Polychlorinated biphenyls in air and water of the North Atlantic and Arctic Ocean

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[1]   Air and seawater samples were collected on board the R/V *Polarstern* during a scientific expedition from Germany to the Arctic Ocean during June–August 2004. The air data show a strong decline with latitude with the highest polychlorinated biphenyl (PCB) concentrations in Europe and the lowest in the Arctic. Σ_{ICES} PCBs in air range from 100 pg m^{-3} near Norway to 0.8 pg m^{-3} in the Arctic. A comparison with other data from previous and ongoing land-based air measurements in the Arctic region suggests no clear temporal decline of PCBs in the European Arctic since the mid-1990s. Dissolved concentrations of Σ_6PCBs (28/31, 52, 101, 118, 138, 153) in surface seawater were <1 pg L^{-1}. Dominant PCBs in seawater were 28/31 and 52 (0.1–0.44 pg L^{-1}), with PCBs 101, 118, and 138 < 0.1 pg L^{-1}. In seawater, PCB 52 displayed the highest concentrations in the northernmost samples, while PCBs 101, 118, and 138 showed slightly decreasing trends with increasing latitude. Fractionation was observed for PCBs in seawater with the relative abundance of PCBs 28 and 52 increasing and that of the heavier congeners decreasing with latitude. However, in air only 15–20% of the variability of atmospheric PCBs can be explained by temperature. Owing to large uncertainties in the Henry's Law constant (HLC) values, fugacity quotients for PCBs were estimated using different HLCs reported in the literature. These indicate that on average, deposition dominates over volatilization for PCBs in the Arctic region with a strong increase in the middle of the transect near the marginal ice zone (78–79°N). The increase in fugacity ratio is mainly caused by an increase in air concentration in this region (possibly indirectly caused by ice melting being a source of PCBs to the atmosphere).

1.   Introduction

[2]   Polychlorinated biphenyls (PCBs) are industrial chemicals that have been used in most industrialized countries. Production of PCBs peaked in the 1960s in Europe and the United States. They were ultimately banned in the late 1970s/early 1980s [*de Voogt and Brinkman*, 1989]. The most recent inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tons [*Breivik et al.*, 2007]. Approximately 97% of this has been used in the Northern Hemisphere, mostly between 30°N and 60°N [*Breivik et al.*, 2002]. PCBs are persistent, ubiquitous, and prone to undergo long-range atmospheric transport (LRAT). As a result, they have been found in the Arctic [*Bidleman et al.*, 1999; *Harner et al.*, 1998; *Stern et al.*, 1997] and shown to bioaccumulate and biomagnify in marine mammals, polar bears, and humans [*Kucklick and Baker*, 1998; *Halsall et al.*, 1998]. There is concern for the health of indigenous Arctic people and wildlife, due to the toxicity, persistence, and bioaccumulation potential of these compounds [*Gilman et al.*, 1997]. Their regulation has become an international policy issue based upon their possible effects on human health and potential environmental risks [*United Nations Economic Commission for Europe*, 1998].

[3]   The atmosphere has been regarded as the most important and rapid route of transport for PCBs to the Arctic. *Wania and Mackay* [1993] put forward the hypothesis that the more volatile congeners would be transported and condensed in colder regions, while the less volatile congeners would be deposited in warmer regions/closer to sources. This would result in a relative enrichment of the

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more volatile compounds in colder (polar) areas over time. Global fractionation of chemicals depends on various physical-chemical properties, processes such as deposition, volatilization, and environmental variables. Many investigators have found evidence of fractionation of PCBs in environmental media such as air and seawater, but uncertainties remain over whether environmental reservoirs act as sources or sinks and whether primary or secondary sources are controlling the levels of PCBs in the environment [*Meijer et al.*, 2003; *Jaward et al.*, 2004; *Sobek and Gustafsson*, 2004; *Gioia et al.*, 2006]. Furthermore, fractionation (or a change in the mixture of PCBs) can also be the result of other processes, such as enhanced removal or settling of the more hydrophobic compounds, to the deep ocean and degradation.

[4] There are several studies reporting PCB concentrations in Arctic biota [e.g., *Arctic Monitoring and Assessment Program*, 2004; *Macdonald et al.*, 2000; *Van Oostdam et al.*, 1999]. Most data to date has been obtained as part of the Canadian-operated *Northern Contaminants Program* [2003] and the Arctic Monitoring and Assessment Program (AMAP) [*Hung et al.*, 2005]. However, there are very few studies of their air and seawater concentrations over the open oceans [*Iwata et al.*, 1993; *Schulz-Bull et al.*, 1988; *Harner et al.*, 1998; *Sobek and Gustafsson*, 2004] despite their importance in supplying food chains and the regional/global cycling of POPs.

[5] Deep oceans are believed to be a final sink of these pollutants, removing them from the "recyclable pool" in the environment [*Jurado et al.*, 2004; *Dachs et al.*, 2002]. PCBs can be removed from the atmosphere via air-to-water exchange, partition into organic matter in seawater, and removed via carbon export to the deeper oceans [*Dachs et al.*, 2002]. Knowledge of the equilibrium status and/or net direction of the flux between air and water is essential to understand the global cycle of these pollutants. Despite the importance of partitioning between air and water for these pollutants, few simultaneous air and seawater measurements over open oceans such as the Atlantic are reported in the literature. This may be because of the difficulties in collecting reliable air and seawater samples on board ships and the large volumes of seawater needed to detect PCBs.

[6] This study presents air and seawater concentrations of PCBs from samples taken on the R/V *Polarstern* during June–August 2004, during a cruise from Germany through the Norwegian Sea, the Greenland Sea, and the Arctic Ocean (see Figure 1). Mechanisms of PCB transport to and within the Arctic are investigated by looking at compound concentrations and latitudinal variations in compound mixtures. The state of equilibrium and net direction of flux between the air and the seawater is also discussed.

