



RESEARCH ARTICLE

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Persistent organic pollutants in ocean sediments from the North Pacific to the Arctic Ocean

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Key Points:

- Bering-Chukchi shelf sediments are an important regional sink for POPs
- Different chemical concentrations between shallow and deeper ocean regions
- Substantial chemical processing between surface waters and benthic sediments

Supporting Information:

- Supporting Information S1

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Abstract Concentrations of polychlorinated biphenyls (PCBs), organochlorine pesticides (OC pesticides), and polybrominated diphenyl ethers (PBDEs) are reported in surficial sediments sampled along cruise transects from the Bering Sea to the central Arctic Ocean. OCs and PCBs all had significantly higher concentrations in the relatively shallow water (<500 m depth) of the Bering-Chukchi shelf areas (e.g., Σ PCB 286 ± 265 pg g^{-1} dw) compared to the deeper water regions (>500 m) of the Bering Sea and Arctic Ocean (e.g., Canada Basin Σ PCB 149 ± 102 pg g^{-1} dw). Concentrations were similar to, or slightly lower than, studies from the 1990s, indicating a lack of a declining trend. PBDEs (excluding BDE-209) displayed very low concentrations (e.g., range of median values, 3.5–6.6 pg/g dw). In the shelf areas, the sediments comprised similar proportions of silt and clay, whereas the deep basin sediments were dominated by clay, with a lower total organic carbon (TOC) content. While significant positive correlations were observed between persistent organic pollutant (POP) concentrations and TOC (Pearson correlation, $r = 0.66$ – 0.75 , $p < 0.05$), the lack of strong correlations, combined with differing chemical profiles between the sediments and technical formulations (and/or marine surface waters), indicate substantial chemical processing during transfer to the benthic environment. Marked differences in sedimentation rates between the shallow and deeper water regions are apparent (the ~ 5 cm-depth grab samples collected here representing ~ 100 years of accumulation for the shelf sediments and ~ 1000 years for the deeper ocean regions), which may bias any comparisons. Nonetheless, the sediments of the shallower coastal arctic seas appear to serve as significant repositories for POPs deposited from surface waters.

1. Introduction

Persistent organic pollutants are globally distributed chemicals that are present in the Polar Regions and remote ocean environments [MacDonald *et al.*, 2000]. The chemicals possess physical-chemical properties that allow them to reside in a variety of environmental compartments (air, water, soil, and sediments) where they can enter and accumulate in marine and terrestrial foodwebs [Lohmann *et al.*, 2007]. Chemicals such as organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and, to a lesser extent, polybrominated diphenyl ethers (PBDEs) have been widely reported in the global environment over the last few decades and are included in the UNEP Stockholm Convention on POPs (<http://chm.pops.int/>). For legacy chemicals, like PCBs, questions arise regarding their long-term fate as they continue to cycle between environmental media with evidence now showing a gradual reduction in concentrations in both air and biota from remote locations [Hung *et al.*, 2010; Riget *et al.*, 2010].

The long-term global sinks for these chemicals are considered to comprise (i) soils, particularly those at relatively high latitudes which are rich in organic matter [Dalla Valle *et al.*, 2005]; (ii) photooxidation in the atmosphere [Brubaker and Hites, 1998]; and (iii) transfer to the ocean environment and burial in benthic sediments [Dachs *et al.*, 2002]. For (iii), there are relatively few studies that have measured concentrations in deep ocean waters or bottom sediments [Iwata *et al.*, 1994; Schulz-Bull *et al.*, 1998], although processes for transferring POPs from surface to deep waters are varied and include subduction of surface ocean currents via the thermohaline circulation [Lohmann *et al.*, 2006], the transfer of sediments in coastal regions to continental shelf areas [Jonsson *et al.*, 2003], and particle settling from well-mixed surface waters [Dachs *et al.*, 1999; Dachs *et al.*, 2002]. For remote pelagic environments like the North Pacific, North Atlantic, and Arctic

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Oceans, particle settling could be a significant removal process for hydrophobic chemicals (i.e., those possessing high K_{ow} values) and, in part, could be driven by the settling fluxes of particle organic carbon associated with primary production by phytoplankton (i.e., the 'biological pump') [Galban-Malagon *et al.*, 2012].

Examining the presence of POPs in the deep ocean environment will therefore help to understand important sinks for these chemicals and aid hemispheric/global mass balances now that chemical production for some chemicals (e.g., PCBs) has effectively ceased. Recent work in a trans Arctic Ocean assessment has revealed only a very small fraction of the global inventory of PCBs reside in surface ocean media across the Arctic [Carrizo and Gustafsson, 2011]. This indicates that the majority of PCBs reside closer to source regions and/or intra-Arctic transfer processes are efficient at removing chemicals from surface media to other sinks such as the deep ocean environment [Sobek and Gustafsson, 2014]. To examine this further, this study presents the results of ocean sediment measurements conducted on a ship-based transect from the North Pacific to the central Arctic Ocean (via the Bering Strait). The aim was to examine spatial variations in sediment-bound concentrations, comparing different regions as well as deep ocean versus shallow water sites, and to explore the influence of sediment properties on chemical concentrations and composition.

2. Experimental Section

2.1. Sampling Cruise

Marine sediment samples were collected onboard the ice-breaker R/V *Xuelong* (*Snow Dragon*) during two Chinese National Arctic Research Expeditions. Specifically, 0–5 cm sediment samples were collected during the 4th Arctic expedition between July and September 2010 (CHINARE 4). The sampling stations roughly follow a latitudinal northward transect across the Bering Sea through Bering Strait and cover both the Chukchi Sea and Canadian Basin (53–88°N). In addition, 0–2 cm sediment samples were collected during the 5th Arctic expedition between July and September 2012 (CHINARE 5). The samples were taken from the Bering Sea across the Bering Strait to the Chukchi Sea, and then through the Northeast Passage to the Amundsen Basin and directly to Iceland (54–88°N). In these two cruises, marine sediments were collected with a stainless steel grab sampler and scooped using a precleaned stainless steel scoop and placed into baked and solvent-rinsed aluminum containers. All samples were stored at -20°C until further analysis.

2.2. Sample Preparation and Cleanup

The CHINARE 4 cruise samples were freeze-dried, and then gently ground and homogenized. Five method blanks of an artificial sediment matrix each consisting of a mixture of 9 g sodium sulfate and 1 g C_8 resin were made, and treated/handled in the same way as the samples. The CHINARE 5 cruise samples were dried by Buchner filtration before the sediment was ground and homogenized. 15 g of the dried sediment (samples for both CHINARE 4 & 5) together with sodium sulfate was Soxhlet extracted in dichloromethane (DCM) for 16 h; immediately prior to extraction, the sediment was spiked with a recovery standard containing ^{13}C -labeled PCBs 28, 52, 101, 138, 153, 180 and 209 and BDEs 51, 128, and 190. A two-step cleanup was then employed to purify the extract; firstly the extract was applied to a 23 mm id chromatography column containing 15 g acidified silica (2:1 w/w silica: sulfuric acid) and eluted with 200 mL of *n*-hexane; second the eluent was reduced to ~ 1 mL under N_2 and subjected to gel permeation chromatography (GPC) (6 g bio-beads). The column was eluted with a 1:1 v/v mixture of DCM and *n*-hexane—the first 16 mL was discarded as waste and a following 35 mL fraction was collected and further reduced under N_2 into 25 μL of *n*-dodecane keeper containing the following internal standards: PCB-30, ^{13}C -labeled PCB-141, ^{13}C -labeled PCB-208 and PBDE-69 and 181. In addition to the five method blanks, five procedural blanks (per cruise batch) each consisting of a Soxhlet thimble containing only sodium sulfate were subject to the same clean-up and concentration steps and analyzed alongside the sediment samples.

