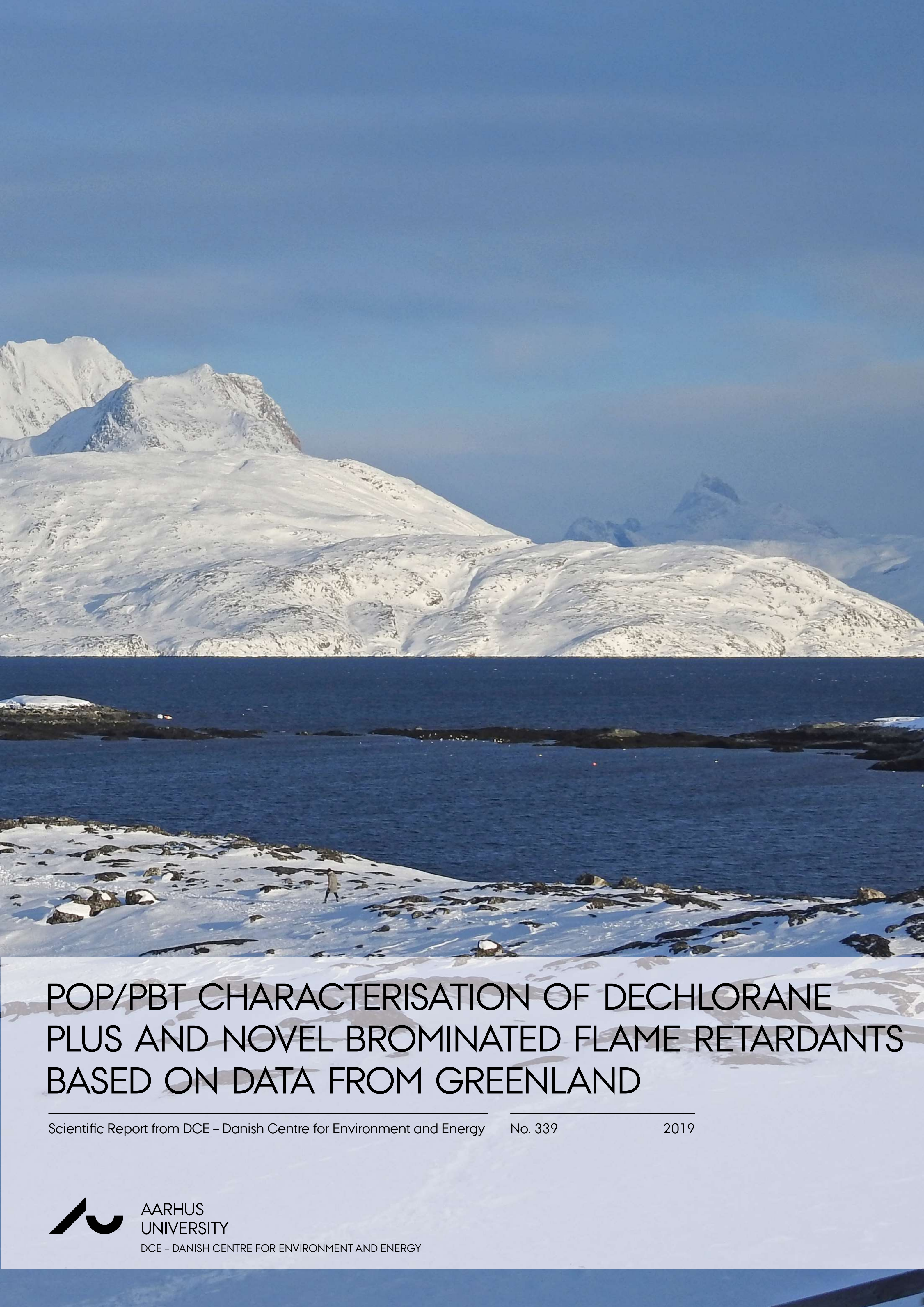

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Scientific Report from DCE – Danish Centre for Environment and Energy No. 339 2019

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Data sheet

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Abstract: Halogenated flame retardants (FRs) are used in inflammable petroleum-based polymers. Dechlorane plus (DP) and so-called novel brominated flame retardants (NBFRs), alluding to the ban of polybrominated diphenyl ethers (PBDEs), have been detected in air and biota of the Arctic. Assessments of whether or not a compound is a persistent organic pollutant (POP) or persistent/bioaccumulative/toxic (PBT), can include monitoring data. Therefore, chemical analyses of DP and NBFRs have been carried out in Arctic air, based on samples from Villum Research Station in Northeast Greenland, and high-trophic level animals from Greenland. In addition, PBT data have been compiled and reviewed, and mammalian toxicity has been addressed through databases and toxicogenomics. All compounds except 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) were detected in Arctic air. The values for DP and decabromodiphenylethane (DBDPE) were surprisingly high in some samples, which warrant verfication, as they might be affected by local sources or contamination. The concentrations in biota were generally low, with few exceptions, e.g. 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) in narwhal *(Monodon monoceros)*, BTBPE in killer whale *(Orcinus orca)* and DBDPE in Arctic char *(Salvelinus alpinus)*. All compounds except DP were found in landlocked Arctic char, suggesting atmospheric deposition as a pathway of contaminant exposure. The PBT review suggested persistence for all compounds of this study. Bioaccumulation was indicated for DP, DPTE and BTBPE and toxicity for all compounds except DP. However, the data availability is limited. Existing no-observed-adverse-effect-concentrations were much higher than concentrations measured in the Greenland environment. In summary, the new data indicate persistence and some degree of bioaccumulation in the Greenland environment, while biomagnification was not apparent from our data.

Keywords: Arctic; bioaccumulation; emerging contaminants; long-range transport; persistence; REACH; Stockholm Convention; toxicity

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Supplementary notes: There was no steering committee for this project.
The Danish Environmental Protection Agency and the Ministry of Environment and Food of Denmark had the opportunity to comment on a draft version of the report.
The following comments were received: a) two typing errors were pointed out; b) one acronym had not been defined; c) a map of the sampling locations should be added.

Contents

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1 Acknowledgements

This study was funded by the Danish Cooperation for Environment in the Arctic (DANCEA) of the Danish Environmental Protection Agency, grant number MST-112-00239, under the Ministry of Environment and Food of Denmark. The authors of this report are solely responsible for all results and conclusions presented in the report, which do not necessarily reflect the position of the Danish Environmental Protection Agency, the Ministry of Environment and Food of Denmark or the Greenland Government.

The air samples collected by high volume sampling at Villum Research Station in Northeast Greenland were made available from the AMAP Core air monitoring programme, also funded by DANCEA (project leader: Henrik Skov). The AMAP Core air programme collects air samples every week of which 13 samples from 2014 were provided for this study. The project group thanks all individuals assisting with the logistics and operation of Villum Research Station.

Some of the biota samples (Arctic char, glaucous gull and ringed seals) originated from the Environmental Specimen Bank of the AMAP Core Programme for biota. This programme has been in operation since 1994, also funded by DANCEA (project leader: Frank Rigét), and regularly collects biota samples from Central East and West Greenland as well as Northwest Greenland, for immediate analysis as well as specimen banking.

Additional samples of high trophic animals (narwhal, killer whale, hooded seal, harp seal, bearded seal, glaucous gull) were kindly provided by Rune Dietz and Christian Sonne. The samples originated from the projects UNEXPECTED, PREDATOR and NOW, details are given in chapter 6.1 of this report. The project group gratefully acknowledges this contribution to the project.

Stable isotopes of carbon and nitrogen in all biota samples were determined by Igor Eulaers, kindly providing valuable additional data for the interpretation of food chain accumulation. The project group would further like to thank Annegrete Ljungqvist, Birgit Groth and Christel Christoffersen for the skilful chemical analyses of the samples in the laboratory.

2 Sammenfatning

Flammehæmmere er brugt i brændbart materiale, såsom syntetiske polymerer, for at nedsætte risikoen for brand. Flammehæmmergruppen polybromerede diphenyl ethere (PBDE) er udfaset i dag, men er blevet erstattet af andre flammehæmmere, heriblandt muligvis det klorholdige dechloran plus (DP) og en gruppe af såkaldte nye bromerede flammehæmmere ("novel brominated flame retardants", NBFR). DP[1] og NBFR[2] er tidligere påvist i luft og biota i Arktis. Overvågningsdata fra Arktis kan indgå i en foreløbig vurdering af stoffernes potentielle egenskaber som sværtnedbrydelige organiske stoffer ("persistent organic pollutants", POPs) i forhold til Stockholm Konventionen eller som PBT-stoffer ("persistent, bioaccumulative, toxic") i forhold til kemikaliereguleringen REACH i den Europæiske Union.

På denne baggrund blev DP og NBFR analyseret i en række luftprøver fra Villum Research Station i Nordøstgrønland samt i prøver af grønlandske dyr, der er placeret højt i fødekæden. Eventuelle geografiske forskelle blev undersøgt vha. prøver af ringsæl *(Pusa hispida)* og gråmåge *(Larus hyperboreus)* fra forskellige lokaliteter i Grønland. Derudover er der analyseret prøver af fjeldørred *(Salvelinus alpinus)* fra en sø i Sydgrønland, der kun modtager kemikalier fra luften. I tillæg til de kemiske analyser blev der sammendraget PBT-data på DP og NBFR fra forskellige rapporter fra Europa, USA og Canada.

Alle stoffer på nær BTBPE (se fodnoter for stofnavne) blev påvist i luftprøverne fra Villum Research Station. Enkelte værdier for DP og DBDPE virkede dog usædvanlig høje og bør verificeres, da de muligvis er påvirket af lokale kilder eller kontaminering. Koncentrationerne i biotaprøver var generelt lave, dvs. betydeligt lavere end typiske POP-niveauer i de samme dyr, med enkelte undtagelser: EH-TBB i narhval *(Monodon monoceros)*, BTBPE i spækhugger *(Orcinus orca)* og DBDPE i fjeldørred kunne detekteres i koncentrationer, der var tættere på typiske POP-niveauer. Målinger fra forskellige lokaliteter tydede på højere koncentrationer af EH-TBB og DPTE i Øst- end i Nordvest-grønland, men pga. de lave niveauer var det svært at vurdere eventuelle geografiske mønstre. Alle stoffer med undtagelse af DP blev påvist i fjeldørred, hvilket tyder på atmosfærisk tilførsel.

PBT-vurderingen tydede på begrænset nedbrydelighed ("persistence") for alle stoffer, potentiale for bioakkumulering for DP, DPTE og BTBPE og toksicitet for alle stoffer, på nær DP. Datamaterialet var dog begrænset, og flere undersøgelser var årtier gamle. Det Europæiske Kemikalieagentur (ECHA) har klassificeret DP som "very persistent, very bioaccumulative". Tærskelværdier for effekter var generelt meget højere end de koncentrationer, der er fundet i Grønland i denne undersøgelse.

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[1] Dechloran plus (DP), CAS nummer: 13560-89-9

[2] 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), CAS nummer 183658-27-7; bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP), CAS nummer 26040-51-7; 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), CAS nummer 35109-60-5; 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), CAS nummer 37853-59-1; decabromodiphenylethane (DBDPE), CAS nummer 84852-53-9

Sammenfattende tyder undersøgelsen på begrænset nedbrydelighed og en vis bioakkumulering af DP og NBFR i det grønlandske miljø, mens biomagnificering i fødekæden ikke blev påvist.

3 Introduction

3.1 Background

Roughly 150 000 chemicals have been registered for use in Europe and the USA in the last 30 years (AMAP, 2017). Despite stringent registration processes, these may include compounds, which, once emitted to the environment, are persistent enough to be transported over long distances, eventually to the Arctic. If they also accumulate in food chains and exhibit adverse (eco)toxic effects, they likely meet the definition of persistent organic pollutants (POPs). Well-known POPs include polychlorinated biphenyls (PCBs) or polybrominated diphenyl ethers (PBDEs). The latter is a group of brominated flame retardants (BFRs) now globally banned via the Stockholm Convention (see chapter 3.2).

Emerging or less-studied compounds are regularly included in the AMAP Core Programme, the environmental monitoring programme of Denmark and Greenland, in terms of screening studies or retrospective time trends (Rigét et al., 2016). In this context, dechlorane plus (DP) and a selection of current-use BFRs, so-called novel brominated flame retardants (NBFRs), were analysed in samples from Greenland[3]. The compounds are further described in chapter 4 and represent a selection of potential replacement products of phased out BFRs, mainly PBDEs.

DP and some novel BFRs were detected in air and biota samples from Greenland, the latter including ringed seal blubber, glaucous gull liver, black guillemot eggs and polar bear adipose tissue (Vorkamp et al., 2015). The concentrations were generally low (Figure 1), and only DP, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and 2,4,6-tribromophenyl 2,3-dibromopropyl ether (DPTE) were detected in > 90% of the biota samples. However, these first detections in the Greenland environment raised concern about their potential persistence, long-range transport, bioaccumulation and toxicity.

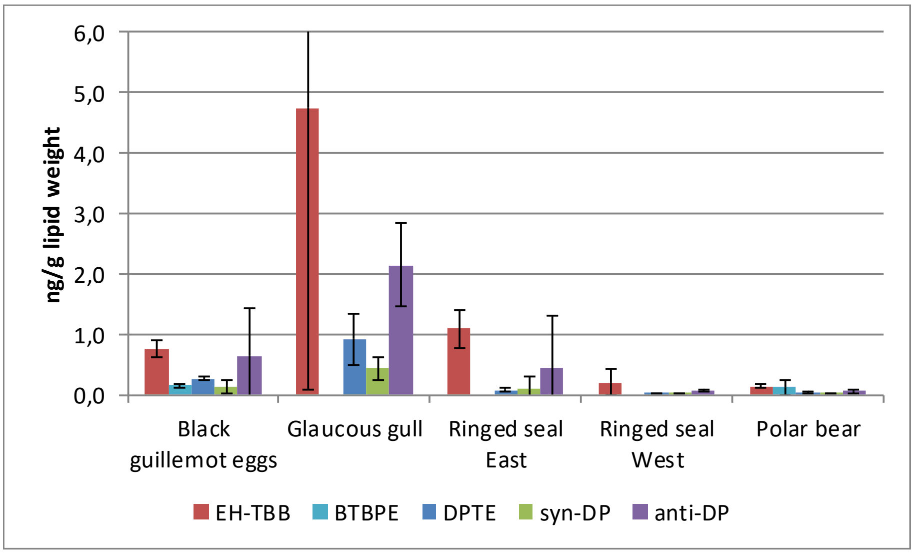

Figure 1. Dechlorane plus (DP) and novel brominated flame retardants in marine animals from Greenland (Vorkamp et al., 2015).

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[3] DANCEA-project "Monitering af grønlandske dyr og den grønlandske atmosfære" (MST-112-00126)

3.2 Stockholm Convention

The Stockholm Convention on POPs is a global treaty under the auspices of the United Nation Environmental Programme, with the objective to protect human health and the environment from POPs. It is based on the recognition that the long-range transport of POPs requires global rather than national action. The Stockholm Convention entered into force in 2004 and has currently 182 parties (www.pops.int). Its main provisions include

- Elimination of production, use, export, import of intentionally produced POPs (Annex A)
- Restriction of production, use, export, import of intentionally produced POPs (Annex B)
- Elimination and reduction of unintentionally produced POPs (Annex C)
- Management of POP-containing stockpiles and wastes
- Targeting of additional POPs.

When the Stockholm Convention entered into force in 2004, twelve POPs were regulated, the “dirty dozen” (Table 1). Several POPs have been added subsequently, increasing the current number of POPs to 28 (Table 1). Furthermore, the insecticide dicofol (CAS no. 115-32-2) and the perfluorinated substances perfluorooctanoic acid (PFOA, CAS no. 335-67-1) and perfluorohexane sulfonate (PFHxS, CAS no. 355-46-4) are currently under review for inclusion in the Stockholm Convention.

The Stockholm Convention defines POPs according to a set of screening criteria for long-range transport (LRT), persistence (P), bioaccumulation (B) and toxicity (T) (Table 2). The table shows that the criteria include specific cut-off values as well as other data and evidence, which become subject to further evaluation in the screening and review process. Monitoring data can be included for the assessment of the three criteria LRT, P and B, and have been included in previous evaluations. For example, the decision to review hexabromocyclododecane (HBCDD) says with regard to persistence (UNEP, 2009): “Monitoring data show that the substance is found in samples from remote areas, e.g., in air and in fish, mammals and birds in the North Atlantic and Arctic regions. An increasing temporal trend of HBCDD concentrations has recently been reported in a range of Arctic biota.”

Thus, environmental data from Greenland can provide relevant information with regard to the screening criteria of the Stockholm Convention. This “indicator function” of Arctic data has previously been used in attempts to identify new POPs (e.g. Lambert et al., 2011). A recent report of the Arctic Monitoring and Assessment Programme (AMAP) has assessed new data on “Chemicals of Emerging Arctic Concern”, including their POP characteristics (AMAP, 2017). Furthermore, Arctic monitoring has addressed the effectiveness of the Stockholm Convention by focusing on the concentration development of the regulated compounds (AMAP, 2016).

Table 1. List of POPs currently regulated by the Stockholm Convention.

Compound	**Acronym**	**Use**	**Year of addition**	**Annex**
Aldrin	-	Insecticide	2004	A
Chlordane	-	Insecticide	2004	A
Dichlorodiphenyltrichloroethane	DDT	Insecticide	2004	B
Dieldrin	-	Insecticide	2004	A
Endrin	-	Insecticide	2004	A
Heptachlor	-	Insecticide	2004	A
Hexachlorobenzene	HCB	Insecticide, industrial chemical	2004	A, C
Mirex	-	Insecticide	2004	A
Polychlorinated biphenyls	PCBs	Industrial chemicals	2004	A, C
Polychlorinated dibenzo-*p*-dioxins	PCDDs	-	2004	C
Polychlorinated dibenzo-*p*-furans	PCDFs	-	2004	C
Toxaphene	-	Insecticide	2004	A
Chlordecone	-	Agricultural pesticide	2009	A
Hexabromobiphenyl	HBB, PBBs*	Industrial chemical (Flame retardant)	2009	A
Hexa- and heptabromodiphenyl ether	PBDEs*	Industrial chemical (Flame retardant)	2009	A
Alpha-hexachlorocyclohexane	α-HCH	Insecticide byproduct	2009	A
Beta-hexachlorocyclohexane	β-HCH	Insecticide byproduct	2009	A
Gamma-hexachlorocyclohexane; lindane	γ-HCH	Insecticide	2009	A
Pentachlorobenzene	PeCB	Industrial chemical	2009	A, C
Perfluorooctane sulfonate and perfluorooctane sulfonyl fluoride	PFOS and PFOSF	Industrial chemical	2009	B
Tetra- and pentabromodiphenyl ethers	PBDEs*	Industrial chemical (Flame retardant)	2009	A
Endosulfan	-	Insecticide	2011	A
Hexabromocyclododecane	HBCDD	Industrial chemical (Flame retardant)	2013	A
Hexachlorobutadiene	HCBD	Industrial chemical	2015, 2017	A, C
Pentachlorophenol	PCP	Pesticide	2015	A
Polychlorinated naphthalenes	PCNs	Industrial chemicals	2015	A, C
Decabromodiphenyl ether	DecaBDE; PBDEs*	Industrial chemical (Flame retardant)	2017	A
Short-chain chlorinated paraffins	SCCPs	Industrial chemicals	2017	A

* Collective compound group name

Table 2. Screening criteria of the Stockholm Convention on POPs.

Property	**Abbreviation**	**Criteria**
Long-range transport	LRT	Atmospheric half-life > 2 days or monitoring data/measurements or multimedia modelling data
Persistence	P	Half-life in water > 60 days, half-life in soil or sediment > 6 months or other evidence
Bioaccumulation	B	Bioconcentration factor > 5000, $\log K_{OW} > 5$ or monitoring data
Toxicity	T	Toxicity/ecotoxicity data

3.3 REACH PBT/vPvB assessment

REACH abbreviates “Registration, evaluation, authorization and restriction of chemicals” in the European Union (EU). The objectives of REACH are to protect human health and the environment, while enhancing competitiveness of the chemical industry in the EU. Companies producing or importing chemicals (including those in manufactured goods) need to register these chemicals with the European Chemicals Agency (ECHA). In order to comply with the regulation, the companies must identify potential health and environmental risks and propose their management.

ECHA and EU member states have developed a screening approach to identify chemicals of potential concern (ECHA, 2015). This screening can lead to a need for further assessment, for example regarding PBT or “very persistent, very bioaccumulative” (vPvB) properties of a given compound. A PBT / vPvB evaluation or other concern places a compound on the candidate list of “Substances of very high concern”. The current PBT / vPvB substances are listed in Table 3, with DP being one of the latest additions (ECHA, 2018). This will be further specified for DP in chapter 7.

Table 3. Current list of PBT/vPvB compounds under REACH. Compounds marked with bold are also included in (or considered for) the Stockholm Convention on POPs. n.a.: not available

Compound	CAS no.	Year of decision
Dechlorane plus	13560-89-9	2018
Benz[a]anthracene	56-55-3	2018
Chrysene	218-01-9	2018
Perfluorohexane sulfonate (PFHxS)	**355-46-4**	**2017**
Perfluorodecanoic acid (PFDA)	335-76-2	2017
Benzo[a]pyrene	50-32-8	2016
UV-327	3864-99-1	2015
UV-350	36437-37-3	2015
Perfluorononaoic acid (PFNA)	375-95-1	2015
5-sec-butyl-2-(2,4-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane; 5-sec-butyl-2-(4,6-dimethylcyclohex-3-en-1-yl)-5-methyl-1,3-dioxane	n.a.	2015
UV-328	25973-55-1	2014
UV-320	3846-71-7	2014
APFO	3825-26-1	2013
Perfluorooctanoic acid (PFOA)	**335-67-1**	**2013**
Decabrominated diphenyl ether (DecaBDE)	**1163-19-5**	**2012**
Henicosafluoroundecanoic acid	2058-94-8	2012
Heptacosafluorotetradecanoic acid	376-06-7	2012
Pentacosafluorotridecanoic acid	72629-94-8	2012
Tricosafluorododecanoic acid	307-55-1	2012
Anthracene oil (and related products)	90640-81-6 / 91995-15-2 / 91995-17-4 / 90640-82-7	2010
Pitch, coal tar	65996-93-2	2010
Musk xylene	81-15-2	2008
Short-chain chlorinated paraffins (SCCPs)	**85535-84-8**	**2008**
Bis(butyltin)oxide (TBTO)	56-35-9	2008
Hexabromocyclododecane (HBCDD)	**134237-50-6 / 124237-51-7 / 134237-52-8 / 25637-99-4**	**2008**

The screening criteria for identification of PBT / vPvB compounds are similar to those of the Stockholm Convention (Table 4). However, long-range transport is not a specific criterion in EU REACH, in line with its regional / supranational rather than global approach to chemical regulation. The bioaccumulation criterion is stricter than that of the Stockholm Convention, with a bioconcentration factor (BCF) of 2000 as a cut-off value in contrast to BCF > 5000 of the Stockholm Convention. The BCF used by the Stockholm Convention characterises a substance as "very bioaccumulative" according to EU REACH (Table 4). The toxicity criteria are described more explicitly than under the Stockholm Convention. Similarly, the other criteria are also defined more specifically. *A priori* they do not suggest using monitoring data for PBT / vPvB classifications.