2. Methodology

2.1. Sample Collection

[7] Air and seawater samples were collected on board the R/V *Polarstern* (Alfred Wegener Institute, Germany) during June–August 2004 from 55°N to 85°N. A total of 37 air samples were taken on the observation deck, 20 m above the sea level, using a high-volume air sampler (Hi-Vol; Tisch Environmental TE-PNY1123 accuvol modified PUF sampler, Factory Cleves, Ohio, USA) placed windward and

operating at $0.25–0.27$ m^3/min. Twelve to forty-eight hours integrated air samples were collected ranging from 150 m^3 in the North Sea to 800 m^3 in the Arctic Ocean. Particulate and gas phase compounds were captured on a glass fiber filter (GFF, 110 mm diameter, Whatman International Ltd., Maidstone, UK) and two polyurethane foam (PUF; 5 cm diameter, 6.5 cm length, Klaus Ziemer GmbH, Langerwehe, Germany) plugs, respectively. The samplers were operated in "good conditions," when the relative wind direction was between $0°–90°$ and $270°–0°$ to avoid sampling air coming from the ship's funnel. After sampling, the PUFs and GFFs were transferred into solvent rinsed aluminum tins and stored in freezers at $-20°C$. These were analyzed at Lancaster University.

[8] Seawater samples were collected from a stainless steel pipe at 8 m depth, using the ship's intake system located in the keel. The average flow rate was about 1.2 L min^{-1}. Both particle and dissolved seawater phases were collected using a GFF (GF/F 52 with 0.7 μm nominal pore size) and a 95 mL XAD-2 resin (Supelco, Germany) column, respectively. After sampling, samples were stored at $-4°C$ until analysis at the Institute for Baltic Sea Research (IOW).

2.2. Processing of Air Samples

[9] PUF plugs were preextracted with dichloromethane (DCM, HPLC grade, Fischer Scientific, Loughborough, UK) using a Dionex accelerated solvent extractor (Dionex UK Ltd, Surrey, UK), while GFFs were precombusted at 450°C. Samples were handled and extracted in a dedicated clean laboratory, which has filtered, charcoal-stripped air and positive pressure conditions. Each sample was spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners (^{13}C-labeled PCB 28, 52, 101, 138, 153, 180; CIL, Cambridge, USA) and extracted in a Buchi extraction unit (Lab Plant, Huddersfield, UK) for 18 h with hexane (HPLC grade, Fischer Scientific, Loughborough, UK). The extracts were concentrated using rotary evaporation and nitrogen evaporation. Each sample was eluted on a 9 mm id column with 1 g alumina (BDH neutral Alumina, Merck, Darmstadt, Germany), 2 g silica gel (Merck Silica 60, Darmstadt, Germany), and 1 cm of sodium sulphate (VWR, Pade, UK) all baked at 450°C overnight. The extracts were then eluted through gel permeation columns containing 6 g of Biobeads SX 3 (BIO RAD Laboratory, Hercules, California, USA). Each sample was concentrated to about 100 μL under N$_2$ gas (BOC Gases, Surrey, UK) and solvent exchanged to 25 μL of dodecane containing PCB 30 and [$^{13}C_{12}$] PCB 141 as internal standards. The samples were analyzed by gas chromatography-mass spectrometry (GC-MS Finnigan Trace by Thermo Fischer Scientific, Loughborough, UK) with an EI+ source operating in selected ion mode (SIM). Details of the instruments, temperature program, and monitored ions are given elsewhere [*Thomas et al.*, 1998; *Gouin et al.*, 2002]. The following congeners were analyzed: tri-PCBs 18, 22, 28, and 31; tetra-PCBs 44, 49, 53, 70 and 74; penta-PCBs 87, 90/101, 95, 99, 105, 110, 118 and 123; hexa-PCBs 138, 141, 149, 151, 153/132 and 158; hepta-PCBs 170, 174, 180, 183 and 187; octa-PCBs 194, 199 and 203.

2.3. Processing of Seawater Samples

[10] Water samples were processed at IOW. XAD resins were precleaned by consecutive Soxhlet extractions with
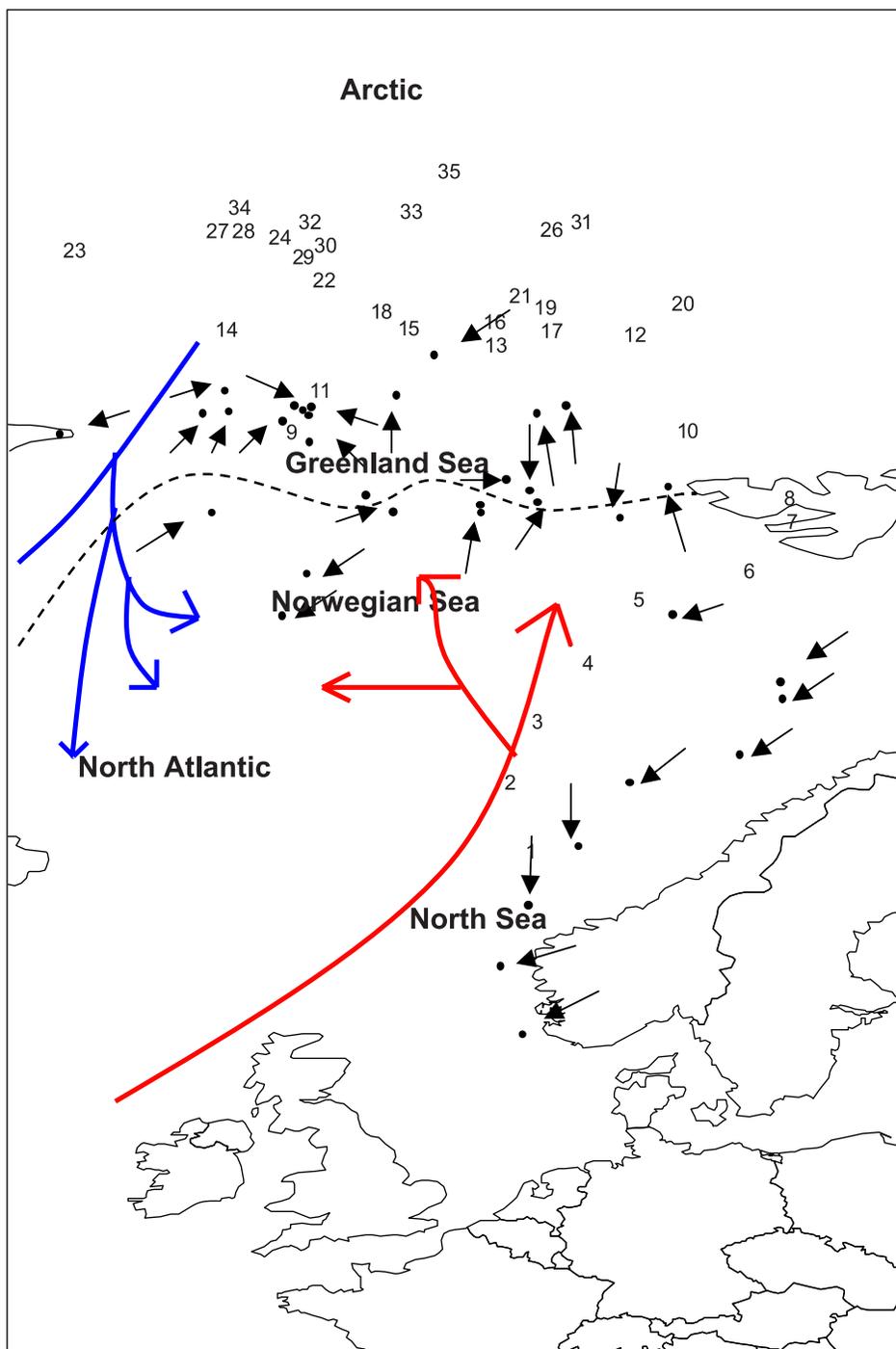
Figure 1. Mean air sampling locations during June–August 2004 on board the R/V *Polarstern*. The black arrows broadly indicate air mass origin for each sample. The red and blue arrows indicate general surface oceanic currents. The red arrows indicate warmer water coming from the North Atlantic; the blue arrows indicate deep cold water descending from the Arctic Ocean. The dashed black line indicates the average ice cover during sampling.