2.3. Chemical Analysis

The samples were analyzed on Thermo "Trace" GC-MS, fitted with a Tri-Plus autosampler and analytes separated on a 50 m 0.25 μm id Varian CP-SIL8 CB Pesticide column. Specific analytes included hexachlorobenzene (HCB), *cis*-chlordane, *trans*-chlordane, DDT (*o*, *p'*-DDT and *p*, *p'*-DDT), DDT metabolites DDE (*o*, *p'*-DDE and *p*, *p'*-DDE) and DDD (*o*, *p'*-DDD and *p*, *p'*-DDD), PCBs (18, 22, 28, 31, 30, 41, 44, 49, 52, 54, 56, 60, 64, 70, 74, 87, 90, 101, 95, 99, 104, 105, 110, 114, 118, 123, 132, 138, 141, 149, 151, 154, 155, 156, 157, 158, 167, 170, 174, 180, 183, 187, 188, 189, 194, 199, 203), and PBDEs (17, 28, 32, 35, 37, 47, 49, 51, 66, 71, 75, 77, 85, 99,

100, 118, 119, 126, 128, 138, 153, 154, 166, 181, 183, 190, 196, 197). All nonlabeled PCB and OC standards were purchased from Wellington Laboratories Inc., Guelph Ontario and all ^{13}C -labeled and PBDE standards were purchased from Cambridge Isotope Laboratories, Andover, Massachusetts, except for BDEs 51 and 128 which were obtained from AccuStandard Inc, New Haven, Connecticut.

2.4. QA/QC

Glassware and sodium sulfate was baked for 5 h at 450°C, and glassware subsequently rinsed (3×) with *n*-hexane, DCM, and acetone prior to use. All solvents were HPLC grade. Method detection limits (MDLs) were derived based on the presence of the analytes in the method blanks, where the MDL is defined as the mean concentration in the blank plus 3*standard deviation. For analytes not quantified in the blanks, then the MDL was simply the instrumental detection limit expressed as a concentration for the mass of sediment extracted (15 g). The MDLs were 1.66 pg/g for PCBs, 3.33 pg/g for OCs, and 4 pg/g for PBDEs. To ensure instrument precision, a quality control (QC) standard consisting of a mixture of tri to octa-PCBs and PBDEs within the calibration ranges of 1–100 pg/μL for PCBs and 2.5–250 pg/μL for PBDEs were run alongside each batch of 10 samples with an acceptable precision of ±10%. Mean recoveries ranged between 75–105% for PCBs/OCs and 60–90% for PBDEs.

2.5. Carbon Content

Each sediment sample (5 g) was extracted in 35 mL deionized water on an orbital shaker for 24 h before filtration through 11 μm-pore Whatman filter paper. Extracts were measured for total organic carbon (TOC) content using a Shimadzu 5000A TOC Analyser (Shimadzu Europa GmbH, Duisburg, Germany) fitted with an infra-red analyser to measure CO_2 . Total carbon (TC) was determined by injecting sediment extracts onto a combustion tube filled with oxidation catalyst heated to 650°C and combusted to CO_2 , whereas inorganic carbon (IC) was converted to CO_2 by reaction with phosphoric acid. TC and IC were measured against a calibration curve of 0–10 ppm or 0–100 ppm TC and IC standards, respectively, in a linear range. TOC was calculated by subtracting IC from TC for each sample.

2.6. Particle Size Analysis

Dried sediments were sieved to <2 mm and lightly ground to remove aggregates. The sediments were then coned and quartered to obtain a representative sample; 3 g of sediment was digested in 35% hydrogen peroxide for 48 h and every 10th sample was repeated in triplicate to assess method precision. Sediments were then analyzed for particle size on a Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK) fitted with a Hydro 2000MU dispersion unit (Malvern Instruments Ltd, Worcestershire, UK) with a 800 mL sample volume containing 2.5 %/20% w:v sodium hexametaphosphate as a surfactant, with every 10th sample measured in triplicate.

3. Results and Discussion

3.1. Geographic Distribution of POPs

To assess the spatial distribution of the contaminants, then the sampling sites were separated into six geographical areas: Bering Sea, Bering Strait, Chukchi Sea, Canadian Basin, Amundsen Basin, and Iceland stations, with a summary of the chemical concentrations for the combined CHINARE 4 and CHINARE 5 campaigns presented in Table 1. The spatial distribution of HCB along the cruise tracks is shown in supporting information Figure S1a. HCB concentrations in the marine sediment ranged from <MDL to 97.2 pg g⁻¹ dry weight (dw), with an average of 18.5 ± 22.2 pg g⁻¹ dw. Analysis of variance (ANOVA) demonstrated significant differences in the mean concentrations in the six geographical regions. Generally, higher HCB concentrations were found in the Chukchi Sea and Bering Strait, with a mean of 37.5 ± 17.3 pg g⁻¹ dw and 28.3 ± 27.4 pg g⁻¹ dw, respectively. The highest HCB levels were observed at site BM04 in the Bering Strait (97.2 pg g⁻¹ dw) and site SR10 in the Chukchi Sea (78.2 pg g⁻¹ dw) during the two expeditions. However, HCB was not observed, or was present at extremely low levels in the deeper ocean sediments of the Pacific-Arctic sector, such as the Bering Sea and Canadian Basin, where average concentrations were generally below the method detection limits. The HCB concentrations in the Bering Strait and Chukchi Sea shelf are comparable to those observed during 1990 and 1993 in the same region [Iwata *et al.*, 1994; Strachan *et al.*, 2001]. Similarly concentrations in the Canada and Amundsen Basins are akin to those previously measured in the Beaufort Sea [Hargrave *et al.*, 1989], although concentrations in the Bering Sea of our study were

Table 1. Summary of OCs, PCBs, and PBDEs Concentrations (pg g d.w.) in the Surface Sediment of the Bering Sea, Bering Strait, Chukchi Sea, Canadian Basin, Amundsen Basin and Iceland Stations for Both CHINARE 4 and CHINARE 5 Expeditions^a

