

Investigation of new brominated and organophosphorous flame retardants in Svalbard benthic marine food web; FlammePlank





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MILJØVERN FOND

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REPORT

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Summary

The aim of this pilot-study was to use silicone rubber-based passive samplers to measure novel brominated flame retardants (nBFRs), polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in seawater and air around Longyearbyen as well as investigate the presence of those compounds in sediment and biota (amphipods, *Gammarus* spp.) nearby Longyearbyen. Passive samplers require no electricity and provide an integrated picture of the levels of the targeted compounds over time. The results were combined with the sampled sediment and *Gammarus* spp. to assess concentrations in the environment. Out of all substances under study, PBDE-47 and -99, α - and β -tetrabromoethylcyclohexane (TBECH), syn- and anti-DP were detected in all investigated matrices. Freely dissolved water concentrations of Σ DPs (3 pg/L) were in line with recent Arctic studies, while Σ PBDEs (3 pg/L) were comparable to urban rivers in southern Norway. Nevertheless, for some compounds, especially the lighter and most volatile ones, long-range transport is most likely a more important contribution to observed levels than local sources. For other compounds, e.g. PBDEs, local sources might still play a role for the load of contaminants into the surrounding environment.

The present study is the first to report a suit of nBFRs and DPs in Arctic benthic fauna. Many of the nBFRs and DPs were detected in sediment and in the amphipods. We recommend further studies with respect to measurements of concentrations over time, and in other species as well, to better understand whether the nBFRs and DPs are common in the marine environment on Svalbard. We recommend that local sources of flame retardants in remote areas receive more attention in the future.

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Preface

This report presents the results from the project “Investigation of new flame retardants in Svalbard benthic marine food web; FlammePlank” (Nye flammehemmere i biota –kommer dem fra nærområdet eller med langtransport? -FlammePlank). The project has been funded by Svalbard Environmental Fund with NIVA as project manager in close cooperation with Akvaplan-niva, University in Oslo, NILU and Research Centre for Toxic Compounds in the Environment (RECETOX, Brno). Pernilla Carlsson has been the project leader at NIVA. Sampling of sediments was carried out in collaboration with UNIS students. Deployment and collection of passive samplers and collection of amphipods were done by Pernilla Carlsson and Øystein Varpe. Analyses and calculations of data were performed at RECETOX by Jaromír Sobotka and Branislav Vrana. Outreach and communication during the project has been handled by Pernilla Carlsson. The report is written by Pernilla Carlsson with support from Øystein Varpe, Jaromír Sobotka and Branislav Vrana, Katrin Borgå and Pernilla Bohlin Nizzetto. Roar Brænden reported the data into the Vannmiljø database. Sissel Ranneklev and Ian Allan did the QA of the report. All participants are grateful for the possibility to perform this project and acknowledge Svalbard Environmental Fund for this opportunity.

Tromsø, 27.03.2018

*Pernilla Carlsson,
Project leader*

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Summary

The aim of this pilot-study was to use silicone rubber-based passive samplers to measure novel brominated flame retardants (nBFRs), polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DP) in seawater and air around Longyearbyen as well as investigate the presence of those compounds in sediment and biota (amphipods, *Gammarus* spp.) nearby Longyearbyen. Passive samplers require no electricity and gives an integrated picture over time of the targeted compounds. These samplers were deployed twice in both water and air; once in 2015 and once in 2016. The results were combined with the sampled sediment and *Gammarus* spp. to assess concentrations in the environment. The PBDE-47 and -99, α - and β - tetrabromoethylcyclohexane (TBECH), *syn*- and *anti*-DP were detected in all investigated matrices. The DPs were found in higher concentrations in the air than reported from other remote Arctic areas. Water concentrations of Σ DPs (3 pg/L) were in line with the Σ PBDEs (3 pg/L) concentrations. The sum of nBFRs was 37 pg/L in the water samples. The sediment samples were dominated by PBDEs and the average concentrations of the different PBDE congeners varied between 0.1-1.9 ng/g dw. The amphipods were dominated by Σ DPs (average: 213 pg/g ww). Nevertheless, for some compounds, especially the lighter (low molecular weight) and smaller ones, long-range transport is most likely a more important contribution than local sources. For other compounds, e.g. PBDEs, local sources might still play a role for the load of contaminants into the surrounding environment.

The present study is the first to report a suit of nBFRs and DPs in Arctic benthic fauna. Many of the nBFRs and the DPs were detected in sediment and in the amphipods and we recommend further studies on them regarding concentrations over time and in other species as well to better understand whether the nBFRs and DPs are common in the marine environment on Svalbard.

We recommend that local sources of flame retardants in remote areas receive more attention in the future.

Sammendrag

Målet med denne pilotundersøkelsen var å bruke silikonbaserte passive prøvetakere for å undersøke nye bromerte flammehemmere (nBFR), polybrominerte difenyletere (PBDE) og dechloran plus (DP) i sjøvann, luft, sediment og biota (amphipoder, *Gammarus* spp.) i nærheten av Longyearbyen. Passive prøvetakere krever ingen elektrisitet og gir et tidsintegrert bilde av konsentrasjonene av stoffene vi undersøker. Prøvetakingen i vann og luft ble gjennomført i 2015 og 2016. Resultatene ble kombinert med prøver fra sediment og av *Gammarus* spp. for å vurdere konsentrasjoner i miljøet rundt Longyearbyen. PBDE-47 og -99, α - og β -tetrabrometylcykloheksan (TBECH), *syn*- og *anti*-DP ble påvist i alle matriser og DP-ene ved høyere konsentrasjoner i luften enn rapportert fra andre fjerne arktiske områder. Vannkonsentrasjonene av Σ DP var i prinsipp (gjennomsnitt: 2,6 pg/L) samme som for Σ PBDEer (gjennomsnitt: 2,9 pg/L). Summen av nBFR var 37 pg/L i vannprøvene. For noen forbindelser, spesielt de mest volatile og mindre molekylene, er langtransporte tilførsler sannsynligvis et viktigere bidrag enn lokale kilder. For andre forbindelser, f.eks. PBDEer, kan lokale kilder fortsatt spille viktig en rolle for tilførsel av miljøgifter til de nærmeste omgivelsene.

Denne studien er den første som prøvetar og analyserer flere nBFRs og DP-er i bentiske invertebrater fra Arktis. Mange av nBFR-ene og DP-ene ble funnet i sedimenter og i amphipodene, og vi anbefaler videre studier om dem og med fokus på konsentrasjoner over tid samt i andre arter for å bedre forstå hvor nBFR og DP finnes i miljøet på Svalbard og om det tas opp videre i næringskjeden her.

Vi anbefaler at lokale kilder til flammehemmere i arktiske strøk får mer oppmerksomhet i fremtiden.

