

RESEARCH LETTER

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Key Points:

- Deep waters of the Fram Strait carried highest concentrations of polychlorinated biphenyls and dichlorodiphenyltrichloroethane
- A fractionation of organic pollutants with depth was observed; contributions of the more hydrophobic compounds increased with depth
- There is a net export of hexachlorocyclohexanes and hexachlorobenzene from the Arctic Ocean through the deepwater passage Fram Strait

Supporting Information:

- Supporting Information S1

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Concentrations and Water Mass Transport of Legacy POPs in the Arctic Ocean

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Abstract The Arctic Ocean is known to be contaminated by various persistent organic pollutants (POPs). The Fram Strait, the only deepwater passage to the Arctic Ocean (from the Atlantic Ocean), represents an unquantified gateway for POPs fluxes into and out of the Arctic. Polyethylene passive samplers were deployed in vertical profiles in the Fram Strait and in air and surface water in the Canadian Archipelago to determine the concentrations, profiles, and mass fluxes of dissolved polychlorinated biphenyls (PCBs) and organochlorine pesticides. In the Fram Strait, higher concentrations of Σ PCBs (1.3–3.6 pg/L) and dichlorodiphenyltrichloroethanes (Σ DDTs, 5.2–9.1 pg/L) were observed in the deepwater masses (below 1,000 m), similar to nutrient-like vertical profiles. There was net southward transport of hexachlorobenzene and hexachlorocyclohexanes (Σ HCHs) of 0.70 and 14 Mg/year but a net northward transport of Σ PCBs at 0.16 Mg/year through the Fram Strait.

Plain Language Summary Persistent organic pollutants can reach the Arctic Ocean by long-range atmospheric transport, ocean currents, and inputs from the large Arctic rivers. Polychlorinated biphenyls (PCBs) and organochlorine pesticides, which have been extensively used since the 1930s, were banned and listed in the United Nations Environment Programme Stockholm Convention on persistent organic pollutants in 2001. We performed the first pan-Arctic deployments of passive samplers to gain knowledge of the occurrence, transport, and fate of these legacy contaminants in the remote Arctic. Our results demonstrated the ubiquitous presence of persistent industrial and agricultural contaminants across the Canadian Arctic and throughout the water column of the Fram Strait. While atmospheric transport seems mostly responsible for the presence of these pollutants in the surface Arctic Ocean, in the Fram Strait, concentrations of PCBs and dichlorodiphenyltrichloroethanes (DDTs) increased in deep waters, indicating their penetration to the deep ocean environment. Our results also showed the legacy hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB) are released from the Arctic Ocean to the Atlantic Ocean via the deepwater Fram Strait, while PCBs are still loaded from the Atlantic Ocean to the Arctic Ocean.

1. Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are groups of legacy persistent organic pollutants (POPs) present in the remote Arctic (Hung et al., 2010; Ma et al., 2015; Muir & de Wit, 2010). The relative distribution of these chemicals between environmental compartments, including air, water, and sediment, depends on their physicochemical properties (Lohmann et al., 2007), enabling their migration to the Arctic Ocean by long-range atmospheric transport, ocean currents, and inputs from the large Arctic rivers (Carrizo & Gustafsson, 2011a).

The Arctic Ocean comprises vast continental shelves and connecting waterways with the Atlantic Ocean and Pacific Ocean. Inflows to the Arctic Ocean include a major influx of North Atlantic water through the eastern Fram Strait and Barents Sea and a minor influx of Pacific water through the Bering Strait. All outflows of the Arctic Ocean are to the Atlantic Ocean, estimated as 72% through western Fram Strait, 24% through the Canadian Archipelago, and 4% through ice removal (Li et al., 2004). Therefore, the Fram Strait, which represents the unique deepwater channel to the Arctic Ocean, is most important for the transport of legacy

POPs in ocean water between the North Atlantic Ocean and the Arctic basin (Beszczynska-Moeller et al., 2012). This transport generally occurs in two opposite ocean currents: the northward West Spitsbergen Current in the eastern Fram Strait and the southward East Greenland Current along Greenland (Hop et al., 2006). Decades after the usage and subsequent ban of POPs, it is not clear whether the Arctic Ocean is still a net sink of these legacy contaminants, or whether the export of POPs via ocean currents exceeds their inflow.

A wealth of studies has described the occurrence of legacy organic pollutants in open ocean seawater (Cai et al., 2012; Carrizo & Gustafsson, 2011a; Gioia et al., 2008; Iwata et al., 1993; Lohmann et al., 2009). Their presence in deep ocean waters lacks data, due to the logistical challenges in sampling, although the transfer to the deep ocean environment is considered one of the long-term global sinks for POPs (Dachs et al., 2002). In the 1990s, the advective outflow of hexachlorocyclohexanes (HCHs) was detected in the deep waters of the eastern Arctic Ocean (Harner et al., 1999). Moreover, vertical profiles with increasing concentrations of PCBs and dichlorodiphenyltrichloroethane (DDT) with depth were demonstrated in the central Arctic Ocean basin in samples collected in the early 2000s (Carrizo et al., 2017; Sobek & Gustafsson, 2014). Recently, the penetration of PCBs and OCPs into the deep ocean were also reported for the tropical Atlantic and the North Atlantic Ocean (Sun et al., 2016). Unusually high concentrations of PCBs were also detected in the endemic amphipod fauna in the deepest ocean trenches (>10,000 m; Jamieson et al., 2017). Results from these studies strongly suggest that POPs dynamics in deeper water masses are important for their ocean cycling.

In this research, polyethylene (PE) passive samplers were deployed at two deep mooring stations in eastern and western Fram Strait from 2014 to 2015 and in air and surface water in the Canadian Archipelago in 2015 and 2016, respectively (Figure 1). By combining samplers from these two locations, we were able to investigate trends of POPs in surface water, and their exchange with air, and contrast surface water results with vertical ocean profiles. The objectives of this research were to (i) determine the occurrence, composition, and vertical profiles of freely dissolved PCBs and OCPs in the Canadian Archipelago and Fram Strait, (ii) to provide knowledge of the fate and environmental behavior of these legacy contaminants in remote deep ocean waters, and (iii) to derive mass fluxes of these legacy contaminants through the deepwater passage Fram Strait.

2. Experimental Section

2.1. Sampling

Fifty-one micrometer PEs were pre-spiked with performance reference compounds (dibromobiphenyl [PBB 9], tetrabromobiphenyl [PBB 52], pentabromobiphenyl [PBB 103], octachloronaphthalene [OCN]) via a method based on Booij et al. (2002). The PEs were deployed in air, lakes, and marine surface seawaters of the Canadian Archipelago, as well as in different water depths of two moorings deployed in the eastern and western Fram Strait (Figure 1). For details and hydrographic conditions, see supporting information.

