Local pollution and the risks of OPFR, PBDE and PFAS to the marine ecosystem outside Longyearbyen and Barentsburg in Svalbard

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Quantification, and three risk analyses, of OPFR, PBDE and PFAS in sediment from Adventfjorden and Grønfjorden, in Svalbard

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Abstract

Most of the ecotoxicological research conducted in the Arctic until today has focused on long range transport of pollutants, while fewer studies on local pollution have been published. The aim of this study was hence to investigate if local pollution of organophosphorus flame retardants (OPFRs), polybrominated diphenyl ethers (PBDEs) and perfluorinated alkylated substances (PFAS) occurs outside two settlements in Svalbard; Longyearbyen and Grønfjorden. Furthermore was the aim to examine if the concentration of each substance differs between the settlements. Sediment was sampled in Adventfjorden (outside Longyearbyen), Grønfjorden (outside Barentsburg) and at a reference site in Kongsfjorden. The samples were analysed for the above mentioned substances. In addition a risk analysis was performed, using toxic units to examine the risk of OPFRs, PBDEs and PFAS to the fjord ecosystems.

Results showed that local pollution exist for 10 respectively 8 out of 13 analysed congeners of OPFRs in Adventfjorden and Grønfjorden, with the highest median concentration of tris(2-chloro-1-methylethyl) phosphate (TCPP) (3.17 ng/g dw respectively 15.2 ng/g dw). Of the PBDEs only 2,2´,4,4´,5-pentabromodiphenyl ether (BDE99) was detected, with the highest median concentration of 28.8 pg/g dw respectively 16.7 pg/g dw in Adventfjorden and Grønfjorden. Three of 21 analysed congeners of PFAS were assumed to originate from local sources, where perfluorooctansulfonic acid (PFOS) had the highest median concentration in Adventfjorden (0.18 ng/g dw) and perfluorotetradecanoic acid (PFTeA) in Grønfjorden (0.49 ng/g dw).

The wastewater effluent in Longyearbyen and a landfill site in Barentsburg had the highest pollution. None of the substance groups constitutes a risk to the marine ecosystem at the present concentrations; however the risk to individual organisms and a combined effect of the examined substances and other compounds which might be present in the fjords should not be excluded.

Abbreviations

DDT	Dichlorodiphenyltrichloroethane
EC50	Effective concentration for 50% of the population
K_d	Water-sediment partitioning coefficient
K_{OC}	Organic carbon-water partitioning coefficient
K_{OW}	Octanol-water partitioning coefficient
LC_{50}	Lethal concentration for 50% of the population
LOD	Limit of detection
MEC	Measured environmental concentration
OPFR	Organophosphorus flame retardant
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PEC	Predicted environmental concentration
PFAS	Perfluorinated alkylated substances
PNEC	Predicted no effect concentration
SSD	Species sensitivity distribution
TU	Toxic unit

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Introduction

Until today, most of the ecotoxicological research conducted in the Arctic has focused on long range transport of pollutants (AMAP, 2009; Kallenborn et al., 2007; Vorkamp and Rigét, 2014). A limited number of results on local contamination have been published in peer review journals. However, extensive amounts of data exist from both the US and Canadian Arctic, Denmark and Norway, but these are published in various languages and difficult to find. Results from the Norwegian Arctic have mostly investigated the presence of older substances, such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and polycyclic aromatic hydrocarbons (PAHs) (Hop et al., 2001; Evenset et al., 2009; Jartun et al., 2009), while few studies on new, emerging substances, included in the Stockholm convention after the initial dirty dozen, have been performed.

Brominated flame retardants (BFRs) and perfluorinated alkylated substances (PFAS) are such new groups of substances, which have been found in the nature around the world (Law et al., 2014; Butt et al., 2010; Ahrens et al., 2010). Indications of local sources to pollution of BFRs in air, sediment and biota closer to settlements compared to remote areas have been observed around the Canadian Arctic (de Wit et al., 2006, 2010), as well as local contribution to contamination of perfluorinated alkylated substances (PFAS) downstream a glacier due to skiing activities in Svalbard (Kwok et al., 2013). Even if indications like these have been observed, available studies examining local contamination in the Arctic are scarce.

Lescord et al. (2015) investigated the extent of PFAS contamination in two lakes known to be polluted from local airports in the Canadian high Arctic. Results from the study showed concentration of PFAS in fish from the polluted lakes to be 100 times higher compared to fish in lakes with background contamination. In the Antarctic Hale et al. (2008) found decreasing concentrations of polybrominated diphenyl ethers (PBDE) in sediment in a gradient from an outlet of untreated wastewater outside two research bases. Due to the decreasing concentrations and the most common congener found being BDE-209, with low mobility, the authors concluded it to be local pollution. Pollution of PBDE as well as other

substances, such as pharmaceuticals, originating from untreated wastewater might also occur in the Arctic since the vast majority of settlements in this area lack adequate wastewater treatment (Gunnarsdóttir et al., 2013; de Wit et al., 2006).

To my knowledge only three studies on local pollution of new substances in the Norwegian Arctic have been performed. One of them, investigating the extent of local pollution of organochlorines, BFRs and PFAS in eggs from black-legged kittiwakes from three areas in Svalbard did not find any difference between the expected polluted sites and the background site (Miljeteig and Gabrielsen, 2009). The result might be explained by the black-legged kittiwakes catching food away from the settlement and is thus not affected by local pollution (Miljeteig and Gabrielsen, 2009). The other two studies examine local contamination of PBDEs and PFAS in sediment, also in Svalbard, were performed by Evenset et al. (2006a and 2009). The presence of PFAS was explained to originate from long range transport since the concentration had a similar range at all sites, including a site which has been unpopulated for 45 years (Evenset et al., 2006a). Local pollution of PBDE is, on the other hand occurring since higher concentrations were detected in Adventfjorden, which is the densest populated area, compared to the other examined fjords (Evenset et al., 2006a). The local contamination of PBDE is further explained by the high concentrations occurring even if the sedimentation rate is rapid in the area. Although local contamination occurs, long range transport is contributing as well (Evenset et al, 2006a). The study from 2009 was a follow up and showed decreasing concentrations of the investigated substances. However, further studies are needed for a more reliable trend (Evenset et al., 2009).

Since the knowledge about local pollution of new substances in the Arctic is limited, it is of importance to investigate. This study will, in association with the Norwegian Polar Institute and Akvaplan-niva and for the interest of the governor on Svalbard, examine how three new substances; PFAS, PBDE and organophosphorus flame retardants (OPFRs) relate to assumed local pollutions sources, and if contamination patterns differ between settlements in Svalbard. In accordance to this, the governor of Svalbard has pointed out a number of point sources of contamination in their interest at two settlements in Svalbard; Longyearbyen and Barentsburg (Sysselmannen 2015a; 2015b). Longyearbyen is a Norwegian settlement while Barentsburg is governed by Russia. The expected polluted areas in Adventfjorden outside Longyearbyen consist of an outlet of untreated wastewater from the municipality and the airport area. One site in the inner parts of the fjord, close to the village, is in addition included in this study as a site expected

to be contaminated by diffuse sources from the whole settlement. In Grønfjorden, outside Barentsburg, the expected polluted sites are situated adjacent to two separate landfills and one greenhouse.

Study aims and research questions

The aim of this study was to investigate if and to what extent local pollution of organophosphorus flame retardants, polybrominated diphenyl ethers and perfluorinated alkylated substances and their congeners occurs from diffuse runoff and sewage outlets in Longyearbyen and landfill areas in Barentsburg in Svalbard. The aim will be pursued by measuring the concentration of the mentioned substance groups in sediment from Adventfjorden, Grønfjorden and one reference point. In order to fulfil the aim the following research questions will be answered:

- Are the settlements Longyearbyen and Barentsburg local sources of OPFR, PBDE and/or PFAS?
    - Are the same compounds detected above limit of detection at the reference point as well as outside the settlements Longyearbyen and Barentsburg?
    - If the same compounds are detected, are the concentrations higher close to the settlements compared to the reference point?
- If local contamination exists, to what extent is it occurring?
    - Which compound of each substance group is most frequently detected and measured at the highest concentration in each of the fjords?
    - Which site has the highest respectively lowest contamination of each substance group in the individual fjords?

Studies examining other pollutants in the area have found differences between the settlements; Kristoffersen et al. (2012) found higher concentrations of PCB in snow bunting eggs from Barentsburg and Pyramiden, Russian settlements, compared to Longyearbyen and Ny-Ålesund, Norwegian settlements. Also Jartun et al. (2009) found higher concentrations of PCBs, in soil, in the Russian settlements compared to Longyearbyen. The high concentrations were explained by weathering from, among others, electrical and construction waste. Since these differences, including the study by Evenset et al. (2009), have been

observed, the aim is furthermore to examine if the concentrations of OPFR, PBDE and PFAS differ between Adventfjorden and Grønfjorden by answering the following question:

- Are the concentrations of individual compounds and the sum of each substance group higher outside one of the settlements compared to the other?

To facilitate the interpretation of measured concentrations and the decision making, the final objective is to investigate if the concentrations of OPFR, PBDE and PFAS are high enough to pose a risk to the aquatic ecosystem in Adventfjorden or Grønfjorden. The risk will be examined by answering the following questions:

- Do the individual compounds or the sum of each and all of the substance groups have concentrations high enough to cause an effect or lethal response for more than 50 % of the most sensitive species in the ecosystem? Are the concentrations of the compounds high enough to cause a toxic unit equal to, or above 1?
- Which congener poses the greatest risk to the ecosystem? I.e. which congener has the highest individual toxic unit in each of the fjords?

Limitations of the study

The study includes sediment samples collected in Adventfjorden, Grønfjorden and Kongsfjorden in Svalbard. Samples taken in Adventfjorden include three sites; the inner part of the fjord, the wastewater effluent site and outside the airport area, while samples from Grønfjorden include sites close to two landfill areas and one greenhouse area. Kongsfjorden was used as a reference site. The samples were analysed for three substance groups; OPFR, PBDE and PFAS. All samples were analysed for OPFR and PFAS, while five sites were selected for the analysis of PBDE. The limitations were done in consideration of time and costs and to the interest of the Governor on Svalbard.

The risk analysis was limited to include congeners with available data on both partitioning coefficients and toxicity (Table 7). Toxicity data was used for organisms found all around the world since none or a limited number of studies are available for site specific species, i.e. Arctic species. Mainly marine organisms were included in the risk analysis. However, as toxicity data for some of the compounds only are available for freshwater organisms, this data was used as well in order to make a more comprehensive analysis. Even though the risk in sediment is examined,

mostly pelagic organisms were included, since data for these species are available while very few data were found for benthic species.

Chemical properties and use

Organophosphorus flame retardants

Organophosphorus compounds are used as flame retardants and plasticisers in a wide range of products, such as textiles, electronic equipment, polyvinyl chloride (PVC), paint, furniture and polyurethane foams (Marklund et al., 2003; Leisewitz et al., 2000; Salthammer et al., 2003). The use of phosphorus flame retardants have increased and is expected to continue to do so, due to the replacement of the banned brominated flame retardants (Reemtsma et al., 2008; van der Veen and de Boer, 2012; Stockholm convention, 2016).

The organophosphorus flame retardants are halogenated or nonhalogenated (Figure 1) (van der Veen and de Boer, 2012; Möller et al., 2012). Like other flame retardants, the OPFRs can be classified as reactive or additive (WHO, 2007). The additive flame retardants are mixed into the polymer while the reactive ones are chemically bound to it. The leakage is greater from additive than reactive flame retardants (Rahman et al., 2001).

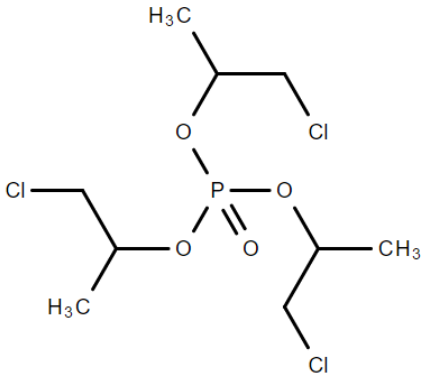

Figure 1. The chemical structure of tris(2-chloro-1-methylethyl) phosphate (TCPP), the most commonly detected OPFR in sediment (van der Veen and de Boer, 2012) (Created using Chemspider (2016)).

Since OPFRs have similar physio-chemical properties as BFRs and have been detected, due to long range transport, in the Arctic, these compounds are suspected to be persistent and bioaccumulating (Hallanger et al., 2015; Liagkouridis et al, 2015). In a comprehensive review Liagkouridis et al. (2015) state that more studies are needed to conclude these substances fate to the environment. In the meantime, they suggest an adoption of the precautionary principle. However, the physio-chemical properties of OPFRs vary between congeners and some show less tendencies to be persistent, bioaccumulative and toxic (Liagkouridis et al, 2015). The water solubility, and hence the absorption to sediment generally decrease respectively increase with molecular weight (van der Veen and de Boer, 2012). The log K_{ow}-values also increase with heavier molecules.

The OPFRs have shown possible neurotoxic, genotoxic and reproductively toxic effects (Wei et al., 2015; van der Veen and de Boer, 2012). The chlorinated OPFRs are also carcinogenic. Some of the congeners have been pointed out as toxic to aquatic organisms, such as; triphenyl phosphate (TPhP), tris(2-chloroethyl)phosphate (TCEP) and tricresylphosphate (TCP/TMPP).

Polybrominated diphenyl ethers

Polybrominated diphenyl ethers are used as flame retardants in a lot of products such as furniture, electronics and textiles (Rahman et al., 2001). Their structure (Figure 2), and hence chemical properties and persistence, are similar to PCBs and DDTs, which have resulted in PBDEs being found in remote areas, such as the Arctic (Rahman et al., 2001; de Wit et al., 2010; Cai et al., 2012). PBDEs are cheap in production and have therefore been used in large quantities, but as their properties are consistent with the criteria for persistent organic pollutants in the Stockholm convention and their abundancy in environmental compartments around the world they are now banned in many countries (Rahman et al., 2001; de Wit et al., 2010; Cai et al., 2012; Law et al., 2014; Vorkamp and Rigét, 2014).

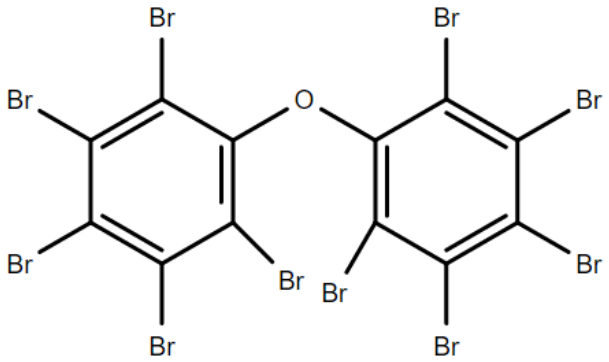

Figure 2. Chemical structure of decabromodiphenyl ether (BDE209), the fully brominated diphenyl ether (Created using Chemspider (2016)).

