations in the dilution rate and phytoplankton growth versus the stream order, for a spring situation (June).

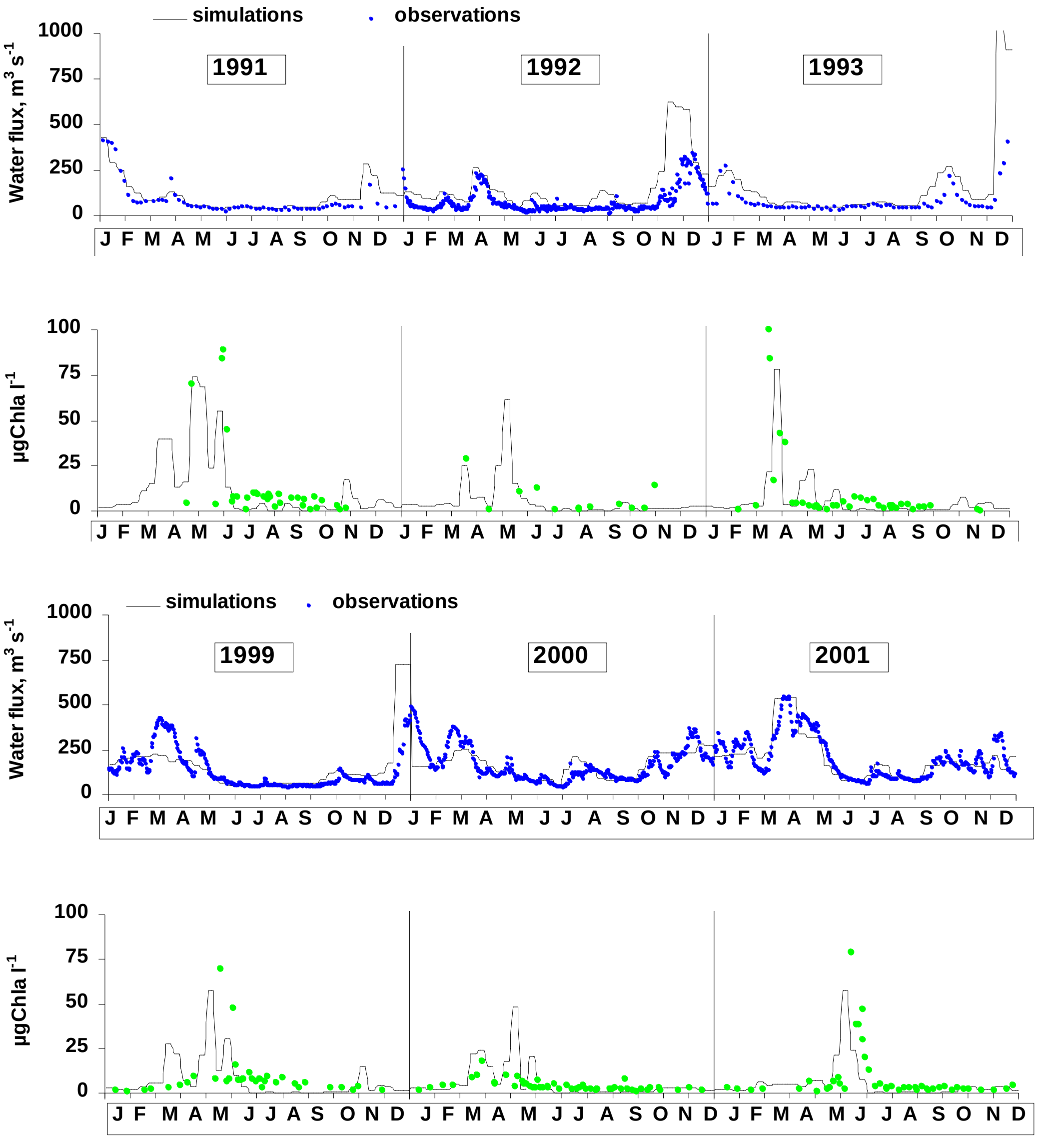

Figure 5.10: Simulated seasonal variations of phytoplankton development (dots) at the outlet of the Marne (Neuilly-sur-Marne) for two three year periods (1991-1993: dry; 1999-2001: wet) throughout a ten year period. Seasonal variations of water fluxes are shown for comparison.

quently change the phytoplankton successions as observed in the Danube (Humborg *et al.*, 1997). In the Seine basin the reservoir impact is not sufficient to markedly lower the silica on the whole basin.

At the sub-basin outlets where the phytoplankton decline occurs, phosphorus and nitrogen are not limiting. Regarding silica, river algal bloom dominated by diatoms may temporarily bring down its concentration to very low levels which would doubtless be limiting for the phytoplankton.

### 5.5.2 Autotrophy vs heterotrophy in eutrophic and/or polluted rivers: the Seine, the Loire, the Mosel and the Scheldt Rivers

Most of major Western European rivers have been extensively studied but rarely in an integrated manner, at the scale of their watershed basins. Because of the modular structure of the RIVERSTRAHLER model, it is possible to adapt the procedure to each case. The four rivers chosen here are situated in morpho-climatic domains similar to that of the Seine (Billen *et al.*, 1995). They can therefore be used to explore an increasing gradient of population density and of agricultural and industrial activity: their watershed basins are fairly small (Table 5.5). At their mouth the stream-orders are 8 for the Loire and the Seine, and 7 for the Mosel and the Scheldt. The hydrological regimes are all characterised by winter and early spring floods and summer low flow. The population density increases clearly from the Loire to the Scheldt according to a South-North gradient. As in the case of the Seine, human activity has greatly contributed to altering the hydrological regime of the rivers (navigation channels, wetlands draining, construction of reservoirs for flood protection). Among the rivers, the Loire is relatively untouched by engineering works, although it has two large dams in the upstream sector, there is no navigation.

As for the Seine River, phytoplankton develops from upstream to downstream in the Loire, Mosel

Table 5.1: Kinetic formulations of the processes taken into account in the RIVE model, and values of the correspon
(in Garnier et al., 1999a)

| Process | kinetic expression | Parameters | | | | |
|---|---|---|---|---|---|---|
| | **phytoplankton dynamics** | | **meaning** | **Diatoms** | **Chloro-phyc.** | |
| Photosynthesis (phot) | kmax (1-exp-( I/kmax)) PHY | kmax* | maximal rate of photosynth. | 0.2 | 0.5 | |
| | | [illegible] | initial slope of P/I curve | 0.0012 | 0.0012 | h-1/( |
| reserves synthesis | srmax M(S/PHY,Ks) PHY | srmax* | max. rate of reserve synthesis | 0.15 | 0.37 | |
| | | Ks | 1/2 saturation cst | 0.06 | 0.06 | |
| reserves catabolism | kcr R | kcr.* | rate of R catabolism | 0.2 | 0.2 | |
| growth (phygrwth) | mufmax M(S/PHY,Ks) lf PHY | mufmax | max. growth rate* | 0.07 | 0.14 | |
| nutrient limitation factor | with lf = M(PO4,Kpp) | Kpp | 1/2 sat. cst for P uptake | 15 | 46 | |
| | or M(NO3 +NH4, Kpn) | Kpn | 1/2 sat. cst for N uptake | 70 | 70 | |
| | or M(Si02 , KpSi) | KpSi | 1/2 sat. cst for Si uptake | 0.42 | - | mg |
| respiration | maint PHY +ecbs phygrwth | maint* | maintenance coefficient. | 0.002 | 0.002 | |
| | | ecbs | energetic cost of biosynthesis | 0.5 | 0.5 | |
| excretion (phyex) | exp phot.+ exb PHY | exp | ”income tax” excretion | 0.0006 | 0.0006 | |
| | | exb | ”property tax” excretion | 0.001 | 0.001 | |
| lysis (phylys) | kdf + kdf (1+ vf) | kdf* | mortality rate | 0.004 | 0.004 | |
| | | vf | parasitic lysis factor | 0 / 20 | 0 / 20 | |
| phyto sedimentation | (vsphy/depth).PHY | vsphy | sinking rate | 0.004 | 0.0005 | |
| NH4 uptake | phygrwth /cn NH4/(NH4+NO3) | cn | algal C:N ratio | 7 | 7 | |
| NO3 uptake | phygrwth /cn NO3/(NH4+NO3) | | | | | |
| PO4 uptake | phygrwth /cp | cp | algal C:P ratio | 40 | 40 | |
| Si02 uptake | phygrwth /csi | csi | algal C:Si ratio | 2 | - | g |
| temperature dependency | $p(T) = p(Topt).exp(-(T - Topt)/dti)$ | Topt | optimal temperature | 18 | 35 | |
| | | dti | range of temperature | 13 | 17 | |
| | **zooplankton dynamics** | | | | **Total zooplankton.** | |
| ZOO growth (zoogwth) | mzox.M(PHY-PHYo),KPHY).ZOO | [illegible] | max. growth rate | | 0.02* | |
| | | KPHY | 1/2 sat cst to PHY | | 0.4 | |
| | | PHYo | threshold phyto conc. | | 0.1 | |
| ZOO grazing | grmx.M((PHY-PHYo) KPHY).ZOO | grmx | max grazing rate | | 0.035* | |
| ZOO mortality | kdz.ZOO | kdz | mortality rate | | 0.001* | |
| temperature dependency | $p(T) = p(Topt).exp(-(T - Topt)/dti)$ | Topt | optimal temperature | | 22 | |
| | | dti | range of temperature | | 12 | |
| | **Lamellibranchs** | | | | **Dreissena.** | |
| Filtration rate | | fmax | max filtration rate | | 0.01* | |
| temperature dependency | $p(T) = p(Topt).exp(-(T - Topt)/dti)$ | Topt | optimal temperature | | 25 | |
| | | dti | range of temperature | | 8 | |
| | **bacterioplankton dynamics** | | | **small bac** | **large bac** | |
| HPi production by lysis | epi . (phylys+bactlys+zoomort) | ep1 | HP1 fraction in lysis pducts | 0.2 | | |
| | | ep2 | HP2 fraction in lysis pdcts | [illegible] | | |
| | | ep3 | HP3 fraction in lysis pdcts | 0.1 | | |
| enzym. HPi hydrolysis | kib.HPi | k1b | HP1 lysis rate | 0.005 | | |
| | | k2b | HP2 lysis rate | 0.00025 | | |
| HPi sedimentation | (vsm/depth).Hip | vs | Hip sinking rate | 0.05 | | |
| Hid production by lysis | de . (phylys+bactlys+zoomort). | ed1 | HD1 fraction in lysis pdcts | 0.2 | | |
| | | ed2 | HD2 fraction in lysis pdcts | 0.2 | | |
| | | ed3 | HD3 fraction in lysis pdcts | 0.1 | | |
| enzym. HDi hydrolysis | eimax. M(HDi,KHi).BAC | e1max | max. rate of HD1 hydrolysis | 0.75 | 0.75 | |
| | | e2max | max. rate of HD2 hydrolysis | 0.25 | 0.25 | |
| | | KH1 | 1/2 sat cst for HD1 hydrol. | 0.25 | 0.25 | |
| | | KH2 | 1/2 sat cst for HD2 hydrol. | 2.5 | 2.5 | |
| direct substr. uptake | bmax. M(S,Ks).BAC | bmax | max. S uptake rate | 0.2 | 0.8 | |
| | | Ks | 1/2 sat cst for S uptake | 0.1 | 0.1 | |
| bact. growth (bgwth) | Y. bmax. M(S,Ks).BAC | Y | growth yield | 0.25 | 0.25 | |
| bact. mortality (bactlys) | kdb.BAC | kdb | bact. lysis rate | 0.01 | 0.1 | |
| bact. sedimentation | (vsb/depth).BAC | vsb | bacteria sinking rate | 0 | 0.01 | |
| ammonification | (1-Y)/Y.bgwth/cn | cn | bact. C:N ratio | 7 | | |
| PO4 production | (1-Y)/Y.bgwth/cp | cp | bact. C:P ratio | 40 | | |
| temperature dependency | $p(T) = p(Topt).exp(-(T - Topt)/dti)$ | Topt | optimal temperature | 25 | 25 | |
| | | dti | range of temperature | 15 | 15 | |

Table 5.5: Simulated reduction in spring phytoplankton biomass (mg L$^{-1}$ of chlorophyll a, mean value in April and May, expressed in percentage) as a function of change factor in total inputs (F = 1 for the reference situation): diffuse and point inputs of nitrogen (N) and phosphorus (P), diffuse inputs of dissolved silica (Si). Results for 1991 at the outlet of the Marne.

| river systems | watershed area, km$^2$ | mean discharge m$^3$s$^{-1}$ | max. order | depth regul. | reservoirs | % arable land | popul density inh, Km$^2$ |
|---|---|---|---|---|---|---|---|
| Seine | 64 500 | 420 | 8 | yes | 3 major | 46 | 195 |
| Loire | 116 000 | 580 | 8 | no | small | 38 | 63 |
| Scheldt | 6 200 | 80 | 7 | yes | none | 39 | 426 |
| Mosel | 17 890 | 300 | 7 | yes | none | 20 | 190 |

and Scheldt (Figure 5.11). At the outlet of the hydrographic network, the level of nutrients and the main pattern of their seasonal variations are found by the model (Figure 5.12).

In classical ecology (Odum, 1971), the trophic state of a system is determined by the equilibrium between the autotrophic metabolism that produces oxygen and the heterotrophic metabolism that consumes it. On this basis, one can therefore establish a diagnosis of the autotrophic-heterotrophic state of a system and its variations in time and space. Autotrophic-heterotrophic diagrams (P/R diagrams) show, on the y-axis, the intensity of the metabolic production of oxygen or carbon in the system (P, algal photosynthesis) and on the x-axis, that of the processes of oxygen consumption or of organic matter degradation (R, respiration of bacteria, zooplankton and the benthos as well as of phytoplankton). In this type of diagram, the systems at equilibrium have an oxygen concentration at saturation level and fall on the diagonal, with increasing distance from the origin as the biological activity rises. Predominantly autotrophic systems, net producers of oxygen, lie above the diagonal (P/R >1) while the systems dominated by heterotrophic processes, net consumers of oxygen, fall below the diagonal (P/R <1), (Figure 5.13). The P/R diagrams are therefore a means of summarising the trophic state of an aquatic system during its evolution in time and space. Although such diagrams can be drawn on the basis of experimental data (Billen *et al.*, 1995), the model, validated at the scale of the hydrographic network, makes it possible to calculate the values of P and R at any point in the network and in all seasons.

According to the river-continuum concept RCC (Vannote *et al.*, 1980) a system not subjected to human intervention has an essentially heterotrophic behaviour in the lower-order streams (1 to 4) even without organic wastes inputs from urban or industrial origins. Their functioning is dominated by allocthonous fluxes of organic matter from their watershed basins and their primary production is weak. The system becomes progressively autotrophic from upstream to downstream.

The comparative analysis by the model of the P/R diagrams at a spatial scale in the 4 large rivers, shows that they, like the Seine, are very eutrophic judging by their high phytoplankton production (maxima of over 2.5 g C m$^2$d$^{-1}$). The case of the Scheldt is a special one, with heavy organic contamination that causes heterotrophic conditions in any order of the drainage network (Figure 5.14).

As in the Seine, the primary production in the

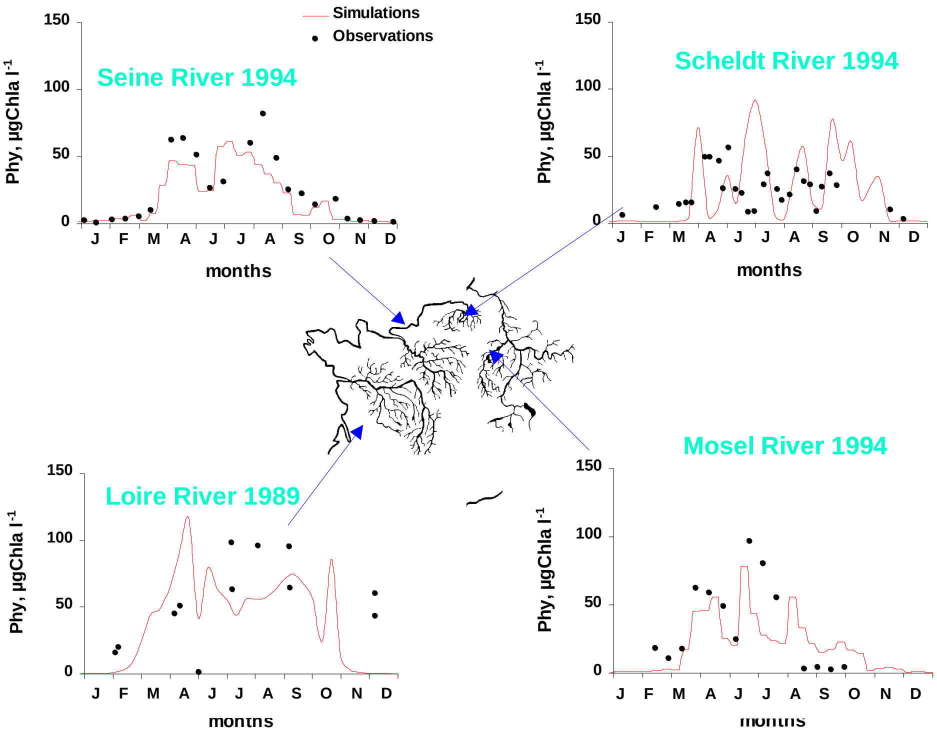

Figure 5.11: Simulations, by the RIVERSTRAHLER model, of phytoplankton biomass (Chl a) in the Seine (1994), the Loire (1989), the Mosel (1994), the Scheldt (1987) at the outlet of the their network.

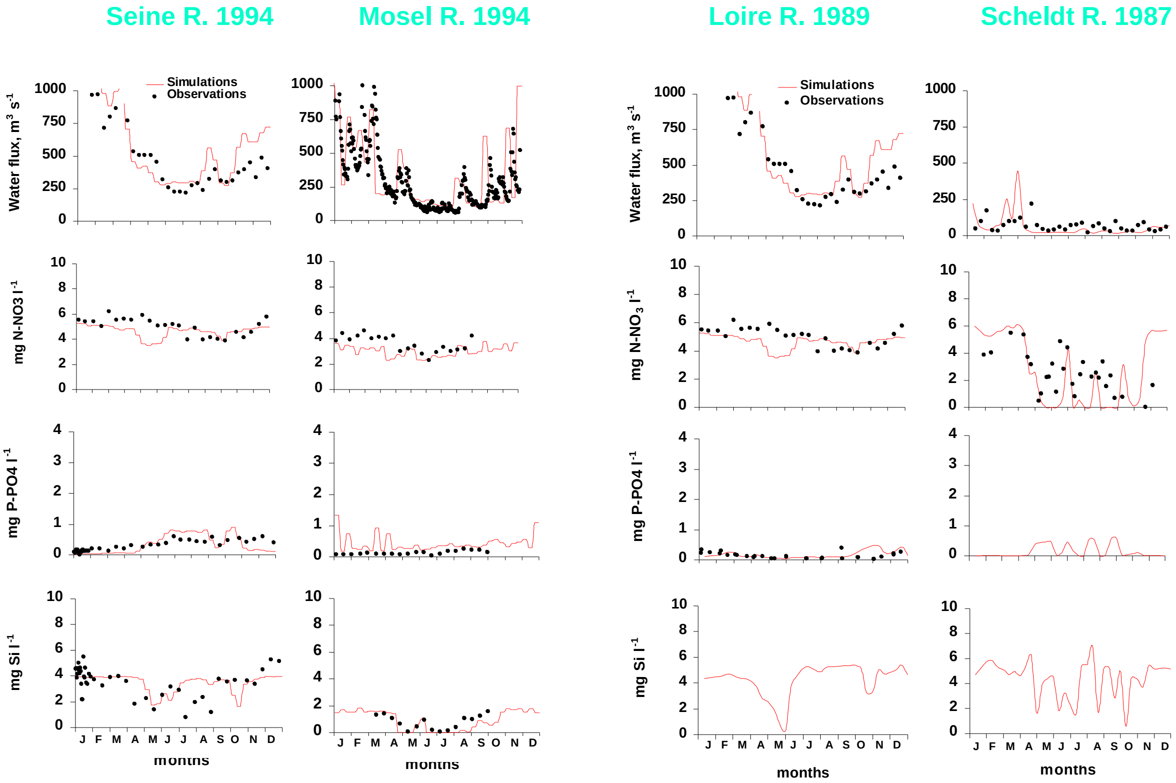

Figure 5.12: Simulation of seasonal variations of water fluxes (m$^3$ s$^{-1}$), nitrates (mg N l$^{-1}$), phosphates (mg P l$^{-1}$), silica (mg Si l$^{-1}$) in the Seine, the Loire, the Mosel an d the Scheldt.

Table 5.4: Simulated reduction in spring phytoplankton biomass (mg L$^{-1}$ of chlorophyll a, mean value in April and May, expressed in percentage) as a function of change factor in total inputs (F = 1 for the reference situation): diffuse and point inputs of nitrogen (N) and phosphorus (P), diffuse inputs of dissolved silica (Si). Results for 1991 at the outlet of the Marne.

| F | N | P | S |
|---|---|---|---|
| | | Chl a % | |
| 0.01 | 47.8 | 25.9 | 19.3 |
| 0.1 | 94.2 | 44.3 | 22.8 |
| 0.3 | 99.4 | 76.9 | 39.5 |
| 0.5 | 100.0 | 96.6 | 48.6 |
| 1 | 100.0 | 100.0 | 100.0 |
| 1.5 | 100.0 | 101.9 | 119.2 |
| 3 | 100.0 | 103.3 | 125.0 |

Mosel and Loire increases from upstream to downstream, beginning in orders 4 to 5. In contrast to the Seine and the Mosel, sudden declines of the phytoplankton production, leading to heterotrophy, occur only in the estuary of the Loire. In the Mosel, the system becomes heterotrophic already at Hauconcourt, the upstream part of the canalised principal axis, and remains so until the confluence with the Rhine (Detzem). Regarding the Seine, the system becomes heterotrophic downstream of Paris, but recovers after 150 km, at Poses, where the estuary begins, only to return to heterotrophy inside the estuary (Figure 5.14).

The analysis of the P/R diagrams at a seasonal scale in the Oise and the Marne tributaries of the Seine shows that the basin outlets are often heterotrophic, except in April and May, whereas the zones further upstream are always autotrophic (Figure 5.15). The most autotrophic sectors are those where the phytoplankton is always in the growth phase with still moderate allochthonous inputs (point sources). These sectors are then permanently oxygenated but the intense algal activity may increase the pH which poses problems for drinking water treatments (De Dianous *et al.*, 1995). The degradation of insufficiently treated discharges, which increase from upstream to downstream, then overtakes the algal production at the outlet of the sub-basins; phytoplankton biomass may become an autochtonous input of highly labile organic matter that leads to heterotrophic conditions (Figure 5.15). From the beginning of the transit through the Paris urban area, heterotrophic conditions dominate all year round (Figure 5.15). Downstream of Paris, after the impact of the treatment plant at Achères, these conditions become even more pronounced. A restoration phase that re-establishes an autotrophic state occurs at Poses, at the mouth of the estuary.

P/R diagrams analysis led to an interpretation of the upstream-downstream functioning of these large impacted and regulated rivers as a succession of heterotrophic and autotrophic sequences. The diagrams confirm the RCC theory but show clearly how the systems have been changed by human intervention and allow to quantify the effect of these interventions. It is clear that the strong human pressure on the Seine contributes to an increase in the alterations between heterotrophic and autotrophic conditions in the system; when the pressure is extreme, as in the case of the Scheldt, the sequence is limited to heterotrophy.

## 5.6 Combating eutrophication in the Seine river and the Seine Bight: scenarios analysis

### 5.6.1 In the upstream basins

As practical examples of management options, various scenarios of phosphate removal were tested on the strongly eutophicated Marne river. The modelling strategy was to consider separately 9 sub-basins and the main branch, to which was coupled a model of the reservoir. After the model was validated through its ability to reproduce available water quality observations (Garnier *et al.*, 2004b),

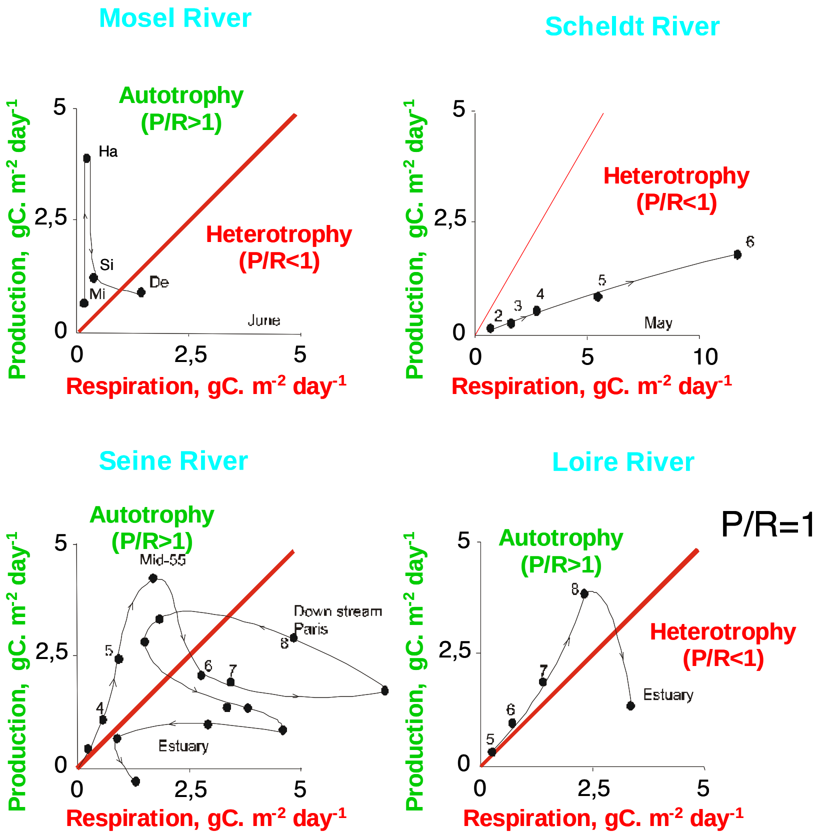

Figure 5.14: Geographical variations of Production vs. Respiration (mg C m$^{-2}$ day$^{-1}$) ), in the Mosel (1993, from upstream to downstream at order 5: Mi: Millery; Ha: Hauconcourt; Si: Sierck; De: Detzem), and from upstream -order 2 to 4-, to downstream -order 6 to 8- in the Scheldt (1987), in the Seine (1991) Loire (1989). Spring situations (June).

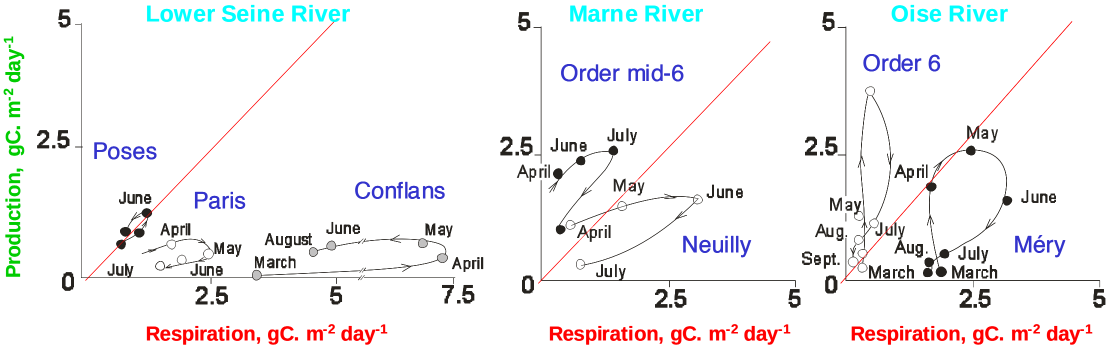

Figure 5.15: Seasonal P/R variations (1991) in the Marne, Oise basin, and in the main axis of the low Seine river. Model outputs at a) Paris, Conflans (upstream the Oise confluence and downstream the waste water effluents of the largest Waste Water treatment Plant of the Seine Basin, 6.5 10$^{6}$ inhabitant equivalent), and Poses the limit of the freshwater estuary: b) two Marne stations (La Ferté, 2/3 of order 6 and Neuilly, near the Seine-Marne confluence, order 6) and two Oise stations (Compiègne: Oise-Aisne confluence, order 6; Méry: Oise, upstream Seine confluence, order 7).

different realistic scenarios of future reduction of phosphorus load can be tested, in various hydrological conditions (dry and wet years). The effect of hydrological variations as well as the phosphorus loading from both point and diffuse sources can be explored.

Under dry hydrological conditions, eutrophication by phytoplankton remains a major problem for drinking water production, even after the implementation of drastic programmes of point source reduction down to 85% of the present loading, although already been reduced to 65% of the 1990 level. Diffuse phosphorus sources from agriculture is found to be important, especially because a high proportion of particulate phosphorus originating from soil erosion is exchangeable with the dissolved phase (Némery, 2003; Némery *et al.*, 2004) and available for phytoplankton growth.

When the present conditions of diffuse and point sources were applied to the hydrological conditions of 1991, the driest in our data base, phytoplankton development reached values similar to those really observed for the year 1991, before the reduction in point sources (Figure 5.16). This result shows that, in hydrological conditions that are not extreme compared to 1976 and 2003 for example, the hydrosystem remains eutrophic, despite the reduction of phosphorus point sources by a factor of 3. Phytoplankton biomass can reach 80 µg Chl a $l^{-1}$, as the phosphorus concentration is higher due to the weaker dilution of the point inputs by low water flow. These results tend to show that further or additional P treatment efforts are needed to prevent phytoplankton development.

Recently constructed wastewater treatment plants in the Seine basin (e.g. the Colombes treatment plant downstream from Paris), using advanced tertiary treatment technology are able to reduce the specific phosphorus load to less than 0.2 g P $inhab^{-1}d^{-1}$ (Garnier *et al.*, 2004a). A value of 0.15 g P $inhab^{-1}d^{-1}$ in the discharge of all wastewater treatment plants in the Marne would decrease the point load from the present one of 1260 kgP $d^{-1}$ in 2000 to 200 kg P $d^{-1}$. The lower P value has a significant effect on phytoplankton biomass, which remains however as high as 60 µg Chl a $l^{-1}$ during the spring bloom (Figure 5.16).

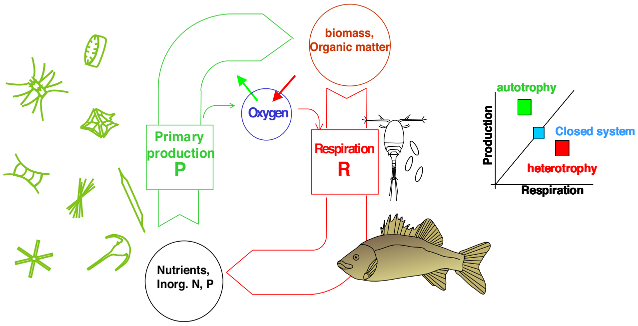

Figure 5.13: Schematic representation of P vs. R diagrams. For closed system, without nutrient input primary production and respiration are equilibrated, P vs R point being situated on the diagonal. When nutrients are added to the system, primary production increases and oxygen is super saturated, P vs. R point being above the diagonal, the system is autotrophic. In a system enriched in organic matter, mineralization increase and oxygen is consumed, P vs. R point being below the diagonal, the system is heterotrophic.

It appears clearly from these results that action aimed solely at the point sources is not sufficient to completely prevent eutrophication. A further test by the model consisted in reducing diffuse sources of phosphorus. For that purpose, we reduced by a factor of 2 the phosphate concentrations in surface and groundwater runoff and considered an additional 50% riparian retention of suspended solids. In these conditions, the spring bloom falls below 40 µg Chl a $l^{-1}$ (Figure 5.16).

Clearly, measures for reducing phosphorus emissions from WWTPs are not sufficient to completely control freshwater eutrophication but must be accompanied with reduction of diffuse sources linked to agricultural leaching and erosion.

### 5.6.2 In the coastal zone

The occurrence of episodic blooms of toxic dinoflagellates of the Seine Bight has led to investigate its relationships with human activity in the Seine watershed. The RIVERSTRAHLER model has been linked to SiAM-3D/ELISE, a model of coastal zone including the estuary; this latter model is a 3D hydrodynamic coupled to an ecological model of the Seine Bight allowing to repro-

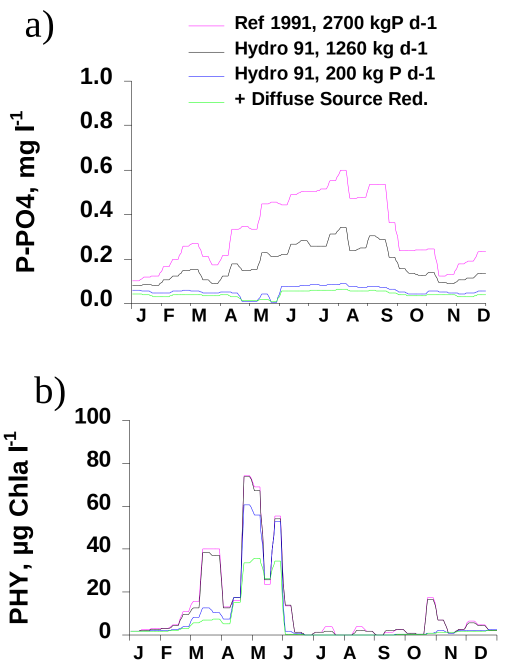

Figure 5.16: Response of the model to a reduction of point source phosphorus in the hydrological conditions of 1991 (2700 kg P d$^{-1}$: phosphorus load in 1991, 1260 kg P d$^{-1}$: phosphorus load in 2000; 200 kg P d$^{-1}$: further reduction tested, 200 kg P d$^{-1}$ + Diffuse source reduction); a) variations in the phosphorus concentrations; b) variations in the phytoplankton biomass levels given in chlorophyll a concentrations.

duce the spatio-temporal variations of sediment transport, thermo-haline stratification and phytoplanktonic development in the plume of the Seine river (Cugier, 1999; Cugier & Le Hir, 2002; Cugier *et al.*, 2004b).

Once the chain of models have been validated by their ability to reproduce observed trends of interannual variations of nutrients delivered by the Seine, as well as the response of the marine biocenose in terms of diatoms and dinoflagellates development (Cugier *et al.*, 2004a), various scenarios of human activity in the watershed can be simulated with alternative policies of wastewater nitrogen and/or phosphorus treatment in terms of marine eutrophication reduction (Figure **??**).

As the proportion of phosphorus point sources increases from the upstream to downstream in regards to diffuse sources, at short term a possible control actions able to reduce nutrient contamination at the coastal zone is the improvement of wastewater phosphorus treatment. An efficient reduction of the nitrate in term of eutrophication is more uncertain due to its dominant diffuse origin (especially from agricultural soils) and the time lag caused by nitrate accumulation in the aquifers (Gomez, 2002; Gomez *et al.*, 2002). We however explore the effect of phosphorus and/or nitrogen tertiary treatments of urban wastewater treatment plants, assuming that the diffuse sources of nutrients are constant, although, due to the time lag caused by nitrate accumulation in the unsaturated soil zone and in the aquifers, prospective models of ground- and surface water contamination in the Seine basin predicts further increase of nitrate concentration during the next decade, even for the hypothesis of a systematic improvement of farming practices (Gomez, 2002; Gomez *et al.*, 2002).The scenarios are run under dry hydrological conditions, shown to be the most critical for the development of potentially harmful algae.

Whereas, a drastic reduction of the phosphorus load discharged with domestic and industrial effluents is technically feasible at the scale of the entire Seine watershed, nitrogen treatment of wastewater is technically more complex. The ordinary activated sludge process retains about 20% of the raw nitrogen load in the produced sludge but can be increased to 50%, by re-circulating a part of nitrified effluents at the head of the biological treatment for denitrification. A reduction of nitrogen from 70% to 90%, in wastewater is technically possible but at a much higher cost, by using methanol or ethanol as external electron donor for the denitrification.

Several hypotheses of phosphorus and/or nitrogen treatment of urban wastewater in the basin were therefore tested. For phosphorus, a generalized 90% reduction throughout the year was tested. For nitrogen, scenarios with 50%, reduction of point sources have been considered. A combined P and N reduction was then explored (Figure **??**).

The phosphorus reduction of wastewater (P 90% trt) appears as a quite effective measure to reduce the potentially harmful algal blooms in the Seine Bight (Figure **??**). Diatom maximum biomass is divided by a factor of 2, and that of flagellates by a factor of 10, phosphorus becoming the limiting factor. Treating phosphorus during the productive period only gives approximately the same result on flagellates as when the treatment is conducted the all year long (Cugier *et al.*, 2004a). In the Seine Bight, flagellate blooms especially occur in the river plume area directly under the influence of nutrient inputs. The Seine river flow and the tidal dynamics lead to a short resident time of freshwaters in that area. Therefore, winter nutrient inputs are rapidly exported into the English Channel, so that the phytoplankton production is mostly dependent on recent nutrient inputs. Regarding the reduction of nitrogen point sources, whereas it does not affect the diatom biomass, the flagellate biomass, limited by nitrogen with a 50% reduction, decrease by a factor of 2. Silica remains the limiting factor whatever the degree of nitrogen treatment of the wastewaters (Figure **??**). Combining a 50% nitrogen reduction and a 90% phosphorus reduction of point sources in the watershed does not provide any significant improvement in terms of flagellate blooms compared to the sole phosphorus treatment. In fact, the nutrient limiting effect due to phosphorus for the P 90% trt scenario is greater than the one due to nitrogen in the N 50% trt scenario.

It is now recognized that increased phosphorus and nitrogen inputs cause silicon to be the main limiting factor for diatom production, favouring flagellate summer blooms which use the nitrogen and phosphorus left over after diatoms have depleted silica (Lancelot *et al.*, 1987; Lenhart *et al.*, 1997; Rousseau *et al.*, 2002; Turner *et al.*, 2003). The recent decreasing trend of phosphorus per capita load (Foy *et al.*, 1995; Billen *et al.*, 2001; Garnier *et al.*, sumbitted) and the feasibility, at relatively low cost, of phosphorus treatment of wastewater, should in the nearby future allow a shift of the ecosystem from silica and nitrogen to a general phosphorus limitation, leading to a significant reduction of harmful algal blooms in the Seine Bight. However on one hand, the impact of nitrogen in excess over silica and phosphorus in surrounding marine areas is not fully understood, and on the other hand the future trend of phosphorus load from agriculture sources (fertilizers, farm effluents) is not known.

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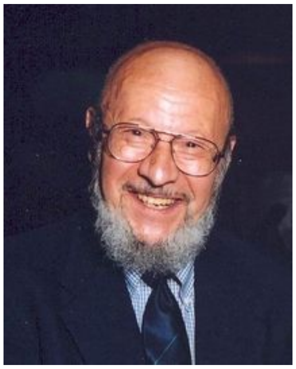
# Part III

# Pelagic block

# Chapter 6

# Eutrophication and phytoplankton



Theodore J. Smayda
Graduate School of Oceanography
University of Rhode Island
Kingston, RI 02881
tsmayda@gso.uri.edu

## 6.1 Introduction

The role of nutrients in regulating the seasonal and regional abundance of phytoplankton, their blooms, species successions, and carbon production (*primary production*) is a classical problem in biological oceanography. The natural fertility of marine waters varies greatly because the amount of nutrients supplied through natural processes to support photosynthesis and growth of the phytoplankton varies regionally and seasonally. The Sargasso Sea, for example, is well known for its poor nutrient supply and oligotrophic nature, in contrast to the high productivity and fisheries yield of nutrient-rich upwelling regions. Nutrient enrichment of oligotrophic waters can benefit food chains, but coastal ecosystems, which are intrinsically productive because of natural nutrient recycling processes, can become degraded through excessive enrichment with anthropogenic nutrients (Ærtebjerg *et al.*, 2003; Cloern, 2001; Jørgensen & Richardson, 1996). Analyses and mitigation of the impact of eutrophication on coastal phytoplankton behaviour require an understanding of the photosynthesis – nutrient relationship. This coupled physiology regulates the basic, cellular responses of the phytoplankton to nutrient enrichment, while the population that develops is modified by food web processes. This physiology, and eutrophication as a process will be reviewed briefly before describing some specific responses of the phytoplankton to nutrient enrichment.

The phytoplankton (*primary producers*) require four primary inorganic macro-nutrients ($NH_4$, $NO_3$, $PO_4$, $SiO_2$) and five *micro-nutrients* (Fe, Cu, Zn, Mn, Mo) to fix carbon during photosynthesis. The photosynthesis equation can be written as an oxidation-reduction reaction having the general form:

$$2H_2O+CO_2+Light \rightarrow (CH_20)+H_2O+O_2 \quad (6.1)$$

with the reaction mediated by the pigment chlorophyll a. Light energy is used to oxidize water yielding gaseous molecular oxygen (Falkowski & Raven, 1997). The $CO_2$ reduced during photosynthesis is temporarily fixed to an organic molecule ($CH_20$) which serves as the substrate used in subsequent biosynthetic reactions to manufacture amino and nucleic acids, lipids, proteins, enzymes, etc. required for cellular growth and reproduction. This biosynthesis requires the concurrent assimilation of essential nutrients (nitrogen, phosphorus, micro-nutrients, etc.) during photosynthesis. The rate of nutrient assimilation is a function of its concentration, and increases hyperbolically with this (Figure 6.1). There are two kinetic characteristics of the nutrient uptake curve which vary among species and influence their responses to nutrient enrichment (or limitation) in competition with other species (Smayda, 1997): the maximum velocity of cellular uptake ($V_{max}$) and the concentration of nutrient ($K_s$) at which uptake is one-half $V_{max}$. The half-saturation constant, $K_s$, is particularly important since it determines the efficiency with which species take up nutrients at low concentrations. The higher the $K_s$ constant, the less able the species in question to assimilate nutrients at low concentrations. On this basis, it might be expected that eutrophication would favor species less efficient in nutrient uptake.

Numerous experiments have shown that at increased rates of nutrient uptake cellular growth is stimulated, and an increase in population abundance results. Similar to the nutrient uptake curve (Figure 6.1), the population will increase up to an asymptotic level and remain relatively constant irrespective of further increases in nutrient concentration. The population at this upper (non-grazed) level corresponds to the *carrying capacity* for that particular species growing in response to the nutrient being supplied. The carrying capacity of a given nutrient level is not constant; it varies with nutrient type, concentration, accompanying growth factors, and among species. Excessively high nutrient levels, particularly $NH_4$, can be inhibitory (Thomas *et al.*, 1980). The amount of light (Eq. 6.1) available influences the effect of nutrients on photosynthesis at the cellular (individual) level, a relationship found also for natural populations (Cloern, 2001). Photosynthesis when deprived of light ceases, or decreases when nutrients are in short supply. During these conditions, the reverse reaction in Eq. 6.1 predominates or is favoured; i.e. oxygen is consumed (*respiration*) leading to the production of $CO_2$. If the respiration pathway is prolonged and the ratio of photosynthetic oxygen production to respiration drops below 1.0, the decreasing oxygen level will push the water body towards hypoxia or, in extreme cases, to anoxia. Thus, nutrient loading can oxygenate and de-oxygenate a nutrient-enriched watermass (Rabalais & Turner, 2001).

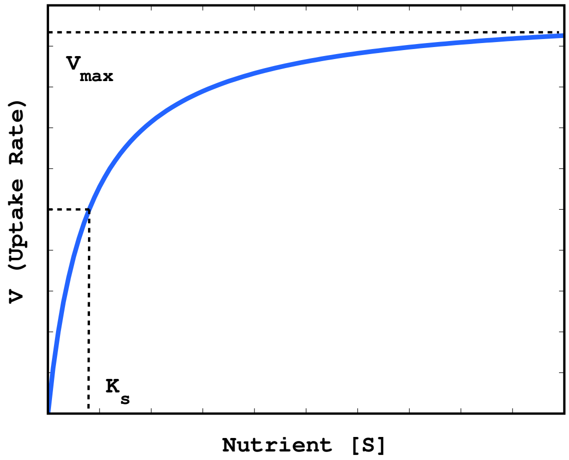


Figure 6.1: Hyperbolic relationship between the uptake of a nutrient (V) and its concentration [S]. $V_{max}$ is the maximum velocity of uptake, and Ks the nutrient concentration at which the uptake rate is one-half that of $V_{max}$. A hyperbolic relationship also occurs between population abundance and nutrient concentration, with the linear portion of the curve corresponding to the yield-dose response to increasing nutrient levels. An equilibrium level is reached at a threshold nutrient concentration, above which the species carrying capacity (population abundance) remains constant despite any further increase in nutrient concentration, and if not inhibitory causing the population to decline (see text for details).

In summary, the amount and types of nutrients available influence two coupled, cellular responses: the rate of nutrient uptake (Figure 6.1) and the rate of photosynthesis (Eq. 6.1). These responses, in turn, regulate the rates of cellular (species) growth and population growth (abundance). Eutrophication also has two distinct modes of ecosystem impact — primary and secondary — with the impacts of the nutrient disturbance further influenced by the other habitat conditions. The primary (direct) effect of nutrient enrichment is on the phytoplankton, both their abundance and species responses. This altered behavior impacts upper trophic level processes and components whose responses develop as secondary (indirect) effects of nutrification. Thus, both bottom-up (nutrient-phytoplankton responses) and top-down (grazer-phytoplankton responses) manipulations accompany nutrient enrichment of marine coastal systems. This complexity, the nutrient-photosynthesis relationship, the nine major macro- and micro-nutrients that regulate phytoplankton growth, and differences in species' nutritional physiology and kinetics make analysis of the influence of eutrophication on phytoplankton difficult. The following overview is therefore subject to modification as knowledge of eutrophication as a process and as a stress on marine ecosystems increases.

## 6.2 Nutrient Limitation and Eutrophication as a Process

Are marine phytoplankton communities responsive and even vulnerable to anthropogenic nutrient enhancement? Numerous field and experimental studies suggest that the supply of nitrogen for primary production in marine waters is the critical nutrient and process. This has led to the paradigm that marine phytoplankton growth is nitrogen-limited, unlike fresh water communities which are phosphorus-limited. Hecky and Kilham (1988) have questioned whether marine coastal waters are more N-limited than P-limited, and attribute this view to experimental artifact. Nonetheless, the bulk of the experimental and field evidence favors widespread N-limitation. The notion of nutrient limitation is an old concept, extrapolated from Liebig's Law of the Minimum formulated for agricultural systems (see de Baar, 1994) and applied to the sea a century ago (Brandt, 1899). The essence of this concept is that the amount of nutrient (i.e. nitrogen or phosphorus) available regulates phytoplankton growth and biomass through a *yield-dose* response. In this relationship, there is usually a linear, direct increase in phytoplankton abundance in response to nutrient supply, and which corresponds to the first (linear) segment of the hyperbolic (curvilinear) relationship shown for nutrient uptake (Figure 6.1). However, should nutrient loading continue to increase, there is a threshold concentration at which the population carrying capacity is reached, and above which the response to further increases in nutrient loading is similar (hyperbolic) to that in Figure 6.1.

The yield-dose response is one aspect of the relationship; changes in phytoplankton species composition and bloom dynamics can also accompany nutrient enrichment, will be discussed. The focus on nitrogen has tended to ignore evidence that phosphorus, silicon and iron also can limit marine phytoplankton growth. Silicon can limit the *in situ* growth of diatoms. Diatoms are unique among the phytoplankton in their requirement for silicon (Conley & Malone, 1992). Documentation of iron limitation remains an intense line of research (Sunda & Huntsman, 1995; Hutchins, 1995). While the N limitation hypothesis underpins marine eutrophication research, it is important to recognize that eutrophication alters the total sum of macro- and micro-nutrients that affect phytoplankton, either as growth stimulants or inhibitors. As a result, there may be multiple, concurrent nutrient limitation involving N, P, Si, Fe which have different impacts on, and targets different floristic components (species, functional groups) within the phytoplankton community.

It is essential that eutrophication be recognized as a process of impact and change that progresses through various phases in response to the intensity, nature and degree of nutrient loading (see Jørgensen & Richardson, 1996); *eutrophication is not a trophic state.* Seki & Iwami (1984) recognized four stages in the eutrophication of habitats, progressing from an oligotrophic state (believed to be the original state of natural waters) to an advanced hypereutrophic state reached after passing through intermediate mesotrophic and eutrophic stages. Transitions from one stage to the next are gated by thresholds in habitat parameters that are modified during nutrient enrichment. Seki & Iwami used the ratio of particulate to dissolved organic matter in relation to the total organic content, and produced in response to enrichment, to designate the thresholds at which transition into the next eutrophication stage occurs. The relationship between the turnover time of soluble amino acids vs. inorganic nitrogen levels was also used. Seki & Iwami emphasized that in focusing on the phytoplankton the heterotrophic microbial community must not be neglected; indeed, the metabolic contribution of the latter to nutrient-enhanced, organic cycling progressively increases with eutrophication intensity. *That is, the importance of phytoplankton relative to bacteria will progressively diminish in its biochemical regulation of the saprobic water quality that accompanies increasing eutrophication.* In a slightly different approach, Nixon (1995) used the total annual supply of carbon from primary production within the system (autochthonous carbon) and introduced from external sources (allochthonous carbon) to classify trophic states along the eutrophication pathway. He also recognized four eutrophication stages, including a terminal hypertrophic stage when nutrient enrichment is particularly high (Table 6.1). The Seki & Iwami and Nixon classification schemes link the definition of eutrophication as a process to the metabolism or total supply of organic carbon, rather than to the fluxes and concentrations of specific inorganic nutrients, the parameter usually focused upon. For example, the UK Comprehensive Studies Task Team (CCST, 1994, 1997) uses winter concentration of '*dissolved available inorganic nitrogen*' (DAIN) to classify eutrophication status. A state of hypernutrification is considered to be present and a precursor to eutrophication when/where winter DAIN concentrations significantly exceed 12 mM m$^{-3}$ and there is at least 0.2 mM dissolved inorganic phosphorus m$^{-3}$. The CSTT considers a habitat to be eutrophic if summer chlorophyll concentrations regularly exceed 10 mg chl m$^{-3}$.

Table 6.1: Trophic classification of marine systems based on annual organic carbon supply, g C m$^{-2}$ y$^{-1}$ (from Nixon, 1995)

| Trophic State | g C m$^{-2}$ y$^{-1}$ |
|---|---|
| Oligotrophic | <100 |
| Mesotrophic | 100 – 300 |
| Eutrophic | 301 – 500 |
| Hypertrophic | >500 |

While the Nixon classification distinguishes between cause and effect, Ærtebjerg *et al.* (2003) point out that it [and the Seki & Iwami classification to a lesser extent] does not take into account the ecosystem structural (trophic) and qualitative (species) changes induced by nutrient enrichment. That is, the biotic changes that occur in direct (primary) response (phytoplankton) and indirect (secondary) response (grazers) to nutrient enrichment are not incorporated into existing definitions of eutrophication as a process. The need to classify, predict and mitigate the biotic and ecosystem changes that accompany eutrophication is important because it is these responses that impact the quality and cultural use of coastal waters. As Ærtebjerg *et al.* (2003) also point out, existing marine monitoring programs and time series data sets seldom include measurements of all the variables needed to estimate the total supply of organic matter to a given system, or its fractionation into dissolved and particulate components. This compromises general use of existing classification schemes. *There is need to redefine eutrophication, incorporating into the definition appropriate diagnostic descriptors of biotic changes that accompany eutrophication.*

## 6.3 Eutrophication and Phytoplankton: the Mass Balance Approach

Operationally, two different approaches have been applied in analyzing the effects of eutrophication on phytoplankton: a mass balance approach and an organismal approach. The eutrophication classification schemes discussed above, i.e. the increased rate of supply of organic carbon to an ecosystem (Nixon); the ratio of particulate to dissolved organic carbon, the soluble amino acid turnover times (Seki & Iwami); winter dissolved inorganic nitrogen levels and summer chlorophyll (= biomass) levels (CSTT) are mass balance approaches. These classifications emphasize the abundance (yield) of phytoplankton that develops in response to added nutrient (dose). Conceptually, the mass balance approach applies the photosynthesis-respiration reaction (Eq. 6.1) in combination with the stoichiometric relationships (Redfield Ratio) that occur between nutrients (nitrogen, phosphorus) and the photosynthesis and respiration of organic matter. In this relationship, nitrogen (N) and phosphorus (P) are bound and released during the synthesis and respiration of organic carbon (C) which, in turn, result either in the production or utilization of oxygen (O):

$$O : C : N : P \tag{6.2}$$

The quantities of the four elements processed in this biochemistry, known as the Redfield Ratio, can be expressed in terms of atoms (Eq. 6.3), or by weight (Eq. 6.4):

$$O : C : N : P = 212 : 106 : 16 : 1 \tag{6.3}$$

$$O : C : N : P = 109 : 41 : 17.2 : 1 \tag{6.4}$$

Thus, during photosynthesis (primary production) for every atom of P assimilated, 16 atoms of N will be assimilated and 106 atoms of C fixed into organic matter (from $CO_2$ — see Eq. 6.1), liberating 212 atoms of O. This assimilation of N and P leads to phytoplankton growth (i.e. biomass = carbon, chlorophyll, etc.) and oxygenates the watermass. Ideally, from a knowledge of the amount of N and P available, for example the DAIN concentrations recommended by CSTT, one can estimate the amount of C that would be produced to evaluate potential eutrophication effects. And, from the biomass level, i.e. the summer chlorophyll (= biomass) levels applied by CSTT as an index of eutrophication status, one can estimate the amount of N and P needed to produce and sustain that biomass level. In that case, one needs to know the C:Chlorophyll a ratio, which varies from ca. 40:1 to 150:1 (by weight) and depends on the phytoplankton group present and their nutritional status. Note that the Redfield Ratio, as in Eq 6.2, describes a reversible process, i.e. the respiration or decomposition of biomass. The break down of C will consume $O_2$ and liberate N and P. A good example of such mass balance behavior with adverse effects is provided by blooms of the dinoflagellate genus *Ceratium* which sometime result in hypoxic or anoxic events. Blooms of ceratian species can be stimulated by nutrient enrichment (Braarud, 1945; Granéli *et al.*, 1989). Hypoxic and anoxic ceratian blooms have been reported in the Kattegat (Granéli *et al.*, 1989), German Bight (Dethlefsen & Westernagen, 1983) and New York Bight (Falkowski *et al.*, 1980), among other areas. During such events, the ceratian species respond in yield-dose behavior to available nutrients, with the population increasing until essential nutrients become exhausted. Nutrient exhaustion then prevents further growth and is even unable to support the existing biomass. The population becomes physiologically stressed; the cells loose their motility and sink to the bottom sediments where they rot. During their decomposition, $O_2$ is utilized (Eq 6.2) which decreases *in situ* concentrations and pushes bottom water towards hypoxia or anoxia. Such occurrences and the degree of deoxygenation depend upon the amount of ceratian biomass being decomposed and the degree to which the bottom waters are ventilated by physical oceanographic processes (see Ærtebjerg *et al.*, 2003). Regions of bottom water stagnation, particularly during summer–autumn when ceratian blooms[1] predominate, are predisposed to hypoxic blooms. Anoxic ceratian blooms are also facilitated by reduced grazing pressure on *Ceratium* species because their large cell size leads to predator-prey mismatches (Nielsen, 1991). Anoxic events can accompany blooms of other dinoflagellate species (Jones *et al.*, 1982; Legovic *et al.*,

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[1] blooms dominated by *Ceratium* species

1994), silicoflagellates (Fanuko, 1989), cyanobacteria (Galat & Verdin, 1989), *Phaeocystis* (Rogers & Lockwood, 1990), and diatoms (Delafontaine & Flemming, 1997). However, it is often difficult to find a definitive link between the hypoxia (anoxia) developing during phytoplankton blooms and nutrient enrichment.

## 6.4 Eutrophication and Phytoplankton Species Selection and Responses

The relationships between eutrophication and phytoplankton biomass are more evident than the effects of anthropogenic nutrient enrichment on individual phytoplankton species. Field studies have detected changes in species composition and abundance in a variety of nutrient-enriched environments, including the Dutch Wadden Sea (Cadee & Hegeman, 1986; Riegman *et al.*, 1992), the Baltic Sea (Kahru *et al.*, 1994; Olli, 1996), the Black Sea (Bodeanu, 1993; Bodeanu & Ruta, 1998) and New York Bay (Mahoney & McLaughlin, 1977). As already pointed out, the increase in nutrients during the initial phase of eutrophication leads to higher phytoplankton biomass through yield-dose kinetics. During these initial stages, particularly during the winter-spring period, the indigenous flora (most often diatoms) usually increases in abundance without novel changes in species behaviour occurring. The Si-requiring diatoms are generally considered to be the 'most desirable' bloom species with regard to grazer suitability, trophic value and water quality. Should nutrification continue to increase, a change in the species composition and the size structure of the phytoplankton community may result and potentially affect energy flow in the impacted ecosystem (Dortch *et al.*, 2001). In extreme cases, the impacts of altered phytoplankton species composition, abundance, size structure and bloom events in response to nutrient enrichment will cascade through upper trophic levels and reform food web structure (Turner, 2001). This latter (secondary) effect will tend to blur the primary responses (i.e. phytoplankton behavior) to eutrophication and mask cause and effect. The nutrient-induced reformation of ecosystems is an extremely complex and poorly understood ecological process.

The shift in phytoplankton species that has attracted the most interest is the shift in abundance (blooms) from diatoms to other non-motile species and flagellates — a *functional group* shift. Functional groups and their shifts are of interest because of significant differences in their physiology and ecological impacts. There is special interest in the diatom:flagellate ratio as a potential indicator of eutrophication since the global increase in harmful microalgal blooms (HABs) is primarily a flagellate species phenomenon [see also Chapter 7, this volume]. It has been hypothesized that the diatom:flagellate ratio should decrease with increasing nutrient enrichment, and consequently might serve as an indicator of eutrophication status. There is some supporting evidence for this from Kastela Bay, Croatia, where a progressive, long-term increase in anthropogenic nutrient has been accompanied by a 10-fold decrease in the ratio of diatom to flagellate abundance (Maresovic & Pucher-Petkovic, 1991). The primary nutrient expected to regulate the shift in functional groups from diatoms to flagellates is silica, which is required by diatoms but not by other microalgal groups exclusive of silicoflagellates (Officer & Ryther, 1980; Smayda, 1990). Silica concentrations and ratios with N and P are altered by eutrophication, with the degree and pattern of change influenced by the chemical nature of the waste water being discharged (Officer & Ryther, 1980; Conley *et al.*, 1994). Silica is assimilated by diatoms stoichiometrically in the Redfield Ratio (Eq. 6.2) in atomic proportions of 1:1 with N, and 16:1 with P. At Si:N supply ratios of <1:1, diatoms will be Si-limited, and N-limited at Si:N supply ratios >1:1. Smayda (1990), based on an evaluation of long-term blooms and nutrient conditions in various regions, has suggested that anthropogenic enrichment of N and P has led to long-term declines in the ratios of Si:N and Si:P which potentially favor non-diatom blooms in such impacted regions. Mescocosm experiments led Egge *et al.*

(1992) to suggest that there is a threshold of approximately 2 $\mu$M Si, below which "*diatoms, as a group, are outcompeted by the 'flagellate group'*". The merit of the Si ratio and threshold concepts as eutrophication switches that result in species shifts and altered community abundance is still under investigation (see the EU SIBER project page). But it is clear that the species-specific responses to these proposed Si effects are under multifactorial control rather than are simple linear responses. For example, Sommer's (1994) experiments showed that diatoms became dominant at Si:N ratios >25:1, while flagellates were superior competitors at lower ratios. Although irradiance did not significantly influence the competition between diatoms and flagellates in these experiments, it was important in the competition among diatom species.

There has been much greater interest in N:P ratios since N and P have been the primary nutrients focused on by phytoplankton ecologists. Niemi (1979) was among the first to invoke N:P ratio control of cyanobacterial blooms of *Nodularia* and *Aphanizomenon* species in the Baltic Sea. In his view, these N-fixing species were able to capitalize on the elevated phosphorus levels occurring then, leading to their competitive advantage over other functional groups. Similar N:P regulation of *Nodularia spumigena* in a P-enriched Australian estuary has been reported (Lukatelich & McComb, 1986). In Tolo Harbour, Hong Kong, a long-term increase in harmful algal and red tide blooms has accompanied eutrophication associated with a marked increase in the human population (see Smayda, 1990). Hodgkiss and Ho (1997) report that the annually averaged N:P ratio decreased from 20:1 to 11:1 over a seven year period, during which the number of dinoflagellate blooms increased. In the Dutch Wadden Sea, a long-term increase in abundance of *Phaeocystis pouchetii* and its dominance of the annual phytoplankton cycle has occurred in response to nutrient enrichment via riverine discharge (Lancelot *et al.*, 1987). Altered nutrient ratios appear to have played a important role in this exploitation. Riegman *et al.* (1992) have shown that the average annual dominance of *Phaeocystis* was inversely related to the average N:P ratio during its growth season (April – September), and that the ratio of $NH_4$:$NO_3$ influenced life cycle stage. In laboratory experiments, Riegman (1995) found that *Phaeocystis* in competition against other species became dominant at N:P molar ratios of $\leq 7.5$ and approached monospecific bloom formation at N:P ratios of 1.5. The successful competition of *Phaeocystis* against diatoms in achieving Wadden Sea preeminence was also linked to lower Si concentrations (Egge & Aksnes, 1992). The catastrophic bloom of *Chrysochromulina polylepis* in the Kattegat and Skagerrak during 1988 has been linked to N:P ratio effects on bloom magnitude and toxicity (Maestrini & Granéli, 1991), although the role of nutrients in this bloom remains controversial. Additional information on the effects of nutrient ratios on phytoplankton species selection will be found in Anderson *et al.* (2002) and Granéli (Chapter 7, this volume).

## 6.5 Eutrophication, Indicator Species and Harmful Blooms

Although marine phytoplankton respond to nutrification by increasing their biomass and through altered species behaviour, most of the results derive from uncontrolled experiments and qualitative field evidence. There is currently inadequate quantification of the eutrophication-phytoplankton response to predict the species-specific responses to acute or chronic nutrient loadings, and whether this altered behaviour will benefit or disrupt a given ecosystem. Recognition that eutrophication is a process with distinct stages in the evolution from oligotrophy to eutrophy represents a major step forward towards achieving this needed quantification. A major stumbling block lies in identifying the relevant habitat features during nutrification and the life-form requirements of the species being selected. Sellner *et al.* (2001) based on evidence from a eutrophicated branch of the Chesapeake Bay have concluded that stratified watermasses exposed to excessive nutrient enrichment are predisposed to dinoflagellate blooms. However, Smayda & Reynolds (2001) recognize nine different combinations of watermass mixing/stratification and nutrient combinations, and associated dinoflagellate life-form types having distinctive morphotype-features and habitat preferences, with three different primary strategies present. This complexity may explain why specific phytoplankton indicator species of eutrophication have yet to be found despite the long-term search for such (see Braarud, 1945). Smayda & Reynolds (2001) in their phytoplankton life-form concept recognize the occurrence of invasive, small- to intermediate-sized colonist species (C-strategists) which often predominate in chemically-disturbed water bodies, and whose characteristics are as follows:

- Found in chemically disturbed habitats subject to sustained nutrient loading
- Typically invasive, colonist species of small cell size (ca $10^3$ µm$^3$); competitive; typically r-selected species
- High cell surface area:volume ratio (µm$^{-1}$) promotes rapid nutrient uptake and growth; flagellates exhibit high motility rates
- Prominent bloom species; achieve great abundance
- When toxic, primarily ichthyotoxic
- Representative C-strategists species: *Gymnodinium, Heterocapsa, Prorocentrum and Scrippsiella spp. Alexandrium minutum; Heterosigma akashiwo, Phaeocystis pouchetii*

They suggest that habitat selection for life-form is primary, while the species to be selected and conforming to this life-form are less predictable and even stochastic. It may be that as eutrophication progresses through its various stages, changes in life-form conditions occur which determine which life-form type of phytoplankter will predominate. Perhaps it is this feature rather than the search for specific indicator species that should be pursued in future research.

In discussion of the effects of eutrophication on phytoplankton species, frequent reference has been made to harmful blooms and red tides. This partly reflects the type of information available. But a word of caution is in order with regard to the increasingly frequent and general invocation that nutrient enrichment is the cause of the global expansion and increase in harmful blooms in marine coastal waters. There is increasing reference by regulatory agencies, in work shop reports (for example, Lipiatou, 2002), and among scientists that elevated nutrient concentrations are the major cause of the HAB epidemic and, therefore, this justifies the need to reduce nutrient loadings. While the latter is certainly desirable, there is no convincing evidence that increased nutrient loading is the general mechanism driving and accounting for most HAB events in global coastal waters (Smayda, 2002). There are certainly examples of an increased HAB – nutrient relationship in certain regions and nutrient driven nuisance blooms such as *Phaeocystis* and certain cyanobacteria (Smayda, 1989, 1990), but most toxic blooms do not appear to be nutrient-stimulated (see also Anderson *et al.*, 2002). Long-term changes in climate, the impacts of overfishing, ballast water introductions of invasive species, and even natural variability are also contributory and intersect.

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# Chapter 7

# Eutrophication and Harmful Algal Blooms

Edna Granéli
Marine Sciences Department
University of Kalmar
SE-39182 Kalmar, Sweden

## 7.1 Introduction

In many aquatic ecosystems not influenced by Man, Harmful Algal Blooms including those of cyanobacteria, are normal phenomena. However, blooms of algae causing detrimental effects on aquatic ecosystems, such as water discoloration, health problems due to intoxicated fish, shellfish etc. as well as direct toxicity to fauna, including fish kills and human fatalities (the latter due to consumption of microalgal toxins accumulated in shellfish) are for sure a disturbance for the aquatic ecosystems where they occur (Dahl & Tangen, 1993; Subba Rao *et al.*, 1988; Kononen & al., 1993; Granéli *et al.*, 1999); see Figures 7.1, 7.2, 7.3, 7.4.

An indirect effect of some Harmful Algal Blooms is oxygen deficiency in deep waters and, as a consequence, mass mortality of benthic animals and fish kills (Granéli *et al.*, 1989). These kind of algal blooms for simplicity of expression are called HABs = Harmful Algal Blooms.

Although as stated above many HABs with disastrous consequence for the marine environment do occur naturally, evidence is gathering that they have increased in number, areal distribution and biomass per unit water surface or volume during the last decades (see e.g. Granéli, 1987; Anderson, 1989; Lam & Ho, 1989; Hallegraeff, 1993; Figure 7.5).

This is certainly true for many marine coastal areas and semi/enclosed seas, where the influence of Man on water quality can be substantial. From long term data only in the Baltic Sea it has been possible to corroborate the assumption that the increase of HABs is to a great extent connected to the increased input of nitrogen and phosphorus to these waters. Sediment cores from anoxic zones in the Baltic Sea, shows that some of these HAB species existed already 7000 years ago, however it is only after 1963 that there is a dramatically increase in the algal biomass (Poutanen & Nikkilä, 2001; Finni *et al.*, 2001); see Figures 7.6, 7.7.

This is a direct consequence of the increased input of mostly N to these waters after the 1940s due to artificial agriculture fertilizers. Thus it took a delay of about 20 years between the input of nitrogen to be expressed in the increase in these algal biomass. For other parts of the world, al-

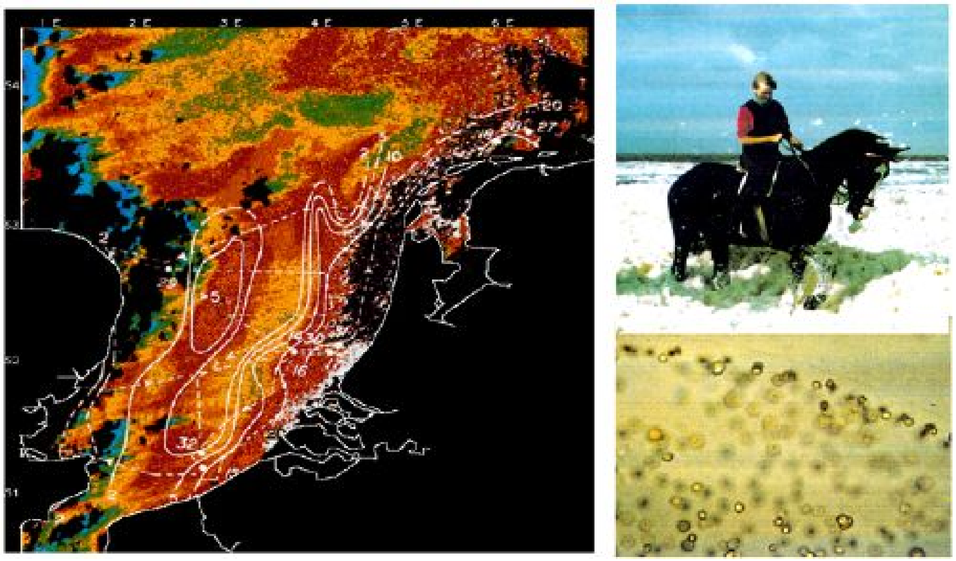

Figure 7.1: Satellite images showing chlorophyll a in *Phaeocystis* bloom outside the Netherlands coast, May 1986 (left), (Photo courtesy of Remote Sensing group at CCMS Plymouth Marine Laboratory), foam origin from a *Phaeocystis* bloom covering the coast outside The Netherlands (upper right). (Photo: M. Veldhuis) and a micrography of a *Phaeocystis* colony. (Photo V. Rousseau. In Granéli *et al.*, 1999) (lower right).

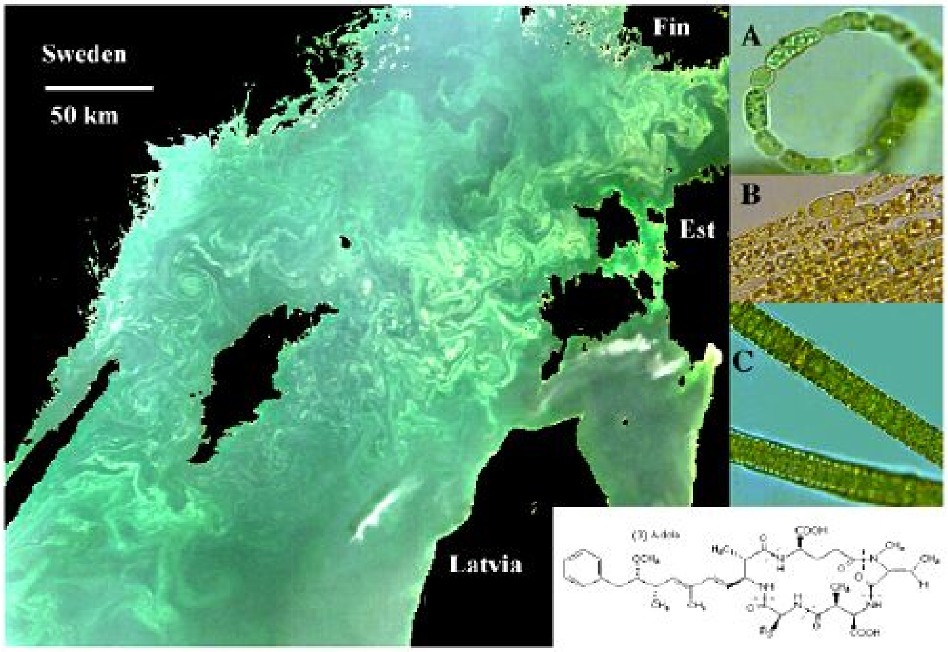

Figure 7.2: Satellite images showing cyanobacteria bloom in the Baltic Sea, August 1983 (Photo courtesy of Remote Sensing group at CCMS Plymouth Marine Laboratory) (left). The Baltic Sea cyanobacteria species *Anabaena* sp, (A) *Aphanizomenon* sp. (B) *Nodularia spumigena* (C) (Photo C. Esplund) and the structure of nodularin.

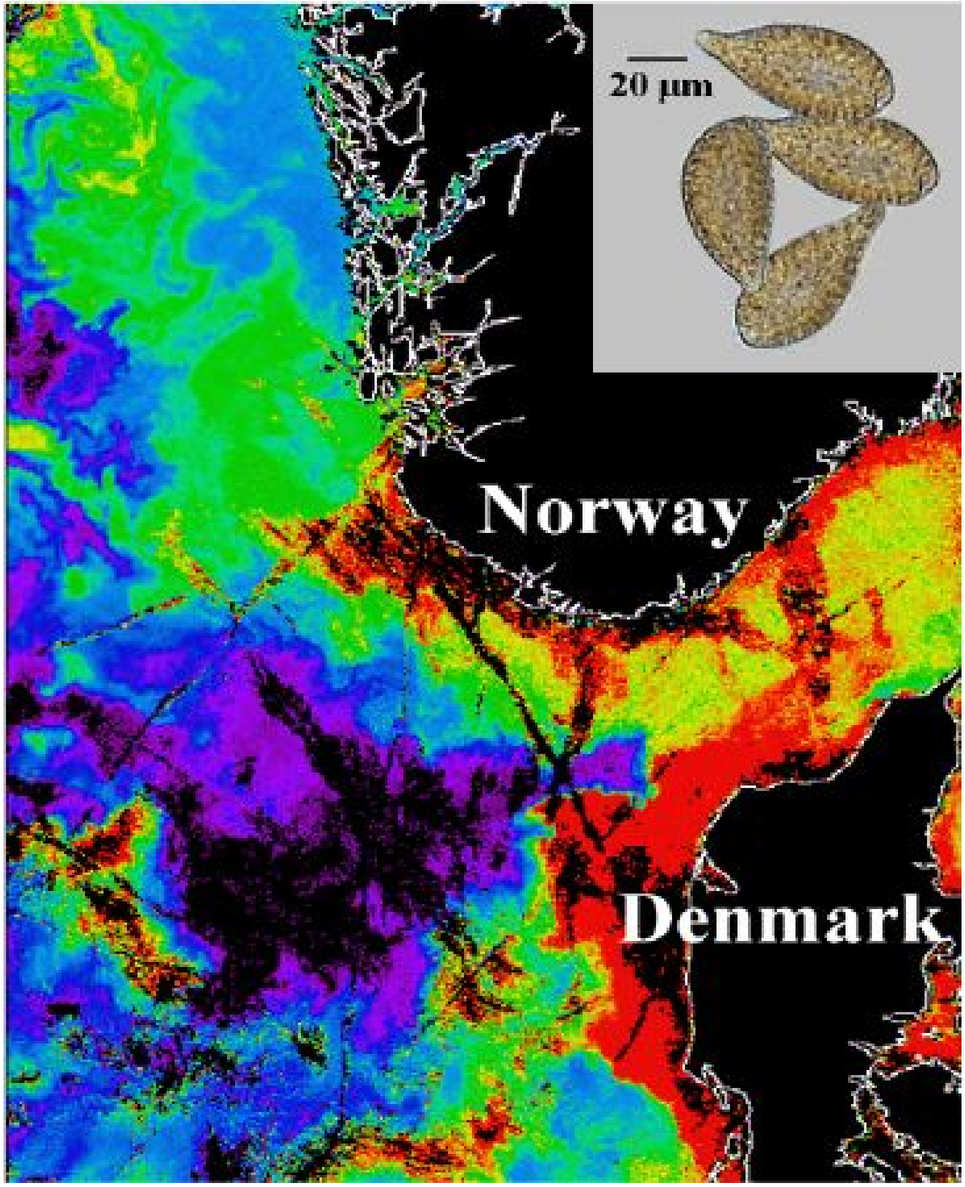

Figure 7.3: Satellite images showing *Chatonella verruculosa* bloom outside the Norwegian and Danish coasts, May 1998 (Photo courtesy of Remote Sensing group at CCMS Plymouth Marine Laboratory) and *Chattonella* sp. cells.

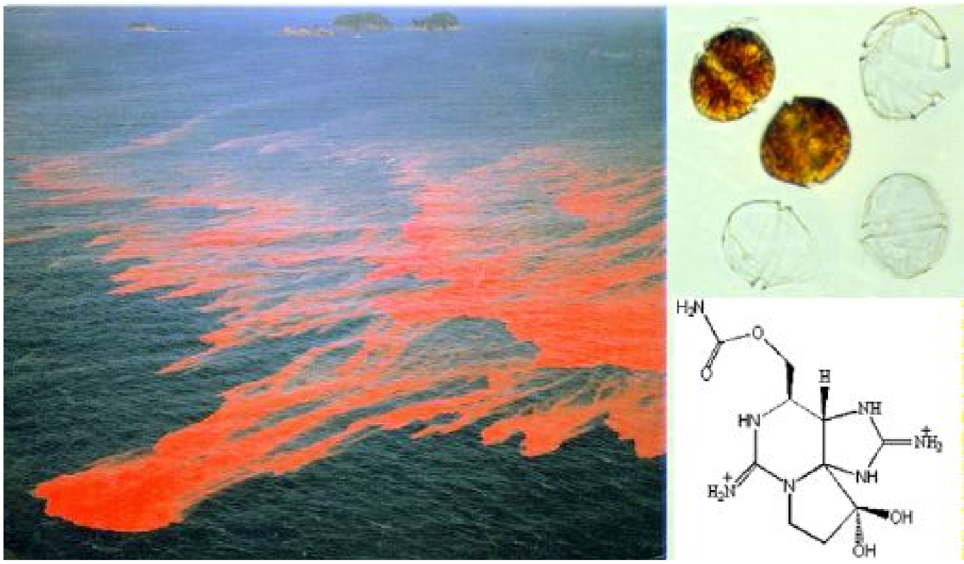

Figure 7.4: Red Tide formed by a bloom of the flagellate *Noctiluca scintillans* (from: Glibert & Pitcher, 2001) (left). Cells and empty theca's from *Alexandrium tamarense*, one of the most toxic Red Tide species (upper right), producing saxitoxin, one of the toxins responsible for Paralytic Shellfish Poisoning, PSP (Photo C. Esplund). The structure of saxitoxin (lower right).

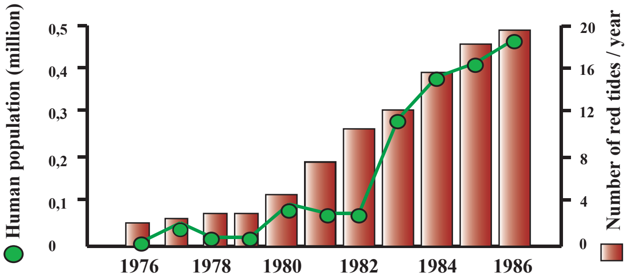

Figure 7.5: Increase in human population and number of red tides in Tolo Harbour, Hong Kong. Redrawn from Lam & Ho (1989).

though not possible to show with certainty an increase in harmful algal blooms occurrence, it has been shown that by reversing eutrophication the number of harmful algae can decrease. This is the case for the very eutrophied Seto Inland Sea, Japan, where the number of HAB have continuously decreased in numbers to 50% since the discharge of industrial and domestic effluents to these coastal waters have decreased (from about 300 to 150 blooms/year) (Okaichi, 1989).

The most damaging HABs are those caused by toxin-producing algal species. The number of species that normally or perhaps only under specific environmental conditions, contain toxins is quite low (≈100). Toxins produced by HAB can be transferred within aquatic food chains. While information on zooplankton feeding or avoidance for some HAB cells exists (Turner *et al.*, 2000), the scattered and species-specific results do not yet allow for generalisations, as HAB species vary greatly in their morphology, nutritional/toxin content and nature of toxins. Recent experimental and field data indicate that HAB toxins can accumulate through vectorial transfer in marine food chains (Maneiro *et al.*, 2000). It is also well known that some HAB toxins accumulate in commercially important shellfish (Marino *et al.*, 1998) and can contaminate humans.

