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Concentration, distribution and sources of perfluoroalkyl substances and organochlorine pesticides in surface sediments of the northern Bering Sea, Chukchi Sea and adjacent Arctic Ocean

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H I G H L I G H T S

- PFAS and OCPs were determined in surface sediments of the adjacent Arctic Ocean.
- OCPs were orders of magnitude greater than the observed PFAS.
- PFOA was the main compound, and the most abundant OCPs were HCHs and DDTs.
- Industrial activities may be responsible for high levels of PFAS in the Bering Sea.
- An increasing latitudinal trend of OCPs were observed.

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Perfluoroalkyl substances (PFAS) and organochlorine pesticides (OCPs) in surface sediments were investigated from the Bering Sea, the Chukchi Sea and adjacent Arctic Ocean in 2010. Total concentrations (dry weight) of Σ_{14} PFAS in surface sediments ($0.85 \pm 0.22 \text{ ng g}^{-1}$) of the Bering Sea were lower than that in the Chukchi Sea and adjacent Arctic Ocean ($1.27 \pm 0.53 \text{ ng g}^{-1}$). Perfluoro-butanoic acid (PFBS) and perfluoro-octanoic acid (PFOA) were the dominant PFAS in these areas. The concentrations of Σ_{15} OCPs in the sediment of the Bering Sea ($13.00 \pm 6.17 \text{ ng g}^{-1}$) was slightly higher than that in the Chukchi and Arctic Ocean ($12.05 \pm 2.27 \text{ ng g}^{-1}$). The most abundant OCPs were hexachlorocyclohexane isomers (HCHs) and dichlorodiphenyltrichloroethane (DDT) and its metabolites. The composition patterns of HCHs and DDTs indicated that they were mainly derived from the early residues via river runoff. Increasing trends of PFAS, HCHs and DDTs in surface sediments from the Bering Sea to the Arctic Ocean were found, indicating oceanic transport. In summary, the concentrations of OCPs were orders of magnitude greater than the observed PFAS concentrations, and the concentrations of PFAS and OCPs in surface sediments from the Bering Sea to the Chukchi Sea and adjacent Arctic Ocean are at the low to moderate levels by comparing with other coastal and marine sediments worldwide.

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1. Introduction

Persistent organic pollutants (POPs) are toxic chemicals that adversely affects human health and the environment around the world. Chemicals such as Perfluoroalkyl substances (PFAS), and

organochlorine pesticides (OCPs) have been detected ubiquitously in many locations, including locations in the remote polar and Alpine regions. These pollutants are persistent against typical environmental degradation processes, potential bioaccumulation through food webs and toxicity to humans and wildlife (De Silva et al., 2009; Zhao et al., 2012; Yang et al., 2019). These chemicals carry physical-chemical properties that allow them to exist in a variety of environmental compartments (air, water, soil, and

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sediments) where they can enter and accumulate in marine and terrestrial food web (Wu et al., 2019).

PFAS are synthetic chemicals with straight or branched chain carbons bonded to fluorine (Kumar et al., 2009), widely used in numerous industrial and commercial applications (Kissa, 2001). Approximately 3,000 PFAS are now or have been estimated in the global market (Wang et al., 2017). Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are typical commercial chemicals that comprises of eight carbon chains. Because of their unique chemical and physical characteristics such as both hydrophobic and oleophobic, which are widely used as industrial surfactants, electrical wire casing, fire, and chemical resistant tubing, fire fighting foams for over 50 years (ATSDR, 2015). PFOS (and its salts) have been recognized as POPs and have been added by the OSPAR Commission to the list of chemicals for priority action (Commission, 2006) and also on the list of 'new contaminants' being observed by the Arctic Monitoring and Assessment Program (Assessment, 2002). The worldwide distribution of PFAS was reported in urban and remote areas including deep oceanic water of up to 5000 m (Yamashita et al., 2005). Detectable concentrations of PFAS in the Arctic environment have provided strong evidence for atmospheric transportation and deposition. PFAS precursors were recognized as another important source in remote areas (Stock et al., 2007). Unfortunately, most of the previous studies of PFAS have focused on water and biological matrices. Little information about PFAS concentrations in the sediments of Arctic Ocean is available.

Organochlorine compounds (OCs) have been considered as ubiquitous contaminants in the marine environment (Kláňová and Matykieviczová, 2008) and are proclaimed as POPs and/or endocrine disrupting chemicals (EDCs), which are being extensively used for pest and insect control of vector-borne diseases since the 1940s. OCPs pose toxicity, persistence and bioaccumulation to the ecosystem (Pazi et al., 2011) and also adverse health effects, including carcinogenesis, immunological and reproductive disorders in living organisms including humans and wildlife (Nizzetto et al., 2010). Although OCPs have been officially prohibited or regulated for over 30 years, some OCPs such as hexachlorocyclohexanes (HCHs), chlordanes (CHLs), and DDTs are still being used against agriculture in some countries around the tropical and subtropical belts. Residues of OCPs have highly contaminated the foods, soils, sediments and biota (Verweij et al., 2004). OCPs have a strong affinity for suspended particulate matter and afterward settle down in sediments due to low water solubility (from 700 mg L^{-1} to $21,300 \text{ mg L}^{-1}$) and high n-octanol/water partition coefficients ($\log K_{ow}$) values (3.9–6.2) (Yang et al., 2005). Particle settling in the North Pacific and Arctic Oceans could be a significant removal process of hydrophobic chemicals (Ma et al., 2015). Organic pollutants in sediments can be released to seawater through the suspension of sediments and also act as secondary sources of these persistent pollutants and greatly affect their fate in the environment (Jones and De, 1999; Palm et al., 2004). In recent studies, OCPs are subject to long-rang transport (LRT) due to their semi-volatile property and from the mid- and low-latitude sources that are thought to be the most important input-pathway to the Arctic environments. The OCPs are also transported to Arctic region through ocean currents, river outflows, continental runoff and ice-drift (Muir and de Wit, 2010). In the Arctic Ocean, the importance of currents as POPs pathways has been recognized. α -HCH is mostly transported through the atmosphere, more water soluble and less volatile β -HCH is mostly transported through the ocean (Li et al., 2002; Pucko et al., 2013; Lohmann and Belkin, 2014). Therefore, it is necessary to evaluate the transport of OCPs in sediments around the Arctic Ocean and

adjacent areas.