	Bering Sea Range	Median	Mean	Bering Strait Range	Median	Mean	Chukchi Sea Range	Median	Mean
HCB	ND-2.7	ND	ND	5.4-97.2	19.6	28.3	13.6-78.2	34.0	37.5
cis-Chlordane	ND	ND	ND	2.4-27.0	4.0	7.5	2.8-17.5	4.9	6.3
trans-Chlordane	ND	ND	ND	ND-11.3	2.6	3.0	ND-7.0	ND	ND
ΣDDTs	0.1-89.0	16.5	24.4	ND-115.9	29.8	46.9	6.5-84.0	59.0	53.3
tri-PCBs	ND-27.6	5.5	7.9	ND-173.2	16.2	44.8	ND-204.8	41.7	57.3
tetra-PCBs	ND-41.2	18.0	18.0	ND-232.3	37.2	67.8	ND-361.2	78.2	96.8
penta-PCBs	ND-43.1	14.2	15.4	ND-229.0	27.4	60.9	ND-373.0	50.3	90.7
hexa-PCBs	ND-18.9	ND	3.8	ND-66.5	3.8	17.3	ND-91.6	17.3	27.4
hepta-PCBs	ND-6.8	4.2	3.8	2.1-19.2	7.1	8.9	ND-39.4	10.2	13.1
octa-PCBs	ND-2.9	ND	ND	ND-1.4	ND	ND	ND-4.2	ND	ND
ΣPCBs	5.4-87.7	57.3	49.9	2.1-708.1	139.8	199.8	9.8-1005.0	222.6	285.8
tri-BDEs	ND-3.7	ND	ND	ND-6.4	ND	ND	ND-4.9	ND	ND
tetra-BDEs	ND-2.9	ND	ND	ND-11.9	ND	ND	ND-6.7	ND	ND
penta-BDEs	ND-8.0	ND	ND	ND-4.7	ND	ND	ND-9.6	ND	ND
hexa-BDEs	ND-10.2	ND	ND	ND-6.5	ND	ND	ND-36.2	ND	ND
hepta-BDEs	ND-7.7	ND	ND	ND-5.0	ND	ND	ND-11.8	ND	ND
octa-BDEs	ND	ND	ND	ND-13.4	ND	ND	ND-10.4	ND	ND
ΣBDEs	0.3-26.0			ND-29.8			ND-67.8		
	Canada Basin Range	Median	Mean	Iceland Stations Range	Median	Mean	Amundsen Basin		
HCB	ND-6.8	ND	ND	5.5-10.0	8.0	7.8	11.6		
cis-Chlordane	ND	ND	ND	ND-0.6	ND	ND	ND		
trans-Chlordane	ND	ND	ND	ND	ND	ND	ND		
ΣDDTs	0.5-39.5	13.5	16.0	11.7-98.1	19.4	43.1	13.9		
tri-PCBs	1.1-52.4	15.2	20.4	ND-59.7	6.8	22.2	ND		
tetra-PCBs	5.9-243.4	32.8	68.3	ND-73.2	24.5	32.6	ND		
penta-PCBs	8.2-101.1	17.3	30.3	ND-62.8	38.7	33.8	ND		
hexa-PCBs	2.0-108.4	7.2	22.8	ND-2.1	ND	ND	ND		
hepta-PCBs	ND-17.0	5.7	7.1	7.1-11.4	9.4	9.3	12.7		
octa-PCBs	ND-2.6	ND	ND	ND	ND	ND	ND		
ΣPCBs	23.7-329.8	127.9	149.1	13.5-202.8	79.4	98.6	12.7		
tri-BDEs	ND-3.0	ND	ND	ND-2.9	ND	ND	ND		
tetra-BDEs	ND-5.8	ND	ND	ND-4.8	ND	ND	ND		
penta-BDEs	ND-11.7	ND	ND	ND-4.5	ND	ND	ND		
hexa-BDEs	ND-8.6	ND	ND	ND-4.3	ND	ND	ND		
hepta-BDEs	ND-14.2	ND	ND	ND	ND	ND	ND		
octa-BDEs	ND	ND	ND	ND	ND	ND	ND		
ΣBDEs	ND-33.3			ND-9.1					

^aND = not detected or below method detection limits. Mean/medians also reported as 'ND' if majority of samples were on or below method detection limits

significantly lower than those reported in 1993 [Strachan *et al.*, 2001]. Table 2 provides contaminant concentrations in sediments from a number of studies around the Arctic, including an earlier investigation in the Mediterranean Sea. Importantly, data from the earlier CHINARE 3 campaign [Hong *et al.*, 2012] are included for comparative purposes.

Concentrations of chlordane in the sediments were relatively lower compared to HCB, with supporting information Figure S1b presenting the spatial distribution of both *cis*-chlordane (CC) and *trans*-chlordane (TC) isomers. Concentrations of $3.6 \pm 5.3 \text{ pg g}^{-1} \text{ dw}$ (<MDL-27.0 $\text{pg g}^{-1} \text{ dw}$) and $3.3 \pm 2.3 \text{ pg g}^{-1} \text{ dw}$ (<MDL-11.3 $\text{pg g}^{-1} \text{ dw}$) for CC and TC, respectively, were observed along the two cruises. Specifically, in the Pacific-Arctic sector, both of the isomers were only detected in the sediments of the Bering Strait and Chukchi Sea, with the highest concentration observed at site BB06 in the Bering Strait (CC: 27.0 $\text{pg g}^{-1} \text{ dw}$, TC: 11.3 $\text{pg g}^{-1} \text{ dw}$). Both CC and TC were below detection limits in the Bering Sea and Canadian Basin, the Amundsen Basin and the Icelandic stations during the expedition of 2012.

Chlordane isomers have been measured at relatively low concentrations in the surface seawater of the Bering Sea, Chukchi Sea, and Canadian Arctic archipelago, ranging from ND to 4 pg L^{-1} during the studies conducted in the 1990s [Hargrave *et al.*, 1997; Iwata *et al.*, 1993; Jantunen and Bidleman, 1998]. While for HCB the concentrations observed in surface seawater of the same region averaged $\sim 15 \text{ pg L}^{-1}$ [Hargrave *et al.*, 1997; Strachan *et al.*, 2001] and these differences may account for the relatively lower concentrations of the chlordanes observed in the marine sediments along the cruise tracks of this study.

Table 2. Comparison of POPs Concentrations in Marine Sediments (pg/g d.w.)

Study Region (year)	HCB	ΣChlor ^a	ΣDDTs	ΣPCBs	Number of PCB Congeners Reference
Kara Sea Area		ND	440 ± 300 ^b	410 ± 340	55 <i>Sericano et al.</i> [2001]
Mediterranean (Gulf of Lion)	39–85		47–890 ^c	800–1000	<i>Burns and Villeneuve</i> [1987]
Beaufort Sea	17				<i>Hargrave et al.</i> [1989]
Hudson Bay, Canada				40–150	<i>Kuzyk et al.</i> [2010]
Bering Sea (Bristol Bay) (1990)	42		70 ^c	240	36 <i>Iwata et al.</i> [1994]
Gulf of Alaska (1990)	67–79	40	92–170 ^c	470–2000	36 <i>Iwata et al.</i> [1994]
Bering Strait (1990)	61	7.5	6.4 ^c	130	36 <i>Iwata et al.</i> [1994]
Chukchi Sea (1990)	35	9.3	8.6 ^c	140	36 <i>Iwata et al.</i> [1994]
Bering Sea (1993)	100				<i>Strachen et al.</i> [2001]
Bering Strait (1993)	40–80				<i>Strachen et al.</i> [2001]
Chukchi Sea (1993)	130				<i>Strachen et al.</i> [2001]
Bering Sea (2008)				22–150 (71) ^d	14 <i>Hong et al.</i> [2012]
Chukchi Sea (2008)				60–640 (190)	14 <i>Hong et al.</i> [2012]
Canadian Basin (2008)				24–600 (150)	14 <i>Hong et al.</i> [2012]
Bering Sea (2010)	ND	ND	16–89 ^b	56–88 (66)	46 this study
Bering Sea (2012)	ND	ND	ND–5 ^b	5–32 (19)	46 this study
Bering Strait (2010)	5–54	6–38	28–81 ^b	75–219 (166)	46 this study
Bering Strait (2012)	12–97	2–21	0.6–116 ^b	2–708 (214)	46 this study
Chukchi Sea (2010)	19–78	5–25	52–84 ^b	124–1005 (387)	46 this study
Chukchi Sea (2012)	14–52	3–7	7–83 ^b	10–357 (185)	46 this study
Canadian Basin (2010)	ND–7	ND	0.5–40 ^b	24–330 (149)	46 this study
Amundsen Basin (2012)	12	2	14 ^b	13	46 this study
Iceland Station (2012)	5–10	ND–3	12–98 ^b	14–203 (99)	46 this study

^aSum of cis- and trans-chlordane.