PBDEs are additive flame retardants (de Wit et al., 2010). They exhibit properties such as persistency, potential for bioaccumulation and toxicity, as well as they are subject for long range transport (Rahman et al., 2001; Gouin and Harner 2003; de Wit et al., 2010; Letcher et al., 2010). PBDEs are hydrophobic and do therefore accumulate in lipids, sediment and soil, where they are largely partitioning to organic carbon (Gouin and Harner, 2003; de Wit et al., 2010). The higher brominated congeners have low volatility and high sorption to sediment which makes them less mobile compared to the lower brominated congeners with higher water solubility and volatility and larger potential to bioaccumulate (Watanabe and Sakai, 2003).

PBDEs have been shown to be endocrine disrupters, have a negative impact on the neurodevelopment, and they are in some cases carcinogenic (McDonald, 2002; Morgado et al., 2007; Darnerud, 2008). In vitro studies from the Arctic have mostly shown endocrine effects to the wildlife (Letcher et al., 2010).

Perfluorinated alkylated substances

Perfluorinated alkylated substances are, due to their physio-chemical properties, both non-polar and polar. Due to their properties they are used in a wide range of products; firefighting foams, textiles, paints, repellents etc. (Kissa, 2001; Kelly et al., 2009; Herzke et al., 2012). The majority of PFAS released to the environment are from direct sources, such as production and use of products containing fluorochemicals (Butt et al., 2010; Prevedouros et al., 2006). However, releases from indirect sources, such as degradation of precursor substances, do also occur. The most common PFAS are perfluorooctanoate (PFOA) and perfluorooctane

sulfonate (PFOS) which belong to the perfluorinated carboxylates (PFCAs) respectively the perfluorinated sulfonates (PFSAs) (Figure 3) (Butt et al., 2010). Both PFCAs and PFSAs are persistent and bioaccumulative, were PFOS seems to biomagnify to a higher degree than PFOA (Butt et al., 2010; Tomy et al., 2004; Kannan et al., 2005). Furthermore, the properties of PFAS are related to its fluorocarbon chain length; longer chained PFCAs ($\geq C_7$) and PFSAs ($\geq C_6$) are more susceptible to sorb to particles and have a higher tendency to bioaccumulate than the shorter-chained compounds, which have higher water-solubility (Ahrens and Bundschuh 2014). PFAS have, due to their physio-chemical properties and ability to undergo long range transport, been voluntary phased out around the world. In addition have PFOS and its precursors been added to the Stockholm convention (Stockholm convention, 2016; Ahrens and Bundschuh, 2014).

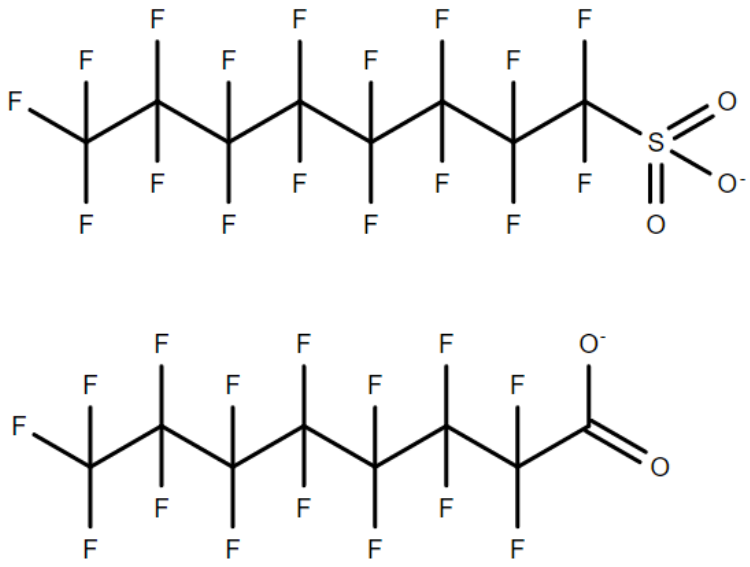

Figure 3. Chemical structure of the most common PFAS; PFOS (above) and PFOA (below) (Created using Chemspider (2016)).

The understanding of PFAS toxicity is ongoing. It has this far been shown to affect organisms by developmental effects, endocrine disruption and changes in the lipid metabolism (Lau et al., 2007; Jensen and Leffers, 2008).

Methodology

Study sites and sample collection

Sediment sampling was conducted outside three settlements; Longyearbyen, Barentsburg and in Kongsfjorden, in Svalbard during September 2015.

Samples in Adventfjorden outside Longyearbyen were collected in areas with specific interest to the governor of Svalbard (Sysselmannen, 2015a) at two expected point sources of contamination; a sewage pipe with release of untreated wastewater (Table 1, Figure 4a; A2) and the area outside the local airport (Table 1, Figure 4a; A4). In the airport area firefighting foams have been used and contamination of, among others, PFOS has been quantified in the terrestrial environment (Rudolph-Lund, 2012). In addition one site in the inner part of the fjord, close to the settlement was sampled, as it might be exposed to diffuse contamination from different parts of Longyearbyen (Table 1, Figure 4a; A1). While one sample each was taken outside the airport and close to the settlement, two samples were taken by the sewage pipe; one approximately by the mouth of the pipe and one 100 meters from the pipe (Table 1, Figure 4a; A3).

In Grønfjorden, outside Barentsburg, three sites were sampled, chosen in agreement with Sysselmannen (2015a, 2015b). The sites are situated close to expected point sources; two landfills (Table 1, Figure 1b; G1 and G2) and a greenhouse area (Table 1, Figure 4b; G4). The landfills contain a wide variety of waste, including electronical waste, hence a mixture of contaminants is suspected to leak to the surrounding environment (Sysselmannen, 2015b). By the greenhouse area DDT and HCB have been measured, still, contamination of other substances may also occur (Sysselmannen, 2015b). Even though point sources of contamination are the main focus, the sampled sites may also be influenced by contamination from diffuse sources in Barentsburg. By one of the landfills (G2) and outside the greenhouse two samples each were collected (G3 respectively G5).

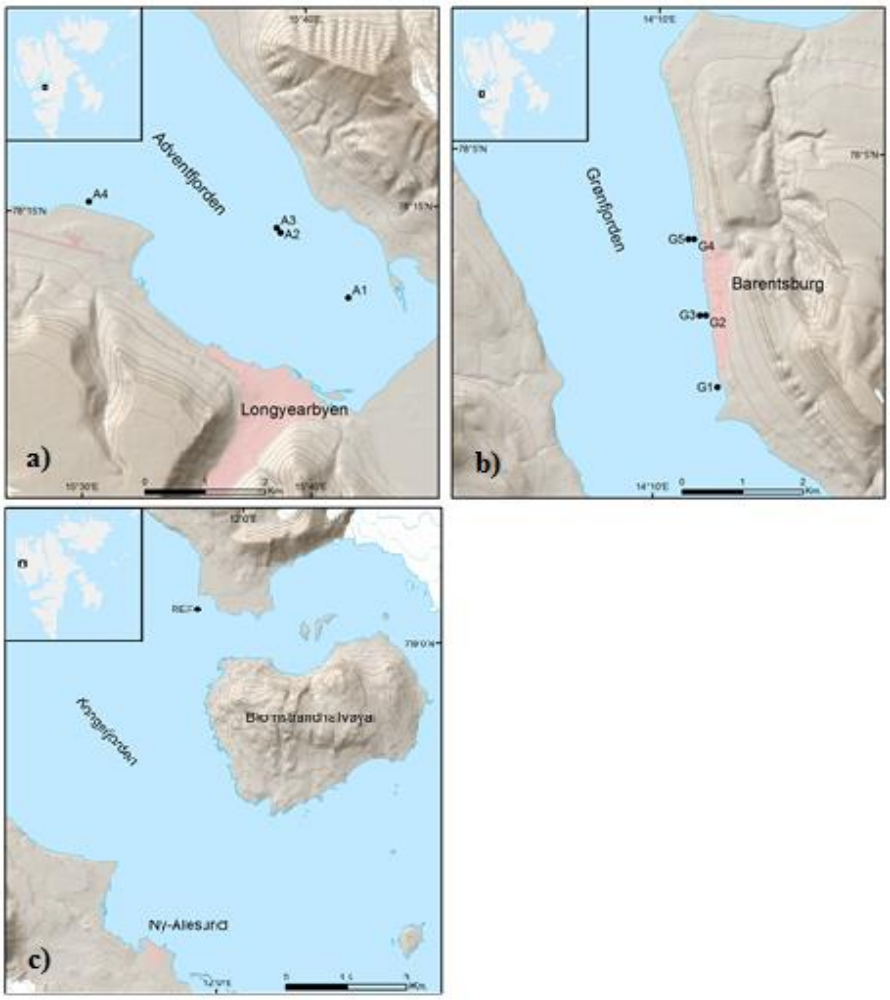

Figure 4. Sampling sites in **a)** Adventfjorden outside Longyearbyen, **b)** Gronfjorden outside Barentsburg, **c)** The reference point in Kongsfjorden. (Norwegian polar institute).

The reference sample was collected in Kongsfjorden (Table 1, Figure 4c; REF). The point is situated about 9 km from the settlement Ny-Ålesund, on the other side of the fjord, close to Blomstrandhalvøya. The site was selected as a reference point since the settlement, Ny-Ålesund, is situated far from large cities and anthropogenic activities, as well as it is a small village with about 35 inhabitants in winter and 180 during summer (Kingsbay, 2016). Presently the area around Ny-Ålesund is primarily used for research. The reference site should hence be virtually free from current local contamination and any levels of contaminants found would probably originate from long range transport.

The field work was performed on a Polarcircle boat in Adventfjorden and Grønfjorden and at MS Teisten in Kongsfjorden. The sediment was collected with a van Veen grab with a volume of about 2 dm^3 in Adventfjorden and Grønfjorden, and with a volume of 10 dm^3 in Kongsfjorden. Three replicates were taken at each sampling point[1]. In Adventfjorden and Grønfjorden three duplicates were sampled for each replicate to get enough sediment. Sampling occurred at different depths (Table 1). From the grab, emptied into a big plastic container, the top two centimetres of sediment was collected and put in Rilsan® (Tub-ex, Denmark) bags until analysis. Rilsan bags have low migration and are suitable for material aimed to be analysed for contaminants. All equipment used was rinsed between each sample taken, to avoid contamination. The samples were frozen, at -18°C, as soon as possible after sampling for later analysis.

Table 1. Overview of sampling points; Sample ID-No., i.e. the name of the sampling site which will be referred to in the text, Number of replicates, GPS-coordinates, depth, distance from point source and short description of area.

Sample ID-No.	No. of replicates	Coordinates N	Coordinates E	Depth	Distance from point source	Comments
A1	3	78°14,182	15°41, 736	25 m	-	Inner part of Adventfjorden
A2	3	78°14,781	15°38,804	55 m	0 m	Sewage pipe
A3	3	78°14,824	15°38,639	58 m	108 m	Sewage pipe
A4	3	78°15,078	15°30,422	13 m	100 m	Airport
G1	3	78°02,871	14°12,721	4 m	50 m	Landfill
G2	3	78°03,522	14°12,187	17 m	36 m	Landfill
G3	1	78°03,522	14°11,917	60 m	136 m	Landfill
G4	3	78°04,213	14°11,638	10 m	100 m	Greenhouse area
G5	1	78°04,213	14°11,392	55 m	200 m	Greenhouse area
REF	3	79°00,288	11°57,169	13 m	-	Reference point

[1] Due to bad bottom conditions only one replicate was taken at sampling point G3 and G5.

Chemical analysis

Chemical extraction and analysis was performed at the Norwegian Institute for Air Research (NILU) in Tromsø. In order to avoid contamination all equipment (i.e. spoons, spatulas, beakers, lids etc.) used from division until analysis were carefully rinsed before handling each sample. All metallic equipment was rinsed in isopropanol and thereafter cleaned in ultrasound bath in acetone, for 10 minutes. Beakers and glass containers were rinsed with acetone and cyclohexane and thereafter burned, covered with aluminium foil, at 450 degrees for 8 hours. Polypropylene centrifuge tubes (PP-tubes), used for PFAS extraction, were rinsed with methanol before use. Lids were cleaned in the ultrasound bath in acetonitrile for 10 minutes. The turbovap, when used, was rinsed and run with acetone before and between each sample.

Preparation of sediment

Division

All samples were defrosted in room temperature and darkness overnight. The thawed samples were mixed well and divided into different containers for respective analysis (Table 2). All handling of the sediment in this step occurred in a clean cabinet or outdoor to avoid contamination of OPFRs and PBDEs, which are both found on dust particles in indoor air. The sediment remaining after division was frozen.

Table 2. Included analyses and the amount of sediment used for each of them.

Analysis	Approx. wet weight (g)	Dry weight (g)
OPFR	20	5
PBDE	30	10
PFAS	2.5	-
TOC	10	0.2
Grain size	100	50
Water content	2	-

Drying and storage

Some samples were dried after division; OPFR, PBDE and water content. The samples for OPFR-analysis were stored in room temperature until drying; thereafter dried in the clean cabinet for three days. The dry samples were stored in room temperature until extraction. The PBDE-samples were stored in fridge, at 6°C, before they were dried in 30±5°C

until a constant weight was reached, about three days. They were thereafter stored in glass jars covered with aluminium foil and lid in room temperature until extraction. The samples for water content were dried in 105°C until a constant temperature was reached, i.e. three days.

The remaining samples were not dried before extraction; PFAS was stored in fridge, at 6°C, while samples for TOC and grain size were given to the Akvaplan-niva laboratory for analysis there.

Extraction, clean-up and analysis

Organophosphorus flame retardants

Organophosphorus flame retardants were analysed in all samples. In addition, three blanks (silica burned at 450°C for 8 hours) were included in the analysis. To avoid contamination, all handling with the samples occurred in the clean cabinet, except when using the ultrasound bath and the Turbovap, at these times, the samples were covered with aluminium foil.

The applied methodology for extraction of OPFR has been verified in the laboratory but has not been published earlier, hence the performance will be described step by step. About 5 g of crushed sediment was transferred to a centrifuge tube and 20 µL internal standard; PFR I 1 ng/µL (2015.10.15) was added to the sample, which then had to soak for 30 minutes. Internal standard is used to later quantify the congeners of the analysed substance and to calculate how much of the actual substances that remain after extraction and clean-up by comparing the internal standard with a recovery standard.

To extract the OPFRs, 10 mL of acetonitrile was added to the sample and the mixture was vortexed and put in the ultrasound bath for 10 minutes. The sample was thereafter centrifuged in 10°C, with a speed of 2000 rpm for 10 minutes. The supernatant was transferred to a new centrifuge tube. This procedure was repeated three times.

The sample was transferred to a turbovap glass, using acetonitrile to make sure all extract was transferred, and concentrated to 0.5 mL in the Turbovap.

For clean-up of the sample, a Solid phase extraction (SPE)-station with an Oasis HLB 6cc (500mg) LP Extraction cartridge[2] was used. The

[2] For sample B41 a column with the same properties, but another producer, was used; Supel – select HLB SPE 500 mb/12 mL tube.