Table 4. Screening criteria for a PBT/vPvB compound classification under EU REACH.

Property	Abbreviation	Criteria
Persistence	P	Half-life in marine water > 60 days, half-life in freshwater > 40 days, half-life in soil or freshwater sediment > 120 days or half-life in marine sediment > 180 days
Very persistent	vP	Half-life in marine water or freshwater > 60 days, half-life in marine or freshwater sediment > 180 days or half-life in soil > 180 days
Bioaccumulation	B	Bioconcentration factor > 2000
Very bioaccumulative	vB	Bioconcentration factor > 5000
Toxicity	T	No-observed-effect-level or concentration $(EC)_{10}$ for aquatic organisms < 0.01 mg/l, carcinogenic, mutagenic or toxic for reproduction or other evidence of chronic toxicity

3.4 Objectives of the study

Based on the initial detections of DP and NBFRs in the environment of Greenland (Figure 1), a more detailed study was initiated to expand the data currently available for these compounds from Greenland. As monitoring data are relevant for a screening of compounds with regard to LRT and B according to the Stockholm Convention (Table 2), the first objective of this project was to acquire additional data from Greenland.

Specifically, air monitoring data have been generated from a remote location in Northeast Greenland (Villum Research Station), which will be used to assess LRT properties (and implicit persistence) of the selected compounds. With regard to bioaccumulation, DP and NBFRs have been determined in high trophic level animals (whales, seals, seabirds), which supplement the species previously analysed in the AMAP Core Programme (Figure 1).

The second objective of this project was to increase the sparse knowledge of the environmental fate of DP and NBFRs in Greenland. Spatial variation has been addressed by adding two new locations to the previously obtained data for ringed seals and glaucous gull (Figure 1). Furthermore, samples of landlocked Arctic char have been analysed, based on a hypothesis of atmospheric deposition of DP and NBFRs as pathway for uptake into food chains.

As a third objective, PBT characteristics were addressed in a review of existing information in regulatory databases. Mammalian toxicity was addressed specifically, based on existing data and toxicogenomics.

4 Dechlorane plus and novel brominated flame retardants

The chemical structures and Chemical Abstract Service (CAS) numbers of the selected compounds are given in Table 5 and Table 6. Table 7 summarises some of their physical-chemical properties.

4.1 Dechlorane plus

4.1.1 Compound history

Dechlorane plus (DP) was introduced as a replacement flame retardant for mirex in the USA in the 1960s (Hoh et al., 2006). Today, there are two production sites for DP, at Niagara Falls, NY, USA and at Huai'in in the Jiangsu Province, China (Wang et al., 2010a; Xian et al., 2011). The Chinese production has been in operation since 2003 (Wang et al., 2010b). DP is classified as a high production volume chemical by the US Environment Protection Agency (EPA), with an annual production (or import) volume of at least 450 tonnes (Sverko et al., 2011). The annual production volume in China was 305-1020 tonnes[4] (Wang et al., 2010b). Wang et al. (2010b) estimated the cumulative worldwide DP production to be 2100-7100 tonnes[5]. For comparison, the total global production of DecaBDE (BDE-209) was estimated to be 1.1-1.25 million tonnes between 1970 and 2015 (Abbasi et al., 2015).

For flame retardant purposes, DP is incorporated into polymer matrices where it can account for 10-35% (Wang et al., 2010a). It is typically added to thermoplastics (nylon, polyester, acrylonitrile butadiene styrene (ABS), rubber, polybutylene terephthalate, polyproplylene, styrene butadiene rubber (SBR)) and thermosets (epoxy and polyester resins, polyurethane foams, polyethylene, silicone neoprene, ethylene propylene diene) (Canada, 2016a). This source specifies that the content in silicone can reach 40%. The polymers are typically used as coatings for commercial electrical wires and cables, in connectors used in computers and in plastic roofing material (OxyChem, 2004).

The chemical structure of DP and its physical-chemical properties are similar to those of internationally banned organochlorine pesticides, such as aldrin, dieldrin, chlordane, heptachlor and mirex, which were among the initial "dirty dozen" of the Stockholm Convention (Table 1) (Wang et al., 2010a). The commercial DP product consists of two stereoisomers (Table 5). The DP composition is usually characterised by the fraction of the concentration of anti-DP, relative to the total DP concentration (Equation 1). In the commercial DP production, f_{anti} is 0.65-0.75 (Sverko et al., 2008; 2011).

Equation 1

$$f_{anti} = \frac{c(anti-DP)}{c(syn-DP)+c(anti-DP)}$$

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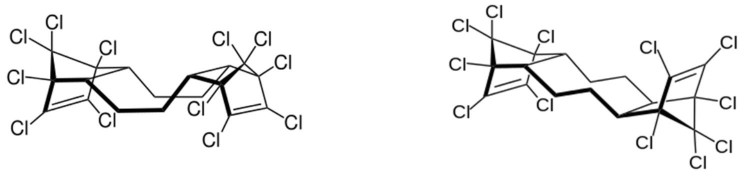
[4] Converted to metric tonnes from 300-1000 tons (Wang et al., 2010b)

[5] Converted to metric tonnes from 2100-7000 tons (Wang et al., 2010b)

Table 5. Chemical structures of syn- and anti-dechlorane plus (DP)



Syn-DP
Anti-DP

CAS no: 13560-89-9

Despite its long time on the market, the first report on DP in the environment was published in 2006 (Hoh et al., 2006): Taking offset in air monitoring under the Integrated Atmospheric Deposition Network of the Great Lakes region, DP had been identified in air, fish and sediment of the Great Lakes, including air samples from remote stations. Some air and sediment concentrations were comparable to those of BDE-209. Since then, many studies and several review articles have been published on DP in the environment (Xian et al., 2011; Sverko et al., 2011; Feo et al., 2012; Wang et al., 2016), generally documenting the omnipresence of DP in the environment.

Along with other flame retardants, DP has also been detected in dust and indoor air (Newton et al., 2015; Fan et al., 2016), indicating additional exposure sources in the indoor environment. The presence of DP in human matrices, such as human serum or human milk, has been shown in Europe, North America and Asia (Zhou et al., 2014; Fromme et al., 2015; Qiao et al., 2018). Little information is available on toxicity. Acute toxicity seems to be low (Feo et al., 2012). According to Wang et al. (2016), toxicity was mainly observed at the transcriptome and metabolome level.

Besides syn- and anti-DP, several DP derivatives have been detected in the environment, e.g. dechloranes 602, 603 and 604, DP monoadducts (e.g. 1,3-DPMA) or the transformation products anti-Cl_{10}DP and anti-Cl_{11}DP. However, these compounds have not been part of the present study.

4.1.2 Dechlorane plus in the Arctic

The early review articles on DP in the environment concluded that DP was a global pollutant, which implied transport to polar regions (Xian et al., 2011; Sverko et al., 2011; Feo et al., 2012). This conclusion was mainly based on the detection of DP in air and water samples on transects to the Arctic and Antarctic (Möller et al., 2010; 2011a; 2011b). Analyses of seawater-air exchange indicated atmospheric transport of DP and net gaseous deposition (Sverko et al., 2011).

A first circumpolar literature review of DP was published in 2014, with a focus on indications of long-range transport and bioaccumulation (Vorkamp and Rigét, 2014)[6]. It concluded that initial evidence existed for long-range transport and bioaccumulation. Additional air data had been published from

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[6] DANCA-project "Nye kontaminanter med relevans for det grønlandske miljø" (MST-112-00299/00040)

Alert, the High Arctic monitoring station in Canada (Xiao et al., 2012). However, few data were available in biota at the time, and some measurements of DP in high trophic level animals had resulted in non-detects. Following this literature review, initial data were generated for DP in biota from Greenland, as described in chapter 3.1, showing high detection frequencies, but relatively low concentrations (Vorkamp et al., 2015).

The recent AMAP report on "Chemicals of Emerging Arctic Concern" included a chapter on chlorinated flame retardants, which focussed on DP (AMAP, 2017)[7]. The database on DP in air had been extended, now also including data from Svalbard, Sweden and sub-Arctic Canada, and updated regarding the data from Alert. DP had been widely detected in seawater and sediment (Na et al., 2015). The same study also included biota data from the terrestrial environment, showing DP concentrations in the low ng/g dry weight range for moss, soil and reindeer dung from Svalbard. Only few additions were made on marine biota, which confirmed previous conclusions of low concentrations: DP was not detected in polar bears from the Hudson Bay and found in concentrations < 0.1 ng/g wet weight in seabird eggs from the Norwegian coast (Huber et al., 2015; Letcher et al., 2018). The conclusion of the AMAP assessment is given in Box 1.

A recent study on contaminants in peregrine falcon eggs from South Greenland[8] confirmed the presence of DP in all samples, with ΣDP levels up to 38 ng/g lipid weight (lw) (mean concentration 8.4 ng/g lw) (Vorkamp et al., 2018). These levels are clearly higher than those reviewed in the AMAP assessment report. However, as the peregrine falcons migrate to Central and South America in the winter, their contaminant exposure does not exclusively take place in the Arctic. Interestingly, the time trend analyses over the sample collection period from 1986-2014 showed tendencies of increases for DP.

Box 1: Conclusions for dechlorane plus (DP) (and related DP derivatives) in the recent AMAP assessment report "Chemicals of Emerging Arctic Concern" (AMAP, 2017).

DP and its analogs are currently unregulated, yet demonstrate similar properties to POPs, including long-range transport to the Arctic. DP has consistently been detected in Arctic air. The majority of studies have found an *anti/syn* ratio similar to that of the technical product, but deviations have been reported. Inconclusive observations exist as to whether the *anti/syn* ratio changes with distance from potential sources of DP.

Although detection in Arctic biota is inconsistent, several recent studies have shown DP and its analogs in terrestrial and marine fauna, including reindeer, seabirds, seals, beluga and polar bears. Concentrations were generally low and challenge analytical detection limits.

Additional monitoring studies are needed to understand the significance of these compounds to the Arctic, specifically regarding freshwater systems for which data are lacking. Including dechlorane transformation products (e.g. dechlorinated derivatives and monoadducts) in screening studies would be useful, because these related compounds have been identified, but not widely screened for in Arctic media and biota, thus their origin and significance remain unclear. Lastly, given the recent detection of dechloranes in apex predators of the Arctic, targeted isomer-specific studies to assess the bioaccumulation potential of these compounds are warranted.

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[7] DANCEA-project "Dansk-grønlandsk bidrag til det internationale AMAP POP assessment" (MST-112-191)

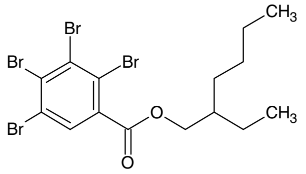
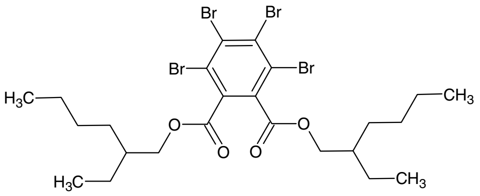
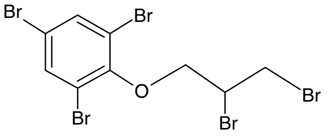
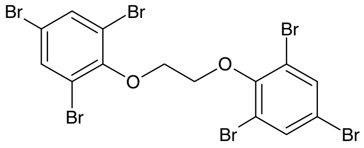
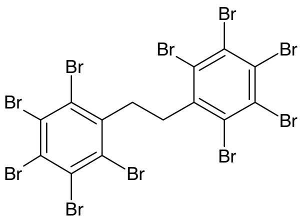
[8] DANCEA-project "Nye og opdaterede tidstrends af svært nedbrydelige organiske stoffer og deres effekter i vandrefalkeæg fra Grønland" (MST-112-00197)

4.2 Novel brominated flame retardants

4.2.1 Compound histories

The selection of NBFRs built on that of the previous project (Vorkamp et al., 2015), based on the objective of the present project to expand the environmental data available for these compounds from Greenland. It obviously is a small selection of the roughly 75 BFRs that have been produced commercially, but also including those that have now been banned (Covaci et al., 2011). EH-TBB/BEH-TEBP, BTBPE and DBDPE were chosen because they had specifically been described as likely replacement compounds of the Penta-, Octa- and DecaBDE products after those were banned (Kierkegaard et al., 2004; Hoh et al., 2005; Stapleton et al., 2008).

Table 6. Chemical structures of the novel brominated flame retardants (NBFRs) included in this study

Acronym	Full name	Structure	CAS no.
EH-TBB	2-Ethylhexyl-2,3,4,5-tetrabromobenzoate		183658-27-7
BEH-TEBP	Bis(2-ethylhexyl)tetrabromophthalate		26040-51-7
DPTE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether		35109-60-5
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)-ethane		37853-59-1
DBDPE	Decabromodiphenyl ethane		84852-53-9

EH-TBB and BEH-TEBP are components of the Firemaster BZ-54 and the Firemaster 550 products, the latter also containing phosphorous flame retardants. The products have been on the market since 2003 and are mainly used in polyurethane foam where they replace PentaBDE (Covaci et al., 2011). BEH-TEBP is also used in the flame retardant mixture DE-54 and as a plasticizer (Andersson et al., 2006; Davis and Stapleton, 2009). The production volume of BEH-

TEBP in the USA was between 450-4500 tonnes/year[9] in 2012, while that of EH-TBB was unknown (Knudsen et al., 2016).

DPTE was produced under the tradename Bromkal 73-5PE in Germany until 1985 (Vetter et al., 2010). Recent updates have suggested that the compound is still being used in Germany today, however, no further information is currently available on its production and use (Vetter et al., 2017). BTBPE is structurally similar to DPTE, as it also includes a 2,4,6-tribromophenol moiety (Table 6). It has been produced in the USA under the tradename FF-680 since the early 1970s, but the production was decreasing after 1998 (Hoh et al., 2005). Verreault et al. (2007) gave a worldwide production (or estimated use) of BTBPE of about 15000 tonnes[10], but if BTBPE replaces OctaBDE (Hoh et al., 2005), these numbers will likely be outdated. In the EU, BTBPE is classified as a low production volume chemical (EFSA, 2012). Similarly to OctaBDE, BTBPE has mainly been used in hard plastics, including ABS and high impact polystyrene (HIPS) (Andersson et al., 2006).

DBDPE was introduced in the mid-1980s or early 1990s and has had the same applications as DecaBDE (Kierkegaard et al., 2004; Covaci et al., 2011). Its tradenames (of US producers) are Saytex 8010 and Firemaster 2100. DBDPE is considered a low production volume chemical in the EU (EFSA, 2012), which refers to an import into the EU of roughly 1000-5000 tonnes (Covaci et al., 2011). DBDPE is also produced by at least two manufacturers in China, with increasing developments in production volume (Covaci et al., 2011).

EH-TBB and BEH-TEBP were first detected in dust samples from the USA, at median levels of roughly 150 ng/g for each compound, which was about half of the concentration of HBCDD in the same samples (Stapleton et al., 2008). The review by Covaci et al. (2011) also includes reports of EH-TBB and BEH-TEBP in sewage sludge and biota. DPTE was first detected in marine samples by Vetter (2001), and its identity was confirmed in samples of blubber extracts of hooded seal (*Cystophora cristata)* (von der Recke and Vetter, 2007). Interestingly, its concentration exceeded that of PBDEs. It has now also been detected in the indoor environment, specifically in dishcloths of everyday use, where concentrations were comparable to BDE-209 (Gallistl et al., 2017).

BTBPE was identified in samples of the Integrated Atmospheric Deposition Network of the Great Lakes region (Hoh et al., 2005), shortly before the first detection of DP in this monitoring programme (chapter 4.1.1), but had also been reported previously, for example in the indoor air of an electronics recycling plant (Sjödin et al., 2001). DBDPE was first quantified in sewage sludge, sediment and workplace indoor air samples from Sweden and the Netherlands (Kierkegaard et al., 2004). The levels were generally lower than those of BDE-209 (2-70% of BDE-209). Since then, DBDPE has been detected in a variety of indoor and outdoor environmental samples, including multiple types of biota samples (Covaci et al., 2011).

Little information is available on toxicity (see chapter 7), however, the structural resemblance of BEH-TEBP to DEHP has raised concern about its endocrine disruption potential (AMAP, 2017).

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[9] Converted to metric tonnes from 1,000,000-10,000,000 lb (Knudsen et al., 2016)

[10] Converted to metric tonnes from 16710 tons (Verreault et al., 2007)

Table 7. Physical-chemical properties of dechlorane plus and the novel brominated flame retardants (NBFRs) included in this study.

Compound	**logK$_{OW}$**	**logK$_{OA}$**	**Water solubility**	**Vapour pressure**	**References**
Dechlorane plus	8.8; 9.3; 10.7-11.6	14.5-15.8	44 ng/L - 249 µg/L (insoluble); 2.85×10^{-7} mg/L; $1.58\times10^{-8} – 6.63\times10^{-7}$ mg/L	6.57×10^{-11} Pa (25°C); $1.58\times10^{-9} – 7.94\times10^{-6}$ Pa	OxyChem (2004); Canada (2016a); Zhang et al. (2016)
EH-TBB	8.3-8.8	12.0-12.4	1.26×10^{-5} - 3.16×10^{-3} mg/L	3.16×10^{-7} - 3.98×10^{-4} Pa	Zhang et al. (2016)
BEH-TEBP	10.08; 10.9-12.4	16.9-17.5	1.60×10^{-6} g/L (25°C); 2.00×10^{-9} - 2.00×10^{-6} mg/L	1.55×10^{-11} Pa (25°C); 1.00×10^{-1} - 5.01×10^{-7} Pa	Covaci et al. (2011); Zhang et al. (2016)
DPTE	5.9; 6.3-6.5	10.6-11.1	1.58×10^{-3} - 7.94×10^{-2} mg/L	8.29×10^{-5} Pa (25°C); $7.94\text{-}10^{-6}$ - 2.51×10^{-2} Pa	Vetter et al. (2010); Zhang et al. (2016)
BTBPE	3.1; 7.88; 8.6-9.2	14.5-15.7	1.90×10^{-5} g/L (25°C); 2.00×10^{-4} - 6.31×10^{-7} mg/L	3.88×10^{-8} Pa (25°C); 1.26×10^{-10} - 3.98×10^{-6} Pa	Karlsson et al. (2007); Covaci et al. (2011); Zhang et al. (2016)
DBDPE	11.1; 12.2-13.6	18.2-19.2	7.2×10^{-4} g/L (25°C); 2.10×10^{-7} g/L (25°C); 1.26×10^{-12} - 1.00×10^{-6} mg/L	6.0×10^{-15} Pa (25°C); 5.01×10^{-16} - 1.00×10^{-8} Pa	Dungey and Akintoye (2007); Covaci et al. (2011); Zhang et al. (2016)

4.2.2 Novel brominated flame retardants in the Arctic

All NBFRs of this study were included in a review on new and current-use contaminants in the Arctic (Vorkamp and Rigét, 2014)[11]. DPTE was present in Arctic air and seawater, showing a net deposition from air, while BEH-TEBP was found more sporadically (Möller et al., 2011a; 2011b). EH-TBB was measured at the atmospheric monitoring station Alert. BTBPE and DBDPE had been widely detected in abiotic media of the Arctic. In biota studies, DPTE had generally been below detection limits, while BTBPE, EH-TBB and BEH-TEBP had been detected in most, but not all studies, at generally low concentrations. DBDPE was generally undetectable or found in low concentrations (Vorkamp and Rigét, 2014).

The recent AMAP assessment report on “Chemicals of Emerging Arctic Concern” includes additional air data for BTBPE, EH-TBB and BEH-TEBP from Alert, showing detection frequencies close to 100% for all three compounds and tendencies of increasing concentrations for EH-TBB and BEH-TEBP (AMAP, 2017)[12]. Monitoring data have also become available for EH-TBB, BEH-TEBP, DPTE and BTBPE from Little Fox Lake (Yukon, Canada) and Svalbard (the latter except DPTE, but including DBDPE). At all three stations, EH-TBB and BEH-TEBP were the compounds with the highest concentrations in air. Additional data in abiotic media (sediment, ice etc.) have been published for some of the compounds. Strikingly high concentrations of DBDPE, i.e. exceeding those of BDE-209, were found in Arctic sediment (Cai et al., 2012).

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[11] DANCA-project ”Nye kontaminanter med relevans for det grønlandske miljø” (MST-112-00299 / 00040)

[12] DANCEA-project ”Dansk-grønlandsk bidrag til det internationale AMAP POP assessment” (MST-112-191)

Box 2. Conclusions for the novel brominated flame retardants of this study in the recent AMAP assessment report ”Chemicals of Emerging Arctic Concern” (AMAP (2017)

DPTE has been detected in air and seawater of the Arctic as well as in some biota. DPTE seems to be widely present in the Arctic environment. Its detection in sewage sludge might indicate additional sources, besides atmospheric long-range transport. While concentrations of DPTE in abiotic media were roughly comparable to those for PBDEs, most concentrations in biota were lower than those for PBDEs, but exceptions exist.

The database on **BTBPE** in the Arctic has been extended considerably since the previous AMAP assessment. The air, snow and ice measurements show that BTBPE is transported to the Arctic and deposited in the Arctic environment. Studies from outside the Arctic indicate bioaccumulation and biomagnification of BTBPE. The compound has been detected in Arctic biota (polar bear, seabirds, ringed seal, and several fish species including Greenland shark), but most studies also include non-detectable concentrations. There is no clear link in the present dataset between concentration and trophic level, but it could be masked by the heterogeneity of the data in terms of location and detection limit. Canadian temporal trend studies on landlocked Arctic char and ringed seal indicate increasing concentrations of BTBPE, which would be in line with its increased use as a PBDE replacement. However, the present air time series do not show the same trend.

More studies have focused on **BEH-TEBP** and **EH-TBB**, which are replacement products of PentaBDE and might thus be applied widely. Although models do not predict a long atmospheric half-life for BEH-TEBP, it is sufficiently stable to reach the Arctic. Levels of BEH-TEBP and EH-TBB in Arctic air are comparable to those of PBDEs and have shown signs of increase. In combination with increasing trends observed in the Great Lakes region, this might reflect the anticipated increase in use as a replacement for pentaBDE. Both compounds have been detected in fish, seabirds and marine mammals from the Arctic indicating that bioaccumulation occurs. Most levels were relatively low, i.e. lower than those of PBDEs, but polar bear plasma from Svalbard, for example, contained slightly higher levels of EH-TBB. The preliminary data do not show biomagnification of BEH-TEBP, but more data will be needed for firm conclusions.

