Alternative Halogenated Flame Retardants versus PBDEs in the Global Marine Environment

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Occurrence, Distribution and Long-Range Atmospheric Transport toward the Polar Regions

Kumulative Dissertationsschrift zur Erlangung des akademischen Grades
Doktor der Naturwissenschaften (Dr. rer. nat.)
an der Fakultät Nachhaltigkeit
der Leuphana Universität Lüneburg

Vorgelegt von
Axel Möller
geboren am 25.04.1984 in Lübeck

Lüneburg, November 2012

Erstgutachter: Prof. Dr. Wolfgang Ruck
(Fakultät Nachhaltigkeit, Leuphana Universität Lüneburg)

Zweitgutachter: Prof. Dr. Ralf Ebinghaus
(Institut für Küstenforschung, Helmholtz-Zentrum Geesthacht/
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Abstract

Halogenated flame retardants (HFRs) have been applied since the 1960s in various industrial and consumer products to protect humans as well as private and public possessions. In the past decade polybrominated diphenyl ethers (PBDEs), formerly the major applied HFRs were widely restricted and adopted as Persistent Organic Pollutants (POPs) in the Stockholm Convention due to their adverse effects on humans and the environment as well as their ubiquitous occurrence in the global environment. Besides PBDEs, various alternative HFRs have been applied for decades as well, or were recently developed to replace PBDEs. However, their potential adverse properties, environmental distribution and fate are largely unknown. Therefore, this thesis addresses the global occurrence, distribution and transport of alternative HFRs versus PBDEs in the marine atmosphere and seawater toward the Polar Regions in order to examine their long-range atmospheric transport (LRAT) potential. This thesis presents the first data on alternative HFRs in the atmosphere of the marine environment and the Polar Regions.

Alternative brominated flame retardants (BFRs), Dechlorane compounds and PBDEs were investigated in high-volume air and seawater samples taken along several sampling transects in the Atlantic Ocean, Pacific Ocean and Indian Ocean toward the Polar Regions of the Arctic and Antarctic. In addition, three sampling cruises were conducted in the German Bight, North Sea. Several alternative HFRs were detected in the global marine atmosphere and seawater with hexabromobenzene (HBB), pentabromotoluene (PBT), pentabromobenzene (PBBz), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and Dechlorane Plus (DP) being the predominant compounds which were observed in concentrations similar or even higher than PBDEs. Total atmospheric concentrations ranged from <1 pg m^{-3} over the open oceans up to 42 pg m^{-3} over the East Indian Archipelago. Seawater concentrations ranged from <1 pg L^{-1} in open ocean seawater up to 21 pg L^{-1} in coastal regions, while estuarine concentrations reached up to 6800 pg L^{-1}. Overall, the comparison revealed that alternative HFRs dominate versus PBDEs in air and seawater, both in coastal regions as well as the Polar Regions, showing a shift from PBDEs toward alternative HFR in the marine atmosphere and seawater.

The distribution in the global atmosphere was strongly influenced by the proximity to potential source regions and the pathway of the sampled air masses. Highest concentrations were observed in continentally influenced air masses, while low background concentrations occurred during sampling of oceanic remote air masses. In general, Western Europe, East and Southeast Asia but also Africa were identified as source regions for the marine environment, especially for alternative HFRs as well as BDE-209. In contrast, relatively low peak concentrations of the PBDE congeners of the Penta- and OctaBDE mixtures under continental influence were observed, indicating limited emissions of legacy PBDEs.

The dry air-seawater gas exchange estimation showed that the atmosphere is a source for seawater resulting in net deposition into the global oceans after atmospheric emissions and transport, both in coastal regions as well as in the open oceans. Besides atmospheric depositions, riverine discharge was shown to act as source for coastal environments.

The investigation of sampling transects toward the Polar Regions revealed that several alternative HFRs – in particular HBB, PBT, DPTE, PBBz and DP – undergo LRAT toward the Polar Regions in an extent similar to PBDEs and, therefore, meet the LRAT criterion of POPs under the Stockholm Convention. DP was found to undergo LRAT attached to airborne particles whereby stereoselective LRAT differences were shown for the two DP stereoisomers. With respect to LRAT, the results of this thesis therefore imply that alternative HFRs – in particular HBB, PBT, DPTE and DP – aren't suitable replacements for PBDEs, but chemicals of emerging global environmental concern and possible future POPs.

Zusammenfassung

Halogenierte Flammschutzmittel (HFRs) werden seit den 1960er Jahren vielfältig in Industrie- und Konsumgütern eingesetzt um Menschen sowie private und öffentliche Besitztümer zu schützen. Im letzten Jahrzehnt wurden die ehemals meist verwendeten HFRs, die polybromierten Diphenylether (PBDEs), aufgrund ihrer nachteiligen Eigenschaften für Mensch und Umwelt und ihres ubiquitären Vorkommens in der Umwelt weitreichend reguliert und als Persistente Organische Schadstoffe (POPs) in die Stockholmer Konvention aufgenommen. Neben PBDEs wurden verschiedene alternative HFRs ebenfalls seit Jahrzehnten verwendet oder erst kürzlich als Ersatzstoffe für PBDEs entwickelt. Ihre möglichen negativen Eigenschaften und Verteilung und Transport in der Umwelt sind aber weitgehend unbekannt. Daher befasst sich diese Arbeit mit dem globalen Vorkommen, der Verteilung und dem Transport von alternativen HFRs in der marinen Atmosphäre und im Meerwasser im Vergleich mit PBDEs, um so das mögliche Potential atmosphärischen Langstreckentransports (LRAT) zu untersuchen. Diese Arbeit zeigt die ersten Daten zu alternativen HFRs in der Atmosphäre der marinen Umwelt und den Polarregionen.

Alternative bromierte Flammschutzmittel (BFRs), Dechlorane und PBDEs wurden in hochvolumigen Luft- und Meerwasserproben entlang verschiedener Probenahmetransekte in dem Atlantischen Ozean, Pazifischen Ozean und Indischen Ozean bis in die Polarregionen der Arktis und Antarktis untersucht. Zusätzlich wurden drei Probenahmekampagnen in der Deutschen Bucht der Nordsee durchgeführt. Verschiedene alternative HFRs wurden in der globalen marinen Atmosphäre und im Meerwasser nachgewiesen. Dabei dominierten besonders Hexabrombenzol (HBB), Pentabromtoluol (PBT), Pentabrombenzol (PBBz), 2,3-Dibrompropyl-2,4,6-Tribromphenylether (DPTE) und Dechlorane Plus (DP) welche in vergleichbaren und sogar höheren Konzentrationen als PBDEs gefunden wurden. Die Gesamtkonzentration in der Atmosphäre lag zwischen <1 pg m^{-3} über den offenen Weltmeeren bis maximal 42 pg m^{-3} über dem East Indian Archipelago. Konzentrationen im Meerwasser lagen zwischen <1 pg L^{-1} in den offenen Weltmeeren bis maximal 21 pg L^{-1} in küstennahen Regionen, wobei in Ästuaren Konzentrationen bis zu 6800 pg L^{-1} auftraten. Der Vergleich von alternativen HFRs mit PBDEs hat aufgezeigt, dass alternative HFRs mittlerweile in Luft und Meerwasser sowohl aus Küstenregionen als auch den Polarregionen dominieren.

Die Verteilung in der globalen Atmosphäre zeigte sich stark beeinflusst von der Entfernung zu möglichen Quellenregionen und der Luftmassenherkunft. Die höchsten Konzentrationen traten bei kontinentalen Luftmassen auf, wohingegen ozeanische Luftmassen zu niedrigen Hintergrundkonzentrationen führten. Westeuropa, Ost- und Südostasien aber auch Afrika wurden allgemein als Quellenregionen besonders für alternative HFRs und BDE-209

identifiziert. Im Gegensatz dazu wiesen relativ geringe Spitzenkonzentrationen von PBDE-Kongeneren der Penta- und OktaBDE Mischungen unter kontinentalen Luftmasseneinflüssen auf limitierte Emissionen der verbotenen PBDEs hin.

Die Abschätzung des Gas-Wasser Austauschs zwischen Atmosphäre und Meerwasser hat aufgezeigt, dass die Atmosphäre eine Quelle für HFRs in Meerwasser darstellt, was folglich, nach Emissionen von HFRs in die Atmosphäre und atmosphärischem Transport, zur Deposition aus der Atmosphäre sowohl in küstennahe Regionen als auch offene Weltmeere führt. Neben atmosphärischen Depositionen wurden Einträge über Flüsse als Quelle für Küstenregionen identifiziert.

Die Untersuchung entlang von Transekten bis in die Polarregionen hat gezeigt, dass verschiedene alternative HFRs – speziell HBB, PBT, PBBz, DPTE und DP – in gleichem Maße wie PBDEs über lange Strecken atmosphärisch bis in die Polarregionen transportiert werden und somit das Kriterium zu Langstreckentransport von POPs der Stockholmer Konvention erfüllen. DP wird gebunden an atmosphärische Partikel über lange Strecken transportiert, wobei stereoselektive Unterschiede im Transportverhalten der beiden Stereoisomere von DP beobachtet wurden. Basierend auf dem Potential zu Langstreckentransport zeigt diese Arbeit, dass alternative HFRs – speziell HBB, PBT, DPTE und DP – keine geeigneten Ersatzstoffe für PBDEs sind, sondern vielmehr Chemikalien von wachsender globaler Umweltrelevanz und mögliche zukünftige POPs.

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Preface

The work underlying this cumulative dissertation was conducted from October 2009 to November 2012 at the Department for Environmental Chemistry of the Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research. This thesis consists of an extended summary including introduction into the research field (chapter 1+2), the objectives of the thesis (chapter 3+4) and the methods (chapter 5). Further, the comprehensive results are presented and discussed in chapter 6, and overall conclusions and future perspectives are given in chapter 7. In the Appendix A to the extended summary, declarations to the publications are given. The cumulative dissertation consists of six scientific papers all of them published in international peer-reviewed journals, and all of them focused on the distribution and transport of alternative halogenated flame retardants in the global marine atmosphere and seawater. They are re-printed at the end of this thesis.

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List of abbreviations

$aCl_{10}DP$	twofold dechlorinated species of antiDP [-1Cl+1H]
$aCl_{11}DP$	onefold dechlorinated species of antiDP [-2Cl+2H]
BC	before Christ
BCF	bioconcentration factor
BFRs	brominated flame retardants
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane
CFRs	chlorinated flame retardants
DBDPE	decabromodiphenyl ethane
DCM	dichloromethane
Dec 602	Dechlorane 602
Dec 603	Dechlorane 603
Dec 603	Dechlorane 604
DecaBDE	technical decabromodiphenyl ether mixture
DP	Dechlorane Plus
DPTE	2,3-dibromopropyl-2,4,6-tribromophenyl ether
E&E	electrical and electronic equipment
ECNCI	electron capture negative chemical ionization
EHTBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
EU	European Union
e-waste	electronic waste
FR	flame retardant
f_{syn}	ratio of synDP to the sum of the isomers
GC	gas chromatograph
GDAS	Global Data Assimilation System
GFF	glass fiber filter
H·	hydrogen radical
H	Henry's Law Constant
HBB	hexabromobenzene
HBCD	hexabromocyclododecane
HCB	hexachlorobenzene
HFRs	halogented flame retardants
K_{OA}	octanol-air partitioning coefficient
K_{OW}	octanol-water partitioning coefficient

LC50	concentration which is toxic to 50% of the test organisms
LPVC	low production volume chemical
LRAT	long-range atmospheric transport
m/z	mass-to-charge ratio
MDL	method detection limit
MS	mass spectrometer
n.a.	not analyzed
n.d.	not detected
NCEP	National Centers for Environmental Protection
NOAA	National Oceanic and Atmospheric Administration
NOEC	no observed effect concentration
OctaBDE	technical octabromodiphenyl ether mixture
·OH	hydroxyl radical
PAHs	polyaromatic hydrocarbons
PBBA	pentabromobenzylacrylate
PBBz	pentabromobenzene
PBDEs	polybrominated diphenyl ethers
PBDFs	polybrominated dibenzofurans
PBEB	pentabromoethylbenzene
pbt	persistent, bioaccumulative, toxic
PBT	pentabromotoluene
PCBs	polychlorinated biphenyls
PentaBDE	technical pentabromodiphenyl ether mixture
p_L^0	subcooled liquid vapor pressure
POP	Persistent Organic Pollutant
PTV	programmable temperature vaporizer
PUF	polyurethane foam
Q	quantifier
QA	quality assurance
QC	quality control
Q1-3	qualifier 1-3
S/N	signal-to-noise ratio
SD	standard deviation
SIM	selected ion monitoring
TBBPA	tetrabromobisphenol-A

TBC	tris(2,3-dibromopropyl)isocyanurate
TBPH	bis(2-ethylhexyl)-tetrabromophthalate
U.K.	United Kingdom
U.S.	United States of America
U.S. EPA	United States Environmental Protection Agency
UNEP	United Nations Environmental Program
vPvB	very persistent very bioaccumulative

Extended Summary

1. Introduction

Ongoing rapid industrialization and globalization in the 20th and 21st century has led to the development of thousands of different anthropogenic chemicals being manufactured and applied in various industrial and household applications. In the last decades, chemicals of special environmental concern have been chemicals with persistent, bioaccumulative and toxic (pbt-) properties, especially the so-called Persistent Organic Pollutants (POPs) which additionally have the adverse potential to undergo long-range atmospheric transport (LRAT) toward remote regions. In 2004, twelve initial POPs were banned on a global scale under the Stockholm Convention on Persistent Organic Pollutants[1], a global treaty under the United Nation Environmental Program (UNEP). All twelve initial POPs are halogenated, i.e., chlorinated, such as polychlorinated biphenyls (PCBs). Halogenation makes a chemical less volatile, less water soluble and more stable which are attractive properties for industrial applications. Controversy, exactly these properties lead to their global distribution and threat for humans and the environment, including sensitive ecosystems far away from human activities and place of application such as the Arctic and Antarctica. Despite the regulatory actions that have been taken, many of these chemicals are still present in the global environment due to their extreme stability.

In 2009, nine additional POPs were included into the Stockholm Convention, among them the technical penta- and octabromodiphenyl ether mixtures (PentaBDE and OctaBDE, respectively) which have been applied as flame retardants (FRs) for several decades *(1)*. Resulting from restrictions on the one hand but ongoing demand of special chemicals on the other hand, the banned ones are replaced by non-restricted chemicals, e.g., polybrominated diphenyl ethers (PBDEs) are simply replaced by non-restricted non-PBDE halogenated flame retardants (HFRs) *(2, 3)*. In order to meet the requested properties of their banned predecessors – flame retardancy for PBDEs – they are structurally related to PBDEs. Along with the flame-proofing properties, they also likely keep the adverse properties for humans and the environment. These so-called "alternative", "alternate", "novel" or "emerging" FRs are certainly not new per definition. Among them, several compounds have been historically developed and produced along with the banned PBDEs, but have been simply out of scientific and political focus for decades. Their possible adverse effects, fate and long-term consequences on the environment are largely unknown. But, detections in the environment including Arctic organisms *(4)* are alarming and

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[1] The POPs criteria under the Stockholm Convention are defined as follows: persistence = half-life in water >2 months, or half-life in soil/sediment >6 months; bioaccumulation = bioaccumulation/-concentration factor >5000 in aquatic species, or $\log K_{OW}$ >5, or high accumulation in other species; toxicity = evidence of adverse effects to human or to the environment, or toxicity/ecotoxicity data indicating the potential for damage to human or to the environment; LRAT = occurrence at remote locations in concentrations of potential concern, or monitoring data showing long-range transport via air or water, or predicted long-range transport potential via environmental fate properties/models, i.e., atmospheric half-life >2 days.

indicate their potential to be global PBDE-like pollutants. Therefore, it is essential to investigate whether these chemicals show PBDE-like and consequently POP-like behavior in the environment.

2. Background

2.1. Halogenated flame retardants

FRs are not an invention of modern history. 450 BC, Egyptians used alum to prevent woods from fires, and 200 BC the Romans applied a mixture of alum and vinegar to protect wood buildings from fire attacks by their enemies *(5)*. In the middle 20th century, rapid development in polymer sciences led to increasing introduction and production of synthetic organic polymers, i.e., plastics. Metals and woods are continuously replaced by synthetic polymers, which have several advantages such as low costs, reduced weight and high flexibility. On the other hand, they are inherently inflammable. Therefore, the modern raison d'être of FRs, including HFRs, is to reduce the risk of fires caused by the high inflammability of synthetic polymers used in daily life in order to protect humans from fire injuries and deaths as well as private and public possessions. Nowadays, FRs are mainly used in electronic equipments, textiles, furnishings, transportations and building materials. Their application is requested by fire safety standards with the most prominent one being the Technical Bulletin 116 and 117 of the state of California, United States of America (U.S.) *(6, 7)*. Related but generally less strict regulations have been enacted in the European Union (EU), such as the Technical Standard EN 60065:2002/A11:2008 regulating the fire safety of audio, video and similar electronic apparatus *(8)*.

These days, more than 175 different FRs are available which can be generally divided into four classes *(9)*:

- inorganic FRs
- organohalogen FRs (HFRs)
- organophosphorus FRs
- nitrogen-based FRs

In 2007, the global FR market was 1.8 million tons with HFRs representing a major group contributing 30% (23% brominated, 7% chlorinated) *(10)*. During combustion processes, HFRs act in the gas phase interrupting the combustion process by stopping the exothermic process, cooling down, and the reduction of flammable gases *(11)*. During this process free radicals (H· and ·OH) which act as oxidizing agents propagating the combustion process are trapped by halogens which are emitted by the degradation of the HFR. The organic backbone of the HFR is designed to provide suitable stability/decomposition temperature, and to allow mixture with or integration into the polymer structure *(12)*. Brominated flame retardants (BFRs) are the most cost-effective and most applied HFRs. Chlorinated flame retardants (CFRs) are used, too, but are less cost-effective and have limited applications *(11)*.

More than 75 different BFRs are commercially available *(12)*. By means of structure, BFRs can be categorized into aromatic (e.g., PBDEs), aliphatic (e.g., dibromoneopentyl glycol) and cycloaliphatic BFRs (e.g., hexabromocyclododecane (HBCD)), while aromatic BFRs are generally more stable than (cyclo-)aliphatic BFRs *(9)*. By mode of application, they can be categorized into reactive, additive and monomeric BFRs *(12)* which is a key factor in their (environmental) life cycle. While reactive BFRs such as tetrabromobisphenol-A (TBBPA) are chemically bond to the polymer and monomeric BFRs are incorporated into the polymer backbone, additive BFRs, such as PBDEs, are simply mixed with the polymer. As a result, additive BFRs can easily leach from the product into the environment *(13)*. This leads to higher environmental concern of additive BFRs than reactive BFRs, though TBBPA has raised concerns due to its occurrence in the environment *(14)*, too, but the levels are significantly lower than PBDEs.

Therefore, this thesis is focused on additive HFRs including PBDEs, several aromatic non-PBDE BFRs as well as Dechlorane compounds which are additive CFRs.

2.2. PBDEs

2.2.1. Classification, properties and usage

PBDEs are diphenyl ethers with one to ten hydrogen atoms being substituted by bromine atoms (see Figure 1) leading to 209 possible congeners. Due to the structural similarity, the numbering system proposed by Ballschmiter and Zell *(15)* for PCBs is commonly used for PBDEs as well, and is applied in this thesis.

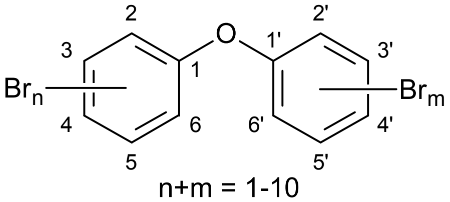


Figure 1. Molecular structure of PBDEs.

Among the PBDE congeners, the properties and, therefore, mobility in the environment depends on their degree of bromine substitution. PBDEs are non-volatile to semi-volatile with subcooled liquid vapor pressures (p_L^0) from 4.6 x 10^{-6} Pa for BDE-209 *(16)* to 0.26 Pa for BDE-3 *(17)*. They are highly hydrophobic with a logK_{OW} value from 5.9–6.2 for tetra-BDEs up to 10 for BDE-209 *(18)*. Similarly, the logK_{OA} increases with increasing degree of bromine substitution, i.e., from 9.3–9.5 for triBDEs *(19)* to 15.3 for BDE-209 *(20)*. The Henry's Law Constant ranges from 0.04 Pa m^3 mol^{-1} for BDE-209 to 4.83 Pa m^3 mol^{-1} for BDE-28 indicating a relatively low (re-)volatilization tendency from the aquatic environment into the atmosphere of lighter PBDEs whereas heavier PBDEs are unlikely to volatilize. Hence, the higher the degree of bromine substitution the lower the mobility between environmental compartments, and the higher the tendency to be distributed to suspended particulate matter in the aquatic environment and airborne particles in the atmosphere, respectively.

The manufacturing of PBDEs as FRs started in 1965 *(21)*. Three technical PBDE mixtures have been produced: (1) PentaBDE with BDE-99 > -47 as major congeners, (2) OctaBDE containing mainly hepta-BDEs (with BDE-183 as predominating congener) and octa- and hexa-BDEs, and (3) DecaBDE which is typically composed of 92–97% BDE-209 *(22)*. After their market introduction, PBDEs became a major group of commercially applied FRs with an estimated contribution of 40% on the global FR market in 1978 *(21)*. Resulting from the worldwide restrictions, DecaBDE can be expected to be the sole BDE-mixture to be currently available on the world market. No current production of Penta- and OctaBDE is registered, but production might still take place *(23)*. The global market volume of DecaBDE was 73000 tons in 2008 *(24)*, which is comparable to the global market of total PBDEs in 2001 (68000 tons, cited in *(25)*) before major restrictions came into force. This indicates a shift toward DecaBDE, but no general global production reduction of PBDEs in the last decade.