In this study, the purposes are (i) to determine the concentration and composition of PFAS and OCPs in surface sediments of the Bering Sea, the Chukchi Sea and adjacent Arctic Ocean, and also to compare with those from the adjacent areas of the Arctic Ocean; (ii) to elaborate the latitudinal trends and potential sources of PFAS and OCPs in surface sediments; (iii) to evaluate the ecological risk of OCPs and PFAS in surface sediments.

2. Materials and methods

2.1. Sampling

The Bering Sea is one of the largest marginal seas in the world and is surrounded by the Alaska Peninsula, the Aleutian Archipelago, Kamchatka Peninsula and Siberia (Niebauer et al., 1999). The Bering Strait act as the Pacific gateway to the Arctic Ocean and all Pacific waters found in the Arctic must cross the Chukchi Sea to reach the Arctic Ocean shelf-break at ca. 73°N . The Chukchi Sea is an epicontinental sea, with a water depth of $\sim 50 \text{ m}$, in the south of the Arctic Ocean and located between northern Alaska and the Siberian coast. The Chukchi Sea surrounds one of the largest continental shelves and its northern location puts it at the crossroads of recently observed changes in the global climate (Grebmeier et al., 2010). In this study, twenty surface sediment samples for PFAS and 12 surface sediments for OCPs were collected from the northern Bering Sea, the Chukchi Sea and adjacent Arctic Ocean during the 4th Chinese National Arctic Research Expedition (CHINARE) in July–September 2010 (Fig. 1). The geographical position of each station was presented in Table S1 (See in supporting information SI). Surface sediments for PFAS and OCPs were retrieved from 20 sampling stations with a stainless grab sampler. Surface sediments for PFAS were collected using a clean, methanol rinsed polypropylene (PP) spatula and was stored in pre-cleaned 50 mL polypropylene (PP) tubes. The surface sediments for OCPs were collected using a pre-cleaned stainless scoop and stored in solvent-rinsed aluminum containers. All samples were kept frozen at -20°C until further processing in the laboratory.

2.2. Analytical procedure

In the laboratory, all sediment samples were freeze-dried, grounded to pass through a 0.2 mm sieve to separate the stone, leaves and dead invertebrates from the samples and fully homogenized. Prior to the extraction of PFAS, about 2 g of dried sediment sample was transferred to 50 mL methanol-rinsed polypropylene (PP) tubes and spiked with 2 ng mass-labeled PFAS mixture (Table S2). Then, 2 mL methanol (200 mmol L^{-1} NaOH) was added to the PP tube to achieve more efficient recovery rates. The mixture was soaked for 30 min 10 mL of methanol was added to the PP tube and sonicated in an ultrasonic bath for 30 min and centrifuged for 12 min at 3000 rpm. The supernatant was collected in methanol-rinsed polypropylene tubes. Sonication was repeated three times, yielding a total of 30 mL supernatant. Finally, the volume of sediment extraction was reduced to 0.5 mL under a stream of pure nitrogen. Oasis WAX cartridges (Waters, 150 mg, 6 cm^3 , $30 \mu\text{m}$) were used for SPE. The pretreatment of the cartridges and the extraction processes were described with minor modification (Naile et al., 2010). Briefly, the cartridges were first preconditioned by 4 mL ammonia methanol (0.1%), 4 mL methanol and 4 mL pre-cleaned Millipore water, were then loaded with samples at a speed of two drops per second. These cartridges were centrifuged to remove water. Afterward, they were sealed in aluminum bags and stored at -20°C until eluted. The dried cartridges were washed with 4 mL methanol and 4 mL of 0.1% ammonia in methanol. The eluate was

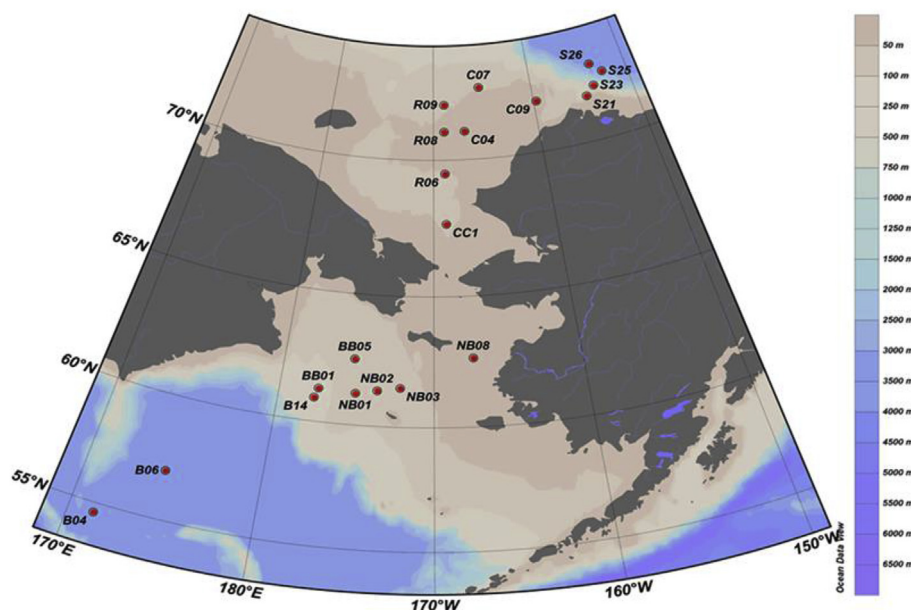


Fig. 1. Map of the study area with the locations of all stations visited during Fourth Chinese National Arctic Research Expedition (CHINARE-4) in 2010.

concentrated using a gentle stream of nitrogen until volume became 0.5 mL. The SPE eluent was cleaned up using another preconditioned CNWBOND Carbon - GCB SPE cartridges to remove the co-eluted interfering compounds and were reduced to 0.5 mL under a gentle stream of nitrogen. Before being injected into the instrument the eluates were diluted to 1 mL with 1:1 methanol and Millipore water.

