4-1-2017

Persistent organic pollutants in the Atlantic and southern oceans and oceanic atmosphere

Jenna L. Luek
University of New Hampshire, Durham, Jenna.Luek@unh.edu

Rebecca M. Dickhut
College of William and Mary

Michele A. Cochran
College of William and Mary

Renee L. Falconer
Colorado School of Mines

Henrik Kylin
Linköping University

Comments

This is an Accepted Manuscript of an article published by Elsevier in Science of The Total Environment in 2017, available online: https://dx.doi.org/10.1016/j.scitotenv.2016.12.189. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

Recommended Citation

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. Science of the Total Environment 583, 64-71.

Persistent Organic Pollutants in the Atlantic and Southern Oceans and Oceanic Atmosphere

Jenna L. Luek[1,2], Rebecca M. Dickhut[1^], Michele A. Cochran[1], Renee L. Falconer[3], Henrik Kylin[4,5]

Science of the Total Environment, accepted manuscript. Published article can be found at:
http://dx.doi.org/10.1016/j.scitotenv.2016.12.189

[1] Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, VA, USA
[2] Chesapeake Biological Laboratory, University of Maryland Center for Environmental Sciences, Solomons, MD, USA
[3] Colorado School of Mines, Golden, CO, USA
[4] Department of Thematic Studies – Environmental Change, Linköping University, SE-581 83 Linköping, Sweden
[5] Norwegian Institute for Air Research, Fram Centre, NO-9296 Tromsø, Norway
[^] Author deceased

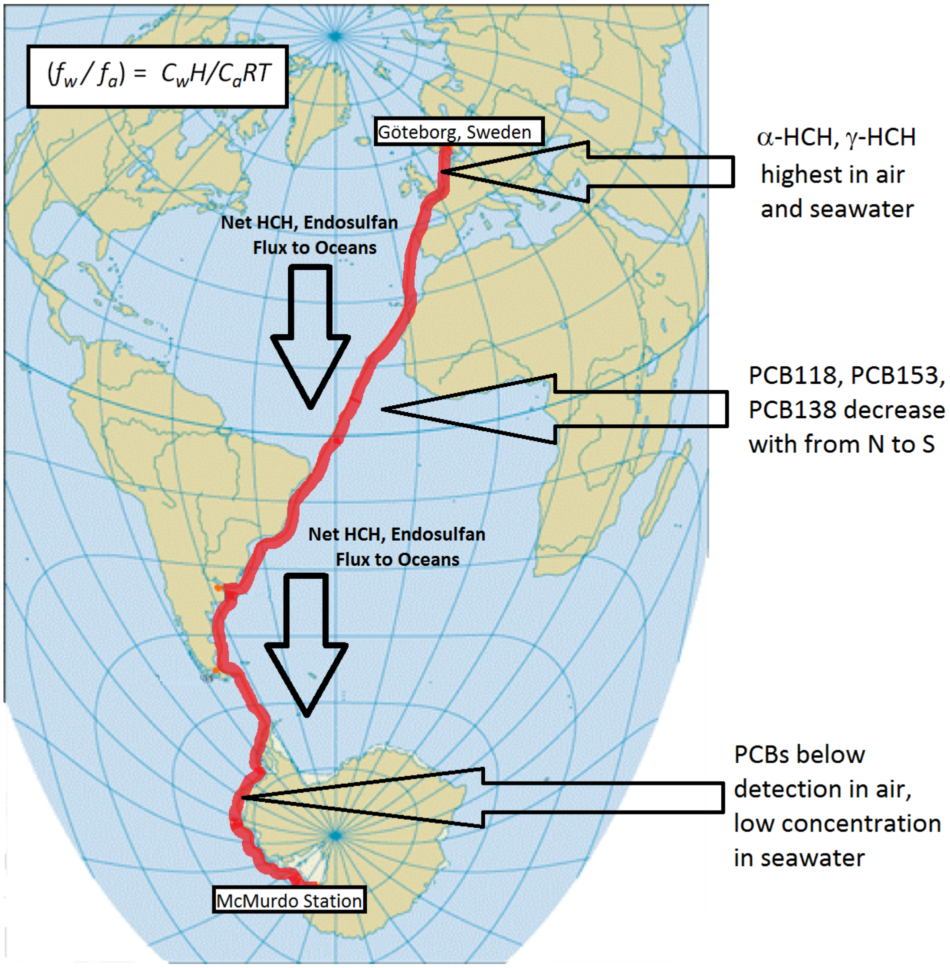
Corresponding Author Contact:
Jenna Luek
Chesapeake Biological Laboratory
146 Williams Street

PO Box 38
Solomons, MD, 20688
jluek88@gmail.com, 412-605-4898

Highlights

- Samples were collected between Sweden and Antarctica about R/V Oden in 2007
- Air and seawater samples were analyzed for persistent organic pollutants (POPs)
- Air and seawater POP concentrations were higher in the northern hemisphere
- Net fluxes for α-HCH, γ-HCH, and Endosulfan were from air to seawater
- Ocean continues to act as a sink for legacy pesticides

Graphical Abstract



Abstract

Persistent organic pollutants (POPs) continue to cycle through the atmosphere and hydrosphere despite banned or severely restricted usages. Global scale analyses of POPs are challenging, but knowledge of the current distribution of these compounds is needed to understand the movement and long-term consequences of their global use. In the current study, air and seawater samples were collected Oct. 2007- Jan. 2008 aboard the Icebreaker Oden en route from Göteborg, Sweden to McMurdo Station, Antarctica. Both air and surface seawater samples consistently contained α-hexachlorocyclohexane (α-HCH), γ-HCH, hexachlorobenzene (HCB), α-Endosulfan, and polychlorinated biphenyls (PCBs). Sample concentrations for most POPs in air were higher in the northern hemisphere with the exception of HCB, which had high gas phase concentrations in the northern and southern latitudes and low concentrations near the equator. South Atlantic and Southern Ocean seawater has a high ratio of α-HCH to γ-HCH, indicating persisting levels from technical grade sources. The Atlantic and Southern Ocean continue to be net sinks for atmospheric α-, γ-HCH, and Endosulfan despite declining usage.

Key words

POPs, organochlorine pesticides, air-sea flux, hexachlorocyclohexane, Endosulfan

Introduction

International regulation of persistent organic pollutants (POPs) is controlled by the Stockholm Convention of the United Nations Environment Programme (UNEP, 2016), which originally identified twelve pollutants to be monitored globally and their emissions to the environment reduced. This list included organochlorine pesticides including chlordane, hexachlorobenzene, and DDT, as well as polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins and –furans. Additional chemicals identified as POPs continue to be added to this international treaty, including hexachlorocyclohexane (HCH) and Endosulfan (UNEP, 2016). POPs are distributed worldwide by various partitioning processes across interfaces between, e.g., air, water, and biota in aquatic and terrestrial environments (Jones and De Voogt, 1999; Wania and Mackay, 1996). Global scale studies of the atmospheric transport and air-sea exchange of POPs have had a major impact on our understanding of POP movement in the environment and the impact of POPs on remote locations (Dachs et al., 2002; Iwata et al., 1993; Pozo et al., 2009, 2006). According to the hypothesis of cold condensation, semi-volatile organic pollutants are constantly cycled from the gaseous phase in warmer latitudes to the cooler polar regions and deposited in aquatic and terrestrial environments where revolatilization is minimal (Wania and Mackay, 1996). Such chemicals have been found to accumulate in polar regions where they bioaccumulate in biota and may reach concentrations in top predators that potentially have adverse effects (Braathen et al., 2004; Brault et al., 2013; Goerke et al., 2004; Oskam et al., 2004; Sonne, 2010). Although substantial work has been done in the Arctic to monitor these compounds and their impacts, studies on POP distribution and movement in the Southern hemisphere and particularly the Antarctic have been much more limited. Changes in polar regions are of particular interest as legacy use compounds may be released to the aquatic environment and atmosphere during the melting of ice sheets and general warming (Cabrerizo et al., 2013; Cincinelli et al., 2016; Geisz et al., 2008; Goerke et al., 2004).