For surface water sampling, stainless steel cages were used to hold PE sheet samplers fixed to subsurface floats at ~4- to 5-m depth. For deepwater sampling, the cages were fastened to moorings in the eastern Fram Strait (79.010°N, 4.328°E) and the western Fram Strait (78.528°N, 2.764°W) for around 1 year. Passive samplers were deployed at 213, 468, 1,173, and 2,535 m (eastern Fram Strait) and 248, 511, 1,242, 1,747, and 2,496 m in the western Fram Strait. Current velocities and current directions were measured from the nearest current meters for each depth during the entire sampling period. Air PEs were fixed inside two inverted bowls to protect them from direct solar radiation and rainfall and generally deployed at ~1- to 2-m height. After the PE samplers were recovered, they were stored in baked aluminum foil, placed into an air-tight bag, shipped back to the University of Rhode Island on ice and kept frozen until analysis.

For comparison, active sampling of Canadian Arctic surface water was also conducted by filtering large volumes (average 250–300 L) through columns filled with XAD-2 resin during ice-covered and open water conditions, respectively.

2.2. Sample Analysis and QA/QC

The extraction, purification, and analytical procedure were conducted as described earlier (Khairy et al., 2014; Liu et al., 2016). In brief, PEs were spiked with surrogate standards ($^{13}\text{C}_{12}$ -PCBs 8, 28, 52, 118, 138, 180, 209 and $^{13}\text{C}_{12}$ -*p,p'*-DDT, $^{13}\text{C}_6$ -HCB) and extracted in hexane twice overnight. The extracts were concentrated down to

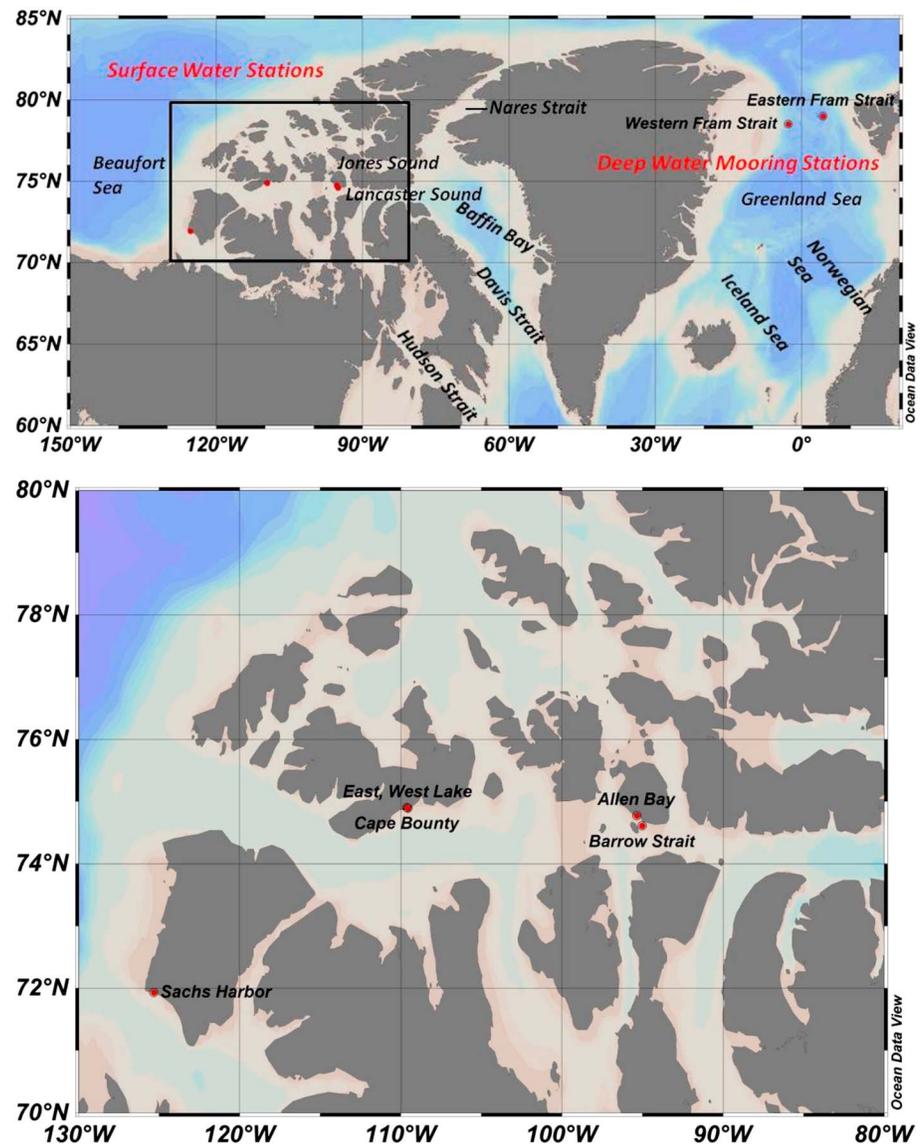


Figure 1. Sampling sites in the Canadian Archipelago and the Fram Strait.

~100 μ l and spiked with tribromobiphenyl as the injection standard. Then, PCBs and OCPs were analyzed on a 6890N GC (Agilent, USA)—Quattro Micro tandem MS (Waters, Micromass, UK) with a DB5-MS fused silica capillary column (30 m \times 0.25 mm, J&W Scientific). Sampling rates of each PE were derived based on performance reference compound loss. Ambient air concentrations and freely dissolved water concentrations were calculated as detailed previously and described in the supporting information (Khairy et al., 2014; Liu et al., 2016). With each batch of samples, matrix spikes, field, and/or procedure blanks were performed. Concentrations of all analytes were recovery corrected and blank subtracted; average recoveries of surrogate standards ranged from 61% \pm 10.1% to 133% \pm 17.8% (Table S2). The method detection limits were calculated by the average plus 3 times the standard deviation (3σ) of field blanks (Table S3).

3. Results and Discussion

3.1. Dissolved PCBs in the Canadian Archipelago

The sum of dissolved PCB congeners in surface waters (Σ PCB_{diss}) of the Canadian Archipelago ranged from 0.65 to 43 pg/L and averaged 14 \pm 16 pg/L (Table S6). For seawater sites, relatively high PCB concentrations were detected in the western Archipelago (Sachs Harbor, 11 pg/L) and the central Archipelago (Allen Bay,

7.1 pg/L), while the PCB concentration in the open waters of Barrow Strait was much lower (1.2 pg/L). For $\Sigma\text{PCB}_{\text{diss}}$ in the East and West Lake at Cape Bounty (Melville Island), samples collected during June and July ranged from 1.9 to 6.5 pg/L, while samples collected during August, when large amounts of snow had already melted, were much higher, at 40–43 pg/L. Our results are generally comparable to samples collected by active large volume sampler (XAD-2 columns) at the same sites; higher PCB concentrations were also detected during end of July and August (39–100 pg/L) than May and June (7.2–23 pg/L) 2016 (Tables S7 and S8).