Hydrophilic-lipophilic balance (HLB) columns were cleaned with 10 mL of acetonitrile and thereafter conditioned with 5 mL of HLB cleaned milli-Q water. The sample was diluted with 10 mL of HLB cleaned milli-Q water and thereafter transferred to the HLB column with a speed of 1-2 drops per second. When the liquid had past the column the sample was cleaned with another 10 mL of HLB cleaned milli-Q water and thereafter with 5 mL of 5 % acetonitrile in HLB cleaned milli-Q water. The columns were completely dried with a portable membrane pump (creating vacuum) at -20 mmHg for about 30 minutes, after clean-up. A new centrifuge tube was thereafter put into the SPE-station. 12 mL of acetonitrile was added to the column, to extract the analytes, which were collected in the centrifuge tube with a speed of 1-2 drops per second.

The extract was concentrated from 12 mL to 0.2 mL[3] in the RapidVap, starting at a speed of 40 %, pressure of 250 mbar, temperature of 40°C and running for 20 minutes. The speed was increased to 50 % and the pressure decreased to 170 mbar. The time varied depending on the amount of extract left in the tube[4]. After concentration, the samples were transferred to a 2 mL vial for storage in the fridge until analysis. The centrifuge tubes were rinsed with acetonitrile to make sure all extract was transferred.

The samples were analysed and quantified by professional staff at NILU using an ultrahigh pressure liquid chromatography column coupled to a triple quadrupole mass spectrometer (UPLC/MSMS, Vantage, Thermo Scientific) and electrospray ionization (ESI) for ionization. The congeners analysed for is presented in Table 3.

Table 3. Congeners of OPFR analysed using UPLC/MSMS and ESI.

Name	Abbreviation
Butyl diphenyl phosphate	BdPhP
Dibutylphenyl phosphate	DBPhP
2-Etylhexyldiphenylphosphate	EHDP
Tris(2-butoxyethyl) phosphate	TBEP
Tris(2-chloroethyl)phosphate	TCEP

[3] Some samples accidently dried out during evaporation, these were dissolved in some drops of acetonitrile.

[4] Some samples were dried out in the RapidVap, to dilute the analytes in these samples, some drops of acetonitrile was added.

Name	Abbreviation
Tricresylphosphate	TCP
Tris(2-chloro-1-methylethyl) phosphate	TCPP
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP
Tris(2-ethylhexyl)phosphate	TEHP
Triethyl phosphate	TEP
Triisobutyl phosphate	TiBP
Tri-n-butyl phosphate	TnBP
Tripropyl phosphate	TPP
Tripropyl phosphate	TPrP

Polybrominated diphenyl ethers

Polybrominated diphenyl ethers (PBDEs) were analysed in ten samples, two replicates from each sampling point; A1, A2, G1, G2 and REF. In addition, one blank with silica (burned at 450°C for 8 hours) was analysed. Before extraction, the extraction thimbles and purified cotton was rinsed running the soxhlet with dichloromethane (about 150 ml) passing the extractor three times.

The whole methodology applied for extraction of PBDE in this study have not been published earlier, it will hence be described step by step, even though, it has been performed and verified in the laboratory before.
10 g of dried and crushed sediment (<2mm) and 200 µL of internal standard; PBDE-I 17.14, (Tromsø 2015.02.02) 1 to 10, were added to the extraction thimble. A bit of purified and cleaned cotton was put on top to prevent the sediment for going out of the thimble. The soxhlet was run with 150 mL of dichloromethane for approximately 20 hours. The extract was transferred from the round bottom flask (rinsed once with dichloromethane to ensure all extract was transferred) to a Turbovap-glass and evaporated to 0.5 mL in the Turbovap. The concentrated extract was transferred, using dichloromethane, to a vial and stored in darkness in the fridge until next step.

Next step included clean-up; here interferents were removed using Gel permeation chromatography (GPC). A calibration solution was injected to the GPC and the timespan for collecting sample was recorded manually due to an error between the GPC and the computer. The chromatogram consisted of five peaks (Figure 2; Table 4).

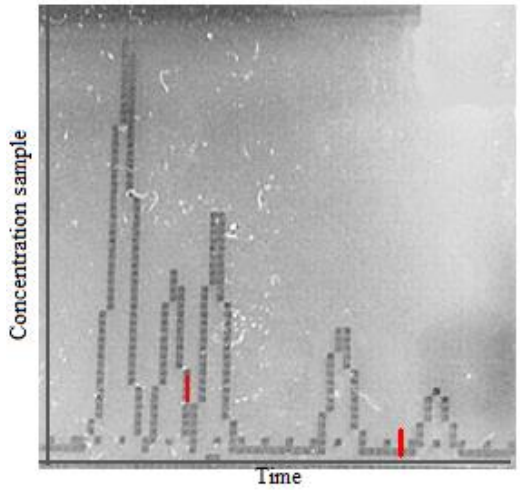

Table 4. List of compounds representing each peak in the chromatogram.

Peak	Compound
1	Corn oil
2	Bis(2-ethylhexyl)phthalate
3	Methoxychlor
4	Perylene
5	Sulphur

Figure 5. Chromatogram over calibration curve of GPC. The y-axis represent the concentration of the sample and the x-axis the time. No values or units are presented due to errors with the connection between GPC and computer, the time was recorded manually. Sample was collected between times 13:40 and 21:20, represented as the two red lines in the chromatogram.

The PBDE-congeners appear between the end of the second peak and just before peak five (Figure 5). Hence, the compounds removed are long chained fats and other long-chained substances, some phthalates and sulphur. The GPC was, after calibration, installed to start sample collection after 13 minutes and 40 seconds, and continue for 7 minutes and 40 seconds. The samples were individually injected to the GPC. Dichloromethane was injected between each sample to rinse the column. The syringe was rinsed with dichloromethane twice after every injection and thereafter cleaned in dichloromethane in the ultrasound bath for 10 minutes. About 1 mL of extract was used, to get the exact amount; the container with extract was weighted before and after GPC aliquot.

The chromatography purified sample was collected in a turbovap glass and run in the Turbovap for concentration of the sample to 0.5 mL. After concentration, the extract was transferred to centrifuge glasses, using dichloromethane for rinsing.

1 mL of hexane was added to each sample, which then was concentrated to 0.5 mL at 35°C, 600 mbar and a speed of 50 % for 20 minutes in the RapidVap. They were thereafter cleaned once again, to remove the remaining interferents, using a SPE-module in the RapidTrace. The extraction columns were rinsed with dichloromethane

and prepared with frits (cleaned in dichloromethane in the ultrasound bath for 10 minutes) in the bottom and top of the column and with 1 g of florisil (burned at 450°C for 8 hours) in between the frits before clean-up. 10 % dichloromethane in hexane was used as solvent to extract the analytes from the column.

After clean-up, ten drops of isooctane was added to the samples, which then were concentrated to 0.2 mL in the RapidVap, starting at 600 mbar, a speed of 50 % and 20 minutes with a gradually decrease down to 250 mbar, increase of speed to 60 % and shorter time intervals. The temperature was kept constantly on 35°C. The samples were thereafter transferred to vials with insert, using dichloromethane to make sure all liquid was transferred. The dichloromethane were removed using nitrogen gas for evaporation.

Analysis and quantification was performed by professional staff at NILU using gas chromatography with a quadrupole mass spectrometer (GC/MS, Quattromicro, Waters) and electron ionization (EI) for ionization. The congeners of PBDE analysed are presented in Table 5.

Table 4. Congeners of PBDE analysed using GC/MS and EI.

Name	Abbreviation
2,4-Dibromophenyl 2-bromophenyl ether	BDE 17
2,4,4´-Tribromodiphenyl ether	BDE 28
2,2´,4,4´-Tetrabromodiphenyl ether	BDE 47
2,2′,4,5′-tetrabromodiphenyl ether	BDE 49
2,3′,4,4′-Tetrabromodiphenyl ether	BDE 66
2,3′,4,6′ -Tetrabromodiphenyl ether	BDE 71
3,3′,4,4′-Tetrabromodiphenyl ether	BDE 77
2,2′,3,4,4′-pentabromodiphenyl ether	BDE 85
2,2´,4,4´,5-Pentabromodiphenyl ether	BDE 99
2,2´,4,4´,6-Pentabromodiphenyl ether	BDE 100
2,3',4,4',6-pentabromodiphenyl ether	BDE 119
3,3′,4,4′,5-Pentabromodiphenyl ether	BDE 126
2,2',3,4,4',5'- hexabromodiphenyl ether	BDE 138
2,2',4,4',5,5'-hexabromodiphenyl ether	BDE 153
2,2',4,4',5,6-hexabromodiphenyl ether	BDE 154
2,3,3',4,4',5- hexabromodiphenyl ether	BDE 156
2,2',3,4,4',5',6-heptabromodiphenyl ether	BDE 183
2,2',3,4,4',6,6'- heptabromodiphenyl ether	BDE 184
2,3,3',4,4',5',6- heptabromodiphenyl ether	BDE 191
2,2',3,3',4,4',5,6'-octabromodiphenyl ether	BDE 196
2,3,3',4,4',5',6- heptabromodiphenyl ether	BDE 197
2,2',3,3',4,4',5,5',6- nonabromodiphenyl ether	BDE 206
2,2',3,3',4,4',5,6,6'-nonabromodiphenyl ether	BDE 207

Perfluorinated alkylated substances

PFAS was extracted in all samples, as well as in three blanks with silica burned at 450°C for 8 hours. For extraction the Powley method (Powley et al., 2005) was adapted, for exact amounts and performance see appendix.

Analysis and quantification was performed by professional staff at NILU using an ultrahigh pressure liquid chromatography column coupled to a triple quadrupole mass spectrometer (UPLC/MSMS, Vantage, Thermo Scientific) and electrospray ionization (ESI) for ionization. The analysed PFAS-congeners are presented in Table 6.

Table 5. PFAS-congeners analysed using UPLC/MSMS and ESI.

Name	Abbreviation
6:2 Fluorotelomer sulfonate	6:2 FTS
Branched perfluorooctansulfonic acid	br-PFOS
Perfluorobutanoic acid	PFBA
Perfluorobutane sulfonate	PFBS
Perfluorodecanoic acid	PFDcA
Perfluorodecanoic acid	PFDcS
Perfluorododecanoic acid	PFDoA
Perfluoroheptanoic acid	PFHpA
Perfluoroheptane sulfonate	PFHpS
Perfluorohexanoic acid	PFHxA
Perfluorohexane sulfonate	PFHxS
Perfluorononanoic acid	PFNA
Perfluorononane sulfonate	PFNS
Perfluorooctanoic acid	PFOA
Perfluorooctansulfonic acid	PFOS
Perfluorooctane sulfonamide	PFOSA
Perfluoropentanoic acid	PFPA
Perfluoropentane sulfonate	PFPS
Perfluorotetradecanoic acid	PFTeA
Perfluorotridecanoic acid	PFTriA
Perfluoroundecanoic acid	PFUnA

TOC, grain size and water content

To examine the local pollution it is of interest to classify the sediment characteristics in order to elucidate that the difference in concentration of each substance between the expected polluted sites and the reference site is caused by local pollution. Total organic carbon and grain size was hence measured as well. It was determined by the Akvaplan-niva laboratory. TOC was determined by releasing CO_2 and then measure it with

photometric infrared light. The amount of CO_2 is proportional with TOC. The grain size was determined by sieving the wet sediment in a 0.063µm sieve, which then was dried and the weight percent calculated. Water content was decided by weighting the sample in wet and dry condition. The percentage of water was calculated by dividing the difference of the wet and dry sample with the weight of the wet sample. The water content was used by the laboratory staff to calculate the dry weight (dw) concentration of each substance in the samples.

Statistical analysis

The data obtained from the chemical analysis have been visualised and analysed using IBM SPSS Statistics 22. An independent-samples Mann-Whitney U test was performed to test differences in total organic carbon concentration and the concentration of substances detected above limit of detection between the fjords and the reference site. Mann-Whitney U test was used due to the small dataset and since all of the data were not normally distributed even after transformation.

To test if total organic carbon influences the concentration of the investigated substances a Pearson correlation was performed between each substance and TOC. All concentrations were in addition TOC-normalised by dividing the substance concentration by the % TOC per dw sediment. For the congeners with significant correlation with TOC, this concentration will be stated in the text together with the non-normalised concentration. If significant correlation was obtained and a difference in TOC-concentration between either the reference site or the expected polluted sites or between Adventfjorden and Grønfjorden exist a Mann-Whitney test was run with TOC-normalised values as well.

The grain size data was classified after the dominant (above 50%) grain size, >0.063mm respectively <0.063mm. A chi-square test was then performed between each of the sampling areas to test if there is a difference in grain size between them. If the grain size differed, a correlation with the compound-concentrations was performed.

For all visualisation and the analysis the sum of congeners was calculated for each substance group and location. Results were considered significant when $p \leq 0.05$ for all tests performed.

Risk analysis

A risk analysis for each group and the sum of all substances in each of the polluted sites was performed using the data obtained from the chemical analysis and from scientific articles.

To obtain the risk each substance pose to the marine environment a toxic unit, based on the equation for concentration addition in Könemann and Pieters (1996) was calculated (Equation 1). Concentration addition can be used since the congeners of a substance group all exhibit similar mode of action.

$$TU_c = \sum \frac{PEC_{c_i}}{PNEC_{c_i}} \qquad \text{(Equation 1)}$$

TU is the toxic unit, PEC the predicted environmental concentration (ng/L), PNEC the predicted no effect concentration (ng/L), c the compound and i a specific congener of the compound. To estimate the overall risk the sum of toxic units were calculated. The ecosystem is affected when TU=>1.

Predicted Environmental Concentration (PEC)

The predicted environmental concentration (PEC) was calculated by using the equilibrium partitioning (EqP) theory (Toro et al., 1991). The EqP assume pore water concentrations being the source of toxicity for sediment organisms. However, as the EqP also assumes equilibrium between phases; sediment and pore water, the organism will receive an equivalent exposure from all phases in the system, i.e. either from respiration in pore water, ingestion of sediment or a mix of both.

The predicted environmental concentration (PEC) was obtained using the measured environmental concentration ($MEC_{sediment}$), achieved from the chemical analysis. In cases where the concentration was below limit of detection the LOD-value was used since the true concentration is unknown and it is impossible to state that it is far below the LOD-value. PEC represents the dissolved concentration of the substance, i.e. the concentration in pore water ($C_{porewater}$), which can be equalised to the bioavailable fraction. $MEC_{sediment}$ is the total concentration of the substance in sediment. The concentration in pore water was derived using the partitioning coefficient of sediment-water (K_d) (Equation 2).

$$K_d = \frac{MEC_{sediment}}{C_{porewater}} \qquad \text{(Equation 2)}$$

K_d is the sediment-water partitioning coefficient (L water/kg sediment), $MEC_{sediment}$ the concentration of the examined substance in sediment (ng/kg) and $C_{porewater}$ the concentration in pore water (ng/L water) (Toro et al., 1991). Since the fraction of organic carbon is greater than 0.2%, the organic carbon is the principal phase of sorption in sediment, which is adjusted by equation 3 (Toro et al., 1991).

$$K_d = K_{OC} \times TOC \qquad \text{(Equation 3)}$$

K_{OC} is the partitioning coefficient between organic carbon-water (L water/kg organic carbon) and TOC the total organic carbon (kg TOC/kg sediment).