Toxic phytoplankton species have been known for more than a century. However, in recent years more and more species able to produce toxins have been detected, and new toxins have been chemically characterized (Yasumoto & Murata, 1993). All these mentioned processes are furthermore connected to the intracellular chemical composition of HAB cells and most of all, their toxin

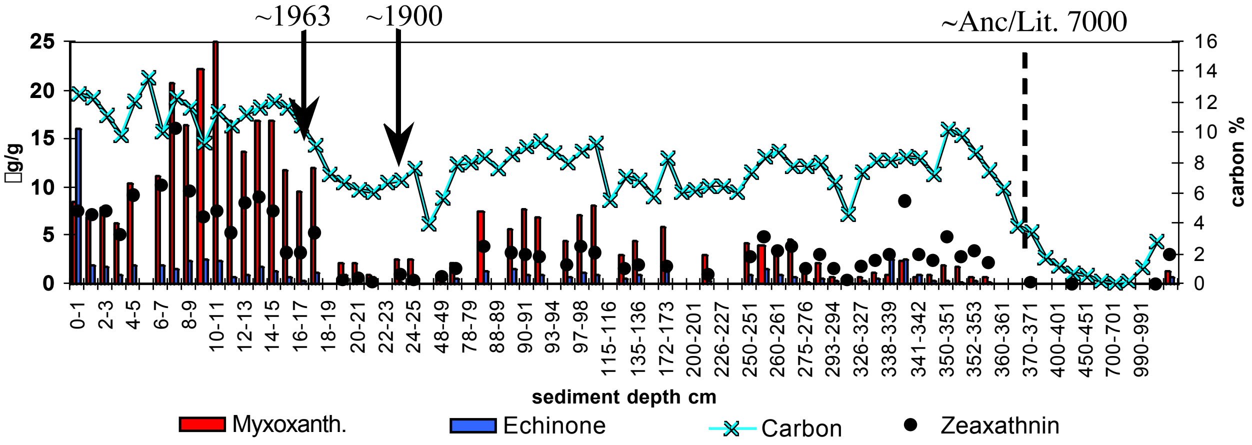

Figure 7.6: Pigments from cyanobacteria in the Gotland Deep (Baltic Sea) sediments and organic carbon. Redrawn from Poutanen & Nikkilä (2001).

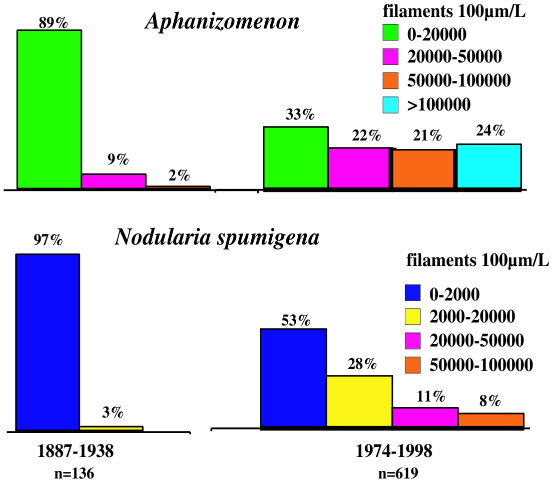

Figure 7.7: Abundances in percentage of *Aphanizomenon* sp. and *Nodularia spumigena* filaments (100$\mu$m length L$^{-1}$) from 1887 to 1938 and from 1974 to 1998. Redrawn from Finni *et al.* (2001).

content, which varies depending on the N and P concentrations in the water. Intracellular toxin content in HAB species has been shown to increase when the cells grow under nitrogen and/or phosphorus unbalanced conditions (in relation to their optimum) (Edvardsen & Paasche, 1998; Johansson & Granéli, 1999; Flynn *et al.*, 1994). For the ichtyotoxic species (Figure 7.8), when these species are either nitrogen or phosphorus deficient, the limiting nutrient (N or P) will be in very low concentrations inside the cells while the surplus nutrient will be in excess (Johansson & Granéli, 1999).

Consequently the intracellular N/P ratios will then vary broadly. A strong relation can be found between the intracellular N/P ratios and the respective toxin concentrations i.e., toxin increases when the cells are more N and or P limited (low and high N/P ratios) (Figure 7.9). For the organisms producing toxins accumulating in the food chain, only under P limitation (excess of nitrogen) (Figure 7.10) there is an increase in toxin production. The reason seems to be that under stress, e.g. lack of an essential nutrient to grow, the HAB cells by producing higher amounts of toxins are able to deter grazers more effectively (Johansson & Granéli, 1999; Hansen *et al.*, 1992; Huntley *et al.*, 1986) and by releasing greater amount of allelopathic substances will kill other phytoplankton species competing for the same scarce limiting nu-

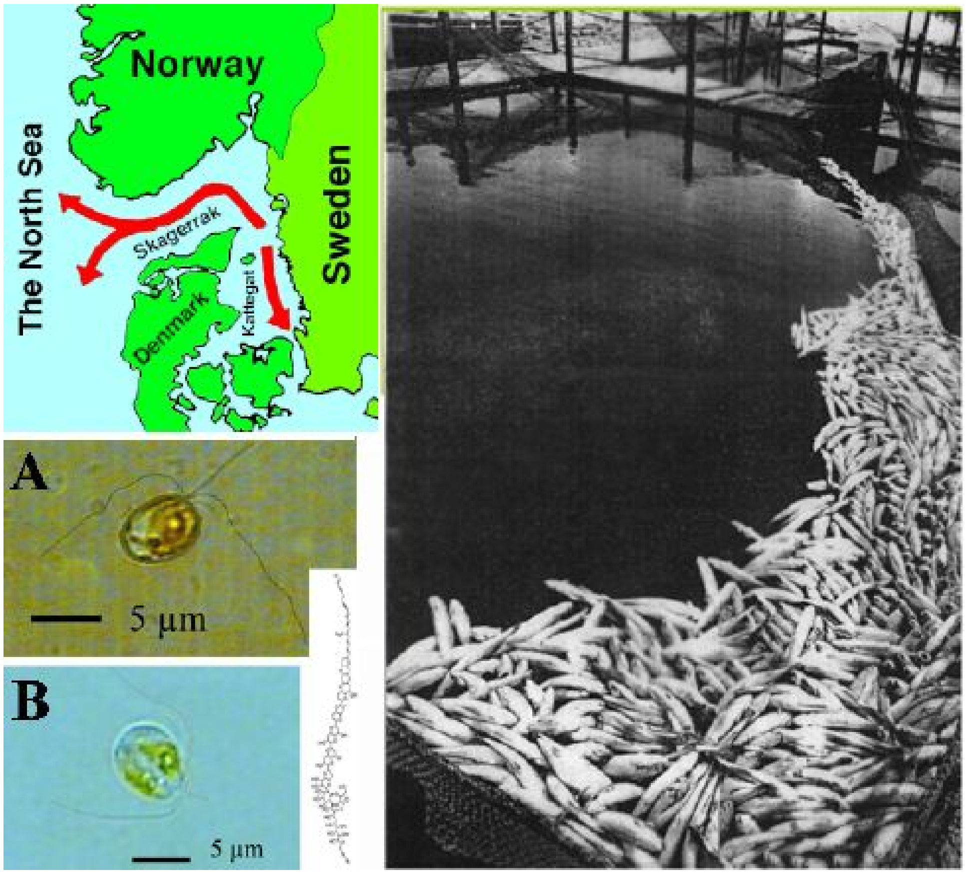

Figure 7.8: The ichtyotoxic species *Chrysochromulina polylepis* (A) caused major fish kills along the Swedish and Norwegian marine waters 1988 (Map) (Photo: O. Tollesby. In Granéli *et al.*, 1999). *Prymnesium parvum* (B) with the structure of its toxin prymnesin-2 (Micrographs: C. Esplund).

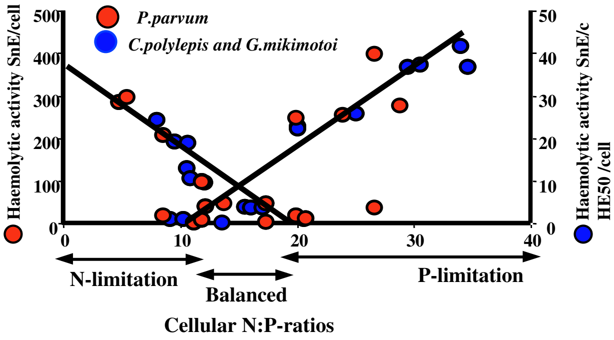

Figure 7.9: Relation between toxicity and nitrogen/phosphorus for ichthyotoxic species (Redrawn from Johansson & Granéli, 1999).

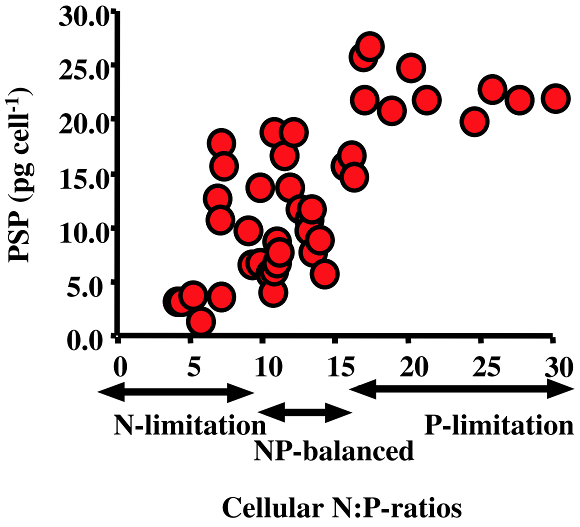

Figure 7.10: Relation between toxicity and nitrogen/phosphorus for for the Paralytic shellfish toxin producing species *Alexandrium tamarense*.

trient (Granéli & Johansson, 2003; Igarashi *et al.*, 1998). For the ichtyotoxic species, the higher toxicity under N or P limitation can be explained by the fact that the molecular structure of these toxins are made of C, O and H, thus there is no need of N or P to synthetise these compounds. For the HAB producing toxins accumulating in the food chain, higher toxicity is only found under P-limitation as these toxins (besides, C, O and H) also need nitrogen in these molecules. Unbalanced N and P conditions are often recurrent in marine waters due to the increase in anthropogenic discharges of N and P to these waters. Thus, it is possible that even if HABs have not increased in size, the deleterious effect of these blooms on the ecosystems is stronger nowadays since toxin levels in the cells are higher.

## 7.2 Possible reasons behind the increase in harmful algal blooms

Special weather and hydrographical conditions are thought to be prerequisites for the development of massive blooms of harmful algae to develop. Unfortunately no general scenario favouring a bloom of a specific species can be visualized. Blooms may be triggered by unusual weather events, occurring sporadically, as e.g. a rainy winter (runoff rich in nitrogen compounds and metals) followed by a sunny calm weather during the spring months (as was the case in the *Chrysochromulina polylepis* bloom, Maestrini & Granéli, 1991). It is also possible that 'global change', e.g. greenhouse effects, have altered the potential for bloom development in general or the conditions for specific species. Even if special weather and hydrological (e.g. with respect to vertical stability of water masses) conditions are a prerequisite for bloom formation, they are probably not sufficient to cause a bloom to develop.

For a large biomass of phytoplankton to build up, a sufficient store or a continuous supply of nutrients is necessary. Thus, eutrophication, i.e. anthropogenically increased additions of nutrients to the aquatic environment, is probably an important factor behind increased harmful blooms events and especially the severity and longevity of the blooms (Okaichi, 1989).

### 7.2.1 Are only inorganic nutrients utilized by HABs to grow?

Eutrophication symptoms, e.g. blooms of algae, some of them toxic, seem to be increasing, not decreasing, as e.g. in the Baltic Sea as a whole, in

Figure 7.11: *Heterocapsa triquetra* blooms in Stockholms archipelago, June 1998. Foto: T. Nilsson.

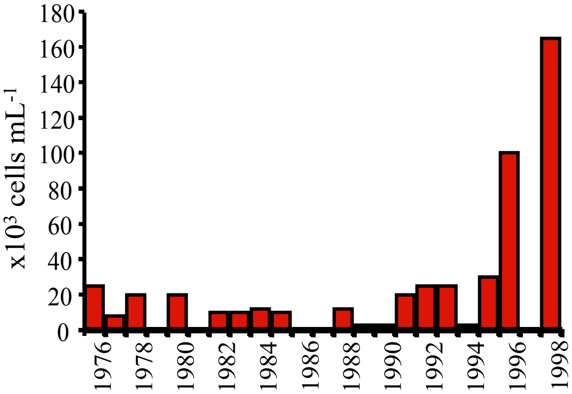

Figure 7.12: *Heterocapsa triquetra* blooms in the Baltic Sea, June – September. Redrawn from Larsson *et al.* (2001).

spite of the countermeasures taken to reduce N and P in these waters. The reason may either be that nitrogen loading does not control algal growth, or — perhaps more likely — that the system reacts slowly due to large internal stores of nutrients and a long residence time (>20 years). For example blooms of the dinoflagellate *Heterocapsa triquetra* (Figure 7.11), colouring many coastal embayments/fjords along the Baltic Sea during the month of June, have increased( Figure 7.12) during the last 30 years (Larsson *et al.*, 2001).

Besides the resilience of the ecosystem with respect to inorganic nutrients, other factors may be involved in the continuation or even increase in HABs. One of those is organic nitrogen bound to humic material, which can directly or indirectly stimulate phytoplankton growth (Carlsson & Granéli, 1993), especially HABs within the group of dinoflagellates (Figure 7.13) and flagellates (Granéli *et al.*, 1985; Granéli & Moreira, 1990; Carlsson *et al.*, 1998); (Figures 7.14, 7.15). However, other phytoplankton species can also utilize humic material as e.g. *Nodularia spumigena*, a toxic cyanobacterium species responsible for blooms covering a major part of the Baltic Sea Proper during late summer, is able to utilize phosphorus from humic compounds to increase it's nitrogen fixation (Panosso & Granéli, 2000). The loading of river-transported, high molecular weigth dissolved organic matter (humic and fulvic acids) to coastal waters can contain a major proportion of the total nutrient input. For the Baltic Sea for example, organic nitrogen bound to riverine humic material may contribute 50% of the total nitrogen being discharged (Wulff *et al.*, 1996).

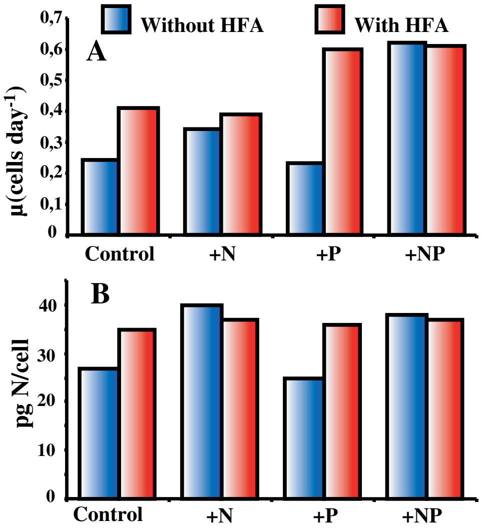

Figure 7.13: Growth rate (A) and cellular nitrogen (B) for *Prorocentrum minimum* growing in Laholm Bay water with or without additions of humic and fulvic acids (HFA) or with additions of nitrogen (N) or/and, phosphorus (P). Redrawn from Granéli *et al.* (1985).

Humic coloring of fresh water systems (lakes, rivers) in the Southern part of Sweden has been steadily increasing. For example, Romare and Cronberg (2001) reported that in Lake Bolmen

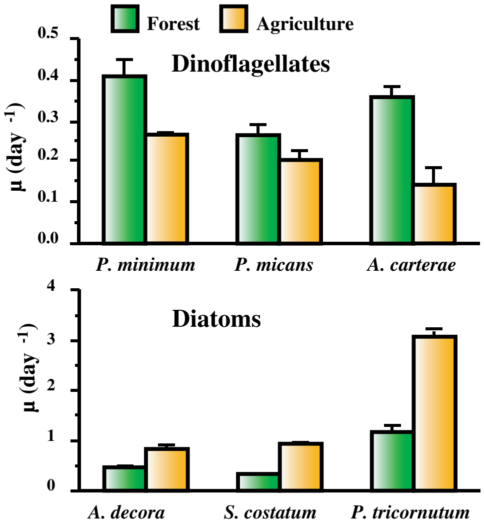

Figure 7.14: Mean growth rates of three dinoflagellates (*Prorocentrum minimum*, *P. micans* and *Amphidinium carterae*) and three diatoms (*Attheya decora*, *Skeletonema costatum* and *Phaeodactylum tricornutum*) grown as batch cultures (80% Laholm Bay and 20% forest or agriculture draining river water. Redrawn from Granéli & Moreira (1990).

(SW Sweden), water color (≈ organic matter content) increased from 20 to 60 mg Pt L$^{-1}$ (platinum) during 1996 – 2000, and in some of the lake's already very humic tributaries it doubled (e.g. from 150 to 300). The same trend is found for the tributaries of Lake Vättern, the second largest lake in Sweden. Between 1970 and 2000, organic carbon content increased by 50% (Lindell, 2003) in tributaries. Many of these humic waters ultimately discharge into the Baltic Sea. An increase in the input of humic substances to the Baltic Sea was in fact noted already during the 1980s (Andersson *et al.*, 1991).

To decrease HABs and improve water quality in the Baltic Sea a threshold based mainly on the loading of inorganic N and P has been discussed. In those values organic nitrogen or phosphorus was thus not included, and until recently there has been only scanty knowledge on the availability of organically bound nutrients for HAB growth. Even now we are far from understanding what nutrients in e.g. humic matter represents for HAB biomass production in the Baltic Sea. One thing we can be rather confident about is that if there has been an increase in the number and severity of HABs over, say, the last 50 years (which there are strong indications for), it is safe to assume that the increase has to do with human activity. This may be due to direct pollution, but also indirectly through e.g. the greenhouse effect causing increased leakage of humic matter. Disruption of the entire food chain ending up in HABs due to overfishing (Figure 7.17) (lack of 'top down' control, Granéli & Turner, 2002) is also a consequence of Man's activities. Thus not only loading of inorganic nutrients, but also organic matter loadings and fishing activities should be subjected to thresholds to manage algal blooms.

Several harmful algal blooms have been connected to an increased discharge of trace metals from land (see e.g. Wells *et al.*, 1991). The 'killer' algae *Chrysochromulina polylepis* has been shown to be stimulated by cobalt additions (Figure 7.16) (Granéli & Risinger, 1994), while other algae were indifferent or even slightly inhibited by elevated levels of Co (Granéli & Haraldsson, 1993). Cobalt levels 20 km from the coastline in the Kattegat are of the order of 0.35 nM and in the inner part of some fjords up to 3 nM, which is two orders of magnitude higher than in the open oceans (Granéli & Haraldsson, 1993).

Aquaculture, represented by the shellfish industry and fish farming in many European countries, is of extreme local importance in some areas. Aquaculture has suffered large economic losses during the last decades due to the occurrences of toxic/harmful phytoplankton blooms. However, we cannot discard the possibility that aquaculture itself (at least fish farming) by releasing extra nutrients (and by the use of antibiotic) might be one of the factors contributing to the development of HABs in enclosed small water bodies.

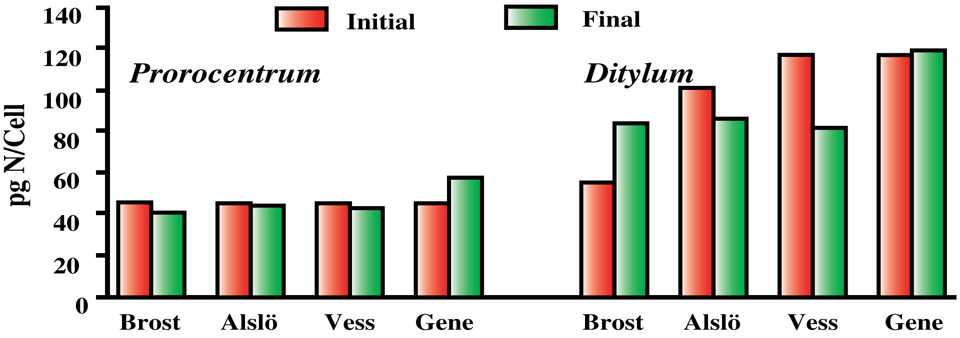

Figure 7.15: Cellular nitrogen of *Prorocentrum minimum* and *Ditylum brightwellii* cells growing in f/2 medium and in mixtures of 90% Laholm Bay and 10% water from the forest rivers (Brostorpsån, Alslövsån and Vess ingeån) and the agricultural river (Gene vadsån). Redrawn from Granéli & Moreira (1990).

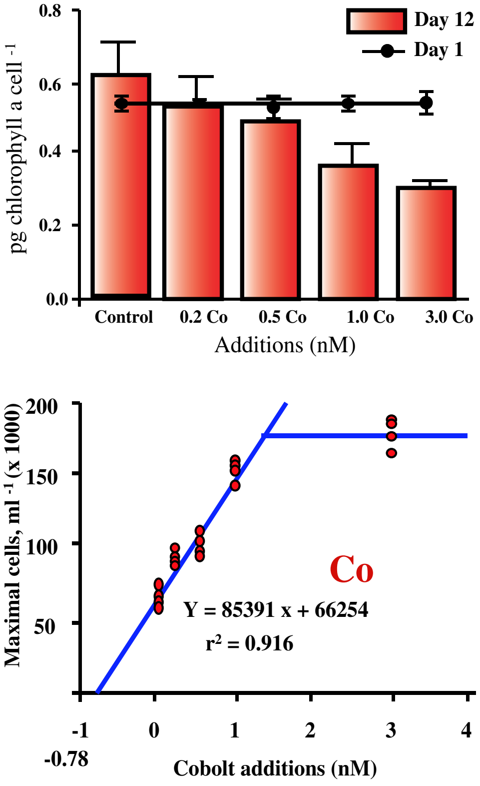

Figure 7.16: *Chrysochromulina polylepis*. Chlorophyll a per cell, initially (Day 1) and at the end of the experiment (Day 12). Error bars = SD (n=4) in the controls and Co additions and maximal numbers of cells produced in relation to Co concentrations (Redrawn from Granéli & Risinger, 1994).

## 7.3 Are there any way to diminish or at least mitigate HABs?

Current strategies for the management of some HABs include monitoring of toxic algal cells and toxins in shellfish, harvesting and sales restrictions for contaminated products, and the towing of aquaculture pens away from HABs. While these management strategies have enhanced our ability to protect public health and affected resources, there are virtually no strategies to reduce the threat from an existing or developing bloom. One promising approach in this regard involves the use of dispersed clay particles to flocculate and cause sedimentation of HAB cells. This method has only been used in SE Asia against ichthyotoxic species. Clay dispersal can effectively remove HAB species from the water column (Lewis *et al.*, 2000). Clays are generally inexpensive, readily available in large quantities, and easy to use in field operations. In addition to the use of clay, it is well known that phytoplankton grazing by mussels is very efficient. Therefore, protective mussel 'curtains' are another alternative that can be used to stop HABs from reaching fish cultured in cages. The EC funded project FATE is just now testing the feasibility and impact of these two mitigation techniques in Europe (Hagström & Granéli, 2003).

The first results(Figure 7.18) show that at the same cell densities, removal efficiency by clay is

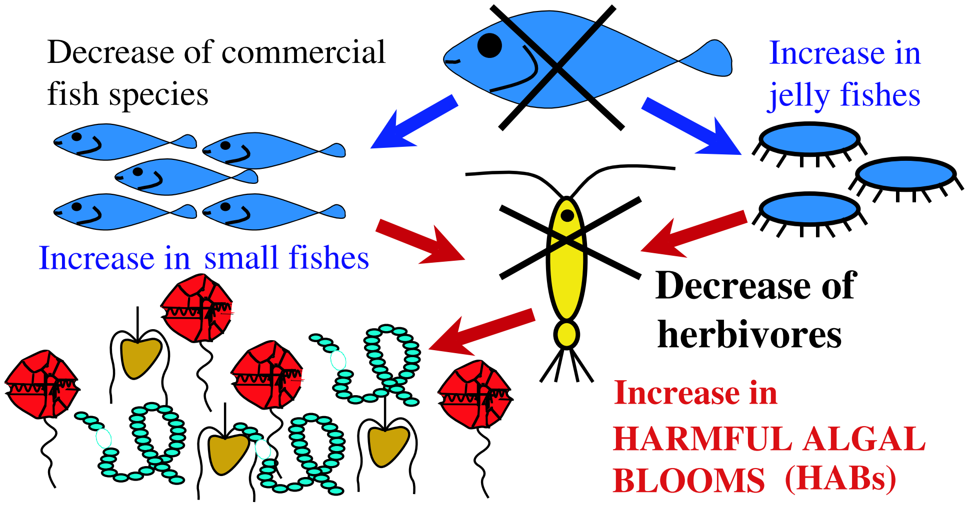

Figure 7.17: Possible pathway for HAB formation when the 'Top-down control' of the food chain is disrupted, as e.g. by overfishing.

100% while when the cells are nutrient deficient not more than 50% of the cells are removed. Although the above mentioned mitigation techniques are to be used in emergency situation, we need to understand how the different HABs function, so this information can later be used in environmental policy concerning countermeasures for the control of:

1. Industrial emissions
2. Nitrogen from agriculture and airborne nitrogen in precipitation from the burning of fossil fuels, including traffic
3. Acidification of soils (mobilization of trace metals)
4. Nitrogen and phosphorus from municipal sewage
5. Coastal management with respect to, e.g., aquaculture
6. Environmental monitoring
7. Commercial fisheries

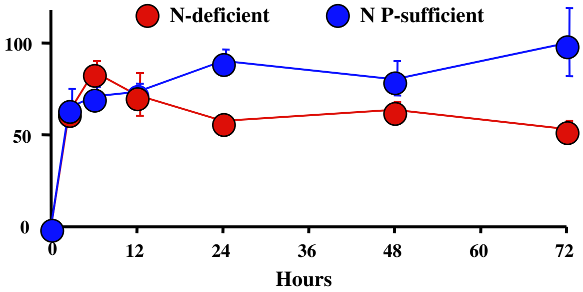

Figure 7.18: Removal efficiency by phosphatic clay on *Prymnesium parvum* cells in different cell concentrations and different nutrient status. Redrawn from Hagström & Granéli (2003).

## 7.4 Conclusions

To decrease HABs and improve water quality in coastal marine waters a threshold based mainly on the loading of inorganic N and P has been discussed. In those values organic nitrogen or phosphorus are thus not included, and until recently there has been only scanty knowledge on the availability of organically bound nutrients for HAB growth. Even now we are far from understanding what nutrients in e. g. humic matter represents for HAB biomass production in the Baltic Sea, even less in other seas as attention have not been devoted yet to this subject. One thing we can be rather confident about is that if there has been an increase in the number and severity of HABs over, say, the last 50 years (which there are strong indications for), it is safe to assume that the increase has to do with human activity. This may be due to direct pollution, but also indirectly through e.g. the greenhouse effect causing increased leakage of humic matter. Disruption of the pelagic food chain due e. g. to selective fishing or overfishing, also a consequence of human activity, may also promote HABs. Thus not only loading of inorganic nutrients, but also organic matter loadings and fishing activities should be subjected to thresholds to manage algal blooms.

Ultimately decreasing or mitigating harmful algal blooms will have a positive impact on natural marine and inland waters by restoring them to near pristine conditions, with very large economic benefits with respect to biodiversity, aquaculture, harvesting of wild fish and recreational activities.

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I wish to thank Christina Esplund for helping me out with the preparation of the figures and the document layout. This work was financed by the European Commission (Research Directorate General Environment Programme — Marine Ecosystems), through the FATE project "Transfer and Fate of Harmful Algal Bloom (HAB) Toxins in European Marine Waters" (contract number EVK3-2001-00050). The FATE project is part of the EC EUROHAB cluster.

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# Chapter 8

# Interactive impacts of human activities and storm events on coastal nutrient loading and eutrophication

Hans W. Paerl
University of North Carolina at Chapel Hill, Institute of Marine Sciences
Morehead City, North Carolina 28557, USA
hpaerl@email.unc.edu

## 8.1 Introduction

As we enter the third millenium, more than 70% of the world's human population resides within 100 km of the coast (Vitousek *et al.*, 1997). Large increases in pollutant discharge have accompanied agricultural and urban development in coastal watersheds. Deterioration of coastal ecosystems as a result of increasing urbanization of their watersheds is accelerating, yet there is a paucity of information on how primary producer and higher-ranked consumer communities are being altered by these perturbations. Understanding how human-induced ecological change (e.g. decreasing biodiversity, water quality, and fisheries) affects ecosystem composition and functioning is a major research challenge worldwide. For estuarine and coastal systems (jointly termed coastal here) that receive and process a bulk of human pollutants, two troubling changes have been nutrient enrichment (Nixon, 1995) and a decrease in grazer and higher consumer populations (e.g. shellfish, finfish) (Jackson *et al.*, 2001). The combined effect of increased nutrient loading and the reduction in grazers has dramatically increased coastal phytoplankton stocks. Increases in phytoplankton have been linked to significant changes in nutrient (C, N, P, Si) cycling, water quality and ecosystem health (Boesch *et al.*, 2001; Paerl *et al.*, 1995). Decreases in water clarity, expanding zones of low-oxygen water (Rabalais & Turner, 2001), increases in harmful algal blooms (Paerl, 1988; Richardson, 1997) may result from increased nutrient input to coastal waters.

Coastal ecosystems are also under the influence of natural perturbations such as droughts, hurricanes and flooding, the intensity and frequency of which appear to be increasing (Goldenberg *et al.*, 2001). During Fall 1999, Hurricanes Dennis, Floyd and Irene (Figure 8.1) inundated coastal North Carolina with up to 1 m of rainfall, causing a 100 year flood in the watershed of the Pamlico Sound, the USAs second largest estuary and key

Figure 8.1: Pamlico Sound Estuarine System as adjacent Atlantic Ocean coastal waters of eastern North Carolina, USA, as observed by the true ocean color satellite remote sensing system SeaWiFS (photos courtesy NASA). Left frame: 11 September, 1998, exactly one year before hurricane Floyd, under quiescent conditions. Insert: 16 September, 1999, during landfall of hurricane Floyd. Right frame: 23 September, 1999, approximately one week after Floyd. Note the brown-stained floodwaters discharging into Pamlico Sound and overflowing into the coastal Atalntic Ocean. Some of the turbid, sediment-laden water is being carried out to sea by the Gulf Stream which passes closely by the North Carolina coastline (from south to north).

fisheries nursery for the mid- and southeast Atlantic regions. Sediment and nutrient-laden floodwaters displaced over 80% of the Sounds volume, depressed salinity by 70%, and accounted for half the annual nitrogen (N) load to this N-sensitive system (Paerl *et al.*, 2001) (see Figure 8.2).

Biogeochemical and ecological effects included hypoxic ($<4$ mg $O_2$ $L^{-1}$) bottom waters, major changes in nutrient cycling, a 3-fold increase in algal biomass, altered fish distributions, catches, and an increase in fish disease (Paerl *et al.*, 2001). Predicted elevated hurricane activity may cause long-term biogeochemical and trophic change in this and other coastal fisheries nursery habitats. Distinguishing and integrating the impacts of these natural events from anthropogenic impacts are difficult but essential to understanding and managing coastal biotic resources.

The effects and manifestations of human and natural perturbations are usually most readily detectable and consequential at the microbial level, where a bulk of ecosystem energy and nutrient flow is mediated. Microbes have fast growth rates, and respond to low levels of pollutants and environmental perturbations. These features make them sensitive, meaningful, and useful indicators of ecological change. Here, we will examine how the dominant primary producers, phytoplankton, respond and adapt to nutrient and climatic perturbations. We will consider how anthropogenic stressors interact with natural forcing features to determine the composition, distribution and activities of phytoplankton communities in North Carolinas Pamlico Sound System, which has been heavily impacted by both human (nutrient enrichment) and climatic (hurricanes) perturbations over the past few decades.

## 8.2 Anthropogenic nutrient stressors: Their interaction with hydrology

Nitrogen availability most frequently controls microbial and higher plant primary production in estuarine and coastal waters (Ryther & Dunstan, 1971; Nixon, 1995). Concentrations and loading rates of this nutrient also most directly reflects

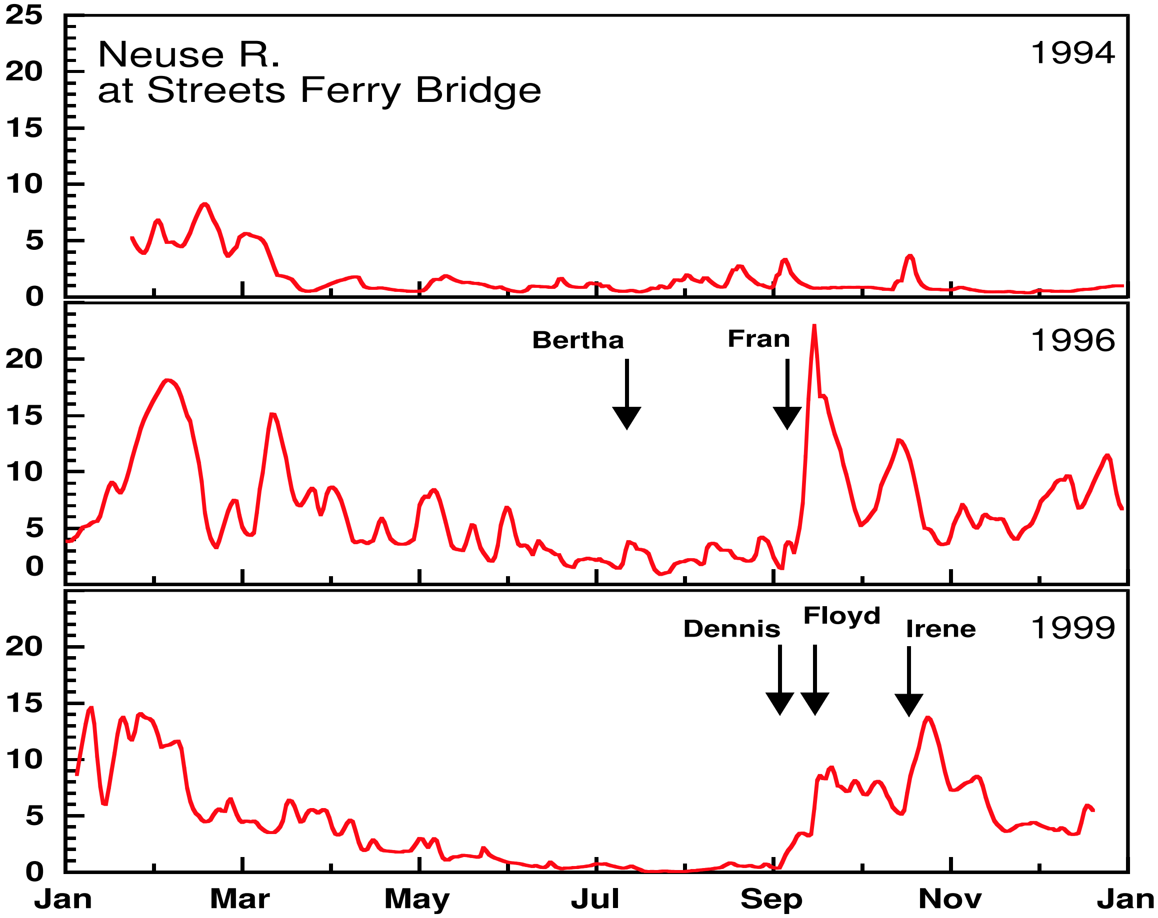

Figure 8.2: Total nitrogen (dissolved and particulate inorganic and organic) loading recoded at the entrance to the Neuse River Estuary (Streets Ferry Bridge) during non-hurricane and hurricane years. Typically, a large percentage of annual N loading in non-hurricane years occurs during the rainy late-winter early-spring period from January through early-May. This is shown for a relatively dry year (1994), as well as more 'normal' years (1996 and 1999). Note that during drought conditions (early summer of 1999), very little N loading takes place. Also shown are N inputs due to hurricanes that impacted the Neuse River Estuary watershed with heavy rainfall. During 1996, Hurricanes Bertha (minimal hurricane) and Fran (category 3 hurricane) impacted the watershed, while in the summer-fall of 1999, Dennis (category 2), Floyd (category 3) and Irene (category 2) sequentially impacted the watershed within a 6 week period. Note that the amounts of N loading due to large hurricanes (Fran and Floyd) accounted for large percentages of annual N loading to this estuary.

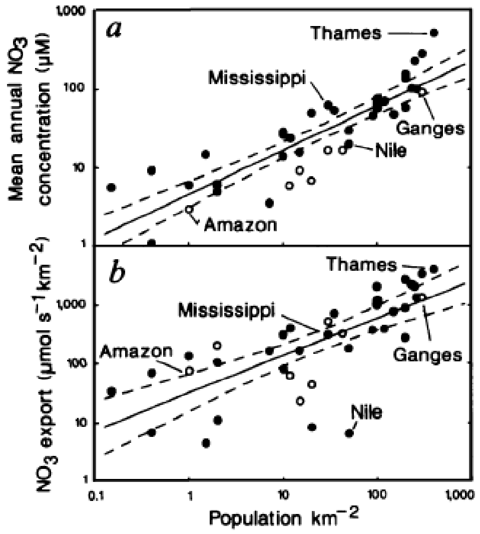

Figure 8.3: Direct relationships between nitrogen (N) concentrations and N export measured in major rivers, and the population density of these rivers' watersheds. Figure adapted from Peijerls et al., (1991).

human population density and activity in coastal water- and airsheds (Peierls *et al.*, 1991) (Figure 8.3). N inputs appear to control rates of primary production in most coastal waters worldwide (Figure 8.4). Not surprisingly, excessive N loading is a key causative agent for accelerating primary production, or eutrophication (Nixon, 1995; Paerl *et al.*, 1995). Symptoms include phytoplankton blooms (Figure 8.5), which may accumulate as ungrazed organic detritus in the sediments, providing the 'fuel' for large-scale oxygen consumption and depletion in bottom waters and sediments. This chain of events is particularly problematic in salinity or temperature-stratified (no-mixed) waters, where oxygen cannot be replenished from the atmosphere (Figure 8.6). Under these conditions, persistent low oxygen or 'hypoxic' conditions can alter nutrient (N, P, trace metals) cycling and promote fish disease and mortality (Diaz & Rosenberg, 1995; Paerl *et al.*, 1998).

A key factor promoting these negative impacts on coastal water quality is freshwater discharge (runoff). Discharge delivers nutrients to the coastal zone and determines hydrologic properties (flushing or residence time), vertical stratification, turbidity and color of the water column, all of which mediate productivity, nutrient cycling, dissolved oxygen dynamics and habitability in an interactive manner of coastal waters (Figure 8.7). For example, the rate of water discharge to estuaries, embayments and fjords controls their hydraulic residence time. Residence time, in turn, plays a critical role in determining the availability and rate of use of nutrients by phytoplankton and higher plants. Because discharge controls transport of phytoplankton through of these systems, it plays an interactive role with nutrient supply in controlling growth, competition and succession among members of the phytoplankton community. For example, high rates of freshwater discharge reduce the salinity and residence time. These conditions favor fast-growing oligohaline phytoplankton, such as chlorophytes (green algae). In contrast, low discharge conditions promote long water residence, high salinity conditions, which favor slower growing, halophyllic taxa, such as dinoflagellates and certain cyanobacteria. The differential impacts of discharge on phytoplankton community composition can be seen in the Neuse River Estuary, NC (Figure 8.8) and Chesapeake Bay, MD/VA (Figure 8.9).

Using diagnostic chlorophyll and carotenoid photopigments as indicators of major phytoplankton functional groups (i.e., diatoms, dinoflagellates, chlorophytes, cyanobacteria, cryptomonads), we have examined the interactive effects of nutrient and hydrologically-driven changes of phytoplankton community composition and activity in the Neuse River Estuary (NRE), Pamlico Sound (PS) and Chesapeake Bay (CB). High performance liquid chromatography (HPLC), coupled to photodiode array spectrophotometry (PDAS) can be used to determine phytoplankton group composition based on the diagnostic photopigments. Pigments include specific chlorophylls (a, b, c), carotenoids and phycobilins. A statistical procedure, ChemTax (Mackey *et al.*, 1996) partitions chlorophyll a (i.e., total microalgal biomass) into the major algal groups, to determine the relative and absolute contributions of each group. In the

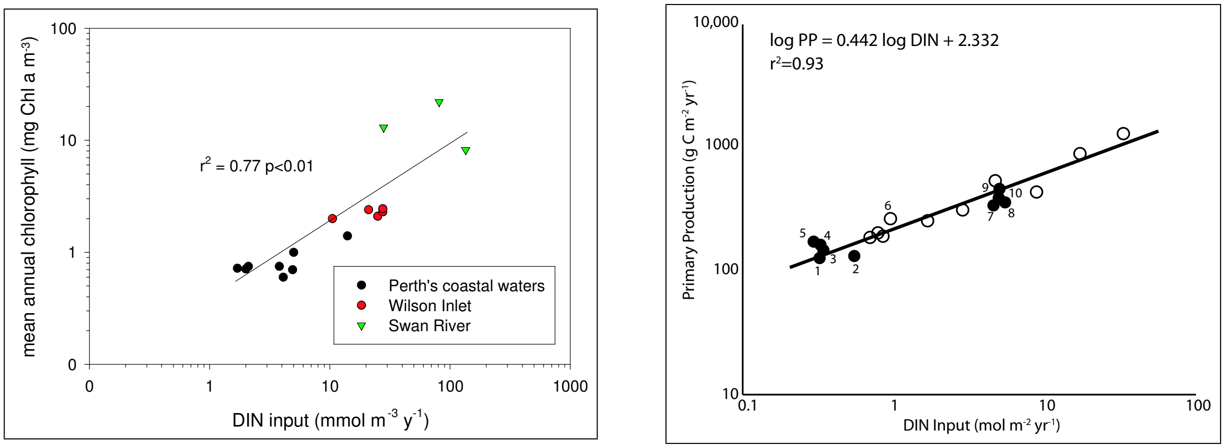

Figure 8.4: Left frame — Direct relationship between dissolved inorganic N input and phytoplankton biomass, as mean annual chlorophyll a content of several Western Australian estuarine systems. Figure adapted from Twomey et al., 2000. Right frame — Direct relationships between dissolved inorganic N input and primary production in a various North American and European estuarine and coastal ecosystems. Figure adapted from Nixon et al., 1995. Details of systems: The open circles are for large (13 $m^3$, 5 m deep) well-mixed mesocosm tanks at the Marine Ecosystems Research Laboratory (MERL) during a multi-year fertilization experiment (Nixon et al. 1986; Nixon 1992). Natural systems (solid circles) include (1) Scotian shelf DIN from Houghton et al. (1978), production from Mills & Fournier (1979), (2) Sargasso Sea — DIN from Jenkins (1988), production from Lohrenz et al. (1992) mean of 1989 and 1990 values of 110 and 144 g C $m^{-2}$ $yr^{-1}$, (3) North Sea — DIN from Laane et al. (1993) assuming that the ratio of DIN/TN in the input from the Atlantic equals that in the Channel, production from Seitzinger & Giblin (this volume), (4) the Baltic Sea — DIN and production from Ronner (1985), including DIN flux across the halocline, (5) North Central Pacific — DIN from Platt *et al.* (1984), production from Tupas et al. (1993, 1994) mean of 1992 and 1993 values of 150 and 185 g C $m^{-2}$ $yr^{-1}$, (6) Tomales Bay, CA, DIN and production form Smith (1991), (7) Continental shelf off New York — DIN and production from Walsh *et al.* (1987), (8) Outer continental shelf off southeastern U.S., DIN and production from Verity et al. (1993), (9) Peru upwelling — DIN calculated from annual mean upwelling rate of 0.77 m $d^{-1}$ (Guillen & Calienes 1981) and an initial 20 M concentation of $NO_3$ in upwelled water (Walsh et al. 1980), production off Chimbote from Guillen & Calienes (1981), (10) Georges Bank — DIN from Walsh et al. (1987), production from O'Reilly *et al.* (1987). The equation is a functional regression.

Figure 8.5: Examples of phytoplankton blooms resulting from excessive nutrient loading is estuarine and coastal waters. Upper left: Cyanobacterial (blue-green algal) bloom in the Gulf of Finland region of the Baltic Sea. Upper right: Dinoflagellate red tide bloom near the Japanese Coastline (Sea of Japan). Lower left: Cyanobacterial bloom in the St Johns River Estuary, near Jacksonville, Florida. Lower right: Mixed cyanobacterial-chlorophyte bloom in a coastal lagoon, North Island, New Zealand.

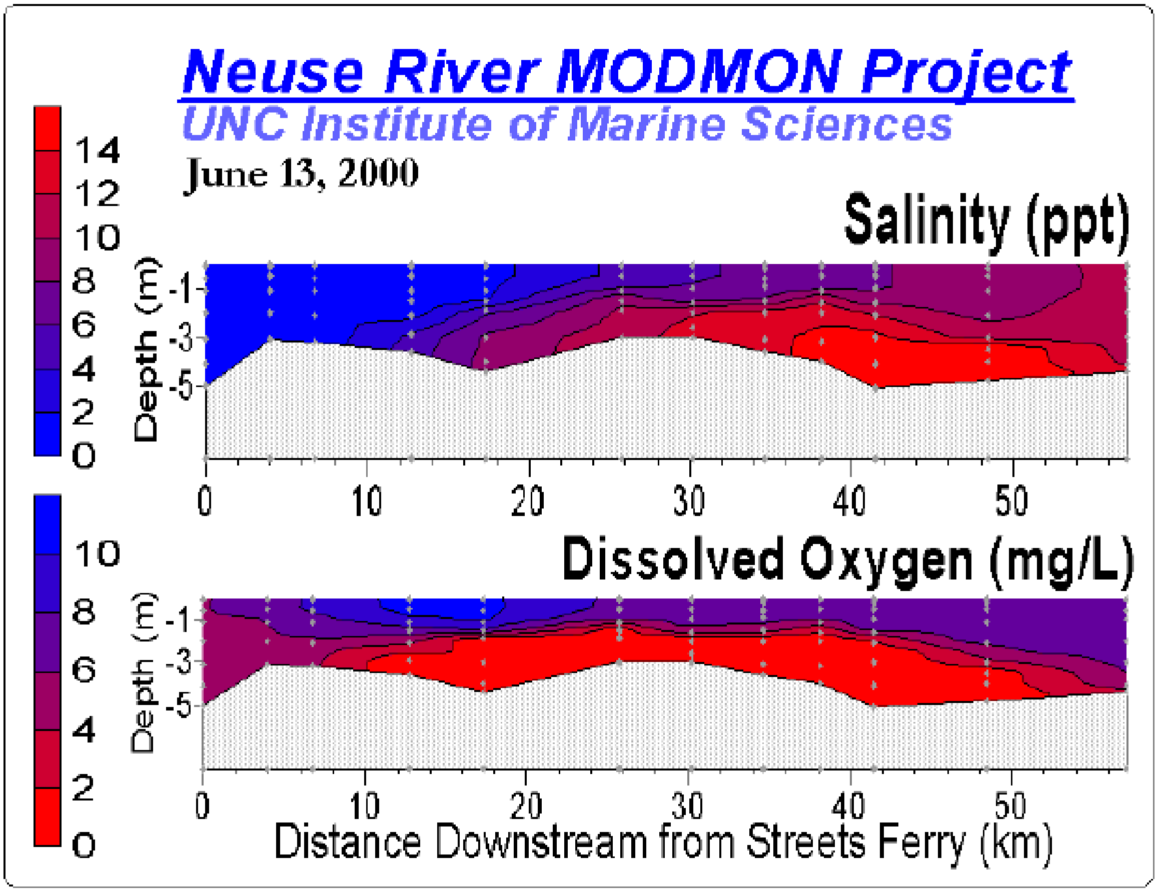

Figure 8.6: Vertical section of the eutrophic Neuse River Estuary, NC, ranging from the freshwater head of the estuary (left hand side) to the mesohaline entrance to Pamlico Sound. Data on which these graphs were plotted were obtained from the biweekly Neuse River Modeling and Monitoring Program, ModMon The upper frame illustrates the strong vertical salinity stratification that results from light freshwater inflow 'sandwiched' over denser salt water entering from Pamlico Sound. Stratifiaction persists during the summer months. The lower frame shows hypoxia that characterizes the bottom water as a result of persistent vertical stratification. This causes the bottom water to become isolated from the well-mixed, aerated, highly-productive surface water. Phytoplankton biomass formed in the surface waters sinks into the bottom, thus serving as the fuel for decomposition and oxygen consumption. Nutrient-stimulated phytoplankton blooms are a large source of oxidizable organic matter, which can exacerbate bottom water oxygen consumption and hypoxia. See the ModMon website for more extensive data sets that show this process on seasonally and interannually.

NRE, key photopigment markers include Chl b and lutein (chlorophytes), zeaxanthin, myxoxanthophyll and echinenone (cyanobacteria), fucoxanthin (diatoms), peridinin (dinoflagellates) and alloxanthin (cryptomonads).

HPLC pigment analyses can be adapted to routine monitoring programs (Pinckney *et al.*, 2001). In addition, HPLC measurements can be used to calibrate remotely-sensed (aircraft, satellite) phytoplankton distributions on the ecosystem and regional scale. Using data from ongoing studies in the NRE (1994-present), PS (1999-present) and Chesapeake Bay (1993-present), it can be seen that these estuarine systems have experienced the combined stresses of anthropogenic nutrient enrichment, droughts (reduced flushing combined with minimal nutrient inputs), and in the NRE/PS since 1996, elevated hurricane activity (high flushing accompanied by elevated nutrient inputs). These distinct perturbations have allowed us to examine impacts of both anthropogenic and natural stressors on phytoplankton community structure. Seasonal and/or hurricane induced variations in river discharge, and the resulting changes in flushing rates and hence, estuarine residence times, have differentially affected phytoplankton taxonomic groups as a function of their contrasting growth characteristics. For instance, the relative contribution of chlorophytes, cryptophytes, and diatoms to the total chl a pool appeared strongly controlled by periods of elevated river flow in the NRE. It is hypothesized that these effects are due to the efficient growth rates and enhanced nutrient uptake rates of these groups. Cyanobacteria, on the other hand, showed greater relative biomass when flushing was minimal (i.e., longer residence times) during the summer.

Further evidence that hydrologic changes have altered phytoplankton community structure is provided by the observed historical trends in dinoflagellate and chlorophyte abundance in the NRE. Both decreases in the occurrence of winter-spring dinoflagellate blooms and increases in the abundance of chlorophytes coincided with the increased frequency and magnitude of tropical storms and hurricanes since 1996. The relatively slow growth rates of dinoflagellates may have led to their reduced abundance during these high river discharge events. These results indicate that phytoplankton composition has been altered since 1994 in conjunction with major hydrologic changes, specifically floods following hurricanes. These phytoplankton community changes could have potentially altered trophodynamics and nutrient cycling in the NRE during these years.

The reconstructed taxonomic composition for Chesapeake Bay (Figure 8.9) also shows strong contrasting responses between dominant phytoplankton groups during spring and summer due to the variability of freshwater flow and nutrient loading. This pattern is strongest in the spring – early summer wherein high flow alleviates N limitation of the mid to lower estuary and supports diatom blooms in the spring, and sometimes in the summer. Low flow produces improved photic conditions but causes an expanded zone of N limitation in the main stem of the bay during the summer, thereby changing phytoplankton dominance to those groups that can grow efficiently under these conditions.

Depending on its source, path of travel and fate, runoff contains distinct amounts and types of nutrients. Much depends on how the watershed has been modified and impacted by human activities, including agriculture, urbanization, and industry. Therefore, when and where storms impact the watershed, their rain content and intensities significantly affect nutrient makeup and amounts discharged to coastal waters.

Freshwater discharge, in addition to its nutrient content, strongly controls vertical stratification of the water column, which in turn determines hypoxia potentials, internal nutrient regeneration and availability (Figures 8.4, 8.5, 8.6, 8.7), which in turn controls phytoplankton growth and bloom potentials. In turn, the magnitudes and aerial extent of blooms affect hypoxia potentials by controlling the formation and downward flux of organic matter providing the fuel for bottom water oxygen consumption. Therefore, the interacting and feedback effects of physical structuring with

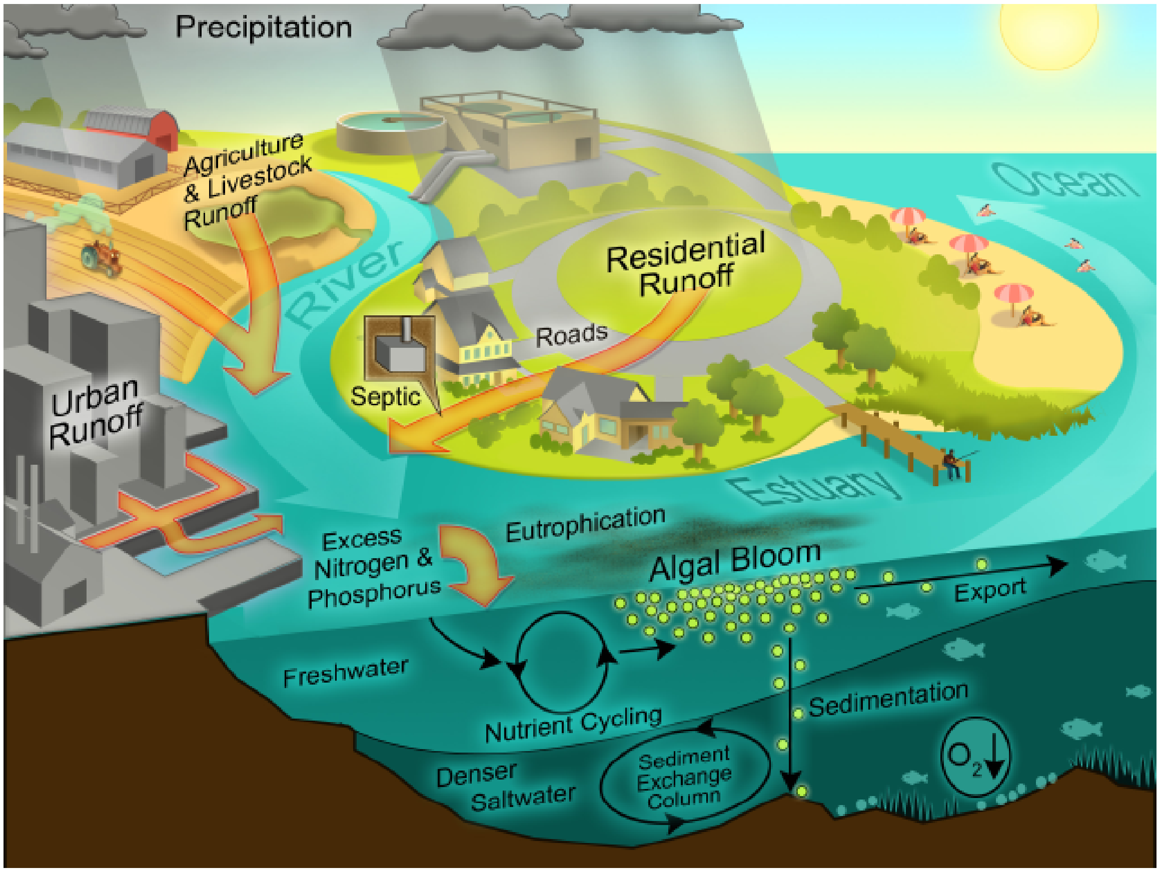

Figure 8.7: Conceptual figure, showing the various watershed and airshed anthropogenic nutrient sources, their input to estuarine and coastal waters via freshwater discharge, the establishment of hypoxia due to freshwater overlaying denser saltwater and the stimulation of primary production (eutrophication) and algal booms due to coastal nutrient enrichment. Note the linkage between nutrient enriched primary production and hypoxia as phytoplankton sink into stratified bottom water. Also, note potential negative impacts of hypoxia on bottom dwelling finfish and shellfish as well as submersed aquatic vegetation communities, all of which require oxic conditions.

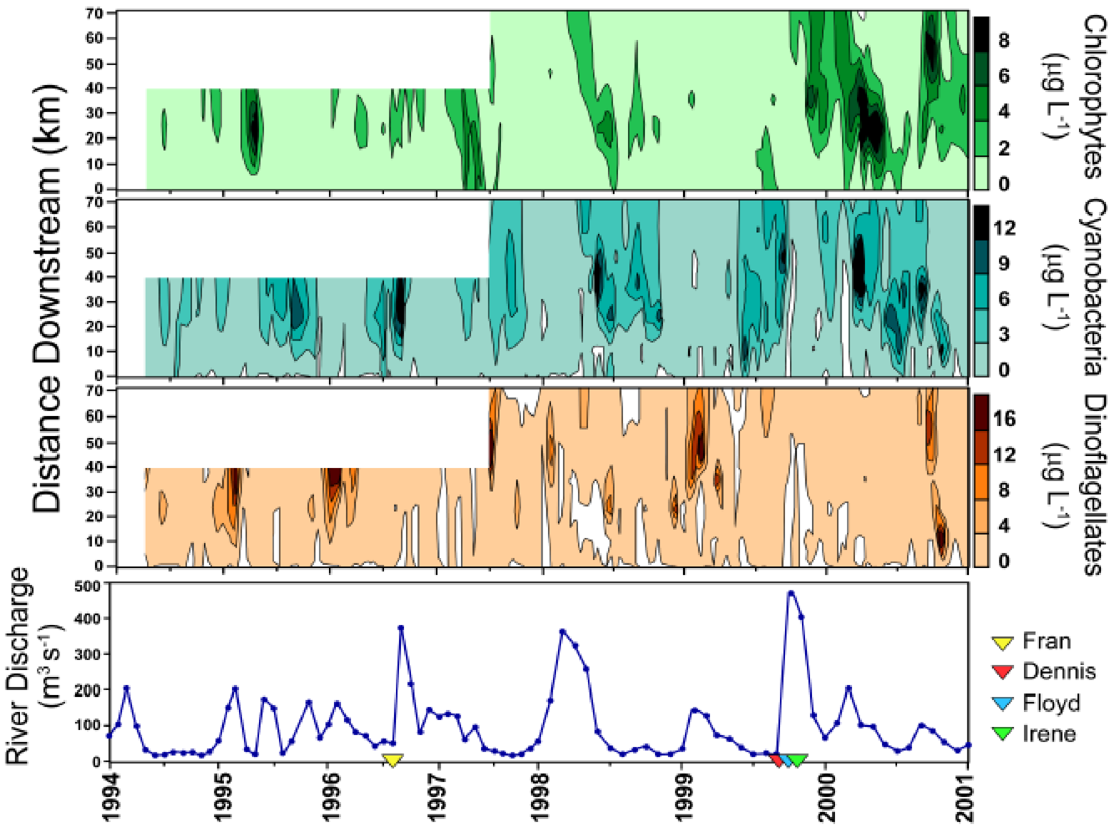

Figure 8.8: Concentrations of chlorophyll a (mg Chl a L$^{-1}$) contributed by chlorophytes, cyanobacteria and dinoflagellates. Values were derived using ChemTax for surface water at a mesohaline location (Station 120, see Figure of the Neuse R.) Estuary during 1994–2000. Data were collected bi-weekly and were temporally extrapolated. White areas indicate instances where data were not collected. ChemTax data were plotted along with freshwater discharge at the head of the estuary. The dates of landfall of the four major hurricanes that have significantly affected flow since mid-1996 are shown.

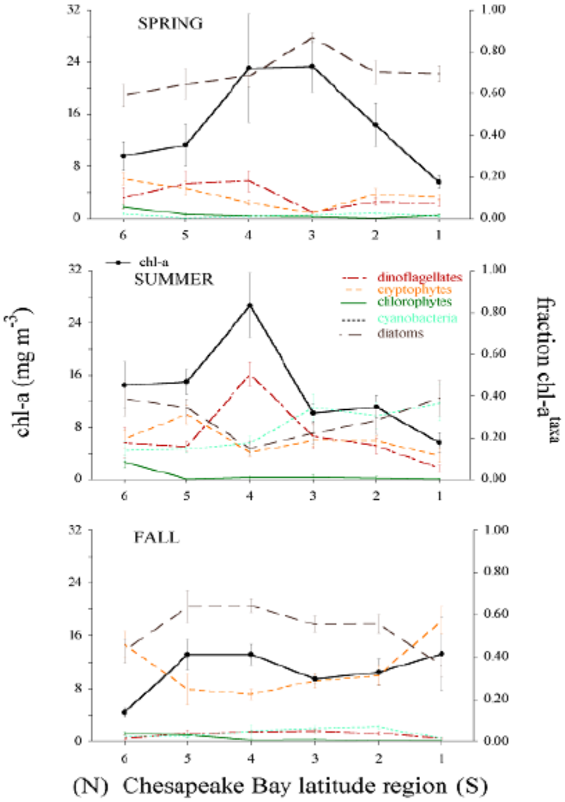

Figure 8.9: Regional means s.e. (1995 – 2000) for chl-a (mg m$^{-3}$) and the relative abundance (fraction chl-a$^{taxa}$) of phytoplankton groups determined by ChemTax for Chesapeake Bay (mid-Bay location). One approach to developing indicators from measurements of phytoplankton biomass and composition is to define the 'average' conditions, as shown above, and then conduct analyses of deviations (seasonal, regionally, inter-annually) in relation to differences in environmental forcing functions and patterns of primary production. Data courtesy L. Harding, Univ. of Maryland Horn Point Laboratory, Cambridge, Maryland.

nutrient availability are key variables determining eutrophication and hypoxia dynamics.

In most instances, it is very difficult to control water quality and eutrophication by manipulating freshwater discharge. Exceptions would include aquaculture and retention ponds, small lagoons and reservoirs, where water input and flow can be tightly controlled. However, in large coastal watersheds, flow controls are neither technically nor economically feasible and realistic because large unpredictable weather events such as hurricanes as well as droughts tend to dominate hydrologic characteristics of these systems. This leaves nutrient and sediment inputs as the chief controllable variables.

## 8.3 Managing coastal eutrophication under hydrologically-variable conditions

Integrated monitoring, research, and assessment are essential ingredients for a nutrient management programs in coastal systems affected by large-scale climatic and hydrologic variability. These programs should address the following questions:

- What type of assessment program is necessary and sufficient to adequately address the full range of ecosystem nutrient and habitat impacts resulting from major storms?
- What are the specific issues that are unique to monitoring on the short-term episodic and longer-term chronic event scales?

Monitoring and assessment should be able to answer the following questions:

- How far away from 'normal' conditions was the system changed by climatic events?
- To what extent do these systems recover? What conditions are required for recovery?
- Are there permanent changes to the ecosystem, and what are they?

- How do human activities affect recovery?
- Are any of the changes (short-term or permanent) detrimental to human use and resources?

Lessons learned from the 1999 hurricanes that struck coastal North Carolina stress the need for long-term monitoring and assessment. These assessments must be able to detect and quantify these events over appropriate spatial and temporal scales, have realistic and sustainable efforts and financial resources, and achievable assessment criteria and goals. Important features of a long-term monitoring and assessment program include:

- Sampling to detect 1) trends, 2) changes in state equivalent to a step function, and 3) consequences of infrequent, but large-scale events.
- Both a routine monitoring and event-response components.
- Spatially- and temporally-extensive monitoring of key environmental variables, using continuous and time-integrative sampling of water quality, productivity and turbidity, possibly making use of satellite- and aircraft-remote sensing, large-scale, long term, real time monitoring using existing infrastructure such as bridges, platforms, commercial and government vessels, ferries. (Buzzelli *et al.*, 2003: www.ferrymon.org)
- Measurement of water quality and habitat responses using meaningful, sensitive and easily-deployed indicators of environmental stress.
- Assessment of sediments. Sediments contain a wealth of paleo-climate and paleo-sea level information for the past 10,000 years of coastal history.
- Aggregation of meteorological data on storm paths, winds, rainfall and flooding to provide a quantitative context for catastrophic storms.
- Assessment of effects of hydrologic, chemical and sediment loading on biotic communities impacting production, nutrient cycling, finfish and shellfish habitats, including water column, salt marsh, seagrass, and open sediment habitats, including:
  - The response of phytoplankton, associated nutrient cycling and grazing communities to storm-related physical-chemical perturbations.
- Fish community behavioral, physiological and health responses to variation in water depth, salinity, temperature and dissolved oxygen.
- Analysis of historical and contemporary data on fisheries landings and how landings respond to intense storm activity.

We may need to reevaluate the relationship between human activities in coastal watersheds and their effects on water quality and fisheries under conditions of more frequent storm events.

A vital component of an effective and broadly-utilized integrated assessment program is cooperation and coordination among state, federal and private research and monitoring entities. The North Carolina 1999 hurricane experience proved that a strong working relationship among these entities was essential for sharing resources and expertise *and* utilizing research aimed at understanding and managing a large system impacted by interacting human and climatic forcing features. Cross-cutting multi-disciplinary, multi-agency approaches and analyses provide the necessary broad perspective that is needed to assess ecological change in a system that simultaneously affects and is affected by human economic, cultural and activities and values.

Synthesis and modeling of watershed, water quality, habitat and fisheries effects of intense storms is a key component of an integrated assessment program and is an important tool for synthesizing information and providing options for environmental management. Extension of model predictions to cover over a wide range of infrequent and extreme conditions and validation of those predictions is both a challenge to, and requirement of, an effective assessment program. In lieu of that, models become minimally usable for understanding these macro-events. The challenge to simulating effects of macro storm events is to find ways to quickly integrate the results of various independent models to aid in the scientific and management response to these events.

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# Chapter 9

# Eutrophication, primary production and vertical export

Paul Wassmann
Norwegian College of Fishery Science
University of Tromsø
N-9037 Tromsø, NORWAY
paulw@nfh.uit.no

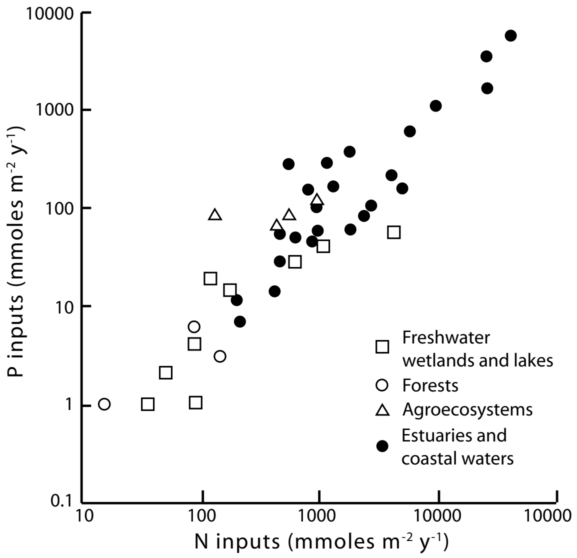

Figure 9.1: Nitrogen and phosphorous loadings to different types of ecosystems (redrawn from Eos, 1992).

## 9.1 Introduction

The effects of global and local changes are most prominent at the land-sea margins where presently population growth is greatest. For example, the population of coastal counties of the USA has roughly doubled since 1960 (Eos, 1992). This gives rise to increased pressure on natural resources and a large number of disturbances to coastal regions. Presently, eutrophication of coastal waters is probably the most important environmental effect (Gesamp, 1991). The effects of nutrient enrichment thoroughly change coastal ecosystems and occur virtually worldwide. Nutrients move across the land-sea margins at such high rates that coastal waters and estuaries are the most fertilized ecosystems on earth (Figure 9.1).

The discharge of nutrients to the coastal zone increased strongly during the last centennial. The increase in human population, the use of fertilisers, increased intensity in agriculture, logging and increased atmospheric deposition are the main cause for this intensification. However, significant periods of eutrophication took place much earlier. Already during pre-Roman time significant amounts of the mixed woods in the Mediterranean disappeared. During pre-Viking times natural woods disappeared in Denmark, during the Middle Ages most of the original woods from central and northern Europe. Europe developed into the cultural landscape that we encounter today, unrecognisable and widely different compared to the pristine state. The removal of woods and the introduction of agriculture had a strong impact on the leaching of nutrients all over Europe and periodically eutrophication in the Baltic and North Seas must have been significant over the last 1000 years. *Cultural* eutrophication, intense as it may be at present, is thus nothing new, but a close and well-known companion of human civilisation, mainly through the introduction of agriculture that paved the road for human development *and population explosion.*

Coastal ecosystems can accommodate large amounts of nutrients, but there is certainly the danger that increased loading gives rise to increases in suspended biomass, far beyond the range of natural concentrations. For scientists and managers alike the question arises how much nutrient discharge a specific recipient can accommodate per unit time before undesirable consequences occur. Can we determine the primary production rates where excessive biogenic matter is exported to the bottom water and the sediment that result in bottom fauna changes and ultimately anoxia?

## 9.2 Eutrophication

The term eutrophication derives from the Greek roots *eu* ('well') and *trope* ('nourishment') and could thus be translated into well-fed, well-nourished. With the term eutrophication we imply that the ecosystem, not an individual, is well-nourished and that nutrients or biomass are supplied to a particular recipient. Eutrophication is not a clearly defined term and there are various definition such as:

1. The process of changing the nutritional status of a given water body by increasing the nutrient resources (Richardson & Jørgensen, 1996)
2. An increase in the rate of organic carbon *production* in an ecosystem (Nixon, 1995)

In most cases we use definition 1 and this will also be the case in the present text. Thus we focus upon the supply to and the dynamics of nutrient resources in a water body. Eutrophication can entail either the *process* or the *result*. One has further to distinguish between *natural eutrophication* that is caused by winter accumulation, precipitation, vertical mixing, upwelling, river run-off and entrainment of nutrients. Climatic variability obviously influences and modulates the nutrient availability of a recipient and natural eutrophication thus varies over time. The natural variability in eutrophication is often poorly known, in particular because it may be camouflaged by *cultural eutrophication*, which is any type of nutrient discharge caused by anthropogenic activity, e.g agriculture run-off (see Sections 3), sewage, atmospheric deposition (see Sections 1), changes in water discharge etc.

## 9.3 Primary production and vertical export: Background considerations

Primary production consists of *new production* ($P_N$) that is based on allochthonous, i.e. externally supplied nutrients, and *regenerated production* ($P_R$), which is based on autochthonous, i.e. internally recycled nutrients (Dugdale & Goering, 1967). Hence total primary production ($P_T$) is the sum of $P_N$ and $P_R$. The amount of carbon that enters the aphotic zone is entitled *export production* ($P_E$) (Figure 9.2).

The concept of new production is of utmost importance for understanding natural and eutrophicated ecosystems because the fraction $f = P_N/P_T$ represents the upper limit of organic matter and energy which can be removed or extracted from the surface waters of the system without de-

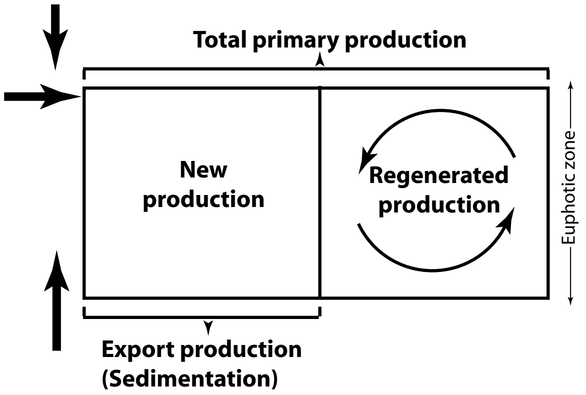

Figure 9.2: New and regenerated production are based on (a) the supply of the limiting (allochthonous) nutrients from the aphotic zone, by advection, run-off or from the atmosphere (straight arrows) and (b) the recycled (autochthonous) nutrients in the euphotic zone (circular arrows), respectively. New and regenerated production comprise total primary production. Export production is the amount of sinking organic carbon at the bottom of the euphotic zone.

stroying the long-term integrity of pelagic systems (Vezina & Platt, 1987; Iverson, 1990; Legendre, 1990). $\mathrm{P_N}$ represents thus the biomass that has to be handled by an eutrophicated recipient (e.g. mineralization, accumulation, harvestable biomass and export of biomass to adjacent recipients). Given the importance of $\mathrm{P_N}$ for the overall cycling of organic matter, considerable emphasis has recently been given to estimating $\mathrm{P_N}$ in coastal (e.g. Wassmann, 1990b) as well as oceanic environments (e.g. Knauer et al. 1990). New production represents the *carrying capacity* of a marine ecosystem. New production represents the *maximum production* capacity of an ecosystem or the *harvestable production*. New production is a *critical component* of marine primary production that limits the supply of food to the benthos, zooplankton, fish, and extensive aquaculture as well as the removal rate of atmospheric $\mathrm{CO_2}$ by the marine biota. New production estimates are of great interest for understanding eutrophication. Increased new production results in additional biomass that the ecosystem has to deal with in terms of grazing, vertical export to the bottom and pelagic and benthic degradation.

Given the practical difficulties in estimating $\mathrm{P_N}$ for lengthy periods of time, sediment traps can be used to estimate $\mathrm{P_N}$. $\mathrm{P_E}$ estimates as measured by sediment traps come close to $\mathrm{P_N}$, but are always smaller because it comprises only the particulate fraction and some transformation takes place from ammonium to nitrate even in the upper layers. Calculations of the productivity index $f$ by applying $\mathrm{P_E}$ give, therefore, rise to underestimates (Wassmann, 1993). As a consequence, the term $e = P_E/P_T$ can be applied and used as an approximation of $f$. In boreal, coastal areas where steady state, if at all, cannot be assumed for intervals of less than the length of the productive period, $e$ is meaningful as a base for estimating $f$ for lengthy periods only (e.g. $>$ 6 months). Therefore, the term $< e >$, representing $e$ for lengthy periods of time will be applied.

## 9.4 Nutrient supply, primary production, retention and vertical export

Increased supply of nutrients to the euphotic zone gives rise to increased production of algae which sooner or later sink to deeper water and the sediment, resulting in increased sediment-water exchange rates, at times in mass mortality of macrofauna and fish eggs (Rosenberg & Loo, 1988; Morrison *et al.*, 1991) and finally in anoxia (Rosenberg, 1985; Graf, 1987). During the last decades widespread occurrence of low oxygen concentrations or anoxia in bottom waters, decreased catches of fish and blooms of toxic algae threatening aquaculture as well as stocks of wild animals have been reported with increasing frequency (Rosenberg & Loo, 1988). These changes seem to be caused by increased inputs of nutrients to aquatic areas from sewage, agricultural run-off and atmospheric fall-out, giving rise to various degrees of eutrophication of fresh-water as well as marine, coastal environments (e.g. Wulff et al., 1990).

Figure 9.3 shows the principle processes of atmospheric $\mathrm{CO_2}$ uptake and release, primary production, suspended biomass and vertical export to the bottom. Seawater takes up $CO_2$ from the atmosphere that is either taken up by phytoplankton or released again to the atmosphere. The phytoplankton uptake of $CO_2$ is caused by primary production and first and foremost dependent on photosynthetic active radiation and nutrients. In addition it is influenced by the residence time of phytoplankton in the euphotic layer (determined by vertical mixing and stratification). *Phytoplankton accumulates in the upper layers if grazing and degradation rates are lower than primary production, i.e. a bloom takes shape.* A part of the suspended biomass, consisting of phytoplankton cells and detritus will inevitably escape grazing and degradation and sink into the aphotic zone and further to the bottom. The export of biogenic matter to the bottom is a complex function of the total amount of suspended matter, the sinking velocity of the sinking particles and the degradation impact of the pelagic heterotrophs. For example, low suspended biomass, low pelagic degradation and high sinking rates give result in a similar sedimentation rate at depth than high suspended biomass, high pelagic degradation and low sinking rates. Degradation of organic matter in the water column or the sediment results in nutrients that sooner or later can be taken up by phytoplankton.

If the limiting nutrient is nitrogen the new primary production depends on the allochthonous nutrient nitrate while the remaining primary production is based upon the autochthonous nutrient ammonium that derives from internal recycling by heterotrophic organisms. The basic principle to use nitrogen species to determine how much of the total primary production comprises new production (in case nitrogen is the limiting element) is difficult to apply in shallow water where the cycle of nutrients is rapid and where particulate nitrogen supplied to the bottom can be recycled to nitrate that is available for primary production. In this case nitrate is not new, but regenerated. Thus some of the nitrate is not ‘new’ and does not comply with the basic assumption of new production. In countless eutrophicated regions ammonium and urea are supplied as allochthonous nutrients. Also

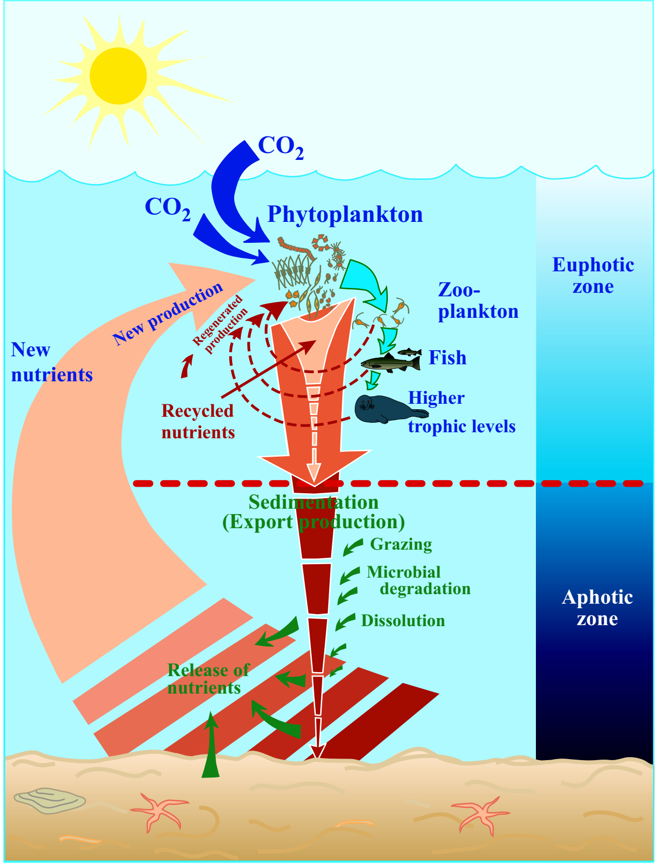

Figure 9.3: Primary production, vertical flux and regeneration of nutrients in a coastal marine ecosystem. Also shown are some of the involved organisms such as phytoplankton, zooplankton, higher trophic levels and benthic organisms. The massive and narrow vertical arrows indicate scenarios of substantial and insignificant vertical flux. (Illustration courtesy: dr. Alexander Keck.)

in this case the traditional method to distinguish new from regenerated production is not possible because some of the per definition autochthonous nutrients are allochthonous. New production is thus impossible to measure in eutrophicated waters.

The state of an ecosystem during a transient bloom is basically characterised by *export food chains* with high vertical export. The amount of regenerated production increases, as the planktonic system develops and becomes more complex during the post bloom phase. Sedimentation of organic material is low and the ecosystem is characterised by *retention food chains*. In the non-eutrophicated coastal zone export chains are based upon new production and represent episodic events on the background of a continuous, seasonally variable regenerated production based on the recycled nutrients from retention chains. If eutrophication continues, i.e. nutrients are supplied in a steady manner, a new steady state with a mixture of export and retention food chains will develop.

In conclusion, an estimate of new/net/harvestable production as a consequence of eutrophication in coastal zones is difficult to measure, among other reason because our terminology and measuring techniques are inadequate.

## 9.5 Algorithms of primary production versus vertical carbon export

An overview on algorithms predicting export production on the base of total primary production in marine environments on an annual scale has been presented by Wassmann (1990b; 1993) (Figure 9.4). Significant variability with regard to the $P_E$ versus $P_T$ relationship was detected. What algorithm should be selected for a global or coastal eutrophication carbon flux model? Obviously, there is no universal algorithm that would fit all ecosystems. Does the variability of the algorithms reflect real difference in the $P_E$ vs. $P_T$ relationships in the various ecosystems from which they were derived (Figure 9.5)? If so, then different algorithms should be applied in different regions.

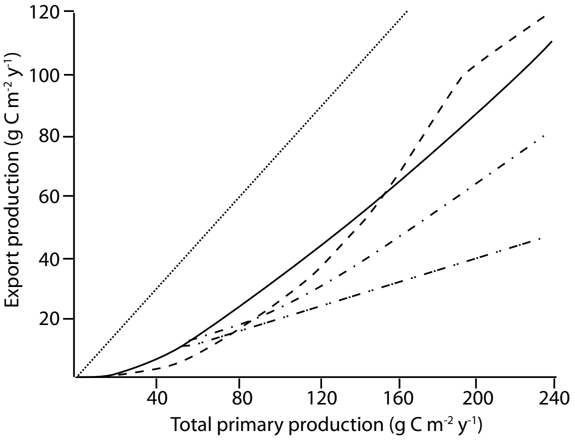

Figure 9.4: Export production as a function of total primary production on an annual scale in marine ecosystems. Algorithms from various publications are presented. Suess (1980) (..........), Eppley & Petersen (1979) (- - - - -), Betzer et al. (1984) (-.-.-.-.-), Pace et al. (1987) (-..-..-..-) and Wassmann (1990) (—). Source: Wassmann (1990b, 1993).

