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1   **New brominated flame retardants and dechlorane plus in the Arctic: local**

2   **sources and bioaccumulation potential in marine benthos**

3

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16

18

Abstract

20   The aim of the present study was to investigate the presence and bioaccumulation of new flame

21   retardants (nBFRs), polybrominated diphenyl ethers (PBDEs) and dechlorane plus (DDC-CO)

22   in the marine environment close to an Arctic community. Passive sampling of air and water and

23   grab sampling of sediment and amphipods was used to obtain samples to study long-range

24   transport versus local contributions for regulated and emerging flame retardants in

25   Longyearbyen, Svalbard. BDE-47 and -99, α- and β-tetrabromoethylcyclohexane (DBE-

26   DBCH), *syn-* and *anti-*dechlorane plus (DDC-CO) were detected in all investigated matrices

27   and the DDC-COss at higher concentrations in the air than reported from other remote Arctic

28   areas. Water concentrations of ΣDDC-COSs were low (3 pg/L) and comparable to recent Arctic

29   studies. ΣnBFR was 37 pg/L in the water samples while ΣPBDE was 3 pg/L. In biota, ΣDDC-

30   COSs dominated (218 pg/g ww) followed by ΣnBFR (95 pg/g ww) and ΣPBDEs (45 pg/g ww).

31   When compared with other areas and their relative distribution patterns, contributions from

32   local sources of the analysed compounds cannot be ruled out. This should be taken into account

33   when assessing long-range transport of nBFRs and DDC-COs to the Arctic. High

34   concentrations of PBDEs in the sediment indicate that they might originate from a small, local

35 source, while the results for some of the more volatile compounds such as hexabromobenzene

36 (HBBz) suggest long-range transport to be more important than local sources. We recommend

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

38

1. Introduction

40 Brominated flame retardants (BFRs) have been extensively used during the last decades

41 (AMAP, 2017). The polybrominated diphenyl ethers (PBDEs) have been shown to

42 bioaccumulate, be toxic and undergo long-range transport in the environment (de Wit et al.,

43 2006, 2010). As a consequence, three commercial mixtures (c-penta-, c-octa-, and c-deca-BDE)

44 and the congener groups included (tetra-, penta-, hexa-, hepta- and deca-BDE) have been

45 subject to regulatory measures and added to the list of persistent organic pollutant (POPs) under

46 the Stockholm Convention and the Aarhus protocol of the Convention on Long-range

47 Transboundary Air Pollution (CLRTAP) (UNECE, 2018). Parties of the conventions must take

48 measures to eliminate the production and use of the PBDEs (Stockholm Convention, 2015).

49 However, PBDEs are still present in the environment, and still pose a possible environmental

50 threat. After regulation of the PBDEs, the industry has introduced alternative BFRs as

51 replacements. These new BFRs (nBFRs) comprise a wide range of individual compounds and

52 the list is continuously growing. Examples of nBFRs are listed in the supplementary

53 information (Table A1, A3) while structure and properties are covered by Bergman et al.

54 (2012). Several chlorinated flame retardants such as *syn-* and *anti-* dechlorane plus (*syn*-DDC-

55 CO and *anti*-DDC-CO) are also produced. Analytical methods are under development and as a

56 result, halogenated FRs are being analysed and detected in the environment at sites all over the

57 world, including the Arctic (AMAP, 2017).

58

59 Among the regulatory criteria for the Stockholm convention (persistent, bioaccumulative and

60 toxic), the "persistent" criteria is considered to be fulfilled if a compound reaches the Arctic.

61 The target compounds of the present study have been found in air, glacier and biota from high

62 trophic levels within the Arctic (AMAP, 2017; de Wit et al., 2010; Hermanson et al., 2010;

63 Verreault et al., 2007; Vorkamp et al., 2015; Vorkamp and Rigét, 2014). Examples of nBFRs

64 found in biota at higher trophic levels are 2,3-dibromopropyl- 2,4,6-tribromophenyl-ether

65 (TBP-DPBE, former DPTE) in hooded seals *(Cystophora cristata)* from the Barents Sea and

66 decabromodiphenylethane (DBDPE) in various biota from Svalbard: Brünnich's guillemot

67 *(Uria lomvia)* eggs*,* polar cod *(Boreogadus saida)* and polar bear *(Ursus maritimus)* plasma (de

68 Wit et al., 2010; Harju et al., 2013; Sagerup et al., 2010; von der Recke and Vetter, 2007). De

69 Wit et al. (2010) concluded that 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) can undergo

70 long-range transport and that it bioaccumulates in the Arctic food web. Vorkamp and Rigét

71 (2014) concluded that DDC-COs can undergo biomagnification while 2-ethylhexyl-2,3,4,5-

72 tetrabromobenzoate (EH-TBB) and BTBPE might biomagnify. There are several other nBFRs

73 available on the market and little is known about the bioaccumulation potential, toxicity and

74 persistency of these compounds. These features need to be investigated for the nBFRs in order

75 to provide a sound management of these compounds, especially with regards to the vulnerable

76 Arctic environment (AMAP, 2017). There is to date a lack of information regarding uptake and

77 concentrations at low and medium trophic levels in the marine Arctic food web, although some

78 information for higher trophic levels and air exist from Greenland (AMAP, 2017; Vorkamp et

79 al., 2015; Vorkamp and Rigét, 2014). Furthermore, the exposure and uptake links between

80 abiotic matrices (e.g. water, sediment, air) and biota are not well understood, and studies are

81 needed to fully understand the fate and environmental behavior of nBFRs.

82

83 BFRs are used in a large suite of materials such as textiles, plastic and electronic equipment. In

84 2013, 280 tonnes of BFRs were used in Norway alone (Norwegian Environment Agency, 2017).

85 With increased human activity and larger, modern settlements in the Arctic, the use of flame

86 retarded goods will most likely increase in these settlements. Hence, even if some of the nBFRs

87 might not undergo long-range transport, they could still be present in the Arctic due to local

88 sources. It is important to understand the impact of local sources on the nearby environment as

89 well as knowing the concentrations and distribution patterns in the environment to disentangle

90 local sources from long-range transport. There are examples where pollution at Arctic sites

91 mainly comes from local sources and not from long-range transport, such as PFAS from airports

92 in remote parts of Canada, PCB from abandoned settlements and siloxanes from local sewage

93 outlets in Svalbard (Pedersen et al., 2011; Stock et al., 2007; Warner et al., 2010).

94

95 As pointed out in the new AMAP assessment on contaminants of emerging concern in the

96 Arctic, there is a need for more research and information on the distribution, sources and

97 pathways of these chemicals (AMAP, 2017). The present study aims to fill some of these

98 knowledge gaps and investigate whether an Arctic community with about 2000 inhabitants

99 impacts the concentrations of new and regulated flame retardants in local air and its marine

100 surroundings. This study is also a pilot study on the accumulation of BFRs and DDC-COs in

101 marine, relatively long-lived amphipods in comparison to their environmental surroundings.

2. Materials and methods

2.1. Sample collection

Four matrices were sampled in this study: sediment, biota (littoral amphipods), water and air. The BFRs in water and air were sampled using passive samplers while biota and sediment were sampled directly (grab sampling). A total of 24 samples were collected within Longyearbyen during 2015-2017 (78°13'N, 15°38'E, Table 1, Figure 1) All equipment used for sampling was pre-cleaned with acetone and *n*-hexane to minimise contamination by the sampling equipment. The handling of samples indoors was kept at a minimum to minimise the risk of contamination. All samples were wrapped in aluminium foil and frozen (-20°C) directly after sampling and kept frozen until analysis.
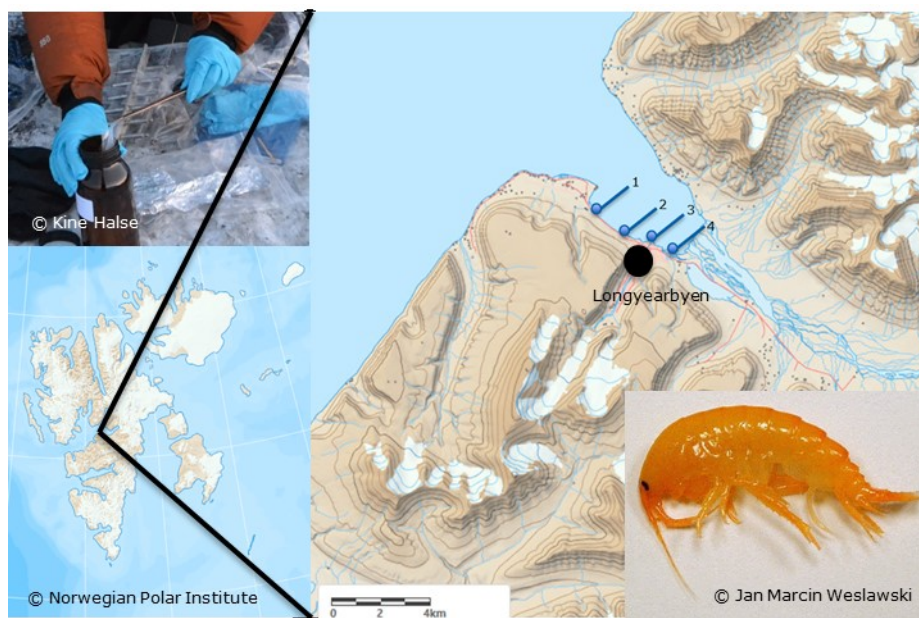
Figure 1. Map over Svalbard, the settlement of Longyearbyen and sampling sites. The water, air and sediments were sampled at the sampling station 1 and one additional sediment sample was taken from station 3. The amphipods (e.g. *Gammarus setosus,* lower right corner*)* were sampled from stations 1-4 along the beaches in Longyearbyen. Deployment of the silicone rubbers (SRs) for passive air and water sampling is shown in the upper left corner.