It is notable that similar PCB concentrations were present in seawater samples collected during May and June and lake samples collected during June and July (Figure S1). These lake samples represent only atmospheric deposition of PCBs, implying that atmospheric deposition continues to be important for PCBs detected in surface water samples. Of course, Arctic rivers are a major influx of POPs to the Arctic Ocean, which could also have originated from atmospheric long-range transport and deposition into the watersheds (Carrizo & Gustafsson, 2011b). The influence of atmospheric long-range delivery is also supported by PCB congener distribution, which is dominated by the lighter PCBs for these samples (Figure S2). The higher PCB concentrations detected during August might be influenced by freshwater sources and snowmelt, which are much more significant in the Canadian Archipelago than for the open ocean (Dickson et al., 2007). The contribution of higher chlorinated PCBs increased greatly during August for these lake samples (Figure S2), indicating catchment inputs of particle-bound heavier PCBs (Dachs et al., 1999). The significant contribution of snowmelt runoff to the inputs of POPs has also been demonstrated in the Resolute Passage of Canadian Arctic during the transition period from winter to summer (Pucko et al., 2017).

Moreover, our dissolved PCB concentrations in the seawater of the Canadian Archipelago are generally higher than earlier reported for the Arctic pan-shelf sea, including European, Asian, and American sectors alike (~1 to ~2 pg/L), as well as the interior Arctic basin regions (<1 pg/L; Carrizo & Gustafsson, 2011a). The concentrations were also higher than those detected in the North Atlantic, including the Norwegian, Greenland, and North Seas (<1 pg/L, Table S9; Gioia et al., 2008). These comparatively high PCB concentrations might be influenced by seawater originating from the Beaufort Sea entering the Archipelago and picking up PCBs from local (secondary) sources. Water circulating in the Beaufort Gyre is relatively old (≈ 7 years) but also had more time for PCBs to be removed via settling (Carrizo & Gustafsson, 2011a). PCBs currently circulating in the Gyre are only slowly released, mainly through the western and northwestern parts of the Canadian Archipelago (Bidleman et al., 2007).

3.2. Gaseous PCBs and Air-Water Exchange Gradients

The sum of gaseous PCB congeners ($\Sigma\text{PCB}_{\text{gas}}$) at Cape Bounty averaged 1.3 ± 0.32 pg/m³ (Table S10). These PCB concentrations were much lower than atmospheric PCBs sampled during early 2000s in the open Arctic Ocean (Gioia et al., 2008) and land-based sites in the Norwegian and Canadian Arctic (Hung et al., 2005, 2010). Long-term monitoring of atmospheric PCBs from 1993 to 2012 also displayed slowly decreasing temporal trends in the Arctic air (Hung et al., 2016).

Air-water fugacity ratios (f_a/f_w) of most PCB congeners were $\ll 1$ (Table S11), indicating that they were in the process of volatilization. That might be explained by PCBs in water becoming *secondary sources*, especially during summer time with more open waters due to reduced ice coverage and increased water temperature (Jantunen et al., 2007).

3.3. Dissolved OCPs in the Canadian Archipelago

Of the targeted OCPs, only HCHs, HCB, and DDTs were regularly detected in both atmosphere and surface water. In the surface water, HCH was the most abundant OCP observed. Interestingly, different from PCBs, relatively high concentrations of α -HCH were detected in Barrow Strait (590 pg/L), followed by α -HCHs in seawater at Sachs Harbor (280 pg/L), whereas the lake water in the same area had quite low concentrations (~100 pg/L); γ -HCH could only be detected in one sample from East Lake of Cape Bounty (59 pg/L). As expected, these concentrations were generally comparable to HCH levels observed in the North Pacific (Cai et al., 2012) and earlier research conducted in the Canadian Arctic, including Beaufort Sea, Labrador Sea, and Hudson Bay (Wong et al., 2010) but higher than concentrations detected in the North Atlantic (Table S9; Lohmann et al., 2009).

HCB was only detected in Barrow Strait seawater and lake water samples. Similar to α -HCH, higher concentrations were present in the Barrow Strait (9.4 pg/L) than lake water samples in the area (average: 2.8 ± 1.6 pg/L). These results were comparable to those observed in the North Pacific, North Atlantic, and Arctic Oceans (Table S9) (Barber et al., 2005; Cai et al., 2012; Lohmann et al., 2009; Wong et al., 2010).

Total DDT residues ranged from non-detect to 2.5 pg/L, with the highest concentration detected in the West Lake at Cape Bounty. The detection frequency of DDT (<10%) and its metabolites (<30%) was rather low, indicating the absence of new sources of DDT to the Arctic. These results were comparable to earlier reported concentrations in Chukchi Sea and North Atlantic (Table S9; Iwata et al., 1993; Lohmann et al., 2009).

Generally, our results for all dissolved OCPs were comparable to those collected by active large volume sampler. The influence of snowmelt runoff in elevating OCP concentrations was not as important as for PCBs (Tables S7 and S8).

3.4. Gaseous OCPs in the Canadian Archipelago

For the atmospheric samples, α -HCH and HCB concentrations averaged 0.84 ± 0.73 and 0.75 ± 0.72 pg/m³, respectively, while DDTs concentrations were lower at 0.15 pg/m³ (Table S10). Concentrations of HCH and HCB present in this study were 1 to 2 orders of magnitude lower than those observed in the Western and Norwegian Arctic atmosphere during 1990s and 2000s; however, no decreasing trends were observed for DDTs (Becker et al., 2012; Cai et al., 2012; Iwata et al., 1993). Similar to PCBs, fugacity ratios of most detected OCPs were $\ll 1$ (Table S11), indicating volatilization from the surface waters to the atmosphere.

In summary, HCHs and HCB were the dominant detected OCPs, and the dissolved OCP concentrations derived from PE samplers are within the range previously observed, but gaseous OCP concentrations were much lower. Dissolved OCPs, which displayed greater concentrations in seawater than in the Arctic lakes, underwent net volatilization to the atmosphere during the summer/sampling period.