Information on air-sea fluxes of individual POPs is important to understand if a particular area of the sea acts as a sink or a source, which, in turn, is essential for the understanding of the global distribution and environmental fate of these contaminants. Without environmental distribution and fate information, environmental risks cannot be estimated. A particular advantage of long geographical transects is that information from a wide range of environmental conditions and distances from anthropogenic sources can be collected.

This study took place during the expedition “Oden Southern Ocean 2007-2008” (OSO 07-08). The objective was to collect information on the distribution and air-sea fluxes of several POPs in a north-south transect of the Atlantic Ocean and a west-east transect in the Southern Ocean between the Western Antarctic Peninsula and the Ross Sea.

Methods

Sample Collection. Air and surface seawater samples were collected aboard the Swedish Icebreaker Oden on a transect between Göteborg, Sweden and McMurdo Station, Antarctica from 23 October through 4 January 2008 (**Figure 1, Table S1**). Samples were analyzed for 26 current and past-use organochlorine pesticides and 21 polychlorinated biphenyls (PCBs) using gas chromatography combined with mass spectrometry (**Table S2**). Gas and dissolved phase concentrations were then used to calculate air-sea fluxes.

Figure 1. Cruise track for the Swedish Icebreaker Oden, Oct. 2007 – Jan. 2008.

Air samples were collected using two high volume samplers consisting of 150 mm diameter glass fiber filters (GFFs) to collect aerosol samples and two polyurethane foam (PUF) plugs (8 cm diameter x 7.6 cm) to collect gas phase samples of approximately 500 m^3. The air samplers were deployed in front of Deck 5, approximately 18 m above the sea surface with the bulk of the bridge shielding the samplers from the stack and, except during storms, out of the sea spray. Sampling took place only while under way, but regardless of wind direction. Prior to use, the GFFs were baked for 4 h at 400 °C and the PUFs Soxhlet extracted with acetone and petroleum ether (24 h each). GFFs were stored in envelopes of aluminum foil baked at 400 °C and PUF plugs were stored in precleaned glass jars, both at -20 °C after sampling, until extraction.

To increase sample volume, some PUF gas phase samples were composited such that sample volumes ranged from ~500-1400 m^3 for Atlantic samples and ~600-2000 m^3 for Antarctic samples. Only Atlantic aerosol samples were analyzed as part of this study and were also composited prior to extraction to increase sample volumes (3500 - 6500 m^3). Antarctic aerosol analyses have been reported previously (Dickhut et al., 2012). A surrogate standard mixture of perdeuterated α-hexachlorocyclohexane (d_6-α-HCH) and PCB 204 was added and PUF plugs were Soxhlet extracted with acetone and petroleum ether (24 h each). Anhydrous sodium sulfate was added to the sample extracts to remove residual water, and extracts were reduced to 10 mL using rotary evaporation (Buchi) and/or a Turbovap II (Zymark), exchanged into hexane, and further reduced to 3 mL using a gentle stream of ultra-high purity N_2. Aerosol extracts and approximately half the gas phase extracts were acid treated using concentrated sulfuric acid. The sample extracts were then cleaned up using silica column chromatography (Chiuchiolo et al., 2004), and an internal standard (d_6-γ-HCH) was added prior to volume reduction to ~100 µl using ultra high purity N_2.

Seawater samples were collected via a direct inlet line from the bottom of the ship (app. 8 m depth) into the laboratory. The entire inlet system was made of acid resistant stainless steel with the exception of PTFE pump impellers. Large volume seawater samples (~110 L for Atlantic Ocean and ~150-160 L for Southern Ocean) were collected in steel holding tanks and treated according to Dickhut et al., 2005. The water was extracted by passing through a column (35 cm x 25 mm i.d.) of Amberlite XAD-2 resin (Sulpeco, Bellefonte, PA). The XAD-2 resin columns were stored at 4 °C until extraction. For analyses, the XAD-2 resin was Soxhlet extracted with acetone and hexane (24 h each) after the addition of the surrogate standard mixture described above. The acetone fractions were back-extracted using hexane and hexane-extracted water three times via agitation for three minutes, and the resulting hexane was combined with the hexane extract and reduced in volume by rotary evaporation. The hexane extracts were then cleaned and analyzed as described above.

Quantification. Samples were analyzed on a Hewlett-Packard 6890 Gas Chromatograph with a 5973 Mass-Selective Detector in negative chemical ionization mode using a J&W DB-35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and selective ion monitoring. Method parameters for analysis were as follows: 70 °C initial hold time of 1 min; 70-150 °C at 20 °C min^{-1}; 150-280 °C at 4 °C min^{-1}, hold for 15 min; 280-295 °C at 5 °C min^{-1}, hold for 2 min; source temperature 150 °C. The carrier gas for both methods was helium at 1.0 mL min^{-1} with a velocity of 39 cm s^{-1} (Chiuchiolo et al., 2004).

Quality Assurance and Quality Control. Quality control procedures included the collection and analysis of laboratory and field blanks, selected duplicate samples, and breakthrough on PUF plugs, non-sequential sample extraction ordering, quantitation of surrogate standard and internal standard recoveries, and the use of a conservative method detection limit.

Laboratory and field blanks were collected and analyzed as quality control procedures. One laboratory blank of baked GFF filters was extracted alongside composite particulate filters (1 laboratory blank to eight samples), as were two laboratory blanks of cleaned PUF not taken in the field. Paired air and seawater field blanks were collected across the Atlantic leg every seven samples (three total), and four air field blanks (30s on high volume air sampler) and two seawater field blanks were collected during the Antarctic leg. Field duplicate Antarctic PUF samples were collected, but most were combined to increase sample volume. Two PUF field duplicates were analyzed separately, and for one pair analytes agree well (most NQ, γ-HCH 0.99 pg m^{-3} vs. 0.83 pg m^{-3}; HCB 23 pg m^{-3} vs. 24 pg m^{-3}). For the second pair, the values are similar for α-HCH - NQ (MDL 0.11 pg m^{-3}) vs. 0.12 pg m^{-3}, but γ-HCH and HCB concentrations were not similar (γ-HCH 1.9 pg m^{-3} vs. <MDL; HCB 99 pg m^{-3} vs. 20 pg m^{-3}). Two duplicate seawater samples were collected during the Atlantic leg, but unfortunately one of these had no surrogate standard recovery so analytes could not be quantified.