2.1.1. Air and water

Air (freely hanging ~1 m above surface) and water (surface water, deployed at the bottom at ~1 m depth) samples were collected at station 1 using passive samplers based on silicone rubbers (SR) from Altesil (Altec, UK, sheet thickness 500 µm). Before deployment in the field, the SRs were pre-cleaned with methanol and spiked with a suite of 14 performance reference

124 compounds (PRCs; including perdeuterated biphenyl and 13 PCB congeners that do not occur
125 in technical mixtures (PCB-1, -2, -3, -10, -14, -21, -30, -50, -55, -78, -104, -145 and -204))
126 according to the procedure described by Smedes and Booij (2012). The PRCs were partially
127 released from the sampler during exposure and could therefore be used for evaluation sampling
128 rates in the individual samplers. The SRs were deployed for three months in 2015 and 2016 at
129 the small boat harbour in the vicinity of Longyearbyen, Svalbard (Figure 1, Table 1) Due to
130 waves and currents, the SRs deployed in water (2016) were pushed into shallow water and were
131 exposed to air during parts of the low tide at the time they were collected. After retrieving the
132 SRs, any visible particles were wiped off with clean tissues. One field blank SR for each
133 campaign was exposed to air when the SRs were deployed and when collected. In addition, two
134 un-exposed SRs were kept in the freezer at all time as a reference for the initial PRC
135 concentrations. The average daily temperatures in the air during the sampling period varied
136 between -15°C and +6°C (The Norwegian Meteorological Institute, 2017). The surface water
137 temperature of Adventfjorden was in the range of -0.5°C to +4°C and is ice-free all year round
138 nowadays (Norwegian Institute for Water Research, 2017).
139
140 ### 2.1.2. Sediment
141 Surface sediments (n=8, upper 3 cm of sediment, Table 1) were sampled by Van Veen-grab
142 from Adventfjorden, in the vicinity of the small boat harbour (station 1, Figure 1) in January
143 2016. One additional sediment sample was collected from station 3 (Figure 1) in March 2017.
144 The wet sediment was covered with aluminum foil and dried at 30°C in a drying oven for 3-4
145 days before sieving (0.5 mm mesh sieve). A bulk sample consisting of a composite mixture of
146 all replicates from station 1 was prepared from dry sediment for additional analyses at a
147 different laboratory.
148
149 ### 2.1.3. Biota (amphipods)
150 Amphipods (n=9 pooled samples) were collected in the littoral zone of the Adventdalen estuary
151 and from Adventfjorden littoral zone (station 1-4, Figure 1, Table 1) in July-August 2016. The
152 amphipods hide under stones and can be accessed by turning stones during low tide. Individuals
153 were picked from the sediment surface or from the underside of the turned stones. For practical
154 reasons the amphipods were not allowed empty their gut contents before freezing. The
155 amphipods collected were *Gammarus spp.*, especially *G. setosus* (Ambrose and Leinaas, 1990;
156 Weslawski, 1994). It is unlikely that this spatial distribution impacted concentrations or relative
157 distribution to any extent that would be larger than natural variability and the analytical

variance. Hence, they were treated as one group for comparison with the sediment, water and air samples.

2.2. Analysis

All samples were analysed for a suite of eight PBDEs, 22 nBFRs, *anti-* and *syn*-DDC-CO, and Dechlorane Plus Mono Adduct (DPMA) at RECETOX, Masaryk university, CZ except for total organic carbon (TOC) in all sediment samples, one sediment sample from 2017 and a bulk sediment sample of the 2016 samples that were analysed at NIVA (Oslo, Norway) instead-. The reason was to compare results between the laboratories. CAS number, log K_{ow}, log K_{oa}, internal standards (IS) and m/z for quantification and qualification masses are listed in Tables A1-A3. The passive SR samplers were also analysed for 18 organophosphorous flame retardants (OPFRs). The passive samplers were analysed for OPFRs as well. However, due to little information on K_{pw} in cold temperatures for SRs, these data are not discussed within the paper, but are presented in Table A8 together with the analytical method. All halogenated standards were purchased from Wellington Laboratories, Guelph, Canada (except BDE-118, which was purchased from AccuStandard, New Haven, CT). All glassware was heated at 150°C for two hours, and all equipment used was cleaned with acetone and *n*-hexane right before use.

TOC was analysed at NIVA (accredited laboratory, ISO 17025). Briefly, the homogenised sediment samples were mixed with hydrochloric acid, flushed with air to remove the inorganic and volatile carbons. Afterwards, the samples were burned and the amount of CO_2 (proportional to the amount of TOC) was measured with infra-red light.

2.2.1. Passive samplers for air and water

All passive samplers were spiked with ^{13}C labelled internal standards (IS) for the BFRs and DDC-COs (Table A2) and three non-labelled PCBs (PCB 4, 29 and 185) that do not occur in technical mixtures before extraction. As recovery and method control, five non-exposed passive samplers were spiked with the target BFRs and DDC-COs and further treated in the same way as the real samples. Two solvent blank samples were also processed. The samples were Soxhlet extracted for eight hours in methanol and thereafter evaporated by Kuderna-Danish apparatus to ~2 mL before solvent exchange to *n*-hexane and further evaporated to ~2 mL.

2.2.2. Sediment

The sediment samples from station 1 (n=8, 10 g each) were spiked with ^{13}C-labelled IS for PBDEs, nBFRs and DDC-COs (Table A2) before Soxhlet extraction for eight hours in DCM followed by evaporation by Kuderna-Danish to ~2 ml and solvent exchange to *n*-hexane. One composite bulk sample of sediment (station 1, 2016 samples) and one sediment sample from spring 2017 (station 3) were analysed at NIVA for PBDEs as a comparison between the two laboratories. The NIVA method differs slightly from RECETOX' method and is described in the appendix. All reported PBDEs were analysed at both laboratories except for BDE-49, -196, -209 which were analysed only at NIVA (bulk sample and the sediment sample from station 3) and BDE-66 and -85 which were analysed at RECETOX only.

2.2.3. Biota

The amphipods were thawed, and water and sediment particles were removed before homogenisation with a kitchen blender. Each sample (n=9) contained 3-8 g of amphipods. ^{13}C-labelled IS of PBDEs, nBFRs and DDC-COs (Table A2) were added to each sample before the homogenates were freeze dried for 50 h. Dried samples were Soxhlet extracted for eight hours in dichloromethane (DCM) and thereafter evaporated using Kuderna-Danish apparatus to ~2 mL, solvent exchanged to *n*-hexane and further evaporated to ~2 mL.

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

Sample type	Number of samples	Time period for sampling	Station number within Longyearbyen
Water	3; 1 in 2015, 2 in 2016	March-May 2015, Feb-May 2016	1
Air	3; 1 in 2015, 2 in 2016	March-May 2015, Feb-May 2016	1
Sediment	10*; 8 in 2016, 1 in 2017	Jan 2016, March 2017	1 (n=8), 3 (n=1)
Amphipods	9 (pooled individuals)	July-Aug 2016	1 (n=3), 2 (n=1), 3 (n=3), 4 (n=2)

*One bulk sample (station 1) of 2016 samples is also included in the total number of analyses but is not included in the station column.