In particular data from the boreal coastal zone from the North Atlantic were investigated. The data used was mainly selected from simultaneous, time-integrated measurements derived over intervals covering most of the productive season (>6 months). Through a regression analysis $P_E$ was positively and nonlinearly correlated with total production $P_T$ (Figure 9.5). Best fit ($r^2 = 0.94$) was found by a power model calculated by the equation:

$$P_E = 0.049 P_T^{1.41} \tag{9.1}$$

The $< e >$ ratio was also calculated and both $< e >$ and $P_R$ were found to be positively, nonlinearly correlated with $P_T$. The upper limit for $< f >$ was calculated to be about 0.5 in boreal coastal environments, i.e. at most about 50% of $P_T$ may be exported through sedimentation to below the euphotic zone. *The curvilinear nature of the relationship implies that vertical export of biogenic matter increases relatively more than total primary production.*

The results of the model of Aksnes & Wass-

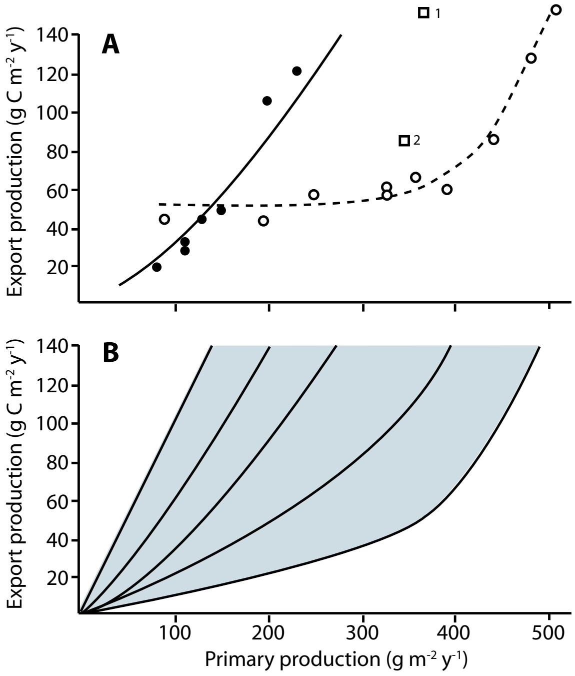

Figure 9.5: (A) Export production as a function of total primary production from the North Atlantic, boreal coast (Wassmann, 1990; full line) and subalpine lakes (Aksnes & Wassmann, 1993; broken line) on an annual scale. The zooplankton of the former ecosystems is often dominated by copepods, the latter one by cladocerans. Also shown are two data points from Dabob Bay, a boreal, North Pacific fjord, and a tropical lagoon, Kaneohe Bay on Hawaii (open squares, 1 and 2, respectively). (B) Schematic diagram on the conceivable relationship between annual export production and total primary production in miscellaneous ecosystems with different production, recycling and export regimes. The functional lines of the various ecosystems could be spread in the shaded area. The relationships could fall onto a suite of lines contrasting between maximum export (steep angle, straight relationship) and high retention (flat angle, strong curvature) efficiencies.

mann (1993) indicate that domination by copepods in the marine and cladocerans in lakes can give rise to very different relationships between primary versus export production (Figure 9.5). Meso-zooplankton species composition obviously influences the pelagic-benthic coupling: for example, copepods and cladocerans have different reproductive strategies (hence different grazing pressure), and cladocerans do not produce distinct faecal pellets. A comparison of retention and export food chains, and vertical flux in lakes dominated by copepods (e.g. Lake Baikal) or marine environments strongly influenced by cladocerans (e.g. the eastern Baltic Sea), would be advantageous to analyse in greater detail the contrasting scenarios of copepod and cladoceran dominance for pelagic-benthic coupling.

In case the algorithms depicted in Figure 9.5 are truly predicting annual $P_E$ on the base of $P_T$, why are there significant differences? In the case of subalpine lakes and boreal coastal areas we have already recognised that differences in the zooplankton community species composition result in the observed variance. The question can be raised if the results presented in Figures 9.4 and 9.6 suggest that various types of top-down regulation are the base for the observed variability? The few data which do exist from non-boreal environments outside the North Atlantic suggest that coastal areas and tropical bays in the North Pacific Ocean experience more efficient retention in the upper layers and less vertical export (Figure 9.5). This interpretation is in consistency with the notion that *tropical environments are characterised by effective retention food chains*. This may also be true for the North Pacific Ocean where at least the open ocean is characterised by extensive micro-zooplankton grazing which prevents major accumulation of phytoplankton biomass (Frost, 1991; Dagg, 1993). $P_E$ as a function of $P_T$ in miscellaneous ecosystems with different production, recycling and export regimes could fall onto a suite of lines falling between maximum export (steep angle, straight line = bottom-up regulation) and high retention (flat angle, curved line = top-down regulation) efficiencies (Figure 9.6). The

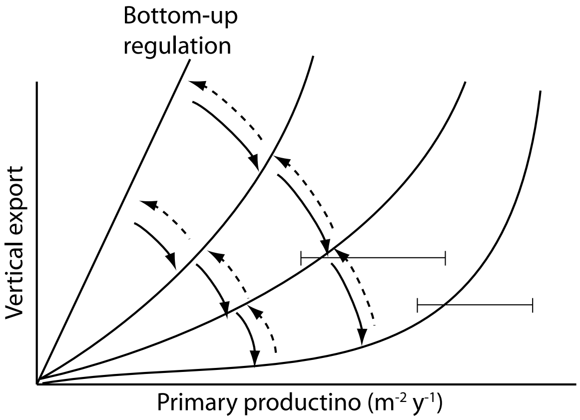

Figure 9.6: Schematic representation of annual primary production and vertical export during a phytoplankton bloom. Increased new production drives the relationship along the linear relationship total primary production = new production = export production. Planktonic heterotrophs reduce vertical export. As the grazing capacity of the planktonic heterotrophs increases with increasing primary production (full arrows), a curvilinear relationship emerges. Note the horizontal bars that indicate threshold intervals where the curvature of the primary production vs. vertical export relationship increases rapidly. Carnivory (stippled arrows) counteracts the retention of suspended biomass by the herbivores and detrivores.

balance between bottom-up and top-down regulation shapes the curvilinear nature of the $\mathrm{P_T}$ vs. $\mathrm{P_E}$ relationship. Not only $\mathrm{P_T}$ varies as a function of climate variability and eutrophication, also the $P_T/P_E$ ratio is not constant, but varies in accordance with the composition and dynamics of the heterotrophic plankton community. 'The' $\mathrm{P_T}$ vs. $\mathrm{P_E}$ relationship does that not exist.

On a daily scale the $\mathrm{P_T}$ vs. $\mathrm{P_E}$ relationship is characterised by irregularities (Figure 9.7). Primary production varies greatly between days and contributes to in different degrees to the suspended pool of biogenic matter (a function of total production, the $f$-ratio, grazing etc.) that may sink. *Although short-term variability in vertical flux takes place, that of primary production is greater.* The phase plot in Figure 9.7 illustrates the spiky nature of primary production as compared to the buffered rates of vertical export. The 5 days running average plot indicates the loop-type relationship between daily $\mathrm{P_T}$ and $\mathrm{P_E}$, as predicted by Wassmann (1998). Increased bottom-up regulation by eutrophication will increase the 'loopy' nature of the $\mathrm{P_T}$ vs. $\mathrm{P_E}$ relationship. In contrast, increased top-down regulation will decrease the loop size. Increased top-down regulation will eventually force the loop onto a retention line and remove excessive vertical export.

## 9.6 Increases in primary and export production: Examples from the Gullmaren Fjord and the Kattegat

Two cases studies illustrate that a 'threshold interval' in primary production exists where vertical export increases strongly. The pelagic ecosystem of the Gullmar fjord situated on the west coast of Sweden and adjacent waters has been studied since the late 1970s, principally in relation to oceanographic variability in the Skagerrak and the possible influence of climatic forcing on this area (Lindahl and Hernroth, 1983; Andersson and Rydberg, 1993; Heilmann et al., 1994; Lindahl et al., 1998; Belgrano et al., 1999). Primary phytoplankton productivity has been a part of these studies and a measuring program in the mouth area of the Gullmar Fjord is ongoing since 1985. An evaluation of this time series was carried out in 1994 (Lindahl, 1995), suggesting that even when elevated values of primary production are observed during the spring period (March-April), the main contribution to the annual production was found during the period May-September.

More recently a first attempt was carried out to study the effect of weather/climatic forcing on the physical-chemical processes related to the primary productivity. These results suggested the presence of an indirect link between the North Atlantic Oscillation index (NAO), the supply of nutrients to Kattegat, wind direction and the primary production (Lindahl et al., 1998; Belgrano et al., 1999). The development of primary production was reconstructed by combining measurements in the Gullmaren fjord with older measure-

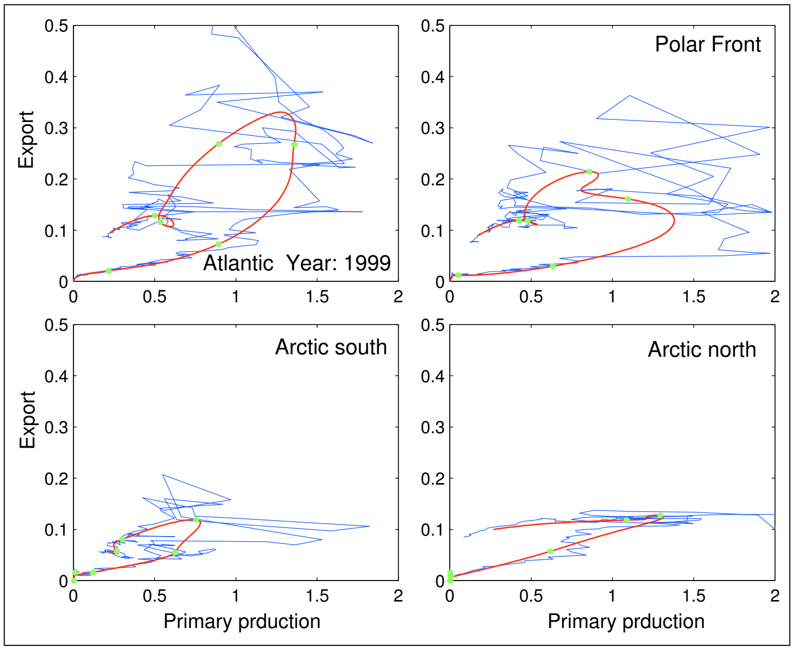

Figure 9.7: Unpublished results from a physically-biologically coupled 3D model presenting primary production versus export production in 4 different regions in the Barents Sea (pers. com., D. Slagstad). The scattered line is the daily variability in the phase diagram while the loops are the 5 day running average.

ments from the Kattegat (Figure 9.8). The striking increase in the 70s and 80s seems caused by eutrophication, while the slight rise is interpreted as a function of climate change. Applying the relationship suggested by Wassmann (1990b), the export production in the 1950/60 period was about 30 g C m$^{-2}$ year$^{-1}$ ($P_T = 100$ g C m$^{-2}$ year$^{-1}$) while at present it is about 120 g C m$^{-2}$ year$^{-1}$ ($P_T = 240$ g C m$^{-2}$ year$^{-1}$). If the assumptions behind these calculations are true, they imply the vertical C export increased four times over a time interval of 50 years! The carbon loading of the basin water of the fjord is obviously far greater today then during the more 'pristine' times prior to 1960.

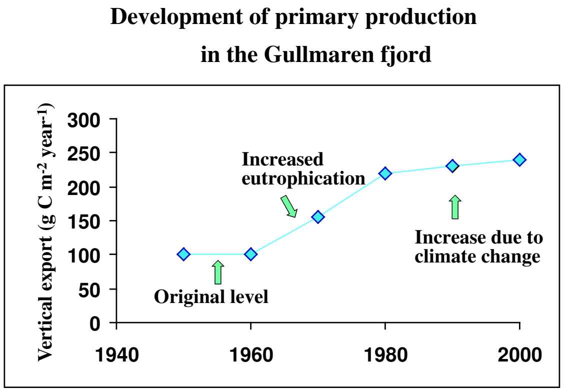

Figure 9.8: Development of primary production in the Gullmaren fjord over the last 30 years.

But even over the recent period significant increases in the organic load to the deep part of Gullmaren Fjord below the euphotic zone can be calculated. $P_E$ has increased from approximately 105 g C m$^{-2}$ y$^{-1}$ in 1985 to almost 123 g C m$^{-2}$ y$^{-1}$ in 2000, corresponding to an increase of the organic load of about 17% over 15 years. One possible result of this process may be the observed decrease in oxygen content of the deep water (>60 m) the beginning of the 1980s. However, it should be pointed out that the decrease in oxygen may be explained by other processes as well, e.g. a change over time in deep-water exchange. Finally, it should be mentioned that the relationship between $P_T$ and $P_E$ in the fjord reflects both eutrophication (which has not increased significantly in recent years due to increased effluent control) and climate changes (variations in NAO, global warming etc.). However, to differentiate between natural and anthropogenic variability is difficult.

Applying again the $P_T$ and $P_E$ relationship of Wassmann (1990b), the vertical export from the upper layers in the Kattegat region appears to

Table 9.1: Increase in primary production in the southern Kattegat over time. Also shown the calculated change in export production (from Wassmann, 1990a).

| Area | Time interval covered (years) | Change $P_T$ (g C $m^{-2}$ $y^{-1}$) | Change $P_E$ (g C $m^{-2}$ $y^{-1}$) |
|---|---|---|---|
| Storebelt | 24 | +63 | +29 |
| Øresund | 44 | +58 | +22 |

have increased 130–250% over a time interval of 20–40 years (Table 9.1; Wassmann, 1990a). This fundamental increase should be adequate to explain the frequently observed oxygen deficiencies in the region (Rosenberg & Loo, 1988), although, as mentioned above, stratification and lack of exchange of bottom water results in anoxic conditions. *The curvilinear nature of the* $P_T$ *versus* $P_E$ *relationship implies that the linear increase in* $P_T$ *causes an exponential type of increase in* $P_E$*, in particular at* $P_T$ *rates >150 g C* $m^{-2}$ $y^{-1}$. It would be advantageous to determine the primary production threshold intervals for various coastal regions where $P_E$ turns out to be greater then oxygen content of or supply to the benthic boundary layer and where undesirable effects (hypoxia, anoxia) develop in the bottom layers.

## 9.7 Variability of vertical export in the pelagic zone

All investigations of export of biogenic matter indicate that the export flux decreases more or less exponentially with depth in the upper part of the ocean, with minor decreases below 200–500 m depth (for algorithms predicting the depth variation of vertical carbon flux see Berger et al. 1989). Resuspension and protrusion of advective, particle rich layers or vertical differences in current direction may alter this general feature of vertical flux. The degradation rate of organic matter in the water column and, in particular for fast sinking particles is of pivotal importance for the quantitative regulation *of* pelagic-benthic coupling. *Depend-*

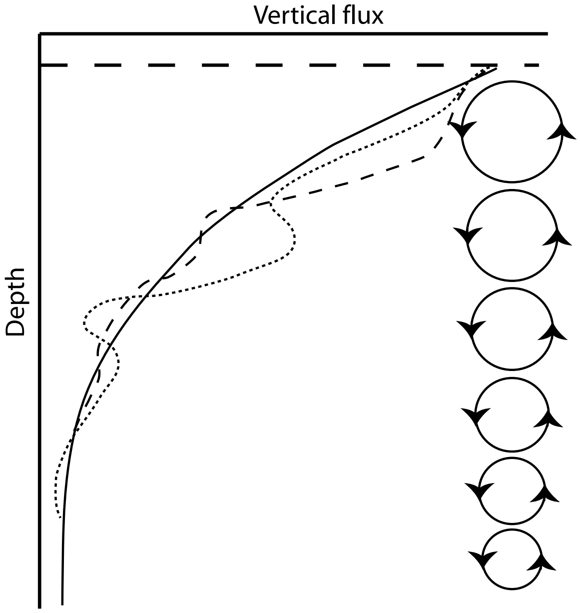

Figure 9.9: Schematic presentation of the 'pelagic mill' in the upper part of the ocean and its regulation of biogenic vertical flux. The full line assumes a continuous mineralisation of export production, giving raise to a decline in flux that follows a power function. The broken line indicates a step-wise decrease in vertical flux caused by extensive grazing at certain depth horizons. The stippled line indicates that vertical flux can increase intermittently due to repackaging. The recycling by the zooplankton community is schematically indicated to the right.

*ing on the degradation rate of fast sinking particles in teh water column, the absolute vertical export of organic matter at a certain depth could be small or large, irrespective the size of the new production from which it derives.*

The current lack of adequate investigations of the vertical export above the depth of 200–500 m where the majority of long-term sediment traps have been deployed, results in difficulties to understand and model vertical carbon flux. There exists a black box of several hundred metres between the surface layers where measurements and algorithms of primary production exists and where data on the carbon export to the ocean interior are available. In this black box, the twilight zone, we face a lack of basic understanding on how vertical export of biogenic matter in general is regulated, let alone in eutrophic regions. In order to guide future investigations of vertical flux attenuation in eutrophicated regions we present an idealised, conceptual model of vertical carbon export and focus upon the 'pelagic mill' and vertical flux regulation in the upper 200 m (Figures 9.3 and 9.9). An adequate understanding of carbon cycling demands not only adequate investigations of primary production, but also concomitant research on the functional biodiversity of the pelagic zone, plankton dynamics, vertical flux and its regulation in the twilight zone.

## 9.8 Seasonal variation in vertical export in eutrophicated coastal areas

Considering the seasonal flux of organic matter in various coastal settings three major modes can be distinguished: one-pulse, multi-pulse and in eutrophicated regions 'buffered' systems (Wassmann, 1991). As an example, we present data from west-Norwegian fjords (Figure 9.10). Non-eutrophicated land-locked fjords represent simple one-pulse systems, where new production, suspended biomass and sedimentation give rise to one major, annual pulse during spring. The relative amplitude of the seasonal signal in flux of organic matter is large, but the average sedimentation rate is low.

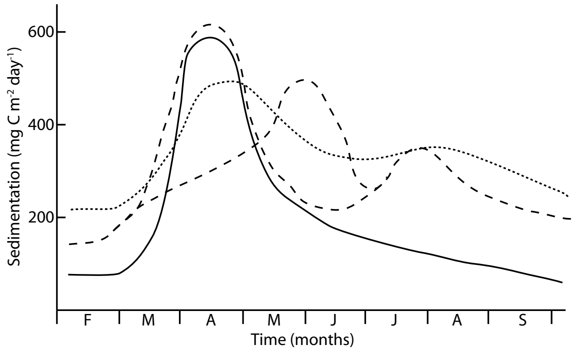

Figure 9.10: Semiquantitative diagram of annual variation of sedimentation of particulate organic carbon (POC) in fjords, eutrophicated as well as non-eutrophicated polls. One-, two- or multi-pulse systems can be distinguished. The characteristic line for eutrophicated fjords is the dotted line (increased average, reduced seasonal variability).

Eutrophicated land-locked fjords show also seasonal variability in organic matter flux, but the relative amplitude of new production, suspended matter and sedimentation is lower (Figure 9.10). The average sedimentation rate, however, is high. The variability in such ecosystems is 'buffered' by the continuous supply of allochthonous nutrients. Eutrophicated land-locked fjords are mainly one-pulse systems, but depending on the supply of nutrients from fresh water run-off, sewage etc. and climatic conditions, several minor summer and autumn blooms may develop. They may thus turn into two- or multi-pulse systems (Figure 9.10).

Open fjords are complicated multi-pulse systems. Pulses in spring and autumn are normally found. However, upwelling of nutrient rich deep water can introduce additional pulses to the system at any time, but normally during late spring and early summer (Figure 9.10). Also, accumulated biomass can be removed from the fjord by large-scale exchange of water. In multi-pulse systems advection represents the most significant element.

Comparing the dynamics of primary production and sedimentation in fjords renders, therefore, difficult because of the differences in time and space scales of these processes.

Primary production is usually estimated in terms of litres and hours, sedimentation, however, integrates the vertical flux at a given depth over the time of trap deployment and is expressed in terms of square meters and days. While the produced biomass can stay in the fjord or is dispersed in adjacent bodies of water, sediment traps might catch organic particles that have been produced and altered throughout the coastal zone. If advection is significant in fjords, the locally measured primary production and sedimentation rates might have little in common, but rather reflect the general productivity and vertical flux regime in all parts of the coastal zones, from the innermost reaches to the open shelf. This has also implications for eutrophication. Eutrophication-derived suspended biomass may be introduced into a non-polluted region from outside or local eutrophication signals may be exported to unpolluted regions.

Ecosystems that receive nutrients continuously or pulsed differ with regard to the pelagic-benthic coupling. Pulsed nutrient addition may cause a higher build-up of phytoplankton biomass, a larger temporal mismatch between herbivores and phytoplankton biomass and a higher sedimentation rate of biogenic matter. This was tested in enclosures (Svensen *et al.*, 2002). Each enclosure received the same total amount of nutrients, but the nutrients were supplied at four different intervals ranging from one single load to continuous additions. Spring bloom-like systems developed where nutrients were added in one or two pulses as they were characterised by high primary production, high suspended biomass of chlorophyll a (Chl a) and particulate organic carbon (POC) and high sedimentation rates. In contrast, the seawater enclosures receiving nutrients about every third day or in a continuous supply resembled regenerated systems with low concentrations of suspended Chl a and POC and with low and stable loss rates. The frequency of nutrient additions had a strong influence on the development of the phytoplankton and vertical flux of biogenic matter as pulsed nutrient addition resulted in the highest vertical export.

## 9.9 Eutrophication and phytoplankton biomass accumulation

The influence of top-down control is obviously important for the flow of nutrients through the food chain or food web. In lakes the cascading effects through the food web by manipulating the top-down regulation is well known (Mazumder *et al.*, 1988). Top-down effects have less-known effects on marine coastal eutrophication. As most of the eutrophicated regions are in the shallow coastal zone some of the peculiarities of these ecosystems have become mixed up into the term eutrophication that is almost analogue with green or brown waters. Do green or brown waters indicate marked increases in marine productivity or eutrophication? In most cases in the coastal zone this is the case, but it could also just reflect the lack of important grazers such as copepods that are excluded from overwintering in shallow waters, resulting in decreased grazing pressure on large-celled bloom phytoplankton. Primarily brown and green waters do not suggest that there is less grazing than phytoplankton production: a mismatch between producers and consumers. Do blue water indicate that marine productivity is low? In some cases this is true, in others not. Blue water reflects a balance between producers and consumers: biomass accumulation does not take place. Production could be high or low. Contradicting to common believe, some blue waters are highly eutrophic (e.g. the north Norwegian shelf; Wassmann *et al.*, 1999) while others are oligotrophic (e.g. the central and eastern Mediterranean Sea). These findings have obvious implications for the interpretation of pigment data and remotely sensed pigments concentrations that traditionally have been applied to construct $\mathrm{P_T}$ fields over regions where $\mathrm{P_T}$ measurements were unavailable. There cannot exist a constant pigment/$\mathrm{P_T}$

ratio, analogous to that no constant $P_T/P_E$ ratio exists. The top-down regulation of phytoplankton biomass is thus important to keep in mind when the eutrophic status of a region is established. Blue water can produce large amounts of detritus and result in large-scale vertical export of biogenic matter, resulting in large supply to the benthos and oxygen deficiency in bottom waters.

The cascading effect of top-down manipulation influenced the plankton community and results in different functional response in the various regions exposed to eutrophication. During the process of eutrophication, the food web structure, timing of fertilisation and alternative grazing/predation strategies of the planktonic heterotrophs have a crucial impact on the retention and loss of nutrients from the pelagic zone (Heiskanen *et al.*, 1996; Svensen *et al.*, 2002).

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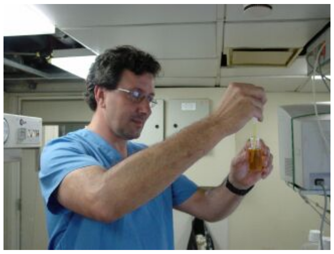
# Chapter 10

# Eutrophication and dose-response relationships in European coastal waters



Carlos M. Duarte[1]
IMEDEA (CSIC-UIB)
Instituto Mediterrneo de Estudios Avanzados
C/Miquel Marques 21
07190-Esporles (Mallorca), Spain

## 10.1 Introduction

Research on coastal eutrophication is lagging at least two decades beyond that in freshwater ecosystems. However, eutrophication problems are widespread in coastal ecosystems throughout Europe (e.g. Vidal *et al.*, 1999), and there is a need to identify research on dose-response relationships for these waters. For an entire range of different coastal ecosystems and mesocosm experiments there seems to exist a universal, robust dose-response relationship between dissolved inorganic nitrogen (DIN) input and primary production (Anonymous, 2000; Figure 10.1). However, frequently increases in autotrophic biomass, not primary production, are used as a measure for eutrophication. Thus the dose-response relationship of nutrient addition and phytoplankton biomass is of primary interest to assess how increases in nutrient supply cause eutrophication effects. Also threshold nutrient levels on a strictly scientific basis and possible 'points of no return' have to be defined in order to support legislation and actions to ensure the sustainability of coastal ecosystems. Because of the potentially vast socio-economic consequences of these measures, it is of utmost importance that the scientific advice be based on solid and robust knowledge. Despite of recent and future (e.g. Chapter 16) improvements of European water quality, in particular freshwater and the innermost coastal zone, substantial further work has to be carried out to adequately understand the dose-response relationships in the waters of the coastal zone. As we will see, there exists no universal nutrient input – phytoplankton biomass dose-response relationship for European coastal waters. This induces significant challenges for the abatement of negative impacts of eutrophication and suggests regional differences in nutri-

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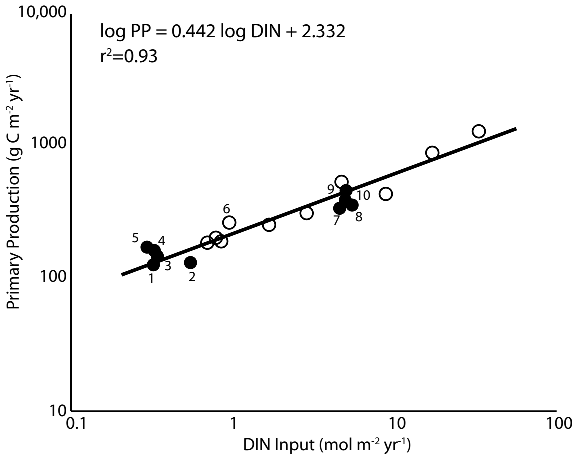

Figure 10.1: Primary production by phytoplankton ($^{14}C$ uptake) as a function of the estimated rates of input of dissolved inorganic nitrogen (DIN) per unit area from marine mesocosms (open circles) and 10, globally distributed ecosystems (solid circles). Modified from Nixon *et al.*, 1986; Nixon, 1992; Nixon *et al.*, 1996 and Anonymous, 2000.

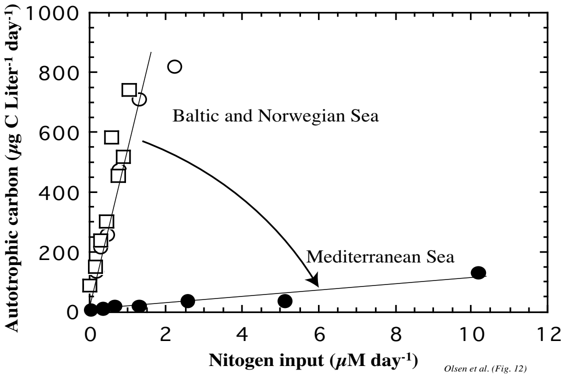

Figure 10.2: The relationship between the average phytoplankton biomass developed in coordinated mesocosm experiments conducted in different regions in relation to nitrogen inputs (Olsen, 1999). Filled circles: Mediterranean Sea. Open circles: Baltic Sea. Open squares: Norwegian Sea. The arrow indicates the effect of increased top-down regulation on autotrophic biomass.

ent thresholds which remain to be defined in most European coastal seas.

## 10.2 Comparative analysis of dose-response relationships

Comparative analyses, both of existing data sources and concerted experiments, can be used to establish threshold nutrient levels, test for possible regional differences in these thresholds, and identify the processes responsible for such differences. Coordinated mesocosm experiments in the Norwegian Sea, the Baltic Sea and the North West Mediterranean Sea by the EU project COMWEB (Comparative analysis of food webs based on flow networks) revealed major differences in dose-response patterns (see also Chapter 15). Mediterranean communities demonstrate significantly lower biomass yield per nutrient input compared to those from the Baltic and Norwegian Sea (Figure 10.2). These results suggest much lower critical nutrient loadings to develop high algal biomass and possible eutrophication problems in Atlantic/Baltic compared to Mediterranean waters. The results suggest that local nutrient emissions to the Mediterranean Sea could possibly be far higher compared to Norwegian or Baltic Sea before unfavourable chlorophyll a concentrations would occur. The results appear surprising and contra-intuitive.

One of the explanations that are offered to account for the difference is the functioning of the food webs in the three investigated regions. Grazing rates by metazoans (Figure 10.3) and DOC release rates by autotrophs (Figure 10.4) were, on average, 3-fold higher in the Mediterranean compared to the Baltic and Norwegian communities for a similar primary production. Hence, the accumulation of autotrophic biomass is far smaller, for a given nutrient input, in the Mediterranean than in the Atlantic, while metazoan production is higher. Also, more autotrophic biomass per primary production is available for other processes than grazing in the Baltic and Norwegian Sea, e.g. vertical export (see Chapter 9). This implies that in the latter seas eutrophication can result in higher supply of organic matter to the benthos, adding to low oxygen and anoxic bottom water conditions.

Evaluating the production of phytoplankton biomass from a strictly bottom-up perspective is obviously inadequate to predict the effect of eu-

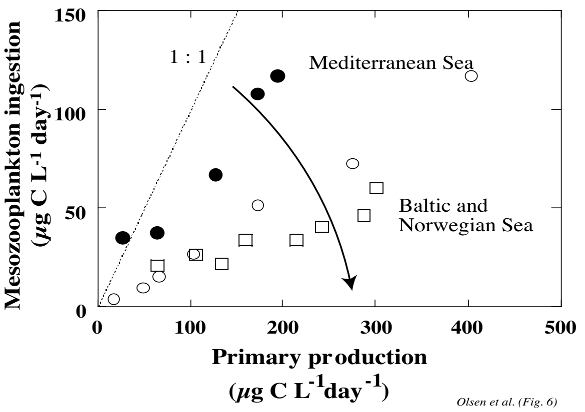

Figure 10.3: The relationship between the average ingestion rate by mesozooplankton grazers and the primary production in coordinated mesocosm experiments conducted in different regions (Olsen, 1999). The 1:1 line indicates that all primary production is grazed by zooplankton. The arrow indicates the effect of decreasing top-down regulation by mesozooplankton.

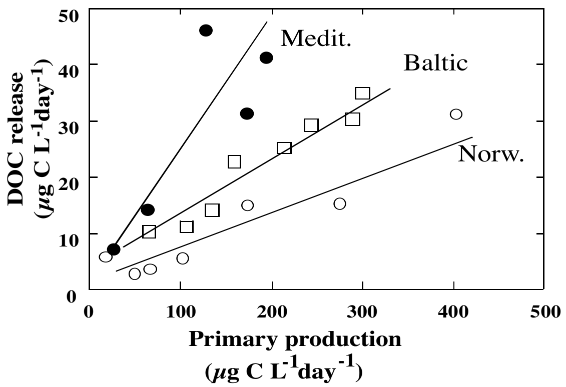

Figure 10.4: The relationship between the average dissolved organic carbon (DOC) release by the food web and the primary production in coordinated mesocosm experiments conducted in different regions (Olsen, 1999).

trophication (Figure 10.2). As discussed in the Chapters 6, 9 and 13, top-down regulation is indispensable to evaluate the effects of variable phytoplankton growth. Food-web analysis is most often not part of eutrophication and HAB studies. Considerable gaps in our knowledge result in that scientific advice regarding the eutrophication of coastal areas cannot be based on sufficiently solid and robust knowledge at present.

## 10.3 Different N:P loadings, dose-response relationships and points of no return

Changing N:P loading ratios may affect the biomass yield for a given input. For instance, the maximum autotrophic biomass yield for a given nutrient inputs was obtained at a N:P ratio of approximately 40, without any further increase in biomass yield at higher loading N:P ratios (Figure 10.5). Nutrients inputs vary between different regions across Europe. For example, there are significant differences between phosphorus and nitrogen loading in the Atlantic and the Mediterranean (Figure 10.6). These differences inN:P ratios of loading result from differences in nutrient sources. In the Atlantic, the main nutrient sources are agriculture, industry and the atmosphere. However, in the Mediterranean they are mainly agriculture and domestic effluents (Duarte and Vidal, unpubl. data). In regional seas and enclosed recipients the variability in N:P ratios of loading can even be higher.

Hence, there are indications, derived both from coordinated mesocosm experiments as well as from comparative analyses, that there are (i) major regional differences in nutrient inputs, both quantity and quality, and (ii) in eutrophication dose-response patterns.

These would, in turn, yield important regional differences in the critical nutrient thresholds that have to be reflected by legislature. There is thus no generic nutrient input — phytoplankton dose-response relationship in European coastal waters. Adequate information regarding these relation-

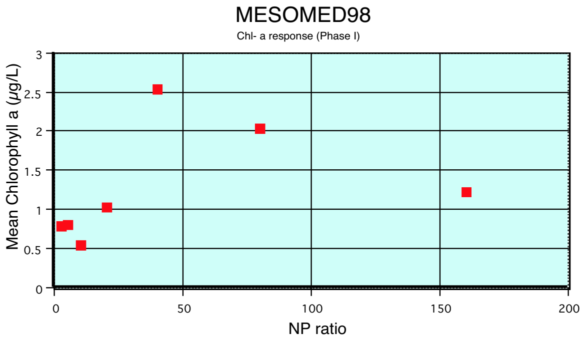

Figure 10.5: The relationship between the mean chlorophyll yield and the loading N/P ratio derived from a mesocosm experiment (MESOMED98) conducted in a Mediterranean coastal ecosystem (Duarte et al., unpubl. results).

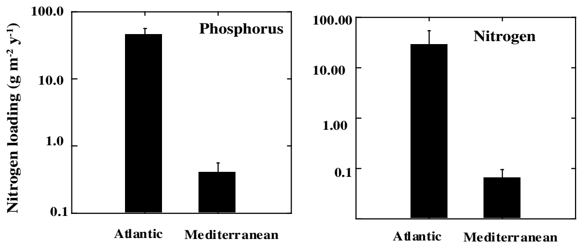

Figure 10.6: The average (±SD) N and P loading to coastal waters in Mediterranean vs. Atlantic coastal waters Vidal *et al.* (1999).

ships does only exist for a selected number of regions.

## 10.4 Autotrophic biomass as an indicator of eutrophication

In predominantly bottom-up regulated ecosystems, autotrophic biomass concentration directly reflects primary production (*de facto* new production). Eutrophication can thus be directly reflected in increased chlorophyll a concentrations and decreased visibility (Figure 10.8). However, in all ecosystems both bottom-up and top-down regulation exists and are closely entangled (see Chapter 9), but the ratio between these regulation modes varies.

The angle of the dose-response relationship is 1:1 when only bottom-up regulation controls phytoplankton growth while top-down regulation (e.g. grazing, Figure 10.3); leakage (Figure 10.4) etc. lowers the slope of the relationship.

The effect of eutrophication is thus reflected in the autotrophic biomass concentration as new production minus the effect of top-down regulation. Chlorophyll a, a standard parameter in environmental monitoring thus reflects the effects of eutrophication only if top-down regulation is low. In the case of the north-western Mediterranean Sea the increase in suspended autotrophic biomass due to increased nutrient input is so small that the impression arises that eutrophication is negligible (Figure 10.1). Autotrophic biomass is thus a convenient, but unreliable, universal measure of eutrophication (Figure 10.7).

Eutrophication is best measured as productivity (e.g. 'new production' (based on limiting nutrients such as N or P) or zooplankton or benthos biomass). Currently such measurements are rarely carried out on a routine basis in eutrophication programmes.

What eutrophication really implies has to be discussed in a system ecological context. It may well be that the DIN input — primary produc-

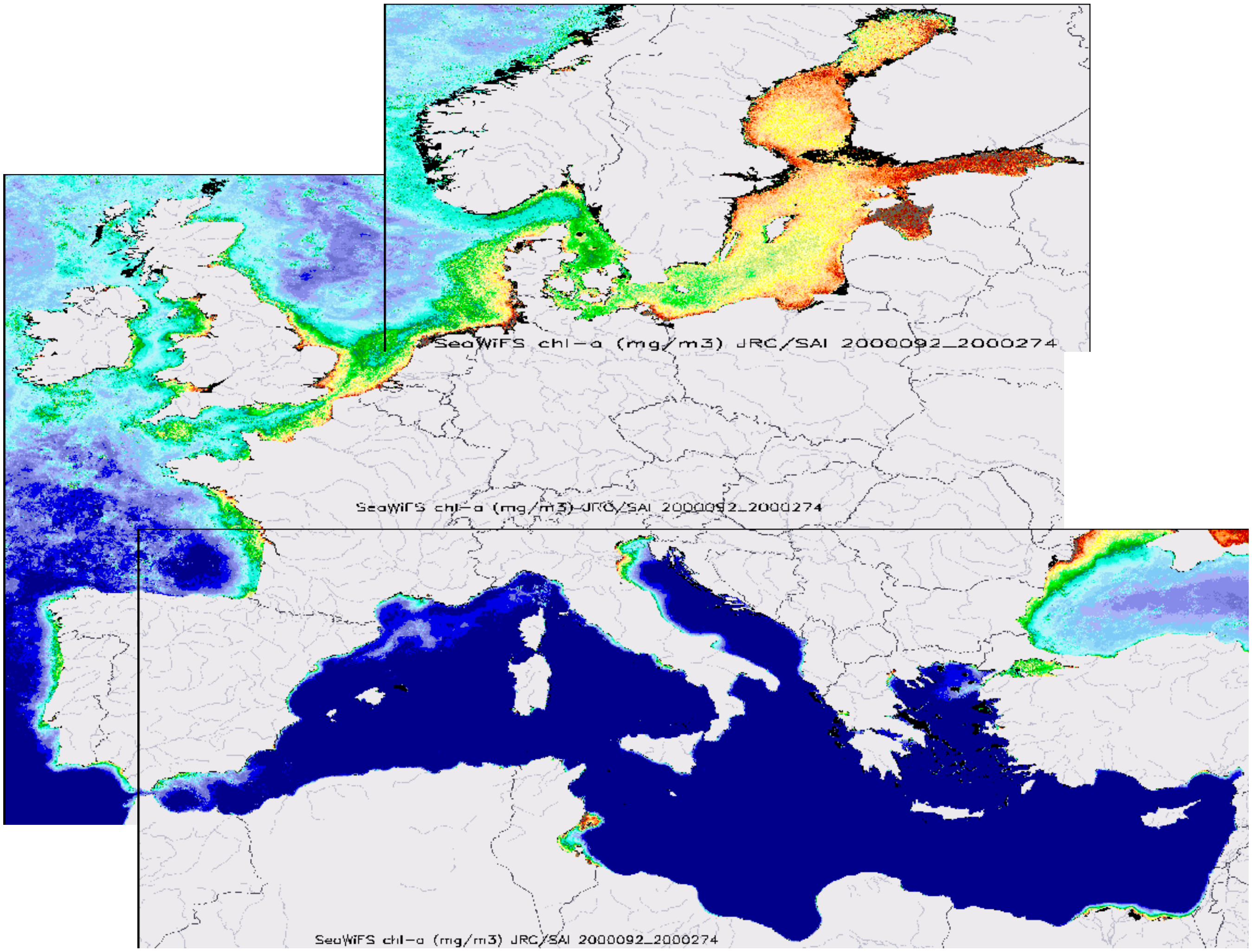

Figure 10.7: Mean spring-summer concentrations of chlorophyll-like pigments in European seas as determined from SeaWiFS satellite observations in 1999. Deep blue = 0.2 µg $L^{-1}$. Yellow = 7–12 µg $L^{-1}$; Red = 20–25 µg $L^{-1}$. Important note: The concentrations are only valid for oceanic waters and overestimate to a large and variable degree the chlorophyll concentrations in coastal seas (e.g. the central and eastern Baltic Sea, Bothnian Bay). Humic substances from rivers play an important role in estuaries and brackish waters. Examples: the Baltic Sea and river mouths such as the Don, Danube, Po, Rhone and Rhine. High chlorophyll concentrations are found in the northern Adriatic Sea, around the western Iberia, the Biskaya, British Isles, the Channel, southern North Sea, Kattegat and Skagerrak.

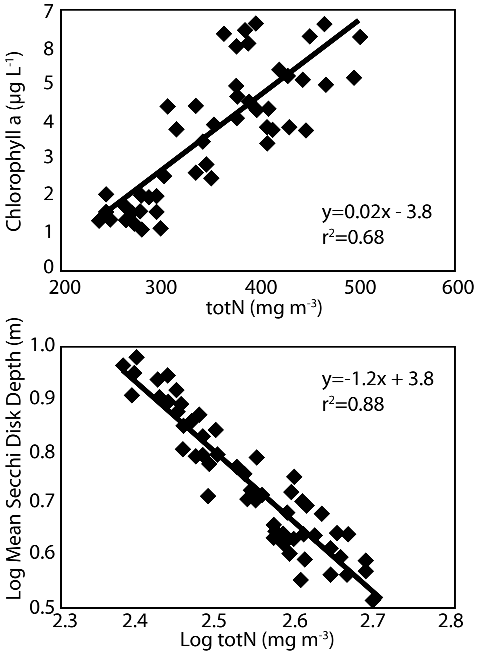

Figure 10.8: Long-term observation from the Himmerfjrden estuary south of Stockholm, Sweden over a period of years in which nitrogen and phosphorous additions were experimentally altered through changes in sewage treatment. The relationship between the mean concentration of total nitrogen and the chlorophyll a in the surface layer (A) and the water clarity (B). Modified after Elmgren and Larsson (1997) and Anonymous (2000).

tion dose-response relationship is universal (Figure 10.1) while top-down regulation influences the DIN input — autotrophic biomass relationship in variable degrees in different ecosystems (Figure 10.2). In order to predict the effect of eutrophication we have to ensure that conventional eutrophication monitoring programmes adequately detect and quantify eutrophication.

## 10.5 'Points of no return' triggered by eutrophication?

Whereas there are experimental and empirical approaches applicable to establish dose-response relationships and definitions of nutrient thresholds those of 'points of no return' are certainly cumbersome. This dilemma — which involves, by definition long-term responses, is not amenable to direct experimentation. The approach to define and understand points of no return must be, therefore, based on

- the identification of bottlenecks for the resilience of ecosystems
- the formulation of models incorporating these bottle-necks and
- the use of existing case studies to test and validate the models.

Only few regional data sets exist in Europe which could serve as a database to investigate points of no return (e.g. Danish and Swedish experience in major reductions in nutrient inputs to coastal ecosystems).

## 10.6 Conclusions/Suggestions

Comparative analyses of mesocosm experiments and ecosystems responses are appropriate tools to define dose-response relationships and to determine and understand thresholds of nutrient inputs. Similar approaches, but involving long-term records, of which Europe has a few, could be used to define 'points of no return'. Evidence of major differences in the magnitude and nature of nutrient inputs to different regions in Europe exists, as well as differential responses of the coastal ecosystems therein. On the basis of these differences, it is suggested that the unit of analysis (and specific legislation) should be *coastal biogeochemical provinces*, which are still to be defined

## 10.7 Acknowledgements

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# Part IV

# Benthic block

# Chapter 11

# Marine eutrophication and benthic metabolism

Ronnie N Glud
University of Copenhagen
Marine Biological Laboratory
Strandpromenaden 5
3000 Helsingør
RNGlud@zi.ku.dk

## 11.1 Introduction

In shallow areas (<30m) sediments can support a significant fraction of the ecosystem primary production. However, at deeper sites the benthic community solely relies on the supply of organic material from the overlying water column. In coastal areas the sediments receive about 50% of the pelagic production while the fraction in the open oceans diminishes to a few percent. The major fraction of this material gets degraded through a complex web of degradation processes, while the remaining refractory material is permanently buried in the sediment. On short time scale sediments thereby acts as a source of inorganic carbon and nutrients insuring a continued production in the water column but on timescales of thousands of years sediments represent the most important sink for burial of organic material.

The organic carbon reaching the seafloor can either be consumed by macrofauna, microfauna or microbes. Typically the activity of the various organisms is coupled so that burrow linings or fecal deposits of macrofauna represent sites with stimulated microbial activity. However, in general bacteria are the main responsible for the degradation of material reaching the seafloor. The following chapter gives an introduction to the benthic microbial processes and the effects of eutrophication. For effects on fauna I refer to the previous chapter.

## 11.2 Benthic primary production and effects of eutrophication

**Benthic microphytic communities.** Benthic phototrophic communities flourish in areas where light reach the sediment surface. In very shallow eutrophic areas phototrophic bacteria like purple bacteria, green sulfur bacteria and green nonsulfur bacteria form vertically laminated communities performing anoxygenic photosynthesis using reduced sulfur compounds as electron donors. They are more or less anaerobic and are equipped with special pigments allowing them to harvest different sections of the long-waved light spec-

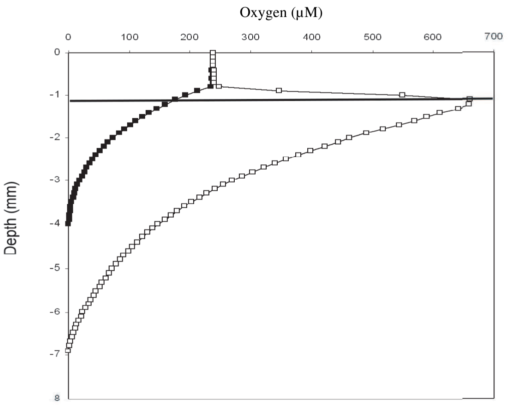

Figure 11.1: Oxygen distribution in a coastal sediment at 18 m water depth during darkness (black symbols) and light (68 $\mu$mol photons m$^{-2}$ s$^{-1}$). The horizontal line indicates the estimated position of the sediment surface. (Glud unpub data)

trum. In most sites they are overgrown by cyanobacteria or diatoms that exploit the shorter wave lengths in their oxygenic photosynthesis. In areas with no metazoan grazing such communities may develop into mm or cm thick microbial mats. Since water efficiently absorbs light of longer wave lengths anoxygenic photosynthesis is seldom of quantitative significance in aquatic environments.

In coastal areas with light exposed sediments diatoms and/or cyanobacteria covers the sediment surface. Here they exploit the nutrients released by the degradation processes occurring in the deeper sediment layers (see below). Thereby they actually put a lid on the sediment depriving the primary producers in the water column a nutrient source. The volumetric photosynthetic activity in these compact communities can be huge and can easily match the integrated activity of the water column. In areas with significant benthic photosynthesis the production and degradation of organic material is tightly coupled spatially and temporally. There exists an almost mutualistic symbiosis were phototrophs leaks low-molecular organic compounds to the aerobic heterotrophic community that on the other hand lower the $O_2$ concentration (and the pH) and release $CO_2$ lowering the photosynthetic stress on the phototrophic community. The dissolved organic material is thereby maintained within the benthic environment. Such communities are of course an excellent food source and are exposed to heavy metazoan grazing keeping the benthic microbial biomass low. Experiments have shown that by eliminating grazing the benthic phototrophic communities quickly grow to an extensive thickness effeiciently absoping nutrients release from the deeper sediment strata. Fixed to the sediment surface the benthic phototrophic community is vulnerable to changes in water turbidity or pelagic blooms impeding the down welling irradiance.

In shallow oligotrophic areas the benthic primary production often dominates the ecosystem. As nutrient loading increases, the advantage of being close to the benthic nutrient source diminish and the pelagic growth limits the light availability. Therefore the ecosystem primary production shift from being dominated by benthic phototrophs in oligotrophic area to pelagic dominated systems in eutrophicated areas. In many temperate coastal areas a similar shift is often seen on a seasonal basis. During late autumn and winter the water is clear, nutrient concentration relatively low and a mixed water column favors a benthic production. However, as water column stratifies during spring (and the nutrient concentration increases) the following pelagic spring bloom shade out the benthic production. During autumn, metazoan grazing decrease, the water column clears and benthic microphytic photosynthesis again becomes important on ecosystem level.

**Nitrogen cycling in microphythic inhabited sediments and the effects of eutrophication.** During active photosynthesis the oxic conditions of the sediment changes dramatically. Oxygen concentration of the surface sediment increases to supersaturation and the oxic zone becomes significantly broader (Figure 11.1).

The benthic microphytes compete with the bacterial community for nutrients in order to sustain the metabolic activity. Nitrogen, primarily in the form of $NH_4^+$, is produced during the anaerobic degradation in the deeper sediment strata (see below). Within the oxic zone nitrifying bacteria oxidize ammonia to nitrate and harvest the released energy according to the following stochiometry: $NH_4^+ + O_2 \rightarrow NO_3^-$. In realty two synthropically coupled groups of bacteria are involved in this process. In many oligotrophic coastal settings microphytes competes successfully with nitrifyers for the ammonia. In such areas the nitrification is almost excluded, while photosynthesis and nitrification coexist in eutrophicated areas with higher concentrations of nutrients. Actually the photosynthetic activity stimulates nitrification in nutrient rich environments due to the broader oxic zone. The benthic microphytes thereby indirectly regulate the activity of the denitrifying community that use nitrate as an oxidant for their heterotrophic metabolism in the anoxic parts of the sediment (see below).

Elevated nutrient concentrations in the water column, stimulates the pelagic production and the light limited benthic microphytic community can be out competed. In those cases nitrification in the sediment gets reduced and a larger fraction of nitrogen leaves the sediment in the form of ammonium. Denitrification is then mainly based on nitrate from the overlying water diffusing down through the oxic zone. If the environment gets further reduced the reduction of nitrate becomes dominated by '*dissimilativ of nitrate to ammonium*' and the removal of nutrients through denitrification ceases. Such transitions are often observed around aquaculture plants with localized eutrophication (e.g. Christensen et al. 2003).

## 11.3 Benthic mineralization processes of aquatic sediments

**Hydrolysis.** The majority of material reaching the seafloor consists of polymers like proteins, lipids, and polysaccarides and nucleic acids (Figure 11.2). Most microbes are not capable of assimilating larger molecules across their cell membranes. In order to cleave the polymers bacteria can actively transport enzymes to the porewater or have specialized enzymes for polymer cleavages attached to their cell membranes. The produced monomers can subsequently be assimilated by the microbes for further intracellular degradation.

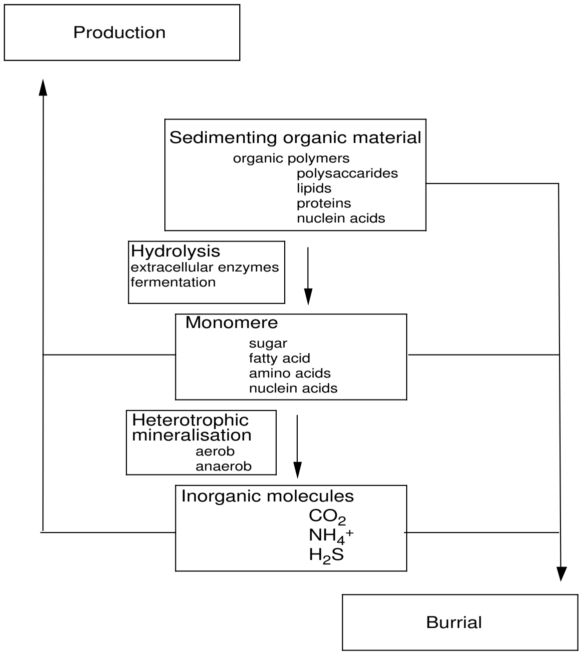

Figure 11.2: A simple scheme illustrating the gradual degradation of organic material reaching the seafloor

**Fermentation.** Initially organic fermentation is an important pathway for restructuring the available organic substrates. Fermentation are metabolic processes where there is redox balance between substrates and products. Well know examples include alcohol fermentation by yeast or homolactic fermentation by e.g. *Streptococcus*:

Alcohol fermentation:

$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$

Homolactic fermentation:

$C_6H_{12}O_6 \rightarrow 2\ CH_3COH_2COO^- + 2H^+$

As can been seen some Carbon atoms have been reduced while others have been oxidized during the process but overall there is redox-balance between the two sides of the equation and no net oxidation has occurred. Only a minor fraction of the available energy is released by fermentation, but it forms small molecules like acetate and propionate that can be used by the majority of the microbes

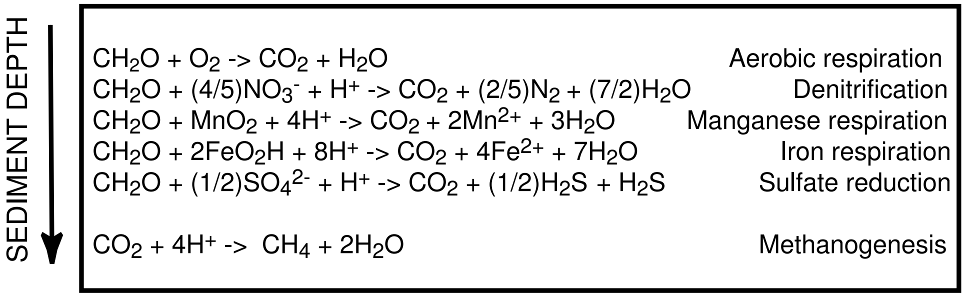

Figure 11.3: A simple scheme over the heterotrphic degradation pathways as they are laminated in the sediment. Methanogenesis is strictly speaking not heterotrophic process but rater a chemoautotrophic pathway.

for further degradation. Inorganic fermentation processes also exist and is in some instances of importance especially during methanogenesis and sulfur cycling but will not be dealt with in any detail.

**Heterotrophy.** The heterotrophic degradation of the various monomers can proceed either aerobically or anaerobically. In the first case bacteria use $O_2$ to oxidize the organic material by a metabolism similar to that of macrofauna (or ourselves) and gain chemical energy. Oxygen is the best available oxidant and consequently it gives the highest growth yield for the bacteria. However, water is a very $O_2$ poor environment and the $O_2$ pool is exhausted in the very upper mm of most aquatic sediments (see Figure 11.1). Below the oxic horizon a number of other oxidants become important: $NO_3^-$, $MnO_x$. $FeO_x$, $SO_4^{2-}$, $CO_2$. During the aerobic and anaerobic heterotrophic activity the organic material gradually becomes degraded into the inorganic components that for the most part get is released to the overlying water column.

The vertical position of the anaerobic degradation pathways are mainly determined by the chemical energy liberated by the redox-process. Therefore denitrification is followed by metal respiration, sulfate reduction and methanogenesis. This laminated sequence is of course a simplification and often there exist overlaps between the different zone and microniches mainly induced by burrowing infauna or uneven sedimentation in the form of aggregates or fecal pellets exists, but essentially the various degradation pathways are sequential structured as outlined below.

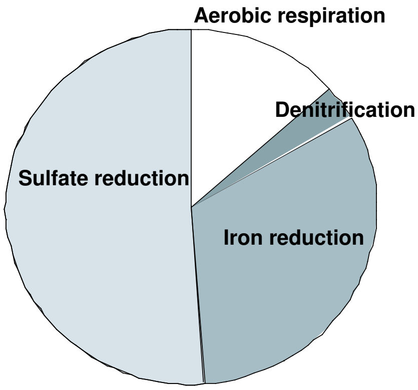

Figure 11.4: The relative importance of the various heterotrophic degradation pathways in a typical marine sediment (380 m in Skagerrak). The microbial mediated manganese oxidation was insignificant (data from Canfield *et al.*, 1993).

The importance of the various pathways depends on the input of organic material to the seafloor and the availability of the involved oxidants (Figure 11.3). In most coastal environments aerobic respiration only plays a relatively minor role but moving towards the deep sea where the input of organic material gradually decreases the importance of $O_2$ as an oxidant becomes increasingly important. This is also reflected in the $O_2$ penetration depth which broadens from a few mm in coastal areas to several cm or dm in the open oceans. Due to the low concentration of $NO^{3-}$ in most aquatic environments, denitrifica-

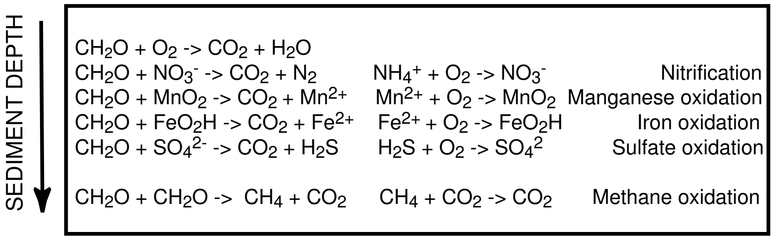

Figure 11.5: Coupled redox processes combining heterotrophic and chemolithotrophic processes.

tion is almost negligible for the degradation of organic material (even though it is a very important process for the aquatic nitrogen cycle). Due to an efficient chemical reduction of maganeseoxides (see below) and the generally low concentrations of manganese in sediments, manganese respiration also only plays a minor role for the benthic diagenesis – even though exceptions exist (see below). The importance of iron respiration for the degradation of organic material has been increasingly recognized during the last decades and it is a major pathway in many coastal environments. This is very explicitly in coastal areas receiving major inputs of terrestic ironoxides like fjords of tropical rainforest. For the vast majority of coastal environments sulfate reduction is the major pathway of benthic carbon degradation (Figure 11.4). This is due to the very high content of sulfate in sea water, which is in the order of 27 mM (at 34‰ seawater) or around 100 times more than the $O_2$ content of air saturated seawater (at 10°C). In marine environment methanogenesis is of less importance, but in limnic settings with their low concentrations of sulfate it can be a quantitatively important process. Strictly speaking most of the methane production in aquatic sediments proceeds by inorganic fermentation: $2CH_2O \rightarrow CO_2 + CH_4$, and is actually not a heterotrophic process.

Figure 11.4 reflects the typical importance of heterotrophic processes in coastal sediments. However, it is important to notice that this is a theme with many variations and the relative importance of the various pathways many differ significantly between environments (Thamdrup, 2000).

**The reoxidation processes for the heterotrophic metabolism.** From the redox equations listed in Figure 11.3 it is apparent that without an efficient reoxidation of the reduced counterparts, sediments would become reduced and the oxidation of organic material would cease. While $N_2$ is a highly inert molecule that escapes to the overlying water without further reactions, $Mn^{2+}$, $Fe^{2+}$ and $H_2S$ are reducing and most molecules are oxidized as they diffuse upwards though the gradually more oxidized sediment layers. The oxidation is exergonic and occurs spontaneously in oxic settings, however, chemolithoautotrophic bacteria are able to efficiently compete with the chemical reactions and can harvest most of the energy. The best know group of bacteria responsible for such activities are the sulfide bacteria *Beggiatoa* spp and *Thiovulum* spp that gain energy from the following reactions:

$H_2S + 2O_2 \rightarrow SO_4{}^{2-} + 2H^+$
$HS^- + O_2 + H^+ \rightarrow S^0$
$S^0 + H_2O + 1\ O_2 \rightarrow SO_4{}^{2-} + 2H^+$

They can store elemental sulfur ($S^0$) intercellular for further redox processes when the environmental settings changes. By their chemosensory behavior these bacteria are capable of maintaining themselves within the $O_2$ — $H_2S$ interface typically characterized by very steep concentration gradients.

Combining the heterotrophic and chemolithotrophic processes introduced above gives a number of coupled redox processes as outlined below.

Since most of the reduced counterparts from the anaerobic degradation ultimately get reoxidized by $O_2$ the total $O_2$ uptake of the sea floor is the

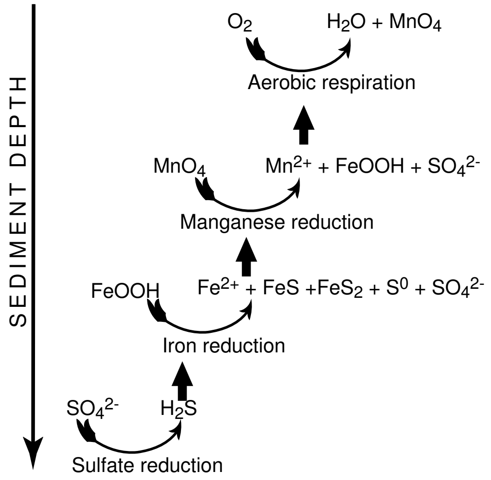

Figure 11.6: A simplified scheme of the redox cascade of marine sediments

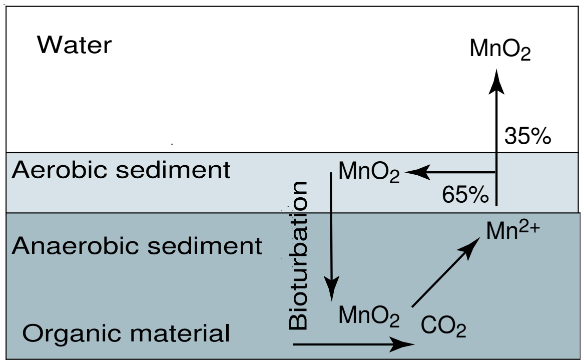

Figure 11.7: An example of manganese cycling in a coastal sediment (16 m, Kattegat). 65% of the manganese ions release during oxidation of the manganese oxides get reoxidized microbially within the 1 mm oxic zone of the sediment, while 35% is chemically reoxidized in the overlying water (data from Thamdrup et al. 1994)

most widely used measure for the benthic diagenesis. This procedure assumes steady state conditions within the sediment. In reality the scheme outlined in Figure 11.5 is an oversimplification. Most of the reoxidation proceeds though a redox cascade rather than direct aerobic activity.

**Metal cycling of marine sediments.** Oxygen only reacts directly with a minor part of the reduced substances from the anaerobic degradation. Instead the reduced counterparts react through a redox cascade as outlined in Figure 11.6.

Most coastal sediments contain significant amounts of ironoxides and in those instances $H_2S$ produced by sulfate reduction reacts with these oxides producing a number of reduced ironsulfides. Pyrite ($FeS_2$) is very stable under anoxic conditions and represents a burial unless the material is brought up to the oxic environments by for instance bioturbation. The reduced ferrous iron ($Fe^{2+}$) and ironsulfides can react with manganeseoxides forming sulfate and ironoxides. In fact most manganges oxidation in marine sediments occur through this reaction and therefore manganese respiration in most sediments only plays a minor role.

Since ironoxides react with reduced sulfur they play a significant role in the benthic diagenesis and are of prime importance for the chemical (and biological) environment of the seafloor. Sulfide is toxic to higher fauna (and flora), but as long as the sediments contains ironoxides the sulfides do not escape to the overlying water but is 'inactivated' by the so called ironoxide-layer. The amount of sulfide that sediments can inactivate is called the sulfide-buffer-capacity (SBC). The SBC decreases during spring and summer where sulfide production (sulfate reduction) gets stimulated by elevated temperature and increased loading of organic material. If the SBC is overloaded the sulfide front will start moving up to the sediment-water interface where sulfide oxidizing bacteria represent the last barrier towards sulfide release to the overlying water. Ironoxides have a large capacity to bind phosphorus, and as they get depleted phosphorus is released to the overlying water, which may further stimulate the pelagic production and the sedimentation of organic carbon. The layer of ironoxides thereby represents an important zone buffering sulfide and phosphor release to the overlying water. A buffering that diminishes and ultimately vanish as eutrophication increase.

Metal oxides ($FeO_2$, $MnO_2$) are solids and are not being transported by diffusion as their reduced counter parts ($Fe^{2+}$, $Mn^{2+}$). Therefore as the reduced solutes reach more oxidized conditions they

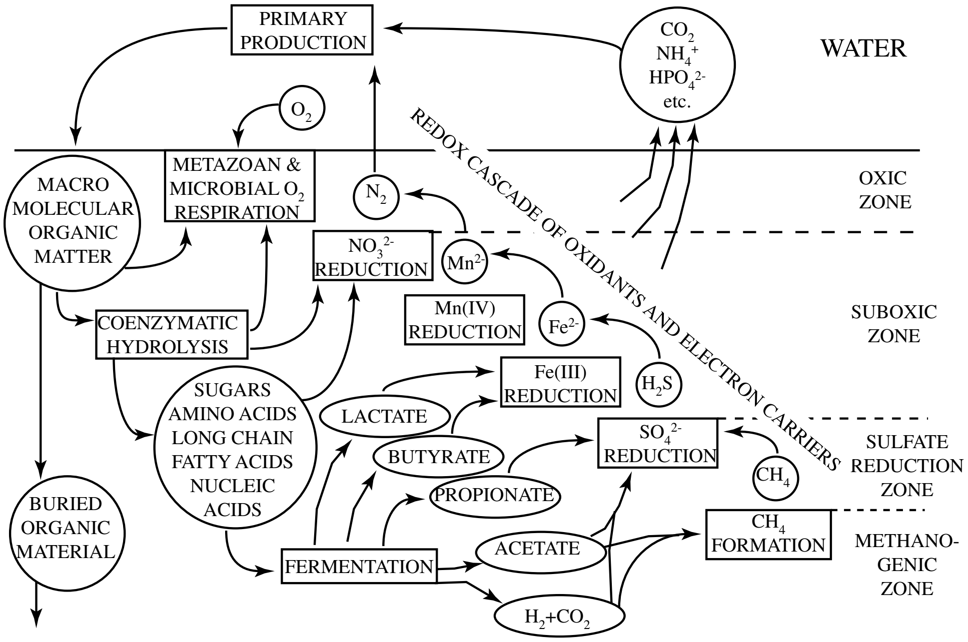

Figure 11.8: A simplified overview of the most important processes involved in the benthic diagenesis (from Jørgensen, 2000).

precipitates and can only act in the heterotrophic carbon mineralization if they are transported to deeper layers either by bioturbation, resuspension or simply by burial. Fauna activity thereby plays an important role for efficient metal cycling in sediments. An example for manganese cycling in coastal sediment is displayed in Figure 11.6.

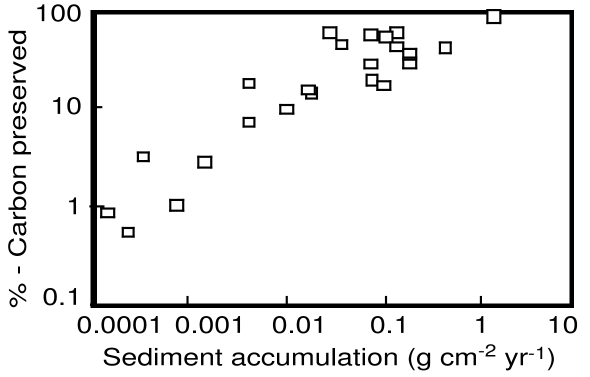

Figure 11.9: Carbon preservations as a function of sediment accumulation in a wide range of coastal sediments (redrawn from Canfield 1994 and Glud et al., 1998).

As can be seen some of the reduced manganese ions escapes to the overlying water, where it spontaneously reacts with $O_2$ forming precipitates that can be transported with bottom currents to sites of deposition. Large amounts of manganese are deposited in central Skagerrak (700 m), and the carbon mineralization is these sediments are completely dominated by manganese respiration due to the very high levels of available manganese oxides (Canfield *et al.*, 1993).

Figure 11.8 gives an overall impression of the benthic carbon degradation of marine sediments combining most of the processes mentioned above.

## 11.4 Eutrophication effects on the benthic diagenesis of coastal sediments

For the benthic microbial community the most prominent effect of eutrophication is the increased loading of organic material to the seafloor. This stimulates the hydrolysis, the fermentation and the heterotrophic activity. Due to higher activity and diminished $O_2$ concentration in the bottom water the oxic zone will shrink and the relative importance of the anaerobic degradation processes will increase. The reoxidation process of $Mn^{2+}$, $Fe^{2+}$ and $H_2S$ will move upward in the more reduced sediment and take place close to the sediment surface. Nitrification and denitification will diminish and nitrogen will leave the sediment in the form of ammonium rather than nitrate and dinitrogen. As the pool of ironoxides in the sediment is getting reduced, phosphorus is released and will diffuse up in the overlying water. The sediment will now become an increasingly important source for phosphorus, which can further stimulate the production in the water column. When the entire pool of ironoxides is used up the sulfide will reach the sediment water interface where a whitish lawn of the sulfide oxidizing bacteria develops. The heterotrophic degradation will now be completely dominated by sulfate reduction and the increased sulfide production may overload the sulfide oxidizers at the sediment surface requiring oxygen (or nitrate) for their activity. At this point sulfide escapes the seafloor and milky plumes of sulfur produced during chemical oxidation of the released sulfide will appear. Stimulated methan production will lead to bubble formations in the sediments. In extreme events bubbles will be released from the sediment leading to resuspension and further $O_2$ depletion of the water column. Such events are commonly observed on a seasonal basis in coastal environments exposed to high levels of eutrophication like: Limfjorden in Denmark or Gulmarsfjorden in Sweden. In most instances the effect of eutrophication does not reach these extreme levels, but depending on the organic carbon loading the sediments will move along this cascade of events until the sedimentation of organic material diminishes.

On a longer time spans the increased loading of organic material affects the fraction of material that is buried in the sediment.

As can be seen above, the fraction of organic material that is buried in the sediments increases with the sedimentation of organic material. Burial in the sediment thereby act as an increasingly important sink for organic material (Figure 11.9). This is not so much an effect of $O_2$ depletion as an effect of exhausting the available oxidants of the anaerobic degradation.

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# Chapter 12

# Benthic phosphorus release from sediment to water

Jouni Lehtoranta
Senior Researcher PhD (Limnology)
Finnish Environment Institute
Research Department
Research Programme for the Protection of the Baltic Sea
Box 140; FIN-00251 Helsinki Finland
jouni.lehtoranta@ymparisto.fi

## 12.1 Introduction

Eutrophication increases the amount of new particulate organic matter in water and the subsequent sedimentation (see also Chapters 11, 9). In estuaries, coastal areas, shallow open sea areas and many lakes a large portion of the autochthonous and allochthonous particulate organic matter reaches the surface of the bottom sediment. Organic matter and nutrients and their processes in sediments therefore play an important role in the nutrient dynamics of these shallow systems. Increased concentrations of labile sediment organic matter leading to higher sediment $O_2$ consumption and the eventual depletion of dissolved $O_2$ in bottom water are a common consequence of eutrophication. The exhaustion of $O_2$ weakens the ability of sediments to retain nutrients. Thus, increase in the release of nutrients from the bottom sediments back to water column is a response to eutrophication.

The bottom area of marine and lake waters can be categorized as erosion-, transport- and sedimentation bottoms. At the erosion bottoms the erosion conditions prevail, whereas at the transport bottoms the settled fine particulate matter can stay for long periods, even for decades, before it is transported to the sedimentation bottom. The fine inorganic and organic particulate matter is eventually buried at the sedimentation bottoms, i.e. areas, where nearbottom water currents can not re-suspend the fine-grained particles back to water. The whole bottom area of the water system does not efficiently release nutrients from sediments to water even under anoxic conditions. The major part of the release usually occurs at the sedimentation areas, where the concentrations of organic matter and nutrients are high in sediments. At the sedimentation areas the renewal of near-bottom water is slow and sediment $O_2$ consumption is high and, thus, they are sensitive to $O_2$ depletion and the subsequent high release rate of nutrients.

The sensitivity of water masses to an excess nutrient load and subsequent eutrophication is largely determined by the geomorphological and hydrographic properties of an area. The longer the residence times of the water and the stronger the stratification due to changes in water density, the greater is the sensitivity. In lake systems water density is largely governed by temperature, but in a brackish water body, for example in the Baltic Sea, the main factors controlling density are salinity and temperature. These result in strong stratifications, namely halocline and thermocline, in the water column. As a consequence, the separate surface and deeper layers may prevent the mixing of $O_2$-rich surface water with the bottom water for years or parts of a year. Due to its unique stratification properties, the Baltic Sea is sensitive to hypoxia i.e. low oxygen concentrations and the high release rates of phosphorus (P) from the sediments (Conley *et al.*, 2002). Changes in hydrographic features affecting stratification in the water body have an effect on biogeochemical processes in the sediments, which may, in turn, affect the pool of P in the water.

## 12.2 Significance of benthic phosphorus flux

Sediments are considered to act as 'sinks' for particulate P. However, a portion of the P is released back into the water as a result of the biogeochemical processes undergone by settled particulate P during burial. The released P may significantly increase the biologically available pool of P in water, counteracting decreases in the external load. Owing to P released from the bottom, the total external load of P does not correspond fully to the pool of algal-available P in water. Thus, reducing the external load of P does not necessarily lead to rapid recovery of the system. In eutrophic lakes and the Baltic Sea, the benthic flux of P can temporarily equal or even exceed the input of P from external sources (Conley *et al.*, 2002; Boström *et al.*, 1985) and can delay recovery of these systems. The P cycle in sediments may take several decades to adjust to changing trophic conditions. In addition, one has to keep in mind that P released from sediment to water is almost completely in the form of dissolved reactive P (orthophosphate), which is, in turn, considered to be completely available for algae. A large part of the external P load enters to water systems as particulate P, which availability to algae is poor. Thus, the algal availability in the load of total P from external sources is not comparable to the efflux from the sediment to water.

In terms of P in sediments, two issues are related to the fate of P: the fraction of settled P that will eventually be buried in the sediments, and the fraction of P that will be transformed into an available form, i.e. one that may potentially contribute to eutrophication, before permanent burial. When P enters the aquatic system, internal processes affect the cycling of P in both water and sediment. In sediments some of the internal processes increase but some decrease the pool of bioavailable P in water. The benthic P efflux, referring to a commonly used term for the internal P load, originates from bottom sediments when dissolved P is released from particles to the pore water and subsequently to the overlying free water. Note that the benthic P efflux can only be based on P transported from external sources. The present section concentrates on the release of dissolved P and thus does not cover the effect of resuspension (i.e. transport of settled particles rich in P back to the water column).

Sediments can, however, bind and release P. A net flux of P into sediments occurs when net sedimentation of P is above zero and P release is lower than gross P sedimentation (Figure 12.1). A net flux of P from sediment to water, in turn, occurs when net sedimentation of P is below zero and release is higher than gross P sedimentation. The flux in and out of the sediments may vary seasonally as well as between years, depending, among other things, on hydrological features. The retention of P in sediments is considered to be largely dependent on (1) net sedimentation of particulate P, (2) early diagenetic cycling and transformations of reactive P compounds, and (3) burial of immobilizable P compounds in deeper sediment layers (Boers *et al.*, 1998).

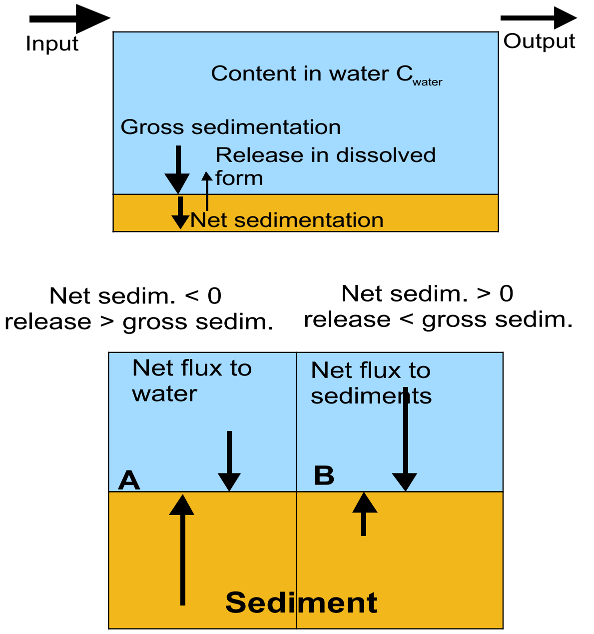

Figure 12.1: Phosphorus balance in water systems and role of sediments.

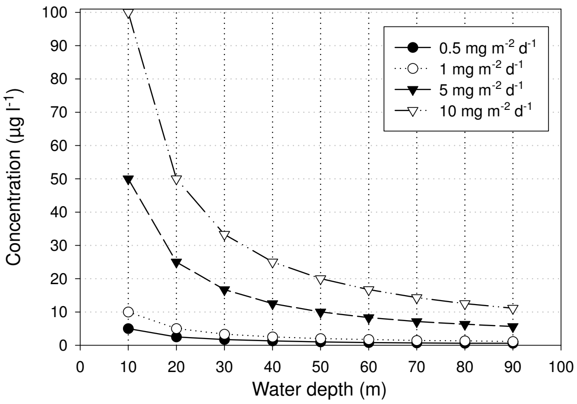

Figure 12.2: Effect of benthic solute efflux (mg m$^{-2}$d$^{-1}$) on concentration in water column above this square meter calculated for 100 d time period.

The release of P from sediment to water can be quantified with mass balance analysis at the whole-system level (mainly lakes), laboratory or *in situ* confinement of sediments in core tubes or benthic chambers, and also by diffusion flux calculations based on measured concentration gradients at the sediment-water interface. The increase in the concentration of dissolved substances in water after their release is controlled by the flux rate of the substances from sediment to water and the volume of water assuming that no back precipitation occurs. In a shallow area, for example, where the water depth is 10 m, an average flux rate of 1 mg m$^{-2}$ d$^{-1}$ during the summer period (100 d) increases the concentration of dissolved substances in the whole water column above this square metre to 10 $\mu$g l$^{-1}$ after complete mixing (Figure 12.2). A similar increase in concentration is achieved at an average flux rate of 5 mg m$^{-2}$ d$^{-1}$ for water at a depth of 50 m.

In the case of nutrients, the issue of whether the benthic flux is high or low depends on the consequences of the efflux related to primary production. For example, the bioavailable P released from the sediments contributes to new production, *i.e.* is a fraction of total primary production. In relatively shallow aquatic environments such as estuaries, continental shelves and bays, the P efflux may support a large proportion of total primary production. In the upper Potomac River estuary, for example, efflux of P can meet 27% of the gross primary production requirements (Callender & Hammond, 1982). In Narrangansett Bay, efflux of P contributes about 50% (Nixon 1981), in the Kiel Bight 20% (Balzer, 1984) and in Århus Bay, Denmark, 15% (Jensen *et al.*, 1995) of the amount needed to support primary production.

Especially in the eutrophic non-stratified shallow lakes the efflux of nutrients from sediment to their rather small water volume may be crucial during productive season. In these systems the nutrients in near-bottom water are rapidly transported to the euphotic water layer during water mixing.

Søndergaard et al. (1991) have reported very high P flux rates up to 200 mg m$^{-2}$ d$^{-1}$ in hyper-eutrophic lake Søbygård (Denmark). These kind of high benthic release rates can be measured only temporarily, but in comparison, the release rate of 200 mg P m$^{-2}$ d$^{-1}$ per one km$^2$ correspond to a daily total phosphorus load of about 67 000 persons, assuming that the total P load of one person per day is 3 g.

Sediment can, however, retain P well. In oligotrophic lakes the release of P from sediment to water is often almost undetectable in oxic conditions and low temperatures in short sediment incubations. For example, in oligotrophic lakes such as Lake Michigan the mean release rate of P 0.05 mg m$^{-2}$ d$^{-1}$ can supply less than 1% of the P utilized for annual primary production (Conley & Quigley, 1988). In addition, agriculturally P loaded Lake Pyhäjärvi in Finland retains in lake — including fish catch — almost 90% of the external total P load (Ekholm *et al.*, 1997).

