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Applying Multivariate Analysis to Developing Electrodialytic Remediation of Harbour Sediments from Arctic Locations

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’Life is like a sewer. What you get out of it depends on what you put into it.’

- Tom Lehrer

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Abstract

Electrodialytic remediation (EDR) is a method for removing pollutants from different materials achieved by acidification and transport processes induced by application of an electric field of low intensity. In the thesis, EDR was shown to be a reliable technology for removal of heavy metals, PAH, PCB and TBT from harbour sediments. The final concentrations of heavy metals met the background criteria (non-polluted) as defined by OSPAR, while further optimisation of EDR is necessary for achieving similar levels of PAH, PCB and TBT.

Multivariate analysis was used to evaluate the efficiency of EDR of the harbour sediments, sampled in the Arctic region (Norway and Greenland). One of the most important factors affecting the outcome was the type of sediment, emphasizing the need for developing site- and sediment specific remediation strategies. Some of the more important sediment properties were cation exchange capacity, content of carbonate, content of organic matter, grain size distribution and how the pollutants were bound in the sediment.

The efficiency of EDR, with regards to metal removal, was tested in two cell designs and a stack, the 2-compartment cell being found to be most efficient with regards to faster acidification of the sediment, faster removal of heavy metals and lower energy consumption. The removal of naturally occurring metals was however also highest and if limiting the removal of these is desirable, future EDR designs may rely on both the 2- and 3-compartment cell designs. The stack was found to be the poorest design with low EDR efficiency and was not recommended in future scaling-up efforts.

The experimental variables found to have the highest influence on the efficiency of EDR depended on the pollutant as well as the EDR design. In general, *current density*, *remediation time* and *temperature* had the greatest influence on the removal of heavy metals, while *stirring rate*, *light* and *temperature* were more important for removal of PAH, PCB and TBT. Optimal settings varied depending on the specific pollutant and in some cases opposite settings were optimal for the different pollutants. High temperatures (20 ^{o}C) were for instance found to improve the removal of heavy metals and TBT due to higher desorption of metals, while low temperatures (4 ^{o}C) increased the removal of PAH and PCB, probably due to microbial communities in the sediments not adapted to higher temperatures. This obviously has implications for future optimisation efforts. However, optimal settings for simultaneous removal of heavy metals, PCB and TBT to satisfactory levels were found by a multivariate model and EDR is hence a promising method for future remediation of harbour sediments.

List of abbreviations

BAC	Background Assessment Concentration
CEC	Cation Exchange Capacity
EAC	Environmental Assessment Criteria
EDR	Electrodialytic Remediation
EKR	Electrokinetic Remediation
ERL	Effect Range Low
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
L/S	Liquid-solid
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polyaromatic Hydrocarbons
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyls
PLS	Projections onto Latent Structures
THC	Total Hydrocarbons
TBT	Tributyltin
VIP	Variable Importance in the Projection

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1 Introduction

The Arctic environment has received increased international focus the past decade due to environmental and geopolitical changes in the region. The effects of global warming have been more profound in the Arctic, compared to the World average, due to polar amplification [1], accumulation of persistent pollutants in remote Arctic areas has been reported [2, 3] and the northern areas are continuously becoming more accessible to transport and thereby the economic exploitation of mineral resources. The direct impact of human activities on the Arctic environment has been made apparent by several studies, strongly indicating the accumulation of persistent organic pollutants and heavy metals in the environment and bioaccumulation in the food chain of Arctic mammals [2, 4-6]. The degradation processes of persistent organic pollutants in the Arctic environment are highly affected by the cold climate, snow/ice coverage and the lack of sunlight for parts of the year leading to slower rates of degradation, making the Arctic environment more vulnerable to accumulation. There is an international consensus that countries outside the Arctic region have an impact on the environment through air- and waterborne transport [3]. In the Arctic Footprint and Assessment project, the European Union (EU) has for instance quantified the impact of human activities in the EU countries on the Arctic environment [7] and the EU is in addition developing an Arctic policy with the aim of supporting industrial development opportunities in an environmental sound way [8].

The increasing human activities in the Arctic connected to the ongoing and expected industrial development, especially within the mining and oil and gas industries in Northern Norway, North-West Russia and Greenland, increase the potential local and regional loads on the environment and accentuate the need for continuous improvement in environmental management systems and technologies aimed at minimising the environmental impact. The main aim of the Environmental Waste Management project (EWMA), managed by UiT - The Arctic University of Norway, was to develop a cluster of competence for dealing with waste management in cold and northern regions, with the main focus on the Arctic oil and gas industries in Northern Norway. The project covers aspects related to assessing environmental impacts of industrial activities as well as developing more environmentally sound technologies for industrial waste management in cold regions. The research conducted during the PhD falls under the latter category and specifically focuses on removal of pollutants from harbour sediments with the intention of reducing the amount of hazardous waste.

1.1 Management of polluted sediments

The discharge of pollutants from human activities into environmental media, whether by local, regional or global sources may lead to the polluted media becoming new sources of pollution and may in themselves be considered hazardous when concentrations exceed quality criteria, as defined by national environmental authorities. Harbour sediments are the final recipient for pollutants from activities in the harbour as well as from on-shore activities, whether this be direct discharges (e.g. from sewer outlets), dispersion of pollution originating on land via ground-, surface- and run-off water, or the illegal dumping of waste in the harbour. The pollution in harbours originates from several sources from both past and present activities and hence often has a complex composition of a wide variety of organic and inorganic pollutants, including heavy metals, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and tribytultin (TBT).

To assess, whether pollutant concentrations pose a risk to human health and/or the environment, sediment quality criteria have been developed both on a national and international level. The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) developed guidelines in the 1990s and has identified substances to be prioritised for action (updated 2010), including PAH, PCB, TBT, Cd, Hg and Pb [9]. OSPAR operates with two sets of criteria; one set corresponding to background levels and one set of criteria for threshold values for which adverse effects on the marine environment is expected. The background concentration (BC) criteria are based on concentrations found in pristine areas of the OSPAR maritime area (North-East Atlantic) and background assessment concentrations (BAC) have been introduced as a statistical measure of the background for which there is a 90% probability that the observed mean concentration will be below BAC when the true mean concentration is equivalent to BC [9]. The environmental assessment criteria (EAC) represent concentrations below which no chronic effects are expected to occur in marine species; for some substances the calculated EAC were however below BAC, in these cases the effects range low (ERL) criteria associated with low biological effect, are used. The national sediment criteria guidelines in Arctic countries are based on the same principals as the OSPAR guidelines; there are however minor differences in the criteria concentrations [10-13] due to national factors and assessments of risk being included in the calculations. Denmark operates with two sets of criteria, like OSPAR, while Norway has defined five levels to distinguish between the extent of adverse biological effect upon the marine environment [12, 13].

The need for action to remediate harbour sediments arises either through development of harbours in which contact with, or removal of polluted sediments is inevitable, e.g. when increasing navigational depths, or through governmental intervention to decrease the adverse effects on the marine environment and human health. The Norwegian Parliament, for instance, adopted an action plan for remediation of polluted seabed (St. meld 14.10) in 2006 and amongst other actions, prioritised 17 municipal harbours for remedial action based on previous environmental investigations (2002-2005) [14]. The majority of the prioritised harbours/fjords have since undergone remedial action, although in most of the harbour and fjords there still remain areas in need of remediation [15]. Another important aspect, besides local harbour development plans and environmental goals of the authorities when undertaking remediation of polluted sediments, is the funding, which ultimately determines the nature and extent of such programs.

The choice of remediation technology in a given situation depends on sediment properties, pollutant composition and quantity, and how these are bound in the sediment as well as cost-effectiveness and site-specific conditions. In-situ technologies are for instance often only relevant in areas for which future contact with the sediments is improbable, since they are often based on decreasing the bioavailability of the pollutants by isolation and/or stabilisation [16] rather than removal of the pollutants. Capping, in which the polluted sediments are covered with a non-polluted material [16], is an example of an in-situ method that would not be relevant to use in areas of harbours where increasing navigational depths is anticipated presently or in the future. The ex-situ management of dredged sediments involves either disposal on land or at sea; or treatment. Disposal at sea may in addition include in-situ treatment to decrease availability of pollutants for the marine environment and for dispersion, e.g. by capping the polluted sediments. When treatment is an option, a first step is often physical separation of the dredged sediment to retrieve the finer fractions, in which the majority of the pollution is bound [17, 18]. The subsequent treatment can be roughly divided into physical, biological and/or chemical technologies including thermal degradation/extraction, biological decontamination, chemical oxidation/reduction/separation, electrokinetics, stabilisation/solidification (STSO) and washing [16-19]. Polluted sediments are however most commonly dredged and disposed of [16] due to practical and cost-efficiency considerations. In the Arctic region, STSO has nonetheless been applied, e.g. in Hammerfest in Northern Norway, where in 2008, 5000 m^3 of polluted sediments were stabilised in the foundations of new constructions next to the harbour [20].

Although investigations into treatment of sediment have been fairly extensive, the implementation of these technologies has been limited compared to disposal options. An increase in the focus of developing and implementing treatment technologies is however anticipated in the future due to increasing focus on promoting/developing sustainable solutions, accelerating the concept of moving towards zero-waste societies. Another aspect is minimising the pollution legacy for future generations, e.g. STSO sediments in constructions may present a future hazardous waste issue. Accordingly, a greater emphasis in identifying and developing methods for separating pollutants from sediments will lead to an increase in the possibilities for recycling the sediments as a non-polluted material and in addition provide the option of recycling pollutants (where desirable) or at the least reduce the amount of hazardous waste. Electrodialytic remediation (EDR) is a method that has proven reliable for separating pollutants from different polluted materials and may be expected to contribute in meeting present and future demands for environmental waste management. In addition, the method may be able to cope with some of the challenges faced with in the Arctic region, such as cold climate, periods of limited sunlight and challenging logistics. For these reasons, EDR was chosen as remediation technology to investigate in this PhD project.

1.2 Electrodialytic remediation

EDR is based on the principles of electrokinetic remediation (EKR) in which applying a low intensity direct current increases the availability of pollutants in polluted waste materials [21]. By making use of ion-exchange membranes, the transport of ions between the electrodes and polluted material is controlled and the introduction of ions from the electrolytes, including H^+ and OH^- generated in electrolysis reactions at the inert electrodes, is prevented. This increases the current efficiency for transport of ions originally found in the polluted material, since the current is not used for transporting ions from the electrolytes through the polluted material [22]. EDR has been extensively used for removing heavy metals from different polluted materials such as soil [23], wood waste[24], sewage [25], harbour sediments [26], fly ash [27] and mine tailings [28].

The removal of heavy metals relies on desorption processes to increase the mobility and transport of the metals as ions or charged species. In materials with a high buffer capacity, e.g. in calcareous soils, this is done by adding desorption agents, for instance ammonia [29] and in materials of low buffer capacity, the mobilisation is ensured by the acidification processes in the polluted material, induced by the electric field. Acidification is achieved mainly due to water splitting at the anion exchange membrane placed next to the anode, the generated hydroxyl ions being transported across the membrane to the electrolyte and the protons transported through the polluted material towards the cathode [30]. Proton leakage at the cation exchange membrane, when the electrolyte is maintained at low pH, may also contribute to the acidification [26]. Once desorbed as ions or charged complexes, the heavy metals are transported by electromigration towards the electrode of opposite charge; the anions towards the anode and the cations towards the cathode. The placement of an anion exchange membrane at the anode and a cation exchange membrane next to the cathode, allows the transport of the mobilised heavy metals out of the polluted material.

EDR has to a lesser extent been used to remove organic pollutants and the few reported studies have relied on combining EDR with other remediation technologies such as chemical oxidation/reduction or bioremediation to achieve sufficient removal efficiencies [31]. The removal of organic pollutants via electroosmosis (transport of fluid induced by the electric field) can be increased by adding pollutant-specific surfactants. An increase in the degradation of organic pollutants relies on applying the electric field for enhancing the availability of pollutants as well as the availability of degradation agents, such as microorganisms, nutrients and/or chemical compounds [32].

EDR has been used to remove Cd, Cu, Pb and Zn from harbour sediments and removal efficiencies of more than 90% have been reported, in some cases the final concentrations were below the BAC levels in the OSPAR sediment quality guidelines [26, 33-36]. EDR has not been used for removing PAH, PCB or TBT from harbour sediments. Results from single studies of removal of PAH and PCB from soil, in combination with other remediation technologies were promising with removal efficiencies above 70% [37, 38].

1.3 Multivariate analysis

EDR has been extensively studied as a remediation method; multivariate analysis has however yet to be used for identifying variable importance and optimal conditions. When applying the one variable at a time (OVAT) strategy, important information on the underlying processes in the EDR method may be retrieved, estimating optima may however deviate from the true value(s) if the studied variables are correlated. The *liquid-to-solid (L/S) ratio* and *current density* have for instance previously been found to be correlated in EDR [39, 40]. Identifying true optima by employing an OVAT approach may in such situations entail conducting numerous experiments and in addition does not take into account other variables that may be correlated in the remediation, such as *time* or *temperature*. Multivariate analysis provides tools for reducing the number of experiments without losing significant information with regards to optima and variable importance within the same studied experimental domain [41]. This is done by conducting experiments in such a way that optimum settings for independent as well as correlated variables are found.

Multivariate analysis provides tools for analysing large sets of data, which is done by reducing the dimensions making it easier to visualise and retrieve trends. Two such tools are principal component analysis (PCA) and projections onto latent structures (PLS) that have been extensively used for development and optimisation in organic synthesis as important data analysis tools and based on this, were broadly employed for data treatment throughout the PhD project. In PCA, differences and similarities in the variation of data are identified by calculating principal components, which are mutually orthogonal vectors that represent independent and uncorrelated variation of the initial descriptors; accordingly correlated descriptors are described by the same principal component. Amongst its many applications, PCA has been used to retrieve information on pollutant distribution in sediment, which can be used to trace sources of pollution by comparing the variation to that in potential pollutant sources [42].

In PLS the quantitative relation between a descriptor matrix, X, and a response matrix, Y, is calculated. For EDR a quantitative relation between experimental variables and removal efficiencies can be calculated and the model may subsequently be used for predicting removal efficiencies by entering new settings for the experimental variables. Information about how variables in the two matrices are related can also be taken from the model and consequently the comparative influence of variables can be evaluated. PLS has been extensively used in organic synthesis [41], but sparingly used in environmental studies; a few examples include identifying natural and anthropogenic sources in ground water [43] and identifying measures for minimising generation of toxic compounds in the incineration of municipal waste [44]. Although PLS has had limited use in remediation studies, it may potentially be a valuable tool for developing site-specific remediation strategies for e.g. harbour sediments taking into account inhomogeneous composition of the sediment, pollutant distribution, remediation objectives and operational limits.

1.4 Objectives and structure of the thesis

The vision of the PhD project was to contribute in strengthening the development of environmental technologies for managing hazardous waste, specifically aimed at the Arctic Region. Electrodialytic remediation provides a method for separating pollutants from contaminated materials thus decreasing the amount of hazardous waste as well as increasing the potential for recycling of the treated non-polluted material and in some cases also the hazardous compounds. It is important to note that the scope of this PhD remained within the EDR technology and did not relate the method to other relevant remediation technologies at the three investigated sites, but rather focused on providing larger portfolio of methods to choose from for future stakeholders and decision makers.

The overall objective of the PhD was to contribute to the further development of EDR, and specifically in developing the method for simultaneous removal of several pollutants from harbour sediments and providing basis for future scaling-up of EDR. An important element of this was to evaluate the potential and the applicability of multivariate analysis in doing so. The research was based on sediments/soil sampled at three sites located in cold regions of Greenland, Norway and NW Russia. Sub-objectives of the work included assessing the influence of variables, including sediment properties on EDR, identifying site-specific remediation strategies by determining optimal conditions within the studied domains, evaluating conditions for future scaling-up and assessing to which degree EDR is adaptable to cold regions.

The approach adopted to answer the objectives is illustrated in Figure 1 and included employing multivariate analysis to assess similarities/differences in sediment characteristics and how pollutants are related to these, determining important parameters in different experimental domains and identifying sediment-specific optimal conditions for the remediation. In addition the relation between these different themes was evaluated; i.e. the influence of sediment characteristics on the efficiency of EDR (experimental domains as well as optimal settings), and the influence of EDR on the sediment.

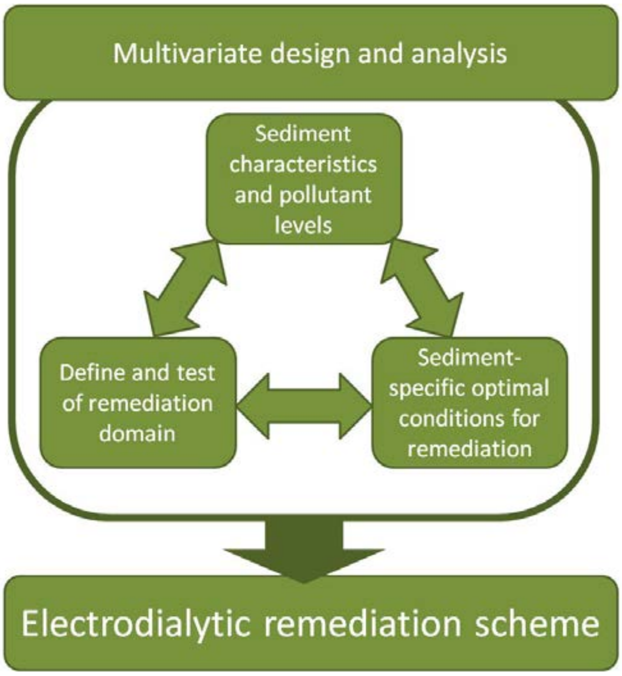


Figure 1: Applied approach to the PhD research.

Structure of thesis

Brief chapters on EDR in relation to soil/sediment remediation design and multivariate analysis as a tool for environmental studies has been included in the thesis (chapter 2.1-2.2). The two chapters are not intended as reviews or in depth analysis, but rather to provide background in relation to topics discussed in the thesis. The methods and materials applied for the research are described in chapters 3.1-3.5.

The results and discussion section (chapter 4.1-4.4) presents the topics investigated in the nine scientific papers produced during the PhD project, in accordance with the overall approach as illustrated in Figure 1. Comparison of sediment properties and how these are related to pollution at the three sites are given in chapter 4.1. In the following chapter 4.2, the experimental domains are identified and assessment of variable importance made. Variables include *EDR cell design*, *current density*, *remediation time*, *liquid-solid* (*L/S) ratio*, *stirring rate*, *temperature*, *suspension liquid* and *light/no light*. Sediment-specific optimal conditions, including energy consumption considerations are presented for selected sediments in chapter 4.3. The arrows of Figure 1, i.e. the relations between sediment properties and developments in EDR are evaluated in chapter 4.4.The final chapter (5) summarises the implications of the findings in relation to present and future development of EDR.

2 Background

2.1 Electrodialytic remediation

Electrodialytic remediation (EDR) was originally developed at the Technical University of Denmark in the early 1990s and was patented in 1995 (PCT/DK95/00209) and is based on the principles of electrokinetic remediation (EKR) in which an electric field of low intensity is applied to a polluted material, which initiates separation processes. EDR and EKR were initially developed for the removal of heavy metals from soil and have the past 20 years been further expanded to include other polluted materials and pollutants.

2.1.1 Principles of electrokinetic remediation (EKR) in brief

The transport processes in porous media under the influence of an electric field include electromigration, electroosmosis, electrophoresis and diffusion [21, 45-48].

Electromigration

Transport of ions and ionic complexes in the pore/suspension liquid

The ions and ionic complexes move towards the electrode of opposite charge, i.e. anions move towards the anode and cations move towards the cathode.

The electromigrational flux depends on the ionic mobility, tortuosity factor, porosity of the media, and charge of the ion, and is the most important transport mechanism for ions in porous media.

Electrophoresis

Transport of charged particles such as colloids, clay particles, organic particles and droplets

Electrophoresis is generally of limited importance in compacted soil systems, but can be significant if micelles are generated, e.g. for biocolloids or slurries, in which negatively charged clay particles for instance may be transported towards the anode.

Electroosmosis

Transport of water in a porous media

In soil, there is a diffuse double layer of cations around the negatively charged clay particles. When applying an electric field, cations from the diffuse layer are transported towards the cathode, creating a net transport of ions in the same direction resulting in a simultaneous transport of fluid towards the cathode due to the potential difference exerted by the mobilisation of ions. Electroosmosis is mainly dependent on the porosity and zeta potential of the soil and is dominant in fine-grained soils compared to hydraulic flow (dependent on pore size distribution and macropores). In general, electromigration has been found to be a magnitude of order higher than flux caused by electroosmosis. The effect of electroosmosis decreases with decreasing pH and zeta potential and may be reversed.

Water electrolysis reactions at the inert electrodes occur upon the application of the electric field, involving reduction at the cathode and oxidation at the anode:

Cathode: $4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-$ (1)

Anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ (2)

In uncontrolled EKR, the electrolysis reactions result in the formation of an acidic front at the anode and an alkaline front at the cathode. In the zone between the acidic and alkaline fronts, water is generated, the pH changes from acidic to alkaline, resulting in precipitation of species, e.g. cations from the acidic front. Since electromigration dominates the transport process of ions and the effective ionic mobility of the proton is nearly twice as high as for the hydroxyl ion, the acidic front dominates the system. Acidic conditions cause the heavy metals adsorbed to particles in the soil to desorb and be transported, mainly by electromigration, towards the cathode. The rate of acidification in the soil depends on the physical and chemical properties of the soil (given the same experimental settings). A high buffering capacity will for instance retard the acidification, as may high contents of organic species and salts [21, 47, 48].

Secondary reactions at the electrodes include precipitation of metals at the cathode (3) and generation of chloride gas (4). The latter is relevant for harbour sediments with naturally high concentrations of chloride.

Cathode: $M^{n+} + ne^- \rightarrow M^0$ (3)

Anode: $2Cl^- \rightarrow 2Cl_2(g) + 2e^- (s)$ (4)

2.1.2 EDR

In EDR, ion-exchange membranes are installed between the electrodes and the polluted soil to control the transport of ions over the membranes. Between the anode and the polluted soil/sediment an anion-exchange membrane is applied allowing the transport of anions and preventing the transport of cations across the membrane. A cation exchange membrane separates the polluted soil from the cathode allowing the transport of cations and preventing the transport of anions across the membrane. This prevents transport of ions from the electrolytes through the polluted soil; if for instance $NaNO_3$ is used as electrolyte, the ion exchange membranes hinder the transport of Na^+ and NO_3^- through the soil thus making the applied current relatively more efficient for the removal of heavy metals from the soil compared to unenhanced electrokinetic treatment [36, 49]. In addition the application of ion exchange membranes avoids formation of acidic and alkaline fronts by H^+ and OH^- generated in the electrolysis reactions at the electrodes.

Heavy metals must be available as ions in solution in order to ensure removal by electromigration, accordingly acidification of the soil is imperative for attaining optimal desorption conditions. In EDR this is mainly achieved by water splitting at the anion exchange membrane [30]; the produced hydroxyl ions are transported across the anolyte while the protons advance towards the cathode (Figure 2). Several studies have revealed that proton leakage from the catholyte, in cases where this is maintained at a low pH, may also contribute to the acidification process [26, 34, 36, 50-52]. Water splitting at ion-exchange membranes occurs at a limiting current at which there are not enough ions in the immediate vicinity of the membranes to carry the current. In soils, there is an abundance of cations compared to anions due to the negative charge of clay; consequently depletion of anions adjacent to the anion exchange membrane will occur at a lower current than depletion of cations in the vicinity of the cation exchange membrane [30]. The formation of an alkaline front caused by water splitting at the cation exchange membrane is undesirable. Optimal removal of heavy metals is hence achieved at current levels that lie between the limiting currents of the anion and cation exchange membranes. Reported values of limiting current densities of cation exchange membranes for soils lie in the range 0.3-0.75 mA/cm^2 [30, 53].

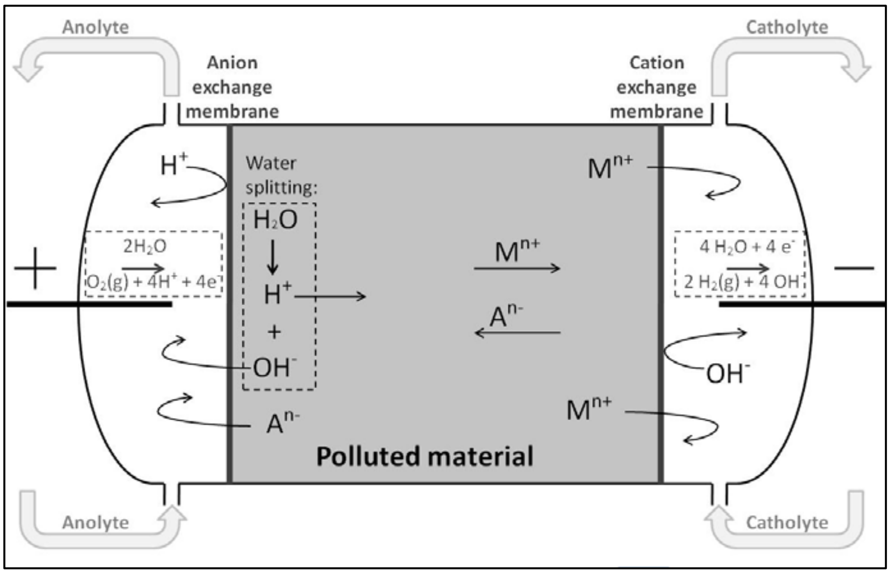


Figure 2: Principles of electrodialytic remediation in a 3-compartment cell design.

When applying inert electrodes, the pH in the catholyte will increase due to the electrolysis reaction [50]. To prevent fouling of the cation exchange membrane, maintaining an acidic pH in the catholyte is necessary, which is most commonly done on a daily basis by manually adding nitric acid to the catholyte [54]. Electrolytes are circulated between two external containers (most often glass bottles) of the anolyte and catholyte and the respective anolyte and catholyte compartment of the electrodialytic cell. The circulation of the electrolytes allows for the removal of gasses generated at the electrodes, amongst these O_2, H_2, Cl_2 [49] and in addition ensures low polarisation at the electrodes [40] and minimises concentration gradients.

The desorption and removal of metals during EDR has been suggested to occur in four consecutive steps [55] and has been confirmed by observations in several studies [26, 56]. During the lag phase, the pH decreases to the threshold value at which desorption of the given metal is initiated and there is limited removal (desorption). Subsequently a fast removal phase, in which the acidification ensures dissolution/desorption of the given metal in the available fraction of the sediment, takes place. This is followed by a slow removal phase in which continuous dissolution/desorption of metals from the less available fractions of the soil occurs and may include dissolution of stable soil minerals. A stationary phase is achieved when removal of the given metal ends. The initiation, duration and removal rates of each phase depend on the given metal and the geochemical properties of the sediment, including metal partitioning [57, 58]. The final concentrations of metals achieved during EDR have been reported as lower than those attained in pure acid desorption experiments of equivalent final pH values [26, 36, 59]. This has been partly attributed to the continuous shifting of chemical equilibrium in the soil during EDR compared to the stationary chemical equilibrium obtained in the acid desorption experiments [26].

EDR was originally developed for removal of heavy metals from soil [23] and has in the past 15 years been further developed to remove heavy metals from other polluted materials such as wood [24], mine tailings [60], harbour sediments [26], fly-ash [27] and sewage sludge [25]. It has recently also been used for recovering phosphorous from fly-ash [61] and sewage sludge ash [62]. The main focus of the EDR studies has been removal of heavy metals and applying EDR to the removal of organic pollutants has been limited to a few studies [37, 38], while development of EKR in this field has been more comprehensive. The transport of hydrophobic contaminants under the influence of an electric field is dominated by electroosmosis [32, 63, 64], and it has been acknowledged that to achieve sufficient clean-up levels, EDR/EKR should be combined with enhancement efforts such as addition of surfactants for increasing the mobility of hydrophobic contaminants and/or other remediation technologies, e.g. bioremediation or chemical oxidation/reduction [31, 32, 65, 66].

2.1.3 Enhancement of EDR

Optimisation efforts carried out for EDR of soil/sediments are related to increasing availability of contaminants and reducing the transport time through the polluted soil/sediment and have included addition of desorbing agents, changes to the design (set-up) and experimental settings depending on the soil/sediment properties.

Desorbing agents

To enhance the removal of heavy metals from soil/sediments, desorbing agents have been used for increasing the availability for electromigration under acidic or alkaline conditions, depending on the initial buffer capacity of the soil/sediment. HCl, NaCl, lactic acid, citric acid and ammonium citrate did not significantly improve the removal of Cd, Cu, Pb and Zn from harbour sediments [51]. The same was the case for organic acids as desorbing agents for the removal of Pb from soil; nitric acid was found however to be more effective as a desorbing agent [67]. Addition of ammonium citrate to a calcareous soil made it possible to remove Cr and Cu under alkaline conditions [68]. Ammonia has also been found to be an effective desorbing agent for the removal of As and Cu from calcareous soils without dissolving carbonates [29, 53]. The previous studies have revealed that addition of desorbing agent(s) is not always necessary for improving removal efficiencies or meeting remediation objectives. However when assessed necessary, the choice of desorbing agent should be based on the targeted metal(s) for remediation, metal partitioning as well as the soil and sediment properties.

The availability of organic pollutants during EDR can be increased by adding surfactants, since these increase desorption of hydrophobic pollutants and transfer them into aqueous micelles by solubilisation [38]. Tween 80 is an example of a surfactant that efficiently removed PAH from soil [37]; it was however not sufficient in increasing PCB removal from a soil and saponin proved to be a better solution [38]. The choice of surfactant during EDR hence depends on the targeted pollutant for remediation.

Design of EDR units

Optimisation efforts with regards to EDR unit designs have included test of different cell designs, applying pulsed current and/or applying a stirred rather than a stationary set-up.

EDR has been developed based on cells consisting of 2-5 compartments. The original cell design consisted of 3 compartments; a centre compartment containing the polluted media and two end compartments in which electrodes are placed and electrolytes are circulated (Figure 2). 1-2 compartments may be applied between the electrode compartments and the polluted material compartment. Ion-exchange membranes between the different compartments control the transport of ions in the cell. In a 5-compartment cell with 2 compartments on either side of the polluted material, the cell can be designed to avoid transport of cations to the cathode and anions to the anode compartments, hence preventing precipitation of metals on the electrodes and generation of chlorine gas at the anode [26]. Recently, a 2-compartment cell was designed in which the anode was placed directly in the polluted material and a cation exchange membrane separated the polluted material and cathode compartment. Few studies have been conducted for the direct comparisons of the different cell designs. In a study of harbour sediments, higher removal efficiencies of Cu and Pb were observed in the 5-compartment cell compared to the 3-compartment cell, while there was not a significant difference for Cd and Zn. The 3-compartment cell appeared to be more vulnerable to pH in the electrolytes in regards to proton leakage than in the 5-compartment cell [26]. In the 2-compartment cell, acidification was caused by the direct supply of protons due to the electrolysis reaction at the anode and was faster than in the 3-compartment cell [69]. In addition, higher conductivity, lower final pH and lower resistance in the 2-compartment cell were observed [69].

