Small Arctic rivers transport legacy contaminants from thawing catchments to coastal areas in Kongsfjorden, Svalbard☆

Maeve McGovern [a,b,*], Katrine Borgå [c], Eldbjørg Heimstad [d], Anders Ruus [a,c],
Guttorm Christensen [e], Anita Evenset [b,e]

[a] Norwegian Institute for Water Research (NIVA), Økernveien 94, 0579, Oslo, Norway
[b] Department of Arctic Marine Biology, UiT, The Arctic University of Norway, 9027, Tromsø, Norway
[c] Department of Biosciences, University of Oslo, 0316, Oslo, Norway
[d] NILU-Norwegian Institute for Air Research, Fram-High North Research Centre for Climate and the Environment, 9296, Tromsø, Norway
[e] Akvaplan-niva, Fram-High North Research Centre for Climate and the Environment, 9296, Tromsø, Norway

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ABSTRACT

Decades of atmospheric and oceanic long-range transport from lower latitudes have resulted in deposition and storage of persistent organic pollutants (POPs) in Arctic regions. With increased temperatures, melting glaciers and thawing permafrost may serve as a secondary source of these stored POPs to freshwater and marine eco-systems. Here, we present concentrations and composition of legacy POPs in glacier- and permafrost-influenced rivers and coastal waters in the high Arctic Svalbard fjord Kongsfjorden. Targeted contaminants include poly-chlorinated biphenyls (PCBs), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs), hexa-chlorocyclohexanes (HCHs) and chlordane pesticides. Dissolved (defined as fraction filtered through 0.7 μm GF/F filter) and particulate samples were collected from rivers and near-shore fjord stations along a gradient from the heavily glaciated inner fjord to the tundra-dominated catchments at the outer fjord. There were no differ-ences in contaminant concentration or pattern between glacier and tundra-dominated catchments, and the general contaminant pattern reflected snow melt with some evidence of pesticides released with glacial melt-water. Rivers were a small source of chlordane pesticides, DDTs and particulate HCB to the marine system and the particle-rich glacial meltwater contained higher concentrations of particle associated contaminants compared to the fjord. This study provides rare insight into the role of small Arctic rivers in transporting legacy contam-inants from thawing catchments to coastal areas. Results indicate that the spring thaw is a source of contami-nants to Kongsfjorden, and that expected increases in runoff on Svalbard and elsewhere in the Arctic could have implications for the contamination of Arctic coastal food-webs.

1. Introduction

The adverse effects of persistent organic pollutants (POPs) for humans and wildlife have been well documented since they were first brought into the public spotlight by Rachel Carson in the 1960's (Car-son, 1962). While current international agreements are in place that restrict the use of some of these compounds, including polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), dichlorodiphenyltri-chloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and chlordane pesticides (Kaiser et al., 2000; Stockholm Convention, 2013), decades of contamination by global industries have resulted in their widespread presence in the environment. POPs are persistent and easily mobilized by warm temperatures and transported by air and ocean currents. Those produced in the Northern Hemisphere typically have a northern tra-jectory, with a fraction gradually making their way to the Arctic due to global wind patterns and atmospheric distillation (Wania and Mackay, 1993; Simonich et al., 1995). Thus, decades of transport and deposition at high latitudes has resulted in stores of these pollutants in Arctic areas (Aslam et al., 2019; Garmash et al., 2013; Hermanson et al., 2020), where they have remained trapped (Blais et al., 1998; Wania & Mackay, 1993), and/or have accumulated in Arctic food-webs (Borgå et al., 2001, 2004; Evenset et al., 2016; Fisk et al., 2001; Hoekstra et al., 2003; Muir

& Norstrom, 1994; Ruus et al., 1999).

While concentrations of these legacy contaminants are steadily declining in air and sediments (AMAP, 2011; Evenset et al., 2007; Wong et al., 2021), and top predator tissues (Riget et al., 2019), following decreased emissions orchestrated by the Stockholm Convention (Stockholm Convention, 2013), climate change could potentially alter these trends by increasing the importance of secondary sources (Carlsson et al., 2012; Kallenborn et al., 2012; UNEP/AMAP, 2011; Nizzetto et al., 2010; Ma et al., 2011). Current climate warming, which is occurring most rapidly in polar regions (IPCC, 2019), and subsequent melting of the Arctic cryosphere (Mercier et al., 2021), is leading to increased inputs from the terrestrial environment to downstream marine ecosystems. In the high-Arctic archipelago Svalbard, melting glaciers have led to a 35% increase in annual runoff since 1980 (Adakudlu et al., 2019). As previously stored contaminants become mobilized, including PCBs and pesticides from Svalbard glaciers (Garmash et al., 2013; Hermanson et al., 2005; Ruggirello et al., 2010), these terrestrial inputs can be expected to have implications for the contamination of the coastal zone (Macdonald et al., 2005; McGovern et al., 2019; Pouch et al., 2017, 2018).

Thus, the objective of this study is to investigate the occurrence and composition of legacy POPs in a transect of glacial and tundra meltwaters draining into Kongsfjorden, on the West Coast of Spitzbergen, Svalbard (Fig. 1). Water samples were collected from rivers and fjord stations along the fjord gradient with the expectation that meltwater samples would represent a source of contaminants to the fjord. The contaminant pattern (i.e. the fraction of the different POPs relative to the sum of POPs) was expected to shift along the fjord transect from the glacier-dominated inner catchments to the tundra-dominated outer fjord catchments in accordance with their physicochemical properties. Furthermore, due to the tendency for hydrophobic POPs to adsorb to particles and organic matter, a higher fraction of the total concentration of POPs was expected to be associated with the particulate vs. dissolved fraction of the water sampled.
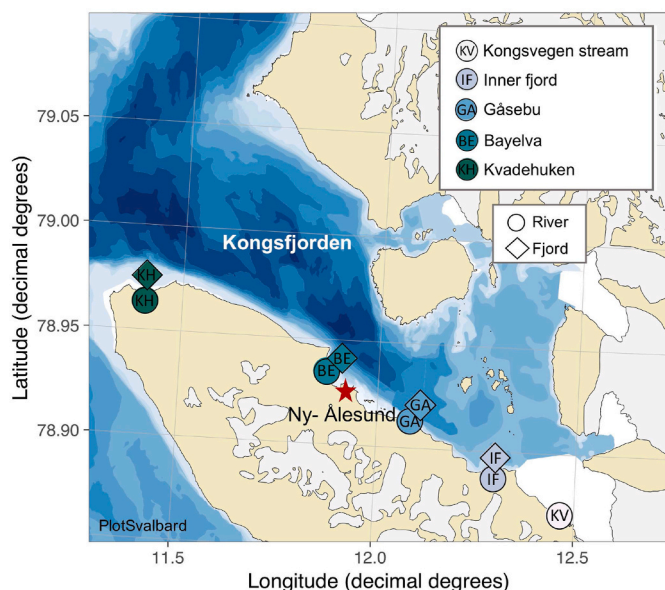