^bSum of o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT and p,p'-DDT.

^cSum of p,p'-DDD, p,p'-DDE and p,p'-DDT.

^ddata in the bracket is the average value.

Total DDT residues, including *p,p'* and *o,p'*-isomers of DDT, DDE, and DDD, were in the range of ND–116 pg g⁻¹ dw and with an average of 36.7 ± 33.2 pg g⁻¹ dw. For the different geographical regions, the ΣDDT concentrations were in the following order: Chukchi Sea (53.3 ± 24.3 pg g⁻¹ dw) > Bering Strait (46.9 ± 43.8 pg g⁻¹ dw) > Iceland (43.1 ± 47.8 pg g⁻¹ dw) > Bering Sea (24.4 ± 32.6 pg g⁻¹ dw) > Canada Basin (16.0 ± 11.9 pg g⁻¹ dw) > Amundsen Basin (13.9 pg g⁻¹ dw), with the spatial distribution presented in Figure 1 (CHINARE 4) and supporting information Figure S1d (CHINARE 5). Notably high levels of DDTs were observed at stations BM01 (116 pg g⁻¹ dw) and BS02 (112 pg g⁻¹ dw) in the Bering Strait during the CHINARE 5 expedition as well as Station B06 in the Bering Sea (89.0 pg g⁻¹ dw) and Station IS-3 near Iceland (107.8 pg g⁻¹ dw).

PCBs were detected in all of the marine sediments collected as part of the CHINARE 4 and CHINARE 5 expeditions and displayed in Figure 1 and supporting information Figure S1e. The highest average Σ₄₆PCBs (sum of the 46 detected PCB congeners) concentrations were observed in Chukchi Sea (286 ± 265 pg g⁻¹ dw) and Bering Strait (200 ± 246 pg g⁻¹ dw), followed by sample stations in the Canadian Basin (149 ± 102 pg g⁻¹ dw) and around Iceland (98.6 ± 96.1 pg g⁻¹ dw), while the Bering Sea (49.9 ± 28.1 pg g⁻¹ dw) and Amundsen Basin (12.7 pg g⁻¹ dw) had the lowest average concentrations. In the Pacific-Arctic ocean sector, high Σ₄₆PCBs concentrations were observed at sites R06 (1005 pg g⁻¹ dw) and SR12 (639 pg g⁻¹ dw) in the Chukchi Sea during the cruise of CHINARE 4, with high Σ₄₆PCBs concentrations at sites BS02 (708 pg g⁻¹ dw) and BM01 (550 pg g⁻¹ dw) in the Bering Strait during the cruise of CHINARE 5. PCB levels in the Atlantic-Arctic ocean sector were markedly lower than the Pacific sector for broadly the same latitudes. Compared with previous studies, PCBs in the Bering Strait and Chukchi Sea were a little higher than those observed in the 1990s, while the concentrations in the central Bering Sea were lower than those measured at Bristol Bay and the Gulf of Alaska [Iwata et al., 1994]. PCBs in the sediments of the Canadian Basin were comparable to those in the Kara Sea (Russia Arctic) [Sericano et al., 2001] (see Table 2). The PCB concentrations measured in this study fall into the same ranges as those measured recently in the Bering Sea, Chukchi Sea, and Canada Basin during the CHINARE 3 cruise in 2008 [see Hong et al., 2012] as well as those observed by Kuzyk et al. [2010] in Hudson Bay, Canada.

The concentrations of PBDEs in the marine sediments were low. The Σ₂₄PBDEs (sum of the 24 detected PBDE congeners) varied from <MDL to 67.8 pg g⁻¹ dw, with an average of 9.8 ± 11.9 pg g⁻¹ dw along the

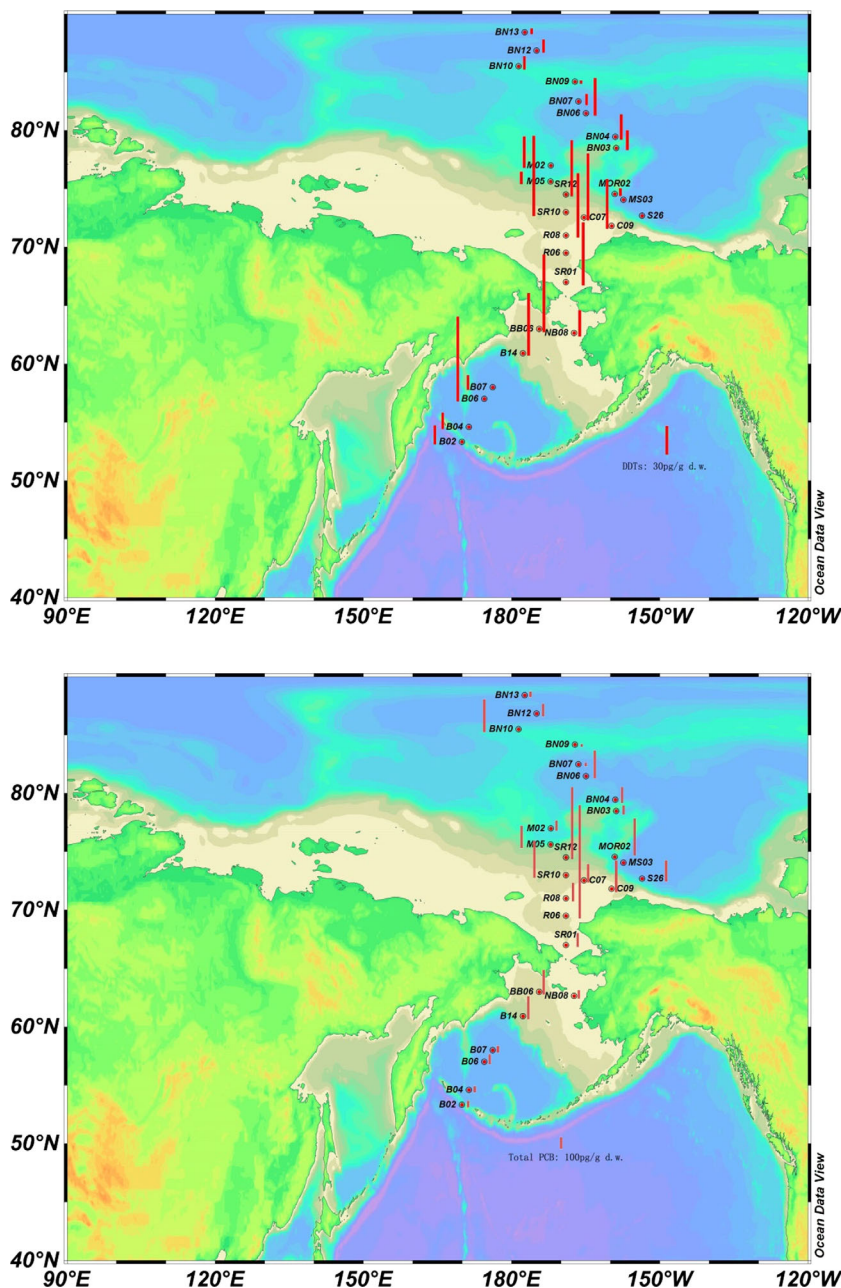


Figure 1. Concentrations of DDTs, Σ₄₆PCBs, and Σ₂₄PBDEs in the surface marine sediment along the sampling cruise of CHINARE 4.