214

2.2.4. Clean-up of all sample matrices

All samples were further cleaned up using silica columns and GPC (for biota and sediment only). Details are provided in the appendix.

218

2.2.5. GC-MS analyses

PBDEs, nBFRs and DDC-COs

Analyses of PBDE, DDC-COs and nBFRs and PRCs were performed using a gas chromatograph connected to a mass spectrometer (GC-MS). Details are provided in the appendix.

224

2.3. Quality assurance and control

Two blanks made of solvent pre-extracted cotton wool were processed together with the sediment and biota samples. The field blanks and reference SRs were processed together with the air and water SRs. 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) were not reported for the biota and sediment samples due to their partial destruction during sample clean-up with silica gel with sulfuric acid. A standard reference material (SRM 1944 from National Institute of Standards and Technology (NIST)) was analysed for PBDEs in sediment at NIVA and the median deviation from the reference value for PBDEs were 12%. The limit of detection (LOD) was defined as 3×S/N (signal to noise-ratio) when a compound was not detected in the blank, otherwise the average blank concentration + 3×standard deviation in the blanks (and reference SRs for air and water) were used. LOQ for the matrix water was calculated by inserting the amount of a target compound detected in the field blank to the formula for calculation of water concentrations (equation 2). Detection frequency is listed in Table A4 and the LODs are listed in Table A5. The field blank concentrations are listed in Table A6. The sample results were not blank subtracted. Samples with concentrations <LOD was not included in statistical analyses and all values are presented based on concentrations >LOD together with a note on the frequency of detection.

243

244

245

246

247   2.4.   Calculations of atmospheric and aqueous concentrations of BFRs

248   The performance reference compounds (PRCs) indicated the degree of equilibrium reached by

249   the passive sampler for compounds with a range of partition coefficients; K_{pa} (SR/air) or K_{pw}

250   (SR/water). The rate that PRCs are leaking out from the passive sampler is known by laboratory

251   experiments and this rate can be related to accumulation of (similar) compounds into the passive

252   sampler. The concentrations left in the SRs after exposure indicated that the samplers were far

253   from equilibrium with the sampled matrix for most compounds. Hence, the sampling was

254   assumed to be fully integrative for all targeted compounds. In this situation, concentration of

255   compounds in the air can be calculated as in equation 1.

256

257    $$C_a = \frac{N_{SR}}{R_S t}$$ (Eq 1)

258

259   Where N_{SR} is the concentration of the analyte in the sampler (pg/sampler) at the exposure time,

260   t is time of exposure (in days), R_s is the sampling rate of the compound (m^3/day) where generic

261   values from Okeme et al. (2016) were used.

262

263   Aqueous concentrations, C_w, of individual compounds were calculated from the mass absorbed

264   by the SRs, N_{SR}, the degree of equilibrium DEQ (equation 3) that the compound attained during

265   sampler exposure, the mass of sampler, m_{SR}, and their sampler-water partition coefficients $K_{SR,w}$

266   as described in Booij et al (2007). This is shown in equation 2.

267

268    $$C_w = \frac{N_{SR}}{K_{SR,w}\, m_{SR}\, DEQ}$$ (Eq 2)

269

270    $$DEQ = \left(1 - \exp\left(-\frac{R_{S,SR}\, t}{K_{SR,w}\, m_{SR}}\right)\right)$$ (Eq 3)

271

272   The sampling rate $R_{S,SR}$ of individual compounds by SR passive samplers was modeled as a

273   function of molar mass M by the water boundary layer (WBL) controlled uptake model with

274   an exposure-specific parameter B: $R_{s,SR} = B \times M^{-0.47}$ (Rusina et al., 2010). The parameter B was

275   estimated from the dissipation of PRCs from samplers during exposure using nonlinear least

276   squares method (Booij and Smedes, 2010). This method considers the fraction of individual

277 PRCs that is retained in sampler after exposure as a continuous function of their sampler-water
278 partition coefficient $K_{SR,w}$.

279

280   2.5.   Bioaccumulation calculations

281 The bioaccumulation factor (BAF; equation 4) was estimated using the average concentrations
282 measured in the passive water samplers (C_{water}; dissolved water concentrations) and amphipods
283 (C_{biota}; lipid weight normalised concentrations). The lipid content in the amphipods were
284 assumed to be 10% based on species and locality (Nygård et al., 2010; Szaniawska and
285 Wolowicz, 1985). To take the seasonal lipid variability into account, estimations with lower
286 (5%) and higher (15%) lipid content were included. For biota-sediment accumulation (BSAF,
287 equation 5), the average TOC-normalised sediment concentrations ($C_{sediment}$) were used.

288

289     $Log\ BAF = \text{Log}(\frac{C_{biota}}{C_{water}})$ (Eq 4)

290

291     $Log\ BSAF = Log(\frac{C_{biota}}{C_{sediment}})$ (Eq 5)

292

3. Results and discussion

294 All samples were collected within the same fjord. Any contribution from long-range transport
295 should therefore impact all samples equally, although the compound distribution and uptake
296 patterns will differ due to the different properties of the matrices. Concentration data are
297 presented in Table 2.

298

299

300   3.1.   Distribution patterns in the Longyearbyen samples

301   3.1.1. Air

302 Seven halogenated FRs were detected in more than 50% of the passive air samples; BEH-TEBP,
303 EH-TBB, α- and β-DBE-DBCH, PBT, *syn*- and *anti*-DDC-CO. In addition, PBEB were
304 detected in one of the samples (Table 2) The PBDE congeners BDE-47 and -99 were detected
305 in all samples -while BDE-100 was detected in two of the air samples. This is consistent with
306 results from outdoor calibration studies of another type of passive air sampler (polyurethane
307 foam; PUF) (Bohlin et al., 2014). As a comparison on the relative contribution of all
308 halogenated FRs analysed, BEH-TEBP was the predominating compund (55%, 1867 pg/m³)

309 followed by *syn-/anti*-DDC-CO (20% together, 356 and 349 pg/m^3, respectively, Figure 2,

310 Table 2). The samples where PBEB (<LOD-0.02 pg/m^3) and PBT (<LOD in one sample, 0.03-

311 0.06 pg/m^3 in the other) were >LOD showed comparable (PBEB) but higher (PBT)

312 concentrations than previously reported from passive sampling at other Arctic sites. The range

313 of PBEB concentrations at other Arctic sites were <LOD-0.11 pg/m^3 in Barrow and St.

314 Laurence Island (Alaska, USA), Stórhöfði (Iceland) and Ny-Ålesund (Svalbard, Norway))

315 while the PBT concentrations were <LOD-0.005 pg/m^3 at the same stations except Iceland

316 where they PBT was not analysed (AMAP, 2017).

317

318

319

320
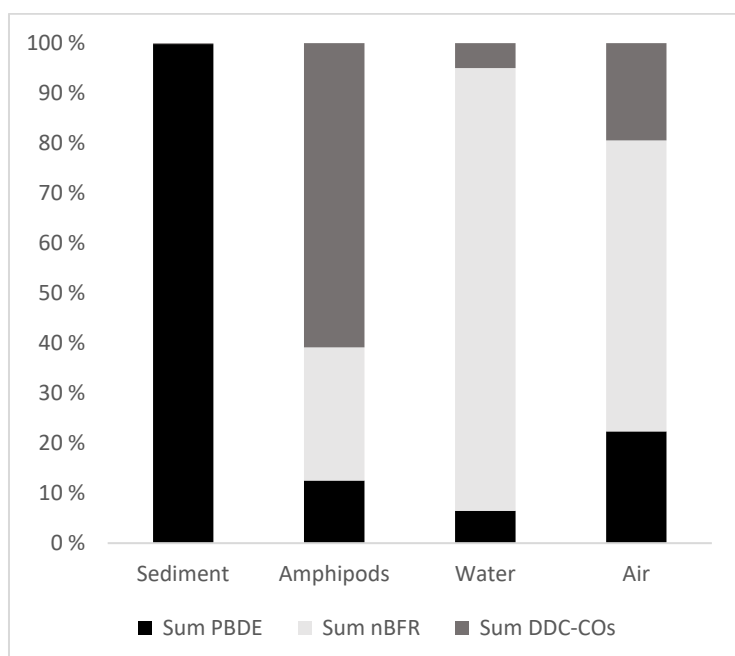
322 **Figure 2.** Relative distribution of ΣPBDE, ΣnBFR and ΣDDC-COs in all samples.