Fig. 1. Map of sampling stations in Kongsfjorden. Shapes indicate station type (diamond = Fjord station, circle = River station). Colors correspond to station names and the catchment characteristics (glacial (white-blue) vs. tundra (green)). This map was made using the PlotSvalbard R package (Vihtakari, 2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2. Methods

2.1. Study area

Kongsfjorden is located on the western side of Spitsbergen, Svalbard. The Kongsfjord drainage basin is roughly 1440 km^2, with 80% of it covered by glaciers (Pramanik et al., 2020). Kongsfjorden receives freshwater inputs from both land and marine-terminating glaciers. The land terminating glaciers are positioned mainly on the southern side of the fjord, and are drained by several rivers flowing into Kongsfjorden. The largest and most well-studied river is Bayelva, which receives runoff from the two small land-terminating glaciers Austre and Vestre Brøggerbreen. The glaciers positioned on the north side and eastern end of the fjord are mostly marine-terminating glaciers including Kongsvegen, Kronebreen, Kongsbreen, Conwaybreen, and Blomstrandbreen. Kronebreen and Kongsbreen are fed by the icefields Holtedahlfonna and Isachsenfonna, which contribute the most freshwater runoff to the fjord (Pramanik et al., 2018). Both freshwater inputs and Atlantic water inflow from the West Spitsbergen current have strong impacts on fjord circulation (Cottier et al., 2005) and biogeochemical conditions (Halbach et al., 2019). While Kongsfjorden was an historically seasonally ice-covered fjord, increases in Atlantic water inflow have resulted in ice free conditions since 2006 (Pavlova et al., 2019). The fjord is located far from most local contaminant sources, but a small research community, Ny-Ålesund, is located on the southern side about mid-way between the inner and outer fjord. In the wintertime, 30–35 people inhabit the settlement, but during summer the number generally increases to ca. 120.

2.2. Sample collection

Fieldwork took place in Kongsfjorden, Svalbard in June 2012. Samples were collected from 5 rivers and 4 adjacent fjord stations (Fig. 1) along a gradient from a Kongsvegen meltwater stream at the heavily glaciated inner fjord (marine-terminating glaciers) to the tundra-dominated Kvadehuken. In the fjord, high volume *in situ* water samples were collected using a stainless steel-titanium McLane Water Transfer System (McLane, USA), equipped with a 180 μm stainless steel pre-filter, as well as a similar sampler made by the University of Oslo. Pre-combusted glass fiber filters (GF/F; diameter 293 mm, nominal pore size 0.7 μm) were used to collect the particle phase and associated POPs, and solvent washed (n-hexane/diethyl ether (9:1)) polyurethane foam (PUF) were used for adsorption of POPs present in the dissolved phase. At fjord stations, the *in situ* sampler was deployed on a rig 5 m below the surface.

In the rivers, a similar but non-submersible system was used to sample high water volumes. A hose submersed in the river pumped water directly through the GF/F filter, and then through the stainless steel chamber, where PUFs sampled the dissolved fraction. The water was then discharged into a stainless steel bucket, and sampled volume determined. Water volumes varied between all stations (64 L–442 L). Filter and PUF samples were packed individually in pre-combusted aluminum foil, placed in zip-lock bags and stored at −20 °C. A set of field blanks (filter and PUF) was collected at each station following the same sampling and storage procedures. In addition, salinity and temperature profiles of the water column on fjord stations were collected using a conductivity-temperature-depth (CTD) profiler (911 plus probe, SeaBird; Washington, USA).

2.3. Chemical analyses

Water samples were analyzed for 48 compounds including 21 polychlorinated biphenyls (PCBs), 7 dichlorodiphenyltrichloroethanes and metabolites (DDTs), 4 hexachlorocyclohexanes (HCHs), 2 chlorobenzenes including hexachlorobenzene (HCB) and pentachlorobenzene (PeCB), and 17 pesticides, including chlordanes (Table S1). All laboratory work was conducted at the Norwegian Institute for Air Research's

(NILU) laboratory in Kjeller, Norway, and followed the extraction method and analysis of Hallanger et al. (2011) with minor changes. Prior to extraction, all PUFs and GF/F filters were spiked with the appropriate mass-labeled standards of analytes of interest. As a first step, the wet PUF samples were extracted with acetone, followed by extraction with n-hexane/diethylether (9:1). The GF/F filters and the corresponding PUF plugs were extracted separately. Extracts were concentrated and cleaned using acid treatment and silica fractionation. Before quantitative analysis, 20 μL of unlabelled tetrachloronaphthalene (TCN, 100 pg/μL) was added as recovery standard (RS). Identification and quantification of the PCBs and pesticides was carried out using a high-resolution gas chromatography coupled to a high-resolution mass spectrometer as detector (HRGC/HRMS). The analyses were performed in Electron Impact ionization mode (EI: PCBs, HCB, HCHs, DDTs) and Negative Ion Chemical Ionization mode (NICI: Chlordanes) using selected ion monitoring (SIM) for the respective compound groups.

The analytical method was quality assured through measurements of laboratory blanks and standard reference material (1588 b cod liver oil from The National Institute of Standards and Technology, Gaithersburg MD). The limit of detection (LOD) was defined as 3 times the signal to noise ratio for the analyzed matrix or blank value for each sample. The LOD was a function of the analytical noise in chromatograms and thus varied among samples. LOD ranged from 0.001 pg to 78.3 pg, depending on the chemical and sample in question (Table S2). Data was automatically corrected for recovery of the 13C labeled compounds, which averaged 76% (range:19–118%) for the PCBs, 71% (range: 24–111%) for the DDTs, 44% (range: 0–68%) for HCHs, 31% (range: 11–50%) for chlorobenzenes and 68% (range: 31–103%) for the Chlordanes. The lowest recoveries were reported for the particulate fractions from the GF/F filters (Table S3). Analytical quality is certified by the regular participation of the NILU laboratory in round robin trials such as the Arctic Monitoring and Assessment Program (AMAP) ring test for POPs in plasma, and Quality Assurance of Information on Marine Environmental Monitoring in Europe (QUASIMEME).