two cruises. Only one very high concentration was observed at Station SR12 located toward the edge of the continental shelf of the Chukchi Sea ($67.8 \text{ pg g}^{-1} \text{ dw}$) during CHINARE 4, although this value is well within the range of ΣPBDE (without BDE-209) concentrations measured in the Canada Basin sediments during CHINARE 3 [Cai *et al.*, 2012]. The PBDE levels did not exhibit large geographical differences between the Bering Sea, Bering Strait, Chukchi Sea, Canadian Basin, and Iceland Stations (supporting information Figure S2), with arithmetic averages of $7.7 \pm 9.5 \text{ pg g}^{-1} \text{ dw}$, $7.9 \pm 10.0 \text{ pg g}^{-1} \text{ dw}$, $12.6 \pm 16.6 \text{ pg g}^{-1} \text{ dw}$, $10.7 \pm 10.5 \text{ pg g}^{-1} \text{ dw}$, $7.1 \pm 1.8 \text{ pg g}^{-1} \text{ dw}$, respectively. Generally, PBDEs in the present study were lower than those detected in the marine sediments in temperate latitudes of the Pacific region [Mai *et al.*, 2005; Moon *et al.*, 2007; Wang *et al.*, 2009] and also relatively lower than other marine and freshwater sediment of the Norwegian and Canadian Arctic [Evenset *et al.*, 2007; Jiao *et al.*, 2009; Stern *et al.*, 2005]. In comparison to the earlier

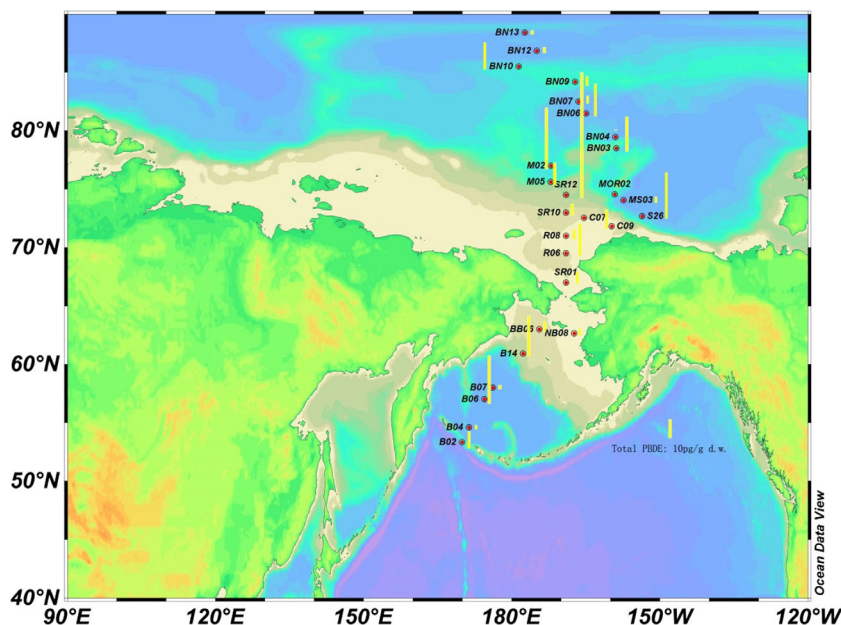


Figure 1. (continued)

CHINARE 3 campaign [Cai *et al.*, 2012] which broadly followed the same cruise track as this study (i.e., CHINARE 4 and 5), the PBDE (excluding BDE-209) concentrations show a reduction from 2008 to 2012, specifically for the Bering Sea, Bering Strait, and Chukchi Sea regions. However, given the intersite variability within this study and the differences in analytical techniques between this study and that of Cai *et al.*, then this temporal trend is unlikely to be significant. Nonetheless, there is some evidence that tissue concentrations for a range of Arctic biota for the lower brominated PBDEs have declined between the mid to the late-2000s in the western Canadian Arctic [see *de Wit et al.*, 2010].

3.2. Variation in Sediment Concentrations With Depth

Clear differences were evident between samples grouped as shallow water sites (<500 m) to those grouped as deep water sites (>500 m). Shallow water areas included all sites located on the continental shelf areas of the Bering Strait and Chukchi Sea as well as Site IS-3 near Iceland. Figure 2 illustrates the shallow versus deep sediment concentrations for the various contaminants. For example, the average HCB concentration in shallow water sediments was $32.5 \pm 22.3 \text{ pg g}^{-1} \text{ dw}$, which was significantly higher ($p < 0.05$) than deep water sediments, with an average of $3.5 \pm 3.6 \text{ pg g}^{-1} \text{ dw}$. Similarly, chlordane in shallow water sediments displayed higher average concentrations of 6.7 ± 5.7 (CC) and 2.5 ± 2.7 (TC) $\text{pg g}^{-1} \text{ dw}$, with very low concentrations in the sediment of the deep water regions that in the main were below detectable concentrations. While concentrations of DDTs in the sediment of shallow waters (mean of $53 \pm 35 \text{ pg g}^{-1} \text{ dw}$) were higher than those observed in deep waters (mean of $18 \pm 19 \text{ pg g}^{-1} \text{ dw}$), although the difference is not as marked as HCB and the chlordanes. For PCBs, concentrations in the shallow water areas (mean of $248 \pm 250 \text{ pg g}^{-1} \text{ dw}$) were nearly twice as high as those in the deep water regions (mean of $104 \pm 94 \text{ pg g}^{-1} \text{ dw}$). However, little variation was seen in PBDE concentrations relating to the depth of water, with $10.5 \text{ pg g}^{-1} \text{ dw}$ and $9.1 \text{ pg g}^{-1} \text{ dw}$ shown in the sediment of shallow and deep water regions, respectively. It should be noted that different sedimentation rates in shallow and deep regions will contribute to the variation in sediment POP concentrations with depth and this is examined further in section 3.4.