3.5. Dissolved PCBs and OCPs at the Fram Strait Mooring Sites

Dissolved PCB congener concentrations were hundreds of femtograms per liter or less in the Fram Strait. The sum of PCB congeners ranged from 0.7 to 3.6 pg/L and 0.9 to 1.6 pg/L in the eastern and western Fram Strait, respectively (for details, see Table S12). PCB concentrations of this study were comparable to those previously reported for deepwater samples (Table S13; Booij et al., 2014; Sobek & Gustafsson, 2014; Sun et al., 2016).

Generally, OCP concentrations in the Fram Strait were higher than PCB concentrations. For all compounds, α -HCH was present at highest concentrations in deep water, at hundreds of picograms per liter, followed by γ -HCH and HCB at tens of picograms per liter, while DDT and its metabolites were at several picograms per liter or less (Table S12). HCH concentrations we detected were lower than those reported during the 1990s (Table S13) in Eastern Arctic Ocean deep waters (Harner et al., 1999). A continuous decline of HCHs due to degradation (microbial and hydrolysis) and export is expected (Harner et al., 1999; Li et al., 2004). Both HCB and *p,p'*-DDE concentrations in the present study were of the same order of magnitude as previously reported in the eastern Fram Strait, Irminger Sea, and the central Arctic Ocean Basin (Booij et al., 2014; Carrizo et al., 2017; Sun et al., 2016).

3.6. Depth Profiles of Dissolved PCBs and OCPs in the Fram Strait

3.6.1. PCBs

Depth profiles of PCBs at both the eastern and western Fram Strait mooring sites generally showed higher concentrations of dissolved PCBs in the deepwater masses and thus, a similar shape as nutrient profiles in the open ocean (Figure 2). While we could not measure PCBs and OCPs in the Fram Strait surface waters directly, a comparison to previous work supports our notion that surface water concentrations were likely lower than results deeper in the water column (Carrizo et al., 2017; Carrizo & Gustafsson, 2011a; Lohmann et al., 2009). Sorption of PCBs to (settling) particles (Galbán-Malagón et al., 2012), as well as complex water sources and water mixing processes in the Fram Strait will contribute to such vertical profiles. In contrast, the less hydrophobic PCB congener 44 displayed a flat vertical profile, as it is not moved as effectively with settling particles to deeper waters as the other PCB congeners.

We observed a change of the PCB composition with depth, whereby the contribution of higher-chlorinated PCBs increased with depth. The contribution of heavier PCBs (hepta and hexa PCBs) increased from ~40% at 200-m depth to >50% at the depth below 1,500 m. The most hydrophobic heptachlorinated PCBs were only

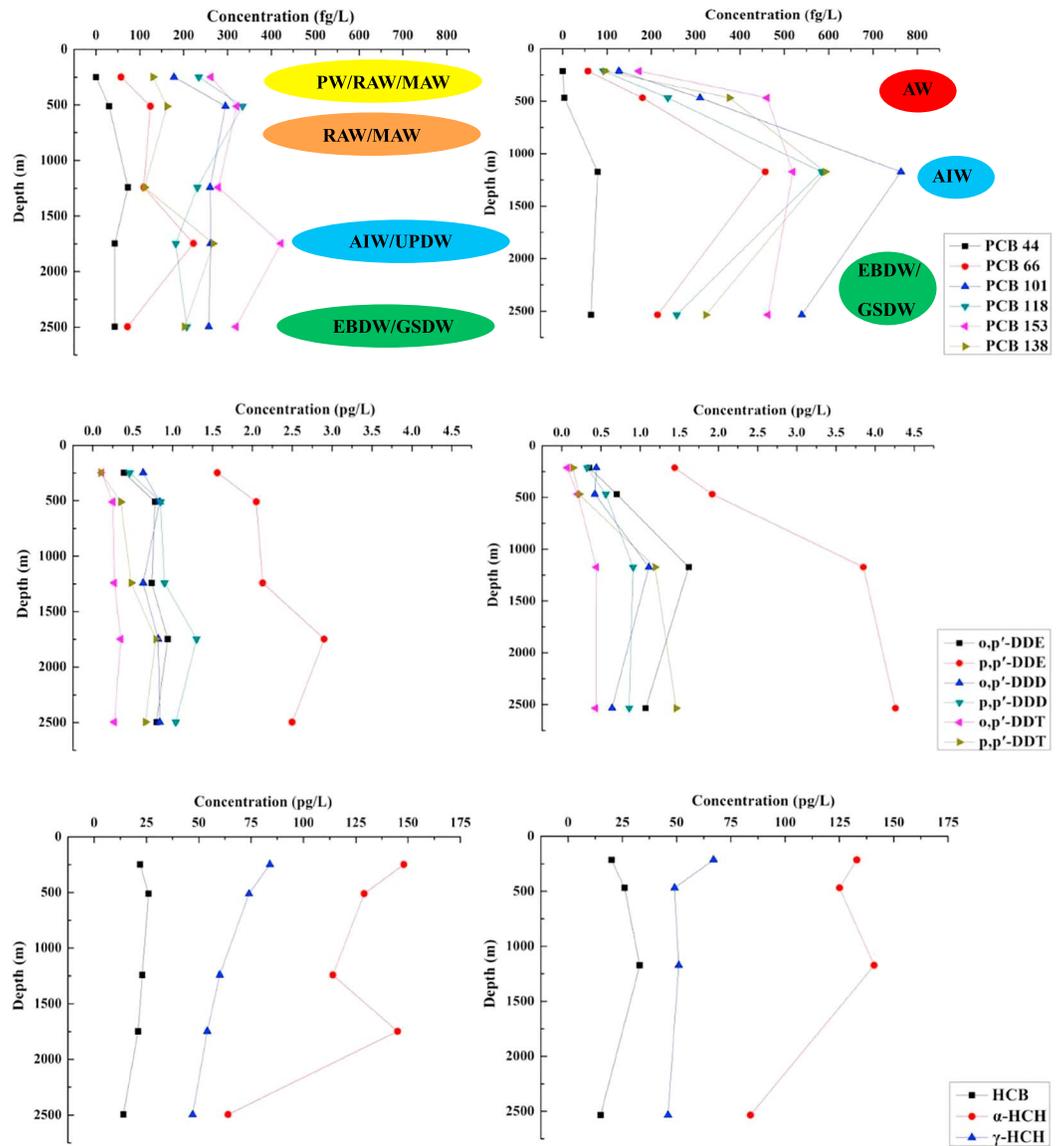


Figure 2. Depth profile of detected PCBs and OCPs in the western (left) and eastern (right) Fram Strait, as well as water mass distributions at both sites. HCB = hexachlorobenzene; PCB = polychlorinated biphenyl; DDT = dichlorodiphenyltrichloroethane; HCH = hexachlorocyclohexane. Water mass definitions: AW = Atlantic Water; AIW = Arctic Intermediate Water; PW = Polar Water; RAW = Recirculating Atlantic Water; MAW = Modified Atlantic Water; UPDW = Upper Polar Deep Water; EBDW = Eurasian Basin Deep Water; GSDW = Greenland Sea Deep Water.

detected below 1,000-m water depth (Figure S3). The higher-chlorinated PCBs are more hydrophobic, with higher octanol-water partitioning (K_{ow}) values and tend to bind more strongly to particles (Dachs et al., 1999). Thus, particles settling could be an important removal pathway for these PCBs from well-mixed surface waters, while dissolution and/or mineralization of settling particles could release these chemicals back to deeper water masses.