2.4. Data analysis

A total of 34 water samples were analyzed for contaminant concentration (sampled volumes were missing for 8 samples) and 42 samples for composition. Compounds which were below LOD for many of the samples (>45%) were excluded from analysis (Table S1). Thus, analysis was carried out on the remaining 31 of the 50 targeted compounds within the groups of PCBs, DDTs, HCHs and chlordane pesticides (Table S1). Statistical analyses were performed using R version 4.0.2 (R Development Core Team, 2020). If field blanks were > LOD, data were field blank corrected. For all samples, values below LOD were replaced with randomly generated values from 0.5 LOD to LOD (Helsel, 2011). Wilcoxon rank sum tests were used to test differences in contaminant concentrations between fjord and river samples as well as dissolved and particulate fractions.

3. Results and discussion

3.1. The thawing terrestrial cryosphere is a secondary source of POPs to coastal areas

Rivers sampled in this study represent a source of organochlorines to Kongsfjorden's coastal waters. Analysis of dissolved and particulate samples led to quantification of compounds from all targeted contaminant groups, with the mean sum of targeted organochlorines at 42.1 ± 17.9 pg L^{-1} (range = 20.5–76.9 pg L^{-1}) in the dissolved fraction and 24.5 ± 39.2 pg L^{-1} (range = 1.09–107.7 pg L^{-1}) in the particulate fraction. River water dissolved fractions were dominated by HCHs and HCB, and the particulate fraction by HCB and PCBs (Fig. 2, Table S4).

While results indicate that the rivers are a source of contaminants to coastal waters, the measured concentrations were generally lower than at nearshore fjord stations (ΣOCs; dissolved: 80.3 ± 17.9 (range: 57.3–108.6 pg L^{-1}) and particulate: 24.4 ± 39.2 (range: 1.5–4.8 pg L^{-1}), Fig. 2A, Table S4). In particular, PCBs and HCHs were higher in the fjord than in the rivers (Fig. 2B and C). At the fjord stations, a fresh surface water layer was present during the time of sampling (Figure S1), and sampled waters were part of the Intermediate Water Mass (Salinity 34.0–34.7, Temperature >1.0 °C Cottier et al., 2005; Figure S2). Therefore, fjord samples do not represent a pure marine Atlantic water signal, but rather represent a mix of contaminants transported with Atlantic water from the shelf, and contaminants associated with freshwater runoff from rivers and glacier front ablation.

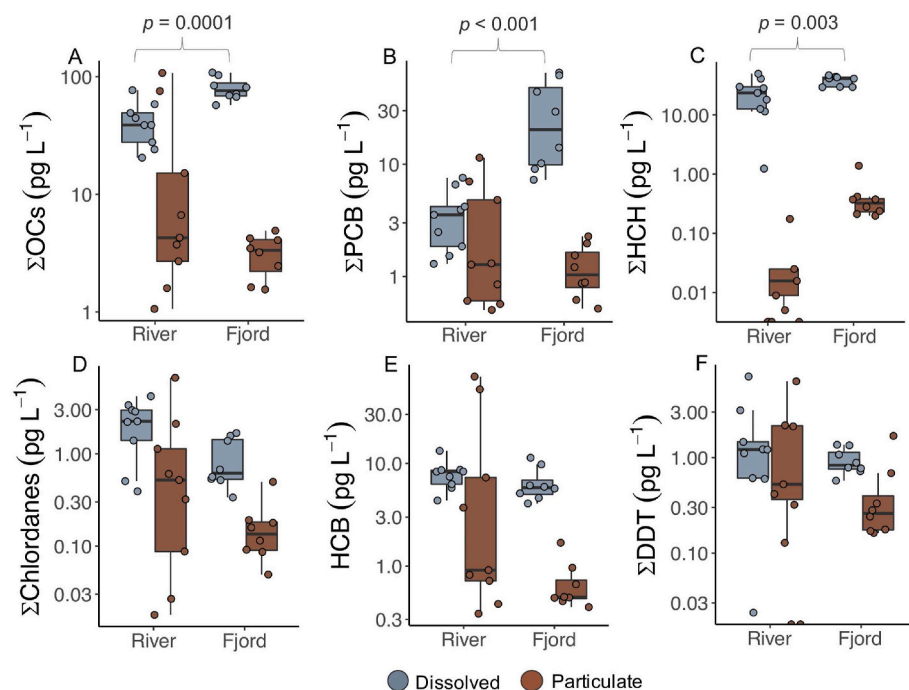PCB concentrations in Kongsfjorden surface waters were higher than

Fig. 2. Boxplots with concentrations (pg L^{-1}) of main contaminant groups in dissolved (blue) and particulate (brown) fractions of water samples collected from river and fjord stations in Kongsfjorden using active water samplers. Individual points represent each sample replicate. Note that the y-axis varies between plots. The fjord had higher dissolved concentrations of total organochlorines compared to the rivers (Wilcoxon Rank Sum, p-value = 0.0001). In addition, the fjord had higher mean concentration of dissolved PCB$_{17}$ and HCH than the rivers (Wilcoxon Rank Sum; PCB$_{17}$: p-value=<0.001; HCH: p-value = 0.003). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

reported for Atlantic water inflow: In the dissolved phase, PCB_7 concentrations were 2–3 times higher (13.05 ± 9.96 pg L^{-1}; range: 3.21–26.35 pg L^{-1}) compared to outer Kongsfjorden (ΣPCB_7: 3.11–5.99 pg L^{-1}; Hallanger et al., 2011), and high compared to the Fram Strait (ΣPCB_{16}: 1.3–3.6 pg L^{-1}; Ma et al., 2018), and the Arctic Ocean ($\Sigma PCB_{12/13}$: 0.3–2.8 pg L^{-1}; Carrizo & Gustafsson, 2011; Gioia et al., 2008). Fjord concentrations (ΣPCB: 7.8–67.8 pg L^{-1} for dissolved + particulate phases) were in the same range or slightly higher than those reported from the same area in 2009 (ΣPCB_9: 19–29 pg L^{-1}) in full water samples (Papale et al., 2017). While concentrations in Kongsfjorden surface waters did not reflect river inputs or Atlantic water inflow, the dominance of lower-chlorinated PCB congeners, PCB 52 and 28, could indicate that glacial front ablation or direct atmospheric deposition are dominating sources of PCBs to the fjord.