Sample extractions were performed in a non-sequential order to prevent laboratory changes over time from imitating geographic trends, and at least every other set of four soxhlet extractions included either a laboratory or field blank control sample. The front and back PUF plugs were analyzed and quantified separately to determine the breakthrough of individual analytes. The average breakthrough of α-HCH and γ-HCH from the front to the back PUF was 21±18 and 24±11%, respectively. Breakthrough for hexachlorobenzene (HCB) was highest (33±8%) and α-Endosulfan was lowest (13±11%). As expected, breakthrough was greater for lower molecular weight compounds and more volatile compounds. Breakthrough was also higher at lower latitudes and warmer temperatures compared to higher latitudes, which should be considered when sampling over a wide range of latitudes or during a variety of seasons. The PUF had also been used once prior to sampling, which may have degraded its ability to collect. Alternatively, a longer PUF column length may be necessary to improve the extraction efficiency for more volatile compounds.

Surrogate standard recovery of d_6-α-HCH in gas phase air samples was 65±6% and 81±8% for PCB 204 (average ± confidence interval, $\alpha = 0.05$). Surrogate standard recovery of aerosol samples was 89±33% for PCB 204. Surrogate standard recoveries in seawater samples were 85±4% for d_6-α-HCH and 115±5% for PCB 204. Reported sample concentrations are not corrected for surrogate standard recoveries.

Method detection limits (MDLs) were conservatively calculated as three times the average field and lab amount in pg and divided by the average sample volume in m^3 or L (Dickhut et al., 2012). In cases where no quantifiable peak was identified for a given compound in any blanks, the MDL was set to 0.05 pg m^{-3} (air) and 0.13 pg L^{-1} (seawater) as these were on the low end of calculated MDLs for individual analytes.

Results and Discussion

The most frequently identified compounds in the gas phase and seawater were α-HCH, γ-HCH, HCB, α-Endosulfan, heptachlor, and PCB congeners 118, 138, 153, 180, and 187 (**Figure 2**, **Figure 3, Table S3, Table S4).** α-HCH, γ-HCH, HCB, α-Endosulfan, and heptachlor were also detected in the eight composite aerosol samples (**Figure S1, Table S5**). High concentrations of heptachlor were identified in both aerosol and gas phase blanks and are therefore not reported. In samples collected while the ship was breaking ice, with frequent backing up and ramming, a grey color was observed on the filters indicating influence from the smoke stack. But even when ship contamination was expected (e.g., Dec. 29-Jan. 1), most compounds were not quantifiable in field blanks. Thus, although ship influence is possible, it is not expected to contribute to the specific analytes or influence the interpretation of the results with the exception of Antarctic HCB concentrations.

Hexachlorocyclohexane. α-HCH and γ-HCH concentrations in gas phase samples ranged from below method detection limits (MDLs) (0.11 pg m^{-3} and 0.18 pg m^{-3}) to 13 and 23 pg m^{-3}, respectively. α-HCH and γ-HCH concentrations in aerosol samples were low and close to MDLs (0.06 pg m^{-3} and 0.10 pg m^{-3}, respectively), with only γ-HCH detected above the method detection limit at one site. The highest concentrations of gas phase HCHs were found in the northern hemisphere with a sharp drop off below the equator (**Figure 2**). HCHs were significantly higher (Student's t-test, $p < 0.01$) in the northern versus southern hemisphere. The highest concentrations of both isomers were observed off the Western European coastline (45° N, 8° W). In the Southern hemisphere, α-HCH consistently declined southward but γ-HCH concentrations increased slightly near 50S, potentially indicating recent South American use. These values are consistent with the spatial and temporal patterns reported over the past two decades, including Eastern Atlantic transects in 1999 and 2008 (Lakaschus et al., 2002; Xie et al., 2011). Since 1987, a clear decline of nearly an order of magnitude has been observed in HCH concentrations across this transect (Xie et al., 2011).

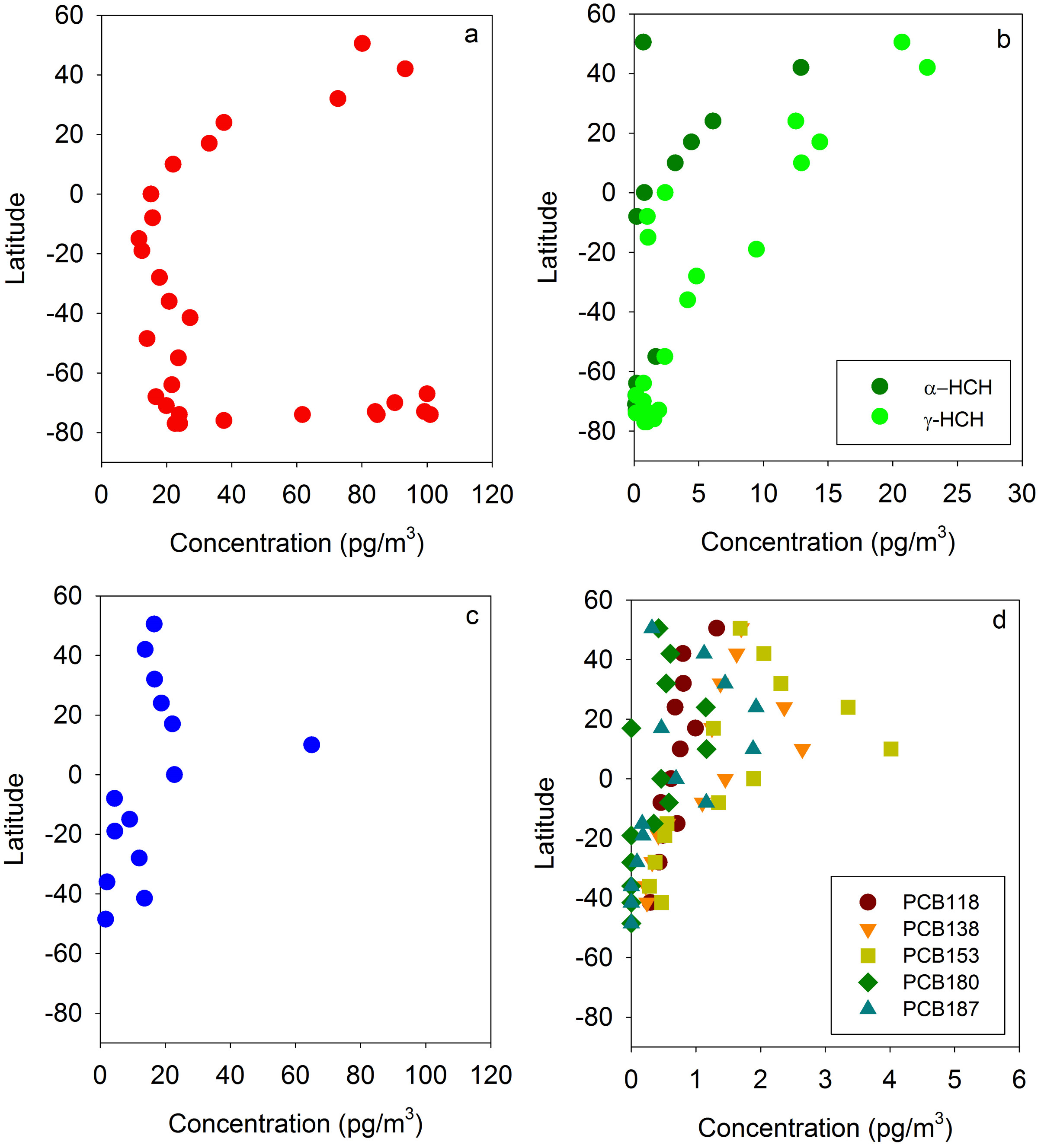


Figure 2. Gas-phase air concentrations of a) hexachlorobenzene b) hexachlorocyclohexanes c) Endosulfan I d) polychlorinated biphenyls in the Atlantic and Southern Oceans, Oct. 2007-Jan. 2008. <MDLs and NQ not shown.