2.2.2. Environmental concerns of PBDEs

The congeners of Penta- and OctaBDE mixtures are persistent, have bioaccumulation (and -magnification) potential, are toxic and have the potential for LRAT *(20, 26)*. Even though BDE-209 is believed to be less bioavailable, less persistent and to have limited mobility due to its extreme hydrophobicity and involatility, it still raises direct, but also indirect risks for the environment as highlighted in the following.

Persistence. PBDEs are highly resistant to photolytic, chemical and biological degradation processes in various matrices with typical half-lives from days (atmosphere) to >1 year (sediment)

(20). However, the overall environmental persistence depends on the degree of bromine substitution and the distribution and transport pathways in the environment. Under the influence of sunlight PBDEs, including BDE-209, can be debrominated by direct photolysis leading to the consecutive formation of lighter PBDEs *(27-30)* as well as to polybrominated dibenzofurans (PBDFs) *(29, 31-33)* which both are more persistent, bioaccumulative and toxic than BDE-209 showing its indirect environmental risk.

Bioaccumulation and -magnification. PBDEs are easily accumulated by organisms from the aquatic environment and can biomagnify within the food web toward higher trophic levels *(34, 35)*. The bioconcentration factor (BCF) generally increases with increasing logK_{OW} and therefore with increasing degree of bromine substitution, but decreases again for highly brominated congeners with a logK_{OW} above 6–7 *(36)*. However, bioaccumulation and -magnification along food webs strongly depends on in vivo biotransformation rates and routes of the individual congeners, along with interspecies differences. BDE-209 has been shown to metabolize to lower brominated congeners, predominantly to nona-, octa-BDEs (and hepta- and hexa-BDEs) which can then be further metabolized to lower brominated DEs having higher bioaccumulation potential *(37, 38)*.

Toxicity. While the acute toxicity of PBDEs is considered to be low *(39)*, the toxic potential is based on various (long-term) effects on animals and humans. The most critical endpoints are developmental neurotoxicity and effects on thyroid hormones which are key components in the hormone and enzyme system as well as metabolic regulation *(26, 40)*. In humans, the prenatal exposure to PentaBDE has been associated to adverse effects on motor, cognitive and behavioral outcomes *(41)*. PBDEs have been further associated to reduce female fertility *(42)*, as well as to reduced male sperm count *(43)*. DecaBDE has been shown to cause liver and thyroid cancer *(44)* and can be classified as possible carcinogen to human *(45)*. In wildlife, adverse effects such as thyroid hormone alteration as well as reduced survival rate of seal pups have been observed which were, at least partially, attributed to PDBE exposure showing PBDEs to be possible endocrine disrupting compounds at environmental concentrations *(46-49)*.

Long-range transport potential. PBDEs have the potential to be atmospherically transported over (very) long ranges from source regions toward remote regions. First concern about their global transport was raised following their detection in seals from the Arctic Ocean in 1987 *(50)* indicating PBDEs to be global pollutants. Their LRAT potential has been further shown by their occurrence in various matrices in remote regions such as the Arctic (see

Environmental occurence) and by predictions using environmental fate models *(20, 51, 52)*. Congeners with low- to intermediate bromine substitution such as BDE-47 were modeled to undergo LRAT and reach remote regions like the Arctic in an extent similar to PCBs while a lower LRAT potential was ascribed to BDE-209 due to its involatility and association to airborne particles *(20)*. However, during strong winds and without particle removal from the atmosphere (i.e., limited precipitation) the application of environmental fate models shows a significant increase of the LRAT potential of BDE-209 *(52)*. In addition, BDE-209 has been observed in the Arctic atmosphere attached to airborne particles in concentrations similar to lower brominated congeners *(53, 54)* showing that it can undergo particle-bound LRAT.

Environmental occurrence. PBDEs do not naturally occur in the environment *(39)*. They were first reported in 1979 in soil and sludge close to a manufacturing site in the U.S. *(55)*. In organisms they were first detected in 1981 in fish from a Swedish river and bay *(56)*. Since then, they have been intensively studied and detected in various environmental compartments (e.g., air, sediment and soil, (sea-)water, sewage sludge, marine and terrestrial organisms and humans) all over the world resulting from their decade-long production and application along with emissions into the environment as summarized in various review papers *(4, 18, 25, 34, 35, 57-61)*. Thereby, the major congeners of the technical mixtures, e.g., BDE-47, -99, -183 and -209 typically dominated the environmental congener pattern. Due to increasing production and usage, temporal trends generally showed increasing concentrations from the 1970s to 2000s, both in humans and the environment *(18, 25)*, even in the Arctic *(62)*. Common sources of PBDEs are emissions from manufacturing *(63)* and from their end of life cycle, i.e., waste treatment facilities *(64-66)*, landfills *(67)*, and recycling processes such as recycling of electronic waste (e-waste) which has been reported as important source for e-waste recycling regions such as China *(68-70)*. Since PBDEs are semi-volatile and not chemically bond to the manufactured product, another major source, especially for the atmospheric environment is the direct leaching and abrasion from manufactured products during their life cycle. After leaching into the surrounding environment, predominantly indoor environments, they are transported to the outdoor environment by air exchange *(71, 72)*. This results in 10–50 times enhanced concentrations in indoor air *(73, 74)* compared to outdoor air concentrations which typically range from <1 pg m^{-3} to a few hundred pg m^{-3}. Strong decreasing gradients from urban to rural and further toward remote areas have been observed due to the generally higher usage and emissions of PBDEs in urbanized regions *(75-78)*.

Resulting from LRAT, PBDEs have been detected in remote air of the Arctic and the global oceans. Typical Arctic air concentrations were in the low one to two digit pg m^{-3} range, i.e., 0.78–

48 pg m^{-3} at Alert, Canadian Arctic *(54)* and 0.14–3.26 pg m^{-3} at Nuuk, Greenland *(79)*. BDE-47 and BDE-99 were the most prominent congeners in Arctic air, along with their predominance in the technical PentaBDE *(22)* and their LRAT potential *(80)*, whereas BDE-209 was not analyzed or not reported in most studies. Nevertheless, BDE-209 was first reported in oceanic Arctic air in 2005 at concentrations from <0.5 to 41.4 pg m^{-3} (attached to airborne particles only) *(53)*. Along the cruise leg from the Bohai Sea toward the Arctic Ocean, atmospheric PBDEs were strongly influenced by the proximity to source regions (i.e., China) as well as the wind direction during sampling leading to enhanced concentrations up to 199 pg m^{-3} in the Bohai Sea. Similarly, Wurl et al. *(81)* reported concentrations up to 16 pg m^{-3} in proximity to Indonesia over the Indian Ocean while concentrations over the open ocean were as low as 1.5 pg m^{-3}.

Even though PBDEs are highly hydrophobic and semi-volatile, they have been observed in surface waters but data, in particular on seawater, are very limited. In the North Sea and the river Scheldt estuary, concentrations from 0.1–5 pg L^{-1} were observed *(82)*. Higher concentrations were reported for the San Francisco Estuary at 3–513 pg L^{-1} *(83)*, and coastal waters from Hong Kong with up to 297 pg L^{-1} *(84)*, while data on open oceans are generally lacking.

2.2.3. Regulatory actions

The first regulations on production and application of PBDEs were introduced in the late 1980/90s in Europe, i.e., voluntary phase out of the marketing of PentaBDE by the German industry in 1986, and ban of PentaBDE in Sweden in 1999 *(85)*. Contrary, the production of PBDEs in the U.S. was not prohibited and still increased during that time. In 2004, the usage (>0.1% in manufactured products) of PentaBDE and OctaBDE was restricted in the EU *(86)*. Current restrictions on DecaBDE in the EU are limited to electrical and electronic equipment (E&E) while it can still be used for other applications *(87)*. Norway is currently the sole country that banned DecaBDE in applications besides E&E with a very few exemptions *(88)*. In the U.S., the production of Penta- and OctaBDE was voluntarily phased out by 2004 *(89)*, but no general restrictions on DecaBDE exist. Recently, a voluntary phase out of the DecaBDE production in the U.S. was announced for 2012/13 *(90)*. In China, the usage of Penta- and OctaBDE in E&E was restricted in 2007 *(91)*, but no restrictions on DecaBDE exist. On a global scale, Penta- and OctaBDE were adopted into the annex A (elimination of production and use of all intentionally produced persistent organic pollutants) of the Stockholm Convention on Persistent Organic Pollutants in 2009 forcing the global ban of PBDEs *(1)*.

2.3. Alternative halogenated flame retardants – classifications

Exact numbers on commercially available and applied alternative HFRs are not available. Harju et al. *(92)* listed 21 BFRs other than PBDEs, HBCD and TBBPA including additive, reactive and monomeric BFRs as well as aromatic and (cyclo-)aliphatic BFRs. They estimated an overall annual production volume of ~100000 tons for these 21 and possible other alternative BFRs. For additive aromatic non-PBDE BFRs, a fair estimate of the annual production would then be several ten thousand tons. None of the alternative HFRs given below is restricted or regulated, neither nationally nor globally. In the following, the alternative HFRs included in this thesis are briefly reviewed.

2.3.1. Traditional alternative non-PBDE brominated flame retardants

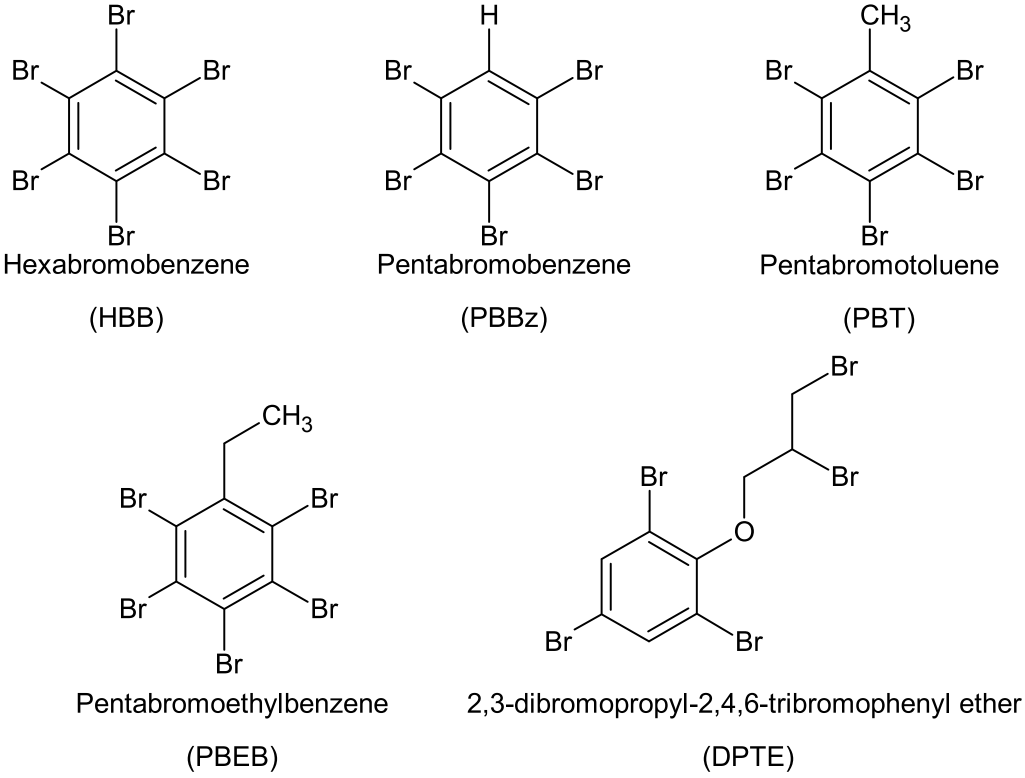


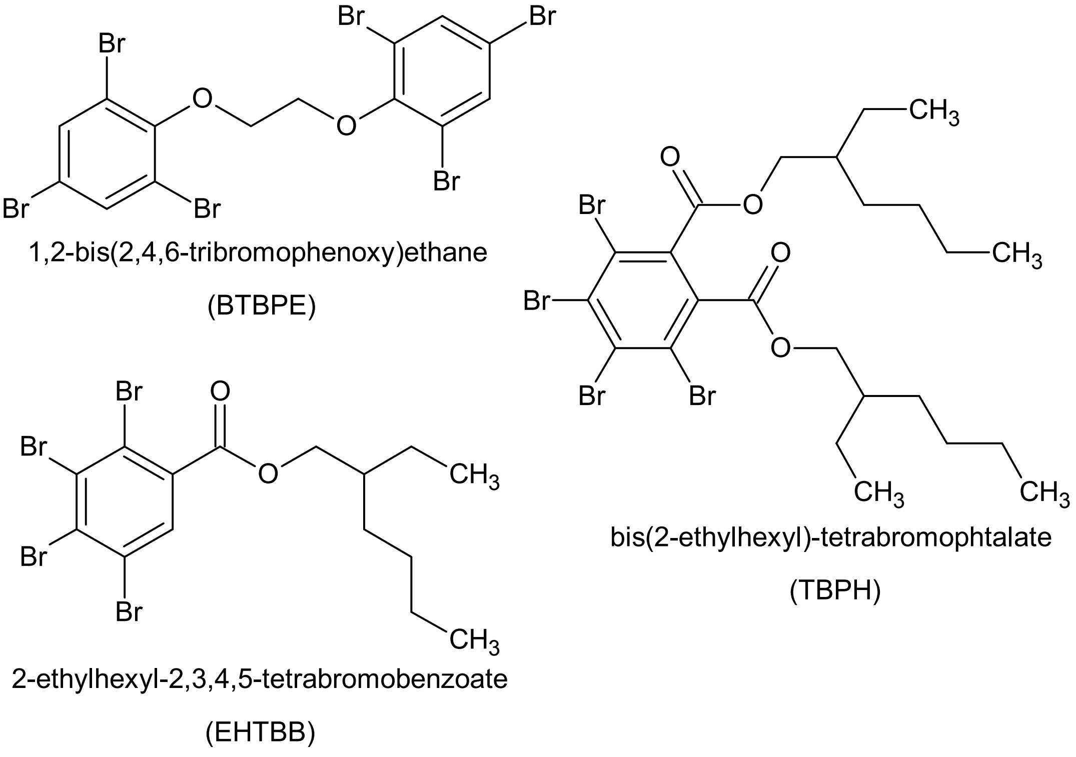
Figure 2. Chemical structures of traditional alternative non-PBDE brominated flame retardants.

Hexabromobenzene (HBB) is a common BFR used since the 1980s *(93)*. It was historically produced in Japan (270 tons per year in 1983 *(93)* and 350 tons per year from 1994-2001 *(94)*), and in the U.S. with 4–225 tons in 1998 yet no use was reported after 2002 *(95)*. It is additionally reported to be currently produced in China at 600 tons per year *(96)*. Pentabromobenzene (PBBz) is not known to be applied as FR.

Pentabromotoluene (PBT) has been used as FR for decades *(97)* with an estimated production volume of 1000–5000 tons per year *(9)*. Similar to HBB, a production of 600 tons per year has been reported for China *(96)* and it is reported to be produced and distributed in the U.S. *(98)*. Pentabromoethylbenzene (PBEB) has been produced during the 1970s and 1980s in the U.S. while production stopped in the late 1980s *(99)*. In the EU, both PBT and PBEB are registered as low production volume chemical (LPVC) indicating production/import of 10–1000 tons per year *(100)*.

2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) is a classical FR which has been manufactured by a German company in the 1980s *(9, 101)*, but the production stopped in 1985 *(102)*. No current production or marketing of DPTE is known.

2.3.2. PBDE replacements


1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)

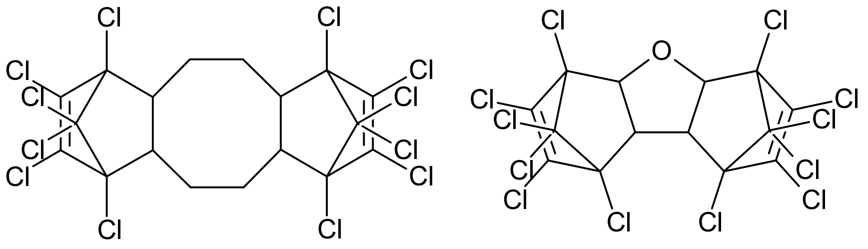
bis(2-ethylhexyl)-tetrabromophtalate (TBPH)

2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB)

Figure 3. Chemical structures of PBDE replacements.

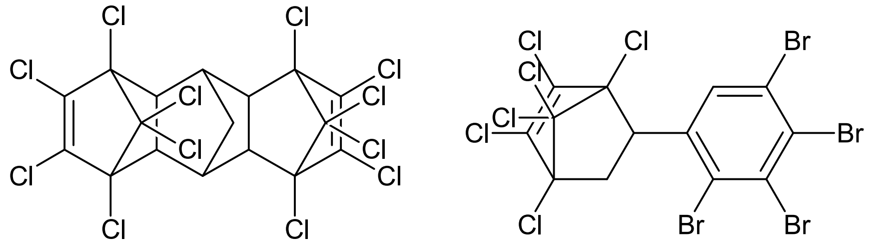
1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-tetrabromophthalate (TBPH) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) can be classified as PBDE replacements since they have been announced to replace PentaBDE (TBPH and EHTBB manufactured in Firemaster 550) and OctaBDE (BTBPE manufactured in Firemaster 680), respectively *(2, 89)*. Despite, BTBPE production started back in the 1970s *(103)* with production taking place in the U.S. with 4500–22500 tons between 1986 and 1994, which decreased to 450–4500 tons per year after 1998 *(99)*. However, the production can be expected to re-increase due to its marketing as PBDE replacement. BTBPE is registered as LPVC in the EU *(100)* and a global production/usage of 17000 tons was estimated for 2001 *(104)*. TBPH has been produced since the 1990s *(105)*. Even though TBPH and EHTBB are applied as mixture in Firemaster 680 in the U.S., only TBPH is listed as LPVC in the EU *(100)*.

2.3.3. Dechloranes



Dechlorane Plus (DP)

Dechlorane 602



Dechlorane 603

Dechlorane 604

Figure 4. Chemical structures of Dechloranes.

Mirex, a legacy pesticide banned under the Stockholm Convention, was widely marketed as pesticide in the 1960s and 1970s, but also as FR under its trade name Dechlorane by Hooker Chemical, now known as OxyChem *(106)*. In the 1960s, substitutes for Dechlorane were developed: Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), Dechlorane 604 (Dec 604) and Dechlorane 605, with the common trade name Dechlorane Plus (DP) *(107, 108)*. The ban of Dechlorane in the late 1970s led to its replacement by the other Dechloranes, in particular DP *(109)*.

Technical DP consists of two stereoisomers – synDP and antiDP – manufactured as a mixture consisting of 59 to 80% antiDP *(110)*. DP is a high production volume chemical in the U.S. with a production volume of ~5000 tons per year *(107)*. Additional production is known to take place in China with 300 tons per year *(111)*. DP is registered as LPVC in the EU, and the annual import volume was reported to be 800 tons for 2000 *(112)*. Since DP was suggested as replacement for DecaBDE by the EU *(113)*, the usage in Europe can be expected to increase in the future.

Even though Dec 602, 603 and 604 are patented for fire retardancy, very little is known on production and usage *(108)*. While Dec 602 is reported to be applied in fiberglass-reinforced nylon and Dec 604 is an ingredient of silicone grease, respectively, Dec 603 is currently not known to be applied as FR *(114)*.

2.4. pbt-properties and long-range atmospheric transport potential of alternative halogenated flame retardants

Even though some alternative HFRs have been applied for decades and are structurally related to PBDEs and Mirex, their physicochemical properties, pbt-properties and environmental fate are poorly investigated. Generally speaking, the physicochemical properties of non-PBDE BFRs and Dechloranes are similar to those of PBDEs, e.g., highly hydrophobic and semi-volatile to non-volatile. PBT, PBBz, DPTE, HBB and PBEB are semi-volatile with physicochemical properties in the range of tri- and tetra-BDEs such as BDE-47, while EHTBB, TBPH, BTBPE as well as Dechloranes have properties related to higher brominated DEs such as BDE-183 and BDE-209 representing non-volatile HFRs. A summary of their physicochemical properties is given together with BDE-47 and -209 in Table 1.

Table 1. Physicochemical properties of alternative HFRs included in this thesis estimated using U.S. EPA EPI Suite 4 *(115)* and, if available, given in the literature (at 25 °C if not marked otherwise). p_L^0 = subcooled liquid vapour pressure, H = Henry's Law Constant, S_W = solubility in water, n.a.=not analyzed.

