Organophosphate Esters in the Canadian Arctic Ocean


ABSTRACT: Eleven organophosphate esters (OPEs) were detected in surface water and sediment samples from yearly sampling (2013–2018) in the Canadian Arctic. In water samples, \( \sum \) chlorinated-OPEs (Cl-OPEs) dominated with median concentrations of 9.9 ng L\(^{-1}\). In sediment samples, \( \sum \) Cl-OPEs and \( \sum \) nonchlorinated-OPEs had similar median concentrations of 4.5 and 2.5 ng g\(^{-1}\), respectively. Eastern Hudson Bay appeared to be affected by local sources. High concentrations of OPEs in samples from the Mackenzie River plume suggest riverine discharge as an OPE source to the Canadian Arctic. The prevalence of OPEs at other sites is consistent with long-range transport. The OPE inventory of the Canadian Arctic Ocean representative of years 2013–2018 was estimated at 450–16,000 tonnes with a median \( \sum \) OPE mass of 4100 tonnes with >99% of the OPE inventory estimated to be in the water column. These results highlight the importance of OPEs as water-based Arctic contaminants subject to long-range transport and local sources. The high OPE inventory in the water column of the Canadian Arctic Ocean points to the need for international regulatory mechanisms for persistent and mobile organic contaminants (PMOCs) that are not covered by the risk assessment criteria of the Stockholm Convention.

1. INTRODUCTION
Organophosphate esters (OPEs) are a class of high production volume chemicals with a wide range of physical–chemical properties and applications. Chlorinated OPEs (Cl-OPEs) are commonly used as flame retardants, whereas nonhalogenated OPEs (non-Cl-OPEs) are mostly used as plasticizers and antioxidant plastic additives.

Since the international bans and phase-outs of polybrominated diphenyl ethers (PBDEs) in the 2000s, the market share of OPE flame retardants has increased considerably. In 2016, OPEs had reached 18% of the global market share of flame retardants with a consumption of around 500,000 tonnes per year. Initially, OPEs were marketed as a potential "environmentally friendly" alternative for PBDEs due to their supposed low persistence in the environment, low bioaccumulation potential, and presumed lack of long-range transport potential (LRTP). However, these assumptions have come under increasing scrutiny due to the frequently detected and high environmental concentrations of OPEs, including in remote environments such as the Arctic. Following reports of concentrations exceeding those of PBDEs in Arctic air, water, and sediments, Sühring et al. investigated long-range transport mechanisms for OPEs. They found that non-Cl-OPEs were likely transported into the Canadian Arctic through air, whereas most Cl-OPEs were likely transported through water, including potential riverine transport. However, available reports of OPEs in the Arctic are predominantly for a single medium only, which made a comprehensive assessment of the transport pathways difficult.

Rodgers et al. argued that, based on their physical–chemical properties (e.g., very low Henry’s law constant), OPEs are expected to have high water concentrations and especially for Cl-OPEs; once in water, Cl-OPEs seem to be resistant to degradation. They concluded that OPEs, and specifically Cl-OPEs, should be characterized as persistent and mobile organic compounds (PMOCs). PMOCs have recently come into scientific as well as regulatory focus because the current regulatory frameworks based on persistence, bioaccumulation potential, and toxicity (PBT) can underestimate the environmental risk of persistent and toxic chemicals that are not necessarily bioaccumulative but are “mobile” in the aquatic environment, including mobility into groundwater.

An effective global management framework for PMOCs is lacking, even though they present a recognized risk for drinking water resources.

Regulatory efforts that include substances that fall in the PMOC category are currently predominantly aimed at human health protection (e.g., in the case of pharmaceuticals or
2. MATERIALS AND METHODS

Surface water samples (n = 69) and surface marine benthic sediments (n = 49) were collected opportunistically across the Canadian Archipelago at 51 sites (water) and 40 sites (sediment) as part of yearly ArcticNet expeditions in collaboration with the Northern Contaminants Program, on board the CCGS Amundsen. Water samples were collected in 2013–2018, while sediments were collected in 2014, 2015, and 2017 (Figure S1). All solvents and reagents were of chromatographic quality, and all glassware including sampling bottles, sodium sulfate, and thimbles were baked at 400 °C overnight before use.