## 12.3 Binding of phosphorus in sediments

The phosphate ion (PO$_4^{3-}$) is a highly particle-reactive anion and thus the sorption properties of sediment are crucial for P-retention capacity. Generally, aerobic conditions are considered to promote P sorption and anoxic conditions to favour P release. After the dissolution of particulate P into inorganic form in sediments, PO$_4^{3-}$ ion is easily sorbed into inorganic particulate form. The storage of surplus P by microorganisms can, however, compete with the chemical immobilization of P (Hupfer & Uhlmann, 1991). Normal bacteria have a low P content in living cells but some bacteria accumulate polyphosphate (poly-P) intracellularly in very large amounts, up to *ca.* 20% of their dry weight. These bacteria store P under aerobic conditions and release intracellular P via enzymatic hydrolysis when conditions turn anaerobic (Deinema *et al.*, 1985). In organic-rich lake sediments, microorganisms are able to take up and release P, depending on redox conditions, and sterilization of oxic sediments can reduce the microbial take up of P (Gächter *et al.*, 1988). Both nonbiological and biological binding mechanisms of P are able to keep the pore water P concentration low and reduce the release of P from sediment to water.

Owing to surface area effects, the sorption reactions of P caused by inorganic particles are enhanced as a function of decreasing sediment grain size. The main fine-grained ($<2$ $\mu$m) constituents of sediments are silicates, *i.e.* clays, carbonates, Fe and Al oxides, and humic acids. The surfaces of fine-grained minerals such as Fe and Al oxides, clay minerals with surficial Fe and Al (hydr)oxides, and possibly also Mn oxides adsorb P efficiently. Humic compounds containing Fe and Al can also sorb P. Silicates and carbonates in larger particles such as sand adsorb P poorly.

It is widely accepted that sedimentary P cycling is linked mainly to the Fe cycle in lake (e.g. Einsele, 1938; Mortimer, 1941, 1942) and marine systems (Jensen *et al.*, 1995; Sundby *et al.*, 1992). In marine sediments, however, most of the total Fe (60–80%) is bound to sheet silicates (e.g. chlorite; see alsoSubsection 11.3). Adsorption of P by silicate-bound Fe is insignificant compared to that by Fe(III) oxides, which are considered to be the main Fe compounds in P binding. Sediments contain a multitude of Fe(III) oxides, often in complexed mixtures, that range widely in degree of crystallinity, particle size, available surface area, reactivity and oxidation state (Lovley, 1991). The P sorption capacity of amorphous, i.e. poorly crystallized, Fe(OH)$_3$ and lepidocrocite (-FeOOH), is about 20 times that of crystalline Fe(III) oxides such as goethite (%-FeOOH) and hematite (%-Fe$_2$O$_3$).

Other negatively charged anions can also compete with the PO$_4^{3-}$ of adsorption sites in sediments. For example, the effect of pH can be related to competition for adsorption sites, because desorption of P from clay minerals and Fe and Al (hydr)oxides is based on ligand exchange, in which P is substituted for by OH$^-$. An increase in pH can also increase the negative charge of the sorbing oxides (Hartikainen & Yli-Halla, 1996). A significant decrease in P sorption to Fe(III) oxides occurs at pH >6.5. Silicon (Si) may also compete with P for adsorption sites (Tallberg, 2000). Silicate ($SiO_4$) and P are sorbed onto the surfaces of hydrated Al and Fe oxides by the same specific mechanism and, thus, $SiO_4$ may chemically compete with $PO_4^{3-}$ for adsorption sites.

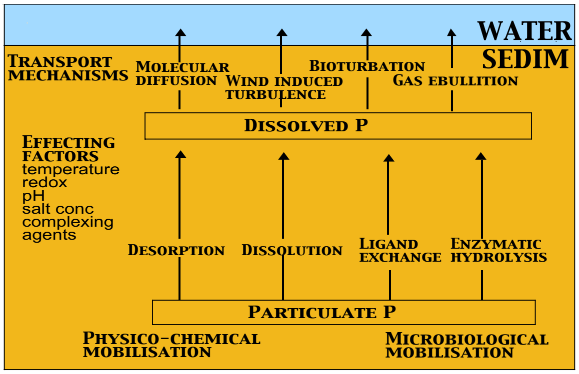

Figure 12.3: Dissolution of particulate P and transport mechanisms of dissolved P into water column (Boström *et al.*, 1982).

## 12.4 Release mechanisms of phosphorus from sediment to water

After settling, particulate P begins to undergo chemical and biological reactions that will lead to dissolution of P (Figure 12.3). Two mechanisms have to occur simultaneously or within a short period before P is released from sediment to water: first, dissolution of P bound to particles or aggregates and its transfer to the pool of dissolved P in the pore water and, second, a transport process responsible for the release of dissolved P from sediment to water (Boström *et al.*, 1982). In sediments, P bound to particles is mobilized into dissolved form in desorption, dissolution, ligand exchange and enzymatic hydrolysis. The driving force behind the released P may be the rate at which dissolved P is generated in the pore water by splitting mechanisms of particulate P. In sediment, the dissolved P generated can be adsorbed, complexed with (in)organic cations, precipitated as authigenic minerals, and taken up by bacteria and benthic microalgae before being released to water.

The main physical factors enhancing the exchange of P between sediment and water are molecular diffusion, temperature, water turbulence, gas ebullition and bioturbation. In stagnant anoxic hypolimnetic and non-bioturbated sediments, molecular diffusion is considered to be the main mechanism for P release. There is usually a pronounced difference in P concentrations between the overlying water and the surface pore water. The steeper the concentration gradient of P between the free water and the sediment pore water, the higher is the rate of diffusion. An increase in sediment solid matter content decreases free diffusion owing to the increase in collisions of molecules with the particles in sediments.

Temperature can have a major effect on the release rate of P from sediment to water. The changes in temperature affects on the microbially and chemically mediated redox reactions in sediments. An increase in temperature accelerates also the diffusion rate as a result of increased Brownian movement. However, temperature also has an indirect effect on P release, because an increase in temperature raises the metabolic rate of bacteria and subsequently the mineralization rate of organic matter.

In addition to molecular diffusion physical water movement can transport solutes from sediment to water. Physical water movement is a much faster transport mechanism than diffusion. Advective flux denotes transport of dissolved chemical species due to transport of water by water turbulence at the sediment-water interface, gas convection, seepage and organisms. The measured solute flux, for example by incubations, is usually higher than the calculated diffusion flux. Physical pore water movement is increased by water currents at the sediment-water interface and by gases formed in microbial reduction processes in sediments. In addition, bioturbation promotes physical water movement and affects the binding capacity of P in sediments.

Sediments are often inhabited by abundant and diverse populations of burrowing macroinvertebrates; these influence nutrient binding and release. A significant variation exists in the behaviour of different burrowing macroinvertebrate species, and so the effect of solute transport in and out of the sediments may vary considerably between species (Matisoff & Wang, 1998). The most common mechanism by which they promote sediment-water exchange is, however, thought to be physical: through their pumping movements (digging and irrigation) in burrows the animals increase the contact between interstitial water and the overlying water. Further, benthic macroinvertebrates can alter sediment properties and chemical exchange between sediment and water by their respiration, feeding and defecating activities.

Burrowing has a three-way effect on the cycling of P in sediments: first, it increases the concentration of $O_2$ in the burrows, thereby improving the P-binding capacity of sediment, but it also promotes the transport of pore water P from sediment to water; second, an abundance of macroinvertebrates increases the rate of mineralization (Hansen *et al.*, 1998), or the acceleration of their digestive and excretory processes (Gardner *et al.*, 1981) furthers the dissolution of P; and third, burrowing animals move particulate oxidized compounds down to the reduced zone and reduced compounds up to the oxic zone, thus affecting Fe(III) oxide reduction and re-oxidation in sediments (Canfield *et al.*, 1993).

## 12.5 Early diagenetic cycling and transformations of phosphorus compounds in sediments

### 12.5.1 Settling of phosphorus in sediments

The main transport mechanism of P to sediments is clearly the settling of particulate matter, although influx of dissolved P to sediment may also occur. The surface of the sediments receives a mixture of particulate inorganic and organic compounds containing P. In sediments, the settled particulate inorganic P can be divided into Fe-, Mn-, Al- and Ca-bound P, whereas the particulate organic P consists of living and dead algae, plant debris, zooplankton, bacteria and detritus. Part of the settled particulate P behaves as inert material and is buried in its original form, whereas part of the P (i.e. mobile P) is involved in various physico-chemical and biological reactions before final burial as inert material in sediments. Mobile pools of loosely sorbed P, Fe-bound P and fresh organic P may constitute over 50% of the surface TP but are largely depleted below a depth of a couple of centimeters. The nonmobilized, buried P consists mostly of stable minerals such as apatite and refractory organic P, whereas the Fe-bound P constitutes only a minor proportion of the burial flux of P.

Particulate organic P is considered to be the main compound transporting P to sediments. In marine regions with marked seasonality such as at the northern temperate latitudes, the settling of the spring bloom with its high P content carries a large portion of the organic particulate P to the surface of the sediment. In the Baltic Sea, for example, seasonal short-term changes in the phytoplankton biomass in the water column are due to the rapid sedimentation of phytoplankton (Heiskanen, 1998). Large part of dissolved phosphorus may be stripped from the entire water column by this event. Although organic matter is mineralized during sinking, a substantial portion of the settled particulate organic matter decomposes within the sediments in relatively shallow environments. In estuaries, however, the sedimentation of particulate matter may be accentuated by salt-induced flocculation of colloidal and particulate matter containing P (Edzwald *et al.*, 1974); further, the dissolved P may precipitate on Fe(III) oxides (Gunnars *et al.*, 2002). The precipitation on Fe(III) oxides in water may be a major binding process of P in water column depths, where biological uptake is minor.

Labile organic matter rich in P tends to increase the release of P from sediment to water within a period of days after settling. The settling and subsequent mineralization of labile organic matter does not, however, necessarily lead to the immediate release of P from sediment to water, owing to the sorption capacity of P in sediments. A major portion of the organic P in sedimentation flux can be mineralized in sediments, but the mineralized P is partitioned between the pore water and adsorption sites of the sediment. The proportion of organic P may then decrease but that of Fe(III) oxide-bound P increase in surface sediment. In Århus Bay, a large part of the P precipitated in spring is mineralized at the sediment surface and subsequently retained in the pool of Fe-bound P (Jensen *et al.*, 1995). Efficient release of Fe(III) oxide-bound P has nonetheless been observed later, that is, in August. In the study of Sundby et al. (1992), the settling matter had a much higher proportion of organic P (35% of TP) and a lower proportion of P bound to metal oxides (25% of TP) than was measured on the sediment surface (6% and 50% of TP, respectively).

Therefore, although the settling of particulate organic P is an important transport mechanism of P into sediment, the P is partly bound to inorganic compounds after mineralization in sediments. However, neither fresh organic P nor Fe(III) oxide bound P is efficiently buried, because organic P is mineralized and Fe-bound P is dissolved in the reduction of Fe(III) oxides in sediments (Jensen *et al.*, 1995). In the Gulf of St. Lawrence, for example, approximately half of the sedimentation flux of particulate P is released from sediment back to water (Sundby *et al.*, 1992), whereas in Århus Bay, 65% of the net sedimentation of P is released back to water (Jensen *et al.*, 1995).

**When does the release of P occur?** In eutrophic lakes and marine coastal areas at northern temperate latitudes the increase of P concentration in near-bottom water occurs usually during summer and autumn, when the external P load is low due to the low river discharges. For example, in shallow lakes of Denmark, there is a clear seasonal pattern in the concentrations of P in water column in the eutrophic lakes, whereas no similar pattern is observed in the oligotrophic ones (Figure 12.4). The increase in P concentration can be explained with benthic P efflux. In the coastal Gulf of Finland, Baltic Sea, the P concentration increases in the near-bottom water and the increase can be explained with enhanced benthic P efflux (Figure 12.4).

Several coinciding factors may explain the increase in benthic flux of P in mid-summer and early autumn. The settling of the phytoplankton serves as a fresh energy source for microorganisms, which in turn enhances microbial activity in sediments in summer. Seasonal changes in hydrographic features may also increase the benthic flux during the summer period. In summer, density stratification is strengthened due to the formation of the thermocline. Density stratification prevents the efficient mixing of surface and deep water layers, resulting in a prolonged residence time of the near-bottom water. Owing to this prolonged residence time and the high sediment $O_2$ consumption caused by a high sediment organic matter content, the near-bottom $O_2$ concentration decreases in summer. Although $O_2$ is not depleted from the near-bottom water, the lowered $O_2$ concentration may cause anoxia at the sediment-water interface, thus favouring the release of P. It is also likely that anoxia in sediment in summer permits anaerobic microbial Fe(III) oxide and $SO_4^{2-}$ reduction close to the sediment-water interface, which in turn affects the cycling of Fe, S and P in surface sediments.

### 12.5.2 Biological and nonbiological iron oxide reduction in sediments

Heterotrophic microbial reduction of electron acceptors during mineralization is considered to be a controlling factor in sediment P cycling (Berner, 1974, see Section 11.3). The redox potential in sediment differs drastically from that in the oxic water mass, which affects P equilibrium between the solid and solution phases, i.e. sorption capac-

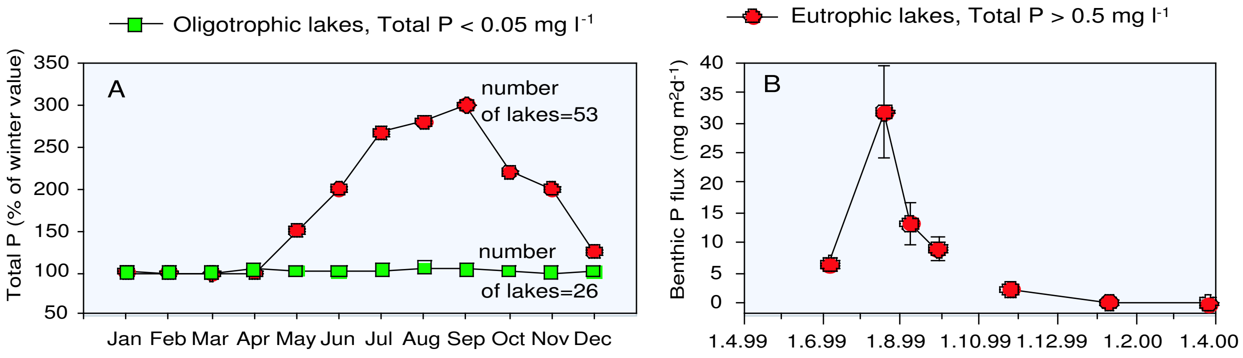

Figure 12.4: (A) Seasonal variation in TP (monthly mean) as percent of winter values (1. Jan. 31. Mar.) in shallow oligotrophic and eutrophic lakes (Søndergaard *et al.*, 1991) and (B) seasonal variation in benthic P efflux at the Gulf of Finland (Lehtoranta 2003).

ity of sediment. Thus, the transformation of previously unavailable forms of P into available ones may necessitate a temporary benthic step.

> In nature, P is predominantly in the oxidation state +V and does not significantly change the valence state in natural biological or nonbiological chemical reactions. Thus, the $PO_4^{3-}$ ion itself does not participate in redox reactions in sediments but redox conditions affect the binding capacity of P in sediments.

Heterotrophic microorganisms that reduce oxidized compounds using organic matter as an energy source are directly or indirectly responsible for most of the redox reactions in sediments (see Section 11.3). Phosphorus dissolved in pore water originates mainly from both Fe(III) oxides and organic matter, which constitute the main mobile P-binding pools in sediments. The bulk of the P, however, is thought to be released in sediment from Fe(III) oxides undergoing reduction. There are two main processes that can reduce Fe(III) oxides in sediments: first, enzymatic microbial dissimilatory reduction and, second, nonenzymatic reduction by the sulphide formed in microbial dissimilatory $SO_4^{2-}$ reduction (Lovley, 1991).

Microorganisms are important in the reduction of Fe(III) oxides, because the storage under anaerobic conditions of readily reducible, synthetic, poorly crystalline Fe(III) oxides or sterilized sediment containing Fe(III) oxides does not result in detectable Fe(III) reduction, even after long periods. As well as anaerobic conditions, the Fe(III) oxide-reducing bacteria need direct contact with particles to reduce Fe(III). When direct contact is prevented, Fe(III) oxides are not reduced (Lovley, 1991). In microbial dissimilatory Fe(III) oxide reduction, Fe(III) is used as an external electron acceptor and Fe(III) is reduced to soluble Fe(II), organic C being the electron donor. Dissimilatory microbial Fe(III) reduction leads to the simultaneous accumulation of Fe(II) and P in anoxic pore water.

Although the concentration of $O_2$ in near-bottom water is high, the anoxic zone develops within a few millimetres beneath the sediment-water interface in organic-rich, fine-grained marine sediments. $O_2$ may be depleted, but the nitrate ($NO_3^-$) present can still inhibit Fe(III) reduction in sediments and so prevent the release of P from Fe(III) oxides to anoxic water (Andersen, 1982). Extensive release of P may occur after depletion of $O_2$ due to the fact that nitrification is inhibited after the exhaustion of $O_2$, leading rapidly to depletion of nitrate.

In marine systems, Fe(III) oxides are probably reduced mostly by $H_2S$, because $SO_4^{2-}$ reduction is the dominant anaerobic respiration process (see Section 11.3). In Århus Bay, for example, partial oxidation of $H_2S$ accounts for 63% of the estimated Fe(III) reduction, whereas the contributions of microbial Fe reduction to carbon mineralization are considered to be small (Thamdrup *et al.*, 1994). The rate and extent of microbial Fe(III) oxide reduction is controlled by the surface area and site concentration of the solid phase. Microbial reduction of poorly crystalline Fe(III) oxide is about 20 times that of goethite, which is about 50 times that of hematite (Roden & Edmonds, 1997). This result is consistent with the decrease in particle size and increase in surface area and crystallinity of these oxides. In accordance with microbial Fe(III) oxide reduction, poorly crystalline Fe(III) oxide minerals are more reactive towards sulphide than are crystalline goethite and hematite. Thus, Fe(III) oxides that effectively adsorb P are the same forms as those that are effectively reduced by Fe(III) oxide reducing microorganisms and by $H_2S$ formed in microbial $SO_4{}^{2-}$ reduction in sediments.

### 12.5.3 Cycling of iron bound phosphorus in sediments

A classic P cycling model is based on the Fe cycle in sediment: insoluble Fe(III) oxides are reduced to soluble Fe(II) ions, after which the P bound to Fe(III) oxides is released into pore water. When reduced soluble Fe(II) is diffused to an oxic environment (sediment surface or near-bottom water) it is oxidized to Fe(III) oxides having a high capacity to sorb P. Hence, sediments overlain by aerobic waters often have an Fe(III) oxide-rich surface layer. The precipitated Fe(III) oxides present in the surface layer are considered to effectively prevent P from entering the euphotic surface of water. Adsorption of P onto Fe(III) oxides may occur rapidly, because Fe(II) is oxidized within minutes or hours in the presence of $O_2$. As well as chemically, Fe(II) is oxidized by lithotrophic Fe(II) oxidizing bacteria in surficial sediments (Sobolev & Roden, 2001). Due to the cycling of Fe in sediments, P can be desorbed and adsorbed several times before its permanent burial or release to water. The P-rich surface layer is in a dynamic state and over time moves upwards as new sediment accumulate.

However, back in 1948, Hasler and Einsele suggested that $SO_4{}^{2-}$ increases the availability of P, a hypothesis that was later substantiated by Sugawara et al. (1957). Recent studies have also revealed the tight coupling between Fe, S and P in marine sediments (Roden & Edmonds, 1997; Rozan *et al.*, 2002). The coupling of Fe with S leads to differences in P cycling between $SO_4{}^{2-}$-poor and $SO_4{}^{2-}$-rich systems (Figure 12.5). As pointed out earlier, $SO_4{}^{2-}$ reduction does not itself release P, but it indirectly promotes P mobilization and reduces the P retention capacity. $SO_4{}^{2-}$ has a double effect on the P cycle via reactions with Fe: first, Fe(III) oxides are effectively reduced by sulphide formed in microbial $SO_4{}^{2-}$ reduction and, ultimately, even very stable crystalline Fe(III) oxides are converted to $FeS_2$ in sulphidic sediments (Canfield *et al.*, 1993); second, dissolved Fe(II) is quickly and effectively removed from pore waters by the precipitation of solid FeS, and the formation of $FeS_2$ in the presence of $H_2S$ formed in $SO_4{}^{2-}$ reduction. Co-precipitation of Fe and S leads to permanent burial of FeS minerals (Canfield *et al.*, 1993). The FeS minerals formed adsorb P poorly at neutral pH. As a consequence, the upward flux of dissolved Fe(II) is decreased, thereby reducing or preventing the reformation of an Fe(III) oxide-rich surface layer able to adsorb P efficiently. However, the P solubilized from Fe(III) oxides is maintained in pore water.

Due to FeS formation, the dissolved Fe:P ratio is higher in freshwater than in brackish-marine systems under anoxic conditions (Gunnars and Blomqvist 1997). When conditions turn oxic, the newly formed colloidal Fe(III) oxides scavenge P ions in lake-water sediment. For example, in Finland several hundreds of small lakes suffered from oxygen deficiency during winter 2002/2003. In these lakes both Fe and P concentrations increased in the whole water column, but after the ice melt and the increase of oxygen concentration in water both Fe and P concentrations went down. In marine sediments, though, P is less efficiently scavenged, and significant amounts remain dissolved in the overlying water (Gunnars and Blomqvist 1997). It has been suggested that the molar ratio of Fe:P dissolved in pore water governs the fate of

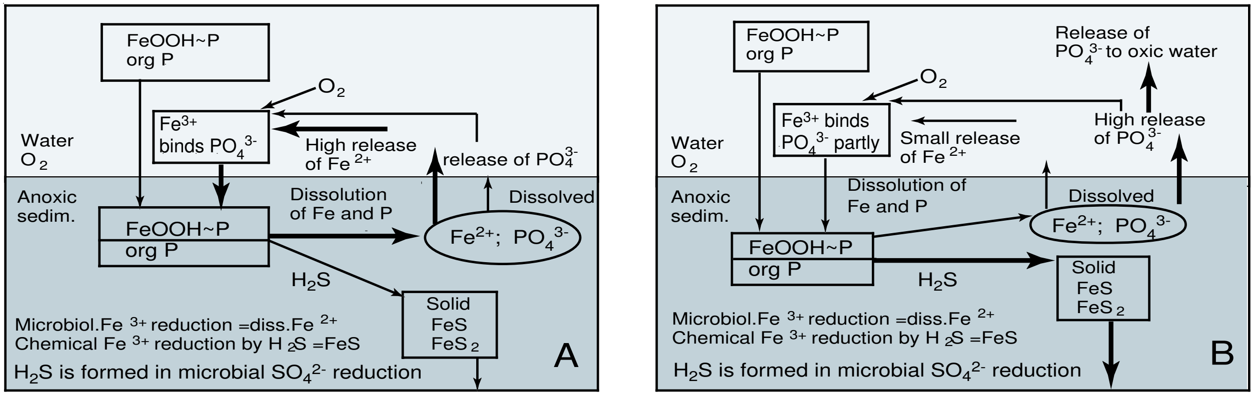

Figure 12.5: Cycling of iron (Fe), sulphur (S) and phosphorus (P) in a (A) $SO_4^{2-}$ -poor and (B) $SO_4^{2-}$ -rich aquatic environment

P when these elements are transported to the oxic zone in sediment. The predominant Fe:P surface complexation ratio of Fe(III) oxide is suggested to be 2 (Gunnars *et al.*, 2002; Gunnars & Blomqvist, 1997). When the dissolved Fe:P molar ratio is under 2, the available Fe is in too short supply to bind all the dissolved P. In marine systems, the Fe:P ratio is under 2 and in lake-water systems (calcareous lakes not included) almost invariably above 2 under anoxic conditions. (review by Gunnars & Blomqvist, 1997).

The benthic flux of P increases when conditions turn from oxic to anoxic in lake (e.g. Einsele & Vetter, 1938; Mortimer, 1941, 1942), brackish-marine (Gunnars and Blomqvist 1997) and marine systems (e.g. Andersen, 1982; Balzer *et al.*, 1983). Several studies have, however, confirmed the occurrence of significant aerobic P release in both lake and marine systems (e.g. Bates & Neafus, 1980; Boers, 1986; Sinke & Cappenberg, 1988; Conley *et al.*, 1997). In $SO_4^{2-}$ rich systems, a low concentration of dissolved Fe(II) may lead to insufficient Fe(III) oxide formation. The Fe(III) oxides formed can then only partially retain the flux of P, and the benthic efflux of P may occur even though the overlying water is oxic. In $SO_4^{2-}$ poor lakes, however, a portion of the P released to oxic water may originate from P bound to organic matter in sediments.

Owing to the low reserves relative to the requirements of algae in most lakes, P is a key factor in lake-water eutrophication (Vollenweider, 1968). In marine and brackish systems, including the Gulf of Finland, however, primary production in the photic zone tends to be N limited (Hecky & Kilham, 1988). The difference in nutrient limitation can be partly attributed to the lower sediment P-binding ability due to the higher $SO_4^{2-}$ concentrations in brackish and marine sediments than in lake waters (Roden & Edmonds, 1997).

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## Chapter 13

# Benthic-pelagic coupling and eutrophication: the case of the silicate pump

Olivier Ragueneau, Laurent Chauvaud, Jacques Grall
UMR CNRS 6539
Institut Universitaire Européen de la Mer
Place Copernic
Technopôle Brest-Iroise
29280 Plouzané, France
Olivier.Ragueneau@univ-brest.fr

## 13.1 Abstract

The present chapter is devoted to the role played by benthic suspension feeders in ecosystem functioning, through their importance in a coastal silicate pump. Following a brief review of pelagic-benthic coupling and eutrophication (Section 13.2, based on the recent review of Grall and Chauvaud 2002), the focus is placed on the Bay of Brest, an eutrophic macrotidal ecosystem of Western Europe subject to both excessive N inputs from the watersheds and the proliferation of an invasive suspension feeder. N river inputs have led to reccurent limitation of diatoms by silicic acid availability. At the same time, *Crepidula fornicata* has been proliferating, constituting today the main benthic suspension feeder in the Bay. There exist in the literature only few examples of a direct interaction between suspension feeders and the Si cycle. Such an interaction is described in Section 13.3 of this chapter, based on a working hypothesis described by Chauvaud *et al.* (2000) and tested by Ragueneau *et al.* (2002a). Suspension feeder activity, stimulated by the proliferation of the invasive species *C. fornicata*, would be the driving force of a biologically active silicate pump which would

1. retain Si within the bay during spring and
2. provide the Si necessary for diatoms during summer

During the year 2000, this hypothesis was successfully tested. Direct evidence of DSi limitation has been provided, and during summer, benthic fluxes measured at a site with high density of *C. fornicata* are one order of magnitude higher than those measured at the site with no *C. for-*

*nicata*. Seasonal budgets of Si inputs and diatom demand demonstrated that diatom production during summer depends strongly upon Si recycling at the sediment-water interface. In the last section of this chapter, the short-term (seasonal) consequences are explored from an ecological viewpoint, with a major emphasis on the role played by invasive species. The long-term (interannual) consequences are also explored but from a more biogeochemical viewpoint, based on Ragueneau *et al.* (2003). It is suggested that enhanced biodeposition, through the proliferation of invasive species (both accidental or for aquaculture purposes), could constitute a third means (beyond eutrophication and river manipulation) by which the Si cycle may be perturbated along the land-ocean continuum.

## 13.2 Benthic-pelagic coupling and eutrophication

### 13.2.1 Pelagic production as food for benthic fauna

Oxygen deficiency in temperate coastal waters has led to an increased awareness of vertical particle flux to bottom waters (see Chapter 9). In recent years, particular attention has been paid to coupling and energy transfer between the benthos and plankton. It has been postulated that suspension-feeding communities can self-organize to enhance the efficiency of food capture and thus establish boundary systems capable of successfully exploiting the less structured planktonic system (Gili & Coma, 1998). Others studies demonstrated that in temperate coastal waters the most prominent event in the annual flux of organic material to the benthos is usually the spring diatom bloom (Smetacek, 1985; Harding *et al.*, 1987; Wassmann, 1991; Olesen & Lundsgaard, 1995).

In coastal (and also temperate and polar) seas this rapidly sinking phytoplankton is often dominated by diatoms that reach the sea floor relatively intact without being ingested by zooplankton (see Smetacek, 1985 for a review; Alldredge & Gotschalk, 1989). Seasonally sedimented phytoplankton blooms are a major source of nutrients that are processed rapidly through the benthic system in open coastal areas (Gili & Coma, 1998; Graf *et al.*, 1982). Information from field studies supports the hypothesis that suspension feeders ingest a wide spectrum of particle sizes (Ribes *et al.*, 1989; Coma *et al.*, 1995; Pile *et al.*, 1996). Many suspension feeders are capable of utilizing any type of food, and are limited only by morphological constraints (Riisgard & Manriquez, 1997).

For the case of suspension-feeding bivalves, food quality and quantity have been shown by Willdish and Kristmanson (1997) and Rosenberg and Loo (1988) to be a limiting factor. For example, infaunal bivalve growth was shown to be positively correlated with both the chlorophyll input to the sediment and the diatom availability in the near-bottom waters (Thompson & Nichols, 1988; MacDonald & Thompson, 1985; Wildish & Kristmanson, 1997). It has been widely recognized that benthic suspension feeders, which are among the main contributors to the biomass of benthic communities of coastal and estuarine ecosystems world-wide, benefit directly from pelagic primary production in the overlying water column (Graf *et al.*, 1982; Christensen & Kanneworff, 1986). Thus, suspension feeders are responsible for a considerable share of the energy flow from the pelagic to the benthic system, in addition to secondary production in benthic environments (Petersen & Black, 1987; Gili & Coma, 1998).

### 13.2.2 Regulation of benthic production by the benthic fauna

**Direct control of phytoplankton biomass.** There are strong indications that phytoplankton biomass may be severely reduced or regulated by active suspension feeders in shallow ecosystems (Cloern, 1982; Smaal *et al.*, 1986; Hily, 1991; Chauvaud *et al.*, 2000). From these studies, it can be concluded that the secondary trophic level is dominated by the benthic ecosystem where active suspension feeders can even regulate pelagic pri-

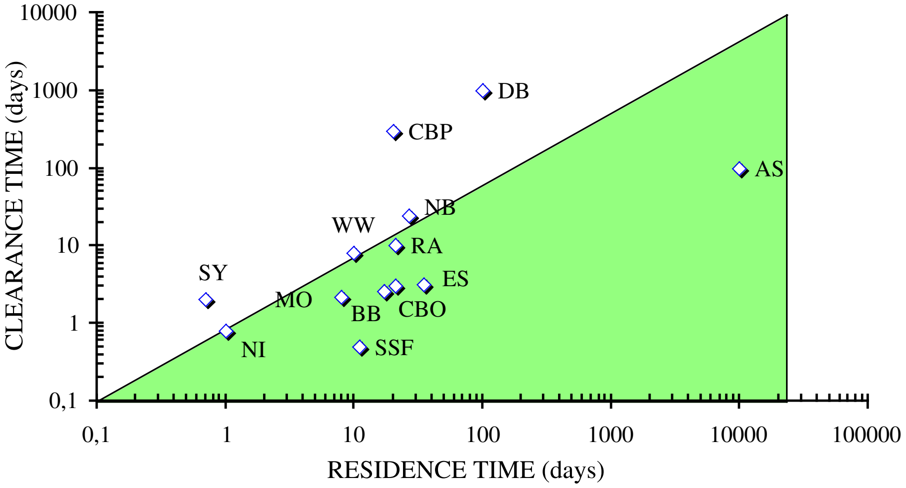

Figure 13.1: Graphical comparison of water mass residence time and clearance time in suspension feeder-dominated ecosystems. Ecosystems situated in the shaded area are potentially regulated by suspension feeders where clearance time is shorter than clearance time. AS: Ask Bay. SSF: South San Francisco Bay. OS: Oosterschelde. CBO: Chesapeake Bay, past. BB: Bay of Brest. MO: Marennes-Olron Bay. RA: Ria de Arosa. WW: Western Wadden Zee. NI: North Inlet. NB: Naragansett Bay. SY: Sylt, Eastern Wadden Zee. DB: Delaware Bay. CBP: Chesapeake Bay, Present. In Dame (1996). From Grall and Chauvaud (2002).

mary production when the water body is shallow, the residence time is long, and the suspension-feeding biomass is high (Cloern, 1996). Figure 13.1 illustrates the fact that suspension feeders are able to consume potentially high amounts of suspended food where the clearance time is shorter than the residence time of the water in the bay. Rates of suspension-feeding are a function of food supply for a variety of taxa, but since the process of filter-feeding uses a variety of different particle-trapping mechanisms and ranges from passive to active filter feeding, the relation between suspension feeders abundance and distribution is highly complex. Hydrodynamic factors may be critical in determining the food supply. The availability of food depends on the three-dimensional nature of the fluid and particulate fluxes to the benthic ecosystem (Fréchette *et al.*, 1989). Herman and Scholten (1990) proposed three reasons why benthic suspension feeders may have a stabilising influence in benthic ecosystems. First, benthic suspension feeders are a stable component of the ecosystem. Secondly, the filtration rate of suspension feeders does not stabilise as food availability increases. Finally, the biomass of suspension feeders has a slow turnover rate. Together these three observations suggest that suspension feeders may limit the intensity and duration of phytoplankton blooms. In contrast, the zooplankton biomass increases in response to phytoplankton blooms and thus do not reach such an effective filtration level during the bloom period.

**Suspension feeders and nutrient cycling.** Mussel or clam beds and oyster reefs may also supply nutrients in high amounts to the overlying water column and promote phytoplankton production. Thus suspension feeders are not only important in terms of direct control, but also affect nutrient recycling and sedimentation or resuspension of organic particulate matter (Figure 13.2). When the amount of food filtered by bivalves exceeds the needs of the individual, pseudofaeces are produced that incorporate the excess particulate organic matter. The formation of these pseudofaeces facilitates the sedimentation of POM and thus increases the overall sedimentation rate. Biodeposits are also a source of food for benthic or-

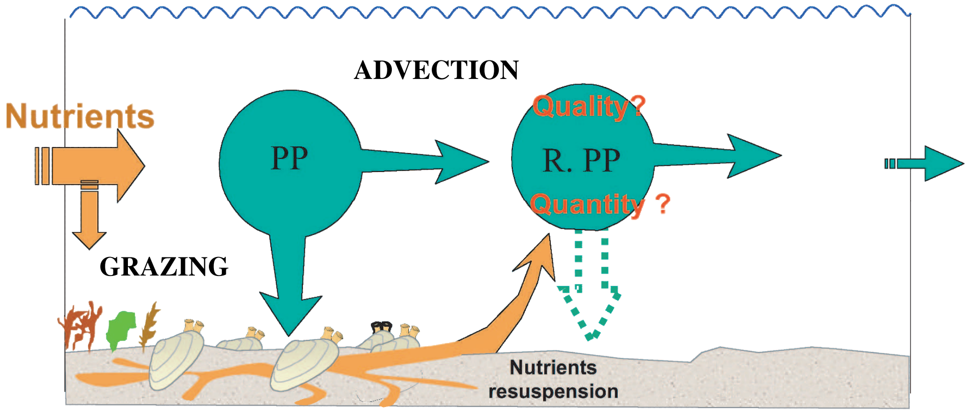

Figure 13.2: Schematic representation of the nutrient fluxes and pelagic primary production dynamics in a suspension feeder-dominated ecosystem. PP = Primary Production. RPP = Regenerated Primary production. From Grall and Chauvaud (2002).

ganisms such as bacteria, meiofauna and macrofauna (Graf, 1992). Faeces and pseudofaeces contribute to enhance bacterial activity on a day scale basis, while meiofauna and macrofauna populations rather respond on a week and month scale basis respectively (Grenz *et al.*, 1990; Smaal & Prinz, 1993). Fauna may either feed directly on the organic matter of the biodeposits or on bacteria, which contributes to secondary production in the benthos but also to increase the turnover of nutrients (Graf, 1992; see below). Kautsky and Evans (1987) argued that the role of suspension feeders in energy transfer may be minimal compared with the role they have in carbon and nutrient cycling in coastal ecosystems. In areas controlled and stabilized by suspension feeders and subject to increasing nutrient loads, the ecosystem is then highly vulnerable to changes in the suspension feeder community (see also Chauvaud *et al.* 2000).

**Nutrient absorption/regeneration and zoobenthic communities.** Several studies have shown experimentally that degradation of organic matter was faster and more efficient in sediments with macrofauna populations. It has been suggested by various authors that the proportion of nutrient export from the benthic ecosystem to the water column due to macrofaunal activity supplies a significant proportion of the phytoplankton requirements (Asmus, 1986; Smaal & Prinz, 1993). However, there is no clear agreement on the amount. Published estimates range from 0 to 100%, with a mean of 28 – 30% (Doering, 1989). A recent study by Grenz *et al.* (2000) showed that during a phytoplankton bloom, nutrient fluxes from the sediment represented 20% (Si), 16%, (P) and 9% (N) of the primary production demand. Experimental studies in mesocosms with an intact benthos have showed that measured annual apparent primary production increased by 23% relative to mesocosms lacking benthos. Furthermore, in another experimental study, Christensen *et al.* (2000) showed that nutrient release to the water column depends on the species function (both behavior and biology) in the system; $NH_4$ and $NO_3$ release were 3 times higher in sediments which had the polychaete *Nereis diversicolor* as suspension feeder, and were just 1.5 times higher in sediments which included *N. virens* as a deposit feeder. The presence of *Nereis* in the sediment increased both $NO_2$ and silicate fluxes by two orders of magnitude. Magni *et al.* (2000) showed that macrofauna rapidly and efficiently recycle the inorganic forms of nitrogen and phosphorus, thus playing a role in the process of nutrient regeneration. Using an open flow-through system, Asmus and Asmus (1991) have shown that the potential for primary production induced by the nutrient release of an intertidal mussel bed was higher than the uptake of phytoplankton by the mussel bed itself. Thus, if benthic communities are able to reduce significantly the phytoplankton biomass, then they also have the potential to maintain eutrophication (De Casabianca *et al.*, 1997).

Oviatt *et al.* (1986) note that as primary production increases, respiration and thus recycling of nutrients in the water column also increases. The pelagic production fuelled by nutrients derived from the benthos could then result in higher pelagic recycling rates. De Casabianca *et al.* (1997) argued that the concentration of dissolved inorganic nitrogen did not vary much as a function of the presence or absence of a benthos, but rather in recycling of nutrients either in bottom sediments or in the water column. Thus, the effects of the benthos on pelagic production are two fold: supplying nutrients directly, and indirectly increasing regeneration rates in the overlying water column.

In the following section, we will explore the influence of benthic suspension-feeders on phytoplankton dynamics, in an ecosystem (the Bay of Brest, France) experiencing both excessive N inputs from the watersheds (leading to silicic acid limitation) and the proliferation of an invasive suspension-feeder, *Crepidula fornicata* (leading to enhanced biodeposition). Short-term ecological and long-term biogeochemical consequences of such an interaction will be explored in Section 13.4 of this chapter.

## 13.3 The case of the silicate pump in the Bay of Brest

### 13.3.1 Si and coastal food webs

Evidence is growing that the nutrient silicic acid (DSi) is playing a major role in the functioning of coastal ecosystems in many regions of the world (Conley *et al.*, 1993). The reason is linked to the importance of diatoms in marine food webs (Cushing, 1989), and to anthropogenic influences on watersheds and rivers. When DSi is missing, diatoms become replaced by other phytoplankton groups that do not have any requirement for this nutrient, such as dinoflagellates (Officer & Ryther, 1980). A wide variety of coastal ecosystems has been documented, where increasing frequency and magnitude of harmful algal blooms have been associated to decreasing Si:N and Si:P ratios, with important consequences for pelagic and benthic food webs (Smayda, 1990). Decreasing Si:P and Si:N ratios first find their origin in eutrophication. Urbanization, agricultural and industrial activities have led to large increases in the delivery of N and P along the land-ocean continuum. On a global basis, the fluxes of these elements to the oceans have increased by a factor two; at the same time, in rivers unaffected by human activities, DSi fluxes have remained constant, as the major source of DSi to rivers comes from natural silicate rock weathering (Maybeck, 1989). The second source of decreasing Si:N and Si:P ratios is river manipulation, especially the build up of dams (Humborg *et al.*, 2000). In the reservoirs behind the dams, growth and sedimentation of diatoms remove biogenic silica ($BSiO_2$) from the water column, leading to decreased DSi concentrations (Conley *et al.*, 1993). Whatever the type of perturbation, decreasing Si:N and Si:P ratios in rivers imply potential DSi limitation for diatoms (Dortch & Whitledge, 1992), which becomes true limitation when DSi concentrations decrease below the half saturation constants in the receiving coastal water bodies (e.g. Nelson & Dortch, 1996).

### 13.3.2 The Bay of Brest example

The Bay of Brest is an ecosystem where Si:N ratios in riverine inputs have decreased by a factor of 3 in the past 30 years, mostly due to excessive N inputs from agricultural practices (Le Pape *et al.*, 1996). Indirect evidence of DSi limitation has been provided, on the basis of declines in diatom populations coinciding with DSi concentrations becoming lower than 1 µM by early spring (Ragueneau *et al.*, 1994). DSi limitation has then been directly demonstrated from kinetic uptake experiments using the $^{32}$Si radioactive isotope Del Amo, 1996; see also Figure 13.2). Despite DSi limitation during spring, diatoms typically continue to dominate the phytoplankton during the entire productive period (Del Amo *et al.*, 1997). Several factors have been hypothesized to account for this (apparent lack of) response of the Bay to excessive N inputs. They include the export out of the bay of most of this N during winter (Le Pape *et al.*, 1996), the well-mixed nature of the water column which does not favor the development of flagellates (Ragueneau *et al.*, 1996), and the intensity of Si recycling both in the water column and at the sediment-water interface (Ragueneau *et al.*, 1994; Del Amo *et al.*, 1997).

Although Si recycling has recently been shown to be accelerated under high bacterial activity (Bidle & Azam, 1999), it remains slower than the recycling of N and P, which are biologically mediated (Officer & Ryther, 1980). In the open ocean, this differential recycling rate is at the basis of the so-called silicate pump (Dugdale *et al.*, 1995), which removes DSi from surface waters for a long time period. In coastal waters, especially in the semi-enclosed Bay of Brest, the effects of the silicate pump may well be reversed, because of the tight temporal and spatial coupling between sediment and surface waters: following the first diatom blooms and the sedimentation of diatom cells, Si can be retained within the Bay, at the sediment-water interface, instead of being exported to the adjacent coastal ocean; it then becomes directly available for regenerated diatom production, because of the shallow depths of the well-mixed waters (Del Amo *et al.*, 1997).

### 13.3.3 The working hypothesis

Synthesizing 20 years of studies of the Bay of Brest ecosystem, both from a pelagic and benthic point of view, Chauvaud *et al.* (2000) suggested that the functioning of this coastal silicate pump is under the control of benthic suspension-feeders. Suspension feeders dominate the benthic megafauna in the Bay of Brest (Thouzeau *et al.*, 2000). Introduced in 1950, the gastropod *Crepidula fornicata* is now the main benthic suspension feeder in the Bay (Chauvaud, 1998). Chauvaud *et al.* (2000) have suggested that increased suspension-feeding activity during early spring (filtration and subsequent production of enormous quantities of biodeposits) could lead to an increase in the temporary retention of $BSiO_2$ in the sediments of the bay, thereby limiting the export of Si out of the bay. Subsequent $BSiO_2$ dissolution during late spring and summer, enhanced by increasing temperature and bacterial activity, would provide the necessary DSi required by diatoms to maintain their dominance throughout the productive period. It is essential to note that the enormous amount of biodeposits produced by *C. fornicata* has no equivalent in the ecosystem.

### 13.3.4 Testing the working hypothesis

During the year 2000, the hypothesis of a 'biologically active silicate pump' was tested. Figure 13.3 shows the physical, chemical and biomass parameters recorded weekly at the monitoring SOMLIT station located near the bay entrance. These parameters characterize the productive season which begins in late March in the bay with the increase in chlorophyll a corresponding to the decrease in nutrient concentrations. A succession of phytoplankton blooms occurred throughout the spring and summer. By late July, DSi and DIP start to accumulate again in the water column, followed by DIN two months later, when the productive period ends.

**Direct evidence of DSi limitation in the Bay of Brest.** Direct evidence of DSi limitation during spring has been obtained through two kinetic experiments performed when the diatoms *Rhizosolenia* sp. and *Chaetoceros* sp. where dominating the phytoplankton population (Figure 13.4). Having similar $K_m$ values close to 1.3 µM, these diatoms were both limited to only 20% of their maximal uptake velocity by late spring/early summer. Note that *Chaetoceros* sp. exhibited a $V_{max}/K_m$

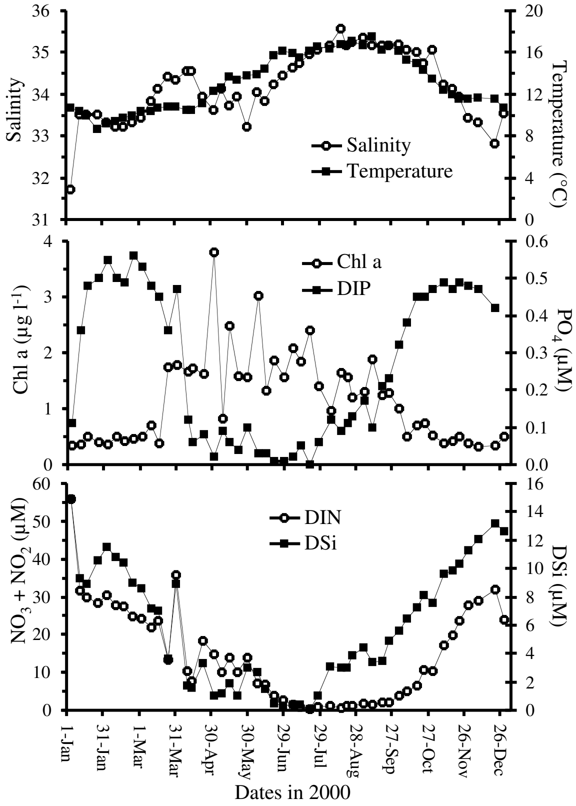

Figure 13.3: Physical, chemical and biological parameters measured at the SOMLIT site in the Bay of Brest during the year 2000. (a) temperature and salinity. (b) phosphate and chlorophyll a. (c) silicic acid and nitrate. From Ragueneau *et al.* (2002a).

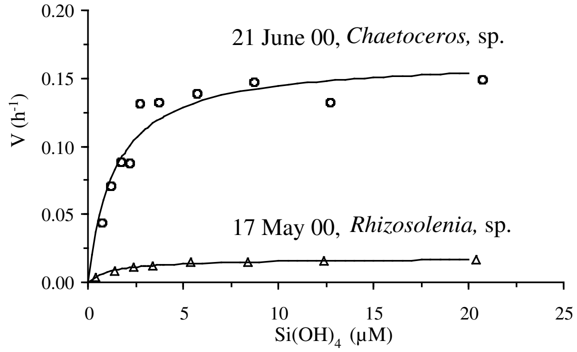

Figure 13.4: Two kinetic experiments performed on 17 May 2000 when the diatom *Rhizosolenia* was dominating and on 21 June 2000 when the diatom *Chaetoceros* was dominating. Experiments have been performed using the $^{32}$Si radioactive isotope (Tréguer *et al.*, 1991). A 3L water sample has been distributed into eight 250 ml polycarbonate incubation bottles. These bottles have been enriched with silicic acid up to 20 µM, spiked with $^{32}$Si and incubated for 24 hours at light saturation. Following liquid scintillation counting (Laynaert *et al.*, 1996), the specific uptake rate (V) is plotted against the Si(OH)$_4$ concentration of the flasks at the beginning of the incubation. These Michaelis-Menten type of curves have been fitted using the non-linear regression method of Wilkinson (1961), allowing the determination of the maximal uptake velocity (V$_{\mathrm{max}}$) and the half saturation constant (K$_{\mathrm{m}}$). From Ragueneau *et al.* (2002a).

ratio ten times higher than that of *Rhizosolenia* sp., suggesting a higher affinity and thus, a higher ability to take up DSi at low concentrations. Thus, diatoms were clearly limited by ambient DSi concentrations and were dependent upon Si recycling during early summer. By late summer, DSi was accumulating again in the water column, suggesting that DSi inputs exceeded the diatom demand by that time.

**Direct effect of *C. fornicata* on DSi benthic fluxes.** To study the possible effects of benthic suspension feeders on DSi recycling at the sediment-water interface, benthic fluxes were measured seasonally at two contrasting sites, displaying respectively low (ca. 30 ind. m$^{-2}$) and high (ca. 1700 ind. m$^{-2}$) concentrations of *C. fornicata*. Sediment cores were retrieved manually at 20 m depth using scuba diving; 3 replicates were taken at each site. Following a time zero sampling at sea, cores were then rapidly (within 1 – 2 hours) incubated in the laboratory at the temperature of the bay waters (from 8°C during winter to 16°C during summer; Figure 13.3). The DSi concentration in the water overlying the sediment was monitored every hour during the first 6 hours, and then two to three times between 20 and 24 hours following the core collection. Homogenisation of the overlying water was ensured by pumping water, using a peristaltic pump, 2 – 3 cm above the sediment water interface and redistributing it near the water surface. The flow rate was adjusted so that one water volume was renewed every hour. The slopes of the DSi increase measured in the cores during their incubation show a 20-fold difference, during late summer, depending on whether *C. fornicata* was abundant or rare (Figure 13.5). The corresponding DSi fluxes are typical of those encountered in coastal environments (Friedrich *et al.*, 2002; Yamada & D'Elia, 1984, and references therein). Mean values at these two contrasting sites were measured every two months, throughout the productive period (Figure 13.6). Two important observations can be made. First, whatever the season considered, fluxes are always higher at the site with *C. fornicata* compared to the site where *C. fornicata* is absent. Being only of a factor of two by late spring, the difference between the fluxes measured at the two sites becomes more than one order of magnitude by midsummer and fall. Secondly, maximum DSi fluxes were measured in late spring at the site without *C. fornicata* and in late summer at the site with *C. fornicata*. Thus, both the amplitude of the DSi benthic flux in the presence of *C. fornicata* and the delay in the timing of the maximum of these fluxes provide strong evidence that the $BSiO_2$ produced during spring is indeed being retained by the activity of the suspension feeders and then gradually released to the overlying waters, following dissolution. Owing to the well-mixed nature of the water column in this macrotidal ecosystem, DSi is then immediately available for diatoms production (Ragueneau *et al.*, 1996).

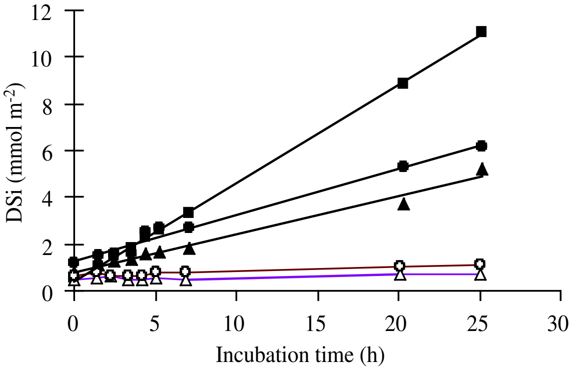

Figure 13.5: Sediment core incubation experiments conducted during late summer in the Bay of Brest. Sediment cores were collected at Rozegat using diving, at two sites located within 300 m but exhibiting contrasted densities of the suspension feeder *Crepidula fornicata*. Filled symbols: site Rozegat with high densities (1243 ind. m$^{-2}$) of *C. fornicata*, (Thouzeau *et al.*, 2000). Open symbols: site Rozegat without any *C. fornicata*. Note the factor of 20 between the mean flux measured at the site with *C. fornicata* (triplicates, mean: 6.3 mmol Si m$^{-2}$ d$^{-1}$) and the mean flux measured at the site without *C. fornicata* (duplicates, mean: 0.3 mmol Si m$^{-2}$ d$^{-1}$). From Ragueneau *et al.* (2002a).

**Validation at the bay scale.** Before budgeting Si fluxes within the bay of Brest ecosystem, a simple, albeit important, calculation provides strong support that the working hypothesis has significance at the scale of the whole system. $11 \times 10^3$ t of dry organic matter are produced by suspension feeders (Chauvaud *et al.*, 2000). By analogy with zooplankton fecal pellets in surface waters (Tande & Slagstad, 1985), we can make the hypothesis that these biodeposits are enriched in biogenic silica because Si is not retained by these organisms for their metabolism. Typically, in the open ocean, the Si:C ratio increases by a factor of ca. 5 between food and feces, between production and export in surface waters, or between the deposition at the sediment-water interface and the accumulation below the bioturbated layer (Ragueneau *et al.*, 2002b). Using this factor and a typical Si:C ratio of 0.04 – 0.09 for the bay phytoplankton (Ragueneau *et al.*, 1994; Del Amo, 1996) yields a Si:C ratio in the biodeposits close to 0.2 – 0.5. Thus, the biodeposits can lead to the temporary

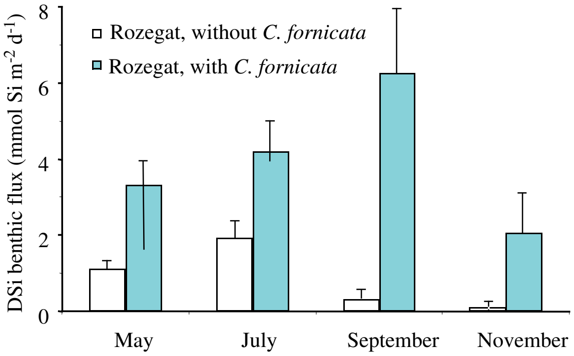

Figure 13.6: Synthesis of DSi benthic fluxes measured at the two contrasting sites during the productive period in the Bay of Brest. Black bars: site Rozegat with *C. fornicata*; white bars: site Rozegat without *C. fornicata*. These fluxes represent the mean values of the fluxes measured in triplicates (see Figure 13.3). From Ragueneau *et al.* (2002a).

deposition of 167 – 417 × $10^6$ mol Si. Distributed spatially over the 180 $km^2$ of the Bay and temporally over the whole year, this leads to a potential DSi benthic flux of 2 – 6 mmol Si $m^{-2}$ $d^{-1}$. Interestingly enough, this range is of the same magnitude as the fluxes measured using core incubations (Figure 13.6).

**Preliminary budgets.** Having provided direct evidence for (i) DSi limitation and (ii) a direct influence of suspension feeders on $BSiO_2$ retention and DSi availability, one needs to compare the magnitude of the DSi benthic fluxes with both river inputs and the diatom demand (silica production). Nutrient river inputs were measured on a weekly basis in the Aulne and the Elorn rivers, which bring most of the freshwater to the Bay of Brest, by members of the ECOFLUX network (Prohel *et al.*, 2001). For comparison purposes, benthic DSi fluxes have been extrapolated to the whole bay (180 $km^2$) by applying the fluxes measured at the site with *C. fornicata* to the area of the bay covered by *C. fornicata* (90 $km^2$) and the fluxes measured at the site without *C. fornicata* to the area still unaffected (90 $km^2$). Reasonable estimates of integrated silica production can be obtained on the basis of primary production measurements and the use of appropriate Si:C ratios (Pile *et al.*, 1996). Under nutrient replete conditions, diatoms grow with a Si:C ratio close to 0.13 (Brzezinski, 1985). In the Bay of Brest, this ratio is typically twice as low, due to the coupled influence of DSi limitation and the presence of non-siliceous algae (Ragueneau *et al.*, 1994; Del Amo *et al.*, 1997). A ratio of 0.06 has therefore been chosen as a reasonable mean of converting C primary production into a BSi production that can then be compared to river and benthic fluxes (Figure 13.7).

Four budgets were made for the productive season (Figure 13.7), neglecting DSi inputs from the adjacent ocean, as they represent less than 5% of the diatom demand during the productive period (Ragueneau *et al.*, 1994). These budgets clearly demonstrate the importance of suspension-feeder activity on the Si cycle allowing for DSi to be available for diatom production during late spring and summer. By early spring, river Si inputs can sustain nearly 100% of the diatom demand; diatoms do not depend upon recycling at the sediment-water interface, especially if we add the winter stock of DSi that can account for one third of the initial diatom demand (Ragueneau *et al.*, 1994). By late spring, river inputs have decreased by a factor of three and can sustain only 30% of the diatom demand. The rest must be met by recycling at the sediment-water interface. By mid-summer, river inputs are even smaller and DSi benthic fluxes alone can sustain diatom demand. Because recycling also occurs in the water column, DSi is probably available in excess and starts to accumulate in the water column (Figure 13.3). Note that in September, DSi inputs exceed the diatom demand by about 140×$10^4$ mol Si $d^{-1}$(Figure 13.7). The Bay volume is close to 2×$10^9$ $m^3$ on average, which means that DSi should accumulate at a rate of roughly 0.07 µmol $L^{-1}$ $d^{-1}$. From late July onwards, DSi increases linearly from 0 to 12 µM in 5 months (Figure 13.3). This corresponds to a rate of 0.08 µmol $L^{-1}$ $d^{-1}$, which is very consistent with the above budget calculation. During fall, diatom demand decreases sharply whereas benthic fluxes are still high and river inputs have increased again due to rainfall. DSi continues to accumulate in the water column at the mean rate calculated above and will soon reach its winter maximum concentrations. The budgets presented demonstrate unambiguously the importance of recycling at the sediment-water interface in sustaining diatom demand throughout the productive period.

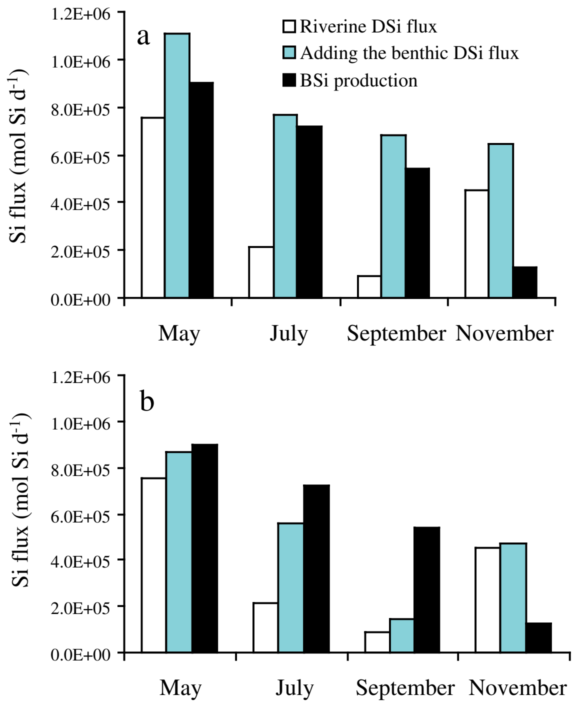

Figure 13.7: Seasonal budgets of DSi fluxes in the Bay of Brest. All data in mol Si $d^{-1}$. White bars: river fluxes. Grey bars: sum of river and benthic fluxes. Black bars: estimates of silica production. See text for explanations on budget calculations. (a) Benthic DSi fluxes have been extrapolated to the whole Bay by applying the fluxes measured at each site (Figure 13.4) to half of the Bay, i.e. the present extension of the invasive *C. fornicata*. The grey bars do not represent only the benthic fluxes shown on Figure 13.4 and extrapolated to the whole Bay; they represent the sum of the river and benthic DSi inputs, which can be directly compared to the diatom demand (black bars). (b) Same description, only *C. fornicata* has been artificially removed from the system by applying the benthic flux measured at the site without *C. fornicata* to the whole Bay and not only to half of it. From Ragueneau *et al.* (2002a).

## 13.4 Ecological and biogeochemical implications

### 13.4.1 Ecological implications in the Bay of Brest

Until quite recently, the Bay of Brest did not experience any sign of 'true eutrophication', and more subtle shifts towards non-diatom species have been sparse. Our results suggest that it is the proliferation of the invasive *C. fornicata* which may well have masked for years the potentially negative effects of elevated N and P inputs, through its role on the coastal silicate pump mechanism.

It has been suggested that *C. fornicata* be removed from the ecosystem, since this invasive species has drastically reduced the native *P. maximus* fishery in the Bay of Brest. A theoretical removal of *C. fornicata* was made in 2000 by applying the DSi benthic fluxes measured at the site without slipper limpets (Figure 13.6) to the whole Bay of Brest (Figure 13.7). The budget suggests that during summer DSi inputs from rivers and from the sediment-water interface would not be sufficient to sustain diatom demand. Diatoms would then probably be replaced by other algae not requiring DSi leading to the potential of harmful algal bloom with severe consequences for pelagic and benthic food webs. The massive bloom of the toxic dinoflagellate *Gymnodinium nagasakiense*, encountered during the summer of 1995 in the Bay of Brest, illustrates this theoretical removal scenario. *C. fornicata* was present but inactive. Indeed, feeding activity has been deeply affected by the mass sedimentation of the diatom bloom that occurred by late spring, through either gill clogging or oxygen depletion (Lorrain *et al.*, 2000; Chauvaud *et al.*, 2001). As a consequence, biodeposits were produced in much lower quantities and Si was exported out of the Bay in the form of $BSiO_2$, instead of being stored at the sediment-water interface as biodeposits. Less DSi was then available for diatoms during late spring and summer, especially as river inputs were particularly low, and *G. nagasakiense* dominated the phytoplankton throughout the summer (Chauvaud *et al.*, 2000).

The 1995 *Gymnodinium* event, explained by a complete stop of the silicate pump mechanism, had dramatic effects on benthic food webs. In particular, it has led to a major interruption in the growth of *P. maximus* (Chauvaud *et al.*, 2000; Lorrain *et al.*, 2000), and to differential larval and/or post-larval mortality, depending on the species sensitivity to toxic substances.Interestingly, most indigenous species are more sensitive to *Gymnodinium* toxicity than the introduced mollusk (Chauvaud, 1998), suggesting that nutrient enrichment would indirectly favor the successful colonization by non-indigenous species.

It is important to note that the silicate pump mechanism described herein has important implications for the ecosystem functioning, primarily because of DSi limitation induced by excessive inputs of N compounds from the watersheds. An interesting project is starting in the Bay of Brest, associating environmental and social sciences. Truely, *C. fornicata* endangers benthic biodiversity (Chauvaud *et al.*, 2000) and the development of *P. maximus* (Thouzeau *et al.*, 2000), which has important social and economical implications. At the same time, the proliferation of *C. fornicata* had beneficial effects for phytoplankton dynamics in the bay, reducing the effects, for phytoplankton dynamics in the bay, of the Si:N distrophy observed at the river output. Thus, paysants working on the watersheds may well have a different perception of the invasion than the fishermen working in the Bay. Therefore, it will be very important, in the coming years, to further investigate the mechanism of the silicate pump in the Bay (how long will it be efficient?) and launch a large discussion among the various actors of the Bay, to ensure its sustainable development for all. The case study presented herein thus provides a good example of an integrated approach, from the watershed to the coastal zone and from environmental to social sciences, to study the response of an ecosystem to two of the seven stressors described by Cloern (2001), namely nutrient enrichement and proliferation of invasive species.

### 13.4.2 The increasing importance of invasive species in ecosystem functioning

The mechanism described herein is also affecting primary production seasonality, with important feedbacks for benthic food webs. The Bay of Brest is showing a long-term change in the seasonal timing of phytoplankton biomass development (Chauvaud *et al.*, 2000). The spring blooms have become smaller in amplitude but the summer biomass has become higher. These subtle seasonal-scale changes might lead to positive or negative feedbacks in the benthic system and in other components of coastal ecosystems (Grall & Chauvaud, 2002). How these responses might be used as early-warning indicators of systemic responses to nutrient enrichment (Cloern, 2001) warrant further investigations. Mass population of invasive mollusks are developing throughout the world as a result of human introduction. Biotic invasions are an important component of human-driven aquatic alteration as major agents of global change (Mack *et al.*, 2000; Grosholz, 2002). Invasive species often outcompete native fauna for food and space, in the process altering the interactions between multiple components in the affected ecosystem (Chauvaud, 1998). The most famous example is the invasion of San Francisco Bay by the asian clam, *Potamocorbula amurensis* in 1986 (Carlton *et al.*, 1990). Within two years the clam had proliferated to more than $10\times10^3$ individuals per meter squared, and accounted for up to 95% of the benthic biomass in colonized areas (Nichols *et al.*, 1990). In the northern basin of the bay, this dense population directly controls the phytoplankton biomass (Cloern, 1982, 1996; Lucas *et al.*, 1999) and affects the zooplankton community by predation, or food competition (Kimmerer *et al.*, 1994). The appearance and proliferation of this species has altered the food web of the entire ecosystem (Nichols *et al.*, 1990; Thompson, 1999). The Bay of Brest and San Francisco Bay examples show how spreading of exotic species in the benthic ecosystem and eutrophication can be interconnected and how these species can alter the ecosystem functioning when the population is high enough to control primary production in the overlying water column (Cloern, 1982; Chauvaud *et al.*, 2000), and alter the cycling of nutrients such as carbon (Dame & Patten, 1981; Doering *et al.*, 1987), oxygen (Effler & Siegfried, 1994), nitrogen (Dame, 1993), phosphorus (Asmus *et al.*, 1995) or silica (Chauvaud *et al.*, 2000). Benthic community compositions have been profoundly modified by the proliferating invading species, threatening the benthic biodiversity at the ecosystem scale (Chauvaud *et al.*, 2000). Stachowicz *et al.* (1999) demonstrated experimentally that increased species richness significantly decreases invasion success, thus the impact of mild eutrophication on biodiversity should be included in further studies.

### 13.4.3 Biogeochemical implications for the Si cycle

Short-term, ecological, consequences of enhanced Si retention at the sediment-water interface, due to the proliferation of invasive species of suspension feeders, have been explored in Section 13.3 of this chapter. Long-term, biogeochemical, consequences will now be explored, discussing the so-called silica depletion hypothesis.

**The silica depletion hypothesis.** Decreasing Si:P and Si:N ratios occur through excessive inputs of N and P through anthropogenic activities in the watersheds, such as urbanization, agriculture and industry. Decreasing Si:P and Si:N ratios also occur through a modification of the Si cycle along the land-ocean continuum, following the so-called ‘silica depletion hypothesis’: enhanced production of diatoms leads to increased deposition and preservation of biogenic silica in sediments, which in turn leads to decreasing water column DSi concentrations. Enhanced diatom production is caused either by eutrophication or by the build up of reservoirs in river systems. Caused by eutrophication, this hypothesis has first been formulated for the North American Great Lakes by Schelske and Stoermer (1971). Conley *et al.* (1993) then described many examples of eutrophicated coastal areas where this hypothesis has been verified. Caused by river manipulation, the artificial lake effect has first been described by van Bennekom and Salomons (1981). A good example is the build up of the iron gates on the Danube river in 1972, which has led to a 50% decrease in the DSi concentrations of the coastal Black Sea (Humborg *et al.*, 1997, 2000). Other similar examples have been presented, such as along rivers from Sweden and Finland (Conley *et al.*, 2000).

Both causes of this silica depletion hypothesis, eutrophication and river manipulation, involve enhanced diatom production, although the trapping of phytoliths in dam reservoirs could also play a role. Here, it is suggested that increased biodeposition by suspension feeders, as evidenced in Section 13.3 of this chapter, could constitute a third means of depleting water column DSi concentrations.

**The biodeposition mechanism.** Biodeposition in beds of suspension-feeding bivalves results from the active filter feeding by a bivalve, which leads to nondigested material being excreted to the sediment surface as feces and pseudofeces (Norkko *et al.*, 2001). Bivalves, therefore, strongly affect physical, chemical and biological properties near the sediment-water interface (review in Graf & Rosenberg, 1997). In particular, these processes typically result in local deposition rates that exceed that of passive physical sedimentation (Dame, 1993; Dobson & Mackie, 1998) and create an enrichment of sediments in C and N (Kautsky

& Evans, 1987).

Diatoms are taken up by benthic suspension feeders in the process of feeding with regeneration of silicic acid from the biodeposits in the sediments (Asmus *et al.*, 1990). Only very few investigations of bivalves and bivalve beds as sources and sinks of silicon exist in the literature (Asmus, 1986; Dame *et al.*, 1991; Doering *et al.*, 1987; Prins & Smaal, 1994) where high rates of DSi release are observed from sediments probably occurring through the silicate pump mechanism described above for the Bay of Brest (Chauvaud *et al.*, 2000; Raguenau *et al.*, 2002a). Benthic filter feeders produce such high quantities of biodeposits that the subsequent dissolution of BSi allows for high rates of benthic DSi fluxes (see Section 13.3). However, due to the importance of biodeposition, even if only a small fraction of the BSi embedded in bivalve feces and pseudofeces gets preserved, the accumulation of BSi may represent an important flux, which needs to be quantified on annual and interannual time scales. In this perspective, a preliminary budget of annual Si fluxes has been built in the Bay of Brest (Figure 13.8). The establishment of such a budget (Raguenau *et al.*, 2003) is briefly described below, with a special emphasis on the demonstration that biodeposits are enriched in silica and constitute an environment favouring subsequent preservation of biogenic silica.

**Enrichment of biodeposits with Si.** In theory, biodeposits should be enriched in Si relative to C, compared to the corresponding Si:C ratio in the food: bivalves do not have any silicon requirements; they consume diatoms to get their energy, and therefore, should release feces with a Si:C ratio higher than in their food as seen for zooplankton in surface waters (Tande & Slagstad, 1985; Dagg *et al.*, 1993). Ragueneau *et al.* (2002b) have shown that both pelagic and benthic grazers participate actively in the Si:C decoupling in the world ocean. The Si:C ratio increases by a mean factor of ≈ 6 between production and export, and by a mean factor of ≈ 4 between deposition at the sediment-water interface and accumulation below the bioturbated layer. In contrast, the Si:C ratio remains almost constant during the descent through the deep water column. These authors hypothesized that grazers are responsible for the observed vertical decoupling between Si and C cycles. Bacteria also participate in this process, as shown recently (Bidle *et al.*, 2002).

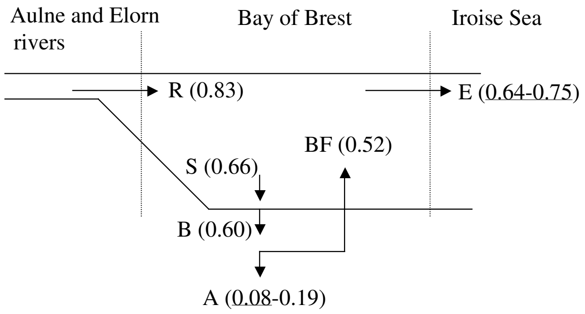

Figure 13.8: A first annual budget of DSi fluxes in the Bay of Brest ecosystem. All fluxes given in parentheses are in mol Si $m^{-2}$ $y^{-1}$. R stands for River fluxes, S for net Sedimentation, B for Biodeposition, BF for Benthic Fluxes, A for Accumulation and E for Export out of the Bay. Note that numbers underlined correspond to estimates obtained by difference: A (minimum estimate) = B - BF, and E = R - A. All other numbers have been quantified directly (See Ragueneau *et al.* 2003).

To provide an estimate of the silica enrichment factor in suspension feeders faeces, we have performed a simple experiment (Moriceau, 2002). The proliferating gastropod *C. fornicata*, collected in the Bay of Brest, has been fed with a diatom *Chaetoceros calcitrans* after a 48 h period of starvation. A Si:C molar ratio of 0.049 ±0.002 was measured in the food. The Si:C measured in the feces after 24 hour was 0.118 ±0.002. Thus, in this experiment, the Si:C ratio has increased by a factor 2.4 between the phytoplankton and the faeces. The experiment described herein needs to be repeated with other bivalves and it remains to be established whether this result is due to the feeding activity of the bivalve itself, or to the associated bacterial activity. Whatever the mechanism, this result confirms that grazers actively participate in the decoupling between Si and C. Biodeposits are thus enriched in silica, suggesting that it would be important to determine how much of this BSi embedded in biodeposits, eventually gets preserved in the sediments. In the absence of direct measurements of annual Si accumulation data, we have performed two indirect, but independent, estimates of BSi preservation efficiency in the sediments of the Bay of Brest.

**Annual accumulation of Si in the Bay.** Chauvaud *et al.* (2000) have estimated the biodeposition of C in the Bay of Brest to be 3.5 mol C m$^{-2}$ yr$^{-1}$. The Si:C ratio in the biodeposits is close to 0.17 and has been estimated using the mean Si:C of phytoplankton during the productive period (Ragueneau *et al.*, 1994; Del Amo *et al.*, 1997), and multiplying it by the factor of 2.4 determined during the experiment with *C. fornicata*. Multiplying the C biodeposition by this ratio of 0.17 yields an annual Si biodeposition close to 0.6 mol Si m$^{-2}$ yr$^{-1}$. Interestingly, this number amounts to 72% of the DSi inputs from the Aulne and Elorn rivers, as measured during 2001 (Prohel *et al.*, 2001). Of course, most of this retention is temporary and we have seen how important recycling at the sediment-water interface can be for pelagic primary production (Section 13.3). The annual DSi benthic flux, estimated from monthly measurements of benthic silicic acid fluxes, amounts at at 0.52 mol Si m$^{-2}$ yr$^{-1}$ for the year 2001. The annual accumulation can be calculated by substracting from biodeposition, this estimate of the annual benthic flux. The first estimate of annual Si accumulation is therefore 0.08 mol Si m$^{-2}$ yr$^{-1}$, i.e. 10% of annual river inputs. A second estimate can be obtained independently. Using inverse modelling, Jean (1994) estimated the annual C accumulation to be 0.32 mol C m$^{-2}$ yr$^{-1}$. To derive the Si accumulation, we can use a Si:C ratio of 0.6, derived from a compilation of Si and C accumulation on continental margins, recently published by DeMaster (1981). The result is 0.19 mol Si m$^{-2}$ yr$^{-1}$, i.e. 23% of annual river inputs. Thus, these simple calculations suggest that the annual retention of Si in the Bay of Brest ranges between 10 and 23%, which seems reasonable when compared to other temperate estuaries (DeMaster, 1981).

Figure 13.8 synthesizes the above calculations and provides a preliminary budget of annual Si fluxes in the Bay of Brest ecosystem. The important information to be derived from this budget is the role that biodeposition is playing in the system. It leads to the temporary retention of 72% of DSi river inputs. Of the BSi being biodeposited, from 13 to 32% eventually accumulates on an annual basis. This preservation efficiency of the BSi embedded in biodeposits approaches that measured in the Southern Ocean (range from 8 to 40%, Raguenau *et al.*, 2002b), whereas that measured values in other deep-sea settings range from 5 to 15% (Raguenau *et al.*, 2002b). It suggests that the sediment conditions induced by biodepositing organisms provide a means of efficiently preserving the biogenic opal.

The annual retention of Si in the Bay of Brest ranges between 10 and 23% of DSi river inputs. It is important to note that it would be much lower in the absence of the invasive species *C. fornicata*, which proliferation leads to both increased deposition rates and sedimentary conditions favorable to BSiO$_2$ preservation. Sediment cores will soon be collected at sites exhibiting contrasted densities of *C. fornicata*, to test this hypothesis by reconstructing changes in the accumulation rates of sediment, organic C, BSiO$_2$ and diatom assemblages.

As noted in Subsection 13.4.2, biological invasions will continue, as mollusk aquaculture production is growing rapidly (www.fao.org ) and expanding international commerce accelerates the translocation of fauna (Carlton & Geller, 1993). Thus, it will be important to test the role of increasing biodeposition in lowering the DSi water column concentrations, as it may already be very important in some ecosystems, and will most probably become even more important in the coming years.

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# Part V

# Mariculture, ecological quality and cultural eutrophication

# Chapter 14

# Maricultures and eutrophication

Marianne Holmer
Institute of Biology, University of Southern Denmark
Campusvej 55, DK-5230
Odense M.
holmer@biology.sdu.dk

## 14.1 Introduction

Aquaculture is an essential industry providing important products to the globally growing demand for marine food products. Most of the aquaculture takes place in poor and food-deficit countries, where the knowledge on environmental effects of aquaculture productions is still scarce. Finfish culture is the most important aquaculture in the industrialized part of the world, whereas aquaculture is more diverse elsewhere. Kelp, shellfish and shrimps dominate the world production over finfish production. The intensive cultures, where fishes and shrimps are raised on artificial feeds cause greater environmental impacts than the more extensive methods used for cultures of herbivorous fish and shellfish. The artificial feeds are produced from industrialized fishing products, and intensification of aquaculture increases the risks of local pollution due to the direct loss of waste products. Most of the nitrogen-containing waste products are released in the dissolved form and may lead to eutrophication events in the water column, whereas the phosphorus compounds primarily are released as particulates and settle in the vicinity of the fish farms. The settling waste products have high organic contents and increase the oxygen demand on the seafloor, which may have detrimental impacts on the benthic fauna right below the net cages. This organic loading of the sediments increase the bacterial activity and regeneration of nutrients back to the water column. The environmental effects of marine fish farming vary greatly between sites and also over geographical regions. Under oligotrophic conditions fish farming may ultimately stimulate the productivity of the ecosystem, whereas eutrophic locations suffer from the additional inputs of nutrients and organic matter.

## 14.2 Environmental effects of marine fish farming

Aquaculture is growing rapidly all over the world due to the declines in natural fisheries and the increasing demand for marine food products by the increasing human population. Aquaculture is still dominated by fresh water activities (57%), but is expanding rapidly into the coastal zones, and at present there are major efforts to move the industry further off-shore in bigger farms. One of the reasons for the move are the conflicts often encountered in industrialised countries, where farms are located in areas with great natural beauty, and where it is difficult to balance the benefits of aquacultures with the local population and tourists in the area. There are similar problems in the tropics, where for example the use of mangrove forest for shrimp farming has created massive conflicts with local users.

Finfish cultures and shrimp farming has become increasing intensive during the last 2–3 decades, where the production has increased almost exponentially. The environmental concerns are many extending from the demand for wild resources to eutrophication effects of the marine ecosystems. The use of aquafeeds produced from industrial fisheries has increased with almost 30% each year for the last few years (Davenport *et al.*, 2003), and although the harvest is from stocks of abundant pelagic fish there is a concern over the potential competition between industrial fisheries, commercially important human consumption, and wildlife conservation interests. *The amount of industrial fish used for production of for instance salmon is very high, about 3.8 kilos pr. kg salmon produced*, and there is a strong pressure on the industry to try to lower this amount by introducing terrestrial compounds in the diets. This high amount of feed needed also means that there is a large loss of waste products from the intensive cultures. *The conversion efficiency of feed to aquaculture product is around 20% at best*, meaning that about 80% of the inputs are wasted (Davenport *et al.*, 2003). The waste products are either released in dissolved form to the water column or as particulates, which may settle in the vicinity of the farms depending on the current regime of the location (Figure 14.1).

The dissolved compounds are primarily nutrients in the form of ammonium from the fish excretion, and $CO_2$ from fish respiration (see Section 14.3) but also toxic and chemical compounds may be released in dissolved forms. *Intensive aquaculture is dependent on the use of chemicals and medicines to control the biological environment within the cage system.* A wide range of chemicals is used, including antibiotics, antiparasitics, fungicides, herbicides and disinfectants. The environmental effects of these chemicals will depend on their toxicity to local species and their dispersion and persistence in the environment. Vaccines are now available for some of the cultured species, such as salmon, and the use of antibiotics has declined significantly since the early 90'ies (Alderman, 2002). Studies of the fate of antibiotics have shown small accumulations of antibiotics in the sediments, whereas the major sink remain unsolved (Capone *et al.*, 1996). The antibiotics have a large variability in residence time in the sediments, but increased bacterial resistance has been found in the underlying sediments, which potentially can be a major environmental risk (Willis, 2000). Another problem is the fouling of the physical structures of the farms which is a major problem, in particular in the tropics with rapid growth of fouling organisms from bacteria to seaweeds and epifauna. Mostly, fouling organisms are removed manually, e.g. by frequent wash of the nets, but it can also be necessary to use antifouling paints. This has lead to increased concentrations of heavy metals such as cupper in the surrounding sediments (Schendel *et al.*, 2004).