Moreover, the water masses with the highest PCB concentrations (Σ PCBs of 3.6 pg/L) observed in eastern Fram Strait at ~1,200 m was typically Arctic Intermediate Water (see Figure 2); high concentrations of PCBs have been reported previously for Arctic Intermediate Water (Sobek & Gustafsson, 2014). A similar nutrient-like vertical profiles of PCBs were reported in samples gathered in the central Arctic Ocean in 2001, with greater concentrations in both intermediate and deep waters than in surface polar mixed waters (Sobek & Gustafsson, 2014). These studies indicate the fractionation of PCBs with depth. In contrast,

decreasing concentration profiles of PCBs in both solution and suspension were reported earlier for the North Atlantic (Schulz et al., 1988; Schulz-Bull et al., 1998) and for particle-bound PCBs in the Mediterranean Sea (Dachs et al., 1997). Those different results might be due to relatively shorter time for them to develop subsurface concentration maxima when sampled back in the 1980s.

3.6.2. DDTs

The depth profiles of DDTs (including *o,p'* and *p,p'* isomers of DDE, DDD, and DDT) in the eastern and western Fram Strait are shown in Figure 2. DDTs displayed similar vertical profiles to PCBs, and the highest concentrations occurred in the deeper water layers; *p,p'*-DDE concentrations also increased with depth in the Makarov and Amundsen Basins of the central Arctic Ocean (Carrizo et al., 2017).

The composition of DDT isomers along the depth profile is shown in Figure S4 (Table S14). It is notable that DDEs (dominated by *p,p'*-DDE) were most abundant throughout the water column (average $59\% \pm 4.4\%$), followed by DDDs (average $28\% \pm 5.4\%$), and DDTs (average $14\% \pm 4.9\%$). Recent research also reported *p,p'*-DDE as the only detectable DDT in the intermediate and deep waters of the central Arctic Ocean (Carrizo et al., 2017). Ratios of *o,p'* and *p,p'* isomers of DDT and DDE and DDT compositions suggest the DDTs we observed represent historical inputs (see supporting information for more details).

3.6.3. HCHs and HCB

The depth profiles of HCHs and HCB were quite different from those found for the more hydrophobic PCBs and DDTs, which bind to particles (Galbán-Malagón et al., 2013). Profiles of HCHs and HCB were similar to PCB 44, which all represent more soluble compounds. We observed greater concentrations of α -HCH, at approximately 130–150 pg/L, both at ~1,000- to 2,000-m and at ~200-m water depth, while γ -HCH generally exhibited a decreasing trend with depth at both sites. Moreover, there were no significant changes of (the persistent) HCB concentrations through the water column at both sites (Figure 2), indicating its utility as a geochemical tracer. In contrast, α -HCH decreased in the deepest samples due to its slow degradation (hydrolysis and/or microbial) over time (Harner et al., 1999).

The ratios of α -HCH and γ -HCH (α/γ -HCH) were in the range of 1.3 to 2.8 (Table S14). Technical HCHs were one of the most extensively used pesticides worldwide in the twentieth century, comprising 55–80% α -HCH, 5–14% β -HCH, and 8–15% γ -HCH (Li, 1999). γ -HCH, also known as lindane, continued being used in some countries of Europe and in North America after technical HCHs were phased out in the 1990s (Li & Macdonald, 2005). Relatively low α/γ -HCH and decreasing trend of γ -HCH through the water column detected in this study might be affected by the continued application of lindane after technical HCH was no longer used.

The net air-sea gas exchange of α -HCH has been shown to change from net deposition to net volatilization in the Arctic Ocean due to decreased worldwide emissions (Jantunen & Bidleman, 1995); the ablation of sea ice also contributed greatly to this change (Wu et al., 2010). Re-emitted α -HCH could then redeposit to the surface seawaters (Cai et al., 2012). Therefore, the relatively higher concentrations of α -HCH observed at ~200-m depth might be influenced by its iterative environmental behavior including deposition, volatilization to the atmosphere, and redeposition in the background of decreasing primary sources and climate change.

In summary, most legacy hydrophobic POPs are not good water mass tracers due to their binding to particles (PCBs and DDTs), reactivity (HCHs), environmental recycling, and varying emission strengths. Exceptions are the less hydrophobic and recalcitrant compounds such as HCB and PCB 44.

3.7. Mass Transport of PCBs and OCPs Through the Fram Strait

Based on the observed depth profiles of PCB and OCP concentrations, we derived POP mass fluxes through the Fram Strait. We used a water volume flux based on long-term measurements of 6.6 ± 0.4 Sv northward and 8.7 ± 2.5 Sv southward (Bieszczynska-Moeller et al., 2012; de Steur et al., 2014). These estimates were derived from direct high-density observations from current meter moorings (Table S15). As the PE samplers were not equally spaced in the water column, we derived average values based on the trapezoidal integration of the contaminant concentrations through the water column. The estimated mass transport fluxes are listed in Table S16 (Figure 3). For HCHs and HCB, the southward mass fluxes (Arctic export) were greater than the northward mass fluxes (Arctic import) through the Fram Strait, with a net transport from the Arctic to the North Atlantic. This means that these legacy OCPs, which have been loaded to the Arctic since the 1930s,