Water samples (4-1 L) were collected by surface grabs or from a Rosette water sampler. The samples were stored in glass bottles, refrigerated, and shipped back to the lab for processing and analysis. Sediments were collected using a stainless steel Reineck-type spade-foot corer with 0.25 m² surface area that penetrates ~40 cm. Sediment samples were collected by scraping the top 1–5 cm or from push core subsamplers. Samples were stored in glass jars with Teflon lids at −20 °C until analysis.

Table S1 lists all OPE analytes, acronyms, CAS numbers, solubility, and log Kow. All water samples were spiked with three OPE-labeled surrogates (Table S2) and were extracted by liquid–liquid extraction using dichloromethane (DCM).

The sediment was homogenized, and approximately ~30 g of wet weight sediment was weighed out. It was spiked with OPE-labeled surrogates, dried by mixing with sodium sulfate, and then stored in glass jars with baked sodium sulfate in glass jars overnight.

Volume reduction of both water and sediment extracts was done by rotary evaporation under a gentle stream of nitrogen and then solvent-exchanged into iso-octane for a final volume of ~1.0 mL. Water extracts did not undergo cleanup, whereas sediment extracts were passed through a Florisil column (Supelco, Supelclean, ENV1-Florisil SPE) to remove organic matter. Mirex was added to each sample as an internal standard for volume adjustment and as a time reference standard. Native mirex was checked in random samples, and none was found.

Percent moisture was determined in the sediment samples by comparing the weight of ~20 g of wet sediment and of dry sediment after drying it at ~100 °C overnight. The organic carbon content of selected sediment samples taken in 2014 and 2017 was quantified based on loss of ignition. The dried sediment was fired at 800 °C in a muffle furnace until a constant weight was achieved. The organic carbon was low with a median of 8.1%, ranging from 0.7 to 14%, with one high value at 34%.

Chemical analysis was performed by gas chromatography mass spectrometry on an Agilent 6890 GC-5973/75 MSD using methods as described in SI (Section 2, Table S2). Table S3 lists target/qualifier ions and limits of detection (LODs) and method detection limits (MDL) for OPEs in water and sediment.

2.1. QA/QC. Water blanks consisted of a clean 4-L bottle shipped to the field, opened during sampling collection, recapped, and returned to the lab for extraction and analysis in the same manner as the samples. Sediment blanks were obtained by placing ~30 g of baked sodium sulfate in glass jars used for sediment samples, shipping it to the field, opening it on the deck during sampling, and following the same sample extraction and analytical methods. For a sample value to be designated as significantly higher than the blank, the sample value must have exceeded the average of the field blanks plus three times the standard deviation of these blanks. Samples were field-blank-corrected.

The recovery of the labeled OPEs in both water and sediment samples ranged from 58 to 119%, and the samples were recovery-corrected (Table S2). Since not all OPE compounds have isotopically labeled analogues, spikes of all native compounds were also done for both water and sediment samples (n = 3 of each); recoveries ranged from 69 to 107%.

2.2. Statistical Analysis. Statistical analysis was performed using RStudio (version 1.1.456) and Microsoft Excel, 2016. Spatial analysis was performed using Ocean Data View (version 5.1.2). Pearson correlations and Student’s t-tests were performed for nearly normally distributed data sets. Values below the MDL were set to “0” for summary statistic calculations unless specifically stated as “based on detectable concentrations” in which case only detected concentrations were used in the calculation.

2.3. Inventory Calculation. Using the weighted-average gridding interpolation method included in Ocean Data View, \(\sum_{\text{Cl-OPe}}\) and \(\sum_{\text{non-Cl-OPe}}\) concentrations in water [ng L\(^{-1}\)] and sediments [ng g\(^{-1}\)] were calculated for the Canadian Arctic Ocean (SI Section 3). The product of the interpolated concentrations and the volume of sediment and water were used to estimate an OPE mass inventory for water and sediments, respectively, across the Canadian Arctic Ocean that is representative of a point in time during the span 2013–2018 (over which concentrations were measured). Given the uncertainties in the dataset, different scenarios were explored using a Monte Carlo uncertainty analysis (SI Section 4).