Tittel: Undersøkelser av nye brominerte flammehemmere i et bentisk næringsnett på Svalbard;
FlammePlank

År: 2018

Forfatter(e): Pernilla Carlsson, Branislav Vrana, Jaromír Sobotka, Katrine Borgå, Pernilla Bohlin Nizzetto, Øystein Varpe

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1 Introduction

Brominated flame retardants (BFRs) are used in a large suit of materials such as textiles, plastic and electronic equipment. In 2013, 280 tonnes of BFRs were used in Norway only (Norwegian Environment Agency, 2017). With increased human activity and larger, modern settlements in the Arctic, the usage of flame retardants will most likely increase in these settlements. Hence, even if some of the nBFRs might not undergo long-range transport, they could still be present in the Arctic due to local sources. It is important to understand the impact of local sources on the nearby environment as well as knowing the concentrations and distribution patterns in the environment and disentangle local sources from long-range transport. There are examples where pollution at Arctic sites mainly comes from local sources and not from long-range transport, such as PFAS from airports in remote parts of Canada, PCB from abandoned settlements and siloxanes from local sewage outlets in Svalbard (Pedersen et al., 2011; Stock et al., 2007; Warner et al., 2010).

The polybrominated diphenyl ethers (PBDEs) have been shown to bioaccumulate, be persistent, toxic and undergo long-range transport in the environment and has therefore been added to the list of persistent organic pollutant (POPs) under the Stockholm Convention and the Aarhus protocol of the Convention on Long-range Transboundary Air Pollution (CLRTAP) (de Wit et al., 2006, 2010)(UNECE, 2018). PBDEs are still present in the environment and impose a possible environmental harm. After regulation of the PBDEs, the industry has introduced alternative BFRs as replacements. These novel BFRs (nBFRs) include a wide range of individual compounds and the list is continuously growing. There are also chlorinated flame retardants such as *syn*- and *anti*- dechlorane plus (*syn*-DP and *anti*-DP) in production today.

One of the PBT (persistent, bioaccumulative and toxic) criteria for environmental pollution compounds is fulfilled if a compound reaches the Arctic since the compound then is persistent enough to undergo long-range transport. The target compounds of the present study have been found in air, glacier and biota from high trophic levels within the Arctic, including Svalbard, but there is very little information available on concentrations of flame retardants in low trophic levels, and especially in the Arctic. As examples can be mentioned that 2,3-dibromopropyl- 2,4,6-tribromophenyl-ether (DPTE) was found in hooded seals (*Cystophora cristata*) from the Barents Sea and decabromodiphenylethane (DBDPE) has been reported in biota from Svalbard such as egg from Brünnich's guillemot (*Uria lomvia*), polar cod (*Boreogadus saida*) and plasma from polar bears (*Ursus maritimus*) (de Wit et al., 2010; Harju et al., 2013; Sagerup et al., 2010; von der Recke and Vetter, 2007).

There is a need to investigate and get to know the concentrations and environmental fate of the novel BFRs (nBFRs) in Arctic environment to provide data for a sound management of these compounds. This need is especially prominent on lower-medium trophic levels in biota as well as the long-range transport pathways; atmospheric and oceanic currents. Without understanding the environmental fate on these levels, it will be difficult to fully understand the environmental fate and transport higher up in the food web.

As pointed out in the new AMAP assessment on contaminants of emerging concern in the Arctic, there is a need for more research and information on the distribution, sources and pathways of these chemicals (AMAP, 2017). The present study aims to fill some of these knowledge gaps and investigate whether an Arctic community with about 2000 inhabitants impacts the concentrations of new and regulated flame retardants in local air and its marine surroundings. This study is also a pilot study on the accumulation of BFRs and DPs in marine and relatively long-lived amphipods in comparison to

their environmental surroundings. We deployed passive samplers in air and water during two field campaigns and collected sediment and biota (amphipods) from the Adventfjorden area to investigate the presence of flame retardants in the area.

2 Material and methods

2.1 Sample collection

A total of 24 samples of sediment, benthic fauna (littoral amphipods), water and air were collected within Longyearbyen during 2015-2017 (78°13'N, 15°38'E, Table 1, Figure 1). All equipment used for sampling was pre-cleaned with acetone and n-hexane to minimise contamination by the sampling equipment. The handling of samples indoors was kept at a minimum to minimise the risk of contamination. All samples were kept frozen from sampling and until analyses.

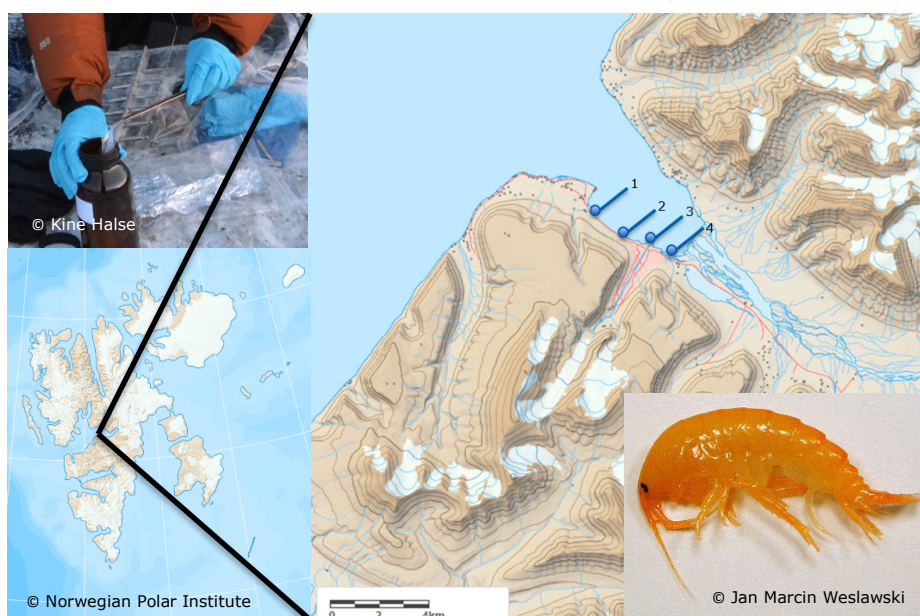


Figure 1. Map over Svalbard and Longyearbyen. The water (PS), air (PS) and sediments were sampled at the sampling site 1 “Small boat harbour”. One sediment sample was also taken from site 3. The amphipods (e.g. *Gammarus setosus*, lower right corner) were sampled from all four sites (1-4) along the beaches in Longyearbyen. Deployment of the passive samplers are shown in the upper left corner. Maps from Norwegian Polar Institute.

2.1.1 Air and water

Air and water samples were collected using pre-cleaned passive samplers (PS) based on silicone rubbers (SR). The PSs were spiked with performance reference compounds (PRCs) before deployment in the field to be able to evaluate the uptake of the target compounds since the PRCs are partially released from the sampler during exposure in a pace that can be related to the uptake of the target compounds and used for calculations of the concentrations of target compounds in e.g. air or water. The PSs were deployed for three months at the small boat harbour (Station 1, Figure 1) at 1m height (air) and 0.5 m depth (water). A picture of the samplers is shown in Figure 2. The time when sampling was conducted is shown in Table 1. Due to waves and currents, the PSs deployed in

water (2016) were pushed into shallow water and had been exposed to air during parts of the low tide at the time they were collected. Field blanks were used to control for any kind of unwanted contamination during handling of the samplers and were exposed to the environment when the samplers were deployed and collected.



Figure 2. Retrieval of passive samplers from water after three months of exposure in the small boat harbour. Photo: Pernilla Carlsson.