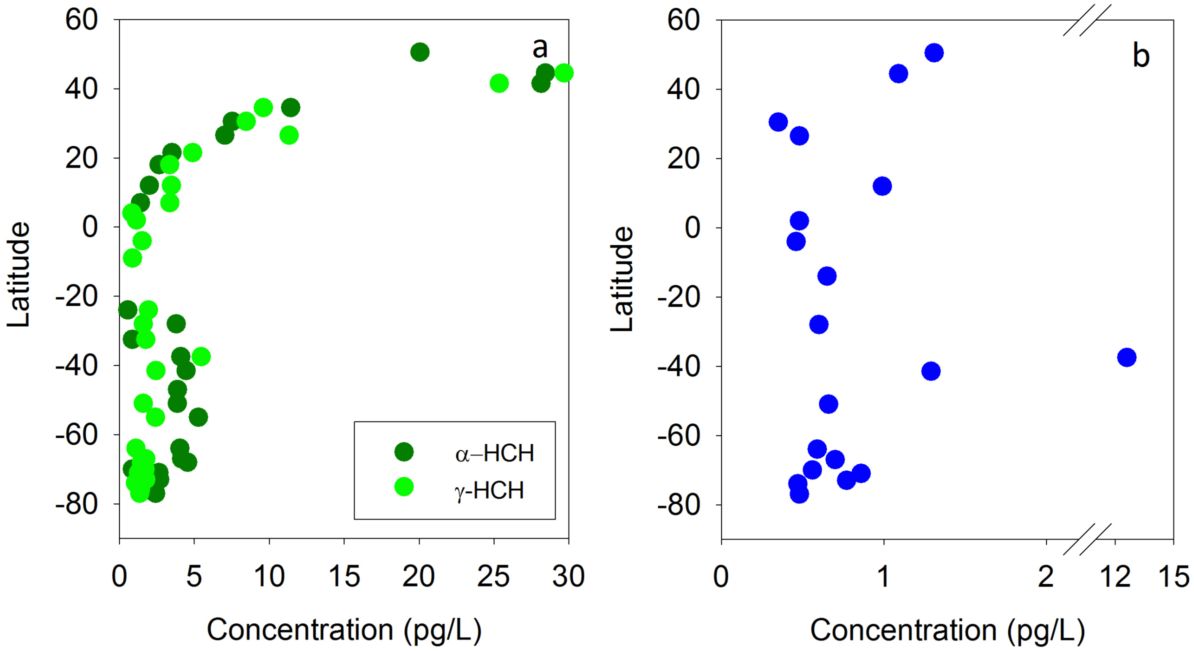


Figure 3. Seawater dissolved phase concentrations of a) hexachlorocyclohexanes *not showing point at 50.5N, 77 pg L^{-1} for scaling reasons b) Endosulfan I in the Atlantic and Southern Oceans, Oct. 2007-Jan. 2008. Samples <MDLs and NQ not shown.

Gas phase samples collected at latitudes below 60° S in the present study had concentrations of α-HCH and γ-HCH that ranged from below MDLs to 0.99 and 1.9 pg m^{-3}, respectively. These are similar to levels reported in 2001- 2002 in the Western Antarctic Peninsula (0.05-0.52 pg m^{-3} for α-HCH, and 0.06-2.4 pg m^{-3} for γ-HCH) (Dickhut et al., 2005). Antarctic atmospheric α- and γ-HCH concentrations measured in this study are consistent with declines seen over the past twenty-five years (Bidleman et al., 1993; Dickhut et al., 2005; Jantunen et al., 2004; Tanabe et al., 1983). Given that HCHs have been shown to have half-lives of ~3 years in Antarctic air (Dickhut et al., 2005), the similar levels measured in 2007-2008 compared to 2001-2001 may indicate that current sources, such as continued agricultural use, may contribute HCHs to the Southern Ocean atmosphere. Alternatively, if agricultural use has declined, a possible source of HCHs is volatilization from the western Antarctic ice sheet, which has been shown to be a source of other legacy use pesticides to the aquatic environment (Cincinelli et al., 2016; Geisz et al., 2008).

The ratios of α-HCH to γ- HCH in the gas phase were computed to investigate the presence of technical grade HCH versus the purer lindane (γ- HCH) in samples where both isomers were above method detection limits; a ratio greater than one represents higher amounts α-HCH isomer associated with technical grade HCH that has been phased out (**Figure S2**). Atmospheric α-HCH concentrations are lower than γ-HCH concentrations across the Atlantic transect, which is consistent with a global reduction in technical HCH usage (Li et al., 1998), but may also imply continued sources of current use γ-HCH. α-HCH appears to be longer lived in the atmosphere ($t_{1/2}$ of 120 vs. 96 d) (Harner et al., 1999; Li et al., 2004), but γ-HCH may be degraded to α-HCH (Walker et al., 1999) complicating the meaning of this ratio.

Seawater α- and γ-HCH concentrations ranged from below MDLs to 28 and 77 pg L^{-1}, respectively (MDL α-HCH = 0.13 pg L^{-1}, γ-HCH = 0.13 pg L^{-1}) (**Figure 3, Table S4**). Similar to HCHs in air, a spatial trend with significantly higher concentrations in the northern hemisphere and lower concentrations in the southern hemisphere was observed (Student's t-test, $p < 0.01$). This latitudinal trend has been observed over the past two decades by several researchers (Harner et al., 1999, 1999; Iwata et al., 1993; Lakaschus et al., 2002; Schreitmueller and Ballschmiter, 1995; Xie et al., 2011). Current concentrations also followed a temporal decline noted by Lakaschus et al., (2002). A 2008 Eastern Atlantic sampling cruise also observed a slight increase in α-HCH near 50S (Xie et al., 2011). This may be caused by regional technical HCH use (Pozo et al., 2006) or by the isomerization of γ-HCH to α-HCH in the environment (Walker et al., 1999).

A somewhat bimodal distribution was observed in the ratios of α-HCH to γ-HCH in seawater samples (**Figure S2**), where the northern and southern latitudes had higher ratios and tropical latitudes had lower ratios (or were not calculated due to non-detection of one of the two isomers). However, the southern latitudes had 3.5 times as much α-HCH as γ-HCH, where as northern latitudes hover at or below 1. Consistently higher α- to γ-HCH ratios in Antarctic seawater versus air indicate that α-HCH may be longer lived in the seawater environment than γ-HCH, or represent an older pool of HCH dominated by technical grade containing α-HCH. The apparent half-life of ΣHCHs in the Antarctic seawater environment has previously been estimated as 2 y and 3.4 y in two separate studies (Chiuchiolo et al., 2004; Galbán-Malagón et al., 2013), which is similar to half-lives reported Antarctic air (3 y) (Dickhut et al., 2005). However, much longer half-lives of 5.9 years and 23.1 years for the (+) and (-) enantiomers of α-HCH and 18.8 years for γ-HCH were reported in the Eastern Arctic Ocean during a 1996 cruise (Harner et al., 1999). It is unclear why such a high ratio of α-HCH persists in Southern Ocean seawater and not in the overlying atmosphere, but is likely driven by current and historical usage patterns as well as differing degradation rates and isomerization from γ-HCH to α-HCH (Harner et al., 1999; Li et al., 1998; Walker et al., 1999).