The following data were used for the inventory calculations:

- Area of the Canadian Arctic Continental shelf: \(1.2 \times 10^6\) km\(^2\) = \(1.2 \times 10^{12}\) m\(^2\)
- Average depth of the Canadian Arctic Ocean: 1038 m
- Total volume of the Canadian Arctic Ocean: \(1.2 \times 10^{15}\) m\(^3\)
- Water column inventory: \(\sum_{\text{Cl-OPe}}\) and \(\sum_{\text{non-Cl-OPe}}\) concentrations in water [ng L\(^{-1}\)] and sediments [ng g\(^{-1}\)] were calculated for the Canadian Arctic Ocean (SI Section 3).

2.3.1. Water Column Inventory. The scenarios were based on the measured depth of the epipelagic zone (EZ) at the sampling stations that ranged from 8 to 45 m. McDonough et al.\(^10\) reported OPE concentrations from deep water moorings in the Arctic Ocean. They found OPEs throughout the water column (including in depths >2000 m). On average, concentrations for OPEs in deep water samples were ~10-fold lower than in surface samples.

Based on these observations, we used the following scenarios for estimating the inventory of OPEs in the water column of the Canadian Arctic Ocean:

1. Minimum: Mixing depth = minimum observed EZ depth (8 m) (OPEs were assumed to be only present in the first 8 m of the water column)
2. Average: Mixing depth = maximum observed EZ depth (45 m) (OPEs were assumed to be only in the first 45 m of the water column)

3. Worst-case: Mixing depth = maximum observed EZ depth (45 m). For the remainder of the water column, OPE concentrations were assumed to be 1/10 of the average observed CI-OPE and non-CI-OPE concentrations at the surface (as reported by McDonough et al.10)

2.3.2. Sediment Inventory. The following assumptions were made:
- A mixing depth of 2 cm (for comparability with Ma et al.)
- The average density of the sediment of 1.7 g cm\(^{-3}\).

2.3.3. Monte Carlo Uncertainty Analysis. The analysis was performed for \(\sum\text{CI-OPEs}\) and \(\sum\text{non-CI-OPEs}\) in water and sediments by multiplying each estimate in the respective inventories 200 times with a pseudorandom value between 0.1 and 10 to account for uncertainties in the extrapolated concentrations. A detailed description of the calculation methods for the inventory and the Monte Carlo uncertainty analysis is presented in SI Section 4.

3. RESULTS AND DISCUSSION

3.1. OPE Concentrations and Profiles in Water. Eight OPEs were detected in water samples from the Canadian Arctic Ocean: the three CI-OPEs, that is, tris(2-chloroethyl)-phosphate (TCEP), tris(2-chloropropyl)phosphate (\(\sum\text{TCP,}\) sum of three isomers), and tris(1,3-dichloro-2-propyl)-phosphate (TDCCP) and five non-CI-OPEs, namely, triphenyl phosphate (TPhP), tri-n-butyl phosphate (TnBP), ethylhexyldiphenyl phosphate (EHDPP), tris(2-isopropylphenyl)phosphate (T2IPP), and tris(2-ethylhexyl)phosphate (TEHP) (Figure 1). TEHP was only detected in water samples collected close to the colony of Arctic seabirds in Hudson Bay and was therefore excluded from the \(\sum\text{non-CI-OPE}\) parameter. This is discussed below.

Concentrations of \(\sum\text{OPEs}\) had a median concentration of 11 ng L\(^{-1}\) and ranged from 0.02 to 306 ng L\(^{-1}\). \(\sum\text{Cl-OPEs}\) had the highest contribution to the \(\sum\text{OPEs}\) with a median concentration of 9.9 ng L\(^{-1}\) (0.02–300 ng L\(^{-1}\)) and 100% detection frequency. \(\sum\text{non-CI-OPEs}\) were detected at concentrations ranging from < LOD to 67 ng L\(^{-1}\) (median: 1.3 ng L\(^{-1}\)) with a detection frequency of 81% (Table S4, Figure 1).