2.1.2 Sediment

Surface sediments (Table 1) were sampled with a Van den Veen grab close to the small boat harbor (Station 1, Figure 1) in January 2016. One additional sediment sample was collected from the littoral zone of Adventfjorden (Station 3, Figure 1) in March 2017. The sediments were dried and sieved at UNIS before freezing.

2.1.3 Biota (amphipods)

Amphipods were collected in the littoral zone of the Adventdalen estuary and along the beaches (station 1-4, Figure 1) in July to August, 2016. The amphipods hide under stones and can be accessed and picked by turning stones during low tide. Nine samples of pooled individuals were collected (Table 1). The amphipods collected were *Gammarus spp.*, especially *G. setosus* (Ambrose Jr and Leinaas, 1990; Weslawski, 1994). Any sediment particles were removed and the samples were packed in the field and handled as little as possible in the laboratory before freezing. Figure 3 shows sampling of the amphipods in the Adventfjorden estuary.

Table 1. Overview of collected samples for flame retardants analyses, sites, number of samples and time period for sampling campaigns. Locations of site numbers are shown in Figure 1.

Sample type	Number of samples (total and per year)	Time period for sampling	Site within Longyearbyen
Water	3; 1 in 2015, 2 in 2016	March-May 2015, Feb.-May 2016	1
Air	3; 1 in 2015, 2 in 2016	March-May 2015, Feb-May 2016	1
Sediment	10*; 8 in 2016, 1 in 2017	Jan. 2016, March 2017	1, 3
Amphipods	9	July-Aug. 2016	1, 2, 3, 4

*One bulk sample (site 3) of 2016 samples is also included in the total number of analyses.



Figure 3. Sampling of amphipods at low tide. One sample is around 5-10 gram amphipods to get enough material for chemical analysis. Photo: Øystein Varpe.

2.2 Analysis

All samples were analysed for a suit of eight PBDEs, 22 nBFRs, anti- and syn-DP, and Dechlorane Plus Mono Adduct (DPMA). A list of the compounds is shown in appendix 1 and the average concentrations (including minimum and maximum concentrations and standard deviations) are shown in appendix 2. The passive samplers were also analysed for 18 organophosphorus flame retardants (OPFRs). For details, please see Carlsson et al. (2018). Analyses of air, water, amphipods and individual sediment samples were done at RECETOX, Czech Republic. Analysis of bulk sediment sample and sediment sample from site 3 were done at NIVA, Oslo.

Total organic carbon (TOC) in sediments was analysed at NIVA (accredited laboratory, ISO 17025) as a supporting parameter analysis. Briefly, the homogenized sediment samples were mixed with hydrochloric acid, flushed with air to remove the inorganic and volatile carbons. Afterwards, the samples were burned and the amount of CO₂ (proportional to the amount of TOC) was measured with infra-red light.

2.2.1 Analyses of nBFRs, PBDEs, DPs and PRC compounds

The detailed description of the clean-up and instrumental methods are described in Carlsson et al. (2018). The amphipods were cleaned from sediment particles on the outside (however, it was not practically feasible to allow them to clean their gut in clean sea water before freezing) before homogenization. Briefly, all samples were thawed, spiked with internal standards and Soxhlet extracted before evaporation and a following silica clean-up step. The passive samplers were extracted with methanol while amphipods and sediment were extracted with dichloromethane (DCM). The sediment and biota samples required gel permeation chromatography clean-up, followed by acidified silica and copper treatment of the sediment as well. Due to the acidic treatment of the samples, the OPFRs and the nBFRs «2-ethylhexyl-2,3,4,5-tetrabromobenzoate; EH-TBB» and «bis(2-ethylhexyl)tetrabromophthalate; BEHTBP» couldn't be analysed in biota and sediment due to their partial destruction during sample clean-up with sulfuric acid. All samples were analysed by gas chromatography-mass spectrometry (GC-MS) The MS was operated in electric ionization (EI+) mode at the resolution of >10 000 for PBDEs, nBFRs and DPs at RECETOX, but in negative chemical ionization (NCI) mode at NIVA for PBDE-analysis of sediment.

2.2.2 Organophosphorous flame retardants (OPFRs)

The passive samplers were analysed for OPFRs as well, but due to little information on the participation coefficient between passive sampler and water (K_{pw}) in cold temperatures for silicone rubbers, the data is not discussed, but it is presented based on the measured concentrations in the passive samplers in appendix 3. K_{pw} is used to calculate the water concentration based on the concentrations measured in the passive sampler. The analytical method is similar to the method for the BFRs regarding clean-up, while the analysis was as follows: the samples were analysed with a GC-MS/MS using a 6890N GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 µm Rxi 5Sil MS column (RESTEK) coupled to a Quattro Micro GC tandem mass spectrometer (Waters, Micromass, UK). The MS was operated in (EI+) using two MRM transitions for each compound. Injection was done in splitless mode with 2 µL at 250°C, and He as carrier gas at 1.4 mL min⁻¹. The GC temperature program was 80°C (1 min hold), then 40°C min⁻¹ to 230°C (5 min hold), followed by 5°C min⁻¹ to 300°C and 20°C min⁻¹ to 320°C (6 min hold).

2.3 Calculations of atmospheric and aqueous concentrations of brominated flame retardants and dechlorane plus

PRCs indicated the degree of equilibrium reached by the sampler for compounds with a range of partition coefficients; K_{pa} (SR/air) or K_{pw} (SR/water). The concentrations left in the passive samplers after exposure indicated that the samplers were far from equilibrium with the sampled matrix for most compounds. Hence, the sampling was assumed to be fully integrative for all compounds. In this situation, concentration of compounds in the air can be calculated as:

$$C_a = \frac{N_{SR}}{R_s t}$$

Where N_{SR} is the concentration of the analyte in the sampler (pg/sampler) at the exposure time, t is time of exposure (in days), R_s is the sampling rate of the compound (m^3/day) as generic values from Okeme et al. (2016).

Aqueous concentrations, C_w , of individual compounds were calculated from the mass absorbed by the passive samplers (SRs), N_{SR} , the degree of equilibrium, DEQ , that the compound attained during sampler exposure (further calculations and references to e.g. usage of PRCs are provided in Carlsson et al. (2018), the mass of sampler, m_{SR} , and their sampler-water partition coefficients $K_{SR,w}$ (Booij et al., 2007).

$$C_w = \frac{N_{SR}}{K_{SR,w} m_{SR} DEQ}$$

2.4 Bioaccumulation calculations

The bioaccumulation factor (BAF) described how much of a compound that is accumulated in the biota. The BAF can be estimated from concentrations in the water and amphipods. The lipid content in the amphipods was assumed to be 10% based on species and locality, although we also included calculations with 5 % and 15 % lipids to take seasonal and individual variations into account (Nygård et al., 2010; Szaniawska and Wolowicz, 1985). The BAF calculation is shown below, where C_{biota} is the concentration of a compound per lipid weight and C_{water} is the dissolved concentrations in water. For biota-sediment accumulation (BSAF), C_{water} is replaced by the concentration in the sediment, which has been normalised for total organic carbon (TOC). The BSAF calculation is also shown below.