Hexachlorobenzene. HCB was ubiquitous in gas phase air samples with concentrations ranging from 12 to 100 pg m^{-3} (MDL = 1.3 pg m^{-3}). HCB in aerosol samples (MDL = 0.21 pg m^{-3}) was frequently below detection limits with only two samples above the MDL. The highest concentrations of HCB in the gas phase were observed in the northern Atlantic and Antarctic air while lower concentrations were measured in tropical and South Atlantic air. A comparison of front and back PUF indicated high levels of HCB breakthrough in the Atlantic samples that were collected at temperatures greater than 20 °C (54±3%). In a 2009 Atlantic transect (N-S and E-W), HCB concentrations were lowest near the equator although concentrations were nearly an order of magnitude lower than reported here for most samples (Lohmann et al., 2012). However, breakthrough information was not reported for these samples.

Southern Ocean HCB concentrations ranged from 17-100 pg m^{-3} with no discernible pattern over the concentration range, slightly higher than the range reported during a 2008 -2009 sampling expedition along the Western Antarctic peninsula (Galbán-Malagón et al., 2013a). However, air mass back trajectories (Stein et al., 2015) did not indicate unique air masses for high versus low concentration sampling periods (**Figure S3, Table S6**). Lab and field blanks extracted and analyzed at the same time are similar and do not indicate a contamination event during the high HCB concentration sample extractions. It is noteworthy, however, that the high concentration events all are from the highest latitudes. This opens up for two explanations: 1) emission of legacy HCB from the melting continental or shelf ice as suggested by (Geisz et al., 2008) or, 2) contamination from the ship during icebreaking. The second explanation is, perhaps, the more likely, as release of legacy POPs from melting glaciers would probably also lead to locally increased air concentrations of, e.g., HCHs, which is not observed. Elevated air concentrations of HCB during icebreaking have not been observed during previous expeditions with Oden, but in this case the bunker fuel was from a different source than normally used.

A further indication that it might be conditions during icebreaking that caused the high concentrations of HCB at high latitudes is that in one case, a duplicate pair collected from the same time and location had vastly different concentrations (20 vs. 99 pg m^{-3}). With a strong side wind, it is likely that one of the air samplers picked up more of a locally produced contamination than the other.

An autumn 2001 sampling cruise found atmospheric HCB levels in air that averaged 19 (±7.6) pg m^{-3} on the Western Antarctic Peninsula north of 68° S (Dickhut et al., 2005). More recently, the Norwegian Troll long term monitoring station in Dronning Maud Land, [Antarctica] observed consistent 22 pg m^{-3} HCB concentrations from 2007-2010, with an austral winter peak (Kallenborn et al., 2013). The highest recent Antarctic HCB measurements (2008-2009) peaked at 49.7 pg m^{-3} (Galbán-Malagón et al., 2013a) along the Western Antarctic Peninsula, but are not as high as the highest HCB concentrations observed in this study.

A high HCB MDL was calculated for the seawater samples (8.0 pg L^{-1}) and therefore HCB was only above the MDL in one seawater sample collected at 50° N (11 pg L^{-1}). In previous transects, HCB has only been observed in seawater at concentrations of 1 pg L^{-1} or less (Lohmann et al., 2012, Zhang and Lohmann, 2010, Galbán-Malagón et al., 2013).

Endosulfan. Endosulfan (α-Endosulfan) concentrations in gas phase air samples ranged from below the MDL (0.21 pg m^{-3}) to 65 pg m^{-3} with significantly higher levels in the northern versus southern hemisphere (Student's t-test, $p = 0.03$). Endosulfan in aerosol samples (MDL = 0.03 pg m^{-3}) was frequently below detection limits with only three samples above the MDL. High Endosulfan gas phase concentrations were observed off the West African coast, where an air mass back trajectory indicated air of continental origin. Inland passive air sampling in West Africa observed extremely high levels of Endosulfan (sum of α-, β-, and -SO_4) in passive air sampling (~2400 pg m^{-3} in 2004-2005) indicating that these high levels are likely due to regional agricultural applications (Pozo et al., 2009, 2006). Although atmospheric Endosulfan peaked off the African coast, seawater concentrations did not, yielding further support that atmospheric conditions were influenced by a continental air mass rather than long-term equilibration with seawater and the overlying air masses. Although banned in more than fifty countries, Endosulfan continues to be used on major crops including coffee, soy, cotton, and tobacco, but will be phased out over the next decade due to inclusion on the Stockholm Convention (UNEP, 2016). In the Antarctic atmosphere, low Endosulfan levels (0.2-0.8 pg m^{-3}) were detected with only three of thirteen samples above the method detection limit. On King George Island, Endosulfan was found to be the most prevalent and abundant organochlorine pesticide (average 27 pg/m^3) during multi-year monitoring (2005-2007) (Baek et al., 2011). Prior to that study, Endosulfan had not been detected in Antarctic air, but may be because Endosulfan was rarely included as an analytes (Pozo et al., 2006). Based on these results and similar Arctic findings (Weber et al., 2010), Baek and colleagues suggested that Endosulfan is extensively transported to polar regions (Baek et al., 2011). However, air mass back trajectories in the current study indicate air of oceanic origin, potentially explaining why low of Endosulfan was observed in the present study rather than at levels similar to King George Island which is more likely influenced by direct South American air masses.

Seawater Endosulfan concentrations (**Figure 3**) were consistently low and showed no clear latitudinal trends. No clear hemispheric difference is consistent with approximately equivalent northern and southern hemisphere applications and continued Endosulfan use (Weber et al., 2010). Concentrations ranged from below the MDL (0.13 pg L^{-1}) to 1.3 pg L^{-1} with a single outlier of 13 pg L^{-1} measured at 37° S. This outlier was collected near shore in the Rio de la Plata estuary, the second largest drainage basin in South America, draining large agricultural and urban regions where Endosulfan have been used recently and continue to persist at high concentrations in agricultural stream beds (Hunt et al., 2016). Endosulfan concentrations in seawater have not been previously reported along an Atlantic transect or in the Antarctic. Arctic sampling has shown low Endosulfan concentrations (mean 2.3 pg L^{-1}) similar in magnitude to these findings (Weber et al., 2010).

Polychlorinated Biphenyls. Twenty different PCB congeners were analyzed in the gas phase samples, but only congeners 118, 138, 153, 180, and 187 were consistently detected (**Figure 2**). PCBs were quantified in two aerosol samples but all were below MDLs. Gas phase concentrations were highest in the northern hemisphere and were nearly undetectable in the air over the South Atlantic and Southern Ocean (MDLs ranged from 0.05 pg m^{-3} to 0.26 pg m^{-3} for individual congeners). In an Atlantic sampling cruise in 2008, PCBs 153 and 180 were reported to have concentrations similar to those observed for the tropical Atlantic (Lohmann et al., 2012). In the present study, PCB153 and PCB180 levels were approximately twice those reported by Lohmann north of the equator, likely because sampling occurred on the Western Atlantic (present study) versus the Eastern Atlantic (Lohmann et al., 2012). Previous studies have shown high atmospheric PCB concentrations in these coastal waters (including those identified here, PCB118, 138, 153, and 180), with mass back trajectories indicative of a known West Africa source (Gioia et al., 2011, 2008).