Abbreviation	**CAS**	**S_w [mg L^{-1}]**	**p_L^0 [Pa]**	**H [Pa m^3 mol^{-1}]**	**logK_{OW}**	**logK_{OA}**
BDE-47	5436-43-1	1.5 x 10^{-3} 1.5 x 10^{-2} *(17)* 9.3 x 10^{-3} *(116)*	2.1 x 10^{-4} 1.9 x 10^{-4} *(17)* 3.2 x 10^{-4} *(117)* 8.2 x 10^{-5} *(116)*	0.30 1.5 *(17)* 0.85 *(118)*	6.8 6.6 *(17)* 6.8 *(119)* 6.7 *(116)*	10.7 10.5 *(19)*
BDE-209	1163-19-5	2.8 x 10^{-11} 4.2 x 10^{-9} *(20)* 1.3 x 10^{-8} *(116)*	6.3 x 10^{-7} 3.0 x 10^{-9} *(20)* 5.4 x 10^{-11} *(116)*	0.0012 0.04 *(118)*	12.1 11.1 *(116)*	18.4
HBB	87-82-1	2.2 x 10^{-3} 3.0 x 10^{-3} *(17)* 1.1 10^{-4} *(120)*	5.7 x 10^{-3} 3.2 x 10^{-4} *(120)* 7.5 x 10^{-4} *(17)*	2.2 11 *(120)* 0.14 *(17)* 0.25 *(121)*	7.3 6.1 *(120)*	9.1
PBBz	608-90-2	3.4 x 10^{-3}	3.1 x 10^{-2}	5.5	6.4	9.1
PBEB	85-22-3	2.9 x 10^{-4}	8.5 x 10^{-3}	8.0	7.5	10.0
PBT	87-83-2	9.4 x 10^{-4}	1.6 x 10^{-2}	6.0	7.0 5.4 *(122)*	9.6

DPTE	35109-60-5	1.8 x 10^{-3}	1.6 x 10^{-3}	0.048	6.3	11.1
BTBPE	37853-59-1	6.6 x 10^{-7}	3.2 x 10^{-6}	0.00074	9.2	15.7
EHTBB	183658-27-7	1.4 x 10^{-5}	1.7 x 10^{-4}	0.64	8.8	12.3
TBPH	26040-51-7	2.0 x 10^{-9}	3.6 x 10^{-7}	0.030	12	16.9
DP	13560-89-9	1.7 x 10^{-8} 4.4 x 10^{-4} *(123)*[a] 2.5 x 10^{-1} *(123)*[a]	7.9 x 10^{-6} 8 (200 °C) *(123)*	0.75	11.3 9.3 *(123)*	14.8
aCl$_{10}$DP	n.a.	4.2 x 10^{-4}	3.8 x 10^{-5}	6.1	10.2	12.8
aCl$_{11}$DP	n.a.	1.7 x 10^{-7}	1.1 x 10^{-5}	2.1	10.4	13.4
Dec 602	31107-44-5	1.7 x 10^{-5}	5.9 x 10^{-5}	0.00027	8.1	15.0
Dec 603	13560-92-4	2.5 x 10^{-8}	2.1 x 10^{-5}	0.25	11.2	15.1
Dec 604	34571-16-9	3.7 x 10^{-8}	1.3 x 10^{-5}	0.11	10.6	14.9

[a] different solubilities of the two stereoisomers are reported, but not specified.

From their structural and physicochemical similarities to PBDEs, their pbt-properties and LRAT potential can be expected to be similar, too, but risk assessments are lacking and studies on their pbt-properties and LRAT potential are hardly available. A few screening studies on industrial chemicals including some but not all of the alternative HFRs focused in this thesis with respect to their pbt-properties and LRAT potential are however available *(92, 124-127)*. Nevertheless, the screenings and predictions partly show controversial results. In the OSPAR Convention, PBEB as well as HBB and PBT are categorized as chemicals for priority action *(128)* and chemicals of possible concern *(129)* for the marine environment, respectively[2]. Fisk et al. *(126)* categorized PBEB, PBT and DPTE as pbt-substances and DP, TBPH and Dec 602 as very persistent and very bioaccumulative (vPvB)[3] substances. Strempel et al. *(127)* categorized DPTE and PBBz as pbt-substances while PBT, PBT, HBB and PBEB were ascribed a lack of bioaccumulation potential, while Howard and Muir *(125)* identified PBEB, HBB, BTBPE, TBPH and DP as persistent and bioaccumulative chemicals. Empirically, the occurrence of several non-PBDE BFRs and DP in organisms further indicates their liability to bioaccumulation and magnification *(96, 130)*, but data are still very limited and partly controversial. However, a higher bioaccumulation potential of HBB and BTBPE than PBDEs was observed as well as biomagnification potential of HBB, PBEB, PBT, BTBPE and DP *(131-137)*.

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[2] OSPAR = The Convention for the Protection of the marine Environment of the North-East Atlantic. The pbt cut-off values in the OSPAR Commission are defined as follows: persistence = half-life in the marine or freshwater environment >50 days; bioaccumulation = bioaccumulation/-concentration factor >500, or logK_{OW} >4; toxicity = acute LC50 ≤1 mg L^{-1}, long-term NOEC ≤0.1 mg L^{-1}, or carcinogenic, mutagenic and toxic for reproduction, or chronic toxicity.

[3] The vPvB cut-off values used for screening were as follows: persistence = half-life in the marine or freshwater >60 days or >180 days in marine or freshwater sediment; bioaccumulation = bioaccumulation/-concentration factor >5000, or logK_{OW} >5.

The estimated atmospheric half-life (versus reaction with ·OH radicals) of DPTE, HBB, PBBz, PBEB, PBT and Dec 604 exceeds the LRAT threshold of 48 h defined in the Stockholm Convention (see *Appendix C* for estimated half-lives). Furthermore, the estimation of the LRAT potential using "The Tool" *(138)* shows a high potential for HBB, PBBz, PBEB and PBT which is similar or even higher than PBDEs and other legacy POPs (see *Appendix C* for results of the prediction using "The Tool"). Similarly, Harju et al. estimated a high LRAT potential of HBB, PBT and PBEB based on the approach of "Arctic contamination potential" *(80, 139, 140)*. Besides these semi-volatile compounds, several highly hydrophobic alternative HFRs might be transported attached to airborne particles. This has been shown to be sufficient for transport of BDE-209 to the Arctic *(53)*.

2.5. Environmental occurrence of alternative halogenated flame retardants

Similar to PBDEs, none of the targeted alternative HFRs has been reported to naturally occur in the environment. Even though first reports on several non-PBDE BFRs in the environment trace back to the 1970/80s, e.g., PBT was detected in sewage sludge in 1975 *(97)*, and HBB was observed in sediments and humans in the 1980s *(93, 141)*, they were omitted from most environmental investigations until the 2000s. Since then, scientific interest and reports on their occurrence increased rapidly and, meanwhile, they have been detected in various matrices including indoor air and dust, outdoor air, water, sediment, soil, sewage sludge, wildlife and humans *(96)*. Most studies focused on regions close to known sources in the U.S. and China, while investigations on the European as well as the global marine environment are still very limited.

In the atmosphere, several papers reported concentrations of non-PBDE BFRs similar to PBDEs. Ma et al. *(142)* observed TBPH and EHTBB in air from the Great Lakes region at 0.05–55 pg m^{-3} and 0.11–290 pg m^{-3}, respectively, which is similar to PBDEs in this region *(143)*. However, TBPH and EHTBB showed an increasing temporal trend, whereas PBDEs decreased. HBB was detected in Japan up to 610 pg m^{-3} *(144)* and Arp et al. reported HBB in Norwegian air at 4.3 ± 5.3 pg m^{-3} attached to airborne particles *(115)*. Again in the Great Lakes region, Salamova and Hites *(145)* reported HBB, PBEB and BTBPE in the atmosphere. The highest HBB concentration was observed at a rural site at 6.4 ± 0.9 pg m^{-3} which was about 80% of the PBDE concentration (sum of congeners in the gas phase), while PBDEs were substantially higher than HBB at other urban sites.

Despite its decade-long production, DP was first reported in 2006 in the atmosphere and sediments from the Great Lakes region *(107)*. Concentrations ranged up to 490 pg m^{-3} close to a

DP manufacturing site which is similar to reported BDE-209 concentrations. Its ubiquitous detection in air from China *(146)*, and in tree bark from Germany and Italy *(147)* first indicated that its environmental distribution is of global relevance. The highest atmospheric concentrations so far were reported in China close to a manufacturing site with up to 27 ng m^{-3} *(110)*. After its first detection in the environment almost 100 scientific papers focused on the occurrence and fate of DP in different environmental compartments were published, most of them again focusing on the Great Lakes regions and on the Chinese environment as summarized in three recent review papers *(130, 148, 149)*. Besides the parent compound, possible dechlorination products of DP, the one- and twofold dechlorinated species of antiDP ($aCl_{11}DP$ and $aCl_{10}DP$, respectively) have been reported, e.g., in sediment *(150)*, human serum *(151)* and biota *(152)* with concentrations typically one order of magnitude lower than DP.

Dec 602, 603 and 604 were first reported in the environment in sediment and fish from the Great Lakes in 2010, with Dec 602 concentrations in fish exceeding those of DP due to its higher bioavailability *(108)*. They were further reported in lake, river and coastal sediments *(153-155)* and oysters *(154)* from the Great Lakes region and Chinese coastal regions. There is only one report for the European environment reporting their occurrence in bird eggs from Spain *(152)*, but in concentrations similar to DP.

In comparison to PBDEs, only very few studies focused on alternative HFRs in remote regions, in particular the Arctic. Nevertheless, several alternative HFRs have been reported in Arctic organisms indicating that they can reach and enrich in the Arctic. BTBPE was reported in bird eggs from the Faroe Islands *(156)*, and HBB, PBT, PBEB and BTBPE were reported in birds from the Norwegian Arctic whereby HBB showed the highest concentrations *(104)*. DPTE was reported in blubber and brain from harp seals from East Greenland Sea (*Phoca groenlandica*) sampled in 1991 *(157)*. Interestingly, the concentrations were higher than typical PBDE concentrations in Arctic seals *(158)*, and DPTE showed a high potential to enrich in brain. Despite reports in biota, data on remote abiotic samples, in particular the atmosphere, are even more limited. Hermanson et al. *(159)* reported BTBPE and PBEB in ice cores from Svalbard, Norwegian Arctic with a deposition flux of <6 pg cm^{-2} $year^{-1}$, while BDE-209 dominated with a flux up to 320 pg cm^{-2} $year^{-1}$. Only recently, Xiao et al. *(160)* reported BTBPE, EHTBB, TBPH, HBB, PBT and DP in the atmosphere from Alert, Canadian Arctic. BTBPE, EHTBB and TBPH dominated with maximum concentrations of a few pg m^{-3}. It needs to be noted that only a very few concentrations, and even none of the reported BTBPE and synDP concentrations, were above their analytical detection limit which limits the significance of the results.

3. Point of departure of the thesis

Starting research on this thesis, PBDEs had just been adopted as POPs into the Stockholm Convention on Persistent Organic Pollutants and the production of the Penta- and OctaBDE mixtures had already been stopped on a global scale. Their usage and application had been restricted by (inter-)national laws, including the third technical PBDE mixture – DecaBDE – at least for usage in E&E in the EU. Several alternative HFRs had popped up in the environment, predominantly in urbanized and industrialized regions such as the Great Lakes region, Canada and in China. Global concern on alternative HFRs raised from first reports in Arctic biota indicating the LRAT potential of alternative HFRs, but their transport pathways toward remote regions together with their occurrence and distribution in the marine environment had not been investigated at all. The identification of this scientific knowledge gap as one key question for future research on alternative HFRs was the point of departure for this thesis.

4. Research objectives

The overall objective of this thesis was to investigate whether alternative HFRs do undergo LRAT from source regions to the marine environment and further toward remote regions. This was hypothesized for several alternative HFRs based on their structural similarity to PBDEs and their occurrence in Arctic biota. The first aim was to identify which alternative HFRs are present in the marine atmosphere, and to further describe the current status of alternative HFRs in the global marine atmosphere including the Polar Regions of the Arctic and Antarctica. If detected in the marine atmosphere, the aim was to investigate their (continental) source regions together with their transport pathways toward the open oceans and further toward the Polar Regions. Since about 71% of the earth's surface is water and the major gateway to the Polar Regions is the transport over the global oceans, the third aim was to investigate the exchange between the atmosphere and the underlying surface seawater influencing the transport potential and loadings into the aquatic environment. Surface waters can act as buffers between the atmosphere and the deep sea *(161)*, and have a significant contribution to the cycling and transport in the environment *(162, 163)*. Therefore, this thesis is focused on marine boundary layer air as well as surface seawater. Among all objectives, special emphasis was given to the comparison of the investigated alternative HFRs versus PBDEs in order to evaluate the LRAT behavior and sources of the alternative HFRs compared to the legacy PBDEs, since LRAT is one key criterion for chemicals to be of global concern and classified and restricted as POPs. The papers included in this thesis are generally focused on individual oceanic regions which, all together, represent the investigation of the global marine environment. The specific aims of the individual papers were:

Paper I: to investigate the occurrence and distribution of DP in the atmosphere and seawater from the European Arctic, the Atlantic and the Southern Ocean, in order to evaluate whether DP undergoes particle-bound LRAT in an extent similar to BDE-209. This had been highlighted as important research gap after the first detection of DP in the environment *(3)*. Further objectives were the investigation of possible stereoselective differences of the two DP stereoisomers during atmospheric transport and the identification of source regions,

Paper II: to investigate non-PBDE BFRs together with PBDEs over the marine European Arctic in order to study the role of Western Europe as source region for the European Arctic. Furthermore, the exchange between the atmosphere and seawater was estimated to study the LRAT behavior and sources for the marine environment,

Paper III: to investigate the transport of non-PBDE BFRs and PBDEs over the North and South Atlantic Ocean toward Antarctica with respect to the possible source regions Europe and Africa as well as exchange between the atmosphere and seawater,

Paper IV: to investigate the short term as well as seasonal variation of alternative HFRs and PBDEs over a marginal sea with strong continental influence – the German Bight, North Sea – with respect to exchange between the atmosphere and seawater as well as riverine discharge,

Paper V: to investigate the transport of alternative HFRs and PBDEs over the North Pacific Ocean toward the Arctic, with emphasis of East Asia as potential source region and the exchange between the atmosphere and seawater, and

Paper VI: to investigate the transport of alternative HFRs and PBDEs over the Indian Ocean, with emphasis of Southeast Asia as well as Australia as potential source regions, and the temperature dependence of the occurrence, distribution and transport in the atmosphere.

5. Experimental

5.1. Sampling

High-volume air samples as well as high-volume seawater samples were simultaneously taken during several research cruises from 2008 to 2011:

Table 2. Summary of sampling cruises included in this thesis.

region/transect	research vessel	cruise name	date	samples	paper
East Greenland Sea	Polarstern	ARK-XXIV/3	08/2009-09/2009	air: 10 water: 16	I+II
Northern Atlantic Ocean – Southern Atlantic Ocean – Southern Ocean	Polarstern	ANT-XXV/1+2	11/2008-12/2008	air: 10 water: 16	II+III
German Bight, North Sea	Heincke	H319, H325, H331	03/2010, 05/2010, 07/2010	air: 20 water: 36	IV
Rivers Elbe and Weser	Ludwig Prandtl	–	02/2011	water: 8	IV
East China Sea – Northern Pacific Ocean – Arctic Ocean – East China Sea	Xuelong (snow dragon)	CHINARE-4	06/2010-09/2010	air: 17 water: 18	V
East Indian Archipelago – Western Australia – Indian Ocean – Southern Ocean – East Indian Archipelago	Xuelong (snow dragon)	CHINARE-27	11/2010-03/2011	air: 20	VI

Air samples were taken via a high-volume air sampler placed in front of the most upper deck of the respective research vessel. Air samples were taken for one day (~300 m^3) for samples in marginal seas as well as coastal areas and up to several days (>1000 m^3) in remote regions. Airborne particles were trapped on glass fiber filters ([GFF], Macharey Nagel GF/F, diameter 150 mm, pore size 0.7 µm) and the gaseous compounds were trapped on self packed glass cartridges filled with polyurethane foam (PUF) and Amberlite XAD-2 (top to bottom). Integrated high-volume seawater samples (~100 L for marginal seas up to >1000 L for remote oceans) were taken via the ship's intake pump. 5 L grab stainless steel bucket samples were taken aboard R/V Ludwig Prandtl. The seawater was passed over GFFs (Whatman GF/C, diameter 142 mm, pore size 1.2 µm) to trap suspended particulate matter followed by a self packed glass cartridge filled with Serdolit PAD-2 (SERVA Electrophoresis) to trap the dissolved compounds (Serdolit PAD-3 for CHINARE-4 and aboard R/V Ludwig Prandtl). Air columns and filters were stored at -20 °C and water columns at 0–4 °C until extraction, respectively.

5.2. Extraction and analysis

Samples were extracted with dichloromethane ([DCM], hexane/DCM 1:1 for air samples of ARK-XXIV/3 and ANT-XXV/1+2, respectively) for 16 h in a Soxhlet apparatus. Before extraction, the samples were spiked with known amounts of surrogate standards (200 pg of each ^{13}C-BDE-77 and ^{13}C-BDE-138 for ARK-XXIV/3 and ANT-XXV/1+2; 200 pg of each ^{13}C-BDE-77, ^{13}C-BDE-138, ^{13}C-HBB, ^{13}C-synDP and 2000 pg ^{13}C-BDE-209 for other samples). The extracts were concentrated in a rotary evaporator to 1–2 mL, and purified on a 10% water deactivated silica column (2.5 g) topped on sodium sulfate (3 g), eluted with 20 mL hexane. The eluates were reduced under a gentle nitrogen stream (1.5–2 bars) to a final volume of 30 µL and 1 ng ^{13}C-hexachlorobenzene (^{13}C-HCB) was added as recovery standard prior to injection (500 pg PCB-207 for CHINARE-27).

Analysis was done via gas chromatography coupled to a mass spectrometer (GC-MS) with electron capture negative chemical ionization (ECNCI) in selected ion monitoring (SIM) mode. The GC-MS (Agilent 6890 GC/5975 MSD) was equipped with a programmable temperature vaporizer (PTV) inlet operated in pulsed-splitless mode with an injection pulse of 20 psi for 2 min. The inlet program was 60 °C for 0.1 min, raised at 500 °C to 280 °C and held for 20 min. The GC was equipped with 30 m HP-5MS column (0.25 mm inner diameter x 0.25 µm film thickness, J&W Scientific). The GC oven was 60 °C for 2 min, 30 °C min^{-1} to 180 °C, 2 °C min^{-1} to 280 °C, 30 °C min^{-1} to 300 °C and held for 6 min, 30 °C min^{-1} to 310 °C and held for a final 25 min. In paper VI, a 15 m column was used for the analysis of BDE-209 (see paper VI for details). The MS transfer line was held at 280 °C and the ion source and quadrupole temperature was 150 °C.

Since several alternative HFRs were recognized as HFRs of emerging interest during ongoing research of this thesis, or suitable analytical standards just became commercially available, not all target compounds were included in all papers, e.g., PBBz was included only in paper IV, V and VI and Dec 602, 603 and 604 were included only in paper V and VI. BDE-209 was not included in paper II due to bad chromatography. The final method includes 10 PBDE congeners, 8 non-PBDE BFRs and 6 Dechlorane compounds as listed together with the monitored mass-to-charge (m/z) values of all target compounds, surrogates and internal standards in Table 3. Analytical standards were obtained from Wellington Laboratories, except ^{13}C-HCB, ^{13}C-synDP (Cambridge Isotope Laboratories), PCB-207 (Dr. Ehrenstorfer GmbH) and Dec 602, 603 and 604 (Toronto Research Chemicals). DCM and hexane were picograde and were obtained from Promochem.

Quantification was done based on peak areas using internal calibrations based on response factors between the target compound and the respective surrogate standard. Thereby, all results were recovery corrected.

Table 3. m/z values used as quantifier (Q) and qualifiers (Q1-3) for analysis of target HFRs, surrogate standards and recovery standards.

Abbreviation	Q	Q1	Q2	Q3
^{13}C-HCB	289.8	255.8		
PCB-207	463.7	461.7		
^{13}C-HBB	559.6	479.6		
^{13}C-BDE-77, -138	79	81		
^{13}C-BDE-209	494.6	413.8		
^{13}C-synDP	667.8	633.8		
BDE-28	79	81	161	327
BDE-47, -66, -85, -99, -100	79	81	161	
BDE-153, -183	79	81		
BDE-154	79	81	563.7	482.8
BDE-209	486.5			
PBBz	79	81	472	474
PBT	79	81	485.7	
PBEB	79	81	499.7	421.6
DPTE	79	81	159.8	
HBB	549.5	473.7		
EHTBB	356.7	79	81	470.9
BTBPE	79	81	251.8	
TBPH	384	464		
aCl$_{10}$DP	583.8	549.9	513.8	
aCl$_{11}$DP	617.8	583.7	547.7	
synDP, antiDP	653.8	617.9	583.9	
Dec 602	613.7	340.8		
Dec 603	637.7	601.7		
Dec 604	79	81		

5.3. QA/QC

In order to prevent sample contamination by the sampling material itself, the sampling columns were cleaned by Soxhlet extraction with solvents of different polarity (e.g., methanol, acetone and hexane) before usage. GFFs were baked at 450 °C for 12 h before usage for sampling. If possible, the application of any plastic material was avoided, e.g., metal tubes were used for the sampling of seawater. To prevent contamination by the ship itself, air sampling was conducted during “good” weather conditions only, i.e., no sampling during station time, back winds and wind speeds <3 m s^{-1}. Air columns were wrapped with aluminum foil during sampling as well as during extraction in the lab to avoid degradation of the target compounds by sunlight.

Sample handling was conducted in a clean lab class 10000. All used glass ware was baked at 250 °C for 10 h and rinsed with the respective solvent before usage. Silica gel and sodium sulfate was baked at 450 °C before usage, too, and rinsed with hexane before application for the sample clean-up. Field blanks and method blanks were taken during each cruise and blank levels were kept at a very low range, generally in the one- to two-digit absolute pg range as presented in the individual papers which was essential to enable proper identification of the target HFRs in remote regions.