$$\text{Log BAF} = \frac{C_{biota}}{C_{water}}$$

$$\text{Log BSAF} = \frac{C_{biota}}{C_{sediment}}$$

2.5 Quality assurance and control

The average recoveries of PBDEs varied between 52-165% for amphipods, 42-147% for sediment and 70-121% for the passive air and water samples. The recoveries for nBFRs and DP (BTBPE, syn- and anti-DP, PBBz and HBBz) varied between 32-85% (amphipods), 19-33% for the sediment samples and 102-129% (passive samplers). The limit of detection (LOD) was defined as $3 \times S/N$ when a compound was not detected in the blank, otherwise the average blank concentration + $3 \times$ standard deviation in the blanks (and reference passive samplers for air and water) were used. The limit of quantification (LOQ; set to $3 \times$ LOD) for the matrix water was calculated by inserting the amount found in the field blank to the formula for calculation of water concentrations – given in section 2.3. The sample results were not blank subtracted or recovery corrected. Samples $<LOD$ was not included in statistical analyses and all values are presented based on compounds $>LOD$ together with a note on the percentage of samples $>LOD$. Concentrations in the field blanks are presented in appendix 4 and LODs are presented in appendix 5.

3 Results

The analytical results for PBDEs, nBFRs and DP in all matrices are listed in appendix 2. All individual concentrations are reported in the Vanmiljø database. OPFR Concentrations measured in the passive samplers in water and air are listed in appendix 3 but not discussed in depth due to the lack of appropriate coefficients in the cold environment for conversion of concentrations in samplers to quantitative concentrations in water/air. The partial exposure to air of the water samplers could have affected the results, although the concentrations in the samplers differ and hence, the impact is considered to not have a major impact on the results. An overview of the nBFR, PBDE and DP results, including an indication for percent of samples above detection limits are given in Table 2.

Table 2. Average concentrations of compounds in sampled matrices. The colour codes show the % of samples $>LOD$. LODs are presented in appendix 5. Sample concentration ranges are presented in appendix 2.

	Air	Water	Sediment	Amphipods		Air	Water	Sediment	Amphipods
PBBz	<LOD	<LOD	1.2	3.8	PBDE28	<LOD	<LOD	<LOD	<LOD
BTBPE	<LOD	<LOD	<LOD	0.5	PBDE47	234	1.6	1 910	39
HBBz	<LOD	<LOD	1.8	3.5	PBDE66	<LOD	<LOD	NA	<LOD
PBEB	16	<LOD	2.5	1.1	PBDE85	<LOD	<LOD	NA	<LOD
PBT	45	<LOD	<LOD	7.3	PBDE99	295	1.3	1 840	30
α -TBCO	<LOD	30	<LOD	<LOD	PBDE100	96	<LOD	330	14
BEHTBP	1 867	7.1	NA	NA	PBDE153	<LOD	<LOD	<LOD	<LOD
EH-TBB	86	<LOD	NA	NA	PBDE154	<LOD	<LOD	100	<LOD
TBP-AE (ATE)	<LOD	<LOD	<LOD	0.1	PBDE183	<LOD	<LOD	<LOD	<LOD
TBP-DPBE (DPTE)	<LOD	<LOD	<LOD	5.5	PBDE196	NA	NA	1 730	NA
β -TBECH	31	0.3	1.3	0.3	PBDE209	NA	NA	<LOD	NA
α -TBECH	48	0.3	1.1	0.4	HCDBCO	<LOD	<LOD	<LOD	<LOD
synDP	356	1.5	6.2	82	BATE	<LOD	<LOD	<LOD	<LOD
antiDP	349	1.1	9.6	131	T23BPIC	<LOD	<LOD	<LOD	<LOD
DPMA	<LOD	<LOD	2.1	4.9	TBCT	<LOD	<LOD	<LOD	<LOD
pTBX	<LOD	<LOD	0.8	<LOD	PBBA	<LOD	<LOD	<LOD	<LOD
β -TBCO	<LOD	<LOD	<LOD	<LOD	Colour coding:	0-25% >LOD	25-50% >LOD	50-75% >LOD	75-100% >LOD

Units: air: pg/m³, water: pg/L, sediment: pg/g dw, amphipods: pg/g ww.

3.1.1 Air

The air samples were dominated by BEHTBP (55%, 1867 pg/m³) and *syn-/anti*-DP (20% together, 356 and 349 pg/m³, respectively (Figure 4). Among the analysed compounds, the following five nBFRs/DPs were detected in more than 50% of the air samples; BEHTBP, α - and β -TBECH, *syn*- and *anti*-DP. Only three of the PBDE compounds (BDE-47, -99 and -100) were detected in the air. One of the sample contained pentabromoethylbenzene (PBEB) at comparable concentrations (0.02 pg/m³) to other Arctic sites where the PBEB concentrations ranged from below the detection limits and up to 0.11 pg/m³ in Barrow, St. Laurence Island, Stórhöfði and Ny-Ålesund (AMAP, 2017). Two of the samples in the present study that contained PBT showed higher concentrations (0.03 and 0.06 pg/m³) than what has been reported from remote atmospheric measurements in the Arctic; <LOD-0.005 pg/m³ at Barrow, St. Lawrence Island and Ny-Ålesund (AMAP, 2017).

3.1.2 Water

The water samples were dominated by α -TBCO (48% and 76% in 2015 and 2016, respectively) followed by BEHTBP (14-23%). The PBDEs contributed to 5% and 15% (2015 and 2016, respectively) of all BFRs/DPs analysed. The relative distribution is shown in Figure 4. The PBDE concentrations were slightly higher in the water around Longyearbyen compared with East Greenland Sea, which could be related to the location of the samplers in the present study; close to a village (Möller et al., 2011). *Syn*- and *anti*-DP contributed to 13% in 2015 but decreased to 3% in 2016.

3.1.3 Amphipods

Syn- and *anti*-DP contributed to an average of 61% of the analysed compounds detected in the amphipods (Figure 4). The PBDEs were below the detection limits in four of the samples. For the other samples, where PBDEs were detected, the congeners BDE-47, -99 and -100 dominated and contributed to 5-26% of the compounds analysed. The concentration of BDE-47 was 39 pg/g ww on average in the samples where it was detected. To our knowledge, nBFRs have not been analysed in Arctic benthic fauna and PBDEs have not been analysed in Arctic littoral amphipods before. The amphipods were analysed without cleaning the gut and hence, the samples may reflect the contaminant distribution within the sediment.

3.1.4 Sediment

PBDEs dominated extensively among the analysed compounds analysed in the sediment samples, followed by *syn*- and *anti*-DP. The dominating compounds were BDE-47 and -99, with concentrations in the bulk sample of 1910 and 1840 pg/g dw, respectively, followed closely by BDE-196 (1730 pg/g dw in the bulk sample). Average, minimum and maximum concentrations and standard deviations for the individual samples are provided in appendix 2.