Of the CI-OPEs, TCEP had the highest water concentrations, followed by \(\sum\text{TCP, TDCiPP}\) (Figure 1). The only CI-OPE with 100% detection frequency was \(\sum\text{TCEP}\), followed by TCEP with 94% detection frequency and TDCiPP with 85% detection frequency (Table S4).

In water, non-CI-OPEs were generally detected in lower concentrations than CI-OPEs (Figures 1 and 2) as well as at lower detection frequencies (Table S4). TPhP and TEHP (only at the seabird colony) were exceptions, with concentrations similar to those of the individual CI-OPEs, but with lower detection frequencies (Figure 1, Table S4). Ranked by their median concentration, the following four non-CI-OPEs were detected in water samples from the Canadian Arctic Ocean: TEHP (only at the seabird colony) > TPhP > TnBP > EHDPP > T2iPPP. None of the non-CI-OPEs had 100% detection frequency in water samples, and only TPhP, TnBP, and EHDPP were detectable in >50% of the water samples (Table S4).

The observed OPE concentrations were about an order of magnitude higher than OPE measurements in Fram Strait10,22 but similar to other OPE measurements in surface sea water from the Canadian Arctic, with mean CI-OPE concentrations between LOD and 4.4 ng L\(^{-1}\) in Barrow Strait.10

OPE concentrations in water samples had widely varying concentrations across the sampling area with no apparent correlation with longitude or latitude (Pearson \(r < 0.5\)) (Table S5). Nevertheless, interesting local spatial patterns were identified for CI-OPEs and non-CI-OPEs. Eastern Hudson Bay had notably elevated concentrations compared to the average OPE concentrations in Hudson Bay for TCEP, TCIPP, TDCiPP, and TnBP, respectively (Figures S2–S4). Elevated concentrations of \(\sum\text{TCP, TDCiPP}\) were also observed within the Mackenzie River plume (Figures S3 and S4), TnBP at Resolute Bay (Figure S6), and TPhP and T2iPPP (only detected in one sample) north of Banks Island (Figures S5 and S8). Seven of 51 sampling locations showed \(\sum\text{non-CI-OPE concentrations} > \sum\text{CI-OPE concentrations}\) (Figure 2). The high \(\sum\text{non-CI-OPE concentrations}\) at these sites were driven entirely by high TPhP concentrations, apart from the sampling location near a seabird colony in Hudson Bay that is discussed below. The locally elevated concentrations for TPhP and other individual OPEs such as TnBP with locally elevated concentrations could indicate the presence of local sources (e.g., airport nearby Resolute Bay for TnBP) or of local environmental conditions (e.g., residence time of the water, local currents, turbidity, organic carbon content in the water, etc.) that could lead to relatively elevated levels of these compounds.
3.1. OPE Concentrations and Patterns Close to the Seabird Colony in Northern Hudson Bay. An interesting case of an apparently locally distinct OPE concentration pattern was observed in water sampled close to a long term (30+ years), a larger breeding colony of ~30,000 pairs of thick-billed murres (Uria lomvia) in northern Hudson Bay (Table S6, n = 6 samples). These seabirds are migrating seasonally to northern Labrador.

At most other sampling stations, CI-OPEs contributed >80% of the OPE concentrations and non-CI-OPEs were dominated by TPhP. However, close to the colony, TEHP had the highest median concentrations among the OPEs with 6.6 (0.047–13) ng L\(^{-1}\) and 100% detection frequency, despite being < LOD in all other water samples from across the Canadian Arctic. TPhP and TnP were also had high average concentrations and high detection frequencies nearby the seabird colony in comparison to water samples from other areas in the Canadian Arctic, but the median concentrations were not significantly different from other areas (Figure 1, Table S6).

CI-OPEs, on the other hand, were detected at lower average concentrations compared to water samples that were taken at distance from the seabird colony. TCEP was only detected in two water samples with concentrations of 1.2 and 5.1 ng L\(^{-1}\) compared to 94% detection frequency with a median concentration of 5.5 ng L\(^{-1}\) in other water samples (Figure 2, Table S6).