Four of the five PCB congeners consistently observed in samples (118, 138, 153, 180) were reported by Lohmann (Lohmann et al., 2004) as congeners which concentrations may potentially be influenced by shipboard contamination. It is possible that some PCBs found in the samples were due to shipboard contamination, as PCBs were detected in some field blanks at low levels. However, shipboard contamination would be expected to impact air samples collected throughout the cruise, and the consistently low levels (<MDL) of PCBs found in the gas phase samples collected throughout the South Atlantic indicates that the measured concentrations are likely representative of actual atmospheric levels with a clear decline from northern to southern latitudes. It should be noted that Oden was built and commissioned 16 years after all uses of PCB were banned in Sweden. As far as has been possible to check among ship documents, no PCB containing equipment has ever been taken aboard. Also, H. Kylin has repeatedly investigated various parts of the ship for contamination of PCB and organochlorine pesticides. This has included screening all batches of paints, etc. used for the ship (particularly those used in the laboratory/sampling areas) prior to application. To date, no sources of contaminants have been identified on board, but there is a risk for contamination with incineration-derived compounds (e.g., HCB) from the industrial activities around the shipyard where Oden is refurbished prior to each expedition.

Similar to air samples, PCB118 and PCB153 were most commonly detected PCBs in seawater. However, these analytes also had high MDLs (**Table S4**) and therefore PCB118 was below MDLs in all samples and PCB153 was below MDLs in all but three samples. PCBs 137, 180, and 187 were also detected in several seawater samples and were above MDLs, where concentrations ranged from below MDLs to 2.6 pg L^{-1} (PCB138) at 7° N. The highest PCB187 and PCB180 concentrations (0.50 pg L^{-1} and 1.1 pg L^{-1}) were also detected in this sample. PCBs in seawater were only detected in the tropics, likely related to the local West Africa source (Gioia et al., 2011). Peak concentrations in seawater PCBs near the equator with very low overall PCB concentrations have also been reported previously in a north-south Atlantic transect, although within the Eastern South Atlantic (Gioia et al., 2008). The only exception was the detection of PCB138 at 78 degrees south (0.98 pg L^{-1}), perhaps influenced by McMurdo Station.

In multiple Antarctic cruises, PCB118 and 153 concentrations ranged from 0.02-0.64 and 0.03-0.46 pg L^{-1}, and PCB99/101 had the highest observed concentrations (Galbán-Malagón et al., 2013). PCB concentrations in the Antarctic are decreasing with an apparent half-life of 5.7 years, likely driven by loss to depth via the biological pump (Dachs et al., 2002; Galbán-Malagón et al., 2013).

Air/Seawater Exchange. The relative concentrations of air and seawater were examined by calculating the water/air fugacity ratios (f_w / f_a) as shown below (Mackay and Paterson, 1981):

$$f_w / f_a = C_w H / C_a R T$$

where water (C_w) and air (C_a) concentrations are in pg m^{-3}, H is the Henry's law constant [Pa m^3 $mole^{-1}$], R is the gas constant [8.314 Pa m^{-3} K^{-1} $mole^{-1}$], and T is the temperature in K. Calculations were done using average daily air and seawater temperatures measured during individual sample collection and temperature appropriate Henry's Law constants (Cetin et al., 2006; Sahsuvar et al., 2003; Shen and Wania, 2005).

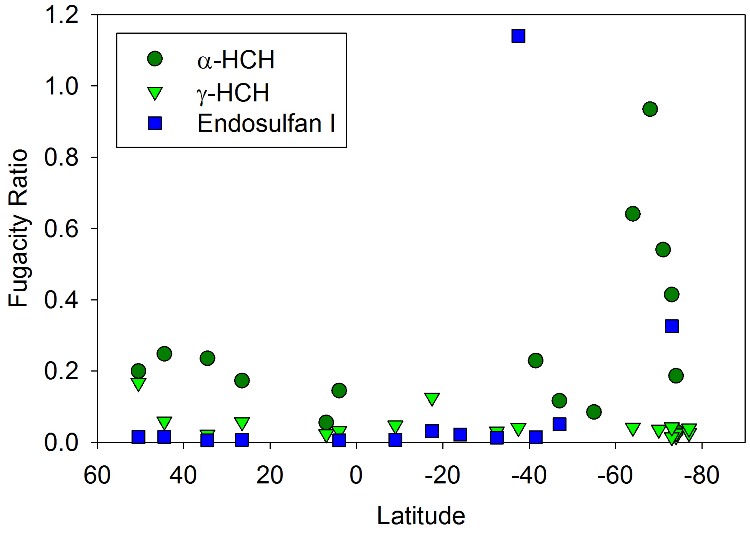


Figure 4. Fugacity ratios of α-HCH, γ-HCH, and Endosulfan I

Calculated HCH fugacity ratios indicated that the Atlantic and Southern Oceans continue to act as a sink for α- and γ-HCH (F<1) (**Figure 4, Table S7**). Fugacity ratios were not calculated for some tropical regions as where one or both isomers were below detection in seawater, still supporting continued net deposition in this region. Similarly, a 2008 Atlantic cruise observed consistent HCH deposition from 45° N to 67° S (Xie et al., 2011). A 1990-1991 cruise observed net deposition of ΣHCHs in the North Atlantic (Schreitmüller and Ballschmiter, 1995); however a 1999-2000 cruise found that ΣHCHs were near air-sea equilibrium in the North Atlantic (Lakaschus et al., 2002). Over a series of Atlantic cruises during the 1990s, γ-HCH was found to be near equilibrium in the tropical Atlantic, but depositing in the northern and southern Atlantic (Weber et al., 2006). A portion of Southern Ocean samples observed near equilibrium (0.3>F<3) conditions for α-HCH, similar to reports in Arctic Ocean samples (Bruhn et al., 2003; Lohmann et al., 2009). However, a similar trend is not observed for γ-HCH in the Southern Ocean, consistent with recent observations of net deposition of γ-HCH in the Southern Ocean (Bigot et al., 2016).

The fugacity ratio of Endosulfan indicates net deposition is occurring across the Atlantic, with the exception of the Rio de la Plata sample outlier (**Figure 4**). Although now being phased out, Endosulfan was still in use during the time of sampling and air concentrations were still relatively high in Endosulfan (Pozo et al., 2009, 2006). Data collected between 1990 and 2004 noted a net deposition of Endosulfan throughout the Atlantic (Lohmann et al., 2009; Weber et al., 2006), and the lack of quantifiable concentrations of Endosulfan in a number of surface seawater samples supports continued deposition from air to water. Fugacity ratios were not calculated for PCBs or HCBs due to the high MDLs in seawater and therefore few gas phase and seawater overlapping data points. Errors associated with these calculated fugacity ratios (Bigot et al., 2016) were not computed due to a lack of replication in individual air/sea water values. Although the error associated with individual values may be considerable, the consistency across samples gives further support to the conclusions reported of continued net deposition of these POPs.