Also disease outbreaks has to be considered as an environmental risk of aquaculture, and rearing fish in net cages can cause stress, which undermine their resistance and increase the risk of disease. Diseases can be prevented by optimizing growth conditions and development of new vaccines. As farms are often placed close to each other a disease outbreak may lead to significant production losses in the area and may eventually affect the wild stocks (Coutant, 1998). In addition to transfer of disease the potential genetic effects on wild fish of accidentally released cultured fish has been of concern, in particular for salmon, where the wild stocks are highly priced (Youngson *et al.*, 2001). Rearing of fish usually leads to reduced levels of genetic variability and differences in genetic composition compared with wild fishes. Interactions between cultured escapees and wild stocks

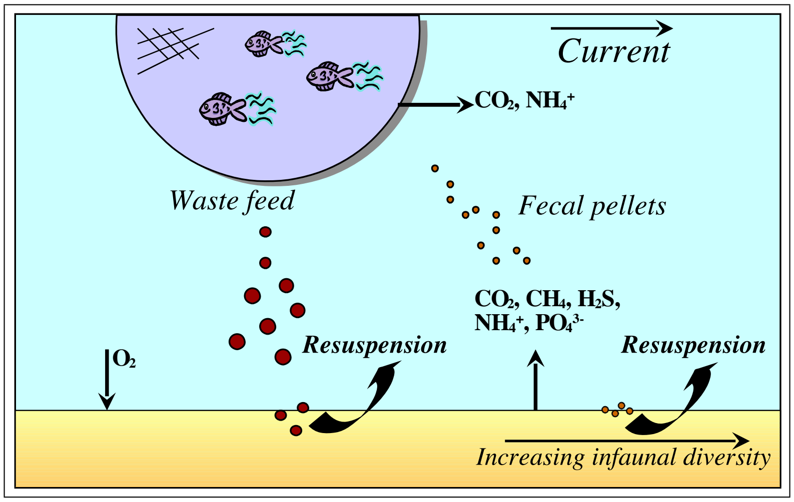

Figure 14.1: Schematic presentation of the fate of waste products from finfish farming in net cages. (Modified from Davenport *et al.*, 2003).

can reduce the fitness of wild populations. Nearly 40% of all known introductions of alien and exotic species to the aquatic ecosystem have been related to aquaculture (Davenport *et al.*, 2003). Many of these species have little known effects, whereas others, such as several shellfishes have caused major damage.

## 14.3 Water column and eutrophication in fish farm surroundings

As the culturing of marine fish takes place in open cages the dissolved losses are released directly into the water column in a highly biologically active form. The dissolved compounds related to eutrophication are both inorganic and organic nutrients. The inorganics are primarily released as ammonium and phosphate, and for the organics it is DOC, DON and DOP which are released (Hall *et al.*, 1990, 1992; Holby & Hall, 1991). The waste products are released directly as excretion products from the fish or are dissolved from feed or faecal particles (Figure 14.1). Although a significant fraction of the waste products from aquaculture operations are in the dissolved form, only small increases in nutrient concentrations can be measured in the surroundings (Nordvarg & Johansson, 2002). Even in sheltered areas the water exchange may be high resulting in low residence times, which allow a rapid dispersion of the dissolved waste products. It is therefore seldom to detect major changes in water quality around fish farms and water quality is not considered as a strong indicator of fish farm impacts. Increased nutrient concentrations have been found during feeding events typically with enhanced concentrations for 1–2 hours after feeding (Karakassin *et al.*, 2001). Due to the relatively long generation times of phytoplankton when considering the rapid dispersion of nutrients in fish farm surroundings, phytoplankton growth is generally not considered to be a good indicator of environmental impacts. The increased nutrient concentrations during feeding events are too short to allow phytoplankton to respond in growth (Karakassin *et al.*, 2001). It has therefore been speculated that the loss of dissolved nutrients is not of importance for the marine ecosystem due to the rapid dilution of nutrients to background level, but a new technique with the use of bio-assays have documented that the nutrient availability is higher in fish farm surroundings in particular under oligotrophic conditions (Dalsgaard unpublished results). The principle behind the bio-assays is to enclose the natural phytoplankton community without grazers in a dialysis bag, which allows the nutrients released from the farms to enter the bags for uptake. The bio-assays can be placed with increasing distance from the farms to show distance related changes in nutrient availability compared to control sites far away from the farm. The bags are left for a few days to allow the phytoplankton to grow, and rates are determined from increases in chlorophyll a concentrations and nutrient uptake by nutrient concentrations. Increased concentrations of chlorophyll a has been measured in distances up to several hundreds meters downstream from fish farms in the Mediterranean showing that although the nutrient concentrations are low, the phytoplankton is able to take up the nutrients (Figure 14.2). It is, however, not possible to detect increased phytoplankton growth in the vicinity of the farms due to the rapid dispersion and a significant grazing pressure. This suggests that the dissolved nutrients are dispersed over large areas and that they may enter the nutrient cycles again as zooplankton faecal pellets. The same technique can be applied for macroalgae, where growth is measured as increase in size, as has been done for *Ulva lactuca*. Increased macroalgae growth has been detected near fish cages (Dalsgaard unpublished results). It is quite common to find increased algae growth on the mooring structures (Honkanen & Helminen, 2000) and the higher nutrient availability is also reflected in the benthic flora, such as seagrasses, where increased nutrient concentrations have been found (Deldago *et al.*, 1999). There have been several attempts to grow macroalgae in the vicinity of fish farms to reduce the loss of nutrients to the environment (Hernandez *et al.*, 2002), but it has not yet been implemented in large scale operations.

Bacterioplankton have much shorter generation times than the phytoplankton, and increased growth, e.g. on the released organic nutrients have been found around Mediterranean fish farms (Tsapakis unpublished results) and in the tropics (Agawin unpublished results). In a study of the bacterial abundance and production during summer in the surroundings of a Japanese fish farm increased numbers were found (Sakami *et al.*, 2003). The bacterial response was strongly related to the release of dissolved organic compounds from the farm, suggesting that the organic nutrients play an important role in the nutrient cycling.

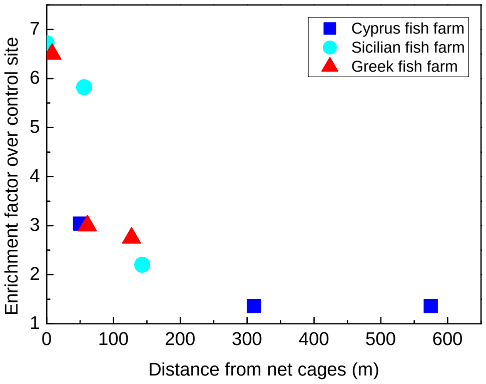

Figure 14.2: Enrichment of chlorophyll a concentrations in phytoplankton bioassays deployed with increasing distance from 3 fish farms in the Mediterranean. Natural seawater was filtered to remove grazers and placed in dialysis bags for up to 5 days at the field site. The chlorophyll a concentrations are given as the ratio between the examined fish farm site and a control site located up to 5 km away from the farms. (Dalsgaard, unpubl. results)

Primary productivity in marine waters is often limited by nutrients, in particular under oligotrophic conditions in the subtropical and tropical regions. In temperate systems nutrient limitation often shows a seasonal variation with phosphate limiting the spring bloom and nitrogen limitation in the summer, whereas phosphate is considered as the most important limiting nutrient in the tropics. Fish farming in temperate regions may, due to the release of dissolved nitrogen directly through excretion of ammonium from the fish during summer, lead to a stimulation of the nitrogen-limited primary producers. Increased chlorophyll a concentrations and periphyton growth has been linked to fish farming activities in the Archipelago Sea in SW Finland (Honkanen & Helminen, 2000), and in non-stratified shallow waters the high mineralization rates in the sediments further increase the nutrient loading of the water column. The study of the Archipelago Sea in Finland is one of the first to show an ecosystem effect on primary production under eutrophic conditions. It is often argued, in particular by fish farmers, that the nutrient release from fish farms in eutrophic regions is negligible compared to the other sources of nutrients, e.g. run-off from agricultural land, but the density of fish farms in the Archipelago was so high that there were direct effects of the industry. *The main problem is that the nutrients are released during the season, where the primary producers usually are limited by nutrients, whereas most of the run-off from land occurs in the winter with low primary productivity.* There have only been a few attempts to find the carrying capacity of tropical ecosystems where the assimilation capacity is expected to be high, but extreme events with mass killings of cultured fish due to blooms of toxic dinoflagellates clearly show, that there is a threshold of nutrient loading (Holmer *et al.*, 2003b). Coral reefs are very sensitive to increased nutrient loads and particle loading caused by land erosion (Barber *et al.*, 2001), but some studies have shown that coral growth is stimulated for selected species when grown in aquaculture surroundings probably by the increased nutrient availability (Bongiorni *et al.*, 2003). The effects of dissolved release from fish farms are not easy to predict.

There have been major concerns that maricultures have stimulated harmful algae blooms (HABs), as observed in the North-Atlantic in late 80's (Gjøsæter *et al.*, 2000) and in the Irish and Scottish Seas around the century. HABs are intensifying globally also in areas with intensive maricultures. There are, however, many possible causes in addition to maricultures, such as climatic changes and intensified agricultural activities. HABs are a major threat to the industry itself, as it may lead to mass killings, such as observed for salmon during the *Chrysochromulina* bloom in late 80's (Gjøsæter *et al.*, 2000) and for the mussel scallop industry in Ireland and Scotland in 2000–2001 (Davenport *et al.*, 2003).

## 14.4 Sediment and eutrophication in fish farm surroundings

There is a significant loss of particulate waste products from fish farms, as finfish primarily are fed with dry pellets. Recent expansion of the tuna industry has resulted in a 'historic return', as the tuna feed on trash fish, which was used before dry pellets. The environmental impacts by use of trash fish were quite serious, and as the tuna farms are much larger than the historic farms the environmental impacts are of major concern and are under intense investigation in these years. The settling of particulate waste products from dry feeding is dependent on the shape and size of the pellets and of the current velocity in the area. Uneaten feed pellets sink fast to the seabed, if they are not consumed in the water column or from the seafloor by wild fish (Figure 14.1). The size and consistency of faecal pellets vary significantly between fish species and for some species such as seabass the faecal pellets tend accumulate directly under the cages, whereas for other species such as seabream the faecal pellets are spread over a larger area (Cromey, unpublished results). Due to the high price on aquafeed, direct feed loss during farming is considered to be minimal, and faecal material is considered as the most important sources of particulates. The pellets are often broken down to smaller particulates during passage in the water column and lead to sedimentation far away from the farms (Cromey *et al.*, 2002).

Settling of feed or faecal pellets increases the organic content of the underlying sediments with highest accumulation at sheltered sites (Brooks & Mahnken, 2003; Holmer *et al.*, 2003b). Fish farms are located in many different types of locations, and in the industrialised part of the world often at more remote and exposed areas, whereas farms can be found in sheltered areas in the tropics due to the low-technology applied and the harsh weather conditions experienced during hurricane seasons. Many Mediterranean and tropical locations are characterised as oligotrophic and the sed-

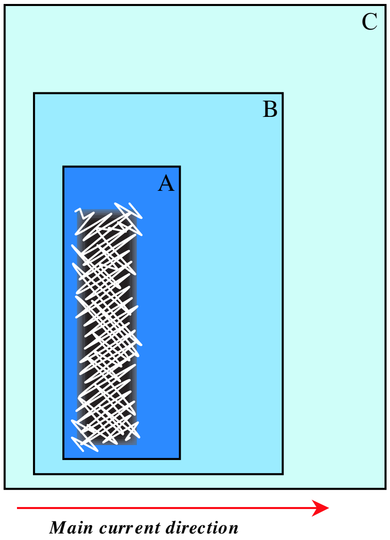

Figure 14.3: Illustration of fish farm (hatched area) and the three impact zones: A) The local zone,. B) The intermediate zone and C) The regional zone.

iments have low organic contents. Fish farming activities may thus alter the sediment conditions significantly compared to eutrophic sites with high organic pools in the sediments. The settling organic matter is, however, of a much higher quality than the natural sedimentation in the marine environment. The feed pellets are rich in carbohydrates, fish oil and fish protein, whereas the faecal pellets are less rich in proteins. The waste products may thus have a relatively high C:N ratio, but on the other hand the contents of organic carbon and nitrogen is much higher than in phytoplanktonic detritus, and the microbial activity in the sediments is usually stimulated. Microbial activity is up to several orders of magnitude higher compared to unimpacted sediments (Hall *et al.*, 1990; Hargrave *et al.*, 1993; Holmer *et al.*, 2003b). Also phosphorus accumulates in the sediments. Phosphorus is primarily released as particulates and settles in the underlying sediments, and may be used as an indicator of fish farm sediments.

The distribution of organic enriched fish farm sediments varies between locations and is among many factors determined by the bathymetry of the site, the current speed and direction, tidal range and production characteristics of the farm (size of farm, type of food, cultured species, season). At sheltered sites with low currents the affected area is typically found right under the cages and in distances up to 50 m, whereas larger areas up to 100 m away may be affected at more exposed sites (Brooks & Mahnken, 2003). The area affected is typically divided into 3 zones (Figure 14.3): A) The local zone, where most of the food pellets settle which usually is under or close to the net cages. B) The intermediate zone, which is the main area of sedimentation of smaller organic particles such as faecal pellets, and of deposition of resuspended matter from the local impact zone. C) The regional zone, which consists of adjacent areas and water bodies, mainly influenced by nutrients from the fish farm.

The effect of organic matter deposition caused by eutrophication on the microbial activity has been described in detail in Chapter 11. The same reactions take place in fish farm sediments, but directly under the net cages sulfate reduction and methanogenesis are often the two dominating processes due to exhaustion of the other electron acceptors ($O_2$, $NO_3^-$, $Fe^{3+}$) (Hall *et al.*, 1990; Holmer & Kristensen, 1996). The organic matter from fish farms is of much higher quality and can easily be decomposed by the bacteria. Oxygen supplied from the water column to support aerobic mineralization is thus rapidly consumed, which also limits the production of nitrate by nitrification, as this is an aerobic process. Oxygen is also needed for reoxidation of reduced iron, as the pools of oxidized iron are quite limited in coastal sediments (Figure 14.4). In extreme cases the sediment will be completely anoxic either with a white cover of the sulphide-oxidizing bacteria *Beggiatoa* or totally black from precipitation of ironsulfides with bubbles of methane coming up from the deeper layers (Figure 14.4). In this case, there will be no macrofauna present in the sediments and there is a risk for oxygen depletion events during calm periods. Under less extreme conditions sulfate reduction still appears to be an important process for mineralization of organic matter and it is often enhanced in the area where increased sedimentation is found (Figure 14.5). In

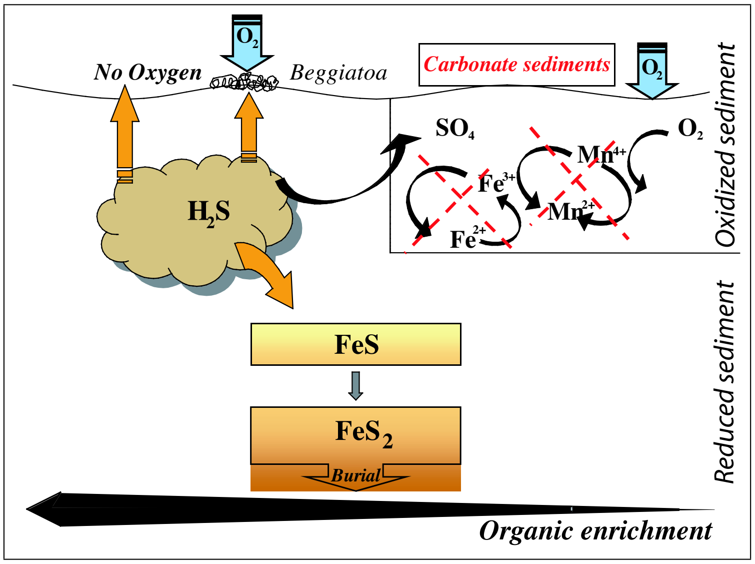

Figure 14.4: Conceptual figure on the fate of sulfides produced by sulfate reducing bacteria along an organic-enrichment gradient, such as approaching a fish farm. If the sediments are oxidized, sulfide may be reoxidized by reaction with oxidized iron, which is regenerated through consumption of oxygen. In sediments without oxygen, hydrogen sulfide may escape to the water column or be oxidized by the sulfide-oxidizing bacteria *Beggiatoa* at the sediment-water interface. Sulfides are buried in the sediments by reacting with reduced iron and formation of pyrite. In carbonate sediments with low pools of oxidized iron, sulfide is reoxidized directly by oxygen.

sediments with high iron pools, where sulphide is reoxidized back to sulfate by oxidized iron, or bound with iron as pyrite, the sediments may be suitable for meio- and macrofauna and for denitrification. However, in sediments with low pools of iron, such as the carbonate sediments in the Mediterranean and the tropics, sulphide concentrations may remain high and limit other biological processes (Figure 14.4). Denitrification is for instance sensitive to high sulphide concentrations and has been found to be inhibited under a Danish fish farm (Christensen *et al.*, 1999).

The high microbial activity in the sediments results in a rapid regeneration of inorganic nutrients, which become available for uptake by primary producers when they are released across the sediment-water interface. In silty organic-rich fish farm sediments nitrogen is primarily released as ammonium, which can be taken up directly by phytoplankton. During the summer period phosphate is also released from the sediments due to low binding capacities with iron oxides in these sulfidic sediments. In colder months the phosphate release may be less, as phosphate is bound with iron in the oxidized surface layers. The release of inorganic nutrients from the sediments during summer months, where the nutrient concentrations are low in the water column, may stimulate the primary

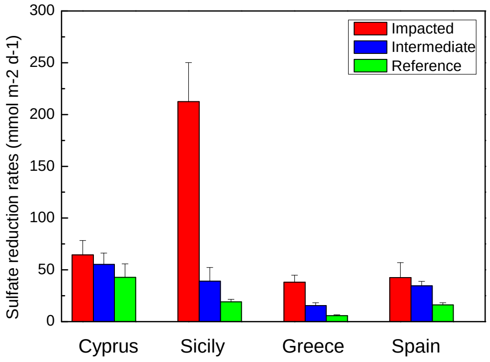

Figure 14.5: Sulfate reduction rates in bare sediments with increasing distance from 4 fish farms in the Mediterranean. The impacted site is right under the net cages, the intermediate is 10–50 meters away from the net cage in the main current direction and the control site is 1–5 km away. Sulfate reduction rates were clearly stimulated at the Impacted and Intermediate stations, except for Cyprus, where the Reference site showed high values. Sulfate reduction accounted for 50–100% of the mineralization in the sediments (Holmer and Dalsgaard unpubl. results).

production. In coarse, nutrient-poor sediments, such as in the Mediterranean, the flux of nutrients is much lower as the sediments appear to have an assimilative capacity, e.g. due to the presence of microphytobenthos to take up N and P. The sediments also have a large calcium-carbonate pool to bind phosphate.

The benthic fauna is affected by the sedimentation of waste products from fish farms, and the fauna distribution in silty sediments often follows the 'Pearson and Rosenberg' pattern along an organic enrichment gradient (Pearson & Rosenberg, 1978) with a grossly polluted zone with presence of the *Beggiotoa* mat and no fauna right under the cages followed by a polluted zone with abundant opportunistic species such as the polychaete *Capitella capitata*. This zone is replaced by a transitory zone, where a peak in fauna biomass and abundance can be found due to the increased input of food in this zone, before the normal zone without impact is reached. In the coarser sediments, the benthic fauna is much different from silty sites, often inhabiting a sparser community of larger species strongly limited in food availability. The input of organic matter tends to stimulate the benthic fauna, but on the other hand, this type of fauna is highly sensitive to environmental changes, which may result in rapid population changes. The dynamics in this type of fish farm sediments have been described as a shifting between of 'successes' and 'catastrophes' (Karakassin *et al.*, 1999).

The stimulated microbial activity and in particular the sulfate reduction may also be important factors controlling the distribution of seagrasses in vicinities of fish farms (Holmer *et al.*, 2003a). Under oligotrophic conditions, where the penetration of light occurs into deep waters (e.g. 20–50 m), the benthic flora is an important component of the coastal ecosystems. Both in the Mediterranean and in the tropics, seagrasses can be found to large depths often at locations with rapid water exchange and coarse sediments, the same sites which are ideal for aquaculture operations. In the Mediterranean the dominating seagrass at large depths is *Posidonia oceanica*, which is a slow growing species highly sensitive to anthropogenic pressures including fish farming activities (Nordvarg & Johansson, 2002; Duarte, 2002). Although the underlying mechanisms have not yet been fully explored *P. oceanica* appears to be negatively impacted by increasing sedimentation rates. The meadows are thus declining in the vicinity of the farms as the seagrass mortality increase and there is no new recruitment of shoots (Figure 14.6). The seagrasses show signs of anoxic stress by accumulation of specific amino acids (Perz and Invers unpubl. results) and shifts in the isotopic composition of sulphur towards the sulphide signal suggesting that the seagrasses have been exposed directly to toxic sulphide (Frederiksen unpubl. results). Also the nutrient contents increase and if there are sea urchins at the location, they may exert a detrimental grazing pressure on the seagrasses. The seagrasses meadows are more sensitive than bare sediments, and the seagrass ecosystem has been found to be affected up to several hundred meters away from the fish farms com-

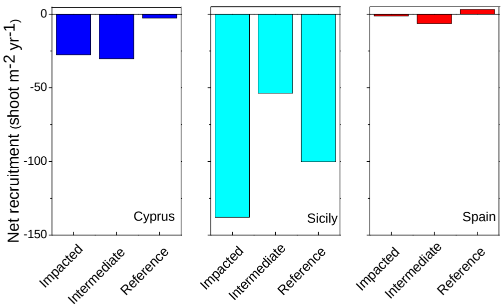

Figure 14.6: Net recruitment of the seagrass *Posidonia oceanica* with increasing distance from 3 fish farms in the Mediterranean. The Impacted site is close to the net cages, where the first seagrasses are found (10–30 m from cages), the Intermediate 30–50 m away from the net cages and the Reference site is 1 km away. Note that the net recruitment is negative for all sites, even the reference sites, except for Spain where the seagrass meadow at the reference site was expanding. This means that *P. oceanica* is generally declining, but the decline is accelerated dramatically close to the fish farms. Observations of plots at the Impacted sites 1 year after in Sicily and Greece showed that the seagrasses were all gone. (C. Duarte unpubl. results).

Figure 14.7: Attraction of wild fish to a net cage at a Greek fish farm. Photo: Marianne Holmer.

pared to less than 100 m for bare sediments.

It is quite common to observe attraction of wild fish to the net cages, and in particular in the Mediterranean where large schools of fish can be observed around the net cages (Figure 14.7, Dempster *et al.*, 2002). The fishes graze on the fouling organisms on the net cages and the anchoring structures or consume waste materials. Also large carnivore fishes and mammals are attracted to the aquaculture operations, and waste material is thus transported further away than just measured by sedimentation traps in the farming area. Evaluations of local fisheries in oligotrophic waters with intensive maricultures have shown increases in fish landings suggesting that the aquaculture operations may increase the productivity of the ecosystems. This has been found in the oligotrophic waters in the Greek archipelago with high farming activities (Machias *et al.*, 2004).

The seasonal variations in the benthic impacts are primarily related to the production activities in the farms and variations in temperature. In temperate regions the farming activity is highest during the summer, where the fish grow the fastest. Here the water temperature is usually at maximum, which influence the bacterial activity in the water column and in the sediments, and the most severe environmental impacts are generally detected during the summer. In winter with low or no activity in the farms, the benthic environment right under the cages may almost return to background conditions with oxygen penetrating into the sediments and benthic fauna recolonising the sediments (Holmer & Kristensen, 1996). The organic matter pools, however, remain high indicating that the sediments are still organic enriched. A following practice, where the fish farms are rotated between different sites, has been suggested to allow the sediments to fully recover, but on the other hand, this exerts a pressure on the coastal zone managers to allocate more space for fish farms. In the tropics there is less seasonal variation in temperature, but the culture periods are often shorter (<4 months) and the farmers have more than one production cycle per year depending on the market value and the hurricane season. The farmer typically allows the site to recover before starting a new production, but very little information is available on the long term effects of fish farming in the tropics (Holmer *et al.*, 2003b).

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# Chapter 15

# Balance between marine resources utilization and ecosystem sustainability, with main emphasis on extensive aquaculture and coastal eutrophication. Results from the MARICULT Research Programme (1996–2000)

Yngvar Olsen
Trondhjem Biological Station
Department of Biology
Norwegian University of Science and Technology
Trondheim, Norway
yngvar.olsen@bio.ntnu.no

## 15.1 Background

The global human population is expected to reach about 10 billion by 2050, and it can be questioned how humans will be able to provide the food needed to feed that population. A sustainable development of the agricultural sector is in all events needed, but the potential of the marine sector for increased contribution is now frequently addressed. An increase in agriculture will require considerable investments in research, wider implementation of intensive agricultural technology, use of genetically improved plants and animals, more efficient distribution of produced food, availability of sufficient freshwater, and a significant increase in new agricultural land. These preconditions call for a precautionary approach; we will need to search for options for food production also outside the agricultural sector. More seafood and food production based on biotechnological methods are among the most obvious options available.

Seafood contains essential lipids and is therefore greatly demanded from nutritional and health perspectives (see e.g. Sinclair and Gibson 1992). The available and prospected bioprotein sources cannot so far replace food of aquatic origin here. Marine fats contain n-3 fatty acids that are essential for humans, and a suboptimal supply may affect the quality of life, because it results in a higher frequency of heart and coronary diseases and in some extreme cases mental health problems, such as deficiencies (Nelson, 1991; Grawford, 1991).

A main motivation for strengthening of the marine sector is the fact that only a very low proportion of human food originates from the ocean. FAO statistics (www.fao.org) show that only about 1 and 5% of human energy and protein consumption, respectively, originates from the fisheries and aquaculture. This is surprising because marine and terrestrial primary production is of the same magnitude, and it implies that the traditional mode of harvesting the marine ecosystem is less efficient than our cultivation and harvesting of the terrestrial ecosystem. It is well known that the production of the world's oceans is temporarily and spatially very patchy. The classic analysis of Ryther (1969) suggested that some coastal upwelling areas are highly productive, whereas the majority of the open ocean is highly oligotrophic, often named marine deserts. The coastal marine systems are normally intermediate. The theoretical analysis of Ryther (1969) suggested that 50% of the global fish and squid production took place in the major coastal upwelling systems of the Earth which constitute only 0.1% of the ocean surface. The next 50% of the production potential was located in the 10% which are coastal waters, whereas the 90% surface which was defined as open ocean, was responsible for <1% of the production. The numbers for upwelling systems cannot be directly evaluated based on fishery statistics — because fish migrate. Even though they are most likely overestimates, they are still representative. An ultimate question is if such high-productive marine ecosystems can be artificially created by some means. This, together with the general low harvesting yields compared to the marine primary production, illustrates a potential call for research to increase the marine food supply for human consumption.

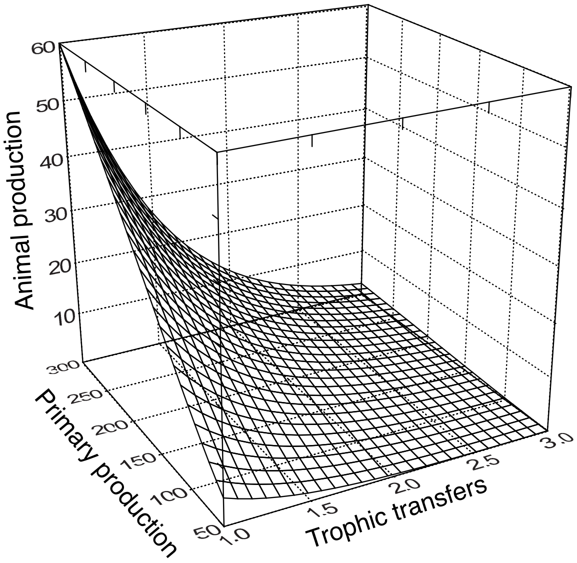

Figure 15.1: Empirical relationship showing secondary production as a function of primary production and the number of trophic transfers that the energy has to pass through before reaching the stock that are harvested. The coefficients used are based on the three cases of systems defined by Ryther (1969). Interpolation is made by assuming coefficients to be continuous functions of primary production and number of trophic transfers through their entire range.

A very simple comparative analysis of production and harvesting strategies in agriculture and fisheries/aquaculture clearly indicates why a major fraction of the food is produced in agriculture. The analysis is based on the simplest principle of food web energetics and empirical knowledge on agriculture and marine food web structures.

Figure 15.1 illustrates the principal relationship between secondary production potential (stocks which are harvested) as a function of the primary production and the number of trophic transfers of energy (based on Ryther 1969). The upper right corner of the figure is representative for the production conditions of coastal upwelling systems, whereas the lower left corner represents the open ocean. The coastal ocean is intermediate, with a primary production of 100 g C m$^{-2}$ yr$^{-1}$ and approximately 2 trophic transfers. The figure shows that:

- When the number of trophic transfers remains constant, the secondary production is *proportional* to the primary production
- For a constant primary production, there is a *sharp exponential decrease* in the secondary production as the number of trophic transfers increases (i.e., as we move up the food web).

The secondary production yield is accordingly more sensitive to variations in the number of trophic transfers than to variation in the primary production. Contrary, as much as 80–90% of the assimilated energy is lost each time something eats something else, or for each trophic transfer of the energy. The total range of variability in secondary production caused by the total variability in primary production (Figure 15.1) is comparable to the variability caused by one single trophic transfer. *The figure clearly shows that the high harvesting potential of the upwelling systems is primarily an effect of the short food webs.* The physical dynamics of upwelling systems are complex and characterized by high natural nutrient supply from deep water and short food webs, which implies few trophic transfers of the assimilated energy and harvesting on lower trophic levels than in other marine ecosystems.

The above conceptual analysis is simple, and therefore also robust to variability in coefficients and empirical input data. Trophic dynamical models are in fact included in most textbooks on ecology. The above conceptual relationships, which are laws of nature, are however not very frequently considered in evaluations of marine productivity and mariculture potential. It may be questioned if our comprehension fails to fully realize the implications of an exponential loss of energy as we move up the food web.

The above considerations explain the marginal contribution of the marine food web in human food supply (1–2% in 1997, www.fao.org). Figure 15.2 illustrates human feeding habits for the

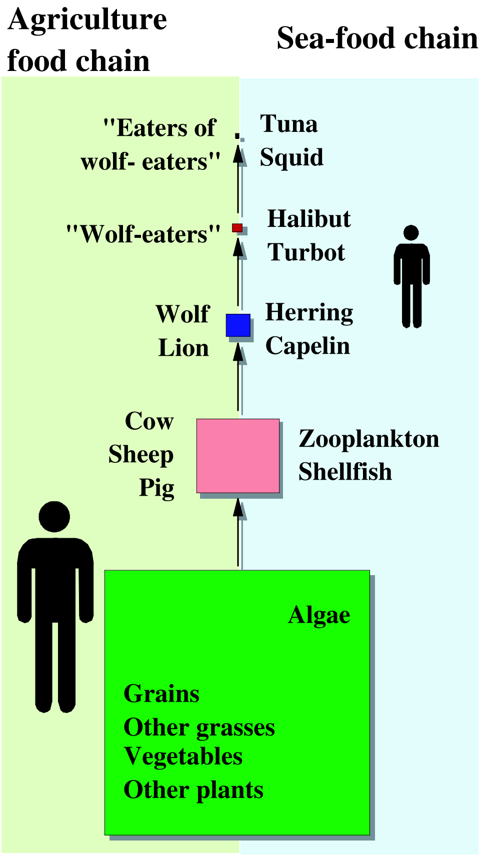

Figure 15.2: Schematic illustration of the human trophic level in the agriculture food chain and the human seafood chain. Our food from the agriculture food chain is harvested approximately 2 levels lower in the food web than in the seafood chain.

products from seafood and agriculture, or the human trophic position for these types of food. In the agricultural food web, humans primarily feed on the primary producers, but also on herbivore animals. Food items from higher trophic levels are well known in many cultures, but such food does not contribute significantly to the global food supply. Accordingly, it may be deduced that we feed between trophic level 1 (plants) and 2 (herbivore animals) in the agricultural food web (herbivore–omnivore), which means 0–1 trophic transfers, closer to 0 than 1 because we eat more plants than meat (see Figures 15.1 and 15.2).

The situation is quite different for seafood. Humans consume some macroalgae and some animals that feed on algae (e.g., mussels and sardines in upwelling systems). 1st carnivore stocks (animals eating herbivore animals, e.g. zooplankton) and species even higher in the food web are the most important commercial resources harvested from the ocean. A significant fraction of the first carnivore stocks is only used indirectly for human consumption, as they are refined through marine aquaculture or agriculture. The overall result is that we most likely feed between levels 3 and 4 ($1^{st}$ and $2^{nd}$ carnivores) in the marine food web, meaning that the primary production have passed 2–3 trophic transfers before human consumption.

The above considerations are again oversimplifications, but still relatively robust.

It nevertheless follows that humans feed about two trophic levels higher in the marine food web than in the typical agricultural one. If the primary production was equal, this is compatible with FAO statistics showing that only 1% of the total energy available to humans originates from marine primary production.

The contribution of proteins becomes higher, because we primarily feed on marine animals. The huge potential to enhance the marine harvesting of bio-resources is to catch the steadily declining carbon before conversion to carbon dioxide during respiratory processes. This implies harvesting and cultivation of organisms at lower trophic levels.

## 15.2 Objectives and programme structure

MARICULT was initiated to examine possibilities for increasing the sustainable culture, harvesting and use of marine resources in the future. A main question is whether increased activity in mariculture will be feasible and acceptable from an environmental point of view. The ultimate goal of MARICULT (1996–2000) has been:

- *To provide a basis for the evaluation of environmental constraints and the potential for increased sustainable provision of food, raw material and energy from the ocean.*

A further exploitation of the marine system should be based on knowledge of how the system functions. Such knowledge was needed to obtain the main objectives of the Programme, and the core activity of MARICULT has therefore been fundamental, strategic research on the marine ecosystem. This represents a main strategic decision meaning that the critical evaluations of both environmental constraints and possibilities for developments in the field of mariculture and marine management must be based on scientific knowledge. New concepts of harvesting and mariculture have to be both sustainable and environmentally acceptable. The production potential of new methods should therefore always be elaborated together with the environmental impact of the methods.

Two main activities were originally planned:

- Sub-programme ‘Marine food webs’
- Sub-programme ‘Marine macroalgae’

Sub-programme ‘Marine macroalgae’ was not implemented, mainly because of problems in obtaining adequate funding for the planned research activities. The environmental perspectives were given the highest priority in Subprogramme ‘Marine food webs’. The research was organized within four main research areas. The main objectives of Subprogramme ‘Marine food webs’ (hereafter denoted MARICULT) were as follows:

Figure 15.3: Examples of mesocosm systems that are land based (left figure) or suspended in the sea (right panel). Land based mesocosms were used for studies of benthic organisms exposed to enhanced concentrations of nutrients whereas suspended mesocosms of variable volumes (2–50 $m^3$) were used for planktonic organisms.

- *To understand how enhanced natural or controlled nutrient supply and appropriate restocking measures of marine systems can affect the marine production and harvesting potential.*

- *To gain insight into the assimilation and cycling of nutrients in pelagic and benthic marine ecosystems and define the conditions which result in undesired environmental situations.*

## 15.3 Environmental constraints and sustainability

The ultimate objective of MARICULT has been to *provide a basis for the evaluation of environmental constraints and the potential for increased sustainable provision of food, raw material and energy from the ocean.* The work carried out to contribute to this ultimate objective involved fundamental research related to food web structure and functioning in the marine ecosystem as well as more applied research and testing of concepts for increasing the harvesting potential. Fundamental aspects are important because the critical evaluations of both environmental constraints and possibilities for exploitation must be based on scientific knowledge. New concepts of harvesting and mariculture must be both sustainable and environmentally acceptable. A research strategy of MARICULT has been that the environmental impact of new concepts should be elaborated together with their production potential and not afterwards.

### 15.3.1 Response of nutrients on lower food web structure and function

Many projects in MARICULT have examined various aspects of the lower pelagic food web, whereas a few projects have treated fundamental aspects of changing the structure and function of benthic communities (see bibliography in Olsen et al 2001; www.maricult.org ). Studies have been undertaken in cultures, in mesocosms (Figure 15.3) and in open marine systems. The project work has supported earlier findings on many points, but also provided substantial support for other less known relations. Some examples of results and conclusions generated in the projects are as follows:

- Balanced N:P:Si nutrient perturbations of NE Atlantic waters support fast-growing diatoms, but this is not necessarily true for Baltic waters.

- Picocyanobacteria form a ubiquitous dominant group in all types of European coastal waters during mid summer and early autumn.

- Picocyanobacteria do often not respond to nutrient perturbations, most likely because they are controlled by grazing or viral infection.
- Many species of eucaryotic phytoplankton, although not all, responded positively and in a predictable way to nutrient enhancement.
- Cell lysis of phytoplankton is an important process in oligotrophic Mediterranean waters, but is not that important in the NE Atlantic.
- Heterotrophic nanoflagellates, ciliates and mesozooplankton all contribute significantly to consumption of primary production, and grazers harvest approximately 50%.
- Smaller grazers feeding on bacteria and picocyanobacteria are, in relative terms, more important in oligotrophic waters than in meso/eutrophic waters, where larger grazers and ciliates become more important.
- Little energy and materials were transferred from the microbial food web to the main food chain; the microbial pathways through heterotrophic nanoplankton and ciliates were insignificant.
- The energy was transferred from primary production through three parallel food webs rather than through a single food web, i.e., autotrophs were the most important food items for all heterotrophic groups.
- Enhancement of nutrient supply blew up the autotrophic fluxes more strongly than the heterotrophic ones.

It can be summarized that there is a relatively tight coupling between the nutrient supply rate to productive waters and the primary production of phytoplankton, which is not very surprising. This has been repeatedly demonstrated both in closed experimental ecosystems and in open natural coastal ecosystems. The responses of animals feeding on phytoplankton and other food sources were slower, less predictive on the species level, but generally positive as well. Horizontal water transport, vertical mixing processes and interactions with benthic communities make registrations of the slower animal responses difficult during experimental exercises, but this does not mean that there is a lack of response. It is, however, important that the predictability of responses on population level will become gradually less as we move up the food web. There is certainly an empirical positive relationship between nutrient supply and secondary production, including fishery yields, on a regional scale, but the predictability is questionable for single populations feeding high up in the food web.

### 15.3.2 Production perspectives

Research in MARICULT has not involved work that may contribute to enhanced value all through the seafood value chain — from management, harvesting technology, the wide spectra of downstream refining activities, logistics and market-related issues. Moreover, the priorities of optional methods of sea ranching were tuned down in the course of the Programme because of legal problems, which are now solved in Norway. It will be important to include aspects of and combinations with sea ranching at a later stage.

The above background discussion of food web energetics based on empirical data and the simplest trophic dynamic model showed that:

- The potential of marine harvesting is, within limits, proportional to the primary production of phytoplankton, which again depends on the physical forcing mediating nutrient supply to productive waters, and
- Inversely exponentially related to the number of trophic transfers that primary assimilated production must pass through before being harvested. As much as 80–90% of the energy (biomass) is lost during each trophic transfer.

The low contribution of fisheries and aquaculture to human food compared to the contribution by agriculture can be understood because:

- Current harvesting of the marine production potential is inefficient because we primarily exploit first and higher carnivores.
- Mariculture has restricted potential because most cultured marine species are secondary or higher carnivores that require marine food.

A general strategy to increase the marine harvesting potential is therefore to harvest at a lower trophic level. There are obvious technological constraints in harvesting small particles like phytoplankton and zooplankton. On the other hand, marine macroalgae represent an easily harvestable resource. There are major cultural and social implications of changes in harvesting strategies and challenges in resource management. The strategy of harvesting at low trophic levels is widely accepted in agriculture.

The general strategies to increase the potential of mariculture are to increase the culture efforts of herbivore/omnivore animals (algal eating/omnivore, e.g. mussels) and to use food resources for traditional carnivore aquaculture that are harvested at primary producer or herbivore level, in accordance with the above strategy.

These general strategies formed the basis of the further identification and evaluation of concepts to obtain higher marine harvesting potential, in accordance with the ultimate objective of MARICULT. There are available options for further elaboration. One major challenge is to harmonize environmental and resource related perspectives of nutrients, which are both resources and potential environmental problems. Concepts that are proposed by MARICULT consider the above general strategies and fulfil the following criteria:

- The potential for enhanced harvesting or cultivation must be significant.
- The activity is environmentally sustainable.
- There is an economic potential that can, within acceptable risks, become realized through further research and developments.
- There is a market, or at least a potential market, for the product.

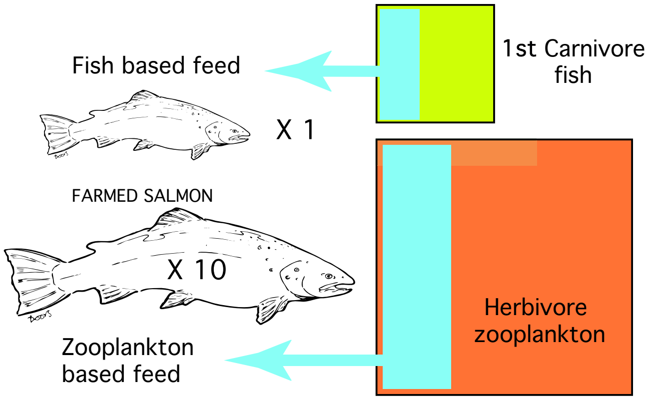

Figure 15.4: Theoretical scheme illustrating the potential benefits of harvesting resources for salmon feed on herbivore zooplankton level. Feed for farmed salmon is currently based on 1st carnivore fish (arbitrary amount for fish farming, illustrated by blue square). If the zooplankton produced on the trophic level below is harvested instead — this zooplankton is the food of 1st carnivore fishes — the salmon production can be increased by a factor of 10.

The following concepts of harvesting and cultivation are proposed:

- Concept 1: Harvesting of herbivore zooplankton resources, including copepods and krill
- Concept 2: Cultivation of benthic, herbivore/omnivore animals, exemplified by blue mussel
- Concept 3: Enhancement of production potential by creation of artificial upwelling systems
- Concept 4: Strategic fertilization or use of available nutrient resources
- Concept 5: Further exploitation of biomass from macroalgae

Figure 15.5: Harvesting of red feed (*Calanus finmarchicus*) using pelagic trawl in the spring in northern Norway.

All concepts involve harvesting or cultivation at low trophic levels, and Concepts 2 and 5 may readily be combined with strategic fertilization or utilization of other available nutrient sources, e.g. from agriculture or aquaculture. It is important to note that some methods are not feasible for all coastal regions. All methods are believed to be well suited for Norwegian waters, but it will for example not be feasible to harvest herbivore zooplankton from oligotrophic waters. Moreover, artificial upwelling systems can, with our current perception, most easily be created in a physical partly enclosed and deep fjord. The potential of mussel production and harvesting or cultivation of macroalgae is more widely distributed.

### Concept 1: Harvesting of herbivore zooplankton resources, including copepods and krill

Some regions of the worlds oceans have large stocks of herbivore copepods and krill that are abundant and potentially exploitable, depending on their distribution in time and space (Figure 15.5). The fact that these zooplanktons are food for important fish stocks brings up a management and political dimension, and the potential interaction with fisheries must therefore have a main focus. It is important to note that 10% of the annual herbivore production will be comparable to the entire production of planktivore (1st carnivore) fish, and that 1% harvesting of this herbivore production is still a significant figure (see example in Figure 15.4). If the zooplankton production in the sea tends to be food limited, we may expect that moderate harvesting primarily will result in less mortality of zooplankton and not necessarily in reduced standing stocks and availability for planktivore fish. If, on the other hand, temperature or advective transport is more important than food limitation, harvesting will have greater impact. These questions are among the major challenges to explore.

The potential of harvesting zooplankton is considerable. It is in particular important to clarify the possibilities, constraints, and consequences of large-scale application of marine zooplankton for fish feed and industrial raw material. It will be important to learn from experience in the current krill fisheries.

### Concept 2: Cultivation of benthic, herbivore/omnivore animals, exemplified by blue mussel

The theoretical down ‘the food web’ potential of culturing herbivore animals in the ocean is high, but there are obstacles that restrict exploitation of primary production in practical mariculture operations. In northern Europe, the blue mussel may represent an interesting species (Figure 15.6). Cultivation requires space in the coastal zone, and appropriate locations must be biologically rich and physically turbulent enough to support an economically feasible production. It is in particular interesting that if we employ appropriate technologies, we can utilize some of the nutrient resources that are residue from agriculture and intense aquaculture for mussel production. These resources, which are released into coastal waters, may be brought back into controlled biological cycling through mussel cultivation. Knowledge of the fate of anthropogenic nutrients and hygienic aspects in the coastal zone will most likely allow such applications, as demonstrated in a MARICULT project in the Larvikfjord.

Mussels are attractive for direct consumption, but a major byproduct of small individuals must be exploited for other purposes. This bulk resource can be used for fish feed. The blue mussel is a species with growth potential high enough to become a feed resource for marine aquaculture. This will require production technologies that are still not invented. It is an attractive option to bring nutrient discharge from intensive aquaculture into blue mussel biomass and then back into fish feed. This will contribute to move the cultured fish species down the food web and secondly to enhance the production potential of cultured fish. The need for knowledge on energy and material cycling in fish farming, its interaction in the coastal ocean, knowledge on threats of disease spreading, and the need to improve production technology suggests that these options are not immediately available.

### Concept 3: Enhance production potential by creation of artificial upwelling systems

The large upwelling areas of the world's oceans are very productive. The fundamental physical and biological mechanisms that result in strong fertilization by deep water, short food webs, and accordingly high harvesting potential, have for long time been a challenge for science. It is important to note that these high productive areas are not recognized as environmental problems. It is a challenging question if smallscale highly productive upwelling systems can be created artificially in suitable locations. An ultimate question is how the nutrient regimes of these ecosystems, driven by their characteristic physical forcing, results in short and highly productive food webs.

MARICULT has supported an initiative to explore the option of improving productivity, primarily as a means of enhancing the potential to cultivate herbivore animals such as mussels, and reduce the problems of toxic algae during mussel cultivation. A submerged freshwater outlet generates the upwelling energy. Preliminary model and background studies have shown that artificial upwelling of nutrient rich deep water in fjords have a potential to increase the phytoplankton production by a factor of 3–4 after the spring bloom and probably also reduce the occurrence of toxic flagellates in the phytoplankton. The Samnangerfjord in western Norway has been identified as a suitable location for testing the effects of artificial upwelling on the biological productivity of macroalgae, mussels and animals of higher trophic levels. The further development of this method will still require research and development, and it is notable that many other deep Norwegian fjords, with available nutrient-rich deep water, will most likely be suitable for this treatment. Related methods, adapted to smaller geographic scale, may be developed and used to detoxify mussels more locally.

### Concept 4: Strategic fertilization or use of available nutrient resources

There is very little doubt that the productivity of marine waters becomes stimulated and controlled by nutrient supply from deepwater. MARICULT has provided experimental data that show in detail how the lower trophic levels of the pelagic food web respond and interact to enhanced nutrient supply. Data are derived from closed experimental ecosystems, but also from experimental activities in an open coastal ecosystem exposed to sustained nutrient addition through the season (Hopavågen, Central Norway). The pattern of responses in food web structure and function are comparable to those found in the southern North Sea, which is affected by anthropogenic nutrient supply (Colijn *et al.*, 2002).

Figure 15.6: Rope cultures of blue mussel (*Mytilus edulis*).

It seems clear that the ability to control the responses of nutrients at species level is very limited for organisms at higher trophic levels. Many alternative food web pathways may become stimulated at trophic levels above herbivore zooplankton; such as primary carnivore fish, jellyfish, other invertebrate predators, or benthic animals. Production yields are therefore not adequately controlled at the species/population level, and it will generally not be feasible to fertilize marine systems to harvest carnivore species. On the other hand, in semi-closed locations, the production yields following nutrient additions may be highly predictable and efficient for macroalgae and for benthic animals that are primarily herbivore, like blue mussel. MARICULT projects have documented growth responses for blue mussels and scallops following the fertilization of an open coastal lagoon.

### Concept 5: Further exploitation of macroalgal biomass

Marine macroalgae (seaweeds) represent a poorly exploited primary biomass, only their polysaccharides are systematically used for industrial purposes. Plant breeding has hardly been applied to these plants and there is a large potential for improvement. Space and access to water are very unlikely to ever limit the cultivation of marine macroalgae. These facts alone make seaweeds particularly interesting as a source of renewable raw materials. It is a main challenge to invent competitive technology for direct utilization of n-3 rich lipids and the conversion of biomass to, for example, fish feed, food ingredients, bulk chemicals, energy carriers and other useful commodities. Another interesting aspect is to use macroalgae for combined biomass production and bioremediation measures for coastal waters.

### 15.3.3 Environmental perspectives

Nutrients are natural elements that are essential for all living organisms and incorporated in all food web components. Because of their stimulating effect on phytoplankton and macroalgal growth, major ecological changes may take place if nutrients are supplied at too high rates. Some ecological changes following enhanced nutrient emission are undesirable and not esthetically accepted because they are associated with ecosystem degradation. *The process of ecosystem enrichment by nutrients is generally denoted eutrophication.* If the process of eutrophication ends up in ecosystem degradation, the process is termed harmful eutrophication. Issues related to coastal eutrophication have been the main focus of MARICULT projects. Some general conclusions are as follows:

- Negative ecological effects caused by enhanced nutrient supply to pelagic ecosystems may occur if the primary production is not being grazed efficiently enough by zooplankton or benthic grazers, dispersed by advection or retained in deep water.
- Phytoplankton responds almost linearly to an enhanced nutrient loading rate during the first weeks of exposure (short-term response). The response on a seasonal scale or longer is more moderate and most likely nonlinear with increasing loading rate, suggesting biological acclimation of food web structure on the longer time scale.
- A wide range of pelagic and benthic buffer mechanisms work to reduce the negative ecological effects of enhanced nutrient emission in the coastal zone.
- Experiments suggest losses of integrity in food web function above a certain nutrient loading rate, suggesting a critical nutrient loading rate for the maintenance of food web integrity.

MARICULT has provided considerable further insight into the responses of pelagic and benthic ecosystems that are exposed to enhanced nutrient supply. Both the structure and function of the plankton food web are altered by enhanced nutrient supply. There are some clear differences how the ecosystems reacts in European marginal seas (Baltic Sea, Mediterranean Sea) and in Atlantic waters, but there are also great similarities. The variability in food web fluxes is much closer related to nutrient loading rates than the variability in biomasses of plankton. However, the latter compartments related better to the total nutrient concentrations in the water.

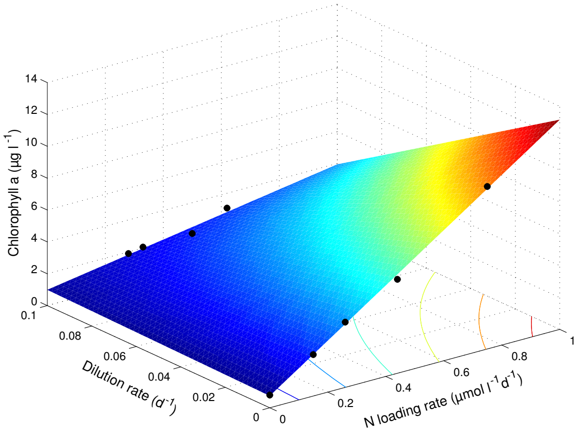

Figure 15.7: Preliminary conceptual nutrient loading model for management purposes, showing phytoplankton biomass ($\mu$g chlorophyll a L$^{-1}$) as a function of nutrient loading rate (here $\mu$mol N L$^{-1}$ day$^{-1}$, P and Si is added in Redfield proportions) and water dilution rate (day$^{-1}$).

Although still at a preliminary stage, the Programme has contributed to a conceptual platform for assessment criteria of ecosystem state and water quality of pelagic coastal waters. Many indices show a common, regionally independent pattern of variation. Primary production, mesozooplankton grazing and growth, fraction of primary production consumed by grazers, and bacterial production relative to primary production, as well as more integrated measures like cycling indices and path lengths, are all well related to the nutrient loading rate. Autotrophic biomass, the ratio of autotrophic to heterotrophic biomass, and the fraction of picocyanobacteria of the total autotrophic biomass are all well related to the total nutrient concentration. These relationships, or other integrated variables based on these, are potential candidates of response functions for nutrient management models for European coastal waters.

The analysis of elemental flow networks of the lower food web suggested an upper critical nutrient loading rate for the maintenance of the integrity of the food web. This means that energy and material transport in the lower food web will not function adequately for loading rates above this critical level. This level must be interpreted as the carrying capacity of coastal waters to accept nutrient loading without co-occurring negative ecological effects. The above biological criteria are therefore fundamental for future site evaluations for aquaculture in coastal waters.

The general response of the phytoplankton and the preliminary framework of a dose-response model for nutrients in the coastal zone are illustrated in Figure 15.7. The nutrient dose stimulated phytoplankton growth whereas the water dilution rate, which is inversely related to the water retention time, is a major modifying factor for the actual ecological effects of the nutrients.

All kinds of food production require a clean and unpolluted environment, and pollution of coastal waters by persistent toxins is a potential threat against mariculture as well as the fisheries. Heavy metals and organic toxins have been steadily phased down in western countries during the last decades, but organic toxins are still a potential problem. We have a long tradition in using the ocean as deposit for wastes, but we cannot afford to continue that practice. The mechanisms of uptake, transport and cycling of toxins in the lower marine food web are not well known, but lipid soluble components will become concentrated up the food web. This calls for attention, because harvesting and cultivation involve first and higher carnivores that may be potentially sensitive to such toxins.

Marine pollution has not been specifically treated in MARICULT. The issue is undoubtedly very important for the fishing and mariculture industries, among other things because of greater public concern about food quality and improved sensitivity and lower detection limits of analytical methods for many substances, e.g. dioxin. It is therefore paramount that the seafood industries phase down their own pollution and that they take major initiatives to reduce toxin emissions from other sources as well.

### 15.3.4 Interaction resources — environment

Coastal eutrophication is a well known environmental problem affecting coastal ecosystems and our quality of life, but nutrients are natural components in the biosphere and are not threatening for human health. The countermeasures against harmful eutrophication are, however, very expensive for society, and it is therefore important to find a sound balance between the use and protection of coastal ecosystems.

The common western principles of nutrient management are hardly sustainable, because we isolate and remove a considerable part of nutrient wastes from the biological cycle instead of putting them back into biological cycling. The principle of reduction at source is in many cases inadequate, because a considerable fraction of the nutrient emission is from diffuse sources that cannot be efficiently reduced. The counter-measure strategy that is still not explored and implemented is to reduce the ecological effects in the coastal zone by using the nutrient resources for controlled mariculture where such nutrient sources are available.

Blue mussel cultivation is an efficient means of retaining anthropogenic nutrients in the coastal zone. The species is very efficient to clear phytoplankton from the water and the food is rapidly converted to mussel biomass. This process of nutrient retention in mussel biomass obviously reduces the nutrient concentrations in the water, and it is important that this is a vital method in situations where no other water purification technologies are available. An example of the particle retention efficiency of mussels is demonstrated in the shallow Öresund Strait between Denmark and Sweden where the massive banks of blue mussels remove practically all the phytoplankton from the water drained from the Baltic Sea. The story may also be turned around; short production time and high mussel meat quality is important for the economic feasibility in mussel farming, and both are supported by high rate of food supply to the mussels. It may in fact be the case that pristine coastal waters in our part of the world may be too nutri-

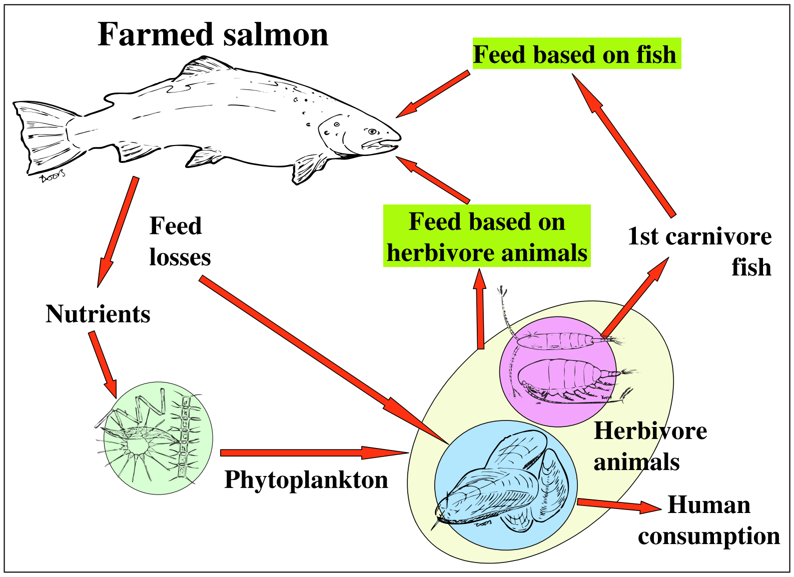

Figure 15.8: Schematic view of the biological cycle of farmed salmon. Zooplankton and blue mussel are both herbivore/omnivore animals that consume small particles of feed and more important phytoplankton produced on nutrients released by the salmon. Blue mussel is like salmon consumed by humans, and blue mussel-salmon thus forms a true polyculture system. Zooplankton is normally the food of 1st carnivore fish, the primary resource currently used for fish feed. Both blue mussel and zooplankton are future potential 'low in food web' resources for fish feed, and their application would reduce pressure on stocks of 1st carnivore fish.

ent deficient for feasible commercial production of blue mussel.

The attractive point of combining mussel production and water purification is that nutrient resources that are out of our control are utilized for food production instead of creating environmental problems and costs for society. This also represents a more sustainable way of nutrient utilization as it contributes to the closing of biological nutrient cycles. The use of anthropogenic nutrients and runoff for blue mussel cultivation has been demonstrated experimentally in the Programme. Additionally, the Limfjord in Denmark and the coastal zone of the Netherlands are both examples where eutrophication has created excellent conditions for mussel production.

Another example may illustrate a great potential. The amounts of nutrients that are released from Norwegian salmon cages represent, if converted to blue mussel biomass, an annu al production of >2 million tonnes. Not all, but a significant part of these nutrients can be retained by controlled mussel production. A schematic view of the biological cycle of farmed salmon is illustrated in Figure 15.8. Blue mussel – salmon forms a polyculture system. Grown together the blue mussel may take advantage of the discarges from the salmon farms.

A more holistic ecological view of management and resource exploitation, where we recognize that we are also components of the ecosystem, is well accepted in eastern Asian countries, but seem to be forgotten in the West. It is important to have a holistic perspective, and it may in turn contribute to more concern about the marine environment. Most people will understand the need to avoid pollution of land areas used for agriculture. The same kind of concern, which is presently not there, is also needed for the marine environment.

### 15.3.5 Contributions and user value

#### Research strategies and policy making

It is a challenge to coordinate fundamental research efforts on national and international levels without active and competent user involvement and such users are rare. Norsk Hydro has been the driving force of MARICULT, as a potential user with long-term perspectives on the issues treated, and the research councils and academic institutions have also contributed. Private funding for strategic fundamental research on the marine ecosystem, in cooperation with public funding agencies, is not common in an international context, and this makes the MARICULT Research Programme quite special. The lesson learned should be considered by research policy makers, because it is a great challenge to involve industry even in fundamental and environmental research and environmental aspects. The uncommon alliance of marine scientists and industry in the field of marine ecology has been powerful, but initially misunderstood by for example environmental organizations.

MARICULT has contributed to both scientific and political agendas, and important contributions have been:

- Significantly higher yields of marine biological resources can only be achieved by new harvesting and cultivation strategies, with stronger focus on exploitation of lower trophic levels.
- A holistic and ecological perspective must form the basis for future cultivation of the sea; an approach which considers that wastes from one organism is food for another.
- Challenging and reconsideration of environmental dogma, for example that nutrients are not toxins but rather resources for production whereas the emission of organic toxins to coastal waters is a potential threat for mariculture and the fisheries.

The understanding of interactions between environmental and production perspectives must be established on an international level. MARICULT projects have, through the channel of the European Commission projects, taken part in the Steering Committee of the ELOISE Programme (European Land-Ocean Interaction Studies), which is the European branch of the international LOICZ Programme.

### User value for management

Fundamental research on coastal eutrophication has been the main focus area of MARICULT, and the results are highly relevant for:

- A better understanding of the marine ecosystem
- The establishment of a user friendly 'nutrient dose–ecological response' model for coastal zone management of nutrient emission
- Quantification of carrying capacity of coastal waters, needed for planning of the further development of the aquaculture industry
- Evaluations of locations for mussel farming and cage aquaculture

It is with minor efforts possible to establish the modelling tools needed to manage nutrient emission in the coastal zone on a scientific basis, and not only based on the principle of a precautionary approach. This is a major step ahead. These methods are the tool needed to quantify the carrying capacity of coastal waters with respect to fish cultivation.

MARICULT has pointed to blue mussel culture as a means of utilizing nutrient wastes from human origin or from intensive aquaculture for mariculture production. These nutrient resources are regarded as potential environmental problems today. Blue mussel feeds marine algae, representing a 'marine cow', and the production potential is therefore very high. Mussel culture has because of many concurring events become prioritized all over Europe during the last few years.

It is also important to emphazise that appropriate co-location of fish cages and blue mussels may contribute to increase the carrying capacity of a location for cage aquaculture. Strategic location of mussel farms in between fish cages will most likely contribute to reduce risk of disease spreading rather than the opposite, and mussels may take advantage of the wastes generated from the cage cultures. Mussels may remove and retain bacteria from the water. These issues should be further explored, because it will reduce the requirements of aquaculture for space in the coastal zone.

### User value for industry

The user value for management is immediately relevant also for industry (see above). MARICULT has additionally provided results that are important for industry in a longterm perspective, but it may be important to identify the ways ahead already now. One example is the availability of marine-based feed for the salmon industry. There are few other options to achieve a steady increasing salmon production based on marine feed than moving the cultured salmon one step down the food web, i.e. to prepare its feed based on herbivore or marine plant biomass (see Figure 15.8).

A precautionary approach is a very important principle for sustainable development, but knowledge is needed to find the balance between sustainable use and protection of the coastal zone. Proper tools to manage nutrient emission in the coastal zone on a scientific basis will also allow the assessment of the carrying capacity of coastal locations and the feasibility of those locations for aquaculture. Steady and predictable conditions for establishment and production are paramount for the industry.

MARICULT has established a conceptual basis for increase of marine harvesting and mariculture, and a number ways to proceed has been suggested. This does not mean that the suggested concepts are the only way ahead. New legislation for sea ranching is now implemented in Norway, and this is but one aspect that should be further evaluated in light of the conceptual basis established by MARICULT. The importance of considering the identified constraints of trophic level and fertilization measures is also very relevant for sea ranching.

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# Chapter 16

# Ecological quality assessment in the EU Water Framework Directive — a new approach for protection of aquatic ecosystem

Anna-Stiina Heiskanen
Wouter van de Bund
Ana Cristina Cardoso
Peeter Nõges
European Commission, Directorate General Joint Research Centre[1]
Institute for Environment and Sustainability
Inland and Marine Waters Unit, TP 290
I-21020 Ispra (VA), Italy
anna-stiina.heiskanen@jrc.it

## Abstract

The Water Framework Directive (WFD) is a new legislative framework to manage, use, protect, and restore surface and ground waters resources and coastal waters in the European Union (EU). The aim is to ensure sustainable water management and to reach good water quality by 2015. The assessment of the ecological status and setting of the practical management goals require several steps. The process has started with the characterisation of the river basins including identification of surface water bodies and types, and identification of significant anthropogenic pressures and impacts. The water bodies will be classified in five quality classes (high, good, moderate, poor, bad) based on Ecological Quality Ratio which is a ratio between reference conditions and current status of the biological quality elements. The current descriptive criteria for high, good and moderate ecological status need to be made operational by the Member States, thus setting the practical quality targets for surface water management. National assessment systems will be harmonised through the WFD intercalibration exercise in order to ensure an equal level of ambition in achieving good surface waters status all over Europe.

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[1] The opinions presented in this paper are those of the authors and do not necessarily represent the position of the European Commission.

## 16.1 Introduction

The Water Framework Directive (WFD, 2000/60/EC) creates a new legislative framework to manage, use, protect, and restore surface and ground water resources within the river basins (or catchment areas) and in the transitional (lagoons and estuaries) and coastal waters in the European Union (EU). The WFD aims to achieve sustainable management of water resources, to reach good ecological quality and prevent further deterioration of surface- and ground waters, and to ensure sustainable functioning of aquatic ecosystems (and dependent wetlands and terrestrial systems). The environmental objectives (WFD, article 2), i.e. the good ecological quality of natural water bodies and good ecological potential of heavily modified and artificial water bodies should be reached in 2015. The implementation timetable requires several intermediate steps in the fulfilment of the technical specifications outlined in the Annexes of the WFD, first of those are already due to end of 2004 (i.e. requirements of the Article 5: Analysis of river basins characteristics, pressures and impacts, and economic analysis).

The overall complexity of the WFD and a very tight implementation timetable create challenges for the fulfilment of the requirements. Moreover, after the enlargement of the EU in 2004, the new Member States will have to implement the WFD in full, meaning that they have the same obligations and timetable as the old Member States. Therefore the European Commission and the Member States started a Common Implementation Strategy (CIS) in 2001 (Anonymous, 2001). This has resulted in a number of guidance documents, where the various technical issues related to the WFD implementation requirements are interpreted according to the common understanding of the Member States (Anonymous, 2003a,e,b,d,f). The guidance documents are based on large number of preparatory documents and expert meetings where various issues were discussed and agreed. They are not legally binding, but present examples of best practises and common understanding of the legal requirements, which may be referred in the future as correct interpretations of the legal implementation requirements.

The WFD stipulates that the ecological status of the surface water is defined as "*. . . an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters, classified in accordance with Annex V.*" (WFD, Article 2: 21). This implies that classification systems for the ecological status should evaluate how the structure of the biological communities and the overall ecosystem functioning are altered in response to anthropogenic pressures (e.g. nutrient loading, acidification, exposure to toxic and hazardous substances, physical habitat alterations, etc.). Such requirements are a novel approach in the European water policy, which has been mostly based on the regulation of emissions at the source through the establishment of emission limit values (ELV), rather than on the regulation of the allowed impacts on the recipient ecosystems. Nature conservation legislation such as the 'Birds Directive' (79/409/EEC) and the 'Habitats Directive' (92/43/EEC) have established a legislative framework for protecting and conserving Europe's wildlife and habitats (creation of a coherent ecological network of protected areas across the EU – NATURA 2000). The Nitrates (91/676/EEC) and Urban Waste Water Treatment (91/271/EEC) Directives already included the requirement for the assessment of the vulnerability/sensitivity of the recipient surface waters to pollution (mostly caused by nitrogen and phosphorus compounds). However, the criteria how the sensitivity should be assessed are subject to different interpretations by the Member States, and the directives do not include any mechanism to harmonize these interpretations.

In this chapter we will discuss the novel approach required by the WFD for a EU wide classification of the ecological quality of surface waters and the requirement for the harmonisation of the classification systems. We will also highlight management implications and some research needs, and review of the WFD legal text and the relevant CIS guidance documents. We present and analyse the agreed approaches outlined in the WFD CIS guidance documents, and discuss the potential problems and benefits of those approaches.

approaches.

## 16.2 Assessment of the surface water ecological status in the WFD

The requirement of the detailed assessment of the ecological status of the water bodies in the river basins is the basis for the protection of the aquatic ecosystems in the WFD. There are several articles which set the timetable and steps for the assessment process and the details of the tasks required to be undertaken are described in the detail in the Annexes of the WFD for different surface water categories (Table 16.1). The first task is to complete a detailed characterization of all surface waters in each EU Member State (Step 1).

The monitoring systems need to be operational only by the end of 2006 (Step 3), which implies that there will be little WFD compatible monitoring data available for carrying out the establishment of the reference conditions. Although Step 4 (Classification of surface water bodies) is only due in 2009 when the classification status of Member States surface waters need to be presented as colour-coded maps as part of the river basin management plans, it really should be already initiated in 2003 for the selection of sites for the intercalibration network (since the process for the intercalibration needs to be initiated already in 2003; step 2), and continued in 2004 in the characterisation and assessment of sites that are in risk to fail the environmental objectives (i.e. those that are likely to be classified as moderate ecological status or below) as a part of step 1 (Figure 16.1).

The first step — characterisation of surface waters — requires an assignment of all rivers, lakes, transitional and coastal waters into geographic units: river basin districts and further to river basins (Anonymous, 2001). This includes identification of surface water bodies, grouping them into types, and the definition of biological and chemical reference conditions (natural baseline) for those types. Water bodies should be discrete and significant sub-units with uniform typology and quality status. Water bodies as such will be the basic unit for reporting and assessing compliance with the directive's environmental objectives (Anonymous, 2003a). Concurrently, the significant anthropogenic pressures must be identified, and their impacts on the surface water status must be analysed (Anonymous, 2003e).

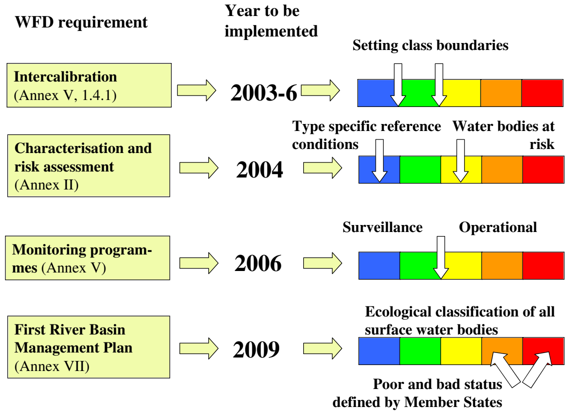

Figure 16.1: . Steps of the Water Framework Directive implementation timetable (with relevant Annexes) which require preliminary setting of the ecological status class boundaries.

### 16.2.1 Typology

The main purpose of typology is to enable type specific reference conditions to be defined which in turn is used as the anchor of the classification system (Anonymous, 2003b). Water body types should be characterised based on geographical, geological, morphological and physical factors. In ecological quality assessment, the purpose of typology is to group sites where the biology is similar in the natural baseline conditions, to enable the detection of the effects of human disturbance. This is only meaningful when the variability of the biological parameters is smaller within types than between types, depending not only on the typology, but also on the biological parameters chosen. The typology should therefore identify physically and morphologically distinct water body groups

Table 16.1: Requirements for the assessment of the ecological status in the WFD. The number of articles where the requirement and time-table for the tasks (only those relevant for the ecological status assessment) are given, and the Annex where the task is described more in detail.

| Step | WFD Requirement | WFD Article No. | Annex No. | Tasks relevant for the ecological status assessment | Year to be completed |
|---|---|---|---|---|---|
| 1 | Characterisation of surface waters | 5 | III | Geomorphological-physical types for all surface waters and type-specific reference conditions for biological quality elements | 2004 |
| 2 | Setting the environmental objectives for protection and restoration of all waters — definition and harmonisation of concept 'good ecological quality' | 4 | V | Identification of criteria for high, good, and moderate according to Tables 1.2.1-5. Harmonization of the ecological quality classification systems between countries (1.4.) ('Intercalibration exercise') | 2006 |
| 3 | WFD compatible monitoring programmes established and operational | 8 | V | Establishment of the surveillance, operational and investigative monitoring programmes | 2006 |
| 4 | River Basin management plans ready and published | 13 | VII | Classification of all surface water bodies using Ecological Quality Ratios based on biological quality elements | 2009 |

enabling comparison of 'like with like' (Anonymous, 2003b,d). This means, for instance, that naturally eutrophic lakes have different reference conditions than oligotrophic lakes, resulting in different scales and requirements for good ecological quality for these different lake types. The WFD allows two different approaches for typology 'System A' and 'System B'. The difference is that System A prescribes how water bodies shall be characterised spatially (ecoregions) and with respect to specific altitude, size and depth intervals, and that System B, besides lacking this prescription, permits the use of additional factors (Anonymous, 2003b).

Validation of different types by evaluating the within-type variability of biological communities requires good quality biological monitoring data from unimpacted sites, which is currently not available from many Member States (Anonymous, 2003b). For many types, most of the water bodies are significantly impacted by human pressures, and therefore it will be difficult to distinguish statistically between the impact of pressures and the type-specific factors that shape the aquatic biological communities.

In the WFD implementation, typology is needed for different purposes. For reporting and intercalibration a typology should ideally be simple and applicable all over Europe for all quality elements. On the other hand, defining reference conditions may require complicated typologies. Different regions and different quality elements may also require different typologies. Typology systems should have a certain level of flexibility, with the possibility to adapt and refine them when more and better biological monitoring data become available.

Two main approaches can be taken in the determination of the surface water body types: 1) types are defined from knowledge of how physical drivers determine biological communities ('*a priori approach*'), and 2) types are distinguished by analysing survey data from reference sites ('*a posteriori*' approach) (Table 16.1).

Table 16.2: Features of '*a priori*' and '*a posteriori*'typology systems

| 'a priori' typologies | 'a posteriori' typologies |
|---|---|
| Should be based on knowledge of how biology is determined by geography/physical conditions | Based on physical and biological monitoring data from reference sites |
| Few data needed to define typology | Typology depends on available data (quality elements, parameters, from which region), and on quality of data |
| Types not necessarily biologically meaningful because of incomplete knowledge — need for validation using targeted field sampling | Types biologically meaningful |
| Reference conditions can be determined by different approaches (expert judgement, spatial, historical/ paleoreconstruction,modelling) | Reference conditions implicit |

System A of the WFD is an example of an '*a priori*' example; system B typologies can be defined using both approaches. The '*a priori*' approach presupposes that biological communities are unambigiously separable, and that we know what drives those biological communities (for example, macrophytes need a certain quantity of nutrients and light, and will therefore always dominate in lakes with geology G, when mean depth <z). However, the '*a priori*' classes are not necessarily biologically meaningful due to an incomplete understanding what drives the biology. An advantage of a verified '*a priori*' typology is that it is likely to be relatively robust, because it is based on knowledge of the biology rather than purely on statistical correlation. The '*a posteriori*' approach requires a sufficiently large number of sites in natural baseline conditions (reference sites) and good quality biological data. An advantage of the '*a posteriori*' approach is that it has a high degree of objectivity. On the down '*a posteriori*' typologies depend on the data available — they are usually specific for a specific quality element.

Only very few countries have established advanced '*a posteriori*' systems for classification and typology. One of the main reasons preventing the development of such systems is that it requires the availability of high-quality data from many water bodies, sampled in a standardised way. The UK RIVPACS approach (Wrigth, 2000), developed to predict reference macroinvertebrate communities in rivers, is a very good example. The potential of this approach is demonstrated in Swedish studies, where RIVPACS-type models (SWEPACS) have been successfully developed for both lake (littoral) and stream (riffle) macroinvertebrate communities (Johnson, 1995). The European research projects STAR[2] and FAME[3] are extending such an approach over a larger geographical area, including wider range of river types, and more biological quality elements collected using harmonised methods. Furthermore, a European research project, CHARM[4] is developing harmonised typology for the coastal Baltic Sea first starting from '*a priory*' typology that will validated using existing biological monitoring data from Baltic Sea countries.

### 16.2.2 Reference conditions and classification

The Directive stipulates that the ecological quality classification "*. . . shall be represented by lower*

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[2] Standardisation of river classifications: Framework method for calibrating different biological survey results against ecological quality classifications to be developed for the Water Framework Directive. WFD on the web: www.eu-star.at

[3] Development, Evaluation and Implementation of a Standardised Fish-based Assessment Method for the Ecological Status of European Rivers. FAME project

[4] Characterisation of the Baltic Sea Ecosystem: Dynamics and Function of Coastal Types. CHARM project

*of the values for biological and physico-chemical monitoring results for the relevant quality elements...*" (WFD, Annex V, 1.4.2). Furthermore it is required that the ecological quality of water bodies should be classified into five quality classes (high, good, moderate, poor, and bad) using Ecological Quality Ratio (EQR), defined as the ratio between reference and observed values of the relevant biological quality elements.

The relevant biological quality elements for the different water body categories are specified in Table 16.2.

The supporting hydro-morphological (such as quantity of water flow in rivers or residence time of water in lakes) and physico-chemical elements (such as salinity, acidification status or nutrient conditions) are required to be used in the classification process in combination of the biological quality elements, especially in the determination of the 'high', 'good' and 'moderate' quality classes (Figure 16.2). For the lower classes biological quality elements needs to be considered only because, if those imply lower quality also hydro-morphological or physico-chemical quality elements are poor or bad by default (Anonymous, 2003d).

Reference conditions can either be spatially based, i.e. defined by collecting biological information from water bodies which are (almost) in natural base-line conditions (sites with minor anthropogenic impacts), or derived by modelling, or by combination of those. If reference conditions are to be defined using modelling, either predictive models or hind-casting using historical, palaeolimnological, and other available data can be applied (Anonymous, 2003d). In many countries there may be no reference sites available or data are insufficient to carry out statistical analysis or validate models. In that case, expert opinion may be the only possibility to define reference conditions. Also the establishment of common networks of reference sites could help in setting type specific reference conditions in a comparable way between different countries.

A stepwise procedure for establishing reference conditions is suggested (Figure 16.3). This would depend on the availability of data form different water bodies types. If there is data available or pressure criteria (Anonymous, 2003b) can be used to select minimally impacted sites for different types, suggested approach would be to establish a network of reference sites, where data for biological quality indicators in reference conditions can be obtained. In combination to that also predictive models can be validated and used to establish reference values for the parameters that represent the different biological quality elements, and apply these models to sites where biological data may be scarce or not available for all quality elements. In some cases collaboration across national borders is required since natural baseline sites for a given types may be found in other countries. If there are no sites with minor anthropogenic impacts, historical monitoring data or paleoecological reconstruction methods should be used to for reconstruction of reference conditions before the time period of significant human impact (Figure 16.3). Expert judgement may be needed to evaluate when the human impact started to increase, and which period would represent conditions with a minor impact. Finally, if no site nor any data is available for a given type, expert judgement remains the only alternative.

A case study for the establishment of reference conditions for lake phosphorus concentrations was carried out for Swedish lakes using combination of different approaches (R. Johnson, pers. comment). The results indicated that variability in the established reference phosphorus concentrations may be large depending on the method. A Danish study on setting the reference conditions for coastal eelgrass (*Zostera marina*) populations comparing the present and past depth distribution of eelgrass, indicated that the reference conditions based on historical data had to be established site specifically, since the variability within the type specific reference conditions was too large which did not allow reliable calculation of EQR values (Krause-Jensen *et al.*, in press).

Schernewski and Neumann (in press) compiled estimations of pre-industrial riverine and atmospheric nutrient loadings to the Baltic Sea using

Table 16.3: Biological quality elements and composition metrics required for the classification and assessment of the high, good, and moderate ecological quality status of different surface waters according to the normative definitions described in the Annex V of the Water Framework Directive. 1 = Taxonomic composition, 2 = Abundance, 3= Biomass, 4 = Plankton blooms, 5= diversity, 6= sensitive taxa (e.g. sensitive vs. insensitive species of organisms), 7 = age structure. * transparency as a proxy of phytoplankton biomass; ** macroalgal cover as a proxy for biomass.

| Quality element | Rivers | Lakes | Transitional waters | Coastal waters |
|---|---|---|---|---|
| Phytoplankton | 1, 2, 3*, 4 | 1, 2, 3, 4 | 1, 2, 3, 4 | 1, 2, 3, 4 |
| Aquatic flora | 1, 2 | 1, 2 | 1**, 2 | 1**, 2, 6 |
| Benthic invertebrates | 1, 2, 5, 6 | 1, 2, 5, 6 | 1, 2, 5, 6 | 1, 2, 5, 6 |
| Fish | 1, 2, 6, 7 | 1, 2, 6, 7 | 1, 2 | – |

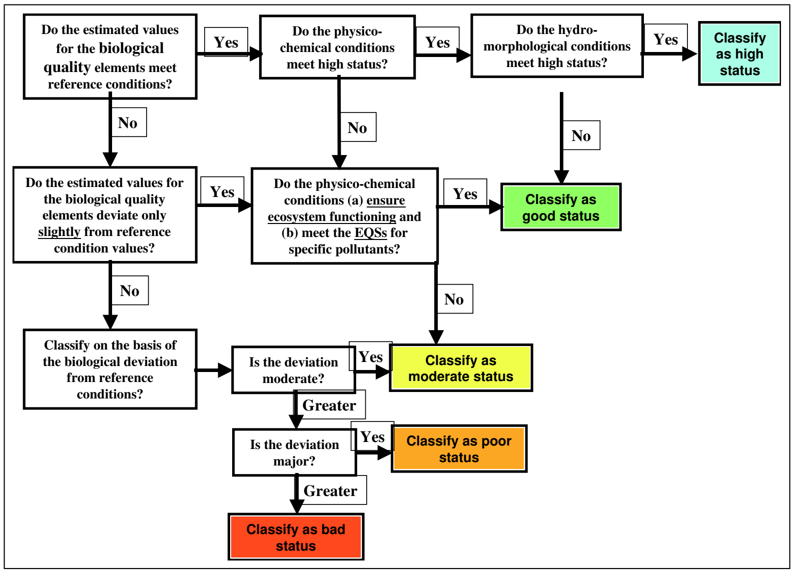

Figure 16.2: Relative roles of biological quality elements and supporting hydro-morphological and physico-chemical conditions in the ecological status classification (modified from Anonymous, 2003b.