Information on OPE concentrations in avian species is limited. In vitro metabolism studies have indicated that OPEs are metabolized rapidly and that non-CI-OPEs have faster rates of metabolism than CI-OPEs.\(^\text{25,24}\) The high contributions of non-CI-OPEs to OPEs in water samples from the seabird colony compared to the majority of water samples sampled at other locations were consistent with OPE patterns observed in other marine avian species. Graeves and Letcher\(^\text{25}\) reported higher non-CI-OPE concentrations compared to CI-OPE concentrations in lipid sampled from Herring Gulls (Larus argentatus) in the Great Lakes, whereas CI-OPE and non-CI-OPE concentrations were similar in Herring Gull muscle tissue and eggs.

Considering the expected fast metabolism of non-CI-OPEs from birds, the observed high contributions of non-CI-OPEs close to the seabird colony indicate that the seabirds are continually exposed to TPhP, TEHP, and TnBP, the sources of which are not evident, especially for TEHP. One source might be microplastics as Provencher et al.\(^\text{26}\) found indications that Northern Fulmar (Fulmarus glacialis) acted as vectors for microplastic contamination around their colonies in the Canadian Arctic from guano that contained microplastics near the breeding colonies. Microplastics could act as carriers for OPEs and “shield” them from degradation. However, this explanation does not account for the pattern of contamination observed. What can be deduced is that the 30,000 pairs of thick-billed murres bioaccumulate OPEs from prey in their foraging area that extends ~50 km from the colony and eliminate these OPEs in guano deposited in the very restricted geographic area of their colony. As such, our data suggest that the seabirds act as “biological concentrators” of OPEs, as has been observed for other species with respect to nutrients and contaminants.\(^\text{27}\) The prevalence of TEHP and other non-CI-OPEs may be related to lower rates of metabolism relative to CI-OPEs, but the ultimate source of TEHP remains an open question.

3.2. OPE Concentrations and Profiles in Sediments. Ten OPEs were detected in sediment samples from across the Canadian Arctic (Table S7). Four CI-OPEs, namely, TCEP, \(\Sigma\)TCP, TDCiPP, and tris-cresyl phosphate (TCP, the sum of three isomers) and six non-CI-OPEs, namely, TPhP, TnP, EHDPP, TEHP, tris(2-butoxyethyl) phosphate (TBOEP), and triisopropyl phosphate (TPrP) (Figure 3). Of the CI-OPEs, TCEP had the highest concentrations, followed by \(\Sigma\)TCP, TDCiPP, and TCP (Figure 3). The ranking of non-CI-OPEs by their median concentration was TPhP > TnP > EHDPP. None of the non-CI-OPEs had 100% detection frequency in sediment samples, and only TPhP, TnP, and EHDPP were detectable in >50% of the sediment samples (Table S7).
Concentrations of ∑_{10} OPEs in sediments ranged from 0.12 to 57 ng g\(^{-1}\) (median: 8.3 ng g\(^{-1}\)). ∑_{4} Cl-OPEs and ∑_{6} non-Cl-OPEs contributed almost equally to the ∑_{10} OPE concentrations with a median concentration of 4.5 ng g\(^{-1}\) (n.d. – 30 ng g\(^{-1}\)) and a detection frequency of 94% for ∑_{4} Cl-OPEs and a median concentration of 2.5 ng g\(^{-1}\) (n.d. to 39 ng g\(^{-1}\)) and a detection frequency of 96% for ∑_{6} non-Cl-OPEs (Figure 3, Table S7).

Similar to the observed OPE patterns in the water column, neither ∑_{6} non-Cl-OPEs nor ∑_{4} Cl-OPEs were correlated with longitude or latitude (Pearson \(r < 0.5\)) (Table S8). Furthermore, none of the detected OPEs were significantly correlated with the organic carbon content of the sediment (Table S8).