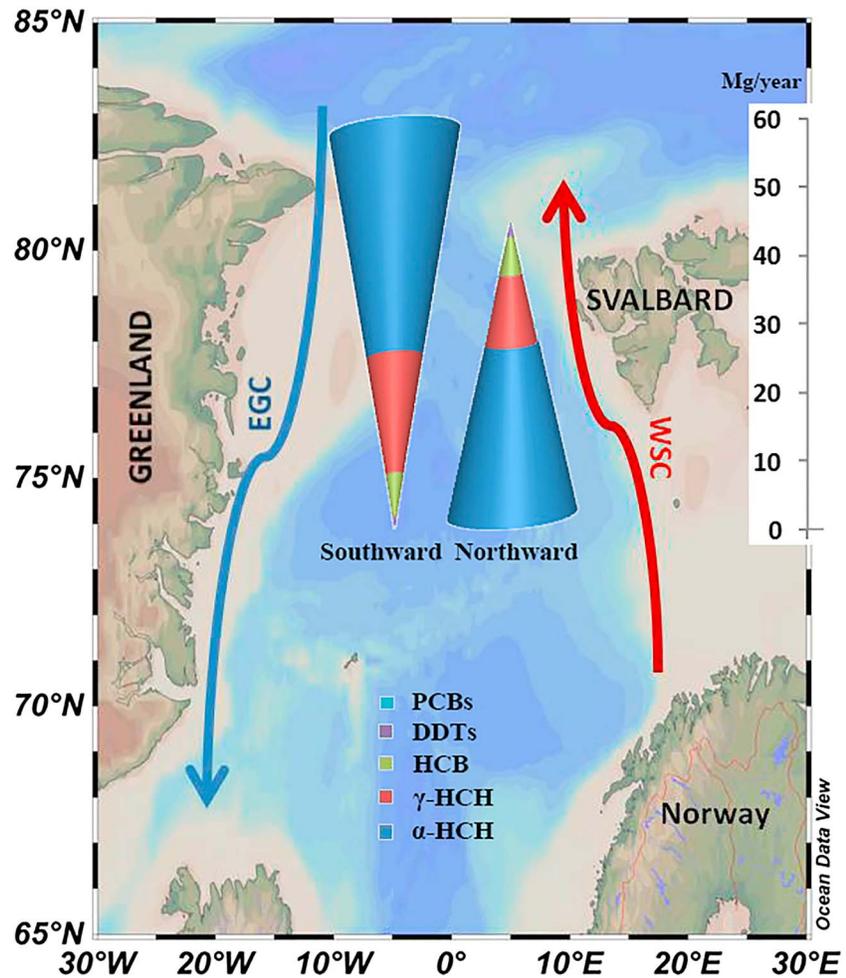


Figure 3. Mass transport of PCBs and OCPs through the Fram Strait (Mg/year). DDT = dichlorodiphenyltrichloroethane; PCB = polychlorinated biphenyl; HCB = hexachlorobenzene; HCH = hexachlorocyclohexane; EGC = East Greenland Current; WSC = West Spitsbergen Current.

are slowly released to the North Atlantic through Fram Strait. However, PCBs are still moving into the Arctic, with net transport from the Atlantic Ocean to the Arctic Ocean.

For the Σ PCBs, the estimated mass transport was 0.55 ± 0.03 Mg/year to the north and 0.39 ± 0.11 Mg/year to the south, with a net northward transport of 0.16 ± 0.12 Mg/year (For the International Council for the Exploration of the Sea (ICES) 7 congeners, the estimated mass transport was 0.39 ± 0.02 Mg/year to the north and 0.29 ± 0.08 Mg/year to the south, with a net northward transport of 0.11 ± 0.09 Mg/year). These fluxes are of the same magnitude as mass fluxes of PCBs from Arctic rivers (0.30 Mg/year) and those estimated for the flux of PCBs into deeper Arctic waters (0.5–0.7 Mg/year; Carrizo & Gustafsson, 2011a).

A novel PCB simulation in a global ocean circulation model (MITgcm, modified from Zhang et al., 2017; for details, see the supporting information) also derived the advective PCB flow for 2015 along a transect at 79°N based on different water flows. The model reproduced observed Arctic surface water concentrations well. Model results also support a net inflow into the Arctic Ocean between 10°W and 15°E. Our estimated mass transports for specific PCB congeners are comparable to the model output (Table S17). The model also estimated that between 1930 and 2015 a total of 80 Mg of the four congeners (PCB 28, 101, 153, and 180) were transported through Fram Strait. Therefore, there is a net inflow of PCBs into the Arctic Ocean, especially in deep waters.

In contrast to PCBs, mass flows of HCHs indicated net export from the Arctic Ocean: For α -HCH, there was a net export of 7.7 ± 9.5 Mg/year (25 ± 1.5 Mg/year into the Arctic and 33 ± 9.4 Mg/year outflow); and for γ -HCH,

there was a net southward transport of 6.3 ± 4.8 Mg/year (10 ± 0.63 Mg/year into Arctic and 17 ± 4.8 Mg/year to the south). An Arctic Mass Balance Box Modal developed by Li et al. (2004) demonstrated that microbial degradation and ocean currents contribute $\sim 50\%$ and $\sim 25\%$ to the disappearance of α -HCH in the Arctic Ocean during 1945–2000, respectively (Li et al., 2004). In this study, the mass transport estimations of α -HCH were similar in magnitude to the output results of Arctic Mass Balance Box Modal (mass flux of α -HCH was estimated as 29 Mg/year to the north by West Spitsbergen Current and 67 Mg/year to the south by East Greenland Current in 1992). For HCB, the estimated net export based on our measurements was 0.65 ± 1.7 Mg/year (5.3 ± 0.32 Mg/year into the Arctic and 5.9 ± 1.7 -Mg/year outflow) from the Arctic Ocean. Finally, the estimated mass flows of Σ DDTs into (1.6 ± 0.45 Mg/year) and out of the Arctic (1.6 ± 0.10 Mg/year) were identical. Considering the Arctic Ocean inventory of DDTs (on the order of several tons, Carrizo et al., 2017), it will take time for DDTs to disappear from the Arctic Ocean via water mass outflow.

4. Conclusions

Results from the first pan-Arctic deployments of passive samplers demonstrated the ubiquitous presence of PCBs and OCPs across the Canadian Arctic and throughout the water column of the Fram Strait. Results also show the importance of atmospheric inputs of POPs from meltwaters and that nearshore areas (such as the archipelago) continue to be influenced by ongoing freshwater inputs. While atmospheric transport is still important for the presence of POPs in the surface Arctic Ocean, air-water fugacity gradients implied net volatilization to the atmosphere during the summer/sampling time for most POPs. In the Fram Strait, higher PCB and DDT concentrations were detected in the deepwater masses, similar to nutrient-like vertical profiles. Based on our measurements, there is net export of legacy HCHs and HCB from the Arctic to the Atlantic Ocean ($\sim 14 \pm 14$ Mg of HCHs and $\sim 0.65 \pm 1.7$ Mg of HCB per year), but import of PCBs from the Atlantic to the Arctic Ocean (0.16 ± 0.12 Mg/year) through the Fram Strait, similar in magnitude to model-based predictions. Finally, estimated mass flows of Σ DDTs into (1.6 ± 0.45 Mg/year) and out of the Arctic (1.6 ± 0.10 Mg/year) were identical.