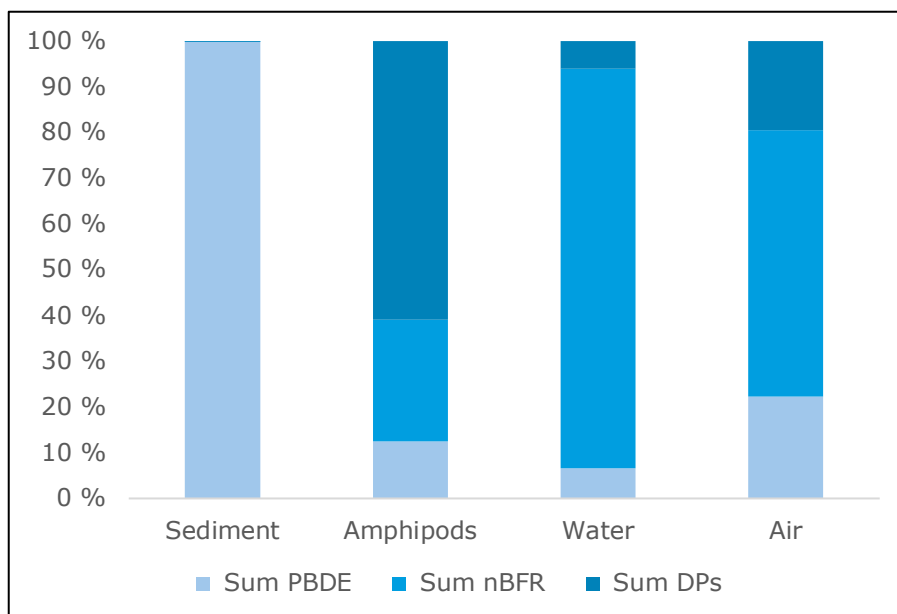


Figure 4. Relative distribution of Σ PBDE, Σ nBFR and Σ DP in all samples. Only concentrations above the detection limits are included.

4 Discussion

4.1 Potential for bioaccumulation

The nBFRs with the smallest molecular weights among the compounds analysed (HBBz, PBEB and PBT) were all detected in the amphipods. The bioaccumulation factor (BAF) was estimated from the dissolved concentrations in the water (PBT was the only one of these, smaller nBFRs detected in the water) and in the amphipods. The lipid content in the amphipods was assumed to be 10% based on species and locality (Nygård et al., 2010; Szaniawska and Wolowicz, 1985; Varpe, 2017). Log BAF for a suit of compounds are presented in Table 3. *Syn*-DP and *anti*-DP also had high log BAFs in these calculations, but the large size of these molecules (654 Da) might hamper bioaccumulation. A common rule of thumb is that molecules larger than 600 Da in general are too large for being able to undergo bioaccumulation. There are a few studies on *syn*-DP and *anti*-DP in the Arctic but with different results regarding detected/non-detected concentrations in biota and hence, difficult to draw any conclusions on the bioavailability and accumulation (AMAP, 2017).

Bioaccumulation calculations are sensitive to the sampling season since lipid concentrations of the organisms impact the calculations (Carlsson et al., 2016), and lipid content of Arctic and high-latitude organisms can vary considerably throughout the year (Nygård et al., 2010; Varpe, 2017). Seasonality is also impacting bioaccumulation in pelagic food webs (Hallanger et al., 2011). This impact of seasonality seems smaller in benthic food webs (Evenset et al., 2016). The log BSAF and log BAF values in the present study Table 3 should be evaluated with age, lipid dynamics and seasonality in mind, especially since the transport pathways of nBFRs and DPs are much less known compared to legacy POPs such as PCBs.

Table 3. Log BAF and log BSAF calculated from concentration data in amphipods, passive water samplers and sediment in the present study. A range of log BAF and log BSAF depending on variations in lipid concentrations are presented. For the sampling season of the amphipods the lipid content is estimated to be around 10% (Nygård et al., 2010).

	Log BAF			Log BSAF		
	15% lipids	10% lipids	5% lipids	15% lipids	10% lipids	5% lipids
PBBz	6.95	7.13	7.43			
PBEB				0.8	1.0	1.3
α-TBECH	6.96	7.13	7.44	0.7	0.9	1.2
β-TBECH				0.6	0.8	1.1
Syn-DP	8.70	8.88	9.18	2.3	2.5	2.8
Anti-DP	8.89	9.07	9.37	2.3	2.5	2.8
DPMA				1.6	1.7	2.0
PBDE47	8.08	8.26	8.56	-1.0	-0.8	-0.5
PBDE99	7.99	8.16	8.46	-1.3	-1.1	-0.8
PBDE100				-0.9	-0.7	-0.4
Bulk sediment sample						
BDE-47				-0.6	-0.5	-0.2
BDE-99				-0.8	-0.6	-0.3
BDE-100				-0.4	-0.2	0.1

Only compounds >LOD in sediment/water and amphipods were included.

^aThe total carbon (TC) was 5.0%

4.2 Potential for local sources

Polybrominated diphenyl ethers (PBDEs)

The concentrations of BDE-47 and -99 in air at Longyearbyen, obtained from the passive air samplers in this study, were two-three orders of magnitude higher than those measured at Zeppelin observatory, using active air samplers, during the same time period; March-May 2015. (Aas and Bohlin-Nizzetto, 2017). The data is shown in Table 4. These results suggest that PBDEs in Adventfjorden harbour area might come from local sources and not solely long-range transport (Ruus et al., 2014). Nevertheless, the PBDEs were not dominating the air, water and biota samples, but they did dominate the sediment samples. Σ PBDE in lake sediments from earlier studies on Svalbard were 5-470 times lower than the present study, ranging from 25.5 pg/g dw in Kongressvatnet, close to Barentsburg in Grønnfjorden and up to 2383 pg/g dw in Åsövatnet on the north-west part of Spitsbergen. The reason for the higher concentrations in Åsövatnet compared to Kongressvatnet and lakes from the same region as Åsövatnet are most likely input from bird colonies, as seen in Ellasjøen at Bjørnøya (Evenset et al., 2007). However, this is not the case for Advetnfjorden, but the elevated concentrations in the present study are most likely a result of a very local contamination within a limited area around the harbour. This is in line with that PBDEs in an additional sample in the present study from the littoral zone (site 3) in Longyearbyen were below the detection limits. With regards to that and earlier analyses of PBDEs in the sediment from further out in Adventfjorden that showed lower concentrations of PBDEs, we believe that the elevated result in the present study is due to human activity, but within a small area. However, it is difficult to know how big/small this area/spot is, if it is a very local spot, or a more diffuse area.