K_{OC} was substituted by equation 4 (Gobas and Morrison, 2000) for OPFR and PBDE, as an inadequate amount of literature values were found for the included congeners of these substance groups.

$$K_{OC} = K_{OW} \times 0.41 \qquad \text{(Equation 4)}$$

K_{OW} is the octanol-water partitioning coefficient, obtained from scientific articles, and 0.41 a constant. Since PFAS are both hydrophobic and lipophobic the K_{OC} might not give the true partitioning between sediment and water, consequently using only the K_d-value, without correcting for organic carbon might give a more reliable result. However, the partitioning of PFAS between sediment and water has been shown to be significantly dependent on the organic carbon content of sediment (Ahrens et al., 2011; Ahrens et al., 2010), the K_{OC}-method should therefore not be excluded. Hence, two calculations have been made, one with K_d-values and one correcting for organic carbon, using K_{OC}-values from literature.

$C_{porewater}$ (ng/L), and hence also PEC, was calculated using equation 5 for OPFR and PBDE, equation 6 for PFAS corrected for organic carbon and equation 2 for PFAS without correction for organic carbon.

$$C_{porewater} = \frac{MEC_{sediment}}{TOC \times K_{OW} \times 0.41} \qquad \text{(Equation 5)}$$

$$C_{porewater} = \frac{MEC_{sediment}}{TOC \times K_{OC}} \qquad \text{(Equation 6)}$$

The values for MEC and TOC were derived from the chemical analysis, while the K_{OW}- and K_{OC}-values were antilogarithmed from scientific data (Appendix: Table 1). If more than one value of K_{OW}, K_{OC} or K_d was found in the literature, the mean was used. For PEC a 95th-percentile was calculated for each fjord and used to calculate the toxic unit.

Predicted No Effect Concentration (PNEC)

To obtain the predicted no effect concentration (PNEC) toxicity data, EC50- or LC50-values, was collected from scientific literature (Appendix: Table 1). If more than one value of a substance were found, the 5^{th}-percentile was calculated and used as PNEC to calculate the toxic unit. The 5^{th}-percentile was used in order to reduce the risk of underestimating the predicted no effect concentration.

Since a lot of toxicity-data on PFOS is available in the literature, a species sensitivity distribution was performed and a hazard concentration of 5% calculated according to Posthuma et al. (2001). The 5^{th}-percentile was calculated for the species with more than one E(L)C50-value.

Results

Local pollution

Total organic carbon and grain size

The median concentration of total organic carbon ranged between 1.10 and 3.24 % dw sediment in the expected polluted sites (Table 7). The median concentration in the reference site was 0.29 % dw sediment. The total organic carbon was similar for all sites within the respective fjords except by the airport (A4) in Adventfjorden and by one of the landfills (G1) in Grønfjorden (Figure 6a). From Mann Whitney U test significant difference were found between Adventfjorden respectively Grønfjorden, and the reference site (p=0.004 respectively p=0.005), while no significant difference was found between Adventfjorden and Grønfjorden (Figure 6b).

Sum of OPFRs and 6 out of 14 analysed congeners were positively correlated with TOC (Table 8). One PFAS congener was positively correlated with TOC, while 4 out of 21 congeners were negatively correlated (Table 9). No correlations were found between the concentration of PBDEs and TOC.

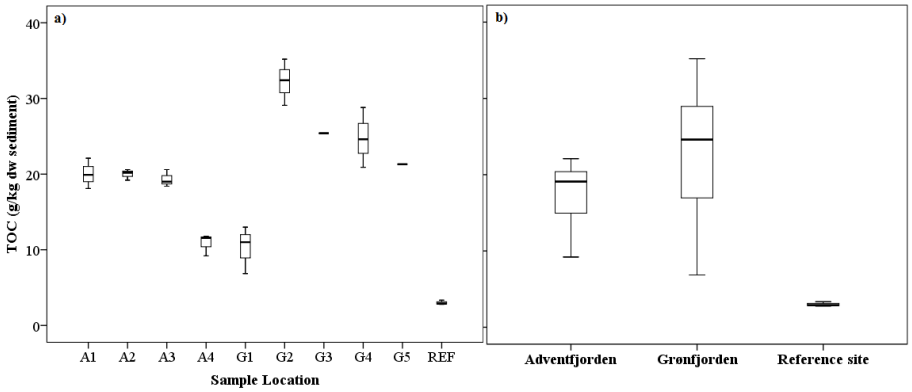

Figure 5. Variance of TOC (g/kg dw sediment) (y-axis) at **a)** the sample sites in Adventfjorden and Grønfjorden (x-axis) and **b)** in the expected polluted sites and the reference site (x-axis). Significant difference was found between each of the fjords and the reference site (p<0.000).

The grain size was <0.063mm for all samples taken in Adventfjorden and >0.063mm for all samples taken at the reference site. Fine grained sediment dominated in Grønfjorden (Table 7). Significant difference was found in a chi-square test between Adventfjorden and the reference site respectively Grønfjorden, while no significant difference was found between Grønfjorden and the reference site.

Significant negative correlation between grain size and OPFR-concentration was found for 2-etylhexyldiphenylphosphate (EHDP) (Pearson correlation 0.52, p=0.007). Significant positive correlation was found between grain size and 6:2 fluorotelomer sulfonate (6:2FTS) (Pearson correlation 0.41, p=0.040) and perfluoroundecanoic acid (PFUnA) (Pearson correlation 0.40, p=0.045), while significant negative correlation was found between grain size and perfluorohexanoic acid (PFHxA) (Pearson correlation 0.64, p<0.001) among the PFAS-congeners. No correlations were found between grain size and the concentration of PBDEs.

Table 7. Median percentage total organic carbon (TOC) of dw sediment and median percentage of grain size above respectively below 0.063mm.

	A1	A2	A3	A4	G1	G2	G3	G4	G5	REF
TOC (% dw sediment)	1.99 (1.81-2.21)	2.02 (1.92-2.06)	1.90 (1.84-2.06)	1.16 (0.92-1.18)	1.10 (0.69-1.30)	3.24 (2.91-3.52)	2.54	2.46 (2.09-2.88)	2.13	0.29 (0.28-0.34)
>0.063mm (%)	5.10 (4.50-6.70)	3.70 (3.70-4.10)	4.10 (4.10-5.40)	26.9 (25.7-32.2)	86.1 (83.6-89.2)	38.5 (61.0-66.3	19.1	53.1 (45.5.-54.9)	33.3	87.5 (74.7-99.1)
<0.063mm (%)	94.9 (93.3-95.5)	96.3 (95.6-96.3)	95.9 (94.6-95.9)	73.1 (67.8-74.3)	13.9 (10.8-16.4)	61.5 (61.0-66.3)	80.9	46.9 (45.1-54.5)	66.7	12.5 (0.90-25.3)

Organophosphorus flame retardants (OPFRs)

Among the analysed organophosphorus flame retardants (14 congeners); butyl diphenyl phosphate (BdPhP), dibutylphenyl phosphate (DBPhP), EHDP, TCEP, TCP, TCPP, tris(2-ethylhexyl)phosphate (TEHP), triethyl phosphate (TEP), tri-n-butyl phosphate (TnBP) and tripropyl phosphate (TPP) were detected in at least one site (Figure 7 and Table 8). No congeners of OPFR were detected in sediment from the reference site. In Adventfjorden 10 congeners were detected, DBPhP was detected in most samples and TCPP had the highest median concentration both per dw sediment and TOC-normalised (0.89 ng/g dw sediment and 58.2 ng/g TOC) (Figure 7). In Grønfjorden 8 congeners were detected and TCEP,

TCP and TPP were detected at most sites while TCPP had the highest median concentration both per dw sediment and TOC-normalised (10.6 ng/g dw sediment and 432 ng/g TOC) (Figure 7).

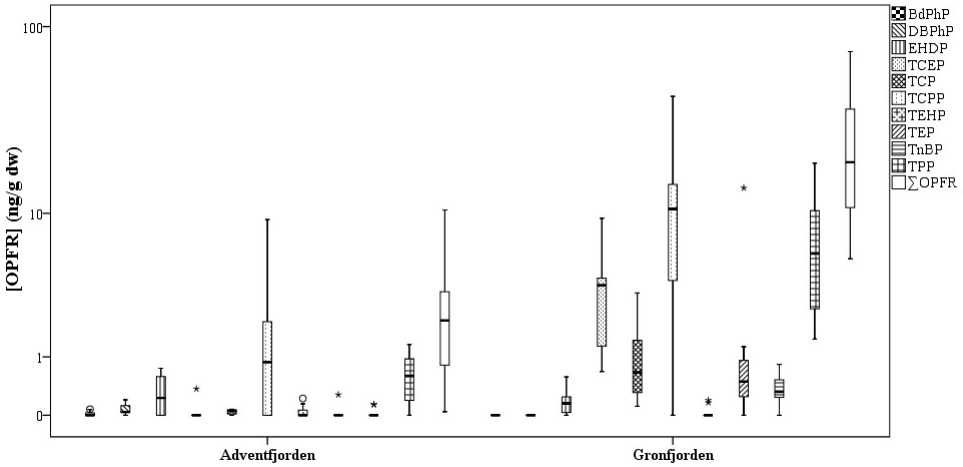

Figure 7. Variance of the concentration (ng/g dw) (median, min and max) of the OPFR congeners (y-axis) measured above limit of detection in Adventfjorden and Grønfjorden (x-axis).

Seven congeners were detected by the wastewater effluent (A2 and A3) and by the airport (A4) in Adventfjorden. However, most number of replicates for congeners above limit of detection was found by the airport (Figure 8a). The highest median concentration of ∑OPFR, both per dw sediment and when TOC-normalised, in the fjord was measured by the wastewater effluent (site A2) (5.68 ng/g dw sediment and 296 ng/g TOC) (Figure 8b). The lowest number of congeners and median concentration of ∑OPFR both per dw sediment and TOC-normalised (0.49 ng/g dw sediment and 22.1 ng/g TOC) was detected in the inner part of the fjord (A1).

In Grønfjorden most congeners were detected at one of the landfills (G2) and the greenhouse area (G4), with 8 congeners each, while fewest congeners were detected at the other landfill (G1) (Figure 8a). The highest respective lowest median concentration of ∑OPFR was measured by the landfills; G2 (47.7 ng/g dw sediment and 1360 ng/g TOC) and G1 (6.46 ng/g dw sediment and 790 ng/g TOC) (Figure 8b). However, when TOC-normalised the concentration was lower by site G3 (270 ng/g TOC) than G1 (Table 8).

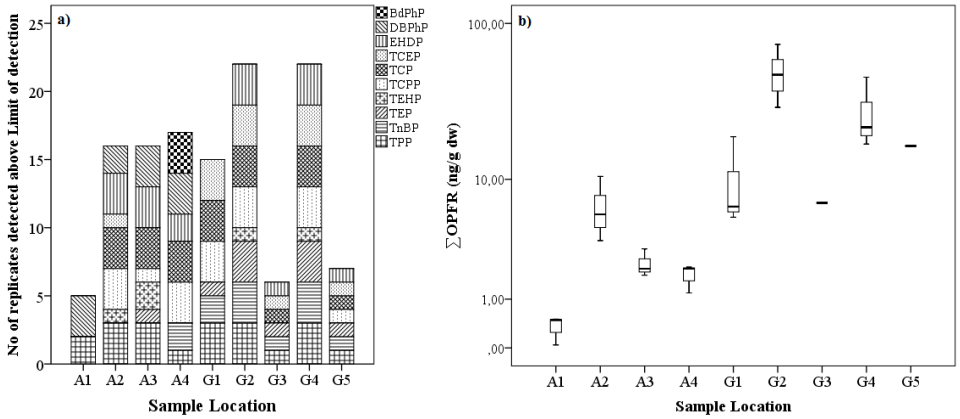

Figure 8. *Level of contamination*; **a)** Number of replicates detected above limit of detection for each congener (y-axis) and each sampling site (x-axis) (n=230) and **b)** variance of total concentration of OPFR (ng/g dw) (median, min and max) (y-axis) at each sampling site (x-axis).

Contamination differences between settlements

All detected congeners of the OPFRs were found in at least one site per fjord, except BdPhP and DBPhP which were only detected in Adventfjorden (Figure 7). Significant differences between sites were found (Mann-Whitney U test) with higher concentrations in Adventfjorden for DBPhP ($p<0.001$) and in Grønfjorden for TCEP ($p<0.001$), TCP ($p<0.001$), TCPP ($p=0.001$), TEP ($p=0.001$), TnBP ($p<0.001$), TPP ($p<0.001$) and the ∑OPFR ($p<0.001$).

Table 8. Pearson correlation between each substance and TOC, p-values are given in brackets, significant correlations are marked with *. Median of concentration per dry weight (ng/g dw) and TOC-normalised concentrations (ng/g TOC) of each OPFR-congener at respective site. Values in brackets by each site represent minimum and maximum values.

	LOD	TOC-correlation	A1	A2	A3	A4	G1	G2	G3[a]	G4	G5[a]	REF
BdPhP	0.01	-0.30 (p=0.136)	<LOD	<LOD	<LOD	0.07 (0.06-0.07)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
BdPhP *TOC-norm*	-	-	<LOD	<LOD	<LOD	6.04 (4.93-8.04)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DBPhP	0.01	-0.26 (p=0.206)	0.06 (0.04-0.07)	0.03 (<LOD-0.03)	0.04 (0.03-0.04)	0.19 (0.17-0.20)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
DBPhP *TOC-norm*	-	-	2.92 (2.36-3.65)	1.38 (<LOD-1.78)	1.82 (1.70-1.96)	16.1 (14.9-21.7)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
EHDP	0.05	0.40* (p=0.046)	<LOD	0.49 (0.39-0.75)	0.61 (0.56-0.62)	0.07 (<LOD-0.09)	<LOD	0.26 (0.23-0.31)	0.12	0.17 (0.15-0.58)	0.07	<LOD
EHDP *TOC-norm*	-	-	<LOD	23.6 (19.1-39.0)	30.1 (29.5-32.9)	7.46 (<LOD-7.49)	<LOD	8.68 (6.99-9.03)	4.72	6.17 (5.98-27.6)	3.13	<LOD
TBEP	5.70	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
TCEP	0.30	0.67* (p<0.001)	<LOD	<LOD (<LOD-0.37)	<LOD	<LOD	0.85 (0.68-2.04)	4.35 (3.81-9.38)	1.12	3.86 (3.68-4.61)	1.43	<LOD
TCEP *TOC-norm*	-	-	<LOD	<LOD (<LOD-19.2)	<LOD	<LOD	99.2 (77.0-157)	134 (131-266)	44.5	150 (134-221)	67.2	<LOD
TCP	0.01	0.69* (p<0.001)	<LOD	0.05 (0.05-0.07)	0.07 (0.07-0.07)	0.05 (0.03-0.07)	0.14 (0.11-0.14)	2.39 (1.38-3.27)	0.54	0.93 (0.66-1.50)	0.51	<LOD
TCP *TOC-norm*	-	-	<LOD	2.57 (2.53-3.82)	3.60 (3.17-3.75)	5.02 (2.59-5.60)	12.4 (10.4-16.4)	67.8 (42.6-112)	21.3	38.0 (31.7-52.0)	23.9	<LOD
TCPP	0.50	0.54* (p=0.005)	<LOD	3.17 (2.30-9.20)	<LOD (<LOD-1.11)	1.17 (0.67-1.79)	3.25 (2.91-13.9)	15.2 (13.4-43.1)	<LOD	5.25 (4.77-29.3)	10.6	<LOD
TCPP *TOC-norm*	-	-	<LOD	165 (112-456)	<LOD (<LOD-58.5)	127 (57.8-152)	425 (296-1070)	459 (432-1330)	<LOD	228 (182-1190)	497	<LOD
TDCPP	0.30	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