Prior to the extraction of OCPs, about 10 g of dried sediment sample was spiked with 50 ng OCPs surrogates (2, 4, 5, 6-Tetrachloro-m-xylene (TCMX)), and 1 g of activated copper powder (to remove sulfur) in a pre-cleaned solvent filter paper. The sediment samples were then extracted by 40 mL DCM: n-hexane: acetone: (1:1:1, v/v) in a Soxhlet apparatus for 18 h. Finally, the sediment extract was transferred to a rotary evaporator bottle. After that, the extract was concentrated to nearly dry by rotary evaporation, then was solvent-exchanged into hexane of about 1 mL. Then, the extract was cleaned by 2:3 (v/v) alumina: silica column chromatography (2.5 g of 80–100 mesh 5% activated silica gel, 1.6 g of 100–200 mesh 1% activated alumina, topped with 1.5 g of anhydrous sodium sulfate). The mixture was eluted with 10 mL of n-hexane/dichloromethane (1:1 v/v), the final volume was then reduced to 100 μ L under a stream of pure nitrogen.

2.3. Instrument analysis

The instrumental analysis of 14 PFAS (Table S2: C4–C12 and C13 PFCAs: perfluoro-butanoic acid (PFBA), perfluoro-pentanoic acid (PFPeA), perfluoro-hexanoic acid (PFHxA), perfluoro-heptanoic acid (PFHpA), perfluoro-octanoic acid (PFOA), perfluoro-nonanoic acid (PFNA), perfluoro-decanoic acid (PFDA), perfluoro-undecanoic acid (PFUnDA), perfluoro-dodecanoic acid (PFDoA), perfluoro-tridecanoic acid (PFTrDA), C4, C6, C8 and C10 PFASs: perfluoro-butanedisulfonate (PFBS), perfluorohexane-sulfonate (PFHxS), perfluoro-octanesulfonate (PFOS), perfluoro-decansulfonate (PFDS)) was performed using a high-performance liquid chromatography interfaced with a tandem mass spectrometry system (HPLC-MS/MS) (Agilent 1290 LC and Agilent 6490 Trip Quadrupole MS, Agilent Technologies, California, USA). The separation column was a Waters Symmetry C18 (150 mm \times 2.1 mm,

5 μ m) column (Waters Corporation). Solvent A is 10 mM Ammonium acetate. Solvent B is 100% methanol. An aliquot (10 μ L) of the sample was injected into the column. The detector was Agilent 6490 tandem mass spectrometer operated in an electrospray interface in the negative ionization mode.

The 15 OCPs (Table S3: hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCHs: α -HCH, β -HCH, γ -HCH and δ -HCH, *trans*-chlordane, *cis*-chlordane, α -Endosulfan, β -Endosulfan, dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDTs: o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, o,p'-DDD and p,p'-DDD)) was analyzed using GC coupled with an electron capture detector (GC-ECD: Agilent 7890 GC-ECD). The capillary column (HP-5 60 m, 0.32 mm i.d., 0.25 μ m film thickness) was used for the analysis. The flow rate of the carrier gas was 1.0 mL min⁻¹ under a constant flow mode. The temperatures of the injector and detector were 250 $^{\circ}$ C and 325 $^{\circ}$ C, respectively. Oven temperature was initially isothermal at 80 $^{\circ}$ C for 1 min, and then linearly ramped from 80 to 210 $^{\circ}$ C at a rate of 10 $^{\circ}$ C min⁻¹, isothermal at 210 $^{\circ}$ C for 10 min, from 210 to 235 $^{\circ}$ C at a rate of 0.5 $^{\circ}$ C min⁻¹, kept for 2 min, from 235 to 300 $^{\circ}$ C at a rate of 10 $^{\circ}$ C min⁻¹, for a total time of 75 min. The targeted compounds were determined on the basis of the retention times and quantified by internal standards. The peak order of OCPs standard was determined by GC-MSD.

2.4. QA/QC of analysis

In this study, all data were subject to strict quality control procedures. Laboratory blanks, spiked blanks and replicate samples were analyzed along with field samples. Compared with the field samples, the blank experiment showed much lower levels of PFAS and OCPs, and so the background PFAS and OCPs in the laboratory could be ignored. Recoveries were determined for all samples by spiking with surrogate standards prior to extraction. Surrogate standards were used to monitor matrix effects and to compensate for losses involved in the sample extraction and work-up. Most of the target PFAS and OCPs had the recoveries ranged from 45 to 120% and 50–119% in the sediment, respectively. The limit of quantification (LOQ) was determined as a signal-to-noise ratio of 10:1. The LOQ (dry weight, d.w.) for PFAS and OCPs in surface

sediments were $0.01\text{--}0.05\text{ ng g}^{-1}$ and $0.02\text{--}1.62\text{ ng g}^{-1}$, respectively. Method recoveries, method detection limits of individual PFAS and OCPs and the field blanks data were shown in Tables S4–S5. It should be noted that the reported concentrations were corrected according to the recoveries of the surrogate standards.

2.5. Statistical analysis

The statistical analysis was performed using SPSS software for window (SPSS, USA). The significant difference analysis of OCPs and PFAS concentration between the Bering Sea and Arctic Ocean were completed by one-way ANOVA method. No significant difference ($p > 0.05$) was observed between the Bering Sea and the Arctic Ocean for most pollutants except for PFOA and PFHxS.

3. Result and discussion

3.1. Concentrations and compositions of PFAS

Overall 14 PFAS in surface sediments were detected in all of the 20 sampling stations in the northern Bering Sea, Chukchi Sea and adjacent Arctic sediments. Concentrations (d.w.) of individual PFAS and Σ PFAS are listed in Table S6. Concentrations of Σ PFAS ranged from 0.55 to 2.66 ng g^{-1} (mean 1.08 ng g^{-1}), whereas concentrations of Σ PFCAs ranged from 0.33 to 2.38 ng g^{-1} (mean 0.80 ng g^{-1}), which were higher than those of Σ PFSAs ($0.10\text{--}0.69\text{ ng g}^{-1}$, means 0.28 ng g^{-1}) in surface sediments of the Bering Sea, Chukchi Sea and Arctic Ocean (Fig. 2). The dominant PFAS in the Chukchi Sea and the Arctic Ocean was PFOA ($0.3\text{--}0.74\text{ ng g}^{-1}$), followed by PFBA ($0.03\text{--}0.68\text{ ng g}^{-1}$) and PFOS ($0.03\text{--}0.18\text{ ng g}^{-1}$). In the Bering Sea, PFOA was the predominant compound, with an average of 0.23 ng g^{-1} , followed by PFBS and PFOS with averages of 0.20 and 0.07 ng g^{-1} , respectively. PFTrDA was not detected in any sediment samples. Compared with the observed PFOA and PFOS concentrations in the other sedimentary regions worldwide, the concentrations of PFAS in surface sediments of the Chukchi Sea and adjacent Arctic Ocean were at a moderate level (Text S1 and Table S7).