Applying a pulsed current was shown to increase removal of Cu from mine tailings [70] and As, Cd and Cu from soil [71] and was in addition shown to reduce the energy consumption in EDR [56, 71-73] due to reducing the resistance in pore fluid and across the cation exchange membrane, which was attributed to re-distribution of ions, decreasing the concentration gradients [71, 72]. The effect of pulsed current on removal efficiencies and energy consumption was revealed to be significant at high current densities; the effect was not visable at lower current densities [72].

The stirred set-up was originally introduced for treatment of a fly-ash suspension and has since been used for soil [39], harbour sediments [33], sewage sludge [25] and mine tailings [74], and has been shown to significantly increase removal efficiencies of heavy metals and PAH compared to a stationary set-up [37, 75]. Applying a stirred set-up is relevant for the development of ex-situ EDR treatment, decreasing the duration of remediation compared to in-situ EDR and hence appears to be a feasible solution when dealing with dredged sediments. In most cases, stirring has been achieved by mechanical stirring; fluidisation by air has however also been introduced for mixing of mine tailing suspensions [74]. Stirring has been revealed to increase oxidation of soil/sediment and may therefore result in a higher release of heavy metals bound in the oxidisable fractions [34, 35]. Faster acidification due to higher dissolution of carbonates in equivalent masses of soil has also been observed [75] and may be attributed to increased mobility/efficiency of H^+ [56] and immediate mixing of protons from interdiffusion at the cation exchange membrane [75]. Due to the lower ionic concentration of suspension liquid compared to pore-liquid in a stationary set-up, the limiting current densities may occur at lower values [75]. Reported limiting current densities for cation exchange membrane are slightly higher for the stationary set-up [30, 39, 53, 54, 76], limiting current densities however appear to be relatively more dependent on soil properties and *L/S ratio* than stirring/non-stirring. In addition to increasing heavy metal removal, the mixing of soil/sediment suspensions may increase the availability of hydrophobic pollutants for chemical/biological degradation. Chemical decomposition of PCB, for instance, increases at low pH (<5), while bioremediation may be inhibited at low pH levels [38, 63]. Optimisation of EDR with the intention of simultaneous removal of several pollutants may therefore involve several steps with different experimental settings.

Experimental settings

Variables that significantly influence the removal of heavy metals during EDR are *time* and *current density* [26, 33, 39]. In general, higher current densities and longer time increases the efficiency of EDR. Due to the depletion of ions in the suspension liquid and water splitting at the cation exchange membrane at higher current densities, there is a limit to increasing the efficiency by adjusting the current density [39, 77]. In addition, the current efficiency with regards to the transport of heavy metals through the EDR cell decreases with time [26], which may partly be related to the different rates of metal desorption in the EDR phases and the increasing amount of protons carried by the current with decreasing pH. Applying a current density as opposed to not applying one, also increases the removal of PAH and PCB during EDR/EKR, which has been attributed to increased proton concentration and increased availability of pollutants, microorganisms and nutrients for chemical/biological degradation [31, 32, 38, 65, 66].

Other variables that have shown to affect the efficiency of EDR are *L/S ratio* and *stirring rate* [26, 33, 34, 39]. The relative importance however depends on the given pollutant and how it is bound in the soil/sediment. Higher stirring rates were for instance revealed to increase the removal of Cu and Pb while not affecting removal of Cd and Zn from harbour sediment [34]. This was attributed to the increasing oxidation of the sediment with higher *stirring rate*, releasing the relatively higher amounts of Cu and Pb bound in the less available oxidisable fraction of the sediment. In turn the *L/S ratio* was revealed to slightly influence the removal of Cu, Pb and Zn, while not significantly affecting the removal of Cd [26, 33].

Soil/sediment properties

Characteristics of soil/sediment that have proven to influence the efficiency of EDR include morphology, geochemical properties as well as the presence of foreign objects e.g. from construction waste.

It has been well established that EDR/EKR is more efficient in the finer soil fractions [45]. Higher resistance across the cell for sandy soils with low content of clay and organic matter have been observed [78]. Removal efficiencies of As and Cr were revealed to be higher when remediating the finer fractions (<63 µm) compared to the original soil and in addition lower resistance and energy consumption were observed for the soil fines [40].

A high content of carbonate increases the buffer capacity and prolongs the acidification process, increasing the remediation time for removing heavy metals in unenhanced EDR [21, 47, 48, 50, 58, 59, 79]. Depending on how metals are bound in the sediment, heavy metals may desorb at higher pH in calcareous than in low calcareous soils, when they are bound in carbonate compounds [50, 59]. Organic matter may contribute to the buffer capacity and retard acidification [21, 47, 48]. The influence of organic matter depends on how the pollutants are bound in the sediment; Cu in a specific sediment was for instance found to be harder to remove than other heavy metals, which was attributed to the relatively higher amount of Cu bound to the organic matter [33]. Another study suggested that removal of heavy metals bound in the organic fraction may be prevented at low pH since organic matter is insoluble at acidic conditions and in addition heavy metals desorbed during acidification may readsorb onto the organic matter amplifying the effect [58].

The presence of foreign objects may decrease the efficiency of EDR. Construction waste in a soil (concrete, brick, stone, screw) was for instance revealed to affect acidification and decrease the removal of Cu [80].

2.1.4 Scaling-up of EDR

Most EDR studies have been conducted in laboratory scale using the 2-5 compartment cell designs as described above. Some attempts at scaling-up EDR have however been made and are based on the 3-compartment cell design. A 3 m^3 pilot plant was for instance designed to treat 100-470 kg of wood waste and consisted of several units containing 0.3 m^3 centre compartments in which the polluted wood waste was placed, and collection compartments in which electrolyte was circulated. Ion-exchange membranes separated the centre and collection compartments and electrodes were inserted in different parts of the plant, the most efficient distance between the electrodes being 60 cm. Remediation times were up to 21 days and high removal efficiencies of As, Cr and Cu were observed [81]. The same design was used for removing Cd from 40 L fly ash suspension applying one unit in the pilot plant. Stirring of the fly ash suspension was done manually [82].

An EDR stack design for bench-scale experiments with a capacity of up to 5 L suspension has been developed for reducing leachability of heavy metals from fly-ash [83]. The stack design is based on the principles of the 3-compartment cell and consists of alternating feed- and concentrate compartments, in which respectively polluted material in suspension and liquid concentrate is continuously circulated ensuring continuous stirring and treatment. The capacity of each feed chamber is approximately 0.3 L. Ion-exchange membranes separate the feed and concentrate compartments and electrodes are placed in the ends of the stack. Acidification in the suspension is ensured by water splitting at the anion exchange membrane as well as proton leakage from the cation exchange membranes, since low pH levels are maintained in the liquid concentrate. The stack was scaled-up to a pilot plant capable of treating 100 L fly-ash suspension, consisting of 50 alternating feed and concentrate compartments [84]. Results from the pilot plant are promising, although optimisation efforts to meet leaching requirements remain to be done [84].

2.1.5 Removal efficiencies for different pollutants

Reported removal efficiencies of different pollutants in soil or harbour sediments, listed in Table 1, show a high potential for using EDR in remediation of both inorganic and organic pollutants. Few studies however exist for organic pollutants.

Although EKR of organic pollutants has been extensively investigated, most of the studies were conducted on spiked soil and the reported high removal efficiencies have not been replicated on aged polluted soils/sediments. In combination with other remediation technologies, removal efficiencies have however vastly improved. Removal efficiencies of up to 60% for TPH have for instance been reported by combining EKR with bioremediation [85]. The use of surfactants has increased removal efficiencies of PAH, albeit still below 30% [66, 86-88]. Lima *et al.* showed that PAH removal efficiency of 79% could be achieved when adding surfactants and applying a stirred EDR set-up [37]. By combining EDR with nanoparticles and maintaining a low pH, removal efficiencies of PCB of up to 80% were achieved [89].

Whilst EDR/EKR has not been applied for removing TBT, other electrochemical methods have been tested. By applying an electric field of high intensity, for instance, removal of up to 83% TBT was observed. The high removal efficiencies were attributed to chemical degradation due to the radicals produced at the electrodes. Removal of heavy metals did however not occur during the treatment [90].

Table 1: EDR of different pollutants – removal percentages

Pollutant	Soil/sediment	Stirred/ non-stirred	Enhancement	Removal (%)	Reference
As	Soil	Non-stirred	Ammonia	30-70	[29]
	Soil	Stirred	n.e	57-67	[52]
	Soil	Stirred	Soil fines	64-79	[40, 59]
Cd	Harbour sediment	Stirred	n.e	93-98	[34, 36]
	Soil	Stirred	Soil fines	92	[59]
Cr	Soil	Non-stirred	n.e	64	[22]
	Soil	Stirred	n.e	2-28	[52, 54]
	Soil	Stirred	Soil fines	55	[59]
Cu	Soil	Non-stirred	n.e	85-86	[22, 23]
	Soil	Stirred	Soil fines	96	[40]
	Soil	Stirred	n.e	67-96	[52, 54]
	Harbour sediment	Stirred	n.e	44-86	[34-36]
Hg	Soil	Non-stirred	n.e	23	[22]
Ni	Soil	Stirred	Soil fines	52	[59]
Pb	Soil	Stirred	n.e	21-96	[39, 54, 59]
	Harbour sediment	Stirred	n.e	62-88	[34, 35]
Zn	Harbour sediment	Stirred	n.e	74-90	[34, 35]
	Soil	Stirred	Soil fines	88	[59]
PAH	Soil	Stirred	Surfactants	79	[37]
PCB	Soil	Stirred	Surfactants, nano-particles	8-76	[38]

n.e. – no enhancement

2.1.6 Effect on sediment

During EDR, the mass of soil/sediment has been observed to decrease, which has mainly been attributed to dissolution of carbonate [35, 56, 59], oxidation of organic matter [35, 59, 91] and to a lesser degree dissolution of other minerals in the soil/sediment [59]. EDR has been shown to accelerate weathering of soil, making metals in all soil fractions more available [92] and removal from both the available and less available fractions of harbour sediment has been observed [35]. In alkaline zone(s) of the soil, heavy metals previously desorbed during acidification may precipitate and be bound in the residual fraction [79].

Applying an electric field to soil has been shown to influence fungal communities negatively at voltage gradient 2V/cm, whereas a limited effect and even an increase in fungal community diversity were observed at 1V/cm [87]. The assessment of applying an electric field on microbial communities has mainly been conducted on the contaminant degrading bacteria, a generally limited affect being detected [32, 63, 64, 85, 87, 93-96], and the electric field may even stimulate microbial activity [96]. Negative impacts on microorganisms during EKR have however been observed and since these occurred adjacent to electrodes, this was attributed to changes in pH rather than the influence of the direct current [97]. This hypothesis was supported by observations of electrodes inhibiting microbial communities if not physically shielded, e.g. by semi permeable membranes [94]. Chlorine and hydrogen peroxide can be generated in secondary electrode reactions and may also inhibit microbial communities adjacent to the electrodes [32].

2.1.7 Design of remediation

EDR has been based on more than 20 years of research and development and is potentially a cost-efficient method. Determining the optimal conditions for remediation in a given situation depends on the polluted material, the pollutants and site-specific conditions. Accordingly, the design of EDR of sediment may vary from time to time; based on previous findings it is however possible to follow a stepwise approach for developing sediment and site-specific remediation.

Approach for sediment- and site-specific remediation

Step 1: Characterisation of the polluted sediment

Step 2: Determining domain of remediation, including enhancement methods

Step 3: Determining best conditions for the site- and sediment-specific remediation

Step 4: Scaling-up of remediation

Step 5: Full scale remediation

It has been made clear that the design of EDR depends on the material at hand and for this reason the first step includes characterisation of the sediment both with regards to geochemical properties and pollutant levels. For soil/sediment, some of the most important parameters to determine are content of carbonate, organic matter and grain size distribution. In addition, it may include assessing the presence of waste (fragments of plastic, timber, concrete, steel, etc.) and possibilities of removing these fragments prior to treatment. In this step it is also important to determine which pollutants are targeted for the remediation and evaluate how these are bound in the soil/sediment.

A good mapping of characteristics in step 1 will give a good foundation for determining the domain of remediation in step 2, which also includes the site-specific conditions for remediation (e.g. in-situ or ex-situ treatment possibilities) and the intended use of sediment after treatment; combined these will determine the desired clean-up levels. The domain of remediation includes relevant experimental variables and use of enhancement methods, e.g. desorbing agents, EDR cell design(s), applying stirred set-up and combination with other remediation technologies.

Based on the chosen domain of remediation, lab- or pilot scale experiments are conducted to determine the optimal conditions for the sediment in step 3. EDR of specific sediment is vulnerable to determining the right combination of variables and settings [39]. Determining the optimal site- and sediment-specific remediation conditions may also include energy-consumption and implementation/operation costs.

The fourth step is scaling-up of the remediation design and the extent will depend on the level of previous practical experience from larger scale experiments of similar domains. The final step is conducting the full scale remediation. These two steps are not touched upon in this thesis, the main focus being on the first three steps, as was illustrated in Figure 1.

2.2 Multivariate design and analysis

Multivariate design and analysis are statistical tools to extract information from large sets of data and has been extensively used in industrial processes to optimise production by for instance eliminating undesired by-products and/or determining optimal settings. Although it has also been found to be useful for tracing pollutant sources, it remains to be applied for optimising remediation technologies. In chemometrics, the multivariate methods used do not assume variables to be independent as in other statistical analysis methods, but actively accept and work with colinearity between variables, thus making them relevant for EDR investigations where experimental variables have been shown to be correlated, e.g. *current density* and *L/S ratio* [26, 33]. This chapter introduces the multivariate methods used in the PhD project, all of them included in the chemometric toolbox.

2.2.1 Experimental design strategy

The selection of experimental design depends on the initial objectives of the experimental work. If the ultimate objective is optimising a process, an understanding of significant variables, possible correlations between variables and preliminary assessments of the space within which optimisation should take place, is imperative. In order to achieve this information, a three-step approach inspired by [41, 98] can be employed:

Step 1: *Determining the experimental domain to be investigated based on prior knowledge*

Step 2: *Screening experiments to identify significant variables*

Step 3: *Optimising the process by determining optimum settings of all variables*

Experimental domain: The experimental variables and ranges in their settings. When more than 2 variables are investigated, the experimental domain covers a multidimensional space.

The first step is to determine the experimental domain to operate within. For EDR of harbour sediments, previous studies have provided a basis of variables important for the process and the approximate maximum settings at which removal of pollutants occurs. Accordingly adequate information is available to determine appropriate experimental domains, including introduction of new discrete variables such as *light/no light*. This preliminary assessment should also include limitations based on practical and economic considerations; in an Arctic location it would for instance obviously not be possible to conduct EDR in a warm climate.

Screening experiments in the second step identifies significant variables in the studied experimental domain. Since variables have been found to be correlated in EDR, it is crucial that the experimental domain employed takes into account both independent and correlated variables.

For optimisation in step 3, variables that were found to be insignificant for the process in step 2 are kept at fixed values and which discrete variables to include is selected [41], e.g. which EDR cell design to proceed with. If optimisation of more than one EDR cell design is desirable, it is necessary to optimise for each one separately [99]. The starting point of optimisation should be based on preliminary assessment of the best settings observed in the second step. Depending on the findings, it may be necessary to repeat the steps described above, e.g. if a new variable is introduced in the experimental domain. By applying systematic designs, as done in multivariate methods, a minimum of additional experiments may however be required for obtaining the essential information on the new variable(s).

In the field of soil/sediment remediation, the objective is to obtain concentrations below site-specific limits and it may not be necessary to find the optimum conditions, which is more important in for instance organic synthesis, where optimal yields are desirable. Depending on objectives of remediation, the best settings found in step 2 with possible adjustments to the experimental domain may be sufficient. In the PhD project, step 1 and 2 have been employed and this chapter hence includes descriptions of multivariate tools for experimental design and analysis of results. For information on achieving optimum settings by multivariate approaches, please refer to e.g. [41].

2.2.2 Experimental design

The objective of step 2 is to determine the influence of the experimental variables and the possible interaction effects between them, which can be achieved by employing a factorial design.

Factorial design

Factorial designs are constructed so that variation in responses can be traced to variation in the experimental variables (factors), making it possible to independently determine both the effects of each factor and interaction effects between the factors [41, 100]. This is achieved by simultaneously varying the factors and investigating all possible combinations of the levels of factors. A two-level factorial design with k-factors hence contains 2^k experiments, as illustrated for a design containing three factors in Figure 3. Each factor is investigated at fixed levels – in a two-level factorial design each factor has two levels [41, 100]. Continuous variables have a low and a high value, which is determined by the experimental domain, and discrete variables have two alternatives (e.g. either *light* or *no light*). Discrete variables can be included in model calculations by arbitrarily assigning the values -1 and 1.

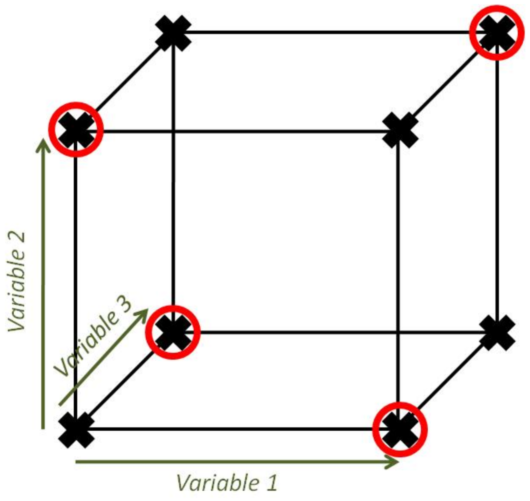


Figure 3: 3-dimensional experimental domain. Two-level factorial design experiments cover all possible combinations of the experimental settings and are located in every corner of the domain (X). The experiments in a fractional factorial design (O) are located as far from each other as possible to cover a large part of the experimental domain.

Factorial designs of 5-7 factors would entail conducting 32-128 experiments, which will often be impractical for an initial screening process. For chemical systems in a limited experimental domain it may be assumed that interaction effects between three or more variables are insignificant compared to main effects and two-variable interaction effects [41], in consequence the number of experiments can be reduced. This is done by constructing designs that are fractions of factorial designs in such a way that it is possible to estimate the desired effects.

Fractional Factorial Design

A fractional factorial design is constructed as a fraction of a complete factorial design and includes experiments which are as widely distributed as possible to cover a maximum variation over the experimental domain [41]. This is illustrated in Figure 3 in which the fractional factorial design is a half fraction of a 2^3 complete factorial design resulting in a 2^{3-1} design. The information on each variable obtained from a fractional factorial design is hence less than from a complete factorial design. This is due to estimates of effects in fractional factorial designs being sums of the true effects. It is however possible to construct the fractional designs in such a way that main effects and two-variable interaction effects are confounded with higher order interaction effects and since these are assumed to be negligible, the fractional designs can be used to obtain good estimates of the true main effects and the true two-variable interaction effects [41].

Generators are introduced as tools for analysing the confounding patterns in fractional factorial designs and can be used to isolate main effects and if necessary, two-variable effects. In the example below, the confounding patterns are based on the 2^3 factorial design matrix; similar approaches can be made to determine confounding patterns of higher factor designs.

As an example a complete factorial design of five factors would entail conducting 32 experiments. A 2^{5-2} fractional design reduces the number of screening experiments to a quarter and generators are used to include the fourth and fifth factor in the matrix of the complete factorial design, which includes main as well as all interaction effects. By defining the variables as **4=12** and **5=13** the following independent generators are obtained; **I=124=135**. All possible multiplications of the independent generators gives the generator **I=2345** giving the complete set of generators; **I=124=135=2345**. Applying the generators in the 2^3 matrix of a complete factorial design gives the following confounding patterns:

I	**1**	**2**	**3**	**12**	**13**	**23**	*123*
124	**24**	**14**	*1234*	**4**	*234*	*134*	**34**
135	**35**	*1235*	**15**	*235*	**5**	*125*	**25**
2345	*12345*	*345*	*245*	*1345*	*1245*	**45**	*145*

This means that by assuming that interaction effects between more than 2 variables are negligible, the main effect of variable **1** is confounded with the interaction effects **24** and **35**, the main effect of variable **2** is confounded with the interaction effect **14**, etc. Similar confounding patterns can be found for fractional designs including 4, 6 or 7 variables (by defining **6=23** and **7=123**) [41]. A summary of the confounding patterns of up to two variable interactions in the fractional factorial designs based on similar generator calculations are compared to a complete 2^3 factorial design in Table 2.

Table 2: Confounding patterns in fractional factorial designs compared to main effects and interaction effects in a complete 2^3 factorial design

2^3 design	2^{4-1} design	2^{5-2} design	2^{6-3} design	2^{7-4} design
1	1+24	1+24+35	1+24+35	1+24+35+67
2	2+14	2+14	2+14+36	2+14+36+57
3	3	3+15	3+15+26	3+15+26+47
12	4+12	4+12	4+12+56	4+12+37+56
13	13	5+13	5+13+46	5+13+27+46
23	23	23+45	6+23+45	6+17+23+45
123	34	25+34	16+25+34	7+16+25+34

In order to estimate the true values of the main effects and/or interaction effects, rather than a sum of these in the fractional factorial designs, additional experiments can be conducted to investigate this. If for instance it is desirable to isolate main effects from the interaction effects in the 2^{5-2} design, the generators **I=-124=-135** can be used, resulting in an additional 8 experiments [41, 100]. Similarly, interaction effects can be isolated, if desirable. Prior to isolating main or interaction effects, insignificant variables can be removed from the design, hence reducing the amount of experiments necessary for obtaining the desired information on significant variables in the experimental domain. This may include analysing the fit of the reduced model to assess which main and/or interaction effects to isolate [41].

Assigning variables with a high or low value in the experimental design of 4-7 variables, is based on the complete factorial 2^3 matrix, which covers every corner of a cube as illustrated in Figure 3. The high or low value of variables 4-7 is based on how variables have been defined, e.g. in the first set of screening experiments the definitions **4=12**, **5=13**, **6=23** and **7=123** were used, (i.e. the values of variable 4 are products of variables 1 and 2; the values of variable 5 are products of variables 1 and 3; the values of variable 6 are products of variables 2 and 3; the values of variable 7 are products of variables 1, 2 and 3) obtaining the following design matrix;

Exp. no.	Variables						
	1	2	3	4	5	6	7
1	-1	-1	-1	1	1	1	-1
2	1	-1	-1	-1	-1	1	1
3	-1	1	-1	-1	1	-1	1
4	1	1	-1	1	-1	-1	-1
5	-1	-1	1	1	-1	-1	1
6	1	-1	1	-1	1	-1	-1
7	-1	1	1	-1	-1	1	-1
8	1	1	1	1	1	1	1

If additional experiments are conducted, the experimental settings are based on the generators used for the design. The use of **I=-124=-135** in a 2^{5-2} fractional factorial design would for instance change the experimental settings of variables 4 and 5, while maintaining the original settings of variables 1-3 [41].

2.2.2 Principal Component Analysis (PCA)

PCA is a tool for visualising the differences and similarities in large data sets by simplifying the variation in the data without loss of systematic information.

A dataset consisting of *N* substances/objects with *K* characteristics (descriptors) can be regarded geometrically for which the descriptors span a *K*-dimensional space [101]. In this multidimensional descriptor space, each of the substances/objects can be described by a point with the coordinates of the descriptor axes corresponding to the values of the characteristics [41]. The *N* objects can then be represented by a swarm of points in the descriptor space. The first principal component vector, p_1, is placed through the swarm of points in the direction in which the data has the largest variation in their distribution [41, 101, 102]. When the vector is anchored in the average point of the descriptor values in the dataset, it is possible to make perpendicular projection of all points in the space on this vector, thus describing the objects of the dataset with coordinates along the vector. These coordinates are the principal component scores, t. If all descriptors are correlated to each other, the swarm of points would describe a linear structure in the descriptor space. If there is more systematic variation not described by the first principal component, a second component vector, p_2, is placed through the swarm of points with the second largest variation. The direction of p_2 is orthogonal to p_1 and anchored through the average point and data points are projected on p_2 to determine the corresponding scores, t_2. If there is still systematic variation left after fitting the two first principal components, additional components, orthogonal to previous components, are determined until all systematic variation has been exhausted [41]. Descriptors which are correlated to each other will be described by the same principal component. Since the principal component vectors are mutually orthogonal, the components will describe independent and uncorrelated variations of the descriptors.

The principles of score plots are illustrated in a 3-dimensional descriptor space in Figure 4, with two principal components. The scores plotted against each other (t_1 vs. t_2) give a graphical illustration of the variation in the dataset and the systematic variation is portrayed using fewer variables than the original 3 descriptors. In a scores plot objects which have similar values of their descriptors will be located close to each other, while objects which are different will be projected apart from each other.

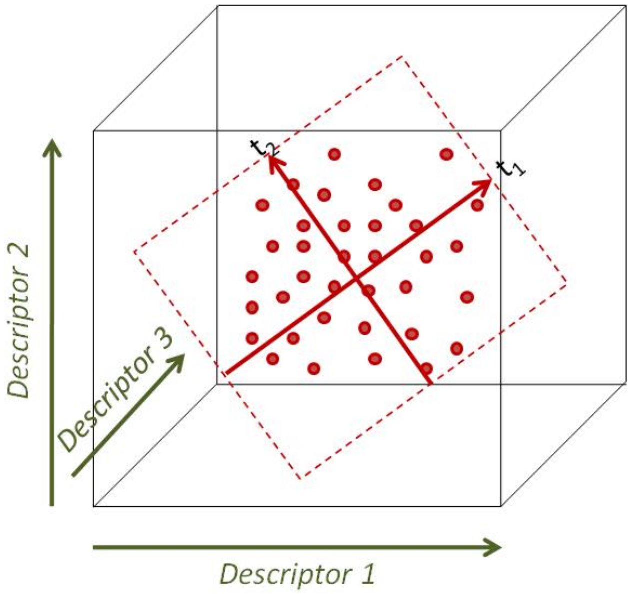


Figure 4: Swarm of data points in a 3-dimensional descriptor space, projected down to two principal component vectors giving coordinates (scores) of the first principal component (t_1) and second principal component (t_2).

The extent to which a descriptor contributes to a systematic variation along the principal component determines how much the direction of the p vector is tilted towards the corresponding descriptor axis. The direction of p is given by cosine of the angle between the descriptor axis and p. This value is the loading of the descriptor to the principal component. If the descriptor does not contribute to the principal component vector, the loading is zero (perpendicular) [41, 103].

After projection onto the first principal component vector it is possible to determine how well this component describes the variation in the data. The distance between the original data point and its projection on the principal component vector (loading vector) is a measure of the variation which is not described by the first principal component [103]. The contribution of the original descriptors to the principal components can then be displayed graphically by plotting the loadings of components against each other in loading plots, p_1 vs. p_2. Descriptors which have strong contributions to the variation of the scores in t_1 will be plotted far from the axis centre and close to the p_1 axis in the loading plot. Descriptors with minor influence are projected close to the axis centre. Descriptors that are positively correlated to each other are projected close to each other. Descriptors that are inversely correlated will be projected opposite to each other with respect to the axis centre [41].

2.2.3 Projections onto Latent Structures (PLS)

PLS models quantify relations between a descriptor matrix, X, and a response matrix, Y and can subsequently be used to calculate expected responses by entering new data into the X-matrix. If the number of independent variables in the X-matrix is given by K and the number of dependent variables in the Y-matrix is M, the objects (e.g. experiments) will be represented as points in the K-dimensional X space (descriptors/variables) and the M-dimensional Y space (responses) [41, 104]. Objects in each space are projected down to PLS components that describe the variation in each space with the constraint that for each PLS dimension, the PLS scores of the Y-matrix (u) should have a maximum correlation to the scores of the X-matrix (t) [41, 102]. New PLS components are iteratively introduced until all the systematic variation in the Y-matrix has been exhausted and only noise remains. Advantages of PLS are that it provides plots of the data compressed to fewer dimensions than the original dataset, it can simultaneously model several responses and it copes with colinearity between variables, noise in both the X and Y matrices and moderate amounts of missing data (<20%) [104-106]. Moreover, since PLS is based on projections, it is possible to have more variables than objects [41].

A model obtained from a small number of objects (<5) will not be precise, the precision will however increase with increasing number of objects and can be updated and refined by including more experimental data as it becomes available [41, 104]. The amount of the variance of the Y-matrix described by the model is R2Y, which accordingly should be high (approaching 1). Q2 is the predictive power, an estimate of the reliability/stability of the model calculated by cross-validation. In order to obtain a high predictive power, R2Y should be high. A value of Q2>0.9 is excellent, while a value above 0.5 is good. With non-significant components, Q2 can even be negative. The difference between R2Y and Q2 should be as low as possible and a difference larger than 0.2-0.3 may indicate outliers or the presence of irrelevant variables in the X-block [41].

The results of the PLS calculations can be presented in different ways, e.g. in score plots, loading plots, combined loading plots, weight plots and Variable Importance in the Projection (VIP) plots. A plot of scores against each other, for instance t_1 against t_2 or u_1 against u_2 will show the scores in the plane spanned by the PLS vectors in respectively the X- and Y-space. A plot of *u* against *t* will show the linear relation between the PLS components. A strong correlation will reveal object points in the score plot fit close to a straight line, while in a weak correlation the scores will be scattered. Loading plots are obtained by plotting the loading vectors against each other; it is however also possible to combine loading plots by plotting p_1 and c_1 against p_2 and c_2. In combined loading plots the variables which are strongly related will be plotted close to or opposite to each other with respect to the axis centre. Weight plots are obtained by plotting the weight vectors, *w*, against each other. These are mutually orthogonal; accordingly these plots show the independent contribution of the X-matrix variables to the systematic variation in the Y-space [41]. VIP plots reflect the relative importance of the parameters in the X-matrix, with respect to their correlations to the responses to each other, in absolute values and variables with high VIP values are most relevant for explaining the responses.

In an inverse PLS the X-block contains the responses and the Y-matrix consists of the variables; accordingly the best settings of the variables can be predicted by entering the desired responses in the X-block. By for instance adding the desired clean-up levels in the X-matrix, it should be possible to predict the best settings of the variables in EDR. In cases where the dimensions of the X-block is lower than the dimensions of the Y-block models can result in an undetermined system, but does none the less provide indicative value [41].

2.2.4 Practical application of chemometrics

Chemometrics was originally developed for pattern recognition in chemical data in the 1970s and has since then been used in a wide variety of scientific fields for obtaining overview of large datasets and retrieving relevant trends. However, the main developments in multivariate tools within chemometrics have been in response to demands and developments within the field of organic chemistry. PCA has, for instance, been used to select new test systems, i.e. the selection of new solvents/reagents in organic synthesis based on score plots to ensure covering a wide range of properties [107-109], or identifying which properties the synthesis of new organic compounds should encompass [110]. In combination with fractional factorial designs, PCA has also been used for determining variable importance and optimal settings within studied experimental domains [111, 112]. Amongst the many uses of PLS are elimination/minimisation of undesirable by-products and predicting optimum conditions [41, 113, 114]. PLS models have in addition been developed to span large experimental spaces making it possible to predict responses of new objects, e.g. a PLS model of quantitative-structure-activity relationships predicted activity of new peptide analogues [115].