While the rivers had lower total organochlorine concentrations, they had higher concentrations of chlordane pesticides, HCB, and DDTs, which were higher in both the dissolved and particulate fractions compared to fjord samples reported here and in the literature (Fig. 2, Table S4; Hallanger et al., 2011). Chlordane pesticides, including cis- and trans-chlordane and cis- and trans-nonachlor, were previously used as insecticides but have been restricted or banned for decades and were officially added to the Stockholm Convention in 2004. These compounds, which are highly volatile, have previously been associated with ice covered areas in the European Arctic (Lohman et al., 2009), glacial runoff to Greenland fjords (Carlsson et al., 2012), and meltwater in Liefdefjorden (Hallanger et al., 2011).

HCB concentrations were slightly higher in river samples compared to the fjord (Fig. 2E), especially in the particulate fraction (which ranged from 0.3 to 70.1 pg L^{-1}). HCB in sediments previously collected from Kongsfjorden demonstrated a strong spatial gradient, with the highest concentrations close to the glacier fronts (Pouch et al., 2018), indicating the importance of glacial inputs on sediment contamination. Our results further emphasize the importance of particulates in glacial meltwater as a transport pathway for HCB stored in catchment glaciers to enter the fjord. However, these results stand in contrast to results from a recent study in Isfjorden, Svalbard, where transport of suspended particulate matter from glaciated catchments were analyzed for HCB and PCBs. Low concentrations in suspended particulate matter resulted in strong dilution of POPs in coastal sediments, leading to strong spatial gradients in sediment concentrations, with increasing concentrations from inner to outer fjord stations (Johansen et al., 2021). A similar picture was presented by Ma et al. (2015), who found that concentrations of many legacy POPs showed a decreasing trend from outer to the inner part of Kongsfjorden, indicating that a marine signal, possibly the North Atlantic Current, could be influencing the distribution of these contaminants to the fjord. Meanwhile, concentrations in the fjord water, which had HCB concentrations ranging from 4.1 to 11.3 pg L^{-1} (mean = 6.6 ± 2.6 pg L^{-1}) in the dissolved fraction, were similar to those previously measured in seawater from Kongsfjorden and Liefdefjorden (4.9–5.2 pg L^{-1}, Hallanger et al., 2011), and off the coast of Western Spitsbergen (2–8 pg L^{-1}, Gioia et al., 2008). When considering findings by Lohmann et al. (2009), who found increasing concentrations of HCB with latitude from Europe to the Arctic, there are indications that release of HCB from secondary sources may be occurring at high latitudes where volatile HCB is easily transported.

DDT, which has been associated with glacial melt in other areas of the Arctic (Macdonald et al., 2005), was found in similar concentrations in river and marine compartments. However, we did find slightly higher concentrations in river samples (Fig. 2F), with the highest concentrations in the Inner Fjord glacial river (IG; 3.5 ± 5.0 pg L^{-1} (range: 0.0–7.1 pg L^{-1}) in both the dissolved (4.2 ± 2.9 pg L^{-1}) and the particulate fraction (2.1–6.3 pg L^{-1}) (Fig. 2, Table S4).

3.2. Meltwater contaminant composition reflects a mixture of snow-melt and glacial-melt water sources

The composition of contaminant isomers and congeners can be used as environmental tracers of contaminant sources in natural ecosystems (Hargrave et al., 1988). Here, contaminant composition indicate that river water samples collected from Kongsfjorden in June were composed of a mix of snowmelt and glacial meltwater. Contaminant composition in freshwater run-off undergoes seasonal shifts as the melt season progresses, with contaminants emerging in accordance with their physicochemical properties (Meyer et al., 2009). Compounds with lower octanol-water partition coefficients (K_{OW}), and therefore higher water solubility, should rapidly partition into the water phase of the melting snowpack, facilitating an earlier release of these compounds into freshwater systems (Meyer and Wania, 2008). Likewise, compounds with higher K_{OW} and higher affinity for particles, will take longer to elute from the snowpack (Garmash et al., 2013).

We see evidence of different stages in snow-melt in the spatial differences in contaminant composition along the river transect (Fig. 3). While the present glacier-to-tundra transect in river stations was chosen to target differences in catchment glacial coverage, it is likely that the differences in contaminant profiles observed are more representative of the variation in melt-season progression among the catchments. The rivers in the inner part of the fjord were characterized by a higher percentage of the lower chlorinated PCBs (PCB-28 and PCB-52), and cis-chlordane in their dissolved fraction compared to the outer fjord stations, suggesting that the melt-season was at an earlier stage (i.e. still early snow-melt). Meanwhile, the outer fjord rivers were characterized by an increased percentage of the higher-chlorinated PCBs (PCB-138, PCB-153 and PCB-180), which is in line with a later stage of the melt season when rivers have a higher sediment load characteristics of catchment erosion and/or glacial inputs.

The abundance of PCB-52 in all samples is consistent with the dominance of this congener in snow (Hermansson et al., 2020) and surface soils and vegetation (Aslam et al., 2019; Bartlett et al., 2019), and is perhaps unsurprising in light of indications that PCB-52 is not currently declining in air samples collected at the Zeppelin Observatory near Kongsvegen (Hung et al., 2016). Thus, the snowmelt period, a time when higher concentrations of dissolved organic carbon have been observed in Svalbard rivers (McGovern et al., 2020) may facilitate the transport of recently deposited PCB-52 and other lighter organochlorines in the dissolved phase to coastal areas where they can accumulate in coastal fauna (Skogsberg et al., in review).

The dominance of snow-melt associated contaminants observed in the rivers suggests that meltwater sampled here represents a younger source of pollutants, and that the expected legacy contaminants associated with glacial runoff were likely only comprising a small percentage of the total contaminant load (e.g. HCBs, Chlordane pesticides, DDTs). While June is typically the peak of the snowmelt-driven spring freshet, previous modelling studies have indicated that snowmelt associated runoff from non-glaciated areas only contributes 16% to the total runoff from the Kongsfjord drainage basin (Pramanik et al., 2018). Rather, in Kongsfjorden, the largest source of freshwater discharge comes from Kronebreen, which is equivalent to around 40% of the total freshwater flux to the fjord and an order of magnitude greater than the runoff from the rivers sampled in this study (Pramanik et al., 2020). Thus, inputs to the fjord from these other large glacier fronts remains a potential source of contaminants to Kongsfjorden, and other Arctic fjords.