	LOD	TOC-correlation	A1	A2	A3	A4	G1	G2	G3[a]	G4	G5[a]	REF
TEHP	0.11	0.22 (p=0.291)	<LOD	<LOD (<LOD-0.22)	0.13 (0.11-0.15)	<LOD	<LOD	<LOD (<LOD-0.19)	<LOD	<LOD (<LOD-0.16)	<LOD	<LOD
TEHP *TOC-norm*	-	-	<LOD	<LOD (<LOD-11.5)	6.99 (<LOD-7.05)	<LOD	<LOD	<LOD (<LOD-6.68)	<LOD	<LOD (<LOD-7.79)	<LOD	<LOD
TEP	0.20	0.38 (p=0.053)	<LOD	<LOD	<LOD (<LOD-0.28)	<LOD	<LOD (<LOD-1.00)	0.66 (0.49-13.9)	0.25	0.25 (0.24-1.26)	0.84	<LOD
TEP *TOC-norm*	-	-	<LOD	<LOD	<LOD (<LOD-13.5)	<LOD	<LOD (<LOD-76.9)	18.4 (16.9-428)	9.74	11.7 (8.62-51.1)	39.5	<LOD
TiBP	0.08	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
TnBP	0.12	0.68* (p<0.001)	<LOD	<LOD	<LOD	0.13 (<LOD-0.14)	0.14 (<LOD-0.23)	0.76 (0.66-0.83)	0.38	0.32 (0.30-0.40)	0.24	<LOD
TnBP *TOC-norm*	-	-	<LOD	<LOD	<LOD	11.5 (<LOD-15.3)	12.9 (<LOD-34.1)	23.6 (22.7-23.6)	15.0	13.8 (12.3-15.2)	11.3	<LOD
TPP	0.40	0.74* (p<0.001)	0.42 (<LOD-0.43)	0.78 (0.76-1.07)	0.97 (0.94-1.32)	<LOD (<LOD-0.45)	2.08 (1.47-2.14)	10.3 (7.55-19.0)	4.45	10.5 (5.81-10.6)	3.00	<LOD
TPP *TOC-norm*	-	-	19.1 (<LOD-21.8)	38.8 (37.0-55.8)	52.8 (45.6-69.3)	<LOD (<LOD-49.3)	189 (164-215)	317 (260-538)	175	369 (278-425)	141	<LOD
TPrP	0.02	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
∑OPFR	-	0.67* (p<0.001)	0.49 (0.04-0.51)	5.68 (3.60-10.5)	2.08 (1.81-3.09)	2.09 (1.19-2.15)	6.46 (5.41-19.2)	47.7 (29.6-74.0)	6.86	22.0 (17.2-46.0)	16.7	-
∑OPFR *TOC-norm*	-	-	22.1 (2.36-25.4)	296 (175-517)	101 (98.4-163)	171 (97.3-226)	790 (587-1470)	1360 (1020-2280)	270	821 (765-1870)	782	-

[a]One replicate

Polybrominated diphenyl ethers

Of the analysed polybrominated diphenyl ethers (23 congeners) only 2,2´,4,4´,5-Pentabromodiphenyl ether (BDE99) was detected. It was detected by the wastewater effluent in Adventfjorden (A2) and by the landfills in Grønfjorden (G1, G2) with median concentrations (min and max) of 28.6 (26.7-30.8) pg/g dw, 16.7 (16.1-17.2) pg/g dw respectively 15.4 (<LOD-22.8) pg/g dw. The highest concentration was detected by the wastewater effluent (A2) in Adventfjorden (Figure 9).

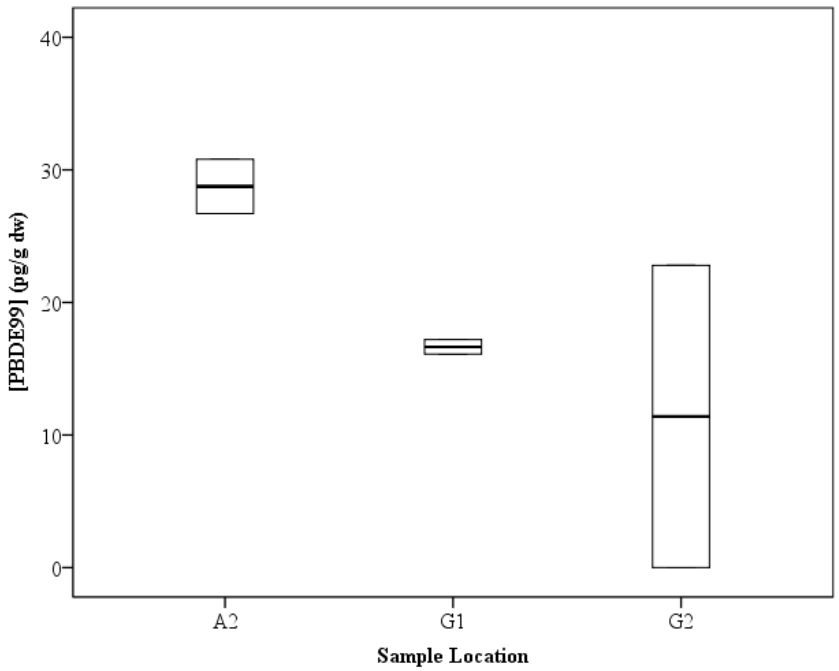

Figure 9. Variance of the BDE99-concentration (pg/g dw) (median, min and max) (y-axis9 at the sites where it was detected (x-axis).

Contamination differences between settlements

No significant difference was found in Mann-Whitney U test between Adventfjorden and Grønfjorden for the concentration of BDE99.

Perfluorinated alkylated substances

Of the analysed perfluorinated alkylated substances (21 congeners) 6:2FTS, perfluorodecanoic acid (PFDcA), perfluoroheptanoic acid (PFHpA), PFHxA, perfluorononanoic acid (PFNA), PFOA, PFOS, perfluorotetradecanoic acid (PFTeA) and PFUnA were detected (Table 9). Of these PFDcA, PFNA, PFOA and PFUnA were detected at all sites, including the reference site (Figure 10). 6:2FTS was only detected at the reference site.

The highest median concentration was measured at the reference point for PFDcA, PFOA and PFUnA, and in Adventfjorden for PFNA. Some individual sites in Adventfjorden and Grønfjorden had higher concentrations than at the reference point (Table 9). However, none of the sites had, in the Mann-Whitney test, significantly higher concentrations of any of the congeners detected at the reference site; the same applies for the TOC-normalised concentrations.

In Adventfjorden four congeners were detected; PFNA was detected at most sites and had the highest median concentration (0.07 ng/g dw (Figure 10). In Grønfjorden four congeners of PFAS were detected; PFNA and PFTeA were detected at most sites while PFTeA had the highest median concentration (0.30 ng/g dw and 11.7 ng/g TOC) (Figure 10).

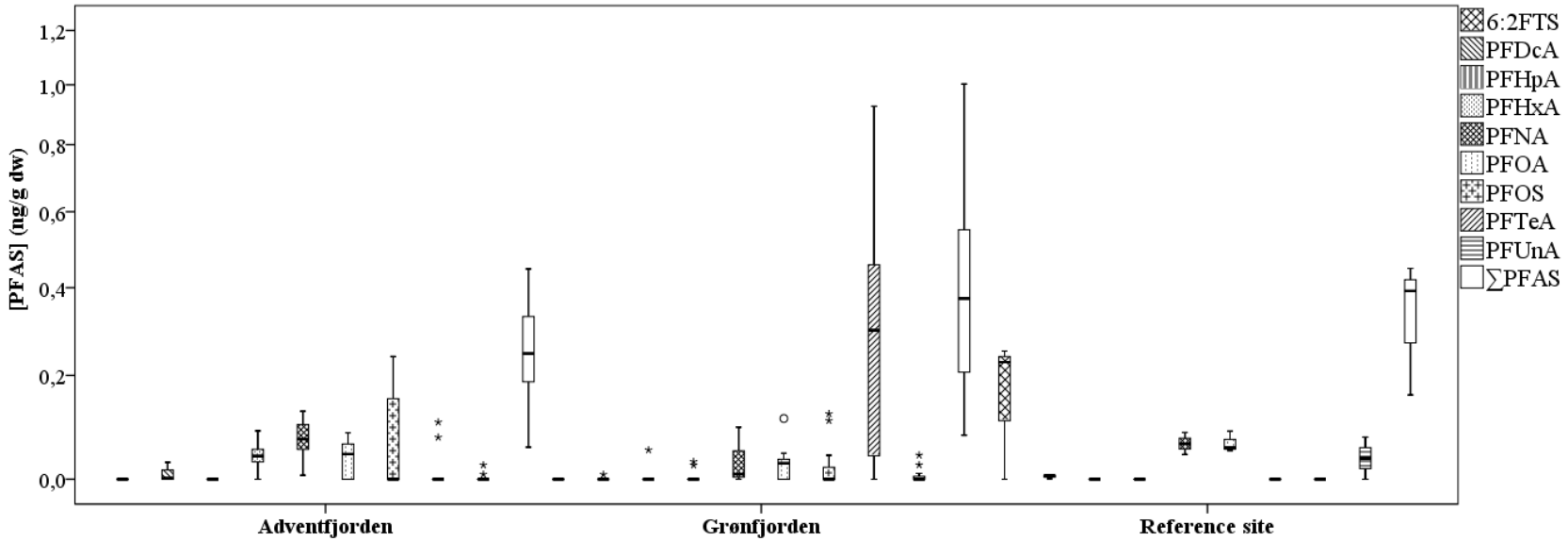

Figure 10. Distribution of the concentration (ng/g dw) (median, min and max) of the PFAS congeners (y-axis) measured above limit of detection in Adventfjorden, Grønfjorden and at the reference site (x-axis).

In Adventfjorden most congeners, 6 out of 21, and the highest median concentration of ∑PFAS (0.38 ng/g dw) was detected by the wastewater effluent (A2) (Figure 11a, b). The lowest number of congeners, 4, was detected in the inner part of Adventfjorden (A1) and the lowest median concentration (0.11 ng/g dw) was measured by the airport (A4) (Figure 11a, b).

In Grønfjorden most congeners, 8 out of of 21, were detected outside one of the landfills (G1), and the highest median concentration of ∑PFAS measured by the other landfill (G2) (0.50 ng/g dw) (Figure 11a, b). Fewest congeners, 2, were detected by the outer part of landfill G2 (site G3), and the site by the outer part of the greenhouse area (G5) had the lowest median concentration of ∑PFAS (0.08 ng/g dw) (Figure 11a, b).

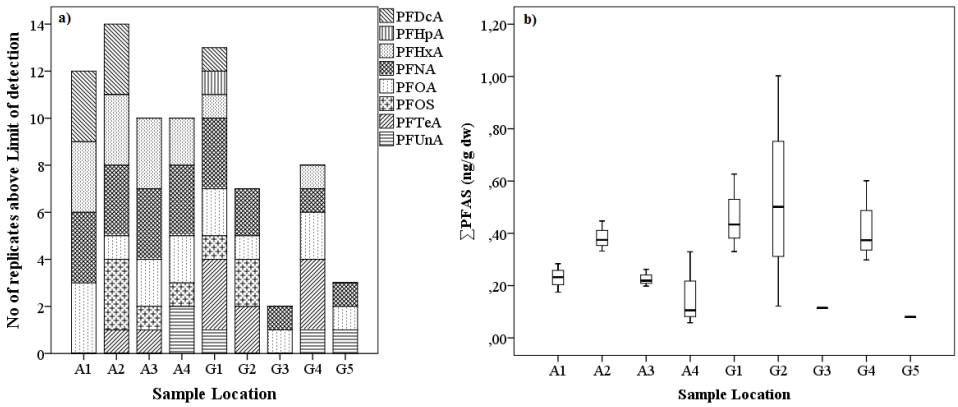

Figure 11. *Level of contamination;* **a)** Number of replicates detected above limit of detection for each congener (y-axis) and sampling site (x-axis) (n=207) **b)** variance of total concentration (median, min and max) of PFAS (ng/g dw) (y-axis) at each sampling site (x-axis).

Contamination differences between settlements

Except for PFHpA, which was only found in Grønfjorden, all congeners of PFAS were detected in both Adventfjorden and Grønfjorden (Figure 10). Significantly higher concentrations in Adventfjorden compared to Grønfjorden were found for PFHxA ($p<0.000$) and PFNA ($p=0.016$), while significantly higher concentration of PFTeA ($p=0.006$) was found in Grønfjorden (Mann-Whitney U test).

Table 9. Median concentration (ng/g dw) of each PFAS-congener at respective site. Values in brackets represent minimum and maximum values.