PCA has been widely used as a tool for obtaining an overview of pollutant patterns in ground water, soil and sediments. Through the distribution patterns of parameters, water quality zones have been identified and reducing the amount of water quality parameters and number of monitoring stations in water quality programs have been suggested, based on the observed correlations between some of the parameters [116, 117]. In addition, the pollutant distribution patterns have assisted in identifying the naturally occurring and anthropogenic sources of heavy metals in groundwater [43]. In soil and sediments, PCA of heavy metal content has been used to retrieve patterns showing different origin, which in some cases have been related to natural or anthropogenic sources [118-122]. Some studies have also combined these patterns with information of site-specific sources to confirm indications of anthropogenic sources [123, 124], and in some cases combining PCA with geographical information systems (GIS) has resulted in graphical overviews of pollutant dispersion in soil/ground water and model predictions of future dispersion of pollution based on geochemical properties and pollutant levels [125, 126].

PCA studies of organic pollutants such as PAH [42, 127], PCDD/F [128] and PCB [129] have also been carried out in order to obtain an overview of distribution patterns, assessing hotspots and establishing remediation boundaries [130, 131]. Relating distribution patterns to pollution sources has been found to work well for point source pollutions. However, if pollution is evenly distributed e.g. due to diffuse sources, PCA will not assist in identifying distinct patterns coupled to sources [132]. If different sources of PAH and PCB pollution exist, this can be visualised by investigating the compound and congener patterns, respectively. Ratios of specific PAH compounds indicate petrogenic or pyrogenic origin, including potential combustion sources (fuel, coal, biomass etc) and PCA has been used to evaluate these ratios in relation to PAH sources [133]. PCA has also been used to assess the distribution of PCB congeners in relation to commercial PCB mixtures [134]. For heavy metals, PLS has been used for assessing correlations between selected naturally occurring metals (e.g. Fe/Mn) and other metal concentrations to evaluate which metals stem from anthropogenic sources [119].

Aside the example above, the use of PLS in pollution studies has been limited. It has however been employed for identifying important factors for production of toxic PCDDs and PCDFs in waste combustion [44] and to assess the influence of soil properties on the chemical oxidation of PAH in soil [135].

3 Methods and materials

3.1 Environmental site investigations and sampling

Environmental site investigations and sampling in the project were made in accordance with Danish and Norwegian guidelines for sediment and soil [136-138]. The sediment/soil sampling was carried out at three locations in cold regions: Hammerfest in Norway, Sisimiut in Greenland and Krasnoe (Arkhangelsk) in NW Russia. The sampling of polluted sediments/soil differed at the three locations and was based on site-specific conditions, including previously conducted environmental site investigations.

Hammerfest was identified as one of seventeen harbours of highest priority for remedial action by the Norwegian National Action Plan for polluted seabed in 2006 [14]. Extensive environmental investigations of the harbour have since taken place [139], revealing a complex composition of many pollutants such as heavy metals, PAHs, PCBs and TBT in the harbour sediments, originating from several sources from the past 60-70 years. In major parts of the harbour, pollutant levels have been identified as very polluted according to the Norwegian sediment quality criteria. In 2008 remedial action to remove and stabilise 5000 m^3 of polluted sediments from parts of Hammerfest harbour were implemented [20]. There, however, still remain large areas in the harbour in need of remedial action to meet the environmental goals of Hammerfest municipality. Sampling of sediments in this project, was based on the previous environmental investigations and remedial actions, and was carried out in five parts of the harbour, in which pollutant levels greatly exceeded the Norwegian sediment quality criteria. Sediments were sampled from the top 10 cm of the seabed using a Van Veen grab.

In Sisimiut, limited environmental investigations of the harbour have previously been conducted. High levels of Cu and Cd in the harbour sediments were however reported in a previous study [140]. In connection with sampling of sediments in assessed hot-spots of the harbour (based on previous/present industrial activities in the harbour), sediments were also sampled in the outskirts of the harbour to assess the dispersion and general level of pollution in the harbour. The environmental investigations comprised a total of nine sampling points and sediments were sampled from the top 10 cm of the seabed using a Van Veen grab.

In Krasnoe, environmental investigations in the frame of the NPA-Arctic (Barents Hot-spots) project were made simultaneously to sampling for the EDR experiments in the PhD project. The source of oil pollution was the former use as a disposal site for discharge of oil-polluted water from vessels, covering an area of 2500 m^2, polluted sandbanks at the site visibly eroding into the Northern Dvina River. Since the source was on-land, it was decided to sample polluted soil from the source rather than the eroded sand in the river sediments. In addition, possible remedial action would primarily be conducted on-land to remove the source, prior to any treatment of the river sediments. Sampling was made by drilling (ø63 mm) and was made in two visible hot-spots, the soil collected at depths of 1-1.5m below the surface (above the subsurface water).

3.2 Environmental risk assessment

Preliminary environmental risk assessments of pollutant levels were made by comparing pollutant levels with the national sediment and soil quality criteria of Denmark, Norway and Russia; and were, in addition, compared to sediment quality criteria of OSPAR and other Arctic countries (Canada and USA). This is the first step in the Norwegian standard for environmental risk assessments [141]. Environmental risk calculations to assess the site-specific risk for human health and environment were not made since the objective of this work was to regard treatment possibilities of dredged sediments and not assess the implications of no-actions or storage in disposal sites.

3.3 Analytical

Major elements and heavy metal concentrations (P, Al, Ba, Ca, Fe, K, Mg, Mn, Na, V, As, Cd, Cr, Cu, Ni, Pb, Zn) were measured based on digestion (Danish standard DS259). Dry sediment (1.0 g, 105°C) and HNO_3 (9 M, 20 mL) were autoclaved (200 kPa, 120°C, 30 min). Solid particles were subsequently removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100 mL. Element concentrations in the liquid were measured by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

Mercury, TBT and organic components (PAH16, PCB7 and total hydrocarbons (THC)) were measured at a licensed laboratory, Eurofins in Moss, Norway. Mercury was measured by Norwegian Standard NS 4768. PAH, PCB and THC were measured by ISO/DIS 16703. The measurements included 16 PAH components and 7 PCB congeners, which were selected based on sediment quality guidelines for Denmark, Norway and OSPAR (originally identified by the USEPA). The PAH components were acenaphtene, acenaphtylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)flouranthene, benzo(k)fluoranthene, benzo(ghi)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorine, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene. The 7 measured PCB congeners were PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180.

Chloride content was measured by agitating dried sediment (10 g) with Millipore water (40 mL) for 20 h. Solid particles were removed by 0.45 µm vacuum filtration and the chloride concentration was measured by ion chromatography.

Carbonate content was measured by treating dried sediment (5.0 g) with HCl (3 M; 20 mL) and the developed CO_2 was measured volumetrically in a Scheibler apparatus, calibrated with $CaCO_3$.

Organic matter was based on loss of ignition of dried sediment (2.5 g), heated at 550 °C for an hour.

Total Carbon (TC) and *Sulphur* (S) were measured by high temperature combustion. Dried sediment (0.5 g) was combusted (1,350 °C) converting all carbon and sulphide into carbon dioxide and sulphur dioxide, respectively. The gasses were passed through scrubber tubes to remove interferences and the carbon dioxide and sulphur dioxide were measured by an infrared detector.

Nitrogen (N) was measured by the Kjeldahl method. Dried sediment (1.0 g) was heated to 370 °C with H_2SO_4 (conc., 15 mL) and K_2SO_4 (7 g) until white fumes were observed (approx. 90 minutes) and subsequent to cooling, 250 mL distilled water was added to the mixture. pH of the mixture was increased by adding NaOH (45 %) and subsequently the mixture was distilled and the vapours were trapped in HCl (15 %, 85 mL). The trapped vapour solution was subsequently titrated with NaOH (5 M).

Cation exchange capacity (CEC) was measured by extraction with NH_4OOCCH_3 and subsequent cation exchange with NaCl. Dried sediment (10 g) was agitated with NH_4OOCCH_3 (1 M, pH 7, 30 mL) for 5 minutes and subsequently centrifuged (2500 rpm, 10 min). The liquid was discarded and the step was repeated two additional times. Subsequently the step was repeated two times using NH_4OOCCH_3 (0.1 M, 30 mL). The sediment was then agitated with NaCl (10 %, 20 mL) for 5 minutes and subsequently centrifuged (2500 rpm, 10 min) and the step repeated three additional times. The liquids from all four NaCl treatments were combined, diluted to 200 mL and ammonium content was measured by flow injection analysis.

pH (KCl). Dried sediment (5.0 g) was agitated with KCl (1 M, 12.5 mL) for an hour and pH was measured using a radiometer analytical electrode.

Conductivity. Dried sediment (5.0 g) was agitated with distilled water (25 mL) for an hour and the conductivity was measured using a radiometer analytical electrode.

Grain size was measured by wet sieving and dry sieving. Wet sediment (75 g), distilled water (350 mL) and $Na_4P_2O_7$ (0.1 M, 10 mL) were agitated for 24 hours. The slurry was then sieved through a 63 µm sieve and the fraction above 63 µm was subsequently dried and sieved for 15 min in a mechanical shaker using sieves with screen openings of 0.063, 0.080, 0.125, 0.25, 1.0 and 2.0 mm. The slurry fraction below 63 µm was transferred to an Andreasen pipette for gravitational sedimentation. Stoke's law was used for estimating the time required for particles to settle 20 cm and samples representing the sizes 40, 32, 16, 8, 4, 2 and 1 µm were measured.

Sequential extraction was made in four steps based on the improvement of the three-step method [142] (also known as BCR) described by Standards, Measurements and Testing Program of the European Union. Air-dried sediment (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL, pH 3) for 16 hours; secondly extracted with hydroxylammonium chloride (0.1 M, 20 mL; pH 2) for 16 hours; thirdly extracted with hydrogen peroxide (8.8 M, 5 mL) for 1 hour, followed by extraction at 85 ^{o}C for 1 hour, followed by evaporation of liquid at 85 ^{o}C, subsequently the cooled solid fraction was extracted with ammonium acetate (1 M, 25 mL, pH 2) for 16 h; and fourthly digestion according to DS259 on the remaining solid particles was run, following the description above.

pH dependent desorption experiments were conducted by agitating 8 samples of dried sediment (5g) with HNO_3 (25 mL) in varying concentrations (0.01 M-1 M). Extractions with distilled water were conducted as a reference. All the extractions were agitated for a week on a horizontal shaker. Subsequently samples settled for 15 min and the pH was measured. The sediment suspensions were vacuum-filtered through a 45 µm filter and digested (as described above).

3.4 Electrodialytic remediation experiments

3.4.1 Materials

3 EDR equipment designs were tested; the 2-compartment cell, 3 compartment cell and stack (Figure 13 in chapter 4.2).

EDR cells

The 2-compartment and 3-compartment cells were designed using the same materials and unit-sizes. The 2-compartment cell consisted of a compartment for the sediment suspension and a cathode compartment; while the 3-compartment cell in addition included an anode compartment. The cell compartments were manufactured from Plexiglas® and the dimensions were: length of electrolyte compartments 3.5 cm; length of sediment suspension compartment 10 cm; inner diameter of all compartments 8 cm. Ion-exchange membranes were from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The electrolyte used was $NaNO_3$ (0.01 M) adjusted to pH 2 by HNO_3 (7 M). Electrolyte liquids (350 mL) were circulated via Pan World pumps between glass bottles (500 mL) and the electrolyte compartments with flow rates of 30mL/min. Platinum coated titanium electrodes were used in each electrolyte compartment and for the 2-compartment cell the anode was placed directly in the sediment suspension. A power supply (Hewlett Packard E3612A) maintained a constant DC current. The sediment suspension was stirred by a RW11 Basic lab-egg (IKA 2830001) with a stirrer consisting of plastic flaps (4cm x 0.5cm) fastened to a glass rod. No light conditions in selected experiments were obtained by covering the EDR cell in tin foil. Temperature of $4^{o}C$ in the cells was achieved by placing the EDR cells in a fridge.

After the EDR experiments the sediment suspensions were gravity filtered and the heavy metal concentration in the suspension liquid and solids were measured. The stirrer, membranes and electrodes were rinsed in HNO_3 (5M) overnight and the heavy metal concentrations in the rinsing liquids and the electrolyte liquids were measured by ICP-OES.

Spacers, ion-exchange membranes and electrodes were assembled into an EDR stack based on the electrodialysis cell design by Jurag Separation A/S. The stack used consisted of 5 feed spacers with alternating concentrate spacers. The feed and concentrate spacers were separated by ion-exchange membranes resulting in 5 feed compartments with alternating concentrate compartments. At each end of the stack an electrode compartment was separated from the adjacent concentrate compartment with ion-exchange membranes. Each feed spacer was 5 mm wide and had an inlet at the bottom and an outlet at the top, both 3 mm wide, enabling sediment with grain sizes <1 mm to pass through the feed compartment without clogging. The concentrate spacer was 0.6 mm wide and also had an inlet at the bottom and an outlet at the top. Each ion-exchange membrane had a surface area of 530 cm2.

External plastic containers initially contained 3l of electrolyte ($NaNO_3$, 0.01 M), 3l concentrate ($NaNO_3$, 0.01 M) and 5 L sediment suspension and circulation of the individual liquids/suspension was achieved by external pumps. Electrolyte liquids from the cathode and anode compartments were mixed in the external electrolyte container. Circulation of the sediment suspension ensured mixing without the need for stirring in the external suspension container.

After the EDR experiments, the sediment suspensions were gravity filtered and the heavy metal concentration in the suspension liquid and solids, liquid concentrate and electrolyte liquid were measured by ICP-OES. The feed compartments of the stack were rinsed with distilled water and the concentrate and electrolyte compartments were first rinsed with HNO_3 (0.1 M) and subsequently with distilled water.

3.5 Multivariate modelling

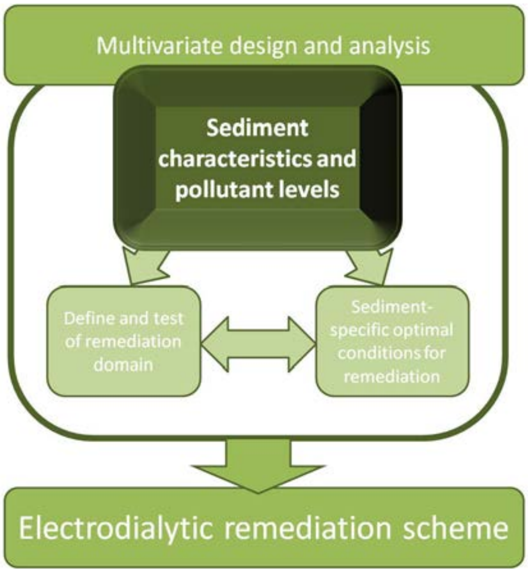
The software MODDE 7 was used to calculate the experimental designs used throughout the PhD project, ensuring that the fractional designs covered as large a part of the experimental domains as possible.

SimcaP 11 was used for multivariate analysis, i.e. calculating PCA and PLS models. The main tools used for PCA model evaluation were R2X, score plots and loading plots. The main tools for analysing the PLS models were R2Y, Q2, VIP values, coefficient plots and weight plots.

4 Results and discussion

4.1 Sediment characteristics and pollutant levels

In order to provide a foundation for evaluating the experimental space for the preliminary screening experiments as well as for assessing the influence of sediment properties on EDR efficiency, this chapter is dedicated to mapping sediment characteristics and pollutant levels. The latter will also form the basis for determining remediation objectives in relation to desirable removal efficiencies of each pollutant.



Presented in this chapter are relevant findings of ***Papers I-II*** as well as additional results from the environmental investigations. As an introduction, brief descriptions of the three sites, including mapping of potential sources of pollution and environmental sampling (*4.1.1*) are given. In order to obtain an overview of the sediments, all the pollutant concentrations compared to quality criteria are presented in *4.1.2*, followed by a summary of sediment characteristics (*4.1.3*). Prior to initiating remediation efforts at polluted sites, it appears essential to consider whether pollution is still occurring. An assessment of historical and current sources, based on results from ***Paper I*** and updated with additional results of the environmental investigations is conducted in *4.1.4*. Subsequently, a brief evaluation of the sediment characteristics and pollutant levels in relation to the outline of screening experiments for EDR is made (*4.1.5*).

4.1.1 Site descriptions including site-specific sources of pollution and sampling

Polluted sediment/soil used in the EDR experiments originate from three sites, each representing cold regions in the northern hemisphere. Hammerfest in Northern Norway and Sisimiut off the western coast of Greenland are located in the Arctic region and Krasnoe, Arkhangelsk, North-West Russia is located in the subarctic region. Similar climatic conditions with long winters and cool, short summer periods prevail at the three locations. Apart from covering a large geographical span of cold regions in the northern hemisphere, the three sites also represent different challenges in managing pollution and minimising the impact of human activities on the Arctic environment. The pollution in Hammerfest has been recognised as a local issue based on national requirements that were not specifically developed for the northern parts of Norway. Since Hammerfest is located in the Arctic region, the pollution in the harbour still represents the challenges in minimising the impact of local sources of pollution on the local Arctic environment, both in regards to past, present and future human activities, based on national quality requirements for the marine environment. In Sisimiut, limited environmental investigations have been conducted in the harbour and the pollution has not been recognised as an environmental issue. Sisimiut hence represents a site at which managing the polluted sediments has a future outlook and due to some similarities with Hammerfest (such as climate and type of pollution) may in a future perspective include transfer of knowledge with reference to mitigation efforts, in order to limit the impact of human activities on the marine environment. Krasnoe has been recognised as a Barents hotspot with the potential of negatively affecting the Arctic environment and is a priority for remediation for the regional authorities in Arkhangelsk. Unlike other Barents hotspots, for which financing may be achieved through investment loans, e.g. wastewater treatment plants, remediation at Krasnoe is highly dependent on grants from Russian and/or international funds. For all three sites it appears imperative that cost-efficient technologies are developed for pollution mitigation, however, prior to any remedial action, obtaining an overview of the pollution is essential. Due to different levels of existing knowledge of pollution at the three sites, the sampling strategies applied differed based on site-specific information on sources of pollution, on previously observed pollution and on local conditions.

Hammerfest, Northern Norway

Hammerfest has direct passage to the Barents Sea and is located at 70.7 degrees north and is hence one of the northernmost towns in the World. Despite its position in the high north, Hammerfest harbour is ice-free year around due to ocean currents. Activities in Hammerfest harbour were for many years dominated by the fishing industry, the petroleum industry has with the establishment of the LNG plant in 2007, however gained importance the past decade.

As a result of the Norwegian act of parliament on remediation of polluted seabed, numerous environmental investigations have been conducted in Hammerfest since 2005, and prior to that fragmented investigations of the harbour had been carried out, confirming a complex composition of pollutants in the harbour sediments [139]. In 2011, leakage of pollutants from land-based sources was confirmed, however due to the various past and present activities in and around the harbour, pollutant sources have not been directly identified [143].

Relevant potential sources of pollution for the sediments sampled in the project are listed in ***Paper I***; the boxes below also include other relevant sources for the entire area of the harbour based on assessments collected by Hammerfest municipality [139, 143-146].

Potential point sources past and present

- *Shipyards (former and present);*
- *Petrol stations;*
- *Oil tanks;*
- *Lumber yard;*
- *Garages;*
- *Sewage and wastewater discharge points;*
- *Snow deposits, located adjacent to the harbour;*
- *Fire 1945, in which the town was burnt down;*
- *Brownfields located next to the harbour;*
- *Storvatn (fresh water lake with outlet into the harbour; pollution in lake sediments and –water has been confirmed);*
- *Leakage of pollutants from wharf constructions.*

Potential diffusive sources;

- *Urban run-off, including snow melting;*
- *Traffic (vessels in harbour, vehicles on land);*
- *Polluted land;*
- *Long-range transport of global pollution;*
- *District heating (albeit limited combustion of waste; mainly renewable resources);*
- *Heating of households by biomass in stoves or oil in boilers.*

The previous environmental investigations revealed that the sediments in Hammerfest harbour were polluted with heavy metals, PAH, PCB and TBT at concentrations assessed as moderate to very high by the Norwegian sediment quality criteria. Dispersion pathways from land-based sources include subsurface water, rainwater, run-off (including snow melting), freshwater outlet and cable routes. Dispersion pathways in the sediments include biodiffusion, resuspension and marine organisms. The resuspension due to shipping, at depths below 20 m, has previously been shown to be the dominant dispersion pathway of the sediments in the western and southern-eastern parts of the harbour [147].

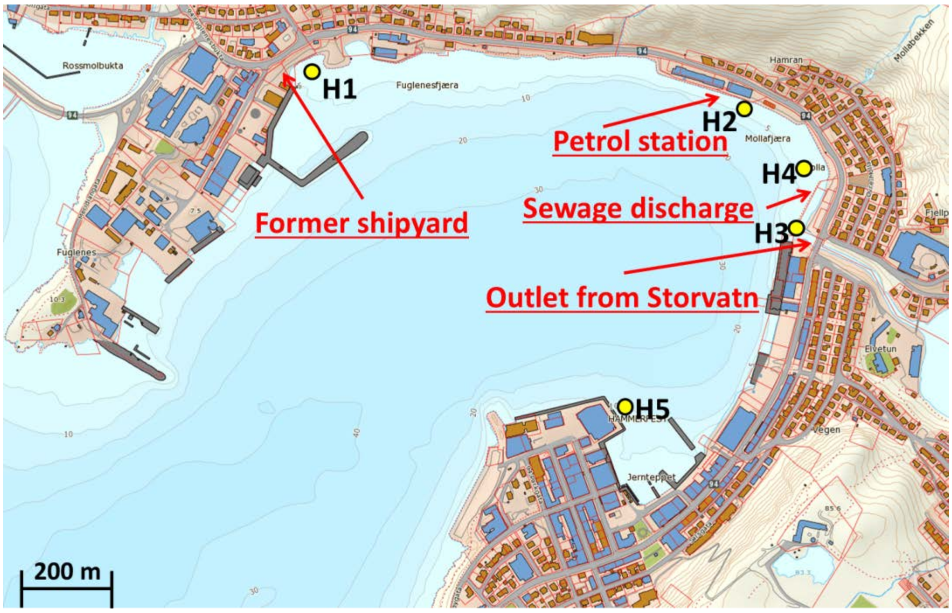


Figure 5: Sampling points and adjacent potential point sources of pollution in Hammerfest harbour.

Based on the extensive environmental investigations already conducted in the harbour, sampling was carried out in confirmed polluted areas of the harbour. Sampling was conducted in October 2010 and 5-10 kg of wet sediment from the top 10 cm as representative of 30-50 years of sedimentation was collected in five locations, H1-H5. The sampling points along with adjacent potential point sources are illustrated in Figure 5.

Table 3: Field observations during sampling in Hammerfest.

Sample point	Depth (m)	Sediment observation			
		Grain size	Colour	Smell	Foreign objects
H1	*13.3*	*Sand, medium-coarse, gravel, coral*	*Brown-grey*		
H2	*7.2*	*Sand, coarse, gravel, coral*	*Brown-grey*		
H3	*16.0*	*Sand, fine-medium, silt*	*Grey-black*	H_2S	*Oil film*
H4	*15.4*	*Sand, organic material*	*Black*	H_2S	*Waste (plastic, wood, steel, etc.)*
H5	*16.2*	*Sand, fine-medium, gravel*	*Brown-grey*	H_2S	

As is obvious from the field observations made during the sampling (Table 3) the sediments had different characteristics in the sampled areas of the harbour. In sample points H1 and H2 the sediment was coarser and contained gravel sized corals. The sediment in H3-H5 were fine grained and smelled of degradation. In the H3 samples oil film in the sediments was observed and sediment from H4 contained organic material and elements of waste such as wood, plastic and steel.

Sisimiut, Greenland

Sisimiut is located at 66.9 degrees north, approximately 75 km north of the Arctic Circle and as in Hammerfest has a year-round ice-free port. Fishing is the main industry and the town contains a fish processing plant located in the harbour. Limited environmental investigations of the harbour have previously been conducted, high concentrations of Cd and Cu in the sediments have however been reported [140]. Potential sources of pollution in Sisimiut harbour are listed in ***Paper I*** and are summarised in the boxes below.

Potential point sources past and present;

- *Fish factory – discharge of processed shrimp/crab (possible biomagnification of pollutants in shells);*
- *Former shipyard;*
- *Petrol station;*
- *Wastewater discharge points;*
- *Discharge from boats;*
- *Leakage of pollutants from wharf constructions.*

Potential diffusive sources;

- *Urban run-off, including snow;*
- *Traffic (boats in harbour, vehicles on land);*
- *Polluted land;*
- *Incineration of waste;*
- *District heating (limited combustion of fossil fuels);*
- *Heating of households by biomass in stoves or oil in boilers;*
- *Long-range transport of global pollution.*

Based on the potential pollutant sources, the harbour sediments may be polluted by heavy metals, PAH, PCB and TBT. As in Hammerfest, dispersion pathways from land-based sources include subsurface water, rainwater, cable routes and snow melting. Dispersion pathways of pollution in sediments include biodiffusion, resuspension and marine organisms.

Since limited environmental investigations of the harbour exist, the sampling included potential hotspots as well as outskirts of the harbour to obtain a better overview of the pollution, resulting in 9 sampling points. Sampling was conducted in August 2012 and 10-20 kg of wet sediment from the top 10 cm was collected at S1, S3, S5 and S6 in potential hotspots, while 1 kg of wet sediment was sampled in the other areas. It should be noted that in ***Paper I*** '*S2*' corresponds to S5 and '*S4*' corresponds to S6 in order to simplify the presentation of results in that paper; the original sampling point denotations have however been kept in this dissertation. The sampling points and potential point sources of pollution are illustrated in Figure 6.

Figure 6: Sampling points and adjacent potential point sources of pollution in Sisimiut harbour.

The sampled sediments appeared to have similar composition according to the field observations (Table 4). In sample point S8 sampling was not possible, which was due to the seabed apparently being covered by large stones in this area. Apart from sediments sampled at S6 and S9, the sediments had a distinct odour of volatile sulphur compounds and had a darker colour (black).

Table 4: Field observations during sampling in Sisimiut.

Sample point	Depth (m)	Sediment observation			
		Grain size	Colour	Smell	Foreign objects
S1	*1.5*	*Sand, fine, silt, few stones*	*Black*	*H_2S, diesel*	
S2	*3.0*	*Sand, fine, silt, few stones*	*Black*	*H_2S*	
S3	*4.7*	*Sand, fine, silt, few stones*	*Black*	*H_2S*	*Waste (plastic, wood, steel, etc.)*
S4	*5.2*	*Sand, fine, silt, few stones*	*Black*	*H_2S*	
S5	*5.2*	*Sand, fine, silt, few stones*	*Black*	*H_2S*	*Waste (plastic, wood, steel, etc.)*
S6	*6.5*	*Sand, fine-medium, silt, stones*	*Grey-black*		*Waste (plastic, wood, steel, etc.)*
S7	*15*	*Sand, fine, silt*	*Black*	*H_2S*	
S8	*8.0*	*No sample*			
S9	*13*	*Sand, fine, seashells, stones, seaweed*	*Grey-black*		

It is important to note that information on pollutant levels in the harbour was not available prior to the field work. The choice, of which sediment to collect for the EDR experiments, was solely based on information of potential hotspots and observations during the fieldwork. Based on assessments in the field, it was decided to proceed with sediment from sample points S1, S3, S5 and S6.

Krasnoe, North-West Russia

5 km north of the settlement Krasnoe, Arkhangelsk Region in North-West Russia lies a landplot located at 64.6 degrees north, along the Northern Dvina River. The climate is similar to those of Sisimiut and Hammerfest with winters of approximately 6 months; the White Sea is however not ice-free in parts of the winter months. In 2008, oil pollution was observed at the landplot due to erosion of polluted sand into the Northern Dvina River (Figure 7). The Dvina Bay was prioritised as a hotspot in the Russian Arctic by the NPA-Arctic (Support to the National Programme of Action for the Protection of the Arctic Marine Environment in the Russian Federation) partly financed by the Global Environment Facility (GEF) and the United Nations Environmental Programme (UNEP) in 2008 [148]. Since the pollution at the landplot was observed to erode, thereby increasing the total environmental load of the Dvina Bay, it was included as one of 16 pre-investment studies of the identified Barents Hotspots in 2010 [149] and subsequently the Nordic Environment Financing Co-operation (NEFCO) financed an environmental site assessment in 2012 [150].

Figure 7: Oil polluted sand from the landplot in Krasnoe, eroding into the Northern Dvina River.

The landplot is manmade and was established in the 1960s by dredging of river sediments and in the 1970s it was used as storage for oil polluted water from ships and vessels. These activities had supposedly ceased by the 1980s, it is however unclear if activities continued through the 1980s and 1990s [150]. The nearest settlement is Krasnoe, located 5 km upstream, so the dumped oil pollution at the site is the main source. Minor sources of the pollution at the site may include the original sediments used to make the landplot and traffic in the river. The environmental investigations conducted at the plot in 2012 revealed concentrations of oil products (as total hydrocarbons) of up to 28000 mg/kg dry matter. Given a polluted volume of 7500 m^3 the total load at the land plot was estimated to be 80 ton of hydrocarbons [150]. Dispersion pathways include subsurface water, transport via pipe systems and erosion into the Northern Dvina River. Approximately 70% of the water in the White Sea originates from the Dvina River. Due to the high quantity of pollution and the continuous erosion into the river, contributing to the total environmental load in the Dvina Bay, the pollution at the landplot was assessed as posing a potential risk for the regional environment [150].

The polluted soil is not directly comparable to the harbour sediments in Hammerfest and Sisimiut, nonetheless pollution levels and environmental risks make it interesting to pursue investigating the potential of EDR for removal/degradation of the oil products. In addition, EDR has not previously been used to remove oil products from polluted material adding another dimension to such investigations.

Sampling of soil at the land plot was conducted in October 2011 at the same time as the environmental investigations in the frame of the NEFCO Barents Hotspot. The top layer at the site was observed to consist of 0.5-1.0 m of brown fine-medium grained sand, followed by 0.5-2.0 m of grey fine-grained sand. Underlying the sand layers were 0.7-1.5 m peat, followed by a sandy loam. Discontinuous subsurface water was connected to the peat layer and in the hotspot free phase oil was observed in the water, just above the peat layer. Sampling for EDR was conducted in two areas of the hotspot; in the first area (K1) samples were taken from the top layer of sand, 0.5 m below ground and in the second area (K2) they were taken from the grey sand just above the peat layer, 2.5 m below ground. Oil was observed to coat the sand and the samples had strong smell of oil.