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References

- Barber, J. L., Sweetman, A. J., Van Wijk, D., & Jones, K. C. (2005). Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Science of the Total Environment*, 349(1), 1–44.
- Becker, S., Halsall, C. J., Tych, W., Kallenborn, R., Schlabach, M., & Mano, S. (2012). Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. *Atmospheric Chemistry and Physics*, 12(9), 4033–4044. <https://doi.org/10.5194/acp-12-4033-2012>
- Beszczyńska-Moeller, A., Fahrback, E., Schauer, U., & Hansen, E. (2012). Variability in Atlantic water temperature and transport at the entrance to the Arctic Ocean, 1997–2010. *ICES Journal of Marine Science*, 69(5), 852–863. <https://doi.org/10.1093/icesjms/fss056>
- Bidleman, T. F., Kylin, H., Jantunen, L. M., Helm, P. A., & MacDonald, R. W. (2007). Hexachlorocyclohexanes in the Canadian Archipelago. 1. Spatial distribution and pathways of alpha-, beta- and gamma-HCHs in surface water. *Environmental Science & Technology*, 41(8), 2688–2695. <https://doi.org/10.1021/es062375b>
- Booij, K., Smedes, F., & van Weerlee, E. M. (2002). Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere*, 46(8), 1157–1161. [https://doi.org/10.1016/S0045-6535\(01\)00200-4](https://doi.org/10.1016/S0045-6535(01)00200-4)
- Booij, K., van Bommel, R., van Aken, H. M., van Haren, H., Brummer, G. A., & Ridderinkhof, H. (2014). Passive sampling of nonpolar contaminants at three deep-ocean sites. *Environmental Pollution*, 195, 101–108. <https://doi.org/10.1016/j.envpol.2014.08.013>
- Cai, M., Ma, Y., Xie, Z., Zhong, G., Möller, A., Yang, H., et al. (2012). Distribution and air-sea exchange of organochlorine pesticides in the North Pacific and the Arctic. *Journal of Geophysical Research*, 117, D06311. <https://doi.org/10.1029/2011JD016910>
- Carrizo, D., & Gustafsson, Ö. (2011a). Distribution and inventories of polychlorinated biphenyls in the polar mixed layer of seven pan-Arctic shelf seas and the interior basins. *Environmental Science & Technology*, 45(4), 1420–1427. <https://doi.org/10.1021/es103542f>
- Carrizo, D., & Gustafsson, Ö. (2011b). Pan-arctic river fluxes of polychlorinated biphenyls. *Environmental Science & Technology*, 45(19), 8377–8384. <https://doi.org/10.1021/es201766z>
- Carrizo, D., Sobek, A., Salvado, J. A., & Gustafsson, Ö. (2017). Spatial distributions of DDTs in the water masses of the Arctic Ocean. *Environmental Science & Technology*, 51(14), 7913–7919. <https://doi.org/10.1021/acs.est.7b01369>
- Dachs, J., Bayona, J. M., & Albaiges, J. (1997). Spatial distribution, vertical profiles and budget of organochlorine compounds in Western Mediterranean seawater. *Marine Chemistry*, 57(3–4), 313–324. [https://doi.org/10.1016/S0304-4203\(97\)00016-9](https://doi.org/10.1016/S0304-4203(97)00016-9)
- Dachs, J., Eisenreich, S. J., Baker, J. E., Ko, F. C., & Jeremiason, J. D. (1999). Coupling of phytoplankton uptake and air-water exchange of persistent organic pollutants. *Environmental Science & Technology*, 33(20), 3653–3660. <https://doi.org/10.1021/es990168o>
- Dachs, J., Lohmann, R., Ockenden, W. A., Mejanelle, L., Eisenreich, S. J., & Jones, K. C. (2002). Oceanic biogeochemical controls on global dynamics of persistent organic pollutants. *Environmental Science & Technology*, 36(20), 4229–4237. <https://doi.org/10.1021/es025724k>
- de Steur, L., Hansen, E., Mauritzen, C., Beszczyńska-Moeller, A., & Fahrback, E. (2014). Impact of recirculation on the East Greenland Current in Fram Strait: Results from moored current meter measurements between 1997 and 2009. *Deep-Sea Research Part I-Oceanographic Research Papers*, 92, 26–40. <https://doi.org/10.1016/j.dsr.2014.05.018>
- Dickson, R., Rudels, B., Dye, S., Karcher, M., Meincke, J., & Yashayaev, I. (2007). Current estimates of freshwater flux through Arctic and subarctic seas. *Progress in Oceanography*, 73(3–4), 210–230. <https://doi.org/10.1016/j.pocan.2006.12.003>