DCM, transferred into glass columns and rinsed with copious amounts of water. XAD columns (two sets of 15 IOW columns of ∼8 cm i.d., 20 cm length, and 20 GSO columns of 3 cm i.d., 20 cm length) were capped and sealed in polyethylene bags. GFFs were precombusted at 450°C for 12 h and wrapped in aluminum foil. After sampling, XAD cartridges were extracted in acetone, ex-changed to hexane, dried over sodium sulphate, and con-centrated by rotary evaporation to ∼150 μL. GFFs were extracted twice by accelerated solvent extraction using hexane: acetone (60:40, V/V) at a pressure of 140 bar at 100°C for 15 min. Extracts were combined, the water phase liquid-liquid extracted with hexane and the hexane phases combined, dried over sodium sulphate, and concentrated by

rotary evaporation to ~150 μL. Samples were cleaned up on a Baker-Bond double column consisting of 3 g inactivated (15% water) aluminum oxide in the upper and 3 g inactivated silica (3.5% water) in the lower column. Samples were eluted with 12 ml hexane and 40 ml dichloromethane: hexane (1:9V/V). The first fraction was used to analyze PCBs. Prior to extraction, internal standards were added ($^{13}C_{12}$-PCBs 28, 52, 101, 153, 138, 180, pp-DDE, and pp-DDT, all at 15 pg μL^{-1}, deuterated PAHs at 100 pg μL^{-1}). A XTI-5 30 m capillary column (inner diameter 0.25mm, film thickness 0,25 μm; Restek, USA) was used to separate analytes in a Thermo Finnigian Trace GC - Automass MS. A 2 μL sample was injected in a programmed temperature vaporizing (PTV) injector, which was ramped from 50 to 280°C at 10°C s^{-1}. The temperature (T) of the GC for PCBs and DDTs ramped from 50°C (3.5 min) at 10°C min^{-1} to 310°C, where it was held for 15 min.

2.4. Quality Assurance/Quality Control

[11] All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks, travel blanks (media that just traveled), and field blanks constituted 10%, 10%, and 30%, respectively, of the total number of samples for air. No analytes were detected in the laboratory blanks (i.e., values were <1 pg μL^{-1} in 25 μL sample on column), showing there was no contamination during sample processing in the laboratory. Travel blanks and field blanks showed similar compound concentration (i.e., <1 pg μL^{-1} in 25 μL sample on column) indicating minimal contamination during storage, sampling, and transport. Samples were blank corrected using the mean of the field blanks. Method detection limits (MDL) were derived as the mean plus 3 times the standard deviation of the field blanks. Air sampling on the ship needs to be consistent and respectful of strict quality control measures, in order to avoid ship contamination and detect low levels of POPs in remote regions [Lohmann et al., 2004]. Passive air samplers (PUF disks) were deployed in different locations in and on board the R/V Polarstern to monitor the background air concentrations of the ship and to determine if the ship had the potential to be a source of contamination for the samples. PCB data resulting from the passive air samplers and active air sampling on board suggest that R/V Polarstern is a clean ship for these compounds [Gioia et al., 2007]. Recoveries were routinely monitored using the $^{13}C_{12}$ PCBs as surrogate standards and they ranged from 85 to 107%. Reported values are not recovery corrected. Extraction and cleanup method efficiencies were monitored by spiking cleaned GFFs and PUFs with validation standards for PCBs and extracting and analyzing those PUFs in the same way as samples. Recoveries ranged from 90 to 110% for all compounds.

[12] Two break-through tests were performed for seawater by filtering water through two XAD columns in series. Sample volumes were 990 and 1260 L. Concentrations on the back-up column of the lighter compounds were around 10–20% of the first column, suggesting that break-through was not a major concern for our samples. Apparent break-through values of heavier weight compounds seemed higher but were close to blank concentrations, confirming that break-through was not of concern. Fortified XAD and GFF blanks at 1 and 10 ng total were coanalyzed with the samples, with recoveries around 100% for all congeners. Average concentrations in the XAD blanks were around 10–20 pg per PCB congener. Detection limits were calculated as the mean blank concentrations plus three standard deviations. Mean blank concentrations were subtracted from the samples.

2.5. Meteorological Data and Back Trajectories

[13] Meteorological data were obtained from PODAS (Polarstern Data System) on board the vessel, an online management system that collects nautical and meteorological parameters from a multitude of measuring devices installed on the ship. NOAA's HYSPLIT model and the NCEP/NCAR Global Reanalysis data set were used to calculate back trajectories (BTs) and atmospheric mixing height. BTs were traced for 7 d with 1 h steps at 0000 coordinated universal time (UTC) at 500 m above sea level. Figure 1 shows the mean sampling location of the transect and prevalent air masses direction.