Higher concentrations of Σ PFAS was observed in sediments of Arctic Ocean at stations S23, S25, S26, R06. To elucidate the spatial concentration of PFAS in surface sediment samples, sampling stations were geographically distributed into two groups: Bering Sea (B04, B06, B14, BB01, BB05, NB01, NB02, NB03, NB08) and Chukchi Sea and adjacent Arctic Ocean (CC1, R06, R08, C04, R09, C07, C09, S21, S23, S25, S26).

Sea and adjacent Arctic Ocean (CC1, R06, R08, C04, R09, C07, S21, S23, S25, S26). Higher concentrations of Σ PFAS was detected in the Chukchi Sea and the Arctic Ocean (stations CC01, R09, S23, and S25). The average concentrations of Σ PFAS had a trend which increased in the following order: Bering Sea < Chukchi Sea and adjacent Arctic Ocean, whereas the northern part of the Canadian Basin (stations S21, S23, S24, and S26) contained the highest concentrations of PFAS. High concentration of PFAS may be due to the transportation of sea ice and atmospheric conditions in the Arctic Ocean (Pfirman et al., 1997). High sedimentation 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). 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. There are three distinct water masses originating from the Bering Sea that flow northward through Bering Strait (Paquette and Bourke, 1981): Alaskan Coastal Water, Bering Shelf Water, and Anadyr Water. They are believed to follow topographically through the direct pathways of the Chukchi Sea to the Arctic basin (Woodgate et al., 2005). Deep ocean in the Arctic get pollutants harder as compared with the continental shelf (Chen et al., 2018). High concentrations of PFAS was found at station S23 (1.44 ng g^{-1}) and S25 (1.37 ng g^{-1}), which were located in the edge of the continental shelf of the Chukchi Sea. Stations S23 and S25 were dominated by PFOA and PFBA. High concentration of PFAS may be due to an input of Canada point sources, atmospheric sedimentation, river runoff etc (Chen et al., 2018). High concentrations of pollutants arrived through the Barrow Point and the Prudhoe Bay offshore area and also clockwise flow of the Beaufort Gyre is helpful to the transportation of pollutants from the Beaufort Sea and North wind Ridge to the northern Chukchi Sea (MacDonald et al., 2000). The Siberian Coastal Water bring pollutants from the Yukon River, flow into the Eastern Chukchi Sea and then turned into the Canadian Basin through the Chukchi Sea shelf, which also contribute to the accumulation of coastal pollutants in this area (Chen et al., 2018).

In the Bering Sea, the concentrations of longer-chained PFCAs, i.e., PFDA, PFUnA and PFDoA, were $0.01\text{--}0.04\text{ ng g}^{-1}$, $0.02\text{--}0.06\text{ ng g}^{-1}$, and $0.02\text{--}0.07\text{ ng g}^{-1}$, respectively. Whereas, concentrations of shorter-chained PFCAs i.e. PFPeA, PFHxA and PFHpA, were $0.02\text{--}0.1\text{ ng g}^{-1}$, $0.02\text{--}0.06\text{ ng g}^{-1}$ and $\text{nd}\text{--}0.02\text{ ng g}^{-1}$, respectively. Low concentrations for short-chain PFCAs in sediment samples are not surprising because short-chain PFCAs are relatively

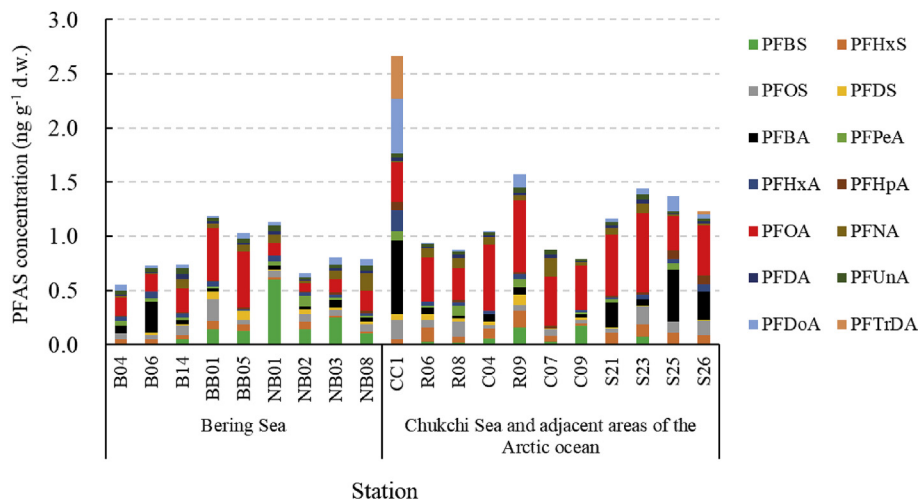


Fig. 2. Concentration of PFAS in surface sediments of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean.

hydrophilic compare to long-chain PFCAs (Yeung et al., 2009). High concentrations of long chain PFCAs was found in sediment samples from Korean rivers and lakes (Lam et al., 2014). The concentration of PFBS was 0.60 ng g^{-1} , with the highest concentration of PFBS at station NB01 in the Bering Sea. A similar PFAS pattern was reported in the sediment samples collected from Pearl River Estuary, South China where PFBS ($0.00\text{--}10.23 \text{ ng g}^{-1}$) was the dominant compound among the targeted PFAS, which may be due to their production and use as PFOS substitutes (Gao et al., 2015). The longer chain PFAS such as PFOS and PFDA were predominant in sediment samples of Korea (Naile et al., 2010).

Composition profiles of PFAS in surface sediments from the Bering, the Chukchi Sea and adjacent Arctic Ocean are shown in Fig. 3. The composition profiles differed between samples and with latitude. There was an increasing composition of \sum PFASs with decreasing latitude (towards south), whereas the FOSA exhibited the opposite relationship. The dominant PFAS compound in the sediments was PFOA, with a contribution of 7.39% to the total PFAS. PFOA was the highest component in shallow sites (stations BB01, BB05) from the continental shelf of the Bering Sea and stations C04, C07, C09, and S21 from the Arctic Ocean. Whereas low PFOA concentrations in deep sites (stations B04, B06) in the Bering Sea and stations S25 and S26 in the Chukchi and the Arctic Ocean were found. Other major components were PFBA (2.58%), PFBS (1.98%), and PFOS (1.67%).