323

324

325 3.1.2. Water

326 The total concentration of halogenated FRs in the passive water samples were 43 pg/L on

327 average. As a comparison on the relative contribution of all halogenated FRs analysed, α-TBCO

328 (48% in 2015 and 76% in 2016) was the predominating compound in the water samples,

329 followed by BEH-TEBP (14-23%). The PBDEs contributed to 15% (campaign in 2015) and

330 5% (campaign in 2016) of all BFRs/DDC-COss analysed (Figure 2). The average ΣPBDE

331 concentrations (2.9 pg/L) were slightly higher in the water around Longyearbyen compared to

332 East Greenland Sea, which could be related to the samplers being located close to a village in
333 the present study (Möller et al., 2011). *Syn-* and *anti-*DDC-CO contributed to 13% in 2015 but
334 decreased to 3% contribution in 2016 of the FRs analysed. This was a consequence of slightly
335 lower DDC-CO-concentrations in combination with increased concentrations of α-TBCO in the
336 2016 water samples. The water samples in 2016 got partially exposed to air due to wind and
337 weather that moved the samplers, but the concentrations measured in 2016 are in the very same
338 range as the results from 2015, and hence, this has probably not affected the concentrations
339 more than the analytical uncertainty.
340

Table 2. Average concentrations >LOD measured in all samples. Compounds/samples without numbers were <LOD.

	Air (pg/m³)				Water (pg/L)				Sediment (pg/g dw)				Sediment (ng/g dw)		Amphipods (pg/g ww)			
	Average >LOD	Min	Max	Std dev	Average >LOQ	Min	Max	Std dev	Average (individual samples) >LOD	Min	Max	Std dev	Composite sample station 1, n=1	station 3. n=1	Average >LOD	Min	Max	Std dev
PBBz	<LOD				1.5	<LOD	1.9	NA	<LOD				NA	NA	3.8	<LOD	5.6	1.3
BTBPE	<LOD					<LOD			<LOD				NA	NA	0.5	<LOD	0.5	0.1
HBBz	<LOD					<LOD			<LOD				NA	NA	3.5	<LOD	6.7	1.6
PBEB	16	<LOD	16			<LOD			2.5	1.2	4.0	1.3	NA	NA	1.1	<LOD	3.5	1.1
pTBX	<LOD					<LOD			0.8	<LOD	0.8		NA	NA	<LOD			
PBT	45	29	61		0.02	<LOD	0.02	NA	<LOD				NA	NA	7.3	<LOD	14	3.2
α-TBCO	<LOD				30	13	55	18	<LOD				NA	NA	<LOD			
BEH-TEBP	1867	459	2588	996	7.1	4.6	10	2.3	NA				NA	NA	NA			
EH-TBB	86	10	164	63		<LOD			NA				NA	NA	NA			
TBP-AE	<LOD					<LOD			<LOD				NA	NA	0.1	<LOD	0.2	0.1
TBP-DBPE	<LOD					<LOD			<LOD				NA	NA	5.5	<LOD	6.8	1.3
syn-DDC-CO	356	65	668	246	1.1	0.3	2.1	0.6	6.2	3.9	8.6	1.6	NA	NA	82	3.8	241	65
anti-DDC-CO	349	72	531	199	1.1	0.5	1.6	0.5	9.6	5.9	17	3.5	NA	NA	130	4.3	329	93
DPMA	<LOD					<LOD			2.1	2.0	2.2	0.1	NA	NA	4.9	<LOD	5.7	0.9
α-DBE-DBCH	48	29	65	15	0.3	0.2	0.5	0.1	1.1	<LOD	1.7	0.5	NA	NA	0.4	0.1	1.4	0.4
β-DBE-DBCH	31	17	46	12		<LOD			1.3	<LOD			NA	NA	0.3	<LOD	0.9	0.2

	Air (pg/m³)				Water (pg/L)				Sediment (individual samples) pg/g dw				Bulk st. 1	St. 3	Amphipods (pg/g ww)			
PBDE28	<LOD				<LOD				34	15	62	15	<LOD	<LOD	<LOD			
PBDE47	234	74	318	113	1.6	0.9	2.5	0.7	4529	2070	6460	1522	1910	<LOD	38.9	<LOD	70	16
PBDE66	<LOD				<LOD				117	34.3	271	81	BDE-49; <LOD	BDE-49; <LOD	<LOD			
PBDE85	<LOD				<LOD				106	<LOD			BDE-126; <LOD	BDE-126; <LOD	<LOD			
PBDE99	295	88	439	150	1.3	0.7	1.7	0.4	5555	2750	11200	2699	1840	<LOD	30	<LOD	47	12
PBDE100	96	<LOD	106		<LOD				1028	404	2120	535	330	<LOD	14	<LOD	14	1
PBDE153	<LOD				<LOD				357	<LOD			<LOD	<LOD	<LOD			
PBDE154	<LOD				<LOD				332	114	930	254	120	<LOD	<LOD			
BDE-183	NA				NA				NA				<LOD	<LOD	NA			
BDE-196	NA				NA				NA				1730	<LOD	NA			
BDE-209	NA				NA				NA				<LOD	<LOD	NA			
ΣPBDEs	593	162	835	306	2.9	1.6	4.1	1.0	11969	5520	21000	5115	5930	<LOD	35	<LOD	132	41

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

Amphipods

Syn- and *anti*-DDC-CO dominated in the amphipods and contributed on average 61% of the total concentration of the analysed compounds that were above LOD in the samples (Figure 2). The PBDE concentrations were below LOD in one of the samples from station 1 and in all three samples from station 3, where also the PBDE concentration in sediment was <LOD. For the other samples, BDE-47, -99 and -100 were the predominant congeners and they contributed 5-26% to the sum of the compounds above LOD analysed in the amphipods (Figure 2). The amphipods were analysed without cleaning the gut and hence, the samples may reflect the contaminant distribution within the sediment from the respective sampling spots. For concentrations and detailed information about the samples, see Table 2 and A4. To our knowledge, nBFRs have not been analysed in Arctic benthic fauna and PBDEs have not been analysed in Arctic littoral amphipods before.

3.1.3. Sediment

PBDEs dominated extensively among the analysed compounds analysed in the sediment samples, followed by *syn-* and *anti*-DDC-CO (Figure 2). The predominant BDE congeners were BDE-47 and -99, with concentrations (bulk sample) of 1910 and 1840 pg/g dw, respectively. The next highest concentration was found for BDE-196 (1730 pg/g dw in the bulk sample; Table 2). Concentrations in the individual samples from station 1 was in the same concentration range (Table 2).

3.2. Potential for bioaccumulation

The lighter nBFRs with a predicted potential for bioaccumulation within the Arctic (HBBz, PBEB and PBT) were all detected in the amphipods although PBT was the only one of these compounds >LOD in the dissolved water phase. PBT showed the highest log BAF value among the compounds analysed in the present study (9.6). For comparison, log BAF was estimated to be 8.3 for BDE-47 and 8.2 for BDE-99 in the present study. This indicates that the uptake/degradation of BDE-47 and -99 at low-medium trophic levels are similar and not impacted to any large extent by e.g. biological degradation. Due to the molecular structure and physical-chemical properties of PBEB and HBBz, there is reason to believe that their BAFs would be cause for concern with regards to bioaccumulation (Harju et al., 2009).

380 Although *syn-* and *anti-*DDC-CO are larger molecules than BDE-47 and -99, they showed high

381 log BAFs in the present study; 8.9 and 9.1, respectively. There are a few studies of these

382 compounds in the Arctic with different results regarding detected/non-detected concentrations

383 in biota and it is difficult to draw any conclusions on the bioavailability, bioaccumulation and

384 biomagnification, as concluded elsewhere (AMAP, 2017; Vorkamp et al., 2015)   The

385 knowledge gaps on uptake and transformation processes need to be further investigated before

386 we can conclude on the bioaccumulation potential of DDC-COs.

387

388 Bioaccumulation calculations are sensitive to the sampling season since lipid content of the

389 organisms impact the calculations, and lipid content of Arctic and high-latitude organisms can

390 vary considerably throughout the year (Carlsson et al., 2016; Nygård et al., 2010; Varpe, 2017).

391 Seasonality, including lipid dynamics also impacts bioaccumulation in pelagic food webs

392 (Hallanger et al., 2011). This impact of seasonality was smaller in a benthic food web in

393 Kongsfjorden compared to the pelagic food web, and this feature may also be valid for

394 Adventfjorden (Evenset et al., 2016). The log BSAF and log BAF values in the present study

395 (Table 3) should be evaluated with age, lipid dynamics and seasonality in mind, especially since

396 the transport pathways of nBFRs and DDC-COs are much less known compared to legacy POPs

397 such as PCBs. Log BAF increased with increasing K_{ow} and compounds with similar K_{ow}

398 showed similar log BAF values (Figure A1).

