



## Low concentrations of persistent organic pollutants (POPs) in air at Cape Verde



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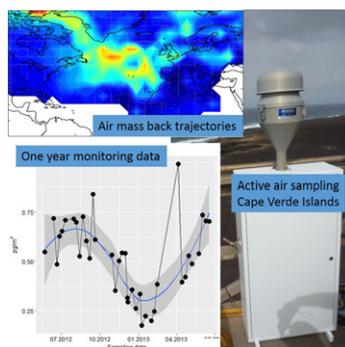
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### HIGHLIGHTS

- One year active air sampling of POPs was performed at Cape Verde Islands.
- Concentrations of several POPs were generally low.
- Air mass back trajectories demonstrated Atlantic Ocean as frequent source regions.
- Volatilization from the ocean was a likely source to several POPs.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Ambient air is a core medium for monitoring of persistent organic pollutants (POPs) under the Stockholm Convention and is used in studies of global transports of POPs and their atmospheric sources and source regions. Still, data based on active air sampling remain scarce in many regions. The primary objectives of this study were to (i) monitor concentrations of selected POPs in air outside West Africa, and (ii) to evaluate potential atmospheric processes and source regions affecting measured concentrations. For this purpose, an active high-volume air sampler was installed on the Cape Verde Atmospheric Observatory at Cape Verde outside the coast of West Africa. Sampling commenced in May 2012 and 43 samples (24 h sampling) were collected until June 2013. The samples were analyzed for selected polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), hexachlorobenzene (HCB) and chlordanes. The concentrations of these POPs at Cape Verde were generally low and comparable to remote sites in the Arctic for several compounds. Seasonal trends varied between compounds and concentrations exhibited strong temperature dependence for chlordanes. Our results indicate net volatilization from the Atlantic Ocean north of Cape Verde as sources of these POPs. Air mass back trajectories demonstrated that air masses measured at Cape Verde were generally transported from the Atlantic Ocean or the North African continent. Overall, the low concentrations in air at Cape Verde were likely explained by absence of

**Abbreviations:** AAS, active air sampling; CVAO, Cape Verde Atmospheric Observatory; ECMWF, European Centre for Medium-Range Weather Forecasts; FLEXPART-f, forecasted FLEXPART emission sensitivities; FLEXPART-r, retrospective FLEXPART emission sensitivities; GC, gas chromatograph; GFS, Global Forecast System; HCB, hexachlorobenzene; MDL, method detection limit; MS, mass spectrometer; NCEP, National Center for Environmental Prediction; PBDEs, polybrominated diphenyl ethers; PCBs, polychlorinated biphenyls; POPs, persistent organic pollutants; PUF, polyurethane foam; QA-QC, quality assurance-quality control.

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major emissions in areas from which the air masses originated combined with depletion during long-range atmospheric transport due to enhanced degradation under tropical conditions (high temperatures and concentrations of hydroxyl radicals).

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## 1. Introduction

Many persistent organic pollutants (POPs) have the potential for atmospheric long-range transport and are ubiquitous in the global environment (Poza et al., 2006; Wania and Mackay, 1996). Over the last decades, several regional monitoring networks have been established to assess the occurrence and trends of POPs in air in support of relevant regulatory programs and Conventions (Hillery et al., 1998; Hung et al., 2010; Kong et al., 2014; Tørseth et al., 2012). Historically, these early monitoring networks have been limited to active air sampling (AAS), but more recent advancements in passive air sampling have facilitated increased spatial coverage (Jaward et al., 2004a; Jaward et al., 2005; Shen et al., 2006) and even temporal trends (Schuster et al., 2011). Still, long-term monitoring stations and/or networks targeting POPs in air based on AAS remain scarce and are mainly limited to industrialized regions in the northern hemisphere (Tørseth et al., 2012) and polar regions (Hung et al., 2010). Comparably less data derived on the basis of AAS are available from developing regions and tropical areas although there are notable exceptions in ship-based cruises (Gioia et al., 2008a, 2008b; Jaward et al., 2004b; Lohmann et al., 2012; Lohmann et al., 2013a; Lohmann et al., 2013b; Xie et al., 2011). Among such studies, there is some previous data available for selected compounds measured at the Cape Verde islands off the West African coast (Garrison et al., 2014; Gioia et al., 2011). Also, there are examples of passive air sampling campaigns in tropical areas (Gioia et al., 2011; Klánová et al., 2009; Lammel et al., 2013).

The current study was performed at Cape Verde islands and aimed to (i) monitor concentrations of selected POPs in air outside West Africa based on active sampling during the course of a year, and (ii) to evaluate atmospheric processes and source regions affecting the measured concentrations.

## 2. Materials and methods

### 2.1. Sampling campaign

Sampling was carried out at the Cape Verde Atmospheric Observatory (CVAO; Fig. 1; 16° 51' 49 N, 24° 52' 02 W) which is a World Meteorological Organization-Global Atmospheric Watch station that has served to provide long-term ground- and ocean-based data since 2006. The CVAO is situated on an island >800 km off the coast of Western Africa in the northern trade winds (heading southward from the Canary Islands and North African continent) region of the tropical eastern Atlantic Ocean (Carpenter et al., 2010).

Between 23 May 2012 and 17 June 2013, 43 air samples were collected with median sampling frequency of 8 days (ranging 1–49 days; see details in Table S1). Twenty-four hours integrated air samples were collected with an average sampling volume of 634 m<sup>3</sup> (0.44 m<sup>3</sup> min<sup>-1</sup>). The sampling was performed using an active high-volume air sampler (DIGITEL Elektronik AG, Hegnau, Switzerland) installed on the roof of the CVAO station (altitude 3 m, sampler installed 30 m above ground). Further, the sampler collects particle and gas phases using a glass microfiber filter and two polyurethane foam (PUF) disks, respectively. Glass microfiber filters (diameter 1.5 cm, GF/C CAT No. 1822–150 from Whatman GF/C, GE Healthcare, Buckinghamshire, UK) were pretreated at 450 °C for 8 h and wrapped in alumina foil. PUF disks (diameter 4.5 cm, thickness 7.5 cm; from Sunde Søm & Skumplast A/S, Gan, Norway) were pre-cleaned using Soxhlet

extraction with toluene for 24 h, acetone for 8 h and finally with toluene for an additional 8 h. After cleaning, the PUF disks were dried in desiccators at 40 °C under vacuum until they were completely dry. Filter holders and glass sampling chambers were pre-cleaned by soaking in a soap solution overnight and rinsed in tap water, followed by acetone and *n*-hexane.

After sampling was completed, the exposed PUF samples were sealed in a gas tight container and glass fiber filters were wrapped in alumina foil and sealed. The samples were stored in a freezer facility at CVAO and sent to the laboratories of NILU at Kjeller, Norway for analyses.

### 2.2. Sample clean-up and analyses

The analytical procedures for PCBs, PBDEs and pesticides were similar to those described by Eckhardt et al. (2009) for PCBs. Prior to extraction, the sample material (filters and PUFs combined) were spiked with internal standards (isotopically labeled analogs of selected analytes; listed in Table S2) before they were Soxhlet extracted for 8–10 h in approximately 250 mL of *n*-hexane/10% diethyl ether. Extracts were concentrated on a TurboVap 500 System (Zymark, Hopkinton, MA, USA) to about 50 mL, and transferred to a graded cylinder. For the majority of samples, 10% (volume) of the extracts were transferred to 10 mL stained vials with screw-caps and stored in a fridge for potential future analyses. The remaining extracts were further concentrated to about 0.5 mL, transferred to a centrifuge tube, adjusted to 2 mL with *n*-hexane, and treated with 2 mL concentrated sulfuric acid. During the acid treatment the clear extract turns to dark yellow, and the treatment was repeated until no more color change was visible (usually 2–3 times). The extract was reduced to 0.5 mL in an evaporation glass and further cleaned up with fractionation with a silica column (15 mm in diameter and 200 mm in length). The column consisted of 4 g of activated silica (Silica gel 60 Merck, pretreated for 8 h at 550 °C) topped with 1 cm anhydrous sodium sulfate (pretreated for 12 h at 600 °C). The column was prewashed with 30 mL *n*-hexane before the samples were eluted with 30 mL *n*-hexane/10% diethyl ether. Extracts were reduced to 0.5 mL by evaporation on the Turbovap and solvent exchanged into iso-octane and transferred to a small vial with a screw-cap. Prior to analyses all extracts were further reduced by a gentle stream of nitrogen to approximately 100 µL and 1,2,3,4-tetrachloronaphthalene was added as recovery standard.