DBDPE has been widely detected in Arctic air. In marine surface sediments, DBDPE has been found at higher and more uniform concentrations than BDE-209. Ice cores documented an increase in DBDPE between 1971 and 1988, but not since then. Most studies on DBDPE in biota have found concentrations close to detection limits, with the exception of one recent Norwegian study which found DBDPE in biota at concentrations of 5–10 ng/g ww, often exceeding those for BDE-47. As the same type of samples from the same area had shown low or even undetectable concentrations previously, these findings suggest either a rapid increase in DBDPE concentrations or other factors affecting DBDPE concentrations in the analysis. Food web studies have indicated biomagnification of DBDPE. On the other hand, DBDPE also seems to be susceptible to rapid biotransformation. More research will be needed to understand the environmental fate of DBDPE in the Arctic. If used as a commercial alternative to BDE-209, large volumes of DBDPE might be produced and potentially emitted to the environment. Thus, updated information on production and use volumes will also be important.

The conclusions of the AMAP assessment report for these five compounds are shown in Box 2 (AMAP, 2017). No new DPTE data were available in biota, except the study performed under the AMAP Core Programme (Vorkamp et al., 2015) (Chapter 3.1). BTBPE still had either undetectable or low concentrations (i.e. < 1 ng/g ww) in biota. More biota data had been published for EH-TBB and BEH-TEBP, but no clear pattern could be found. The data included concentrations below detection limits and up to approximately 8 ng/g ww. The report showed a large variation in the DBDPE concentration in Arctic biota, with some concentrations below detection limits and others exceeding PBDEs. A study from Norway was particularly noteworthy as it showed a widespread occurrence of DBDPE including biomagnification in the food chain (Harju et al., 2013).

In a recent study on NBFRs in peregrine falcon eggs from South Greenland[13], no BTBPE or DBDPE were detected and the concentrations of other NBFRs were relatively low (< 5 ng/g lw) compared with PBDEs and other halogenated compounds in the same samples (Vorkamp et al., 2018). As mentioned for DP, the concentrations in peregrine falcon eggs represent a large geographical area of exposure, including their migration routes and winter habitats in Central and South America. DPTE was the only NBFR showing a significant time trend over the study period (1986-2014), in terms of decreasing concentrations.

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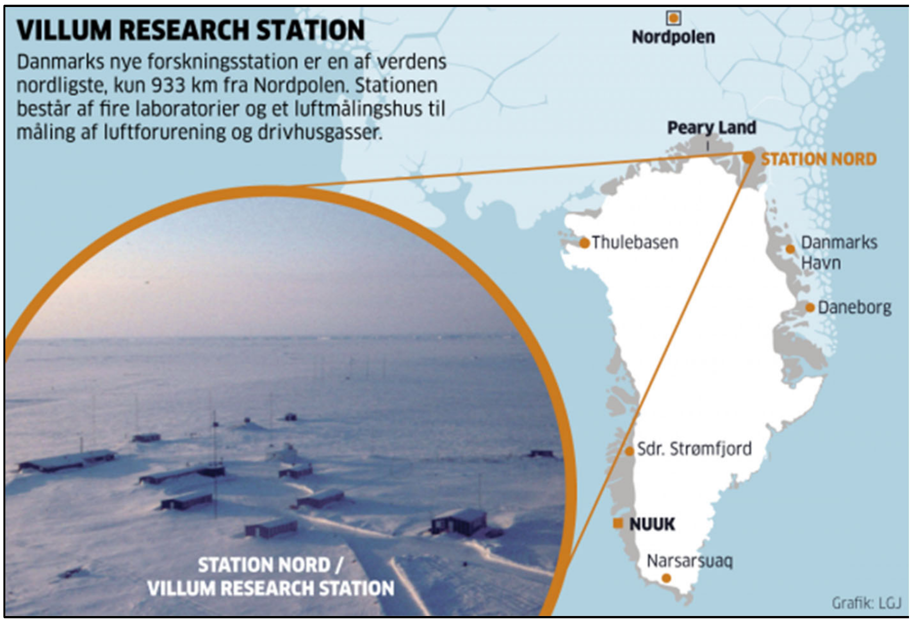
[13] DANCEA-project ”Nye og opdaterede tidstrends af svært nedbrydelige organiske stoffer og deres effekter i vandrefalkeæg fra Grønland” (MST-112-00197)

5 Air measurements

5.1 Samples

The air samples analysed in this project were collected at Villum Research Station / Station Nord (81°36‘ N; 16°40‘ W) in Northeast Greenland (Figure 2; Figure 3).



VILLUM RESEARCH STATION

Danmarks nye forskningsstation er en af verdens nordligste, kun 933 km fra Nordpolen. Stationen består af fire laboratorier og et luftmålingshus til måling af luftforurening og drivhusgasser.

Figure 2. Location of Villum Research Station/Station Nord in Northeast Greenland

Figure 3. View of Villum Research Station in Northeast Greenland. Photograph taken by Bjarne Jensen.

The study included two sets of air samples:

- Monthly samples of the year 2014 (13 samples)
- Short-term sampling (1-2 days) in spring 2016 (13 samples).

The primary focus of the project was on the monthly air samples which should provide information about the long-range transport (and implicit persistence) of DP and the NBFRs. The purpose of the additional short-term sampling was to provide input data of DP for atmospheric transport models back-tracking the transport of DP to Northeast Greenland.

The air samples were collected with a high volume air sampler as described by Bossi et al. (2016). The high volume sampler is placed in a hut at about 15°C and contains a quartz fibre filter (for atmospheric particles) followed by a cartridge packed with polyurethane foam (PUF)/XAD-2/PUF (for gaseous chemicals). Each sample represents a sampling volume of 5000 m^3 sampled continuously over one week. Samples for this study were collected every four weeks, as part of the regular air monitoring at Villum Research Station, leading to 13 samples in total. They roughly represent every month of the year, with two samples at the beginning and the end of March, respectively. The same equipment and air flow was used for the short-term sampling, but the sampled air volume was reduced to 1429 m^3. After sampling, the filters and PUF/XAD-2/PUF cartridges were shipped to Denmark where they were kept at -20°C until analysis.

5.2 Chemical analysis

The PUF and XAD-2 materials were pre-cleaned with dichloromethane, and the quartz fibre filters were baked at 450°C prior to shipment to Greenland and sampling at Villum Research Station.

For the chemical analysis, the quartz fibre filters and PUF/XAD-2 materials were combined for each sample, i.e. the analysis does not distinguish between particle-bound and gaseous forms of DP and NBFRs. The samples were Soxhlet extracted using hexane:dichloromethane (4:1), reduced in volume and cleaned on 2 g silica. After elution with hexane:dichloromethane (1:1), the extracts were evaporated to 100 µl (monthly samples) and 500 µl (short-term sampling), respectively. The finale volume was increased between these two sets of samples to reduce matrix effects observed in the first analyses. The samples were analysed by gas chromatography-mass spectrometry (GC-MS) with electron capture negative ionisation (ECNI).

The two sets of samples were analysed in two batches, each including two blanks. One blank was a cleaned set of quartz fibre filter and PUF/XAD-2/PUF, the other one was a pure solvent blank. In addition, the first batch included a field blank, i.e. a set of PUF/XAD-2/PUF, which was transported to Greenland and back, but not used for sampling. The data were corrected for the amount found in the blank set of quartz fibre filter and PUF/XAD-2/PUF.

The limits of quantification (LOQs) are given in Table 8. They differ for the monthly samples and the short-term sampling because of differences in the sampled air volume and the final extract volume. The latter also varied among the short-term samples as these were analysed in two batches with different final volumes, and the higher LOQ is included in Table 8. Concentrations below LOQs were replaced with zero in calculations of ΣDP, means and median values.

Table 8. Limits of quantification (LOQs) for dechlorane plus (DP) and the novel brominated flame retardants (NBFRs) in air samples from Northeast Greenland (Villum Research Station)

Compound	LOQ monthly samples (pg/m^3)	LOQ short-term sampling (pg/m^3)
Syn-DP	0.00099	0.017
Anti-DP	0.0020	0.016
EH-TBB	0.0099	0.086
BEH-TEBP	0.0020	0.35
DPTE	0.0020	0.017
BTBPE	0.0049	0.086
DBDPE	0.0098	0.17

5.3 Results and discussion

5.3.1 Dechlorane plus

Of the 13 samples analysed from 2014, seven samples were below LOQs for both DP isomers. The remaining samples showed concentrations up to 5.5 pg/m^3 for ΣDP (Figure 4). Averaging over the measurements for one year leads to a mean of 0.64 pg/m^3 (Table 9), while the median value is below LOQ because of the majority of the samples having undetectable levels of DP.

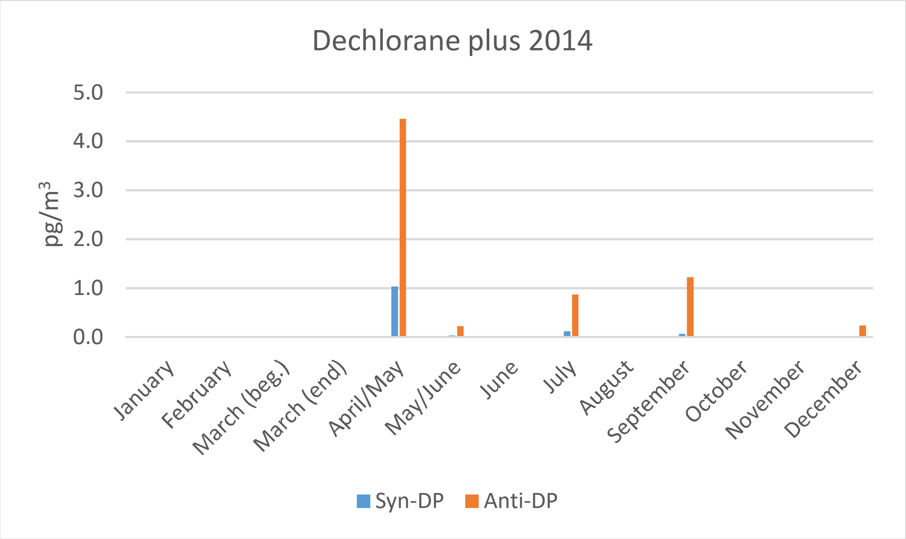


Figure 4. Concentration of syn- and anti-dechlorane plus (DP) in monthly air samples collected at Villum Research Station in 2014.

The detection frequency of DP was higher in the short-term samples, i.e. 92% for anti-DP compared with 46% in the monthly samples (Figure 4). The DP level was generally higher and reached a maximum of 31.7 pg/m^3 for ΣDP (Figure 5). The mean concentration in the short-term samples was 7.8 pg/m^3, while it was 4.2 pg/m^3 in all samples (Table 9).

These concentrations appear unusually high in an Arctic context, in particular those of the short-term sampling. Other studies also included single high concentrations, approximately up to 5 pg/m^3, which would be consistent with the monthly air samples, but lower than the maximum concentrations of the short-term sampling (Table 9). It cannot be excluded that the atmospheric concentration of DP increased since the measurements reported in the literature. However, samples collected at Villum Research Station in 2012 also showed a relatively high concentration of DP (Table 9), which exceeded DP concentration determined at other Arctic locations (Table 9). Unlike the present measurements, the data from 2012 had not been corrected for blanks. The Global Atmospheric Passive Sampling Network (GAPS) included a station in Alaska where a DP concentration of approximately 110 pg/m³ was determined (Sverko et al., 2011). However, in an updated publication, the concentrations at the GAPS site in Alaska was given with < 2 pg/m³ (for each of the DP isomers) in 2014 (Rauert et al., 2018). The same result was reported for all other Arctic GAPS stations (St. Lawrence Island, Alaska; Stórhöfði, Iceland; Ny Ålesund, Svalbard; Pallas, Finland).

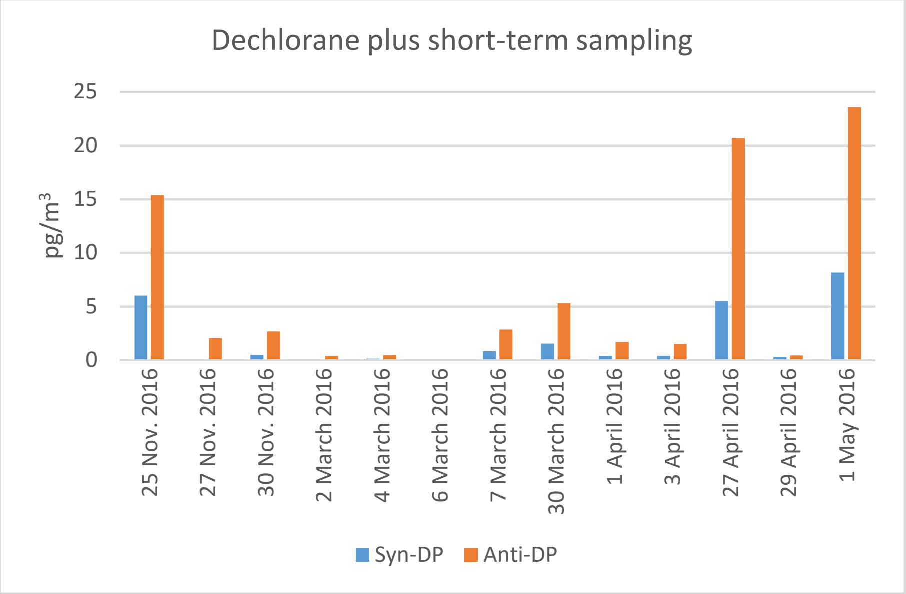


Figure 5. Concentrations of syn- and anti-dechlorane plus (DP) during short-term sampling at Villum Research Station in 2016.

As some of the DP concentrations stand out as unusually high in an Arctic context and the concentration range was relatively large, the question was discussed whether the samples could be affected by local sources. Potential local sources at Villum Research Station included a waste incinerator, which is operated intermittently and could explain that some, but not all samples, had elevated DP levels. Furthermore, it cannot be excluded that contamination can occur during sample shipment. The presence of flame retardants has been documented in airplanes, however, DP has not been sought specifically (Allen et al., 2013). The contamination hypothesis is supported by the field blank, which also showed elevated DP levels.

The recent review of Arctic data, conducted under the AMAP assessment of "Chemicals of Emerging Arctic Concern", concluded that atmospheric concentrations of DP were comparable to those of PBDEs (AMAP, 2017). Although large variations can be expected between locations, this rough comparison also supports DP concentrations at the level of the monthly samples, as the mean ΣPBDE at Villum Research Station was 0.71 pg/m³ (Bossi et al., 2016).

Even though some of the values of this study are uncertain, they indicate that DP is transported over long distances and that it is persistent enough to reach the High Arctic. The long-range transport of DP was also supported in a non-Arctic study which detected DP in lichen from the Tibetan Plateau (Yang et al., 2016). Interestingly, the concentrations (in ng/g dry weight) were comparable to DP in tree bark in urban and industrialised areas, such as the USA (New York) and Germany.

Table 9. Concentrations of syn- and anti-dechlorane plus (DP) in air samples of this study and examples from other Arctic stations.

Location	Year	Mean ΣDP concentration (pg/m^3)	Maximum ΣDP concentration (pg/m^3)	Reference
Villum Research Station	2014-2016	4.2	31.7	This study (all samples)
Villum Research Station	2014	0.64	5.3	This study, monthly samples
Villum Research Station	2012	6.7	41	Vorkamp et al. (2015)
Pallas, Finland	2013/2014	0.039	0.061	Haglund et al. (2016)
Little Fox Lake, Yukon, Canada	2011-2014	~ 0.25	~ 1.8	Yu et al. (2015)
Longyearbyen, Svalbard *	2012/2013	1.2	5.0	Salamova et al. (2014)
Alert, Canada	2007	~ 0.75	2.1	Xiao et al. (2012)

* Particle phase only. DP is mainly associated with particles (Hoh et al., 2006).

5.3.2 Novel brominated flame retardants (NBFRs)

The concentrations of the NBFRs varied considerably in terms of detection frequency and concentration (Table 10). BTBPE was below LOQ in all air samples. EH-TBB, BEH-TEBP and DPTE were found at a similar level, with mean concentrations < 0.3 pg/m^3. DBDPE stood out with much higher concentrations than the other compounds (Table 10).

The lower detection frequency for BEH-TEBP in the short-term sampling is affected by the higher LOQs in this batch. Otherwise, the short-term sampling showed a tendency of higher concentrations than the monthly samples collected 1-2 years previously, which was also found for DP. However, a Student's t-test (two-tailed, performed on ln transformed concentrations) did not indicate a significant differences for the DBDPE concentrations in the two sample sets (p=0.08).

Table 10. Concentrations of novel brominated flame retardants (NBFRs) in air samples of this study.

Compound	Detection frequency (%)	Mean concentration (pg/m^3)
Monthly samples		
EH-TBB	38	0.026
BEH-TEBP	42	0.014
DPTE	15	0.0076
BTBPE	0	< 0.0049
DBDPE	100	3.1
Short-term samples		
EH-TBB	38	0.15
BEH-TEBP	8	0.20*
DPTE	69	0.0075*
BTBPE	0	< 0.086
DBDPE	100	9.7

* Value < LOQ (Table 8). Calculated mean including concentrations < LOQ replaced by zero.

Air concentrations of NBFRs at other Arctic stations are given in Table 11. EH-TBB and BEH-TEBP can be emitted to the environment together as they are ingredients of the same flame retardant product (Stapleton et al., 2008). However, BEH-TEBP can also be used individually, and different physical-chemical properties will likely individualize their environmental fate. As Table 11 shows, the ratio between the two compounds is not constant in atmospheric samples.

The concentrations of EH-TBB and BEH-TEBP at Alert and Little Fox Lake are similar and appear higher than the concentrations at Villum Research Station (Xiao et al., 2012; Yu et al., 2015). The detection frequency of BEH-TEBP was only 38% at Little Fox Lake, as opposed to 78% for EH-TBB, but the maximum concentration was as high as 5.6 pg / m^3, indicating a large concentration variability. Recent updates from Alert showed a near 100% detection of EH-TBB and BEH-TEBP and concentrations of 1.4 and 6.7 pg / m^3, respectively, in 2012 (AMAP, 2017). These levels are approaching those measured in atmospheric particles at Svalbard at the same time (Salamova et al., 2014). These relatively high concentrations, often surpassing PBDE concentrations, are not detectable in Northeast Greenland. Measurements of EH-TBB and BEH-TEBP at Pallas in North Finland were more comparable to the results from this study (Haglund et al., 2016).

The concentrations of DPTE were also lower at Villum Research Station than those reported in the literature (Table 11). At Little Fox Lake in Yukon, Canada, DPTE was detected in 86% of the air samples and the mean concentration was about seven times higher than that at Villum Research Station (Yu et al., 2015). Ship-based measurements in the East Greenland Sea and the Bering / Chukchi Sea showed DPTE in 89 and 100%, respectively, of the gaseous samples (Möller et al., 2011a; 2011b). In the particle phase, it was only detected in the East Greenland Sea samples (Table 11).

Similarly, BTBPE was detectable at other Arctic monitoring stations although not consistently (Table 11). At Little Fox Lake, BTBPE was detected in 24% of the samples (Yu et al., 2015). According to modelling result, 100% of BTBPE would be associated with particles (Xiao et al., 2012), however, gas-phase analysis also showed BTBPE, even though detection frequencies were lower in the gas phase (22%) than in the particle phase (70%) (Möller et al., 2011a). Particle-based analysis at Svalbard resulted in a detection frequency of 53% and relatively low concentrations (Salamova et al., 2014). Unlike these low detection frequencies and concentrations, BTBPE was consistently detected at Alert (Canada) with a maximum concentration of 1.9 pg / m^3 (Xiao et al., 2012).

Table 11. Concentrations of novel brominated flame retardants (NBFRs) in Arctic air (pg/m^3) published from other Arctic stations. The concentrations are arithmetic means. Cells without data indicate that the compound was not analysed.

Location and year	EH-TBB (pg/m^3)	BEH-TEBP (pg/m^3)	DPTE (pg/m^3)	BTBPE (pg/m^3)	DBDPE (pg/m^3)	Reference
Pallas, Finland (2013/2014)	0.008	0.015	-	0.031	0.17	Haglund et al. (2016)
Little Fox Lake, Yukon, Canada (2011-2014)	0.25	0.86	0.049	0.082	-	Yu et al. (2015)
Longyearbyen, Svalbard (2012-2013)*	7.0	2.7	-	0.04	0.53	Salamova et al. (2014)
Alert, Canada (2006-2008)	0.74	0.80	-	0.64	-	Xiao et al. (2012)
East Greenland Sea, ship-based (2009)	-	Gas phase: < LOQ Particle phase: < LOQ-0.12	Gas phase: < LOQ-1.7 Particle phase: 0.005-0.05	Gas phase: < LOQ-0.06 Particle phase: < LOQ-0.02	-	Möller et al. (2011a)
Bering/Chukchi Sea, ship-based (2010)	< LOQ	Gas phase: < LOQ-0.36 Particle phase: < LOQ-0.18	Gas phase: 0.1-0.28 Particle phase: < LOQ	Gas phase: < LOQ-0.17 Particle phase: < LOQ	-	Möller et al. (2011b)

* Particle measurements only

Very few data are available for DBDPE in Arctic air (Table 11). The mean DBDPE concentration in atmospheric particles at Svalbard was similar to the lowest concentration in the air samples from Greenland (Figure 6). In a recent study from China, DBDPE exceeded all other NBFRs by at least one order of magnitude, with a mean concentration of 50 pg / m^3 (Liu et al., 2016). However, in the absence of comparable data, it is uncertain whether this observation of DBDPE clearly dominating the NBFR spectrum is also valid for the remote Arctic. At Pallas, DBDPE also had the highest concentrations among the NBFRs (Haglund et al., 2016), but it was much lower than the concentrations measured in Greenland. DBDPE has had the same applications as BDE-209 (Covaci et al., 2011) and might have replaced it since BDE-209 was banned. However, the mean concentration of BDE-209 at Alert was only 1.6 pg / m^3 in 2002-2004 and had decreased to 0.34 pg / m^3 in 2012 (Su et al., 2007; AMAP, 2017).

As discussed for DP (chapter 5.3.1) we are aware of potential risks of local sources and / or contamination during sampling and transport of the samples. However, DBDPE does not follow the same pattern as DP, neither for the monthly samples nor the short-term sampling. The two compounds are not correlated in the samples, suggesting different sources of DBDPE and DP. The field blank that had been shipped to Villum Research Station for quality assurance / quality control purposes contained DBDPE at a level of approximately 0.5 pg / m^3. Thus, it is possible that a background contributes to the overall DBDPE level. If the concentration in this field blank was subtracted from each sample (instead of the concentration in the blank resulting from cleaned quartz filters and PUF / XAD-2 / PUF cartridges at present), the results would become slightly lower, with mean DBDPE concentrations of 2.7 pg / m^3 for the monthly samples and 7.6 pg / m^3 for the short-term sampling. However, these corrected values would still clearly exceed those published by Salamova et al. (2014) and Haglund et al. (2016) for DBDPE. It will thus be important to verify the high DBDPE levels in the air samples from Greenland to establish a more solid Arctic air level.