When looking into Σ PBDE concentrations in sediment from outside other Nordic settlements, the sediment samples (both on individual and on bulk sample basis) from this study had orders of

magnitude higher concentrations compared to Tromsø harbour (130 pg/g dw), a 75 000 people city in Northern Norway (Fjeld et al., 2004). The concentration and relative distribution pattern of PBDEs in the sediment samples from Longyearbyen were similar to the distribution pattern of those PBDE congeners around Lillehammer (28 000 inhabitants), lake Mjøsa, where there have been point sources (Fjeld et al., 2004). The total concentration (without BDE-209) in Mjøsa were 14 200-16 600 pg/g dw. A recent study of BDE-209 in sediments in Kongsfjorden, close to the research community Ny-Ålesund on Svalbard showed elevated concentrations outside the harbour compared to their stations further out in Kongsfjorden (averages 230 and 100 pg/g dw, respectively) (Ma et al., 2015). Ny-Ålesund also receives several cruise ships during the summer time, which could contribute to elevated concentrations of BFRs around harbours on Svalbard. However, earlier studies as well as the one sample from a local beach in the present study did not show high concentrations within the fjord (Evenset et al., 2009). The concentrations differences between the samples from the local harbour in the present study and the samples further out in Adventfjorden are either a result of a very local “hot-spot” sampled in the present study, or dilution/high sedimentation rates in the fjord that causes low PBDE concentrations there. There is reason to believe that the PBDE in the sediment samples in the present study came from a local “hot spot”, although it might be difficult to identify the source or to re-localise due to sedimentation in the fjord and harbour area. All in all, the results in the present study means that it cannot be out-ruled that some of the PBDE in the environment comes from local sources. Examples of sources that could be investigated further are the sewage outlet, particles and run-off from the roads and the city.

Table 4. Concentration range of PBDEs and DPs in Arctic air (pg/m³ for gas and particulate phase) and water (pg/L) from recent studies.

Area	ΣPBDE in air (pg/m ³)	ΣPBDE in water (pg/L)	Syn-DP in air (pg/m ³)	Syn-DP in water (pg/L)	Anti-DP in air (pg/m ³)	Anti-DP in water (pg/L)
Villum station, Greenland ¹	0.2-6.26 (gas + particles)*					
East Greenland Sea ²	0.06-1.6 (gas)	0.03-0.64	0.29 (gas), 0.47 (particles)	0.04	0.09 (gas), 0.04 (particles)	0.02
Nuuk ³	0.14-3.26 (gas + particles)*					
Svalbard, Ny-Ålesund ⁴	5.3 (gas, passive air sampler)					
Svalbard, Ny-Ålesund, Zeppelin ^{4,5}	ΣPBDE: 0.13-13.9, BDE-47: 0.04 -7.32, BDE-99: 0.01 - 0.19, BDE-100: 0.00 - 0.13 gas+particles).					
Present study	ΣPBDE: 593 (BDE-47: 234, BDE-99: 295) (gas, passive air sampler)	2.9	356 (gas, passive sampler)	1.5	349 (gas, passive sampler)	1.1

* The samplers were inside a hut with large temperature difference compared to the outdoor environment. To avoid problems related to disturbing of the gas-particle phase equilibrium, the gas and particle samples were combined before analyses.

¹ Range for PBDE congeners in air and aerosols during the monitoring at Zeppelin station 2015. ΣPBDE includes PBDE-28, -47, -49, -66, -71, -77, -85, -99, -119, -138, -153, -154, -183, -196, -206, -209.

References: ¹Bossi et al. (2016); ²Möller et al. (2010, 2011), ³Bossi et al., (2008), ⁴Pozo et al., (2006), ⁵Aas and Bohlin-Nizzetto, (2017)

4.2.1 Hexabromobenzene (HBBz) and pentabromobenzene (PBBz)

HBBz and PBBz were detected in two of the sediment samples and in seven and three of the amphipod samples, respectively. The compounds were not detected in any of the air or water samples even though recent studies in Longyearbyen reported HBBz (median 0.12 pg/m³) and PBBz (median 0.04 pg/m³) in the atmospheric particle phase (Salamova et al., 2014). Samples from Ny-Ålesund also contained HBBz in the gas phase (<LOD-0.67 pg/m³) although the LODs in that study were lower than in the present study (AMAP, 2017; Lee et al., 2016). Regarding biota, a recent study reported HBBz below the detection limits in liver samples from kittiwakes, Arctic foxes and ringed seals in Svalbard (Sagerup et al., 2010). The overall few samples where it was detected in the present study, in combination with similar concentrations at remote areas on Svalbard suggests that the source might not be of local origin, although diffuse run-off from local sources cannot be ruled out due to the earlier findings close to the settlement. HBBz is a fairly small and volatile compound that can undergo long-range transport (AMAP, 2017, p. 2017; de Wit et al., 2010). Due to the structural similarities between HBBz and PBBz, there is reason to believe that also PBBz can undergo long-range transport.

4.2.2 *Syn-* and *anti-dechlorane plus*

Syn- and *anti-DP* were detected in all matrices in the study. The concentrations in the sediment samples (average of 15 pg/g dw of Σ DP) were lower than sediments from Great Lakes (the averages of Σ DP ranged between 330-26000 pg/g dw) but in line with sediment from Kongsfjorden at Svalbard, where the concentrations were 6 pg/g dw of Σ DP (Ma et al., 2015; Shen et al., 2010; Sverko et al., 2011). Another recent study from Kongsfjorden showed average concentrations of Σ DP in the sediment that was higher than the present study; 340 pg/g dw (Na et al., 2015). It is also important to keep in mind that there is an analytical uncertainty between laboratories on these relatively little analysed compounds, which could be part of the explanation of the different concentrations between Ny-Ålesund and Longyearbyen. Also, (Na et al., 2015) did not report TOC content in their sediment samples, which makes it very difficult to compare TOC-normalised concentrations. The amount of TOC can impact the concentrations of environmental pollutants present in the sediment.

4.2.3 Pentabromotoluene (PBT) and pentabromoethylbenzene (PBEB)

With the atmospheric behaviour of PBT and PBEB (single/multiple hoppers), it cannot be out-ruled that their presence in amphipods, air and sediment (PBEB) around Longyearbyen originates from long-range transport. When the air samples are compared with even more remote sites in the Arctic, a local contribution from Longyearbyen cannot be excluded either due to higher atmospheric concentrations in Longyearbyen. PBEB ranged between <LOD-16 pg/m³ in Longyearbyen and PBT ranged between <LOD-61 pg/m³. This can be compared to PBT (0.001-0.02 pg/m³) in East Greenland Sea (Möller et al., 2011)). This conclusion is somewhat hampered by the usage of passive air samplers that have an uncertain uptake/accumulation of less volatile compounds.

4.3 Further recommendations

Passive samplers are a suitable tool for sampling in remote areas. However, assessing uptake rates in cold environment needs to be further investigated to fully use the potential of passive samplers in the Arctic. Littoral amphipods are a good matrix for investigations of local contamination based on the easy access to collecting them and their life history. These amphipods will reflect their surrounding environment. Nevertheless, the passive samplers in air and water together with the samples of amphipods and sediments shows the presence of new flame retardants as well as older

flame retardants in the surroundings of Longyearbyen. There is reason to believe that Longyearbyen is a source of these compounds and it should be taken into account when further studies are being made; Longyearbyen cannot be considered as pristine environment with regards to emerging contaminants. However, the concentrations found and only in few samples indicates that there is no need for acute measures, but for the future, the risk of local contamination of the surrounding environment needs to stay in focus during planning and increasing activities in Longyearbyen and Svalbard.

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7 Appendix

Appendix 1. Chemical-physical properties, full name and abbreviations of the analysed compounds.