4.1.2 Preliminary environmental risk assessment of the three sites

Pollutant concentrations at the three sites were compared to sediment quality criteria of OSPAR (Table 5 on page 46). Components not included in OSPAR's criteria, were compared to class 1 (no toxic effects) and class 2 (low toxic effect) of the Norwegian sediment quality criteria (NSQC). Since the soil at the land plot near Krasnoe is continuously eroding into the Northern Dvina River, and is the source of pollution in the river bed, these samples have been included in the comparison.

In Hammerfest, the concentrations of PAH, PCB, TBT, Cu, Hg, Pb and to a lesser degree Zn exceeded the EAC/ERL criteria and hence may have toxic effects on the marine environment in the harbour. These compounds were consequently targeted for remediation in the EDR experiments.

In Sisimiut, the concentrations of PAH, PCB and TBT also exceeded the EAC/ERL criteria as did Cu, Pb and Zn. With the exception of TBT in sample point S9, concentrations of the pollutants were lower in the outskirts of the harbour (S2, S7 and S9) indicating that the potential toxic effect of pollutants is highest in the harbour. The high level of TBT at S9 indicates that the docking of ships in this part of the harbour has had a local toxic effect on the marine environment. The high concentrations of pollutants in the centre of the harbour may indicate dispersion due to resuspension as a result of boat traffic in the harbour. Further investigations are however necessary to confirm these observations.

The soil samples from the landplot near Krasnoe were heavily polluted by PAH and THC, greatly exceeding the Russian soil quality criteria (***Paper IX***). The concentrations of heavy metals and PCB were low and did not appear to pose a risk for the environment. THC is not included in the sediment quality criteria, it however cannot be refuted that the eroded polluted soil may have a toxic effect on the local aquatic environment.

Table 5: Pollutant concentrations at the three sites compared to the sediment quality criteria of OSPAR. Concentrations are given in mg/kg dry matter. Standard deviations were 10-25% for heavy metals; 25-40% for PAH components; 20-25% for PCB congeners; 40% for TBT and 20-30% for THC. Concentrations exceeding background concentrations are highlighted in italics and concentrations exceeding EAC/ERL are highlighted in bold.

Pollutant	OSPAR/NSQC		Hammerfest					Sisimiut								Krasnoe	
	BAC	EAC/ERL	H1	H2	H3	H4	H5	S1	S2	S3	S4	S5	S6	S7	S9	K1	K2
As	25	52**	6.3	4.0	5.0	*21*	5.9	18.7	2.3	9.2	17	8.5	6.6	*28*	1.9	0.6	1.8
Cd	0.31	1.2	0.13	0.25	0.27	*1.10*	0.14	*0.54*	0.12	*0.38*	**1.9**	*0.7*	0.09	0.13	0.1	<0.1	<0.1
Cr	81	81	15.2	8.4	23	47	28	37	12	25	39	24	10	48	4.1	6.2	6.5
Cu	27	34	**116**	*33*	**60**	**167**	**77**	**216**	22	**184**	**170**	**125**	**42**	17	54	11.5	2.4
Hg	0.07	0.15	**0.31**	**0.92**	**0.54**	**1.19**	**0.32**	**0.30**	0.037	*0.09*	**0.329**	*0.10*	0.01	0.005	0.013	n.a.	n.a.
Ni	36	46**	9.5	5.1	15	23	19	18	6.2	18	14	13	6.0	5.4	2.3	4.9	6.4
Pb	38	47	**49**	**220**	**92**	**152**	**58**	**73**	9.9	**57**	**72**	*39*	7.8	5.2	2.6	12.5	0.8
Zn	122	150	83	64	**218**	**537**	105	**343**	53	**957**	**420**	**239**	82	17	82	28	19
Acenaphtene	0.0048*	0.160**	*0.086*	*0.066*	*0.048*	**0.24**	*0.039*	**0.72**	*0.016*	**0.26**	**0.43**	**0.26**	**0.41**	<0.01	*0.014*	**0.74**	*0.015*
Acenaphtylene	0.0016*	0.033**	*0.012*	*0.01*	*0.03*	**0.066**	**0.035**	*0.022*	<0.01	*0.01*	*0.021*	*0.01*	*0.01*	<0.01	<0.01	*0.021*	**0.093**
Anthracene	0.005	0.085	**0.19**	**0.13**	**0.29**	**1.6**	**0.25**	**1.3**	*0.023*	**0.47**	**0.76**	**0.47**	**0.69**	*0.017*	*0.033*	**0.33**	<0.01
Benzo(a)anthracene	0.016	0.261	**0.59**	**0.46**	**0.98**	**8.4**	**0.93**	**4**	*0.068*	**1.5**	**1.3**	**1.5**	**0.84**	*0.039*	*0.039*	**0.28**	*0.097*
Benzo(a)pyrene	0.03	0.430	**0.5**	*0.34*	**0.66**	**4.3**	**0.71**	**2**	*0.071*	**0.74**	**0.97**	**0.74**	**0.55**	*0.036*	*0.035*	*0.12*	*0.048*
Benzo(b)flouranthene	0.046*	0.240**	**0.5**	**0.34**	**0.67**	**4.1**	**0.67**	**2.1**	*0.092*	**0.78**	**0.95**	**0.78**	**0.48**	0.030	0.035	*0.21*	*0.049*
Benzo(k)fluoranthene		0.21**	**0.44**	**0.31**	**0.59**	**3.9**	**0.62**	**1.9**	*0.056*	**0.68**	**0.85**	**0.68**	**0.41**	0.029	**0.029**	**0.057**	0.011
Benzo(ghi)perylene	0.08	0.085	**0.38**	**0.23**	**0.54**	**2.4**	**0.63**	**2.4**	**0.11**	**0.51**	**0.84**	**0.51**	**0.36**	0.027	0.027	*0.053*	0.071
Chrysene	0.02	0.384	**0.63**	**0.48**	**0.96**	**7.8**	**0.94**	**4.2**	*0.11*	**1.5**	**1.2**	**1.5**	**0.83**	*0.035*	*0.050*	**0.95**	*0.40*
Dibenzo(a,h)anthracene	0.012*	0.590**	*0.077*	*0.054*	**0.12**	*0.5*	*0.12*	*0.4*	*0.020*	*0.14*	*0.19*	*0.14*	*0.094*	<0.01	<0.01	<0.02	*0.018*
Fluoranthene	0.039	0.600	**0.93**	**0.77**	**1.4**	**17**	**1.5**	**6.2**	*0.14*	**2.2**	**2.5**	**2.2**	**1.7**	0.084	*0.078*	*0.28*	0.029
Fluorene	0.0068*	0.260**	0.096	*0.069*	*0.082*	**0.46**	*0.08*	**0.79**	*0.016*	**0.27**	**0.41**	**0.27**	**0.47**	<0.01	*0.013*	**1.1**	<0.01
Indeno(1,2,3-cd)pyrene	0.103	0.240	**0.33**	*0.2*	**0.44**	**2**	**0.48**	**2.4**	0.085	**0.55**	**0.75**	**0.55**	**0.39**	0.029	0.026	0.024	0.014
Naphthalene	0.008	0.160	*0.049*	*0.05*	*0.075*	**0.17**	*0.043*	**0.44**	0.01	*0.14*	**0.51**	*0.14*	*0.14*	<0.01	*0.028*	**1.3**	*0.011*
Phenanthrene	0.032	0.240	**0.65**	**0.48**	**0.67**	**4**	**0.78**	**4.4**	*0.078*	**1.5**	**2.1**	**1.5**	**2**	*0.046*	*0.058*	**2.6**	0.010
Pyrene	0.024	0.665	**0.77**	*0.6*	**1.3**	**13**	**1.2**	**4.3**	*0.13*	**1.4**	**1.7**	**1.4**	**1.1**	*0.062*	*0.070*	**2.1**	*0.37*
PAH16	0.30*	2.0**	**6.2**	**4.6**	**8.9**	**70**	**9.1**	**38**	**1.0**	**13**	**15**	**7.6**	**10**	*0.43*	*0.53*	**10**	*1.2*
PCB7	0.001	0.068	**0.084**	*0.034*	**0.28**	**0.55**	**0.078**	**0.18**	*0.021*	**0.14**	**0.518**	**0.218**	*0.015*	*0.002*	*0.005*	<0.001	<0.001
TBT	0.001*	0.005**	**1.8**	**0.29**	**0.071**	**0.110**	**0.032**	**0.59**	*0.004*	**0.160**	**0.440**	**0.220**	**0.014**	<0.001	**6.3**	n.a.	n.a.
THC			410	240	380	1000	340	2600	610	1800	3300	2000	370	120	470	22000	7200

* Norwegian sediment quality criteria class 1 (no toxic impact)

** Norwegian sediment quality criteria class 2 (ERL)

n.a. - not analysed

4.1.3 Sediment characteristics

Sediment characteristics were determined for the 11 sediments that were sampled for the EDR experiments and included more than 20 parameters. In order to obtain an overview of the 11 sediments in relation to the measured geochemical properties, PCA was employed. In ***Paper I*** and ***Paper II***, PCA of the 9 harbour sediments from Hammerfest and Sisimiut revealed that sediments originating from the same harbour exhibited differences in composition, suggesting that treatment of sediment, to remove pollutants has to be designed in accordance with the sediment at hand. In both papers the loading plots showed that many parameters contributed to the first component explaining most of the variation, while the second component was mostly related to the buffer capacity in the sediments. Since EDR of heavy metals is affected by the buffer capacity, these PCA plots appear to be relevant to use in choosing test systems and including more data from other sediments in the future, may also be useful in assessing how EDR can remediate new sediment.

In Figure 8 the Russian soils, K1 and K2 have been included in the PCA calculations and are located in the lower left quadrant of the PCA plot far away from the harbour sediments. This is not surprising since these soils had a higher content of sand (63µm-2mm) and lower contents of organic matter and metals than the harbour sediments; all parameters which highly influence the loading plot.

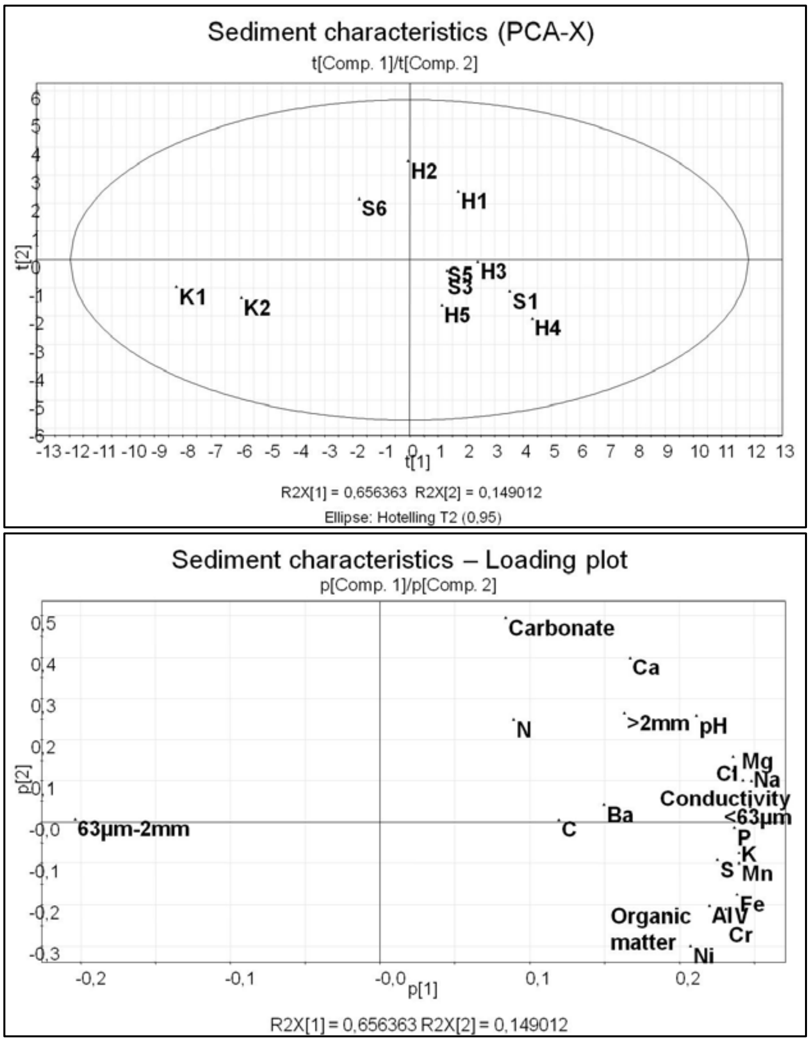


Figure 8: PCA score plot (top) and loading plot (bottom) for the 11 soil/sediments.

As was the case in the PCA plots in ***Paper I*** and ***Paper II***, the second component in Figure 8, explaining 15 % of the variance was dominated by the buffer capacity of the sediments. Another interesting trend in the loading plot is the apparent correlation between conductivity and the dissolvable ions Cl, Mg and Na, which is not surprising. In addition, a correlation between the clay/sand fraction of the sediments (<63µm) and metal concentrations may exist. This was not further investigated in ***Paper I*** and ***Paper II***, since this was beyond the scopes of the two papers. However, since previous studies have shown that EDR is more efficient for the finer fractions of soil, a preliminary investigation of amounts of metal in the different grain fractions is presented here. Due to the high content of oil as well as the low contents of metal in the Russian soils (K1 and K2), these have not been included in the analysis.

The amount of each metal (Al, Fe, K, Mg, Mn, Cr, Cu, Ni, Pb and Zn) found in the fractions[1] coarse sand (0.5-2 mm), medium sand (180-500 µm), fine sand (63-180 µm), silt (4-63 µm)and clay (<4 µm) were calculated and accounted for the X-matrix in a new PCA (R2X 65 %). As was the case for the sediment characteristics above, the sediments' distribution in the scores plot was independent of geographical origin (Figure 9). Apart from Mg, the metals in the clay fraction are clustered in the loading plot indicating similar binding patterns for the metals in the clay fractions. The reason that Mg is an outlier may be due to Mg in the pore water not being separated from the sediment prior to the gravitational sedimentation in the grain size distribution analysis rather than being differently bound in the clay fraction. With the exception of Cu, Pb and Zn, the loading plot also implies correlation between the metals in both the silt and fine sand fractions. The high concentrations of Cu, Pb and Zn in the sediments (Table 5) suggested anthropogenic sources; it is however uncertain whether the loading plot indicates that excessive levels of these pollutants are bound in the silt and fine sand fractions or that there is a difference in mineral composition in these fractions. The metals in the medium and coarse fractions span a wider space of the loading plot and the correlation between the metals is not as distinct as in the finer fractions of the sediment. It is interesting to note that for all the fractions correlations between Al and Fe; and Cr and Ni, respectively, are observed.

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[1] According to ISO 14688-1.

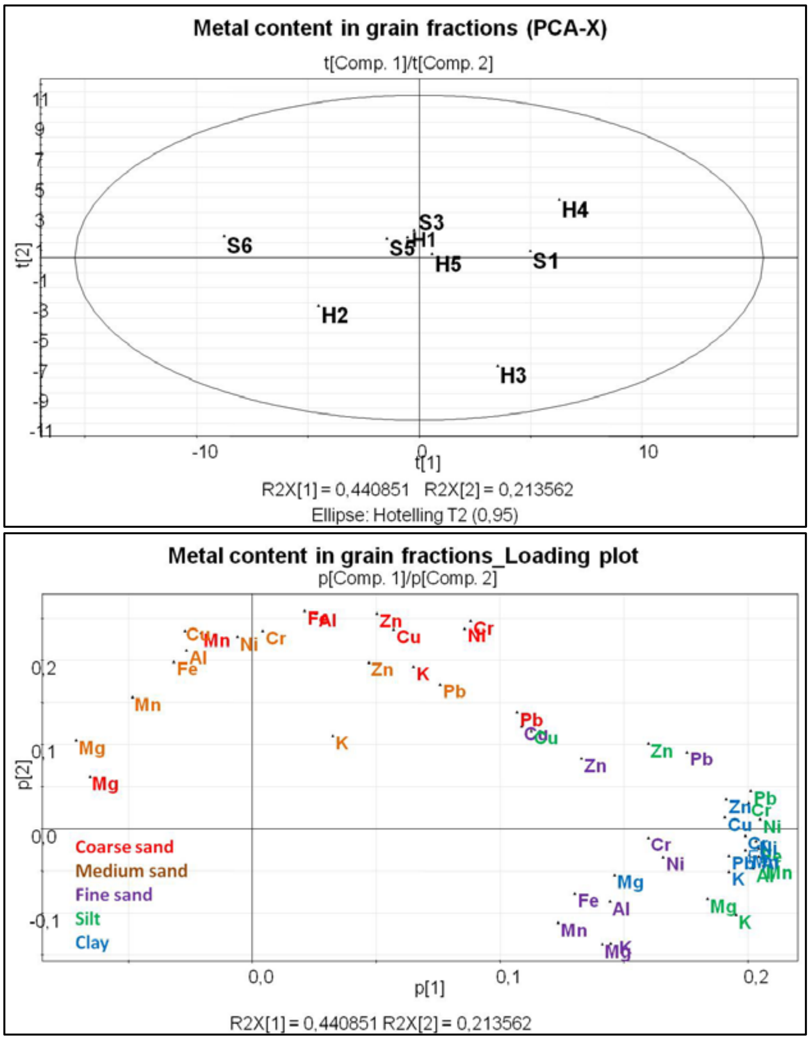


Figure 9: PCA score and loading plots of the metal content in each of the fractions coarse sand, medium sand, fine sand, silt and clay.

The chemical binding of metals in the sediment may also influence the efficiency of EDR. As a consequence, an analysis of metal binding, evaluated by the amount of metal bound in the exchangeable (including metals bound as carbonates), reducible, oxidisable and residual fractions, in the 9 harbour sediments was conducted in ***Paper I***. Metals, which were correlated in each fraction included Al, Fe, K, Mg, Mn, Cr and Ni; while no correlations to or between the heavy metals Cd, Cu, Pb and Zn in any of the fractions were found. This suggests different binding patterns in the sediment due to anthropogenic sources and interestingly, the pollutants appear to bind to all the chemical fractions of the sediments. Accordingly removal of the anthropogenic heavy metals during EDR would entail removal from all fractions.

4.1.4 Assessment of pollution sources

Heavy metals, TBT, PAH and PCB have higher affinity for organic matter than for clay minerals. PCA in ***Paper I*** revealed a general correlation between pollutants and organic matter in the sediments from both Hammerfest and Sisimiut harbour, indicating diffuse sources with similar pollutant loads. Some of the pollutants however showed different trends attributed to differences in sources and/or existence of point sources and although they may still be strongly bound in the organic matter, at different loads compared to the general trend. In Hammerfest this included PAH, PCB, TBT, Pb and Hg, while in Sisimiut it included PAH and to a lesser degree PCB and Zn.

Heavy metals

As pointed out in ***Paper I***, it was, based on the given information of different parameters from the sediments in Hammerfest and Sisimiut, not possible to trace the diffuse sources of heavy metals. Assessments of the binding patterns and concentration distribution in the sediments may however provide more specific information on the pollution. The results of the sequential extraction analysis summarised above, for instance, revealed that Cd, Cu, Pb and Zn had different chemical binding patterns than other elements, and may be indications of partly anthropogenic origin and this is confirmed by the elevated concentrations observed in the harbours (Table 5). Hg was not part of this analysis; nonetheless it is also considered a pollutant due to concentrations exceeding the ERL criteria in both harbours (Table 5). The PCA plot of pollutant concentrations and sediment characteristics in ***Paper I*** revealed similar distributions for Cd, Cu and Zn in Hammerfest and Cd, Cu, Hg and Pb in Sisimiut in relation to the content of organic matter, suggesting diffuse sources of these heavy metals.

Pb and Hg showed different trends in Hammerfest indicating different point sources. The highest concentration of Pb was found at H2 (Table 5), located next to a petrol station (Figure 5) and may be related to use of leaded petrol prior to 1996. The concentration of Hg is also elevated at this location and may be related to the activities at the petrol station; a previous study indicated that car washes may be sources of mercury pollution [151]. It is, however, important to note that a recent environmental investigation did not find significant leakage of pollutants into the harbour from the specific petrol station [143] implying that the sources are historical. The highest concentration of Hg was found at the sewage/waste water discharge point (H4) and may be connected to the untreated waste water. The highest concentration of Zn in Sisimiut was found at S3 (Table 5, Figure 6) and may be related to leakage of wastewater or run-off from the adjacent petrol station.

TBT

In Hammerfest, the content of organic matter and TBT concentrations were not correlated, which, in ***Paper I***, was attributed to the point source found at H1 adjacent to the previous shipyard (Table 5, Figure 5). In Sisimiut the content of organic matter and TBT appeared to be correlated; the PCA plot did however not include samples S2, S4, S7 and S9 since these sediments were not characterised. A very high concentration of TBT is observed in the outskirt of the harbour at S9 (Table 5, Figure 6), probably due to the docking of large ships here. Besides the hotspots, the high concentrations (in regard to toxicity) of TBT in other parts of the harbour may be due to boat traffic and dispersion of TBT from polluted sediments via resuspension, diffusion or marine species.

PCB

In both harbours PCB did not appear to be strongly related to the content of organic matter suggesting different sources of pollution. PCA plots of the seven analysed congeners also revealed a difference in composition (***Paper I***). The PCA plot of the distribution of PCB congeners in the harbour sediments and commercial PCB mixtures has been updated with S2, S4, S7 and S9 in Figure 10, the two components explaining 86% of the variation and in general the distribution of PCB congeners in the sediments were clustered according to which harbour they originated in.

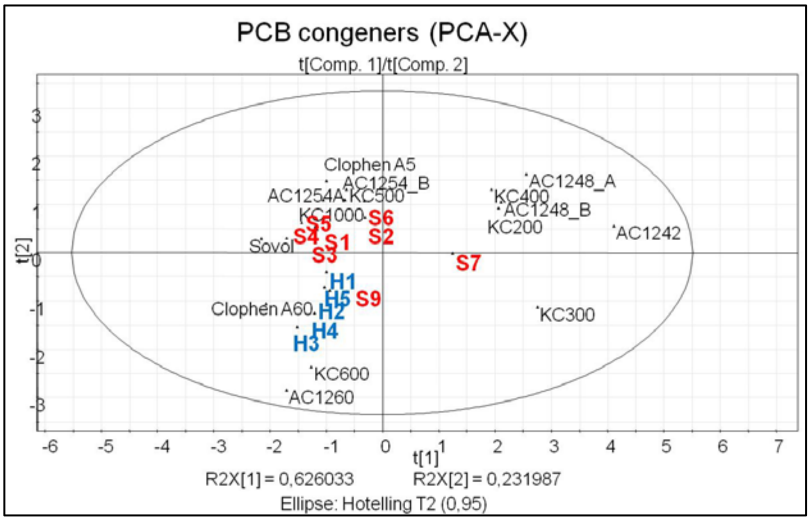


Figure 10: PCA scores plot of 7 PCB congeners – harbour sediments in Hammerfest (H1-H5) and Sisimiut (S1-S9) compared to commercial PCB mixtures.

To get a better overview of the contribution of the different commercial PCB mixtures, a PLS model, in which the X-matrix consisted of commercial mixtures and the Y-matrix consisted of the PCB concentrations in the sediments, has been calculated (not included in ***Paper I***). The correlation factor, R2Y, was 0.98 and the predictive power, Q2, was 0.79, and the weight plot of the model (Figure 11) reveals that the PCB pollution in Hammerfest was mainly related to the Russian (Sovol), German (Clophen) and American (AC – Arochlor) mixtures, while the correlation between the concentrations of PCB in the Sisimiut sediments and the commercial mixtures was more ambiguous. The concentrations of PCB in S7 and S9 were very low and are not necessarily related to different PCB sources than those found elsewhere in the harbour. The clustering of S2 and S6 may be related to marina activities (small boats are also anchored close to S2) and were mostly related to the Japanese mixtures (KC – Kanechlor). The other samples (S1, S3, S4 and S5) had the highest concentrations of PCB in the harbour (Table 5) and were mainly related to the American and Russian commercial mixtures.

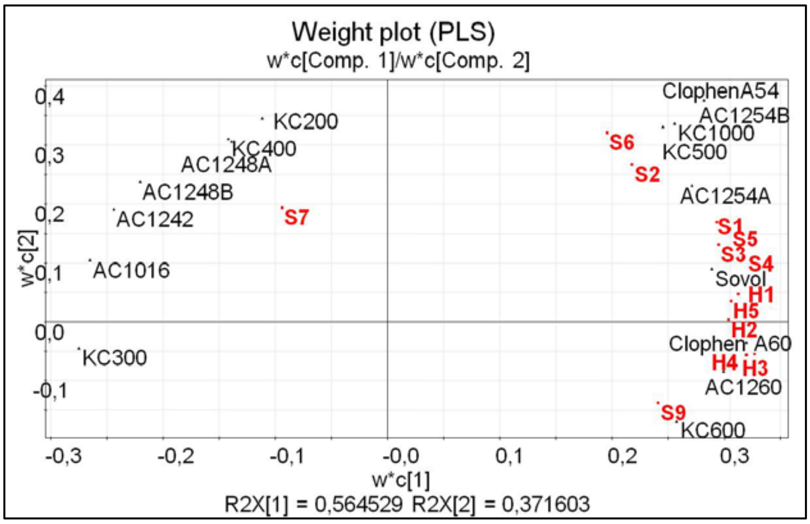


Figure 11: Weight plot of PLS model of 7 PCB congener distribution of commercial mixtures (X-matrix) and harbour sediments from Hammerfest, H1-H5, and Sisimiut, S1-S9 (Y-matrix). The abbreviations for the commercial mixtures used in the plot are KC – Kanechlor and AC – Arochlor.

Despite clustering of the Hammerfest sediments suggesting similar origin, several sources based on similar commercial mixtures may exist and concentration levels in the harbour were different. The highest concentrations of PCB were found at H4 and H3 (Figure 5); the first probably related to the sewage discharge, while the latter may be related to dispersion of PCB pollution from the freshwater lake via the outlet adjacent to H3. The lake sediments have previously been shown to contain elevated concentrations of PCB, stemming from several sources in Hammerfest town [144].

PAH

In ***Paper I***, assessments suggested a point source of PAH at H4, attributed to sewage discharge. Ratios of selected PAH components were subsequently used to identify sources of pollution and it was found that PAH in the sediments in Hammerfest were pyrogenic, mainly from combustion of fuelwood. Combustion of fuel probably also contributes, just to a lesser degree. In addition, some of the PAH pollution may originate from the town fire in 1945.

In Sisimiut, it was found that PAH was not related to the content of organic matter, and was suggested to originate from several diffuse sources. PAH ratios indicated pyrogenic origin from combustion of fuel, coal or biomass; a main contributor was however not found and the PAH pollution may originate from traffic, incineration of waste and household heating by oil boilers. These trends were also found for S2, S4, S7 and S9, not included in ***Paper I*** (Table 6).

Table 6: PAH ratios for sediments from Sisimiut.

	An/(An+Phe)		(Fl/Fl+Py)		Ip/(Ip+Bghip)	
	Ratio	*Source*	*Ratio*	*Combustion*	*Ratio*	*Combustion*
S1	0.23	Pyrogenic	0.59	Coal/biomass	0.50	Coal/biomass
S2	0.23	Pyrogenic	0.52	Coal/biomass	0.44	Fuel
S3	0.24	Pyrogenic	0.61	Coal/biomass	0.52	Coal/biomass
S4	0.27	Pyrogenic	0.60	Coal/biomass	0.47	Fuel
S5	0.21	Pyrogenic	0.58	Coal/biomass	0.49	Fuel
S6	0.26	Pyrogenic	0.61	Coal/biomass	0.52	Coal/biomass
S7	0.27	Pyrogenic	0.58	Coal/biomass	0.52	Coal/biomass
S9	0.36	Pyrogenic	0.53	Coal/biomass	0.49	Fuel

An – anthracene
Phe – Phenantrene
Fl – fluoranthene
Py – pyrene
Ip – ideno(1,2,3-cd)pyrene
Bghip – Benzo(ghi)perylene

Pollution sources in Krasnoe

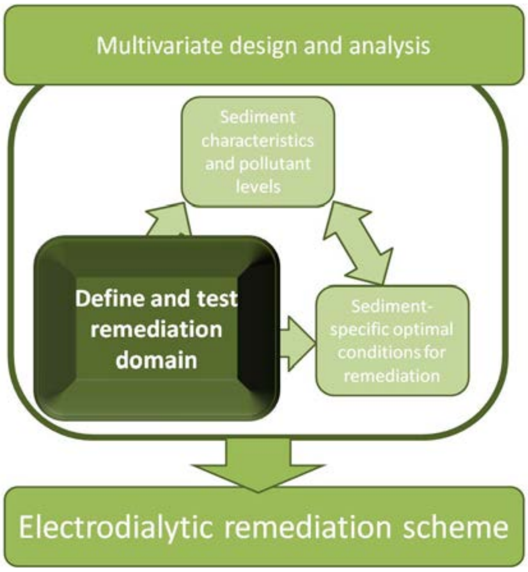
The main source of oil pollution at the landplot was the previous discharge of oil polluted water. PAH ratio calculations (***Paper IX***) revealed that the PAH pollution was related to the oil pollution. Other pollution sources in the area include boat traffic in the river, this possible contribution is however insignificant compared to the oil pollution.

4.1.5 Relevant sediment factors for EDR experiments

Sediments H1, H2 and S6 were found to have higher contents of carbonate and coarser materials (> 2 mm) compared to sediments H3-H5, S1, S3 and S5 (Figure 8). For EDR of heavy metals from the first three sediments, this might entail the use of desorbing agents and possible removal of gravel prior to treatment. For the other harbour sediments removal of heavy metals during EDR could potentially occur without the addition of desorbing agents or pre-treatment. For this reason, sediments S1, S3, H1 and H3-H5 were chosen to proceed with in the EDR experiments. These sediments were in addition clustered in the same quadrant of the PCA plot of sediment properties, potentially displaying such similarities, despite different geographical origin, that similar settings of EDR could be applied to achieve equivalent clean-up levels. The soils K1 and K2 have a higher content of sand fractions compared to the harbour sediments which may make removal of heavy metals more challenging. These were however not the target for remediation and the main focus is removal of oil and PAH. Due to the higher pollutant concentrations in soil K1, this was chosen to proceed with in the EDR experiments.

Assessment of the pollution in both harbours showed anthropogenic sources of Cd, Cu, Hg, Pb, Zn, PAH, PCB and TBT, and are hence the focus substances to remove during EDR. The soil from Krasnoe had high concentrations of oil and PAH and these remain the target for EDR. In this porject, the objectives of remediation have been to reach concentrations equivalent to background levels. In practice, this is seldom the goal, and removal efficiencies are often determined by site-specific conditions, including assessments of risk of exposure to residual pollution. However, the purpose in this project has been to showcase possibilities in the method, so that in the future, limits are set by decision makers and stakeholders and not due to limitations in the method.