3.3. Source Markers

In the marine sediments, the ratio of TC/CC averaged 0.43 ± 0.19 (i.e., reflecting a greater contribution of CC over TC) compared to the ratio in technical chlordane ranging from 1.16 to 1.35 [Jantunen *et al.*, 2000; Patton *et al.*, 1991]. Ratios <1 indicate possible preferential degradation of TC over CC and are typical of contemporary ratios observed in Arctic air [Becker *et al.*, 2012]. Ratios derived from marine sediments may be

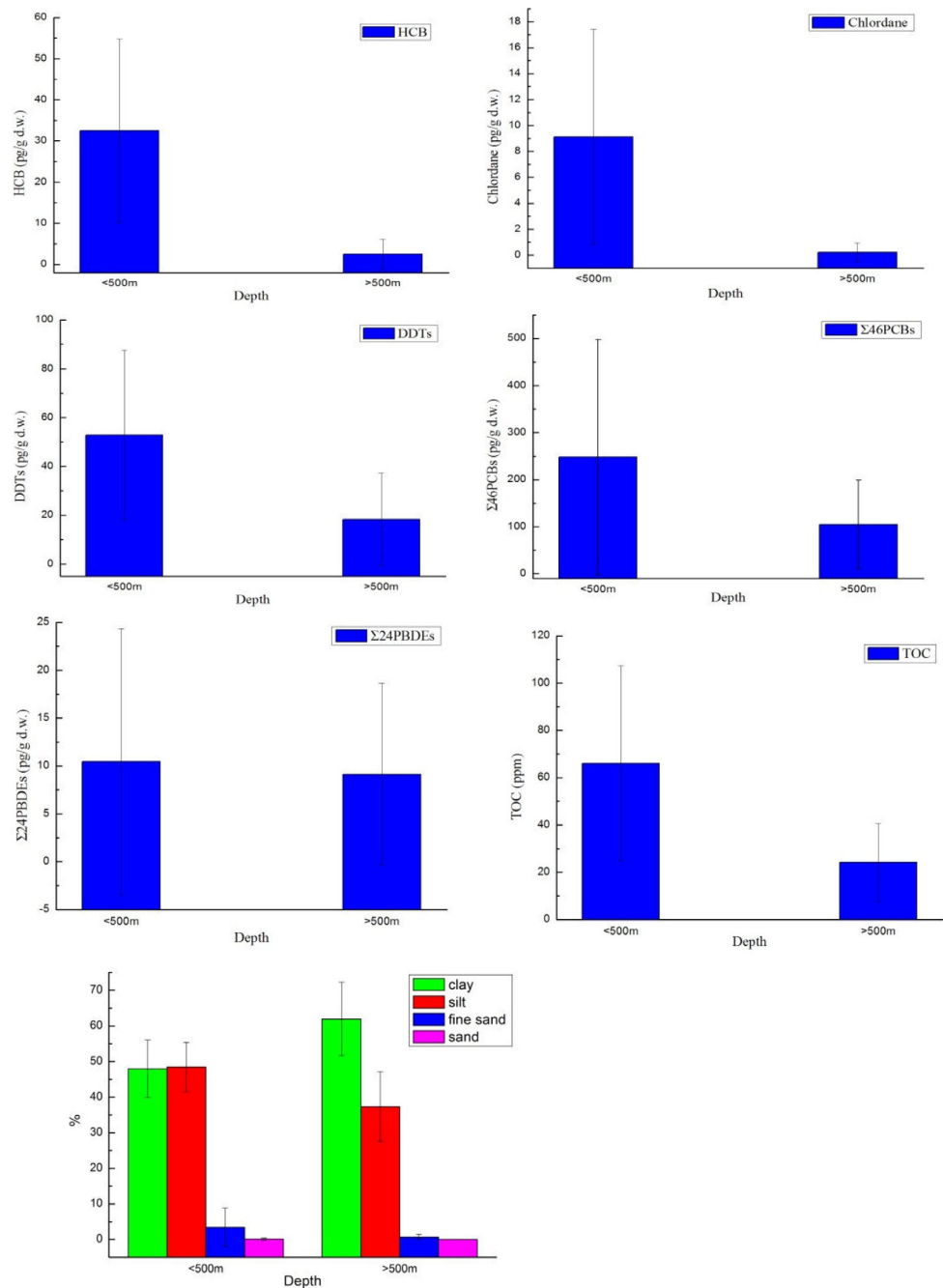


Figure 2. HCB, Chlordane, DDTs, Σ_{46} PCBs and Σ_{24} PBDEs concentrations, TOC levels, percentage of clay, silt, gravel and sand in the shallow water region (0–500 m) and deep water region (>500 m).

further reduced as TC may be preferentially degraded by marine biota and is more readily metabolized to oxychlordane compared to the more stable CC isomer [Kawano *et al.*, 1988].

To examine DDT weathering and hence the age of the DDT signal present in the sediments, then the ratio of *p,p'* and *o,p'*-DDT to the degradates *p,p'*-DDE, *o,p'*-DDE and DDD was examined. Technical grade DDT contains ~80% *p,p'*-DDT, 15% *o,p'*-DDT, with smaller quantities of *p,p'*-DDE and *p,p'*-DDD [Li and Macdonald, 2005]. The average DDT/DDE + DDD values were 2.9 and 4.4 in the deep water regions of the Bering Sea and Canadian Basin, respectively; however, ratios were significantly lower in the shallow water regions of the Bering Strait and Chukchi Sea (average 0.4 ± 0.19). The ratios observed in the deep water locations reflect the upper range observed in Arctic air monitoring programmes from the mid-1990s to mid-2000s

[Becker *et al.*, 2012]. The lower ratios in the sediments of the shallow water regions indicate a more weathered DDT signal. The waters of the Bering Strait and southern Chukchi Sea have high primary production rates with relatively low grazing pressure, resulting in high organic carbon settling rates to the relatively shallow shelf sediments which support a rich benthic food web [Grebmeier *et al.*, 2006; Sambrotto *et al.*, 1984]. Therefore, the abundant phytoplankton in the water column coupled to the high biomass of long-lived benthic fauna may contribute to the biodegradation process of DDT parent compounds relative to the deep water sediment accounting for the relatively lower DDT ratios in these regions.

The ratio of *o,p'*-DDT/*p,p'*-DDT can also be used to distinguish DDT pollution caused by technical DDT from that by dicofol. Dicofol is produced and used in southern Europe, India, China, Israel and Brazil [Van de Plasche, 2003]. However, China has been a major producer of technical DDT and dicofol, accounting for >85% of the global technical DDT production with over half of this amount used to manufacture dicofol. The predominant DDT impurity found in dicofol is *o,p'*-DDT. Generally, *o,p'*-DDT/*p,p'*-DDT ratios range from 0.2 to 0.3 in technical DDT and from 1.3 to 9.3 or higher in dicofol [Qiu *et al.*, 2005]. From this study, a range of 0–0.92, with an average of 0.23, was determined in the various sediment samples along the entire cruise, indicating technical-DDT rather than dicofol as the predominant source of DDT.

In order to relate our results with the PCBs measured in the surface waters of the polar mixed layer (PML), and also examine PCB profiles, a subset of 13 PCB congeners (PCB IUPAC numbers 18, 28, 52, 70, 101, 110, 118, 105, 149, 153, 138, 180, and 194) were selected for further analysis. Consistent with PCBs observed in the PML, higher PCB concentrations were found in the sediments of the shelf seas compared to those in the interior central Arctic [Carrizo and Gustafsson, 2011]. To examine the PCB profile in detail and compare the PCB pattern in the sediments with that present in a range of technical formulations, then cluster analysis was undertaken. The standard technical PCB formulations included Aroclors (1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268), Clophens (A30, A40, A50, and A60), Kanechlors (KC 300, 400, 500, and 600), Sovol, and Trichloridiphenyl (TCD). The results showed that all the sampling stations along the cruise tracks were generally distinguished into four major clusters (supporting information Figure S3), with three clusters having representative technical PCB mixture signals, and dominated by the tri-chlorinated (TCB, A30, KC 300, Aroclor1016, 1242) tetra-chlorinated (A40, KC400, Aroclor1248), and penta-chlorinated (Sovol, A50, KC500, Aroclor 1254) congeners, respectively. The fourth cluster did not align to any particular homolog pattern. The PCB geographical profiles in the sediment samples do not fully align with the PCB profile in the technical formulations. This is not surprising given the environmental transport processes and chemical weathering which will affect the PCB congener pattern in environmental samples. Nonetheless, sediments in the Canadian Basin were grouped in the first and second clusters containing the lighter Aroclor, Clophen and TCD mixtures, whereas sediments from the Bering Strait and Chukchi Sea shelf where clustered separately indicating a different congener pattern.