	Water solubility (mg/L 25°C)	Molecular weight (Da)	Log Kow	Log Koa
Polybrominated diphenyl ethers (PBDEs):				
BDE-28	0.07 (1)	406,90	6,24	9.41 (8)
BDE-47	0.015 (1)	485,79	6,80	10.6 (8)
BDE-66	0.018 (1)	485,80	7,00	10.6 (8)
BDE-85	0.006 (1)	564,69	7,27	11.5 (8)
BDE-99	0.009 (1)	564,69	7,38	11.5 (8)
BDE-100	0.04 (1)	564,69	7,09	11.5 (8)
BDE-153	0.001 (1)	643,59	7,86	11.7 (8)
BDE-154	0.001 (1)	643,59	7,62	11.7 (8)
BDE-183	0.002 (1)	722,48	8,61	11.7 (8)
BDE-209	<0.001 (1)	959,17	9,87	11.7 (8)
DPs:				
Syn-dechlorane plus (<i>syn</i> -DP)	0.00004 (8)	653,72	9,30	11.7 (8)
Anti-dechlorane plus (<i>anti</i> -DP)	0.00004 (8)	653,72	9,30	11.7 (8)
Dechlorane Plus Mono Aduct (DPMA)	No info	380,95	8,00	No info
nBFRs:				
Hexabromobenzene (HBBz)	0.003 (1)	551,49	6,11	9.26 (8)
2,3,5,6-tetrabrom-p-xylene (p-TBX)	0.54 (2)	421,75	6,20	8.00 (8)
Pentabromobenzene (PBBz)	0.0034 (4)	472,59	5,40	7.93 (8)
2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB)	0.000011 (5)	549,92	7,73	11.6 (8)
Bis(2-ethylhexyl)tetrabromophthalate (BEHTBP)	0.0016 (2)	706,14	9,34	11.7 (8)
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	0.2 (3)	687,64	9,15	11.7 (8)

Decabromodiphenylethane (DBDPE)	0.00072 (6)	971,23	10,50	11.7 (8)
Pentabromotoluene (PBT)	0.000935 (3)	486,62	6,99	8.95 (8)
Pentabromoethylbenzene (PBEB)	0.035 (2)	500,65	6,76	8.83 (8)
Bromoallyl 2,4,6-tribromophenyl ether (BATE)	No info	334,83	6,00	No info
2,3-dibromopropyl 2,4,6-tribromophenyl ether (former DPTE, now TBP-DBPE)	0.0883 (7)	530,67	6,30	9.82 (8)
Hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO)	0.0161 (8)	540,76	7,62	11.7 (8)
Allyl 2,4,6-tribromofenyl ether (former ATE, now TBP-AE)	3.42 (8)	370,86	5,00	7.82 (8)
Tris(2,3-dibromopropyl)isocyanurate (T23BPIC)	19.96 (8)	728,69	4,45	11.7 (8)
3,4,5,6-Tetrabromo-2-chlorotoluene (TBCT)	0.22 (8)	442,17	5,70	8.21 (8)
Pentabromobenzyl acrylate (PBBA)	No info	556,67	6,00	No info
α -1,2,5,6-Tetrabromocyclooctane (α -TBCO)	2.56 (8)	427,80	5,28	8.42 (8)
β -1,2,5,6-Tetrabromocyclooctane (β -TBCO),	2.56 (8)	427,80	5,28	8.42 (8)
α -Tetrabromoethylcyclohexane (α -TBECH)	2.63 (8)	427,80	5,50	8.42 (8)
β -Tetrabromoethylcyclohexane (β -TBECH)	2.63 (8)	427,80	5,50	8.42 (8)
Pentabromoethylbenzene (PBEB)	0.24 (8)	500,64	6,76	8.83 (8)
2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE)	1.15 (8)	530,67	6,30	9.82 (8)

1) https://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=496489,
<http://onlinelibrary.wiley.com/doi/10.1002/etc.5620210907/full>

2) <http://www.miljodirektoratet.no/old/klif/publikasjoner/2462/ta2462.pdf>

3) <http://link.springer.com/article/10.1007%2Fs00216-011-4807-8>

(4) <https://chem.nlm.nih.gov/chemidplus/rn/608-90-2>

5) https://www.epa.gov/sites/production/files/2015-08/documents/ffr_hazards.pdf

6) https://www.tri-iso.com/documents/ICL_Flame_Retardant_FR-1410_MSDS.pdf

7) http://www.biomonitoring.ca.gov/sites/default/files/downloads/FlameRetardants_FourMore.pdf

8) <https://comptox.epa.gov/>

Appendix 2. Concentrations measured in all samples. Compounds/samples without numbers were <LOD.

	Air; pg/m ³				Water; pg/L				Sediment; pg/g dw Average (individual samples) >LOD				Amphipods; pg/g ww			
	Average >LOD	Min	Max	Std dev	Average >LOQ	Min	Max	Std dev	>LOD	Min	Max	Std dev	Average >LOD	Min	Max	Std dev
PBBz	<LOD							NA	<LOD				4.4	<LOD	5.6	1.2
BTBPE	<LOD								<LOD				0.5	<LOD	0.5	0.1
HBBz	<LOD								<LOD				5.1	<LOD	6.7	1.1
PBEB	0.02	<LOD	0.02	NA					2.5	1.2	4.0	1.3	1.1	<LOD	3.5	1.1
pTBX	<LOD								0.8	<LOD	0.8	NA	<LOD			
PBT	0.05	0.03	0.06	NA	0.02	0.02	0.02	NA	<LOD				11.7	<LOD	14	2.3
α-TBCO	<LOD				30	13	55	18	<LOD				<LOD			
α-TBECH	0.05		0.06	0.01	0.3	0.16	0.48	0.1	1.1	<LOD	1.7	0.5	0.4	0.1	1.4	0.4
BEHTBP	1.9		2.6	1.0	7.1	4.6	10	2.3	Not analysed				Not analysed			
EH-TBB	0.1		0.2	0.1					Not analysed				Not analysed			
TBP-AE (ATE)	<LOD								<LOD				0.1	<LOD	0.2	0.1
TBP-DBPE (DPTE)	<LOD								<LOD				5.5	<LOD	6.8	1.3
<i>syn</i> -DP	0.4		0.7	0.2	1.5		2.1	0.6	6.2	3.9	8.6	1.6	82.2	3.8	241	65
<i>anti</i> -DP	0.3		0.5	0.2	1.1		1.6	0.5	9.6	5.9	17	3.5	146.3	37	329	87
DPMA	<LOD								2.1	2.0	2.2	0.1	4.9	<LOD	5.7	0.9
β-TBECH	0.03		0.05	0.01					1.3	<LOD			0.3	<LOD	0.9	0.2
PBDE28	<LOD								34	15.0	62	15	0.3	<LOD	0.6	0.2
PBDE47	0.2		0.3	0.1	1.6		2.5	0.7	4529	2070	6460	1522	38.9	<LOD	70	16
PBDE66	<LOD								117	34.3	271	81	<LOD			
PBDE85	<LOD								106	<LOD			<LOD			
PBDE99	0.3		0.4	0.2	1.3		1.7	0.4	5555	2750	11200	2699	30	<LOD	47	12
PBDE100	0.1	<LOD	0.1	NA					1028	404	2120	535	14	<LOD	14	1

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PBDE153	<LOD			<LOD			357	<LOD		<LOD				
PBDE154	<LOD			<LOD			332	114	930	254	<LOD			
BDE-183	Not analysed			Not analysed			Not analysed				Not analysed			
BDE-196	Not analysed			Not analysed			Not analysed				Not analysed			
BDE-209	Not analysed			Not analysed			Not analysed				Not analysed			
ΣPBDEs	0.6	0.8	0.3	2.9	4.1	1.0	11969	5520	21000	5115	38	<LOD	132	42

The individual samples presented here were analysed for all compounds while the bulk sample of these samples was only analysed for PBDEs. The sediment sample from 2017 is shown here, but was discussed separately due to the much lower concentrations (all PBDEs were <LOD) found there.