- Galbán-Malagón, C., Berrojalbiz, N., Gioia, R., & Dachs, J. (2013). The “degradative” and “biological” pumps controls on the atmospheric deposition and sequestration of hexachlorocyclohexanes and hexachlorobenzene in the North Atlantic and Arctic Oceans. *Environmental Science & Technology*, 47(13), 7195–7203. <https://doi.org/10.1021/es4011256>
- 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. *Nature Communications*, 3(1), 862. <https://doi.org/10.1038/ncomms1858>
- Gioia, R., Lohmann, R., Dachs, J., Temme, C., Lakaschus, S., Schulz-Bull, D., et al. (2008). Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean. *Journal of Geophysical Research*, 113, D19302. <https://doi.org/10.1029/2007JD009750>
- Harner, T., Kylin, H., Bidleman, T. F., & Strachan, W. M. J. (1999). Removal of alpha- and gamma-hexachlorocyclohexane and enantiomers of alpha-hexachlorocyclohexane in the eastern Arctic Ocean. *Environmental Science & Technology*, 33(8), 1157–1164. <https://doi.org/10.1021/es980898g>
- Hop, H., Falk-Petersen, S., Svendsen, H., Kwasniewski, S., Pavlov, V., Pavlova, O., & Soreide, J. E. (2006). Physical and biological characteristics of the pelagic system across Fram Strait to Kongsfjorden. *Progress in Oceanography*, 51(2–4), 182–231. <https://doi.org/10.1016/j.poccean.2006.09.007>
- Hung, H., Blanchard, P., Halsall, C. J., Bidleman, T. F., Stern, G. A., Fellin, P., et al. (2005). Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring. *Science of the Total Environment*, 342(1–3), 119–144. <https://doi.org/10.1016/j.scitotenv.2004.12.058>
- Hung, H., Kallenborn, R., Breivik, K., Su, Y. S., Brorström-Lundén, E., Olafsdottir, K., et al. (2010). Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Science of the Total Environment*, 408(15), 2854–2873. <https://doi.org/10.1016/j.scitotenv.2009.10.044>
- 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). *Environmental Pollution*, 217, 52–61. <https://doi.org/10.1016/j.envpol.2016.01.079>
- 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. *Environmental Science & Technology*, 27(6), 1080–1098. <https://doi.org/10.1021/es00043a007>
- Jamieson, A. J., Malkocs, T., Pierny, S. B., Fujii, T., & Zhang, Z. (2017). Bioaccumulation of persistent organic pollutants in the deepest ocean fauna. *Nature ecology & evolution*, 1(3), 51–51. <https://doi.org/10.1038/s41559-016-0051>
- Jantunen, L. M., & Bidleman, T. F. (1995). Reversal of the air-water gas exchange direction of hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 versus 1988. *Environmental Science & Technology*, 29(4), 1081–1089. <https://doi.org/10.1021/es00004a030>
- Jantunen, L. M., Helm, P. A., Kylin, H., & Bidleman, T. F. (2007). Hexachlorocyclohexanes (HCHs) in the Canadian Archipelago. 2. Air–water gas exchange of α - and γ -HCH. *Environmental Science & Technology*, 42(2), 465–470.
- Khairy, M., Muir, D., Teixeira, C., & Lohmann, R. (2014). Spatial trends, sources, and air–water exchange of organochlorine pesticides in the Great Lakes Basin using low density polyethylene passive samplers. *Environmental Science & Technology*, 48(16), 9315–9324. <https://doi.org/10.1021/es501686a>
- Li, Y. F. (1999). Global gridded technical hexachlorocyclohexane usage inventories using a global cropland as a surrogate. *Journal of Geophysical Research*, 104(D19), 23,785–23,797. <https://doi.org/10.1029/1999JD900448>
- Li, Y. F., & Macdonald, R. W. (2005). Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review. *Science of the Total Environment*, 342(1–3), 87–106. <https://doi.org/10.1016/j.scitotenv.2004.12.027>
- Li, Y. F., Macdonald, R. W., Ma, J. M., Hung, H., & Venkatesh, S. (2004). Historical alpha-HCH budget in the Arctic Ocean: The Arctic Mass Balance Box Model (AMBBM). *Science of the Total Environment*, 324(1–3), 115–139. <https://doi.org/10.1016/j.scitotenv.2003.10.022>
- Liu, Y., Wang, S., McDonough, C. A., Khairy, M., Muir, D. C. G., Helm, P. A., & Lohmann, R. (2016). Gaseous and freely-dissolved PCBs in the lower Great Lakes based on passive sampling: Spatial trends and air–water exchange. *Environmental Science & Technology*, 50(10), 4932–4939. <https://doi.org/10.1021/acs.est.5b04586>
- Lohmann, R., Breivik, K., Dachs, J., & Muir, D. (2007). Global fate of POPs: Current and future research directions. *Environmental Pollution*, 150(1), 150–165. <https://doi.org/10.1016/j.envpol.2007.06.051>
- Lohmann, R., Gioia, R., Jones, K. C., Nizzetto, L., Temme, C., Xie, Z., et al. (2009). Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. *Environmental Science & Technology*, 43(15), 5633–5639. <https://doi.org/10.1021/es901229k>
- Ma, Y. X., Halsall, C. J., Crosse, J. D., Graf, C., Cai, M. H., He, J. F., et al. (2015). Persistent organic pollutants in ocean sediments from the North Pacific to the Arctic Ocean. *Journal of Geophysical Research: Oceans*, 120, 2723–2735. <https://doi.org/10.1002/2014JC010651>
- Muir, D. C., & de Wit, C. A. (2010). Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations. *Science of the Total Environment*, 408(15), 3044–3051. <https://doi.org/10.1016/j.scitotenv.2009.11.032>
- Pucko, M., Stern, G. A., Burt, A. E., Jantunen, L. M., Bidleman, T. F., Macdonald, R. W., et al. (2017). Current use pesticide and legacy organochlorine pesticide dynamics at the ocean–sea ice–atmosphere interface in resolute passage, Canadian Arctic, during winter–summer transition. *Science of the Total Environment*, 580, 1460–1469. <https://doi.org/10.1016/j.scitotenv.2016.12.122>
- Schulz, D. E., Petrick, G., & Duinker, J. C. (1988). Chlorinated biphenyls in North-Atlantic surface and deep-water. *Marine Pollution Bulletin*, 19(10), 526–531. [https://doi.org/10.1016/0025-326X\(88\)90543-7](https://doi.org/10.1016/0025-326X(88)90543-7)
- Schulz-Bull, D. E., Petrick, G., Bruhn, R., & Duinker, J. C. (1998). Chlorobiphenyls (PCB) and PAHs in water masses of the northern North Atlantic. *Marine Chemistry*, 61(1–2), 101–114. [https://doi.org/10.1016/S0304-4203\(98\)00010-3](https://doi.org/10.1016/S0304-4203(98)00010-3)
- Sobek, A., & Gustafsson, Ö. (2014). Deep water masses and sediments are main compartments for polychlorinated biphenyls in the Arctic Ocean. *Environmental Science & Technology*, 48(12), 6719–6725. <https://doi.org/10.1021/es500736q>
- Sun, C., Soltwedel, T., Bauerfeind, E., Adelman, D. A., & Lohmann, R. (2016). Depth profiles of persistent organic pollutants in the north and tropical Atlantic Ocean. *Environmental Science & Technology*, 50(12), 6172–6179. <https://doi.org/10.1021/acs.est.5b05891>
- Wong, F., Jantunen, L. M., Pucko, M., Papakyriakou, T., Staebler, R. M., Stern, G. A., & Bidleman, T. F. (2010). Air–water exchange of anthropogenic and natural organohalogen on International Polar Year (IPY) expeditions in the Canadian Arctic. *Environmental Science & Technology*, 45(3), 876–881. <https://doi.org/10.1021/es1018509>
- Wu, X., Lam, J. C., Xia, C., Kang, H., Sun, L., Xie, Z., & Lam, P. K. (2010). Atmospheric HCH concentrations over the marine boundary layer from Shanghai, China to the Arctic Ocean: Role of human activity and climate change. *Environmental Science & Technology*, 44(22), 8422–8428. <https://doi.org/10.1021/es102127h>
- Zhang, X., Zhang, Y., Dassuncao, C., Lohmann, R., & Sunderland, E. M. (2017). North Atlantic Deep Water formation inhibits high Arctic contamination by continental perfluorooctane sulfonate discharges. *Global Biogeochemical Cycles*, 31, 1332–1343. <https://doi.org/10.1002/2017GB005624>