3. Global Orientation and Sampling Locations

[14] The sampling locations in the Norwegian Sea, the Greenland Sea, and the Arctic Ocean represent different regions of the generalized global mass flow in the lower atmosphere and the ocean water. Figure 1 shows representative air mass direction, prevalent surface ocean currents, and sea ice coverage during the sampling period. BT analysis shows that about 60% of the samples are oceanic (12–19, 24–29, 31, and 33), while for the others air masses were partly continental (Canada and Greenland or Russia) and partly oceanic (defined as air that has been away from land for 3 days) (3–11, 20–23, 30, 32, 34, and 35). Only two samples (1–2) in the North Sea had air masses coming predominantly over the land (Scandinavian countries) before sampling.

[15] In parts of the Norwegian and Greenland Seas, cold and saline surface water descends 2–3 km down, forming cold, oxygen-rich deep waters. The North Atlantic Deep Water (NADW) is largely formed in the Labrador Sea and the Greenland Sea by the sinking of highly saline, dense overflow water from the Greenland Sea. The region remains ice-free due to the warm and saline Norwegian Atlantic Current. Lohmann et al. [2006] estimated a subduction flux of ~420 kg PCBs a^{-1} for the Norwegian Sea. All the samples collected in the Arctic Ocean and some in the Greenland Sea (near the coast of Greenland) were characterized by ice cover. There would have been minimal interaction between the atmosphere and the water column because of the ice sheet in between. Weather conditions over the ice were predominantly characterized by low wind and fog.

4. Results

4.1. Air Concentrations

[16] A total of 37 samples were collected during the cruise; ~50% in the Arctic Ocean, ~29% in the Greenland Sea, and ~21% in part of the North and the Norwegian Sea. Table 1 gives a summary of the results for PCB air concentrations in each of the three regions. Atmospheric

Table 1. Summary of Results in Air Samples[a]

Compound	Part of North Sea and Norwegian Sea		Greenland Sea		Arctic Ocean	
	Mean (n)	Range	Mean (n)	Range	Mean (n)	Range
Latitude	$60°-72°$		$72°-78°$		$78°-85°$	
PCB 28	13 (n = 8)	2.3–50	3.4 (n = 10)	1.6–6	4.2 (n = 15)	1.3–22
PCB 52	6 (n = 8)	1–20	2.3 (n = 10)	0.48–8	1.6 (n = 19)	0.42–1.4
PCB 90/101	5 (n = 7)	1.2–12	1.6 (n = 4)	0.55–3.5	3 (n = 3)	1.4–5.0
PCB 118	1.5 (n = 8)	0.36–3.9	0.64 (n = 10)	0.20–1.48	0.3 (n = 15)	0.1–1.6
PCB 138	2.2 (n = 8)	0.65–5	1.0 (n = 10)	0.32–2.7	0.4 (n = 19)	0.13–2.3
PCB 153	2.7 (n = 7)	0.74–6	0.90 (n = 10)	0.30–2.6	0.50 (n = 19)	0.17–2.5
PCB 180	0.81 (n = 8)	0.16–2.5	0.33 (n = 10)	0.1–1.3	0.37(n = 10)	0.08–1.3
Σ_{ICES} PCBs[b]	30	6–100	9	3.5–22	7	0.76–43
Σ_{29} PCBs[c]	83	22–250	30	10–85	21	3.3–130

[a]Air samples are measured in pg m^{-3}. Mean is calculated assuming D.L. PCB is polychlorinated biphenyl.
[b]Σ_{ICES} PCBs is the sum of PCB 28, 52, 90/101, 118, 138, 153, 180.
[c]Σ_{29} PCBs is the sum of PCBs 18, 22, 28, 31, 44, 49, 53, 70, 74, 87, 90/101, 95, 99, 105, 110, 118, 123, 138, 141, 149, 151, 153/132, 158, 170, 174, 180, 183, 187, 194, 199, and 203.

concentrations of the Σ_{29}PCBs ranged from 3.3 to 250 pg m^{-3} over the whole cruise with ca. 70% accounted for by Cl$_3$Bs and Cl$_4$Bs in all three regions. The Σ_{ICES}PCBs (28, 52, 90/101, 118, 138, 153, and 180 identified by the International Council for the Exploration of the Seas (ICES) as markers of the degree of contamination) ranged from 0.76 to 100 pg m^{-3} and contributed to $\sim$30–35% to Σ_{29}PCBs. Highest concentrations were determined for PCB 28, ranging from $\sim$1.3 to 50 pg m^{-3}; PCB 52 was present at concentrations ranging between 0.42 and 20 pg m^{-3}. PCB 101 was only detected in 14 samples and ranged from 0.55 to 12 pg m^{-3}. PCBs 118, 138, and 153 were below

Figure 2. Spatial distribution of Σ_{ICES} polychlorinated biphenyl (PCB) in air along the cruise (n = 37). Note that the bars center on the average sample location. Largest bar is 100 pg m^{-3} (site 2); smallest bar is 0.76 pg m^{-3} (site 31). Black arrows indicate general recent direction of the 72 h back trajectories for each sample.

3 pg m^{-3} in the North and the Norwegian Sea and below 1 pg m^{-3} in the Greenland Sea and the Arctic Ocean. PCB 180 was detected in $\sim$80% of the samples and concentrations averaged $\sim$0.8 pg m^{-3} in the Norwegian Sea, and $\sim$0.3 pg m^{-3} in the Greenland Sea and the Arctic Ocean.

[17] Figure 2 shows the spatial distribution of the Σ_{ICES}PCBs and air mass origin for each sample in the sampling region. Samples collected near the west coast of Norway and Svalbard had the highest concentrations, while samples collected in the middle of the Greenland Sea and the Arctic Ocean had the lowest, with the exception of 3 samples (17, 26, and 35). Sample 35 was collected at the northernmost location; its air mass trajectories originated partly over Russia. Samples 17 and 26 are oceanic samples; it is not clear why they had somewhat (2–3 times) higher concentrations than others taken nearby.

[18] There is clearly a decline in PCB concentration with increasing latitude (from the North and Norwegian Sea to the Arctic Ocean (Table 1 and Figure 2) and a decline in concentration with longitude (i.e., the concentrations decline from east to west across the transect). The eastern samples were influenced by movement from European source regions over previous days, receiving inputs from the continental air masses (air masses originated and traveled predominantly over land). Samples collected at the western part of the cruise transect represent clean oceanic air masses (air masses originated and traveled over the ocean) from the south or partly oceanic and partly continental from Greenland and Canada. This implies that during this campaign Europe was the major source of PCBs to the European Arctic region, but to the rest of the sampling campaign.