Appendix 3. Average concentrations (ng/g sampler) of OPFRs in Longyearbyen air and water, including the blanks. Due to little information on K_{pw} in cold temperatures, the data is presented on a sampler basis and not as concentrations per volume.

Compound	Abbreviation	Water	Air	Blanks	
Tri-n-propyl phosphate	TPrP	<LOD	<LOD	<LOD	
Triisobutyl phosphate	TiBP	12.9	12.5	4.0	
Tri-butylphosphate	TnBP	58.4	44.8	8.9	
Tris(2-chloroethyl)phosphate	TCEP	1.1	<LOD	<LOD	
Tris(1-chloro-2-propyl)phosphate	TCPP	6.1	15.0	1.1	
Dibutylphenyl Phosphate	DBPP	19.0	21.3	<LOD	
Tripentyl phosphate	TPeP	<LOD	<LOD	0.3	
Butyldiphenyl Phosphate	BDPP	2.4	2.1	<LOD	
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP	24.4	7.8	0.1	
Tris(2-butoxyethyl)phosphate	TBEP	<LOD	<LOD	79.4	
Triphenyl phosphate	TPhP	4.5	1.6	0.2	
2-Ethylhexyl diphenyl phosphate	EHDPP	0.7	0.7	0.1	
Tris(2-ethylhexyl)phosphate	TEHP	0.6	0.8	0.1	
Tri-o-tolyl phosphate	ToTP	<LOD	<LOD	<LOD	
Tri-m-tolyl phosphate	TmTP	0.1	0.1	<LOD	
Tri-p-tolyl phosphate	TpTP	<LOD	<LOD	<LOD	
Tris(2-isopropylphenyl) phosphate	TIPPP	0.04	0.1	<LOD	
Tris(3,5-dimethylphenyl) phosphate	TDMPP	<LOD	<LOD	<LOD	
		0-25% >LOD	25-50% >LOD	50-75% >LOD	75-100% >LOD

Appendix 4. Average concentrations detected in blanks. One blank/year was used for the passive samplers and in addition, a reference sample for PRC concentrations and for laboratory contamination control was kept in the lab-freezer and analysed together with the samples, one for each sample year.

air and water				amphipods	sediment	
pg/g sampler				pg/g ww	pg/g dw	
TiBP	3950	PBBZ	4.1	PBBz	0.9	0.6
TnBP	8855	HBB	4.9	HBBz	1.1	0.7
TCPP	1050	PBT	1.3	PBT	3.0	2.0
TPeP	308	α-TBECH	0.6	Syn-DP	1.0	0.6
TDCPP	88	BEHTBP	2.7	Anti-DP	1.9	1.2
TBEP	79432	Syn-DP	1.2	PBDE47	8.3	5.4
TPhP	160	Anti-DP	1.4	PBDE99	6.5	4.2
EDP	129	β-TBECH	0.4	PBDE100	2.1	1.3
TEHP	112	PBDE28	0.2	BTBPE	ND	ND
TPrP	ND	PBDE47	0.7	PBEB	ND	ND
TCEP	ND	PBDE99	0.5	pTBX	ND	ND
DBPP	ND	PBDE100	0.8	α-TBCO	ND	ND
BDPP	ND	BTBPE	ND	α-TBECH	ND	ND
ToTP	ND	PBEB	ND	BEHTBP	ND	ND
TmTP	ND	pTBX	ND	EH-TBB	ND	ND
TpTP	ND	α-TBCO	ND	ATE	ND	ND
TIPPP	ND	EH-TBB	ND	DPTE	ND	ND
TDMPP	ND	PBBA	ND	DPMA	ND	ND
ATE	ND	β-TBCO	ND	β-TBECH	ND	ND
DPTE	ND	PBDE66	ND	PBDE28	ND	ND
BATE	ND	PBDE85	ND	PBDE66	ND	ND
DPMA	ND	PBDE153	ND	PBDE85	ND	ND
T23BPIC	ND	PBDE154	ND	PBDE153	ND	ND
TBCT	ND	PBDE183	ND	PBDE154	ND	ND
HCDBCO	ND					

Appendix 5. Limit of detection (LODs) for nBFRs, DPs and PBDEs for all matrices analysed in this study.

	Amphipods	Sediment	Water ^a	Air	Air ^b
Units	pg/g ww	pg/g dw	pg/L	pg/m ³	pg/g sampler
<i>Anti</i> -DP	5.62	3.64	0.30	0.05	
<i>Syn</i> -DP	2.94	1.91	0.38	0.04	
ATE (TBP-AE)	0.05	0.03	0.01		0.02
BATE (TBP-DPBE)	0.14	0.09	0.01		0.04
BEHTBP	NA ^c	NA ^c	0.43	0.11	
BTBPE	0.38	0.25	0.05		0.10
DPMA	0.29	0.19	0.03		0.10
DPTE	3.65	2.37	0.40		1.10
EH-TBB	NA ^c	NA ^c	0.22		0.60
HBBz	3.29	2.14	1.60		0.70
HCDBCO	0.26	0.17	0.03		0.10
PBBA	1.38	0.89	0.15		0.40
PBBz	2.73	1.77	0.03	0.08	
PBEB	0.06	0.04	0.01	0.0001	
PBT	9.13	5.93	0.32	0.02	
pTBX	0.04	0.03	0.004		0.01
T23BPIC	2.57	1.67			0.80
TBCT	0.21	0.14	0.02		0.10
α-TBCO	0.35	0.23	0.04		0.10
α-TBECH	0.03	0.02	0.003	0.01	0.01
β-TBCO	0.79	0.51	0.08		0.20
β-TBECH	0.13	0.08	0.01	0.004	0.04
PBDE28	3.57	1.01	0.03		1.00
PBDE47	24.9	16.2	0.17	0.01	
PBDE49		0.10			
PBDE66	18.3	3.02			1.20
PBDE85	21.0	7.60	0.16		3.10
PBDE99	19.6	12.7	0.08	0.01	
PBDE100	6.20	4.02	0.16	0.02	
PBDE153	69.3	6.63	0.12		1.60
PBDE154	37.0	1.99	0.10		1.20
PBDE183	21.3	28.7	2.90		20.6
PBDE196		0.30			
PBDE209		50			

^a Limit of quantification (LOQ) is given for water instead of LODs.

^b For compounds not present in the air samples, a LOD based on pg/g sampler is provided instead of as pg/m³.

^c NA: Not analysed.

Compounds and matrices left blank are not calculated/analysed for that specific matrix.

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