Analyses of the i) PCB congeners and HCB were performed using an Agilent 7890A gas chromatograph (GC) coupled to a Waters high resolution mass spectrometer (MS) in electron impact mode (Halse et al., 2011); ii) PBDE congeners were performed with an Agilent 6890 N GC and a low resolution Waters AutoSpec MS in electron impact mode; and, iii) pesticides (*trans* chlordane, *cis* chlordane, *oxy*-chlordane, heptachlor, *trans* nonachlor, *cis* nonachlor and mirex) were performed by a Agilent 6890 N GC coupled to a low resolution Waters Autospec MS in electron capture negative ion mode (Halse et al., 2015). Details of the instrumental conditions (e.g. column and temperature program) and all compounds analyzed are presented in Table S3.

The quantification was performed according to the isotope-dilution method, an internal standard method, which is applied in all modern standard methods dealing with analysis of POPs as for example the US-EPA method 1625B for semivolatile organic compounds (US EPA Method 1625, 1984). These methods inherently correct the analyte

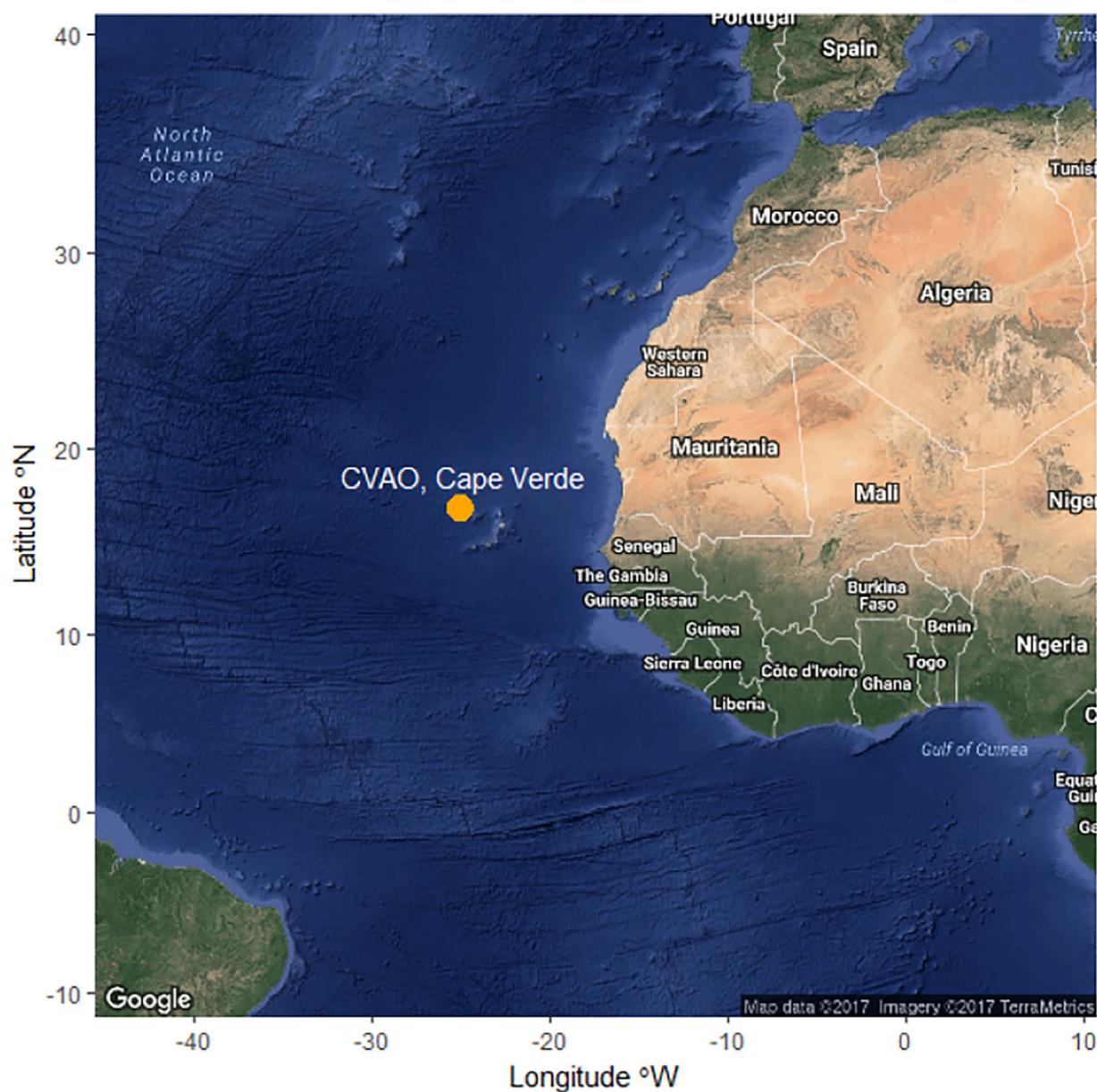


Fig. 1. Location of the Cape Verde Atmospheric Observatory (CVAO) at the Cape Verde Islands.

concentration according to the measured recovery of the added isotopically labeled surrogate.

### 2.3. Quality assurance and quality control (QA-QC)

Two field blanks were collected during the yearlong monitoring campaign and, in 2015, post sampling blanks were collected and analyzed (field = 2, transport = 2 and laboratory = 2). One field blank from 2013 was analyzed along with the samples in 2012/2013 and the other in 2015 along with the extra blank samples. The variation among concentrations in blanks was large and a conservative approach was chosen to determine the method detection limit (MDL; see details in Table S4). The MDL was set from the average + 3 \* standard deviation of all blank data (when blank concentrations were below instrumental detection limits, this limit divided by two represented the value for that blank sample). Also, results are only presented for samples with recoveries of internal standards higher than 40%.

For two samples, the filter and PUFs were analyzed separately to assess partitioning of POPs in the particle and gas phase (Table S5) but

concentrations in the main text are presented for filter and PUFs combined.

### 2.4. Particle dispersion modelling of PCB-28

FLEXPART is a Lagrangian particle dispersion model that calculates trajectories of 'tracer particles' and simulate their long-range and meso-scale transport, diffusion, degradation by hydroxyl radicals, dry and wet deposition (Eckhardt et al., 2009; Stohl et al., 2005; Stohl et al., 1998). This model was employed to indicate source regions for air masses sampled at the CVAO station and coupled to spatially resolved emission estimates for PCBs and atmospheric fate properties of PCBs to provide simulated concentrations at the measurement site and geographical distribution of their sources.

Based on previous studies using the FLEXPART model in Norway, PCB-28 was chosen as model compound (Eckhardt et al., 2009; Halse et al., 2013). For each measurement FLEXPART was run 20 days backward in time for an air tracer representing the chemical properties of PCB-28. Two sets of time-variant emission estimates for PCB-28 were used in simulations, specifically the maximum emission scenarios

described by Breivik et al. (2007) and by Breivik et al. (2016). The main difference between these two global emission scenarios is that the latter accounted for exports of waste electric and electronic equipment (e-waste) into developing regions, whereas the former did not. Further details for the model simulations were described by Eckhardt et al. (2009) and Halse et al. (2013).