Although previous studies have suggested that the open ocean will move towards being a source of POPs to the atmosphere (Bruhn et al., 2003; Schreitmueller and Ballschmiter, 1995; Weber et al., 2006; Xie et al., 2011), removal of these compounds to the deep ocean bound to particles or organisms, or via the degradative pump (Galbán-Malagón et al., 2012; Goerke et al., 2004; Lohmann et al., 2004; Zhang et al., 2013) may continue to keep surface water concentrations low and indicate net deposition from the atmosphere. Future trends in atmospheric and open ocean concentrations and fluxes of legacy use organochlorines will likely be affected by a number of issues. Changing wind patterns and warming surface water temperatures, as well as new sources of legacy pesticides from melting ice sheets (Cincinelli et al., 2016; Dickhut and Gustafson, 1995; Geisz et al., 2008) all have the potential to alter the predicted decline of phased out POPs. How exactly these physical, chemical, and biological climate change factors will affect this equilibrium has yet to be understood.

Acknowledgements

We sincerely thank the late Rebecca M. Dickhut for her foresight, hard work, friendship and mentorship. The expedition “Oden Southern Ocean 2007-2008” was organized by the Swedish Polar Research Secretariat in cooperation with the United States Antarctic Program. We thank the officers and crew of the R/V *Icebreaker Oden*, and Heidi Geisz and Elizabeth MacDonald for laboratory assistance. The authors gratefully acknowledge the NOAA Air

Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication. Thanks to two reviewers for providing helpful comments. This project was funded by Swedish Research Council, the National Science Foundation Office of Polar Programs Award 0741379 and NSF Research Experience for Undergraduates Award 0552612. VIMS contribution XXXX.

References

Baek, S.-Y., Choi, S.-D., Chang, Y.-S., 2011. Three-Year Atmospheric Monitoring of Organochlorine Pesticides and Polychlorinated Biphenyls in Polar Regions and the South Pacific. Environ. Sci. Technol. 45, 4475–4482. doi:10.1021/es1042996

Bidleman, T.F., Walla, M.D., Roura, R., Carr, E., Schmidt, S., 1993. Organochlorine pesticides in the atmosphere of the Southern Ocean and Antarctica, January–March, 1990. Mar. Pollut. Bull. 26, 258–262.

Bigot, M., Muir, D.C.G., Hawker, D.W., Cropp, R., Dachs, J., Teixeira, C.F., Bengtson Nash, S., 2016. Air–Seawater Exchange of Organochlorine Pesticides in the Southern Ocean between Australia and Antarctica. Environ. Sci. Technol. 50, 8001–8009. doi:10.1021/acs.est.6b01970

Braathen, M., Derocher, A.E., Wiig, Ø., Sørmo, E.G., Lie, E., Skaare, J.U., Jenssen, B.M., 2004. Relationships between PCBs and Thyroid Hormones and Retinol in Female and Male Polar Bears. Environ. Health Perspect. 112, 826–833. doi:10.1289/ehp.6809

Brault, E.K., Goebel, M.E., Geisz, H.N., Canuel, E.A., Dickhut, R.M., 2013. Inter-Annual Variation of Persistent Organic Pollutants (POPS) in an Antarctic Top Predator *Arctocephalus gazella*. Environ. Sci. Technol. 47, 12744–12752. doi:10.1021/es403577f

Bruhn, R., Lakaschus, S., McLachlan, M.S., 2003. Air/sea gas exchange of PCBs in the southern Baltic Sea. Atmos. Environ. 37, 3445–3454. doi:10.1016/S1352-2310(03)00329-7

Cabrerizo, A., Dachs, J., Barceló, D., Jones, K.C., 2013. Climatic and Biogeochemical Controls on the Remobilization and Reservoirs of Persistent Organic Pollutants in Antarctica. Environ. Sci. Technol. 47, 4299–4306. doi:10.1021/es400471c

Cetin, B., Ozer, S., Sofuoglu, A., Odabasi, M., 2006. Determination of Henry's law constants of organochlorine pesticides in deionized and saline water as a function of temperature. Atmos. Environ. 40, 4538–4546. doi:10.1016/j.atmosenv.2006.04.009

Chiuchiolo, A.L., Dickhut, R.M., Cochran, M.A., Ducklow, H.W., 2004. Persistent Organic Pollutants at the Base of the Antarctic Marine Food Web. Environ. Sci. Technol. 38, 3551–3557. doi:10.1021/es0351793

Cincinelli, A., Martellini, T., Pozo, K., Kukučka, P., Audy, O., Corsolini, S., 2016. Trematomus bernacchii as an indicator of POP temporal trend in the Antarctic seawaters. Environ. Pollut. 217, 19–25. doi:10.1016/j.envpol.2015.12.057

Dachs, J., Lohmann, R., Ockenden, W.A., Méjanelle, L., Eisenreich, S.J., Jones, K.C., 2002. Oceanic Biogeochemical Controls on Global Dynamics of Persistent Organic Pollutants. Environ. Sci. Technol. 36, 4229–4237. doi:10.1021/es025724k

Dickhut, R.M., Cincinelli, A., Cochran, M., Ducklow, H.W., 2005. Atmospheric Concentrations and Air−Water Flux of Organochlorine Pesticides along the Western Antarctic Peninsula. Environ. Sci. Technol. 39, 465–470. doi:10.1021/es048648p

Dickhut, R.M., Cincinelli, A., Cochran, M., Kylin, H., 2012. Aerosol-Mediated Transport and Deposition of Brominated Diphenyl Ethers to Antarctica. Environ. Sci. Technol. 46, 3135–3140. doi:10.1021/es204375p

Dickhut, R.M., Gustafson, K.E., 1995. Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls to southern Chesapeake Bay. Mar. Pollut. Bull. 30, 385–396.

Galbán-Malagón, C., Berrojalbiz, N., Ojeda, M.-J., Dachs, J., 2012. The oceanic biological pump modulates the atmospheric transport of persistent organic pollutants to the Arctic. Nat. Commun. 3, 862. doi:10.1038/ncomms1858

Galbán-Malagón, C., Cabrerizo, A., Caballero, G., Dachs, J., 2013a. Atmospheric occurrence and deposition of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic Peninsula. Atmos. Environ. 80, 41–49. doi:10.1016/j.atmosenv.2013.07.061

Galbán-Malagón, C., Del Vento, S., Berrojalbiz, N., Ojeda, M.-J., Dachs, J., 2013b. Polychlorinated Biphenyls, Hexachlorocyclohexanes and Hexachlorobenzene in Seawater and Phytoplankton from the Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas). Environ. Sci. Technol. 47, 5578–5587. doi:10.1021/es400030q

Galbán-Malagón, C., Del Vento, S., Cabrerizo, A., Dachs, J., 2013c. Factors affecting the atmospheric occurrence and deposition of polychlorinated biphenyls in the Southern Ocean. Atmospheric Chem. Phys. 13, 12029–12041. doi:10.5194/acp-13-12029-2013

Geisz, H.N., Dickhut, R.M., Cochran, M.A., Fraser, W.R., Ducklow, H.W., 2008. Melting Glaciers: A Probable Source of DDT to the Antarctic Marine Ecosystem. Environ. Sci. Technol. 42, 3958–3962. doi:10.1021/es702919n

Gioia, R., Eckhardt, S., Breivik, K., Jaward, F.M., Prieto, A., Nizzetto, L., Jones, K.C., 2011. Evidence for Major Emissions of PCBs in the West African Region. Environ. Sci. Technol. 45, 1349–1355. doi:10.1021/es1025239