Method detection limits (MDLs) were calculated based on mean blank values plus three times the standard deviation (SD), or, for those compounds showing no blank contamination, at instrumental signal-to-noise ratios (S/N) of three. Depending on the sampling volumes and blank levels, typical MDLs were in the one to two digit fg m^{-3} and fg L^{-1} range, respectively, while higher MDLs up to a few pg m^{-3} and pg L^{-1}, respectively, were observed for BDE-209. Breakthrough tests using tandem columns were conducted showing no breakthrough of the target compounds (i.e., concentrations in the lower column below MDL). The completeness of the extraction was proved exemplarily by second extractions of the samples showing no residues above the MDL. Recoveries of the surrogates were monitored in each sample and recoveries of the target analytes were regularly checked by spike tests. Recoveries of target compounds as well as surrogates generally ranged from 60 to 100%. Individual QA/QC parameters are presented in the respective papers.

5.4. Air mass back trajectories

In order to identify possible source regions and atmospheric transport pathways of detected target compounds, air mass back trajectories (BTs) were calculated for each air sample using NOAA’s Hysplit 4.9 model *(164)*. Meteorological data was provided from the NCEP Global Data Assimilation System model (GDAS). Air masses were traced back for five days and BTs were recalculated every four to six hours, while the arrival position was adjusted to the corresponding position of the ship. The arrival height was set to the sampling height.

5.5. Air-seawater exchange

To estimate the exchange between air and seawater of semi-volatile compounds distributed in the gaseous phase, the direction of the dry air-seawater gas exchange was predicted using the ratio of the fugacities in air and seawater. The net dry air-seawater gas exchange was estimated using the modified version of the Whitman two-film resistance model *(165, 166)*, a model commonly used to estimate the net dry gaseous flux between air and water, including open oceans *(162, 167-169)*. To properly estimate the flux, the Henry's Law Constant was adjusted to the given water temperature and salinity, and the flux was calculated based on the respective air and water temperatures as well as wind speeds as monitored during sampling aboard the research vessel. Fugacity ratios and net air-seawater gas exchange were estimated for the simultaneously taken air and seawater samples using the gaseous and dissolved fraction only. Details on the calculations are given in *Appendix B*.

The dry deposition of particle-bound compounds was estimated based on the obtained particle-bound concentrations of the target compounds and estimated particle deposition velocities. For open oceans (paper I, II, III, V) a deposition velocity of 0.1 cm s^{-1} was adopted according to deposition measurements for polyaromatic hydrocarbons (PAHs) in the Atlantic Ocean *(170)* and global marine deposition velocity observations *(171)*. A higher velocity of 0.2 cm s^{-1} was used for the German Bight, North Sea (paper IV) representing marine aerosols with continental influence *(172)* and a value of 0.3 cm s^{-1} was used for the samples along the Asian coast (paper V) according to observations in Chinese coastal regions *(173)*.

6. Results and Discussion

This thesis resulted in several contributions which significantly improve the knowledge on occurrence, fate and transport – in particular LRAT – of alternative HFRs as well as PBDEs in the global (marine) environment. Since alternative HFRs are semi-volatile (or non-volatile) and have limited water solubility, the discussion in the following chapters is mainly focused on the atmosphere being their predominant medium of transport in the marine environment. Nevertheless, detailed discussions on alternative HFRs and PBDEs in seawater are given in the individual papers. The results of this thesis are summarized and discussed in the following chapters, addressing:

- Occurrence – alternative halogenated flame retardants versus PBDEs
- Global distribution and long-range atmospheric transport potential

- Atmospheric transport – from the continents toward the open oceans
- Alternative halogenated flame retardants – do the (un-)known sources explain the occurrence?
- Dechlorane Plus: stereoselective transport
- Exchange between air and seawater

6.1. Occurrence – alternative halogenated flame retardants versus PBDEs

Apart from PBDEs, which are known to be present ubiquitously in the global environment *(4, 25)*, this thesis presents the first observations of various alternative HFRs in the *global* marine atmosphere representing a first basic dataset. DP, HBB, PBT, DPTE and PBBz were the predominant compounds with detection frequencies from 86% for PBBz to 100% for synDP. TBPH, EHTBB and BTBPE were detected in 42%, 28% and 21% of all air samples, respectively. The other Dechloranes – Dec 602, 603 and 604 – as well as $aCl_{11}DP$ were observed in <20% of the samples, while $aCl_{10}DP$ and PBEB were not detected in any air sample. Alternative HFRs as well as PBDEs were detected both in the gaseous and the particulate phase, while the phase distribution generally followed the trend of their $\log K_{OA}$ values. Lighter HFRs such as PBBz, PBT and HBB were distributed mainly into the gaseous phase (median particle-bound fraction of 0 ± 0.2%, 0 ± 13% and 3 ± 6%, respectively) and heavier HFRs such as BDE-209, DP and TBPH were predominantly distributed into the particulate phase with a median particle-bound fraction of 100 ± 34% for BDE-209, 60 ± 30% and 68 ± 32% for syn- and antiDP, respectively, and 100 ± 35% for TBPH (see Table 1 for $\log K_{OA}$ values).

While PBDEs have historically been the dominating HFRs in the global atmosphere, this thesis shows that this is in general no longer the case, at least for the global *marine* atmosphere (see Figure 4 for contributions of individual HFRs in air samples from the entire thesis). Even though PBDEs still dominated in the European Arctic (paper I+II, median contribution of Σ_{10}PBDEs of 44 ± 21%), non-PBDE BFRs had higher contributions in all other investigated regions, e.g., up to 76 ± 23% for $\Sigma_8$non-PBDE BFRs over the Pacific and Indian Ocean (paper VI). Overall, HBB was the predominating compound with a median contribution of 18 ± 21%, followed by DP with 9 ± 18% (sum of syn- and antiDP) and DPTE with 8 ± 9%, respectively. Among PBDEs, the common Penta-, Octa- and DecaBDE congeners – BDE-47, -99 and -209 – generally dominated. However, the composition of alternative HFRs, as well as the contribution of the individual PBDE congeners displayed global, regional and temporal differences caused by differences in sources and meteorological impacts as discussed in the individual papers and summarized in the following chapters.

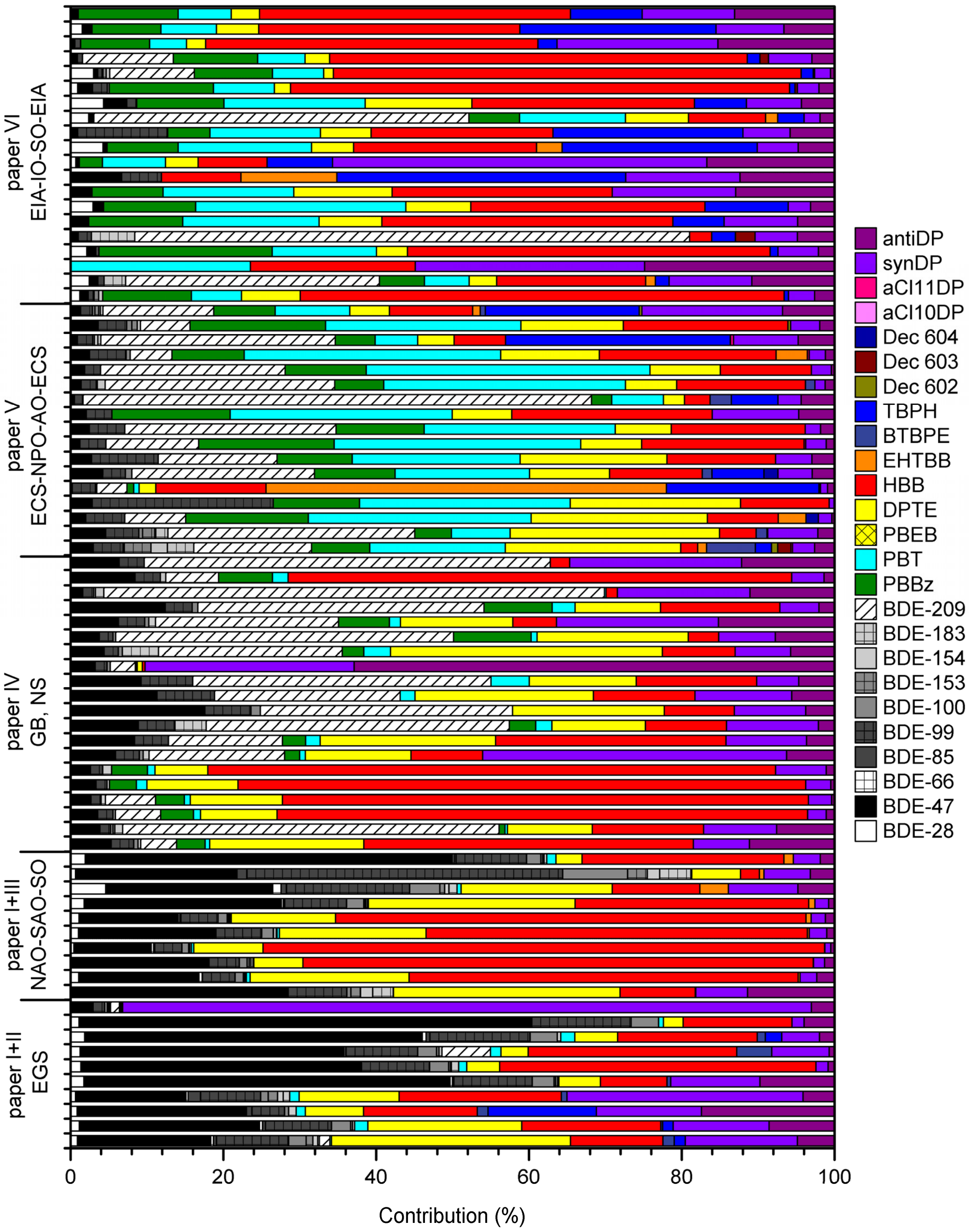

Figure 5. Relative contributions of individual HFRs in the atmosphere from the sum of investigated HFRs. Note that not all target compounds were included in all papers as explained in chapter *Experimental.* EGS = Greenland Sea, NAO = North Atlantic Ocean, SAO = South Atlantic Ocean, SO = Southern Ocean, GB = German Bight, NS = North Sea, ECS = East China Sea, NPO = North Pacific Ocean, AO = Arctic Ocean, EIA = East Indian Archipelago, IO = Indian Ocean.

Total concentrations (sum of gaseous and particulate phase) ranged from <MDL to 11 pg m^{-3} for Σ_{10}PBDEs, 0.02 to 34 pg m^{-3} for $\Sigma_8$non-PBDE BFRs and from 0.006 to 22 pg m^{-3} for Σ_6Dechloranes, with concentrations <1 pg m^{-3} over the open oceans and enhanced concentrations over the marginal seas as discussed in chapter *Atmospheric transport – from the continents toward the open oceans*. The individual concentrations of the predominating compounds are presented in Table 4 together with available literature data on the marine atmosphere.

The observed PBDE concentrations were in a range similar to those reported for marine concentrations, with the exemption of data published by Wang et al. *(53)* who reported concentrations one to two orders of magnitude higher for the similar transect as investigated in paper V. This might be a result of the ongoing restriction of the production and usage of PBDEs, in particular Penta- and OctaBDE, leading to decreasing concentrations in the past decade. Alternative HFR concentrations similar to those over the open oceans in this thesis have been reported for continental remote sites, e.g., for DP, HBB, BTBPE, PBBz and PBT in the Great Lakes region *(107, 145, 174, 175)*.

Table 4. Atmospheric concentrations (in pg m^{-3}, sum of gaseous and particulate phases) of PBDEs, HBB, PBT, DPTE and DP over the global oceans and their marginal seas (n.a. = not analyzed, n.d. = not detected). Note that the number of individual congeners included in ΣPBDEs varies in the literature. Modified from paper VI.

oceanic region	**Year**[a]	**BDE-47**	**BDE-209**	**ΣPBDEs**	**HBB**	**PBT**	**DPTE**	**DP**	**Reference**
Atlantic Ocean	2008	0.57–8.3	n.a.	0.86–6.4	n.a.	n.a.	n.a.	n.a.	ref*(176)*
Atlantic Ocean	2008	0.18–2.3	n.a.	0.43–3.3	0.10–11	0.01–0.05	0.10–2.3	0.05–1.6	paper I+III
Atlantic Ocean (North Sea)	2010	0.10–0.79	n.d.–9.4	0.31–10.7	0.09–6.3	n.d.–0.24	n.d.–2.5	0.13–22	paper IV
Pacific Ocean	2010	0.04–0.11	n.d.–2.0	0.22–2.3	0.10–2.5	0.12–0.64	0.18–0.41	0.01–0.86	paper V
Pacific Ocean [b]	2003	0.88–17	<0.5–27	1.4–37	n.a.	n.a.	n.a.	n.a.	ref*(53)*
Pacific Ocean (East Asian Seas)	2010	0.07–0.76	0.13–3.9	0.31–8.1	0.26–0.57	0.36–4.5	0.26–5.9	0.52–1.4	paper V
Pacific Ocean (East Asian Seas) [b]	2003	<0.16–112	<0.50–29	2.3–199	n.a.	n.a.	n.a.	n.a.	ref*(53)*
Pacific Ocean (East and South China Seas)	2008	0.41–13	n.a.	2.9–29	n.a.	n.a.	n.a.	n.a.	ref*(176)*
Pacific Ocean (East Indian Archipelago and Philippine Sea)	2010/11	0.14–0.32	n.d.–4.0	0.14–4.6	3.7–19	0.71–2.2	0.44–2.3	1.7–11	paper VI
Indian Ocean	2008	0.57–8.3	n.a.	1.15–13	n.a.	n.a.	n.a.	n.a.	ref*(176)*
Indian Ocean	2004/05	<3.4–13	<0.6	1.5–16	n.a.	n.a.	n.a.	n.a.	ref*(81)*
Indian Ocean	2010/11	n.d.–0.49	n.d.–6.5	n.d.–6.6	0.15–26	n.d.–2.8	n.d.–1.1	0.26–2.1	paper VI
Arctic Ocean	2010	0.03–0.04	n.d.–4.0	0.07–4.1	0.16–0.42	0.22–0.79	0.10–0.19	0.05–0.44	paper V
Arctic Ocean [b]	2003	<0.16–31	<0.50–41	<2.58–61	n.a.	n.a.	n.a.	n.a.	ref*(53)*
Arctic Ocean (Greenland Sea)	2009	0.06–0.95	n.d.–0.07	0.09–1.8	0.08–0.66	n.d.–0.02	0.01–1.7	0.02–4.2	paper I + II
Southern Ocean	2008	0.58	n.a.	0.78	0.32	0.02	0.04	0.07	paper I+III
Southern Ocean	2010/11	0.08	n.d.	0.13	0.12	n.d.	n.d.	0.31	paper VI

[a]year of sampling; [b]only aerosols

In seawater, total concentrations (sum of dissolved and particulate phase) ranged from <MDL to 10 pg L^{-1} for Σ_{10}PBDEs, <MDL to 5.7 pg L^{-1} for $\Sigma_8$non-PBDE BFRs and from <MDL to 18 pg L^{-1} for Σ_6Dechloranes. Concentrations <1 pg L^{-1} were observed in the open oceans while enhanced concentrations occurred at coastal sites, i.e., in the German Bight, North Sea (paper IV). Overall, DP was the dominating compound (median contribution of 19 ± 20%, followed by DPTE (18 ± 20%), BDE-209 (9 ± 27%) and BDE-47 (7 ± 11%), with individual concentrations of <MDL–18 pg L^{-1}, <MDL–5.7 pg L^{-1}, <MDL–9.3 pg L^{-1} and <MDL–1.1 pg L^{-1}, respectively. As expected, the phase distribution between the dissolved and particulate phase generally followed the logK_{OW} values, i.e., BDE-47, DPTE and HBB were predominantly distributed into the dissolved phase (median particle-bound fractions of 0 ± 27%, 0 ± 24% and 0 ± 33%, respectively), while BDE-209 was attached to suspended particulate matter at 94 ± 31%. In the estuaries of the rivers Elbe and Weser (paper IV), concentrations up to 6800 pg L^{-1} for Σ_{10}PBDEs (dominated by BDE-209 contributing 96 - 100%), 105 pg L^{-1} for DP and 70 pg L^{-1} for DPTE were observed. This thesis presents the first data on PBDEs as well as alternative HFRs in seawater from the open oceans, while for the North Sea coastal region similar PBDE concentrations were reported *(82)*, except for BDE-209 which was observed in lower concentrations. The observed estuarine and riverine concentrations were generally similar to those observed in other coastal regions *(83, 177)*, while much higher concentrations up to 19 ng L^{-1} were reported for the Pearl River Delta, China *(178)*. Literature data on alternative HFRs in surface and seawaters are even more limited than for PBDEs. DP was reported in coastal seawater from China, but concentrations were 10–100 times higher than in this thesis *(155)* while riverine concentrations in Chinese rural regions were similar to those in the rivers Elbe and Weser *(179)*.

6.2. Global distribution and long-range atmospheric transport potential

Based on the results of the individual papers, a global distribution pattern is presented in Figure 6 for the dominating individual compounds – HBB and DP – as well as for Σ_{10}PBDEs and $\Sigma_7$non-PBDE BFRs (excluding HBB). This pattern demonstrates that several alternative HFRs, in particular HBB, PBT, DPTE, PBBz and DP are present in the global marine atmosphere showing that they are pollutants of global environmental concern. More strikingly, their occurrence over the Arctic and Southern Ocean, representing regions without sources of FR, shows that they can undergo LRAT toward remote regions. Thereby, HBB, PBT, DPTE and PBBz undergo LRAT as gases similar to legacy POPs. DP on the other hand was shown to undergo particle-bound LRAT similar to BDE-209 as previously demonstrated *(53)*. The fact that the composition pattern along the sampling transects toward remote regions did not significantly change in favor of PBDEs showed that the potential to undergo LRAT and the current extent of LRAT of alternative HFRs – namely HBB, PBT, PBBz, DP and DPTE – is similar to PBDEs. This is further supported by significant correlations between PBDEs and several alternative HFRs along the sampling transects, e.g., between BDE-47, HBB and DPTE in East Greenland Sea and BDE-47, PBBz, PBT, DPTE and DP from East Asia toward the Arctic. These findings from the field observations are well consistent with results from predicted LRAT potentials (see *Appendix C*) which also showed the highest LRAT potentials exactly for HBB, PBT and PBBz, which is even higher than for PBDEs. Even though the potential of DPTE was predicted to be lower than for PBDEs, its atmospheric half-life is still sufficient for LRAT which is supported by its occurrence in remote regions in this thesis.

On a global scale, the highest concentrations in air were generally observed in four regions with close adjacency to the continents: The German Bight, North Sea (paper IV), the West African coast (paper II), the East Asian Seas (paper V) and the East Indian Archipelago (paper VI) – while the ranking varied for the individual compounds. Exemplarily, the highest BDE-209 as well as DP concentration was observed over the North Sea, while the highest HBB concentrations appeared over the East Indian Archipelago. Overall, the highest concentrations were observed in the East Indian Archipelago with a sum concentration of all target compounds up to 42 pg m^{-3}, dominated by HBB up to 26 pg m^{-3}. In global comparison, the concentrations in the Northern Hemisphere, both of alternative HFRs as well as PBDEs were somewhat higher over the Pacific Ocean than over the Atlantic Ocean. This might be a result of the higher production and usage of HFR in East-Asia and North America than in Europe and Africa. The same coherence was obvious for the Southern Hemisphere, where the concentrations over the Pacific and Indian Ocean were several times higher than over the Atlantic Ocean, caused by the close adjacency to South-East Asia and Australia compared to Africa. However, it needs to be noted that this might vary for other regions of the global oceans, i.e., when comparing the Western Atlantic Ocean versus Eastern Pacific Ocean. Comparing the Polar Regions of the Arctic and the Southern Ocean, the Arctic concentrations were relatively higher, likely caused by its closer adjacency to source regions such as Northern America, Asia and Europe.