4.2. Seawater Concentrations

[19] Figure S1 and Tables S1–S2 show the mean sampling locations for seawater samples.[1] Individual [PCB]$_{diss}$ were below 1 pg L^{-1} (Table S2). [PCB]$_{diss}$ decreased with increasing degree of chlorination. Highest concentrations were determined for PCB 28/31, ranging from $\sim$0.2 to 0.4 pg L^{-1}; PCB 52 displayed concentrations from 0.1 to
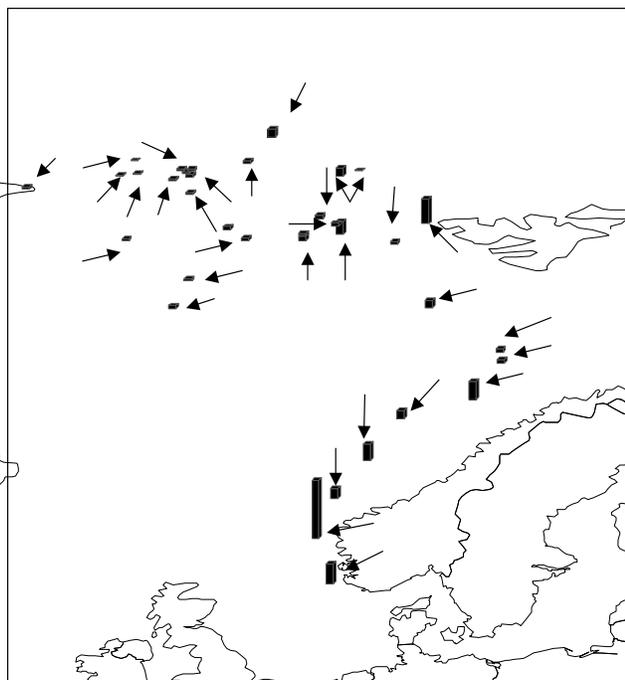

0.4 pg L^{-1}. PCBs 101, 118, and 138 occurred at dissolved concentrations < 0.1 pg L^{-1} in all samples. For PCB 28/31, highest concentrations occurred both in the southernmost (0.43 pg L^{-1}) and in the northernmost samples (0.36 pg L^{-1}). PCB 52 displayed highest concentrations in the northernmost samples, while PCBs 101, 118, and 138 tended to decline slightly with increasing latitude.

[20] Only PCBs 138 and 153 were detected in the particulate phase (Table S2). Highest particulate-associated concentrations of PCB 138 were obtained near Europe (0.2 pg L^{-1}), with the remaining samples being lower in concentration (<0.1 pg L^{-1}). For PCB 153, ∼50% of samples were below d.l. Highest concentrations were determined in the southernmost sample (0.4 pg L^{-1}), with the remaining samples displaying concentrations of <0.1 pg L^{-1}.

[21] [PCBs]$_{diss}$ were comparable to the few previous studies. *Sobek and Gustafsson* [2004] reported total (dissolved + particulate) concentrations of around 50–500 pg L^{-1} for PCBs 28 and 52, consistent with the results obtained here, and a slightly wider range and higher concentrations for PCBs 118 and 138.

[22] PCB data collected in the North Atlantic on a previous cruise on R/V *Polarstern* (ARK XVI in 1999) are presented, for comparison. PCB data from this cruise are presented for comparison in Table S2. PCBs 28/31 and 52 dominated at 0.1–0.7 pg L^{-1}.

5.   Discussion

5.1.   Comparison With Land-Based Measurements and Other Data Sets From the Arctic

[23] This study provides one of the first comprehensive data sets of PCBs in the European Arctic atmosphere over the open ocean. These compounds have been routinely measured at land-based sites in the Canadian Arctic since 1993, for the Northern Contaminants Program and in the European Arctic since 1991, under AMAP [*Hung et al.*, 2005] at Zeppelin mountain, Ny Ålesund, Svalbard (78°54′N, 11°53′E, 474 m above sea level). Σ_{ICES}PCBs ranged from 2.8 to 20 pg m^{-3} in samples collected at Zeppelin (cordially provided by the Norwegian Institute for Air Research, the Zeppelin monitoring program is funded by the Norwegian state pollution control authorities) during the cruise, in line with measurements made here over the Greenland Sea and the Arctic Ocean. BT analysis at the Zeppelin site showed that PCB concentrations are higher when air masses have traveled over European countries and lower when air masses have originated and traveled over ocean water and Canada.

[24] Similar PCB concentrations have also been measured at Amderma, Russia in 1999–2000 and Kinngait II in Canada in 2000–2001, where the sum of 10 PCB congeners (28, 31, 52, 101, 105, 118, 138, 153, 156, and 180 called the AMAP subset) was 4.0 and 3.3 pg m^{-3}, respectively [*Hung et al.*, 2005]. Data from 1999 at Alert, Canada and from 1994 at Dunai in Russia averaged 5.6 pg m^{-3} and 5.9 pg m^{-3}, respectively, in the same range as those reported in this study and those at Zeppelin station. However, annual means of PCBs (10 AMAP congeners) from 1995 and 1996 at Spitsbergen, Norway and Storhofdi, Iceland were 19 and 17 pg m^{-3}, respectively, 3–4 times higher than those reported in this study. These comparisons generally suggest

no clear temporal trend of PCBs in the Arctic atmosphere. This was also suggested by *Berg et al.* [2004], who did not find any evidence to support declining PCB concentrations in the Arctic region.

[25] PCBs in seawater have been measured on several studies into the Northern Atlantic and Arctic Ocean [*Schulz-Bull et al.*, 1988; *Sobek and Gustafsson*, 2004]. *Schulz-Bull et al.* [1988] determined PCBs at different depths in the North Atlantic in 1993. Their concentrations reflect the export flux of PCBs to 200 or 300 m depth, and are not comparable to the surface water concentrations determined in this study. In contrast, the studies by *Sobek and Gustafsson* [2004] and from ARKVI measured surface water concentrations in the northern oceans in 2001 and 1999, respectively. However, no clear time trend is apparent. For the samples close to Europe, dissolved PCB concentrations from this study were lower than those determined by *Sobek and Gustafsson* [2004] by about a factor of 2. However, similar concentrations were obtained in the samples north of 80°N. PCB concentrations on a previous R/V *Polarstern* cruise (ARKXVI) were either higher or comparable to concentrations reported here (Table S1). In view of the different analytical procedures used by the groups, and the difficulty of comparing results from different years and somewhat different locations, the agreement between these three measurements is encouraging. However, it does restrict speculation on any trends or their absence.