However, studies have suggested that smaller glaciers, where more recent layers of snow and ice contribute to runoff, may be greater sources of legacy contaminants deposited in the post-industrial era compared to older larger icecaps, where emerging ice may be from preindustrial times, and therefore contribute more to dilution of contaminants in receiving waters (Johansen et al., 2021, Macdonald et al., 2005). Additional seasonal sampling of these rivers draining small land-terminating glaciers through July and August is required to
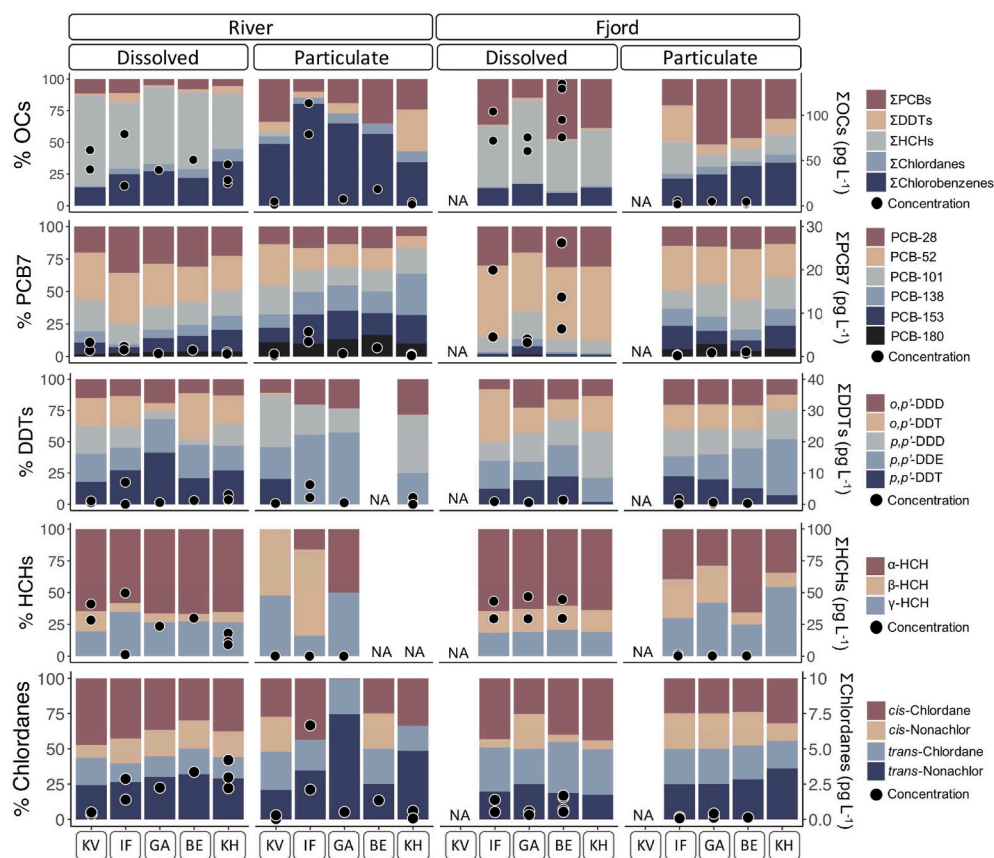
Fig. 3. Compositional changes (%; left axis) in compounds along the gradient and total concentration of quantified contaminants for each respective group (pg L^{-1}; right axis). Stations are arranged along the gradient from the glacier-dominated Inner Fjord to tundra-dominated Kvadehuken; KV= Kongsvegen stream, IF= Inner Fjord, GA = Gåsebu, BE=Bayelva, KH=Kvadehuken. Compositional data is based on means of stations replicates while concentration data is shown for all replicates. Compounds include (a) PCB$_7$, (b) DDTs, (c) HCHs, (d) Chlordane pesticides. NA= No data available (DDT and HCH were ruined for some samples (BE, KH River particulate) and filtered volume could not be measured from the KH fjord samples, thus the composition can be read, but not the concentrations).

determine whether a greater fraction of the glacial-bound contaminants would eventually be released as the melt season progresses.

3.3. Low organochlorine concentrations in filtered particulate matter

Due to the hydrophobic nature of organochlorines, concentrations in water are generally low in the dissolved phase, as they have a tendency to sorb to particulate matter. Thus, the observed dominance of organochlorines in the dissolved fraction of both the river and fjord was surprising. Indeed, the ratio of particulate:dissolved concentrations for most of the targeted contaminant groups were <1, especially in the fjord (Fig. 4). Even the rivers, which tended to have higher suspended sediment loads, had higher total contaminant concentrations in the dissolved vs. particulate fractions (Fig. 2). However, the dissolved fraction here is defined by its ability to pass through a 0.7 μm GF/F filter, and thus could include compounds that are not truly dissolved, but attached

to very small suspended particles. Furthermore, the rivers did have higher particulate:dissolved ratios for most contaminant groups compared to the fjord, and these ratios increased with K$_{OW}$ as expected, reaching >1 for the higher chlorinated PCBs 180 and 138 (Fig. 4).

The sorption of some organochlorines to riverine suspended particles and dissolved organic matter has implications for the fate of these contaminant groups in the marine environment. At the land-ocean interface, sedimentation of suspended sediments and flocculation of organic matter can act as removal pathways for contaminants to leave the water column, where they can be buried in marine sediments and removed from circulation in the environment (Lohmann et al., 2007). In contrast, organochlorines remaining in the dissolved fraction or sorbed to very small particles have the potential to be transported farther from the river outlet, and potentially re-volatilized to the atmosphere or to be taken up in the food-web. Thus, higher dissolved concentrations suggests that remobilized contaminants may remain in circulation for long
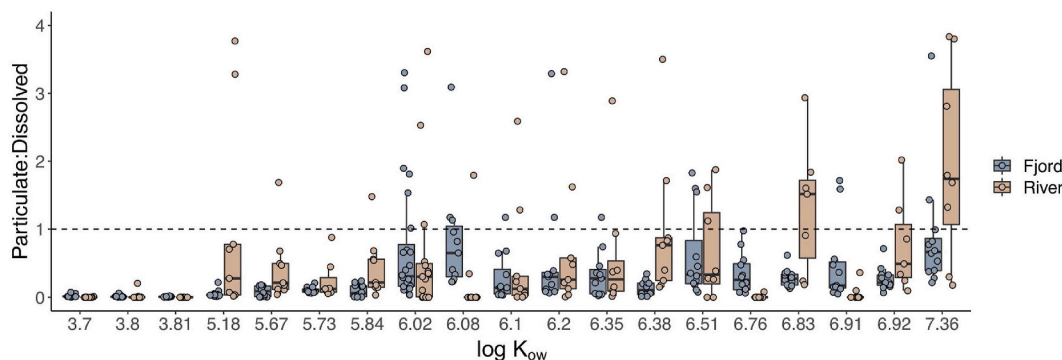