3.2. Concentrations and compositions of OCPs

Fifteen type of Organochlorine pesticides were measured in surface sediment samples of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean (Fig. 4). The dominant OCPs in surface sediments of the Bering Sea was \sum HCH, followed by HCB, \sum DDT, \sum Endosulfane, and \sum Chlordane. The highest concentrations (d.w.) of OCPs was observed at stations BB05 (19.56 ng g^{-1}) and BB14 (15.84 ng g^{-1}) near the coast of the Eurasian continent (Table S8). The total OCP concentrations in surface sediments of the Chukchi Sea and adjacent Arctic Ocean ranged from 9.06 to 15.68 ng g^{-1} . The concentrations of OCPs in these areas followed the order: \sum DDTs (the sum of DDT, DDD, and DDE) > \sum HCH > HCB > \sum Endosulfan > \sum Chlordane.

The concentration ($4.67 \pm 1.64 \text{ ng g}^{-1}$) of the total DDT (\sum DDT: p,p' -DDT + p,p' -DDE + p,p' -DDD + o,p' -DDT) with range of $2.68\text{--}7.81 \text{ ng g}^{-1}$ in surface sediments of Chukchi Sea was found.

High concentrations of DDTs was observed at stations R06 (7.81 ng g^{-1}) and C07 (5.05 ng g^{-1}). \sum DDT concentrations were in the following order: Chukchi Sea and adjacent Arctic Ocean > Bering Sea. The average concentration of HCB in surface sediments of the Bering Sea was $4.06 \pm 3.27 \text{ ng g}^{-1}$. The highest concentration of HCB (6.95 ng g^{-1}) was found in station BB05 and the lowest concentrations of HCB (0.24 ng g^{-1}) was observed at station B06. The highest concentration of α -HCH (3.05 ng g^{-1}) in the sediment was found in the Chukchi Sea and adjacent Arctic Ocean (station S21). Concentration of α -HCH ($0.29\text{--}3.05 \text{ ng g}^{-1}$) in sediment of Chukchi Sea and adjacent Arctic Ocean were higher than that in the Bering Sea. The concentration of α and β -Endosulfan (1.13 ng g^{-1}) in the sediment from the Bering Sea was higher than the sediment (0.61 ng g^{-1}) from the Chukchi Sea and adjacent Arctic Ocean, and the concentration of α -endosulfan was slightly higher than that of β -endosulfan. Endosulfan is an insecticide that is still widely used in different part of the world including in circumpolar countries. α -endosulfan and its oxidation product, endosulfan sulfate are predominant chlorinated organics in Arctic abiotic environments (Muir and de Wit, 2010). Endosulfan is persistent in the environment with upper range of field-based half-lives >6 months in soil and sediments (α -, β -, and sulfate), with half-lives highly dependent on the dominant environmental conditions. An increasing trend in the concentration of α -endosulfan was observed from the Bering Sea to Bering Strait. The increasing trend of α -endosulfan was observed at station R08, C07, and S26 from the Chukchi Sea to the adjacent Arctic Ocean. No significant increasing trend of β -endosulfan was observed in the Bering Sea, the Chukchi Sea and the Arctic Ocean. Concentrations of \sum Chlordane in sediment samples varied between 0.15 and 1.11 ng g^{-1} with a average concentration of 0.62 ng g^{-1} , and the concentrations of *trans*-chlordane were higher in all surface sediment samples of the Bering Sea, Chukchi Sea and Arctic Ocean than that of *cis*-chlordane. In general, the concentrations of OCPs in surface sediments of the Chukchi Sea and adjacent Arctic Ocean were at a moderate level compared with the other regions in the worldwide (Text S2 and Table S9).

In the aquatic environment, the total organic carbon (TOC) in sediments was an important factor for controlling the distribution of OCP compounds. Generally, high total concentrations of OCPs are accompanied by the high TOC since OCPs are usually removed from the water column and adsorbed by the particulate matters due to their high affinity for organic matter (Mai et al., 2002).

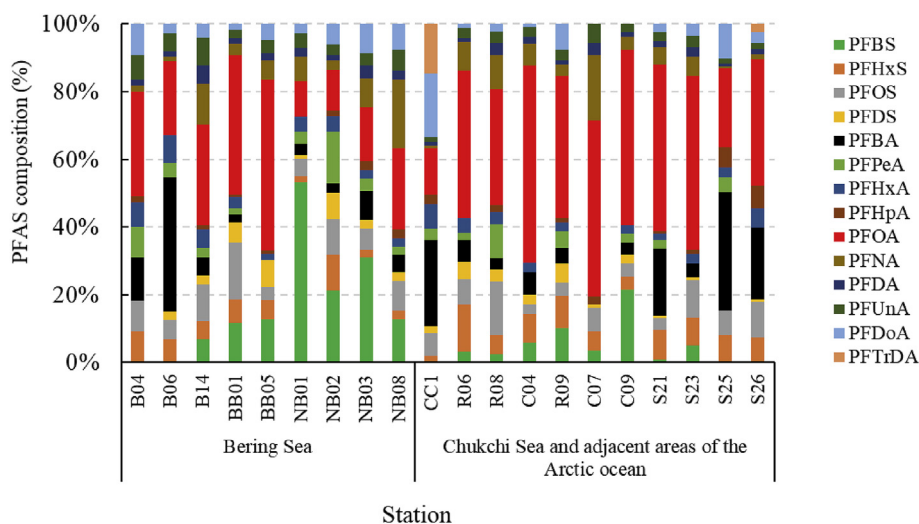


Fig. 3. Spatial distribution and composition of individual PFAS in surface sediments of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean.

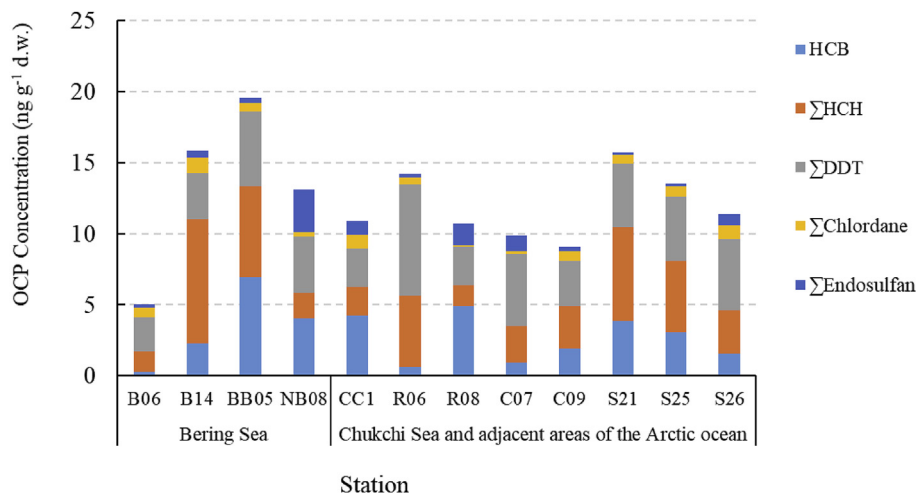


Fig. 4. Concentration profiles of OCPs in surface sediments of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean.