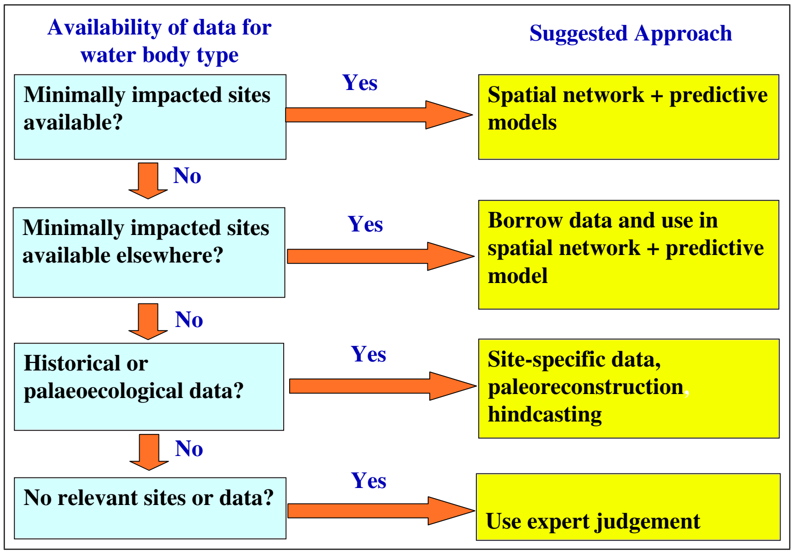

Figure 16.3: A step-by-step approach for selection of the method for determination of reference conditions for surface water bodies depending on available information and data.

long-term monitoring data from rivers and various literature sources. These loadings were used as input to an integrated biogeochemical physical ecosystem model to obtain reference nutrient and chlorophyll concentrations for different coastal areas of the Baltic, as well as the central Baltic Sea. They estimated that in the central Baltic Proper the average annual chlorophyll concentrations were reduced 20–40% from those of 1980's, and in the eastern coastal Baltic even 60% reduction of chlorophyll was obtained in the model calculations. However, one has to treat model calculations with caution, especially if the models are validated based on present day conditions and data can be used to simulate nutrient dynamics more than 100 years ago when conditions may have been quite different. Alternatively Andersen et al. (sumbitted) have used palaeoecological approach to determine pre-industrial nitrogen concentrations in some coastal locations in the Baltic. Their approach was based on analysis of fossils diatom assemblages from sediment cores sampled, and using calibrated transfer functions to evaluate former nitrogen concentrations in those locations. Although these models are useful tools for estimation of past nutrient concentrations, still reference conditions for the biological quality elements will also be required, in order to obtain EQR-values for the coastal types

In the WFD, high ecological status is defined as 'slight' or 'minor' deviation from the reference conditions of a surface water body type, while the good status is defined as 'small' deviation. The CIS guidance documents suggest that due to the variability of type specific reference conditions, it will be more practical to consider that high status is equal to reference conditions (Anonymous, 2003b,d). In order to be able to set the quality classes and their borders, more detailed criteria are needed. There should be also an agreement of how the quality borders are set statistically (Anonymous, 2003b). The WFD requires a 'one out – all out' approach for classification, potentially using a high number of quality elements, and the status of a site should be determined by the lowest value of the quality elements used. Various quality elements have different sensitivity to pressures, thus they may reflect the impacts of pressures differently. Because all quality elements have a certain error (that can be very high), the potential of misclassification is amplified by the number of quality elements included in the 'one out – all out' system. A recent guidance prepared by the WFD CIS working group on Ecological Status provides recommendations how different quality elements could be grouped in the process of classification depending for which pressures those would be sensitive for (Anonymous, unpublished).

At the moment there is no scientific basis for setting the class boundaries to be corresponding to the normative definitions in Annex V (1.2.1-5). In 'good' status the biological quality elements should indicate only 'slight' deviation from reference conditions, and the hydromorphological, physico-chemical, and chemical quality elements should ensure ecosystem functioning (Anonymous, 2003b). However, it is not clear how the ecosystem functioning in good status should be defined. The functional diversity of the ecosystems trophic structure may display high variability of response (Kassen *et al.*, 2000; Chase & Lieibold, 2002) when subjected to human impacts such as nutrient loading (Worm *et al.*, 2002).

One possible approach would be to establish functional relationships (i.e. dose-response models) between pressures and biological quality element (or parameters) which are sensitive for those pressures and specific for surface water categories and types. The quantitative changes of the parameter values could then be matched with the normative definitions in the Annex V of the WFD, in order to enable identification of 'very minor' and 'slight' changes from the reference conditions, and further setting of the quantitative values for the class boundaries 'high-good' and 'good-moderate' (Figure 16.4). However, in order to verify that in good ecological status physico-chemical conditions should enable 'ecosystem functioning' conceptual understanding of the linkages between ecosystem components as response to major pressures would be required. This is also in line with the requirement of the 'one-out-all-out' principle where the

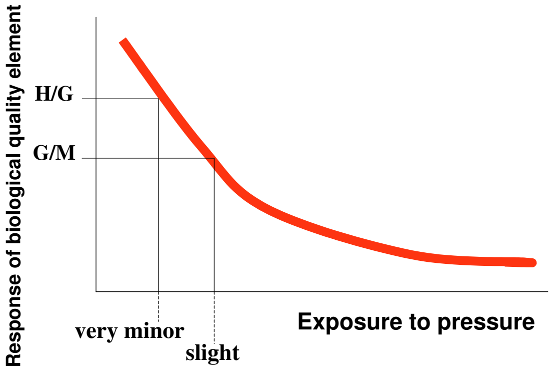

Figure 16.4: Schematic presentation of a possible 'dose-response' relationship between biological quality element (or an indicator/ parameter representative for that) and a pressure gradient. Such functional relationships could be used for defining quantitative changes of the indicator values (as response to increase in pressure) which can be linked to the normative definitions 'very minor' and 'slight' as described in the Annex V of the WFD, and further used in the setting of quantitative values for the classification boundaries high-good (H-G) and good-moderate (G-M).

lowest of the quality elements will determine the final classification status of the water body. Ultimately impacts on one trophic level will have consequences also to other components of the ecosystem and therefore all biological quality elements should be considered (if the natural variability is small enough to allow detection of impacts).

### 16.2.3 Intercalibration

In order to ensure comparability of the classification results based on the Ecological Quality Ratio (EQR) scales between the different EU countries and to obtain comparable criteria for the interpretation of the normative definitions for different quality classes (i.e. there needs to be a common understanding of the good ecological status of surface waters) all over EU, harmonisation of the ecological classification systems is needed. To achieve this, the directive requires an intercalibration exercise, that will be completed by the end of 2006. Prior to this an intercalibration network consisting of selected intercalibration sites needs to be established by the end of 2004 (Anonymous, 2003f).

Member States have agreed on common intercalibration types for the network, as well as pressures and quality elements that will be the focus for the intercalibration. Each of these common types is shared by a number of countries forming geographical intercalibration group (GIG). Currently (November 2003) there are sixteen (16) GIGs identified for both inland and coastal waters in the draft register forming the intercalibration network (Table 16.4).

Many countries belong to two or three GIGs of the same water category (Table 16.5), linking the different regions of Europe. These GIGs will make groups of countries that will carry out intercalibration exercise together using the selected intercalibration sites as common test sites to compare their national assessment systems for surface water ecological quality.

For example, in the northern GIG for lakes, currently (status in November 2003) seven common types have been identified for the draft intercalibration register (Table 16.6). These types are shared by five countries, which will select water bodies to the intercalibration network.

Water bodies for intercalibration should be selected so that their present quality status should be provisionally representative for the border between high and good or good and moderate classes. In the selection process either pressure criteria (Anonymous, 2003b) and/ or available biological and chemical data can be used. Each country should select at least two sites for each quality border (Figure 16.5), resulting in a number of comparable sites for each type within each GIG (Anonymous, 2003f).

The aim of the intercalibration exercise is to set EQR values for the relevant class boundaries (high-good, good-moderate). The selection of the intercalibration sites will reflect the Member States perception of the quality classes. Since the WFD compatible monitoring program are not yet operational during the intercalibration process (Anonymous, 2003c), the site selection and the exercise have to base on existing data. Since current biological monitoring data is scarce, or even non-existing in many EU countries, intercalibration ex-

Table 16.4: Overview of Geographical Intercalibration Groups (GIGs) with numbers of countries belonging to the GIG, numbers of common intercalibration types, and numbers of sites currently (status in November 2003) submitted to the draft intercalibration register (n.d: not defined)

| GIG | | Number of Countries | Number of Types | Number of sites |
|---|---|---|---|---|
| RAL | Alpine rivers | 6 | 2 | 104 |
| RBA | Baltic rivers | 4 | 4 | 19 |
| RCE | Central rivers | 16 | 6 | 225 |
| REC | Eastern continental rivers | 9 | n.d. | 5 |
| RME | Mediterranean rivers | 7 | 5 | 104 |
| RNO | Northern rivers | 5 | 8 | 130 |
| LAL | Alpine lakes | 8 | 8 | 38 |
| LAT | Atlantic lakes | 4 | 3 | 27 |
| LBA | Baltic lakes | 4 | 5 | 36 |
| LCE | Central lakes | 10 | 8 | 41 |
| LEC | Eastern continental lakes | 9 | n.d. | 1 |
| LME | Mediterranean lakes | 7 | 9 | 40 |
| LNO | Northern lakes | 5 | 7 | 90 |
| CBA | Baltic Sea | 8 | 10 | 19 |
| CME | Mediterranea Sea | 6 | 7 | 5 |
| CNE | North-East Atlantic | 11 | 10 | 76 |
| TOTAL | | | 92 | 915 |

ercise has to be focused on biological quality elements and assessment methods that have been most commonly used in Europe to assess impacts of most widespread pressures (Anonymous, 2003f). This implies that the assessment methods for the 'ecological status' will not be compared and harmonized as whole, but merely 'eutrophic status' or 'organic pollution status' depending on availability of data and methods for the intercalibration exercise.

Although not required by the WFD, revision of the intercalibration network and repetition of the intercalibration exercise would be useful also after 2006 when WFD compatible monitoring data begins to be available. This would enable setting revised management targets for the next river basin management cycle (revision of the characteristics and reference conditions of water body types is required after every six years by the Article 5 of the WFD), and finally intercalibration of the ecological status of surface waters as a whole.

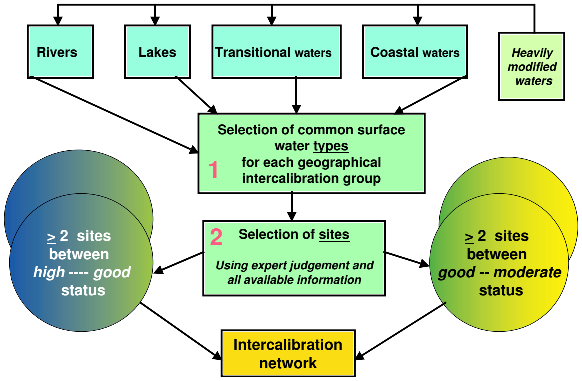

Figure 16.5: Process for the selection of common surface water types and selection of sites for the register forming the intercalibration network. All surface water categories are included. Artificial and heavily modified water bodies need to be assigned to the category which is closest to their characteristics, and if necessary also those can be included in the network.

Table 16.5: Distribution of countries by Geographic Intercalibration Groups (GIGs) and water categories, with numbers of sites currently (status in November 2003) selected from each country to the draft register forming the intercalibration network.

| Country | RBA | RNO | RCE | RAL | RME | REC | LBA | LNO | LAT | LCE | LAL | LME | LEC | CBA | CNE | CME |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Estonia | | 3 | | | | | | 14 | | | | | | | 0 | |
| Latvia | 4 | | | | | | 6 | | | | | | | 0 | | |
| Lithuania | 7 | | | | | | 4 | | | | | | | 1 | | |
| Poland | 5 | | 8 | | | | 12 | | | 10 | | | | 4 | | |
| Finland | | 1 | | | | | | 2 | | | | | | 5 | | |
| Sweden | | 16 | 0 | | | | | 21 | | | | | | 7 | 3 | |
| Norway | | 74 | | | | | | 46 | | | | | | | 1 | |
| UK | | 31 | 42 | | | | | 12 | 12 | 4 | | | | | 36 | |
| Ireland | | 8 | 17 | | | | | 9 | 15 | | | | | | 16 | |
| Denmark | | | 14 | | | | | | | 0 | | | | 0 | 0 | |
| Netherlands | | | 17 | | | | | | | 7 | | | | | 8 | |
| Belgium | | | 24 | | | | | | | 5 | | | | | 1 | |
| Luxemburg | | | 0 | | | | | | | 0 | | | | | | |
| Germany | | | 25 | 9 | | | | | | 11 | 13 | | | 2 | 9 | |
| France | | | 33 | 21 | 8 | | | | | 4 | 7 | 0 | | | 2 | 0 |
| Spain | | | 10 | 7 | 45 | | | | 0 | | 1 | 21 | | | 0 | 0 |
| Italy | | | 0 | 0 | 0 | | | | | | 0 | 0 | | | | 0 |
| Slovenia | | | 4 | 0 | | 0 | | | | | 1 | | 0 | | | 1 |
| Austria | | | 10 | 20 | | 4 | | | | | 15 | | 0 | | | |
| Czech Republic | | | 21 | | | 0 | | | | 0 | | | 0 | | | |
| Slovakia | | | 0 | | | 0 | | | | 0 | 0 | | 0 | | | |
| Greece | | | | | 10 | 0 | | | | | | 0 | 0 | | | 3 |
| Portugal | | | | | 35 | | | | 0 | | | 15 | | | 0 | |
| Cyprus | | | | | 5 | | | | | | | 4 | | | | 1 |
| Hungary | | | | | | 0 | | | | | | | 0 | | | |
| Bulgaria | | | | | | 0 | | | | | | | 0 | | | |
| Romania | | | | | | 1 | | | | | 1 | | 1 | | | |
| Malta | | | | | 0 | | | | | | | 0 | | | | |
| TOTAL | 19 | 130 | 225 | 104 | 104 | 5 | 36 | 90 | 27 | 41 | 38 | 40 | 1 | 19 | 76 | 5 |

## 16.3 Conclusions

Implementation of the WFD requires a setting of operational definitions for 'high', 'good', and 'moderate' ecological status classes in order to establish practical targets for the environmental objectives of the directive. Classification of water bodies into ecological status classes requires establishment of reference conditions and identification of boundaries between 'high–good' and 'good–moderate' quality classes. The boundary between good and moderate status will be especially important because it will set the targets for restoration and improvement plans of water bodies which are in risk to fail the environmental objectives. Biological monitoring data will be needed in order to have a sound basis for the establishment of the class boundaries, since the classification of the ecological quality should not only be based on the hydromorphological and physico-chemical conditions, but also on the biological status of the water bodies. The implementation timetable of the WFD does not completely match with the order of steps that are needed to fulfill classification requirements. This requires Member States to take a pragmatic approach to the classification task, and to start to evaluate the ecological status of their water bodies based on pressure criteria and available biological data although the current monitoring networks of the most Member States are not WFD compliant. The required harmonization (i.e. intercalibration exercise) of the ecological quality classification scales in 2005 and 2006 will be probably difficult because of the heterogeneity of national assessment systems and scarcity of biological data available. However, WFD requires only one intercalibration exercise with the aim to fix the relevant class boundaries for management purposes. Hopefully, a new intercalibration and a revision of the ecological status class boundaries could be possible also after 2006, when new biological data will become available from the restructured monitoring systems, compliant with the WFD requirements.

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Table 16.6: Common intercalibration types currently (status November 2003) selected for northern lakes which are shared by the countries in the same geographical intercalibration group (FI= Finland, IE = Ireland, NO = Norway, SE = Sweden, UK = United Kingdom)

| Characterisation of the common lake type | FI | IE | NO | SE | UK |
|---|---|---|---|---|---|
| 1. Lowland, shallow, siliceous, moderate alkalinity, large | X | X | X | X | X |
| 2. Lowland, shallow, siliceous, low alkalinity, large. | X | X | X | X | X |
| 3. Lowland, shallow, peat, large | X | | X | X | |
| 4. Boreal, large, very shallow, siliceous, moderate alkalinity | X | | X | X | |
| 5. Boreal, shallow, siliceous, low alkalinity, large | X | | X | X | X |
| 6. Boreal, shallow, peat, large | X | | X | X | |
| 7. Highland, shallow, siliceous, low alkalinity, large | X | | X | X | |

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# Chapter 17

# Cultural eutrophication: perspectives and prospects

Paul Wassmann
Norwegian College of Fishery Science
University of Tromsø
N-9037 Tromsø, NORWAY
paulw@nfh.uit.no

## 17.1 History of cultural eutrophication

Cultural eutrophication is old as *Homo sapiens.* In particular after the introduction of agriculture and larger settlements eutrophication has been mans faithful companion. During the pre-agricultural hunting and picking stage only probably a couple million humans inhabited the world and cultural eutrophication was negligible. The 3 orders of magnitude increase in population has changed this considerably. Human population growth and mans present existence is entirely based upon the development and efficiency of agriculture. Seafood delivers only a small percentage of human food word wide (see Chapter 15). A consequence of the increased population (based on agriculture) has been large-scale cultural eutrophication. This process has accompanied all major civilisations. Mesopotamia, the Golden Crescent, the Mediterranean cultures, central Europe, North America and China all have been affected/suffered from the effects of cultural eutrophication. Some of us may dream about the good old times of the Middle ages when man lived closer to nature, when the word appeared to be 'greener' than today and when life was more 'natural'. This view is based on a misunderstanding. The present eutrophication of the Baltic and North Sea was preceded by similar or even worse eutrophication periods caused by logging and the introduction of large-scale agriculture in Europe. Medieval cities were probably not only unsanitary, but contaminated by organic wastes, nutrients and heavy metals. The cultural eutrophication in major cities must have been immense, far beyond today's imagination. A good example of the ambience of Paris in medieval times is portrayed in Patrick Suesskinds novel 'Perfume'. Cultural eutrophication is thus not a recent phenomenon. It has continuously accompanied mans existence in variable degrees. Locally cultural eutrophication can have been far more significant than today.

The earth's recent development is characterised by accelerating population growth, human migration and immigration patterns (Figure 17.1), mod-

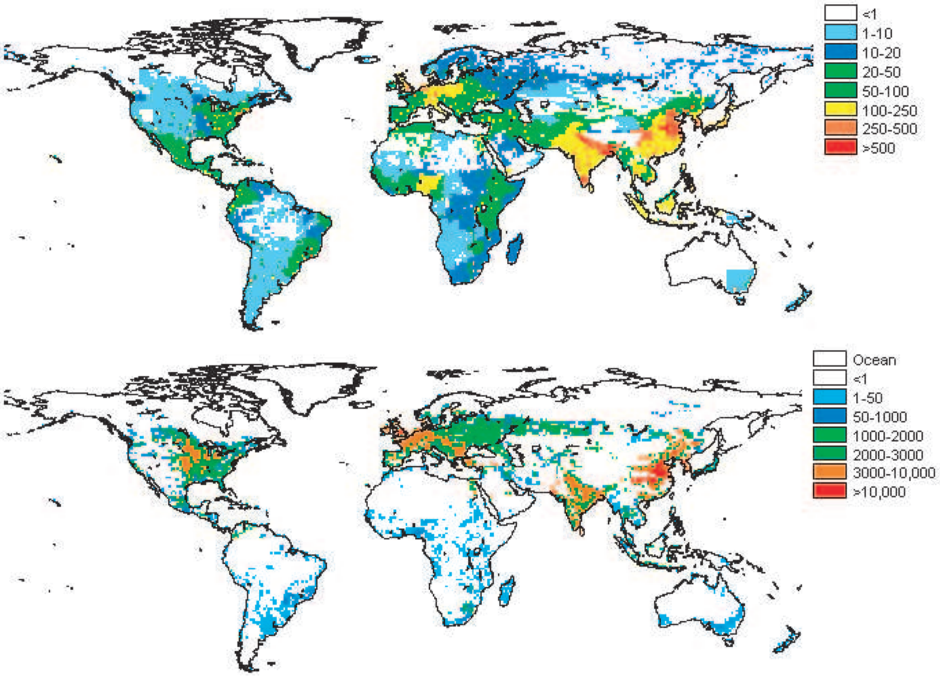

Figure 17.1: Upper panel. Population in 1990 (persons km$^{-2}$). Lerner et al. 1988; updated to 1990 by Bouwman, based on U.N. statistics. Lower panel. Nitrogen fertilizer use in 1990 (kg N km$^{-2}$ y$^{-1}$). Bouwman et al. (1995) and FAO statistics. Remark the high fertilizer application in north-eastern North America and central Europe that is not accompanied by high population density. In the case of India and China the population density is high, but the fertilizer application is moderate. In Africa and South America the application of fertilizers is low relative to the population density.

ern agriculture and fundamental changes in nutrient and water cycles. Cultural eutrophication has become a global issue, in particular due to interference with the local and regional nutrient and water cycles. Substantial amounts of nutrients are discharged into rivers, lakes and estuaries. They reach the ocean more and more rapidly. Eutrophication is thus, in general, highest in the estuaries as nutrient concentration and population density increases along the rivers pathway from the interior to the coastal zone.

Many industrialised countries import not only fertilisers but also nutrients in the form of food. Often they even import the limited resource water in the form of food. For example, 1 kg of wheat demands 1 $m^3$ of water; 1 kg of rice needs 2 $m^3$ of water while 1 kg of beef requires 10 $m^3$ of water. Densely populated countries that have the financial means to buy food from outside, e.g. the Netherlands with plenty of water, is a large-scale importer of water. Thus not only nutrients and biomass are moved over long distances, connections between otherwise separated ecosystem, biogeochemical cycles and resource-limited societies are established. Many of the most developed countries are net-importers of nutrients, in particular nitrogen. The nitrogen supply can be several times greater than the natural standing stock, and that inevitably results in eutrophication. Resources from obviously resource-limited regions (food, water, and fertilisers) are deviated into resource-rich ones. However, here they can cause large-scale eutrophication.

The focal point of cultural eutrophication is the fundamental changes in cycling of carbon, nutrients and water. The recirculation inside small region that was characteristic for the ecological setting in earlier days when the means of transportation were limited, is changed and the nutrient and water circles are first *opened* (i.e. the natural space and times scales are exceeded) and subsequently *widened* to global scales. Due to this the biogeochemical cycles are significantly changed. Stored carbon (coal, oil, gas, wood, soil) are reassigned with the consequence that the atmospheric $CO_2$ concentration has increased from 240 to 380 ppm since the industrial revolution (Figure 17.2). We move phosphorus in the form of apatite from the Kola Peninsula to cover the worlds needs for phosphate. We fix nitrogen gas from the atmosphere in similar amounts than nitrogen fixers (Figure 17.2). We dam and channel rivers, change their discharge patterns and focus sewage into sewers. By fracturing existing biogeochemical and water cycles we change the original cycling, introducing a new, global cycling pattern that changes the overall functioning of the globe. Despite that nutrient discharge can be minimised by effective management in the drainage area, losses inevitably occur. Human population growth, altering global biogeochemical cycles, and increased eutrophication are therefore two aspects of the same cause.

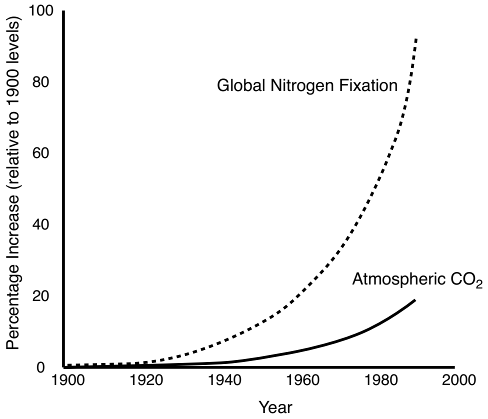

Figure 17.2: The relative change in nitrogen fixation caused by human activities globally compared to the relative increase in carbon dioxide in the atmosphere since 1900. Note that humans are having greater influence on nitrogen availability than they are on the production of carbon dioxide, an important greenhouse gas (modified from Vitousek *et al.* 1997).

## 17.2 Cultural eutrophication: regions, ecosystems, changes and organisms

An important concept for cultural eutrophication is the residence time of nutrients in the recipient. Low water exchange results in high residence times and that increases the effect of the supplied nutrients and vice versa. The volume of the recipient influences its flushing time that determines the nutrient residence time (Figure 17.3). In addition the supply rate by discharge from the drainage basin influences the degree of eutrophication. In concert these factor can give rise to a large range of eutrophication scenarios, both on an annual and seasonal scale. High residence times will be encountered in land locked ecosystems such as fjords with high sills, the Baltic Sea and the Black Sea, while shallow regions or enclosed regions with lower threshold such as the northern Adriatic, the North Sea, Kattegat and many Norwegian fjords take an intermediate position. The degree of eutrophication is determined by the supply rate of nutrients. If the supply is high, such as the Kattegat, Baltic Sea, southern North Sea and certain estuaries and fjords, the combination of highs supply and increased residence times create a scenario for extensive cultural eutrophication.

If the organic matter supply is greater than the degradation and oxygen reserves or its hydrodynamic supply seasonal or long-term hypoxia or anoxia will develop. This phenomenon has been encountered in increasing frequency and has been often been interpreted as a sign of eutrophication although changes in vertical mixing and stratification also can cause hypoxia or anoxia. Further, an increasing Harmful Algal Bloom (HAB) frequency have been interpreted as a consequence of eutrophication (Figure 17.4; see also Chapter 7). In the Seto Inland Sea, one of the most important aquaculture regions in Japan, a large-scale increase in HABs was encountered from the 60s and onwards. Increasing control of the effluents in the region in the 80s and onwards has resulted in a sharp decrease in HAB. However, it is not easy to indicate with confidence if the increased frequency of HABs all over the world is accelerated by eutrophication. For this we have too few reports from the days prior to aquaculture and to few long time series of phytoplankton. HABs have been observed throughout the times: The first HABs report can be found in the Old Testament (Exodus 7: 20-21). "...and all the waters that were in the river were

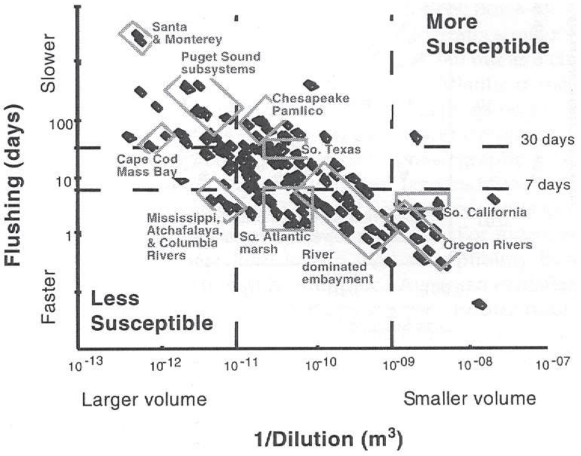

Figure 17.3: Coastal systems can be classified according to their dilution and mixing capabilities. Here 138 coastal systems of the U.S. are classified according to dilution (volume of estuarine water above the pycnocline) and flushing (based on time to replace estuarine volume by freshwater inflow or tidal prism volume). Coastal systems falling in the lower left region of the graph are those with extreme large dilution volumes and short flashing times. One can expect these systems to be least susceptible to eutrophication. Systems in the upper right region of the graph have the smallest dilution volumes and longest flushing times. One can expect these systems to be most susceptible to eutrophication. From Anonymous (2000).

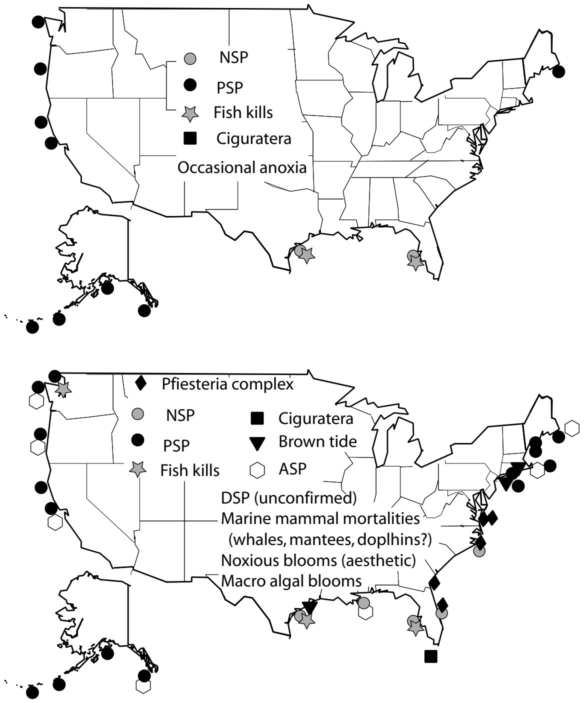

Figure 17.4: Expansion of harmful algae bloom (HAB) problems in the U.S.. These maps depict the HAB outbreaks known before and after 1972. This maps are rather indications of outbreaks than exhaustive compilations of all events. Remark the increasing frequency of HAB events along the coast with the highest population densities. There has been no increase in HAB event frequencies in low-populated regions such as Alaska and Hawaii. NSP = Neurotic shellfish poisoning; PSP = Paralytic shellfish poisoning; ASP = Amnesic shellfish poisoning. From Anderson 1996 and Anonymous 2000.

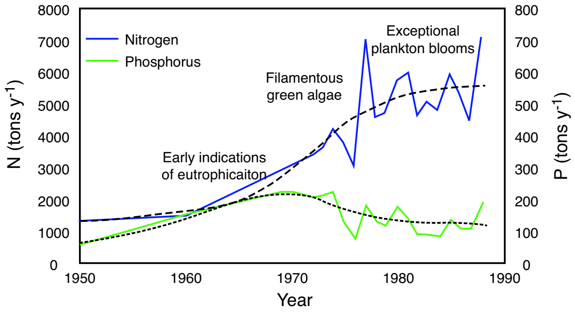

Figure 17.5: Emission of nutrients to Laholm Bay, Sweden. Note the increasing difference in P and N emission. Three phases of eutrophication are indicated: Early indications of eutrophication (colour, visibility), filamentous green algae and exceptional plankton blooms (accompanied by fish kills). From Rosenberg et al. (1990).

turned to blood. And the fish that was in the river died; and the river stank, and the Egyptians could not drink the water of the river . . . ". On the background of the extensive changes in ecosystem structure and composition increased HAB frequencies seem most likely.

Advent of opportunists and introduced species in eutrophicated regions is well known. For example, 3/4 of the benthic biomass of the Rhine River is comprised by inadvertently introduced species. There is great concern worldwide what happens to lacustrin and marine ecosystems under the impact of introduced and alien species. The number of alien species, often introduced by ballast waters, transport of aquaculture organisms, channels or voluntary introduction, is ever increasing. The long-term consequences are more or less unknown.

## 17.3 Phases of cultural eutrophication

We distinguish between three principle, consecutive phases: (A) enrichment phase, (B) initial and secondary effects and (C) extreme and ultimate effects (Figure 17.5). During the enrichment phase increases in pelagic and benthic biomass, fish and mussel yields are recorded. There are several lines of evidence that moderate eutrophication can result in increases in harvestable production and resources attractive to humans. Thus moderate eutrophication can be considered beneficial if increased harvest of fish and shellfish is the focus of our attention. In each ecosystem, there is a level of nutrient availability over which no increase in harvestable resources takes place. This is by definition the end of the enrichment phase. 'Points of no return' (beyond these the ecosystem does not return to its original state after a driver such as nutrient supply is reduced) lay somewhere between B and C.

When the enrichment phase comes to an end the initial and secondary effects of eutrophication become visible. There exists an entire range of phenomena and processes that are characteristic for the second phase of eutrophication. We can observe changes in species composition, e.g. certain benthic algae disappear or certain polychaets domiante. Similar processes can be observed for phytoplankton species. In the Southern North Sea extensive blooms of *Phaeocystis globosa* reflect eutrophication (see also Chapter 20). Further, the increase in relative contribution of flagellates to the phytoplankton biomass is interpreted as a sign of eutrophication, reflecting increased N and P supply while that of Si declines, mainly due to dam constructions (for Si decline see also Chapter 13). Reduction in light penetration caused by increased bloom density and turbidity decrease the depth of the euphotic zone and reduces the area where benthic algae prosper. The increasing frequency of hypoxic episodes belongs also to the initial and secondary effects of eutrophication.

The phase of extreme and ultimate effects is characterised by the large-scale disappearance of sensitive species and that opportunists take over. Mass proliferation of benthic algae such as *Ulva* and *Cladophora* are also characteristic for this stage. Mass mortality and anoxia are the ultimate stage of eutrophication.

## 17.4 Evaluating the sources of cultural eutrophication

The natural sources of nutrients (streams, lakes, rivers) derived from natural (erosion) and human activity. Today the flux of nutrients from their sources to the coast is strongly influenced by anthropogenic activities. Human population growth does not cease in the near future and in all already high agricultural production regions (such as the U.S., central Europe, but in particular in India and China) the application of fertilizers will in crease (Figure 17.6). In addition, clear-cutting trees, drainage of wetlands, fertilising fields and meadows, intensive husbandry, building dams and towns, in essence all anthropogenic activities, contribute to the prevailing picture of cultural eutrophication (see Chapter ). Only a small fraction of applied fertilizers ends up in human food while most is discharged to streams and the atmosphere (Figure 17.7; Chapter 2). The main nutrient sources are diffuse with agriculture as the contributor. Point sources such as towns play a moderate role in the complex scenario of nutrient discharge. The so far strong dedication to reduce eutrophication through point sources such as towns and factories implies that the most important sources for eutrophication have not been sufficiently focussed upon. Even in industrialised countries the main contribution of nutrients derives from agriculture, husbandry and forestry.

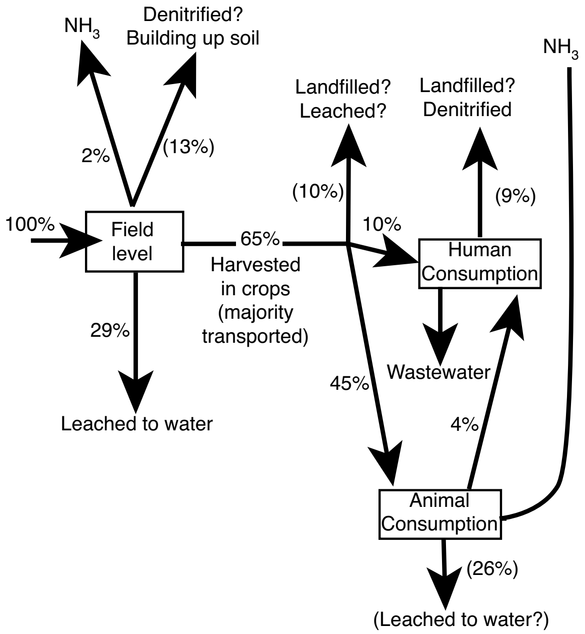

Figure 17.7: The average fate of nitrogen fertilizer applied to agricultural fields for North America. The numbers in parentheses are calculated by difference, and the other numbers are direct estimates. Remark that man only consumes 15% of the applied nitrogen fertilizer, that 46% is leaching into water, that 17% is emitted to the atmosphere. Note also that production on fields, husbandry and human consumption most often take place in separate region, connected by transport. From Anonymous (2000).

As an example we select intensive husbandry with Denmark as an example. Here are 13 million pigs that produce faeces and urine corresponding to 3 person equivalents. Pig farms alone produce probably 6 times more nutrients in Denmark then its population, which is connected to sewer

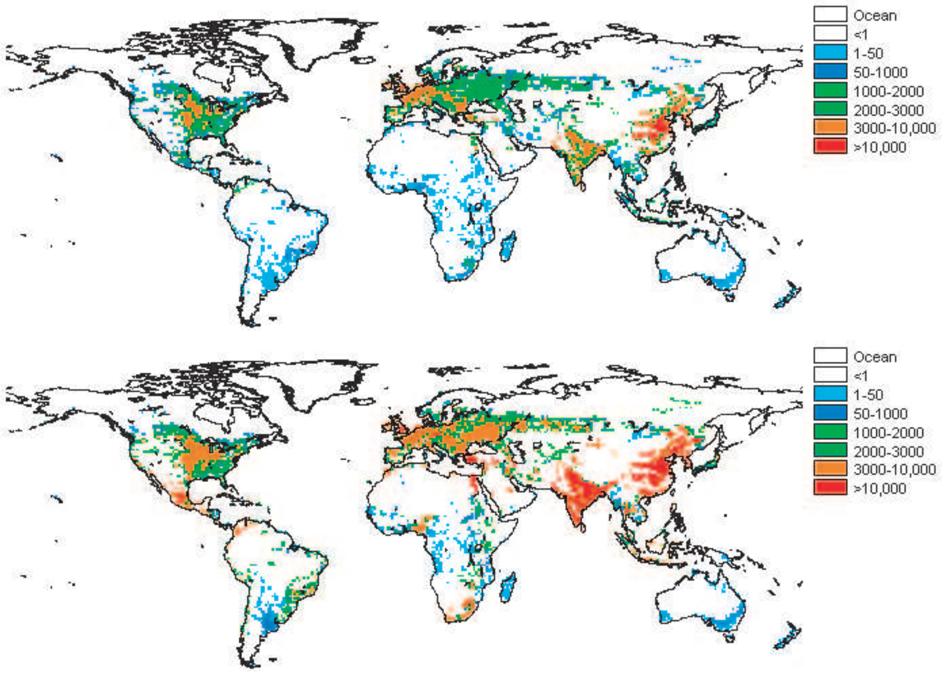

Figure 17.6: Nitrogen fertilizer use in 1990 (upper panel) and prediction for 2050 (lower panel) (kg N km$^{-2}$ y$^{-1}$) Bouwman et al. 1995 and Bouwman 1997. Note the significant increase in future fertilizer consumption world wide, but particular in India, Eastern Europe, Turkey, Egypt, Mexico and South Africa.

systems. In addition there is the remaining husbandry and extensive agriculture production. In total, person equivalents of more than hundred million persons are discharged into the Danish aquifer and the coastal zone. Some of these millions are channelled through sewer systems, but the majority is discharged without significant limitation. Eutrophication of Danish coastal waters is thus not surprising. Locally towns and smaller settlements may cause it, but on a larger scale it is the agricultural practice, the intensity of crop growing and our choice of food (meat vs. vegetables and cereals) that determine most of cultural eutrophication. Sustainability in the coastal zone is thus, bye and large, a question of how we produce food, which food we prefer and what environmental constrains we select for the environment we live in.

Recent investigations indicate that 30% or more of the annual nitrogen supply can come from the atmosphere and burning of oil/gas and intensive husbandry are the reason. Everybody contributes to this large-scale eutrophication. Point sources of nitrogen are of minor significance (in the case of Denmark only 3%) while 66% derive from river discharge with agriculture as the main contributor. Should we attempt to reduce cultural eutrophication we must start where the gain is greatest. Thus we have to attempt to reduce the diffuse emission of nutrients and not focus mainly on the point sources that do only play a minor role in the total picture. This implies that the emissions from agriculture into aquifers and the atmosphere have to be reduced and regulated. There is no indication that this can take place in the near future. Little public debate about this matter exists and attempts to create such a debate in the media appear to result in no major public interest. We have to confront us with this debate if we wish to have an adequate opinion about sustainability.

## 17.5 An adequate understanding of cultural eutrophication

An adequate understanding of eutrophication is for the moment not effortlessly available. The main reason for that is the fragmentation of interest, education and responsibility. Despite of a basic understanding how nutrients flow through an aquifer and into the coastal zone, there exist few institutions and composite research groups that study the entire route and the involved processes simultaneously and from a superior perspective. Eutrophication of the coastal zone, freshwater, run-off from forests, agriculture, industry and sewage treatment are usually dealt with by different scientist and institutions that have few contacts. Education of students and scientists is separate too and we have at present not the adequate expertise and the will that binds the different sectors together.

While industry and citizens pay taxes for the damages of the environment to the costs for sewage treatment plants no such costs are imposed on the by far main contributor of cultural eutrophication, i.e. agriculture and in certain regions forestry. The public focus is directed to point sources that play only a minor role. While industry and cities give raise to environmental problems, the most significant contributors to cultural eutrophication are characterised as nature friendly. Sector thinking prevents holistic solutions or accomplishments that are proportional with the environmental damage. For an environmental impact that has probably a most important environmental effect (Gesamp, 1991) and occurs virtually worldwide, this inadequacy is surprising. A public debate that attempts to focus upon the most important global environmental effect, that is not characterised by sector interest, and that does not hesitate to focus upon the key problem, is indispensable. Emphasis has to be given to normal praxis regarding negative environmental impact — i.e. the polluter pays for the negative environmental effects. The greatest contributor to cultural eutrophication is exempted from this obligation, probably because the public is not aware of the full extent of the problem and is afraid to pay more for food. However, food has become a comparatively minor cost in our budget. In addition, all industrialised countries significantly subsidise agriculture. It must be puzzling that many societies subsidise activities that can cause anoxic bottom waters, reduced water quality, harmful algae blooms, reduced fisheries, prevent aquaculture etc. Obviously a holistic perspective is needed to solve this apparently inconvincible dilemma. At the end of the day we all pay for our approach to deal with cultural eutrophication, either through food costs, subsidies, environmental taxes or a negative development of the environment.

Assuming a connection between agriculture subsidies and increased production, taking notice of the lack of nutrient discharge appropriate limitations from agriculture and husbandry and considering the consequential eutrophication, a connection exists between subsidies, demands for inexpensive food, decreased environmental quality, reduced fisheries and increased HAB. Can removal of agricultural subsidies give rise to increased costal zone environmental quality and fisheries? It is timely to promote these type of questions and study the complete costs of food production and environmental losses.

## 17.6 Remediation of cultural eutrophication

An obvious mode to reduce the effects of cultural eutrophication is reduction of resource use in the drainage area. This could be achieved by a reduction of fertilisers use and limitations of husbandry. An obvious step would be to reduce nutrient discharge to the aquifer. This implies that steps are taken that effluents from fields, intensive husbandry towns and factories are strongly regulated. By regulating gullies and tiles in agricultural regions significant declines of nutrient discharge can be achieved (Figure 17.8; Chapter 2). With regard to point sources removal of nutrients by additional sewage plants could be an option. Low-price biological removal plants should be considered. Harvesting weeds in ponds and bringing them back to the fields or include them into compost is an option that is not adequately considered.

In marine environments growing blue mussels in river mouths can reduce eutrophication. By removing the rapidly growing mussels and transport them into the aquifer (compost, waste disposal sites etc.) the nutrient residence time can be significantly increased (see also Chapter 15). This is an efficient and low-cost manner to decrease the discharge of nutrients into coastal regions. One can also decrease the direct discharge of effluents to small rivers and streams by planting bushes and trees, which in recent decades have been removed by agricultural means to increase the farm area. To collect water from ditches that drain the tillage from fields into dams, is another manner to decrease direct and rapid losses of nutrients from agriculture (e.g. Figure 17.8). Taking fields out of production and destroying tillage is still another option that should be considered in times when overproduction of food is a predominant characteristic of agriculture in Europe.

A natural manner to get rid of nitrogen is denitrification. How can we increase denitrification in a drainage area? Denitrification is highest in waterlogged soils that are not efficient for agriculture. The height of water in ditches, the presence of dams and the amount of wetlands are important aspects of increasing denitrification. In many cases converting fields into wetland implies transferring them back into their original state. Often wetlands and waterlogged soils have been converted into farmlands previously. Wetland restoration is by far the most efficient and cheapest manner to reduce nitrogen supply to rivers and coastal zones, with ramifications for biodiversity and ecosystem variety.

The increasing imbalance between nutrients is of major concern. While nothing can be done with the decreasing discharge of Si unless dams are removed, the balance of the N and P discharge could be improved. So far the major goal has been to

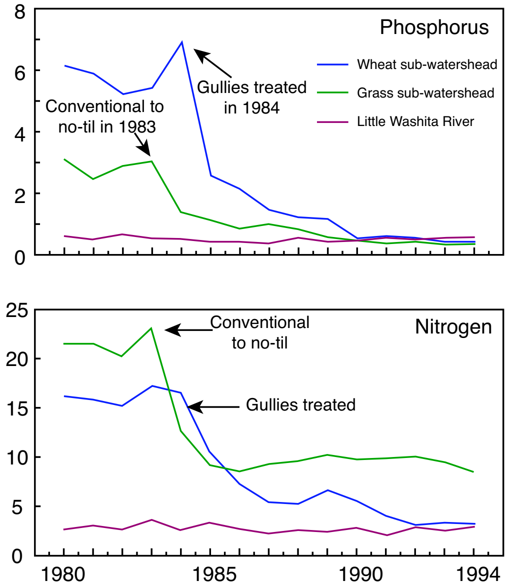

Figure 17.8: Annual nitrogen and phosphorous loss into the Little Washita River from a wheat- and grass-dominant sub-watershed. Note the reduction in both nutrients after the eroding of the gullies in the grass watershed were treated in 1984 and conventional tillage was replaced with no-till in 1983 in the watershed growing wheat (modified from Sharpley and Smith 1994; Sharpley et al. 1996, from Anonymous 2000)

reduce nutrient discharge *per se*. While this is a first, important step, the next must be to figure out if the discharge of N and P could be closer to the Redfield ratio to achieve a more environmental friendly composition.

The basic goal for reducing the eutrophication in streams, lakes and coastal waters is fist of all to increase their residence time on land and omit the present short-circuits in the nutrient cycles. This would decrease fertilizer use and result in a higher net-utilization of nutrients by man. Returning marine biomass back to the drainage area and spreading human and animal excrements efficiently in the drainage area is an option that has been previously applied and should be reconsidered. Decreased meat consumption (Figure 17.8) or more spread meat production are additional options that would decrease nutrient discharge.

## 17.7 Controlled cultural eutrophication and aquaculture

Agriculture has been the backbone of human existence that created the base for the 3 orders of magnitude increase in human population. While intensive agriculture often is considered negative for the productivity in adjacent aquatic environments (e.g. too high nutrient supply, major deviations in nutrient composition, large-scale modifications of water sheds and water supplies) the exploitation of aquatic ecosystems in Europe has until recently been dominated by various forms of fish and shellfish. Compared to agriculture, fishery is still based on the hunter and picker approach that agriculture left several thousand years ago: wild resources are exploited rather than cultivated. While various aquaculture techniques, often in combination with agriculture, have been widely applied in many countries (e.g. China and Japan), aquaculture in sea- or landbased enclosures first developed into a major economy in European countries in recent decades. Aquaculture can now be of similar or even greater significance than natural fish and shellfish catches. The majority of marine fish aquaculture depends on feed that derives from natural fish resources. The supply of nutrients that causes eutrophication in coastal regions may support a higher fishery, but this effect has not been quantified. One problem is that the nutrients are not added in close to Redfield ratio proportion and that pollutants such as heavy metals, pesticides and detergents are dumped in concert with the nutrients. For a general discussion of marine production and seafood; see Chapter 15.

Is it possible to leave the 'hunter and picker stage' of fisheries and introduce aquaculture in the meaning of agriculture, i.e. fertilising a region, manipulate the organisms and channel the nutrients into crops that are harvestable items of human food consumption? Can we control the fertilisation of aquatic recipients by using a limiting resource (i.e. nutrients), which at present is dumped into what we wish to be pristine regions or can we generate a controlled fertilisation of certain regions by adding fertilisers? Could we turn the waste of resources that result in eutrophication into a benefit, resources that benefit humans? The lack of knowledge how nutrients are channelled through manipulated food webs prevents extensive sustainable aquaculture in the foreseeable future. However, it is important to investigate the base for a future aquaculture (see Chapter 15), in parallel with the development of agriculture that took place several thousand years ago. There is no reason to assume that aquatic environments are in essence so different compared to terrestrial environments that significant aquaculture should be out of question. In particular not in a world that is short in food.

To build up a modern aquaculture know-how that would allow extensive aquaculture if the need arises would be a good investment in future prosperity of coastal populations. This knowledge would simultaneously contribute to a better understanding of eutrophication. Some attempts to obtain such knowledge have been already obtained by the MARICULT programme (see Chapter 15). To endeavor a controlled fertilization of coastal waters (in contradiction to our current uncontrolled experiment) to be subsequently utilized by fisheries or extensive aquaculture is an approach that has not found wide acceptance. On the contrary, the common attitude is rather to prevent eutrophication of coastal water or dump nutrients at depth. This attitude is opposed to use the already and in most poor regions of the world perpetuate eutrophied coastal waters for extensive aquaculture, in analogy to agriculture. There exists a conflict between the wish to (a) experience non-eutrophied coastal waters, (b) to use these waters eventually for aquaculture and fertilize them and (c) todays approach to dump nutrient at large-scale without considering (a) or (b). It can be questioned if option (b) is the best manner to cope favorably with the negative aspects of eutrophication. This in order to support the sustainability of the coastal zone that is rapidly decreasing in many regions (e.g. some estuaries and fjords, the southern North Sea or the 'death zone' in the Gulf of Mexico).

In Japan where aquaculture has played a vital role throughout the last thousand years examples exists showing that eutrophication and aquaculture can co-exist without destroying the long-term integrity of aquatic ecosystems. Edo, the capital of Japan during the Tukagawa regime (at present Tokyo), was densely populated and transported manure from the city to fields outside the town. Also, they harvested the undoubtedly eutrophicated bight outside the city through extensive aquaculture establishments (e.g. scallops, fish, seaweed etc.). The discharge and cycling of biomass and nutrients was so balanced that no negative episodes of eutrophication (e.g. HAB, anoxic bottom water) have been reported. The wisdom concealed in the case of Edo reflects a balanced solution, in a setting where resources (here nutrients/food) were strictly limited. The example shows that sustainable development is possible if appropriate techniques are applied. In many respects eutrophication functions like the waste of a limited resource, in this case nutrients. In a phase of our development characterised by excessive use of resources, phenomena such as eutrophication are difficult to omit. In times to come, when the negative consequences of our resource mismanagement will become difficult to cope, and resource and food shortage are difficult to deal with, the waste of nutrients and the accompanied negative effects have to be carefully evaluated. Extensive aquaculture combined with recycling of nutrients back to arable land may be one option to alleviate this conflict.

## 17.8 Epilogue

It is obvious that cultural eutrophication is tightly coupled to the development of man, his techniques, food production and dietary habits. Can cultural eutrophication be omitted as long as *Homo sapiens* exists? The answer to this question is frankly no. With few exceptions (the utmost outskirts of civilization) the surface of the earth has been transformed from nature into a cultural landscape. Not so visible for the human eye also the sea has been turned into a cultural landscape. We have various forms of marine pollution that can be encountered worldwide. We reduced the number of large mammals in *Homo sapiens* earliest days and recently also overfishing has taken place: Medium- and large-sized fish have declined to about 25% of what was found in the 50ties. The seafloor has become a deposition site for scrap, dredged material, constructions, ammunitions, chemical waste etc. Each $m^2$ of the North Sea or Kattegat is subjected to bottom trawls several times a year. What we in colloquial terms call *nature* is to a large extent actually *culture*, also in the ocean. And with regard to the latter the term culture reflects a rather uncultured attitude. We think highly about the ocean, but could not care less.

For obvious reasons, mankind is increasingly worried about the quality of its environment. What is a clean and healthy environment in times when most of the earth carries the signature of environmental change, habitat destruction and pollution? Given the strong increase in human populations over the last 1000 and particular the last 100 years, until when were our environments clean and healthy? When did the coastal regions where people live, stop to be clean or healthy? In 1900, 1500, 500 or 500 A.D.? There is no scientific definition for the terms clean and healthy. Clean and healthy have operational definitions that we have to generate. Most environmental standards are rather based on 'common sense' than scientific reasoning. Environmental standards must include the impact of humans, unless we wish to exterminate ourselves for the benefit of nature *per se*. Prior to a clean-up of our polluted coastal zones we have to decide *how clean* they should become and which point in time we wish to refer to that is *acceptably clean and healthy*.

Culture means alienation from nature. But culture is the very base of human existence; it is what makes us humans. We can thus not ignore alienation from nature. Even an environmentalist is alienated with regard to what he/she wishes to protect. This creates a basic problem for environmental protection that easily can result in sustainable development confrontations. Sustainable development implies that mans demands for natural resources such as food are covered inside the 'buffer capacity' of an ecosystem. Sustainability also implies that organic matter and energy harvesting from an ecosystem must not threaten the long-term integrity of ecosystems. In aquatic systems sustainable development is limited by new production, in other words the ecosystems carrying capacity, its maximum production capacity and harvestable production. Sustainability can only be maintained at harvest levels that are much lower than the carrying capacity. Where this limit is to be set is the great challenge that depends on our definition of sustainability which has not absolute, but an operational meaning.

Ecosystems changes are a direct consequence of our existence. There is no way to stop cultural eutrophication. Any attempt to target a clean environment without radically reducing human populations and thoroughly changing our life commodities, is utterly naïve. Technology (for the educated and wealthy) can only *help*, but does not fundamentally change the state of affairs. Thus we can only ask "What eutrophication, how much eutrophication and where should eutrophication preferentially take place"? The question is not cultural eutrophication or not, but *what type* of eutrophication, *how much* and at *what price* for nature and humans. Most aquatic ecosystems are thus a cultural 'landscape', which cannot be turned into nature or a sanctuary without removing humans from the entire watershed. And even this will not help as the atmosphere supplies nutrients from adjacent regions. We have to bear the responsibilities in a setting where we cannot run away from the consequences, but modify our management. We live in the environment that we deserve. And the recent growth in human population has probably resulted in that we have passed already the Earths point of no return. Most of the Earth has developed irreversibly into a cultural landscape. Cultural eutrophication is a facet of this process.

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# Part VI

# Case studies

# Chapter 18

# Northern Adriatic Sea

Serena Fonda Umani
Laboratory of Marine Biology
University of Trieste
Italy
labbioma@univ.trieste.it

## 18.1 Introduction

As in many coastal environments throughout the world, the watersheds of the Adriatic Sea are regions of rapid population growth and changing land-use patterns that have led to increases in nutrient loading and changes in freshwater flow patterns to coastal waters that have been especially pronounced during the last 100 years. The Adriatic region is characterized by intensive land-based and sea-based activities, including urban growth and development, agriculture, commercial and recreational fisheries, tourism, and multinational commerce. Changes in these activities are widely believed to have elicited significant degradation of water quality, manifested as mucilage events, oxygen depletion of bottom water, harmful algal blooms, outbreaks of gelatinous zooplankton, invasions of non-indigenous species, loss of habitat and instability of fisheries. Individually, these phenomena may not be cause for concern. But taken as a whole, they may be indicative of a pattern of environmental stress that threatens the health of coastal ecosystems of the Adriatic.

Although there are many uncertainties, it was concluded that the weight of scientific evidence from the Adriatic and elsewhere supports the hypothesis that mucilage events, oxygen depletion, harmful algal blooms, and the sustainability of fisheries may be related to each other and to increases in nutrient loading from human sources. The common denominator in this scenario is the response of the food web to nutrient inputs and the harvesting of fish (from the WORKSHOP REPORT on "Nutrient and Trophic Dynamics in the Adriatic Sea: Toward a Coordinated Adriatic Observing System." Rovinj, Croatia, 17–23 October 1999).

## 18.2 An oceanographic overview

The Adriatic Sea has an extension by latitude of about 800 km, and by longitude from 100 to 200 km. It consists of a series of three basins, characterized by decreasing depth from the southern to the northern one. An 800 m deep sill partly separates the southern basin, whose depth is greater than 1200 m, from the Ionian Sea, and a second sill, of about 130 m, separates the southern from the central basin, a transversal trench of 270 m maximal depth. Northward a steep slope separates it from the northern basin, whose bottom gently slopes from the 100 m isobath to the 30–40

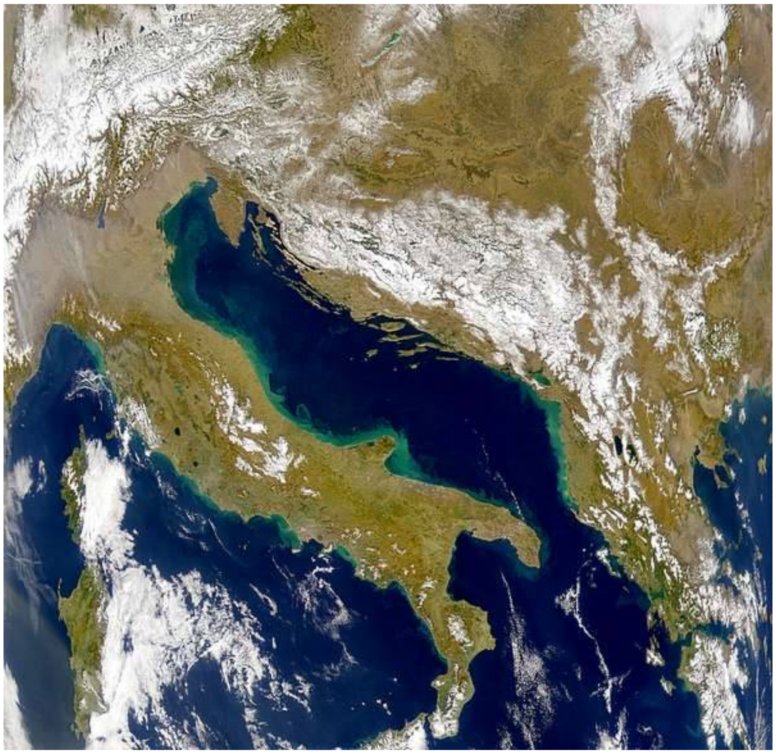

Figure 18.1: Seawift image of the Adriatic Sea

m average depth of this shallow area (Figure 18.1).

The circulation and the distribution of the water masses is strongly influenced by the morphological features of the Adriatic Sea bottom. The sills control the circulation of the dense waters in the deeper part of the central and southern basins, while the thermohaline characters of the waters are strongly influenced in the southern basin by the exchange with the Ionian Sea, and in the northernmost basin by riverine inflow, mainly from the western coast.

The renewal of the whole Adriatic water is estimated to be in the range of 3 to 10 years, whereas every sub-basin and water layer within them show very different renewal time scales, owing to their different volumes, degrees of stratification and relationships between forcing factors. In all basins the small volume of water closer to the coast shows similar characters and phenomenologies, related to physical processes of mixing and circulation with short time and space scales, which also have considerable importance in a part of the shallow northern basin during some periods of the year, in relation to the vertical and cross frontal exchanges of energy and matter.

The circulation is always cyclonic, with a northward flow along the eastern side, and a southward one along the western coast. Both the extension and the intensity of flow in the opposite sides of the basin show large seasonal variations (Figure 18.2).

## 18.3 Southern and central basins

In the deeper basins the water column is divided into three layers: the superficial one is constituted by waters of low density, influenced along the western side by the indirect effects of riverine dilution; the intermediate one, with waters of high salinity of Ionian origin; and the deep one, constituted of dense waters, generated during the wintertime.

The intermediate layer is strongly influenced by

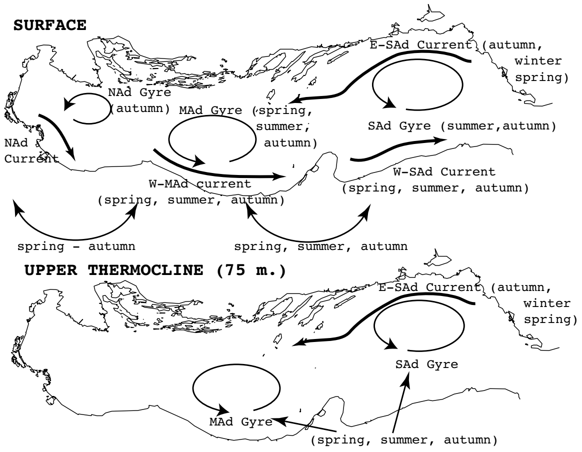

Figure 18.2: Schematic representation of the Adriatic Sea baroclinic circulation according to Artegiani et al., 1993

Levantine Intermediate Water (LIW). This water mass originates in the eastern Mediterranean during the wintertime, by vertical convective mixing of water of low temperature (15 °C) and high salinity (39.1‰), and occupies a layer between 200 to 600 m depth. This water layer, which is entrained by the circulation in the Otranto Channel, enters into the southern basin, and is propagated along the whole Adriatic Sea, by different mixing and transport processes. The ingression of saline waters is highly variable, showing pluriannual fluctuations.

In summer the general circulation shows a cyclonic gyre extending to both the central and southern basins, with a noticeable transversal flow in the former. The gyre is vertically strongly stabilized by the thermal fluxes at the surface, and is affected by the advection of western diluted waters, deflected towards the east by the irregularities of the coastline, and of southern waters from the intermediate layer.

During the winter the circulation generates two semi-stationary cyclonic gyres, situated in the northern area of the southern basin and in the central basin. In both areas the isopycnal surfaces assume a dome-like shape: the intense evaporative thermal fluxes at the surface, driven by the NE wind (Bora), generate high-density water in the central zone of the gyres and vertical convection. Afterward this dense water flows along the western side of the Otranto Channel, feeding the deep water of the Ionian Sea.

The dense water generated in similar conditions in the central and the northern basin, characterized by higher densities (up to 1029.5 kg $m^{-3}$), fills the deepest part of the central basin.

The distribution of dissolved matter is driven by the vertical and horizontal density and motion fields described above. Nutrients are found in low concentrations in the surface layer, and in relatively greater one in the saline intermediate water inflowing into the southern basin, and in the dense deep water. The transfer by turbulent diffusion from the intermediate water core advected from the Ionian basin is the major source of nutrients for the surface layer of the southern Adriatic, coastal runoff playing a secondary role. By the dense water outflow, nutrients produced by mineralization processes in the lower part of the water column are brought into the Ionian and eastern Mediterranean deeper basins.

## 18.4 Northern basin

The oceanography of the northern Adriatic Sea is influenced by the physiography of the basin and by the meteorology of the area. The wide periodical modification of the density field and of the water column vertical stability is a result of the above factors, the density structure of the basin varying from complete instability in winter to a highly stratified pattern during the rest of the year.

The most important factors driving the processes, which determine the annual modification of the thermohaline characteristics of the water, the generation of water masses and their circulation is the wide fluctuation of the surface heat fluxes and the large volume of fresh water inflowing into the shallow basin.

During the winter, when the total heat budget is negative, the cold waters diluted by the western riverine inflow remain confined in a coastal belt, separated from the offshore waters by a frontal system, and flowing southward. In the offshore area of the basin the waters are highly saline, being advected from the southern basins: they are actively mixed by wind driven surface cooling and mechanical stirring. Under these conditions of vertical instability, high density waters are generated, which flow towards the central basin during periods of strong NE (Bora) wind. In the early spring the inversion of the total heat budget leads to the generation of a thermocline, and the vertical stabilization of the surface layer to the injection of Po River waters. The dilution increases the buoyancy of the surface layer, which expands to a large part of the northern Adriatic. Successive heating and dilution processes, wind mixing, and advection from the southern basins in the summer generate highly stratified water column, in which as a rule three layers can be identified, separated by strong density gradients. The increase in hydrostatic stability resulting from the pycnoclines reduces the vertical turbulent diffusion and affects vertical mixing, and in different ways the transport processes of dissolved and particulate matter.

During the wintertime a significant part of the nutrient input from river sources is retained inside the coastal water belt, in which their concentration becomes very high (e.g. up to 100µM for nitrate-nitrogen). In offshore saline water the nutrients show quite low concentrations, and seem to originate mainly by recycling, by advection from the southern basin, or, to a lesser extent, by cross frontal turbulent diffusion from the coastal waters. Both in the coastal and in the offshore zone the vertical mixing causes a homogeneous distribution along the water column of dissolved and suspended matter.

In spring and summer diffusive transport of the terrigenous and riverine inputs are the prevailing mechanism of nutrient transfer to the basin waters. Part of the input from sources distributed along the coast is retained in the coastal waters, but a large part of the input from the River Po, driven by the river plume dynamics, is distributed with the fresh diluting water over the whole basin. In the surface layer the nutrient concentrations range from one to three orders of magnitude from the input point to the periphery of the diluted area, as an effect both of turbulent diffusion and of biological uptake, and of sedimentation of the particulate matter produced in the deeper layers.

The vertical flux of nutrients in the dissolved and particulate phases is strongly discriminated by the density condition. The decrease of vertical turbulence at the pycnoclines hinders the diffusive transport of dissolved matter between the layers, and the steep density gradients regulate the downwards diapycnic flux of different dimensional ranges of the biogenic particulates, through the control of their settling speed. The level of nutrient concentrations becomes periodically high in the dense water mass, confined by the deep pycnocline. In this layer the stock of dissolved nutrients increases in consequence of the mineralization processes of the organic matter settling from the overlying layers, with a related decrease of dissolved oxygen. A significant fraction of the nutrients advected in the surface layer by the River Po is stored in this way into the near bottom layer, from which is very slowly released upwards through turbulent diffusion, or periodically exported by lateral advection, and quantitatively diffused into the upper part of the water column only during the early winter mixing phase.

## 18.5 Distribution of chlorophyll and primary production

The rivers draining into the northern Adriatic are the major sources of external nutrient input, especially during stratified periods. The water mass exchange between the northern region and the remainder of the essentially oligotrophic Adriatic, as well as the major influence of Ionian water in the south, has a great influence on the productivity and standing crops of different sub-areas. A terrigenous supply of nutrients in some semi-enclosed bays and channels of the eastern coast and all along the western coast via run-off influences the productivity of a relatively narrow coastal belt, and consequently the biomasses and production rates are spatially very variable. Buljan 1964 who made an estimate of the productivity of the Adriatic Sea on the basis of its hydrographic properties, suggested its division into four productivity zones: open waters of the central and southern Adriatic having low production; the shallow northern Adriatic including a narrow coastal belt along western coast, characterized by permanent high production; the area of moderate production occupying the eastern coastal waters and finally the limited zones with high production under strong coastal influences (lagoons and embayments) along the eastern and also western shore.

The northern Adriatic has been recognized for many years as a region of high marine production at several trophic levels from phytoplankton to fish, but recently the external nutrient input is thought by some authors to be the source of the eutrophication problem of this area (Degobbis, 1989).

A region of high but variable phytoplankton biomass and production was quantified off the delta of the River Po and related to the spreading of its plume, and a marked west to east gradient of the standing crop and production was observed. The mean water column chl a (2.87 mg $m^{-3}$) in the western zone under the direct influence of the River Po is about twice as high as in open north Adriatic waters, which in turn have a significantly higher biomass than the eastern North Adriatic zone (mean 0.9 mg chl a $m^{-3}$), which is under the influence of oligotrophic waters of more southern origin. Very high chl a values are found along the western coast of the Italian region of Emilia-Romagna, where close to the coast the annual mean chl a has values over 10 mg $m^{-3}$, falling below 8 mg $m^{-3}$ at about 2 km offshore (Fonda Umani, 1996).

Similar trends are evident for primary production (PP) data, with maxima over 30 µg C $l^{-1}$ $h^{-1}$ in the western and below 10 µg C $l^{-1}$ $h^{-1}$ in the eastern part. Minimal values are similar for both regions <1 µg C $l^{-1}$ $h^{-1}$. More recently one of the most important results of ELNA Project was the estimation of annual PP rates in the three Northern Adriatic areas, identified by means of their respective fresh water contents: 1 — the so called dystrophic area, close to the Po River mouth where mean annual PP was equal to 183 g C $m^{-2}y^{-1}$; 2 — the neighbor eutrophic area with an average PP of 94 g C $m^{-2}y^{-1}$ and 3 — the open waters where PP was 64 g C $m^{-2}y^{-1}$ (Hopkins, 1999).

## 18.6 Red tides

Conditions favoring dinoflagellate bloom development are most often observed in the coastal areas of Emilia Romagna. Here nutrient loads are higher than in all other parts of the basin due to freshwater inputs of the Po River and of minor rivers along the coast. Peak flows in spring and autumn, and less frequent, summer pulses, lead to enhanced phytoplankton production in general, and, since 1975, dinoflagellate blooms particularly (Table 18.1). The typical seasonal distribution in this region proceeds as follows: low water temperatures prevent bloom expression in the winter. After early spring diatom increases, dinoflagellate blooms generally commence in March-April. The principal contributors are *Noctiluca miliaris* and *Glenodinium lenticula*, followed by early summer blooms of *Prorocentrum micans*, *P. scutellum*, *Scrippsiella trochoidea*, and *Gymnodinium foliaceum*. In summer-fall, *Gymnodinium corii*, *Lingulodinium polyedra*, and *Heterocapsa rotundata* prevail. In most cases, they occur in patches along the axes of the coastal belt, decreasing in intensity from north to south. The patchy distribution of the blooms also reflects variability in small tributary discharge in the area, with blooms localized to mouths of the small rivers.

Other regions of the basin and coastal bays are typified by bloom-forming species with regional variability in distributions of bloom-forming taxa more frequently observed in the early summer (Table 18.2). For example, in June 1977, a bloom of *N. miliaris* was noted in the Gulf of Trieste, persisting one week and concentrated in the inner and more confined part of the harbor. The bloom was triggered by a sudden increase in surface temperature (2–3°C in a few days) associated with an increase in tributary runoff of nutrient-

Table 18.1: Along Emilia Romagna coasts. (mean duration — 2/4 weeks)

| year | month | species |
|---|---|---|
| 1968 | October/November | *P. depressum* |
| 1969 | May | *P. depressum* |
| 1975 | September | *C.karstenii* |
| 1976 | July | *P.micans* |
|  | from August to December | *G.corii* |
| 1977 | July | *G.polyedra G.corii* |
|  | August | *P.micans* |
|  | October | *G.corii* |
| 1978 | March | *N. miliaris* |
|  | August/September | *G.polyedra* |
|  | September/October | *G. corii* |
| 1979 | June | *G. foliaceum* |
|  | August/September | *G.polyedra* |
|  | October/November | *G.corii* |
| 1980 | March | *N. miliari* |
|  |  | *K.rotundatum* |
|  |  | *G.lenticula* |
|  | June | *P. micans* |
| 1981 | March | *G.lenticula* |
|  | June | *K.rotundatum* |
|  | August/September/October | *Gymnodinium sp.* |
|  | October | *K.rotundatum* |
| 1982 | April | *G.lenticula* |
|  | June | *P.scutellum* |
|  | July/August | *G.polyedra* |
|  | August | *G. tamarensis* |
|  | September | *P. trochoideum* |
| 1983 | September | *Gymnodinium sp.* |
| 1984 | August/September | *G.polyedra* |
|  |  | *Gymnodinium* |
|  |  | *Massarthia* |
|  | October/November | *Gymnodinium* |
| 1985 | July/August | *G.polyedra* |
| 1986 | August | *P.trochoideum* |
| 1987 | October/November | *Gymnodimium* |
| 1990 | March/April | *N. miliaris* |
|  | August | *G.polyedra* |
|  |  | *S.trochoidea* |
|  |  | *Cochlodinium* |
| 1991 | July | *S.trochoidea* |

Table 18.2: Northern Adriatic Sea. (mean duration — 1/2 weeks)

| year | month | species | area |
|---|---|---|---|
| 1973 | August | *P. ovum* | Gulf of Trieste |
| 1977 | June | *N. miliaris* | Gulf of Trieste |
| 1968 | .. | dinoflagellates | Pula harbour |
| 1978 | September | *G. polyedra* | Gulf of Trieste |
| 1980 | June | *N. miliaris* | North Adriatic |
| 1981 | June | *E. marina* | Trieste harbour |
| 1982 | September | *G. polyedra* | Gulf of Trieste |
| 1983 | May | *S. faeroense* | Gulf of Trieste |
|  | September | *G.polyedra* | Gulf of Trieste |
| 1984 | October | *Gymnodinium sp.* | North Adriatic |
| 1987 | September | *S. trochoidea* | Gulf of Trieste |

rich freshwater. In the same summer, some of the same taxa noted above in the seasonal distribution of bloom forming taxa, *G. corii* and *L. polyedra*, were observed along the Emilia Romagna coast, lasting from July 19th to the 27th, followed in August by a *P. micans* red tide. In June 1980, another bloom of *N. miliaris* occurred but was far more widespread, affecting the whole northern portion of the Adriatic, from the coast of Istria to Venice. This taxon was not observed along the Emilia Romagna coast where another *P. micans* bloom was note. At the end of summer, frequently only one bloom-forming species has impacted the entire whole northern basin. *L. polyedra* was observed in September 1978 and again from August-September 1982; late summer densities were generally lower than densities reported for early summer blooms.

Occasionally, blooms have been noted late in the year. In fall, 1984, a *Gymnodinium* bloom was observed throughout the northern Adriatic Sea, persisting from September until December and resulted in chl a levels extgreater 700 mg m$^{-3}$. The bloom developed along the Emilia Romagna coast after a collapse of dense blooms of diatoms and later of *L. polyedra*, and extended 20 km offshore. New nutrient influx was responsible for the bloom: heavy precipitation led to high freshwater inputs and associated new nutrient loads from the scouring of river bed nutrient stocks that had accumulated in a meteorologically calm period prior to mid-August.

Dinoflagellate blooms along the Emilia Romagna can contribute significantly to total biomass, at least in the northern most part of the basin directly influenced by the Po River. For example, during the August 1981 bloom of *G. corii*, chlorophyll concentrations exceeded 1000 mg m$^{-3}$ and densities reached $2.3\times10^8$ cells L$^{-1}$. Similarly, chlorophyll concentrations exceeded 40 mg m$^{-3}$ during an August 1986 bloom of *Peridinium trochoideum.*

The *G. corii* bloom covered the Emilia Romagna region from the Po River delta to Mount Conero with highest chl a concentrations noted in the northern portion of the region, declining to >200 mg m$^{-3}$ in southern areas. Although productivity data are not available, these biomass levels were likely responsible for very high productivity along the entire coast. Oxygen concentrations in surface waters were supersaturated (>170%) and anoxia typified bottom waters of the area. The bloom and its associated oxygen-rich surface waters were subsequently displaced offshore by the upwelling of anoxic bottom waters generated by strong offshore winds.

Annual blooms of individual bloom-forming species are not typical of most of the Northern Adriatic Sea. Only isolated bays on the coast and near-shore waters south of the Po River delta have conditions favoring frequent bloom activity. These conditions include: (1) a near continuous supply of new nutrient from the Po and small rivers, (2) tidal- or meteorologically-induced mixing of remineralized nutrients, vegetative cells and resting stages from the shallow bottom, (3) persistent, stable fronts (convergences) between the nutrient-rich plume and oligotrophic offshore water, and (4) wind-induced upwelling of deep, nutrient-rich bottom water from intermediate or deep basin water immediately to the east. In most years, summer river discharge is minimal so that nutrients delivered in the eastward-spreading summer plume are quickly diluted, restricting bloom development to the western-most portions of the basin. Nutrient uptake at depth via vertical migration provides little substrate for maintaining bloom populations due to nutrient-depleted intermediate water. Further, remineralized nutrient pools as well as 'seed populations' in deep bottom waters are rarely introduced into surface waters due to strong vertical stratification and depth, thereby restricting surface production to new nutrient in the plume and surface regeneration in increasingly oligotrophic water. Thus, blooms in the basin would reflect new nutrient inputs and tend to be short-lived due to rapid exhaustion of nutrient pools.

Dinoflagellate blooms occur most frequently along the western margin of the northern Adriatic, probably as a consequence of the combined affects of the discharge of buoyant, nutrient-rich water and physical processes that confine the discharges from the Po and smaller rivers to the western margin under most circumstances. Three bloom periods characterize the region: 1) following the late spring-early summer diatom bloom period when surface nutrients are depleted and the water column has become thermally stratified, dinoflagellates are able to bloom by migrating between nutrient-rich, sub-thermocline water and the surface layer where light levels are higher; 2) during summer, surface waters remain nutrient depleted and dinoflagellates rapidly respond to local nutrient enrichment from river discharges or coastal upwelling; 3) rainfall-induced freshets in autumn lead to brief diatom blooms followed, as in spring, by blooms of dinoflagellates. The duration of spring and summer blooms appear to be limited by nutrient availability while autumn events appear to be more dependent on stable meteorological conditions and perhaps intense recycling of local production.

The October 1984 *Gymnodinium* bloom exemplifies this latter process. Intense precipitation in mid-August brought new nutrients previously accumulated in river beds into the coastal basin leading to an initial diatom bloom, subsequently replaced by the *Lingulodinium.* In September *Lingulodinium* was in turn replaced by *Heterocapsa* in the north and *Gymnodinium* in the south. With winds blowing seaward (Libeccio), the bloom spread over a large area, later invading the whole northern basin.

A coastal plume of less saline, nutrient-rich water is always found south of the Po River delta, with strongest flow and widest extent from autumn to spring. With surface warming and summer thermohaline circulation, much of the Po River's plume extends eastward into the basin from the eastern delta, confining some of the southern flowing coastal plume on shore as it moves to the southeast. Nutrients from terrestrial drainage are utilized and recycled in the water column of the coastal area and partially retained in its sediments. Dissolved nutrient concentrations are maintained at relatively high levels with an apparently positive balance between the inputs and outputs from the system. Phytoplankton is found in the plume and along discontinuities resulting from thermohaline circulation and the salt gradient between the coastal plume and more oligotrophic basin waters. Localized blooms result from spatial and temporal heterogeneity in nutrient inputs, vertical stratification, and frontal convergence. Few if any blooms are initiated from recycled nutrients delivered from the bottom al-

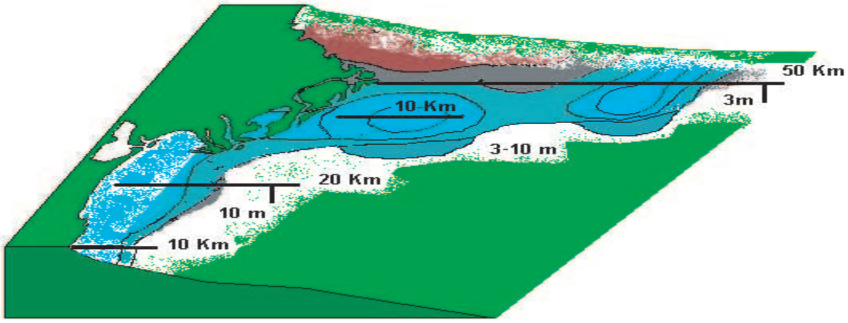

Figure 18.3: Scheme of Po River plume and Emilia Romagna coastal region dynamics.

though perpetuation of existing blooms has been suggested.

Extension of the Po River plume into the oligotrophic basin of the Northern Adriatic in the low discharge summer period or, alternatively, during winter Bora, should also lead to aperiodic blooms, reflecting increased buoyancy, nutrient enrichment as well as dinoflagellate accumulation at convergences between the lower salinity plume and basin surface waters. However, although elevated chlorophyll levels are reported during the eastern extensions of the plume, there is only one study containing taxonomic information (*Gymnodinium*, see above) that dinoflagellates dominated plume autotrophic biomass.