Fig. 4. Ratio of contaminant concentration in each sampled water fraction (particulate: dissolved) for all fjord and river stations vs. the log K$_{ow}$ of each contaminant. Individual points in the box plot represent each sample replicate.

periods of time, which is concerning when considering exposure to the marine food-web.

3.4. Future perspectives

Contaminant profiles of Arctic rivers draining glacial and tundra catchments into Kongsfjorden were dominated by HCHs, PCBs and HCB, and while they only comprised a small fraction of the total contaminant load, rivers contained higher concentrations of HCB, chlordane pesticides and DDTs compared to the fjord. These results support findings from previous studies suggesting that glacial/snowmelt is a source of pesticides to coastal Arctic areas (Carlsson et al., 2012; Hallanger et al., 2011; Kallenborn et al., 2012, McGovern et al., in review).

The total discharge from Bayelva in 2012 (June–October) was 29×10^6 m^3 (Zhu et al., 2016). Based on these discharge data, collected from hourly-averaged instrumental record (Zhu et al., 2016), and contaminant concentrations reported here, uncertain estimations of fluxes indicate an annual discharge of 1.43 g organochlorines in the dissolved phase in 2012. For PCB$_{17}$, which constituted a small fraction of the total contaminant load in the sampled rivers, the extrapolated annual flux of 0.11 g (0.06 dissolved and 0.05 particulate) for Bayelva is small compared to fluxes from the six Great Arctic Rivers (Ob, Yenisey, Lena, Indigirka, Kolyma, and Mackenzie), with estimated ranges of 3.9–184 kg PCB$_{13}$/year (Carrizo and Gustafsson, 2011). This is not surprising, given the huge differences in river sizes and discharge. While samples collected only in June cannot account for seasonal variability in contaminant concentrations and composition, these estimations indicate that the contribution of contaminants from glacial rivers to the Kongsfjorden system is generally low. Results of this study suggest that freshwater inputs from land-terminating glaciers are a small secondary source of contaminants, but also highlight the need for higher resolution seasonal data from high Arctic catchments.

Author statement

Maeve McGovern: Methodology, Data curation, Writing – review & editing.**Katrine Borgå**; : Conceptualization, Investigation, Data curation, Writing – review & editing.**Eldbjørg Heimstad**: Funding acquisition, Writing – review & editing. **Anders Ruus**: Conceptualization, Investigation, Writing – review & editing.**Guttorm Christensen**: Investigation, Writing – review & editing.**Anita Evenset**: Concept**ualization, Fun**ding acquisition, Project administration, Investigation, Writing – review & editing.

Data availability

The dataset (Akvaplan-niva, 2021) and source code (McGovern, 2021) are openly available online.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.envpol.2022.119191.

References

Adakudlu, M., Andresen, J., Bakke, J., Beldring, S., Benestad, R., Bilt, W., et al., 2019. In: Norwegian Environmental Agency (Miljodirektoratet), N.E.A. (Ed.), Climate in Svalbard 2100 – a Knowledge Base for Climate Adaptation, p. M-1242.

Akvaplan-niva, 2021. Raw Lab Data for COPOL II Study of Persistent Organic Pollutants in Kongsfjorden. Zenodo, Svalbard. https://doi.org/10.5281/zenodo.4686619 [Data set], Version 1.0.0.

Amap, 2011. AMAP Assessment 2011: Mercury in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway.

Aslam, S.N., Huber, C., Asimakopoulos, A.G., Steinnes, E., Mikkelsen, Ø., 2019. Trace elements and polychlorinated biphenyls (PCBs) in terrestrial compartments of Svalbard, Norwegian Arctic. Sci. Total Environ. 685, 1127e1138.

Bartlett, P.W., Isaksen, E., Hermanson, M.H., 2019. New unintentionally produced PCBs in the Arctic. Emerging Contaminants 5, 9–14.

Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B., 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature 395, 585–588.

Borgå, K., Fisk, A.T., Hoekstra, P.F., Muir, D.C.G., 2004. Biological and chemical factors of importance in the bioaccumulation and trophic transfer of persistent organochlorine contaminants in arctic marine food webs. Environ. Toxicol. Chem. 23, 367–2385.

Borgå, K., Gabrielsen, G.W., Skaare, J.U., 2001. Biomagnification of organochlorines along a Barents Sea food chain. Environ. Pollut. 113, 187–198.

Carlsson, P., Corneliussen, G., Bøggild, C.E., Rysgaard, S., Mortensen, J., Kallenborn, R., 2012. Hydrology-linked spatial distribution of pesticides in a fjord system in Greenland. J. Environ. Monit. 14, 1437–1443.

Carrizo, D., Gustafsson, O., 2011. Pan-Arctic river fluxes of polychlorinated biphenyls. Environ. Sci. Technol. 45, 8377–8384.

Carson, R., 1962. Silent Spring. Houghton Miffin Company, Boston, USA.

Cottier, F., Tverberg, V., Inall, M., Svendsen, H., Nilsen, F., Griffiths, C., 2005. Water mass modification in an Arctic fjord through cross-shelf exchange: the seasonal hydrography of Kongsfjorden, Svalbard. Journal of Geophysical Research-Oceans 110.

Evenset, A., Carroll, J., Christensen, G.N., Kallenborn, R., Gregor, D., Gabrielsen, G.W., 2007. Seabird guano is an efficient conveyer of persistent organic pollutants (POPs) to Arctic lake ecosystems. Environ. Sci. Technol. 41, 1173–1179.

Evenset, A., Hallanger, I.G., Tessmann, M., Warner, N.A., Borgå, K., Gabrielsen, G.W., Christensen, G.N., Renaud, P.E., 2016. Seasonal variation in accumulation of persistent organic pollutants in an Arctic marine benthic food web. Sci. Total Environ. 542, 108–120.