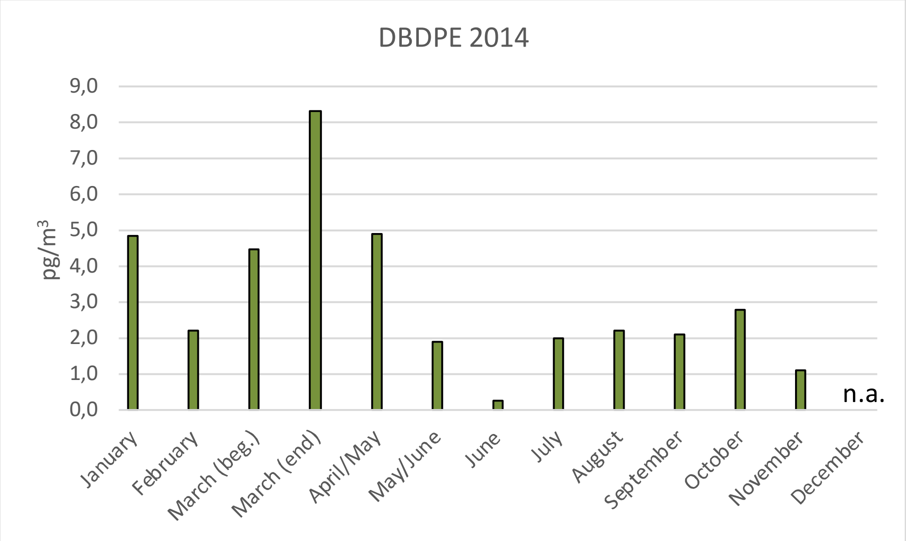


Figure 6. Concentration of decabromodiphenyl ethane (DBDPE) in monthly air samples collected at Villum Research Station in 2014. n.a.: not available.

5.4 Conclusions

DP was detected in some, but not all monthly samples collected at Villum Research Station. The concentrations were comparable to other studies, but maximum concentrations were in the high end of the published range. However, the additional short-term sampling gave reasons to discuss contributions from local sources as these concentrations appeared unusually high.

EH-TBB, BEH-TEBP, DPTE and BTBPE followed a general pattern of somewhat lower concentrations at Villum Research Station than otherwise published for Arctic air. BTBPE was not detected in the air samples from Northeast Greenland. EH-TBB, BEH-TEBP and DPTE were detectable, but at a low level, i.e. < 0.3 pg/m^3 on average. It can thus be concluded that these three compounds are transported to the Arctic, but are not major contaminants in Arctic air. However, indications may exist in our study and the literature of increasing concentrations of EH-TBB and BEH-TEBP in Arctic air. As EH-TBB and BEH-TEBP mainly replace the PentaBDE mixture in the USA (Stapleton et al., 2008), their use and emissions might have increased since the ban of PBDEs. Little is known about the actual use of DPTE, but a recent study on peregrine falcon eggs showed a significant decrease of DPTE between 1986 and 2014 (Vorkamp et al. 2018), further suggesting that DPTE is not a major contaminant in Arctic air.

The concentration of DBDPE clearly exceeded those of the other NBFRs. It also appears higher than the Arctic air concentrations of BDE-209, which it is supposed to replace. As little information is available for comparison of DBDPE levels in Arctic air, these findings warrant verification.

6 Biota

6.1 Samples

Biota samples were analysed to provide information on the potential bioaccumulation of DP and NBFRs (see chapter 3.4). Based on the analogy to POPs accumulating in biota tissue over time and biomagnifying through the food chain, high trophic level animals were selected for the analysis (Table 12). The sampling locations are indicated in Figure 7.

Since the first analyses of DP and NBFRs in wildlife from Greenland (see chapter 3.1), additional samples of ringed seal blubber and glaucous gull liver have been analysed to consolidate the original data set. These samples were collected in East Greenland in 2014 and analysed under the AMAP Core Programme 2014-2016[14] (Table 12). They are included to extend the database of this project and to enable comparisons between different locations.

As a third aspect, samples of land-locked Arctic char were analysed as these chars are mainly exposed to contaminants from atmospheric deposition. To some extent, the lake can also receive contaminants from melting snow, but this can be considered an indirect way of transferring contaminants from the atmosphere to the lake.

Table 12. List of biota samples analysed for dechlorane plus and novel brominated flame retardants.

Species	Latin name	Sampling location	Sampling year	Original sampling purpose	Tissue for analysis	Age/Sex	Number of individuals
Arctic char	*Salvelinus alpinus*	Isortoq	2014	AMAP Core Programme	Muscle	Age unknown/F and M	6
Glaucous gull*	*Larus hyperboreus*	Northwest Greenland ("Thule")	2015	Project "NOW"	Liver	Adult/M	6
Ringed seal	*Phoca hispida*	Northwest Greenland ("Thule")	2014	AMAP Core Programme	Blubber	1-3 years/F and M	6
Harp seal*	*Pagophilus groenlandicus*	Ittoqqortoormiit	2015	Project "UNEXPECTED"	Blubber	Adult/F	4
Hooded seal*	*Cystophora cristata*	Ittoqqortoormiit	2015	Project "UNEXPECTED"	Blubber	Adult/F	4
Bearded seal*	*Erignathus barbatus*	Ittoqqortoormiit	2015	Project "UNEXPECTED"	Blubber	Subadult	5
Narwhal*	*Monodon monoceros*	Ittoqqortoormiit	2015	Project "UNEXPECTED"	Blubber	Subadult/F and M	8
Killer whale*	*Orcinus orca*	Tasiilaq and Kulusuk	2012-2013	Project "PREDATOR"	Blubber	Subadults and adults/F and M	11
Glaucous gull**	*Larus hyperboreus*	Ittoqqortoormiit ("East")	2014	AMAP Core Programme	Liver	Adult/F and M	8
Ringed seal**	*Phoca hispida*	Ittoqqortoormiit ("East")	2014	AMAP Core Programme	Blubber	0-10 years/ F and M	5

* Samples provided by Rune Dietz and Christian Sonne; ** Samples analysed under the AMAP Core Programme 2014-2016.

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[14] DANCEA-project "Long-term monitoring of contaminants in Greenlandic animals and in the atmosphere of Greenland 2014-2016" (MST-112-190)

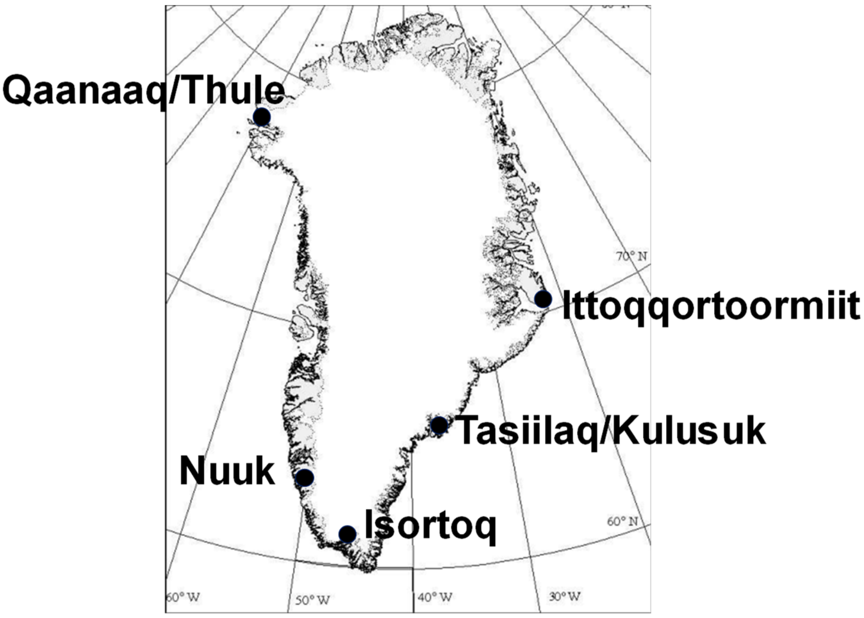

Figure 7. Sampling locations for the biota samples analysed for dechlorane plus and novel brominated flame retardants.

6.2 Chemical analysis

The analysis of DP and NBFRs in the biota samples followed the methods applied in the previous project (chapter 3.1). The homogenized samples were spiked with recovery standards and ^{13}C-BEH-TEBP and Soxhlet extracted using hexane:dichloromethane (1:1). The extracts were split in half for separate clean-up of extracts containing the acid-labile BEH-TEBP (by gel permeation chromatograpy (GPC) and silica) and extracts containing the remaining compounds (by acid silica and aluminium oxide). For the analysis of Arctic char and glaucous gull (Thule), two separate samples were extracted for BEH-TEBP and the remaining compounds, respectively, because of the larger sample intake. Elution was with hexane:dichloromethane (1:1) in both clean-up procedures.

The column clean-up (on acid silica and aluminium oxide) was applied twice to account for the high lipid content of most of the samples. The extracts for GPC clean-up were split into five sub-samples for more efficient lipid removal and re-combined after GPC clean-up. As previous analyses had shown incomplete recovery from the GPC clean-up, some loss of BEH-TEBP had to be expected. To some extent, this can be compensated by the ^{13}C-labelled internal standard, unless the BEH-TEBP residue drops below detection limits. The extracts were originally evaporated to a final volume of 100 µl, but based on evaluations of matrix effects and detectable concentrations, this was increased in subsequent batches. The samples were analysed by GC-MS (ECNI) in the same way as the air samples (chapter 5.2). BEH-TEBP and DBDPE were analysed on a 15 m GC column, while the other compounds were analysed on a 60 m GC column.

The samples of this project were analysed in three batches each containing a blank for GPC and column clean-up, respectively. The glaucous gull and ringed seal samples of the AMAP Core Programme had been analysed in their own batch previously. A small, relatively constant amount of DP was found in all blanks and subtracted from the amount in the samples. The LOQs are given in Table 13, for blubber samples and Arctic char muscle samples analysed in this project. The LOQs differ between these two types of samples because of differences in sample intake and volume of the final extract. The glaucous gull samples have intermediate LOQs. Within the blubber samples, narwhals and killer whales had slightly higher LOQs than the seal species, because of differences in final volume. In these cases of variations between samples, the highest LOQ is given in Table 13.

Table 13. Limits of quantification (LOQs) for dechlorane plus (DP) and the novel brominated flame retardants (NBFRs) in biota samples from Greenland. ww: wet weight

Compound	LOQ blubber (ng/g ww)	LOQ Arctic char muscle (ng/g ww)
Syn-DP	0.059	0.00057
Anti-DP	0.053	0.00052
EH-TBB	0.29	0.0028
BEH-TEBP	0.032	0.026
DPTE	0.059	0.00057
BTBPE	0.11	0.0011
DBDPE	0.59	0.0057

The lipid content of the samples was determined according to Smedes (1999). The dry matter content was determined by drying a sub-sample at 105°C until constant weight.

6.3 Results and discussion

6.3.1 Dechlorane plus

Concentrations in high trophic level animals

The concentrations of DP in biota were generally low and below quantification limits for several species. Only glaucous gull liver had detectable DP concentration in all six samples of this project (Thule) and in all but one sample of the previous analyses (East Greenland)[15]. This also agreed with the first analyses of DP in 2012, in glaucous gull liver from East Greenland (see chapter 3.1), which had also shown detectable DP concentrations in all samples.

Table 14 summarises the outcome of the analyses of DP. The concentrations are normalised to the lipid content of the sample. Neither of the two DP isomers was found in any sample of ringed seal (Thule). In ringed seals (East), Arctic char and narwhals, only the anti-DP isomer was present, which generally occurred in slightly higher concentrations than the syn-DP isomer.

The low concentrations of DP in marine Arctic biota are consistent with other Arctic studies. In glaucous gull samples from the Cape Dorset (Nunavut) in the Canadian Arctic, the maximum detection frequency of DP was 65% in liver samples from 2012 (Verreault et al., 2018). This was the case for males, while the detection frequency was only 21% in females. Mean concentrations were only calculated for male birds, and were 0.18 and 0.16 ng/g wet weight (ww) for syn- and anti-DP. Converted to wet weight, the concentrations in our glaucous gull samples from Thule were 0.012 and 0.049 ng/g ww for syn- and anti-DP, respectively, i.e. even lower than the results from Canada.

DP was only detected sporadically in ringed seals from multiple locations in the Canadian Arctic (Houde et al., 2017). Detectable levels of syn-DP ranged

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[15] The LOQ for this specific sample was about ten times higher than for the other samples because little material was available for analysis. This sample is not included in Table 13.

between 0.04-0.41 ng/g lw, while the detectable range for anti-DP was 0.04-6.3 ng/g lw. The detection frequency was presumably < 20%. Minke whales *(Balaenoptera acutorostrata)* and beluga whales *(Delphinapterus leucas)* from the St. Lawrence Estuary as well as beluga from the Canadian Arctic have also been studied (Simond et al., 2017). In 2013, the mean ΣDP concentration for these three populations was 0.31 (minke whales, St. Lawrence Estuary), 0.44 (beluga, St. Lawrence Estuary) and 1.28 ng/g lw (beluga, Arctic). The highest concentration of 1.28 ng/g lw in the Arctic population was different from the generally observed contaminant distribution, which usually showed higher concentrations at more southern locations, and could not be explained. For comparison, the ΣPBDE concentration in these three populations was 257, 1068 and 276 ng/g lw, respectively (Simond et al., 2017). The authors described that belugas were second in contaminant exposure behind killer whales in Canadian waters. As shown in Table 14, only two individuals of killer whale (detection frequency of 18.2%) had quantifiable levels of anti-DP, roughly in the same order of magnitude as the beluga from St. Lawrence estuary or the Canadian Arctic.

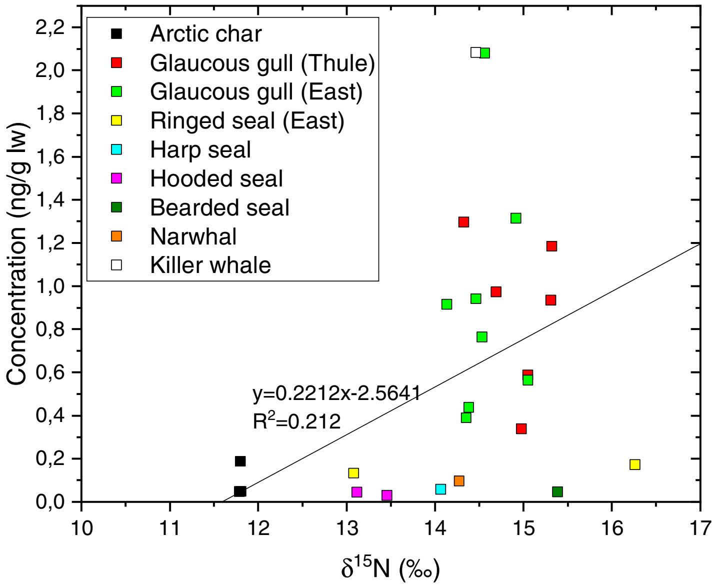
Table 14. Concentrations (ng/g lipid weight) and detection frequencies (DF) of syn- and anti-dechlorane plus (DP) in biota samples from Greenland. Lipids (%) describes mean lipid content of the samples. Concentrations < LOQ were set to 0 in the calculations of means.

Species			syn-DP			anti-DP	
	Lipids (%)	DF (%)	Mean	Range	DF (%)	Mean	Range
Arctic char	0.69	0	<0.13	<0.13	50	0.047	<0.030-0.19
Glaucous gull (Thule)	5.3	100	0.22	0.076-0.35	100	0.89	0.34-1.2
Ringed seal (Thule)	92	0	<0.018	<0.018	0	<0.017	<0.017
Harp seal	95	25	0.008 [a]	<0.018-0.032	25	0.014 [a]	<0.017-0.058
Hooded seal	92	50	0.013 [a]	<0.017-0.033	50	0.019	<0.017-0.045
Bearded seal	88	20	0.004 [a]	<0.017-0.019	20	0.009 [a]	<0.015-0.045
Narwhal	90	0	<0.065	<0.065	12.5	0.012 [a]	<0.039-0.096
Killer whale	98	9.1	0.040 [a]	<0.038-0.44	18.2	0.19	<0.037-2.1
Glaucous gull (East)	5.3	87.5	0.24	<0.55 [b]; 0.079-0.54	100	0.93	0.39-2.1
Ringed seal (East)	90.6	0	<0.014	<0.014	50 [c]	0.076	<0.013-0.17

[a] value near or below detection limits; [b] very low sample intake (0.31 g); [c] detected in two out of four samples, in the fifth sample the peak could not be integrated.

Stable isotope data for nitrogen were available for the samples of this project, allowing an estimation of the relative trophic positions, which the samples represented. Figure 8 shows the quantifiable concentrations of anti-DP as a function of the δ^{15}N data available for the same samples. Anti-DP has been chosen over syn-DP or ΣDP as more results were available for this isomer. Since Figure 8 does not include the concentrations below LOQs, it presents a bias towards higher concentrations. The figures might indicate a tendency towards higher concentrations at higher trophic levels, however, the linear regression line was not significant (p=0.068). A second regression was calculated where all data were used and values below detection limits were estimated statistically, but this regression line had a lower slope and is less likely to be significant (p=0.67).

Figure 8. Quantifiable concentration of anti-dechlorane plus (ng/g lipid weight) in the biota samples of this study, as a function of their δ¹⁵N value, indicating trophic level.



Regarding glaucous gull and Arctic char alone, the concentrations are clearly higher in the higher trophic level glaucous gulls. However, the pinniped and cetacean species do not show the same pattern. Rather than a continuous accumulation and biomagnification in the food chain, these results indicate species-specific bioaccumulation of DP, possibly related to differences in exposure and/or transformation capacity. Of all the species included in this study, only glaucous gull showed a consistent accumulation of DP in their liver tissues.

The previous study, based on samples from 2012, included adipose tissue of polar bear from East Greenland, the apex predator of the Greenland marine food chain. Mean DP concentrations in those samples were 0.025 and 0.065 ng/g lw for syn- and anti-DP, respectively (Vorkamp et al., 2015), i.e. in the lower end of the values shown in Figure 8. Recent analyses of DP in polar bear from the Hudson Bay in Canada, called a contaminant hot spot in the publication, resulted in concentrations below detection limits for DP (Letcher et al., 2018). These findings support the results of this study, of limited or no biomagnification of DP in the Arctic marine food chain. As discussed above, bioaccumulation can occur in some species, furthermore, the proximity to emission sources can play a role in the detection of DP in high trophic level species (de la Torre et al., 2012).

These results of no or limited biomagnification are different from a biomagnification study in a freshwater food web in China where Trophic Magnification Factors (TMFs) of 11.3 and 6.6 were found for syn- and anti-DP, respectively (Wu et al., 2010). The study included different carp species, prawn *(Macrobrachium nipponense)*, water snake *(Enhydris chinensis)* and other freshwater organisms. These TMFs were similar to those for PCBs. Tomy et al. (2007) studied the bioaccumulation and biomagnification of DP in Lake Winnipeg and Lake Ontario in Canada and found differences between isomers as well as between the two lakes. One of the findings for Lake Winnipeg was that anti-DP dominated at high trophic levels, while syn-DP dominated at low trophic levels. In Lake Ontario, the DP concentrations were generally highest in lower trophic level animals. Consequently, no TMF was determined for Lake Ontario. For Lake Winnipeg, the TMF was 2.5 for anti-DP, but < 1 for syn-DP. These two studies, in combination with our results, indicate some complexity in the DP bioaccumulation and biomagnification where ecosystem differences can play a role.

Isomer composition

The fraction of anti-DP in the commercial DP production (Equation 1) ranges between 0.65-0.75 (Sverko et al., 2008; 2011), corresponding to an anti-/syn-DP ratio of about 3. In the glaucous gull samples, the mean f_{anti} was 0.82 ± 0.021 and 0.76 ± 0.062 in samples from Northwest Greenland ("Thule") and East Greenland, respectively. These relative standard deviations are small (2.7 and 8.3%, respectively), indicating the high correlation between the DP isomers. The relative standard deviations of the absolute concentrations were much higher, i.e. 41 and 60% for anti-DP in glaucous gull from Thule and East Greenland, respectively. Due to the low concentrations in the remaining samples, f_{anti} could only be calculated for one sample each of killer whale (f_{anti}=0.82), harp seal (f_{anti}=0.65) and bearded seal (f_{anti}=0.71) as well as for two samples of hooded seal (f_{anti}=0.48 and 0.71).

Our previous study showed an f_{anti} value of 0.83 ± 0.049 for glaucous gull liver from East Greenland (Vorkamp et al., 2015), which is similar to the results obtained here. The other species included in our previous project (ringed seals, polar bears, black guillemot, all from East Greenland) showed mean f_{anti} values of 0.72-0.84 (Vorkamp et al., 2015). All these results are close to the value of the commercial product, but indicate a tendency toward slightly more anti-DP, i.e. a preferred accumulation of anti-DP and/or a degradation of syn-DP. The results for hooded seal do not entirely match this pattern. However, there is only one deviating sample and the concentrations are close to detection limits.

Only few studies of Arctic biota have discussed f_{anti}, mainly because of generally low DP concentrations. Glaucous gull liver from the Canadian Arctic had an f_{anti} value of 0.55 in males (Verreault et al., 2018). The concentrations were lower in females, but also similar for syn- and anti-DP. Whale species from the Canadian Arctic also showed f_{anti} values that were lower than those of the technical mixture (Simond et al., 2017). In a study on terrestrial animals on Svalbard, f_{anti} was 0.66-0.67 for reindeer and birds (Na et al., 2015). As discussed above, biomagnification studies are inconclusive regarding the isomer-specific DP enrichment (Tomy et al., 2007; Wu et al., 2010). Black guillemot eggs from the Faroe Islands showed an f_{anti} value of 0.72 (Schlabach et al., 2011). In other studies reporting low concentrations, anti-DP has often been the only isomer above detection limits (e.g. Huber et al., 2015). The results of our study do not indicate a preferential accumulation of syn-DP in high trophic level marine biota from Greenland, but the overall reports in the literature are inconclusive.

Geographical differences

As mentioned above, spatial differences in DP concentrations were assessed, based on the analysis of the same species from different locations:

a) Glaucous gull liver from Thule and East Greenland

   Glaucous gull liver from East Greenland had been collected in 2012 and 2014 for DP analysis. The results from the 2012 analyses were part of the previous study (Vorkamp et al., 2015). In addition, glaucous gull liver collected in Northwest Greenland in 2015 has been analysed in this study. The mean concentrations and standard deviations for these three groups of samples are shown in Figure 9.

A Wilcoxon rank sum test (α=0.05) was used to test for differences in the DP concentrations between sample groups. No significant difference was found for syn-DP between the 2012 and 2014 samples of glaucous gull from East Greenland, nor between glaucous gull from East Greenland and Northwest Greenland (Thule). For anti-DP, the 2012 concentration at East Greenland was significantly higher than the 2014 concentration, whereas no significant difference was found between the 2014 samples in East Greenland and the 2015 samples from Northwest Greenland (Thule).

Based on these data, the concentration of anti-DP varied more between years than between locations. This appears somewhat surprising, but indicates a relatively uniform geographical presence of DP in the Greenland environment. As discussed above, the DP concentrations in the glaucous gull liver samples from Greenland were exceeded by corresponding samples from the Canadian Arctic by a factor of 5-10 (Verreault et al., 2018).