	LOD	TOC-correlation	A1	A2	A3	A4	G1	G2	G3[a]	G4	G5[a]	REF
6:2FTS	0.23	-0.50* (p=0.009)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.23 (<LOD-0.25)
6:2 FTS ***TOC-norm***	-	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	68.1 (<LOD-90.8)
brPFOS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBA	0.18	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFBS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDcA	0.003	-0.03 (p=0.874)	0.01 (0.004-0.03)	0.02 (0.004-0.03)	<LOD	<LOD	<LOD (<LOD-0.01)	<LOD	<LOD	<LOD	<LOD	0.01 (<LOD-0.01)
PFDcA ***TOC-norm***	-	-	0.55 (0.20-1.47)	1.00 (0.21-1.57)	<LOD	<LOD	<LOD (<LOD-0.63)	<LOD	<LOD	<LOD	<LOD	1.83 (<LOD-2.63)
PFDcS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFDoA	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpA	0.04	-0.16 (p=0.427)	<LOD	<LOD	<LOD	<LOD	<LOD (<LOD-0.05)	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpA ***TOC-norm***	-	-	<LOD	<LOD	<LOD	<LOD	<LOD (<LOD-4.78)	<LOD	<LOD	<LOD	<LOD	<LOD
PFHpS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFHxA	0.006	0.06 (p=0.789)	0.05 (0.04-0.06)	0.06 (0.04-0.09)	0.04 (0.02-0.05)	0.02 (<LOD-0.04)	<LOD (<LOD-0.03)	<LOD	<LOD	<LOD (<LOD-0.02)	<LOD	<LOD
PFHxA ***TOC-***	-	-	2.61 (1.87-	2.86 (2.01-	1.94 (0.82-	2.14 (<LOD-	<LOD (<LOD-	<LOD	<LOD	<LOD (<LOD-	<LOD	<LOD

	LOD	TOC-correlation	A1	A2	A3	A4	G1	G2	G3[a]	G4	G5[a]	REF
norm			2.76)	4.61)	2.86)	4.48)	2.41)			0.87)		
PFHxS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFNA	0.01	-0.40* (p=0.043)	0.12 (0.07-0.13)	0.05 (0.04-0.09)	0.08 (0.05-0.11)	0.06 (0.01-0.07)	0.07 (0.04-0.10)	0.01 (<LOD-0.01)	0.08	<LOD (<LOD-0.01)	0.01	0.06 (0.04-0.09)
PFNA ***TOC-norm***	-	-	6.37 (3.27-6.40)	2.70 (2.16-4.59)	4.43 (2.78-5.49)	4.77 (0.58-8.00)	5.15 (3.22-14.0)	0.21 (<LOD-0.25)	3.22	<LOD (<LOD-0.63)	0.42	22.2 (16.0-25.5)
PFNS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFOA	0.03	-0.41* (p=0.038)	0.07 (0.05-0.07)	<LOD (<LOD-0.05)	0.03 (<LOD-0.09)	0.04 (<LOD-0.06)	0.05 (<LOD-0.11)	<LOD	0.03	0.03 (<LOD-0.04)	0.03	0.06 (0.05-0.09)
PFOA ***TOC-norm***	-	-	3.62 (2.23-3.66)	<LOD (<LOD-2.37)	1.69 (<LOD-4.62)	3.61 (<LOD-6.76)	4.24 (<LOD-8.66)	<LOD	1.31	1.19 (<LOD-1.78)	1.33	20.4 (15.4-30.5)
PFOS	0.04	0.09 (p=0.680)	<LOD	0.18 (0.15-0.24)	<LOD (<LOD-0.13)	<LOD (<LOD-0.15)	<LOD (<LOD-0.11)	0.04 (<LOD-0.12)	<LOD	<LOD	<LOD	<LOD
PFOS ***TOC-norm***	-	-	<LOD	8.70 (7.51-12.5)	<LOD (<LOD-6.40)	<LOD (<LOD-16.6)	<LOD (<LOD-15.8)	1.22 (<LOD-3.76)	<LOD	<LOD	<LOD	<LOD
PFOSA	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPA	0.07	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFPS	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PFTeA	0.05	0.41* (p=0.036)	<LOD	<LOD (<LOD-0.11)	<LOD (<LOD-0.08)	<LOD	0.30 (0.09-0.42)	0.49 (<LOD-0.93)	<LOD	0.31 (0.29-0.55)	<LOD	<LOD
PFTeA ***TOC-norm***	-	-	<LOD	<LOD (<LOD-5.11)	<LOD (<LOD-4.02)	<LOD	27.2 (6.61-61.7)	17.0 (<LOD-26.3)	<LOD	11.7 (10.9-26.4)	<LOD	<LOD
PFTriA	0.03	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

	LOD	TOC-correlation	A1	A2	A3	A4	G1	G2	G3[a]	G4	G5[a]	REF
PFUnA	0.01	-0.45* (p=0.022)	<LOD	<LOD	<LOD	0.01 (<LOD-0.03)	<LOD (<LOD-0.03)	<LOD	<LOD	<LOD (<LOD-0.01)	0.04	0.04 (<LOD-0.08)
PFUnA ***TOC-norm***	-	-	<LOD	<LOD	<LOD	0.72 (<LOD-2.17)	<LOD (<LOD-1.95)	<LOD	<LOD	<LOD (<LOD-0.42)	2.02	13.5 (<LOD-22.9)
∑PFAS	-	0.16 (p=0.434)	0.23 (0.18-0.28)	0.38 (0.33-0.45)	0.21 (0.20-0.26)	0.11 (0.06-0.33)	0.43 (0.33-0.63)	0.50 (0.12-1.00)	0.12	0.37 (0.30-0.60)	0.08	0.39 (0.16-0.45)
∑PFAS ***TOC-norm***	-	-	12.8 (7.92-14.3)	18.2 (16.4-23.3)	11.9 (10.4-12.7)	9.08 (4.90-35.8)	39.4 (25.4-91.5)	17.2 (3.8-28.5)	4.53	13.0 (12.1-28.8)	3.77	133.9 (55.3-141)

[a]One replicate

Potential risk to the ecosystem

Organophosphorus flame retardants

The toxic unit for organophosphorus flame retardants in Adventfjorden was 7.93 x 10^{-05} and 5.33 x 10^{-04} in Grønfjorden (Table 10). Among the examined congeners, TPP are the one with the highest toxic units (3.81 x 10^{-05} and 2.97 x 10^{-04}), while TEHP has the lowest toxic units (2.02 x 10^{-11} and 2.25 x 10^{-11}) in Adventfjorden respectively Grønfjorden.

Table 10. Toxic unit (TU) for each and the sum of examined congeners.

Congener	TU Adventfjorden	TU Grønfjorden
EHDP	5.22 x 10^{-07}	2.69 x 10^{-07}
TBEP	6.27 x 10^{-06}	7.71 x 10^{-06}
TCEP	4.93 x 10^{-06}	4.15 x 10^{-05}
TCP	2.90 x 10^{-11}	4.95 x 10^{-10}
TCPP	2.06 x 10^{-05}	8.77 x 10^{-05}
TDCPP	1.41 x 10^{-06}	1.74 x 10^{-06}
TEHP	2.02 x 10^{-11}	2.25 x 10^{-11}
TEP	7.39 x 10^{-06}	9.70 x 10^{-05}
TiBP	3.66 x 10^{-08}	4.50 x 10^{-08}
TPP	3.81 x 10^{-05}	2.97 x 10^{-04}
∑TU	7.93 x 10^{-05}	5.33 x 10^{-04}

Polybrominated diphenyl ethers

The toxic unit for all examined congeners of polybrominated diphenyl ethers in Adventfjorden respectively Grønfjorden is 8.98 x 10^{-07} and 2.21 x 10^{-06} (Table 11). The substances with the highest respectively lowest toxic units in the fjords are 2,2´,4,4´-Tetrabromodiphenyl ether (BDE47) and 2,2',4,4',5,6-hexabromodiphenyl ether (BDE154) (8.45 x 10^{-07} and 5.11 x 10^{-11}) in Adventfjorden and BDE47 and BDE154 (2.09 x 10^{-06} and 1.27 x 10^{-10}) in Grønfjorden.

Table 11. Toxic unit (TU) for each and the sum of examined congeners.

Congener	TU Adventfjorden	TU Grønfjorden
BDE28	3.93×10^{-09}	9.72×10^{-09}
BDE47	8.45×10^{-07}	2.09×10^{-06}
BDE99	7.79×10^{-09}	1.10×10^{-08}
BDE100	2.20×10^{-10}	5.45×10^{-10}
BDE154	5.11×10^{-11}	1.27×10^{-10}
BDE183	4.05×10^{-08}	1.00×10^{-07}
∑TU	8.98×10^{-07}	2.21×10^{-06}

Perfluorinated alkylated substances

The toxic unit for perfluorinated alkylated substances calculated by using K_d respectively K_{OC} is for Adventfjorden 1.35×10^{-09} and 225 and for Grønfjorden 7.84×10^{-10} and 153 (Table 12). The congener with the highest TU in both of the fjords and for both K_d and K_{OC} is PFOS.

Table 12. Toxic unit (TU) for each and the sum of examined congeners of PFAS, both calculated using Kd and KOC, in Adventfjorden and Grønfjorden.

Congener	TU Adventfjorden	TU Grønfjorden
K_d		
PFOS[a,b]	1.22×10^{-09}	6.77×10^{-10}
PFHxA	8.11×10^{-11}	3.18×10^{-11}
PFOA	9.44×10^{-11}	9.59×10^{-11}
PFNA	1.91×10^{-12}	1.40×10^{-12}
∑TU	1.35×10^{-09}	7.84×10^{-10}
K_{OC}		
PFOS[a,c]	232	159
PFHxA	9.72×10^{-08}	3.51×10^{-08}
PFOA	1.33×10^{-06}	1.55×10^{-06}
PFNA	2.26×10^{-08}	3.03×10^{-08}
∑TU	225	153

[a]TU calculated using HC5 from SSD.
[b]$TU_{Adventfjorden}$ 1.92 x 10-10 and $TU_{Grønfjorden}$ 1.07 x 10-10 if 95th-percentile from exponential distribution used.
[c]$TU_{Adventfjorden}$ 36.6 and $TU_{Grønfjorden}$ 24.0 if 95th-percentile from exponential distribution used.

Discussion

Local pollution & differences between settlements

Organophosphorus flame retardants

10 respectively 8 out of the 13 analysed OPFRs were detected outside Longyearbyen and Barentsburg in Svalbard. The presence of the congeners in these areas but not in the reference site is indicating local pollution. However, positive correlation between the concentration of some of the congeners and total organic carbon were found, which means that more organic carbon will increase the concentration of these substances in sediment. The TOC differed significantly between both Adventfjorden respectively Grønfjorden and the reference site, with lower concentrations by the reference site. Due to the fairly high correlation (ranging between 40-74%) between TOC and EHDP, TCEP, TCP, TCPP, TnBP and TPP and the difference of total organic carbon between the sites it cannot be stated that contamination of these substances are not occurring by the reference point and neither that the pollution in Adventfjorden and Grønfjorden is solely caused by local sources. Long range transport might hence, contribute as well, but further studies are needed in order to draw such a conclusion. Correlation with grain size was only found for one congener; EHDP, which also had a correlation with TOC, further confirming the above stated assumption. However, as the concentrations of the same congeners differ between the fjords, the contamination is mainly assumed to originate from local sources.

The most polluted site in Adventfjorden was by the wastewater effluent (A2, A3) where the highest concentration of ∑OPFR was measured and most congeners detected above limit of detection. This result was expected since no wastewater treatment is occurring and OPFRs are common in furniture, carpets, textiles etc. used in households. However, the same number of congeners was also detected outside the airport (A4), while fewer were detected in the inner part of the fjord (A1), resulting in it being the least polluted site of OPFRs.

BdPhP and TnBP were only detected outside the airport, while DBPhP was measured at the highest concentration at this site. These

substances are known to be used in hydraulic fluids used in aircrafts (Solbu et al., 2011; Sundkvist et al., 2010). This can explain the presence of them outside the airport, while not being detected or measured at low concentrations at the sites in the inner part of the fjord.

Of the congeners detected by both the effluent and outside the airport; EHDP, TPP, TCP and TCPP, but with higher concentration by the effluent are EHDP, TCP and TPP used in hydraulic fluid and as flame retardants, in plasticizers, paint etc. (Sundkvist et al., 2010). The application of these substances in a wide range of products used in houses could thus be an explanation to the higher concentration by the effluent.

The most contaminated site outside Barentsburg was by one of the landfills (G2, G3). The same number of substances was also detected outside the greenhouse area (G4, G5) where the concentration of ∑OPFR was lower. However, the concentration of most of the detected congeners at this site, except TCP, TCPP and TEP, were in the same range as outside the landfill. TPP was the only substance measured at higher concentration by the greenhouse area compared to the landfill. The presence of OPFRs by the landfill is quite expected since the landfill contains products treated with OPFRs, which will, through leakage, end up in the leachate and hence, the fjord (Wei et al., 2015).

The high concentration of OPFRs outside the greenhouse area could be explained by the mouth of the stream receiving wastewater being situated close to the sampling point. More contamination at one of the landfills (G2, G3) and by the greenhouse area compared to the other landfill (G1) could further be explained by point G2-G5 being located right outside the village, while point G1 is situated a bit south of the settlement. G2-G5 might hence receive more contamination from diffuse sources in the settlement compared to site G1. There might also be a content difference of waste between the two landfills.

Grønfjorden is significantly more polluted by TCEP, TCP, TCPP, TEP, TnBP and TPP than Adventfjorden, which is more polluted by DBPhP in the sampled locations. TCPP was measured at the highest concentration in both fjords, which is consistent with studies from other areas, also finding TCPP being the dominant congener of OPFRs in sediment (Leonards et al., 2011; Cristale et al., 2013a; van der Veen and de Boer, 2012). The concentration of TCPP in sediment range between below limit of detection (0.15 ng/g dw) and 54 ng/g dw in the marine environment outside wastewater treatment plants at mainland Norway, with highest concentration in Oslo (Leonards et al., 2011). In rivers influenced by sewage treatment plant effluents and industries in Spain the concentrations are ranging from below limit of detection (4.5 ng/g) and 365 ng/g (Cristale et al., 2013a). The concentrations from these areas are

up to about eight times higher than the ones measured in this study, even though the concentrations from Adventfjorden and Grønfjorden are quite high (highest measured concentration of TCPP being 43.1 ng/g at site G2) taking into account the difference in population size compared to mainland Norway and Spain. The concentration of OPFRs is higher in Grønfjorden compared to Adventfjorden, even though Longyearbyen is denser populated. However, as the pollution sources differ between the sites, the landfills in Barentsburg might release more OPFRs than the wastewater effluent in Adventfjorden causing higher concentrations in Grønfjorden. The different level of OPFRs might furthermore be explained by difference in usage pattern between the two settlements, which, in such a case, also explain the variance of congeners detected in the two fjords.

Polybrominated diphenyl ethers

The only congener of the PBDEs detected was BDE99. It was measured in three out of four sites with the highest concentration by the wastewater effluent in Adventfjorden (A2) and with similar concentrations by the two landfills in Grønfjorden (G1 and G2), while it was not detected in the inner part of Adventfjorden (A1). The presence of it by the point sources and not in the reference site indicates local pollution. No correlations existed either between the concentrations of BDE99 and TOC or grain size, strengthening the conclusion of local pollution. However, the general detection of PBDEs is low and the presence of BDE99 can hence only indicate local pollution, while a comprehensive study on PBDEs are needed to draw any firm conclusions.

BDE99 have been banned in Europe since 2003 (Directive 2003/11/EC). Nonetheless, it might still occur in products produced before the legislation. The presence of BDE99 indicates penta-BDE being the mixture of PBDEs used in products in Svalbard, as the mixture is dominated by BDE99 and BDE47 (La Guardia et al., 2006). BDE47 could hence also be expected to be detected in the area. As the limit of detection for this congener was higher than the measured concentration of BDE99 it might be present but it cannot be confirmed due to the high LOD-value.

The higher concentration of BDE99 in Adventfjorden than Grønfjorden is consistent with the study by Evenset et al. (2009) and can partly be explained by the denser population. However, since the examined sources in Adventfjorden and Grønfjorden are different it is difficult to draw such a conclusion. The concentration of BDE99 (28.8 pg/g dw) by the wastewater effluent is similar to the concentration of 20.0 pg/g dw respectively 29.7 pg/g dw measured by Evenset et al. (2006b; 2009) outside the previous wastewater effluent in Adventfjorden. They did

also find elevated concentrations of BDE47 and BDE209 in 2009 and of BDE209 in 2006. BDE209 was not analysed for in this study, but the presence of BDE47 in the studies by Evenset et al. further indicate penta-BDE being one of the most common mixtures of PBDE in the area.

None of the sampled sites in Grønfjorden from this study and the studies by Evenset et al. (2006b; 2009) are the same; no site specific comparison can hence be made. However, the concentration of BDE99 in Grønfjorden, taken by Evenset et al. (2006b; 2009) were in 2006 38 pg/g dw and did in 2009 range between 2.84 pg/g dw and 4.03 pg/g dw, which can be compared to the measured concentration in this study ranging between below limit of detection (7.90 pg/g dw) and 22.8 pg/g dw.