399

400

401 **Table 3.** Log BAF and log BSAF calculated from concentration data in amphipods, passive water samplers and

402 sediment in the present study[a]. The table also illustrates the differences in BSAF values between an average of the

403 individual sediment samples and the results from the bulk sample analysis.

	Log BAF			Log BSAF[a]			
% lipids in amphipods:	15%	10%	5%	15%	10%	5%	**Log Kow**
PBBz	7,2	7,4	7,7				5,4
PBEB				0,8	1,0	1,3	6,8
PBT	9,4	9,6	9,9				
α-DBE-DBCH	7,0	7,1	7,4	0,7	0,9	1,2	5,5
β-DBE-DBCH				0,6	0,8	1,1	5,5
syn-**DDC-CO**	8,7	8,9	9,2	2,3	2,5	2,8	9,3
anti-**DDC-CO**	8,9	9,1	9,4	2,3	2,5	2,8	9,3
DPMA				1,6	1,7	2,0	8,0
BDE-47	8,2	8,4	8,7	-0,9	-0,7	-0,4	6,8
BDE-99	8,2	8,4	8,7	-1,1	-0,9	-0,6	7,4
BDE-100				-0,7	-0,5	-0,2	7,1

Composite sediment sample				
BDE-47	-0,5	-0,3	-0,03	6,8
BDE-99	-0,6	-0,4	-0,1	7,4
BDE-100	-0,2	-0,01	0,3	7,1

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

405 [a] The TOC content in the sediment samples was 2.3% and the total carbon (TC) was 5.0%.

406

407

408 ### 3.3.   Potential local sources

409 ### 3.3.1. Polybrominated diphenyl ethers (PBDEs)

410 The concentrations of BDE-47 and -99 in air at Longyearbyen, obtained from the passive air

411 samplers in this study, were two to three orders of magnitude higher than those measured at

412 Zeppelin Observatory, using active high-volume air samplers, during the same time period

413 (March-May 2015, Table A7) (Aas and Bohlin-Nizzetto, 2017). These results suggest that

414 PBDEs in Adventfjorden harbour area might come from local sources and not solely from long-

415 range transport (Ruus et al., 2014). Nevertheless, the PBDEs were not the predominant FRs in

416 the air, water and biota samples, but they did predominate the sediment samples. This feature

417 could be due to the longer historical usage of PBDEs, the affinity of PBDEs for sediment

418 particles, and a high content of coal particles in the sediment. The coal is present due to the

419 geology of the area, but mostly as a consequence of the coal storage along the shoreline close

420 to the sampling area (few 100 metres away). However, several of the nBFRs are similar enough

421 in their structure to PBDEs that they also would be associated with the coal particles, but the

422 concentration of ∑nBFRs in the sediment was around a factor 200 lower compared to the

423 ∑PBDEs in the bulk sediment sample.

424

425 The concentrations of the PBDEs in the sediment samples from the present study are two orders

426 of magnitude higher than those at remote areas in Bering Sea, Chukchi Sea and the Canada

427 Basin where the BDE-47 and -99 ranged between <LOD-75.6 pg/g dw (Cai et al., 2012).

428 ∑PBDE in lake sediments from earlier studies (sampled 2004-06) on Svalbard were 2-470 times

429 lower than the present study (Table 2), ranging from 25.5 pg/g dw in Kongressvatnet, close to

430 Barentsburg in Grønnfjorden and up to 2383 pg/g dw in Åsövatnet on the north-west part of

431 Spitsbergen (Christensen and Evenset, 2008). Åsövatnet is impacted by bird guano input.

432 However, bird guano is not a likely explanation for explaining the high concentrations in the

433 present study. Instead the close distance between sampling site and a harbour is more likely to

434 be of importance. There is reason to believe that the higher concentrations measured in the

present sediment samples are caused by local sources, most likely more influenced by harbour activities and other activities happening on land close to the sampling area. The local sewage outlet was not a source as effluents are released into a different water mass than the one sampled.

Compared to PBDE concentrations in harbour sediment from the 75 000 people city Tromsø in Northern Norway (ΣPBDE: 130 pg/g dw), the sediment sample concentrations from this study were one order of magnitude higher (Fjeld et al., 2004). The concentration and relative distribution pattern of PBDEs in the sediment samples from Longyearbyen were similar to the distribution pattern of those PBDE congeners around Lillehammer (28 000 inhabitants), Lake Mjøsa, where there have been point sources (Fjeld et al., 2004). Only congeners analysed at both sites were considered in this comparison (BDE-28, -47, -99, -100, -153, -154 and -183) and the total PBDE concentrations (excluding BDE-209) in Lake Mjøsa sediments were 14 050-16 480 pg/g dw. BDE-99 contributed to 47% in Longyearbyen sediment and 49-51% in the Lillehammer sediment while BDE-47 had a slightly higher relative contribution in Longyearbyen sediment of 38% compared to 26-28% in Lillehammer (Fjeld et al., 2004). The higher relative contribution of BDE-47 in Longyearbyen might be caused by long-range transport, but the concentration in the present study are too high to be explained only by long-range transport. A recent study of BDE-209 in sediments in Kongsfjorden, Svalbard showed elevated concentrations outside the Ny-Ålesund harbour there compared to stations further out in the fjord (230 and 100 pg/g dw, respectively) (Ma et al., 2015). Ny-Ålesund also receives several cruise ships during the summer time, which could contribute to elevated concentrations of BFRs around harbours on Svalbard. However, earlier studies (Evenset et al., 2009) as well as the one sample from a local beach in the present study did not show high concentrations within Adventfjorden. The concentrations differences between the samples from the local harbour in the present study, and the samples further out in Adventfjorden, are either a result of a very local "hot-spot" sampled in the present study, or dilution/high sedimentation rates in the fjord that causes low PBDE concentrations there. There is reason to believe that the PBDE in the sediment samples in the present study came from a local "hot spot", although it might be difficult to identify the source or to re-localise due to sedimentation in the fjord and harbour area. This is further supported by the results from station 3 (PBDEs <LOD). Taken together, the results in the present study means that it cannot be out-ruled that some of the PBDE in the environment comes from local sources.

3.3.2. Hexabromobenzene (HBBz)

470   HBBz was detected in two of the sediment and three of the amphipod samples although at low

471   concentrations (Table 2 and A4). It was not detected in the water nor the air samples even

472   though recent studies in the same area showed the presence of HBBz (median 0.12 pg/m^3)in

473   the atmospheric particle phase (Salamova et al., 2014). Samples from Ny-Ålesund (gas phase;

474   <LOD-0.67 pg/m^3) were in the same concentration range (AMAP, 2017; Lee et al., 2016).

475   However, the LODs in that study were lower than in the present study. HBBz was not detected

476   in previous studies from Svalbard in liver in biota at medium-high trophic levels such as in

477   kittiwakes, Arctic foxes and ringed seals (Sagerup et al., 2010). The overall few samples -

478   including amphipods- where HBBz was detected in the present study, in combination with

479   similar concentrations at remote areas on Svalbard suggests that the source might not be of local

480   origin. HBBz is a fairly small and volatile compound that can undergo long-range transport

481   (AMAP, 2017; de Wit et al., 2010) Nevertheless, diffuse run-off from local sources cannot be

482   ruled out due to the findings close to the settlement in the present study.

483

484

485   3.3.3. *Syn-* and *anti-*dechlorane plus

486   *Syn-* and *anti-*DDC-CO were detected in all matrices in the study. The average concentrations

487   in the sediment samples (6.2 and 9.6 pg/g dw of *syn-*DDC-CO and *anti-*DDC-CO, respectively)

488   were lower than sediments from the Great Lakes (total DDC-CO concentration ranging between

489   330-26000 pg/g dw) but similar to sediment from Kongsfjorden at Svalbard (1.4 and 4.5 pg/g

490   dw of *syn-*DDC-CO and *anti-*DDC-CO, respectively) (Ma et al., 2015; Shen et al., 2010; Sverko

491   et al., 2011).

492

493   The relationship between *syn-* and *anti-*DDC-CO can be expressed as f_{anti}, which is the fraction

494   of *anti-* compared to the sum of *syn-* and *anti-*DDC-CO. The technical DDC-CO mixture has

495   an f_{anti} of 0.75. The f_{anti}-DDC-CO in air (0.5) and water (0.5) in the present study could indicate

496   that these samples are closer to a source than earlier samples from East Greenland Sea (f_{anti} of

497   0.33), which is also supported by the higher dissolved concentrations reported in the present

498   study (Table A7) (Möller et al., 2010). The *syn-*DDC-CO isomer is suggested to be more

499   persistent to e.g. photodegradation in air compared to the *anti-*DDC-CO, although it might be

500   affected by biodegradation in the sediment and water (Möller et al., 2010; Sverko et al., 2011).