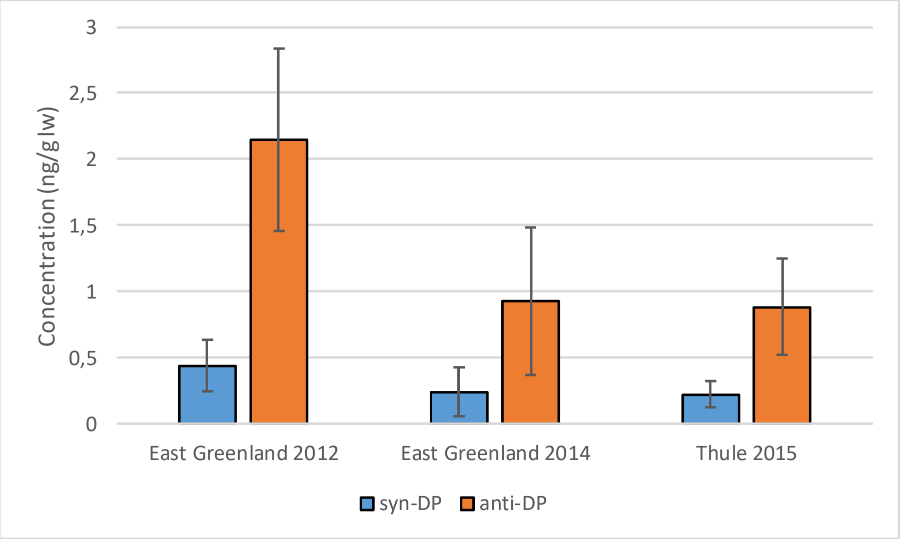


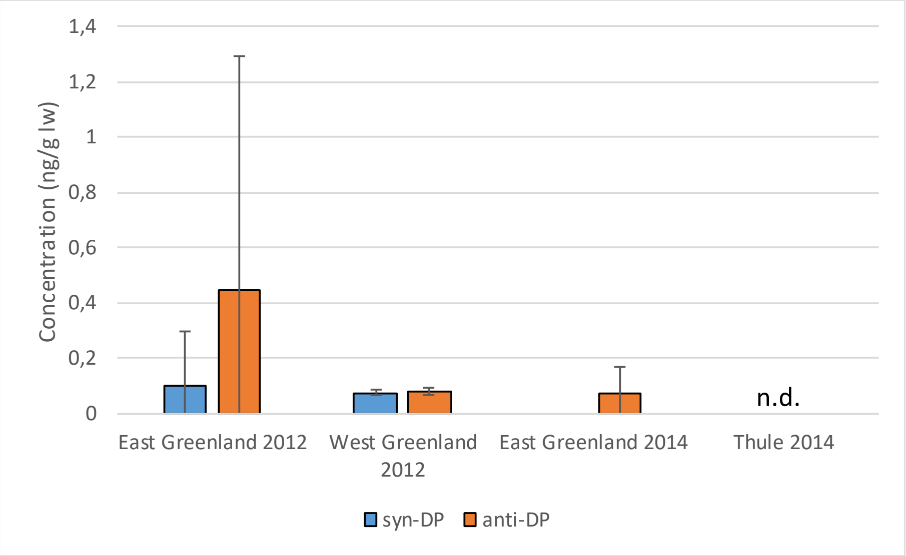
Figure 9. Concentrations and standard deviations of DP-isomers (ng/g lipid weight) in glaucous gull liver samples collected at different locations and time points in Greenland. Concentrations below LOQ are set to zero.

b) Ringed seal blubber from Thule, East and West Greenland

The previous study included ringed seal samples from East and West Greenland collected in 2012, for which DP concentrations could be quantified (Vorkamp et al., 2015). This study included additional ringed seal samples from East Greenland and from Thule, both collected in 2014 (Table 12, Table 14). The results are summarized in Figure 10.

The Wilcoxon rank sum test (α=0.05) did not indicate any statistically significant differences for either syn-DP or anti-DP between the 2012 and 2014 samples from East Greenland, nor between the 2012 samples from East Greenland and West Greenland. Although the mean concentrations from East Greenland 2012 appear higher, their large standard deviations overlap with the concentrations in the other groups. In agreement with the results for glaucous gull, the currently available data for DP do not show any clear spatial differences in marine biota concentrations in Greenland. In a study on ringed seal from Canada, DP was only detected sporadically and no spatial trend could be derived although the study included multiple locations (Houde et al., 2017).

Figure 10. Mean concentrations and standard deviations of DP-isomers (ng/g lipid weight) in ringed seals blubber samples collected at different locations and time points in Greenland. Concentrations below LOQ are set to zero. DP was below LOQ in all ringed seal samples from Northwest Greenland (Thule).



Arctic char as an indicator of atmospheric inputs

As explained above, atmospheric deposition is the main source of contaminants for landlocked Arctic char in a small lake in Southwest Greenland (Rigét et al., 2010). Thus, the contaminant concentrations in landlocked Arctic char are largely indicative of atmospheric contaminant inputs. Additional contaminant sources may exist from melting snow, which also originate from atmospheric deposition.

As shown in Table 14, syn-DP was below quantification limits in all samples of Arctic char analysed in this study. Anti-DP was detected in three out of six samples, at a range of 0.047-0.188 ng/g lw (0.00033-0.00083 ng/g ww). Arctic char from the Faroe Islands (one sample pooled of 12 individuals) had DP levels below detection limit, i.e. < 0.004 ng/g ww (Schlabach et al., 2011). These results are consistent with the findings from Greenland.

The low levels in the Arctic char do not indicate a strong atmosphere input of DP although they are no clear proof of the opposite as DP could in principle be biotransformed in the fish. Assuming limited DP degradation, these results do not support the relatively high DP concentrations that have been found in some air samples (chapter 5.3.1) and that might be influenced by local emission sources or contamination.

In summary, the levels of DP are close to or below limits of quantification in all species included in this study, with the exception of glaucous gull. Thus, they indicate species-specific bioaccumulation of DP rather than food-chain biomagnification. Based on analyses of glaucous gulls and ringed seals, the data indicate a relatively uniform occurrence of DP in marine biota from Greenland, although the low concentrations make comparisons difficult. DP was detectable in Arctic char from a lake receiving contaminants mainly via atmospheric deposition, however, the levels were very low as well and only above LOQs in some samples.

6.3.2 Novel brominated flame retardants

The concentrations of NBFRs in the samples of this project are summarized in Table 15 for EH-TBB and BEH-TEBP and in Table 16 for DPTE, BTBPE and DBDPE. EH-TBB and BEH-TEBP are combined because these compounds are used together in the Firemaster 550 and Firemaster 600 products (Ma et al., 2012; Phillips et al., 2017). The lipid content of the samples was given in Table 14.

Concentrations of EH-TBB and BEH-TEBP in high trophic level animals

EH-TBB could not be quantified in glaucous gull liver and killer whale blubber because an interfering peak in the chromatogram could not be separated from the peak for EH-TBB in these samples. It was possible to quantify EH-TBB in the glaucous gull liver samples from East Greenland (Table 15).

Likewise, the quantification of BEH-TEBP was uncertain in the glaucous gulls from Thule, but the absence of BEH-TEBP was in line with the results from East Greenland. As explained in chapter 6.2, the analysis of BEH-TEBP was particularly challenging because the compound is not stable during the commonly used acid treatment of the samples. Therefore, an alternative clean-up method was used, with higher losses of the target compound. This can be compensated by the use of a ^{13}C-labelled standard, but requires that the loss is so small that the originally low amount in the sample does not drop below detection limits. In addition, the LOQs for BEH-TEBP are slightly higher than for the other NBFRs (Table 13).

Table 15. Concentrations (ng/g lipid weight) and detection frequencies (DF) of EH-TBB and BEH-TEBP in biota samples from Greenland. Concentrations < LOQ were set to 0 in the calculations of means. n.a.: not available.

Species	EH-TBB			BEH-TEBP		
	DF (%)	Mean	Range	DF (%)	Mean	Range
Arctic char	n.a. [a]	0.34 [a]	0.26; 0.42 [a]	100	1.06	0.37-2.7
Glaucous gull (Thule)	n.a. [b]	n.a. [b]	n.a. [b]	0 [c]	<0.023 [c]	<0.023
Ringed seal (Thule)	100	0.15	0.095-0.23	100	0.12	0.072-0.18
Harp seal	100	0.18	0.14-0.26	100	0.099	0.069-0.15
Hooded seal	100	0.76	0.49-0.86	100	0.17	0.059-0.35
Bearded seal	80	0.11	<0.10-0.23	100	0.074	0.057-0.093
Narwhal	100	5.1	2.8-8.9	62.5	0.12	<0.0087-0.24
Killer whale	n.a. [b]	n.a. [b]	n.a. [b]	45.5	0.063	<0.0081-0.38
Glaucous gull (East)	100	8.6	1.9-21	0	<0.24	<0.24
Ringed seal (East)	100	1.5	0.19-5.5	20	0.023	<0.029-0.12

[a] The compound could only be quantified in two out of six samples, because of interferences in the chromatogram. The concentration was above LOQ in these two samples. [b] The compound could not be quantified because of interferences in the chromatogram. [c] Uncertain because of chromatographic difficulties.

Despite the analytical difficulties, the results for BEH-TEBP document generally low levels of this compound in Arctic marine biota, while the levels of EH-TBB were higher, in particular for narwhal, glaucous gull and ringed seal (East). The same ringed seal samples (East) had been analysed for a number of other POPs. For comparison, the mean concentrations of BDE-47 and BDE-99 in the same samples were 27 and 1.6 ng/g lw. The mean concentration of hexachlorobenzene (HCB) was 9.22 ng/g lw, while PCBs had much higher concentrations (mean concentration of CB-153: 200 ng/g lw).

EH-TBB and BEH-TEBP have been included in multiple Arctic studies, but with diverse results. Both compounds were undetectable in Greenland shark, seabird eggs from Northern Norway and polar bears from Canada (Strid et al., 2013; Huber et al., 2015; Letcher et al., 2018). In Arctic char from the Faroe Islands, EH-TBB and BEH-TEBP were the NBFRs with the highest concentrations, i.e. 0.011 and 0.0031 ng/g ww, respectively (Schlabach et al., 2011). The wet weight-based mean concentrations in Arctic char of our study were slightly lower than that, i.e. 0.0026 and 0.0065 ng/g ww for EH-TBB and BEH-TEBP, respectively.

In ringed seals from Canada, EH-TBB had the second highest detection frequency (23%) amongst NBFRs and a maximum concentration of 1.1 ng/g lw (Houde et al., 2017), which is roughly comparable to the results of this study. For BEH-TEBP, the detection frequency in the ringed seals from Canada was 19%, and the maximum concentration was 3.2 ng/g lw. However, most of the detectable concentrations were <0.5 ng/g lw, which is similar to the results from Greenland.

Similar levels were also reported for EH-TBB in glaucous gulls from Canada, while the results for BEH-TEBP were different (Verreault et al., 2018): Detection frequencies of EH-TBB were 36 and 47% in liver of female and male birds, respectively. Maximum concentrations were 0.92 and 0.85 ng/g ww in females and males, respectively. Converted to ng/g ww the mean concentration in glaucous gull (East) was 0.46 ng/g ww, and the maximum concentration was 1.2 ng/g ww. BEH-TEBP had lower detection frequencies (21 and 12% for females and males, respectively), but higher maximum concentrations of 2.1 and 2.6 ng/g ww, respectively. In our study, BEH-TEBP could not be quantified in any sample of glaucous gull liver (Table 15).

In a study from Svalbard, EH-TBB had detection frequencies of 90-100% in capelin *(Mallotus villosus)*, common eider *(Somateria mollissima)* (liver), Brünnich's guillemot *(Uria lomvia)* (eggs), kittiwake *(Rissa tridactyla)* (liver), ringed seal (liver) and polar bear (plasma) (Sagerup et al., 2010). The mean concentration in ringed seal liver was 0.44 ng/g ww (13 ng/g lw). In polar bear, the mean concentration of EH-TBB was 3.5 ng/g ww (415 ng/g lw). BEH-TEBP was undetectable in polar bear plasma, and the detection frequency in the other species ranged between 50-90%. The concentration of BEH-TEBP in ringed seal liver was 0.57 ng/g ww (17 ng/g lw). A second study from Svalbard did detect BEH-TEBP in polar bear plasma (0.15 ng/ml; 16.5 ng/g lw) (Harju et al., 2013). Furthermore, BEH-TEBP was also found in ringed seal plasma, at a concentration of 0.04 ng/ml (5.7 ng/g lw). These lipid-normalised concentrations in ringed seal were considerably higher than the ringed seal concentrations in our study, but they are based on liver and plasma, while blubber was analysed in our study.

Figure 11 shows the measured concentrations of EH-TBB as a function of $\delta^{15}N$, which characterizes the trophic level of the species. Due to the low levels of EH-TBB in bearded seals and ringed seals (East), which have a high trophic level, there is no significant increase of EH-TBB with trophic level. The Norwegian report highlighted the large increase in EH-TBB concentration from ringed seal to polar bear (by a factor of 30), which could indicate biomagnification (Schlabach et al., 2011). On the other hand, there was no increase from capelin to its predatory species (Brünnich's guillemot, kittiwake and ringed seal). Polar bear adipose tissue was analysed in our previous study and contained EH-TBB at a level of 0.12 ng/g lw, i.e, much lower than the levels reported from Svalbard and lower than the mean concentration in ringed seals (Table 15). In vitro experiments with human liver and rat microsomes have shown a rapid metabolisation of EH-TBB to 2,3,4,5-tetrabromobenzoic acid (TBBA) (Roberts et al., 2012), as also discussed in chapter 7.

Figure 11. Concentrations of EH-TBB (ng/g lipid weight) in the biota samples of this study, as a function of their δ15N value, indicating trophic level.

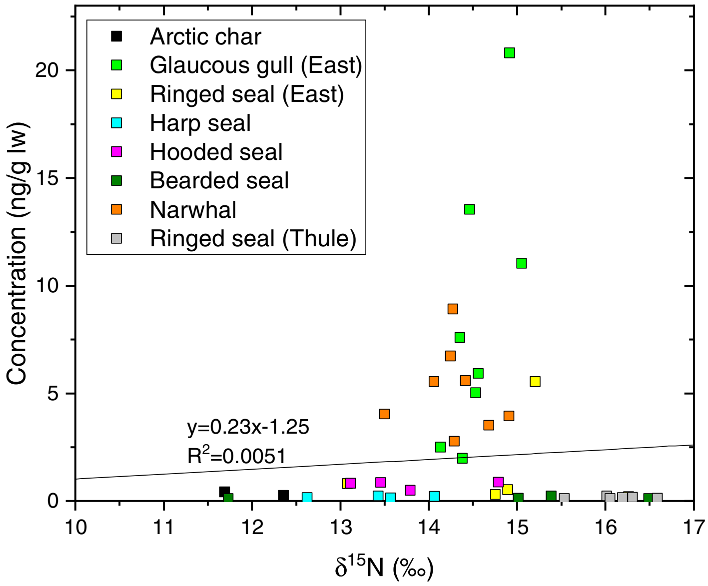
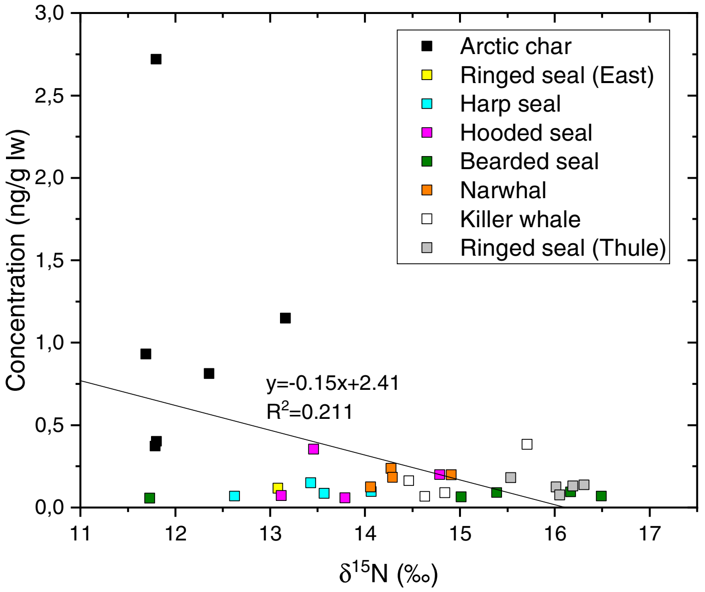


Table 15 shows the highest lipid-normalised concentrations of BEH-TEBP in Arctic char muscle. This is also illustrated in Figure 12 where the concentrations decrease with increasing position in the food chain, compared with Arctic char. Figure 12 only includes the detectable concentrations, but adding the concentrations below LOQ as zero will not change the result much. A similar result of indications of decreasing concentrations of BEH-TEBP towards higher trophic levels was also reported from Norway, however, with the caveat of no significant trend (Sagerup et al., 2010). BEH-TEBP is a brominated analog of di(ethylhexyl)phthalate (DEHP), and phthalates are known to be metabolized to monoesters (Koch and Calafat, 2009). *In vitro* studies with human liver and rat microsomes have shown this reaction for BEH-TEBP as well, however, it was slower than for DEHP (Roberts et al., 2012). Toxicity is further discussed in chapter 7.

Figure 12. Quantifiable concentrations of BEH-TEBP (ng/g lipid weight) in the biota samples of this study, as a function of their δ15N value, indicating trophic level.



Geographical differences of EH-TBB and BEH-TEBP

As described in chapter 6.3.1, glaucous gull and ringed seal samples were analysed from two and three locations, respectively: Glaucous gull samples were available from East Greenland (2012 and 2014) and Thule (2015), while ringed seal samples were available from West Greenland (2012), East Greenland (2012 and 2014) and Thule (2014). The samples from 2012 were included in the previous study (Vorkamp et al., 2015). The results for EH-TBB and BEH-TEBP in ringed seals are shown in Figure 13. For glaucous gull, no spatial difference could be analysed as it had not been possible to integrate the peak for EH-TBB in samples from Thule, leaving only samples from East Greenland (2012 and 2014).

The previous study had indicated higher concentrations of EH-TBB in ringed seals from East Greenland than from West Greenland (Vorkamp et al., 2015), which seems to be confirmed by the additional data from 2014. A Wilcoxon rank sum test ($\alpha=0.05$) did not indicate any statistically significant differences between EH-TBB in ringed seals from East Greenland collected in 2012 and 2014 ($p=0.22$). The concentration in ringed seals from Thule is similar to that from West Greenland.

BEH-TEBP could not be detected in the previous study, however, detection limits were slightly higher (Vorkamp et al., 2015). The current data indicate relatively low levels of BEH-TEBP in ringed seals from East Greenland. However, as mentioned above, the results are probably more uncertain for this compound because of challenges with the chemical analyses.

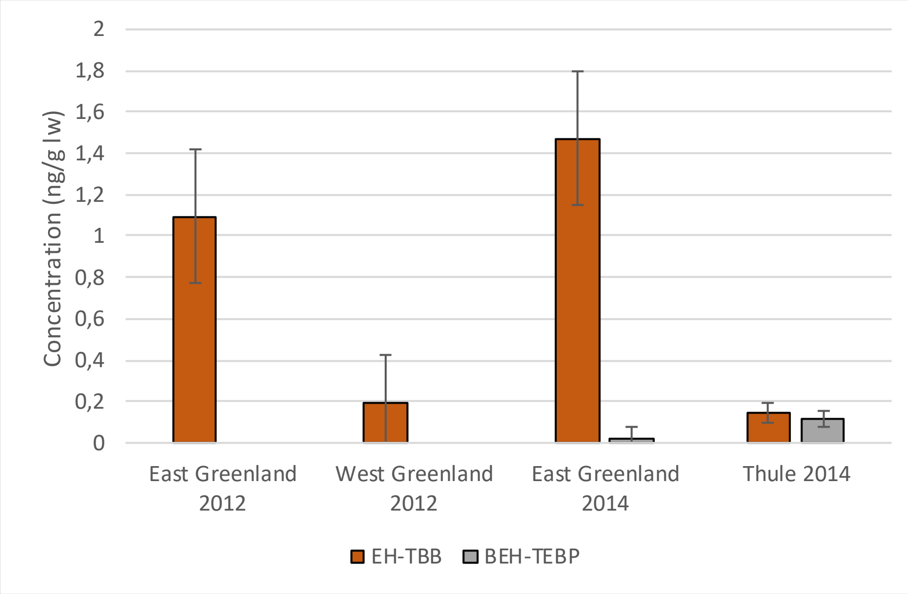


Figure 13. Concentrations of EH-TBB and BEH-TEBP (ng/g lipid weight) in ringed seal from different locations in Greenland.

Arctic char as an indicator of atmospheric inputs of EH-TBB and BEH-TEBP

Both compounds could be detected in Arctic char. As discussed above, the concentrations are similar to, but slightly lower than those detected in Arctic char from the Faroe Islands (Schlabach et al., 2011). Lipid-normalised concentrations of BEH-TEBP were higher in Arctic char than in the other species of this study. These results suggest an atmospheric input of EH-TBB and BEH-TEBP into the lake system and an uptake by freshwater fish.

The presence of EH-TBB and BEH-TEBP in air samples was shown in this study (Table 10). These concentrations were relatively low compared to studies from the Canadian Arctic and Svalbard (Table 11). However, the samples originated from Villum Research Station in Northeast Greenland and might thus not be representative of the region in Southwest Greenland where the Arctic char samples had been collected.

Concentrations of DPTE, BTBPE and DBDPE in high trophic level animals

The results for DPTE, BTBPE and DBDPE are summarised in Table 16. DPTE was detected in all species, but not in all individuals of glaucous gull (Thule) and the four seal species. In contrast to the samples from Thule, DPTE was detectable in the glaucous gull and ringed seal samples from East Greenland, as they had also been in the previous project (Vorkamp et al., 2015). BTBPE could not be quantified in glaucous gull samples from Thule because of chromatographic problems, which was also the case for EH-TBB (Table 15). BTBPE was also detected in all species, but not all individuals, and killer whales had relatively high concentrations of BTBPE. DBDPE was detected less frequently, but also has higher LOQs. It was not detected in any species of narwhal, hooded seal or ringed seal (East).

Table 16. Concentrations (ng/g lipid weight) and detection frequencies (DF) of DPTE, BTBPE and DBDPE in biota samples from Greenland. Concentrations < LOQ were set to 0 in the calculations of means.

Species	**DPTE**			**BTBPE**			**DBDPE**		
	DF (%)	**Mean**	**Range**	**DF (%)**	**Mean**	**Range**	**DF (%)**	**Mean**	**Range**
Arctic char	100	0.18	0.067-0.34	100	0.33	0.16-0.59	100	3.2	1.8-5.9
Glaucous gull (Thule)	83.3	0.22	<0.016-0.54	n.a. [a]	n.a. [a]	n.a. [a]	33.3	0.13	<0.16-0.56
Ringed seal (Thule)	33.3	0.0094	<0.017-0.030	50	0.022	<0.016-0.063	50	0.20	<0.17-0.68
Harp seal	50	0.0092	<0.018-0.037	50	0.0093	<0.018-0.037	100	0.77	0.43-1.6
Hooded seal	50	0.011	<0.017-0.022	100	0.050	0.022-0.099	0	<0.20	<0.20
Bearded seal	40	0.0085	<0.016-0.024	40	0.022	<0.016-0.091	80	0.29	<0.18-0.52
Narwhal	100	0.50	0.16-0.79	50	0.035	<0.042-0.083	0	<0.64	<0.64
Killer whale	100	0.47	0.14-1.1	100	3.2	1.2-6.3	9.1	0.037	0.41 [b]
Glaucous gull (East)	100	0.88	0.28-2.9	25	0.13	<0.16-0.56	25	0.24	0.87; 1.0
Ringed seal (East)	100	0.095	0.066-0.14	60	0.024	<0.014-0.079	0	<0.28	<0.28

[a] The compound could not be quantified because of interferences in the chromatogram. [b] Only quantifiable in one individual.