5.2.   Observations of Latitudinal Fractionation

[26] Changes in the relative abundance of PCB congeners in air were observed from Europe toward the Arctic. This fractionation is shown in Figure 3, where the relative abundance of each ICES congener over the total is plotted versus latitude and temperature. The relative abundance of PCB 28 and PCB 52 increases with increasing latitude (R^2 = 0.23, p = 0.007 and R^2 = 0.15, p < 0.01, respectively) and increases with decreasing temperature (R^2 = 0.24, p < 0.005 and R^2 = 0.11, p < 0.01). The heavier PCB congeners show the opposite trends with a decrease in their relative abundance with increasing latitude and with decreasing temperature.

[27] Distance from source regions and air/surface temperatures are confounding variables, which influence the mixture in air. However, such fractionation is consistent with diffusive primary sources controlling current ambient levels and LRAT being responsible for the delivery of PCBs to the Arctic region [*Meijer et al.*, 2003; *Jaward et al.*, 2004; *Gioia et al.*, 2006]; it is in line with congener-specific differences in atmospheric characteristic travel distances. If a mixture of congeners is assumed to be emitted together from a primary source region, the heaviest ones are predicted to be preferentially deposited close to the source area [*Wania and Mackay*, 1996]. Even though Figure 3 displays a slight PCB fractionation in air, only 15–20% of the variability of atmospheric PCBs can be explained by temperature and therefore by temperature-driven fractionation. Still, other fractionation processes may be occurring during transport.

[28] Clear changes in the relative abundance of the PCBs in seawater were seen (Figure S2). The contribution of PCB 28 stayed relatively constant from near Europe to the high Arctic, at ∼40–50% of Σ_6PCBs. In contrast, the contribu-
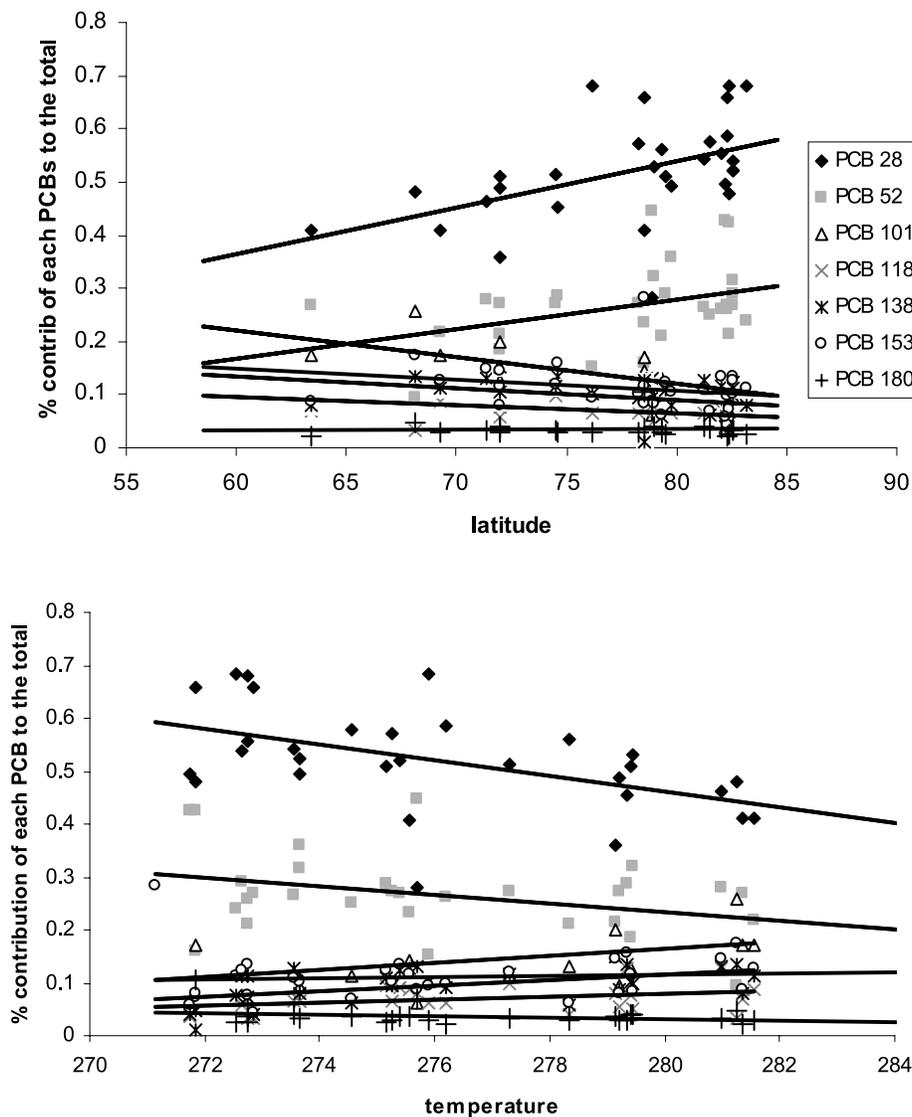
Figure 3. Percentage contribution of different International Council for the Exploration of the Seas PCB congeners in air samples versus latitude and temperature.

tion of PCB 52 increased from 60° to 84°N, from ~30% to almost 50%, while the contribution of PCBs 101, 118, and 138 decreased strongly. These results suggest evidence of the fractionation hypothesis, which predict increasing concentrations with latitude for the lower chlorinated congeners, and decreasing trends for PCBs containing four or more chlorines. The first two samples, taken close to Europe, were not consistent with the others, presumably because they were directly influenced by ongoing primary emissions from Europe.

[29] *Sobek and Gustafsson* [2004] reported a correlation of the relative increase of PCBs from near Europe to the high Arctic with compound subcooled liquid vapor pressure. PCBs with higher vapor pressures were relatively more abundant in the northernmost samples relative to less volatile congeners. A similar correlation was observed in this data set.

[30] Therefore, it seems clear that there is a fractionation of PCBs in seawater, but a decrease of highly chlorinated PCBs with increasing latitude could not only be due to a temperature driven process but also due to fractionation of water column PCBs due to selective transport to deeper waters of the more hydrophobic congeners associated to particulate matter.