FLEXPART was here driven by global model-level data from the European Centre for Medium-Range Weather Forecasts (ECMWF, 2002) and by pressure-level data from the Global Forecast System (GFS) model of the National Center for Environmental Prediction (NCEP). Both data sets have a temporal resolution of 3 h (analyses at 0, 6, 12, 18 UTC; 3 h forecasts at 3, 9, 15, 21 UTC) and a horizontal resolution of  $1^\circ \times 1^\circ$ . The GFS data are available on 26 pressure levels between 1000 hPa and 10 hPa, while the ECMWF data have 60 model levels. We used 2 different meteorological datasets, as the horizontal resolution is better for the ECMWF data, but real-time forecasting data were only available for the GFS dataset. We will further refer to the forecasting mode of FLEXPART using GFS as FLEXPART-*f* and the retrospective mode of FLEXPART using ECMWF as FLEXPART-*r*.

After completion of the yearlong monitoring in June 2013, FLEXPART-*f* was run daily across the winter of 2014 and 2015 to predict the origin of air masses at CVAO the following day to allow for possible targeted sampling. If forecasts indicated air masses coming from suspected source regions emphasizing known destinations of e-waste imports, e.g. Ghana and/or Nigeria (Schluep et al., 2011), air masses were sampled the following day. This aspect was largely motivated by past observations from ship based cruises which had indicated elevated levels of PCBs and halogenated flame retardants in air outside West Africa (Gioia et al., 2008a, 2008b; Jaward et al., 2004c; Xie et al., 2011). Two targeted 24-h samples were indicated as potentially influenced by air from the West African continent (5 November and 10 December 2013) and were analyzed for POPs.

### 2.5. Calculation of atmospheric degradation of gas phase concentrations as a function of time

An evaluation of atmospheric degradation of gas phase concentrations of POPs under tropical conditions is relevant for evaluating long-range atmospheric transport in the context of the monitoring results at Cape Verde (Wania and Daly, 2002; Webster et al., 1998). For PCB-28, PCB-153, HCB, *trans* nonachlor and *cis* chlordane, atmospheric degradation rates were calculated using Eq. 1 (Wania et al., 2006).

$$k_{RA} = k_{RAref} * [OH]^* e^{\frac{AE_A}{R} * \left( \frac{1}{298.15K} - \frac{1}{T_A} \right)} \quad (1)$$

where,  $k_{RA}$  is the rate of atmospheric degradation in  $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  and  $k_{RAref}$  is the estimated rate constant at 298 K.  $k_{RAref}$  is obtained in  $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for PCBs (Brubaker and Hites, 1998a), for HCHs and HCB (Brubaker and Hites, 1998b), and for chlordanes (US EPA, 2016).  $[OH]$  is assumed to be  $3 \cdot 10^6$  radicals/ $\text{cm}^3$  (Lelieveld et al., 2004).  $AE_A$  is activation energy in air, here assumed to be  $1 \cdot 10^4$  J/mol (Brubaker and Hites, 1998b),  $R$  is the gas constant,  $T_A$  is the ambient temperature in K and assumed to be 303.15 K (30 °C).

Degradation of the initial concentration up to 7 days was calculated using Eq. 2 as a fraction of the initial concentration.

$$C(x) = C_0 * e^{-k_{RA} * t} \quad (2)$$

where,  $C(x)$  is the concentration of the chemical at a distance  $x$  km from the emission point,  $C_0$  is the concentration of the chemical at the point of the emission, here assumed to be 1, and  $k_{RA}$  was obtained from Eq. (1) and  $t$  was time in seconds.

### 2.6. Data handling and statistical analyses

A total of 43 samples were collected and analyzed for POPs, still the number of data points presented varies between compounds due to MDL and QA-QC censoring (Table S4). Summary statistics for compounds with detection frequencies above 40% are presented in Table 1. For compounds detected in <80% of samples, the summary measures were calculated using the Kaplan-Meier method with the NADA package for R according to Helsel (2005). For values that were below compound-specific MDLs, the values were substituted with the value divided by half prior to any further data analyses. Statistical analyses were executed using R, ver.3.1.1., and statistical significance was defined as  $p < 0.05$ . Correlations between components are presented as Spearman's rank correlations. Presentation of trends was performed with the ggplot2 package in R.

## 3. Results and discussions

### 3.1. Yearlong monitoring revealed low POP concentrations

The concentrations of the POPs from high-volume active air sampling at Cape Verde from May 2012 to June 2013 are summarized in Table 1. There are limitations to the data as there were variable recoveries (no correlation between sample recovery and quantified concentrations) and the number of blank samples should have ideally been higher. Still, stringent strategies chosen during data treatment were deliberately selected in the attempt to reach sound results. The trends across the sampling period varied between the different compounds and are presented for PCB-28, HCB and *cis* chlordane in Fig. 2 (selected others are presented in Fig. S1). PCB-28 (Fig. 2A) appeared to decrease across the sampling period and trends were similar for PCB-52 and PCB-153 although less apparent (Fig. S1). Concentrations of HCB from the early sampling period were missing due to low recovery for those samples in particular but trends appeared to increase from the period in October 2012–January 2013 compared to April–July 2013 (Fig. 2B). However, concentrations of *cis* chlordane (Fig. 2C) demonstrated clear seasonal variation with maximum concentrations in July to October. Temporal changes in concentrations of *trans* and *cis* nonachlor as well as Mirex resembled those of *cis* chlordane (Fig. S1) but those for *trans* chlordane did not display any clear trends. Inter-compound

**Table 1**  
Summary statistics in  $\text{pg}/\text{m}^3$  for the measurements of POPs obtained by 24 h active air sampling between May 2012 to June 2013.

Compound	Mean	SD <sup>a</sup>	Median	Min <sup>b</sup>	Max <sup>c</sup>	MDL <sup>d</sup>	Samples above MDL <sup>e</sup>
PCB-18	0.16	0.05	0.15	<MDL	0.31	0.07	38/40
PCB-28	0.20	0.06	0.19	<MDL	0.36	0.12	34/40
PCB-31	0.18	0.06	0.17	<MDL	0.32	0.11	35/40
PCB-33 <sup>f</sup>	0.08	0.02	0.07	<MDL	0.26	0.09	26/40
PCB-52	0.22	0.06	0.22	<MDL	0.48	0.12	39/40
PCB-66	0.12	0.04	0.12	<MDL	0.20	0.08	25/40
PCB-153	0.15	0.11	0.11	<MDL	0.60	0.07	36/40
PBDE-47 <sup>f</sup>	0.16	0.15	0.11	<MDL	1.07	0.17	15/37
PBDE-49 <sup>f</sup>	0.02	0.02	0.01	<MDL	0.12	0.02	17/37
<i>trans</i> Chlordane	0.41	1.74	0.11	0.06	11.00	0.02	39/39
<i>cis</i> Chlordane	0.77	1.59	0.53	0.17	10.40	0.03	39/39
<i>trans</i> Nonachlor	0.63	1.50	0.39	0.16	9.70	0.02	39/39
<i>cis</i> Nonachlor	0.12	0.44	0.05	0.02	2.80	0.005	39/39
HCB	11.35	3.34	10.80	6.95	19.30	0.48	23/23
Mirex	0.31	1.37	0.08	<MDL	8.40	0.01	35/37

<sup>a</sup> SD = Standard deviation.