Normalization of nonpolar organic compounds to TOC content is valid only if the TOC content in the sediments is greater than 0.2%. At TOC concentrations less than 0.2%, other factors that influence partitioning of the sediment pore waters (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important (Di Toro et al., 1991).

In terms of the individual OCPs distributions (Fig. 5), it was found that β -HCH were predominant of total HCHs in the sediment samples from NB08, CC1, R08 and C09. Among four HCH isomers, β -HCH is more persistent and accumulates in sediment because of its

lowest vapor pressure. β -HCH is a known metabolite product of the biodegradation of γ -HCH and α -HCH in the sediments (Wu et al., 1997). Our results for β -HCH showed no significant trend in the Bering Sea, the Chukchi Sea, and the Arctic Ocean. However, a slightly decreasing trend was seen for γ -HCH isomer in the Chukchi Sea and the Arctic Ocean. As for δ -HCH, a decreasing trend was also observed in the Chukchi Sea and the Arctic Ocean with latitude. In the Bering Sea, a decreasing trend was seen in α -HCH. As shown in Fig. 5, the more dominant p, p'-DDD accounted for 31.81%, o, p'-DDE, p, p'-DDT, o, p'-DDD, and are the three other isomers of DDT that accounted for 24.45%, 15.62%, and 13.03% respectively. Whereas p, p'-DDE and o, p'-DDT accounted for only 8.93% and 6.17%. Concentrations of Σ DDT increased with the increasing north latitude.

3.3. Latitudinal trend of PFAS and OCPs

The Arctic Ocean is considered a sink for global pollution because of the flow of oceanic and atmospheric currents. It is a delicate ecosystem exposed by land-based sources of pollution particularly POPs and heavy metals (Lystsov, 2006). A increasing trend of PFAS from station B04 to BB01 of Bering Sea and S21 to S23 of Chukchi Seas was found in this study. Moreover, concentrations of PFOA elevated at station S21 and S23. During the last decades, main loadings of POPs to the Arctic Ocean occurred by atmospheric transport and air-water exchange, precipitation and riverine input, and migration through the north-flowing ocean currents (Li et al., 2004). A USSR/US investigation begun in 1984 in the Bering and Chukchi Seas to study the transport of agricultural chemicals such as pesticides and other persistent pollutants (Chernyak et al., 1995). The results showed that α -HCH concentrations ranged from 810 to 1220 $\mu\text{g L}^{-1}$ on the transect from the Sea of Japan to the Bering Sea, and a trend of increasing concentration with increasing latitude was observed ($r^2 = 0.88$). This trend for α -HCH concentration may reflect the effect of much colder surface water temperatures in the polar seas, because of the Henry's law constant of α -HCH decreases with the decreasing water temperature, thus, favoring deposition to the water phase. The concentration of α -HCH in surface sediments showed a general increasing trend with latitude such as in the Chukchi Sea and adjacent Arctic Ocean. α -HCH is more volatile and less water soluble than γ -HCH, therefore the high concentration level in the Arctic Ocean is due to the air-water exchange of α -HCH through the cold condensation effect (Cai et al., 2010). For α -HCH, long-range transport is operated throughout the transport

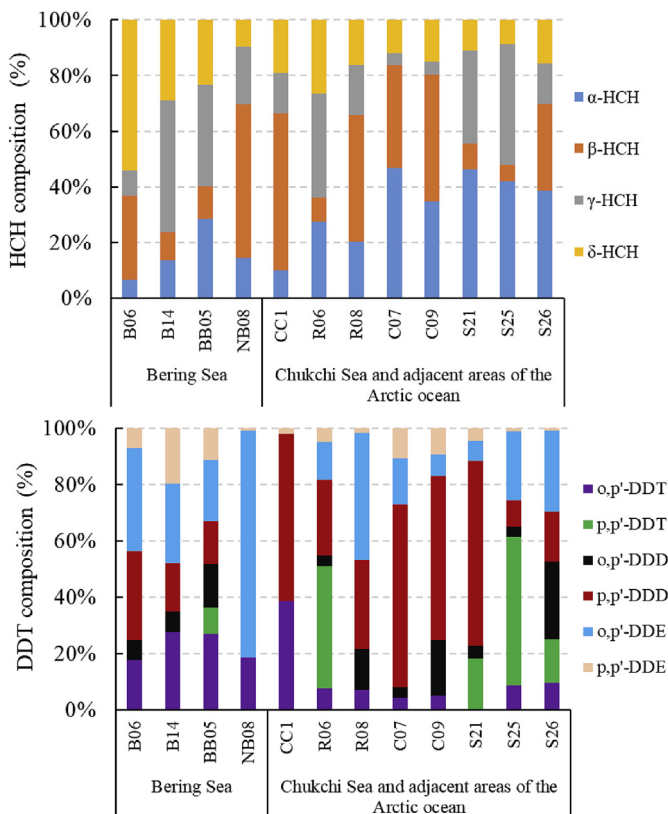


Fig. 5. Compositions of HCH and DDT in surface sediments of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean.

route from the emission region to the Arctic. Once the atmospheric γ -HCH was depleted through dry and/or wet deposition, the special thermodynamic properties of γ -HCH made it impossible for the LRT to enter the Arctic Ocean. The geographical distributions of OCPs showed different patterns according to their physicochemical properties. The concentrations of HCHs and HCB showed rather uniform distribution, pointing their transportable nature in long-range atmospheric transport. For semi-volatile compounds that partition HCH strongly into cold water, an inevitable loading of Arctic aquatic reservoirs have been seen. Strong HCH emission reductions have been rapidly followed by reduced atmospheric burdens with the result that the major reservoir and transport agent has become the ocean (Macdonald et al., 2000). In the Arctic, it will take decades for the upper ocean to clear HCH. In this study, the concentration of HCB is higher in the Bering Sea than the Chukchi Sea and adjacent Arctic Ocean which indicate an increasing trend with northward latitude. DDTs was predicted to be less transportable through the atmosphere due to the decreasing trends of residue levels in sediments from south to north (Iwata et al., 1994). The increasing trend of DDTs was observed in surface sediments from south to north. The decreasing trends of both chlordane and endosulfan were observed in northward latitude. Overall, PFAS and OCPs had similar distribution trend which increased from 54.59° N to 62.54° N of the Bering Sea and 71.81° N to 71.93° N of the Chukchi Sea.