Our results show that DPTE and BTBPE are widely present in marine biota from Greenland, but at relatively low levels. DBDPE is detected more sporadically, possibly influenced by slightly higher detection limits. Arctic char from the Faroe Islands had DPTE and DBDPE concentrations below detection limits (Schlabach et al., 2011). However, BTBPE was detected at a level of 0.012 ng/g ww, which was about 5 times higher than our mean concentration (0.0024 ng/g ww). Likewise, DPTE was below detection limits in all the species (capelin, common eider, Brünnich's guillemot eggs, kittiwake, ringed seal and polar bear plasma) of the Norwegian study, while BTBPE and DBDPTE were detected in 40 and 10%, respectively, of Brünnich's guillemot eggs (0.66 and 0.58 ng/g ww, respectively) (Sagerup et al., 2010).

BTBPE and DBDPE were below detection limits in glaucous gull liver from the Canadian Arctic (Verreault et al., 2018). In a previous study on glaucous gull samples from Svalbard, detection frequencies in egg yolk and plasma were 29 and 5%, respectively, and the maximum concentrations were 0.96 and 0.26 ng/g ww (Verreault et al., 2007). The maximum concentration of BTBPE in our study was 0.025 ng/g ww for glaucous gull liver from East Greenland, i.e. lower by an order of magnitude provided that it can be compared with the results for plasma and eggs. BTBPE had a mean concentration of 0.61 ng/g lwin Greenland shark from waters around Iceland, while DPTE was undetectable and DBDPE was not included in that study (Strid et al., 2013). All three compounds were undetectable in polar bears from Canada (Letcher et al., 2018).

Studying ringed seals from multiple locations around Canada, Houde et al. (2017) detected DPTE and BTBPE in 18 and 11% of the samples, respectively, at a range of 0.02-0.2 and < 1 ng/g lw, respectively. This is very similar to the results of this study (Table 16). In contrast to these findings, levels in harp seal blubber and brain, for animals from the Barents Sea and Greenland Sea, were 322-470 and 130-340 ng/g ww, respectively (von der Recke and Vetter, 2007).

Relatively high concentrations of DBDPE were reported for seabirds from Northern Norway, i.e. 0.36-1.5 ng/g ww. Furthermore, the detection frequency of DBDPE was 100% in polar cod, common eider and kittiwake eggs as well as glaucous gull, ringed seal and polar bear plasma, all from Svalbard (Harju et al., 2013). The concentrations in the plasma samples were 460, 765 and 775 ng/g lw for glaucous gull, ringed seal and polar bear, respectively, and thus higher than concentrations of BDE-47. In addition, indications of biomagnification were found for DBDPE (Harju et al., 2013).

Figure 14 shows the quantifiable DBDPE concentration in the biota samples of this project, as a function of their $\delta^{15}N$ content. The figure does not contain the samples below the limit of quantification, as explained for DP in chapter 6.3.1. Unlike the Norwegian results (Harju et al., 2013), the concentration does not increase with increasing $\delta^{15}N$ content of the samples. It has to be noted that the samples of this project do not present a coherent food chain, which they do in the study by Harju et al. (2013). As such, the studies are not directly comparable. No corresponding figures are shown for DPTE and BTBPE, as the trend line in the figures was close to a horizontal line, not showing any relationship between $\delta^{15}N$ content and NBFR concentration.

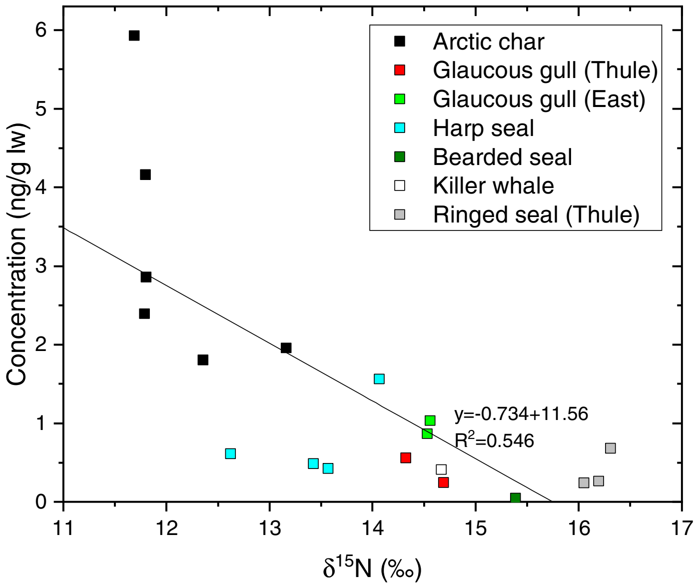
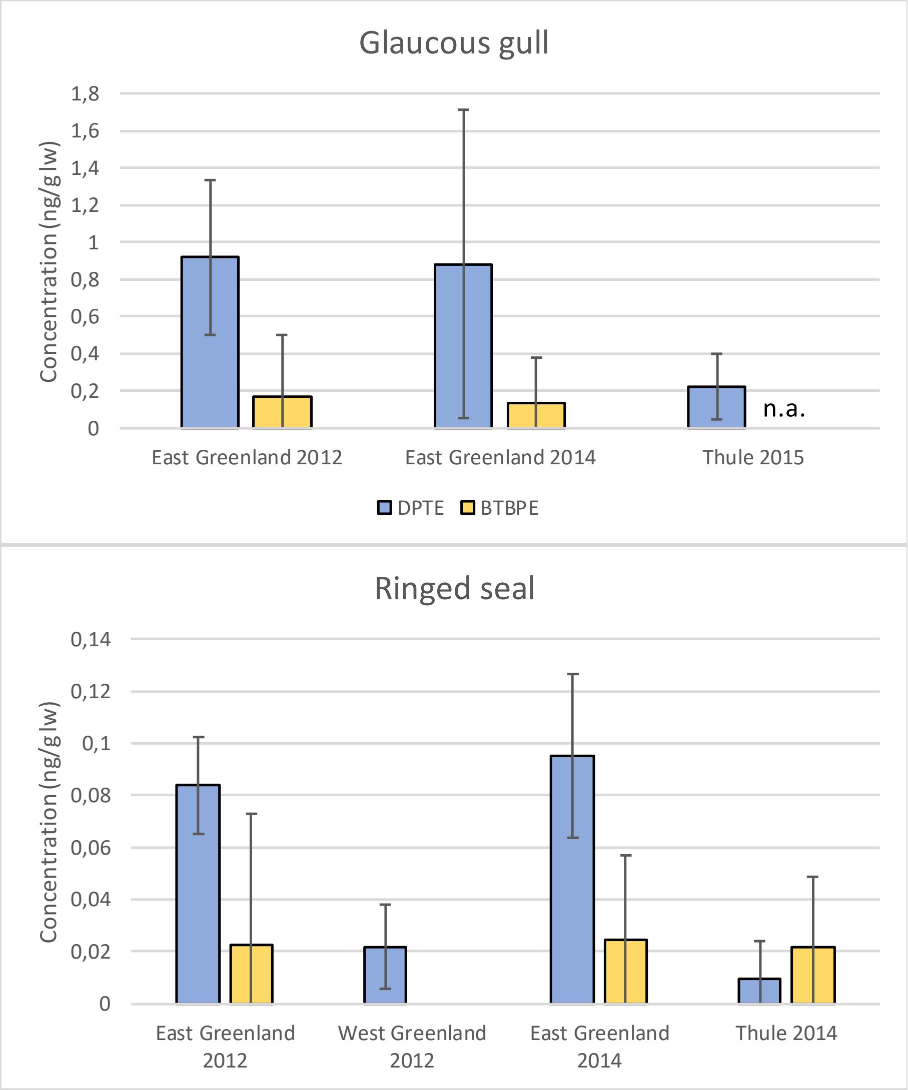


Figure 14. Quantifiable concentrations of DBDPE (ng/g lipid weight) in the biota samples of this study, as a function of their $\delta^{15}N$ value, indicating trophic level.

Geographical differences of DPTE, BTBPE and DBDPE

The concentrations of DPTE and BTBPE in ringed seal and glaucous gull from different locations in Greenland are shown in Figure 15. DBDPE is not included in the figure because of its low detection frequencies (Table 16). The lipid-normalised concentrations were higher in glaucous gull than in ringed seals.

Figure 15. Concentrations of DPTE and BTBPE (ng/g lipid weight) in ringed seal and glaucous gull from different locations in Greenland. BTBPE could not be determined in glaucous gull samples from Thule because of chromographic interferences (n.a.: not available).



A Wilcoxon rank sum test (α=0.05) did not indicate any statistically significant differences between DPTE in glaucous gull from East Greenland collected in 2012 and 2014 (p=0.44). The same was the case for DPTE in ringed seals (p=0.84) and for BTBPE in glaucous gull (p=0.46) and ringed seal (p=0.10). BTBPE was not detectable in ringed seals from West Greenland (2012). These samples had significantly lower DPTE concentrations than the ringed samples from East Greenland (Vorkamp et al., 2015).

The Wilcoxon rank sum test (α=0.05) indicated statistically significant differences between DPTE in glaucous gull samples from Thule and East Greenland ($p < 0.05$). No difference was seen for BTBPE in ringed seals (p=0.10). In terms of spatial differences, the results for DPTE are similar to those for EH-TBB. BTBPE on the other hand was more similar to DP, showing relatively uniform concentrations for all locations.

Arctic char as an indicator of atmospheric inputs of DPTE, BTBPE and DBDPE

All three compounds had a detection frequency of 100% in Arctic char indicating inputs of these compounds to the freshwater system and uptake in the foodchain. DBDPE had the highest concentrations in Arctic char of all the NBFRs and DP analysed in this study. DPTE and BTBPE also had higher concentrations in Arctic char than observed for DP.

A previous study on Arctic char from the Faroe Islands reported the following concentrations for DPTE, BTBPE and DBDPE, respectively: <0.0042, 0.012 and <0.16 ng/g ww (Schlabach et al., 2011). Based on wet weight, the mean BTBPE concentrations of our study was 0.0024 ng/g ww, which is lower than the results from the Faroe Islands. The DPTE and DBDPE concentrations of our study (0.0012 and 0.021 ng/g ww, respectively) are consistent with values below the detection limits of the Faroese study.

As discussed in chapter 5.3.2, the air measurements at Villum Research Station resulted in relatively high levels of DBDPE in air, exceeding previously published concentrations and warranting verification. However, they could be consistent with the findings of DBDPE present and accumulating in Arctic char from a lake receiving contaminants from Arctic air. More data will be needed to establish these links, which remain only indicative at present.

6.4 Conclusions

DP and NBFRs have been analysed in various animals from Greenland, including high trophic level species. In general, the levels were relatively low, i.e. clearly below those typically measured for POPs in the same or similar samples. Detection frequencies were below 100% in several combinations of species and compounds.

The results for DP were comparable to data available for some of the same species (e.g. ringed seals, glaucous gull, Arctic char) from other locations in the Arctic. The concentrations of DP in glaucous gulls exceeded those in other species. Thus, no clear increase of lipid-normalised concentration with increasing trophic level, which would indicate biomagnification, has been found, but indications exist of bioaccumulation in certain species, such as glaucous gull.

Similarly, EH-TBB showed relatively high concentrations (a few ng/g lw) in some species, such as narwhal and glaucous gull, but not for all species. Since a Norwegian study found increases in EH-TBB concentration from ringed seal to polar bear, a different approach involving prey-predator species might reach different conclusions. Likewise, a study from Norway reported BEH-TEBP in ringed seal and polar bear plasma in much higher concentrations than observed in their blubber or fat tissue. Our study suggested low concentrations of BEH-TEBP in high trophic animals. For both BEH-TEBP and DBDPE, highest lipid-normalised concentrations were found in Arctic char. The biomagnification reported for DBDPE from Svalbard was not found here, but differences in study design might play a role. DPTE and BTBPE were found consistently in nearly all samples, but at relatively low levels.

The comparison of different locations indicated higher concentrations of EH-TBB and DPTE in East Greenland than in Northwest Greenland, but a more uniform occurrence of DP and BTBPE. BEH-TEBP and DBDPE could not be assessed in the same way because of lower detection frequencies.

The detection of nearly all the compounds in Arctic char is an interesting observation that relates back to the occurrence of these compounds in air and their long-range transport. The levels in Arctic char are comparable to or lower than those reported for Arctic char from the Faroe Islands. The detection frequency of DP in Arctic char was lower than those of NBFRs, for which our study indicates atmospheric transport and deposition. In summary, DP and the NBFRs do not form a uniform picture in terms of their occurrence in Greenland wildlife. Their current concentrations in Arctic biota are generally low, with exceptions for some compounds in some species.

7 PBT review

7.1 Introduction

Data regarding the PBT status of DP and the NBFRs are generally sparse and disperse. This chapter presents a compilation of reviews undertaken by international regulatory bodies or other organizations. Table 17 summarizes the sources that have been included.

Table 17. Documents and databases searched for PBT information on dechlorane plus (DP) and novel brominated flame retardants.

Compound	EU registration[16]	ECHA Annex XV[17]	USEPA TSCA Reports[18, 19]	TOXNET[20]	Canada
DP	√	√		√	√[21]
EH-TBB			√		√[22]
BEH-TEBP	√		√	√	√[22]
DPTE	√[23]				
BTBPE	√[24]			√	
DBDPE	√			√	√[25]

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[16] https://echa.europa.eu/web/guest/information-on-chemicals/registered-substances

[17] Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57. https://echa.europa.eu/documents/10162/2b729df8-a54f-1485-f77b-185457d96fbd

[18] USEPA TSCA Report 740-Q1-4002. TSCA Work Plan Chemical. Technical Supplement - Use and exposure of the brominated phthalates cluster (BPC) chemicals. https://www.epa.gov/sites/production/files/2015-09/documents/bpc_data_needs_assessment_technical_supplement_use_and_exposure_assessment.pdf

[19] USEPA USEPA TSCA Report 740-Q1-4003. TSCA Work Plan Chemical. Technical Supplement – Hazard assessment of the brominated phthalates cluster (BPC) chemicals. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100N3UC.PDF?Dockey=P100N3UC.PDF

[20] TOXNET database; US National Library of Medicine. https://toxnet.nlm.nih.gov

[21] Draft Screening Assessment Report of the Government of Canada (for dechlorane plus) http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=FDE6572D-1

[22] Draft State of the Science Report of the Government of Canada (for EH-TBB and BEH-TEBP) http://www.ec.gc.ca/ese-ees/844D1EBA-1839-4857-A796-0CBDDDB3E38C/DSOS_OFRs%20%28TBB-TBPH%29_EN_octobre2016.pdf

[23] Not registered, but included in an Annex III inventory (DPTE): https://echa.europa.eu/en/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.047.596

[24] Not registered, but included in an Annex III inventory (BTBPE): https://echa.europa.eu/en/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.048.794

[25] Draft Screening Assessment Report of the Government of Canada (for DBDPE) http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=926BF22A-1

We focused on the following regulatory assessments and databases:

- ECHA registrations;
- the ECHA Annex VI assessment of DP as a potential Substance of Very High Concern (ECHA, 2017);
- two USEPA Technical Substances Control Act (TSCA) reports addressing EH-TBB and BEH-TEBP (USEPA, 2015a; 2015b);
- the USEPA TOXNET database including the Hazardous Substances Data Bank (HSDB) and the High Production Volume Information System (HPVIS) and
- reports of the Government of Canada, produced by Environment and Climate Change Canada and Health Canada (Canada, 2016a; 2016b; 2016c).

BTBPE is listed on the Domestic Substance List of Canada, but no further information could be found. The Government of Canada issued a request for information on BTBPE in 2001, 2009 and 2017 (Canada, 2001; 2009; 2017). In addition to the review of the PBT status of the compounds, based on these assessments and databases, we will briefly present their toxicogenomic profile in terms of possible health impacts on mammals.

7.2 PBT review results

Below are the results for the PBT review based on the sources in Table 17. In the column to the right ("Conclusion"), we have added our conclusion for each compound, based on the data summarized in the tables.

Table 18. Summary of evaluations of persistence (P) for dechlorane plus (DP) and novel brominated flame retardants. EH-TBB and BEH-TEBP were assessed together in the Canadian document. vP: very persistent; (v)B: (very) bioaccumulative; T: toxic

Compound	EU registration	ECHA Annex XV	USEPA TSCA Reports	TOXNET (USEPA)	Government of Canada	Conclusion
DP	An autonomous expert panel determined the substance to be vPvB based on weight-of-evidence, but this conflicts with the manufacturer's analysis. The manufacturer is compelled to acknowledge the conclusion of the expert panel and will manage the substance as if it were a PBT / vPvB.	The European Chemical Agency has classified DP as vP (ECHA, 2018).	Not included (see Table 17)	Hazardous Substance Data Bank (HSDB): Various degradation tests in sewage sludge inoculated water and soil. Based on these screening test results, biodegradation is expected to be very slow in the environment (aerobic and anaerobic). Not expected to undergo hydrolysis due to the lack of functional groups that can hydrolyze under environmental conditions. DP does not contain chromophores that absorb at wavelengths > 290 nm and is therefore not susceptible to photolysis by sunlight. Indications exist that some high trophic level species can degrade DP. High Production Volume Information System (HPVIS): Same conclusions; photodegradation half-life is 24 years in water.	Model predictions support experimental findings that aerobic and anaerobic biodegradation of DP is very limited and that DP is expected to be persistent in water, soil, and sediment. Modelled predictions for DP persistence in air are not consistent, and suggest a half-life < 0.5 day for photolysis and a half-life of 160 days for ozone reaction. However, DP sorption to airborne particles is expected, which would lower the photolysis rate and result in a longer half-life in air. An overall persistence (P_{ov}) of 260 days is predicted by the OECD POPs tool.	vP
EH-TBB	Not registered	Not included (see Table 17)	2-Ethyl-1-hexanol[26] and 2,3,4,5-tetrabromobenzoic acid[27] are main dissipation products.	No entry in HSDB or HPVIS. Some information available under BEH-TEBP (e.g. biodegradation to 2,3,4,5-tetrabromobenzoic acid).	Consideration of the empirical lines of evidence for hydrolysis, photodegradation, and biodegradation gives an overall expectation for persistent behaviour	Indications of P

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[26] CAS number 104-76-7

[27] CAS number 27681-13-1

			EH-TBB has been detected in ambient air at remote locations.		of EH-TBB and BEH-TEBP in the environment. The empirical abiotic hydrolysis data corroborates with the notion of slow hydrolysis due to steric hindrance and sparing water solubility. Photodegradation was only directly studied in hydrogen atom donating organic solvents as opposed to a more environmentally relevant aquatic system. The empirical data also suggest an overall low biodegradation potential of EH-TBB and BEH-TEBP. Generally, model predictions neither fully support nor refute the empirical findings that biodegradation of EH-TBB and BEH-TEBP is limited. Considering all lines of evidence, EH-TBB and BEH-TEBP are expected to be persistent in water, soil, and sediment. Regarding the gas-phase, sorption to fine particulates, resulting in greater persistence, and consequent atmospheric transport, is a potential explanation for the presence of these compounds in the Canadian North despite short predicted half-lives in the gas phase. Metabolites of EH-TBB and BEH-TEBP are likely to be similarly persistent.	
BEH-TEBP	Decision deferred on the substance from the list of potential PBT or vPvB substances.[28] Substance included in the Community Rolling Action Plan (CoRAP) (ECHA, 2019). The substance is hydrolytically unstable showing half-lives at 50°C of 30 hours at pH 4, 44 hours at pH 7 and 78 hours at pH 9. One transformation product was identified as tetrabromophthalic acid.	Not included (see Table 17)	BEH-TBEP has been detected in ambient air at remote locations.	HSDB: Expected to be degraded by sunlight on soil surfaces and in water. Expected to hydrolyze in soil and water under basic conditions. Not expected to be degraded by microbes. Hydrolysis of BEH-TEBP is expected to be important, based on calculated hydrolysis half-lives of 30 days (at pH 7) and 3 days (at pH 8). BEH-TEBP contains chromophores that absorb at wavelengths > 290 nm and therefore, may be susceptible to direct photolysis by sunlight. It was reported to photodegrade in water to form a tribromo anhydride. Adsorbed BEH-TEBP had dissipation half-lives of 25 and >200 days in suspended solids and sediment, respectively. Biodegradation data in soil and water were not available. BEH-TEBP can be metabolized by porcine esterases to mono-(2-ethyhexyl) tetrabromophthalate (TBMEHP). HPVIS: Calculated atmospheric half-life of approximately 6 hours. Stability in water: Calculated half-life of 29		Inconclusive, indications of P, but also degradation to TBMEHP.