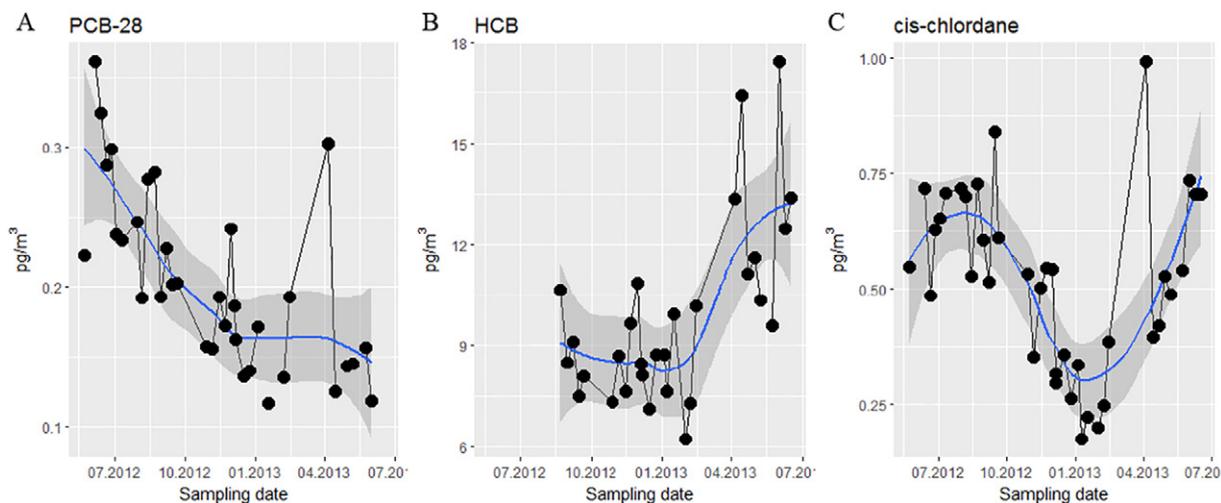
<sup>b</sup> Min = Minimum.

<sup>c</sup> Max = Maximum.

<sup>d</sup> MDL = Method detection limit.

<sup>e</sup> Of the 43 samples obtained, a variable number of samples were not quantifiable for each compound due to low recovery of the internal standards. See also Table S4.

<sup>f</sup> Descriptive summaries estimated using approach for censored results below 80% detection (see methodology Section 2.6. in the main text).

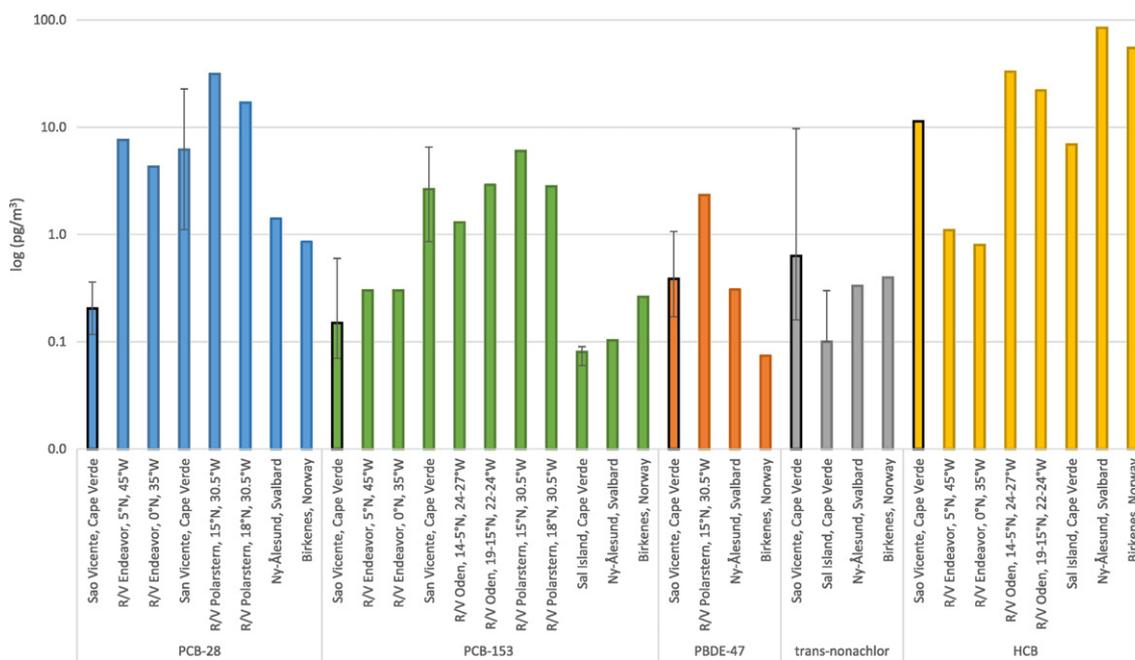


**Fig. 2.** One year monitoring trends between May 2012 and June 2013 as concentrations of A) PCB-28, B) HCB and C) cis chlordane in  $\text{pg}/\text{m}^3$ . The trend line was estimated by locally weighted scatterplot smoothing (loess) and the shaded areas designate the 95% confidence intervals of the trend line.

correlations were highest among the PCBs and the chlordanes, but also considerable across the POP groups (Table S6).

Median air concentrations across the sampling period were highest for HCB whereas considerably lower for chlordanes and PCB congeners (Table 1). Results for PCB-28, PCB-153, PBDE-47, *trans* nonachlor and HCB are compared with other remote sites and available data from the Atlantic Ocean in Fig. 3 and Table S7. The presented medians demonstrated low concentrations for PCBs in comparison with studies performed in the eastern tropic Atlantic Ocean or sites in Norway and at Svalbard (EMEP, n.d.; Garrison et al., 2014; Gioia et al., 2011; Gioia et al., 2008a; Gioia et al., 2008b, Lohmann et al., 2012; Luek et al., 2017; van Drooge et al., 2002; Xie et al., 2011). The monitoring results referred to at Svalbard and Norway were analyzed by the same laboratory as those in the present study and implies high comparability between these results (Su and Hung, 2010). However, medians for PBDE-47, *trans* nonachlor and HCB at Cape Verde were similar to the

studies mentioned in Table S7. These results indicate that Cape Verde in this period displayed concentrations within the range of those observed at remote sites. Still, it should be noted that concentrations of especially the more volatile compounds like HCB and lower chlorinated PCBs are likely underestimated due to breakthrough during sampling. This is a known sampling artifact, especially for sampling relatively volatile POPs under high temperatures (Melymuk et al., 2016) as in the present study ( $K_{OA}$  values ranging 7.25–10.30), and is likely to have led to underestimation and variability in concentrations presented. This assumption is further supported on the basis of two samples with filters and PUFs analyzed separately for which a considerable percentage was detected in the second PUF in the sampler (Table S5). Also, the particle phase fraction (represented by the concentrations on the GFF) was <1% for HCB, 1.1%–8% for PCBs and 3.6%–13.5% for the two PBDEs (Table S5). A high fraction of POPs in the gas phase during active air sampling was also observed in a study performed at Tenerife, also in



**Fig. 3.** Comparison of concentrations in air (median/means and range) for selected POPs and monitoring results performed in the region as well as examples of remote sites. Sampling years ranged between 2005 and 2013 and see text and Table S7 for further details. Whiskers represent the variation in the data wherever that information was presented in studies and is not visible for HCB in this study as the variation was miniscule on that scale.

the warmer regions of the Atlantic Ocean (van Drooge et al., 2002). Thus, some loss of the more volatile POPs during sampling is likely to have occurred under the governing conditions (Melymuk et al., 2014; Melymuk et al., 2016) and their bulk concentrations are likely somewhat underestimated. Still, concentrations of HCB are comparable to other studies performed in tropical areas (Table S7). This could be due to relatively uniform concentrations in background air (Barber et al., 2005), but also reflect similarities in sampling artifacts like breakthrough during sampling (Melymuk et al., 2016).