Fisk, A.T., Hobson, K.A., Norstrom, R.J., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater polynya marine food web. Environ. Sci. Technol. 35, 732–738.

Garmash, O., Hermanson, M.H., Isaksson, E., Schwikowski, M., Divine, D., Teixeira, C., Muir, D.C.G., 2013. Deposition history of polychlorinated biphenyls to the lomonosovfonna glacier, svalbard: a 209 congener analysis. Environ. Sci. Technol. 47, 12064–12072.

Gioia, R., Lohmann, R., Dachs, J., Temme, C., Lakaschus, S., Schulz- Bull, D., Hand, I., Jones, K.C., 2008. Polychlorinated biphenyls in air and water of the north atlantic and Arctic Ocean. J. Geophys. Res. Atmos. 113 (D19).

Halbach, L., Vihtakari, M., Duarte, P., Everett, A., Granskog, M.A., Hop, H., Kauko, H.M., Kristiansen, S., Myhre, P.I., Pavlov, A.K., Pramanik, A., Tatarek, A., Torsvik, T., Wiktor, J.M., Wold, A., Wulff, A., Steen, H., Assmy, P., 2019. Tidewater glaciers and bedrock characteristics control the phytoplankton growth environment in a fjord in the arctic. Front. Mar. Sci. 6 https://doi.org/10.3389/fmars.2019.00254.

Hallanger, I.G., Ruus, A., Warner, N.A., Herzke, D., Evenset, A., Schøyen, M., Gabrielsen, G.W., Borgå, K., 2011. Differences between Arctic and Atlantic fjord systems on bioaccumulation of persistent organic pollutants in zooplankton from Svalbard. Sci. Total Environ. 409 (14), 2783–2795.

Hargrave, B.T., Vass, W.P., Erickson, P.E., Fowler, B.R., 1988. Atmospheric transport of organochlorines to the Arctic Ocean. Tellus 40B, 480–493.

Helsel, D.R., 2011. Statistics for Censored Environmental Data Using Minitab and R. John Wiley & Sons. ISBN 1118162765.

Hermanson, M.H., Isaksson, E., Divine, D., Teixeira, C., Muir, D.C.G., 2020. Atmospheric deposition of polychlorinated biphenyls to seasonal surface snow at four glacier sites on Svalbard, 2013-2014. Chemosphere 243, 125324.

Hermanson, M.H., Isaksson, E., Teixeira, C., Muir, D.C.G., Compher, K.M., Igarashi, M., Kamiyama, K., 2005. Current-use and legacy pesticide history in the austfonna ice cap, svalbard, Norway. Environ. Sci. Technol. 39, 8163–8169.

Hoekstra, P.F., O'Hara, T.M., Fisk, A.T., Borgå, K., Solomon, K.R., Muir, D.C.G., 2003. Trophic transfer of persistent organochlorine contaminants (OCs) within an Arctic marine food web from the southern Beaufort-Chukchi Seas. Environ. Pollut. 124, 509–522.

Hung, H., Katsoyiannis, A.A., BrorströmLundén, E., Olafsdottir, K., Aas, W., Breivik, K., Bohin-Nizzetto, P., Sigurdsson, A., Hakola, H., Bossi, R., Skov, H., Sverko, E., Barresi, E., Felin, P., Wilson, S., 2016. Temporal trends of persistent organic pollutants in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). Environ. Pollut. 217, 52–61.

IPCC Report, 2019. IPCC special report on the ocean and cryosphere in a changing climate. In: Pörtner, H.-O., Roberts, D.C., Masson-Delmotte, V., Zhai, P., Tignor, M., Poloczanska, E., Mintenbeck, K., Alegría, A., Nicolai, M., Okem, A., Petzold, J.,

Rama, B., Weyer, N.M. (Eds.), IPCC Report. Available online at. https://www.ipcc.ch/srocc/.

Johansen, S., Poste, A., Allan, I., Evenset, A., Carlsson, P., 2021. Terrestrial inputs govern spatial distribution of polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) in an Arctic fjord system (Isfjorden, Svalbard). Environ. Pollut. 281, 116963. https://doi.org/10.1016/j.envpol.2021.116963.

Kaiser, J., Enserink, M., Kaiser, J., 2000. Environmental toxicology. Treaty takes a POP at the dirty dozen. Science 290 (5499), 2053.

Kallenborn, R., Halsall, C., Dellong, M., Carlsson, P., 2012. The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants. J. Environ. Monit. 14, 2854–2869.

Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: current and future research directions. Environ. Pollut. 150, 150–165. https://doi.org/10.1016/j.envpol.2007.06.051.

Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine pesticides and PAHs in the surface water and atmosphere of the north atlantic and Arctic Ocean. Environ. Sci. Technol. 43, 5633–5639.

Ma, J., Hung, H., Tian, C., Kallenborn, R., 2011. Revolatilization of persistent organic pollutants in the Arctic induced by climate change. Nat. Clim. Change 1, 255e260.

Ma, Y., Xie, Z., Halsall, C., Moeller, A., Yang, H., Zhong, G., Cai, M., Ebinghaus, R., 2015. The spatial distribution of organochlorine pesticides and halogenated flame retardants in the surface sediments of an Arctic fjord: the influence of ocean currents vs. glacial runoff. Chemosphere 119, 953–960. https://doi.org/10.1016/j.chemosphere.2014.09.012.

Ma, Y., Adelman, D.A., Bauerfeind, E., Cabrerizo, A., McDonough, C.A., Muir, D., Soltwedel, T., Sun, C., Wagner, C.C., Sunderland, E.M., Lohmann, R., 2018. Concentrations and water mass transport of legacy POPs in the Arctic Ocean. Geophys. Res. Lett. 45 https://doi.org/10.1029/2018GL078759, 12,972–12, 981.

Macdonald, R.W., Harner, T., Fyfe, J., 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Sci. Total Environ. 342, 5–86.

McGovern, M., 2021. MaeveMcGovern/KongsPOPs: Code for COPOL II Study of Persistent Organic Pollutants in Kongsfjorden, Svalbard (v1.0.0). Zenodo. https://doi.org/10.5281/zenodo.5554686.