On smaller scales, red tides of May-June, 1977, 1980, 1981, and 1983 in the Gulf of Trieste always followed Isonzo River freshets. The river's discharge constitutes the only significant freshwater source for the shallow Gulf of Trieste, with low flows in early winter and summer and high flows in early spring and autumn. Episodic short-lived pulses of high flow may occur in late spring and summer as a result of local storms. Heavy rains in this period have led to high river discharge lowering surface salinity (from >37 to <32) and an enrichment of Gulf surface waters with new nutrients, primarily as nitrates. At the same time, sunny weather can increase surface temperature by 2–3 °C. These hydrological conditions have led to optimal conditions for dinoflagellate growth, with critical depth exceeding the mixing depth yielding a diluted and warm surface layer favoring bloom development. Blooms are more frequently noted in the inner, less hydrodynamic portions of the Gulf, and persist for less than a week followed generally by dispersion from winds from the land, mainly the Bora (ENE) (Sellner & Fonda Umani, 1999).

However there are evidences that significant blooms, particularly red tides occurred with greater regularity in the 1970s and 1980s than in recent years. More recent data collected during late 1980s and 1990s have shown a decrease of phytoplankton biomass as chl a in summer and autumn, due to a decrease frequency of dinoflagellate blooms. These changes can be attributed to a reduction of phosphorus loads with progress in wastewaters treatment in the region, and to the replacement of polyphosphate in detergents throughout Italy. This latter measure resulted in reduced phosphorus concentrations in Po River waters and thereby impacted the receiving waters of the northern Adriatic (Harding *et al.*, 1999).

## 18.7 Mucilage Phenomena

The accumulation of surface mats of mucus are frequent in the northern Adriatic over the last 15 years, inconveniencing coastal inhabitants, reducing tourism, and affecting benthic communities (Figures 18.3  18.4).

Figure 18.4: Mucilage strips.

Figure 18.5: Mucilage surface creamy layer in a small harbour.

The recent history of 'mare sporco' may indicate a basic shift in environmental conditions from those generally favorable to post-spring dinoflagellate blooms to those favoring elevated saccharide production in nutrient-limited diatom populations (Figure 18.5).

The accumulation of large floating masses of mucilage in the northern Adriatic has been documented since 1729. These masses are large complexes of gel-like heteropolysaccharides with glucose the dominant monosaccharide followed by mannose, fructose, galactose, arabinose, ribose, xylose, and fucose. With age, $\alpha$-glucosidic bonds give way to $\beta$-glucosidic linkages, characteristic of refractory polymeric saccharides. Bacteria capsular material is also suggested as a source of heteropolysaccharides as mucilage accumulates. Lipids are found in trace amounts in the matrices while C to N ratios vary widely from about 3, suggesting nitrogen enrichment to 29, indicative of nitrogen-deficient conditions.

Mucilage events have been noted in the northern Adriatic since 1729, followed by events in 1872, 1880, 1891, 1901,1903, 1905, 1920, 1921, 1922, 1924, 1929, 1930, 1949, possibly 1951, and most recent episodes in 1988, 1989, 1991, 1997, 2000 and 2002. In 1976 and 1983, mucilage accumulation was isolated in the Kvarner region. In 1988, 1989, and 1991, the large aggregations of gelatinous masses were noted throughout the Northern Adriatic, spreading along the eastern and western coasts; in 1990, it occurred only in the Kvarner area. In 1997, mucilage was also noted although less visible in the largest part of the northern basin areas than in the other regions. In 2000 and 2002 it was mostly confined in the intermediate layers and few surface mats were noticed.

In general, 'mare sporco' is observed in spring-summer following the spring diatom bloom. There are some data to suggest that areas characterized by early annual minima in flow (e.g., Kvarner region) are typified by earliest mucilage formation as northeastern and eastern regions were the sites for first observation of mucilage in 1988, 1989, 1991, and 1997, usually June-July. Mucilage eventually becomes most concentrated along frontal systems with time, particularly well developed in the western northern Adriatic off the Po delta. Recent findings suggest that the first accumulation might occur in a central nucleus of intermediate water derived from modified LIW intrusions.

Spatial distribution of mucilage in the system is governed by several forces. Vertical distributions are determined from the difference between densities attributable to increasing particle scavenging by the aggregates with time versus buoyancy derived from gas bubble formation in the mucilage.

Once formed, mucilage in the surface mixed layer is moved throughout the NA as a function of winds, the eddy circulation pattern, and surface horizontal current velocities below 20 cm $s^{-1}$.

## 18.8 Mechanisms

Degobbis et al. (1995) have argued that aperiodic discharge of the Po during the early summer delivers nutrients for rapid uptake and assimilation by the late spring diatom community, leading to phosphorus limitation This, in turn, favors the production of high molecular weight exocellular and intracellular saccharides fibrils and through death and decomposition, cell wall debris.

In the Gulf of Trieste, Faganeli *et al.* (1995) provided a chronology for mucilage formation, aggregation, and sedimentation in response to discharge of the Isonzo River, indicating that this phenomenon might occur throughout the NA and its adjoining bays. N, P, and silicon inputs in the spring stimulated phytoplankton production, resulting in increases in particulate protein and carbohydrate. Depletion of nutrients led to decreases in protein while particulate carbohydrate concentrations remained unchanged. Marine snow resulted, followed by macroaggregates. After six weeks, the aggregates were most abundant at 10 m with sedimented macroaggregates typified by the same $\Delta\ ^{13}$C signal, i.e., that of structural heteropolysaccharides, as the initial spring bloom. Later, mucilage was found in superficial bottom sediments.

Accepting the role of P-limited diatom growth

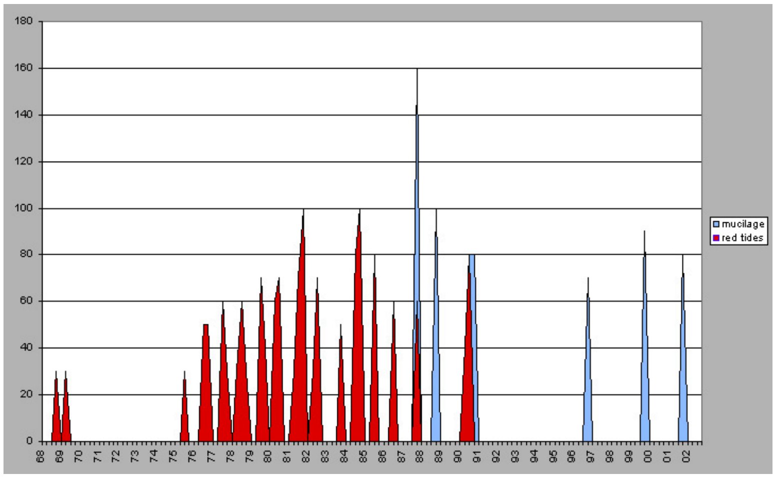

Figure 18.6: Relative appearances of red tides and mucilage events in the Northern Adriatic.

as the initial source of polysaccharides, there are three plausible mechanisms for subsequent development of mass mucilage accumulations in the NA. Differences arise on the fate of diatom production and its role in pelagic carbon and nutrient cycling. The first hypothesis favors lysis of diatom populations and accumulation of cell wall and intracellular polysaccharide materials. This lysis hypothesis has only just been proposed and requires basin-wide research on lytic agent distributions and activities. Two other hypotheses are slightly more plausible due to common foundations on characteristic regional water quality and circulation. In one, advocated by Herndl*et al.* (1992), the diatoms become P-limited and produce large amounts of polysaccharides. Ambient bacteria initially hydrolyze the nitrogenous substrates and $\alpha$-glucosidic polysaccharides, leading to increasing C/N and a more refractory, gel-like aggregate with high proportions of $\beta$-glucosidic saccharides in accumulating matrices. P-limited bacterioplankton produce only small amounts of exocellular enzymes capable of hydrolyzing these compounds as well as large molecular weight compounds, including refractory capsular material, further stabilizing the mucilage. The mucilage matrix sinks to the pycnocline, scavenging plankton and other seston. This scenario also has room for some of the lysis argument in that, as aggregates age, cells lyse, release saccharides into the matrix and extend fibril/stringer-like matrices.

Mucilage accumulating at the pycnocline can rise through the water column as a function of photosynthetic activity. This ascent and nocturnal descent favor continued entrapment of plankton and seston from the water column, leading to enrichment of pico-microplankton in the aggregates. Depending on bubble-induced buoyancy versus net density, aggregates can be trapped at the sea surface to yield a photo-oxidized scum or sink to the pycnocline where aggregations aperiodically cascade to the bottom, leading to bottom water anoxia and mass benthic mortalities.

The third hypothesis, principally advocated by Azam *et al.* (1999), suggests that the persistent phytoplankton blooms in the Northern Adriatic Sea are sustained by efficient P remineralization. Bacteria remineralize P in preference to carbon because of high phosphatase activity relative to glucosidase activity (40–53 fold higher activities), yielding organic matter with high C/P, including slowly degrading polysaccharides. P is remineralized from the saccharide accumulations, perpetuating high productivity and additional high C/P polysaccharides. As noted by Herndl *et al.* (1992), bacterial capsular material, polysaccharides and mucopolysaccharides, further stabilize the saccharide matrices. Accumulated saccharides rise to the surface not through photosynthetic activity but through bacterial-mediated denitrification and accumulation of $N_2$ in the mats.

The most recent findings (Fonda Umani *et al.*, 2002) indicate that an uncoupling between primary production and bacterial carbon demand can be envisage as one of the most important factor to increasing dissolved organic carbon availability which eventually aggregates as mucilage.

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## Chapter 19

# Pelagic eutrophication in the Gulf of Riga

Paul Wassmann
Norwegian College of Fishery Science
University of Tromsø
N-9037 Tromsø, NORWAY
paulw@nfh.uit.no

### 19.1 Introduction

Quantitative estimates of the fluxes and dynamics in the nutrient load on marine environments, their distribution and channelling through the food web and the effect on the increase of new production, are fundamental and constitute a prerequisite for the planning of actions for water protection measures. The Gulf of Riga is no exception. The Gulf is a semi-enclosed part of the eastern Baltic Sea, surrounded by Estonia and Latvia and has one major outlet, the Irbe Straight Sound, and one minor one, the Muhu Sound. The Gulf of Riga has a surface area of 19,000 km$^2$, is up to 67 m deep, has a relatively simple topography and a volume of 420 km$^3$ (Figure 19.1). The Gulf is eutrophicated and most of the pollution loads in the Gulf can be attributed to human activities in the drainage basin, which covers 135,700 km$^2$, or more than seven times the surface area of the Gulf itself. In pelagic environments the fate of organic matter produced by an increased supply of nutrients, the regulation of vertical flux and in particular the pelagic-benthic coupling are not well known in general, let alone in the Gulf of Riga. Since the beginning of this century Estonian, Latvian, Lithuanian and Russian scientists have already carried out a substantial body of work in various disciplines in the Gulf of Riga and its drainage area (summarised by Ojaveer 1995). From 1993–1997 Nordic and Baltic scientists joined forces in an international project, the 'Environmental Research in the Baltic Sea', also referred to as the 'Gulf of Riga Project' (GoR). The objective was to study environmental problems in the Gulf and its drainage area, and to determine their impact on the rest of the Baltic Sea in general and the Baltic Proper in particular (Figure 19.2).

The investigations reviewed here aim at to understand the Gulf of Riga as an ecosystem by analysing

1. the dynamics of the runoff of nutrients and their supply to the Gulf
2. the distribution of nutrients in the Gulf

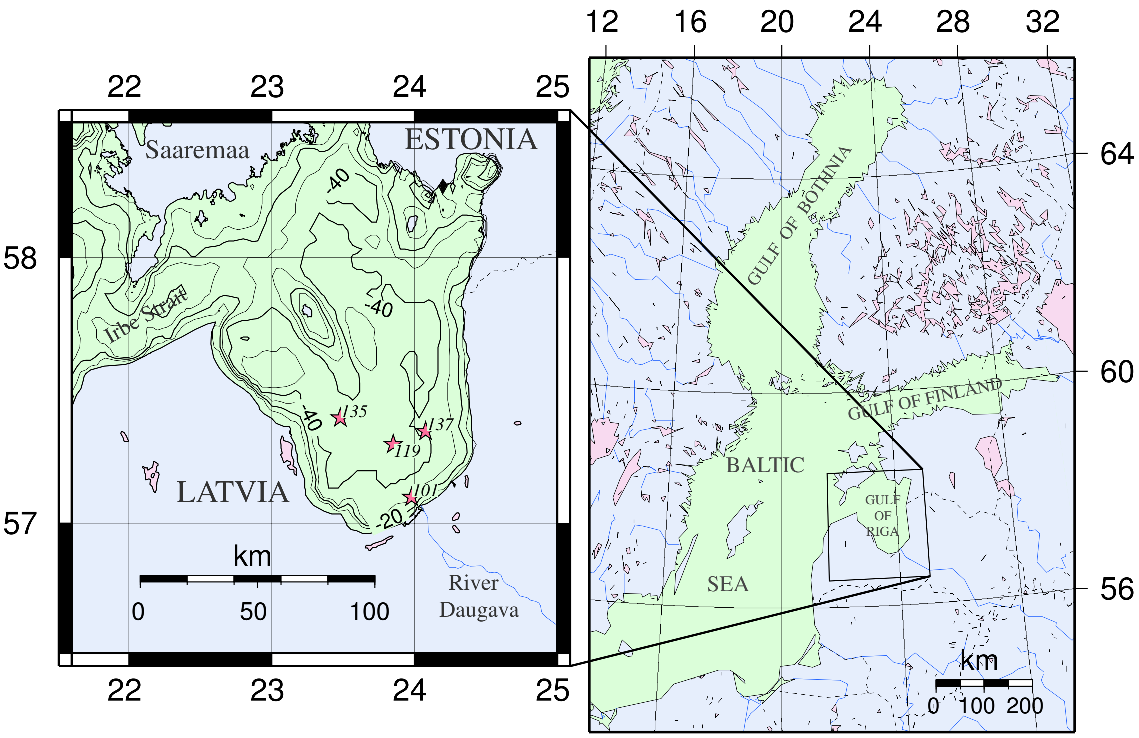

Figure 19.1: The Gulf of Riga between Estonia and Latvia. Also shown are some of the stations that were investigated

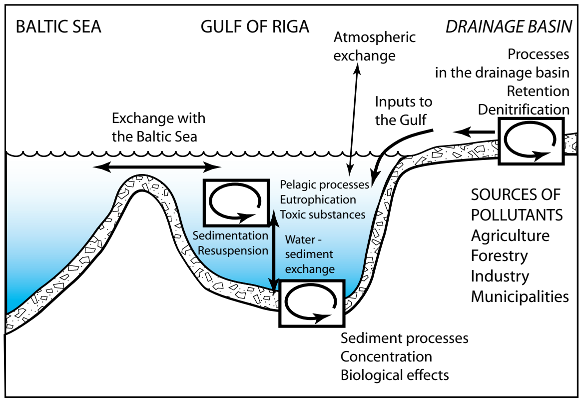

Figure 19.2: A conceptual scheme of the Gulf of Riga project.

3. the production and distribution of plankton and organic matter and

4. the processes involved in settling and the vertical export of organic matter

This chapter rests upon 14 publications from the project 'Pelagic eutrophication and sedimentation' (Wassmann & Tamminen, 1999); see also J. Mar. Syst, Vol 23.

## 19.2 The riverine input of nutrients is high, area-specific loads are low

The Gulf of Riga receives more than 140,000 t of nitrogen and 3,000 t of phosphorus annually (Laznik *et al.*, 1999). Most of this pollution load can be attributed to the activities in the drainage basin of the Gulf of Riga. The two largest drainage basins are those of the Daugava and Lielupe River,

Figure 19.3: The town of Riga, the river Daugava and the adjacent coast in the southern coast of the Gulf of Riga.

which cover 78% of the total drainage area (Figure 19.4). On an annual basis, runoff corresponds to 9% of the total water volume of the Gulf. Thus, the impact of the rivers on the Gulf of Riga is substantial. River supply to the Gulf of Riga is by far the most important pathway of nutrients. Approximately 113,000 t of nitrogen (79% of the total load) and 2,050 t of phosphorus (68% of the total load) are annually transported by the rivers to the Gulf. In addition, the Gulf receives approximately 65,000 t $yr^{-1}$ of silica. Bio-available forms of nitrogen and phosphorus were shown to be responsible for 55% and 74% of the total loads of nitrogen and phosphorus, respectively. The share for the inorganic nitrogen is comparable with other Baltic Sea rivers, whereas the share for phosphate is somewhat higher (P. Stålnacke, pers. comm.). The high N:P ratio (>50 on an average annual basis, w:w) suggests that rivers entering the Gulf of Riga are phosphorus-limited, and that their discharge contributes to phosphorus limitation in the Gulf, which was suggested by Yurkovskis et al. (1993).

Although the riverine input of nutrients is high, the area-specific load from the catchment area of the Gulf of Riga is low or moderate compared to loads from other areas in the Baltic Sea region. For example, Stålnacke (1996) reported annual area-specific riverine exports of 12.2 kg $ha^{-1}$ for nitrogen and 0.42 kg $ha^{-1}$ for phosphorus in the Western Baltic sub-basin (i.e. Kattegat, The Belts, Øresund) compared to 8.3 kg $ha^{-1}$ for nitrogen and 0.15 kg $ha^{-1}$ for P reported for the Gulf of Riga catchment area by Laznik et al. (1999). These relatively low values are unexpected in view of the generally inefficient sewage treatment for the 4.5 million inhabitants in the drainage basin and the previously intensive agriculture (approximately 40% of the catchment area is used for agricultural production) with e.g. inefficient and inappropriate handling and spreading of manure and commercial fertilisers.

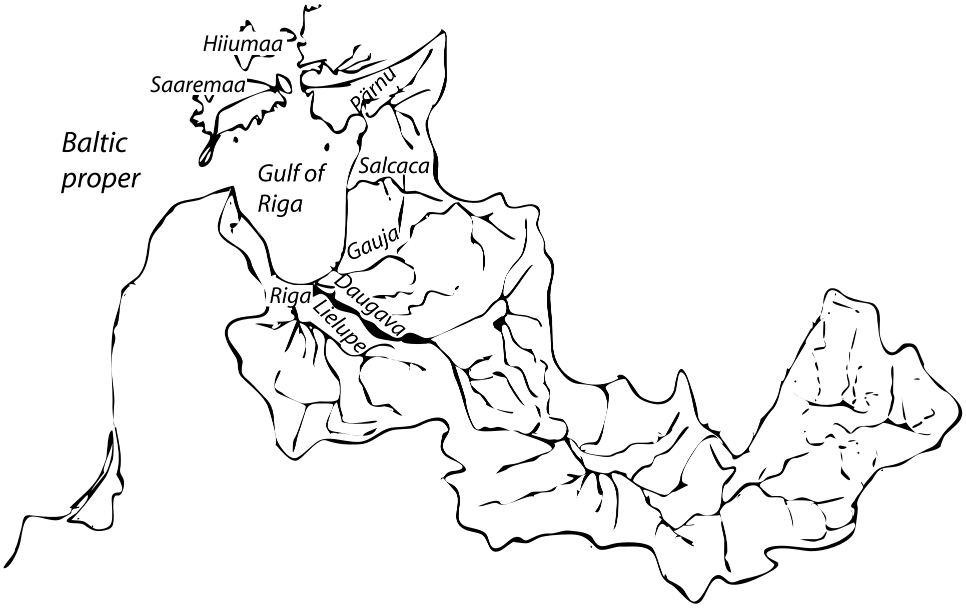

Figure 19.4: The water shed of the rivers discharging into the Gulf of Riga.

## 19.3 Temporal variation in riverine loads is substantial

The temporal variation in riverine loads of nutrients to the Gulf of Riga is substantial and characterised by both large interannual and seasonal variations. Most of these variations can be explained by natural fluctuations in runoff (Laznik *et al.*, 1999). The large interannual variation in the nutrient loads can be exemplified by the nutrient loads for 1984 and 1990, which differed by a factor of two for all major nutrient constituents. The seasonal distribution in load also correlates well with the variability in runoff. Comparatively low loads normally follow a pronounced peak during the spring flood during the low-flow period in summer. For example, the phosphorus load of the Daugava River in April usually accounts for 20% of the total annual load, whereas the corresponding loading during summer is much lower.

The annual loads in the period investigated (1993–1995) were, when compared with a 20-year average, relatively normal. Thus the biological investigations of the present study were carried out in a runoff scenario that resembles the average over the last 20 years. However, in recent years increased nitrate concentrations were observed in the Daugava River (P. Stålnacke, pers. comm.). No definite and clear evidence of downward trends in the nutrient loadings related to the rapid economical recession (particular agriculture: fertiliser application decreased to 20%) in the catchment area in the former republics of the Soviet Union (i.e. Baltic Republics and Belarus) can be noted. The decrease in annual loadings that can be observed in certain periods is almost solely due to a decrease from the high runoff observed during other periods.

## 19.4 Riverine runoff dominates hydrography in spring, variable atmospheric forcing during summer — a shift from lateral to vertical processes

At the beginning of the annual plankton succession, the spring flood period dominates the growth conditions of phytoplankton not only because of the nutrient supply factor, but also because of the physical conditions. The density difference between the high riverine runoff and the well-mixed basin water results in a strong, diffusive river plume. Salinity differences are the main agent for springtime stratification, and the buoyancy transport from springtime river runoff can re-stratify the Gulf after winter homogenisation in a period of about 5 weeks. During summer this would take about 1 year, indicating that the river runoff plays a major role in the creation of stratification only in spring (Stipa *et al.*, 1999).

The springtime river plume implies a formation of distinct horizontal gradients within the basin, whereas during summer conditions the weak river plume quickly dissolves and creates spatial variability in the southernmost basin only. The horizontal stratification gradients during spring have significant effects on the depletion of wintertime nutrients from the water column, and thus on the forthcoming growth conditions of planktonic communities during the stratified period. The areas in the middle and northern Gulf are mixed down to the bottom far later than the southern basin, which is under immediate river plume influence (Stipa *et al.*, 1999). Therefore significant nutrient reserves remain in the intermediate and deep layers of the southern basin after spring, whereas the northern basin is depleted of nitrate and especially phosphate down to deep layers (Tamminen & Seppälä, 1999).

After the establishment of thermal stratification the surface fluxes take over the buoyancy forcing by lateral freshwater eddy fluxes, and the mixed layer starts to deepen due to more variable atmospheric forcing. This implies higher temporal variability in the growth conditions of the planktonic community, and also more variability of lateral heterogeneity than during spring. An especially important feature of the vertical processes is the relation between mixed layer deepening and the depth of the euphotic zone, which in the Gulf of Riga is typically around 10 m as in adjacent Baltic Sea. Towards early autumn, the depth of the mixed layer clearly exceeded the euphotic zone, with dramatic consequences for the nutritional and production preconditions of the planktonic biota (Tamminen & Seppälä, 1999; Olesen *et al.*, 1999).

## 19.5 The Gulf is basically nitrogen-limited

The total nutrient pools in the Gulf of Riga show significant seasonal changes. Springtime levels of ca. 400 *mug* N l$^{-1}$ and 30 µg P l$^{-1}$ in the whole basin (1995) except for the southern River Daugava plume, where concentrations of >>600 µg N l$^{-1}$ and up to 40 µg P l$^{-1}$ have been detected. During the summer stages, total nutrient pools levels are lowest (on average, 270 µg N l$^{-1}$ and 17 µg P l$^{-1}$ in June 1994), increasing slightly from midsummer and onwards (Tamminen & Seppälä, 1999). The annual cycle of total nutrients with maximum in spring, minimum in early summer and gradual increase towards autumn is well established for adjacent Baltic areas like the Gulf of Finland, and overall total nutrient levels were comparable to long-term data from the coastal areas of the middle and eastern Gulf of Finland (HELCOM, 1996). Thus the total nutrient pools of the Gulf of Riga indicate a rather similar overall degree of eutrophy as other Baltic subareas.

The early spring 1995 nutrient distributions clearly indicated that the spring bloom period in the Gulf of Riga is potentially N-limited, since during the homothermal and deep-mixing season, inorganic N/P ratios were markedly and uniformly below the Redfield ratio in the whole basin, with the exception of the River Daugava plume (Tamminen & Seppälä, 1999). In early summer 1994, the mixed surface layer was effectively depleted of inorganic nutrients (both phosphate, nitrate and ammonium), yielding low (<Redfield) inorganic N/P ratios, except for the southernmost basin, which had high ammonium levels because of a strong mixing event. In mid-July 1994, very low inorganic nutrient concentrations and very low inorganic N/P ratios prevailed over the whole Gulf in the surface layer. Under this strongly N-limited productive layer, cumulative mineralization of am-

monium and phosphate took place in the relatively warm intermediate layers, as well as near to the bottom. A strongly N-limited productive layer, and equally strongly N-surplus deeper strata below the mixed layer characterize the summer stages in the Gulf of Riga as long as distinct separation of these layers prevail (Tamminen & Seppälä, 1999).

It is obvious that physical mixing events can produce drastic temporary fluctuations in the limitation pattern by introducing the significant nitrogen reserves from deeper water into the euphotic zone. When the effectively mixed surface layer depth exceeds significantly the depth of the euphotic zone towards the end of the stratified period, the production preconditions of planktonic autotrophs deteriorate, and consequently so do their capacity to utilise the nutrient pool of the mixed surface layer. As the considerable accumulations of nutrients in deep layers are also mixed into the surface layer, a combined result could be a sharp increase of inorganic nutrients in the euphotic zone.

Deep mixing during the stratified period promotes P-limitation, whereas a thin or moderate mixed layer promotes N-limitation, as previously observed in the outer estuary of the River Neva, eastern Gulf of Finland (Pitkänen & Tamminen, 1995). During the stratified period, strong mixing events due to physical forcing can abruptly change the prevailing N limitation into a P-limited phase, but unless deep mixing is prolonged, N-limitation is likely to be re-established in the surface layer. The probability of P-limited phases should increase towards the end of the stratified season, both due to the hydrographical development towards deep mixing, and to cumulative increase of subthermocline N reserves. The Gulf of Riga appears therefore to be characterized by considerable, hydrographically driven interannual and within-season variability with regard to surface layer inorganic nutrient concentrations and limitation patterns, in spite of the essential N limitation of the basin. The limitation scenario suggested by Tamminen and Seppälä (1999), which contradicts the conclusions of Yurkovskis et al. (1993) and Suursaar (1995) suggesting P limitation of the Gulf, is supported by experimental evaluation of nutrient limitation of the natural planktonic communities (Seppälä *et al.*, 1999).

Figure 19.5: *Cladophora*, a filamentous algae that is characteristic species in eutrophicated, marine and brackish water regions, growing on a stone in the Gulf of Riga.

## 19.6 Spatial variability of phytoplankton and pigments of the entire Gulf is high

During the spring bloom in 1995, the spatial structures of the high phytoplankton biomass and chlorophyll a were well explained by common factors such as inorganic N, total N and P, salinity and the depth of the mixed layer (Seppälä & Balode, 1999). Contrary to our expectations, the SW part of the Gulf was more influenced by the freshwater flow from the river Daugava than the SE part. Furthermore, the bloom was more pronounced in the SW part of the Gulf. Also in the central region of the southern gulf are influenced by the freshwater load. The river plume can move towards the centre and the western part of the Gulf instead of the anticipated north-easterly direction suggested by the general circulation pattern. This is obviously caused by the predominating wind strength and direction and suggests that wind plays a significant role for the spreading of surface and river plume water in the Gulf of Riga.

During the middle of the spring bloom diatoms prevail over the entire Gulf, but algal biomass and chlorophyll a can quickly decrease during week-long periods, although considerable amounts of inorganic N and P are still available (Seppälä & Balode, 1999; Tamminen & Seppälä, 1999). The dinoflagellate *Peridiniella catenata* can be an important constituent of the phytoplankton spring community. The reduction of the silicate pool over the last ten years in the Gulf of Riga (Yurkovskis & Kostrichkina, 1996), which is probably the result of decreased runoff (Laznik *et al.*, 1999), could be one of the factors stimulating the development of dinoflagellates in late spring, as dissolved silicate becomes a limiting nutrient for diatoms. The proportion of diatoms/non-silicate demanding phytoplankton species varies in accordance to the annual and climatological variations in runoff. Strong stratification of the water column appeared to enhance sedimentation of diatoms while the motile dinoflagellates controlled their position in the water column in spring (Olli, 1999; Olli & Heiskanen, 1999). In the most stratified region in the southern Gulf a clear dominance of diatoms, however, remained.

The early summer stage is characterized by a homogenous distribution of algal biomass and low concentrations of inorganic N and P. Picoplankton was dominating the phytoplankton community in the outer Gulf (Seppälä & Balode, 1999). The small relative fraction of picoplankton in the regions affected by nutrient load in the southern part of the Gulf is in accordance with the conclusions of Kuparinen and Kuosa (1993). The dominating species of green algae, *Monoraphidium contortu*m was probably favoured by eutrophic conditions (Kononen, 1988); the opposite seemed to be true for dinoflagellates.

An intense bloom of the cyanobacterium *Aphanizomenon* sp. took place in the middle of the summer of 1994 after an increase in temperature of the surface layer. Similar to the situation in spring, the abundance of *Aphanizomenon* sp. was related to the common structure of N, P and freshwater, and the bloom was most dense in the southern Gulf (Seppälä & Balode, 1999). It has been postulated that the recent increase of cyanobacteria blooms is caused by the decreasing DIN/DIP ratio (Balode, 1994; Balode & Purina, 1996). During the cyanobacteria bloom in 1994, the DIN/DIP ratio was rather low (0.7–6.4 w:w). As during the early summer stage, the contribution of picoplankton was lower in the most eutrophicated, southernmost areas (Tamminen & Seppälä, 1999). Cyanobacteria are obviously supported by the high nutrient status of the river runoff. Less eutrophic conditions in the central and northern parts of the Gulf favoured the growth of cryptomonads and diatoms.

The early autumn phase in 1993 (after an intense bloom of cyanobacteria which covered the entire Gulf; Kahru *et al.*, 1994) was characterized by high heterotrophic activity and the phytoplankton community was dominated by cryptomonads (on average 50% of the total biomass). Diatoms were relatively more abundant in the most nutrient-rich southern Gulf. Cryptomonads, as main constituents of the phytoplankton community, were most abundant on the western side of the Gulf or generally in areas with less total N or P.

Basin-wide the distribution of phytoplankton variables correlated clearly, except during the early autumn stage, with environmental factors such as salinity, stratification and nutrients. Thus, the distribution of phytoplankton variables followed closely the patterns of nutrient-rich freshwater (Seppälä & Balode, 1999). The nutrient load from the rivers obviously generates a south-north gradient of phytoplankton biomass while the east-west gradient is more variable, probably depending on the predominating winds. The differences in phytoplankton biomass or chlorophyll a along the north-south axis were 3 to 6 fold. It seems to be clear that the nutrient load from rivers in the southern Gulf of Riga is the reason for higher phytoplankton biomass in the southern Gulf, especially during blooms.

## 19.7 Temporal variability dominates over spatial variability in the central and southern Gulf

High seasonal differences in the phytoplankton community structure and sedimentation characterise the southern Gulf of Riga (Olli & Heiskanen, 1999). However, the high within-season temporal variability dominates over the variability between different areas of the southern Gulf. For most of the suspended and sedimented parameters studied at the spatial stations, the recorded variability is significant in all seasons (Lundsgaard *et al.*, 1999; Reigstad *et al.*, 1999). The temporal variation found in the centre of the Gulf was even higher than the spatial variation. The situation off the mouth of the Daugava river is, however, different. This station is affected by resuspended matter at depth and by the suspended loads from the river runoff in the upper water column.

The sedimentation in the southern and central Gulf of Riga is influenced by river discharge, stratification and wind (Reigstad *et al.*, 1999). Wind causes high temporal variability in nutrients, suspended matter and vertical fluxes. In particular the wind direction changes the concentration of suspended matter and influenced stratification of the surface water that is influenced by both the river Daugava and by water entering through the Irbe Straight. The influence from the river on the sedimentation rates and retention of nutrients in the Gulf is difficult to evaluate since short-term variation exceeded the spatial variation in the Gulf.

## 19.8 Moderate primary production and high community respiration rates

Plankton community production and respiration rates in relation to wind, solar radiation, biomass and nutrients revealed that the predominant limiting factor for phytoplankton growth is nutrient supply during spring and summer (Olesen *et al.*, 1999). In autumn, the combination of low light levels and deep vertical mixing due to wind leads to conditions of light limitation. The growth conditions are in all three situations, however, strongly affected by the stabilising (solar heating) and destabilising (wind) forces acting on the system. Depending on the relative strength of these forces, day-to-day primary production varies by a factor of two. Under conditions of nutrient limitation mixing may lead to increased photosynthesis, which is a consequence of improved exploitation of incident light and of available nutrients in the deeper mixed layer.

Primary production and respiration measurements indicate that the gross primary production is generally high during the productive season, on average about 2 g C $m^{-2}$ $d^{-1}$ (Olesen *et al.*, 1999). Assuming that this estimate is representative for a presumed growth period March/April to October (approximately 200 days), the total annual primary production is estimated to range between 300 and 400 g C $m^{-2}$ (Olesen *et al.*, 1999). High respiration estimates (on average about 4 g C $m^{-2}$ $d^{-1}$) demonstrates that the pelagic system is rather based on regenerated than on new production. This is supported by simultaneous vertical flux measurements (Lundsgaard *et al.*, 1999) that indicate that the export of autochthonous matter out of the euphotic zone, relative to the standing stock and primary production, is small. Compared to many other coastal areas, the pelagic system of the Gulf of Riga appears exceptionally efficient in recycling and its ability to retain biogenic matter and nutrients in the upper layers.

## 19.9 Phytoplankton assemblages and the limited vertical export of phytoplankton cells

During spring the Gulf is characterised by an intensive dinoflagellate (mainly *Peridiniella catenata*) dominated spring bloom while the diatom

*Thalassiosira baltica* contributed most (80 to 90%) to the settling phytoplankton biomass. As mineral nutrients are abundant during the bloom it is suggested that the differential sedimentation of species is caused by physical factors (Olli & Heiskanen, 1999).

During summer the phytoplankton biomass is dominated by high abundance of the filamentous cyanobacterium *Aphanizomenon* sp., autotrophic nanoflagellates and picoplankton. The primary vertical flux of phytoplankton is mainly due to non-motile species and aggregate-bound picoplankton and *Aphanizomenon* sp. Below the pycnocline, resuspended dormant diatom populations cause a significant secondary flux. Large heterotrophic dinoflagellates (*Gyrodinium/Gymnodinium*) are abundant in the middle layers and associated with ammonium regeneration. The phytoplankton assemblage appears to have three major functional groups, which build up roughly equal parts of the total biomass (Olli & Heiskanen, 1999):

1. Large filamentous cyanobacteria (*Aphanizomenon* sp.). These are mainly inedible by the majority of the ambient zooplankton community in the Baltic Sea (Sellner *et al.*, 1994, 1996). As with the grazing losses, the sedimentation loss rates of this group are very low. Consequently, the fate of this biomass is probably to disintegrate in the water column and to fuel the detrital and microbial pathways of the food web.

2. Nanoflagellates (e.g. *Teleaulax* spp., *Plagioselmis prolonga*, *Pyramimonas* spp., *Pedinelle* spp. and *Pseudopedinella* spp., *Chrysochromulina* spp., *Heterocapsa rotundata*). These are usually considered as readily available for mesozooplankton grazing. Their abundance points at the importance of the grazing food chain and represents the 'efficient' part of the energy transfer in the food web to higher trophic levels. The sedimentation of this compartment is also insignificant. It is suggested that most of the nanoflagellates are grazed, and that their abundance is the result of an equilibrium between their growth and herbivory.

3. Picoplankton. This includes picocyanobacteria and pico-sized eucaryotes. The abundance of picocyanobacteria is quite common everywhere in the Baltic during summer. It is suggested that this compartment is an important food source for ciliates and cladocerans. Surprisingly, the sedimentation of picocyanobacteria was consistent. A likely mechanism is sedimentation within detrital aggregates.

The only significant sedimentation of fresh phytoplankton biomass took place in spring, in particular for *Thalassiosira baltica*. In the other seasons phytoplankton sedimentation appears unimportant. The matter that sedimented was detritus. Consequently, there must be mechanisms that prevent vertical export of phytoplankton cells and promote recycling of bioelements in the pelagic ecosystem of the Gulf of Riga.

## 19.10 The importance of microbial and viral loops in carbon cycling

In the planktonic ecosystem bacteria are the main consumers of dissolved organic carbon, and bacterial carbon production can be as much as half, or at times even higher than the primary production because carbon can be recycled several times through the microbial loop (Giorgio *et al.*, 1997). This seems to be the case in the Gulf of Riga during summer, when bacterial production was as high as primary production (Tuomi *et al.*, 1999). The carbon fixed by the phytoplankton is released by direct exudation, cell lysis and directly from the higher trophic levels (e.g. sloppy feeding). All this dissolved organic matter can be utilised by bacteria. Viral lysis of bacterioplankton is thought to make the bacteria-DOM-bacteria loop even more important (Thingstad *et al.*, 1993). Thus, there are several routes by which the carbon from the primary producers ends up in bacteria and can be cycled several times through bacteria. One important route is the lysis of the cells due to viral infection. On average more than half of the bacterial production in the Gulf of Riga was lost through viral lysis (Tuomi *et al.*, 1999). This bacterial carbon is recycled back to bacteria. Unfortunately it is not possible to estimate how much of the other plankters in the Gulf were lysed. In particular phytoplankton blooms may be attacked by viral infection.

Grazing by heterotrophic nanoflagellates and viral lysis have been recognised as two main reasons for bacterial mortality in aquatic ecosystems (e.g. Fuhrman & Noble 1995). Viral lysis of bacterial biomass produces dissolved organic matter to be utilised again by bacteria, while grazing can transfer bacterial carbon and other elements to higher trophic levels. In the Gulf of Riga heterotrophic nanoflagellates were estimated to consume on average one third of the bacterial production (Tuomi *et al.*, 1999). Due to respiration and sloppy feeding, only part of this carbon finally ends up to higher trophic levels.

It appears that a larger proportion of the carbon channelled into bacteria is recycled among the bacteria than is transferred to the higher trophic levels in the Gulf of Riga. Between trophic levels bacteria are thus more a sink than a link. Viral lysis of the cells seems to be very important at least among the bacteria. This results in the consumption of carbon among the bacteria and fast turnover of mineral nutrients. While the amount of carbon recycled through bacteria is as high as the primary production during summer, the bacterial production is lower during the other seasons, where bacterial production comprised 13 to 45% of primary production (Tuomi *et al.*, 1999). Thus the importance of the microbial loop in the carbon cycling of the whole plankton community is less pronounced.

## 19.11 P retention depends on the complexity of the pelagic food web

indexphosphorus!retention indexpelagic!nutrient retention

Although increased vertical export of C and N was recorded along with the export of phytoplankton cells at the end of the spring bloom (Olli & Heiskanen, 1999), pelagic retention of P is already high in late spring, resulting in low vertical loss rates of P. It is suggested that increased export of C, N and P to the benthos may take place during the spring bloom *before* the pelagic system develops sufficient complexity to greatly reduce vertical losses. The main supply of phytoplankton biomass to the benthos in the Gulf of Riga is thus determined by the time window characterised by low trophic complexity in spring. Retention of P was also high during summer and early autumn. In regions where nutrients are continuously supplied both from allochthonous and autochthonous sources, C and N are lost in excess while P is recycled from the pelagic system throughout the productive season (Heiskanen *et al.*, 1996). However, species-specific differences in bloom dynamics and sedimentation (i.e. dinoflagellates vs. diatoms) give rise to episodic events which are crucial for the further channelling of the assimilated nutrients and produced biomass into pelagic or benthic food webs (Heiskanen, 1998). Seasonal and annual variations in nutrient supply through rivers (Laznik *et al.*, 1999), in particular with regard to dissolved silicate, will possibly contribute to the differences in dinoflagellates vs. diatoms prevalence and thus induce interannual changes in the pelagic-benthic coupling.

The efficiency of P retention depends on the complexity of the pelagic food web and is enhanced by the increasing complexity of the trophic structure in the system over time. Increased P retention will also counteract the P deficiency induced by river runoff (Laznik *et al.*, 1999) and contribute to the complex N vs. P limitation scenarios recorded from the southernmost Gulf (Seppälä *et al.*, 1999). Through this response P limitation may be eliminated and the P requirements of phytoplankton are adequate. The trophic complexity of the planktonic community in the southern and central Gulf of Riga and the variable, but continuous supply of nutrients by rivers such as Daugava give rise to a high 'buffering capacity' of the pelagic ecosystem throughout the productive season. Thus retention rather than export food chains are favoured and the effect of external perturbations, such as increased nutrient supply, is reduced.

## 19.12 Sources of settling material: Aggregation and zooplankton mediated fluxes

Despite the relatively high suspended biomass during summer situation, and the presence of suitable physical conditions, significant aggregate formation and export did not take place (Lundsgaard *et al.*, 1999). Contrary to expectations aggregation was not involved during mass sedimentation of diatoms during spring (Lundsgaard *et al.*, 1999). A positive correlation between sedimentation of detritus aggregates, sedimentation rates of biogenic matter and sedimentation velocities/specific loss rates of POC and phaeopigments is encountered. Aggregation of detritus may thus partly control the sedimentation dynamics, but it did not correlate with turbulent shear as expected according to classical coagulation theory. The aggregates are possibly fragile and form only during periods of low turbulence. The correlation between phaeopigments and aggregate sedimentation, the observed disintegration of faecal pellets into amorphous detritus, and the inclusion of pellets in the larger aggregates indicate that faecal matter constitutes an important component of sedimenting matter (Lundsgaard *et al.*, 1999). This points at the significance of the larger planktonic heterotrophs in the food web of the Gulf.

The food web composition in spring is characterised by a relatively high biomass of large phytoplankton and a dominance of protozoa (mainly ciliates), while mesozooplankton are almost absent. During midsummer a medium phytoplankton biomass is encountered with significant quantities of mesozooplankton (both copepods, cladocerans and rotifers). However, all other heterotrophic components increase their biomass as well, and a complicated food web prevails. The early autumn is characterised by low phytoplankton biomass and a heterotrophic system with decreasing biomass. Protozoa (ciliates) increase their importance relative to metazoa. Bacterial production is reduced.

The relative export of biogenic matter in summer is possibly low due to a high potential for retention, disintegration and decomposition of detritus by heterotrophic organisms. The high concentrations of mesozooplankton during summer result in a disintegration of the larger detritus particles and aggregates. Or they disintegrate or ingest faecal pellets by mechanisms such as coprophagy or coprorhexy (*sensu* Noju 1991). Strong wind action may also affect the disintegration of aggregates. Furthermore, picoplankton and the microbial food web are important in the organic carbon flow and for regeneration. Ciliates were dominant among the large protozoa, and cladocerans as well as rotifers constitute a significant fraction of the metazoa. Contrary to copepods, these organisms produce faecal particles that easily disintegrate.

## 19.13 Eutrophication in the Gulf of Riga: fiction or reality?

Assuming that the bioavailable N and P from the rivers (Laznik *et al.*, 1999) would be spread over the entire Gulf, the annual supply would be 0.57 and 0.016 g m$^{-2}$ for N and P, respectively. Assuming further that the euphotic zone is 10 m deep and that the nitrate and phosphate concentrations at the end of the winter are 20 and 0.6 µM, respectively (Suursaar, 1995), it becomes obvious that the river supply to the winter-accumulated N and P in the euphotic zone is moderate: 20 and 15%, respectively. However, as the spreading of fresh-

Figure 19.6: A river meets coast of the Gulf of Riga in winter

water in the Gulf is dependent on runoff variations and meteorological forcing (Stipa *et al.*, 1999), the effect of nutrient supply (Turner & Rabbalais, 1994) and suspended biomass (Reigstad *et al.*, 1999; Babichenko *et al.*, 1999) in the southern part can vary considerably. Also, wind mixing induces new nutrients to the euphotic zone. The greatest impact of nutrients is confined to the southern area and consequently new production is significantly increased.

A rough estimate of the autochthonous supply of P to the euphotic zone shows that it is less than half of what is delivered to the Kattegat. As compared to the high primary production rate (Olesen *et al.*, 1999), the relatively small vertical export of biogenic matter from the euphotic zone (Lundsgaard *et al.*, 1999), the small new production (Olesen *et al.*, 1999), the insignificant contribution of phytoplankton cells to the vertical export after the vernal bloom (Olli & Heiskanen, 1999) and the prevalence of detritus and faecal matter (Lundsgaard *et al.*, 1999) point at high pelagic recycling efficiency in the Gulf. The buffering capacity of excess suspended biomass in the pelagial causes the prevalence of retention rather than export food chains. Consequently, the effect of external perturbations such as increased nutrient supply is reduced accordingly. The main supply of fresh biogenic matter to the benthos is defined by the extent of the vernal bloom and the complexity and efficiency of the seasonal development of the planktonic community structure. As the duration and start of the spring bloom can change as a consequence of variable seasonal and annual nutrient discharge to the Gulf as well as climatic factors such as ice-cover, wind forcing, solar radiation and the spectral light composition (clouds, fog etc.), the time window in which vernal phytoplankton is exported to the benthos is variable.

As the supply of nutrients to the Gulf depends strongly on the seasonal and interannual variability in river runoff, which can double during years of increased precipitation as compared to dry years, the allochthonous supply of nutrients varies accordingly. Thus also the interannual new production and the extent of eutrophication vary. Nutrient removal of bioavailable N and P from coastal point sources would only relieve the N budget of the Gulf by 9%, that of P however by 44% (Laznik *et al.*, 1999). Obviously a removal of P from coastal point sources would reduce the P budget of the Gulf significantly and even N removal would to some extent mitigate the N burden.

Nutrient removal from point sources such as the city of Riga will reduce the eutrophication in both the southern littoral zone as well as in those offshore areas of the Gulf that are under direct influence of the river Daugava. Clear evidence of downward trends in the nutrient loadings of rivers related to the rapid economical recession in the catchment area were so far not recorded (Laznik *et al.*, 1999). Thus, the allochthonous supply of nutrients to the Gulf by rivers from diffuse sources (e.g. agriculture) will basically continue in the future. The general eutrophication of the Gulf will probably only decline when both nutrient removal at coastal point sources is introduced and the use of fertilisers and manure is kept continuously low over lengthy periods of time. Also, measures ought to be taken to limit the effect of modern forestry on nutrient discharge, to constrain the introduction of deserted farms into modern agriculture, to eliminate drainage of former wetland areas and to increase the vegetation along rivers and small streams in intensive agricultural areas. These measures will jointly increase the denitrification in the drainage basin or constrain the discharge of nutrients to small catchment areas. Finally, reduced emissions of P and organic matter from point sources in the drainage basin may, under certain conditions, reduce the denitrification capacity in rivers (Chesterikoff *et al.*, 1992). Therefore, it cannot be ruled out that the N loads to the Gulf of Riga may increase in the future, regardless of modernisation in the agricultural sector and nutrient removal from point sources along rivers (Stålnacke *et al.*, 1999). Accordingly, it is difficult to predict changes in both the total nutrient discharge to the Gulf and the N-P-DSi composition of the waters in the Gulf.

Eutrophication in coastal waters is not only characterised by substantial additions of P and N, but also by the fact that the supply of DSi is more or less constant or subjected to natural runoff patterns (Skjoldal, 1993; van Bennekom & Salomons, 1981). There is also a tendency for DSi supply to the sea to decrease over time in many eutrophied rivers (Turner & Rabbalais, 1994). This is explained by increased growth of freshwater diatoms in the river due to increased N and P concentration, and subsequent sedimentation of diatoms behind dams. There seems to be evidence for declining DSi supply also from the Gulf of Riga (Laznik *et al.*, 1999). However, there are several dams along the river Daugava that were built already before nutrient records became available. Thus, DSi supply to the Gulf must have been reduced already for several decades. Scenarios where the relative concentration of DSi is decreased while that of N and P is increased, favour the growth of non-DSi dependent forms such as flagellates. The resulting change in phytoplankton species composition results in increased residence times of the phytoplankton-derived organic matter in the upper layers because aggregate formation and the relative contribution of rapidly sedimenting diatom blooms decreases. DSi obviously plays an important role for eutrophication as emphasised by Officer and Ryther (1980), Conley et al. (1993); see also Chapter 13. The increasing gap between decreasing DSi, but increasing N supply results in a decreasing significance of diatom and increased potential of nuisance blooms.

The high buffering capacity of the pelagial confines the vertical supply of biogenic matter to the benthos. However, the supply of biogenic matter to the benthos and the main accumulation bottom derives probably from advective transport from the slope, the river plume and the littoral zone where erosion of fine biogenic matter results in a predominance of hard substrate (D. Conley, pers. comm.). The effect of frequent resuspension episodes, weather-controlled bottom currents which regularly and easily entrain organic matter from the sediment-water interface (Floderus *et al.*, 1991), as well as sediment focusing, add to the supply of food for the benthos at depth. Here biogenic matter from the surface accumulates on an area which is less than half that of the entire surface area, creating favourable growth conditions for the benthos.

Statements that regard the Gulf of Riga as an eutrophic to hypertrophic area seem not to be valid. The data of Laznik et al. (1999) and Tamminen and Seppälä (1999) indicate that the nutrient supply to the Gulf, as well as the concentrations in the water body, are similar to or less than that of other Baltic Sea areas (e.g. the middle/eastern Gulf of Finland or the Kattegat. In contrast to previous assumptions the Gulf of Riga is basically N- and only periodically P-limited. Furthermore, it has a high pelagic buffering capacity with regard to nutrient discharge induced by efficient recycling by the pelagic food web, which limits the occurrence of massive algal blooms. Nevertheless, the pollution loads from the rivers, in particular those originating from the catchments of the Daugava and the Lielupe rivers, have contributed to an overall eutrophication of the Gulf of Riga, with a continuously shifting gradient between the southern and northern halves of the Gulf. As the simple and exposed topography of the basin makes it exceptionally prone to physical forcing, it is obvious that episodic mixing events can cause considerable interannual and within-season variability in the production preconditions and nutrient limitation of the planktonic community, especially towards late summer and early autumn.

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Figure 19.7: Spectacular sunsets are characteristic on the shores of the Gulf of Riga.

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## Chapter 20

# Pelagic eutrophication in the North Sea

Beatriz Balino
Bjerknes Centre for Climate Research
Allgaten 55, N-5007 Bergen, Norway
beatriz.balino@bjerknes.uib.no
www.bjerknes.uib.no

## 20.1 Introduction

The North Sea is an area of rich natural resources and home of an abundant flora and fauna. It is an important nursery for juvenile fish and one of the most productive fishery grounds in the world. The North Sea is also subject to intense human activities by the approximately 164 million inhabitants in its catchment area, ranging from heavily populated areas in the Netherlands and Belgium (>1000 inhabitants km$^{-2}$) to less populated regions ($\leq$ 50 inhabitants km$^{-2}$) along the coastlines of Norway and Scotland (NSTF, 1993a). Fisheries is one of the most important activities and accounts for up to 5% of the world catch of fish. The area is one of the busiest shipping routes in the world and maintains an important tourist and recreational industry.

Due to these intense human activities, the North Sea is also the receptacle of a considerable amount of waste products. In particular, there has been a sustained increment of the amount of nutrient inputs of anthropogenic origin to coastal areas in the past decades. Man-made inputs add to natural nutrient sources, primarily in the form of sewage, agricultural run-off of excess fertiliser, industrial effluents and combustion of fossil fuel. Most of the land-derived anthropogenic nutrients end up in the rivers and consequently, rivers carry nowadays several times as much nitrogenous compounds and phosphate to the North Sea as they did a century ago. In addition, the polluted atmosphere contributes with additional nitrogen loads, which are estimated to be of the same order of magnitude as the riverine ones (NSTF, 1993a). Increments in man-made nutrients are of concern because of their potential impact upon primary producers and thereby, the possibility of leading the ecosystem through a process of eutrophication.

Signs of eutrophication have become visible in the marine ecosystem at the regional scale and correlates with the increase in scientific literature on marine eutrophication in the past 30 years (Nixon, 1995). For instance, oxygen deficiency bottom waters were detected in the German Bight and off the Danish Coast, (Brockmann *et al.*, 1988) as well as an alleged increase in the frequency of nuisance and toxic phytoplankton blooms and the occurrence of 'exceptional blooms', particularly in coastal areas and embayments (Fransz & Verhagen, 1985). This claim is partly supported by an apparent shift in dominance from diatoms to non-diatom phytoplankton, amongst which most of the toxic blooming species belong to (Taylor, 1990), which can be ascribed to the shift in nutrient ratios in coastal waters because river loads discharge nutrients in different proportions to the natural (Redfield) ratio found in marine waters and inside algal cells. Nutrient inputs deficient in silicate with respect to N and P will reduce the competitive advantage of diatoms and will favour non-silica demanding species, such as flagellates (Conley *et al.*, 1993). In addition, the toxicity developed by *Chrysocromulina polylepis* during the exceptional bloom of 1988 in the Skagerrak, until then recorded as a non-toxic species, has been related to P-limitation (Edvardsen *et al.*, 1990) which directly associates with P-removals in river water by sewage treatment.

Conversely, many argue that it is our awareness about algal blooms what has increased because of their economic consequences upon industrial (e.g. aquaculture) and recreational (e.g. tourism) activities. Sudden or gradual changes in the ecosystem do not necessarily arise as a consequence of human activities but can very well be ascribed to the natural conditions or variability of the system or to climatic factors.

This review compares the development of anthropogenic nutrient inputs to the North Sea with observational data on phytoplankton biomass and production trends, in a preliminary assessment of pelagic eutrophication signs in the North Sea in recent decades until the mid-nineties.

## 20.2 The hydrography of the North Sea

The North Sea is a shallow sea with a surface area of 575,000 km$^2$ and a volume of $40\times10^3$ km$^3$ (Reid *et al.*, 1988). Its bathymetry is characterized by a depth gradient increasing northwards, from the shallow Southern Bight (<30 m) to the passage between Norway and the Shetlands, at the edge of the continental shelf (about 200 m); the greatest depths are found at the Norwegian Trench (725 m) (Figure 20.1). It is subject to the Atlantic Ocean influence from the north and the southwest via the English Channel, and is connected to the Baltic Sea via the Skagerrak. The general circulation pattern of the North Sea is a composite of wind and density-driven circulation and tidal motion (Otto *et al.*, 1990) that results in a long-term anti-cyclonic movement arising from the prime external inflow of the Atlantic water from the north and, to a lesser extent, through the Channel. The pattern reflects the dominance of a westerly wind component in each seasonal wind field and the influence of the topography (NSTF, 1993a; Figure 20.1).

The inflow of Atlantic water in the north branches in two components: the largest branch of oceanic water from the upper 500 m, flowing between the Shetlands and Norway, and a minor branch between the Shetlands and the Orkneys (the Fair Isle Current), a mixture of oceanic water from the upper 200 m of the continental slope and Scottish coastal water. The southern North Sea receives Atlantic water from through the Strait of Dover. This flow mixes with offshore water from the southern North Sea and the continental coastal water, which are strongly influenced by river runoff. These water masses join the Jutland Current and enter the Skagerrak. Ultimately, all the water flowing into the North Sea will leave the area as the Norwegian Coastal Current (NCC) whose magnitude roughly balances the inflow to the North Sea (31–$57\times10^3$ km$^3$ y$^{-1}$). The Skagerrak outflow alternates between blocking and outbreaking regimes controlled by the prevailing winds south-westerly winds block the outflow while during weak westerlies or easterlies, outbreaks of Skagerrak water occur (Aure & Sætre, 1981).

The water masses of the North Sea are quite diverse and have been classified into 6 basic units (Table 20.1) leaving the water from the central

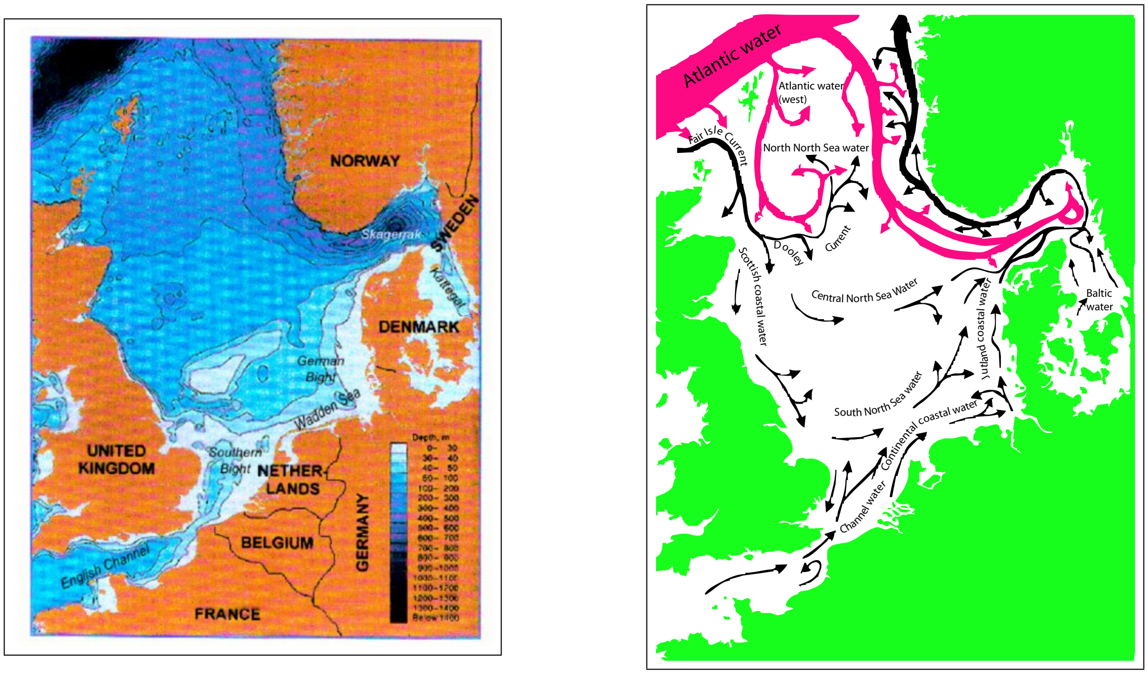

Figure 20.1: The North Seas (left) bathymetry and (right) general circulation and water masses (width of arrows indicate magnitude of volume transports; From NSTF, 1993a).

and southern North Sea as a mixture of the others (Lee, 1980). The position of each water mass is seasonal and most of the North Sea is sufficiently shallow so that the water masses can be considered to extend from the surface (or below the surface stratification) to the sea bed. Exceptions are the Skagerrak and the Norwegian Trench where depths are much greater than average and the water column is occupied by two or more water masses (Reid *et al.*, 1988). On average it takes 36 months for the water in the German Bight to leave the North Sea, whereas water in the northern North Sea may remain for only 6 months (NSTF, 1993a). Conversely, the turnover time for the upper layers (0–10 m) is much shorter and of the order of days as it is determined by the intensity of the wind stress on a daily basis.

Tidal motion is one of the dominant features in the dynamics of the North Sea and differences in the influence of tides and topography divides the Sea into two main sub-regions: a shallow, tidally dominated area of the southern and central parts, and the deeper northern area, where tidal influence is less important. Fronts and frontal zones are characteristic near-shore features of the North Sea and have a significant ecological impact in the dynamics, spreading and mixing of water masses, in addition to being areas of enhanced biological activity (Otto *et al.*, 1990).

Surface temperatures exhibit a strong seasonality (0-17°C) while the salinity distribution is similar throughout the year (Otto *et al.*, 1990) reflecting the influences of oceanic and coastal water masses: high salinities (>35‰) in the north decreasing to the south. Only in very shallow, coastal waters receiving large freshwater discharges such as the Skagerrak/Kattegat (outflows from the Baltic) and the Norwegian and continental coast (from river freshwater discharges) there is a variable haline stratification (Reid *et al.*, 1988).

## 20.3 Nutrient dynamics in the North Sea

The dynamics of nutrient contents in North Sea waters is a function of physical, chemical and bi-

Table 20.1: Characteristic winter and summer temperatures, salinity and inorganic nutrient contents in the water masses of the North Sea, according to Lee (1980)

| | Temperature (°C) | | Salinity | Inorganic nutrients (µM) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Winter | Summer | | | Winter | | | Summer | |
| Water mass | | | | Phosphate | Nitrate | Silicate | Phosphate | Nitrate | Silicate |
| North Atlantic | 6–8 | 12–14 | >35 | 0.6–0.8 | 10 | 4–6 | 0.1–0.4 | 1–4 | 2 |
| Channel | 5–7 | 16–17 | 34–34.75 | 0.3–0.5 | 7 | 6 | <0.1 | <1 | <1 |
| Skagerrak | 2–5 | 14–17 | <34 | <0.4 | <7 | <4 | 0.1–0.2 | – | – |
| Scottish Coastal | 4–6 | 12–14 | 34–35 | 0.6 | – | – | 0.2 | 0.5–1 | 2 |
| English Coastal | 4–6 | 14–18 | 34–34.5 | 0.7–1.2 | 35 | 14 | 0.1–0.4 | 1-Apr | <1 |
| Continental Coastal | 2–4 | 17–19 | <34 | 2–3 | 45 | 20–30 | 0.1–0.4 | Oct-20 | 1-Feb |

ological processes. Nutrients are transported horizontally, either by inflowing water from the Atlantic or by river loads; and vertically, by atmospheric deposition or transport from deep waters when gales and storms in the fall mix the entire water column. During the growing season, biological activity depletes the nutrients in the surface layers of thermally stratified water columns. Spatial and temporal variability of these factors and processes impose characteristic regional and seasonal differences in the distribution of nutrients in the area.

In the winter, biological production is low so the nutrient distribution in the North Sea reflects the chemical contents of the different water masses. An exception is the Dogger Bank, where the activity of primary producers is high throughout the year (Potsma, 1978). The inflow of nutrient-rich Atlantic water imprints the northern water masses. The bulk of the central North Sea, on the other hand, is mainly influenced by the Fair Isle current which is a mixture of oceanic water from the continental slope and coastal water and lower nutrient contents. River loads heavily influence the coastal waters in the south and thus they exhibit the highest nutrient concentrations and large gradients decreasing offshore.

During the spring, the development of a thermocline dominates the nutrients dynamics in northern and central regions of the North Sea. During the growth season, nutrients in the surface layers are rapidly depleted, senescent phytoplankton cells sink through the thermocline and the fixed nutrients are mineralised in deep waters. At the thermocline, dissolved and particulate organic substances accumulate and an intense mineralization occurs, products of which are re-utilised in the upper layer (Brockmann *et al.*, 1988). Recycling occurs at a high rate since increments in nutrient concentrations are hardly detected. Because a strong thermocline hinders the vertical supply of nutrients during most of the productive season, a strong nutrient limitation upon primary production is a characteristic feature of the central and northern regions of the North Sea (Potsma, 1978). In early autumn, gales and storms cause the breakdown of the seasonal thermocline and a vigorous mixing of the whole water column takes place, bringing nutrients from deeper waters back to the surface layers which may lead to the development of a fall bloom.

In the Southern North Sea, the inflow of Atlantic water through the Channel during the growing season gets progressively enriched by mixing with plume water from the Thames and Humber estuaries on the west and the Scheldt and Rhine, on the east. Primary production in the highly turbid waters along the Belgian and Dutch coasts is light limited due to river runoff and the non-utilised riverine nutrients are transported to neighbouring areas (Joint & Pomroy, 1992).

## 20.4 Nutrient inputs to the North Sea

The nutrients contents in the North Sea are a combination of natural sources and human activities (anthropogenic). Natural sources are

1. plant and animal decomposition
2. animal excretion
3. air-sea exchanges
4. ocean mixing and advection

The mixing with the Atlantic water, both through the northern and southern limits, is by far the most important natural nutrient input to the North Sea (Anonymous, 1987).

Anthropogenic nutrient inputs, on the other hand, originate from domestic wastes (i.e. sewage), agricultural practices (e.g. runoff of excess fertiliser), animal wastes from extensive livestock units, aquaculture, industrial effluents and combustion of fossil fuel. The importance of various sources vary as industrial and agricultural practices differ among the different regions and/or countries. Nutrients resulting from human activities reach the sea through different routes, the main ones being: river runoff and direct discharges from land, dumping at sea, and atmospheric deposition.

On an annual basis, the North Sea receives about 6 million tons of N and 755,000 tons of P from both natural and anthropogenic sources (Table 20.2). Atlhough anthropogenic inputs are moderate compared to the natural sources, most of the man-made inputs (rivers) are discharged on a relatively limited geographical area of slow moving water in the southern North Sea and impose a major regional impact on the biochemical components of the coastal ecosystem. The large N and P inputs from the North Atlantic inflow through the northern limit, on the other hand, are insignificant for the productivity of the southern North Sea.

table.20.2

Table 20.2: Annual mean inputs (in tons) of nitrogen (N) and phosphorus (P) to the North Sea. (a) Estimations based on inflow data from Lee (1980) and North Sea Task Force (1993a) and nutrient concentrations from Table 20.1, averaged for winter and summer. (b) Data according to the North Sea Task Force (1993a). The atomic N/P ratio of each source is shown

| Sources | N<br>103 tons | % | P<br>103 tons | % | N/P |
|---|---|---|---|---|---|
| **Natural**[a] | | | | | |
| North Atlantic | 3 940 | 94 | 663 | 95 | 13 |
| Channel | 258 | 6 | 36 | 5 | 16 |
| **Anthropogenic**[b] | | | | | |
| Rivers | 910 | 59 | 48 | 86 | 42 |
| Direct inputs & dumpings | 126 | 8 | 8 | 13 | 37 |
| Atmospheric[1] | 520 | 33 | n.i | – | – |
| Natural | 4 198 | 73 | 699 | 93 | 13 |
| Anthropogenic | 1 556 | 27 | 56 | 7 | 62 |
| Total | 5 754 | 100 | 755 | 100 | |

### 20.4.1 Rivers and direct inputs

Estimations for 1990 show that the total amount of nutrients (inorganic + organic) discharged by rivers and direct inputs to the North Sea were of the order of 1 million tons of nitrogen (N) and about 55 thousand tons of phosphorous (P). Most of the nitrogen originates from agriculture practices while phosphorus derives primarily from sewage. An important feature of riverine nutrient inputs is the seasonality as well as the N/P ratio of the loads. The freshwater discharge of continental rivers follow the precipitation pattern, exhibiting a maximum in winter and a minimum in the summer. In Scandinavia, on the other hand, runoff is frozen as ice and snow during the winter, hence, river flows are at minimum in winter while the maximum occur in summer pacing with the ice-melting, although hydroelectrical energy production tend to counteract this pattern. Another major characteristic of riverine inputs is that the average ratio of riverborne nitrogen to phosphorus is usually much higher (23–42; see Table 20.2) than the Redfield ratio. The dynamics of N/P ratios from continental rivers follow a similar seasonal pattern as the freshwater discharges: high in the winter/spring and low in summer/autumn.

### 20.4.2 Atmospheric deposition

Atmospheric inputs of nitrogen oxides and ammonia originate mainly from emissions of fossil fuel combustion, from cattle and liquid manure and sewage treatment (read also Chapter 1). It is assumed that $N_2$-fixation is negligible. P and Si deposited by the atmosphere are, on the other hand, considered negligible (Reid *et al.*, 1988). During 1990, nitrogen inputs to the North Sea via the atmosphere were about half million tons, i.e. in the same order of magnitude as riverborne loads.

## 20.5 Trends

### 20.5.1 Anthropogenic nutrients

Nutrient contents in river water from countries bordering the North Sea have substantially and steadily increased during the last century, and particularly after the Second World War. For instance the Rhine, the largest river in Western Europe, flows through several densely populated and industrialised areas of Switzerland, Germany, Netherlands, and drains parts of France and Luxembourg. The development in the nutrient contents in Rhine for nitrogen (ammonium and nitrate) and phosphorus (phosphate and particulate phosphorus) is shown in Figure 20.2. Population growth and increased industrialisation together with the introduction of phosphate detergents for domestic and industrial use at the beginning of the 60's caused a ten-fold increase of riverine phosphate. Regulations on the use of detergents in the early 80's and secondary treatment in sewage purification plants in Germany since 1970, are reflected in the sharp decrease of phosphate and particulate P in river water, respectively. Ammonium and nitrate contents in Rhine water raised also steadily until the 70's as a consequence of population growth, increased use of fertilisers (mainly in Germany) and increased manure production in the Netherlands. Ammonium contents decreased due to sewage treatment in Germany from 1970 while the trend in nitrate contents is steady and by 1990 the contents of N in the Rhine was six times higher compared to 1950.

### 20.5.2 Influence of river loads on coastal and offshore waters

#### Southern Bight

Colijn et al. (1992) compared the winter phosphate content distribution in the Southern Bight from 1986 and 1989 with data from the winter 1935/1936 in order to calculate the fractional increase in phosphate during the period. They showed that phosphate levels increased 3–4 times in the coastal strip of the southern and eastern North Sea, probably due to the cumulative impact of nutrient inputs from the Rhine, Ems, Weser and Elbe (Figure 20.3). This means that, in absolute terms, the phosphate contents in coastal waters increased from about 0.6 to 2.0 µM-P at a salinities 33‰ while there was no evidence of P increase outside the coastal band. Increments of dissolved nitrogen in coastal waters between 1940 and 1990 are comparable to those for P (NSTF, 1993b).

#### German Bight

The impact of riverine nutrients in the German Bight has also been monitored at Helgoland Roads, 60 km offshore from the discharges of the river Elbe (Hickel *et al.*, 1993). A 30-year time-series of inorganic nutrients and phytoplankton surface data show that phosphate concentrations increased steadily until the beginning of the 80's. From 1982 and onwards, the concentrations decreased significantly, probably due to similar phosphorus reducing measures mentioned above. Increments in nitrate contents occur only since 1980/81 and are correlated to flood events of the Elbe.

#### Western North Sea: the English coast

A compilation of all available winter nitrate measurements along the British coast (North Sea west

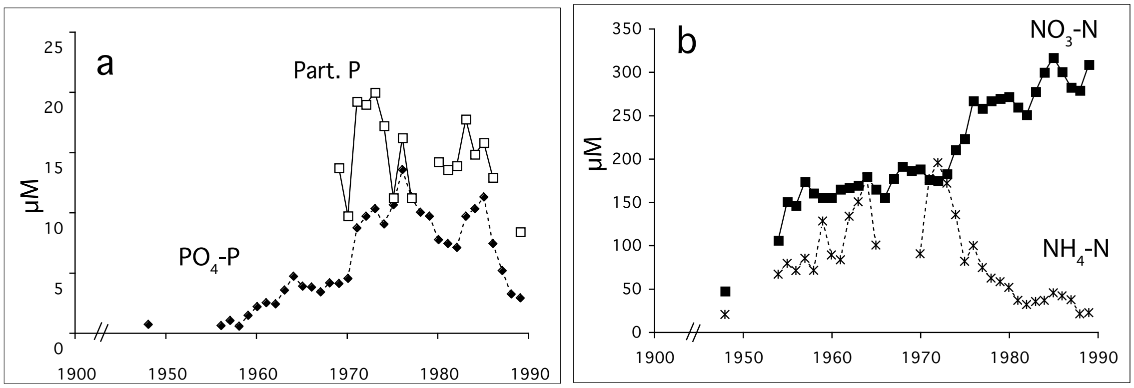

Figure 20.2: Concentrations of (a) phosphorus (as phosphate and particulate phosphorus) and (b) nitrogen (as nitrate and ammonium) in the Rhine, between 1950 and 1990. Annual averages measured at Lobith, at the German-Dutch border (Source: International Commission for the protection of the Rhine against Pollution)

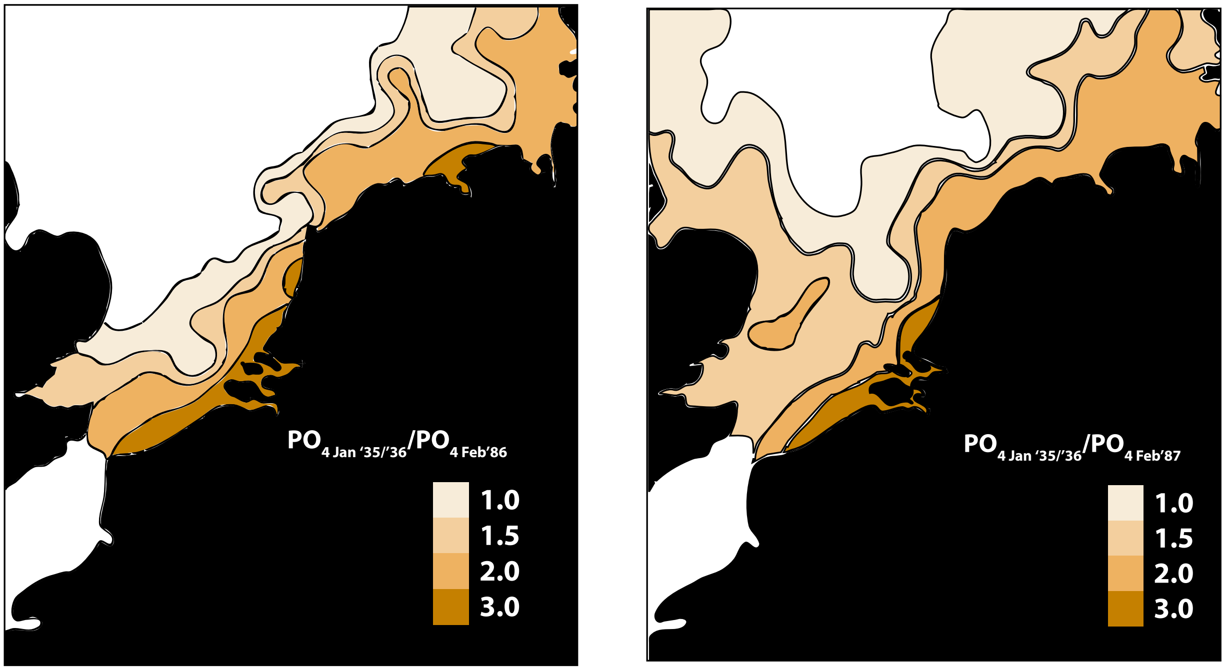

Figure 20.3: Ratio of surface phosphate during winter of 1935/36 to winter phosphate during 1986 and 1989 (redrawn from Colijn *et al.* 1992).

of 3°E) between 1960 and 1987 did not show the same positive trend observed in nitrate loads from UK rivers, even though the use of fertilizer N increased from 60 ktons to 1600 ktons between 1930–1985 (Dickson *et al.*, 1988). The variation pattern of nitrate was similar along the entire UK coast and such uniformity along a coast subject to major regional differences in river discharges, estuary type, land use, etc., reinforce the idea that this might be a regional ('natural') trend, rather than anthropogenic one.

**Kattegat and Skagerrak**

It is assumed that the Kattegat and inner Skagerrak were oligotrophic in its pristine conditions since it is a strongly stratified system with a marked halocline separating the Baltic outflow and the Norwegian coastal current from the underlying water from the North Sea or the Atlantic (Skjoldal & Dundas, 1989). The situation in the past decades has changed dramatically, where very high concentration of nutrients with excess in nitrate are now a regular feature both in the Kattegat and the Skagerrak (Aure *et al.*, 1990; Skjoldal & Dundas, 1989).

Since the *Chrysocromulina polylepis* bloom in the spring/summer of 1988, there has been a large awareness of the role played by the Jutland current as a transport route of nutrients from the southern North Sea (Skjoldal & Dundas, 1989). During the winter, water masses loaded with nutrients from river discharges in the south are transported with the Jutland Current into the Skagerrak. As the growing season proceeds, the excess of nitrogen which remains following the depletion of phosphorus and silicate after the spring bloom will also be transported with this current. The vertical mixing with this N-enriched water will primarily affect the algae at the pycnocline where there is typically a post-bloom chlorophyll maximum (Rosenberg *et al.*, 1990). This is one of the backgrounds suggested for the 1988 bloom (Skjoldal, 1993). However, it was argued that the pool of nutrients present in the upper layers were sufficient to sustain the densities achieved by *C. polylepis* and hence, environmental mechanisms other than eutrophication must have been responsible for the development of the bloom. Lately, the role that exceptional hydrographical conditions in 1988 must have played in the formation of the bloom, rather than the long-term eutrophication of the southern North Sea, has been stressed (Granéli *et al.*, 1993).

## 20.6 Assessment of the pelagic eutrophication in the North Sea

According to Gray (1992), the process of eutrophication in marine environments exhibits different stages of development: from an *enrichment* (due to increased nutrient inputs that enhances the biomass at all trophic levels but not necessarily part of an eutrophication process, e.g. upwellings); through *initial and secondary effects*, where further nutrient inputs will lead to changes in species composition (e.g. shifts from diatoms to flagellates among the phytoplankton) and deleterious effects (shading, euphotic depth reduction; nuisance blooms), and ultimately *extreme and ultimate effects*, the final stages of eutrophication: massive growth of opportunistic species, toxic plankton blooms and anoxic sediments. This general model is applicable to enclosed or semi-enclosed bodies of water, i.e. lakes, estuaries, bays, fjords, or large areas with limited water exchange with the open sea where eutrophication effects have been detected, such as the Wadden Sea (Beukema & Cadeé, 1986) and the Kattegat and Skagerrak (Rosenberg *et al.*, 1990).

In more open coastal and offshore waters, on the other hand, effects of eutrophication are usually not so straightforward. These areas are subject to highly variable hydrodynamics so that changes due to natural variability are difficult to distinguish from man-made effects. Circulation patterns may play a major role in the dispersal/concentration of the pollutant matter in the different area or the effects may be felt in regions distant from the eutrophication sources.

In the North Sea in particular, claims about the extent of eutrophication of this area has been the topic of debate among politicians and researchers in the last decades. This is a consequence of a series of events that could well be ascribed to eutrophication, such as the occurrence of oxygen deficiency in bottom sediments and of exceptional toxic and/nuisance phytoplantkon blooms. Still, many have legitimately argued that the increase in the frequency of plankton blooms is due to an increased monitoring effort and to our growing awareness about these events and its consequences to mariculture/aquaculture activities and tourism. Because of the general lack of long-term data series, incomplete regional databases or inadequate time-series for the establishment of reliable trends, this argument cannot yet be refuted.

In the next section, evidence of changes in aspects of phytoplankton populations (biomass and primary production, species composition and changes in bloom frequency and toxic or novel blooms) in different areas of the North Sea is reviewed and will be related to trends in anthropogenic nutrient inputs.

### 20.6.1 Phytoplankton biomass and production

#### Skagerrak and Kattegat

Enhancement of primary production along the coastal waters of Denmark, following an increasing trend in the local supply of nitrogen and phosphorus has been recorded in the past decades although regional variations occur. Still, it is emphasised that unusual meteorological and hydrographical conditions in combination with nutrient increments are most likely the root cause of the occurrence of massive blooms (Nielsen & Ærtebjerg, 1984).

#### Wadden Sea

The monitoring of phytoplankton since the early 1970's in the Marsdiep, the westernmost tidal inlet of the Wadden Sea, showed an increase in phytoplankton biomass and primary production until mid-80's with subsequent stabilization towards the end of the decade (Cadeé, 1991). The increments in phytoplankton biomass were primarily due to flagellates, particularly *Phaeocystis* with a concomitant extension of the blooming period of *Phaeocystis* from 30 to 150 day. Only since 1983 and onwards, have these increments been correlated to Rhine runoff, although the enrichment of the Rhine waters was evident already in the 50's. Between 1950 and 1970, however, the nutrient concentrations in the Wadden Sea have remained fairly constant due to retention (primarily of P) in the sediments of Lake Ijseel. Thus, the response of the phytoplankton and phytobenthos to eutrophication showed a time lag (van der Veer, 1989). But by late 1970's, saturation in the sediments was reached and the P accumulated started being released to the water column and made available for the algae. The fact that an intensive mussel culture was taken place in the western Wadden Sea between 1950–1960 (stabilized since then) might have had a counteracting effect on the eutrophication in the area (van der Veer, 1989). It was concluded that the changes observed in Marsdiep are clearly related to a eutrophication process (NSTF, 1993c).

#### Dutch coastal waters

Long-term changes in phytoplankton abundance in the North Sea between 1948 and 1975 were evaluated by using data from the Continuous Plankton Recorder (CPR) (Gieske & Kraay, 1977). From the late 60's and onwards, a general increase in the colour of the CPR silks, interpreted as a sign of increment in the biomass of microflagellates, occurred in the whole North Sea but much more pronounced along the Dutch coast. In the period 1976–1991, yearly median values of chlorophyll a concentrations along the Dutch coastal waters show large annual variations but no trends (North Sea Task Force 1993b) and have been attributed to fluctuations in Rhine loads (Gieske & Schaub, 1990).