### 3.2. Potential source regions and atmospheric processes influencing POPs at Cape Verde

Concentrations in air are controlled by a combination of factors including proximity to (primary and secondary) sources, atmospheric transport times and origins, and processes controlling atmospheric reaction and net atmospheric deposition (Wania and Daly, 2002; Wania and Mackay, 1996; Webster et al., 1998). Evaluations of key factors controlling the concentrations observed at Cape Verde have been assessed separately for (i) air mass transport trajectories, (ii) estimated atmospheric degradation, and (iii) seasonal changes and potential influence from secondary sources.

#### 3.2.1. Source regions indicated by air mass transport trajectories

The particle dispersion model FLEXPART was used to indicate source regions for the POPs in sampled air masses at Cape Verde. Overall, FLEXPART-*r* demonstrated that the air masses to Cape Verde during the summer generally originated from the open Atlantic Ocean and southwestern areas of Europe, while from the surrounding ocean and northwestern areas of the African continent during winter (data not shown). Similar seasonal variations in wind patterns have been observed in previous studies (Gioia et al., 2011; Müller et al., 2010; Xie et al., 2011). We used FLEXPART-*r* emission sensitivities, which are proportional to the particle residence times and represent the likelihood of surface emission uptake, to specify possible source regions for low/high measurement samples. These were normalized by the mean footprint in order to indicate regions that contribute to especially high/low concentrations. The ratios of emission sensitivities as high/mean and low/mean of emission footprints for monitoring samples are presented for *cis* chlordane (Fig. 4). Specifically, the indicated source regions for a high sample (average for all footprints corresponding to measurements above the 80th percentile value of monitoring samples) for *cis* chlordane demonstrated that the Atlantic Ocean north of the Cape Verde Islands is the predicted source region for high measurements (high values in Fig. 4A). Conversely, the source regions for a low sample (correspondingly below 20th percentile value of monitoring samples) are likely northwestern Africa and Europe (Fig. 4B). Similar source regions were indicated in the same analyses for PCB-28 (Fig. S2). Underlying these results were footprint emission sensitivity maps for the 80th percentile, the 20th percentile and average of measurements (exemplified for *cis* chlordane; Fig. S3). These results were similar across several substances and support that the general trends in source regions are similar among the POPs studied.

We were particularly interested in using FLEXPART-*r* to indicate potential influence of atmospheric transport episodes in measurements that deviated from the observed seasonal trends as inferred from the statistical analyses. The sample deviating most from the seasonal trends was observed in April 2013 (Fig. 2 and S1) and was evident for PCB-28, PCB-52, *trans* chlordane, *cis* chlordane, *trans* nonachlor (e.g. 158% of the average of the monitoring phase for PCB-28). Thus, this sample was most suspected to be influenced by an episode of long range transport from source areas. The emission footprint map for the air masses predicted for this sample indicated source regions in the Atlantic Ocean and Europe (Fig. S4). Still, the same regions were indicated in emission footprint maps observed for sample measurements with lower concentrations. The Cape Verde Islands are far from major historical source

regions of e.g. PCB in industrialized countries, but long-range transport from contemporary source regions related to informal e-waste disposal and recycling in countries like Ghana (Breivik et al., 2016; Gioia et al., 2011) could potentially have influenced measurements at the islands. Accordingly, air sampling on ship cruises closer to the continent had earlier shown high concentrations of PCBs and PBDEs and suggested sources on the West African continent (Gioia et al., 2011; Gioia et al., 2008a, 2008b; Xie et al., 2011). Still, the concentrations observed at Cape Verde are lower compared to concentrations reported closer to the coastal regions. Also, the predicted time series for PCB-28 during the monitoring period were similar regardless of whether the emission scenarios employed incorporated emissions from e-waste or not (~5% difference between measurements and predicted values; Fig. S5 and S6).

POP concentrations and indicated source regions for the two samples analyzed from the targeted sampling period are presented in Table S8 and Fig. S7. The concentrations for these targeted samples (Table S8) were within the range of samples from the yearlong monitoring sampling and FLEXPART-*r* confirmed negligible influence from any emissions in countries like Ghana and Nigeria on these measurements. Taken together, the air measurements from CVAO did not capture any distinct transport episodes with elevated concentrations attributed to direct transport from West African countries that have been implicated as major destinations for e-waste.

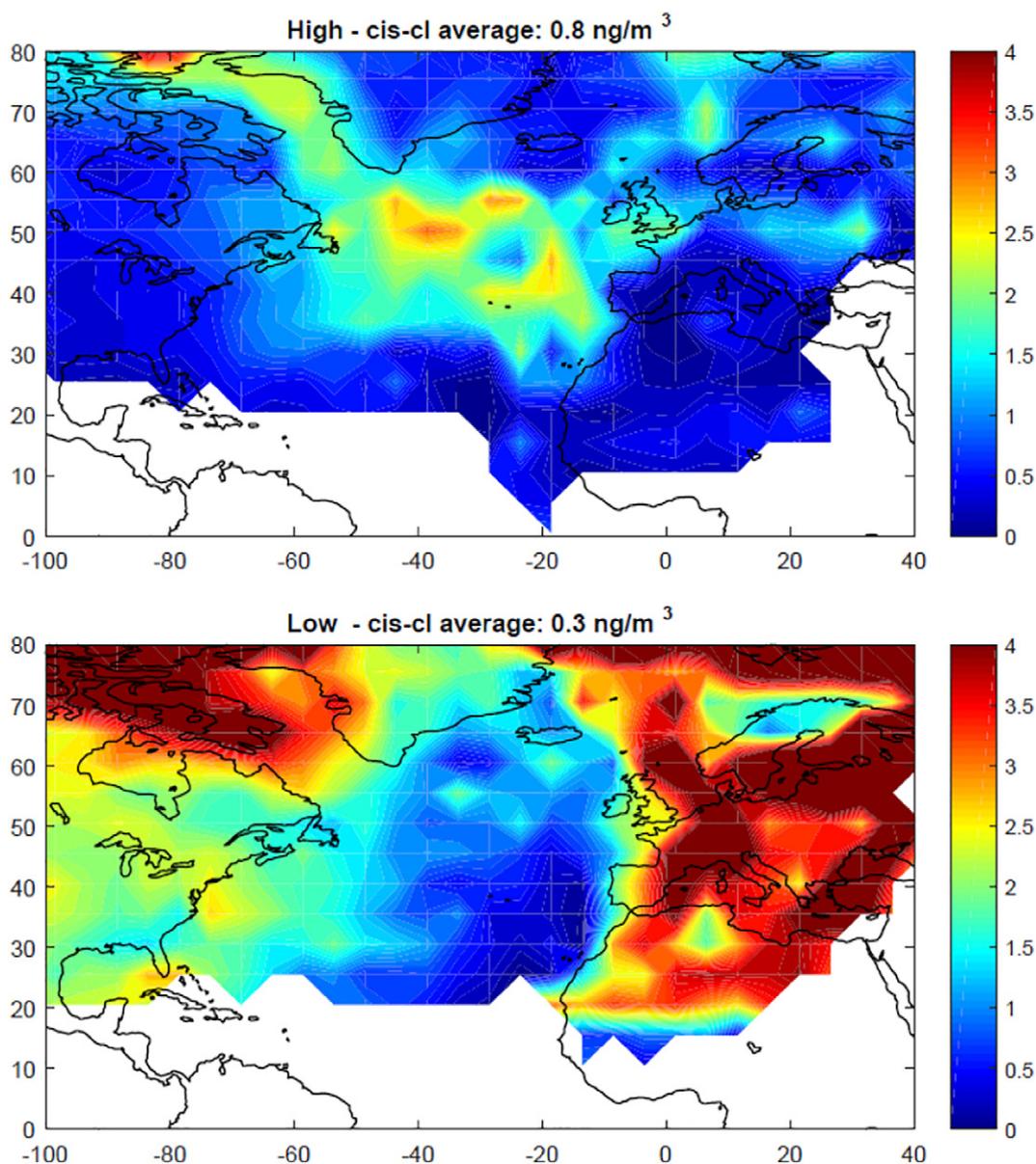
#### 3.2.2. Evaluation of potential atmospheric degradation of gas phase concentrations