3.4. Sources of PFAS and OCPs

3.4.1. Sources of PFAS

Precursor PFAS are volatile and they can be transported via the atmosphere. Precursor PFAS can be degraded to PFCAs and PFSAs, then accumulated via wet and dry deposition. Elevated concentrations were observed in snow samples, indicating that atmospheric deposition is an important source of PFAS (Yeung et al., 2017). Oceanic current is the second pathway to transport PFAS from contaminated coastal areas to the Arctic marine environment. PFAS were only detectable above 150 m depth in the polar mixed layer (PML) and halocline. PFOS concentrations declined rapidly after 2002 in the surface mixed layer (half-life: 1–2 years) but are still increasing below 1000 m depth. Results pointed out that in 2015, 60% of the cumulative PFOS that were discharged from North America and Europe are still present in the North Atlantic and 30% had entered the Arctic Ocean. Most of the remaining fraction was transported to the South Atlantic. The lifetime of PFOS in the surface ocean is less than 5 years due to rapid penetration into deeper waters where it persists for decades or longer before being transported to other basins (Zhang et al., 2017). The concentration of PFAS decreases at stations B04, B06 and B14 in the Bering Sea. However, increasing trend of PFAS was observed at station BB01, BB05, NB01 of the Bering Sea. This can be explained by the impact of the industrial regions, such as Japan and China and the Alaskan current, which causes runoff from the urbanized and industrialized areas of Northern American regions to move toward the Bering Sea (Cai et al., 2012). In the Chukchi Sea and adjacent Arctic Ocean, the same trend of PFAS concentration was observed at stations R06, R08, C04, R09, C07, C09, S21, S23, S25, and S26 which can be caused by the dilution effect from the Bering Sea, ice melting, surface ocean currents and river runoff. The concentration of Σ PFAS at station CC1 was higher than the station NB08 in the Bering Sea. However, the composition of PFAS was the same between stations NB08 and CC1. This indicates that stations NB08 and CC1 have the same sources and pathways of PFAS that were dominated by the oceanic currents in the Arctic Ocean.

3.4.2. Sources of DDTs

The DDTs and their isomers can be used to evaluate the occurrence of the recent OCP inputs (Hong et al., 2008). Normally, DDT can be biodegraded to DDD because of the reductive dechlorination process by the microbe in anaerobic culture (Yu et al., 2011) and transfer to DDE in aerobic conditions. Ratios of (DDE + DDD)/DDTs and DDD/DDE show their sources and they can also be used to estimate if there is new DDT. We could find the input sources, degradation status, and reduction-oxidation conditions by using (DDDs + DDEs)/DDTs and DDD/DDE ratios.

The ratio of (DDDs + DDEs)/DDTs (>0.5) has often been used to identify aged or weathered technical DDT in the environment (Doong et al., 2002; Zhou et al., 2006). Technical DDT generally, contain p, p' -DDT (75%), o, p' -DDT (15%), and p, p' -DDE (5%) and less o, p' -DDE, p, p' -DDD, and o, p' -DDD. A ratio of (DDDs + DDEs)/DDTs of more than 0.5 indicates long term biotransformation of DDT to DDE and DDD, a ratio of less than 0.5 may indicate recent input of DDT (Hitch and Day, 1992; Zhang et al., 2002). The ratio of (DDDs + DDEs)/DDTs in the Bering Sea, Chukchi Sea and the Arctic Ocean ranged from 0.63 to 21.95 in surface sediments. This indicated that the DDT compounds are mainly obtained from early residues or long-term weathering residues after pesticides were applied and no new DDTs were added. DDTs in surface sediments increased in the Chukchi Sea with the latitude indicating the long-range atmospheric transport. The ratio of o,p'-DDT/p,p'-DDT can also be used to distinguish DDT pollution caused by technical DDT of 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). In this study, a range of 0.16–0.62, was determined in surface sediment samples of the Chukchi Sea and adjacent Arctic Ocean (R06, S21, S25 and S26), indicating that the technical-DDT rather than dicofol was the predominant source of DDT. High percentage of o,p'-DDT from all the Bering Sea samples indicated that dicofol was a dominant source of DDT.

Under anaerobic condition, DDT is mainly degraded into DDD; under aerobic condition, DDT is mainly degraded into DDE. Therefore, DDT content is likely maintained at a high level if DDT is continuously applied; without additional DDT, DDT content is possibly reduced. The corresponding degradation product will likely increase in a continuous pattern. Thus, the ratios of DDD/DDE can be used to trace the degrading environment of DDTs. The ratios of DDD/DDE ranged between 0.51 and 0.99 from stations B06, B14, BB05, S25 and R08, indicating the aerobic degradation of p, p' -DDT. On the other hand, the station of CC1, R06, C07, C09, S21 and S26 recorded the opposite trend where DDD/DDE ratios ranged from 1.67 to 26.6, which indicated the anoxic condition (Kucuksezgin and Gonul, 2012). This difference was associated with geographic locations. Sediment collection stations in the Chukchi Sea are located at a northern latitude, and covered throughout the year, thereby creating an anaerobic environment. Other sediment sample collection stations are located on the Bering Sea at a low latitude and surface sediments are exposed to air for longer periods of time, thereby creating an aerobic environment.

3.4.3. Sources of HCHs

Ratios of α -HCH/ γ -HCH can be used as indicators of contaminant source age. Technical HCH was produced and widely used as an insecticide in different countries. Generally, technical HCH contain isomers in the following percentages: 60–70% of α -HCH, 5–12% of β -HCH, 10–12% of δ -HCH and 6–10% of γ -HCH, respectively (Willett et al., 1998), with the ratio of α/δ -HCH between 3 and 7. Among the isomers of HCHs, β -HCH was the most stable and relatively resistant to microbial degradation. The α -HCH/ γ -HCH ratio in the range of 0.2–1 indicates pollution attributed to lindane.