In studies from other areas BDE209 is the dominant congener, but BDE99 and BDE47 are also frequently detected (Lee & Kim, 2015; de Wit et al., 2010; Cristale et al., 2013a). The concentration measured by the wastewater treatment plant effluent of a permanently manned Australian research station in the Antarctic was 2.9 ng BDE99/g TOC (Wild et al., 2015). This is higher than the organic carbon normalized concentration of BDE99, 1.44 ng/g TOC, measured outside the wastewater effluent in Adventfjorden. The higher concentration by the research base might reflect a lower usage of penta-BDE in the Norwegian community. The lower concentration in Adventfjorden might also be influenced by a high sedimentation rate, but as no information on the sedimentation rate outside the research base in the Antarctic is available no such conclusion can be drawn.

The concentration of BDE99 in Barentsburg are substantially lower than the ones measured by a landfill on mainland Norway; 11 ng/g dw (Fjeld et al., 2004) compared to the highest concentration measured in this study (30.8 pg/g dw). The concentration difference seems however be consistent with the difference in population size between the areas.

Perfluorinated alkylated substances

Of the analysed PFAS-congeners, four were detected at both the expected polluted sites and at the reference site; PFDcA, PFNA, PFOA, PFUnA. None of these congeners had significantly higher concentrations in the expected polluted sites, thus it can be assumed that the contamination originated from long range transport. Four congeners were detected solely in the expected polluted sites; PFHpA, PFHxA, PFOS and PFTeA. Of these PFHpA was only detected in one sample at a concentration close to the limit of detection, while the others; PFHxA, PFOS and PFTeA, were detected repeatedly above limit of detection throughout the sites, indicating local pollution. Of the congeners detected at the expected

polluted sites only PFTeA had a significant correlation with TOC, while none of the congeners correlated with grain size. However, as the concentration of PFTeA differed significantly between Adventfjorden and Grønfjorden and the TOC did not, the pollution is further assumed to originate from local sources. Some of the congeners detected also in the reference site did have a negative significant correlation with TOC, which might be explained by the ability of PFAS to be both polar and non-polar and is an aspect to consider in future studies examine PFAS in sediment.

PFHxA and PFOS were almost solely detected in Adventfjorden, where PFHxA had significantly higher concentrations than in Grønfjorden. The highest concentration was measured by the wastewater effluent, making this the most locally polluted site of PFAS by Longyearbyen. The airport area and the inner part of the fjord had similar detection frequencies and concentrations of these substances, resulting in them being similarly influenced by local pollution.

PFOS has previously been detected on land by the airport area (Rudolph-Lund, 2012), and was assumed to be found in the marine environment as well. However, a lagoon is situated between the airport and the sea and might hence receive larger quantities and prevent leakage of PFOS to the fjord. The sample was taken close to the effluent of the airport, although runoff might occur at other sites around the airport, increasing the concentrations there. Further investigations are needed to make any conclusions.

The concentration of PFOS by the wastewater effluent, 0.18 ng/g dw, is similar to the concentration measured by Evenset et al. (2009); 0.19 ng/g dw and Evenset et al. (2006); 0.10 ng/g dw. An increase rather than decrease has occurred since 2006, contradictory to the ban of PFOS by the Stockholm convention in 2009 (Ahrens and Bundschuh, 2014). In a study by Kallenborn et al. (2004) the concentration of PFOS and PFHxA was measured in sewage sludge from mainland Norway. The concentrations ranged between 0.45 ng/g ww and 1.02 ng/g ww respectively 0.13 ng/g ww. The higher concentrations, which will be even higher when stated in dw, compared to the ones measured by the wastewater effluent in Adventfjorden (ranging between <LOD and 0.24 ng/g dw and 0.02 ng/g dw and 0.09 ng/g dw), can be indicated by a denser population size and by a non-dilution factor as the compounds were measured in sludge and not in sediment. The concentration of PFOS and PFHxA was also measured in Torshavn, a smaller community situated in the Faroe Islands. There the concentrations were 0.24 ng PFOS/g ww and 0.35 ng PFHxA/g ww (Kallenborn et al., 2004). However, the concentration of PFHxA is still higher than the ones measured in Adventfjorden, which might be explained by the non-dilution effect of sludge as well as different

consumer patterns. The concentration of PFOS is in a similar range, although the concentration from Torshavn will be higher when stated in per dry weight. However, as the population size is slightly higher in the Faroe Islands, the concentration in Adventfjorden is rather comparable to the one in the Faroe Islands. PFAS have also been examined in both marine and freshwater sediment from northern mainland Norway, but no detectable concentrations were found for PFOS, PFHxA or PFTeA (Harju et al., 2013).

PFTeA was almost exclusively detected in Grønfjorden, with a significant higher concentration than in Adventfjorden. The highest concentration was measured by one of the landfills (G2), which hence was the most locally polluted site. The concentration was similar by the other landfill (A1) and the greenhouse area (G4), resulting in them being equally polluted. To my knowledge no results on PFTeA in sediment has, neither in marine or freshwater around the world, been reported and no comparison can hence be made. Neither the application for it has been found. It is possible that the chemical composition is different in Russian products since PFTeA was found outside the landfills and mostly in Grønfjorden and as it only was detected in two of twelve replicates from Adventfjorden, compared to eight of eleven outside Barentsburg.

Potential risk to the ecosystem

Organophosphorus flame retardants

The toxic unit for OPFRs was 7.93×10^{-05} in Adventfjorden and 5.33×10^{-04} in Grønfjorden, i.e. the risk of more than 50 % of the organisms being affected is not anticipated as TU<1. However, a risk to a smaller amount of organisms or individual organisms cannot be eliminated before a risk analysis with more comprehensive toxicity data, e.g. EC10-values, is performed. Such data are at the moment not available for the substances included in the study. TPP and TCPP had the highest toxic units, and also the highest and second highest concentration in both of the fjords explaining the distribution of risk contribution among the congeners.

Even though the risk analysis gives toxic units below one, the concentration of some of the congeners is not negligible according to Verbruggen et al. (2006), which might partly be explained by the effect concentrations used being representative for 50% of the organisms, as discussed above. Verbruggen et al. (2006) have developed environmental risk limits for nine OPFRs in sediment. However, while serious risk

concentrations are presented for all examined substances, negligible concentrations and maximum permissible concentrations are not available for TCEP, TCPP and TDCP. TCPP and TCEP were among the congeners with the highest concentration in this study. According to Verbruggen et al. (2006) the median concentration of TCPP (15.2 ng/g dw) and TCEP (4.35 ng/g dw) are well below the serious risk concentration (230 ng/g dw respectively 74 ng/g dw). However, TPP, with the highest toxic unit, is according to Verbruggen et al. (2006) the median concentration (10.45 ng/g dw) above the negligible concentration (0.95 ng/g dw), but below the serious risk concentration (35 ng/g dw). Also the median concentration of TCP (2.39 ng/g dw) is above the negligible concentration (0.090 ng/g dw) but below the serious risk concentration (8.6 ng/g dw).

Polybrominated diphenyl ethers

A risk of PBDEs to more than 50% of the organisms was not predicted to the ecosystem in Adventfjorden or Grønfjorden since the toxic units are well below one. However, as discussed for OPFRs, a risk to a smaller amount of organisms or to individuals cannot be eliminated. The highest toxic unit was calculated for BDE47, even though it was not measured above limit of detection. Anyhow, the LOD of it was high, and it might be present in the fjords as discussed earlier.

The probability that there is a risk to the benthic ecosystem and individual organisms in the area can be reduced since the concentration of BDE99 and an eventual presence of BDE47 is well below the PNEC calculated for penta-BDE in a risk assessment by the European Union; $PNEC_{sediment}$ 0.31 mg/kg dw and $PNEC_{OC\text{-}normalised\ sediment}$ 1.55 mg/kg dw (European Union, 2001). According to the classification of pollutants in sediment in Norway, stated by the Norwegian Pollution Control Authority, the sediment concentration of BDE99 is classified as background levels (Norwegian Pollution Control Authority, 2007). The classification is the same when the limit of detection of BDE47 is added to the BDE99-concentration, further eliminating the risk of PBDE to the benthic ecosystem in the examined sites.

Perfluorinated alkylated substances

Two toxic units were calculated for PFAS, based on K_{OC} respectively K_d. Negliable risk was assessed for Adventfjorden or Grønfjorden when K_d was used, however the toxic unit was well above one when K_{OC} was applied. The highest risk to the ecosystem constitutes of PFOS in both Adventfjorden and Grønfjorden, while PFNA has the lowest risk of the

examined congeners. PFTeA was not included in the risk analysis since data on partitioning or toxicity is not available in the literature. However, it was the compound with the highest measured concentration, the risk of it should hence not be excluded. Since no other studies with results on PFTeA in aquatic ecosystems are available the risk of it cannot be concluded, until more research on its toxicity has been carried out.

The high toxic unit from the K_{OC}-method is solely dependent of the partitioning of PFOS between sediment and water. However, the concentration of PFOS was 0.18 ng/g dw at highest, by the wastewater effluent, which classifies the sediment as good (no toxic effects), according to the Norwegian Pollution Control Authority (2007). The K_{OC}-values used to calculate the toxic unit is hence leading to an overestimation of the risk of PFOS while the K_d-method seems to give a more appropriate result seeing to the risk estimated by the Norwegian Pollution Control Authority.

Both a species sensitivity distribution (SSD) and a distribution with initial, not transformed, values of EC- or LC50 were used to obtain the 5^{th}-percentile and to calculate the toxic unit for PFOS. The SSD gives a higher potential risk than when using the distribution with initial values, which is a result of the SSD giving a lower PNEC than the distribution with initial values. The toxic unit for K_{OC} is also lower with HC_5, but still far above one. If enough data is available it is according to the results of PFOS more accurate to use the SSD than the distribution with initial values to get the 5^{th}-percentile, since the SSD is giving more attention to the sensitive organisms while the distribution with initial values classify all organisms equal. The toxic unit for the other investigated compounds are similar for K_{OC} and K_d, and both methods should therefore be appropriate to use.

The toxic unit approach and Arctic conditions

Even though the risk analysis indicates no risk to the ecosystem for each individual substance group, more factors should be considered before drawing any conclusions. The ecosystem examined is situated in the high Arctic in areas with high glaciation and where the conditions are different compared to temperate areas (Chapman, 2016; Chapman and Riddle, 2005; Huber et al., 2016). For example; the temperature is lower, the species composition differ, the sedimentation rate is higher than in an unglaciated area, as well as the sun is present 24 hours a day in summer while it is totally dark in winter. These conditions are not considered in the methodology used to examine the risk in this study, even though they might affect the risk. Species living in the Arctic have adapted to the conditions there and have, for example, larger lipid content and a slower metabolism which might result in delayed toxicity compared to species

living in temperate areas (Chapman, 2016; Chapman and Riddle, 2005). Furthermore, the physio-chemical properties might differ and affect the toxicity under Arctic conditions (Huber et al., 2016).

The predicted no effect concentration is mainly derived from toxicity data on acute effect concentrations and from species in temperate areas, since such studies on chronic effect concentrations on the included substances and on Arctic organisms is missing. The risk examined is hence acute, while real conditions rather are chronic. The low concentrations obtained in this study might in reality cause a higher effect than the one retrieved since the exposure of a lower concentration for a longer time will have a more adverse effect than for a short period of time. Although some of the species used in the risk analysis exists in the examined area, the characteristics and sensitivity of them might be different compared to the ones assessed in the toxicity tests, since they, as mentioned, live under different conditions and might also be more sensitive than species in temperate areas due to their adaption to the cold environment (Chapman and Riddle, 2005). It is, however, difficult to test if the Arctic organisms are more or less sensitive, as long as toxicity data on field-collected Arctic species is lacking. Studies on differences in toxicity of oil components between Arctic and temperate species have shown small differences and that the data from temperate areas are good to use as a first indication (de Hoop et al., 2011; Camus et al., 2015). Also studies showing slower response, due to delayed toxicity caused by slower metabolism and higher lipid content, among Arctic and Antarctic species do exist (Hansen et al., 2013; Zamora et al., 2015). No such studies are, however, available for the substances included in this paper. Also the sorption of each substance to sediment and hence the bioavailable fraction will affect the toxicity to differ throughout sites, making it even more important to use locally derived toxicity values (Castro-Català et la., 2016). This would, however, be costly, take time, and be contradictory to ethical values as living organisms would be used; in the meantime of an appropriate method or such results I suggest that the precautionary principle is applied.

The toxicity data used are further mainly representing organisms living in the pelagic zone, while the risk is examined for sediment, and hence benthic species. However, very few data on toxicity to benthic species of the examined substances exist. The measured concentrations were hence corrected to pore-water concentrations using the equilibrium partitioning theory. The EqP-theory has been widely debated among scientist and seems to work variously good for different chemicals in comparison with other methods (McDonough et al., 2010; Fuchsman et al., 2006; Vidal and Bay, 2005; Kraaij et la., 2003). Kraaij et al. (2003) found the EqP-method being correct for hydrophobic organic substances

sequestrating to sediment if it is calculated based on the rapidly desorbing sediment compartment rather than the total organic matter. In order to use a rapidly desorbing compartment instead of TOC a determination of bioavailability of each substance in the present sediment would have been required (Lydy et al., 2015). An experiment with passive samplers for OPFRs and PBDEs was conducted in conjunction with the laboratory work, but as the concentrations in sediment were low and the analysis expensive these samples were never analysed, but saved for possible analysis in the future. However, if analysed they would have provided the true bioavailable fraction of OPFRs and PBDEs in the examined sediment. Since PFAS partitioning differ with chain-length it was not included in the passive sample experiment as the method is not supporting substances with these characteristics yet. However, in future studies it might be more accurate to measure the concentration of PFAS in pore-water or water and sediment instead of only in sediment in order to get a more valid bioavailability fraction or the true partitioning between sediment and water in the examined area.

The bioavailability is dependent of the sediment characteristics and the sorption strength of each individual substance. The partitioning theory, based on K_{OC} and the organic carbon fraction, for estimating the PEC might give a value close to the true value of the bioavailable fraction for OPFRs and PBDEs as they are non-ionic organic compounds which are known to bind to the organic carbon fraction in sediment (Burgess et al., 2013). But, as mentioned above, the sequestration of these compound groups might affect the sorption and hence the bioavailable fraction. Another method used for PAHs by McDonough et al. (2010) measuring the concentration of contaminants directly in pore-water showed better prediction of toxicity and non-toxicity than the K_{OC}-method, same as the one used in this paper. However, the K_{OC}-method was applicable for determining toxicity, since it has an over-prediction of the bioavailable fraction but not for predicting non-toxicity which might result in unnecessary remediation (McDonough et al., 2010). Since no test of the true toxicity have been performed in this paper it is impossible to say if the prediction of toxicity and the outcome risk to the ecosystem is as correct it can be.