4.2 Defining and testing experimental domains for EDR



In order to develop EDR and to prepare sediment-specific remediation strategies it is imperative to obtain a better understanding of the experimental space, which is the topic of this chapter. The first step is a preliminary evaluation of experimental variables in order to select relevant experimental domains for further EDR investigations (*4.2.1*). This is followed by assessment of variable importance during EDR over the studied experimental domains, based on ***Papers II-IX*** (*4.2.2*). Subsequently, a preliminary assessment of correlations between variables is given (*4.2.3*) and in the final section (*4.2.4*), important variables for EDR in the studied experimental domains are summarised.

4.2.1 Selecting relevant experimental domains

Prior to initiating the investigations of the environmental space for EDR, a preliminary evaluation in order to identify relevant variables was carried out. The evaluation included assessments of possible/proven effects of the variables on EDR, whether the variable was relevant to pursue and the approximate range of experimental settings. This was initially based on available information on EDR/EKR at the time of planning the experimental designs and in addition on findings of ***Paper II***, in which a PLS model of previous EDR studies of harbour sediments was calculated to determine variable importance of already tested variables. Table 7 and Table 8 summarise the initial evaluations of the discrete and continuous variables, respectively.

These evaluations were subsequently used for selection of relevant domains in the experimental space to be investigated and were revised when results from experiments were available. An update on important variables found in the PhD project is summarised in section *4.2.4*. Based on the evaluation, a total of six studies were conducted all employing fractional factorial designs (***Papers III-IX***) and encompassed testing the influence of the following variables; *current density*, *remediation time*, *stirring rate*, *L/S ratio*, *temperature*, *EDR cell designs*, *sediment*, *suspension liquid* and *light/no light*.

Table 7: Initial evaluation of experimental space, discrete variables

Variable	Preliminary assessment of variable	Constant in experiments	Experimental settings – range
Discrete variables			
EDR cell/stack	***Paper II*** indicated influence of cell design (the 3- and 5-compartment cells), depending on the heavy metal. The supply of H^+ is different in the 2- and 3 compartment cells and may influence acidification and transport of heavy metals, and the degradation of organic pollutants. The stack is based on the 3-compartment cell design; however the distance between membranes is smaller and it is capable of treating larger volumes.		2-compartment 3-compartment EDR stack
Sediment	Type of sediment has previously been shown to influence EDR [33] and ***Paper II*** indicated high influence of sediment properties; sediments H3-H5, S1 and S3 were clustered in the PCA plot of sediment properties (chapter 4.1.3) indicating similar variation in characteristics. Consequently, same settings of EDR may result in similar removal patterns of pollutants from the sediments.		Hammerfest (H1, H3, H4, H5) Sisimiut (S1, S3) Krasnoe (K1)
Suspension liquid	The influence of tap water rather than distilled water as suspension liquid has not been tested, but may be interesting for practical reasons. The influence may be expected to be low, but higher initial ionic concentrations of tap water may influence the immediate transport processes in EDR.		Distilled water Tap water
Light	Influence of light has not been previously investigated and it may be relevant for the Arctic region. A limited influence on removal of heavy metals is expected; however it may influence degradation of organic pollutants.		Light/no light
Desorbing agents	The use of desorbing agents and/or surfactants may increase the efficiency of EDR for both heavy metals and organic pollutants [29, 66] but it was not the focus of the research. In addition the sediments selected for EDR did not appear to need desorbing agents to enhance removal (chapter 4.1.5)	No use of desorbing agent/surfactant	
Electrodes	The influence of using different inert electrodes has not been determined and is not assessed as relevant for these investigations but may be appropriate for scaling-up efforts.	MMO coated titanium	
Electrolyte	Use of electrolyte in EDR has not been tested; due to the use of ion-exchange membranes, it is expected to have limited influence and is not tested.	0.01 M $NaNO_3$	
Ion-exchange membranes	A previous study indicated that transfer numbers of ion-exchange membranes were similar [152] and possible influence on EDR efficiency is not the focus.	Ionics	
Pumps	The type of pumps for circulation of electrolyte has not been tested, it is expected to have limited influence and it is not relevant for the project.	Plastomec PO5	
Tubes/pipes	The type of pipes used for circulation of electrolyte has not been tested; it is expected to have limited influence and is not relevant for the investigations.	PVC tubes	
Power supply	The type of power supply has not been tested and is not relevant.	E3612A	
Stirrer	The influence of the type of stirrer has not been investigated; it is expected to have limited influence and it is not relevant for the present investigations.	RW11 Basic lab-egg	

Table 8: Preliminary evaluation of experimental space, continuous variables

Variable	Preliminary assessment of variable	Constant in experiments	Experimental settings – range
Continuous variables			
Flow rate electrolyte	Circulation of electrolytes ensures low polarisation at the electrodes [40]. The influence of flow rate has not been investigated and is not relevant in the project, but may be interesting in future scaling-up efforts.	30 mL/min	
Current density	Current density has been shown to be an important variable for EDR of heavy metals, confirmed by findings in ***Paper II***. The current density should be kept between the limiting current densities of the anion- and cation-exchange membranes to ensure acidification and prevent OH^- from being introduced into the sediment suspension [39]. Current densities of up to 1.4 mA/cm^2 have been reported for EDR of harbour sediments, the EDR efficiency however decreasing above 1.0 mA/cm^2 [26]. Applying current in EKR has been shown to increase removal of THC [153].		0.04-1.0 mA/cm^2
Voltage	Voltage across the cell is correlated to current density and resistance across the cell. High voltages may distort EDR.	The voltage is not controlled.	
Stirring rate	Stirring rate may influence the removal of some heavy metals, depending on how they are bound in the sediment [34]. ***Paper II*** indicated low influence; however for some of the metals (Cu, Pb) there appeared to be a moderate influence. Influence on organic pollutants has not been tested, but may increase bioavailability.		1-1300 rpm
Flow rate suspension stack	Flow rate of the sediment suspension in the stack may influence efficiency of EDR but is not tested. Relevant for future optimisation of the stack.	5 L/min	
L/S ratio	L/S ratio may influence EDR efficiency depending on the heavy metal to be removed [33]; findings in ***Paper II*** indicated moderate influence. The influence on organic pollutants has not been tested.		2-12 mL/g
Temperature	Preliminary experiments indicate that removal efficiencies of heavy metals improve at higher temperatures [57]. Influence of temperature on EDR of organic pollutants has not been tested. Influence of low temperatures is relevant for regions located in the Arctic.		4-20 ^{o}C
Remediation time	Remediation time has been shown to be an important parameter for EDR of heavy metals and it was amongst the most important variables in ***Paper II***.		48-672 h
pH electrolyte	pH in the electrolyte may affect the transport across the ion-exchange membranes, but has not been tested and is not the focus in the research.	The pH is controlled by continuously adjusting the pH to 2.	
pH suspension	pH of the suspension liquid influences desorption of metals and availability of microorganisms for degradation of organic pollutants. Controlling the pH is not the focus of the research.	The pH is not controlled in the experiments.	

4.2.2 Variable importance

The assessment of variable importance was carried out by calculating PLS models for the different experimental designs employed and tools used for the evaluation were mainly VIP plots and coefficient plots. In the following the main findings for the influence of variables on EDR of heavy metals, PAH, PCB, THC and TBT are presented. It is however important to stress that the data collected is more extensive for the heavy metals than the other pollutants and for this reason some relevant, general findings regarding heavy metals will be reviewed first.

The first experimental design conducted (***Paper III***) revealed that substituting *time* with *time after acidification* improved the stability of the PLS models and this was attributed to the first set of models covering several phases of EDR, i.e. the acidification phase, the fast removal phase and the slow removal phase. Prior to the soil reaching the pH threshold value, at which desorption of a given metal begins, limited removal of the metal occurs; consequently the experiment duration time may include significantly different rates of removal resulting in instable models. In calcareous soils this may be more pronounced since the acidification time is longer. Since including the acidification phase apparently distorted the models, it was henceforth decided to proceed with *time after acidification* as an experimental design parameter (descriptor). The specific pH threshold value at which desorption begins depends on the metal, Ca will for instance be desorbed from the sediment at higher pH values than the heavy metals. Based on the desorption patterns for the heavy metals targeted for remediation (Cu, Pb and Zn), acidification was defined as the point at which the sediment suspensions had reached pH 4. This was a compromise of pH desorption levels for the three heavy metals in the sediments studied (***Paper VIII*** Figure 3); significant desorption of Zn was for instance observed to occur at higher pH; however this generally did not appear to affect model reliability and stability significantly.

An analysis of the influence of selected variables on the acidification time was carried out in ***Paper VIII*** based on the experiments conducted in the 3-compartment cell. This was done by calculating a PLS model in which the X-matrix consisted of *current density*, *stirring rate*, *L/S ratio*, *suspension liquid*, *light/no light* and the *sediment properties* and the acidification time was the response. It was revealed that the type of sediment was most important, suggesting that although some similarities in the sediment properties were originally observed (Figure 8), differences between the sediments significantly affected EDR. The influence of sediment properties is dealt with in chapter 4.4.1 and will not be elaborated upon here. Whilst the sediment properties had the highest influence on the acidification time, some of the experimental variables were also revealed to have a significant impact. The VIP order was *stirring rate* (1.3) > *current density* (0.90) > *L/S ratio* (0.8) > *suspension liquid* (0.7) >> *light* (0.1).

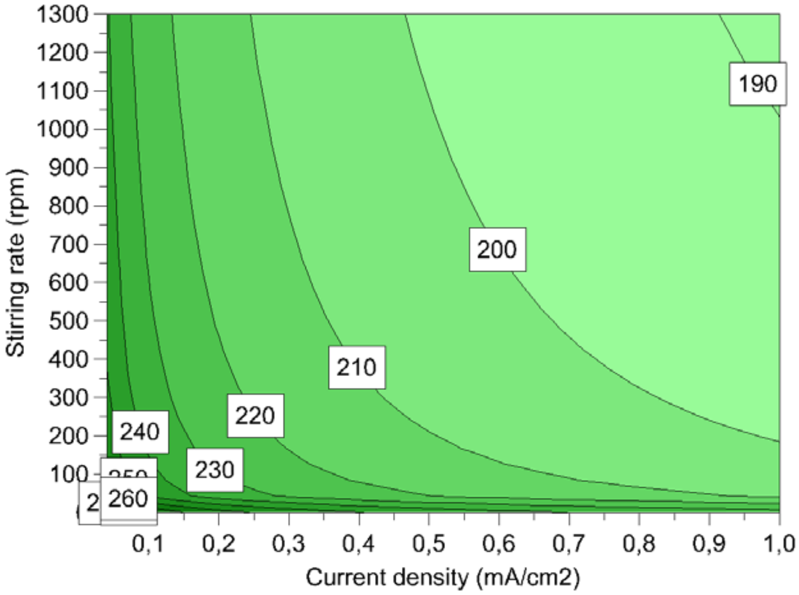


Figure 12: Acidification time (h) as a function of current density and stirring rate based on 47 experiments conducted in the 3-compartment cell. The following experimental variables were fixed: L/S (2 mL/g); suspension liquid (distilled water), light. Sediment properties were set at the centre values.

A contour plot of the acidification time as a function of *current density* and *stirring rate* (Figure 12) illustrates that even a small increase in the *stirring rate* at the minimum setting (1 rpm) had a high effect on reducing the acidification time. Experiments modelled for the *stirring rate* at 1 rpm were in fact not continuously stirred, but stirred once a day and the results hence suggest that continuous stirring of the sediment suspension is important for distribution of H^+ as well as for reducing the transport of H^+ directly to the cathode without affecting the sediment suspension. At continuous stirring (in the modelled experiments 100-1300 rpm), the other experimental variables will have relative higher impact, accordingly *current density*, *L/S ratio* and *suspension liquid* are also important parameters for the acidification time.

Current density

Current density is obviously vital for EDR and the importance in relation to other parameters was studied in ***Papers II-IX***. During the experiments an operational limit of the *current density* was observed (threshold value at which the maximum voltage in the power supply was reached) depending on the sediment at hand, probably due to depletion of ions in solution at the higher current densities. It was hence decided to run experiments under the operational limit and for the harbour sediments it was possible to operate up to 0.52-1.0 mA/cm^2 depending on the specific sediment. For the soil from Krasnoe, it was however not possible to exceed a *current density* of 0.1 mA/cm^2 most likely related to the high concentrations of non/low-conductive oil.

Current density was found to be amongst the most important variables for EDR and was shown to be positively correlated with the removal of heavy metals. Water splitting at the cation exchange membrane did not appear to occur at the highest current densities studied since no changes in voltages during EDR were observed. Proton leakage may have prevented or counteracted water splitting at the cation exchange membrane.

Current density was not as important for the removal of PAH, PCB, TBT and THC within the studied domain. Previous EKR studies found that applying electric current to soil increased removal of organic pollutants attributed to increased availability of pollutants for mobilisation and/or degradation [85, 87, 88, 153]. These findings were however based on stationary set-ups, meaning that the conditions are not directly comparable and may be the reason that applying current as opposed to not applying a current in ***Paper IX*** was found to have limited influence on removal of PAH and THC. In ***Paper VII*** the intensity of current was tested and found to have a low influence on the removal of PCB and TBT, while applying a *current density* of high intensity negatively influenced the removal of PAH. This was attributed to the faster acidification inhibiting the microbial community in the sediment suspension. The reason that the same trend was not observed for PCB and TBT was that chemical exchange and degradation were assessed to be induced by the acidification, thus being more important processes than bioremediation.

Time after acidification

The influence of *time after acidification* was studied in ***Papers III-IX*** and was amongst the most important variables for EDR of heavy metals, which is in line with previous findings [26, 33]. For the organic contaminants and TBT, the influence of *time* was not as significant for the EDR efficiency. In fact the *remediation time* was shown to have limited influence on the removal of PAH and THC. The first experiments were terminated after 48 hours when pH in the sediment suspension had reached a value of 4, accordingly the low influence of time may indicate that most of the degradation had taken place prior to this, which is in line with findings of a study of EKR coupled with bioremediation in which an initial fast degradation rate was followed by slower degradation of PAH [87].The influence of *time* was moderate on the removal of TBT and PCB indicating that removal from the sediment occurred throughout the entire remediation time, supporting the indication that other processes apart from bioremediation were significant for the removal.

Stirring rate

The influence of *stirring rate* in the sediment suspension was investigated in ***Papers III, V, VII and IX*** and was found to generally have a moderate impact on the electrodialytic removal of heavy metals; the influence however depending on the given heavy metal. Higher stirring appeared to have a slightly greater effect on Cu and Pb than on Zn, in line with findings in a previous EDR study [34], ascribed to how the metals are bound in the sediment. Larger amounts of Cu and Pb were bound in the oxidisable fractions of the sediments studied in the PhD and a higher *stirring rate* may have increased oxidation of the sediment thereby increasing the release of metals bound in the oxidisable fraction. The effect of *stirring rate* was also found to be relatively higher in the 2-compartment than the 3-compartment cell (***Paper V***), which was also attributed to higher oxidation of the sediment due to the direct introduction of oxygen via the electrolysis reaction at the anode.

The *stirring rate* had a strong influence on the removal of PCB, TBT and THC, a higher *stirring rate* increasing the removal efficiencies which may be related to the increasing availability of the pollutants for mobilisation, biodegradation and chemical degradation. The optimal setting of the *stirring rate* for EDR of PAH was more ambiguous. In ***Paper IX*** results indicated that a high *stirring rate* increased the removal, while a low *stirring rate* was observed to increase the removal of PAH for the experiments reported in ***Paper VII***. This opposite trend can be related to the difference in acidification of the soil/sediment in the two studies. In the first study, decrease in pH of the soil suspension was not observed, attributed to the high content of oil and the *stirring rate* hence increased the bioavailability without inhibiting the original microbial community. In the second study, acidification occurred, which may have inhibited bioremediation and a lower *stirring rate* may have decreased the effect of acidification.

L/S ratio

The influence of the *L/S ratio* of the sediment suspension on EDR was investigated in ***Papers III, V, VII and IX*** and was found to moderately affect the removal of heavy metals during EDR. The influence depended on the heavy metal, the VIP values were generally higher for Pb and Zn than for Cu, ascribed to relatively more Pb and Zn than Cu bound in the exchangeable fraction. The availability of heavy metals for cation exchange and acid solubilisation is likely to increase with increasing *L/S ratio*.

The *L/S ratio* had a low influence on the removal of PCB and a moderate importance for the removal of PAH, TBT and THC. A low setting increased the removal indicating that the availability of the three pollutants did not increase when using an *L/S ratio* of 4 ml/g as opposed to 2 ml/g (***Papers VII and IX***).

Temperature

The influence of *temperature* was investigated in one study, summarised in ***Paper VII*** and was shown to have a moderate effect on the removal of PAH and a high impact on the removal of heavy metals, TBT and PCB. The fact that high temperatures (20^{o}C) increased the removal efficiencies of heavy metals and TBT, was suggested to be related to increasing desorption and oxidation of the sediment with increasing *temperature*. Lower temperatures (4^{o}C) increased the degradation of PAH and PCB which may be due to the natural microbial communities not adapted to the higher temperatures. Since the study did not include centre point experiments, further investigations are needed to confirm the findings.

EDR cell design

The efficiency of EDR was tested in three EDR cell designs; a 2-compartment cell, a 3-compartment cell and a stack (Figure 13). The latter was able to treat approximately a 10-fold higher quantity of sediment than the cell designs. PLS models indicated that the three set-ups were different, entailing different remediation schemes for each set-up. The stack had the poorest EDR efficiency and needed a magnitude higher electric charge per mass sediment to achieve acidification and comparable removal efficiencies to those in the 2- and 3-compartment cell designs.

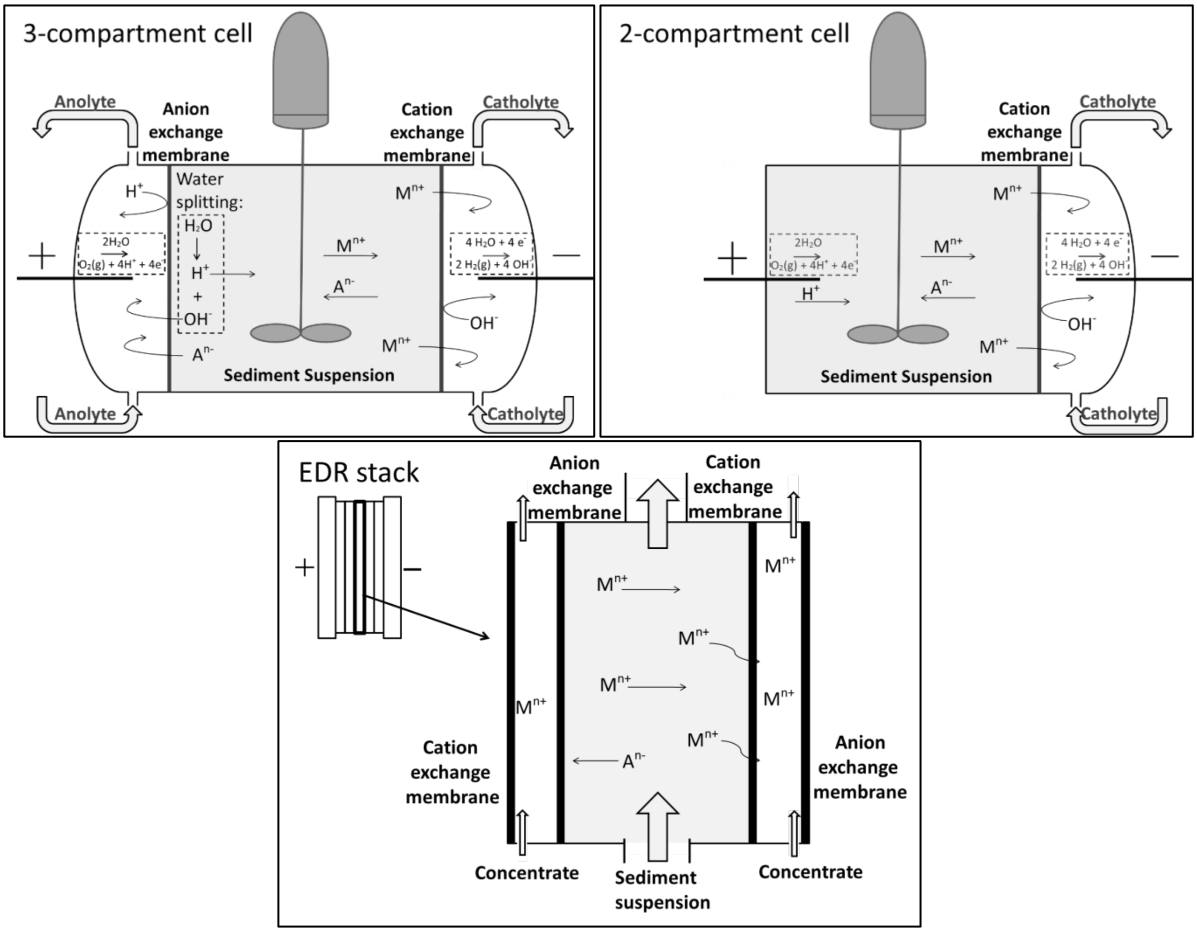


Figure 13: The EDR cell and stack designs; 3-compartment cell, 2-compartment cell and stack.

In the 2-compartment cell, protons and oxygen were directly introduced into the sediment suspension via electrolysis reactions at the anode and in fact the acidification time was found to be lower than in the 3-compartment cell. The EDR efficiency was generally higher in the 2-compartment cell with lower energy consumption levels and higher removal efficiencies. However higher removal of non-targeted elements in the sediment was also observed, potentially negatively affecting the sediment. Although the EDR efficiency was not as good in the 3-compartment cell, it was possible to remove heavy metals to the desired clean-up levels while removing lower amounts of naturally occurring metals, however at higher energy consumption levels.

Sediment

The influence of sediment was investigated in ***Papers III and VII*** and encompassed all three set-ups. It was shown that sediment highly influenced the removal of all the pollutants tested, underlining that remediation requires different strategies based on the specific sediment properties. A more detailed analysis of the influence of sediment properties on EDR based on results of sediments H1, H3, H4, H5, S3 and S5 is presented in ***Paper VIII*** and in chapter 4.4.1.

Suspension liquid

The influence of using tap water as opposed to distilled water as suspension liquid was presented in ***Papers III and V***. The effect was only tested on heavy metals and it was revealed that the type of suspension liquid had a moderate influence; the use of distilled water increased the removal efficiency and it was decided to proceed with using distilled water in later studies.

Light/no light

Experiments to assess the influence of *light* were undertaken in studies reported in ***Papers III, V, VII and IX*** and *light* was shown to have limited influence on removal of heavy metals and THC; and high influence on the removal of PAH, PCB and TBT, indicating that photolysis during EDR was important for degrading these three pollutants. Stirring and the period of midnight sun may have contributed to the influence by ensuring high, uniform exposure to light during these experiments.

4.2.3 Preliminary assessment of correlation between variables

Experiments were designed to determine significant variables and did not necessarily convey possible correlations between the experimental variables. Experiments conducted in the 3-compartment cell however encompass 47 experiments and included test of the sediments H1, H3, H4, H5, S1 and S3, and the variables *time after acidification*, *current density*, *stirring rate*, *L/S ratio*, *suspension liquid* and *light/no light* hence providing a large dataset from which trends regarding correlations between the variables may be retrieved. This analysis was briefly touched upon in ***Paper VIII*** and besides the experimental variables included sediment properties in the X-matrix in the PLS model, which was presently adjusted to include Cu, Pb and Zn in the Y-matrix since these are the heavy metals targeted for remediation. A loading plot of p_1 against p_2 reveals the contribution of the X-matrix parameters to the scores, t and since the PLS model ensures maximum correlation between the scores of the Y-matrix (u) and t, is also related to the responses and can hence illustrate how variables are correlated. In order to give equal weight to the parameters, the loading plot in Figure 14 has been scaled in relation to the X-matrix as well as the correlation.

The parameters plotted close to each other or opposite to each other with respect to the axis centre are correlated and parameters furthest from the axis centre have the biggest contribution to t. It is obvious from Figure 14 that the sediment properties are important for EDR efficiency and correlations between the different sediment parameters can be observed, for instance the clustering of Al, Fe, K, Mn, Cr and Ni, which were also correlated in the original sediments (chapter 4.1.4). The influence and correlations of sediment properties is undertaken in chapter 4.4.1 and will not be further elaborated on here.

Current density and *stirring rate* are located opposite each other with respect to the axis centre hence inversely correlated, implying that by employing a high *stirring rate*, the *current density* can be set at a lower intensity for reaching specified final concentrations of Cu, Pb and Zn and vice versa. Other correlations in parts of the model can be evaluated by regarding the contributions to each component. In the first component, p_1, *current density* and *L/S ratio* are for instance located opposite each other which may be related to the correlation previously observed in EDR studies [39], that the optimal *current density* for removal of heavy metals increases with higher quantities of sediment to treat (lower *L/S ratio*). In the second component, *stirring rate* and *L/S ratio* are oppositely located indicating that higher stirring is necessary for lower *L/S ratios* to obtain similar final concentrations.

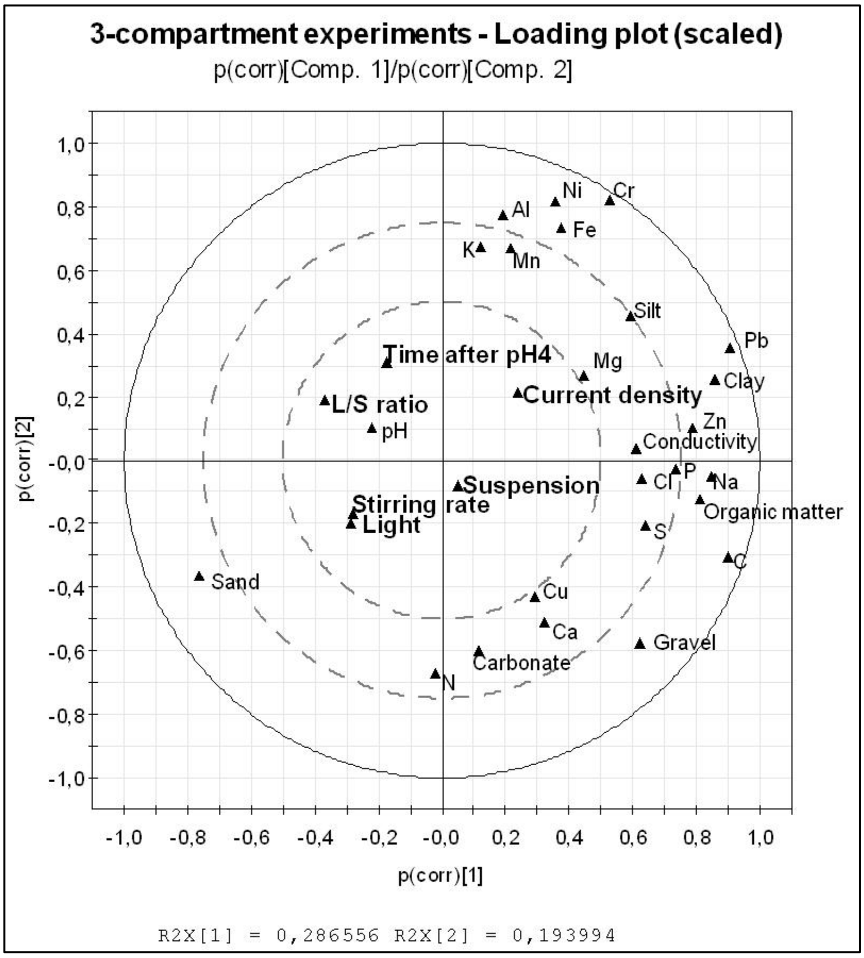


Figure 14: Loading plot (scaled) of X-variables (experimental variables and sediment properties) for the 3-compartment cell experiments encompassing the sediments H1, H3, H4, H5, S1 and S3 and a total of 47 experiments. Correlated variables are plotted close to each other or opposite each other with respect to the axis centre. Experimental variables are accentuated in bold.

Since the sediment properties have a large influence on the PLS model, it may be appropriate to assess correlations between experimental variables in EDR of specific sediment. As examples, the loading plots of experiments conducted in the 3-compartment cell of the H3 sediment and experiments conducted in the 2-compartment cell of the S3 sediment are given in Figure 15. For the H3 sediment *current density* and *time after acidification* are correlated, and *L/S ratio* and *stirring rate* may be correlated to a lesser degree (only correlation in the second component). For the S3 sediment, *current density* and *time after acidification* are correlated in the first component and oppositely correlated in the second component, which may be related to the part of the experimental domain for which increasing *current density* will not significantly increase the removal of heavy metals, e.g. in the slow removal phase.

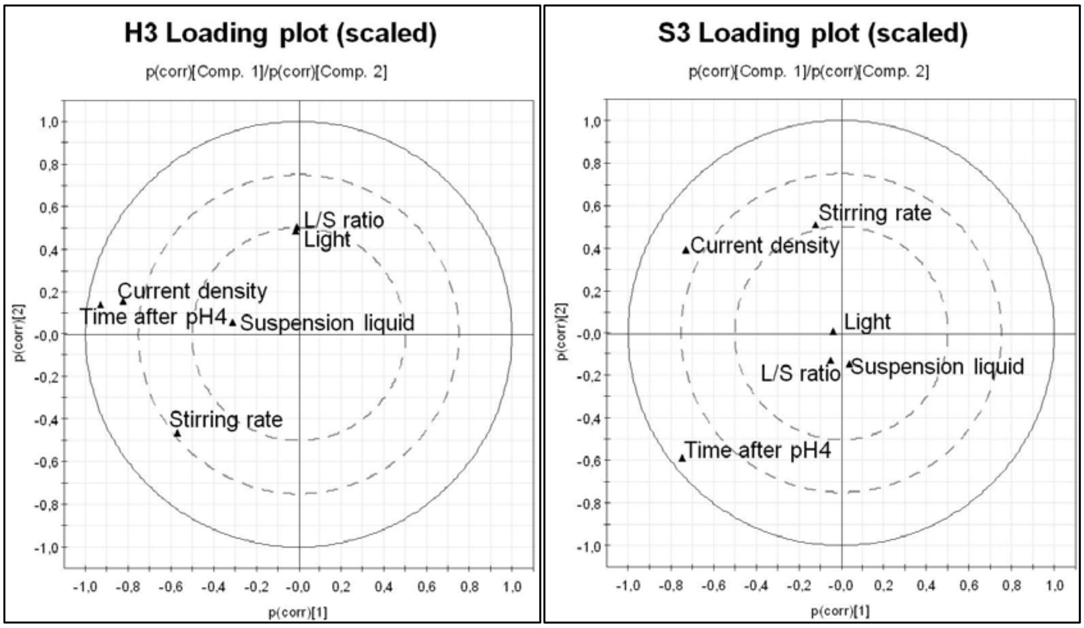


Figure 15: Loading plots (scaled) of variables of the experiments with H3 sediment (3-compartment cell) and the S3 sediment (2-compartment cell). Correlated variables are plotted close to each other or opposite each other with respect to the axis centre.