5.3. Ice Cover as a Possible Influence

[31] Air samples taken from "ice free" and "ice covered" areas of the Arctic part of the cruise were compared and plotted against temperature. No difference between the sample subsets or in their correlations with temperature was found. This further suggests that the effect of temperature on the air concentration variability is subtle. A lack of difference between the sample subsets does not mean that snow/ice or the melting pack ice do not influence Arctic

air PCB concentrations. However, the effects were not measurable from this ice pack, or were not sufficiently strong/localized to exert a measurable effect on the air. PCBs in the Arctic atmosphere could potentially be influenced by volatilization of previously deposited compounds from ice/snow, or through an influence of meltwaters. Indeed, snow/ice have been shown to have a dynamic effect on PCBs deposited to them [*Herbert et al.*, 2005; *Burniston et al.*, 2007]. As the ice breaks up during the summer, direct exchange between air and the previously obscured surface seawater also recommences [*Daly and Wania*, 2004].

5.4. Water Column Biological Activity as a Possible Influence and Comments on Air-Water Equilibrium Status

[32] Processes in the water column, notably dissolved-particle phase partitioning, biological productivity, reactivity, and salting out can influence air-water exchange and hence air concentrations [*Dachs et al.*, 1999, 2002; *Scheringer et al.*, 2004].

[33] Knowledge of whether surface ocean waters are in equilibrium with the atmosphere, or the net direction of flux (i.e., whether absorption or volatilization dominates), is crucial for our understanding of the global cycling and fate of POPs [*Dachs et al.*, 2002]. Previous work suggests that enhanced sinking fluxes of PCBs occur in high productivity areas of high latitudes regions [*Dachs et al.*, 2002], leading to efficient removal of PCBs from the surface waters. Chlorophyll *a* data from 3-year climatological means (obtained from SeaWifs) and fluorescence data from the Ferry Box on the ship indicate an increase in primary productivity in the water column near the ice marginal zone (75°N to 79°N). For example, ice melting can induce blooms, which deplete dissolved phase PCBs, especially the more hydrophobic ones. If sinking fluxes are faster than air-water exchange fluxes, then the system will not be at equilibrium. The flux of gaseous contaminants between the atmosphere and the oceans is driven by concentration gradients and the transport by molecular and turbulent motion. However, this is a highly complex and difficult issue to address. There are large uncertainties in making such estimations [*Axelman et al.*, 2001; *Wania et al.*, 2001; *Bruhn et al.*, 2003]. Determination of the key physico-chemical parameters, notably the HLC required to make such an assessment, are subject to measurement difficulties and artifacts. Different methodologies have been used, which can be a source of variability in the reported data [*Bamford et al.*, 2002; *Li et al.*, 2003; *Goss et al.*, 2004; *Baker et al.*, 2004; *ten Hulsher et al.*, 2006].

5.4.1. Fugacity Quotient

[34] Fugacity quotients were calculated for paired measurements of air and water to evaluate the net direction of the air/sea gas exchange for ice free regions and for comparative purposes in ice covered regions. The fugacity in air (f$_{AIR}$) was calculated according to

$$f_{AIR} = \frac{C_{AIR}RT_{AIR}}{M} \qquad (1)$$

where C$_{AIR}$ is the gas phase concentration (g m^{-3}), R is the gas constant (8.314 m^3 Pa mol^{-1} K^{-1}), T$_A$ is the average air

temperature (K) and M is the molecular mass (g mol^{-1}). The fugacity in the water (f$_w$) was calculated as

$$f_W = \frac{C_W HLC}{M} \qquad (2)$$

where C$_W$ is the concentration of the compound in the dissolved phase (g m^{-3}), and HLC is in Pa m^3 mol^{-1}. Owing to the large uncertainties in reported HLCs for PCBs, the fugacity in the water was estimated, using data from three different sources, namely *Li et al.* [2003], *Bamford et al.* [2002], and *ten Hulsher et al.* [2006]. The HLC values were corrected for temperature and salinity, while the dissolved phase concentration was DOC corrected as reported elsewhere [*Totten et al.*, 2001]. Fugacity quotients are shown in Figure 4 (f$_{AIR}$/f$_W$) for four PCB congeners (28, 52, 118, and 138). PCB 101 is not shown because it was often not detected in air, while PCB 153 and 180 are not shown because they were not detected in the seawater. A quotient higher than 1 indicates a net downward flux (deposition, f$_{AIR}$ > f$_W$), and a quotient lower than 1 indicates net upward flux (volatilization, f$_W$ > f$_{AIR}$). An estimate of the errors around the fugacity quotient due to sampling and analytical error (±1 standard deviation) of air and water, ±10%, and the uncertainty associated with the HLC values, ±20%, is also shown in Figure 4. The propagated error for the calculation of the fugacity quotient is therefore believed to be ∼40%.

[35] The fugacity quotients of PCBs ranged from 5 to 440, using the different published values for the different congeners [*Bamford et al.*, 2002; *Li et al.*, 2003; *ten Hulsher et al.*, 2006] with the highest positive ratio from 75°N to 79°N. Variability in the quotients was rather high (see Figure 4), caused mostly by variability in air concentrations, as water concentrations were more homogeneous.

[36] Given the range of values and the associated uncertainties, the general picture that emerges is of net deposition particularly in the middle of the transect near the marginal ice zone (78°–79°N) for all the PCB congeners, where both ice and no ice cover are present. The increase in fugacity ratio and therefore the net deposition is mainly caused by relatively high air concentration in this region, which suggests very dynamic processes. Possible explanations for this could be as follows:

[37] 1. As noted earlier, ice aging and melting can be a source of PCBs to the atmosphere. *Daly and Wania* [2004] suggested that snow cover functions as a temporary storage reservoir that releases contaminants accumulated over the winter during a short melt period, resulting in temporarily elevated concentrations in air, water, and soil. The intensity of these peaks increases with the length of the snow accumulation period. Organic chemicals of sufficient volatility (log K$_{OA}$ < 9; e.g., light PCBs) can volatilize from the snowpack, resulting in summer time concentration maxima in the atmosphere. Figure S3 shows the fugacity ratios for each different PCB congeners correlated with salinity and temperature gradients. When both salinity and temperature decrease, higher fugacity ratios were observed, suggesting that ice melting may have induced higher atmospheric PCB levels. However, it should be noted that melting ice also can release nutrients and PCBs to the water column. Higher biological productivity in such regions would presumably
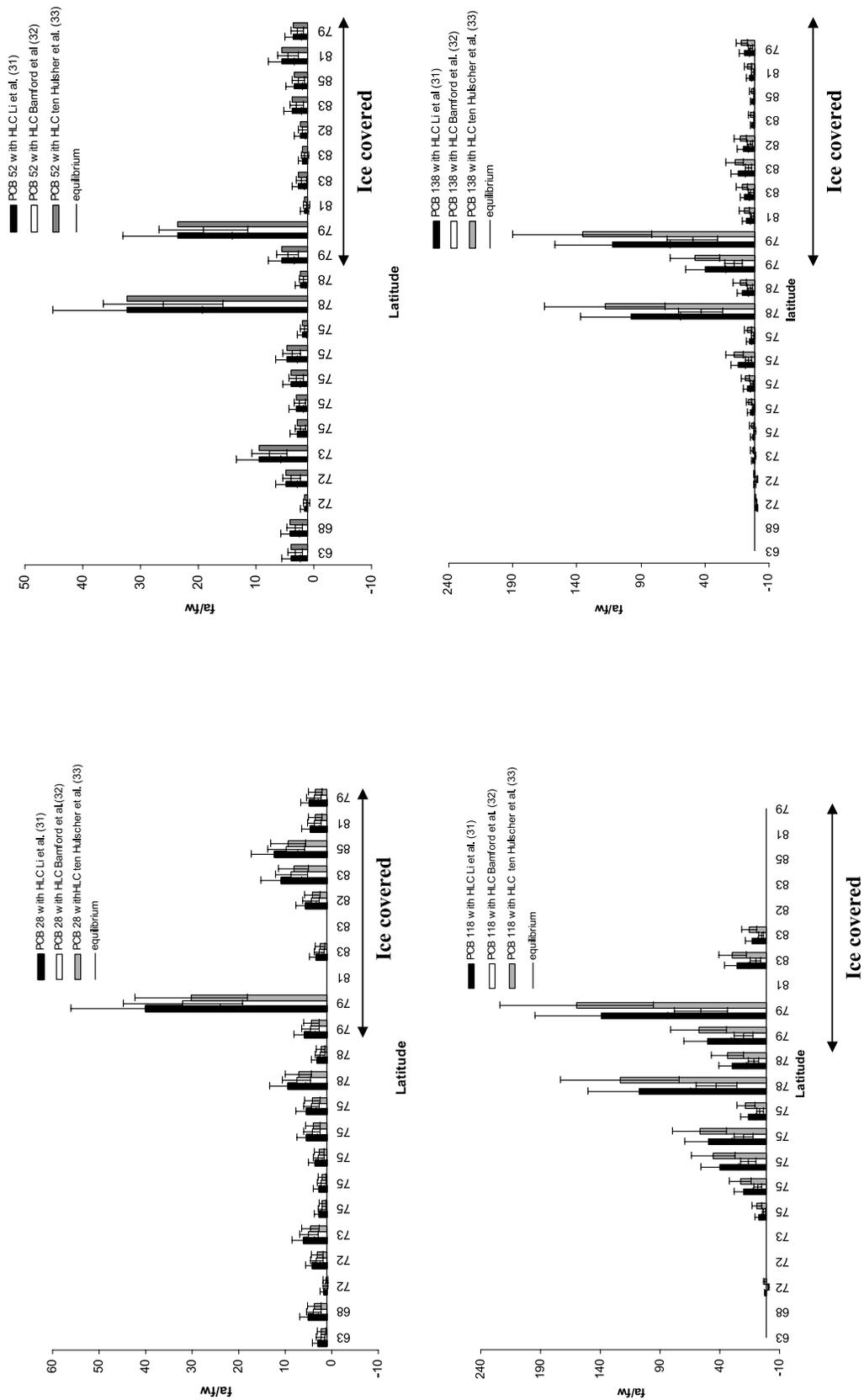
Figure 4. Fugacity fractions of four PCB congeners (28, 52, 118, and 1380 versus latitude. Henry's Law constants were taken from *Bamford et al.* [2002], *Li et al.* [2003], and *ten Hulsher et al.* [2006].

deplete the dissolved phase PCB concentrations and impact sinking fluxes and the relative rates of air-water exchange.

[38] 2. Most of the northernmost samples were taken under foggy conditions, and lower wind speeds. These factors may also have enhanced PCB air concentrations. Early work by *Capel et al.* [1990] showed enrichment of POPs on fog droplets. However, again there was no systematic evidence for an effect of fog when the data set is considered as a whole.

5.4.2. Air-Water Fluxes

[39] Gas exchange rates were calculated (as described in the Auxiliary Material) for the ice free only sites. A negative flux indicates that absorption dominates, while a positive flux indicates that volatilization dominates. The absorptive fluxes were typically more than 90% of the volatilization fluxes. Generally, the tri- and tetra-chlorinated PCBs dominated the flux profiles, accounting for more than 70% of the total estimated PCB fluxes. Total fluxes (defined as the sum of those for PCBs 28, 52, 118, and 138) depended on the HLC values selected. They ranged between -4 and 0.08 ng m^{-2} d^{-1} [*Li et al.*, 2003], -5.6 and 0.05 ng m^{-2} d^{-1} [*Bamford et al.*, 2002], and -6.3 and 0.1 ng m^{-2} d^{-1} [*ten Hulsher et al.*, 2006]. There are very few studies reporting air-water exchange fluxes over the ocean. *Iwata et al.* [1993] reported a Σ_{36}PCBs adsorptive net flux of ~-60 ng m^{-2} d^{-1} in the North Atlantic, ~-100 ng m^{-2} d^{-1} in the Bering Sea, and 80 ng m^{-2} d^{-1} (around $2-3$ times higher than those derived here), based on measurements made in the late 1980s/early 1990s.

6. Conclusions

[40] Concentrations of gaseous PCBs showed no temperature dependency, indicating that PCBs in air and water were neither at nor "near" equilibrium conditions across the region. Furthermore, the calculated fugacity ratios (f_A/f_W) indicate that net deposition was dominating in all the Arctic region. A higher net deposition of PCBs was observed near the marginal ice zone, where PCB air concentrations tended to be higher. However, uncertainties remain over whether this was because melting ice margins were a source of PCBs to the atmosphere or whether more complex ice-water-atmosphere interactions were occurring (e.g., coupled to phytoplankton activity). Current knowledge of contaminant levels in sea ice and the interactions between the ice water and the atmosphere is still sparse and raises major uncertainties over seasonal and longer-term PCBs dynamics in the Arctic.

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