The long-range atmospheric transport potential of POPs will be limited by (net) atmospheric deposition and atmospheric reaction (Anderson and Hites, 1996; Beyer et al., 2003). Of particular interest and relevance to this study is the enhanced atmospheric degradation losses anticipated under tropical conditions. To evaluate potential differences in atmospheric degradation and hence long-range transport potential to Cape Verde for selected individual POPs, we estimated gas phase POP degradation in air as a function of time (Table S9). FLEXPART results indicated that a frequently observed travel time from the west coast of Africa to Cape Verde was three days. For HCB, 99% of the initial concentration was estimated to be present in a given air mass after three days, while this percentage was 87, 37 and 2 for PCB-153, PCB-28, and nonachlors, respectively. From these theoretical considerations, considerable gas phase degradation of many POPs could be expected in the governing tropical conditions i.e. warm temperatures and high concentrations of hydroxyl radicals (Anderson and Hites, 1996; Beyer et al., 2003). It also follows that the concentrations of HCB and PCB-153 at Cape Verde could be influenced by long-range transport while less so for PCB-28 based on expected duration of the air transport. This is supported by predicted general long-range atmospheric transport potentials for HCB and PCBs (Beyer et al., 2000). Concentrations of POPs in air are therefore expected to be low as well as show a “weathered” signal, given the remoteness of CVAO from global source regions in combination with the high reactivity of the atmosphere. As chlordanes are among the more reactive POPs included in our study, the occurrence of these substances may rather indicate possible influence from more local sources and/or secondary emissions from the oceans.

Temperature has major influence on the gas-particle partitioning equilibrium which again influences the atmospheric degradation (Wania and Daly, 2002). The estimations of degradations presented in Table S9 are only valid for gas phase concentrations whereas the degradation was here evaluated for bulk sample concentrations. Assuming that particle bound POP molecules have longer half lives (Wania and Daly, 2002), the degradation rates are somewhat overestimated and the travel time correspondingly underestimated.

#### 3.2.3. Influence of temperature and diffusive air-ocean exchange of POPs

The seasonal trends in concentrations (Fig. 2) are in accordance with those in observed ambient temperatures (Fig. 5) and the strongest



**Fig. 4.** Source regions for sampled air masses at Cape Verde from the FLEXPART-model displayed as ratios of emission footprints for a high sample (80th percentile value of measurements) and a low sample (20th percentile value of measurements) for *cis* chlordane. Values for residence times in the region South of 20° were small and included noise due to a low particle number, thereby hampering calculations in most of that area and the areas are not represented by any color.

relation to temperature was observed for *cis* nonachlor. The Clausius-Clapeyron equation describing the relation between temperature and gas phase air concentrations have been proposed as a tool to evaluate possible influence from secondary sources as driven by volatilization (Halsall et al., 1999; Hoff et al., 1998; Wania et al., 1998). Table 2 presents the temperature-dependence of gas phase concentrations across the sampling period at Cape Verde according to this equation and a negative relation was significant for *cis* chlordane and *cis* nonachlor. These results indicate that air-surface exchange (i.e. most likely air-ocean exchange) governs the atmospheric concentrations of these compounds. Correspondingly, the lack of significant relations for the other POPs (PCBs, HCB) implies that the relative importance of volatilization from proximate surfaces was low compared to long-range transport. The sample measurements deviating from the regression line in the Clausius-Clapeyron plots (Fig. 5) did not have any air mass back-trajectories deviating from those of samples obtained in the same time period and hence no distinct long-range atmospheric transport episodes leading to elevated concentrations were observed.

Although previous studies have found indications of net atmospheric deposition of PCBs in the Atlantic Ocean (Jurado et al., 2004), the fate appear regionally dependent as the tropical Atlantic Ocean has also been described as a secondary source to many PCBs by net volatilization (Lohmann et al., 2012). Also, influencing the interpretation are the general declining trends across time in many areas and in that aspect, the Atlantic Ocean surface waters have been suggested to buffer the general downwards concentrations of many POPs (Hung et al., 2016; Nizzetto et al., 2010). Together with the low concentrations observed in this study, the temperature dependence of several chlordanes could indicate that the temperature-dependent air-ocean exchange is an influential mechanism for the concentrations measured in air at Cape Verde.

### 3.3. Summary of evaluations of suspected source regions and atmospheric processes at Cape Verde

This study presents yearlong monitoring results for a tropical eastern Atlantic site at the Cape Verde Islands. The measured concentrations in air of selected POPs at Cape Verde were assessed based on a

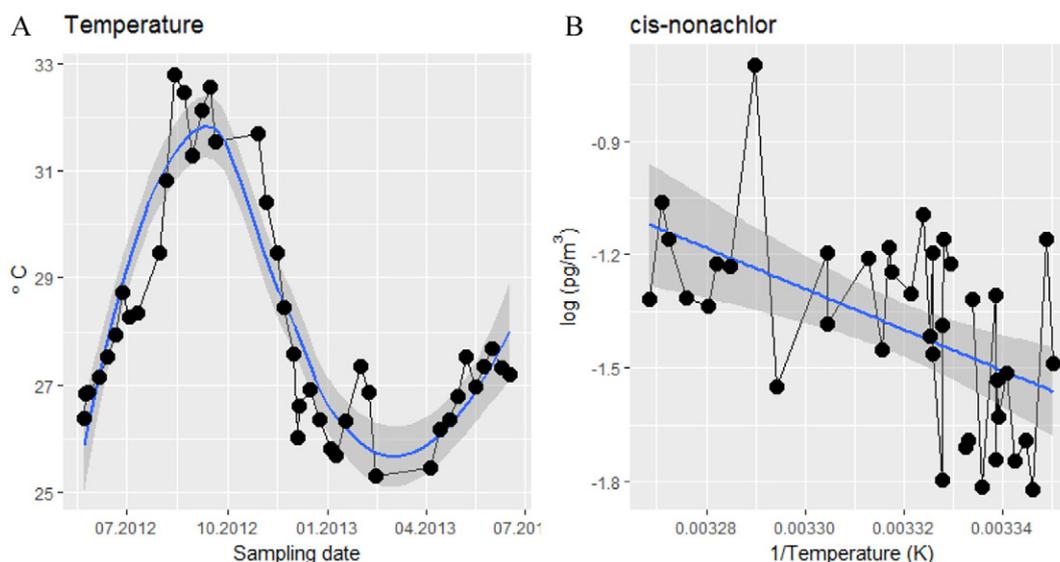


Fig. 5. Atmospheric concentrations of B) *cis nonachlor* (expressed as log, excluding outlier at log-value 0.45) at Cape Verde correlated with A) ambient temperature (K).

combination of air mass transport trajectories, estimated atmospheric degradation (gas phase concentrations), seasonal trends and Clausius-Clapeyron plots. The concentrations of POPs at Cape Verde were generally low and comparable to remote sites in the Arctic for several compounds. Air mass transport trajectories demonstrated air masses typically from the ocean or the North African continent as well as southwestern Europe. We have emphasized general features when evaluating atmospheric processes and source regions affecting the measured concentrations in these discussions. Consistently, both the evaluation of temperature-dependence and air mass transport trajectories implied that the concentrations observed were not strongly affected by long-range transport episodes from suspected or known continental source regions, but rather reflected background concentrations likely influenced by air-ocean exchange over the Atlantic Ocean. While measured concentrations of the more persistent substances (e.g. HCB, PBDEs and higher chlorinated PCBs) in air may be affected by transport from global source regions as indicated by the FLEXPART results, the governing tropical conditions at these latitudes likely favors atmospheric degradation of many POPs (e.g. chlordanes and lower chlorinated PCBs). This may also in part explain the low levels observed at this remote site. Taken together, our results suggested that Cape Verde could represent a suitable location to study background concentrations in tropical

regions. The data also indicated that some POPs, especially chlordanes, were influenced by volatilization, most likely from the ocean.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.08.217>.