Only Cl-OPEs had elevated concentrations in the Mackenzie River plume water, whereas all detected OPEs, except TPrP, had elevated concentrations in Mackenzie River plume sediments (Beaufort Sea) compared to other sampling stations (Figures 4 and S9–S17). TnBP concentrations were not elevated in sediments sampled close to Resolute Bay, unlike water concentrations (Figures S6 and S14). Instead, stations close to Resolute Bay were the only sediment sampling stations at which TPrP could be detected (Figure S17).

Sediment concentrations were up to an order of magnitude higher than those reported by Ma et al.\(^{7}\) from the Central Arctic Ocean, Chukchi Sea, and Bering Strait. Concentrations of Cl-OPEs and TPhP in sediments were in the same order of magnitude as those in two fjords on Svalbard with suspected pollution point sources, with two exceptions for TnBP and EHDPP that were higher in the Canadian Arctic.\(^{28}\)

The high concentrations observed in this study compared to previous studies of Arctic sediments were driven by the high concentrations observed in the Mackenzie River plume. Sediment concentrations in the Mackenzie River plume of all OPEs, apart from TPrP, were significantly higher (Mann–Whitney–U test, \(p < 0.05\)) than sediment concentrations from sampling stations outside the plume (Figures S9–S17). The Mackenzie River has previously been identified as a source of methylsiloxanes and polycyclic aromatic hydrocarbons in sediments.\(^{25,30}\) as well as for hexachlorocyclohexane in water.\(^{31}\)

### 3.3. Transport Pathways for OPEs into the Canadian Arctic

Previous research suggested that Cl-OPEs are PMOC substances where mobility is conferred by waterborne transport.\(^{6,10,12,13,32}\) Furthermore, Sühring et al.\(^{6,12}\) hypothesized that rivers are important transport vectors for Cl-OPEs into the Canadian Arctic.

![Figure 3](https://dx.doi.org/10.1021/acs.est.0c04422)

**Figure 3.** Concentrations (ng g\(^{-1}\)) of OPEs in sediment samples from the Canadian Arctic. The black horizontal line inside each box represents the median based on detected concentrations; the boxes represent the 25th and 75th percentiles of concentrations above the LOD; the black vertical lines mark the 95% confidence interval; and the dots represent outliers based on the 95% confidence interval. OPEs with less than 50% detection frequency have been marked with a blue cross.

![Figure 4](https://dx.doi.org/10.1021/acs.est.0c04422)

**Figure 4.** Spatial distribution and concentrations [ng L\(^{-1}\)] of ∑_{4} Cl-OPEs (green) and ∑_{6} non-Cl-OPEs (blue) in sediments across the Canadian Arctic. The green dots indicate the individual sediment sampling locations. Basemap: ESRI National Geographic, EPSG:3857, WGS 84/Pseudo-Mercator, Projected.
The high concentrations of Cl-OPEs in the water column compared to sediments found here support the hypothesis that Cl-OPEs are PMOC substances subject to long-range waterborne transport into the Canadian Arctic. The elevated concentrations of Cl-OPEs in the Mackenzie River plume, as well as the elevated concentrations of nearly all detectable OPEs in sediments in the Mackenzie River plume, support the hypothesis that riverine transport and discharge is a source for OPEs in the Canadian Arctic. Without measurements along the, e.g., Mackenzie River, it is impossible to determine whether the OPEs originate from local sources, close to the river mouth, or from long-range transport across the watershed. However, local sources are unlikely given the enormous discharge volume of the river of 9.9 km$^3$ s$^{-1}$, the large dilution effect from the Beaufort Sea, and the sparse population of 0.03 persons per square kilometer from ∼40,000 people across the entire Northwest Territories. Potential local sources at specific locations in the Arctic have been reported for TnBP as well as EHDPP. In these studies, airports (TnBP), ships, and harbors (EHDPP) have been identified as local contaminant sources. Similarly to Sühring et al., we identified Resolute Bay as a point source of TnBP and TPrP in this study. The TnBP contamination likely originates from TnBP use in aircraft fire-resistant hydraulic fluid at the Resolute Bay military airport. Local contamination from ship traffic is also possible: ship-based fisheries are an important source of food and income for many Arctic communities, and ship traffic for resource extraction, transport, and tourism has tripled since the 1990s.