Since existing measurements of primary production along the Dutch coast are not suited for trend analysis, Fransz & Verhagen (1985) used mathematical modelling to compare phytoplankton and nutrient conditions in 1980 with the hypothetical pre-eutrophication situation prior to 1930. The simulations indicate that primary production doubled since 1930 and that flagellate biomass had increased by a factor of 2 to 4 within 30 km from the coast.

#### German Bight

Long-time data series from Helgoland Roads indicate that between 1962 and 1985 there was an increase in flagellate abundance and corresponding decrease in diatoms with a concomittant shortening of the period with nutrient limitation (Radach *et al.*, 1990). Including data until 1991, Hickel *et al.* (1993) estimated that there had been a 3–4 fold increase of phytoplankton biomass, although this increase was mostly due to unidentified nanoflagellates, which are easily overlooked or were probably destroyed by fixation in earlier samples. Hickel and co-authros also tried to relate flood events of the river Elbe during the 80's with the development of large phytoplankton blooms in the area. Only during the one flood event there was a massive *Ceratium* bloom, the largest in the area so far; the main difference with the second flood event was the prevailing meterological conditions in the area at the time of the bloom development. Thus, a causal relationship between riverine inorganic nutrients and phytoplankton stock is not conclusive from the Helgoland data as it is for the Wadden Sea, and the authors stress upon the influence of meteorological conditions in the formation of large blooms.

### 20.6.2 Novel phytoplankton blooms

#### Skagerrak and Kattegat

Blooms of not previously recorded species, such as *Gyrodinium aureolum* and *Prorocentrum minimum* are now common in southern Scandinavian waters (NSTF, 1993c). Also changes within local populations have been observed, such as exceptional bloom episodes of indigenous species co-occurring with blooms of immigrant species, i.e. *Ceratium* or the bloom's geographical extension and toxicity exhibited by *Chrysocromulina polylepis* in Skagerrak and Kattegat. Until 1988, *C. polylepis* was recorded an indigenous non-toxic species that rarely formed blooms. Smayda (1990) concluded that in a 25-year period (1964–1988) the waters of the Skagerrak, Kattegat and the Baltic exhibited unusual blooms involving at least 11 taxa together with apparently novel introduced aggressive, toxic bloom-producing species.

#### Wadden Sea

Mass occurrences of the colony forming *Phaeocystis* blooms started to be recorded and later become dominant in the Marsdiep during the late 70's (Cadeé, 1991) at the time P started leaking from the sediments in Lake Ijseel (see above). This confirms laboratory experiments showing that *Phaeocystis* algae is a poor competitor under P-limitation (Riegman *et al.*, 1992).

### 20.6.3 Changes in species/group composition and/or dominance and/or toxicity

Nutrient inputs deficient in silicate with respect to N and P will reduce the competitive advantage of diatoms and will favour the dominance of flagellates (Conley *et al.*, 1993). Evidence of this if found in the eutrophic Dutch Wadden Sea where mass occurrence of *Phaeocystis* colonies dominate during the summer. The prolonged growth period and dominance of *Phaeocystis* colonies is not only due to its competitive ability during situations of nitrogen limitation (i.e. summer) but also when nitrate/ammonium ratios are high. From early 70's and onwards, there has been a shift in the nitrate/ammonium ratio in the discharges of the Rhine due to ammonium removal in water treatment installations (Riegman *et al.*, 1992). Thus, novel nuisance algal blooms are directly linked to shifts in nutrient ratios of riverine inputs.

Distorted nutrient ratios ($N/P \gg 16$) characteristic of anthropogenic inputs (Table 20.2) can promote the development of toxicity in certain phytoplankton species. Examples are two prymnesiophytes, e.g., *Prymnesium parvum* and notably *C. polylepis*, which produce a similar toxin called prymnesin which is induced by P-limitation in combination with other factors (Edvardsen *et al.*, 1990).

### Long-term changes

Most of the recorded exceptional blooms occur in continental coastal waters of the southern North Sea, receptacle for the largest riverine nutrient inputs. Whether a similar linkage occurs elsewhere in the North Sea is difficult to say. Evidence has been sought in the records of the CRP which has recorded changes in the phytoplankton stock of the North Sea and adjacent Atlantic waters since 1940. An increment of the CPRs 'greenes index' between 1950 and 1970 was attributed to an increase in nanoflagellate biomass (Gieske & Kraay, 1977). But because this trend was also observed in North Sea waters not directly affected by river runoff, it is more likely that at least part of part of these changes are due to climate variability.

A document on eutrophication symptoms and problem areas in the North Sea was prepared by the working Group on Nutrients of the Paris Commission (Anonymous, 1991). In there it was concluded that, until the mid-70's, there was an overall positive correlation between nutrient inputs and phytoplankton biomass in the continental coastal waters. By the end of the 80's, algal biomass was (on average) 2 to 3 times higher compared to the early 60's and most likely attributable to the long-term increments in nutrient levels along the coasts. An increased frequency, duration and intensity of blooms of local and novel species had occurred in the whole North Sea, including the Skagerrak and Kattegat. Concomitantly, the role that meteorology and hydrodynamics played in bloom formation, in addition to nutrient availability, was stressed. It was concluded that the observed changes in the relative timing and duration of micro- and dinoflagellate blooms is expected to be a result of anthropogenic eutrophication. The toxicity developed by certain species is also attributed to distortion of nutrient ratios in anthropogenic inputs. The areas identified as eutrophication problem areas in the Convention waters are shown in Figure 20.4

Figure 20.4: Eutrophication problem areas (red) in the North Sea, identified by the Working Group on Nutrients of the Paris Commission (redrawn from Anonymous 1991)

## 20.7 Concluding remarks

Despite the number of observations, monitoring and evidence of changes in restricted areas, it is not yet possible to conclude whether there has been an increase in the incidence of nuisance, toxic and/or exceptional phytoplankton blooms in the North Sea as a consequence of increased anthropogenic nutrient inputs. Other factors, such as meteorological and/or hydrodynamic conditions, must be taken into consideration to explain particular events. The fact that consequences of eutrophication on coastal and offshore waters are by no means straightforward, imposes limitations to the value of traditional sampling, monitoring activities and statistical analyses to establish cause-consequence relationships. Field data is inherently noisy in that it often show such large variations that it is difficult to judge whether extremes in polluted regions fall inside or outside natural ranges. Thus, in order to assess human impact, the natural variability of the system has to be determined and one approach is the use of mathematical models as a synthesising tool.

This review only emphasises the difficulties in the assessment of eutrophication in marine environments, due to the complexity of coastal ecosystems which are characterized by an inherently high natural variability. Mass mortality or gradual changes in the size of populations, two possible outcomes from short- and long-term eutrophication process, can also occur as a consequence of natural events, e.g., cold winters or long-term changes in climate or ocean circulation (Zijlstra & Wolf, 1988). On the other hand, it should be kept in mind that systems or regions that are naturally prone to conditions promoting intense algal growth or oxygen depletion in bottom waters are particularly sensitive to additional nutrient inputs, either natural or anthropogenic, as the extra loads will enhance an existing natural trend.

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# Chapter 21

# Eutrophication of the East African Great Lakes

Mbachi Ruth Msomphora
Norwegian College of Fishery Science
University of Tromsø
N-9037 Tromsø, NORWAY
mbachi@stud.nfh.uit.no

## 21.1 Introduction

The Great lakes of east Africa have similar characteristics. They are perhaps the best-known lakes in the world for their faunal diversity. From a limnological perspective, the distinguishing attributes of these lakes are their large size and tropical location. Their diversity may be attributed to these features, along with their great age, e.g. Lake Malawi has existed in the rift valley for over two million years (Brooks, 1950; Hecky, 1984). Despite their shared characteristics, there are some major limnological differences among Africa's three largest lakes. Compared to Lake Malawi and Tanganyika, Lake Victoria is substantially shallower, younger geologically and has faster water renewal times (Hecky, 1984; Bootsma & Hecky, 1993). Lake Malawi and Tanganyika are similar in morphology and transparency, and are both meromictic, but they are markedly different with regard to hydrology, nutrient dynamics (Hecky & Bugenyi, 1992), plankton composition (Hecky & Kling, 1987), and trophic structure (Hecky, 1984). In contrast to Lake Tanganyika, Lake Malawi consists of a single basin with the greatest depth of about 785 m (Table 21.1). Lake Malawi is about 560 km long and greatest width of about 75 km. It is about 1/3 of the total geographical area of the country (Figure 21.1). Nearly 25% of Lake Malawi belongs to Mozambique and they call it Lake Niassa. In Tanzania Lake Malawi is still called its colonial name, Lake Nyasa (Figure 21.1). Victoria is the largest lake by area in Africa (second largest in the world) but with only one-third the volume of that of Lake Malawi (Table 21.1). Lake Tanganyika is the deepest of these three East African Great Lakes and has the biggest volume of about 18,900 km$^3$ (Table 21.1). The effects of the anthropogenic activities on these lakes may be quite different.

Human benefits gained from Lake Malawi, Tanganyika and Victoria include:

1. Water supply for consumption, agriculture, industry, and hydroelectricity production
2. Fish production, which serves as a source of protein or food in general and cash income

Table 21.1: Morphometric and hydrological data for Africa's three largest lakes. Source: a - Gonfiantini et al. (1979). b - Rzoska (1976). c - Owen et al. (1990). d - Coullter and Spigel (1991). e - Eccles (1979). f - Bootsma and Hecky (1993).i

| | Malawi | Tanganyika | Victoria |
|---|---|---|---|
| Catchment Area (km$^2$) | 100,500 f | 220,000 f | 195,000 f |
| Lake Area (km$^2$) | 28,000 f | 32,600 f | 68,800 f |
| Maximum Depth (m) | 785a | 1470a | 79a |
| Mean Depth (m) | 292a | 580a | 40 f |
| Volume (km$^3$) | 8,400a | 18,900a | 2,760b |
| Outflow (O) (km$^3$ y$^{-1}$) | 11c | 2,7d | 20b |
| Inflow (I) (km$^3$ y$^{-1}$) | 29c | 14d | 20b |
| Precipitation (P) (km$^3$ y$^{-1}$) | 39c | 29d | 100b |
| Evaporation (km$^3$ y$^{-1}$) | 55e | 44d | 100b |
| Flushing time ($V/O$) (years) | 750 f | 7,000 f | 140 f |
| Residence time ($V/(P+1)$ (years) | 140 f | 440 f | 23 f |

3. Aesthetic value, which attracts tourists, biodiversity which supports an aquarium trade in cichlid fishes, and has other noneconomic benefits

4. Scientific value.

Such benefits may perish with the current human activities, which are already threatening these values. In Lake Victoria it is likely that hundreds of haplochromine cichlids have gone extinct in the past decade. Only three species are currently harvested in any numbers (Hecky, 1993). The loss of this trophically diverse group of fishes and reduction to extreme trophic simplicity can be a hypothesis to explain other change in the food web. For example, eutrophication is likely to be considered as one of the effects due to such trophic changes.

Human activities that threaten the lakes include agriculture, urban development, tourism, industrial development, over-fishing, and other human activities in the catchments and alien species introduction. Of special concern are the possible oil exploration activities in Lake Malawi and Tanganyika. However, other phenomena, especially the increase in human and livestock population since the colonialism and following state development, must also be considered. This development together with anticipated sensitivity to eutrophication of the tropical Great Lakes because of their 'endless summer', warm deep water and dominance of direct precipitation in their water budget Hecky & Bugenyi (1992) must be carefully considered.

## 21.2 Differences in the hydrology of Lake Malawi, Victoria and Tanganyika

As indicated above Lake Victoria is much shallower than Lake Malawi and Tanganyika, which have an anoxic deep hypolimnion, hence the monimolimnia[1] of these two latter lakes are N sinks. Very little ammonia regenerated in the monimolimnia reaches the euphotic zone (Figure 21.3),

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[1] Monimolimnion is technically the same as the hypolimnion; i.e. the deepest layer in the lake. In most lakes that mix once or twice y$^{-1}$, it is called the hypolimnion. But in lakes that are permanently stratified, it is called the monimolimnion

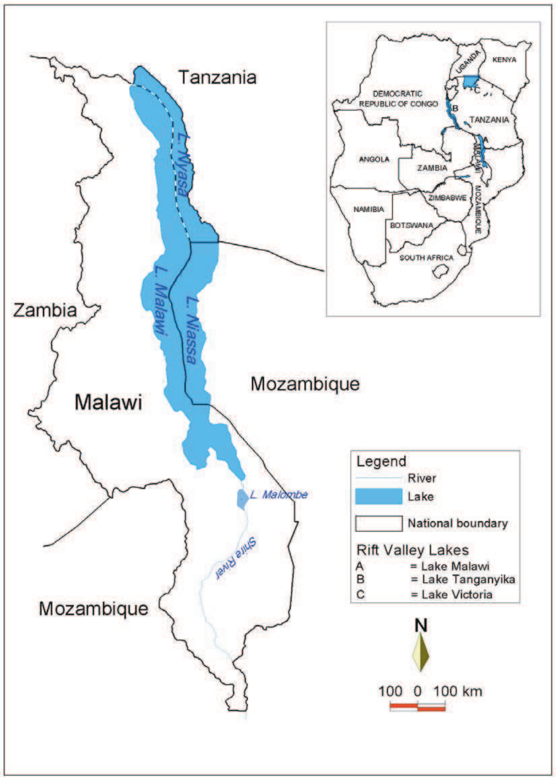

Figure 21.1: Map of Malawi showing the position of Lake Malawi and the bordering countries. The position of Lake Malawi in relation to Lakes Tanganyika and Victoria is also shown on the Map of Southern Africa (http://www.ramsar.org).

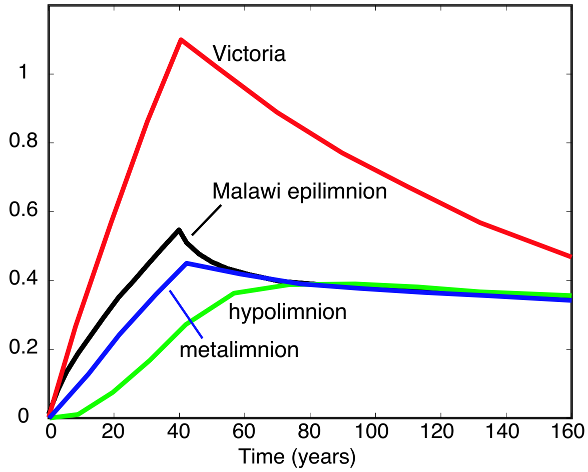

Figure 21.2: Pollution scenario for Lake Victoria and Malawi, in which all inflow rivers contain 5 $\mu$g $l^{-1}$ pollutant for 40 years, followed by complete cessation of pollution input. The model uses the hydrology parameters of Table 21.1; it assumes that the only loss of pollutant is via outflow and that all inflow enters the epilimnion (Bootsma & Hecky, 1999; Gonfiantini *et al.*, 1979).

because it is oxidized to nitrate when it mixes with oxic waters (Bootsma & Hecky, 1999). Lake Victoria in total is currently experiencing eutrophication and its many once common species are no longer found there and maybe extinct. This is not yet true for Lake Malawi and Tanganyika except locally. This demonstrates that the biodiversity vulnerability is not only a function of eutrophication, pollution etc, but also depends on the hydrology of the water body.

The Nile outflow from Lake Victoria is almost twice greater than the Shire flow from Lake Malawi (nearly proportional to the difference in catchment area of the two lakes). Hence the flushing time of Victoria is much smaller (Table 21.1). As a consequence the concentration of introduced pollutants can rise much more quickly in Lake Victoria, but it will also recover much more quickly if their supply would cease (Figure 21.2). On the Great Lakes scale, Lake Erie in North America is the best-known case of substantial recovery from pollution (Sweeney, 1993). Lake Erie is like Victoria, large and shallow, but its flushing time is on the order of five years, allowing it to flush out excess dissolved nutrients and contaminants relatively rapidly (Bootsma & Hecky, 1999). It would take many years for Lake Malawi to recover if it ever experienced pollution concentrations comparable to those that occurred in Lake Erie and what is currently being experienced in Lake Victoria. As such the ability to predict the effects and decisions on how to prevent or mitigate the effect of pollution requires an understanding of the specific limnology of each aquatic system. For Lake Malawi and Tanganyika prevention is the only realistic and affordable policy for maintaining the lakes in healthy condition and insuring their continued beneficial use by the people.

## 21.3 Limiting nutrients in Lake Malawi, Victoria and Tanganyika

While P is the nutrient most often limiting algal growth and biomass in most fresh water systems, this is not necessary the case in tropical lakes. In Lakes Malawi, Tanganyika, and Victoria, concentrations of N and P in surface waters are low (Figure 21.3). Talling and Talling (1965) suggested that low nitrate concentrations in Lake Victoria indicated a potential for N limitation. While phytoplankton in Lake Victoria appears slightly deficient in N, neither N nor P appears to be limiting, based on Redfield ratios. Similarly, particulate nutrient ratios in Lake Malawi suggest N and P deficiency. Evidence suggests that photosynthesis in Lake Victoria is now light limited, but in Lake Malawi Guildford et al. (1994) found that phytoplankton growth is rarely controlled by light. Little work has been done to identify limiting nutrients in Lake Tanganyika, but the fact that the N: P regeneration ratio is close to 16:1 (Hecky *et al.*, 1991), the optimal ratio for phytoplankton, suggests that also this lake is not limited by these nutrients.

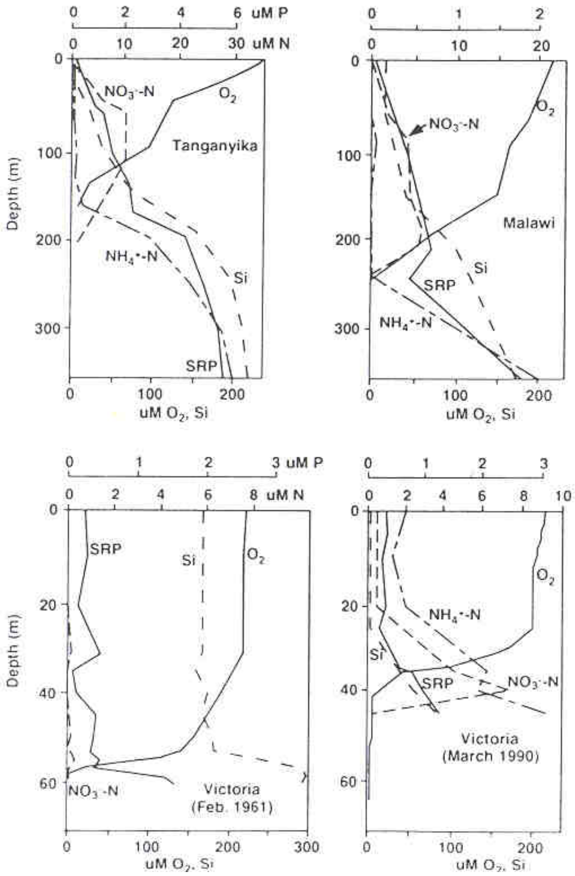

Figure 21.3: Nutrient and oxygen profiles for the three African Great Lakes. SRP = soluble reactive phosphorus (it is mostly phosphate, also called orthophosphate). (Bootsma & Hecky, 1993).

## 21.4 Eutrophication in Lake Victoria as compared to Lake Malawi and Tanganyika

In Africa, burning, deforestation and increasing agricultural activities are all results of increased population density, which have negative impacts in the East-African Great Lakes region. Compared to Lake Victoria, in Lake Malawi and Tanganyika these effects are currently undetectable (Bootsma & Hecky, 1999) because the latter lakes have steep near-shore topographies (Figure 21.4). They are susceptible to soil erosion after disturbance (for example the northeast shores of Lake Tanganyika) but are not attractive for dense human population or cattle grazing. Hence the Lake Victoria catchment is much more densely populated than the other African Great Lakes (Figure 21.5). Nevertheless, cultivation and deforestation increasingly takes place in the latter lakes. A potential exists for land degradation, local increase in sediments and nutrient inputs in the very near future except for the extreme end of Tanganyika where near-shore population densities are presently low around the entire lake (Figure 21.5).

The introduction of the Nile perch in the 1950's and of the water hyacinth in Lake Victoria has also contributed greatly to the dramatic shifts in the lake's ecosystem during the past few years. Currently the presence of water hyacinth has also been reported in Lake Malawi, within the vicinity of Sugar Corporation of Malawi-Dwangwa Mill and Ethanol Company Limited and in the Shire River, the outlet of Lake Malawi (Figure 21.1). This may be of great concern to Lake Malawi. If population growth trend continues at the current rate (2.8% $y^{-1}$) in Malawi, cultivation (e.g. sugar plantation) and deforestation on steep slopes including industrialisation along the lakeshore will definitely lead into increased river runoff. This may result in more nutrient and sediment loading in the lake. Certainly the density of people occupying a catchment and the type of land-use (e.g. agriculture) they employ, will determine the effect the population can have on a lake.

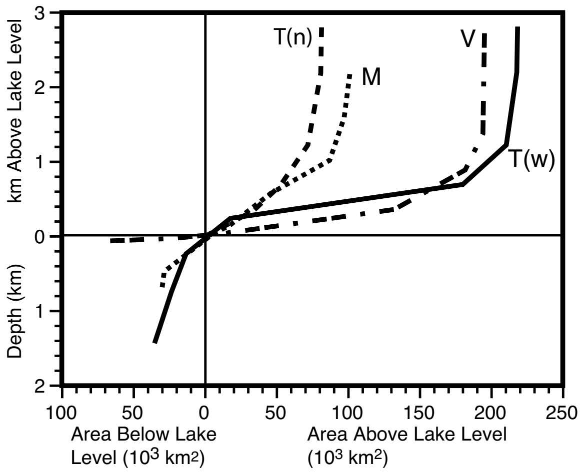

Figure 21.4: Hypsographic curves for the three lakes and their drainage basins. $T_{(w)}$ = entire Tanganyika drainage basins. A separate curve for the Tanganyika drainage basin ($T_{(n)}$) was determined by excluding the eastern plains (area east of dashed line) in order to provide a more accurate description of near shore topography. Note changing scales on each axis. (Bootsma & Hecky, 1993).

## 21.5 Effects of Eutrophication in Lake Malawi, Tanganyika and Victoria

Eutrophication may result into increased sedimentation, which may lead into a rise of the anoxic boundary layer (Figure 21.3), increased bottom water oxygen demand and greater light attenuation. This will reduce the depth of the euphotic zone. Such effects may result in shrinkage of available fish habitat and is detrimental to fisheries. A change in phytoplankton species composition may also result. The nature of these changes will be determined by the absolute and relative input rates of N, P and Si, by hydrodynamics, and by the complex interplay between internal nutrient cycling and the trophic structure. In the Laurentian Great Lakes, eutrophication has been observed to result in lower Si concentrations (Schelske *et al.*, 1988) due to rapid growth and subsequent sedimentation of diatom frustules in rivers. The in-

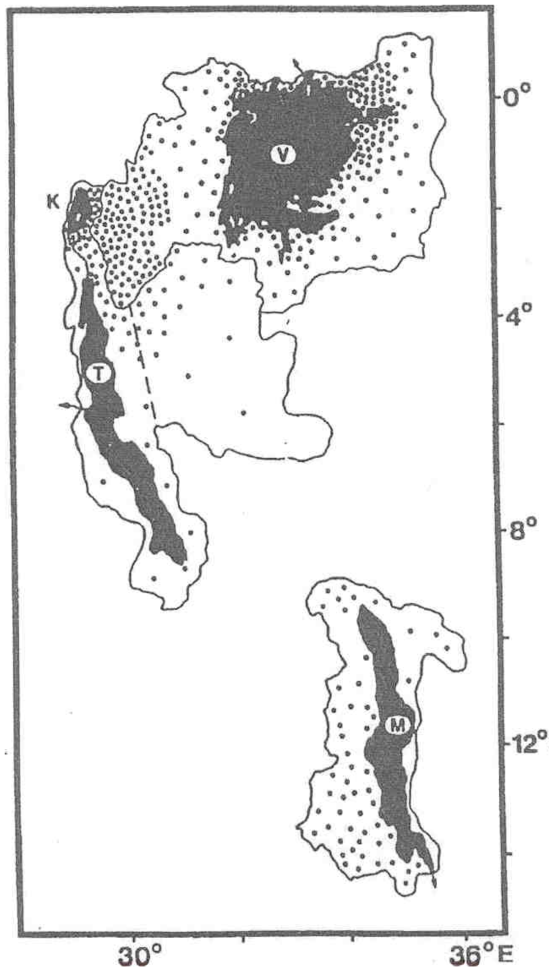

Figure 21.5: Human population densities in the drainage basin of African's largest three lakes. One dot = 100,000 persons. V = Victoria; K = Kivu; T = Tanganyika; M = Malawi (Bootsma & Hecky, 1999).

creased productivity in Lake Victoria during 1991 (Mugidde 1993) relative to 1960–1961 (Talling, 1965, 1966) appears to have had the same effect (Figure 21.3). While diatoms were still abundant in Lake Victoria during 1990, they consisted primary of thinly silicified *Nitzschia* (Bootsma & Hecky, 1993), where as Talling (1986) reported dominance by *Melosira*, a large heavily silicified diatom (which is now absent except perhaps in marginal bays where Si remains available from inflowing streams).

Eutrophication in lakes often results in cynobacteria dominance, although others factors such as temperature (Varis, 1991), light (Zevenboom *et al.*, 1982), and pH (Shapiro, 1973) may also affect the competitive ability of these organisms. This scenario is apparent in Lake Victoria. Relative to that observed during 1960–1961 (Talling, 1966), evidence of increased nutrient input (Hecky, 1993) is accompanied by higher cyanobacteria biomass (Ochumba & Kibaara, 1989). Because denitrification will minimise the influence of additional N input in Lakes Tanganyika and Malawi, eutrophication in these lakes will result in a greater increase in P available than N availability, and the significance of N-fixing cyanobacteria would also increase in these lakes. Such a shift in phytoplankton species composition might result in a lower efficiency of energy transfer to higher trophic levels, since cyanobacteria are generally considered a poor food source (Lampert, 1981; Heerkloss *et al.*, 1984; Haney, 1987). However the ability of some Tilapiines (*Tilapia* and *Oreochromis* species) to digest cyanobacteria (Moriarty, 1973; McDonald, 1987), suggests that eutrophication may result in a more productive fishery dominated by herbivorous fishes. While this would be beneficial with regards to food production (Tilapiines), such an environment would not be favourable for zooplanktivorous fish species, since cyanobacteria are a poor food source for zooplankton.

## 21.6 Particular eutrophication issues to consider for Lake Malaw

The major sources of nutrients such as N and P to Lake Malawi are rivers (Figure 21.6) and atmospheric deposition (Bootsma & Hecky, 1999). Almost all silica entering the lake comes from its tributary rivers. For the epilimnion, both rivers and vertical mixing are important silica sources.

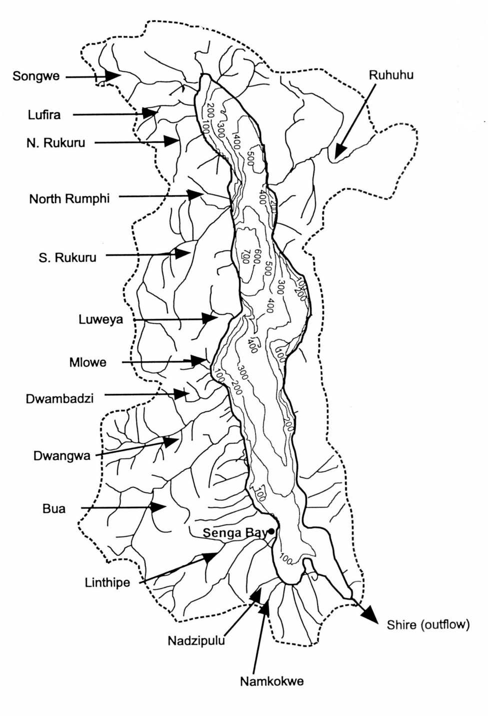

Figure 21.6: General geology and river systems in the Lake Malawi catchment (www.science.uwaterloo.ca).

### 21.6.1 Main source of nutrients in Lake Malawi

#### Rivers

River inflow responds to climatic variability and exhibits large shifts in runoff. The rainy season experiences large inflows, while in the dry or winter season the inflow decreases strongly. The lake surface levels also follow this pattern (Figure 21.7). This may also magnify the loading of nutrients and sediments, especially from river basins with extensive deforestation and agriculture. The annual precipitation regulates for the annual variability of inflow. This is also the case with the runoff and nutrient loading in other lakes or enclosed seas e.g. the Baltic Sea (Vagstad *et al.*, 2001).

A comparison of the 1997 loading with previous estimates of Lake Malawi (Table 21.2) clearly indicates that river loading may play a much more significant role in nutrient loading to the mixed layer of the lake than previously thought. Bootsma and Hecky (1999) reported that sediment and sediment-bound nutrient load is higher in the lake through rivers, which are heavily impacted, (Linthipe, Songwe and Dwangwa Rivers) than rivers that are lightly impacted (Mlowe, Luweya and Dwambazi Rivers; See Figure 21.6. The Linthipe, Songwe and Dwangwa Rivers are heavily impacted because of intensive land-use practices in their catchments. The catchments are characterised with more agricultural activities (e.g. intensive sugar plantation along Dwangwa River) and deforestation, and greater population densities compared to catchments of the lightly impacted rivers. Besides, such rivers are heavily impacted because of topography, urbanisation and improper sewage treatment and disposal (e.g. direct disposal of sewage and industrial waste into rivers). When industries dispose their organic waste, the biological oxygen demand (BOD) can be higher than the recommended (20 mg $l^{-1}$ for the treatment works and 5 mg $l^{-1}$ for the stream), (Anonymous, 1995). The levels of ammonia detected in the receiving waters of Lake Malawi from ethanol effluents are reported to be above the recommended levels for most species in water, ranging between 0.6 to 2 mg $l^{-1}$ (Msomphora, 2000). Even the management of clinical waste seems to be a problem in Malawi. In several basins such practices can alter the patterns of river nutrient/sediment transport. Hence the dilution capacity level of the lake's large water volume may no longer be effective.

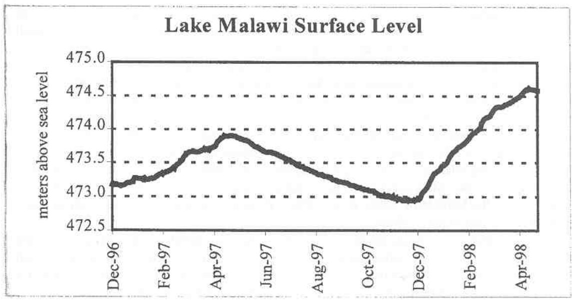

Figure 21.7: Lake levels variability from December 1996 to April 1998. A significant increase in lake level followed a large early season inflow in December 1997 (Bootsma & Hecky, 1999).

Table 21.2: Comparison of 1997 N and P loading estimates with previous estimates. All units are in mmol m$^{-2}$ of lake surface area. Source: Bootsma and Hecky (1993; 1999).

| | 1997 estimate | Previous estimate |
|---|---|---|
| Total dissolved phosphorous | 1.195 | 1.51 |
| Suspended phosphorous | 9.08 | 1.91 |
| Total phosphorous | 10.28 | 3.42 |
| Total dissolved nitrogen | 22.87 | 23 |
| Suspended nitrogen | 178.6 | 12 |
| Total nitrogen | 201.5 | 35 |
| Soluble reactive silica | 298.8 | 220 |

**Atmospheric deposition**

According to Bootsma and Hecky (1999), a larger portion of atmospheric carbon and N deposition in the lake is in the form of soluble organic compounds. Soluble and particulate P deposition is similar in magnitude, with much of the soluble P being organic. Atmospheric deposition of nutrients in to the lake surface is primarily in the form of dry deposition. For instance, mean daily dry deposition is almost twice the mean daily wet deposition (Table 21.3). This may be due to less dust during the rainy season, when the ground is wetter and there is greater vegetation coverage. It is also reported that concentration of solute and particulate nutrients in rainwater near Lake Malawi are not particularly high relative to industrial regions or some other parts of Africa. However higher than average $NH_4^+$, $NO_3^-$, and $K^+$ concentration, suggests that burning is having a significant effect on atmospheric chemistry around the lake. High P deposition may also be linked to burning practises. But although the direct effect of the deposition of these solutes on the lake may not be negative, the burning and soil exposure is. These observations may potentially result in negative impact, such as siltation, accelerated flux of nutrients from soil to the lake, and a decreased and a more variable water supply from rivers as described above.

### 21.6.2 Nutrient cycles in Lake Malawi

Nutrients are renewed in the photic zone of Lake Malawi by vertical transport from the nutrient-rich deep waters. However, most of the time the algae are experiencing balanced growth with their biomass limited by grazing and adequate nutrients supplied through regeneration. The algae community in the lake is adapted to a low, but relatively steady supply of nutrients supplied through the mechanisms of regeneration by grazers and continuous introduction of nutrients from below the epilimnion by mixing. Conducting nutrient enrichment experiments, Bootsma and Hecky (1999) revealed that if nutrients increased in Lake Malawi, chlorophyll a concentrations would increase too and algae species composition would change. Further evidence was seen during January and February (rainy season when the river runoff increases) in the Linthipe River, which is one of the most important nutrient suppliers to the lake. With increasing nutrient loading of P relative to N, the algae community was affected and the chlorophyll a concentration increased. As such it is likely that increased P input to the lake, due to increased erosion, will disrupt the balanced algae growth and favour the development of N fixing, filamentous cyanobacteria such as *Anabaena* species. *Anabaena* blooms were observed in the southern portion of the lake in March and April of 1997 and 1998 (Bootsma & Hecky, 1999).

Table 21.3: Comparison of daily dry and wet deposition of carbon, nitrogen, phosphorous and silicon. Source: Bootsma and Hecky (1993; 1999). Total C Total N Total P Total Si

| | Total C | Total N | Total P | Total Si |
|---|---|---|---|---|
| Mean Wet Dep. ($\mu$mol m$^{-2}$ event 1997/98) | 2465 | 431 | 14.2 | 115 |
| Mean Dry Dep. ($\mu$mol m$^{-2}$ event 1997/98) | 2570 | 560 | 24.7 | 155 |

### 21.6.3 Recent ecological changes in Lake Malawi

There have been quite a few changes in the quantitative phytoplankton flora of Lake Malawi, which creates concern, besides the fish kills reported now and then due to probably ethanol effluents spillage, pesticides and some chemicals from the Sugar Corporation of Malawi-Dwangwa Mill into the lake. Usually there are fish kills due to pesticides and herbicides when knapsacks sprayers are washed or cleaned in the water courses (per.comm). The filamentous chlorophytes of the *Mougoetia/Oedogonium* complex has occurred since the 1960's, but it has been ignored until now. *Planktolyngbya tallingi* has been reported to be appearing in the southern portion of the lake, where it has replaced the dominant species, *Planktolyngbya nyassensis.* This is an indication for increasing nutrient availability and poor light conditions. The filamentous blue-green alga, *Cylindrospermopsis raciborski*, which has toxic forms, has also been reported. This is of concern because usually such algae are typical climax species in highly eutrophic situations. *Anabaena* species blooms are currently reported to be reoccurring, especially inshore in the vicinity of the Linthipe River, during the end of rainy season (March–April). In the past this species was reported to occur only in October–November. The co-occurrence of the dinoflagellates *Peridinium* species with the *Anabaena* species bloom in at least one bloom is also worrisome as both taxa have forms, which can produce toxins (Bootsma and Heckey 1999). Even if such changes in the phytoplankton community composition may yet appear minor, they are indications that greater changes may follow. Due to fragmentary, qualitative and discontinuous availability of earlier studies, the interpretation of data is difficult. It could just reflect natural variability. In Lake Victoria qualitative analysis of phytoplankton did not occur until after dramatic changes had occurred. By then the phytoplankton community had changed within decades to a eutrophic assemblage dominated by potentially toxic blue-green algal species (Mugidde, 1992).

### Summary

Several of the African Great Lakes are distinctive for their very long water residence time >100 years. Incoming nutrients will be retained within the lakes and recovery will be slow even if inputs are reduced. While changes in chemistry and plankton composition of Lake Malawi have not been extreme to date, strong eutrophication is already happening in Lake Victoria, where damage has reduced its biological wealth and human misery may follow (Baskin, 1992). It could be advisable to prevent this happening to Lake Malawi and Tanganyika.

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# Chapter 22

# Large shallow temperate lakes Peipsi and Võrtsjärv: consequences of eutrophication and climate change

Tiina Nõges, Peeter Nõges
Institute of Zoology and Botany
Estonian Agricultural University
Võrtsjärv Limnological Station
61101 Rannu, Tartumaa, Estonia
tnoges@zbi.ee

## 22.1 Introduction

Lake Peipsi (3,555 km$^2$, mean depth 7.1 m) is one of the most important lakes in Europe and has the fourth largest surface area after Lakes Ladoga, Onega, and Vänern. Located on the Estonian-Russian border, Lake Peipsi is a transboundary waterbody and the largest international lake in Europe. The volume of water in Lake Peipsi is 25 km$^3$ at the long-term mean water level (30 m above sea level) and the mean residence time of water is about 2 years (Jaani, 2001). The River Narva contains the outflow of Lake Peipsi and runs into the Gulf of Finland. Lake Võrtsjärv (270 km$^2$, mean depth 2.8 m) is the largest lake belonging entirely to Estonia (Figure 22.1). The watershed of Lake Võrtsjärv (3,104 km$^2$) lies within Lake Peipsi catchment (47,800 km$^2$). Regular investigation of these two large, shallow, nonstratified lakes began in the 1960s. To date, over 35-year time series on water chemistry and biology have been collected.

Riverine transport is the most common pathway for nutrient input into both lakes. The four rivers Väike Emajõgi, Õhne, Tarvastu, and Tänassilma contribute 70–75% of the water inflow into Lake Võrtsjärv and 80–85% of the total load of substances. In Lake Peipsi, the majority of phosphorous and nitrogen compounds (>80%) are carried into the lake by the rivers Velikaya and Emajõgi (outflow from Lake Võrtsjärv), the first carrying biologically treated sewage from the Russian town of Pskov (ca. 200,000 inhabitants) and the latter transporting wastewater from the Estonian town of Tartu (ca. 100,000 inhabitants). A water treatment plant has been in operation in Tartu since the end of 1998; prior to its installation, water from Tartu was untreated. The River Emajõgi contributes approximately 70% of the total nitrogen (TN) and total phosphorus (TP) loading

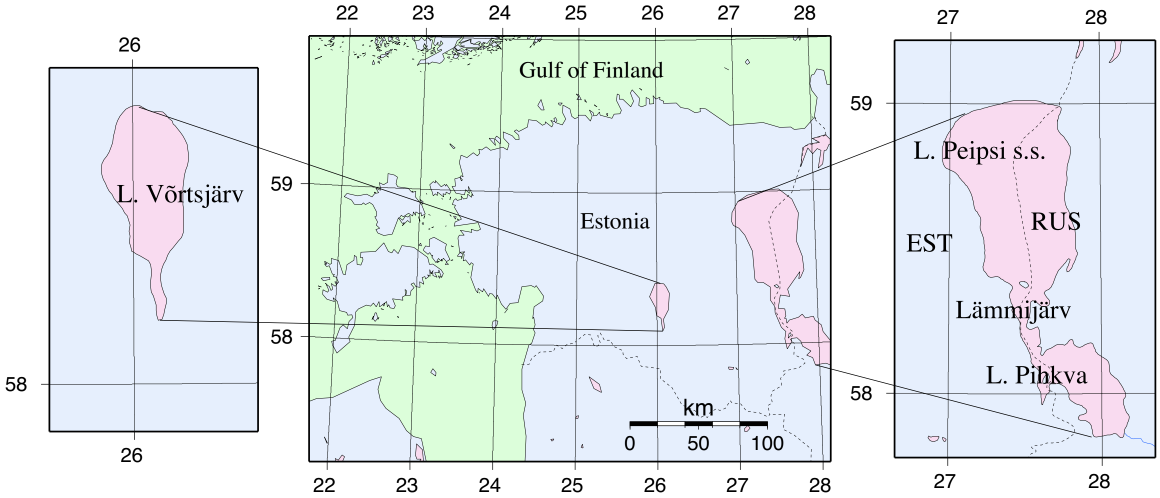

Figure 22.1: Location map of Lakes Peipsi and Võrtsjärv.

into Lake Peipsi from the Estonian territory (Figure 22.2). The Russian River Velikaya contributes about 65% of all nutrient loading into Lake Peipsi (Stålnacke *et al.*, 2002) and about 85% of that comes from the Russian territory.

Lake Peipsi consists of three parts: the largest northern part, Lake Peipsi *sensu stricto*, 2,611 km$^2$, mean depth of 8.4 m and maximum depth of 12.9 m; the southern part, Lake Pihkva, with an area of 708 km$^2$ and mean depth of 3.8 m; and the narrow river-shaped Lake Lämmijärv with an area of 236 km$^2$ and mean depth of 2.6 m that connects Lake Peipsi with Lake Pihkva. The entire catchment area (47,800 km$^2$) involves parts of Estonian, Russian, and Latvian territories. Lakes Peipsi and Võrtsjärv are unstratified and eutrophic, Lake Lämmijärv has some dystrophic features, while the trophic status of Lake Pihkva is the highest reaching even hypertrophic level (Table 22.1).

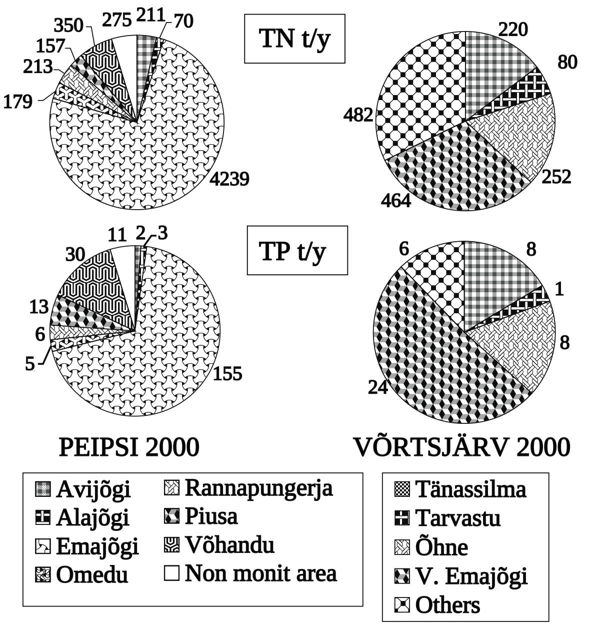

Figure 22.2: Nitrogen and phosphorus loading from Estonian watershed into L. Peipsi and Võrtsjärv in 2000, and the share of different rivers (Nõges *et al.*, 2002).

## 22.2 Changes in nutrinet loading

Riverine discharge of nutrients into Lakes Peipsi and Võrtsjärv increased during the 1980's while a sharp decrease occurred in the early 1990's (Nõges *et al.*, 2003a; Järvet, 2001). This was mainly evi-

Table 22.1: Indices reflecting the trophic status of lakes Peipsi and Võrtsjärv (modified from Haberman *et al.*, 1998; Laugaste *et al.*, 2001; Starast *et al.*, 2001)

| Parameter | Units | L. Peipsi mean | L. Pihkva | L. Lämmijärv | L. Peipsi s.s. | L. Võrtsjärv |
|---|---|---|---|---|---|---|
| TP | mg P $m^{-3}$ | 42 | 63 | 53 | 35 | 54 |
| TN | mg N $l^{-1}$ | 0.77 | 1.01 | 0.9 | 0.68 | 1.6 |
| Chlorophyll *a* | mg $m^{-3}$ | 18 | 26 | 25 | 14 | 24 |
| Secchi depth | m | 1.8 | 1.3 | 1.4 | 1.8 | 1 |

denced in TN loadings (Figure 22.3). The change resulted from the collapse of soviet-type agriculture, which was characterised by extensive use of fertilizers often accompanied by substantial nutrient leakage into water bodies. Significant reductions in fertilizer use, typical for the transitional economy during recent years, diminished nutrient losses from the catchment. Only 5–10% of N, P, and K mineral fertilizers and 30% of manure were applied to agricultural lands at the end of the 1990's compared to the levels at the end of the 1980s (Järvet *et al.*, 2002). As TN loading decreased faster than TP loading, the TN/TP loadings ratio decreased (Figure 22.3).

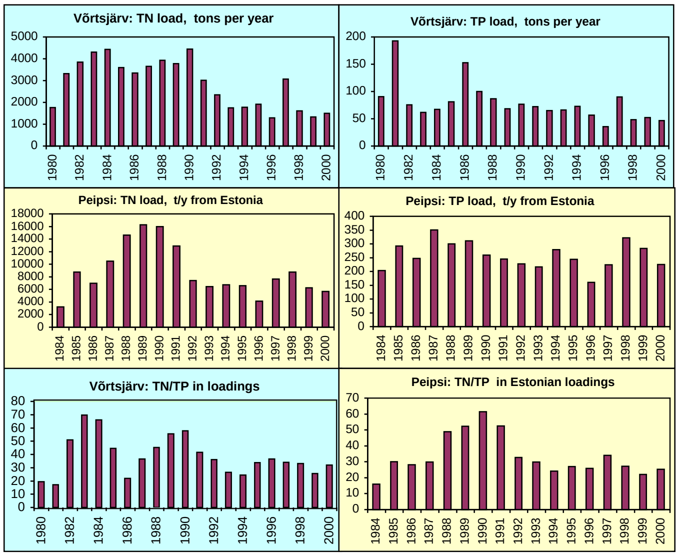

Figure 22.3: Annual runoff of total nitrogen (TN) and total phosphorus (TP) from Estonia into Lake Peipsi in 1984–2000 (Nõges *et al.*, 2003a), and into Lake Võrtsjärv in 1980–2000 (Järvet, 2001) and the resulting TN/TP mass ratio in external loadings.

## 22.3 Relations between changed nutrient loading and phytoplankton

The average phytoplankton biomass in Lake Võrtsjärv from May to October in 1963–2001 was 20 g WW $m^{-3}$ (variation from 1 to 100 g WW $m^{-3}$); in Lake Peipsi proper the respective value for 1962–2001 was 10 g WW $m^{-3}$ (0.35–61 g WW $m^{-3}$). Many species of bloom-forming cyanobacteria use molecular nitrogen at low N/P ratios if N is the limiting nutrient. Observing the changes in cyanobacterial dominance from the beginning of the 1960's in Lakes Peipsi and Võrtsjärv, one can notice an increase during the late 1960's and early 1970s, a decline during the late 1970's and 1980's, and another increase during the late 1990's in both lakes (Figure 22.4, Nõges *et al.*, 2003a). Changes are much less pronounced in Lake Võrtsjärv than in Lake Peipsi. In Lake Võrtsjärv, the dominant cyanobacterial species *Limnothrix planktonica*, *L. redekei*, and *Planktolyngbya limnetica* are not able to fix $N_2$; the main $N_2$-fixing species, *Aphanizomenon skujae*, does not achieve dominant status. In Lake Peipsi $N_2$-fixing species *Aphanizomenon flos-aquae* and *Gloeotrichia echinulata* prevail in summer phytoplankton. Since the beginning of the 1990s, the biomass of $N_2$-fixing species has increased in both lakes.

The increasing dominance of cyanobacteria and the occurrence of algal blooms in both lakes can be caused by reduced nitrogen loading and decreased TN/TP ratio. In Lake Peipsi a TN/TP mass ratio <30 seems to be critical for the development of predominant cyanobacterial species, both $N_2$-fixing (*Gloeotrichia echinulata, Anabaena, Aphanizomenon*) and non-fixing (*Microcystis*) as seen in Figure 22.5.

## 22.4 Water level changes

A long-term sinusoidal fluctuation of the water level (WL) with a period of about 30 years is characteristic of both lakes (Figure 22.6). Smooth and continuous decreases (1928–1940) and increases (1940–1957; 1965–1990) of WL resemble a long-term trend and can be distinguished only in the context of a long time series. Apparent periodicity is probably associated with large-scale fluctuations in solar activity and atmospheric processes. Similar periodic changes have occurred in other large geographic areas: in lakes Saimaa, Ilmen, and Onega WL fluctuations have a spectral density maximum at 28–32 years (Masanova & Filatova, 1985); spectral density maxima ranging from 20 to 30 years were stated for different hydrological elements of Lakes Ladoga (Malinina *et al.*, 1985) and Müggelsee (Behrendt & Stellmacher, 1987).

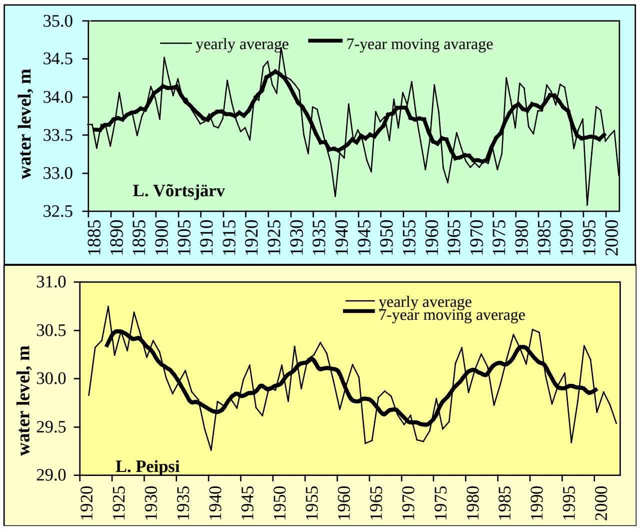

Figure 22.6: Long-term dynamics of the water level of Lakes Võrtsjärv and Peipsi.

## 22.5 Water level, nutrients and phytoplankton

In very shallow L. Võrtsjärv the annual mean amplitude of WL (1.4m) is equal to 1/2 of its mean depth, and the absolute range of WL fluctuations (3.2m) even exceeds the mean depth of the lake. Between the registered absolute minimum and maximum WL the lake area differs 1.4 times, the mean depth 2.5 times, and the volume 3.5 times (Figure 22.7) having a strong influence on the ecosystem (Nõges *et al.*, 2003c). In low-water years, the water column is better illuminated while both phosphorus release and denitrification increase because of more frequent resuspension of bottom sediments (Figure 22.8) bringing about substantially higher phosphorus concentration and lower N/P ratio (Figure 22.9). Such conditions favour the development of phytoplankton, first of all nitrogen-fixing cyanobacteria. In L. Võrtsjärv phytoplankton biomass is substantially higher and the share of $N_2$-fixing species bigger in low-water years (Figure 22.10). In deeper L. Peipsi where seasonal and absolute WL variation ranges make up approximately 1/5 and 1/2 of the mean depth, respectively, the direct influence of the WL is not so obvious.

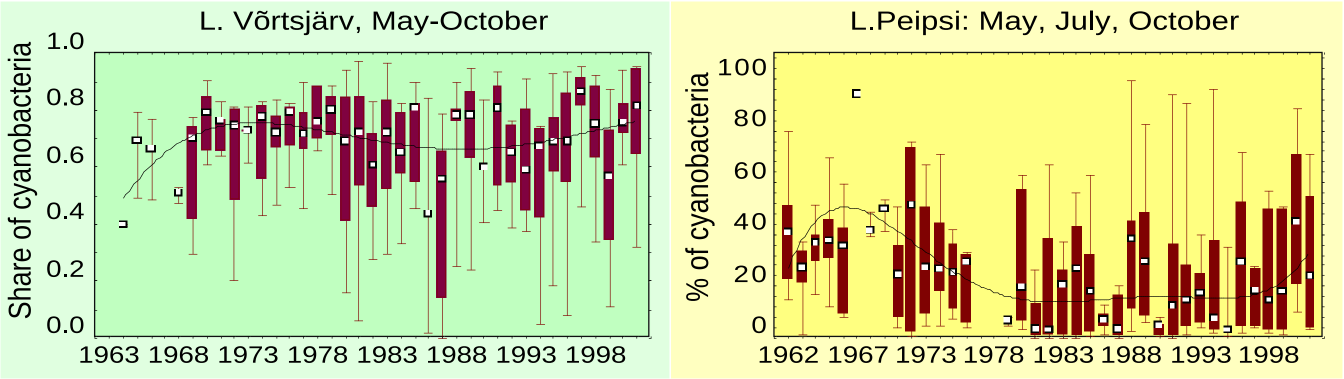

Figure 22.4: Changes in the dominance of cyanobacteria in phytoplankton biomass of Lake Peipsi and Lake Võrtsjärv since the 1960's (from Nõges *et al.*, 2003a).

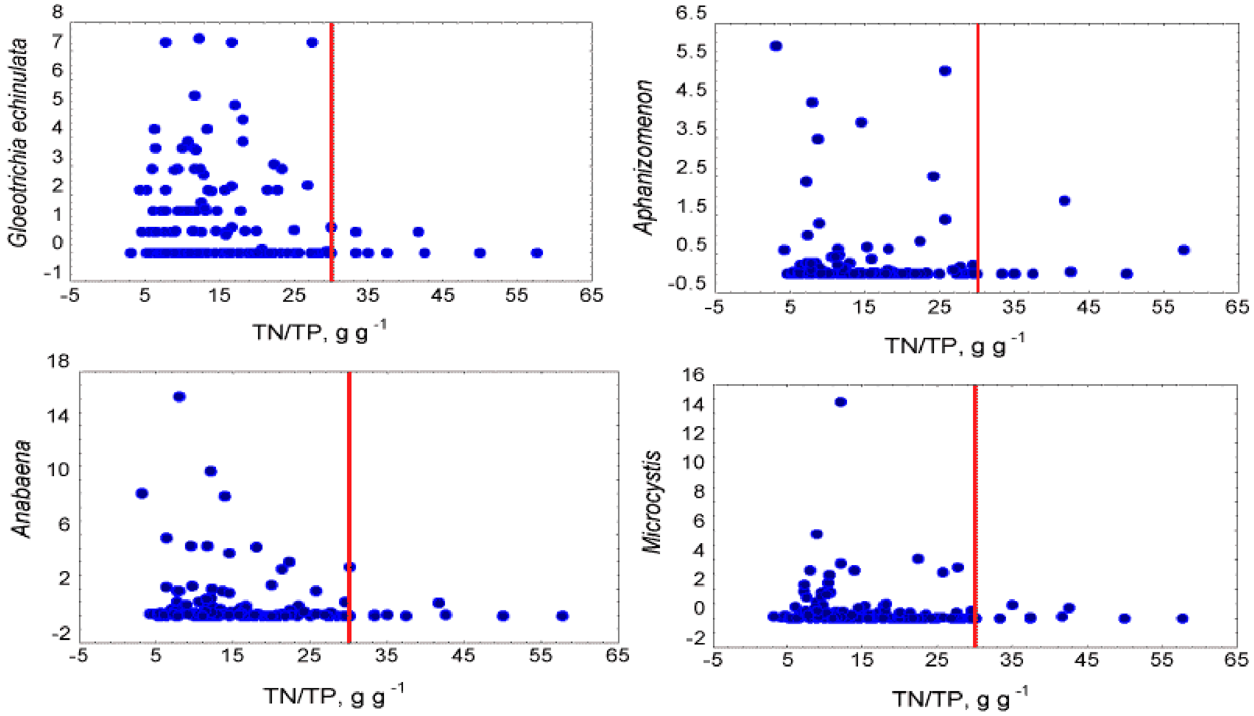

Figure 22.5: Biomass of dominating cyanobacteria gWW $m^{-3}$ at different TN/TP ratios in Lake Peipsi in June-September (Nõges & Nõges, 2004, data from Reet Laugaste)

Figure 22.7: Lake Võrtsjärv at high (1999) and low (1996) water level in southern (left) and northern (right) part of the lake.

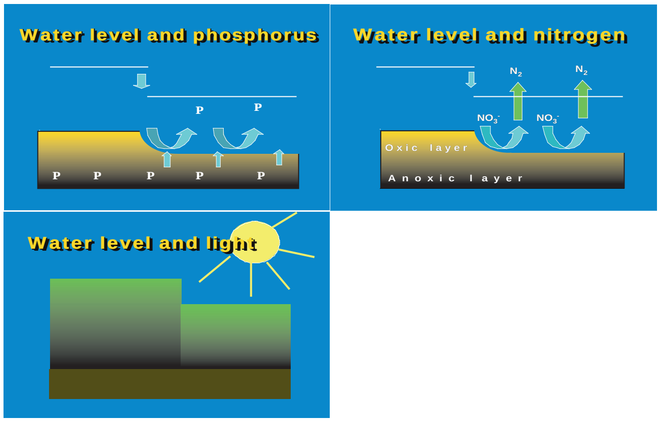

Figure 22.8: In a large and very shallow lake the decrease of water level increases resuspension of bottom sediments enhancing the release of phosphorus. Intensive resuspension denudes anaerobic sediment layers and denitrification increases. The shallower is the mixed water column the better it is illuminated.

## 22.6 Climate, water level and phytoplankton

The North Atlantic Oscillation (NAO), which is defined through the variability of air pressure differences between the north (Iceland) and south (Azores), dictates climate variability over a large area of the Atlantic, North America, and Europe, especially during winter (Hurrell *et al.*, 2001). Variation in heat and moisture transport between the Atlantic and surrounding continents affect water balance components of lakes, such as precipitation, riverine inflow, and evaporation, resulting in changes in water level. In both Lakes Peipsi and Võrtsjärv, mild winters associated with high NAO index bring about higher water level (Figure 22.11).

For the ecosystem of Lake Võrtsjärv, warmer and wetter climate could bring about higher water levels. The deeper the mixed water column, the lower the average light intensity, resulting in reduced phytoplankton biomass (Nõges & Nõges,

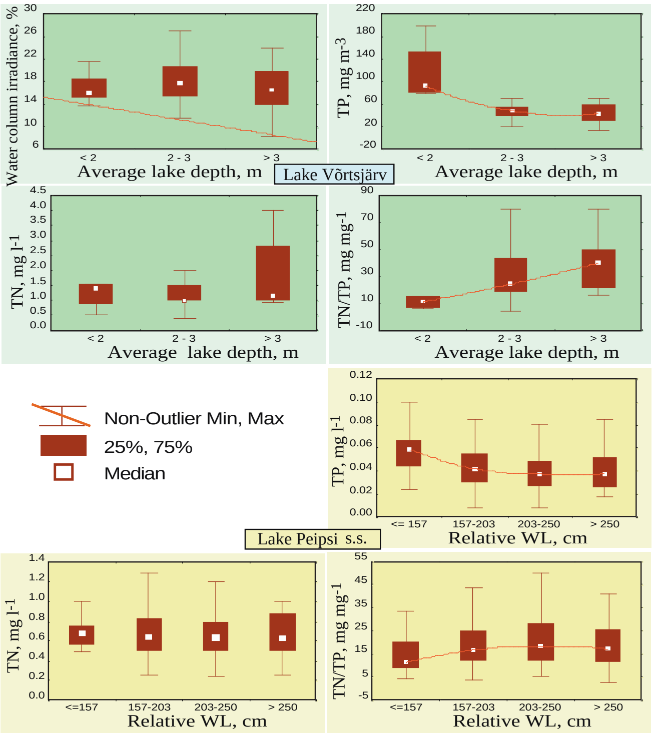

Figure 22.9: Dependence of total nitrogen (TN) and total phosphorus (TP) concentration, of the TN/TP mass ratio and of the average water column irradiance ($I_{mix}$) on the mean depth (or water level, WL) in lakes Võrtsjärv and Peipsi.

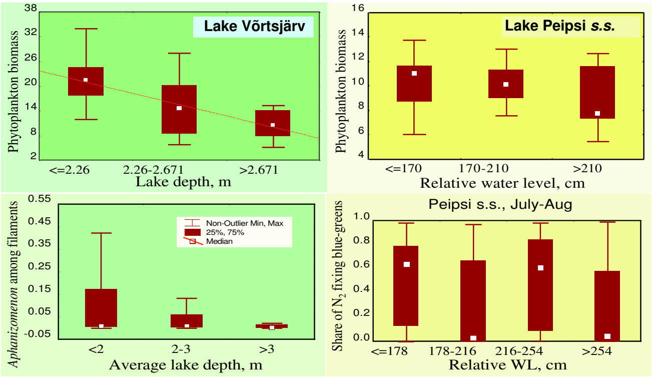

Figure 22.10: Relationship between the mean depth (or water level, WL) and phytoplankton biomass (mg wet weight $l^{-1}$) in lakes Võrtsjärv and Peipsi.

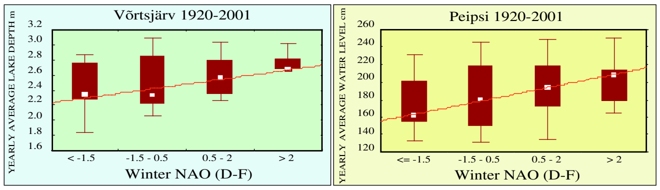

Figure 22.11: Relationship between winter NAO and yearly average water level (WL) or lake depth in lakes Võrtsjärv and Peipsi.

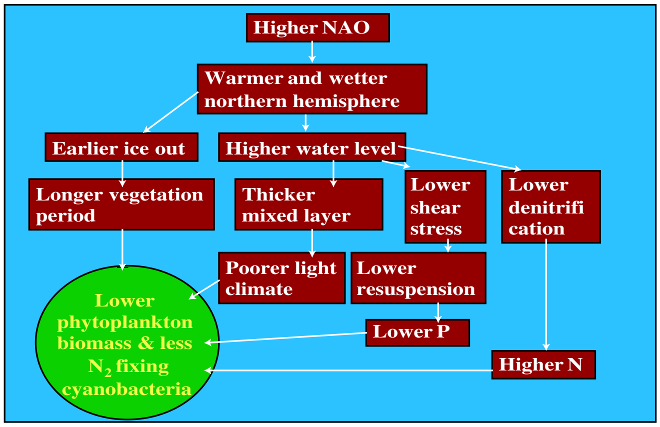

Figure 22.12: The assumed consequences of global warming on the phytoplankton of Lake Võrtsjärv.

1998). Weaker resuspension in deeper water releases less phosphorus from the bottom sediments while lower denitrification rate keeps nitrogen concentration high (Nõges & Nõges, 1999). Consequently, in a warmer world the N/P ratio in Lake Võrtsjärv would probably be higher and $N_2$-fixing cyanobacteria will have less chance to develop (Figure 22.12).

A warmer and wetter climate will also affect watershed processes: reduced soil frost and increasing amount of precipitation will increase nutrient leaching from the soil and accelerate the eutrophication of water bodies. We have noticed that during the 1990's the spring peaks of riverine nutrient discharges shifted from the beginning of April to mid March. It is remarkable that despite abandoning of a substantial proportion of previously cultivated lands and decreased use of fertilisers, wintertime nutrient losses are almost as high as during former years because of increased water discharge and surface runoff in winter. Larger water discharges in winter, in combination with the still large nutrient pools in the soils, could explain the phenomenon that nutrient concentrations in lakes have decreased less than what might be expected from the reduced fertiliser applications.

## 22.7 Climate, nutrients and fish-kills

Several winter fish-kills have been documented in Lake Võrtsjärv during the last century (in 1939, 1948, 1967, 1969, 1978, 1987, 1996). Fish-kills occurred most probably in wintertime and dead fish were subsequently recovered in spring. One reason for these fish-kills could be the depletion of oxygen in low-water years during late winter when the under-ice oxygen concentration dropped faster due to smaller absolute amount dissolved in the smaller volume of water. This kind of oxygen depletion was documented in March 1996 (Nõges & Nõges, 1999) and resulted in a massive kill of eel.

In Lake Peipsi, high water temperature and algal blooms resulted in massive fish-kills during summers of 1959, 1972, and 2002. During algal blooms, phytoplankton biomass is built up faster than can be consumed by zooplankton. Intensive photosynthesis produces much oxygen during the day that partly leaves to the atmosphere when the water becomes oversaturated. At night, when algal masses consume but do not produce oxygen, oxygen deficiency may occur. Such large-scale diurnal fluctuations of oxygen concentration harm fish and make them more susceptible to other stressors. High water temperature associated with algal blooms makes the situation even more dangerous to fish. Other stressors accompanying algal blooms are high water pH caused by intensive photosynthesis and elevated concentrations of ammonium released during the decomposition of organic matter. At high pH (>9) most ammonium is converted to toxic ammonia ($NH_3$), which can kill fish. Moreover, cyanobacterial toxins can also significantly influence fish populations (Figure 22.13).

## 22.8 Fishes and food webs

Lake Peipsi is important for recreation and fishery in both neighbouring countries, Estonia and Russia. Considering its annual fish catches (9,000–12,000 tons or 25–34 kg ha$^{-1}$) L. Peipsi exceeds all large lakes in North Europe. The main commercial fishes are lake smelt (*Osmerus eperlanus eperlanus*), perch (*Perca fluviatilis*), pikeperch (*Sander lucioperca*) and bream (*Abramis brama*), until the 1990's also vendace (*Coregonus albula*). The stock of vendace decreased sharply in the beginning of 1990's and has not recovered. This has been explained by the occurrence of unfavourable spawning conditions in several successive years while the impact of eutrophication can not be neglected either. At the same time, the abundance of pikeperch increased remarkably (Pihu & Kangur, 2001; Kangur *et al.*, 2002).

Lake Võrtsjärv was considered as a ruffe-lake in 1950's and 1960's as small non-valuable fishes, most of all ruffe *Gymnocephalus cernuus* dominated in catches. From late 1960's until early 1970's the fine-meshed trawling was stopped as it was considered to damage the commercially important piscivorous fish, first of all pikeperch. The introduction of glass eels was started to increase the commercial value of fish catches. As the result of these measures, the catches of pikeperch and other valuable fish increased rapidly. By now the value of catches has increased by 3–5 times while the total yearly catch has remained quite stable, 300–400 tons or 10–15 kg ha$^{-1}$ Järvalt *et al.* (2003).

In the food web of a lake large carnivoruos fishes like pike and pikeperch are top predators placed on the highest level of the food pyramide. The amount of fishes and their distribution between planktovores, benthivores and piscivores is determined by the functioning of the whole food chain. The potential productivity at all trophic levels is controlled bottom-up by nutrient/food supply. The 'health' of a lake ecosystem is, however, rather determined by the efficiency of the transformation of the organic matter produced by algae through food chain towards top predators. The more efficient this transformation, the higher is the pro-

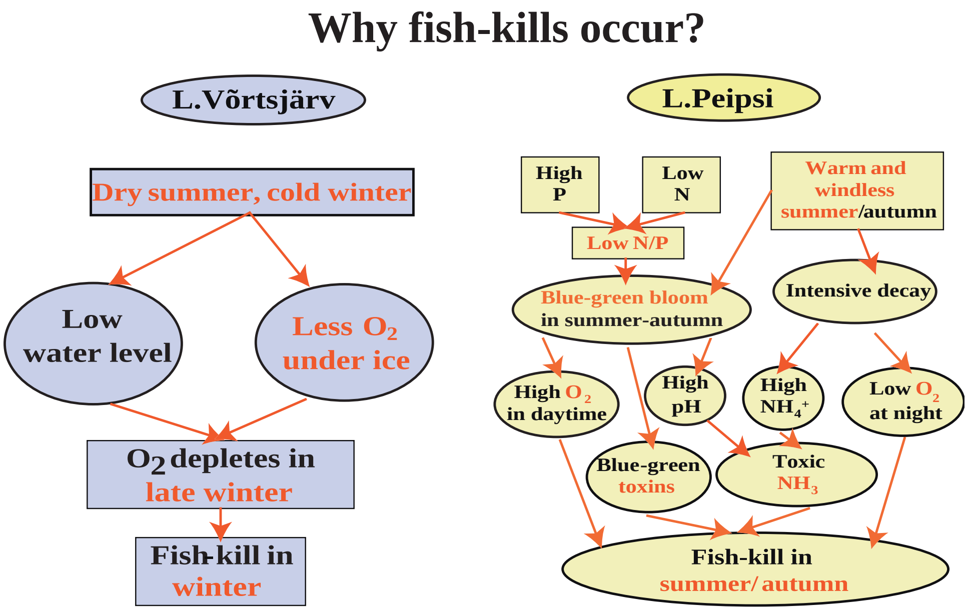

Figure 22.13: Causes of fish-kills in lakes Võrtsjärv and Peipsi.

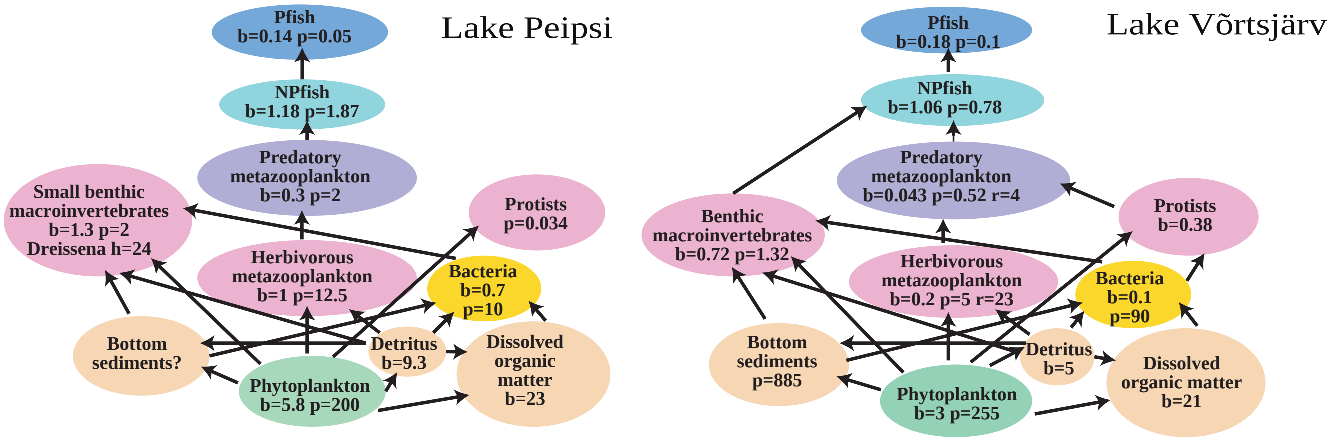

Figure 22.14: Quantified food web structure in Lake Võrtsjärv according to Nõges et al. (1998) and in L. Peipsi where fish biomass and production was calculated by A. Järvalt from data published by Kangur et al. (2003), biomass and production of zoobentos was obtained from Timm et al. (2001) and that of zooplankton from Haberman (2001), other data from Nõges et al. (2001). Symbols: b=bulk, gC $m^{-2}$; p=production, gC $m^{-2}$ $year^{-1}$; r=requested food ration, gC $m^{-2}$ $year^{-1}$. Green arrows denote grazing food chains, blue arrows denote detrital food chains, violet arrows denote microbial loop and black arrows denote other transformations. Ovals of the same colour have an equal distance from the base of the food chain, i.e. belong to the same trophic level. Symbols: NPfish — non-piscivorous fish; Pfish — piscivorous fish; b – bulk, gC $m^{-2}$; p – production, gC $m^{-2}$ $year^{-1}$; r – requested food ration, gC $m^{-2}$ $year^{-1}$. Conversion factor 1 mg WW = 0.1 mg C is used for all links.

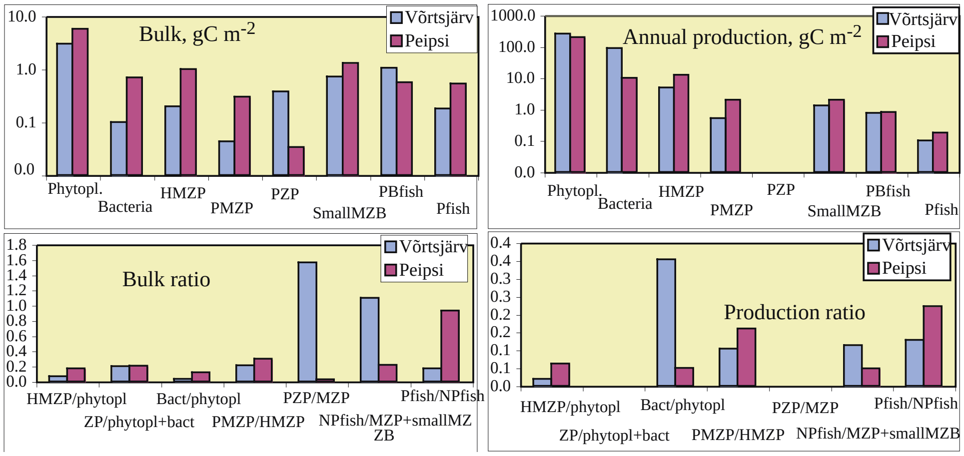

Figure 22.15: The bulk and production ratios of different food web components in lakes Võrtsjärv and Peipsi. Symbols: ZP zooplankton (metazooplamkton + protists), MZP– metazooplankton, PZP – protozooplankton, HMZP - herbivorous metazooplankton, NPfish – non-piscivorous fish; Pfish – piscivorous fish. Data sources used as in previous figure.

duction of 'good' piscivorous fish and the better water quality can be expected. In that sense the composition of fish community in L. Peipsi can be considered 'good' and even improving after the increase of pikeperch since the beginning of the 1990s. The share of piscivores in the fish biomass and production has increased more than three times: from, accordingly, 18% and 4.5% in 1986 up to 48% and 18% by the turn of century (calculated by A. Järvalt from the data of Kangur *et al.*, 2003). However, sharp decrease of clean-water species like vendace may indicate the consequences of eutrophication and cannot be considered as a desirable change (Kangur *et al.*, 2002).

Aquatic food chains usually have four links in the pelagic community: 'phytoplankton → zooplankton → planktivorous fish → piscivorous fish'. The ecological efficiencies of energy flow from one trophic level to another is 5–20%, the widely accepted average being 10%. Besides pelagic food chains macrovegetation can be an important primary producer. A considerable amount of energy can also be channelled through benthic food webs in many lakes. In such systems zoobenthos plays the role of herbivores and serves as food source for bottom-feeding fish like bream, roach etc. In lake Peipsi aquatic macrophytes do not play an important role in primary production because strong wave action disturbs their extensive development in such a large lake. Benthic fauna, first of all the invader *Dreissena polymorpha*, is well developed and benthic food webs are important in L. Peipsi (Timm *et al.*, 2001). A direct relationship between zoo- and phytoplankton in the food chain has been considered to prevail in Lake Peipsi (Nõges *et al.*, 1993, 2001), based on the fact that the production of herbivorous zooplankton forms about 10% of phytoplankton production. It means that zooplankton feeds mostly on live algae, and the dominance of large forms in phytoplankton is the result of high grazing pressure on small algae. The role of the 'detritus food chain' and *microbial loop* seems to be rather modest in L. Peipsi. This is confirmed also by the very small biomass of protozoan ciliates that participate in the *microbial loop* compared with the biomass of metazooplankton acting mainly in the *grazing food chain* (Figure 22.15). In Lake Võrtsjärv the effeciency of the grazing food chain is rather low — the production of herbivores is about 40 times lower than the primary production and the majority of algal production is utilized through detrital food chain. Intensive bacterial production and high ciliate biomass reflect the great importance of the *microbial loop* (Figure 22.14, Nõges *et al.*, 2003b). If to compare the ecosystems of these two large shallow lakes, the specific feature for L. Peipsi is the high ratio of herbivorous zooplankton to phytoplankton, and carnivorous to planktivorous fishes, both indicating an effectively functioning food web. In Lake Võrtsjärv the extremely high biomass of protozooplankton and the high ratio of bacterial to phytoplankton production at low bacterial biomass (Figure 22.15) indicate the important role of *mi-*

*crobial loop* in the food web of this lake.

## Acknowledgements

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# Chapter 23

# Eutrophication related web-sites and web-based publications

## 23.1 National web sites

### 23.1.1 USA

www.epa.gov/maia/html/eutroph.html
wow.nrri.umn.edu/wow/under/primer/page17.html
www.coe.uncc.edu/ jdbowen/neem/

**NASA**

http://visibleearth.nasa.gov/Human_Dimensions/Environmental_Impacts/Eutrophication.html

### 23.1.2 Canada

http://www.umanitoba.ca/institutes/fisheries/eutro.html

### 23.1.3 Australia

http://www.rivers.gov.au/research/nemp/index.htm

### 23.1.4 Norway

http://www.grida.no/soeno97/index.htm
http://www.environment.no/templates/themepage____2126.aspx
http://www.niva.no
http://www.jordforsk.no

### 23.1.5 Sweden

**EPA**

http://www.internat.naturvardsverket.se/index.php3?main=/documents/objectiv/objdoc/obj06.html

**MARE**

http://www.mare.su.se/

### 23.1.6 South-Africa

http://www.unilever.com/environmentsociety/environmentalissues/eutrophication/

### 23.1.7 Northern Ireland

http://www.afsni.ac.uk/Research/eutrophication.htm

### 23.1.8 UK

http://www.wfddatabase.com/
http://agrifor.ac.uk/browse/cabi/708855be4efd9ecd828eff9f5a873e0e.html

### 23.1.9 New Zealand

http://www.qeallc.com/html/eutrophication.htm

### 23.1.10 Finland

http://www.environment.fi/default.asp?node=6024&lan=en

## 23.2 Web site of organisations

**HELCOM** http://www.helcom.fi/pollution/eutrophication.html

**EEA** http://reports.eea.eu.int/topic_report_2001_7/en

**Environmental Litteracy Council** http://www.enviroliteracy.org/article.php/410.html

**International water institute** http://www.iwmi.cgiar.org/textonly/index.htm

**BERNET** http://www.bernet.org/wm125051

**OSPAR** http://www.ospar.org/eng/html/organisation/euc.htm

**ESPERE-ENC** http://www.atmosphere.mpg.de/enid/16e.html

**OECD** http://lakes.chebucto.org/TPMODELS/OECD/oecd.html

**ICES** http://www.ices.dk/products/cooperative.asp
http://www.bmu.de/de/800/js/download/ices_report/

**DG ENV-WFD web-pages** http://europa.eu.int/comm/environment/water/water-framework/index_en.html
http://forum.europa.eu.int/Public/irc/env/wfd/home
http://forum.europa.eu.int/Public/irc/env/wfd/library
http://www.cordis.lu/eesd/ka1/home.html

**Harmonised Modelling Tools for Integrated Basin Management (Harmoni-CA)** http://www.harmoni-ca.info

## 23.3 Web sites of places and regions

**Lakes** http://lakes.chebucto.org/eutro.html

**Black Sea** http://lnweb18.worldbank.org/ECA/ECSSD.nsf/0/f52f5c1b9388a2c685256ae8000559bf?OpenDocum

**Wadden Sea** http://www.waddensea-secretariat.org/management/eut/eut.html

## 23.4 Electronic books

**Nutrients and Eutrophication in Danish Marine Waters A Challenge for Science and Management Edited by Ærtebjerg, G., Andersen, J.H. & Hansen, O.S. National Environmental Research Institute** http://www2.dmu.dk/1_viden/2_Publikationer/3_Ovrige/rapporter/ospar.asp

## 23.5 Project web sites

**STAR on standardisation of WFD River assessment systems** http://www.eu-star.at/

**REBECCA Relationships between ecological and chemical status of surface waters** http://www.ymparisto.fi/default.asp?node=11778&lan=EN

**Benchmark models for the water framework directive BMW** http://www.ymparisto.fi/default.asp?contentid=61465&lan=EN

**Euro-limpacs: effects of future global change on Europe's freshwater ecosystems** http://www.eurolimpacs.ucl.ac.uk/

**CHARM** http://www.dmu.dk/1_Viden/2_Miljoe-tilstand/3_vand/4_Charm/charm_main.htm

**BIOHAB** http://wwwold.nioz.nl/projects/biohab/

**EUROHAB** http://wwwold.nioz.nl/projects/biohab/html/eurohab.html

**IOC Harmful algae programme** http://ioc.unesco.org/hab/GEOHAB.htm

**Mantra-east** http://www.mantraeast.org/

**MEAD** http://www.uea.ac.uk/env/mead/

**IMPACTS** http://www.uea.ac.uk/env/mead/impacts.htm

**EUROHARP** www.euroharp.org

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