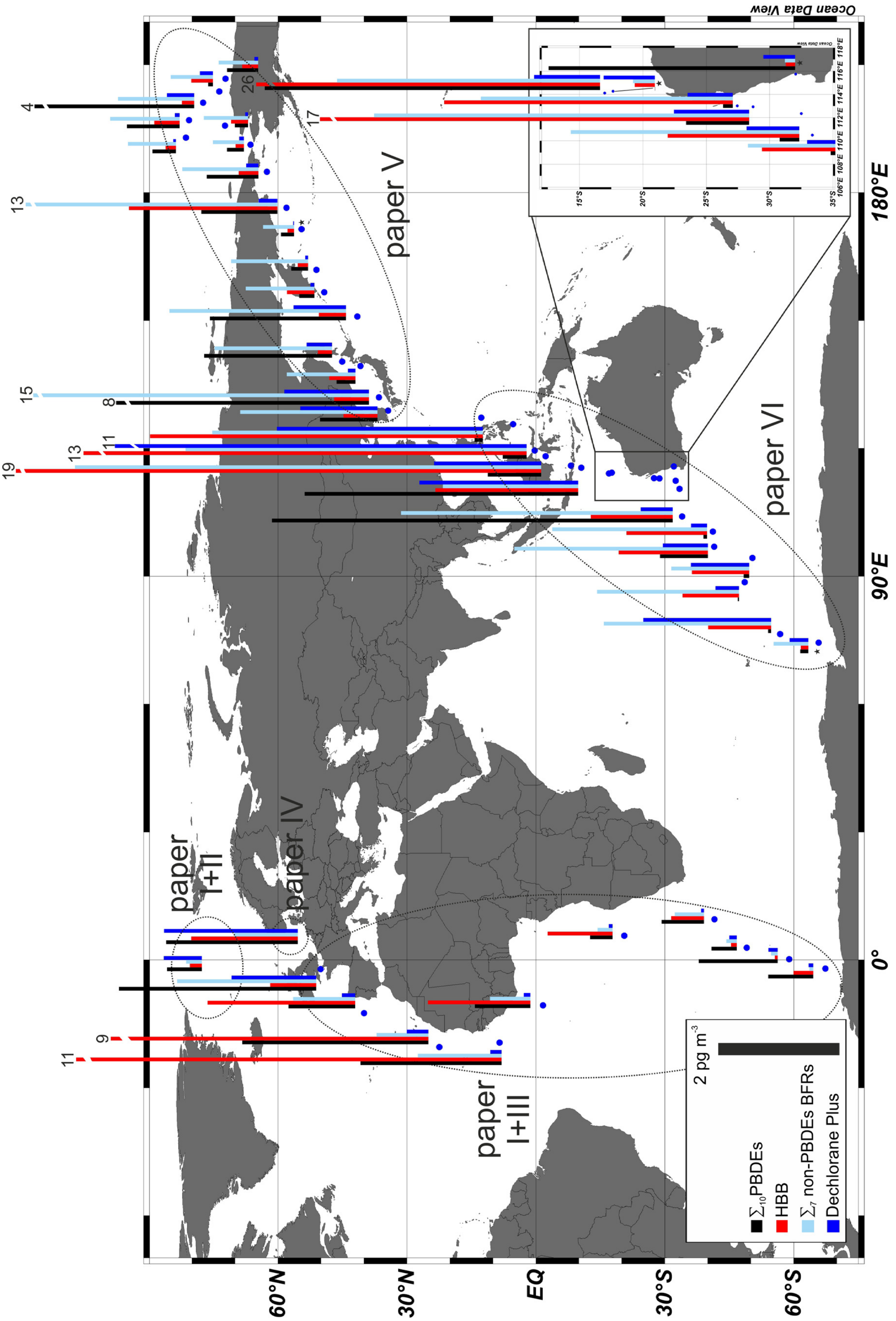

Figure 6. Spatial distribution of Σ_{10}PBDEs, HBB, Σ_7 non-PBDEs BFRs and DP (sum of gaseous and particulate phase, pg m^{-3}) in the global marine atmosphere. Note that values for the North Sea (paper IV) and East Greenland Sea (paper I + II) represent average concentrations. Samples marked with a star represent only the particulate phase. Two samples from paper VI were omitted for presentation, but this does not manipulate the global pattern.

In seawater, the concentrations were generally highest in the marginal seas such as the East Asian Seas (paper V) and the North Sea (paper IV). Concentrations decreased toward the open global oceans where they remained relatively stable representing remote concentrations. On a regional scale, the spatial distribution was demonstrated for the German Bight, North Sea in paper IV. The highest seawater concentrations were observed at coastal stations of the German Bight ranging from ~5 to 21 pg L^{-1} for the sum of all target compounds. A strong decrease from coast-near samples toward the open North Sea down to <1pg L^{-1} was observed showing the continental influence on the HFR contamination by riverine discharges. This was further supported by a negative correlation with seawater salinity (during cruise H331), as well as by the investigation of the rivers Elbe and Weser showing 10–100 times higher concentrations compared to the German Bight, North Sea. In open oceans, concentrations were generally <1 pg L^{-1}. Nevertheless, a spatial trend could even be observed in the East Greenland Sea. In East Greenland Sea, higher concentrations were observed in the western part of the Fram Strait, along the eastern coast of Greenland, compared to the eastern part of the Fram Strait. One reason might be melted Arctic seaice being transported out the Arctic in the westerly part of Fram Strait and glacial meltwater from Greenland. Enhanced HFR concentrations might result from atmospheric transport of HFRs to the Arctic, followed by deposition and accumulation to ice-/snowpacks *(180)* which are then released into the ocean during melt seasons showing the (long-term) impact of atmospheric transport on the aquatic remote environment.

6.3. Atmospheric transport – from the continents toward the open ocean

As stated above, the global distribution of HFRs in the atmosphere was found to be strongly influenced by the distance to land and, even more important, the pathway of the sampled air masses. Lowest concentrations generally coincided with sampling of oceanic air masses with travelling times over the oceans of several days, while enhanced concentrations occurred during sampling of continental air, especially if highly populated regions had been passed. Even if distinct point sources could not be identified due to the limited sampling density in time and space, some general results on source regions were obtained.

In East Greenland Sea (paper I + II), enhanced concentrations of PBDEs, non-PBDE BFRs (in particular HBB and DPTE) as well as DP were observed for air masses passing the United Kingdom (U.K.) and Ireland. This suggests that Western Europe is a source of HFRs, in particular alternative HFRs including particle-bound compounds such as DP, in the European Arctic. This was further confirmed by the three cruises in the German Bight, North Sea (paper IV). In this region, the lowest concentrations were generally observed during northerly winds transporting oceanic or even Arctic air masses, while air masses passing Western Europe including Germany, the Netherlands, France and U.K. showed elevated concentrations, especially of BDE-209 and DP. While BDE-209 was the dominating PBDE congener in continentally influenced samples, BDE-47 was the dominating congener during oceanic or even Arctic air masses showing a higher LRAT of BDE-47, but higher fresh emissions of BDE-209. Very interestingly, HBB was strongly enhanced during the cruise in March 2010 where air masses were dominated by air passing Scandinavia. The concentrations were even ~10 times higher than in July 2010 where air masses passed Western Europe which was suspected to have a higher source potential due to higher population density and degree of industrialization. The predominance and variation of HBB is further discussed in detail in chapter *Alternative halogenated flame retardants – do the (un-)known sources explain the occurrence?*.

Along the transect from the Northern Atlantic Ocean toward the Southern Ocean (paper I + III), concentrations in the English Channel were similar to the North Sea, again resulting from air masses passing Western Europe. More important as well as unexpected, strongly enhanced PBDE, DPTE and HBB concentrations off the African West Coast were observed. HBB (up to 11 pg m^{-3}) was more than ten times higher than in the English Channel. Air masses showed the African continent as likely source. This is untypical, at least on the first view, since industrialized regions producing HFRs such as Europe and Northern America are traditionally source regions of HFRs in the atmosphere rather than Africa *(76, 181)*. Even though initial production and usage of HFRs in Africa might be low, Africa was assumed to act as source region due to receiving e-waste *(182, 183)*, most likely containing significant amounts of HFRs. The rather primitive cycling (burning) might then lead to emissions of HFRs into the atmosphere as further discussed in chapter *Alternative halogenated flame retardants – do the (un-)known sources explain the occurrence?*.

From the East Asian Seas toward the Arctic Ocean (paper V), a clear signal of air masses from East Asia was observed resulting in enhanced concentrations, even though air masses had already traveled over the East Asian Seas for some days. Apart from enhanced concentrations, these air masses transported a high variety of compounds including several alternative HFRs (e.g., BTBPE, EHTBB, Dec 602, Dec 603, $aCl_{11}DP$). These were hardly detected in any other oceanic region, indicating East Asia as a more complex source region of HFRs than Europe, but this needs further investigations. Even though air mass analysis provided important information on the transport pathway and possible sources, they did not explain the entire spatial and temporal variations as observed in the Pacific Ocean and the Arctic. For example, two peak concentrations of HBB, EHTBB, TBPH as well as PBDEs were observed under the influence of air travelled over remote areas such as Siberia and the Arctic Ocean. Certainly, local sources might lead to emissions even in remote regions *(58)*, but still these observations cannot be explained within this thesis.

From Southeast Asia toward Antarctica (paper VI), strongly enhanced concentrations were observed in samples over the East Indian Archipelago toward the West Coast of Australia, a similar trend as observed by Wurl et al. *(81)* for PBDEs. They were mainly traced back to air masses passing the archipelagic states such as Indonesia, which is actually the world's fourth most populated country, as well as from Australia. Again HBB (and PBBz, PBT and DPTE) was strongly enhanced with concentrations more than ten times higher than during oceanic air masses representing a strong impact on the emissions and occurrence of alternative HFRs in the marine atmosphere, in particular in the Southern Hemisphere.

6.4. Alternative halogenated flame retardants – do the (un-)known sources explain the occurrence?

The ubiquitous occurrence of PBDEs in the global atmosphere can be generally ascribed to their decade-long global production and application in high volumes *(12, 25)*. Even though the Penta- and OctaBDE mixtures are banned and most likely no longer produced, they still might be present in products manufactured before restrictions came into force and be continuously released into the environment *(4)*. In addition, the treatment of "old" e-waste containing the banned PBDE mixtures was shown to be an important source at the end of their life-cycle *(68, 70)*. The fact that BDE-209 was the dominating congener in most of the continentally influenced samples, both for Western Europe and East-Asia, reflects its ongoing production and application. In contrast, congeners of the Penta- and OctaBDE mixtures showed much lower peak concentrations in coastal regions showing the effect of the restrictions.

Since alternative HFRs, just like PBDEs, are additive FRs and have similar physicochemical properties, their modes of release into the environment can be assumed to be similar. But, simply taking the scarce available information on production volumes into account (see chapter *Alternative halogenated flame retardants - classifications*), their predominance can hardly be explained. Therefore, rather than explaining the observed concentrations by known sources, possible sources of the predominating alternative HFRs occurring in the global environment can be discussed.

Though alternative HFRs are generally reported to replace PBDEs which implies (re-) increasing production and usage of alternative HFRs since the banishment of PBDEs, specific marked data that underlie this assumption are lacking. Among the predominating alternative HFRs, the most surprisingly detected was DPTE. It was produced in Germany but production stopped in the 1980s *(102)*. Similar to PBDEs, it might still be present in "old" products. But, the fact that enhanced concentrations were several times higher than the banned BDE-47 and were observed both for Western Europe and Asian coastal samples indicates that its global distribution results rather from current productions and application than from old residues, even though current production and application is not known.

HBB has been produced for decades but production volumes were rather low (<1000 tons per year) *(94)* compared to the former Penta- and OctaBDE (and ongoing DecaBDE) production. It is known to be produced and applied in China, too *(96)*, which might be a source for the Asian coastal regions as observed in paper V. However, its predominance in the atmosphere of the German Bight, off the African West coast and over the East Indian Archipelago implies that its sources and emission pathways are related to more complex mechanisms than its initial production and usage. As possible secondary source, HBB was reported to be formed by thermal degradation of PBDEs and polymeric BFRs *(184-187)*. Therefore, the formation during the impact of heat, i.e., treatment of e-waste in open fires might explain its predominance and enhanced concentrations. This fits well to the fact that the highest concentration were observed off the African West coast and the East Asian Archipelago which are e-waste receiving regions *(182, 183)*. Another mechanism could be the formation from photolysis of higher brominated FRs during atmospheric transport, which would again be favored off the West African Coast and over the East Asian Archipelago due to high solar radiation in the equatorial zone. This assumption is supported by the strong temperature dependence of atmospheric HBB (see paper VI) assuming temperature dependent emissions, or even formations of HBB during atmospheric transport. In contrast, enhanced HBB concentrations over the German Bight occurred only during March – during low temperatures and limited solar radiation. Air masses were traced back to Scandinavia where seasonal specific processes, such as burning of woods, waste and fuels during winter time might release HBB. In addition, Arp et al. *(188)* reported a particle-bound HBB concentration of 4.5 ± 5.3 pg m^{-3} for Southern Norway, which can be translated into a total concentrations (gaseous + particulate phase) of ~100 pg m^{-3} showing enhanced concentrations in Scandinavia. HBB is not known to be produced in or imported to the EU supporting the hypothesis that its occurrence does not result from its initial usage. Still the predominance of HBB and its sources cannot be explained in this thesis. This, together with studies of the Great Lakes region *(145)*, where HBB was found to be higher in rural than in urban regions, and Norway *(188)* where its origin could not be explained, too, shows the need of future research.

The same seems to apply for PBBz. It is not known to be applied as FR even though it was suspected to be commercially in use *(175)*. Similarly, PBBz is reported to be formed by thermal degradation of PBDEs, too *(184-186)*, as well as by photolysis of BDE-209 *(32)*. A strong temperature dependence of atmospheric PBBz similar to HBB observed in paper VI, again, supports that it might originate from formation by degradation of higher brominated FRs rather than from direct emissions.

PBT was also reported to be released from thermal degradation of polymeric BFRs *(187)* as well as from decabromodiphenyl ethane (DBDPE) *(189)*, another highly brominated FR, in addition to its initial production and usage as FR *(9)*. As consequence, higher brominated non-volatile FRs such as BDE-209 and DBDPE considered of lower environmental risk, in particular due to a limited LRAT, might lead to the formation of semi-volatile alternative HFRs with then pose a higher environmental risk due to their global distribution and high LRAT potential as discussed in chapter *Global distribution and long-range atmospheric transport potential*. However, studies on distinct sources as well as possible formation mechanism are necessary to evaluate the source strengths of possible formation from higher brominated FRs versus initial production and usage.

The occurrence of DP in the U.S. and China is usually traced back the local production and application *(107, 110, 146)*. Yet its occurrence in the European Arctic and the German Bight together with strong continental influence as discussed in chapter *Atmospheric transport – from the continents toward the open ocean* indicates sources of DP in Western Europe, as well. In fact, DP is marketed worldwide *(146)* and listed as LVPC in the EU *(112)*, but its occurrence and distribution on the European continent together with possible sources has not been reported so far. The results of this thesis indicate point sources of DP in Western Europe, with emissions both into the atmosphere as well as into the aquatic environment as obvious from the enhanced riverine concentrations in the rivers Elbe and Weser. Therefore, it is essential to investigate the sources of DP in Western Europe for further assessment on its possible risk for the environment, especially since it has been proposed as potential DecaBDE replacement *(113)* and the DP concentrations are meanwhile similar to BDE-209.

Few other alternative HFRs, in particular BTBPE, TBPH and EHTBB were detected in enhanced concentrations over the East Asian Seas with East Asia as likely source regions, but not in the German Bight. So far, their production and application has been reported for the U.S. as replacements for PBDEs *(2, 89)*, and, therefore, might be considered as "American" alternative HFRs. From the results of the present thesis, they are likely produced and applied in East Asia, too, which is further supported by their occurrence in the continental Asian environment *(190-192)*. Therefore, distinct sources including production sites of these PBDE replacements can be assumed for East Asia which is in line with the general increasing demand and production of HFRs in East Asia, in particular China *(96, 193)*. In contrast, limited consumption of these

PBDE replacements can be assumed for Western Europe due to their absence in the environment.

6.5. Dechlorane Plus: stereoselective transport

Together with the first detection of DP in the atmosphere of the Great Lakes region in 2006, stereoisomeric differences between the syn- and antiDP isomer during atmospheric transport were reported *(107)*, possibly due to higher stability of synDP against UV-light *(150)* resulting in a relative enrichment of synDP during atmospheric transport. Possible conversion from anti- to synDP has not been reported to occur. Along the transect from the North Atlantic Ocean toward the Southern Ocean (paper I), a shift of the f_{syn} ratio (ratio of synDP to the sum of the isomers) from 0.37 in the English Channel which is close to the mean value of the technical mixture (0.32 *(110)*) up to 0.67 ± 0.03 southwards of the equator which was significantly correlated with the latitude (see Figure 7A). Suggesting Western Europe as source region as demonstrated by the air mass analysis, this supports the findings of Hoh et al. *(107)* assuming a higher stability of synDP in the atmosphere. This was further supported by observations in the atmosphere of the German Bight, North Sea (paper IV) where a significant increase of f_{syn} with decreasing DP concentrations was observed (see Figure 7B).

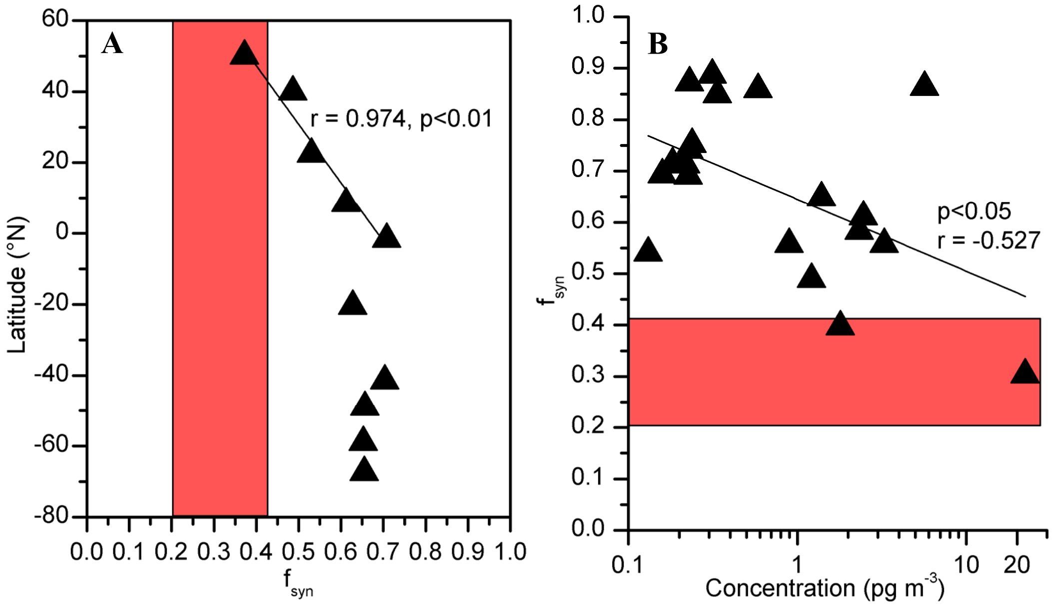

Figure 7. The f_{syn} value in the atmosphere along the Atlantic transect as a function of latitude (A) and the f_{syn} value as a function of DP concentration in the atmosphere of the North Sea (B). The red boxes represent commercial f_{syn} values reported by Wang et al. *(110)*.

Though a similar trend could be expected for the other studied regions, no significant trends were observed and f_{syn} values generally ranged between 0.6 and 0.8 suggesting alteration of the stereoisomer composition during atmospheric transport before sampling. Even if the stereoselective transport as first reported by Hoh et al. *(107)* was confirmed by this study, it needs further detailed long-term investigations to clarify e.g., whether sources with different f_{syn} ratios exist (i.e., alteration of f_{syn} before emission) and which meteorological parameters influence possible alteration.

Similar to the atmosphere, a shift of f_{syn} was observed for the first time in surface waters – from the rivers Elbe and Weser toward the North Sea (paper IV). While the ratio in the rivers and estuaries corresponded to the technical mixture as observed for other rivers *(179)*, f_{syn} increased with decreasing DP concentration towards the North Sea. This might result either from alteration of f_{syn} during transport from the rivers toward the open sea (e.g., by degradation or differences in the solubility and sedimentation process), or the predominance of atmospheric inputs as source of (atmospherically altered) DP in the open North Sea versus aquatic discharges as source of riverine DP. However, the fact that the DP concentration showed a negative linear trend with salinity toward the estuary while the f_{syn} ratio showed an exponential like increase suggests the change in the predominance from aquatic to atmospheric sources to be the driving factor of the shift. As result, seawater from the open oceans in paper I and V generally showed f_{syn} values corresponding to the atmospherically altered f_{syn} ratio. In any case, the f_{syn} ratio in the open oceans was found to be different from rivers and estuaries leading to differences in the DP stereoisomer mixture exposed to aquatic organisms and, therefore, differences in uptake and bioaccumulation rates.

6.6. Exchange between air and seawater

Estimation of the dry air-seawater gas exchange was performed for compounds detected both in the dissolved phase of seawater and the gaseous phase of air samples, namely BDE-47, -99, and DPTE for East Greenland Sea (paper II) and the German Bight, North Sea (paper IV), BDE-47, -99, -100, DPTE and HBB for the transect from the Northern Atlantic Ocean toward the Southern Ocean (paper II), and BDE-47, -99, PBT, HBB and DPTE for the transect from the East Asian Seas toward the Arctic Ocean (paper V). The estimation revealed that the dry air-seawater gas exchange of HFRs is generally dominated by net deposition, which means that the atmosphere is a source of HFRs in seawater, both for marginal seas as well as open oceans including the Arctic and Southern Ocean. Overall, dry air-seawater gas exchange fluxes ranged from -880 (deposition) to 50 (volatilization) pg m^{-2} day^{-1} for BDE-47, -230 to 42 pg m^{-2} day^{-1} for

BDE-99, -50 to -2 pg m^{-2} day^{-1} for BDE-100, -3100 to 230 pg m^{-2} day^{-1} for DPTE, -4800 to -96 pg m^{-2} day^{-1} for HBB and -2200 to -46 pg m^{-2} day^{-1} for PBT. The highest deposition fluxes coincided with elevated air concentrations resulting from continental air masses. Fluxes in remote regions were generally much lower and close to equilibrium resulting from LRAT and ongoing exchange between the atmosphere and the seawater surface. Comparing PBDEs with their alternatives, peak deposition fluxes were observed for non-PBDE BFRs rather than PBDEs suggesting atmospheric transport and dry air-seawater gas exchange as important source of non-PBDE BFRs in the marine environment, while the input of PBDEs is comparably low. The estimated PBDE fluxes were one to two magnitudes lower than in a coastal region in Turkey reported in 2007 *(177)*, which might be a result of ongoing regulations of PBDEs and decreasing emission into the atmosphere. Volatilization was observed for a few stations only and with low net fluxes. However, it was shown that emissions to the aquatic environment by riverine discharges as observed for the German Bight and by meltwater as observed in East Greenland Sea might lead to a change in the flux direction. It needs to be noted that the uncertainty of the estimation of DPTE and PBT is assumed be several times higher than for PBDEs and HBB since no measured Henry's Law Constants were available and need to be investigated in future research to allow more certain estimations (see *Appendix B* for details).