It is clear from the above examples that there are correlations between the experimental variables. The assessment was, however, preliminary and to obtain a better understanding of variable correlations, it appears essential to perform additional experiments of the significant variables to cover the important part(s) of the original experimental domain. In addition, separate assessments of each sediment and EDR cell design should be conducted. Such investigations may be relevant in connection with scaling-up for which the correlations may have practical implications for the site- and sediment-specific remediation strategies.

4.2.4 Important variables for sediment-specific EDR

The evaluation of variable importance provides a foundation for further developing and optimising EDR. For the sediments/soil from Hammerfest, Sisimiut and Krasnoe, the variable importance analysis based on a total of 100 experiments, revealed that remediation strategies should be based on the specific sediment and choice of EDR cell design. The best setting, whether it being the minimum or maximum value in the experimental domain, illustrated that achieving specific remediation goals will also depend on the pollutants targeted for remediation. A summary of the findings are given in Table 9, which provides a matrix for developing and improving the EDR efficiency within the experimental domains of the studied sediments/soil.

Table 9: Summary of variable importance based on 100 EDR experiments. 'High' conveys VIP values > 1, 'moderate' conveys VIP values 0.5-1.0 and 'low' conveys VIP values <0.5. For variables with moderate and high influences on EDR, the best settings for the variables are given (maximum or minimum).

	Heavy metals	TBT	PAH	PCB	THC
Current density	High[1,2,3,4,6] Max value	Low[6]	Moderate[5,6] Min value	Low[9]	Low[5]
Time after acidification	High[1,2,3,4,6] Max value	Moderate[6] Max value	Low[5,6]	Moderate[6] Max value	Low[5]
Stirring rate	Moderate[1,3,6] Max value	High[6] Max value	High[5,6] Max/min	High[6] Max value	High[5] Max value
L/S ratio	Moderate[1,3,6] Max value	Moderate[6] Max value	Moderate[5,6] Min value	Low[6]	Moderate[6] Low value
Temperature	High[6] Max value	High[6] Max value	High[6] Min value	High[6] Min value	Not tested
EDR cell/stack	High[2,3] Cell design	Not tested	Not tested	Not tested	Not tested
Sediment	High[4,9]	High[6]	High[6]	High[6]	Not tested
Suspension liquid	Moderate[1,3] Distilled water	Not tested	Not tested	Not tested	Not tested
Light	Low[1,3,6]	High[6] Light	High[6] Light	High[6] Light	Low[5]

1 Paper III

2 Paper IV

3 Paper V

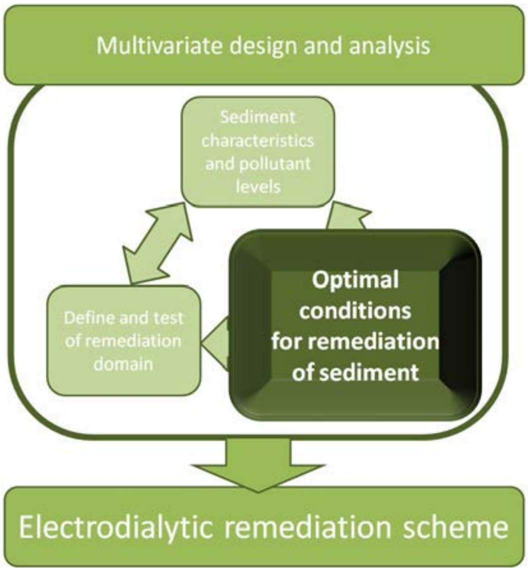
4 Paper VI

5 Paper VII

6 Paper IX

4.3 Optimal conditions for EDR of sediment

In order to determine the optimal settings for EDR of the polluted sediments studied, the PLS models were used to explore the experimental domain in relation to remediation objectives, based on the initial analysis of significant variables in the preceding chapter. Included in this chapter are also evaluations dedicated to highlighting some of the challenges related to exploring and developing optimal settings of EDR.



The findings in this chapter are mainly based on ***Papers III, V, VI and VII***. In the first section (*4.3.1*), the focus remains solely on the removal of pollutants by illustrating how PLS models have been used to find parts of the experimental domain in which simultaneous removal of pollutants have occurred and if not meeting the desired removal efficiencies, identifying starting points for further optimisation. Subsequently, in *4.3.2*, a case study, to illustrate how the PLS model, by adding more responses to the Y-matrix, can include other factors such as effect on sediment and energy consumption in the assessment of optimal settings, is presented. In the final section, *4.3.3*, challenges related to optimisation of EDR of harbour sediments are briefly highlighted.

4.3.1 Optimal conditions for removal of pollutants from sediments

Investigations of variable importance illustrated that specifying optimal settings for EDR depends on the sediment, the cell design used and which pollutant(s) to remove. Although remediation objectives are usually based on site-specific conditions, in the following they have been set to the OSPAR BAC concentrations, in practice a strict goal, nonetheless it will show the resources necessary to achieve high levels of remediation and will in addition increase possibilities for recycling of the sediment.

Three cases of evaluating the optimal settings for EDR of harbour sediments are presented; removal of heavy metals from the H3 sediment using the 3-compartment cell (based on ***Paper III***), removal of heavy metals from the S3 sediment using the 2-compartment cell (based on ***Paper V***) and removal of heavy metals, PCB and TBT from the H4 sediment using the 3-compartment cell (based on ***Paper VII***). It is stressed that some of the PLS models had low predictive powers, which may be due to too few experiments or the experimental domains studied. The models, however, especially considering the inhomogeneous sediment matrix, still provide approximate optimal settings in relation to the remediation objectives.

EDR of Hammerfest sediment (H3) – removal of heavy metals

The sediment sampled from H3 in Hammerfest, was polluted by Cu, Hg, Pb, Zn, PAH, PCB and TBT (Table 5, chapter 4.1.2). The first set of experiments (***Paper III***) focused on the removal of the heavy metals Cu, Pb and Zn. The PCA plot of sediments characteristics in Figure 8 indicated that the sediment contained more carbonate than other sediments (apart from H1 and H2); the content of carbonate was in fact 8 % which is higher than for the other sediments located in the same quadrant of the PCA plot with contents below 2%. Longer acidification times in comparison to these other sediments were also observed during EDR. Including the acidification time in the descriptor *time* resulted in PLS models with low predictive powers illustrating the importance of modelling the different EDR phases separately, when possible. The *time after acidification* was subsequently used in the response models instead of the total time, and although this made the X-matrix slightly skewed, the resulting PLS model made it possible to retrieve general trends.

Adjusting the original PLS model from ***Paper III*** by focusing on the targeted heavy metals, i.e. including the final concentrations of Cu, Pb and Zn in the response matrix resulted in a model with a correlation factor, R2Y, of 0.74 and a predictive power, Q2, of 0.50. The PLS model included the 15 experiments that had been conducted in the 3-compartment cell. The original PLS model (***Paper III***) was used to evaluate the influence of six variables of which the most significant were found to be *current density* and *remediation time*. The evaluation of optimal settings was therefore based on different settings of these two variables and made by using contour plots of the concentrations of the three heavy metals as function of *time after acidification* and *current density* (Figure 16). The other variables were fixed in the contour plots and were based on evaluations of the PLS model. *Stirring rate* and *suspension liquid* had moderate influence on EDR and were fixed at their best settings in the experimental domain. The *L/S ratio* also had a moderate influence with the maximum value being the optimal setting; however since operating with low *L/S ratios* treated four times the quantity of sediment compared to the maximum values, the value was fixed at the minimum value. *Light* did not influence EDR and was set to *light* in the contour plots.

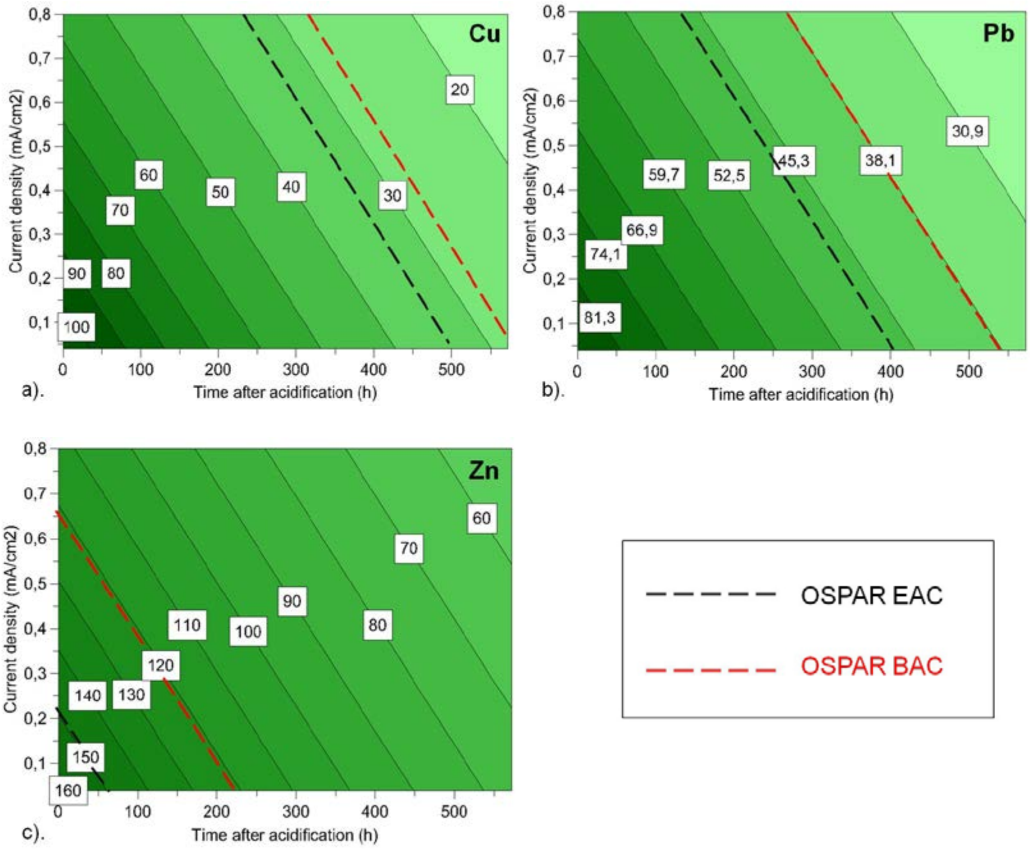


Figure 16: Concentrations (mg/kg dry matter) of a). Cu, b). Pb and c). Zn as function of time after acidification and current density for H3 experiments conducted in the 3-compartment cell. Fixed variables: stirring rate 1300 rpm; L/S ratio 2 ml/g; suspension liquid: distilled water, light.

It is clear from Figure 16 that concentrations of heavy metals in parts of the experimental domain studied are well below the concentrations of OSPAR BAC, as was intended with the experiments. The contour plots illustrate how simultaneous removal of several heavy metals can be accomplished and is thus a valuable tool for planning remediation in accordance with desired clean-up levels, time frames and/or financial limitations.

EDR of Sisimiut sediment (S3) – removal of heavy metals

The S3 sediment was sampled adjacent to the petrol station in Sisimiut harbour (Figure 6, chapter 4.1.1) and pollutants that exceeded the OSPAR EAC/ERL criteria were Cu, Pb, Zn, PAH, PCB and TBT (Table 5, chapter 4.1.2). The focus of this study, however, remained on the removal of heavy metals, thus Cu, Pb and Zn were the targeted pollutants for remediation and both the 2-compartment and3-compartment cell design were tested. The sediment had a low content of carbonate (1.7 %) and shorter acidification times than those for the H3 sediment in the 3-compartment cell were observed. The EDR efficiency was revealed to be better in the 2-compartment cell (***Paper V***) and accordingly evaluation of optimal settings for the S3 sediment was carried out for the 2-compartment cell.

The PLS model (***Paper V***) had a low predictive power, which was attributed to the experimental domain covering several phases of EDR, i.e. the fast removal phase, the slow removal phase and possibly also the stationary phase. The two most important variables for the removal of Cu, Pb and Zn were *time after acidification* and *current density*. *Stirring rate*, however, also had a significant influence on the removal, especially for Cu, ascribed to increased availability of H^+ and oxygen in the sediment suspension due to electrolysis reactions at the anode, the subsequent oxidation of the sediment hence releasing heavy metals bound in the oxidisable fraction of the sediment. The removal of Cu as a function of *stirring rate* and *current density* was illustrated in ***Paper V***; the present evaluation of the optimal settings fixed the *stirring rate* at the maximum setting and illustrated the removal of Cu, Pb and Zn as function of *current density* and *time after acidification* (Figure 17). Compared to ***Paper V***, the models have been updated with 5 extra experiments that were conducted in connection with the comparison of the 2-compartment cell, 3-compartment cell and stack in ***Paper IV*** (giving a total of 15 experiments), providing better overviews of parts of the experimental domains and adjusting the contour plots.

As was the case for the H3 sediment, final concentrations below OSPAR BAC were achieved for all the metals in parts of the experimental domain and once again Cu was the determining heavy metal for the remediation, as it was the most difficult to remove (Figure 17). The *stirring rate* appeared to be more important for Cu than for Pb and Zn, and further optimisation of especially Cu may be achieved by increasing the maximum setting of the *stirring rate*, there may, however, be an operational limit to doing so. In the contour plot for Zn, it is interesting to note that concentrations of Zn were below the OSPAR BAC criterion, 48 hours after the sediment had reached pH 4 and almost 90% of the original amount had already been desorbed from the sediment at this point. The OSPAR BAC criterion for Zn was also met if the fixed values were adjusted to the 'worst' settings. The concentration of Pb meets the criterion of OSPAR BAC in large parts of the experimental domain, but had a much lower initial concentration than Zn. For further understanding of Zn removal during EDR, experimental designs may have to include earlier starting points, e.g. at the time of the onset of Zn desorption.

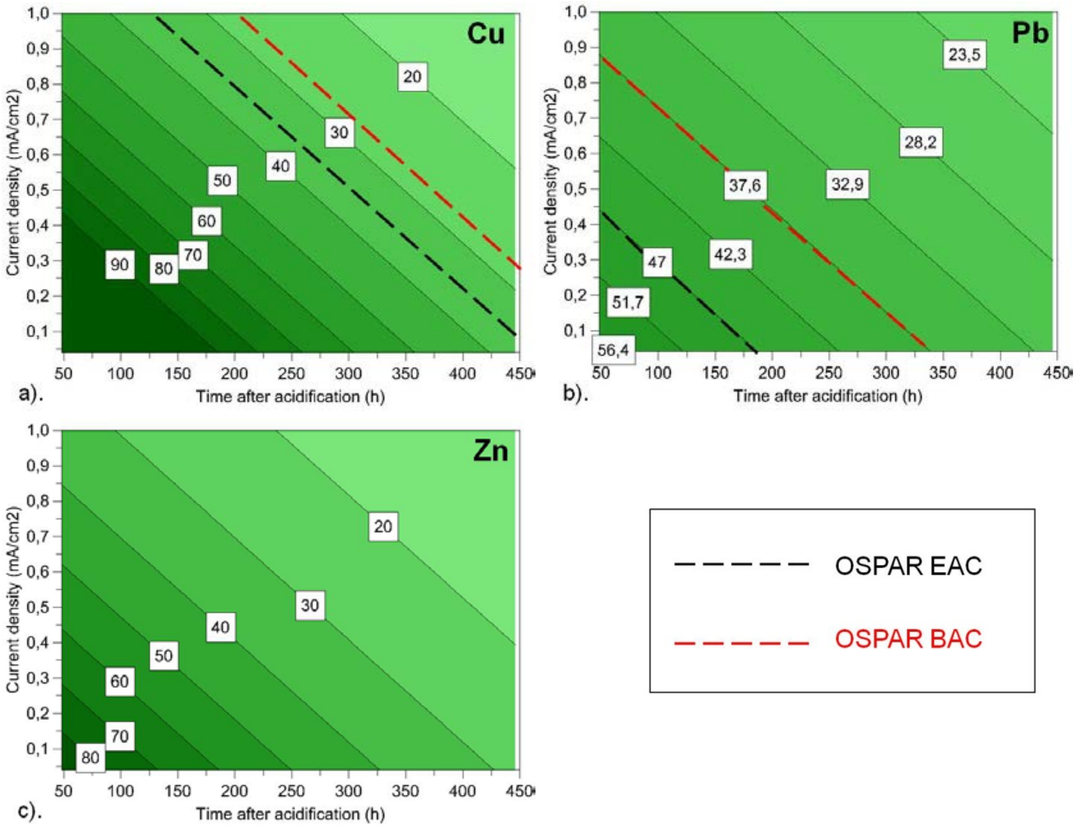


Figure 17: Concentrations (mg/kg dry matter) of a). Cu, b). Pb and c). Zn as function of time after acidification and current density for the S3 sediment experiments conducted in the 2-compartment cell. Fixed variables: stirring rate 1300 rpm; L/S ratio 2 ml/g; suspension liquid distilled water, light.

EDR of Hammerfest sediment (H4) – removal of heavy metal, PCB and TBT

The H4 sediment was sampled adjacent to a sewage discharge point in Hammerfest harbour and was found to be polluted with Cu, Hg, Pb, Zn, PAH, PCB and TBT (Table 5, chapter 4.1.2). The concentrations of the organic pollutants and TBT were very high and are classified in the highest class of the Norwegian sediment quality criteria and are accordingly considered hazardous. The sediment had a low content of carbonate (0.7 %), but had the highest content of organic matter (15%) of all the sediments studied. Eight EDR experiments were conducted in the 3-compartment cell testing the influence of the variables *current density*, *time after acidification*, *stirring rate*, *L/S ratio*, *temperature* and *light/no light* for removal of all the pollutants.

The final concentration of Zn met the criterion of OSPAR BAC in parts of the experimental domain; removal of the other pollutants proved more challenging and did not meet the OSPAR BAC criteria. The removal efficiencies of the H4 sediment were, in fact, lower than those observed for the S1 sediment investigated in the same study (***Paper VII***), which was located close to the H4 sediment in the PCA plot of sediment characteristics (Figure 8, chapter 4.1.3) underlining the need for developing different remediation strategies depending on the sediment properties. The highest removal efficiency of PAH in the H4 sediment was 16 %, resulting in a final concentration still considered hazardous. The degradation appeared to be inhibited by the low pH and it is assessed that other remediation technologies should be combined with EDR to remove PAH from the sediment. Although PCB and TBT had high removal efficiencies of up to 60 % and 50 %, respectively, the final concentrations were still high, i.e. equivalent to the second highest class in the Norwegian sediment quality criteria. The final concentrations of Cu and Pb were, based on the same criteria, considered moderately polluted, and still posing a risk to the marine environment.

In the following the experimental domain is explored to identify the settings for which the highest removal efficiencies were observed to assess the possibilities of optimising EDR with respect to simultaneous removal of Cu, Pb, Zn, PCB and TBT. It is possible to use contour plots of each pollutant to evaluate the experimental domain. However, since there are five pollutants that in addition were shown to have different responses to changes in variable settings (Table 9, chapter 4.2.4) this approach would be very arduous and time consuming. Instead it is possible to employ sweet spot plots, which are essentially several contour plots combined to a single plot illustrating parts of the experimental domain that meet specified removal efficiencies or final concentrations of pollutants. Presently, it is desirable to identify the parts of the experimental domain for which the final concentration of Zn meet the OSPAR BAC; Cu and Pb meet the criteria for moderate pollution and PCB and TBT have high removal efficiencies (>40 %).

Analysis of variable importance (***Paper VII***) revealed that *current density*, *time after acidification*, *temperature* and *stirring rate* heavily influenced the removal of Cu, Pb and Zn. The strong influence of *temperature* and *stirring rate* was attributed to how the metals were bound in the sediment. For PCB and TBT the variables with greatest influence on the removal were *temperature*, *stirring rate* and *light*. In addition to differences in variable importance, the best settings (max/min value of the experimental variables) also varied depending on the pollutant and for some of the variables (e.g. *stirring rate*, *temperature*) opposite settings were optimal for different pollutants (Table 9, chapter 4.2.4). Two sweet spot plots were subsequently made to explore the different parts of the experimental domain in relation to the significant variables (Figure 18). The first sweet spot plot is a function of *time after acidification* and *current density* with the other variables fixed at their optimal settings according to heavy metal removal, apart from the *L/S ratio*, which was set at the low value to maximise the amount of sediment treated per experiment. As is evident in the sweet spot plot, simultaneous removal of the five pollutants is possible and the highest removal efficiencies can be achieved by operating at moderate *current densities* and long *remediation times*.

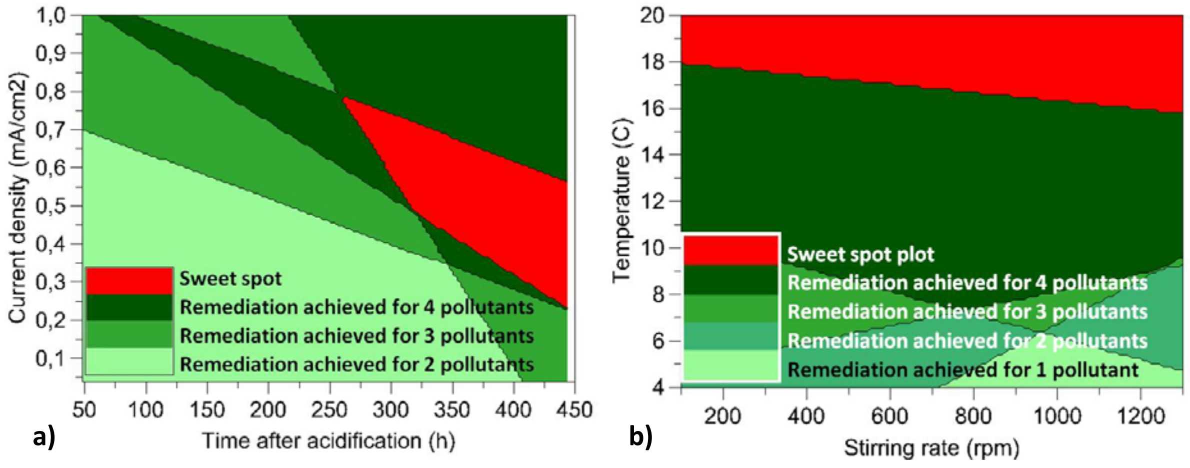


Figure 18: Sweet spot plot for simultaneous removal of Cu, Pb, Zn, PCB and TBT; a) as a function of time after acidification and current density for EDR of H4 (fixed values; Stirring rate 1300 rpm, L/S ratio 2mL/g, temperature 20°C and light); b). as a function of stirring rate and temperature (fixed values; Current density 0.52 mA/cm^2, time after acidification 444h, L/S ratio 2mL/g, light).

Since *temperature* and *stirring rate* were important variables for all pollutants, these two variables were varied in the second sweet spot plot. The effect of *temperature* was in addition interesting to evaluate since opposite settings were best for the heavy metals and PCB/TBT, respectively. The fixed values of *current density* (0.52 mA/cm^2) and *time after acidification* (444 h) were determined based on the first sweet spot plot. Although the removal efficiencies of PCB and TBT were revealed to have optimal settings at lower *temperatures*, the sweet spot plot illustrates that the simultaneous removal of all pollutants required the maximum setting of *temperature* (20^{o}C). The two sweet spot plots illustrate the complexity in the simultaneous removal of several different types of pollutants, but also demonstrate the possibilities to do so and by adjusting the experimental domain, e.g. decreasing the range of *current density* and increasing *time after acidification*, investigations into optimising the simultaneous removal can be commenced. It may also be an idea to include other variables such as acid resistant microorganisms, surfactants and/or nano particles to further enhance removal efficiencies of PCB and TBT, while providing the opportunity of including PAH in the simultaneous remedial action.

4.3.2 Optimal settings for several parameters in site-specific remediation

Above were given examples of how the experimental domain may be explored when removing pollutants is the sole objective in the remediation. Other parameters may, however, be of equal or greater importance in the decision-making of which relevant remediation technologies to proceed with and may include economic costs, practical issues and/or environmental impacts. In order for EDR to be economically competitive with other remediation technologies, the energy consumption by means of electricity used to mobilise and remove pollutants should preferably not be the highest contributor to the total cost, since for instance implementation costs are known to be high. Maintaining low energy consumption levels will also ensure low carbon-foot print, if electric energy is produced by fossil fuels. Another issue in EDR may be the simultaneous mobilisation of pollutants and naturally occurring metals; it may be desirable to limit the latter to maintain multiple recycling options of the sediment (e.g. by ensuring limited disturbance to the sediment) and in addition to prevent leaching of the metals. Inorganic Al is for instance known to be toxic to many aquatic species [154, 155] and Cd, Ni and Pb are included as priority substances in the EU water directive[156], accordingly in situations where these heavy metals are not considered pollutants, limited mobilisation of these are desired.

In ***Paper VI***, the evaluation of sediment-specific EDR in addition to removal efficiencies included energy consumption and mobilisation of naturally occurring metals. The sediment used in the study was the H5 sediment from Hammerfest and the concentrations of Cu and Pb exceeded the OSPAR EAC criteria making them the target pollutants for removal. Based on variable importance of other sediments (as summarised in Table 9, chapter 4.2.4), the experimental design just included *current density* and *time after acidification*; the other variables were kept at fixed values in the experiments. *Temperature* and *stirring rate* were fixed at their highest settings (20^{o}C, 1300 rpm), *L/S ratio* at a centre value (6 mL/g) and the *suspension liquid* was distilled water and the experiments were conducted in both the 2- and 3-compartment cell. Due to earlier findings, the EDR cell designs were considered as two systems and were accordingly modelled separately. In paper 6, different parts of the experimental domain were treated separately (***Paper VI***, Table 1); here all of the experiments are included in the models.

The PLS models (R2Y 0.60-0.65; Q2 0.27-0.45) reveal that in large parts of the experimental domain of both the 2- and 3-compartemnt cells, the final concentrations of Cu and Pb were below the OSPAR BAC criteria as illustrated by the sweet spot plots in Figure 19a and Figure 20a. Consequently, it appears relevant to evaluate surface response plots to assess the amount of naturally occurring metals removed over the experimental domain. In this analysis the major elements Al, Fe, K, Mg and Mn were included as were Cr and Ni, which had low concentrations (Table 5, chapter 4.1.2) and correlation to major elements (chapter 4.1.3) indicating natural origin. During EDR, metals will be mobilised, the focus is therefore on identifying parts of the experimental domain with limited mobilisation of the naturally occurring metals, e.g. amounts equivalent to those found in the more available fractions of the sediment. Accordingly, the criteria for assessing metal removal were set to amounts equivalent to those found in the exchangeable fractions. EDR has been shown to remove pollutants bound in all fractions of the sediment [35], consequently metals bound in other fractions than the exchangeable may be removed, the defined criteria, however, appear to be relevant for a preliminary assessment of metal mobilisation. For later scaling-up or development of site-specific EDR, the criteria can be adjusted to requirements for recycling of the sediment, e.g. leaching.

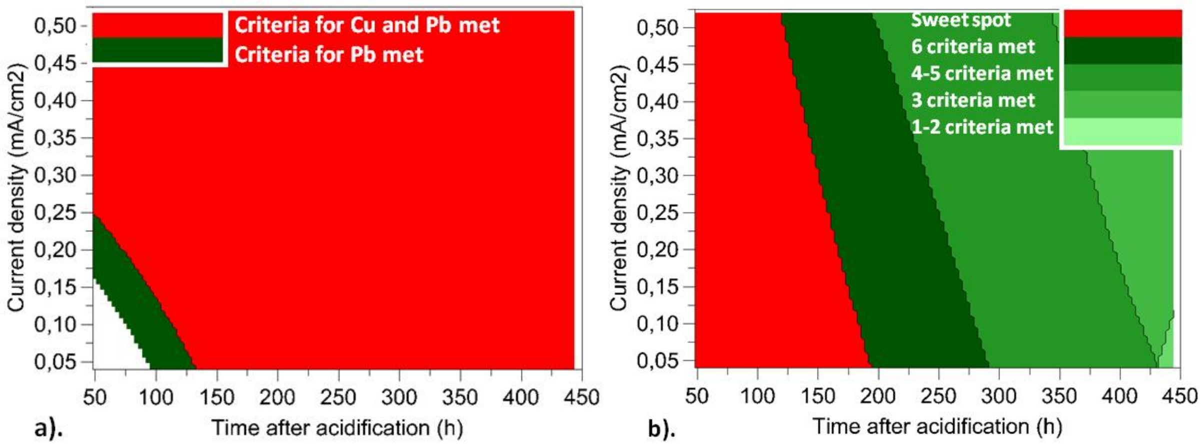


Figure 19: Sweet spot plots of results in the 2-compartment cell illustrating; a). parts of the experimental domain in which final concentrations of Cu and Pb are below the OSPAR BAC criteria; b). parts of the experimental domain for which removal of naturally occurring metals (Al, Fe, K, Mg, Mn, Cr and Ni) did not exceed amounts bound in the exchangeable fraction.

The sweet spot plots for the 2- and 3-compartment cell in Figure 19b and Figure 20b, respectively, demonstrate parts of the experimental domain in which removal of naturally occurring metals is limited to amounts equivalent to those found in the exchangeable fraction of the sediment. It is clear that relatively more removal of naturally occurring metals takes place in the 2-compartment cell compared to the 3-compartment cell, in line with the preliminary findings of ***Paper V***. By combining the sweet spot plots of pollutant and naturally occurring metal removal for each of the EDR cell designs, the experimental domain to operate within to meet remediation objectives and ensure low impact on the sediment can be visualised for the 2- and 3-compartment cell, respectively. From Figure 19 and Figure 20, it is obvious that it is possible to operate within a larger space of the experimental domain for the 3-compartent than for the 2-compartment cell; the time for remediation can however be reduced in the 2-compartemnt compared to the 3-compartment cell.

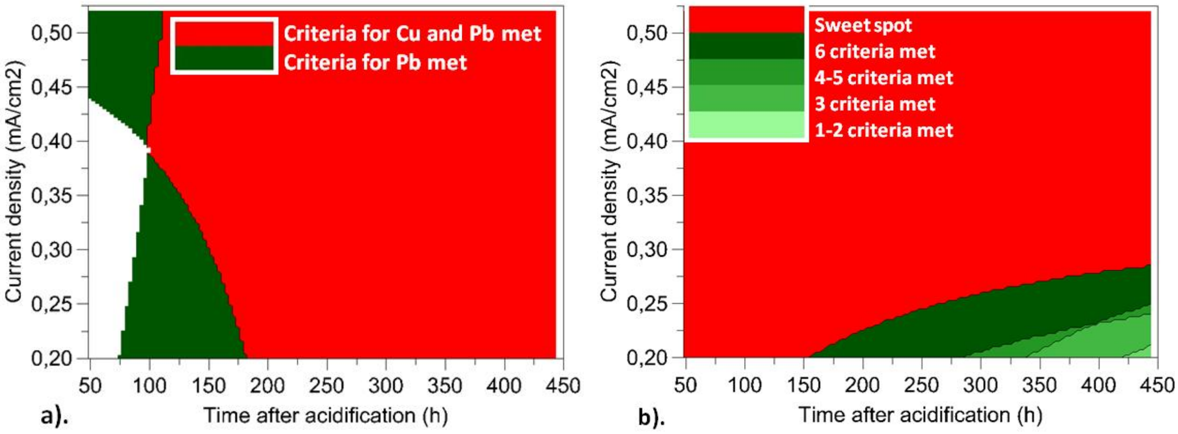


Figure 20: Sweet spot plots of results in the 3-compartment cell illustrating; a). parts of the experimental domain in which final concentrations of Cu and Pb are below the OSPAR BAC criteria; b). parts of the experimental domain for which removal of naturally occurring metals (Al, Fe, K, Mg, Mn, Cr and Ni) did not exceed amounts bound in the exchangeable fraction.