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[28] Explanation on the ECHA website: The substance is a suspected PBT or vPvB, but it is at present not possible to request the generation of the data necessary to achieve a definitive conclusion **or** the substance is a suspected PBT or vPvB, but the substance is not of interest due to zero or low volume used.

				days at pH 7. Not readily biodegradable in aerobic activated sludge-inoculate test (OECD 301B and 301D).		
DPTE	Ready biodegradability model (IRFMN) in VEGA (Q)SAR platform predicts that the chemical is not readily biodegradable (moderate reliability). The Danish QSAR database contains information indicating that the substance is predicted as not readily biodegradable.	Not included (see Table 17)	Not included (see Table 17)	Not included (see Table 17)	Not included. DPTE is on the Canadian Non-domestic Substance List[29].	Indications of P, based on model calculations.
BTBPE	Ready biodegradability model (IRFMN) in VEGA (Q)SAR platform predicts that the chemical is not readily biodegradable (moderate reliability). The Danish QSAR database contains information indicating that the substance is predicted as non readily biodegradable.	Not included (see Table 17)	Not included (see Table 17)	HSDB: BTBPE is not expected to undergo hydrolysis in the environment due to the lack of functional groups that hydrolyze under environmental conditions. The molecule contains chromophores that absorb at wavelengths >290 nm and, therefore, may be susceptible to direct photolysis by sunlight. Microbes are not expected to break down BTBPE. Incubated at concentrations of 1%, 0.01% and 1 ppm, the compound only reached 1.1, 0.53, and 1.41% mineralization, respec-	No information. BTBPE is on the Canadian Domestic Substance List[30].	Indications of P

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[29] http://www.ec.gc.ca/subsnouvelles-newsubs/default.asp?lang=En&n=9454EBA5-1&offset=5&toc=show%20?iframe=true&width=100%&height=100%

[30] https://www.canada.ca/en/environment-climate-change/services/managing-pollution/publications/chemical-abstract-services-registry-gazette/chapter-5.html

				tively, in a 26 to 30 week period using an acclimated sewage and garden soil inoculum. Biodegradation is not an important environmental fate process in soil. Biodegradation data in water were not available. Elimination from fish (exposed to BTBPE) followed first-order depuration kinetics, with a calculated half-life of 54 days. HPVIS: Calculated atmospheric half-life of 8.6 hours. Irradiation of BTBPE on a silica surface resulted in a half-life of 0.4 days. Conclusions for hydrolysis and biodegradation confirmed.		
DBDPE	The substances is not PBT/vPvB according to EU registration dossier. However, DBDPE was included in Community Rolling Action Plan (CORAP)[31] because it was suspected to be PBT/vPvB, because it had a high (aggregated) tonnage and a wide dispersive use.	Not included (see Table 17)	Not included (see Table 17)	HSDB: DBDPE is not expected to undergo hydrolysis in the environment due to the lack of functional groups that hydrolyze under environmental conditions. The molecule does not contain chromophores that absorb at wavelengths >290 nm and, therefore, is not susceptible to direct photolysis by sunlight. Biodegradation data in soil or water were not available. DBDPE biotransformation occurred in rats and other	DBDPE testing under longer-term, environmentally relevant conditions to determine the degradation pathways and transformation products is lacking. Relevant transformation processes for DBDPE include photodegradation, biodegradation and biotransformation, as well as combustion/pyrolysis. DBDPE is expected to be persistent in air, water, soil and sediment. Model predictions are consistent with experimental findings that aerobic and anaerobic biodegradation of DBDPE is	Indications of P

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[31] https://echa.europa.eu/en/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/-/dislist/details/0b0236e1807e3287

	The outcome of the CoRAP was that the registrant had to provide more information (ECHA, 2014).			mammals. DBDPE was widely detected in sediment and sewage sludge. HPVIS: Not included.	limited and that DBDPE is expected to be persistent in water, soil, and sediment. Photodegradation of DBDPE in solvents may be fast; however, photodegradation could take much longer in other matrices/substrates. Modelled predictions for DBDPE in air suggest a half-life > 4 days (gas phase) and an overall persistence (P_{ov}) of 277 days (OECD POPs model).	

Table 19. Summary of evaluations of bioaccumulation (B) for dechlorane plus (DP) and novel brominated flame retardants. vB: very bioaccumulative; (v)P: (very) persistent; T: toxic

Compound	EU registration	ECHA Annex XV	USEPA TSCA Reports	TOXNET (USEPA)	Government of Canada	Conclusion
DP	See information in Table 18. Classical OECD 305 studies by aqueous exposure do not appear appropriate, given the high logK_{OW} and the extremely low water solubility; exposure via diet may lead to accumulation of precipitates in fish tissue, suggesting higher bioaccumulation than by pure absorption.	The European Chemical Agency has classified DP as vB (ECHA, 2018).	Not included (see Table 17)	Hazardous Substance Data Bank (HSDB): DP has been detected in multiple biota species and human samples. Tissue residues in biota did not increase proportionally with dose. Some high trophic level animals could apparently degrade DP. A bioconcentration factor (BCF) range of 14-121 was measured using orange-red killifish (*Oryzias latipes*) exposed over an 8-week period, i.e. below the thresholds for POP/PBT (Table 2; Table 4). Biomagnification factors (BMF) for syn- and anti-DP in rainbow trout exposed for 49 days were 1.9 and 5.2, respectively. However, trophic magnification factors (TMF) of 2.5 and <1 were calculated for anti- and syn-DP in the food web of Lake Winnepeg. High Production Volume Information System (HPVIS): BCF in bluegill *(Lepomis macrochirus)* was 1.97-7.02.	Based on its physical and chemical properties (e.g., moderately large maximum diameter, very low water solubility, high logK_{OW}, and low experimental BCF), DP is expected to have a low bioconcentration potential. However, monitoring studies from many parts of the world have reported measurable DP in aquatic and terrestrial organisms. Data for field-based biomagnification factors (BMF), bioaccumulation factors (BAF), and biota-sediment accumulation factor (BSAF) support that DP bioaccumulation and biomagnification occur. Studies of metabolism in wildlife (fish and birds) show no evidence of metabolic transformation products, suggesting little to no metabolism of DP. Regarding model calculation of bioaccumulation, it should be considered that the logK_{OW} of DP might be outside the model domain.	B-vB
EH-TBB	Not registered	Not included (see Table 17)	EH-TBB has been detected in a wide range of biota samples, including terrestrial and aquatic animals, but the studies also included a number of non-detects.	No entry in HSDB or HPVIS. Some information available under BEH-TEBP (e.g. lack of bioconcentration in fish).	A modelled logK_{OW} of 7.71 for EH-TBB suggests bioaccumulation potential. The logK_{OA} of 11.34 suggests that given a terrestrial dietary exposure, these compounds will have the potential to biomagnify in terrestrial food webs. However, the use of logK_{OW} and logK_{OA} are not sufficient evidence, by	Inconclusive, indications of limited B

			The highest reported concentration was in a freshwater clam (2220 ng/g lipid weight) near a wastewater treatment plant outfall (La Guardia et al., 2012).		themselves, to determine bioaccumulation potential as these are simply partition coefficients and do not account for physiological parameters, such as biotransformation. While the physical chemical properties suggest potential for bioaccumulation of EH-TBB, in the overall weight of evidence, this is substantially outweighed by the published mesocosm and feeding studies with fathead minnows, *in vitro* examinations of metabolic biotransformation, and general absence of increased concentrations in predator-prey relationships in biota monitoring data. These lines of evidence point to limited bioaccumulation potential. Although exposure via gills is less important for these substances, an empirical bioconcentration factor also suggests limited bioaccumulation.	
BEH-TEBP	Decision deferred on the substance from the list of potential PBT or vPvB substances (see Table 18). A study to determine the biomagnification factor (BMF) was conducted according to OECD guideline 305. The resulting BMF of 0.038 (after 28 days for uptake,	Not included (see Table 17)	BEH-TEBP has been detected in a wide range of biota samples, including terrestrial and aquatic animals, but the studies also included a number of non-detects. The highest reported concentration was in finless porpoise *(Neophocaena phocaenoides)* blubber (3859 ng/g lipid weight) from Hong Kong (Lam et al., 2009).	HSDB: BEH-TEBP is not expected to build up in aquatic organisms. However, BEH-TEBP has been detected in biota, e.g. in blubber of finless porpoise *(Neophocaena phocaenoides)* and humpback dolphins *(Sousa chinensis)* from Hong Kong (Lam et al., 2009) and livers of ring-billed gulls from Canada (Gentes et al., 2012). Mesocosms studies with fathead minnows (*Pimephales promelas*) showed a lack of consistent accumulation of EH-TBB and BEH-TEBP. The fish were exposed for 42 days,	Only empirical data are considered for BEH-TEBP as the modelled logK_{OW} value of 10.10 resides outside the domain of bioaccumulation models. Modelled logK_{OW} for BEH-TEBP suggests that BEH-TEBP has a low potential to bioaccumulate. In addition to logK_{OW}, the logK_{OA} of 15.03 suggests that given a terrestrial dietary exposure, these compounds will have the potential to biomagnify in terrestrial food webs. However, the use of logK_{OW} and logK_{OA} are not sufficient evidence, by themselves, to determine bioaccumulation potential as these are simply	Indications of limited B

	and another 28 days for depuration) indicates that BEH-TEBP is not bioaccumulative to *Oncorhynchus mykiss* when applied orally.		BEH-TEBP has also been detected in vegetation and in humans. The humans might have been occupationally exposed.	followed by 28 days depuration in outdoor mesocosm ponds. BEH-TEBP was detected in fish only on day 7 of the 70-day experiment and only in fish from one pond, indicating that it does not bioconcentrate. A bioconcentration factor (BCF) of 13 was calculated in fish, using an estimated logK_{OW} of 11.95 and a regression-derived equation, i.e. below the thresholds for POP/PBT (Table 2; Table 4). BEH-TEBP has been detected in human samples. HPVIS: BCF of 3.162 calculated for BEH-TEBP, using an estimated logK_{OW} of 11.95.	partition coefficients and do not account for physiological parameters, such as biotransformation. The physical-chemical properties, mesocosm and feeding studies suggest a limited bioaccumulation potential for BEH-TEBP, although in general, this may be less due to metabolic biotransformation than in the case of EH-TBB.	
DPTE	The Danish QSAR database contains information indicating that the substance is predicted as bioaccumulative (BCF > 2000 L/kg).	Not included (see Table 17)	Not included (see Table 17)	Not included (see Table 17)	Not included. DPTE is on the Canadian Non-domestic Substance List (see Table 18).	Indications of B, based on model calculations.
BTBPE	No information	Not included (see Table 17)	Not included (see Table 17)	HSBD:BCFs were 8.6-27.1 and 25.4-43.6 at 0.3 and 0.03 ppm, respectively, in an 8-week study using carp (*Cyprinus carpio*), i.e. below the thresholds for POP/PBT (Table 2; Table 4).	No information. BTBPE is on the Canadian Domestic Substance List (see Table 18).	Inconclusive, indications of B

				Juvenile rainbow trout (*Oncorhynchus mykiss*) were exposed to an environmentally relevant dose via their diet for 49 days, followed by 154 days of untreated food. There was a linear increase in the amount of BTBPE in fish during the uptake phase. The derived biomagnification factor (BMF) of 2.3 ± 0.9 suggests that this chemical has a high potential for biomagnification in aquatic food webs. In a mesocosm experiment with fathead minnow, BTBPE was accumulated in the fish tissue (16-4203 ng/g lipid). In experiments with rats, it was conclude that absorption and metabolism of BTBPE by ingestion was limited. HPVIS: BCF for carp repeated.		
DBDPE	The substances is not PBT/vPvB according to EU registration dossier. However, DBDPE was included in Community Rolling Action Plan (see Table 18) because it was suspected to be PBT/vPvB.	Not included (see Table 17)	Not included (see Table 17)	HSDB: A calculated BCF of 7, from an estimated logK$_{OW}$ of 13.64, suggests that the potential for bioconcentration in aquatic organisms is low. However, DBDPE has been observed to accumulate in the tissues of fish from South China. A biomagnification factor (BMF) for fish and its prey was < 1. In a study with blackworm *(Lumbriculus variegatus)*, the bioavailability of DBDPE was poor compared with lower brominated PBDEs. However, after oral administration to rats for 90	The logK$_{OW}$ of 9.89 for DBDPE is considered out of the model domain for typical bioaccumulation models. While DBDPE appears to be bioavailable to some organisms, the available evidence is equivocal with respect to higher bioaccumulation. Based on its physical and chemical properties (e.g., moderately large maximum diameter, very low water solubility, high logK$_{OW}$), DBDPE is expected to have a low bioconcentration potential. Monitoring studies from many	Indications of limited B

				days, DBDPE was found in all tissues (liver, kidney, adipose), but at lower concentrations than some PBDEs. Biotransformation was observed in rats and other mammals (see Table 18). DBDPE was only detected sporadically in animals, tree bark as well as human samples. HPVIS: Not included.	parts of the world have reported measurable DBDPE in aquatic and terrestrial organisms; however, there are also very high proportions on non-detects in biota studies (frequently >50%). Data for field-based biomagnification and bioaccumulation factors are not consistent and have uncertainties to consider. Studies of DBDPE in rats and wildlife suggest that DBDPE may be bioavailable for uptake, and metabolism may occur in some species. Therefore, while it appears that DBDPE may accumulate in the tissues of some organisms to some extent, at present there is not adequate evidence of potential for high bioaccumulation. Currently there are more lines of evidence to suggest that bioaccumulation potential of DBDPE is limited by low bioavailability and dietary assimilation efficiency, steric uptake restriction and some metabolism.	

Table 20. Summary of evaluations of toxicity (T) for dechlorane plus (DP) and novel brominated flame retardants. EH-TBB and BEH-TEBP were assessed together in the Canadian document. (v)P: (very) persistent; (v)B: (very) bioaccumulative

Compound	EU registration	ECHA Annex XV	USEPA TSCA Reports	TOXNET (USEPA)	Government of Canada	Conclusion
DP	The substance does not fulfil the toxicity criterion in REACH Annex XIII and thus is not considered being a PBT substance.	Based on the available ecotoxicity and mammalian data, DP does not currently meet the T criterion. Carcinogenicity data are lacking.	Not included (see Table 17)	Hazardous Substance Data Bank (HSDB): Mild liver and lung effects were observed in laboratory animals following repeated exposure to moderate air levels. No evidence of infertility, abortion or birth defects were observed in laboratory animals exposed to DP before or during pregnancy. DP did not have developmental or reproductive effects in rats; it was not mutagenic in *Salmonella typhimurium*. Regarding ecotoxicity, the following effects were observed in aquatic organisms: Effects on enzymatic and metabolic processes, induced apoptosis, thyroid hormone disruption, oxidative stress. Studies on earthworms also showed oxidative stress and effects on enzyme activity. Little information on effects on human health, but indications that DP can induce adipogenesis. High Production Volume Information System (HPVIS): No acute toxicity observed in rats after oral exposure or inhalation, no acute toxicity in rabbits after dermal exposure. Repeated dose tests	Results from the available empirical aquatic toxicity studies have high uncertainty and questionable applicability because treatment concentrations exceeded the DP water solubility limit. Furthermore, given that DP preferentially partitions to soil or sediment compartments, dissolved phase aquatic toxicity is not the most environmentally relevant form of testing for the effects of this substance. While DP's mode of action may not be completely understood for aquatic organisms (e.g., sediment organisms), its analogues, the cyclodiene insecticides (e.g., chlordane), are generally considered neurotoxicants for terrestrial organisms. Based on the results of sediment and soil chronic toxicity testing, using the analogues chlordane and mirex, DP has the potential to cause effects at low concentrations to soil and sediment organisms. DP does not show potential for effects on wildlife based on current rodent and avian studies. No classifications of the health effects of DP by national or international regulatory agencies were identified. The US EPA has developed screening-level hazard characterization documents for DP.	Limited T

				showed changes in organ weights. No mutagenic effects *in vitro*.		
EH-TBB	Not registered	Not included (see Table 17)	Not on Toxic Releases Inventory of the US EPA. Studies on rodents only with commercial flame retardant mixture. Indications of effects on kidney. Fetal developmental toxicity observed at high dosis. Metabolite might be endocrine disruptor. Acute and chronic aquatic toxicity: See BEH-TEBP.	No entry in HSDB or HPVIS.	Although the majority of EH-TBB and BEH-TEBP released is expected to partition to soil and sediment, neither suitable toxicity data nor analogues with relevant empirical toxicity data could be identified for these compartments. A modest fraction of these compounds is predicted to remain in the water compartment, to which EH-TBB and BEH-TEBP are expected to be released. A mixture of EH-TBB and BEH-TEBP has been demonstrated to have moderate potential for toxicity to aquatic organisms. No classifications of the health effects of BEH-TEBP or EH-TBB by national or international regulatory agencies were identified. No chronic toxicity/carcinogenicity studies were identified. Little information was available for EH-TBB; however, limited data are available regarding the short-term repeat-dose toxicity, acute toxicity and genotoxic effects of BEH-TEBP as well as reproductive and developmental effects of mixtures of EH-TBB and BEH-TEBP.	Uncertain, indications of modest toxicity
BEH-TEBP	No ecotoxicological hazards have been identified. However, all aquatic toxicity tests were performed above water solubility. Waiving for terrestrial toxicity tests seems unreasonable since environmental exposure is expected. No hazards identified for humans.	Not included (see Table 17)	Not on Toxic Releases Inventory of the US EPA. There is a low hazard for acute toxicity. In a screening level dietary study in rats with BEH-TEBP, the potential for liver toxicity was observed by perturbations in clinical chemistry values. However, some liver effects have been attributed to a mode of action, peroxisome proliferation, not considered relevant to humans.	HSDB: The potential for BEH-TEBP to produce toxic effects in humans has not been studied. The potential for BEH-TBEP to cause cancer, birth defects or reproductive effects in laboratory animals has not been studied. BEH-TEBP can be metabolized by porcine esterases to mono(2-ethylhexyl) tetrabromophthalate, which elicited maternal thyrotoxic and hepatoxic effects and induced mononuclear gonocytes in the fetal testes in a rat model. Fathead minnows *(Pimephales promelas)* were orally exposed to		Uncertain, indications of toxicity, possibly related to the metabolite TBMEHP

			Metabolite might be endocrine disruptor. Acute aquatic base-set toxicity data were available for BEH-TEBP/EH-TBB that suggest aquatic invertebrates as the most sensitive species; however, given the low water solubility and high logK_{OW} of BEH-TEBP/EH-TBB and the use of solvents and/or test concentrations above the limit of solubility, there is concern that these effects do not represent environmental conditions. Insufficient experimental data are available to characterize hazard that would result from chronic exposure to wildlife populations. Currently, information from experimental studies that address standard aquatic toxicity endpoints are limited to two chronic invertebrate studies conducted on two different species and two different flame retardant formulations (BZ-54 and pure BEH-	either FM 550, FM BZ54, or the nonbrominated form of BEH-TEBP, di-(2-ethylhexyl) phthalate (DEHP). Significant increases in DNA strand breaks from liver cells (but not blood cells) were observed during the exposure period. HPVIS: No mortality in acute toxicity test in rabbits; decreased body weight, enzyme activity, Ca and P levels in repeated-dose toxicity in the rat; no genotoxic effect *in vivo* (mice); positive genotoxic effect *in vitro* (1000 µg/ml, human cell line).		

			TEBP) that present conflicting conclusions. Long term mesocosm experiments suggest that aquatic and/or sediment dwelling invertebrate populations may be impacted by chronic exposure.			
DPTE	The Toolbox profiler 'Carcinogenicity (genotox and nongenotox) alerts by ISS' gives an alert for carcinogenicity. The Toolbox profiler 'DNA alerts for AMES, MN and CA by OASIS v.1.3' gives an alert for mutagenicity. The Toolbox profiler 'in vitro mutagenicity (Ames test) alerts by ISS' gives an alert for mutagenicity. The Toolbox profiler 'Protein binding alerts for Chromosomal aberration by OASIS v1.1' gives an alert for mutagenicity.	Not included (see Table 17)	Not included (see Table 17)	Not included (see Table 17)	Not included. DPTE is on the Canadian Non-domestic Substance List (see Table 18).	Indications of T, based on model calculations

BTBPE	DEMETRA *Daphnia magna* toxicity model in VEGA (Q)SAR platform predicts that the chemical has a 48 hour EC_{50} of 0.0255 mg/L (moderate reliability) Fish toxicity classification (SarPy/IRFMN) model in VEGA (Q)SAR platform predicts that the chemical is Toxic-2 (between 1 and 10 mg/L) (moderate reliability).	Not included (see Table 17)	Not included (see Table 17)	HSDB: Acute toxicity in laboratory animals was low. Minimal microscopic change in liver were found in rats fed high concentrations for BTBPE for 106 days. Inflammation of the lungs was found in rats breathing in high concentrations of BTBPE in dust for 21 days. Direct contact with BTBPE was slightly irritating to the skin of laboratory animals. No abortions or birth defects in offspring were found after pregnant laboratory animals were exposed to BTBPE. Cancer or effects on neurological development have not been studied in laboratory animals. Based on studies with juvenile rainbow trout *(Oncorhynchus mykiss)*, BTBPE is not a potent thyroid axis disruptor. BTBPE was negative in mutagenicity tests with *Salmonella typhimurium* strains. The potential for BTBPE to produce toxic effects in humans has not been studied. HPVIS: Acute toxicity to *Daphnia magna* (LC_{50} = 50.43 mg/L, calculated); acute toxicity to green algae (EC_{50} = 33.66 mg/L, calculated); no mortality or adverse effects in rabbits; no genotoxic effect *in vitro* (number	No information. BTBPE is on the Canadian Domestic Substance List (see Table 18).	Uncertain, indications of modest toxicity

				of bacterial mutants); NOAEL 10% of diet in reproductive toxicity tests in the rat; NOAEL 10,000 mg/kg in developmental toxicity/teratogenicity in the rat.		
DBDPE	The substances is not PBT/vPvB according to EU registration dossier. No environmental hazard, low hazard to humans. However, DBDPE was included in Community Rolling Action Plan (see Table 18) because it was suspected to be PBT/vPvB.	Not included (see Table 17)	Not included (see Table 17)	HSDB: Liver toxicity, alterations in thyroid hormone and enzyme levels, changes in blood glucose levels and oxidative stress were observed in laboratory animals following repeated exposure to high oral doses of DBDPE. No evidence of maternal toxicity, developmental toxicity or teratogenicity was observed in rats or rabbits. Data on the potential for DBDPE to cause infertility or cancer in laboratory animals were not available. DBDPE was acutely toxic in ecotoxicity studies (48 hours EC_{50}=19 μg/L for water fleas). It reduced the hatching rates of exposed zebrafish eggs and raised the mortality in hatched larvae. A clear dose-respone curve was found in a fish hepatocyte assay, based on the synthesis and secretion of vitellogenin. DBDPE was not genotoxic in bacterial assays. Data on the potential for DBDPE to produce toxic effects in humans were not available. HPVIS: Not included.	Since the vast majority of DBDPE settles in soil or sediment compartments, water-based exposure is not considered an environmentally important pathway for exposure. Based on the results of sediment and soil chronic toxicity testing, DBDPE appears to have the potential to cause effects at high exposure concentrations to reproduction of earthworms as well as plant survival and growth, while no effects were observed for sediment organisms. No overtly toxic effects were found in wildlife, although DBDPE may affect enzyme activity in some test species. This information indicates that DBDPE has the potential to cause ecological harm in Canada. No classifications of the health effects of DBDPE by national or international regulatory agencies were identified. No chronic or carcinogenicity studies using DBDPE were identified. On the basis of the available information regarding genotoxicity, DBDPE is not genotoxic in vitro. No adverse effects were observed in rats exposed to DBDPE orally for 28 or 90 days, up to doses of 1250 or 1000 mg/kg bw/day, respectively. No reproductive studies were identified. In two separate	Uncertain, indications of modest toxicity

					developmental toxicity studies, no treatment related maternal effects were observed in rats and rabbits exposed to DBDPE via the oral route; and no malformations or developmental variations occurred in the offspring. There were no adverse effects observed in experimental animals exposed to doses up to 1000 mg/kg bw/d in their diet in sub-chronic studies.	

Table 21 summarizes the results of the PBT review of the databases and assessment reports based on the conclusions in Table 18 to Table 20.

Table 21. Summary of PBT characterization of dechlorane plus (DP) and novel brominated flame retardants, based on Table 18-Table 20. The brackets show that the uncertainly is high and only indications were found in the PBT review.