In order to take possible inputs of particle-bound HFRs into account, the particle-bound dry deposition estimations resulted in deposition fluxes from 8 to 2900 pg m^{-2} day^{-1}, dominated by BDE-209 and DP which were the predominating compounds in the particulate phase. Again, highest fluxes resulted from continental atmospheric emissions to the marine environment, while the fluxes over the open oceans were generally constant due to limited variations in the particle-bound concentrations of HFRs. However, it needs to be noted that the deposition velocity might vary between the individual HFRs as well as with meteorological parameters and physicochemical parameters of the aerosols. The comparison between dry air-seawater gas exchange and dry particle-bound deposition revealed that dry air-seawater gas exchange dominates versus particle-bound dry deposition as input pathway of semi-volatile HFRs into the marine environment. Again, this is influenced by the ambient air temperature as shown in paper IV for the German Bight, North Sea, where higher air temperatures in summer lead to partitioning into the gaseous phase, resulting in reduced particle bound fluxes and increased gaseous deposition fluxes. In contrast, non-volatile HFRs such as BDE-209 and DP are emitted to the marine environment via dry particle-bound deposition with fluxes comparable to the gas exchange flux of the dominating semi-volatile HFRs, i.e. HBB, DPTE and PBT.

In addition to dry air-seawater gas exchange and dry particle-bound deposition, wet deposition (as well as riverine discharges for coastal regions) needs to be considered to understand and rank the importance of the different input pathways of HFRs. However, for the semi-volatile compounds air-seawater exchange can be assumed to dominate versus wet deposition, due to their partitioning into the gaseous phase and, therefore, the resulting limited washout ratio. Exemplarily, wet deposition fluxes were estimated for the German Bight, North Sea (see *Appendix D*). Dry air-seawater gas exchange was estimated to account for a median contribution of 71 ± 30% and 75 ± 15% of atmospheric inputs (sum of dry air-seawater gas exchange, dry particle-bound deposition and wet deposition) of BDE-47 and DPTE, respectively. In contrast, wet deposition can be assumed to dominate versus dry deposition for particle-bound HFRs such as BDE-209 and DP due to strong washout of atmospheric particles by rain, but particle-bound dry deposition will still dominate during dry seasons. However, a comprehensive mass balance investigation is needed to understand and evaluate the atmospheric input pathways of HFRs, together with spatial and temporal variations, but this is beyond the scope of this thesis.

7. Conclusions and future perspectives

The studies underlying this thesis have demonstrated that several non-PBDE BFRs as well as Dechlorane Plus are ubiquitously distributed in the global marine atmosphere and seawater, with concentrations similar or even higher compared to the legacy PBDEs. This thesis provides first data on alternative HFRs in the marine environment including the Polar Regions of the Arctic and Southern Ocean which, as combined in this cumulative thesis, present a global view on their occurrence, distribution and transport. The overall conclusion is as follows:

Alternative HFRs, in particular traditional non-PBDE BFRs such as HBB, DPTE, PBT and PBBz, as well as Dechlorane Plus, are predominating HFRs versus PBDEs in the marine (atmospheric) environment. From source regions, they are atmospherically transported to the marine environment and undergo LRAT over very long ranges toward the Polar Regions in an extent similar to PBDEs, which are banned on a global scale due to their adverse properties (including LRAT). Hence, several alternative HFRs are emerging pollutants and possible future POP candidates of global environmental concern.

More specific, their occurrence in the global marine atmosphere is strongly influenced by the continental emissions and, therefore by the distance to source regions in combination with the pathway of the air masses as well as their LRAT potential. Both, Western Europe and East/Southeast Asia are important source regions of alternative HFRs in the marine environment, while the variety of individual alternative HFRs was much higher for Asia than for

Western Europe. The predominance of alternative HFRs versus PBDEs in the marine environment demonstrates that it is indispensable to go one step back and investigate their sources and emissions in source regions such as Western Europe, East Asia, but also North America, together with temporal and spatial variations. Enhanced concentrations off the African West coast, in particular of HBB, indicates that the global occurrence and distribution of alternative HFRs is not simply controlled by their production and consumption, but influenced by the global flow of consumer products and, even more important, the global flow of e-waste showing the complexity of the global environmental concern of HFRs.

Alternative HFRs are deposited from the atmosphere into the global oceans, whereby dry air-seawater gas exchange is the dominating input pathway of semi-volatile alternative HFRs. Therefore the atmosphere is the most important transport medium for alternative HFRs on a global scale, especially to sensitive remote regions such as the Arctic, while coastal regions are additionally influenced by riverine emissions. The impact of the different input pathways of HFRs into the marine environment should be investigated in detailed multimedia fate studies to enable overall input estimations as basis for detailed risk assessments for selected marine regions.

The obvious shift from PBDEs toward alternative HFRs might be a result of the banishment of PBDEs and increasing production and application of alternatives, yet underlying long-term observations are lacking. Since the dominating alternative HFRs – HBB, PBBz, PBT, DPTE and DP – are traditional HFRs, they can be assumed to have been widely distributed, but not investigated, in the environment for decades. However, an environmental shift from PBDEs toward alternative HFRs in the last decade is still likely. This is alarming, since none of these HFRs are regulated, neither nationally nor internationally, and data on their environmental fate are still very limited. Nevertheless, PBDEs still need to be investigated in the environment in the future, in particular due to the ongoing production and emission of BDE-209, and its possible transformation into HBB and PBBz. HBB, PBT and PBBz, might have sources others than their initial production and application such as formation under the influence of heat or sunlight, leading to enhanced emissions and, therefore, concentrations in the environment. It should be investigated whether these formations take place, and compare the impact of emissions versus initial production and application as FR. If confirmed, this will provide further indirect evidence for the environmental risk of highly brominated PBDE congeners, as well as other highly brominated FRs such as DBDPE and polymeric BFRs.

This thesis presents evidence that HBB, PBT, DPTE and PBBz undergo LRAT toward remote regions and, therefore, fulfill the criterion of LRAT to be classified as POPs under the Stockholm Conventions. DP was shown to undergo particle-bound LRAT which is sufficient to reach remote regions, too, while differences in the stability of the two stereoisomers – synDP and antiDP – lead to a relative enrichment of synDP during LRAT. The observed LRAT potential was similar or even higher than LRAT potential of PBDEs confirming predictions of environmental fate models. Therefore, focusing on LRAT potential and environmental occurrence and distribution, they aren't suitable replacements for PBDEs, but traditional HFRs of emerging concern. Moreover, they should be considered as possible future POP candidates, since they likely fulfill the pbt-criteria, too. Therefore, there is urgent need to investigate the pbt-properties and the environmental risks besides LRAT of alternative HFRs. Long-term monitoring in remote regions such as the Arctic should be conducted to assess the origins and temporal changes of HFRs in remote regions, together with bioaccumulation- and magnification in marine food webs.

Apart from the alternative HFRs investigated in this thesis, various other alternative HFRs are suspected to be on the global market. Generally, very little public information is available on production and consumption volumes. In many cases even the identity of HFRs is unknown until reported in the environment for the first time as experienced for DP *(107)*. While this thesis has been prepared, several other HFRs popped up in the environment – e.g., tris(2,3-dibromopropyl)isocyanurate (TBC) *(194-196)* and pentabromobenzylacrylate (PBBA) *(175)* – which might again share the adverse properties of PBDEs and, again, might be chemicals of global environmental concern undergoing LRAT. Furthermore, it is still uncertain whether (cyclo-)aliphatic BFRs such as HBCD, which is currently proposed to be listed as POP under the Stockholm Convention, and reactive BFRs such as TBBPA and several of its derivatives have reduced environmental risks compared to PBDEs.

Consequently, dozens of alternative HFRs, if known to be applied as FR, would need to be investigated for pbt-properties and LRAT potential. One solution might be the general restriction of HFRs and replacement by halogen-free, environmental friendly FRs, especially since their benefit for fire safety is still arguable due to increased risk for human health by increased formation of smoke and carbon monoxide (due to reduced conversion of CO into CO_2) at the presence of HFRs which is the much more important cause of fire deaths rather than burning *(197)*. Certainly, FRs are designed to save human life and private and public possessions, but detailed risk versus benefit analysis, including environmental risks, should be conducted *before* the market introduction of new FRs.

Appendix A – Declarations to the individual papers

This cumulative thesis is based on six scientific papers, all of them being published in international peer-reviewed journals. In the following, declarations to the contributions of the authors to the papers and the quality of the publications are given.

Paper I

Large-scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica

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Authorship	Co-authorship: predominant contribution
Contributions	• Axel Möller (70%): concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation • Zhiyong Xie (20%): concept, laboratory work, comments on the manuscript • Renate Sturm (5%): comments on the manuscript • Ralf Ebinghaus (5%): concept, comments on the manuscript
Status	published
Journal	Environmental Science and Technology **2010**, *44 (23)*, 8977-8982
Impact factor	5.228 (2011)
Presentations	• Fifth International Symposium on brominated flame retardants, Kyoto, 5-7 April 2010. http://www.bfr2010.com/ (poster presentation) • SETAC Europe 20th Annual Meeting, Seville, 23-27 May 2010. http://seville.setac.eu/home/?contentid=181&pr_id=180 (poster presentation) • International Polar Year – Oslo Science Conference, Oslo, 8-12 June 2010. http://ipy-osc.no/ (poster presentation) • 30th International Symposium on Halogenated Persistent Organic Pollutants (POPs), San Antonio, 12-18 September 2010. http://www.dioxin20xx.org/ (oral presentation) • SETAC North America 32nd Annual Meeting, Boston, 13-17 November 2011. http://boston.setac.org/ (poster presentation)

The paper was highlighted in the Environmental Science and Technology news: *Kellyn Betts: Chlorinated flame retardant travels the globe. Chemical & Engineering News 88 (46), 5 November 2010, news of the week*. The paper was further highlighted in the public news: *Helga Rietz: Neue Gifte ersetzen alte. Neue Zürcher Zeitung, 1 December 2010.*

Paper II

Polybrominated diphenyl ethers (PBDEs) and Alternative Brominated Flame Retardants in Air and Seawater of the European Arctic

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Status	published
Journal	Environmental Pollution **2011**, *159 (6)*, 1577-1583
Impact factor	3.746 (2011)
Presentations	• Fifth International Symposium on brominated flame retardants, Kyoto, 5-7 April 2010. http://www.bfr2010.com/ (poster presentation) • SETAC Europe 20th Annual Meeting, Seville, 23-27 May 2010. http://seville.setac.eu/home/?contentid=181&pr_id=180 (poster presentation) • International Polar Year – Oslo Science Conference, Oslo, 8-12 June 2010. http://ipy-osc.no/ (poster presentation) • 30th International Symposium on Halogenated Persistent Organic Pollutants (POPs), San Antonio, 12-18 September 2010. http://www.dioxin20xx.org/ (poster presentation) • SETAC North America 32nd Annual Meeting, Boston, 13-17 November 2011. http://boston.setac.org/ (poster presentation)

Paper III

Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean

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Authorship	Co-authorship: important contribution
Contributions	• Zhiyong Xie (55%): concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation • Axel Möller (30%): data evaluation and analysis, discussion, manuscript preparation • Lutz Ahrens (5%): comments on the manuscript • Renate Sturm (5%): comments on the manuscript • Ralf Ebinghaus (5%): concept, comments on the manuscript
Status	published
Journal	Environmental Science and Technology **2011**, *45 (5)*, 1820-1826
Impact factor	5.228 (2011)
Presentations	• SETAC Europe 20th Annual Meeting, Seville, 23-27 May 2010. http://seville.setac.eu/home/?contentid=181&pr_id=180 (poster presentation) • 30th International Symposium on Halogenated Persistent Organic Pollutants (POPs), San Antonio, 12-18 September 2010. http://www.dioxin20xx.org/ (poster presentation) • SETAC North America 32nd Annual Meeting, Boston, 13-17 November 2011. http://boston.setac.org/ (poster presentation)

Paper IV

Occurrence and Air-seawater Exchange of Brominated Flame Retardants and Dechlorane Plus in the North Sea

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Authorship	Co-authorship: predominant contribution
Contributions	• Axel Möller (75%): concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation • Zhiyong Xie (10%): concept, comments on the manuscript • Armando Caba (5%): sampling • Renate Sturm (5%): comments on the manuscript • Ralf Ebinghaus (5%): concept, comments on the manuscript
Status	published
Journal	Atmospheric Environment **2011**, *46*, 346-353
Impact factor	3.465 (2011)
Presentations	• SETAC Europe 21st Annual Meeting, Milan, 15-19 May 2011. http://milano.setac.eu/?contentid=291 (oral presentation)

Paper V

Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic

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Authorship	Co-authorship: predominant contribution
Contributions	• Axel Möller (55%): concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation • Zhiyong Xie (10%): concept, laboratory work, comments on the manuscript • Minghong Cai (5%): concept • Guangcai Zhong (5%): laboratory work • Peng Huang (5%): sampling • Minggang Cai (5%): concept • Renate Sturm (5%): comments on the manuscript • Jianfeng He (5%): concept • Ralf Ebinghaus (5%): concept, comments on the manuscript
Status	published
Journal	Environmental Science and Technology **2011**, *45 (16)*, 6793-6799
Impact factor	5.228 (2011)
Presentations	• 31st International Symposium on Halogenated Persistent Organic Pollutants (POPs), Brussels, 21-25 September 2011. http://www.dioxin20xx.org/ (oral presentation) • SETAC North America 32nd Annual Meeting, Boston, 13-17 November 2011. http://boston.setac.org/ (poster presentation)

Paper VI

Brominated Flame Retardants and Dechlorane Plus in the Marine Atmosphere from Southeast Asia toward Antarctica

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Status	published
Journal	Environmental Science and Technology **2012**, *46 (6)*, 3141-3148
Impact factor	5.228 (2011)
Presentations	• SETAC North America 32nd Annual Meeting, Boston, 13-17 November 2011. http://boston.setac.org/ (poster presentation) • 6th SETAC World Congress/SETAC Europe 22nd Annual Meeting, Berlin, 20-24 May, 2012. http://berlin.setac.eu/?contentid=404 (poster presentation)

Ich versichere, dass alle in diesem Anhang gemachten Angaben jeweils einzeln und insgesamt vollständig der Wahrheit entsprechen.

Hamburg, November 2012

Appendix B – Air-seawater exchange

Fugacity ratios. The fugacity ratio was calculated by:

$$\frac{f_W}{f_A} = \frac{C_W H_{salt,T}}{C_A R T_A} \tag{B1}$$

where f_W and f_A are the fugacities in water and air, respectively, and C_W and C_A are the dissolved and gaseous concentrations in water and air (pg m^{-3}), respectively. R is the gas constant (8.31 Pa m^3 K^{-1} mol^{-1}) and T_A is the air temperature. $H_{salt,T}$ is the Henry's Law Constant (Pa m^3 mol^{-1}) at the given water temperature (T_W) and salinity which was adjusted to the proper temperature according to:

$$\ln H' = A + \frac{B}{T_W} \tag{B2}$$

where H' is the dimensionless Henry's Law Constant according to:

$$H' = \frac{H}{RT_W} \tag{B3}$$

The Henry's Law Constant of BDE-47 and -99 and their temperature dependence was taken from Cetin and Odabasi *(118)* and the Henry's Law Constant of HBB was taken from Tittlemier et al. *(17)*. Since there are no measured or predicted Henry's Law Constants for DPTE and PBT available, they were estimated to be 0.0478 Pa m^3 mol^{-1} and 6.05 Pa m^3 mol^{-1} using US EPA EPI Suite 4.0 *(115)*. The temperature dependence of HBB, DPTE and PBT was estimated to be similar to BDE-47.

The Henry's Law Constant was corrected by the salinity *(198)*:

$$H'_{salt,T} = H' \times 10^{K_S C_S} \tag{B4}$$

where C_S is the salt concentration (mol L^{-1}) and K_S is the Setschenow constant (L mol^{-1}) which was taken from Cetin and Odabasi *(118)* for BDE-47 and -99, respectively, or calculated for HBB, DPTE and PBT following *(199)*:

$$K_S = 0.04 \log K_{OW} + 0.114 \tag{B5}$$

If C_A or C_W were not available, 2/3 of the MDL was used. A fugacity quotient <1 and >1 indicates net dry gaseous deposition and volatilization, respectively, and $f_W/f_A = 1$ indicates thermodynamic equilibrium. The total uncertainty of the fugacity ratio was propagated from the estimated relative standard deviations of the water and air concentrations (± 20%) and the Henry's Law Constant (<13% for PBDEs *(118)*; estimated to be 20% for HBB), and the air temperature during sampling (± 10%) resulting in a total uncertainty of ± 32% for PBDEs and ± 35% for HBB, respectively. Since no measured Henry's Law Constants of DPTE and PBT are available, an uncertainty of a factor of at least three has to be assumed.

Air–seawater gas exchange. The dry air-seawater gas exchange F_{AW} (pg m^{-2} h^{-1}) was calculated as follows *(165, 166)*:

$$F_{AW} = K_{OL}\left(C_W - \frac{C_A}{H'_{salt,T}} \right) \quad \text{(B6)}$$

where K_{OL} (m h^{-1}) is the overall mass transfer coefficient compromising the resistances to mass transfer in both water ($K_{W,}$ m h^{-1}) and air ($K_{A,}$ m h^{-1}). A negative flux indicates deposition from the atmosphere to seawater and a positive flux indicated volatilization to the atmosphere. K_{OL} is defined by *(166)*:

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'} \quad \text{(B7)}$$

where *(200)*:

$$k_A = (0.2U_{10} + 0.3) \times \left(\frac{D_{i,air}}{D_{H_2O,air}} \right)^{0.61} \times 36 \quad \text{(B8)}$$

and:

$$k_W = (0.45U_{10}{}^{1.64}) \times \left(\frac{Sc_i}{Sc_{CO_2}} \right)^{-0.5} \times 0.01 \quad \text{(B9)}$$

D_{air} is the diffusity in air (cm^2 s^{-1}) and U_{10} is the wind speed at 10 m height above sea level (m s^{-1}). D_{air} was calculated using the method described by Fuller et al. *(201)*:

$$D_{i,air} = 10^{-3} \times \frac{T_A{}^{1.75}\left(\frac{1}{M_{air}} + \frac{1}{M_i} \right)^{0.5}}{\rho_{H_20}\left(\overline{V}_{air}{}^{1/3} + \overline{V}_i^{1/3} \right)^2} \quad \text{(B10)}$$

where M_{air} is the molar mass of air (20.1 cm³ mol^{-1}), M_i is the molar mass of the compound of interest, ρ_{H2O} is the density of water (g cm^{-3}), $\overline{V}_{air}$ and $\overline{V}_i$ is the molar volume of air (20.1 cm³ mol^{-1}) and the compound of interest, respectively. The molar volume of BDE-47, -99 and HBB was taken from ref*(121)*, and from ref*(198)* for H_2O, or calculated following ref*(202)* for PBT and DPTE.

Sc is the water phase Schmidt number which was taken from ref*(198)* for CO_2 or calculated according to *(198)*:

$$Sc_i = \frac{\nu}{D_{i,w}} \quad \text{(B11)}$$

where ν is the kinematic viscosity of water (cm^2 s^{-1}) and $D_{i,w}$ (cm^2 s^{-1}) is the diffusion coefficient in water which was calculated following Hayduk and Laudi *(203)*:

$$D_{i,w} = \frac{13.26 \times 10^{-5}}{\eta^{1.14} \overline{V}_i^{0.589}} \tag{B12}$$

where η is the dynamic viscosity of water (centipoise). The overall uncertainty of BDE-47 and -99 was estimated to ± 51% and ± 55% for HBB based on an uncertainty of ± 40% for K_{OL} *(118)*. The uncertainty of DPTE and PBT has to be estimated to at least a factor of three since the uncertainties of both H' and K_{OL} are not known.

Particle-bound dry deposition. The particle-bound dry deposition flux F_d (pg m^{-2} day^{-1}) was calculated according to:

$$F_d = V_d C_p \tag{B13}$$

where V_d is the dry deposition velocity (m day^{-1}) and C_p is the concentration in the particulate phase (pg m^{-3}). Since measured deposition velocities of the target compounds for the investigated oceanic regions were not available, a deposition velocity of 0.1 cm s^{-1} was adopted for open oceans according to deposition measurements for polyaromatic hydrocarbons (PAHs) in the Atlantic Ocean *(170)* and global marine deposition velocity observations *(171)*. A higher velocity of 0.2 cm s^{-1} was used for the German Bight, North Sea representing marine aerosols with continental influence *(172)* and a value of 0.3 cm s^{-1} was used for the samples along the Asian coast according observations in Chinese coastal regions *(173)*. It need to be noted, that the deposition velocity strongly depends on both meteorological parameters, size and physicochemical parameters of the airborne particle and of the pollutant itself *(204)*. Even though deposition velocities were chosen based on literature, the differences in the dry particle-bound fluxes are still mainly a result of differences in the particle-bound concentrations of the target compounds, and higher differences can be expected if the variation of the deposition velocity, both spatially as well as between the target compounds, would be known. Therefore, an uncertainty of a factor of at least three has to be assumed.