501   Hence, a lowered fraction of *anti-*DDC-CO compared to the technical mixture can indicate

502   long-range transported of DDC-COs, which is the case in both Möller et al (2010) and in the

503   present study. Hence, local sources of DDC-COs cannot be excluded as explanation for the

504   presence of DDC-COs in the present study. Both the sediment and amphipod samples in the

505   present study had an average f_{anti} of 0.6 which indicates that there is little selective

506   biotransformation of DDC-COs in the amphipods though, and that sediment poses a larger

507   exposure to the amphipods than water with regards to uptake. Another recent study from

508   Kongsfjorden showed higher concentrations in the sediment; average of 270 and 73 pg/g dw of

509   *syn*-DDC-CO and *anti*-DDC-CO, respectively (Na et al., 2015). Ma et al. (2015) suggest that

510   the detection of DDC-CO in sediment from Kongsfjorden can be caused by transport by water

511   currents from the Fram Strait. However, the highest concentrations measured in Kongsfjorden

512   coincided with the ship route. Thus, contamination from ships could be a plausible explanation

513   for detection of DDC-CO in sediment from Ny-Ålesund as well as from the Longyearbyen

514   sediment samples. The general lack of data, analytical uncertainty between laboratories on these

515   relatively little analysed compounds and lack of TOC data should also be taken into account

516   when data are being compared.

517

518   The similar fraction measured in both air and water could indicate that there is an interaction

519   between these phases where any degradation in one of the phases quickly reaches the other

520   phase, or, the slightly lower f_{anti} ratio in air could also be interpreted as a result of

521   photodegradation in air and a slow delivery of *syn*-DDC-CO from air to water. However, there

522   is very little research on isomer selective photo- and biodegradation of DDC-COs, and other,

523   e.g. microorganisms in the water column might degrade one or both of the DDC-COs.

524   Stereoselective degradation is an important process for the fate of chiral environmental

525   pollutants (Carlsson, 2013; Kallenborn and Hühnerfuss, 2001) and this process may be of high

526   interest for further elucidation of the environmental fate of the chiral *syn*- and *anti*-DDC-CO.

527

528   3.3.4. Pentabromotoluene (PBT) and pentabromoethylbenzene (PBEB)

529   PBT and PBEB are considered as single/multiple hoppers in the atmosphere, meaning that they

530   have the potential to undergo long-range transport Nevertheless, a local contribution from

531   Longyearbyen cannot be excluded due to higher atmospheric concentrations in Longyearbyen

532   (PBEB: <LOD-16 pg/m^3, PBT: <LOD-61 pg/m^3) compared to e.g. the East Greenland Sea

533   (PBT; 0.001-0.02 pg/m^3) (Möller et al., 2011). This conclusion is somewhat hampered by the

534   usage of passive air samplers that have an uncertain uptake/accumulation of less volatile

535   compounds.

536

4. Conclusions

Passive sampling with silicone rubbers is a practical sampling technique for gaseous air and dissolved water fractions of PBDEs, nBFRs and DDC-COs in cold and remote climate where electricity driven sampling is not always feasible. The sampling campaign represents several months and thus shows the concentrations over time instead of a snapshot as with active sampling. In addition to the PBDEs, there is also a bioaccumulation potential for PBT, PBBz, *syn*- and *anti*-DDC-CO, and maybe also for α-DBE-DBCH, BEH-TEBP, HBBz and PBEB, although more data is needed before firm conclusions can be drawn. Many of the nBFRs were present in the sediment and also in the amphipods although not always above the detection limits in the water, which indicates that sediment is an important exposure pathway. Nevertheless, there is very little information available on nBFRs in water and in animals at low to medium trophic levels, and the present study is the first to report nBFRs and DDC-COs in Arctic benthic fauna. This paper contributes to a better understanding of bioaccumulation potentials of nBFRs and DDC-COs in the Arctic benthic ecosystem.

5. Acknowledgement

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1 **Appendix; New brominated flame retardants and dechlorane plus in the**

2 **Arctic: local sources and bioaccumulation potential in marine benthos**

3

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17 **Table A1.** CAS number and m/z used.

Compound	CAS number	Quantitative mass	Qualitative mass
PBDEs			
BDE 28	41318-75-6	405.8027	407.8007
BDE 47	5436-43-1	485.7112	483.7132
BDE 66	189084-61-5		
recovery STD, ^{13}C-BDE-77		497.7513	495.7533
BDE 100	189084-64-8	563.6216	565.6197
BDE 99	60348-60-9	563.6216	565.6197
BDE 85	182346-21-0		
BDE 154	207122-15-4	643.5302	641.5322
BDE 153	68631-49-2	643.5302	641.5322
BDE 183	207122-16-5	721.4407	723.4387
recovery STD, ^{13}C-BDE-138		655.5703	653.5723
nBFRs and DDC-COs			
TBP-AE (ATE)	3278-89-5	369.8027	371.8027
α- DBE-DBCH	3322-93-8	266.9207	268.9187
β- DBE-DBCH	3322-93-8	266.9207	268.9188

p-TBX	23488-38-2	340.7999	342.7979
BATE	Not available	329.7714	331.7693
β-TBCO	3194-57-8	266.9207	268.9187
PBBz	608-90-2	471.5954	473.5934
TBCT	39569-21-6	441.6614	443.6593
α-TBCO	3194-57-8	266.9207	268.9187
DPMA	Not available	344.9353	379.9041
PBT	87-83-2	485.6111	487.6090
PBEB	85-22-3	499.6266	501.6247
TBP-DPBE (DPTE)	35109-60-5	531.6353	529.6372
HBBz	87-82-1	551.5038	549.5059
HCDBCO	51936-55-1	476.6983	474.7003
recovery STD, ^{13}C-BDE-77		497.7513	495.7533
EH-TBB	183658-27-7	420.6720	418.6740
BTBPE	37853-59-1	358.7928	356.7984
syn-DDC-CO	13560-89-9	271.8102	273.8072
anti-DDC-CO	13560-89-9	271.8103	273.8073

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20 **Table A2.** Internal standards used.

Internal standards	Amount added [ng]
^{13}C PBDEs; 28,47,99,100,153,154,183	1
^{13}C HBB, PBBz, *syn*-DDC-CO and *anti*-DDC-CO, DBDPE, BTBPE	1
PCB-4, -29, -185	10

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Clean-up of samples

Silica-clean-up of all sample matrices

26 All samples were further cleaned using silica columns (5 g activated silica gel and 1 g of sodium

27 sulphate) that were conditioned with 20 mL of diethylether (DEE): acetone (9:1; v:v) before the

28 samples were quantitatively transferred and eluted with 40 mL of DEE:acetone (9:1; v:v). The

29 samples were evaporated to ~2 mL and transferred to hexane before a final evaporation to ~1 mL

30 followed by evaporation under nitrogen.

Gel permeation chromatography (GPC) clean-up of biota and sediment samples

To further clean the sediment and biota samples, these samples were cleaned with gel permeation chromatography (GPC). The column was Bio Beads S-X3 200-400 mesh (Tessek Ltd., Czech Republic) and the mobile phase was chloroform. The extract was evaporated under nitrogen to ~0.5 mL before solvent change to n-hexane and again evaporated down to ~0.5 mL before transfer to GC-vials. Because precipitate occurred in the sediment samples when n-hexane was added, the precipitates were removed by filtration through a glass column with a glass wool plug and a PTFE frit. The extracts were eluted with 20 mL of hexane, evaporated under nitrogen to ~0.5 mL and transferred to GC-vials.

Additional clean-up steps of biota and sediment samples

The biota and sediment extracts were split in two aliquots after the GPC clean-up; 70% and 30% before an additional silica column clean-up (5 g activated silica gel, 44% sulfuric acid and 1 g of sodium sulphate). The first fraction of each aliquot was eluted with n-hexane:DCM and evaporated before analyses.For sediment, this fraction was also cleaned with copper powder to remove any sulphur present ^{13}C-BDE-77 (PBDEs, nBFRs, DDC-COs) and ^{13}C-BDE-138 (PBDEs) was added as recovery internal standards.