Another important aspect when assessing suitability of EDR as remediation technology is energy consumption, which can contribute in maintaining low operational expenses. From the energy consumption contour plots in Figure 21, it is obvious that the 2-compartment cell generally consumes less energy than the 3-compartment cell. Maintaining an energy consumption of 0.1 kWh/kg dry sediment results in a total energy cost of maximum 10€/m^3 wet sediment (calculations based on electricity price in Norway 0.13€/kWh; 40% dry weight; 1800kg/m^3), which is less than 10% of the total costs of other soil/sediment treatment methods in Norway, consequently other costs are the limiting factors for the relevance of the method.

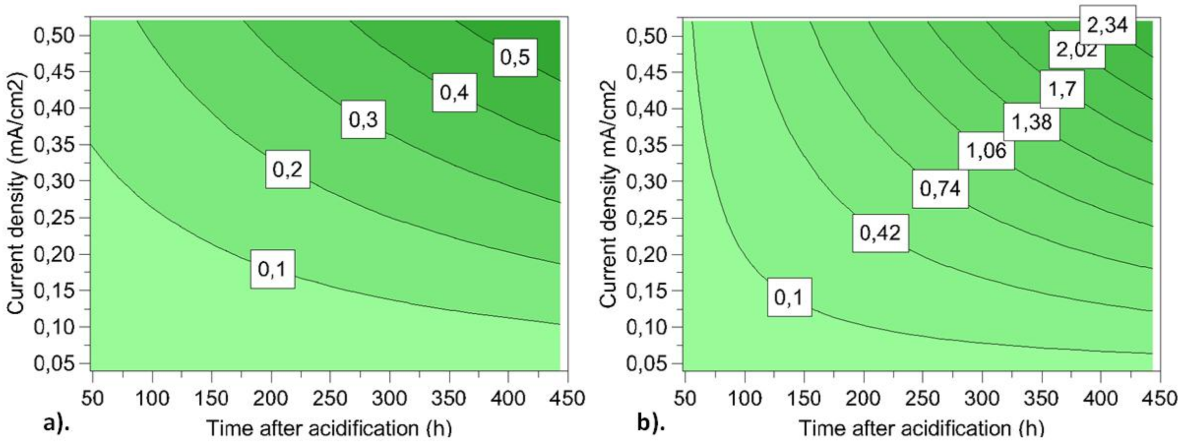


Figure 21: Energy consumption (kWh/kg dry sediment) as a function of time after acidification and current density in a) the 2-compartment cell and b) the 3-compartment cell.

It is worth noting that results in ***Paper VI*** revealed that all criteria for metal removal could be met while maintaining energy consumption below 0.05 kWh/kg dry sediment for low current densities and moderate remediation time, illustrating the importance of scrutinising relevant parts of the experimental domain.

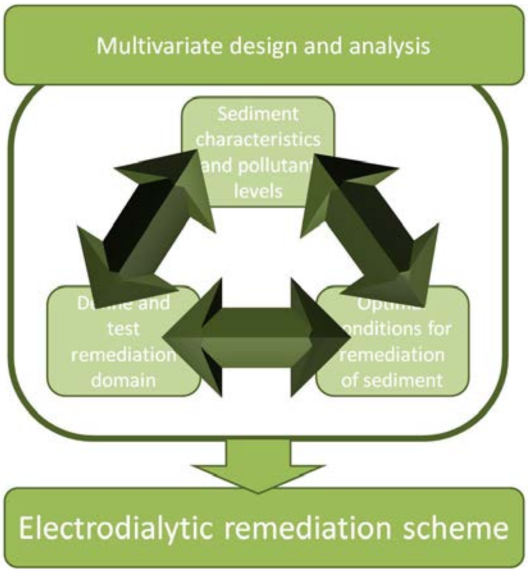
4.3.3 Optimisation of EDR of harbour sediments

The use of PLS models for examining surface response plots based on screening experiments to evaluate optimal settings for removal of heavy metals and naturally occurring metals and requirements for energy consumption has been illustrated in this chapter. Whilst the examples given were based on screening experiments, the models still provided good foundations for optimisation whether within the experimental domains studied or by adjusting/extending them in accordance with the remediation objectives. Including more experiments in the response plots will increase the predictability of the models and adjust the contour plots/sweet spot plots; this may however be tedious since remediation strategies for EDR should be sediment-specific and for practical purposes may not be necessary for sediments H3, S3 and H5 since these models at present provide overviews of the approximate experimental domains to use for meeting remediation objectives.

Asides being sediment-specific, remediation strategies should also take EDR cell design into consideration. For the H5 sediment, criteria for removal of heavy metals and naturally occurring metals as well as energy consumption may be met in both the 2-compartment and 3-compartment cell under specific settings of *current density* and *time after acidification* and the choice of EDR cell design will hence depend on local conditions, e.g. site-specific remediation objectives, time frame. If the energy consumption costs are low compared to other costs of the remediation, these may not be the deciding factor between choices of EDR cell design. In some situations a combination of the cell designs may be appropriate; for the H3 sediment with a higher content of carbonate, the acidification time can potentially be reduced by using the 2-compartment design in the initial phase and the 3-compartment cell design could subsequently be used to ensure limited removal of naturally occurring metals in the later phase of EDR.

4.4 Relations between sediment properties and aspects of EDR

This chapter is dedicated to exploring relations between sediment properties and the different aspects of developing EDR strategies by using multivariate analysis. The first section (*4.4.1*) presents findings related to the influence of sediment properties on EDR, followed by preliminary assessments of the impact, EDR has on the harbour sediments studied (*4.4.2*). Subsequently an evaluation of how PLS modelling can be used to assess experimental domains in relation to new sediment as well as the optimal settings, is conducted (*4.4.3*). In the final section important findings of the relations are related to site-specific conditions (*4.4.4*). All results presented are based on ***Paper VIII*** unless otherwise stated.



4.4.1 Influence of sediment on EDR

EDR experiments summarised in ***Papers IV*** and ***VIII*** revealed that sediment characteristics strongly influence the EDR efficiency. The comparison of sediments included the S3 sediment against the H5 sediment and the S1 sediment against the H4 sediment, located close to each other in the initial PCA plot of sediment characteristics (Figure 8, chapter 4.1.3), suggesting that differences in sediment properties even within the confined area observed in the PCA plot had a significant influence on EDR.

Properties that have previously been shown to affect EKR/EDR of soil or sediment include *CEC*, *carbonate*, *organic matter*, *Cl*, *grain size* and composition and concentration of *major elements* [39, 40, 157-161]. Sediment/soil characteristics and their influence on EDR/EKR have often been studied but not for several parameters simultaneously. Based on the fairly large number of EDR experiments (47) of five harbour sediments in the 3-compartment cell conducted during the PhD project, ***Paper VIII*** investigated the influence of several parameters at once to assess the relative influence of each property and the results may prove essential for future optimisation efforts for more efficient EDR of harbour sediments. The analysis also included experimental variables and since these were already discussed in chapter 4.2.2, they will presently only be touched upon briefly here. In the following a summary of the findings in with regards to the sediment properties is made, including new figures for visualising the results.

Influence of sediment on the acidification time

The type of sediment was revealed to strongly influence acidification (chapter 4.2.2), accordingly and prior to presenting the results of the PLS analysis of influence of sediment properties on the final concentrations of heavy metals, the results of the effect on the acidification time are summarised. The PLS model (R2Y 0.87, Q2 0.64) included the sediment properties of 5 harbour sediments (H1, H3, H4, H5, S1 and S3) and experimental variables in the X-matrix and the acidification time (pH4) as response. The VIP plot in ***Paper VIII*** revealed that the sediments in comparison with the experimental variables had the highest influence on the acidification time, which is also apparent in the weight plot (Figure 22).

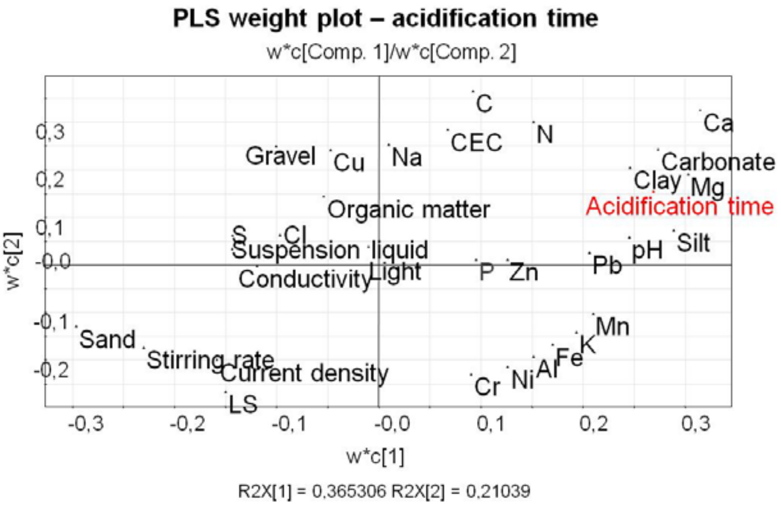


Figure 22: PLS model of acidification time – combined weight plot of X-weights and Y-weights. Correlated variables are plotted close or opposite to each other with respect to the axis centre.

In the weight plot, parameters located furthest from the axis centre have the greatest influence on the acidification time, i.e. *light* has the smallest and *Ca* the highest influence on the acidification time. Parameters located close to each other are positively correlated, while parameters located opposite each other with respect to the axis centre are inversely correlated; accordingly, *carbonate* and *stirring rate* are, for instance, inversely correlated, consequently high *carbonate* content and low *stirring rate* increases the acidification time. Sediment properties with the highest influence on the acidification time include *carbonate*, *pH*, *grain size distribution* and the elements *Ca*, *Mg* and *Pb* to a lesser degree. Not surprisingly, the buffer capacity in terms of *carbonate* and *pH* has a very strong influence on the acidification and the reason for the elements *Ca*, *Mg* and *Pb* also exhibiting great influence suggests that they are partly or substantially (*Ca*, *Mg*) present as carbonates in the sediment. The acidification time increases by high content of *silt/clay* and may be related to the correlation between *clay* and *carbonate*, and decreases with higher contents of *sand* and may suggest that the sand fractions originate from non-carbonaceous igneous rocks (Figure 22). The low influence of *organic matter* suggests that compared to *carbonate*, it does not substantially contribute to the buffer capacity of the sediments at these pH levels.

Influence of sediment properties on the different phases of EDR

The total PLS model included all 47 experiments conducted in the 3-compartment cell and revealed that concentrations and composition of metals/heavy metals in the sediment and grain size were the most influential on the final concentrations of Cu, Pb and Zn. In order to obtain an understanding of the difference in importance between the different phases of EDR, three more PLS models were calculated and each included the experiments that were assessed relevant for the specific EDR phase. The choice of which experiments to include in each model was based on the final pH of the sediment suspensions and the choice of threshold values of pH for each model was based on pH dependent desorption tests of the sediments (***Paper VIII***, Figure 3).

The first model (2a) included the experiments that had final pH above 3.6. According to the pH dependent desorption tests these experiments covered the lag phase of Cu and Pb, whilst also partly covering the fast removal phase of Zn.

The second model (2b) included the experiments that had final pH in the range 2-4. According to the pH dependent desorption tests this was approximately equivalent to covering most of the fast removal phases of Cu, Pb and Zn.

The third model (2c) included the experiments that had final pH below 2. According to the pH dependent desorption tests this was equivalent to the final parts of the fast removal phase, the slow removal phase and for some experiments possibly moving towards the stationary phase.

It is important to note that the sediment properties may present a skewed X-matrix, even if they according to the PCA plot of the initial sediment characteristics afford some spread in properties in one quadrant of the plot. In addition, the models were based on initial properties of the sediment and not possible changes during EDR, e.g. removal of carbonate or oxidation of organic matter. Despite these factors, the models provide indications of changes in relative importance of the sediment properties in the different phases of EDR. Individual models of the focus heavy metals, Cu, Pb and Zn, were presented in ***Paper VIII***. These results are supplemented with results of including all three heavy metals in the PLS model, in the following. Figure 23 summarises the VIP values and Figure 24 illustrates the combined weight plots of the different phases of EDR.

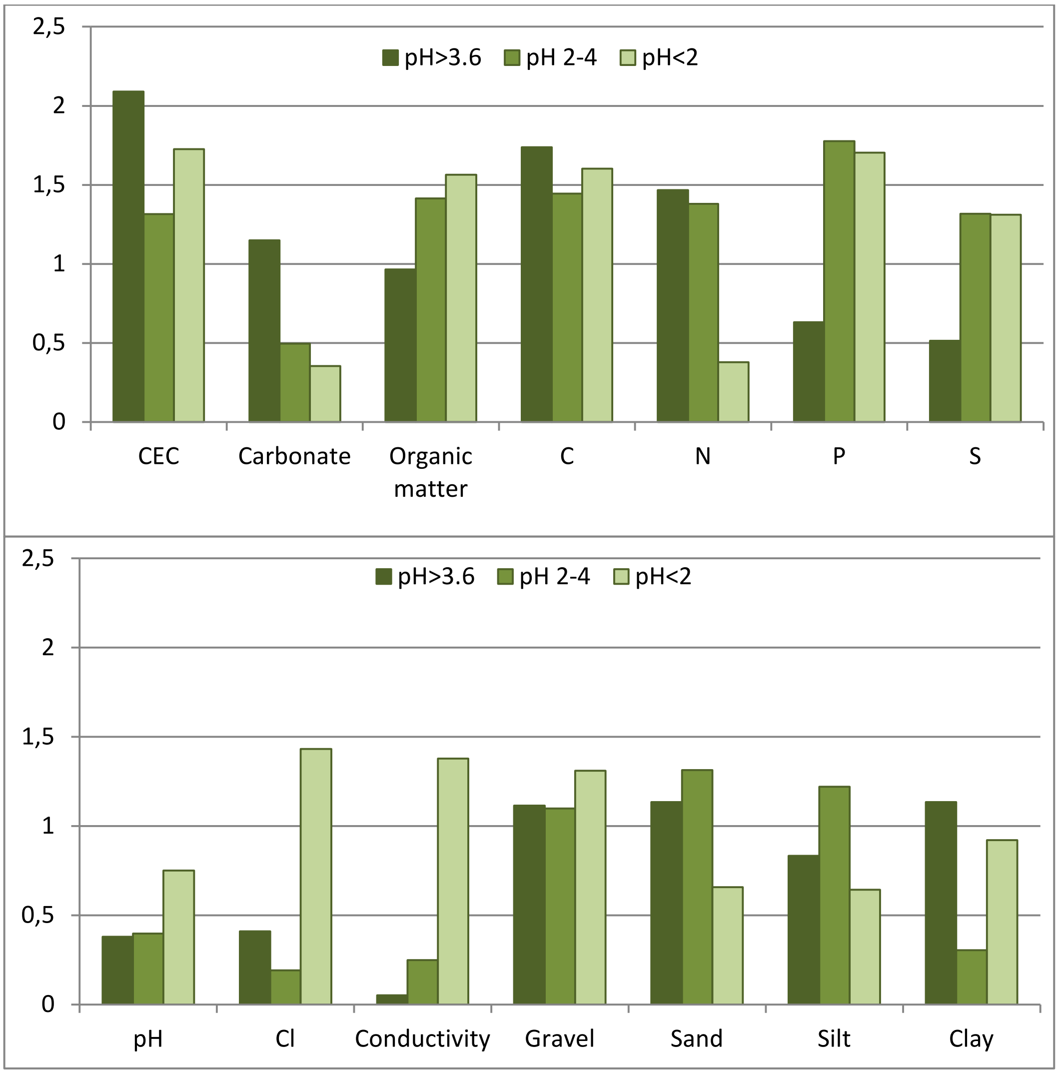


Figure 23: Summary of VIP values for PLS models with Cu, Pb and Zn as responses. Parameters with high VIP values have the highest influence on the models.

The VIP values of *CEC* indicate strong influence on removal of heavy metals during all phases of EDR. Individual models of Cu, Pb and Zn and the weight plots (Figure 24) reveal that in the fast and slow removal phases, *CEC* has relatively greater influence on the removal of Pb and Zn compared to Cu. This is in line with relatively higher amounts of Pb and Zn than Cu bound in the exchangeable fractions (***Paper VIII***, Figure 2). The strong influence of *CEC* for the removal of especially Pb and Zn in all phases of EDR may be an indication of continued removal from the exchangeable fraction during EDR. As may be expected, the influence of *carbonate* decreases as carbonate is depleted. The individual models furthermore indicate that the *carbonate* content has greater influence on the removal of Pb and Zn suggesting that these two heavy metals may be bound as carbonates in the sediment to a larger extent than Cu.

Even though *organic matter* did not appear to significantly influence the acidification time (Figure 22), it influenced the removal of heavy metals during the acidification phase and the importance increased in the fast and slow removal phases of EDR. A high content of *organic matter* resulted in higher final concentrations, indicating that the release of heavy metals from the oxidisable fraction as a result of oxidation of sediment was slow compared to removal of heavy metals bound in other fractions. The individual models revealed that the influence of *sulphur* in the fast and slow removal phases of EDR was higher for Cu than Pb and Zn, which is also implied in the weight plots (especially Figure 24b), suggesting that Cu is bound in sulphur compounds, e.g. as sulphides in the sediment, in line with previous findings of anoxic sediments [34]. The strong correlation between Cu and s*ulphur* in the fast removal phase (final pH2-4) may indicate that Cu remains bound to *sulphur* in this phase, since high initial concentration of *sulphur* result in high final concentrations of Cu. The increasing influence of *phosphorus* in the fast and slow removal phases of EDR may be a consequence of mobilised heavy metals binding to phosphates, thus reducing the removal from the sediment. The individual models in ***Paper VIII*** point to strong influence of *phosphorus* on the removal of Zn in the acidification phase, which may be related to binding of the relative higher amounts of Zn mobilised at this stage. The lower influence of *nitrogen* on EDR in the slow removal phase, may indicate that oxidation of the sediment induces nitrification, the nitrate being depleted in the later phases of EDR.

The increasing influence of *chloride* in the third PLS model is correlated to Pb and Zn (Figure 24c) suggesting that the differences in the final concentrations are related to complexing with chlorides. The reason for *chloride* not having a large influence in the preceding models (i.e. initial EDR phases), for which complexing may be expected, is that other processes dominate the removal; accordingly concentrations at lower pH at which EDR is moving towards the stationary phase, may to a higher degree display this effect. A similar reasoning can be used for the high influence of *conductivity* for Pb and Zn (Figure 24c) in the third model (2c), in that the initially higher conductivities resulted in lower transference numbers for Pb and Zn and the effect not being apparent until EDR of these two heavy metals moved towards the stationary phase.

A moderate to high importance of the initial concentrations and composition of elements on the efficiency in the removal of Cu, Pb and Zn is apparent from Figure 24 and high concentrations may result in lower transference numbers of Cu, Pb and Zn. Ca is, for instance, located close to Pb and Zn in all three weight plots, and not necessarily close to *carbonate*, which may indicate that high concentrations of Ca prevent simultaneous removal of Pb and Zn during EDR. This inhibitory effect of high metal concentrations on heavy metal removal has also been observed in numerous EKR studies [160]. The high influence of *grain size* during EDR indicates that the relative binding of heavy metals in gravel, sand, silt and clay is important for the removal and may be due to the relatively higher amounts of metals bound in clay and silt fractions. The chemical binding of heavy metals in the sediment was also shown to influence the efficiency of EDR (***Paper VIII***). The individual PLS models indicated that there was a difference in importance of the initial binding of heavy metals in the different phases of EDR, depending on the heavy metal, it may therefore be suggested that metal binding changes during EDR. These are however preliminary results that need to be confirmed by more EDR experiments, designed for the purpose.

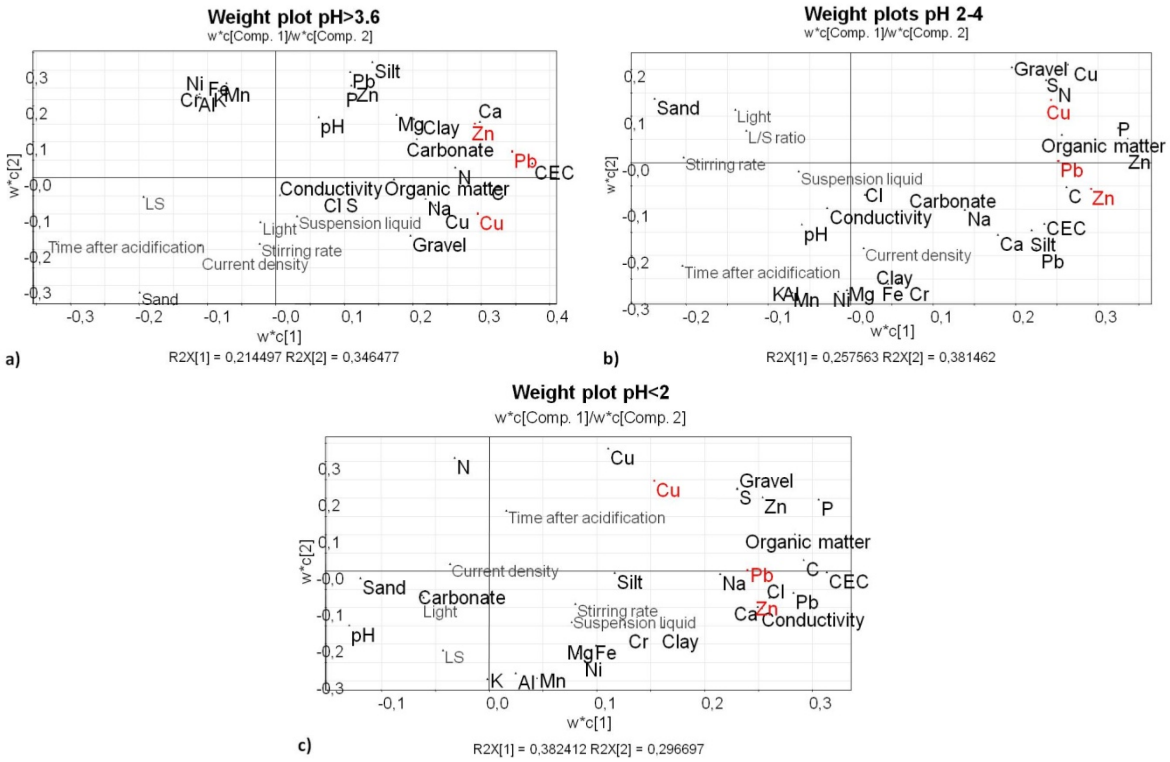


Figure 24: Combined weight plots of X (w*) and Y (c) for the first and second component, for the three PLS models that included experiments with final a) pH>3.6, b) final pH 2-4 and c) final pH<2. Directly correlated X and Y variables are located adjacent to one another. Responses of Cu, Pb and Zn are highlighted in red and experimental variables in grey.

The assessments of the influence of sediment properties above were based on EDR experiments in the 3-compartment cell. It would be interesting to extend the study to investigate the effect in the 2-compartment cell, for instance evaluating the higher influence of oxidation of the sediment (as indicated in paper ***Paper V***) induced by the direct introduction of oxygen via the electrolysis reaction. Since EDR experiments of two harbour sediments in the 2-compartment cell have already been conducted, this may not necessarily entail substantial amounts of new experiments.

4.4.2 Influence of EDR on sediments

Assessing the influence EDR had on the changes in sediment characteristics was not within the scope of the work in this PhD, this is however an important aspect when evaluating the method from a sustainability perspective, e.g. by quantifying environmental impacts and carbon footprint. Whilst investigations with the aim of assessing the impact of EDR on the sediment and environment were not undertaken, some interesting observations related to the topic were made. The first one is obvious, the observed decrease in pH strongly indicated removal of carbonate and hence dissociation of carbonate minerals. In addition, the sediment suspension was observed to change colour during the experiments. At the start of the experiments, the sediment suspension was very dark, almost black and after 2-10 days, the colour changed to light brown/grey. The colour change appeared to be faster in the 2-compartment cell, the time however also apparently depended on other variables. It is speculated whether the change in colour may be an effect of oxidation of the sediment. Another issue is the removal of chloride from the sediment resulting in the formation of chlorine gas at the anode. Chlorine is toxic at high concentrations (>40 ppm; fatal >400 ppm, exposure >30 min) [162] and was previously observed to form during EDR of harbour sediments in the 3-compartment cell [26]. In the first two-three weeks of the EDR experiments a strong smell of chlorine was registered in the anolyte, the same was not the case for the soil experiments. Reducing exposure to chlorine gas may be essential for scaling-up and may be achieved by adding a compartment between the sediment suspension and anode compartments to prevent the transport of chloride to the anode [26].

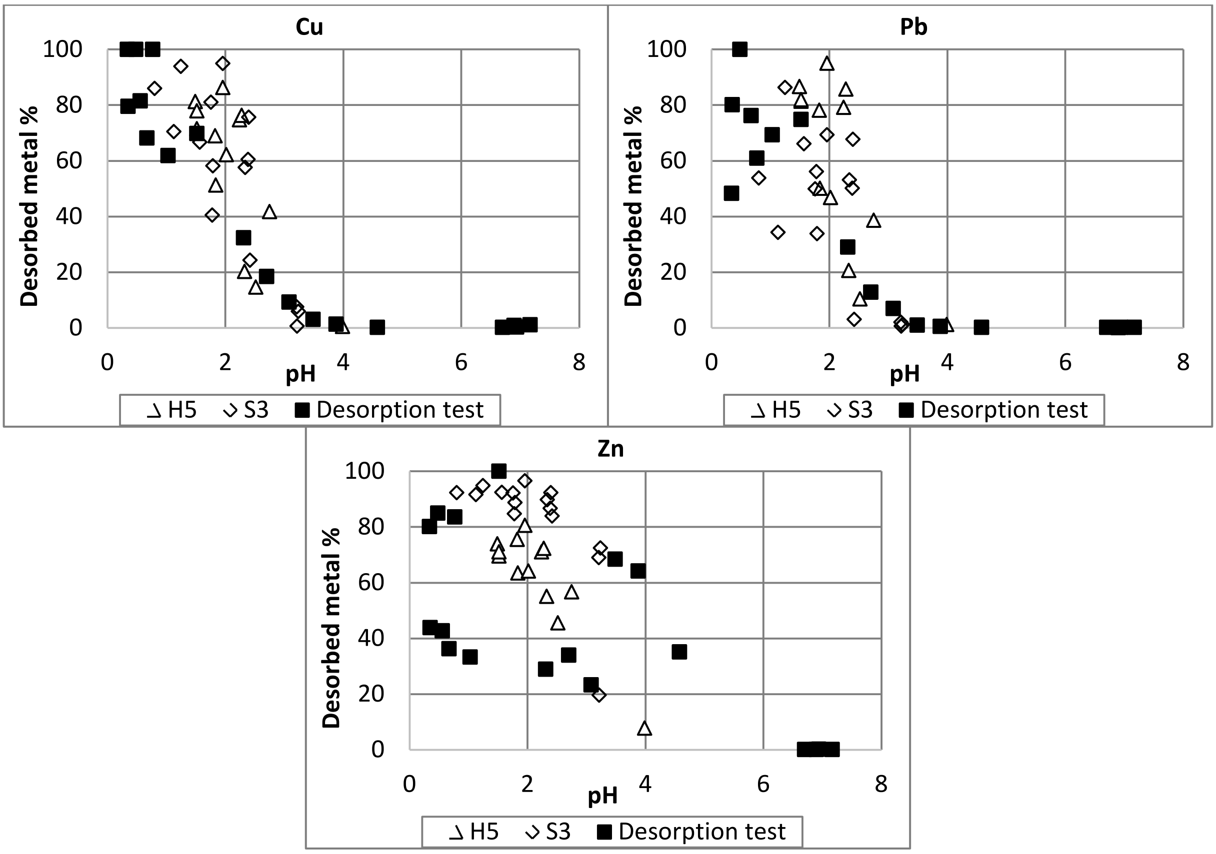


Figure 25: Comparison of relative amounts of Cu, Pb and Zn desorbed during desorption tests and EDR for the two sediments H5 and S3 in the 2-compartment cell. Results from the pH dependent desorption test of the two sediments are not distinguishable in the plots, since they exhibited similar trends in desorption of Cu, Pb and Zn.

Desorption tests of sediments, in which the sediments were mixed with different concentrations of acid until they reached equilibrium, were made to assess the efficiency of EDR in comparison with chemical acidification of the sediment. In the 3-compartment cell, higher levels of desorption of Cu and Pb at the same pH levels was generally observed for the EDR experiments, while similar levels between EDR and desorption tests were observed for Zn (***Paper VIII***, Figure 3). The same trend was observed for the 2-compartment cell (Figure 25), albeit including only the two sediments used during the EDR experiments, i.e. the H5 sediment and the S3 sediment. The difference in mobilisation may be related to equilibrium continuously being shifted during EDR. Since it is possible to remove relatively larger amounts of metals in EDR compared to acid treatment at similar pH levels, the opportunity of operating at higher pH in EDR may limit the relative effect on the sediment.

In order to ascertain whether a similar trend could be observed for the naturally occurring metals, the comparison was extended to these elements, exemplified by plots of Al in Figure 26 and Ni in Figure 27. The reason for picking these two elements is that they represent the general trend for the naturally occurring metals and in addition Al is known to be toxic to the aquatic environment and Ni is a prioriy substance in the EU water framework directive.