Compound	P	B	T
DP	vP	B-vB**	limited T
EH-TBB	(P)	(limited B)*	(T)
BEH-TEBP	(P)*	(limited B)	(T)
DPTE	(P)	(B)	(T)
BTBPE	(P)	(B)* and **	(T)
DBDPE	(P)	(limited B)	(T)

* inconclusive; ** low bioconcentration factors

With regards to persistence, the compounds with data are either vP or P, but the uncertainty was high for most compounds. It is only DP that is currently vB, and we found indications that DPTE and BTBPE might be B. Basically all compounds are questionable with regards to T as few data are available and some ecotoxicity studies used aqueous concentrations above the water solubility of the compound. This causes the dose-response to decline beyond the limit of solubility. Based on their low water solubility and high logK_{OW} value, these compounds are expected to be found in sediment, sludge and soil, rather than in the water phase, hence chronic invertebrate toxicity testing on sediment dwelling organisms should be considered in an assessment of toxicity. DP presently shows limited T, while the other compounds show indications of T.

DPTE is the only compound without any experimental data at all. The conclusions in Table 21 are entirely based on model calculations. The (Q)SAR predictions suggest that DPTE is a PBT. However, experimental data will be needed to reach sound conclusions.

7.3 Mammalian toxicological review

We reviewed the available mammalian toxicological data in order to address potential differences in toxicology of the compounds with regard to the Arctic animals for which we have biota data (see chapter 6). The mammalian toxicity has usually been tested on rodents, which obviously is not directly comparable to the Arctic mammals of this study.

We used the same sources as listed in Table 17, meaning that some of the mammalian toxicity data are included in Table 20. Several reports often refer to the same original studies, but might interpret these studies differently. In addition, we screened the compounds in the Comparative Toxicogenomic Database[32] by the US National Institute of Environmental Health Sciences (NIEHS) to determine potential mammalian mechanisms of action and potential diseases from a toxicogenomic perspective.

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[32] http://ctdbase.org/

7.3.1 ECHA Annex XV

As indicated in Table 17, the ECHA report only addresses DP (ECHA, 2017). Toxicokinetic studies with rats indicated that the uptake, distribution and elimination kinetics were complex, with preferential accumulation of both isomers in the liver rather than in the muscle. DP reached levels of approximately 1000 mg/kg lw in rat liver when dosed at 100 mg/kg/d for 90 days. The residues increased with longer exposure times, and a steady state was not reached. The elimination half-life was about 180, 44 and 24 days for rat liver, muscle and serum, respectively. However, these results were based on only three studies, two of which were unreferenced and from the 1970s, and the third one included some deviations from OECD guidelines.

Table 22 summarizes the No-observed-adverse-effect-levels (NOAEL) given for DP in the ECHA document. Data considered reliable by the authors of the ECHA report were available for oral and dermal exposure as well as for inhalation. No specific organ toxicity is reported in any of the studies, and clinical signs are minimal. Some changes in biochemical parameters in liver tissue (rats, mice) were reported. However, it was not known for the oral repeated dose studies whether DP was completely soluble in the corn oil vehicle. Bacterial and mammalian mutagenicity tests did not indicate genotoxicity of DP. Carcinogenicity was not addressed. It is obvious that the inhalation NOAEC, for example, is much higher than any of the DP concentrations measured in Arctic air (chapter 5.3.1).

Table 22. No-observed-adverse-effect-levels (NOAEL) for dechlorane plus in toxicity studies with rats or mice (ECHA, 2017)

Uptake	NOAEL	Comment
Inhalation	1.524 mg/L air*	OECD TG 412
Oral	5000 mg/kg bw/day	OECD TG 422
Dermal	2000 mg/kg bw/day	OECD TG 410

*No-observed-adverse-effect-concentration (NOAEC)

7.3.2 USEPA TSCA reports

The USEPA documents only addressed EH-TBB and BEH-TEBP (see Table 17) (USEPA, 2015a; 2015b). There is limited information on the toxicokinetics of EH-TBB and BEH-TEBP. EH-TBB has tetrabromobenzoic acid (CAS 27581-13-1) as its final metabolite and this was found in *in vitro* liver tests. The primary metabolite of BEH-TEBP is mono(2-ethyhexyl) tetrabromophthalate (TBMEHP; CAS 61776-60-1), which is ultimately metabolized in mammals to tetrabromophthalic acid (CAS 13810-83-3). However, this was not found in *in vitro* testing and there are no toxicokinetic data available for the compound. No phase II metabolites were found for EH-TBB or BEH-TEBP.

More toxicity data are available for BEH-TEBP than for EH-TBB (Table 23). Some results were reported for tests with Firemaster BZ-54, which is a mixture of both compounds. In a dietary repeated dose study with rats, BEH-TEBP produced a slight body weight decrease in females and clinical biochemistry perturbations. BEH-TEBP was not mutagenic in bacteria *in vitro*, but did induce chromosomal aberrations in mammalian cells *in vitro*. The metabolite TBMEHP did not exhibit anti-androgenic activity in rats, but it did exhibit liver toxicity attributable to peroxisome proliferator-activated receptor (PPAR) α mode of action, similar to effects observed for DEHP and its metabolite.

The studies with Firemaster BZ-54 showed kidney effects and increased levels of serum chloride in a repeated dose study in rats, exposed to the mixture for 28 days. Females appeared more sensitive than males, but the NOAEL was not reported. The lowest-observed-effect-levels (LOEL) was 160 mg / kg / day. The effects observed in a two-generation reproductive toxicity study with Firemaster BZ-54 were mainly reduced body weight and reduced body weight gain.

Table 23. No-observed-adverse-effect-levels (NOAEL) for EH-TBB and BEH-TEBP in toxicity studies with rats (USEPA, 2015b)

Uptake (and endpoint)	NOAEL EH-TBB	NOAEL BEH-TEBP
Oral (repeated dose toxicity)	-	223 mg/kg bw/day
Oral (reproductive toxicity parental)	50 mg/kg bw/day	
Oral (reproductive toxicity offspring)	50 mg/kg bw/day	
Oral (developmental toxicity)	50 mg/kg bw/day	

7.3.3 USEPA Hazardous Substances Data Bank (HSDB)

The USEPA database only holds toxicity information for DP, BEH-TEBP, BTBPE and DBDPE (Table 17), and only few NOAELs are available (Table 24). Summaries of the effects observed on mammals are included in Table 20.

Rats were exposed (by inhalation) to DP at 0.64 and 1.524 mg / L for a period of 28 days. Increased liver and lung weights were observed, the latter only in some dose groups. The HSDB gives a lowest-observed-adverse-effect-level (LOAEL) of 0.64 mg / L and states that a NOAEL was not given for this study. This is slightly inconsistent with Table 22, which includes an NOAEC for the same study, as given in the ECHA document (ECHA, 2017).

The dermal exposure study with DP was performed with rabbits over a period of four weeks. Weight changes in organs were observed, but no corresponding histopathological effects. The NOAEL of 2000 mg / kg bw / day was the highest dose tested. Rats were orally exposed for 90 days, but no statistically significant effects were found, leading to an NOAEL of 100,000 ppm, the highest doses tested. In another study, repeated exposure occurred at four doses and for 28 days and reproductive and developmental toxicity was targeted, but no significant effects were found.

No NOAEL or similar values were available for BEH-TEBP in HSDB. It was noted that BEH-TEBP could be metabolized to TBMEHP, which produced maternal hypothyroidism and maternal hepatotoxicity in rats. It also increased multinucleated germ cells in fetal rat testes. Effects on enzyme activity were observed for TBMEP in mice.

Toxicokinetic studies with BTBPE showed that absorption and metabolisation of BTBPE was limited in rats. The studies used radioactively labelled BTBPE, and most of the radioactivity was found in feces, where one study identified the parent compound while another study found indications of BTBPE being metabolically activated and covalently bound to proteins or lipids. The HSDB also lists changes in liver tissue and inflammation of the lungs after exposure through oral uptake and inhalation, respectively, but no NOAEL values are given.

More information is available for DBDPE. The value in Table 24 is based on prenatal development studies with rats and rabbits orally exposed to different doses of DBDPE. No maternal toxicity, developmental toxicity or teratogenicity was observed at the highest dose (1250 mg/kg bw/day). However, probably referring to a different study, the HSDB reported observations of oxidative stress, elevated blood glucose levels and changes in protein levels and enzyme activity in rats dosed with 100 mg/kg DBDPE for 90 days. In this study, DBDPE was found in all tissues (liver, kidney, adipose) after exposure. Effects on blood glucose level, enzyme activity as well as hormone levels were also observed in mice, and the study concluded that DBDPE had the activity of endocrine disruptors, possibly interfering with enzymes, glucose metabolism homeostasis and thyroid hormone levels. LD_{50} values of 5000 mg/kg bw and 2000 mg/kg bw were given in the HSDB for oral exposure of rats and dermal exposure of rabbits, respectively.

In vitro experiments with human liver cell line indicated that DBDPE was cytotoxic with anti-proliferation effect, and apoptosis was accompanied with overproduction of reactive oxygen species. Biotransformation of DBDPE was found in *in vitro* tests with liver microsomes of Arctic marine mammals.

Table 24. No-observed-adverse-effect-levels (NOAEL) for dechlorane plus (DP) and DBDPE in toxicity studies with rats or rabbits according to the US Hazardous Substances Data Bank (HSDB)

Uptake (and endpoint)	NOAEL DP	NOAEL DBDPE
Inhalation	0.64 mg/L air*	-
Oral (repeated dose toxicity)	100,000 ppm	100 mg/kg*
Oral (reproductive toxicity)	5000 mg/kg bw**	1250 mg/kg bw/day
Dermal (repeated dose toxicity)	2000 mg/kg bw/day	-

* Lowest-observed-adverse-effect-level (LOAEL); ** No-observed-effect-level (NOEL)

7.3.4 Canadian reports

As summarized in Table 17, only DP, EH-TBB, BEH-TEBP (often assessed together, based on studies with the commercial Firemaster BZ-54 mixture) and DBDPE have been assessed in reports prepared by Environment and Climate Change Canada and Health Canada (Canada, 2016a; 2016b, 2016c). NOAEL values are summarized in Table 25. As the Canadian reports frequently refer to both ECHA and USEPA documents, many conclusions agree with those in Table 22 and Table 24. No classification of health effects by other regulatory agencies were identified for any of the compounds.

Results for the genotoxicity database were negative for DP, BEH-TEBP, the EH-TBB/BEH-TEBP mixture and DBDPE. QSAR model predictions confirmed that DBDPE was not genotoxic. No chronic toxicity studies or carcinogenicity studies were identified for any of the compounds.

Toxicokinetic studies showed that DP and DBDPE were poorly absorbed. Main accumulation of DP occurred in the liver, and elimination was slow; half-lives were in the range of 24-179 days, depending on the tissue and the isomer. Human exposure studies showed a relatively rapid transformation of EH-TBB to TBBA, subsequently eliminated, and limited accumulation of EH-TBB. Metabolisation of BEH-TEBP in mammals might be slower. Transformation of BEH-TEBP to DEHP appeared less likely as the bulky bromine atoms may resist complete debromination in mammals. In a study with rodents, most of the EH-TBB and BEH-TEBP was excreted, either as parent compounds or metabolites; the same result of nearly complete excretion was reported for DBDPE.

The NOAEL of 5000 mg / kg bw / day for DP resulted from a combined 28-day repeated dose toxicity study in rats with a reproductive / developmental toxicity screening test, a 90-day subchronic toxicity study with rats and a 10-day exposure study with mice. It was also noted in the Canadian report that the food level of 100,000 ppm for rats (see Table 24) corresponded to a dose of 5000 mg / kg bw / day. In the 90-day subchronic study, clinical chemistry parameters (e.g. enzyme activity) showed decreases already at 100 mg / kg bw / day.

The Canadian report on DP also mentioned the inhalation study listed in Table 22 and Table 24 and concluded on an LOAEL of 0.64 mg / L, based on increases in liver weights, effects on lungs and on liver cells. This value is identical with the conclusions in Table 24. Agreements also exist for the NOAEL value for a dermal study with DP in rabbits. The Canadian report noted that there was a margin of eight orders of magnitude (i.e. a factor of at least 100,000,000) between this NOAEL value and estimates of DP exposure for the Canadian general population.

Regarding BEH-TEBP, a repeated dose toxicity study with dietary exposure of rats for 28 days did not show any signs of toxicological significance. However, changes in alanine aminotransferase and phosphorous levels were observed, leading to the NOAEL value in Table 25. This is the same value as shown in Table 23. The Canadian report highlighted that BEH-TEBP was not likely to have the same mode of action as DEHP.

The assessment of the Firemaster BZ-54 mixture of EH-TBB and BEH-TEBP referred to the same studies as that in Table 23, but the results were interpreted differently. In contrast to the authors of the study, Health Canada interpreted the findings as significant (i.e. findings of reduced body weight, reduced body weight gain and food consumption) leading to a change of an NOAEL value (Table 23) to an LOAEL value (Table 25). The maternal NOAEL in Table 25 originates from a different study and is the same value as that in Table 23. In addition, another study exposing rats to the Firemaster BZ-54 mixture for 28 days showed systemic toxicity and kidney effects.

Altogether, the Canadian report did not expect effects caused by EH-TBB / BEH-TEBP following short-term exposure at concentrations relevant for humans. Additional QSAR analyses did not indicate a potential for EH-TBB or BEH-TEBP to bind to the estrogen or androgen receptor. A margin of about 300,000 was found between the lowest NOAEL and the highest exposure estimate from environmental media.

In a sub-chronic oral study with rats over 90 days, an NOAEL of 1000 mg / kg bw / day was identified, i.e. the highest dose tested. A second study was mentioned with an NOAEL of 100 mg / kg bw / day, which seems to be the same value as that in Table 24. Although changes in clinical parameters were observed, an expert panel of the European Food Safety Authority did not consider them toxicologically significant. A third repeated-dose study over 28 days resulted in an NOAEL of 1250 mg / kg bw / day (Table 25). The study on reproductive toxicity was conducted with rats and rabbits.

Based on the absence of effects at a dose of up to 1000 mg / kg / bw / day and the highest estimate of daily intake of DBDPE from environmental media, a margin of exposure of seven orders of magnitude was found.

Table 25. No-observed-adverse-effect-levels (NOAEL) for dechlorane plus (DP), EH-TBB, BEH-TEBP and DBDPE in toxicity studies with rats, mice or rabbits in the Canadian reports (Canada, 2016a; 2016b; 2016c).

Uptake (and endpoint)	NOAEL DP	NOAEL EH-TBB	NOAEL BEH-TEBP	NOAEL DBDPE
Inhalation	0.64 mg/L air*	-	-	-
Oral (repeated dose toxicity)	5000 mg/kg bw/day	-	223 mg/kg bw/day (LOAEL: 2331 mg/kg bw/day)	100 mg/kg bw/day
		160 mg/kg bw/day		1000 mg/kg bw/day
				1250 mg/kg bw/day
Oral (reproductive toxicity)		Offspring: 15 mg/kg bw/day (LOAEL: 50 mg/kg bw/day) Maternal: 50 mg/kg bw/day		1250 mg/kg bw/day
Dermal (repeated dose toxicity)	2000 mg/kg bw/day	-	-	2000 mg/kg bw/day**

* Lowest-observed-adverse-effect-level (LOAEL); ** Single dose toxicity

7.3.5 Toxicogenomic review

We included a toxicogenomic assessment to determine potential effects the compounds may have on mammals. We therefore screened the toxicogenomic profile of the compounds to assess the potential target sites and mammalian toxic responses they may induce.

The Comparative Toxicogenomic Database (CTD) is a robust, publicly available database that can be used to advance our understanding about how environmental exposures affect human health – also extrapolated to other mammals to assess potential target sites and diseases. It provides curated information about chemical–gene/protein interactions, chemical–disease and gene–disease relationships. These data are integrated with functional and pathway data to aid in the development of hypotheses about the mechanisms underlying environmentally influenced diseases.

Table 26 shows the genes which DP and the NBFRs are most prone to interact with and the diseases the screened compound would be most likely to result in, for humans and potentially other mammals.

Table 26. Toxicogenomic screening results for dechlorane plus (DP) and the novel brominated flame retardants

Compound	Genes	Most probable diseases
DP	ACHE I ANXA4 I NAT2 I SULT1A1 I SULT2A1 I TCP1 I TPD52; CELF2 I CFP I CYBA I RGS5 I SULT2A1; CAT I CYBA I HAMP	Prostatatic neoplasms; Liver chirrhosis; Kidney failure
EH-TBB	PPARG	Carotid Intimal Medial Thickness 1; Leukostasis; Lipodystrophy
BEH-TEBP	PLIN1; ACOX1; PPARG; FABP4	Liver injury; Hypothyroidism; Diabetes; Obesity
DPTE	No data available	-
BTBPE	CYP1A4; CYP1A5; DIO3	Breast neoplasms
DBDPE	No data available	-

There are no toxicogenomic data for DPTE and DBDPE. DP has the most known interactions with genes indicating risks of chirrhosis (reduced capacity) of the liver, kidney failure and prostate neoplasms (tumor and cancer). EH-TBB has mainly gene interactions suggesting disruption of metabolism and cardiovascular effects. The same pattern is seen for BEH-TEBP. BTBPE is mainly associated with breast neoplasms (cancer) possibly suggesting a potential endocrine disruption based on the toxicogenomic analysis.

7.4 Conclusions

All compounds show indications of persistence although the data for BEH-TEBP were inconclusive. This is related to findings of its potential to be hydrolyzed or photodegraded. Biotransformation has been shown for EH-TBB and BEH-TEBP. DP was classified as vPvB by ECHA. DPTE and BTBPE also showed indications of bioaccumulation, but for BTBPE in particular the data were inconclusive, mainly because of low bioconcentration factors. EH-TBB, BEH-TEBP and DBDPE showed limited bioaccumulation potential. For EH-TBB and BEH-TEBP this was mainly related to their biotransformation potential, while DBDPE is a bulky molecule with a high $\log K_{OW}$, which might lead to lower bioavailability. However, all compounds have been detected in biota.

While the data material for DP showed limited toxicity, indications of some toxic potential were found for the other compounds. However, for DTPE, this was completely based on model results as no empirical data were available. Except for DBDPE, acute toxicity was generally low. The LOAEL, NOAEL or NOAEC values compiled from various reports are much higher than the general contaminant level found in the Arctic. However, as high trophic level Arctic animals are known to contain high levels of POPs, combination effects could also occur.

Based on their physical-chemical properties, the compounds can induce metabolic disorders and liver diseases. Moreover, neoplasms in prostate (DP) and breast (BTBPE) are diseases of concern and candidates for diseases for these compounds based upon their toxicogenomic profile. However, the toxicities of the compounds should be seen in relation to the exposure concentrations and the levels found in mammals in the study area to determine the relative risk with a focus on the toxicogenomically most likely sites of action and concern.

The air measurements in this report are in the low pg/m^3, whereas the inhalation NOAEC values are in the low mg/m^3 range, suggesting a low risk to Arctic animals from atmospheric exposures, and that this is not the main exposure pathway of concern. Since at least DP is a vPvB compound, the main exposure pathway is expected to be via oral intake.

8 Conclusions

DP and all NBFRs except BTBPE were detected in Arctic air. While all concentrations were similar to or even lower than concentrations at other Arctic stations, the concentrations for DP and DBDPE exceeded values reported in the scientific literature and warrant verification. For DP in particular there are indications of contamination or influences from local sources that might have compromised some of the measurements. Relatively high levels of DBDPE in air would be consistent with the findings for landlocked Arctic char, but need confirmation as well. Although the absolute levels of DP and DBDPE are uncertain, it can be concluded for all compounds except BTBPE that they are persistent and subject to long-range transport, but that they are not major contaminants in Arctic air at present. This conclusion can also be extended to BTBPE, which was not detected in our study, but at other Arctic stations.

The concentrations of DP and the NBFRs in Arctic animals were low, i.e. clearly below those of commonly measured POPs, even in high trophic level species like killer whale. Slightly elevated levels (i.e. a few ng/g lw) were found for EH-TBB in narwhal, BTBPE in killer whale and DBDPE in Arctic char. DP was close to or even below limits of detection in all species except glaucous gull. The results indicated species-specific bioaccumulation rather than food-chain biomagnification.

The geographical comparison, based on samples of glaucous gull and ringed seal, was limited in its obtainable results due to the low concentrations. It indicated relatively uniform levels of DP, but higher levels of EH-TBB and DPTE in East Greenland than in Northwest Greenland. All compounds were detectable in Arctic char, indicating atmospheric deposition as a relevant source. However, the concentrations of DP were only above LOQ in some samples. The low levels were generally consistent with other findings from the Arctic. However, some studies had reported higher levels of BEH-TEBP and DBDPE, including signs of biomagnification for DBDPE, which were not found here. Different tissues were analysed, which could be of importance.

The review of published assessments indicated persistence for most compounds of this study, but was inconclusive for BEH-TEBP, which can be photolyzed and hydrolyzed. DP was evaluated as vPvB by ECHA. Limited bioaccumulation potential was found for EH-TBB, BEH-TEBP and DBDPE, partly due to biotransformation (EH-TBB, BEH-TEBP), partly due to expected low bioavailability (DBDPE). The data material suggested limited toxicity for DP, but some toxic potential for the other compounds. For DPTE, all assessments were based on model predictions.

In summary, the data indicate persistence and long-range transport for DP and the selected NBFRs although some abiotic degradation might take place for at least BEH-TEBP. The measurements indicate species-specific bioaccumulation, but biotransformation has been observed for some of the compounds in controlled experiments and limited bioavailability has been predicted for DBDPE, which could be consistent with some of the low detection frequencies observed in the study. Toxic potentials exist, but might not be of greatest concern at the low levels currently observed in the Arctic.

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POP/PBT CHARACTERISATION OF DECHLORANE PLUS AND NOVEL BROMINATED FLAME RETARDANTS BASED ON DATA FROM GREENLAND

Halogenated flame retardants (FRs) are used in inflammable petroleum-based polymers. Dechlorane plus (DP) and so-called novel brominated flame retardants (NBFRs), alluding to the ban of polybrominated diphenyl ethers (PBDEs), have been detected in air and biota of the Arctic. Assessments of whether or not a compound is a persistent organic pollutant (POP) or persistent/bioaccumulative/toxic (PBT), can include monitoring data. Therefore, chemical analyses of DP and NBFRs have been carried out in Arctic air, based on samples from Villum Research Station in Northeast Greenland, and high-trophic level animals from Greenland. In addition, PBT data have been compiled and reviewed, and mammalian toxicity has been addressed through databases and toxicogenomics. All compounds except 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) were detected in Arctic air. The values for DP and decabromodiphenylethane (DBDPE) were surprisingly high in some samples, which warrant verfication, as they might be affected by local sources or contamination. The concentrations in biota were generally low, with few exceptions, e.g. 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) in narwhal (*Monodon monoceros*), BTBPE in killer whale (*Orcinus orca*) and DBDPE in Arctic char (*Salvelinus alpinus*). All compounds except DP were found in landlocked Arctic char, suggesting atmospheric deposition as a pathway of contaminant exposure. The PBT review suggested persistence for all compounds of this study. Bioaccumulation was indicated for DP, DPTE and BTBPE and toxicity for all compounds except DP. However, the data availability is limited. Existing no-observed-adverse-effect-concentrations were much higher than concentrations measured in the Greenland environment. In summary, the new data indicate persistence and some degree of bioaccumulation in the Greenland environment, while biomagnification was not apparent from our data.

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