Sediment clean-up and analysis procedure at NIVA

IS was added (18 ng of BDE-119 and -181, and 50 ng of ^{13}C-BDE 209) to 1 g of dried sediment before two extractions with 20 mL and 10 mL DCM for one hour in ultra-sonic bath. The extracts were combined and evaporated down to 2 mL before clean-up with 4 mL of concentrated H_2SO_4. The extracts were evaporated down to ~200 µL and transferred to vials before GC-MS analyses. Details, including temperature programme for PBDE analysis are described in Narváez Valderrama et al. (2016). Briefly, a Hewlett Packard 6890 Plus GC was connected to a Hewlett Packard 5973 MS, which was operated in negative chemical ionisation and single ion monitoring (SIM) mode for analysis of PBDE congeners. The GC was equipped with a DB-5MS (15 m long, 0.25 mm internal diameter and 0.10 µm film thickness) column and injections were done in splitless mode.

GC-MS analyses at RECETOX

PBDEs, nBFRs and DDC-COss

Analyses of PBDE, DDC-COs and nBFRs were performed with a high resolution GC (7890A GC, Agilent, USA) equipped with a 15 m × 0.25 mm × 0.10 µm RTX-1614 column (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ mode at the resolution of >10 000. For PBDEs, the injections were done in splitless mode (2 µL) at 280 °C, with He as carrier gas at 1 mL/min flow. The GC temperature programme was 80 °C (1 min hold),

65   then 20 °C/ min to 250 °C, followed by 1.5 °C/min to 260 °C (2 min hold) and 25 °C/min to 320 °C

66   (4.5 min) hold. For the nBFRs and the DDC-COs, 3 μL were injected in splitless mode (250 °C) with

67   He as carrier gas, and the following GC temperature programme was used: 80 °C (1 min hold), then

68   20 °C/min to 250 °C, followed by 1.5 °C/min to 260 °C (2 min hold), and 25 °C/min to 320 °C (4.5

69   min hold). The method for these compounds is described in Vernier et al. (2016).

70   ## Performance reference compounds (PRCs)

71   PRCs (PCBs and deuterated biphenyls) were analysed in the SRs using GC-MS/MS 6890N GC

72   (Agilent, USA) equipped with a 60 m x 0.25 mm × 0.25μm DB5-MS column (Agilent J&W, USA)

73   coupled to Quattro Micro GC MS (Waters, Micromass, UK) operated in EI+ mode. At least two

74   MRM transitions were recorded for each compound analysed. One μL of extract was injected in

75   splitless mode at 280°C. Helium was used as carrier gas at the flow of 1.5 ml min^{-1}. The GC

76   temperature programme started at 80°C (1 min hold), 15°C min^{-1} to 180°C, and finally 5°C min^{-1} to

77   300°C (5 min hold).

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79   ## Recoveries

80   The average recoveries (at RECETOX) of PBDEs varied between 52-165% for amphipods, 42-147%

81   for sediment and 70-121% for the passive air and water samples. The recoveries for nBFRs and DDC-

82   COs (BTBPE, *syn-* and *anti*-DDC-CO, PBBz and HBBz) varied between 32-85% (amphipods), 19-

83   33% for the sediment samples and 102-129% (passive samplers).

84   **Table A3.** Physical- chemical properties, full names and abbreviations of the analysed compounds.

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

Bis(2-ethylhexyl)tetrabromophthalate (former BEHTBP, now BEH-TEBP)	0.0016 (2)	706,14	9,34	11.7 (8)
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	0.2 (3)	687,64	9,15	11.7 (8)
Decabromodiphenylethane (DBDPE)	0.00072 (6)	971,23	10,50	11.7 (8)
Pentabromotoluene (PBT)	0.000935 (3)	486,62	6,99	8.95 (8)
Pentabromoethylbenzene (PBEB)	0.035 (2)	500,65	6,76	8.83 (8)
Bromoallyl 2,4,6-tribromophenyl ether (BATE)	No info	334,83	6,00	No info
2,3-dibromopropyl 2,4,6-tribromophenyl ether (TBP-DBPE, former DPTE)	0.0883 (7)	530,67	6,30	9.82 (8)
Hexachlorocyclopentenyl-dibromcyclooctane (HCDBCO)	0.0161 (8)	540,76	7,62	11.7 (8)
Allyl 2,4,6-tribromfenyl ether (TBP-AE, former ATE)	3.42 (8)	370,86	5,00	7.82 (8)
Tris(2,3-dibrompropyl)isocyanurate (T23BPIC)	19.96 (8)	728,69	4,45	11.7 (8)
3,4,5,6-Tetrabromo-2-chlorotoluene (TBCT)	0.22 (8)	442,17	5,70	8.21 (8)
Pentabromobenzyl acrylate (PBBA)	No info	556,67	6,00	No info
α-1,2,5,6-Tetrabromocyclooctane (α-TBCO)	2.56 (8)	427,80	5,28	8.42 (8)
β-1,2,5,6-Tetrabromocyclooctane (β-TBCO),	2.56 (8)	427,80	5,28	8.42 (8)
α-Tetrabromoethylcyclohexane (α-DBE-DBCH, former TBECH)	2.63 (8)	427,80	5,50	8.42 (8)

β-Tetrabromoethylcyclohexane (β-DBE-DBCH, former TBECH)	2.63 (8)	427,80	5,50	8.42 (8)
Pentabromoethylbenzene (PBEB)	0.24 (8)	500,64	6,76	8.83 (8)

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89   **Table A4.** Detection frequency of compounds in sampled matrices. LODs are presented in Table 2. Sample
90   concentration ranges are presented in Table A4. Only compounds >LOD in at least one of the samples analysed
91   in the study are presented here. Those BFRs not listed here were not detected in any of the samples analysed.

	Sediment	**Amphipods**	**Water**	**Air**
PBBz	0 %	33 %	67 %	0 %
BTBPE	0 %	22 %	0 %	0 %
HBBz	0 %	78 %	0 %	0 %
PBEB	50 %	78 %	0 %	33 %
pTBX	13 %	0 %	0 %	0 %
PBT	0 %	78 %	67 %	33 %
α-TBCO	0 %	0 %	100 %	0 %
α-DBE-DBCH	50 %	100 %	100 %	100 %
BEH-TEBP	0 %	56 %	100 %	100 %
EH-TBB	0 %	44 %	0 %	100 %
TBP-AE	0 %	44 %	0 %	0 %
TBP-DBPE	0 %	22 %	0 %	0 %
syn-DDC-CO	100 %	100 %	100 %	100 %
anti-DDC-CO	75 %	100 %	100 %	100 %
DPMA	25 %	22 %	0 %	0 %
β-DBE-DBCH	63 %	89 %	100 %	100 %
PBDE28	100 %	0 %	0 %	0 %
PBDE47	100 %	56 %	100 %	10 %
PBDE66	100 %	0 %	0 %	0 %
PBDE85	63 %	0 %	0 %	0 %
PBDE99	100 %	33 %	100 %	100 %
PBDE100	100 %	22 %	0 %	67 %
PBDE153	88 %	0 %	0 %	0 %
PBDE154	100 %	0 %	0 %	0 %

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94   **Table A5.** Limit of detection (LODs) for nBFRs, DDC-COs and PBDEs for all matrices analysed in this study.

	Amphipods	**Sediment**	**Water**[a]	**Air**	**Air**[b]
Units	pg/g ww	pg/g dw	pg/L	pg/m3	pg/g sampler
Anti-DDC-CO	4	2	0.3	0.03	
Syn-DDC-CO	1	1	0.4	0.03	
TBP-AE	0.1	0.03	0.01		0.02
BATE	0.1	0.1	0.01		0.04

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BEH-TEBP	3	2	0.4	0.1	
BTBPE	0.4	0.3	0.1		0.1
DPMA	0.3	0.2	0.03		0.1
TBP-DPBE	4	2	0.4		1
EH-TBB	2	1	0.2		0.6
HBBz	2	1	2		0.7
HCDBCO	0.3	0.2	0.03		0.1
PBBA	1	1	0.2		0.4
PBBz	2	1	0.03	0.05	
PBEB	0.1	0.04	0.01	0.0001	
PBT	3	2	0.3	0.01	
pTBX	0.04	0.03	0.004		0.01
T23BPIC	3	2			0.8
TBCT	0.2	0.1	0.02		0.1
α-TBCO	0.4	0.2	0.04		0.1
α-DBE-DBCH	0.03	0.02	0.003	0.01	0.01
β-TBCO	0.8	0.5	0.1		0.2
β-DBE-DBCH	0.1	0.1	0.01	0.001	0.04
PBDE28	4	1	0.03		1
PBDE47	8	5	0.2	0.01	
PBDE49		0.1			
PBDE66	18	3			1
PBDE85	21	8	0.2		3
PBDE99	7	4	0.1	0.01	
PBDE100	2	1	0.2	0.01	
PBDE153	69	7	0.1		2
PBDE154	37	2	0.1		1
PBDE183	21	29	3		21
PBDE196		0.3			
PBDE209		50			

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

[b] For compounds not present in the air samples, a LOD based on pg/g sampler is provided instead of as pg/m^3.