#### References

- Anderson, P.N., Hites, R.A., 1996. OH radical reactions: the major removal pathway for polychlorinated biphenyls from the atmosphere. *Environ. Sci. Technol.* 30, 1756–1763.
- Barber, J.L., Sweetman, A.J., van Wijk, D., Jones, K.C., 2005. Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes. *Sci. Total Environ.* 349, 1–44.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.* 34, 699–703.
- Beyer, A., Wania, F., Gouin, T., Mackay, D., Matthies, M., 2003. Temperature dependence of the characteristic travel distance. *Environ. Sci. Technol.* 37, 766–771.
- Brevik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2007. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach: 3 An update. *Sci. Total Environ.* 377, 296–307.
- Brevik, K., Armitage, J.M., Wania, F., Sweetman, A.J., Jones, K.C., 2016. Tracking the global distribution of persistent organic pollutants accounting for e-waste exports to developing regions. *Environ. Sci. Technol.* 50, 798–805.
- Brubaker, W.W., Hites, R.A., 1998a. Gas-phase oxidation products of biphenyl and polychlorinated biphenyls. *Environ. Sci. Technol.* 32, 3913–3918.
- Brubaker, W.W., Hites, R.A., 1998b. OH reaction kinetics of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-p-dioxins and dibenzofurans. *J. Phys. Chem. A* 102, 915–921.
- Carpenter, L., Fleming, Z.L., Read, K., Lee, J., Moller, S., Hopkins, J., et al., 2010. Seasonal characteristics of tropical marine boundary layer air measured at the Cape Verde Atmospheric Observatory. *J. Atmos. Chem.* 67, 87–140.

Table 2

Temperature-dependence of gas phase concentrations in  $\text{pg}/\text{m}^3$  of POPs at Cape Verde according to regressions of Clausius-Clapeyron plots. Published  $\log K_{\text{OA}}$  values at the annual average temperature of 28 °C are also presented.

Compound	$\log K_{\text{OA}}$	$R^2$ <sup>a</sup>	$p$ <sup>b</sup>	Slope	S.E. <sup>c</sup> of slope
PCB-28	7.71 <sup>d</sup>	0.06	0.154	−1341	918
PCB-52	8.08 <sup>d</sup>	0.03	0.314	−783	766
PCB-153	9.28 <sup>d</sup>	0.10	0.062	−3122	1620
PBDE-47	10.3 <sup>e</sup>	0.00	0.886	−331	2270
<i>trans</i> Chlordane	8.70 <sup>f</sup>	0.00	0.968	−44	1088
<i>cis</i> Chlordane	8.75 <sup>f</sup>	<b>0.19</b>	0.006	−3255	1122
<i>trans</i> Nonachlor	9.11 <sup>f</sup>	0.05	0.192	−1376	1035
<i>cis</i> Nonachlor	9.49 <sup>f</sup>	<b>0.28</b>	0.001	−5412	1454
HCB	7.25 <sup>g</sup>	0.07	0.154	1161	791

<sup>a</sup>  $R^2$  = percent variance explained by the regression model (bolded values are statistically significant)

<sup>b</sup>  $p$ -value = significance level.

<sup>c</sup> S.E. = standard error.

<sup>d</sup> Li et al., 2003.

<sup>e</sup> Wania and Dugani, 2003.

<sup>f</sup> Shoeib and Harner, 2002.

<sup>g</sup> Shen and Wania, 2005.