Appendix C – LRAT estimation using "The Tool"

The long-range transport potential of alternative HFRs was assessed using the Software "The Tool" – the OECD Overall Persistence and Long-Range Transport Potential Screening Tool – a screening-level multimedia chemical fate model to assess the persistence and long-range transport potential of potential POP candidates for into the Stockholm Convention *(138)*. Applying the model results in the overall persistence in the environment (P_{OV}), based on emission scenarios to soil, water and air. Two indicators describing the long-range transport potential are calculated. As first the characteristic travel distance (CTD [km]) representing the travelling distance at which the initial concentration has dropped to 37%. The second indicator is the transfer efficiency (TE [%]) describing the potential of a chemical to be transported and deposited to remote regions as the ratio of emission flux in a source region to deposition flux in a remote region. The CTD is calculated for emission scenarios to air and water, and the TE for emissions to air, water and soil. Required input parameters are half-lives ($t_{1/2}$) in soil, seawater and air as well as logK_{OW} and logK_{AW} values (i.e., the dimensionless Henry's Law Constant). Since these physicochemical parameters are generally not available for alternative HFRs, they were estimated using models included in the U.S. EPA EPI Suite 4.0 *(115)*, namely BIOWIN3 for half-lives in soil and seawater (transferred according to Aronson et al. *(205)*, assuming similar half-lives in soil and seawater), AOPWIN for half-life in air, KOWWIN for logK_{OW} and HENRYWIN for logK_{AW}. The results of the estimation, together with the input parameters, are shown in Table C-1 and Figure C-1. The two vertical and horizontal lines are defined by the lowest values of six reference chemicals: carbon tetrachloride and the legacy POPs HCB, α-hexachlorocyclohexane (α-HCH) and CB-28, -101 and -180.

Among the alternative HFRs, all except TBPH and EHTBB exceed the P_{OV} benchmark of 195 days as defined by the reference chemicals, and have a POV similar or higher than BDE-47 showing their high persistence in the environment. Among them, only PBT and PBBz exceed the CTD benchmark of 5100 km for long-range transport with CTDs of 11000 and 7600 km, respectively, which are higher than estimated for BDE-47 (3010 km). For the second indicator TE, PBT, PBBz, HBB, DPTE and PBEB and exceed the benchmark of 2.3%, too, with very high predicted values for PBT, PBBz and HBB of 47.0, 21.4 and 20.2%, respectively. They are again higher than predicted for BDE-47 (8.5%). Besides, several Dechloranes and BTBPE show a TE of ~12.7% and CTD of ~2860 km (similar to BDE-209) which is equivalent to the limit of long-range transport of atmospheric particles defined in the model. It needs to be noted that the estimated input parameters are rather uncertain leading to a high uncertainty in the model predictions. Nevertheless, the estimations show a high long-range transport potential for PBT, PBBz, HBB, DPTE and PBEB which is predicted to be sufficient to reach remote regions such as the Arctic, while the long-range transport potential of several highly brominated/chlorinated FRs depends on the transport of airborne particles, which was shown to be sufficient for transport of BDE-209 to the Arctic *(53)*.

Table C-1. Input parameters (estimated via U.S. EPA EPI Suite 4.0 *(115)* if not stated otherwise) and results of the persistence and long-range transport estimation using "The Tool". The red highlighted values are above the benchmark and the yellow highlighted values are similar to the limit of long-range transport of atmospheric particles defined in the model. The benchmarks are defined as defined the lowest values of six reference chemicals: carbon tetrachloride and the legacy POPs HCB, α-HCH, and CB-28, -101 and -180.

Abbreviation	**$t_{1/2}$ air [h]**	**$t_{1/2}$ soil [h]**	**$t_{1/2}$ water [h]**	**logK_{OW}**	**LogK_{AW}**	**P_{OV} [d]**	**CTD [km]**	**TE [%]**
BDE-47	256	5760	5760	6.81[a]	-3.46[c]	346	3010	8.5
BDE-209	7621	17280	17280	11.12[a]	-4.79[c]	1063	2861	12.7
PBBz	535	5760	5760	6.44	-2.66	344	7623	21.4
HBB	1868	17280	17280	6.10[b]	-4.28[d]	1038	4105	20.2
PBEB	223	5760	5760	7.48	-2.50	346	3736	5.1
PBT	1388	5760	5760	6.99	-2.61	346	11232	47.0
DPTE	64	5760	5760	6.34	-4.71	346	1418	2.9
BTBPE	17	17280	17280	9.15	-6.52	1062	2860	12.7
EHTBB	24	2880	2880	8.75	-3.59	173	2233	7.5
TBPH	12	2880	2880	11.95	-4.91	188	2861	12.7
DP	11	17280	17280	11.27	-3.52	1055	2854	12.6
aCl$_{10}$DP	13	17280	17280	10.17	-2.61	1039	2418	8.9
aCl$_{11}$DP	13	17280	17280	10.35	-3.06	1039	2741	11.6
Dec 602	18	17280	17280	8.05	-6.96	1059	2849	12.6
Dec 603	18	17280	17280	11.2	-4.00	1061	2859	12.7
Dec 604	49	17280	17280	10.56	-4.34	1062	2860	12.7

[a]ref *(119)* [b]ref*(120)* [c]ref*(118)* [d]ref*(17)*

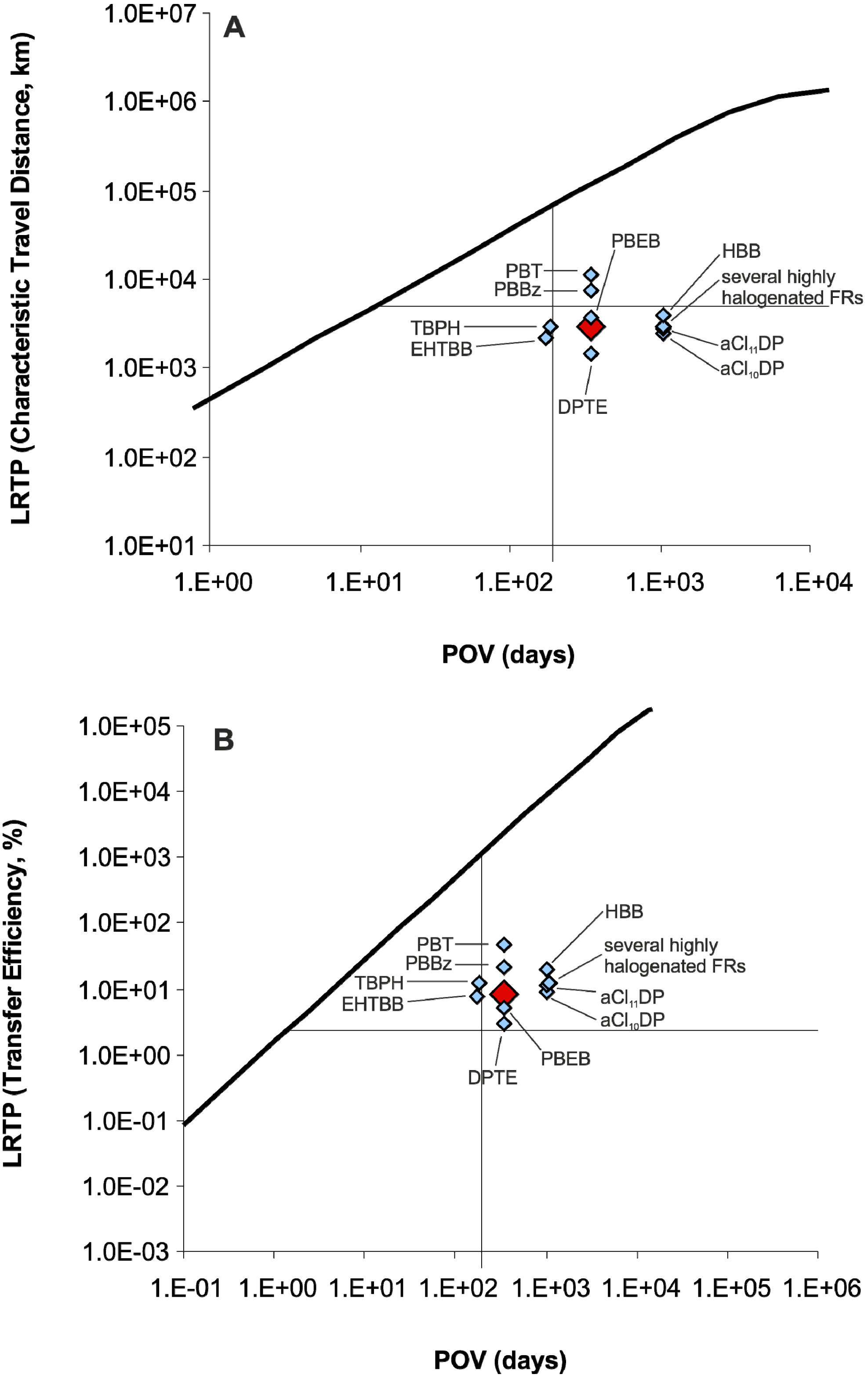

Figure C-1. Results of the "The Tool" estimation of persistence and long-range transport (CTD as indicator in Figure C-1A, TE as indicator in Figure C-1B) of alternative HFRs and BDE-47 and BDE-209 included in this thesis. The red dot represents BDE-47. The two vertical and horizontal lines are defined the lowest values of six reference chemicals, carbon tetrachloride and the legacy POPs HCB, α-HCH, and CB-28, -101 and -180.

Appendix D – Washout ratio and wet deposition estimation

The overall washout ratio W from the atmosphere is defined as *(206)*:

$$W = W_V(1-\phi) + W_P\phi = \frac{C_R}{C_A} \tag{C1}$$

where W_V is the washout from the gaseous phase:

$$W_V = \frac{RT}{H} \tag{C2}$$

W_P is the washout from airborne particles, ϕ is the particle bound fraction, and C_R and C_A is the concentration in rain and air, respectively, and T is the ambient air temperature. If H is sufficiently high, washout from the gaseous phase can be neglected and washout from airborne particles dominates. For a very rough estimation of the wet deposition rates for the German Bight (paper IV) , W_P of BDE-47, -99 and -209 was taken from Li et al. *(173)*, while W_P of DPTE was assumed to be similar to BDE-47, W_P of BDE-100 similar to BDE-99 and W_P of DP similar to BDE-209 because of their physicochemical similarities. W_V was calculated based on the Henry's Law Constant as used for the gas air-seawater exchange estimation (see paper IV).

Table D-1. Estimated deposition fluxes in pg m^{-2} day^{-1} (F_{AW} = dry air-seawater gas exchange; F_d = dry particle-bound deposition; F_W = wet deposition) and percentage contributions of the total estimated atmospheric input (sum of F_{AW}, F_d and F_W). Values in brackets give the median value ± SD.

		BDE47		**DPTE**		**BDE-209**		**DP**	
		flux	**%**	**flux**	**%**	**flux**	**%**	**flux**	**%**
H319	F_{AW}	27-110 (59 ± 32)	31-98 (49 ± 27)	140-1500 (300 ± 540)	47-84 (73 ± 14)	–	–	–	–
	F_d	0-97 (19 ± 38)	0-30 (22 ± 12)	0-100 (31 ± 37)	0-19 (4 ± 7)	0-1200 (72 ± 480)	14	36-250 (51 ± 96)	14
	F_W	1-130 (25 ± 49)	2-39 (29 ± 15)	51-270 (120 ± 87)	14-34 (23 ± 8)	0-7600 (440 ± 3000)	86	220-1500 (310 ± 580)	86
H325	F_{AW}	7-170 (51 ± 54)	22-99 (54 ± 29)	41-710 (150 ± 230)	53-76 (73 ± 10)	–	–	–	–
	F_d	0-120 (13 ±42)	0-34 (20 ± 13)	9-28 (13 ± 8)	3-19 (8 ± 6)	0-140 (40 ± 48)	0-14 (12 ± 6)	23-990 (39 ± 370)	14
	F_W	1-160 (17 ± 55)	1-44 (26 ± 16)	27-190 (37 ± 59)	19-35 (22 ± 6)	29-1000 (270 ± 330)	86-100 (88 ± 6)	140-6000 (240 ± 2300)	86
H331	F_{AW}	8-220 (101 ± 80)	82-99 (99 ± 6)	22-910 (210 ± 370)	68-100 (87 ± 12)	–	–	–	–
	F_d	0-9 (0 ± 3)	0-4 (0 ± 1)	0-28 (0 ± 12)	0-4 (0 ± 1)	51-890 (240 ± 290)	14	32-240 (180 ± 88)	14
	F_W	1-14 (2 ± 5)	1-18 (1 ± 6)	0-270 (30 ± 110)	0-30 (13 ± 11)	310-5400 (1500 ± 1800)	86	160-1500 (1100 ± 540)	86

Using the observed airborne concentrations and an annual precipitation rate of 750 mm m^{-2}, wet depositions were estimated for the three cruises H319, H325 and H331 as summarized in Table D-1. Medium wet deposition fluxes ranged from 2 ± 5 to 25 ± 49 pg m^{-2} day^{-1} and from 30 ± 110 to 120 ± 87 pg m^{-2} day^{-1} for BDE-47 and DPTE, respectively, while much higher fluxes from 270 ± 330 to 1500 ± 1800 pg m^{-2} day^{-1} and 240 ± 2300 to 1100 ± 540 pg m^{-2} day^{-1} were calculated for BDE-209 and DP, respectively. As comparison, dry air-seawater gas exchange is the dominating pathway of atmospheric input of BDE-47 and DPTE into the German Bight with median contributions of 49 ± 27 to 99 ± 6% and 73 ± 14 to 87 ± 12% to the total atmospheric input, respectively, caused by their relatively high Henry's Law Constants and, even more important, their distribution into the gaseous phase limiting the atmospheric washout. Especially during H331 in summer dry air-seawater gas exchange is almost the solely input pathway due to the favoured partitioning of BDE-47 and DPTE into the gaseous phase at higher ambient air temperatures. In contrast, for BDE-209 and DP wet deposition can be expected to dominate versus dry particle-bound deposition due to strong washout from atmospheric particles with contributions >80% of wet deposition of the total input. Nevertheless, during dry seasons dry particle-bound deposition will be the dominating and solely atmospheric input pathway of BDE-209 and DP.

It needs to be noted that neither washout ratios of the target compounds were measured, nor spatial or temporal variations of precipitation rates were taken into account leading to a high uncertainty of at least a factor of four. A detailed investigation of alternative HFR in precipitation as well as dry deposition would be necessary for a more accurate estimation of the input fluxes.

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Cumulative thesis

Paper I

Large-scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica

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Large-Scale Distribution of Dechlorane Plus in Air and Seawater from the Arctic to Antarctica

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Dechlorane Plus (DP), a highly chlorinated flame retardant, was investigated in marine boundary layer air and surface seawater from East Greenland Sea and in the Northern and Southern Atlantic toward Antarctica. The concentrations of DP ranged from 0.05 to 4.2 pg m^{-3} in the atmosphere and from <MDL to 1.3 pg L^{-1} in seawater. The occurrence of DP even in the remote areas of the Arctic and Antarctica suggests that DP is susceptible to long-range atmospheric transport (LRAT). Along the Atlantic atmosphere, the highest concentration was observed in the English Channel originating from continental air passing Western Europe indicating Western Europe as source region of DP in the marine environment. Thereby, the fractional abundance of the syn isomer (f_{syn}) increased with decreasing northern latitude from 0.37 which is close to the commercial mixture ($f_{syn} = 0.32$) to ~0.67 showing a stereoselective depletion of the anti isomer likely caused by UV-sunlight during LRAT. In addition, two degradation products ([-1Cl+1H] and [-2Cl+2H]) were detected in seawater from the Arctic. This paper presents the first report of DP in the marine environment, especially in remote areas, together with stereoselective LRAT potential.

Introduction

Organic halogenated flame retardant (FRs), in particular brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), have been used for several decades to reduce the inflammability of industrial and commercial products (*1*). PBDEs, which have been the most focused FRs in policy and science in the past decade, are known to be persistent, toxic, and bioaccumulative and undergo long-range atmospheric transport (LRAT) into remote areas like the Arctic and Antarctica (*2*). As a result, the technical Penta- and OctaBDE mixtures were banned in the European Union EU in 2004 and were recently included in the Stockholm Convention of Persistent Organic Pollutants (POPs) (*2*). In addition, DecaBDE has been implemented in the EU Directive on the restriction of use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) and was banned in Europe by July 2008 (*3*). Therefore, there is increasing demand and production of nonregulated non-PBDE flame retardants including non-PBDE BFRs but also nonbrominated substances.

Another currently unregulated halogenated flame retardant, the highly chlorinated Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$), was introduced as replacement compound for the toxic Mirex. It has been produced for over 40 years by OxyChem in the United States (*4*) and is used for coating electrical wires and cables, in computer connectors and in plastic roofing material (*5*). The technical DP, containing the syn- and antistereoisomer (synDP and antiDP), has an estimated annual production volume as high as ~5000 tons and is marketed worldwide (*6*). Besides OxyChem, Wang et al. reported an additional annual production of ~300 tons in China (*7*). The usage of DP in the European Union (EU) was 800 tons in 2000 (*8*), while one German company is listed as importer/producer by the European Commission (*9*). Recently, the EU suggested DP to be a possible replacement compound for DecaBDE for several applications (*10*) which might lead to increasing usage in Europe and, therefore, emissions into the environment.

Nevertheless, DP has only recently been detected in the environment. In 2006, Hoh et al. reported DP for the first time in the environment: in air, sediment, and fish from the Great Lakes close to the OxyChem facility (*11*). Further studies were mainly focused on the Great Lakes region and, in increasing numbers, in China close to possible sources including air (*6, 12*), biota (*13, 14*), human serum (*15*), soil (*7, 12, 16*), river water and sediment (*17*). Data on the European Continent have been only published by Qiu and Hites who reported DP in tree bark from Germany and Italy (*18*) and by La Guardia at al. for Spanish sewage sludge (*19*). In this paper, we present the first data on the occurrence and spatial distribution of DP in marine boundary layer air as well as surface seawater, with regard to its partitioning behavior and stereoselective transport into remote areas.

Materials and Methods

Sample Collection. Air and seawater samples were simultaneously taken aboard the German research vessel *R/V Polarstern* during the expedition cruises ARK-XXIV/3 in East Greenland Sea in August and September 2009 (69−80.5°N) and ANT-XXV/1 + 2 along the cruise leg Bremerhaven, Germany - Cape Town, South Africa - Neumayer Station in the Antarctic in November and December 2008. For each cruise leg, 10 two- to six-day air samples (500−2700 m^3) were collected during each cruise at the upper deck (15 m above sea level) using a high-volume air sampler equipped with glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) for atmospheric particles and a glass column packed with PUF/XAD-2 resin for the gas phase. Air columns were protected against UV-sunlight with aluminum foil.

Seawater samples (16 samples for ARK-XXIV/3 and 16 samples for ANT-XXV/1 + 2) were collected via the ship intake system located at the ship's keel operated for 18−20 h to obtain a volume of ~1000 L. The seawater was directly pumped by the ship's intake system consisting only of stainless steel parts through a GFF (GF/C, pore size: 1.2 μm) to collect the particulate phase followed by a glass column packed with PAD-2 (preconditioned with distilled water which was cleaned by passing through a PAD-2 column) for the dissolved phase. All air and seawater columns were precleaned with solvents of different polarity, and GFFs were baked out at 450 °C for 12 h prior to their usage. Seawater samples were stored at 0 °C on *R/V Polarstern* and 4 °C in the laboratory, respectively, and air samples and air/water filter were stored at −20 °C until extraction.

Sampling dates, volumes, and distance covered during sampling are included in Tables S1 and S2 in the Supporting

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Information. Sampling parameters such as latitude, longitude, air and water temperature, and salinity were obtained from the DSHIP Landsystem of the Alfred-Wegener-Institute (AWI). They are included in Tables S1 and S2, too.

Extraction and Cleanup. Extraction and cleanup of the samples was done in a clean laboratory class 10000. All solvents were residue-analysis grade and were distilled prior to use. Samples were spiked with 200 pg of ^{13}C-BDE-138 (Wellington Laboratories) as a surrogate standard prior to extraction. Air sampling columns were extracted in a modified Soxhlet apparatus for 16 h using dichloromethane/hexane (1/1), while dichloromethane was used for the water sampling columns and air/water filter. The extracts were evaporated to 1−2 mL while the solvent was exchanged to hexane. Seawater and seawater filter extracts were frozen before cleanup to eliminate the remaining seawater. They were further cleaned on a silica column (10% water deactivated) topped on 3 g of anhydrous granulated sodium sulfate. The extracts were purified by eluting with 15 mL of hexane and evaporated to the final volume of 30 μL. One ng on ^{13}C-HCB (Cambridge Isotope Laboratories) was added as recovery standard before injection.

Analysis. Samples were analyzed for synDP, anti DP, the onefold dechlorinated antiDP species (aCl$_{11}$DP), and the 2-fold dechlorinated antiDP species (aCl$_{10}$DP) which were obtained from Wellington Laboratories (the dechlorinated species were only analyzed in ARK-XXIV/3 samples). Analyses were done by a GC/MS-system (6890 GC/5975 MSD) in negative chemical ionization mode (NCI) with methane as ionization gas fitted with a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific). The injector was operated in pulsed-splitless mode (injection pulse 20 psi for 2 min) with an inlet temperature program: 60 °C for 0.1 min, 500 °C min^{-1} until 280 °C and held for a final 20 min. The GC oven program was as follows: initial 60 °C for 2 min, 30 °C min^{-1} until 180 °C, 2 °C min^{-1} until 280 °C, 30 °C min^{-1} until 300 °C and held for 6 min, 30 °C min $^{-1}$ until 310 °C and held for a final 25 min. The MS transfer line was held at 280 °C and the ion source and quadrupole temperature was 150 °C. The instrument was operated in selected ion monitoring mode (*m*/*z* 653.8, 617.9, and 583.9 for syn- and antiDP; *m*/*z* 617.8, 583.7, and 547.8 for aCl$_{11}$DP; *m*/*z* 583.8, 549.9, and 513.8 for aCl$_{10}$DP).