[c] NA: Not analysed.

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

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102 **Table A6.** Average concentrations detected in blanks.

air and water pg/g sampler				amphipods pg/g ww	sediment pg/g dw
TBP-AE	ND	β-DBE-DBCH	0.4	PBBz	0.9	0.6
TBP-DPBE	ND	PBDE28	0.2	HBBz	1.1	0.7
BATE	ND	PBDE47	0.7	PBT	3.0	2.0
DPMA	ND	PBDE99	0.5	*Syn*-DDC-CO	1.0	0.6
T23BPIC	ND	PBDE100	0.8	*Anti*-DDC-CO	1.9	1.2
TBCT	ND	PBDE66	ND	PBDE47	8.3	5.4
HCDBCO	ND	PBDE85	ND	PBDE99	6.5	4.2
α-TBCO	ND	PBDE153	ND	PBDE100	2.1	1.3
EH-TBB	ND	PBDE154	ND	BTBPE	ND	ND
PBBA	ND	PBDE183	ND	PBEB	ND	ND
β-TBCO	ND			pTBX	ND	ND
BTBPE	ND			α-TBCO	ND	ND
PBEB	ND			α-DBE-DBCH	ND	ND
pTBX	ND			BEH-TEBP	ND	ND
PBBz	4.1			EH-TBB	ND	ND
HBBz	4.9			TBP-AE	ND	ND
PBT	1.3			TBP-DPBE	ND	ND
α-DBE-DBCH	0.6			DPMA	ND	ND
BEH-TEBP	2.7			β-DBE-DBCH	ND	ND
Syn-DDC-CO	1.2			PBDE28	ND	ND
Anti-DDC-CO	1.4			PBDE66	ND	ND
				PBDE85	ND	ND
				PBDE153	ND	ND
				PBDE154	ND	ND

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108 **Table A7.**
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110 Concentration range of PBDEs and DDC-COs in Arctic air (pg/m^3 for gas and particulate phase) and

111 water (pg/L) from recent studies.

Area	∑PBDE in air (pg/m^3)	∑PBDE in water (pg/L)	*Syn*-DDC-CO in air (pg/m^3)	*Syn*-DDC-CO in water (pg/L)	*Anti*-DDC-CO in air (pg/m^3)	*Anti*-DDC-CO in water (pg/L)
Villum station, Greenland[1]	0.2-6.26 (gas + particles)*					
East Greenland Sea[2]	0.06-1.6 (gas)	0.03-0.64	0.29 (gas), 0.47 (particles)	0.04	0.09 (gas), 0.04 (particles)	0.02

10

Nuuk[3]	0.14-3.26 (gas + particles)[*]					
Svalbard, Ny-Ålesund[4]	5.3 (gas, passive air sampler)					
Svalbard, Ny-Ålesund, Zeppelin[¤,5]	ΣPBDE: 0.13-13.9, BDE-47: 0.04 -7.32, BDE-99: 0.01 - 0.19, BDE-100: 0.00 - 0.13 gas+particles).					
Present study	ΣPBDE: 593 (BDE-47: 234, BDE-99: 295) (gas, passive air sampler)	2.9	356 (gas, passive sampler)	1.5	349 (gas, passive sampler)	1.1

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

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

References: [1]Bossi et al. (2016); [2]Möller et al. (2010, 2011), [3]Bossi et al., (2008), [4]Pozo et al., (2006), [5]Aas and Bohlin-Nizzetto, (2017)
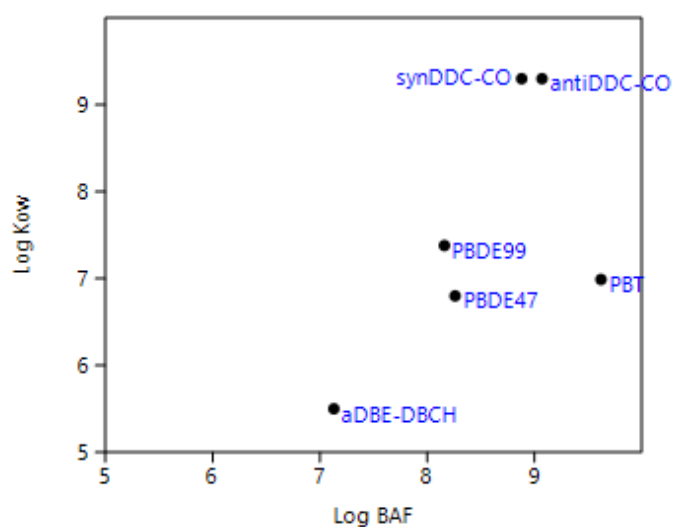
Figure A1. Log BAF based on 10% lipid content in the amphipods (listed in Table 2) versus log K_{ow} (listed in Table S3) for compounds detected both in water and in amphipods in the present study.

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Organophosphorous flame retardants (OPFRs)

The clean-up method was the same as for the nBFR and PBDE analyses of the silicone rubbers. The analytical method at RECETOX was as follows: the samples were analysed with a GC-MS/MS using a 6890N GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 μm Rxi 5Sil MS column (RESTEK) coupled to a Quattro Micro GC tandem mass spectrometer (Waters, Micromass, UK). The MS was operated in (EI+) using two MRM transitions for each compound. Injection was done in splitless mode with 2 μL at 250°C, and He as carrier gas at 1.4 mL min-1. The GC temperature program was 80°C (1 min hold), then 40°C min-1 to 230°C (5 min hold), followed by 5°C min-1 to 300°C and 20°C min-1 to 320°C (6 min hold).

Table A8. Average concentrations (ng/g sampler) of OPFRs in Longyearbyen air and water, including the blanks. Due to little information on K_{pw} in cold temperatures, the data is presented on a sampler basis and not as concentrations per volume. LOD is set as for the FRs; average blank concentration +3*std deviation of the blanks when a compound is present in the blanks.

Compound	Abbreviation	Blk 2015	Ref 2015	Ref 2016	Blk 2016	Lyb air 2015	Lyb air-I 2016	Lyb air-II 2016	Lyb water 2015	Lyb water-I 2016	Lyb water-II 2016
Tri-n-propylphosphate	TPrP					<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Triisobutylphosphate	TiBP	1 886	4 527	6 779	2 607	44 539	<LOD	<LOD	<LOD	<LOD	<LOD
Tri-butylphosphate	TnBP	8 158	6 021	6 522	14 720	76 555	<LOD	<LOD	71 410	<LOD	<LOD
Tris(2-chloroethyl)-phosphate	TCEP					1 861	<LOD	<LOD	1 086	<LOD	<LOD
Tris(1-chloro-2-propyl)phosphate	TCPP	2 602	257	644	696	16 199	<LOD	20 715	<LOD	<LOD	<LOD
Dibutylphenyl-phosphate	DBPP					13 643	9 901	30 757	13 600	23 208	20 154
Tripentylphosphate	TPeP			322	295	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Butyldiphenyl-phosphate	BDPP					2 500	1 925	2 742	2 054	1 554	3 461
Tris(1,3-dichloro-2-propyl)phosphate	TDCPP	146		30		5 513	1 140	922	19 262	21 268	32 657
Tris(2-butoxyethyl)-phosphate	TBEP			55 765	103 100	55 145	9 520	<LOD	41 164	33 664	18 786
Triphenylphosphate	TPhP	231	89			15 931	1 719	2 070	3 609	<LOD	8 970
2-Ethylhexyldiphenyl-phosphate	EHDPP	205		64	118	14 866	<LOD	932	972	<LOD	<LOD
Tris(2-ethylhexyl)-phosphate	TEHP	90	178	76	105	2 782	1 192	828	861	<LOD	<LOD
Tri-o-tolylphosphate	ToTP					<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tri-m-tolylphosphate	TmTP					248	69	74	<LOD	39	82
Tri-p-tolylphosphate	TpTP					<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Tris(2-isopropylphenyl)-phosphate	TIPPP					1 793	55	102	54	25	30
Tris(3,5-dimethylphenyl)-phosphate	TDMPP					<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

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