- Eckhardt, S., Breivik, K., Li, Y., Manø, S., Stohl, A., 2009. Source regions of some persistent organic pollutants measured in the atmosphere at Birkenes, Norway. *Atmos. Chem. Phys.* 9, 6597–6610.
- ECMWF, 2002. European Centre for Medium-Range Weather Forecasts (Datasets available from <https://www.ecmwf.int>).
- EMEP (European Monitoring and Evaluation Programme) under the convention on long-range transboundary air pollution, Measurements (obtained from <http://ebas.nilu.no/>, accessed 01.02.16).
- Garrison, V.H., Majewski, M.S., Foreman, W.T., Genualdi, S.A., Mohammed, A., Massey Simonich, S.L., 2014. Persistent organic contaminants in Saharan dust air masses in West Africa, Cape Verde and the Eastern Caribbean. *Sci. Total Environ.* 468–469, 530–543.
- Gioia, R., Lohmann, R., Dachs, J., Temme, C., Lakaschus, S., Schulz-Bull, D., et al., 2008a. Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean. *J. Geophys. Res. Atmos.* 113 (1984–2012), D19302.
- Gioia, R., Nizzetto, L., Lohmann, R., Dachs, J., Temme, C., Jones, K.C., 2008b. Polychlorinated biphenyls (PCBs) in air and seawater of the Atlantic Ocean: Sources, trends and processes. *Environ. Sci. Technol.* 42, 1416–1422.
- Gioia, R., Eckhardt, S., Breivik, K., Jaward, F.M., Prieto, A., Nizzetto, L., et al., 2011. Evidence for major emissions of PCBs in the west African region. *Environ. Sci. Technol.* 45, 1349–1355.
- Halsall, C.J., Gevao, B., Howsam, M., Lee, R.G.M., Ockenden, W.A., Jones, K.C., 1999. Temperature dependence of PCBs in the UK atmosphere. *Atmos. Environ.* 33, 541–552.
- Halse, A.K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K.C., Breivik, K., 2011. Spatial variability of POPs in European background air. *Atmos. Chem. Phys.* 11, 1549–1564.
- Halse, A.K., Eckhardt, S., Schlabach, M., Stohl, A., Breivik, K., 2013. Forecasting long-range atmospheric transport episodes of polychlorinated biphenyls using FLEXPART. *Atmos. Environ.* 71, 335–339.
- Halse, A.K., Schlabach, M., Schuster, J.K., Jones, K.C., Steinnes, E., Breivik, K., 2015. Endosulfan, pentachlorobenzene and short-chain chlorinated paraffins in background soils from Western Europe. *Environ. Pollut.* 196, 21–28.
- Helsel, R.D., 2005. *Nondetects and Data Analysis. Statistics for Censored Environmental Data*. Hoboken, NJ, USA, Wiley Interscience.
- Hillery, B.R., Simcik, B.F., Basu, I., Hoff, R.M., Strachan, W.M.J., Burniston, D., et al., 1998. Atmospheric deposition of toxic pollutants to the Great Lakes as measured by the integrated atmospheric deposition network. *Environ. Sci. Technol.* 32, 2216–2221.
- Hoff, R.M., Brice, K.A., Halsall, C.J., 1998. Nonlinearity in the slopes of Clausius – Clapeyron plots for SVOCs. *Environ. Sci. Technol.* 32, 1793–1798.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y.S., Brorstrom-Lunden, E., Olafsdottir, K., et al., 2010. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.* 408, 2854–2873.
- Hung, H., Katsoyiannis, A.A., Brorström-Lundén, E., Olafsdottir, K., Aas, W., Breivik, K., et al., 2016. Temporal trends of persistent organic pollutants (POPs) in Arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.*
- Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, K.C., 2004a. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environ. Sci. Technol.* 38, 34–41.
- Jaward, F.M., Barber, J.L., Booi, K., Jones, K.C., 2004b. Spatial distribution of atmospheric PAHs and PCNs along a north–south Atlantic transect. *Environ. Pollut.* 132, 173–181.
- Jaward, F.M., Barber, J.L., Booi, K., Dachs, J., Lohmann, R., Jones, K.C., 2004c. Evidence for dynamic air–water coupling and cycling of persistent organic pollutants over the open Atlantic Ocean. *Environ. Sci. Technol.* 38, 2617–2625.
- Jaward, T.M., Zhang, G., Nam, J.J., Sweetman, A.J., Obbard, J.P., Kobara, Y., et al., 2005. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environ. Sci. Technol.* 39, 8638–8645.
- Jurado, E., Jaward, F.M., Lohmann, R., Jones, K.C., Simó, R., Dachs, J., 2004. Atmospheric dry deposition of persistent organic pollutants to the Atlantic and inferences for the global oceans. *Environ. Sci. Technol.* 38, 5505–5513.
- Klánová, J., Čupr, P., Holoubek, I., Borůvková, J., Příbylová, P., Kareš, R., et al., 2009. Monitoring of persistent organic pollutants in Africa. Part 1: passive air sampling across the continent in 2008. *J. Environ. Monit.* 11, 1952–1963.
- Kong, D.G., MacLeod, M., Hung, H., Cousins, I.T., 2014. Statistical analysis of long-term monitoring data for persistent organic pollutants in the atmosphere at 20 monitoring stations broadly indicates declining concentrations. *Environ. Sci. Technol.* 48, 12492–12499.
- Lammel, G., Heil, A., Stemmler, I., Dvorská, A., Klánová, J., 2013. On the contribution of biomass burning to POPs (PAHs and PCDDs) in air in Africa. *Environ. Sci. Technol.* 47, 11616–11624.
- Lelieveld, J., Dentener, F.J., Peters, W., Krol, M.C., 2004. On the role of hydroxyl radicals in the self-cleaning capacity of the troposphere. *Atmos. Chem. Phys.* 4, 2337–2344.
- Li, N., Wania, F., Lei, Y.D., Daly, G.L., 2003. A comprehensive and critical compilation, evaluation, and selection of physical–chemical property data for selected polychlorinated biphenyls. *J. Phys. Chem. Ref. Data* 32, 1545.
- Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., Bollinger, K., 2012. PCBs and OCPs on a east-to-west transect: the importance of major currents and net volatilization for PCBs in the Atlantic Ocean. *Environ. Sci. Technol.* 46, 10471–10479.
- Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., Bollinger, K., 2013a. Concentrations, fluxes, and residence time of PBDEs across the tropical Atlantic Ocean. *Environ. Sci. Technol.* 47, 13967–13975.
- Lohmann, R., Klanova, J., Příbylova, P., Liskova, H., Yonis, S., Bollinger, K., 2013b. PAHs on a west-to-east transect across the tropical Atlantic Ocean. *Environ. Sci. Technol.* 47, 2570–2578.
- Luek, J.L., Dickhut, R.M., Cochran, M.A., Falconer, R.L., Kylin, H., 2017. Persistent organic pollutants in the Atlantic and southern oceans and oceanic atmosphere. *Sci. Total Environ.* 583, 64–71.
- Melymuk, L., Bohlin, P., Oe, Sáfka, Pozo, K., Klánová, J., 2014. Current challenges in air sampling of semivolatile organic contaminants: sampling artifacts and their influence on data comparability. *Environ. Sci. Technol.* 48, 14077–14091.
- Melymuk, L., Bohlin-Nizzetto, P., Prokes, R., Kukucka, P., Klanova, J., 2016. Sampling artifacts in active air sampling of semivolatile organic contaminants: comparing theoretical and measured artifacts and evaluating implications for monitoring networks. *Environ. Pollut.* 217, 97–106.
- Müller, K., Lehmann, S., Dv, Pinxteren, Gnauk, T., Niedermeier, N., Wiedensohler, A., et al., 2010. Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLE intensive. *Atmos. Chem. Phys.* 10, 2709–2721.
- Nizzetto, L., Lohmann, R., Gioia, R., Dachs, J., Jones, K.C., 2010. Atlantic Ocean surface waters buffer declining atmospheric concentrations of persistent organic pollutants. *Environ. Sci. Technol.* 44, 6978–6984.
- Pozo, K., Harner, T., Wania, F., Muir, D.C.G., Jones, K.C., Barrie, L.A., 2006. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environ. Sci. Technol.* 40, 4867–4873.
- Schluep, M., Manhart, A., Osibanjo, O., Rochat, D., Isarin, N., Mueller, E., 2011. Where are WEEE in Africa. Findings from the Basel Convention e-waste Africa Programme. Châtelaine, Switzerland: Secretariat of the Basel Convention. (Geraadpleegd op <http://www.basel.int/Implementation/TechnicalAssistance/EWaste/EWasteAfricaProject/Publications/tabid/2553/Default.aspx>).
- Schuster, J.K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., Jones, K.C., 2011. Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs. *Environ. Sci. Technol.* 44, 6760–6766.
- Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical – chemical property data for organochlorine pesticides. *J. Chem. Eng. Data* 50, 742–768.
- Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., Xiao, H., 2006. Polychlorinated biphenyls and polybrominated diphenyl ethers in the north American atmosphere. *Environ. Pollut.* 144, 434–444.
- Shoeb, M., Harner, T., 2002. Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. *Environ. Toxicol. Chem.* 21, 984–990.
- Stohl, A., Hittenberger, M., Wotawa, G., 1998. Validation of the Lagrangian particle dispersion model FLEXPART against large-scale tracer experiment data. *Atmos. Environ.* 32, 4245–4264.
- Stohl, A., Forster, C., Frank, A., Seibert, P., Wotawa, G., 2005. Technical note: the Lagrangian particle dispersion model FLEXPART version 6.2. *Atmos. Chem. Phys.* 5, 2461–2474.
- Su, Y., Hung, H., 2010. Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples. *Environ. Pollut.* 158, 3365–3371.
- Tørseth, K., Aas, W., Breivik, K., Fjaeraa, A.M., Fiebig, M., Hjelbrekke, A.G., et al., 2012. Introduction to the European monitoring and evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmos. Chem. Phys.* 12, 5447–5481.
- US EPA, 2016. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.1. United States Environmental Protection Agency, Washington, DC, USA. (Available from <http://www.epa.gov/oppt/exposure/pubs/episutedl.htm>).
- US EPA Method 1625, 1984. Revision B: Semivolatile Organic Compounds by Isotope Dilution GC/MS (Vol. 1625B). US-EPA. United States Environmental Protection Agency, Washington, DC, USA (Available from [https://www.epa.gov/sites/production/files/2015-10/.../method\\_1625b\\_1984.pdf](https://www.epa.gov/sites/production/files/2015-10/.../method_1625b_1984.pdf)).
- Van Drooge, B.L., Grimalt, J.O., Garcia, C.J.T., Cuevas, E., 2002. Semivolatile organochlorine compounds in the free troposphere of the northeastern Atlantic. *Environ. Sci. Technol.* 36, 1155–1161.
- Wania, F., Daly, G.L., 2002. Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. *Atmos. Environ.* 36, 5581–5593.
- Wania, F., Dugani, C.B., 2003. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models. *Environ. Toxicol. Chem.* 22, 1252–1262.
- Wania, F., Mackay, D., 1996. Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.* 30, A390–A396.
- Wania, F., Haugen, J.-E., Lei, Y.D., Mackay, D., 1998. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol.* 32, 1013–1021.
- Wania, F., Breivik, K., Persson, N.J., McLachlan, M.S., 2006. CoZMo-POP 2 – a fugacity-based dynamic multi-compartmental mass balance model of the fate of persistent organic pollutants. *Environ. Model. Softw.* 21, 868–884.
- Webster, E., Mackay, D., Wania, F., 1998. Evaluating environmental persistence. *Environ. Toxicol. Chem.* 17, 2148–2158.
- Xie, Z., Möller, A., Ahrens, L., Sturm, R., Ebinghaus, R., 2011. Brominated flame retardants in seawater and atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* 45, 1820–1826.