Apart from the Mackenzie River and Resolute Bay, eastern Hudson Bay had elevated concentrations of CI-OPEs as well as TnBP compared to OPE concentrations measured at other sampling stations in the eastern Canadian Arctic (Figure 2). These locally elevated concentrations could be an indication for local OPE sources from settlements or from ship traffic in eastern Hudson Bay. The seabird colony in Hudson Bay (and elsewhere) may also “bioconcentrate” and “geoconcentrate” OPEs locally, although this hypothesis warrants further sampling near other breeding colonies across the Arctic and the paucity of sites precludes a definitive analysis of spatial trends and attribution of causes.

### 3.4. OPE Inventory in the Canadian Arctic Ocean

Assuming an average (45 m) mixing depth in the water column and 2 cm mixing depth in sediments, the median $\sum_{-}$CI-OPE inventory for the Arctic Ocean at a time point between 2013 and 2018 was estimated at 3500 tonnes (5th percentile: 400 tonnes, 95th percentile: 1.2 × 10$^4$ tonnes). For $\sum_{-}$Cl-OPEs, the estimated median inventory was 620 tonnes (5th percentile: 50 tonnes, 95th percentile: 4000 tonnes) (Table 1).

The total estimated OPE inventory of the Canadian Arctic Ocean at an assumed average mixing depth of 45 m was between 450 tonnes (5th percentile) and 1.6 × 10$^5$ tonnes (95th percentile) with a median of 4100 tonnes.

Water column OPEs accounted for ∼99% of the total OPE inventory in the Canadian Arctic Ocean. Minimum and worst-case estimated inventories (45 m mixing depth) for $\sum_{-}$Cl-OPEs and $\sum_{-}$non-Cl-OPEs are presented in Tables S9 and S10, respectively.

Ma et al. estimated a median inventory for seven OPEs in the top 2 cm of Central Arctic Ocean sediments of 52 tonnes (17–292 tonnes) or around 10 g $\sum_{-}$OPEs per km$^2$. Similar to our results, Ma et al. reported that TCEP contributes most to the OPE sediment inventory, with a median of 39 tonnes (around 8 g km$^{-2}$). These results are similar to our estimates of 4 tonnes or ∼4 g km$^{-2}$ for TCEP (0–15 tonnes).

As discussed by Ma et al., the sediment inventory of OPEs in the Arctic is very small compared to the 500,000 tonnes annual production volume for OPEs. However, the main inventory of OPEs is in the water column of the Arctic Ocean itself, with a median $\sum_{-}$Cl-OPE mass of 4100 tonnes (equal to 0.8% of the global annual OPE consumption).

To the best of our knowledge, the OPE inventory of the Arctic Ocean has not been estimated before. Our estimates indicate that the $\sum_{-}$Cl-OPE inventory in the Canadian Arctic Ocean (Table 1) is comparable to the estimated peak inventory for $\alpha$-hexachlorocyclohexane ($\alpha$-HCH) of ∼7000 tonnes in the North American Arctic Ocean. $\alpha$-HCH is a persistent organic pollutant with an environmental half-life in water of ∼30–300 days. Incidentally, this range of environmental half-lives for $\alpha$-HCH in water is comparable to the estimated half-lives in water of CI-OPEs that range from 90 to 484 (TCEP) to 180 days (TDGCPP). However, it should be noted that these environmental half-lives are highly uncertain, particularly for cold-temperature climates that can be expected to prolong degradation half-lives.