The K_{OC}-values were calculated using K_{OW}, which is temperature dependent (Bogillo & Bazylevska, 2008). Since the temperature in the Arctic is lower than in temperate areas this might influence the risk analysis further. K_{OW}-values for lower temperatures are possible to calculate from reference temperatures and by knowing the partitioning enthalpy for each individual substance as done in Bogillo & Bazylevska (2008) for a wide range of organochlorine contaminants (OCs) in the

Antarctic. This was not done in the present study, but can be an improvement for future studies if the necessary data is available. The result of partitioning between seawater and sediment in Bogillo & Bazylevska (2008) showed dominating deposition of OCs to sediment. This can be applied also in Svalbard, since the temperature is similar to the ones in the Antarctic, which might result in another distribution of each substance between the water phase and sediment. No conclusion can, however, be drawn since concentrations in water is missing for the studied area. For future studies measurements of water- and biota-samples should be considered in order to avoid recalculations and false assumptions of concentrations in other compartments than the one examined.

To give a more adequate guide for stakeholders to take measures the probability of the toxic unit being greater than one could have been estimated. However, in order to make a simulation and calculate the probability, distributions need to be fitted to the data. Since the dataset is small, distributions cannot be fitted for all parameters, hence the outcome of the simulation will be very uncertain. Simulations can neither be made when the 5^{th}- and 95^{th}-percentiles for PEC and PNEC are used, since these are received from the distribution and used as individual numbers and not as distributions in the calculation of the toxic units, i.e. no input variables are available. It is furthermore not possible to make a simulation of the sum of toxic units, which would be the interesting probability to receive.

Nevertheless, since the toxic units retrieved are well below one and the concentrations measured are lower than on mainland Norway and in other parts of the world, the probability for a risk should be low seeing to each substance group until other studies, with more accurate data, is proving the opposite. Even though the precautionary principle should be taken in consideration as the risk analysis performed is representative for an effect to 50% or more of the ecosystem while there might be a risk to a smaller group of organisms or individuals. Furthermore, the precautionary principle should be considered if new or increased emissions to the fjords arise, which might happen in the future as the human activities in the Arctic are increasing as the climate is changing.

Bioaccumulation and the cocktail effect

Neither bioaccumulation was considered when examining the risk, however as the substances included in this study all have the potential for bioaccumulation the concentration might be higher in the organisms leading to a more severe effect of the low concentrations measured than obtained effect in the risk analysis. Including a bioconcentration factor in

the risk analysis could have compensated for this, as it would have given an estimated value of the concentration in the organisms.

The toxic unit and additive approach allow examining the risk for each individual substance group but cannot be used for all three groups since they have different mode of action. Even if no risk should be assumed for the individual substance groups, the combined effect from the examined substances and compounds not included in this study should be considered. The overall risk should especially be considered as the sources of pollution in both Adventfjorden and Grønfjorden also can contribute with other substances, resulting in a risk from a combination of effects. In Adventfjorden, mainly by the wastewater outlet, pharmaceuticals and other substances used in the everyday life can be assumed to occur as the wastewater is untreated and the local temperatures are low which prevent degradation of substances normally degrading even if not treated in temperate areas. In Grønfjorden elevated concentrations of PCB and DDT have been detected (Evenset et al., 2006b). Even if these concentrations are decreasing (Evenset et al., 2009); the compounds as well as new compounds are and might be present.

As mentioned earlier the human activities in the Arctic is increasing as the climate is changing (Wöhrnschimmel et al., 2013), in addition is the tourism industry, education and research increasing in Svalbard, mainly in Longyearbyen and the former major mining industry decreasing (Sysselmannen, 2016). The change in population size and industry might change the pollution rate and the pollutants released and hence cause an effect to the ecosystem, not seen today. Such an effect might more likely affect the tourism industry, with tasting of locally caught fish and whale watching, harder than the population itself since the community is not dependent on fishery in the same way as for example the Inuit population in Greenland. More studies are however needed before a cocktail effect of all potentially occurring substances and the risk for the ecosystem can be assessed. If the population size or tourism increases, or progress as today, in regards to the result of this study and the precautionary principle a wastewater treatment plant in Longyearbyen and better treatment processes for the landfills and industries in Barentsburg should be considered.

Conclusions

- Of the 13 analysed organophosphorus flame retardants local contamination is assumed to occur for BdPhP, DBPhP, EHDP, TCEP, TCP, TCPP, TEHP, TEP, TnBP and TPP in Adventfjorden and for EHDP, TCEP, TCP, TCPP, TEHP, TEP, TnBP and TPP in Grønfjorden. Even though the contamination is mainly assumed to originate from local sources, long range transport might contribute as well. The highest contamination rate has DBPhP and TCPP in Longyearbyen and TCEP, TCP, TCPP and TPP in Barentsburg.
- Of the 23 congeners of PBDE analysed only BDE99 was detected. It is anticipated to originate from local pollution in both Adventfjorden and Grønfjorden.
- Of the 21 PFAS congeners analysed three; PFHxA, PFOS and PFTeA, were solely detected in the expected polluted sites and are assumed to originate from local pollution. The highest contamination rate constitute PFOS and PFTeA in Adventfjorden respectively Grønfjorden.
- The wastewater effluent in Adventfjorden and one of the landfills in Grønfjorden are overall mostly polluted. The concentration differences between sites in each fjord can partly be explained by the application of each substance in different products.
- Grønfjorden is significantly more locally polluted by OPFRs than Adventfjorden; except for DBPhP which had significantly higher concentration in Adventfjorden. However, Adventfjorden is more locally polluted by BDE99 than Grønfjorden, even though a more comprehensive survey is needed to draw any firm conclusion. Among the PFAS, PFHxA had significantly higher concentrations in Adventfjorden and PFTeA in Grønfjorden.
- None of the substance groups pose an acute risk to the ecosystem, even though individual organisms might be affected. The concentration of TCP in Grønfjorden and TPP in both fjords is not negligible according to Verbruggen et al. (2006). The combined risk of all investigated substances and compounds not included in the present paper as well as an increased risk with future changes in population size, industry and tourism in the Arctic as a consequence of climate change cannot be excluded.

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Appendix

Extraction of Perfluorinated alkylated substances

The sample (about 2.5 g) was spiked with 20 µL ISTD (0.5 ng/µL of 13C PFAS mix in methanol). For extraction 1 mL of 200 mM NaOH in methanol was added to the sample. After the mixture had soaked for about 30 minutes, 100µL 2 M HCl in methanol (already prepared) and 9 mL methanol was added. The sample was thereafter vortex-mixed for about 30 seconds and further extracted in ultrasound bath for ten minutes times three, with vortex-mixing in between. After extraction, the sample was centrifuged at a speed of 2000 rpm and a temperature of 10°C in 5 minutes for sedimentation. 7 mL of the extract was transferred to a 15 mL methanol-rinsed PP-tube.

The extract was evaporated to 2 mL in a RapidVap, at 35-40°C, a speed of 50 % and a pressure of 180 mBar. A 1.7 mL Eppendorf centrifuge tube was prepared with 25 mg of ENVI-Carb and 50 µL glacial acetic acid (already prepared) for clean-up of the sample. 1 mL of the evaporated supernatant methanol extract was added to the Eppendorf tube, which thereafter was vortex-mixed for about 30 seconds. The sample was centrifuged at 10 000 rpm in 10 minutes for sedimentation of the ENVI-carb. 0.5 mL of the supernatant solution and 20 µL of recovery standard; 3,7-dimet PFOA 0.1 ng/µL were added to a 1.5 mL vial, vortex-mixed and stored in the fridge until analysis.

Data for risk analysis

Table 1. Data used in the risk analysis, obtained from scientific literature.

Substance	Log Kow	Toxicity Endpoint	Organism	Value	References
Organophosphorus flame retardants					
EHDP	5.73	EC50 (48h)	Zooplankton	0.31 mg/L	NTP (2016), Cristale et al. (2013)
TBEP	3.75	EC50 (48h)	Zooplankton	38 mg/L	Verbruggen et al. (2005), Cristale et al. (2013)
TCEP	1.78, 1.44	EC50 (15min) EC50 (48h)	Bacteria Zooplankton	323 mg/L 381 mg/L	Verbruggen et al. (2005)
TCP	5.95, 5.11	EC50 (48h) EC50 (96h) EC50 (96h)	Zooplankton Fish Fish	0.31 mg/L 8700 mg/L 9100 mg/L	Verbruggen et al. (2005), Cristale et al. (2013)
TCPP	2.59	EC50 (15min) EC50 (30min) EC50 (48h)	Bacteria Bacteria Zooplankton	172 mg/L 296 mg/L 81 mg/L	Van der Veen & de Boer (2012), Verbruggen et al. (2005), Cristale et al. (2013)
TDCPP	3.8	EC50 (48h)	Zooplankton	7.9 mg/L	Van der Veen & de Boer (2012), Cristale et al. (2013)
TEHP	4.22, 9.42, 9.49	EC50 (48h)	Zooplankton	0.74 mg/L	Van der Veen & de Boer (2012), Verbruggen et al. (2005), Cristale et al. (2013)
TEP	0.8, 7.45	EC50 (96h) LC50 (96h)	Crustacea Fish	950 mg/L 2100 mg/L	Van der Veen & de Boer (2012), Verbruggen et al. (2005)
TiBP	2.12, 3.6	EC50 (15min)	Bacteria	129 mg/L	Van der Veen & de Boer (2012), Verbruggen et al. (2005)
TPP	2.67, 4.59	LC50 (96h) LC50 (96h) LC50 (96h) LC50 (96h)	Crustacea Fish Fish Fish	0.18 mg/L 0.32 mg/L 95 mg/L 98 mg/L	Van der Veen & de Boer (2012), Verbruggen et al. (2005)
Polybrominated diphenyl ethers					
BDE28	5.67, 5.94, 5.98, 6.24	LC50 (48h)	Zooplankton	108 µg/L	Lebrun et al. (2014), Lv et al.

Substance	Log Kow	Toxicity Endpoint	Organism	Value	References
					(2015), Wollenberg et al. (2005), Zhang et al. (2013)
BDE47	5.85, 6.55, 6.8, 6.81, 6.81	EC50 (96h) EC50 (96h) EC50 (96h) EC50 (96h) IC50 (72h) EC50 (48h) LC50 (96h) LC50 (96h) LC50 (48h) LC50 (96h) LC50 (48h) LC50 (96h)	Microalgae Microalgae Microalgae Microalgae Algae Phytoplankton Zooplankton Zooplankton Zooplankton Zooplankton Fish Fish	0.79 µg/L 1.52 µg/L 1.99 µg/L 2.25 µg/L 25.73 µg/L 70 µg/L 57 µg/L 851 µg/L 2370 µg/L 4400 µg/L 27.35 µg/L 14.13 µg/L	Lv et al. (2015), Zhang et al. (2013), Lebrun et al. (2014), Jia et al. (2012), Wollenberg et al. (2005), Zhuo-na et al. (2009), Mhadhbi et al. (2012a), Källqvist et al. (2006), Fengfeng et al. (2013), Breitholtz & Wollenberg (2003)
BDE99	6.39, 7.13, 7.32, 7.38, 7.39	IC50 (72h) LC50 (48h) LC50 (48h) LC50 (96h)	Algae Zooplankton Fish Fish	30.9 µg/L 705 µg/L 38.28 µg/L 29.64 µg/L	Lebrun et al. (2014), Wollenberg et al. (2005), Jia et al. (2012), , Lv et al. (2015), Mhadhbi et al. (2012a)
BDE100	6.23, 6.86, 7.09, 7.24, 7.27	LC50 (48h)	Zooplankton	520 µg/L	Lebrun et al. (2014), Wollenberg et al. (2005), Zhang et al. (2013), Lv et al. (2015), Waszak et al. (2012)
BDE154	6.76, 7.61, 7.82	IC50 (72h)	Algae	243.72 µg/L	Lebrun et al. (2014), Zhang et al. (2013), Lv et al. (2015), Mhadhbi et al. (2012a)
BDE183	7.20, 8.27, 8.61	LC50 (8weeks)	Oligochaeta	0.169 µg/L	Lebrun et al. (2014), Lv et al. (2015), Zhang et al. (2013), Chiu et al. (2012)

Substance	Log K_{OC} ($LogK_d$)	Toxicity Endpoint	Organism	Value	References
Perfluorinated alkylated substances					
PFHxA	2.1, 2.55, 2.62, 2.64 (0.8)	LC50 (24h)	Rotifer	140 mg/L	Guo et al. (2015), Ahrens et al. (2015), Wang et al. (2014)
PFNA	2.35, 2.39, 2.4, 2.5, 2.9, 3.07, 3.56, 3.8 (1.805, 2.2, 2.5, 2.88)	EC50	Mussel	195 mg/L	Higgins & Luthy (2006), Zhao et al. (2012), Guo et al. (2015), Zao et al. (2015), Munoz et al. (2015), Cao et al. (2015, Liu et al. (2014)
PFOA	1.9, 2.06, 2.09, 2.17, 2.53, 2.68, 2.98 (0.58, 1.2, 1.8, 1.9, 2.67)	EC50 EC50 EC50 EC50 (72h) EC50 (96h) EC50 EC50 (48h) EC50 (144h)	Cyanobacteria Bacteria Microalgae Microalgae Zooplankton Mussel Sea urchin Fish	72.3 mg/L 524 mg/L 96.75 mg/L 163.6 mg/L 15.5 mg/L 594 mg/L 110 mg/L 11.9 mg/L	Higgins & Luthy (2006), Zhao et al. (2012), Guo et al. (2015), Cao et al. (2015), Ahrens et al. (2015), Munoz et al. (2015), Rosal et al. (2010), González-Naranjo & Boltes (2014), Mhadhbi et al. (2012b), Liu et al. (2014)
PFOS	2.57, 2.68, 2.97, 3.58, 3.7, 3.75, 3.8, 4.15 (2.3, 2.5, 3.11)	EC50 (72h) EC50 (96h) EC50 (96h) EC50 (96h) EC50 (96h) EC50 (96h) LC50 (96h) EC50 (48h) EC50 (48h) EC50 (48h) EC50 LC50 (96h) EC50 (96h) EC50 (72h) LC50 (96h) LC50 (96h) LC50 (96h) EC50 (144h) EC50 (96h) EC50 (96h) LC50 (96h)	Microalgae Algae Algae Algae Phytoplankton Zooplankton Crustacean Crustacean Crustacean Crustacean Mussel Mussel Oyster Sea urchin Fish Fish Fish Fish Fish Fish Fish	37.5 mg/L 81.6 mg/L 263 mg/L 305 mg/L 3.2 mg/L 6.9 mg/L 3.6 mg/L 8.9 mg/L 9.4 mg/L 9.4 mg/L 33 mg/L 683 mg/L 2.9 mg/L 1.795 mg/L 13.7 mg/L 13.7 mg/L 15 mg/L 0.11 mg/L 7.8 mg/L 9.9 mg/L 22 mg/L	Higgins & Luthy (2006), Zhao et al. (2012), Guo et al. (2015), Cao et al. (2015), Ahrens et al. (2015), Liu et al. (2015), Mhadhbi et al. (2012b), Boudreau et al. (2003), Beach et al. (2006), Liu et al. (2014), Wang et al. (2012), Gunduz et al. (2013)

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