McGovern, M., Evenset, A., Borgå, K., de Wit, H.A., Braaten, H.F.V., Hessen, D.O., Schultze, S., Ruus, A., Poste, A., 2019. Implications of coastal darkening for contaminant transport, bioavailability, and trophic transfer in northern coastal waters. Environ. Sci. Technol. 53 (13), 7180–7182. https://doi.org/10.1021/acs.est.9b03093.

McGovern, M., Pavlov, A.K., Deininger, A., Granskog, M.A., Leu, E., Søreide, J.E., Poste, A.E., 2020. Terrestrial inputs drive seasonality in organic matter and nutrient biogeochemistry in a high arctic fjord system (isfjorden, svalbard). Front. Mar. Sci. 7, 542563. https://doi.org/10.3389/fmars.2020.542563.

McGovern M, Warner N, Borgå K, Evenset A, Carlsson P, Skogsberg E, Søreide JE, Christensen G, Poste AE (in review). Is glacial meltwater a secondary source of legacy contaminants to Arctic coastal food-webs? In Review at Environmental Science & Technology.

Mercier, D., 2021. Climate change and the melting cryosphere. In: Spatial Impacts of Climate Change. John Wiley & Sons, Ltd, pp. 21–41. https://doi.org/10.1002/9781119817925.ch2.

Meyer, T., Lei, Y.D., Muradi, I., Wania, F., 2009. Organic contaminant release from melting snow. 1. Influence of chemical partitioning. Environ. Sci. Technol. 43, 657–662. https://doi.org/10.1021/es8020217.

Meyer, T., Wania, F., 2008. Organic contaminant amplification during snowmelt. A review. Water Res. 42 (8e9), 1847e1865.

Muir, D.C.G., Norstrom, R.J., 1994. Persistent organic contaminants in Arctic marine and freshwater ecosystems. Arctic Research 8, 136–146.

Nizzetto, L.M., Macleod, Borgå K., Cabrerizo, A., Dachs, J., Guardo, A.D., Ghirardello, D., Hansen, K.M., Jarvis, A., Lindroth, A., Ludwig, B., Monteith, D., Perlinger, J.A., Scheringer, M., Schwendenmann, L., Semple, K.T., Wick, L.Y., Zhang, G., Jones, K.C., 2010. Past, present, and future controls on levels of persistent organic pollutants in the global environment. Environ. Sci. Technol. 44, 6526–6531.

Papale, M., Giannarelli, S., Fransesconi, S., Di Marco, G., Mikkonen, A., Conte, A., Rizzo, C., Domenico, E., Michaud, L., Giudice, A.L., 2017. Enrichment, isolation and biodegradation potential of psychrotolerant polychlorinated-biphenyl degrading bacteria from the Kongsfjorden (Svalbard Islands, High Arctic Norway). Mar. Pollut. Bull. 114, 849–859.

Pavlova, O., Gerland, S., Hop, H., 2019. Changes in sea-ice extent and thickness in kongsfjorden, svalbard (2003–2016). In: Hop, H., Wiencke, C. (Eds.), The Ecosystem of Kongsfjorden, Svalbard. Advances in Polar Ecology, vol. 2. Springer, Cham. https://doi.org/10.1007/978-3-319-46425-1_4.

Pouch, A., Zaborska, A., Pazdro, K., 2017. Concentrations and Origin of Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments of Western Spitsbergen Fjords (Kongsfjorden, Hornsund, and Adventfjorden). Environmental Monitoring & Assessment, p. 189175.

Pouch, A., Zaborska, A., Pazdro, K., 2018. The history of hexachlorobenzene accumulation in Svalbard fjords. Environ. Monit. Assess. 190, 360.

Pramanik, A., Kohler, J., Lindbäck, K., How, P., Van Pelt, W., Liston, G., Schuler, T.V., 2020. Hydrology and Runoff Routing of Glacierized Drainage Basins in the Kongsfjord Area, Northwest Svalbard, the Cryosphere Discuss. https://doi.org/10.5194/tc-2020-197.

Pramanik, A., Van Pelt, W., Kohler, J., Schuler, T.V., 2018. Simulating climatic mass balance, seasonal snow development and associated freshwater runoff in the Kongsfjord basin, Svalbard (1980-2016). J. Glaciol. 64, 943–956. https://doi.org/10.1017/jog.2018.80,2018.

R Core Team, 2020. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna.

Riget, F., Bignert, A., Braune, B., Dam, M., Dietz, R., Evans, M., Wilson, S., et al., 2019. Temporal trends of persistent organic pollutants in Arctic marine and freshwater biota. Sci. Total Environ. 649, 99–110.

Ruggirello, R.M., Hermanson, M.H., Isaksson, E., Teixeira, C., Forsstrom, S., Muir, D.C. G., Pohjola, V., van de Wal, R., Meijer, H.A.J., 2010. Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. J. Geophys. Res. Atmos. 115, D1830.

Ruus, A., Ugland, K.I., Espeland, O., Skaare, J.U., 1999. Organochlorine contaminants in a local marine food chain from Jarfjord, Northern Norway. Mar. Environ. Res. 48, 131–146.

Simonich, S.L., Hites, R.A., 1995. Global distribution of persistent organochlorine compounds. Science 269, 1851–1854.

Skogsberg, E.; McGovern, M.; Poste, A. E.; Jonsson, S.; Arts, M.; Varpe, Ø.; Borgå, K. No effect of seasonal glacial run-off on Hg and chlorinated POP concentrations in arctic littoral amphipods. Environmental Pollution in review.

UNEP/AMAP, 2011. Climate Change and POPs: Predicting the Impacts. Report of the UNEP/AMAP Expert Group. Secretariat of the Stockholm Convention, Geneva, p. 62.

Vihtakari, M., 2019. PlotSvalbard: PlotSvalbard – Plot Research Data from Svalbard on Maps. Rpackage, version 0.8.5.

Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio 22, 10–18.

Wong, F., Hung, H., Dryfhout-Clark, H., Aas, W., Bohlin-Nizzetto, P., Breivik, K., Wilson, S., 2021. Time trends of persistent organic pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEAC) in Arctic air from 25 years of monitoring. Sci. Total Environ. 775, 145109.

Zhu, Z.Y., Wu, Y., Liu, S.M., Wenger, F., Hu, J., Zhang, J., Zhang, R.F., 2016. Organic carbon flux and particulate organic matter composition in Arctic valley glaciers: examples from the Bayelva River and adjacent Kongsfjorden. Biogeosciences 13, 975–987. https://doi.org/10.5194/bg-13-975-2016.