Generally, the congener distribution of all stations is substantially skewed toward a higher contribution of lighter PCBs, with the tri, tetra, penta, and hexa-chlorinated congeners contributing 31%, 25%, 23%, and 16% to the Σ_{13} PCBs, respectively. Figure 3 shows the PCB homolog distribution for the main geographical regions. A similar congener distribution was evident in the Bering Sea, Bering Strait, and Canadian Basin, with tri and tetra-chlorinated PCBs comprising ~60% of Σ_{13} PCBs, with the penta, and hexa-PCBs comprising ~30%, although in the sediments of the Chukchi Sea shelf region, the pentachlorinated congeners were more abundant. In the surface seawater of the Chukchi Sea and interior Arctic Ocean, the trichlorinated congeners made up $\geq 50\%$ of the total PCBs and this congeneric pattern suggests the influence of atmospheric long-range delivery [Carrizo and Gustafsson, 2011]. However, for the marine sediment samples collected in the same region, the abundance of the trichlorinated PCBs is lower, especially in the Chukchi Sea shelf region and the Atlantic side of the Arctic toward Iceland. Diffusive air-sea gas exchange is the dominant air to water depositional process for the lower chlorinated PCBs [Totten *et al.*, 2001], and postdepositional processing in the water column including phytoplankton/particle uptake and carbon settling export is likely to change the profile of PCBs from surface to deeper water masses and marine sediment [Schulz-Bull *et al.*, 1998]. These processes are likely to shift the homolog profile in favor of the more chlorinated PCBs given their lower aqueous solubility and higher partitioning coefficients (K_{OC}) which will favor their deposition through the water column via particle settling. Moreover, benthic sediment perturbations (e.g., bio-perturbation) may result in repeated exposure of sediment to the overlying water column resulting in a shift in equilibrium partitioning that favours loss of the lower chlorinated PCBs via partitioning back to the

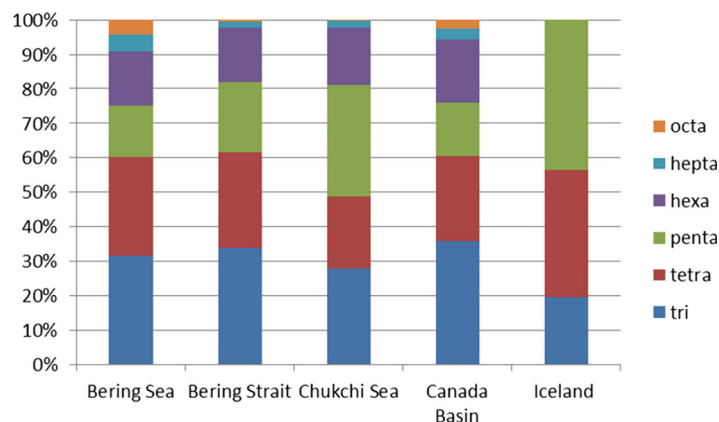


Figure 3. Contributions of different chlorinated congeners to the Σ_{13} PCBs in separated geographical regions.

on grain size φ , where $\varphi = -\log_2 \Phi$ (and Φ is the diameter in mm): clay ($\varphi > 8$, $\Phi < 4 \mu\text{m}$), silt ($4 < \varphi < 8$, $4 \mu\text{m} < \Phi < 63 \mu\text{m}$), fine sand ($2 < \varphi < 4$, $63 \mu\text{m} < \Phi < 250 \mu\text{m}$), and sand ($\varphi < 2$, $\Phi > 250 \mu\text{m}$). In general, the sediments composed of clay (54%) and silt (43%), with low proportions of fine sand (2%) and sand (0.08%) for the entire two cruises. Figure 2 demonstrates that a higher proportion of clay was found in the sediment of the deep water regions, whereas more silt was present in the shallow water regions. The TOC content was in the range of 7.3–144 ppm and the average TOC content in the sediment of shallow water regions (66 ppm) was significantly higher than those in the deep water regions (24 ppm) (supporting information Figure S1c). A Pearson correlation analysis between contaminant concentrations and sediment parameters is presented in Table 3. The strongest relationships were apparent between contaminant concentrations and depth of water (discussed above) as well as TOC content. For TOC, a statistically significant relationship was apparent between HCB, Chlordane and DDTs concentrations with a stronger relationship apparent for the 2010 data set, presumably due to the larger geographical area covered by this campaign and the wider range of TOC concentrations. For PCBs, the positive correlation with TOC increased with degree of chlorination and this is most evident for individual PCB congeners (both the correlation and the level of significance increased from PCB-28 to PCB180). Significant negative correlations were observed for OC concentrations with percentage clay content and yet positive correlations were apparent with silt content (presumably due to the residing organic matter in the silt). Similar trends were also apparent with the PCBs although these were not statistically significant. These relationships with clay and silt reflect the higher clay content in the deep water sediments where contaminant concentrations were lower, and the higher silt content in the shallow water areas where concentrations were relatively higher. Interestingly, these relationships, particularly for the PCBs, are not always significant and this was also the case for sediments collected in earlier campaigns conducted in broadly the same geographical regions as this study (e.g., CHINARE 3). For example, *Hong et al.* [2012] reported no apparent corelations between PCB concentrations and sediment properties including TOC. While the distribution of Σ PCBs in Hudson Bay sediments (a shallow water region) only partly reflect sediment texture ($\Phi < 63 \mu\text{m}$, $r^2 = 0.49$) and organic carbon content ($r^2 = 0.55$) [*Kuzyk et al.*, 2013]. In summary, this would indicate complex processing of organic contaminants following their input—principally deposition from the atmosphere for remote pelagic environments—and final accumulation with benthic particulate matter.

The seasonally ice-covered Bering Strait and Chukchi Seas represent large continental shelf areas that are strongly influenced by nutrient-rich Pacific waters (Bering Shelf-Anadyr Water) together with riverine input associated with the outflowing Yukon River [*Grebmeier et al.*, 2006; *Kuzyk et al.*, 2013]. The carbon cycle, especially the biological pump, has been shown to have a key role in controlling environmental sink processes for hydrophobic organic chemicals, such as burial in sediments [*Nizzetto et al.*, 2012]. The exceptional productivity and subsequent large particle fluxes over these shallow shelf regions will serve to efficiently export contaminants present in the water column to the underlying sediment. Indeed, oceanic regions with high primary productivity lead to a depletion of POP concentrations in the surface mixed layer due to phytoplankton uptake and subsequent export and settling of biogenic particles to deeper water

dissolved phase. However, in the deep water regions marked by lower biological activity (primary production/remineralization), such as the Canadian Basin, this shift in PCB profile is not as apparent as the shallow-water sediments and this is evident from the cluster analysis presented in supporting information Figure S3.