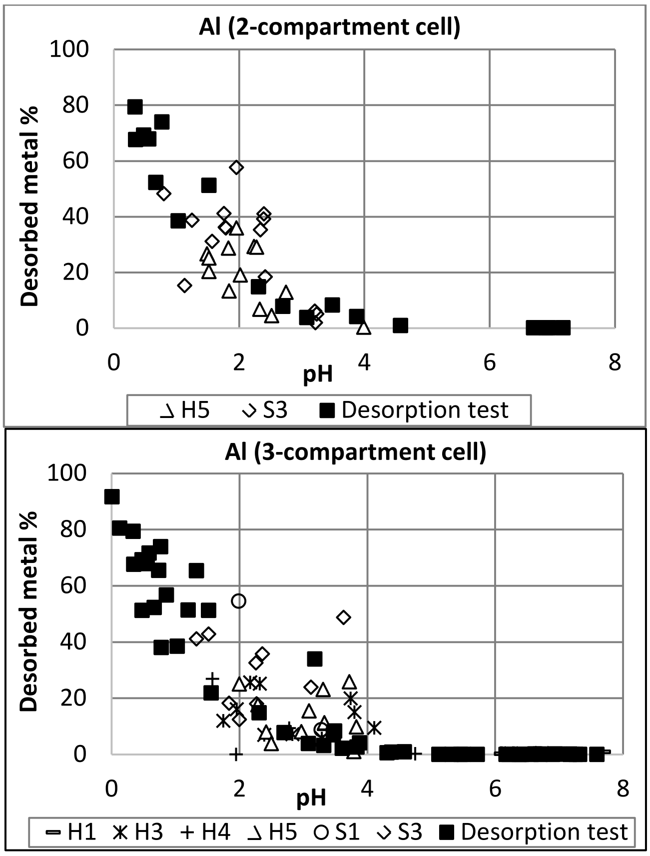


Figure 26: Relative amounts of Al desorbed during EDR in the 2- and 3-compartment cells compared to amounts desorbed in desorption tests of the sediments. Results from the pH dependent desorption test do not distinguish between the sediments since they exhibited similar trends in desorption of Al.

A similar effect for Al and Ni is observed as for the pollutants, i.e. higher desorption occurs during EDR than by acid treatment. The effect is however not as distinct for Al, for which desorption during EDR almost follows the desorption curve of the acid treatment. For Ni, EDR mobilises higher amounts of the metal than the addition of acid does and the effect is especially clear in the 2-compartment cell (Figure 27). These results indicate that EDR has implications for the environment and it appears essential to design EDR for the simultaneous removal of pollutants, while limiting the mobilisation of the naturally occurring metals, as exemplified in chapter 4.3.2. In a future perspective, it may be interesting to compare the difference in leaching of elements after EDR treatment and acid treatment to assess whether the two methods result in different binding patterns in the sediments.

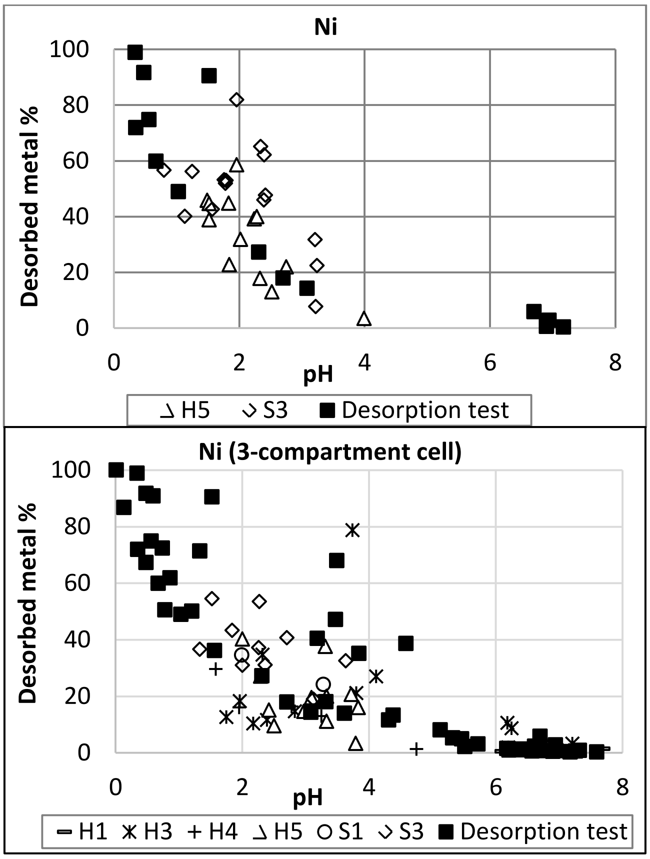


Figure 27: Relative amounts of Ni desorbed during EDR in the 2- and 3-compartment cells compared to amounts desorbed in desorption tests of the sediments. Results from the pH dependent desorption test do not distinguish between the sediments since they exhibited similar trends in desorption of Ni.

The binding of metals in the sediment can be evaluated by sequential extractions and although some drawbacks to the method used in this project (BCR, chapter 3.3) have been reported, e.g. readsorption and redistribution of metals, it has been found to be a repeatable and reproducible method [163]. In this project sequential extraction has been used to assess how strongly the metals were bound in the sediment, e.g. in more available fractions (exchangeable and reducible) or less available fractions (oxidisable and residual). Previous studies have shown that EDR accelerates the weathering of soil and mobilises heavy metals bound in all fractions [35, 92]. Accordingly, it is not possible to determine the release of metals from the specific fractions during EDR by the initial binding patterns in the sediment. However, results in both ***Papers III*** and ***V*** revealed relatively higher removal of elements that to a higher degree were bound in the exchangeable fraction. This may suggest that relatively higher removal from the exchangeable fractions occurred for the harbour sediments studied in this project. Some preliminary trends may thus still be retrieved by comparing the removal percentages of elements to the initial metal partitioning in the sediment. This has been done for the naturally occurring metals, Al and Ni, in Figure 28. The removal percentages for Al in the 3-compartment cell are equivalent to amounts found in the exchangeable fraction, apart from sediment S1. Higher removal of Ni in relation to amounts bound in the available fractions, than was the case for Al, is observed in the 3-compartment cell. In the 2-compartment cell, higher removal percentages were observed and mobilisation from the residual fraction of the sediments definitely occurs. Interestingly, the 2-compartment cell appears to impact the removal of Ni to a higher degree compared to the 3-compartment cell. This may be attributed to the relatively higher amounts of the metal bound in the oxidisable fraction, being released by increased oxidation of the sediment in the

2-compartment cell. It is also interesting to note that although there are differences in the removal of Al and Ni, the trend in difference between the sediments appear to be similar for the two elements, which may also be related to the similar binding patterns of the two metals in the exchangeable fractions of the sediments studied.

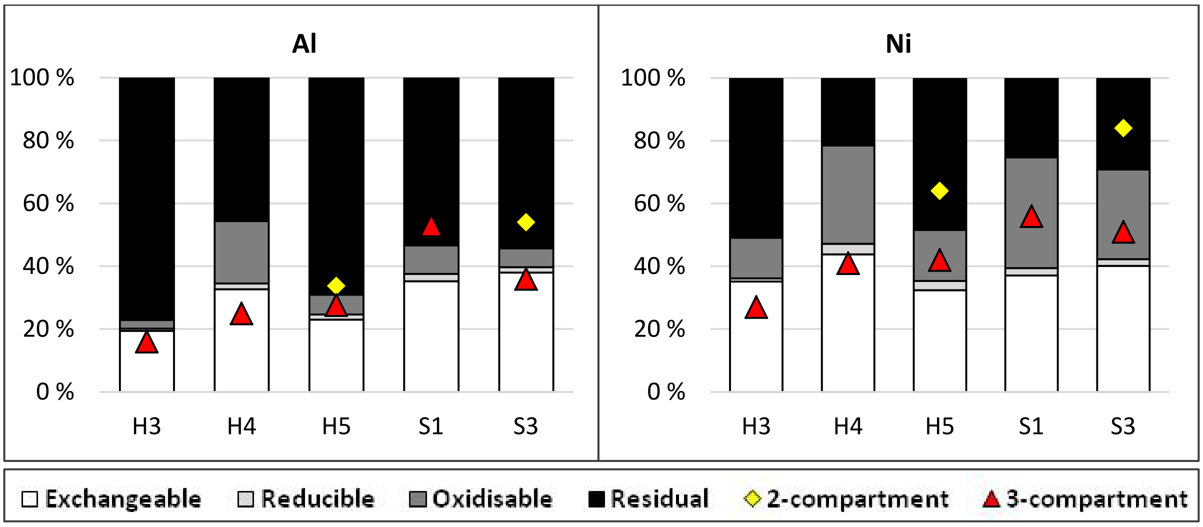


Figure 28: Metal partitioning of Al and Ni in the five sediments used for EDR experiments and comparison with the highest removal efficiencies achieved during EDR in the 2- and 3-compartment cells. EDR experiments of sediments H3, H4 and S1 were not conducted in the 2-compartment cell.

The preliminary assessments of mobilisation of naturally occurring metals revealed that the degree to mobilisation depends on the metal and how it is bound in the sediment. Whilst EDR has proven to be a reliable method for removing heavy metals from harbour sediment, it also mobilises naturally occurring elements, and this emphasises the need for comprehensive investigations into the actual effects of EDR on the sediment.

4.4.3 Predictions based on PLS models

Evaluating the relation between the findings of the experimental domains studied and optimal settings in regard to specific sediment can be done by testing the predictions of the model by new experiments. This was done for datasets of several sediments (***Paper II***) and these findings are complemented here with analyses of the sediment-specific findings presented in chapter 4.3. Previous EDR studies of harbour sediments have differed significantly with regard to the degree of variation in sediment properties (***Paper II***, Figure 2) and therefore a new PLS model, in which the X-matrix consisted of the sediment properties and experimental variables and the Y-matrix consisted of final concentrations of Cd, Cu, Pb and Zn, was calculated and subsequently used to predict experimental settings for a new sediment (H5). The choice of sediment for the prediction was based on the PCA plot of the sediment characteristics and the H5 sediment was chosen due to its location close to the centre of the model sediments ensuring potential contribution of all sediments to the predictions. The calculated PLS model predicted Cu concentrations for the specific properties of the H5 sediment and investigated settings of the experimental variables *current density* and *remediation time*, within the deviations of the observed values of the model (***Paper II***, Figure 6). Slightly higher deviations were observed for Pb, although the actual final concentrations were lower than model predictions, i.e. meeting the remediation objectives. It was suggested that model predictability could be optimised by developing sediment-specific models.

Based on the entire datasets of EDR experiments for sediments H3, H5 and S3, an assessment of sediment-specific model predictions have been made. New PLS models of experiments conducted in the 3-compartment cell were calculated for each sediment, excluding random experiments for later test of model predictability. For sediments H5 and S3, PLS models were also calculated for the experiments conducted in the 2-compartment cell. Experiments chosen for the test were isolated compared to other experiments in the experimental domains. Since naturally occurring metals are mobilised during EDR and may be important design parameters in future development of EDR, final concentrations of Al, Fe, K, Mg, Mn, Cr and Ni were also included in the models. (Cr and Ni were included as naturally occurring metals due to their low concentrations and their previously found correlation with the major elements in the sediments in chapter 4.1.3). Table 10 summarises the experiments used in the new models, the PLS model reliability (R2Y and Q2) and experiments chosen for testing model predictability.

Table 10: Overview of experiments included in PLS models, model reliability and test experiments for model predictions.

Sediment	EDR cell design	PLS experiments	R2Y	Q2	Test experiments
H3	3-compartment	1-13 (*Paper III*)	0.52	0.37	H3.1 (14, *Paper III*) H3.2 (15, *Paper III*)
H5	3-compartment	1-2,4-5 (*Paper II*) 1, 4 ,5, 23, 26 (*Paper IV*) 2a, 8a (*Paper IV*)	0.64	0.46	H5.1 (3, *Paper II*)
H5	2-compartment	9, 10, 12, 13, 24, 25,27 (*Paper IV*) 1b, 4b-6b (*Paper VI*)	0.65	0.53	H5.2 (2b, *Paper VI*) H5.3 (3b, *Paper VI*)
S3	3-compartment	1-4, 9-10 (*Paper V*)	0.62	0.12	S3.1 (2, *Paper IV*) S3.2 (6, *Paper IV*)
S3	2-compartment	5-8, 11-16 (*Paper V*) 8, 14, 15 (*Paper IV*)	0.83	0.48	S3.3 (11, *Paper IV*)

Figure 29 and Figure 30 present the model predictions and observations of the test experiments for the pollutants Cu, Pb and Zn and the naturally occurring metals Ni, Al and K. In general the deviations between model predictions and observations were below 20 %, which is lower than the standard deviations of analysis. There are however some larger deviations for Pb and Zn and new experiments may have to be tuned for these two heavy metals, in order to obtain better predictions. The large deviations between the observed and predicted values of Pb for the H3 sediment experiments may be due to the pH in sediment suspension not having reached the threshold value at which desorption of Pb initiates. Cu and Zn in the same experiments have apparently entered the fast removal phase. It is worth noting that the deviations between observations and predicted values of Cu and Pb observed in ***Paper II***, are lower in the new PLS model solely based on the H5 sediment (H5.1 in Figure 29).

There are some differences in model predictabilities between the sediments which may be related to the experimental domains. In order to optimise the models and hence the assessed optimal settings for remediation, the experimental domains may have to be adjusted and possibly reduced to only changing settings of the significant variables. For the H5 sediment, for instance, the experimental domain only consisted of *current density* and *time after acidification*, while for the sediments H3 and S3 it included six variables. There do not appear to be differences in deviations from predictions in the 2- and 3-comparment cells for the H5 sediment. The differences observed for S3 may be due to fewer experiments being included in the 3-compartment cell, thus decreasing the reliability of the model; this is supported by the low predictability power for the PLS model (Table 10).

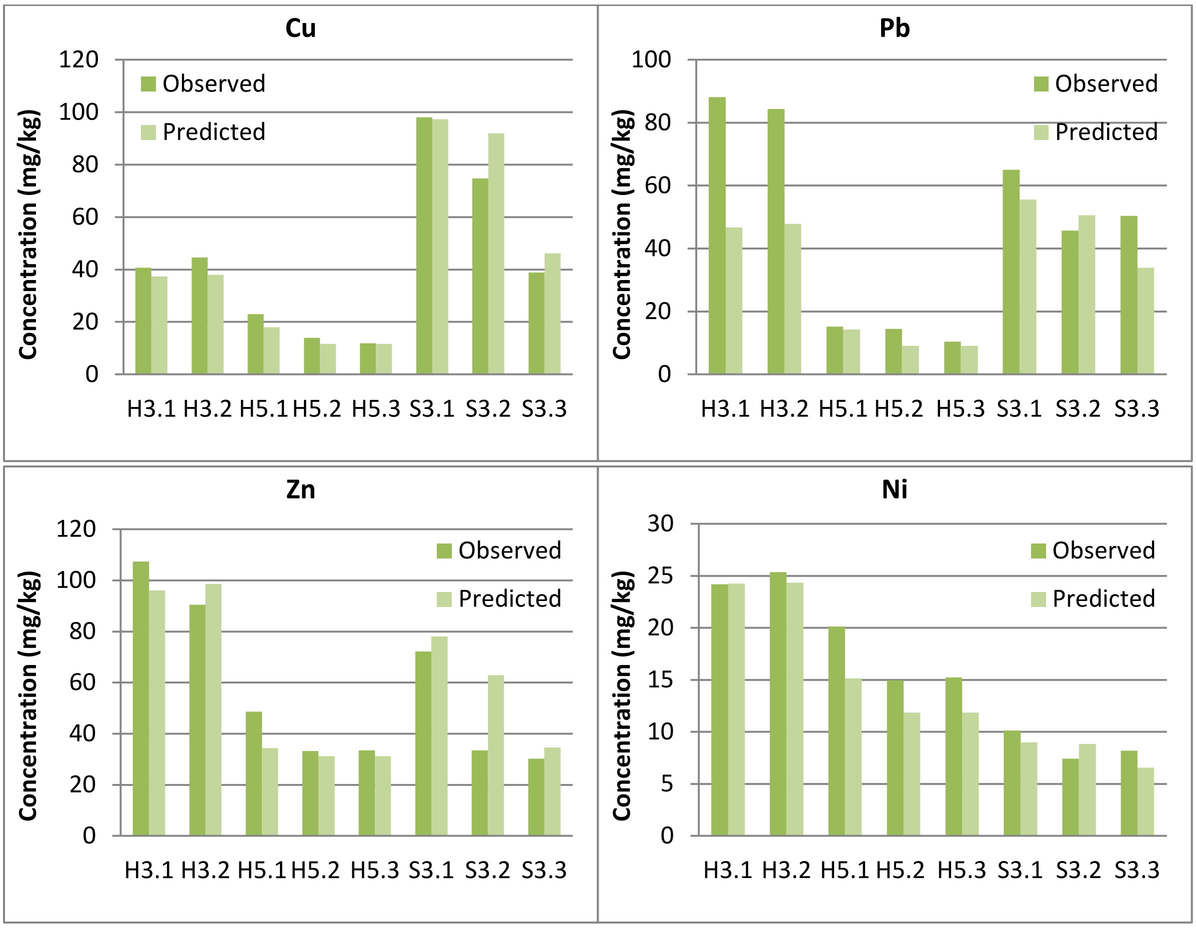


Figure 29: Final concentrations of the heavy metals Cu, Pb, Zn and Ni observed in the experiments and predicted by PLS models.

Differences between observed and predicted final concentrations of the naturally occurring metals, exemplified by Ni (Figure 29), Al and K (Figure 30) indicate that PLS models of each sediment may predict approximate final concentrations of the metals from igneous rocks providing a basis for including requirements for these in the remediation objectives. The slightly higher deviations for Ni may be due to the low final concentrations resulting in higher margins of error.

From a remediation perspective, the PLS models appear to be sufficiently accurate for predicting approximate final concentrations for given experimental settings for specific sediments. Optimisation of models in relation to sediments or targeted heavy metals may be achieved by reducing or adjusting experimental domains. It is however questionable whether such optimisations afford practical implications for site-specific remediation strategies since these results are already within currently accepted limits.

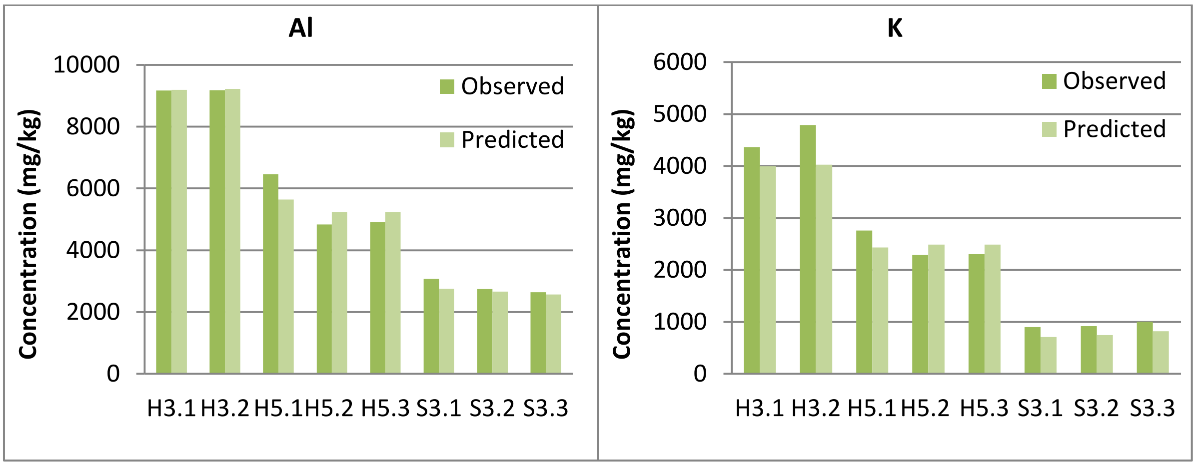


Figure 30: Final concentrations of the Al and K observed in the experiments and predicted by PLS models.

4.4.3 Predicting settings for new sediment according to site-specific conditions

Since the data collected for EDR of harbour sediments in the 3-compartment cell is extensive due to previous as well as the presented studies of the thesis, these may be used to predict settings for remediation of new sediment. This, however, relies on the new sediment having similar variation in properties as those already studied and that the targeted pollutants are Cu, Pb and/or Zn. If these circumstances are met, a PLS model can be calculated to predict settings according to site-specific remediation objectives that may also include requirements for removal of the naturally occurring metals. Depending on the site-specific conditions, it may be necessary to extend the experimental domain, e.g. by preferring the 2-compartment cell or adding *temperature* as a variable in cold regions. In such cases a PLS model of existing data may be used to approximate starting points, which can then be adjusted according to existing knowledge of the conditions, e.g. that removal in the 2-compartment cell is faster than in the 3-compartment cell and that operating at low temperatures decreases the EDR efficiency of heavy metals.

5 Implications for EDR and future perspectives

The overall aim of this PhD project was to contribute in the development of reliable and efficient methods for removal of pollutants from environmental media, thereby reducing the amount of hazardous waste, particularly focused on the Arctic region. This was specifically done by using multivariate analysis to develop and optimise EDR of harbour sediments from Hammerfest in Norway and Sisimiut in Greenland, and of soil from Arkhangelsk in Russia. In the following, important findings are highlighted and the implications on the present and future development of EDR are put into perspective, including considerations of environmental outlooks.

Important findings

- EDR was shown to be a reliable method for simultaneously removal of heavy metals, PCB and TBT from polluted harbour sediment.
- Investigations of different designs revealed that the 2-compartment cell was the most efficient with regards to removal of heavy metals and energy consumption, while the 3-compartment cell ensured limited removal of naturally occurring metals.
- The influence of experimental variables during EDR was revealed to depend on the sediment and specific pollutant and also varied depending on the EDR cell design employed.
- The influence of *temperature* and *light* revealed that EDR can be designed for Arctic conditions. *Temperature* was shown to influence removal of all pollutants, while *light* primarily influenced the removal of PAH, PCB and TBT.
- PLS models were employed as important tools for determining sediment-specific optimal settings for simultaneous removal of pollutants, while maintaining low energy consumption and limited removal of naturally occurring metals.

Prior to undertaking EDR, mapping of sediments in relation to pollutant levels and characteristics was carried out, forming the foundation for environmental risk assessment and subsequent determining remediation criteria. PCA was employed for assessing the potential sources of pollution. Few hotspots in the harbours of Sisimiut and Hammerfest were identified and the pollution, in general, had a complex composition of heavy metals, PAH, PCB and TBT, stemming from several sources. By employing PCA, it was however possible to distinguish pollution in the different parts of the harbour as well as assessing the origin of PAH and PCB. It was, for instance, found that the PCB pollution in the harbours originated from several commercial PCB mixtures. PAH mainly stemmed from several different pyrogenic sources, with contributions from combustion of biomass/waste and to a lesser degree, liquid fossil fuels. Very high concentrations of oil were found in the soil at Krasnoe (Arkhangelsk) and PCA of the PAH pollution also found at the site strongly indicated relation to the oil pollution and not to other sources.

Advancements in multivariate analysis of EDR

Multivariate analysis had not previously been used in EDR studies, and was during the course of the PhD project continuously shown to be a valuable tool for developing site- and sediment-specific remediation strategies for EDR of harbour sediments. Apart from using PCA to illustrate the change in distribution of organic pollutants during EDR, the main tool used for assessing EDR efficiency, was PLS. Significant variables were identified and this provided a basis for analysing the PLS models for optimal settings in relation to the remediation objectives. It was revealed that, besides removal of pollutants, requirements for limiting the removal of naturally occurring metals and energy consumption could also be included in the models. By modelling results of previous EDR studies that included several sediments, it was possible to identify good starting points for treatment of new sediment and it was found that including sediment properties in the X-matrix along with the experimental variables were crucial for model predictability.

Adjusting the descriptor from *time* to *time after acidification*, was revealed to improve the predictive power of the PLS models, illustrating the importance of modelling the different phases of EDR separately. Excluding the initial acidification phase, in which limited removal of metals occurred, was especially shown to improve model reliability. The PLS model predictive powers (Q2) were sometimes still in the lower range, which was mainly attributed to the experimental domains studied, or too few experiments included in the models due to the fractional factorial designs. Deviations between model predictability and experimental observations were however generally below 20 %, which, taking the inhomogeneous sediments into account should be considered acceptable. This is assessed as sufficient for remediation purposes, since the approximate level of pollution rather than exact final pollutant concentrations is adequate.

Since the model predictability was assessed acceptable for remediation of harbour sediments, it appears to be relevant to collect all present and past results of EDR studies in a database, providing a good foundation for predicting approximate settings for removing heavy metals from not previously treated sediments. Data for organic pollutants are not as extensive; a database would, however, provide possibilities of adding new data, when available and thus provide a valuable tool for planning simultaneous removal of sediments during EDR of harbour sediments, in the future. Multivariate analysis may also be adapted to other environmental media such as soil, wood, sewage sludge, mine tailings and fly ash in accordance with specific targets for EDR treatment, potentially including other priority substances. In a long-term perspective, it may also be relevant to extend the use for other remediation technologies, thereby providing foundation for assessing the most appropriate technology according to sediment- and/or site-specific conditions.

Development of EDR – findings

It was well established that the type of sediment greatly affected the final concentrations of heavy metals, organic pollutants and TBT. The comparisons of sediment relied on an initial PCA plot of sediment characteristics and even though only sediments located close to each other were used in the comparisons, they exhibited variations in sediment properties that significantly influenced EDR. PLS models, calculated to assess the influence of sediment properties and experimental variables on the removal of heavy metals in the 3-compartment cell, revealed that sediment properties generally had stronger influence on EDR. The relative importance varied depending on the EDR phase, *carbonate* was for instance found to have a diminishing influence after the acidification phase attributed to the depletion of *carbonate* with increasing acidification of the sediment, while the significance of *organic matter* increased in the fast and slow removal phases. The strong influence of *CEC* in all phases indicated importance of metal binding in the exchangeable fraction, and the initial *metal partitioning* in the sediment was also found to influence removal of metals during the different phases of EDR. Other important properties included *grain size distribution* and the initial *composition* and *concentration* of naturally occurring metals in the sediment. These findings of comparative importance in the different EDR phases are of significance for the future optimisation of EDR in relation to the sediment properties, e.g. by decreasing acidification time or increasing oxidation of sediment for calcareous or organic sediments. It hence appears important to further extend this analysis to include organic pollutants and TBT in the future.

The three cell and stack designs differed in EDR efficiency with regards to heavy metal removal, acidification time and energy consumption and had to be modelled separately. The 2-compartment cell was found to be the most efficient with regards to acidification time, heavy metal removal and energy consumption, followed by the 3-compartment cell. A difference in variable importance was also observed in the two cell designs, *stirring rate* was for instance relatively more important in the 2-compartment cell, ascribed to the higher oxidation of sediment due to the direct introduction of oxygen in the sediment suspension. The removal of naturally occurring metals was, however, also higher in the 2-compartment cell and the final pH levels were lower, potentially impacting the sediment to a higher degree than in the 3-compartment cell. Whether this impact is significant for future possibilities of recycling the sediment, remains to be investigated. Determining requirements for the use of the treated sediment appears vital for future optimising of the EDR cell design, e.g. by combining the two cell designs to ensure optimal acidification and limited removal of naturally occurring metals (if necessary) while removing pollutants to acceptable levels. It would also be interesting to investigate the efficiency on removal of organic pollutants and TBT in the 2-compartment cell, especially in regard to whether the oxygen from the electrolysis reaction at the anode increases degradation of these pollutants. The stack was capable of treating larger quantities of sediment than the cell designs, however the electric charge per unit mass, needed for achieving acidification and similar removal efficiencies were higher. The energy consumption per mass unit in the stack was also an order of magnitude higher than those needed in the cell designs. Based on these results, the future scaling-up of EDR of harbour sediments is hence recommended to focus on developing other designs rather than making efforts to optimise the stack.

Investigations into conditions specific to the Arctic, i.e. *temperature* and *light* revealed that the extent to the influence of these two variables on EDR was specific to the pollutant and sediment. In general, *light* did not influence the removal of heavy metals, but significantly influenced the removal of organic pollutants and TBT. *Temperature* was found to influence the removal of all of the pollutants, although the optimal setting of *temperature* depended on the pollutant. For heavy metals and TBT a high temperature increased removal, attributed to increasing desorption at higher temperatures. Low temperatures increased removal of PAH and PCB and this was suggested to be related to microbial communities in the sediments not adapted to higher temperatures. The influence of *temperature* was based on preliminary investigations and including experiments of different sediments would provide a better understanding of how temperature influences the efficiency of EDR, e.g. for sediments with low contents of organic matter. The implications of conducting EDR in periods of limited light, e.g. in the winter months in Hammerfest and Sisimiut, and/or low temperatures from October to May are generally lower removal of pollutants. Adapting EDR to the Arctic region may hence result in relatively longer remediation times and/or seasonal planning, and may include operational considerations, depending on the targeted pollutants, e.g. the possible heating of the sediment suspension for removal of heavy metals and TBT.

The optimal settings of EDR depended on the sediment as well as on the pollutant. The optimal removal of heavy metals was influenced by metal partitioning and the pH threshold values at which desorption initiated. Zn was for instance revealed to be more readily removed than Cu and Pb; this was attributed to Zn desorbing at higher pH values and being bound in the available exchangeable fraction of the sediments studied to a higher degree than Cu and Pb. Whilst *current density* was essential for the removal of heavy metals, it appeared to have low influence on removal of organic pollutants and TBT. The higher influence of *stirring rate* may indicate that stirring of the sediment suspensions was sufficient to increase the availability of the pollutants for degradation. Acidification of the sediment appeared to positively influence the removal of PCB and TBT, attributed to chemical processes in the sediment suspension, while having a negative impact on the removal of PAH ascribed to inhibition of microbial communities in the sediment. A PLS model of the experimental domain studied, revealed that optimisation of simultaneous removal of PCB, TBT and heavy metals was possible, the concurrent optimisation of PAH removal would, however, require other remedial actions, e.g. addition of acid resistant bacteria. Further investigations of simultaneous removal of all pollutants are necessary to fully assess whether EDR provides a reliable method, or whether a step-wise approach, in which organic pollutants are removed prior to EDR of heavy metals, or vice versa, is the most appropriate remediation strategy.

Environmental outlook

In the present work, higher concentrations of pollutants in the harbour sediments in Hammerfest and Sisimiut, than those reported in remote areas of the Arctic, were observed, emphasising the importance of local pollution sources, sometimes neglected in a global context of assessing environmental impacts of pollution on the Arctic environment. The need for developing remediation methods for pollution mitigation in the Arctic will exist in the years to come, partly due to the persistence and continual local as well as global discharge of pollutants into the environment, and the continuous identification of new priority substances. There is also a risk that banned pollutants are produced as by-products, as is the case for PCB in paint pigments [164].

Challenges present themselves for remediation activities in the Arctic region and include cold climate with prolonged periods of winter, periods of limited light and logistics due to long distances. Remediation technologies need to meet these challenges; it is however also important to acknowledge that remediation impacts the environment, e.g. bioremediation of 91000 kg diesel pollution in an Arctic location in Canada resulted in consumption of 95000 kg diesel [165]. EDR has already proven to be a good method for removing heavy metals from harbour sediments and may be adapted to challenges in the Arctic region. Environmental impacts of EDR have, however, as yet not been assessed or quantified. This appears to be a research field in itself, but is nonetheless crucial in a sustainability perspective and investigations of the environmental impacts in relation to benefits of the method should be undertaken. Important issues may include identifying possibilities for recycling the treated sediment, the possible use of retrieved heavy metals, quantifying generation of black carbon, quantifying the carbon footprint, assessing the impacts of implementation and operation. In conclusion, EDR provides the potential for optimising removal of pollutants from sediments to non-toxic levels, it however seems important that future improvements include actions for developing the method in an environmental sound way.

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