In the Bering Sea, α : γ ranged from 0.28 to 0.71, indicating that the input source was by lindane. However, the values of α -HCH/ γ -HCH at the stations R08, C07, C09, S21 and S26 of Chukchi Sea were greater than 1, indicating that these stations were polluted by industrial HCH. The value of α -HCH/ γ -HCH was less than 1 at S25 and C09 stations of Chukchi Sea, indicating the presence of a possible emission source of lindane nearby this region. A comparison with the former results was shown in Table S10, the α / γ ratio of HCHs in the Bering Sea was less than the data of 1988, 1990, and 1999 (Iwata et al., 1993; Rice and Shigaev, 1997; Yao et al., 2002). Whereas the α : γ ratio of HCHs in the Chukchi Sea was similar to those of 1988 and 1999 (Jantunen and Bidleman, 1995; Yao et al., 2002), but less than the data of the 1993 survey. The observed low α : γ ratio of HCHs in the Bering Sea indicated that OCPs were transported from the low latitude and also the presence of a possible source of lindane. Lindane is expected to continue to be transported to the North Pole from Canada, France, and China.

3.5. Ecological risks

Australian guideline values for maintaining ecosystem health are not available for PFAS in marine sediment. However, a system of classification for the environmental quality of marine sediments contaminated with PFOS has been developed in Norway (PFOA guideline levels are not available). Although, there are currently no provincial or federal SQG values for individual or total PFAS compounds. The Norway sediment quality guideline has included PFOS in their updated effects-based environmental quality guidelines for marine sediment (Bakke et al., 2010) and although their classification system varies from the Ministry of Environment and Climate Change (MOECC) or Canadian Council of Ministers of the Environment (CCME) framework, they identify PFOS concentrations less than 220 ng g⁻¹ in marine sediment as it is unlikely to have toxic effects. Canada has developed a proposed risk management approach for the selection of PFAS (Environment Canada, 2010) and in 2009 PFOS was classified as a persistent organic pollutant by the Stockholm Protocol. The concentrations of PFOS (0.04–0.2 ng g⁻¹) and (0.03–0.18 ng g⁻¹) in surface sediments of the Bering Sea and Chukchi Sea, respectively are well below the Norwegian guidelines (0.17–220 ng g⁻¹).

Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for DDT, DDD, and DDE in freshwater and marine sediments were developed according to the procedures described in CCME (1995) (Table S11). These values were developed using a modification of the National Status and Trends Program (NSTP) approach, with the exception of those values for DDT in freshwater sediments. The database developed by Long and Macdonald, (1990) to derive SQGs for marine and estuarine sediments has been updated. The PEL represents the lower limit of the range of chemical concentrations that are usually or always associated with adverse biological effects. The national SQG and the PEL are used to define three ranges of chemical concentrations for a particular chemical, those that are rarely (<SQG), occasionally (between the SQG and the PEL), and frequently (>PEL) associated with adverse biological effects (MacDonald et al., 1992; Long et al., 1995). The SQG is the concentration below which biological effects are not expected, while the PEL is a level above which adverse effects are likely to occur (Jiao et al., 2009). The potential risk of organochlorine compounds in the sediments from the Bering Sea was evaluated. The comparison of OCP isomers with ISQG or PEL at every station was studied in surface sediments of the Bering Sea (Table S11). It was seen that concentrations of γ -HCH at stations B14 and BB05 are higher than the ISQG. The comparison of \sum HCH and PEL also showed that the HCH in the studied area could have an ecological risk. It is considered that adverse effects of γ -HCH in the

sediments of the studied area are expected to occur. The isomer p,p'-DDD at station CC1 exceed the ISQG, so adverse effects produced by DDT isomer are expected to occur. Whereas in other sampling stations of the Bering Sea, DDT and its isomers (p,p'-DDE, p,p'-DDT) did not exceed the ISQG. Therefore, the adverse effects caused by DDT and other organochlorine pesticide isomers were not expected to occur. In the Chukchi Sea and the adjacent area of the Arctic Ocean, it was observed that the concentrations of γ -HCH at stations R06, S21, and S25 were higher than the ISQG. The comparison of \sum HCH and PEL also showed that the HCH in the studied area could have an ecological risk. The p,p'-DDT isomer does exceed the ISQG at stations R06 and S25 and the adverse effect were expected to occur. Whereas in other sampling stations, DDT and its isomers (p,p'-DDE, p,p'-DDT) did not exceed the ISQG. The ISQG value for \sum Chlordane was not exceeded at any sample locations of the Bering Sea, the Chukchi Sea, and the adjacent Arctic.

4. Conclusion

The concentrations of PFAS in surface sediments of the Bering Sea were lower than the Chukchi Sea and the adjacent areas of the Arctic Ocean. PFOA was predominant among the PFAS in the sediment of the Bering Sea, followed by PFBS, and PFOS. However, in the Chukchi Sea and adjacent Arctic Ocean, PFOA was the predominant among the PFAS followed by PFBA and PFOS, indicating that there might be different sources of PFAS in the sediment of the Chukchi Seas and adjacent Arctic Ocean. The dominant OCPs in surface sediments of the Bering Sea was \sum HCH, followed by HCB, \sum DDT, \sum Endosulfane, and \sum Chlordane. γ -HCH was the most abundant among the four isomers in all the sampling stations of the Bering Sea, followed by δ -HCH, β -HCH, and α -HCH. The possible sources of the HCHs in the sediment of the Bering Sea were mainly from the historical usage of lindane. The main isomer of DDT was o, p'-DDE. It can be suggested from the high percentage of o,p'-DDE that the source of DDTs was the historical usage/input in the area. The concentrations of \sum DDT increased with the increasing latitude. The concentrations of OCPs were orders of magnitude greater than that of PFAS in this study. The concentrations of OCPs and PFAS were at a relatively higher level in the Chukchi Sea and adjacent Arctic Ocean as compared to the Bering Sea. However, the total concentration of OCPs was high in comparison with those reported in Arctic Ocean and lower than the other coastal environment around the world. It was seen that the concentration of γ -HCH above the ISQG value could have an ecological risk. The isomer p,p'-DDT exceed the ISQG, so the adverse effects produced by DDT isomer were expected to occur in the Chukchi Sea and Arctic Ocean.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.06.219>.

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