3.4. Influence of Sediment Composition and Sedimentation Rates

The marine sediments were divided into four parts based

Table 3. Pearson Correlations Between Sediment Properties and OCs, PCBs Concentration

		HCB (2010)	Chlordane (2010)	DDTs (2010)	HCB (2012)	Chlordane (2012)	\sum_{13} PCB	tri-PCB	tetra-PCB
clay	Pearson Correlation	-0.411 ^b	-0.493 ^c	-0.499 ^a	-0.101	-0.176	-0.267	-0.179	-0.338
	Sig. (2-tailed)	0.033	0.009	0.011	0.670	0.459	0.187	0.383	0.091
	N	27	27	25	20	20	26	26	26
silt	Pearson Correlation	0.434 ^a	0.529 ^c	0.550 ^b	0.175	0.208	0.313	0.241	0.370
	Sig. (2-tailed)	0.024	0.005	0.004	0.460	0.379	0.119	0.236	0.063
	N	27	27	25	20	20	26	26	26
fine sand	Pearson Correlation	0.078	0.065	0.033	-0.071	0.001	-0.058	-0.145	0.020
	Sig. (2-tailed)	0.699	0.748	0.874	0.765	0.998	0.779	0.478	0.922
	N	27	27	25	20	20	26	26	26
sand	Pearson Correlation	-0.199	-0.172	-0.203	-0.104	-0.067	-0.189	-0.185	-0.251
	Sig. (2-tailed)	0.319	0.391	0.330	0.662	0.778	0.354	0.364	0.216
	N	27	27	25	20	20	26	26	26
TOC	Pearson Correlation	0.683 ^b	0.660 ^b	0.759 ^b	0.471 ^a	0.445 ^a	0.389 ^a	0.403 ^a	0.527 ^b
	Sig. (2-tailed)	0.000	0.000	0.000	0.036	0.049	0.049	0.041	0.006
	N	27	27	25	20	20	26	26	26
Depth	Pearson Correlation	-0.756 ^b	-0.689 ^b	-0.611 ^b	-0.453 ^a	-0.466 ^a	-0.515 ^b	-0.464 ^a	-0.628 ^b
	Sig. (2-tailed)	0.000	0.000	0.001	0.045	0.038	0.007	0.017	0.001
	N	27	27	25	20	20	26	26	26
		penta-PCB	hexa-PCB	hepta-PCB	octa-PCB	PCB28	PCB52	PCB70	PCB180
clay	Pearson Correlation	-0.227	-0.200	-0.186	-0.180	-0.247	-0.286	-0.357	-0.186
	Sig. (2-tailed)	0.264	0.327	0.364	0.380	0.225	0.157	0.073	0.364
	N	26	26	26	26	26	26	26	26
silt	Pearson Correlation	0.268	0.221	0.232	0.170	0.314	0.326	0.379	0.232
	Sig. (2-tailed)	0.186	0.279	0.254	0.405	0.118	0.104	0.056	0.254
	N	26	26	26	26	26	26	26	26
fine sand	Pearson Correlation	-0.053	0.006	-0.088	0.101	-0.139	-0.027	0.063	-0.088
	Sig. (2-tailed)	0.796	0.977	0.668	0.623	0.499	0.896	0.759	0.668
	N	26	26	26	26	26	26	26	26
sand	Pearson Correlation	-0.131	-0.145	-0.220	-0.112	-0.187	-0.209	-0.269	-0.220
	Sig. (2-tailed)	0.523	0.481	0.281	0.587	0.360	0.306	0.184	0.281
	N	26	26	26	26	26	26	26	26
TOC	Pearson Correlation	0.221	0.362	0.699 ^b	0.269	0.426 ^a	0.480 ^a	0.524 ^b	0.699 ^b
	Sig. (2-tailed)	0.278	0.070	0.000	0.184	0.030	0.013	0.006	0.000
	N	26	26	26	26	26	26	26	26
Depth	Pearson Correlation	-0.351	-0.519 ^b	-0.433 ^a	0.074	-0.541 ^b	-0.581 ^b	-0.616 ^b	-0.433 ^a
	Sig. (2-tailed)	0.079	0.007	0.027	0.718	0.004	0.002	0.001	0.027
	N	26	26	26	26	26	26	26	26

^aBoth environmental variables and contaminant concentrations are log-normally distributed.

^bCorrelation is significant at the 0.05 level (2-tailed).

^cCorrelation is significant at the 0.01 level (2-tailed).

[Dachs *et al.*, 2000]. Therefore, the sediment of the shallow shelf regions of the Bering Strait and Chukchi Sea could be viewed as an important regional sink for PCBs and OCs and is likely to account for the relatively higher concentrations observed in the shallow water areas of this study.

Contrary to such highly productive ocean margins, the relatively lower rates of primary production over the Canada Basin and central Arctic Ocean result in much lower vertical fluxes of organic matter in the water column and corresponding sedimentation rates. Primary productivity in these deeper water regions may be further impeded in a warmer Arctic with less ice [Cai *et al.*, 2010]. Across the study transect there are markedly different sedimentation rates, with high rates occurring in the northern Bering and Chukchi Seas in contrast to much lower sedimentation rates in the central Arctic Ocean [Darby *et al.*, 2009]. Sedimentation rates determined from cores taken along the edge of the continental shelf of the Chukchi Sea with the Canada Basin (i.e., the Chukchi-Alaskan margin) ranged from ~0.4 to 12 m/kyr⁻¹ with average rates of between 1.50 and 3.13 m/kyr. Some of the highest sedimentation rates are likely attributable to rapid sedimentation events (e.g., turbidites) and are probably localized to specific geographic regions (e.g., underwater canyons, etc). Nonetheless, these rates contrast markedly with rates derived from sediment cores taken on several of the major ridges and basins of the central Arctic Ocean, where rates were estimated to be ~0.01–0.02 m/kyr. Therefore, the top 5 cm of surficial sediments collected in this study represent an accumulation period of ~50 years in the Bering Strait and Chukchi shelf regions, ~100 years in the Bering Sea, but a much longer period (>1 kyr) in the Canada Basin and the central Arctic Ocean. In the Bering and Chukchi

shelf regions then sediment representing 50–100 years of accumulation effectively covers the period of POPs production and use (from the 1930s onward), whereas the majority of the sediment sampled in the deep ocean regions predates this period. As such in the deeper ocean sediments a grab sample of ~5 cm in depth will effectively “dilute” the POPs associated with the upper ~0.1–0.2 cm of sediment (i.e., the thin surface layer representing the last ~100 years of accumulation) and therefore care must be taken when comparing the concentrations from regions with wide variations in sedimentation rates.

Generally, the concentrations of OCs and PCBs detected in this study were similar to, or slightly lower than, studies from the 1990s, indicating a lack of a declining trend in contrast to temporal trends observed in other arctic media. The exception, however, are the PBDEs (excluding BDE-209) with evidence of lower concentrations in sediments collected in 2012 compared to 2008, albeit with very low concentrations. Nonetheless, efficient settling of OCs and PCBs is reflected by their elevated concentrations in sediments of the shallow shelf regions especially in the Chukchi Sea shelf region. Therefore, marine sediments in shelf areas of the coastal Arctic seas, where sedimentation rates are at their highest, are likely to serve as an important repository for POPs. These sediments may provide a long-term sink for these chemicals, depending to some degree on the rate of biogeochemical processing of the organic carbon and only for the most persistent/recalcitrant chemicals (e.g., higher MW PCBs).

Acknowledgments

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