Gioia, R., Nizzetto, L., Lohmann, R., Dachs, J., Temme, C., Jones, K.C., 2008. Polychlorinated Biphenyls (PCBs) in Air and Seawater of the Atlantic Ocean: Sources, Trends and Processes. Environ. Sci. Technol. 42, 1416–1422. doi:10.1021/es071432d

Goerke, H., Weber, K., Bornemann, H., Ramdohr, S., Plötz, J., 2004. Increasing levels and biomagnification of persistent organic pollutants (POPs) in Antarctic biota. Mar. Pollut. Bull. 48, 295–302. doi:10.1016/j.marpolbul.2003.08.004

Harner, T., Kylin, H., Bidleman, T.F., Strachan, W.M.J., 1999. Removal of α- and γ-Hexachlorocyclohexane and Enantiomers of α-Hexachlorocyclohexane in the Eastern Arctic Ocean. Environ. Sci. Technol. 33, 1157–1164. doi:10.1021/es980898g

Hunt, L., Bonetto, C., Resh, V.H., Buss, D.F., Fanelli, S., Marrochi, N., Lydy, M.J., 2016. Insecticide concentrations in stream sediments of soy production regions of South America. Sci. Total Environ. 547, 114–124. doi:10.1016/j.scitotenv.2015.12.140

Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, R., 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ. Sci. Technol. 27, 1080–1098.

Jantunen, L.M., Kylin, H., Bidleman, T.F., 2004. Air–water gas exchange of α-hexachlorocyclohexane enantiomers in the South Atlantic Ocean and Antarctica. Deep Sea Res. Part II Top. Stud. Oceanogr. 51, 2661–2672. doi:10.1016/j.dsr2.2004.02.002

Jones, K.C., De Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221.

Kallenborn, R., Breivik, K., Eckhardt, S., Lunder, C.R.., Manø, S., Schlabach, M., Stohl, A., 2013. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmospheric Chem. Phys. Discuss. 13, 6219–6246. doi:10.5194/acpd-13-6219-2013

Lakaschus, S., Weber, K., Wania, F., Bruhn, R., Schrems, O., 2002. The Air−Sea Equilibrium and Time Trend of Hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. Environ. Sci. Technol. 36, 138–145. doi:10.1021/es010211j

Li, Y., Macdonald, R., Ma, J., Hung, H., Venkatesh, S., 2004. Historical α-HCH budget in the Arctic Ocean: the Arctic Mass Balance Box Model (AMBBM). Sci. Total Environ. 324, 115–139. doi:10.1016/j.scitotenv.2003.10.022

Li, Y.F., Bidleman, T.F., Barrie, L.A., McConnell, L.L., 1998. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. Geophys. Res. Lett. 25, 39–41.

Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. Environ. Sci. Technol. 43, 5633–5639.

Lohmann, R., Jaward, F.M., Durham, L., Barber, J.L., Ockenden, W., Jones, K.C., Bruhn, R., Lakaschus, S., Dachs, J., Booij, K., 2004. Potential Contamination of Shipboard Air Samples by Diffusive Emissions of PCBs and Other Organic Pollutants: Implications and Solutions. Environ. Sci. Technol. 38, 3965–3970. doi:10.1021/es035005l

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. doi:10.1021/es203459e

Mackay, D., Paterson, S., 1981. Calculating fugacity. Environ. Sci. Technol. 15, 1006–1014.

Oskam, I., Ropstad, E., Lie, E., Derocher, A., Wiig, Ø., Dahl, E., Larsen, S., Skaare, J.U., 2004. Organochlorines Affect the Steroid Hormone Cortisol in Free-Ranging Polar Bears (*Ursus maritimus*) at Svalbard, Norway. J. Toxicol. Environ. Health A 67, 959–977. doi:10.1080/15287390490443731

Pozo, K., Harner, T., Lee, S.C., Wania, F., Muir, D.C.G., Jones, K.C., 2009. Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study. Environ. Sci. Technol. 43, 796–803. doi:10.1021/es802106a

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. doi:10.1021/es060447t

Sahsuvar, L., Helm, P.A., Jantunen, L.M., Bidleman, T.F., 2003. Henry's law constants for α-, β-, and γ-hexachlorocyclohexanes (HCHs) as a function of temperature and revised estimates of gas exchange in Arctic regions. Atmos. Environ. 37, 983–992. doi:10.1016/S1352-2310(02)00936-6

Schreitmueller, J., Ballschmiter, K., 1995. Air-water equilibrium of hexachlorocyclohexanes and chloromethoxybenzenes in the North and South Atlantic. Environ. Sci. Technol. 29, 207–215.

Shen, L., Wania, F., 2005. Compilation, Evaluation, and Selection of Physical−Chemical Property Data for Organochlorine Pesticides. J. Chem. Eng. Data 50, 742–768. doi:10.1021/je049693f

Sonne, C., 2010. Health effects from long-range transported contaminants in Arctic top predators: An integrated review based on studies of polar bears and relevant model species. Environ. Int. 36, 461–491. doi:10.1016/j.envint.2010.03.002

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. Bull. Am. Meteorol. Soc. 96, 2059–2077. doi:10.1175/BAMS-D-14-00110.1

Tanabe, S., Hidaka, H., Tatsukawa, R., 1983. PCBs and Chlorinated Hydrocarbon Pesticides in Antarctic Atmosphere and Hydrosphere. Chemosphere 12, 277–288.

UNEP, 2016. pops.int [WWW Document]. Stockh. Conv. Persistent Org. Pollut. URL http://www.pops.int (accessed 11.2.16).

Walker, K., Vallero, D.A., Lewis, R.G., 1999. Factors Influencing the Distribution of Lindane and Other Hexachlorocyclohexanes in the Environment. Environ. Sci. Technol. 33, 4373–4378. doi:10.1021/es990647n

Wania, F., Mackay, D., 1996. Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol. 30, 390A–396A.

Weber, J., Halsall, C.J., Muir, D., Teixeira, C., Small, J., Solomon, K., Hermanson, M., Hung, H., Bidleman, T., 2010. Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic. Sci. Total Environ. 408, 2966–2984. doi:10.1016/j.scitotenv.2009.10.077

Weber, J., Halsall, C.J., Muir, D.C.G., Teixeira, C., Burniston, D.A., Strachan, W.M.J., Hung, H., Mackay, N., Arnold, D., Kylin, H., 2006. Endosulfan and γ-HCH in the Arctic: An Assessment of Surface Seawater Concentrations and Air−Sea Exchange. Environ. Sci. Technol. 40, 7570–7576. doi:10.1021/es061591h

Xie, Z., Koch, B.P., Möller, A., Sturm, R., Ebinghaus, R., 2011. Transport and fate of hexachlorocyclohexanes in the oceanic air and surface seawater. Biogeosciences 8, 2621–2633. doi:10.5194/bg-8-2621-2011

Zhang, L., Dickhut, R., DeMaster, D., Pohl, K., Lohmann, R., 2013. Organochlorine Pollutants in Western Antarctic Peninsula Sediments and Benthic Deposit Feeders. Environ. Sci. Technol. 47, 5643–5651. doi:10.1021/es303553h

Zhang, L., Lohmann, R., 2010. Cycling of PCBs and HCB in the Surface Ocean-Lower Atmosphere of the Open Pacific. Environ. Sci. Technol. 44, 3832–3838. doi:10.1021/es9039852