### 3.5. Implications for Regulation

There is currently no global regulatory mechanism for environmental contaminants, such as OPEs, that do not meet the persistent organic pollutant assessment criteria established by the Stockholm Convention. In Europe, the German Environment Agency and the Norwegian Geotechnical Institute have recently started an initiative to give equal weight to the mobility of a chemical as the bioaccumulation potential when deciding on regulatory measures. However, the screening criteria, proposed by the German Environment Agency, based on an organic carbon partitioning coefficient $K_{OC}$ ≤ 4 at an environmentally

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neutral pH, have been criticized by chemical producers as too
vague a criterion for listing substances as potentially PMOC.41
International acceptance of mobility as a risk assessment
criterion equivalent to bioaccumulation in terms of environ-
mental risk could help to implement measures aimed at
reducing environmental concentrations of water-based con-
taminants with potential long-term impacts for the aquatic
environment and drinking water resources. In the case of
OPEs, the mobility criterion would encompass CI-OPEs,
which make up >80% of the OPE contamination in water of
the Canadian Arctic Ocean.
It is important to address the lack of regulatory mechanisms
for PMOC substances such as CI-OPEs because, in contrast to
many legacy persistent organic pollutants, sedimentation is not
an effective sink for these substances in the environment. For
non-CI-OPEs, mobility in water may not be a sufficient
regulatory criterion because their predominant (long-range)
transportation pathway does not seem to be through water.
The origin of non-CI-OPEs detected in the Canadian Arctic
could be atmospheric transport, and for some, local sources.
Mechanisms to reduce local emissions (such as regulations
regarding ship and aircraft fuels) might therefore be needed to
control non-CI-OPE concentrations in the Canadian Arctic
environment. Source controls are required for other non-CI-
OPEs, such as TPhP, that are widely distributed in the Arctic.
For non-CI-OPEs and CI-OPEs alike, the concept of
“essential use” proposed by Cousins et al.42 for determining
when uses of per- and polyfluoroalkyl substances (PFASs) can
be phased out could be a useful mechanism to reduce
nonessential uses and related emissions of OPEs. As discussed
by Cousins et al.42 for PFASs, OPEs that are “not necessary for
the betterment of society in terms of health and safety” or have
“functional alternatives” cannot be considered “essential”. A
phase-out of such nonessential use OPEs as well as a
continuous effort to develop alternatives for currently essential
use OPEs should be implemented.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at
https://pubs.acs.org/doi/10.1021/acs.est.0c04422.

Map of the sampling locations; description of the target
analytes and analytical methods; inventory calculations;
Monte Carlo uncertainty analysis; organophosphate
erester (OPE) concentrations in water and Pearson
correlation coefficients with geographical features;
concentration maps for individual OPEs in water; OPE
congressions nearby a seabird colony; detected
organophosphate ester (OPE) concentrations in sediments;
Pearson correlation coefficients with geographical features;
concentration maps for individual OPEs in sediments; estimated OPE inventories for water and sediments from the Canadian Arctic Ocean; references (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Liisa M. Jantunen — Air Quality Processes Research Section,
Environment and Climate change Canada, Egbert, Ontario
L0L 1N0, Canada; Department of Earth Sciences, University
of Toronto, Toronto, Ontario M5S 3B1, Canada;

orcid.org/0000-0003-3073-5656

**Authors**

Roxana Sühring — Department of Environmental Sciences,
Stockholm University, 114 18 Stockholm, Sweden;
Department of Chemistry and Biology, Ryerson University,
Toronto, Ontario MSB 2K3, Canada; orcid.org/0000-
0002-7285-8044

Miriam L. Diamond — Department of Earth Sciences,
University of Toronto, Toronto, Ontario M5S 3B1, Canada;

Sarah Bernstein — Air Quality Processes Research Section,
Environment and Climate change Canada, Egbert, Ontario
L0L 1N0, Canada

Jennifer K. Adams — Department of Earth Sciences, University
of Toronto, Toronto, Ontario M5S 3B1, Canada

Jasmin K. Schuster — Air Quality Processes Research Section,
Environment and Climate change Canada, Toronto, Ontario
M3H 5T4, Canada

Kim Ferrie — Ecotoxicology and Wildlife Health Division,
Environment and Climate change Canada, Burlington,
Ontario L7S 1A1, Canada; orcid.org/0000-0003-3073-
3208

Kyle Elliott — Department of Natural Resource Sciences,
McGill University, Sainte-Anne-de-Bellevue, Quebec H9X
3V9, Canada

Gary Stern — University of Manitoba, Winnipeg, Manitoba
R3T 2N2, Canada

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.est.0c04422

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