QA/QC. Breakthrough of the target compounds was checked for both seawater and air samples using tandem columns aboard during the sampling campaigns. Both DP isomers were not detected in the lower cartridges. Three field blanks were taken for each sample type during each cruise leg. Seawater field blanks consisted of preconditioned PAD-2 columns which were treated and extracted similar to the real samples. Both DP isomers were detected in the low absolute pg range for ARK-XXIV/3, while no DP was detected in any blanks from ANT-XXV/1 + 2 (see Table S3 for individual blanks). Method detection limits (MDLs) derived from the mean blank values plus three times the standard deviation for ARK-XXIV/3 and from instrumental signal-to-noise (*S*/*N*) ratios of three for ANT-XXV/1 + 2, respectively, ranged from 0.0004 pg m^{-3} in air filter to 0.07 pg m^{-3} in air columns (see Table S4 for individual MDLs). The method recovery was examined by spike tests resulting in mean recoveries of 88 ± 18% and 83 ± 16% for syn- and antiDP, respectively. The mean recovery of aCl$_{10}$DP was 74 ± 10%, while the recovery of aCl$_{11}$DP was only 31 ± 10%. The mean relative recovery of DP against ^{13}C-BDE-138 was 85 ± 7% and 80 ± 7% for syn- and antiDP, respectively, and 72 ± 9% and 29 ± 3% for aCl$_{10}$DP and aCl$_{11}$DP, respectively. Therefore, the analysis of aCl$_{11}$DP in this study was semiquantitative.

Air Mass Back Trajectories. Air mass origins were calculated for the air samples using NOAA's HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php). Back trajectories (BTs) were calculated for each sample in 6 h steps along the sampling cruise. BTs were traced back for 120 h with the sampling height as arrival height (see Figure S1 for individual BTs).

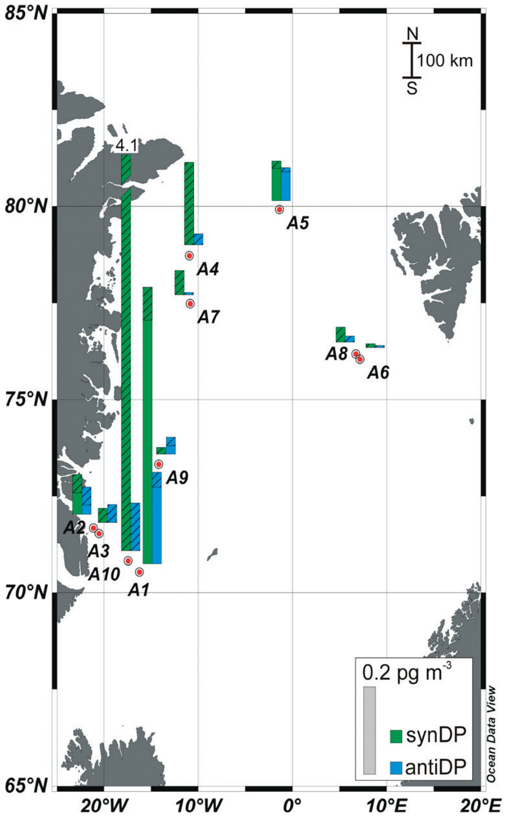

FIGURE 1. Map showing the concentrations of syn- and antiDP in the East Greenland Sea atmosphere. Lined and solid bars represent particulate and gaseous concentrations, respectively. For station A10 only the particulate phase was analyzed.

Results and Discussion

DP in the Marine Atmosphere. Both syn- and antiDP were detected in all air samples mainly associated with the particulate phase with mean fractions of 79 ± 29% and 81 ± 30% for syn- and antiDP, respectively, as a result of its high logK_{OA} of 14 (*6*). Ren et al. (*6*) and Hoh et al. (*11*) reported even higher percentages of 97% and >99%, respectively. The comparably high fraction in the gaseous phase might be caused by the binding to fine aerosol particles (<0.5 μm) in the marine environment, especially in cold areas like the Arctic (*20*) passing the GFF and being trapped on the column. Figures 1 and 2 show the spatial distribution of syn- and antiDP along the sampling cruises (see Table S1 for individual concentrations). In East Greenland Sea, the highest concentrations were observed for stations A1 and A10 at the lowest latitudes of ~70°N, while the lowest concentrations were observed at stations A6 and A8 in the open East Greenland Sea. It should be noted that the sampling stations in Figures 1 and 2 represent mean stations since samples were taken continuously along the cruise leg. BTs showed that station A1 contained continental air masses traveled over United Kingdom (UK) and Ireland. However, air mass back trajectories of sample A10 showed rather diverse air mass origins including oceanic, arctic, and continental (Greenland) air. Mixing of air masses might result in any significant spatial trends within the Arctic. Hence, the origin of the highest concentration of 4.1 pg m^{-3} at station A10 cannot be explained, but there might be also local sources of FRs in the Arctic such as open burning of waste (*21*). Bossi et al. (*22*) observed PBDEs in South-West Greenland from

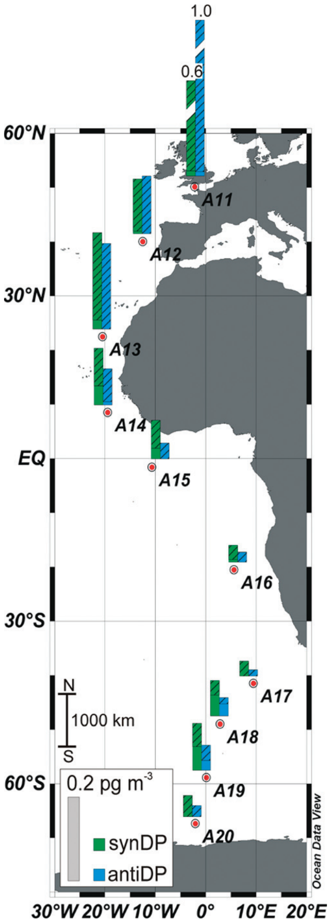

FIGURE 2. Map showing the concentrations of syn- and antiDP in the atmosphere along the Atlantic transect. Lined and solid bars represent particulate and gaseous concentrations, respectively.

0.14 to 3.26 pg m^{-3} and from 0.08 to 1.40 pg m^{-3} for Σ_{11}PBDEs and BDE-47, respectively, showing that DP concentrations in the European Arctic are similar to PBDEs which are regulated as POPs under the Stockholm Convention.

Along the Atlantic transect, the concentration decreased with decreasing northern latitude from 1.6 pg m^{-3} at station A11 in the English Channel to ~0.1 pg m^{-3} in the Southern Ocean. BTs showed continental air masses for station A11 passing Western Europe, in particular the UK, France, Germany, Belgium, indicating Western Europe as source of DP. Similar to PBDEs and other organic FRs, general sources of DP are the production and industrial usage of the technical DP mixture and the use and disposal of consumer products containing DP (*12*). Since no production takes place in the EU, the two latter source types dominate the DP emission into the environment in Western Europe. Station A13 was slightly influenced by European land air masses, too, resulting in a two times higher concentration than observed for station A12 which was dominated by oceanic air masses from northwest. At remote sites in North America, concentrations of 0.15 ± 0.21 pg m^{-3} (<MDL to 0.99 pg m^{-3}) (*11*) and 0.8 ± 0.6 pg m^{-3} and 0.8 ± 0.3 pg m^{-3} (*23*) were reported which are in good agreement with the atmospheric concentrations in the marine environment observed in this study. Ren et al. (*6*) observed concentrations of 15.6 ± 15.1 pg m^{-3} in urban centers in China, while the concentrations in rural areas were approximately 5 times lower showing the urban influence on DP concentrations in the atmosphere.

DP in Seawater. Seawater concentrations of DP are shown in Figures 3 and 4 (see Table S5 for individual concentrations). Similar to atmospheric samples, DP was found predominantly in the particulate phase with mean percentages of 97 ± 9% and 58 ± 33% for synDP and 80 ± 40% and 75 ± 26% for antiDP in East Greenland Sea and the Atlantic transect, respectively. In East Greenland Sea, no spatial correlations were observed for DP. The highest concentrations were observed at stations in the Fram Strait passage between eastern Greenland coast and Spitsbergen (stations W5, W6, and W7). In contrast, station W12 located between station W6 and W7 showed comparably low concentrations. The Fram Strait is characterized by different ocean currents: fresh Arctic water and sea ice flows southwards along the East Greenland Current and while warmer saline water is transported northwards into the Arctic Ocean. Low temperatures <0 °C and a lower salinity at stations W5−7 show an influence from freshwaters. Hence, the samples might be influenced by older Arctic waters with concentrations different than those of saline Atlantic waters. In addition, the sampling campaign took place during the arctic ice melt period in summer resulting in changing ice extents and possible influences of meltwater from glaciers on Greenland.

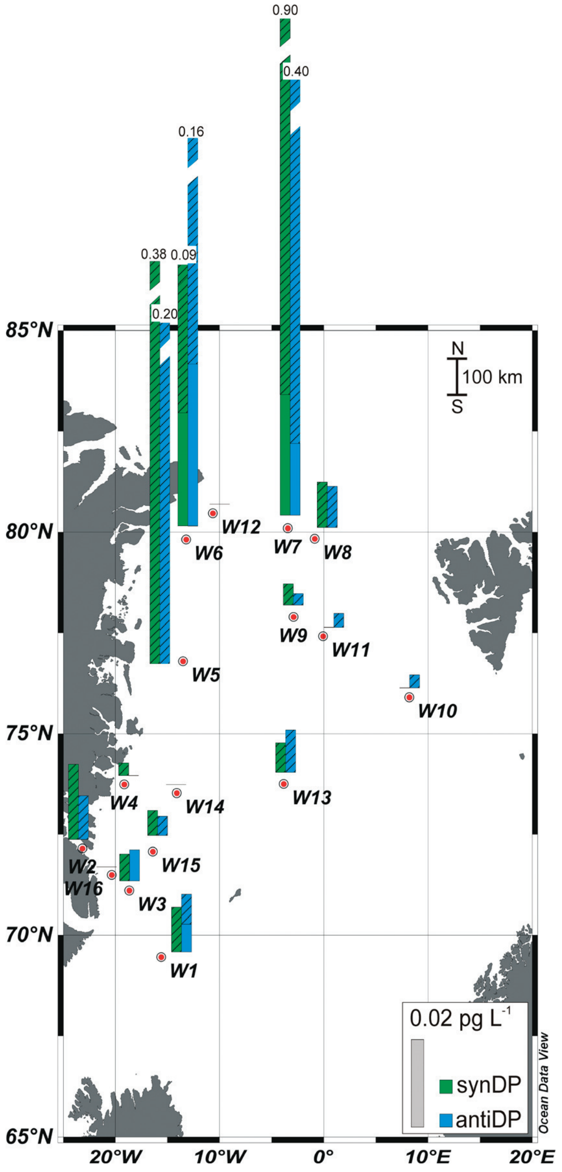

FIGURE 3. Map showing the concentrations of syn- and antiDP in seawater of East Greenland Sea. Lined and solid bars represent particulate and dissolved concentrations, respectively.

Similar to the atmospheric concentrations, the highest seawater concentration along the Atlantic transect was

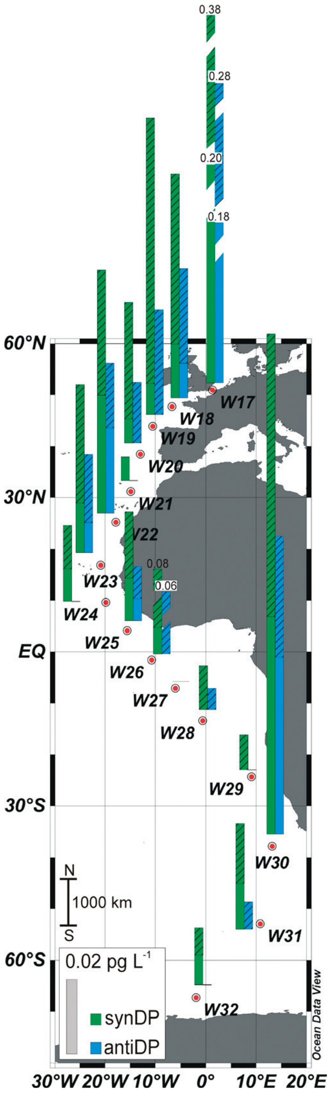

FIGURE 4. Map showing the concentrations of syn- and antiDP in seawater along the Atlantic transect. Lined and solid bars represent particulate and dissolved concentrations, respectively. For station W21 only the dissolved phase was analyzed.

observed in the English Channel (0.66 pg L^{-1}). Southwards of station W18 toward the equator, the concentrations were relatively constant while they were generally higher in the Northern than in the Southern Hemisphere as a result of higher atmospheric deposition from the source region Western Europe (see below). A slight increase was observed for station W30 at the South-African coast. This might be a result of water masses from the Indian Ocean transported via the Agulhas Current derived from a higher water temperature at station W30 compared to station W29 (22.3 and 19.1 °C, respectively). There are currently no data available for comparison of DP in seawater. Qi et al. (*17*) reported a mean DP concentration in Chinese rural riverine surface water of 0.03 ± 0.07 ng L^{-1} which is about two magnitudes higher than in seawater while, again, much higher concentrations were observed in urban regions.

Interestingly, aCl$_{11}$DP and aCl$_{10}$DP were detected between <0.001 and 0.07 pg L^{-1} in the seawater from the Arctic, mainly in the particulate fraction (see Table S6). Sverko et al. (*4*) reported their occurrence in sediment of the Niagara River and Ren et al. found the [-1Cl+1H] species in blood serum of Chinese workers what could be either a result of human metabolism or, before entering the human body, due to degradation in the environment (*15*). It was reported that they could also be formed during analyses by a dirty injector linear (*4*). The linear used for the analysis of the Arctic samples was replaced very frequently, and no decomposition was observed for a standard mixture of DP with a used linear. OxyChem stated that DP is susceptible to aerobic biodegradation, while no speciation between the isomers was given (*24*). However, the decomposition products could be either formed during atmospheric transport by degradation via UV-sunlight or by biodegradation once deposited/emitted into the ocean. On the other hand, they could also be byproduct during the production of DP and therefore emitted directly during the production process or from the products being flame proofed with DP.

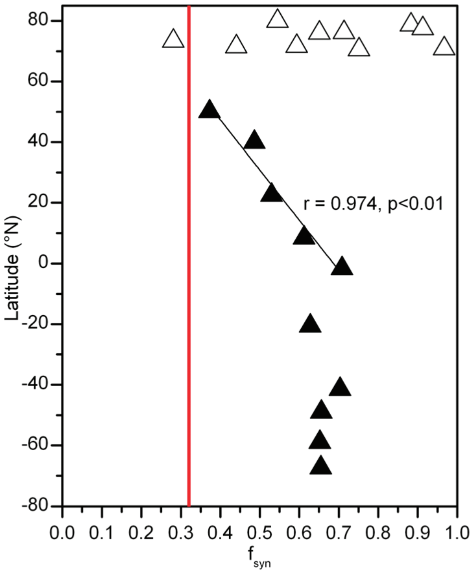

FIGURE 5. The f_{syn} value in the atmosphere of East Greenland Sea (white triangle) and along the Atlantic transect (black triangle) as a function of latitude. The red line of f_{syn} = 0.32 represents the mean commercial f_{syn} value reported by Wang et al. (*12*).

Stereoisomeric Fractionation of DP. The synDP fraction (f_{syn}) expressed as the ratio of synDP to the sum of isomers was calculated for the total concentrations (gaseous+particulate and dissolved+particulate). The f_{syn} value in air samples is shown in Figure 5. The f_{syn} value in the East Greenland Sea atmosphere varied between 0.28 to 0.97 with a mean f_{syn} value of 0.67 ± 0.22 which is much higher than in the commercial mixture (mean f_{syn} = 0.32 (*12*)). Similar to the varying concentrations, the variation in f_{syn} could also be resulted from different air masses during the sampling. In the English Channel, the f_{syn} value was 0.37 which is close to the commercial mixture. Again, this shows Western Europe to be a source region of DP in the marine environment. From station A11 to A15 the f_{syn} value increased with decreasing northern latitude ($r = 0.974$, $p < 0.01$) toward an almost constant value of 0.67 ± 0.03 southwards of the equator. These results suggest that the syn isomer is more stable toward photodegradation leading to a stereoselection during atmospheric transport. Since stations in the Southern Hemisphere contained exclusively oceanic or Antarctic air masses (see Figure S1), the constant f_{syn} value in the Southern Hemisphere represents the isomer mixture derived from LRAT. However, a further study along the Antarctic coast might provide more detailed information on the DP sources and possible alterations of f_{syn} during LRAT to the Southern Ocean. Sverko et al. proved the higher stability of synDP toward photodegradation in a laboratory study (*4*), and a similar spatial trend with increasing distance from the source was observed in the Great Lakes region with f_{syn} values up to ~0.8 within a wide variation (*11*). In contrast, Qiu and

Hites (*18*) observed f_{syn} values in tree bark from Germany and Italy close to the f_{syn} value of the commercial mixture showing a similar atmospheric fate of the isomers.

The mean observed f_{syn} value in seawater was 0.53 ± 0.13 for East Greenland Sea and 0.65 ± 0.07 for the Atlantic transect (excluding stations were only one isomer was detected), and no correlations with the latitude were observed (see Figure S2). These values are well comparable with the mean atmospheric f_{syn} values as a result of atmospheric dry deposition, with prior depletion of the anti isomer by UV-sunlight. Once deposited, there might be further degradation mechanisms such as biodegradation affecting the stereoisomer fractionation of DP in seawater. In sediment, the anti isomer was estimated to be more persistent (*17, 25, 26*), while La Guardia et al. (*19*) reported a mean f_{syn} value of 46% in Spanish sewage sludge what might also be a result of biodegradation but with a higher stability of the syn isomer.

However, the observed trend in the atmosphere along the Atlantic transect clearly indicates a stereoselection with an enrichment of the syn isomer during atmospheric transport which results in a higher LRAT potential of the syn isomer than the anti isomer. Several other parameters might affect the stereoselection of the two DP isomers in different environmental matrices including biodegradation, bioaccumulation, and physicochemical differences and, possibly more important, sources and/or source regions with different isomer profiles. In addition, there might be changes in the isomer profile before emission into the environment, e.g., alteration during waste burning (*15*). Further research is needed to investigate the stereoselective differences in the environmental fate of the DP isomers and mechanisms which alter the isomer profile in the environment.

Dry Deposition. Dry deposition is one important deposition process of POPs into the global oceans and into remote areas (*27, 28*), especially for highly hydrophobic POPs such as heavier polychlorinated biphenyls (PCBs) and BDE209 (*29, 30*). On the other hand, dry deposition of POPs leads to a removal from the atmosphere and, because of a low revolatilization from the surface media, to a limitation of the LRAT potential (*31*). The dry deposition flux of DP was calculated using eq 1

$$F_d = V_d \times C_p \qquad (1)$$

where V_d is the deposition velocity (m d^{-1}) and C_p is the DP concentration in the particulate phase (pg m^{-3}). The deposition velocity depends on meteorological parameters and physicochemical parameters of the particle and the pollutant (*32*). There are no measured velocities for DP available. Del Vento et al. reported deposition velocities of Polycyclic Aromatic Hydrocarbons (PAHs) in the Atlantic Ocean of ~0.1 cm s^{-1} (*33*), and for the open Mediterranean Sea a value of 0.2 cm s^{-1} was used to estimate the deposition of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/Fs) (*34*). Hence, a value of 0.1 cm s^{-1} (86.4 m d^{-1}) was used for the Open Sea conditions in this study. Nevertheless, V_d might vary significantly within the oceans investigated in this study leading to, e.g., higher values in the North Atlantic and in the Southern Ocean as a result of higher particle diameters or high wind speeds (*35*). Therefore, an uncertainty of a factor of 5 was estimated for the dry deposition fluxes within this study. The dry deposition of syn- and antiDP as a function of latitude is shown in Figure 6. In general, the deposition flux was found to be higher in the Northern Hemisphere than in the Southern Hemisphere with decreasing fluxes toward the equator as a result of Western Europe as source of DP in the marine environment of the European Arctic and the Atlantic Ocean. Once deposited into seawater, DP is unlikely to revolatilize due to its low volatility and will therefore be susceptible to oceanic processes such as degradation, bioaccumulation, sedimentation, and transport via the ocean currents. In the Arctic, the presence of ice might reduce the flux into seawater, but DP might be accumulated on the ice/snow surface and released into the ocean during ice melting periods. The dry deposition flux of antiDP was higher than for synDP in the English Channel, while the ratio changed toward the equator and synDP became dominant. In the Southern Hemisphere the deposition flux increased slightly toward Antarctica as a result of lower temperatures with a dominance of synDP. Since the dry deposition was calculated based on a constant deposition velocity, the differences in the fluxes result only from the differences in the particulate DP concentrations. Higher regional differences are expected if the variation of the deposition velocity trends along the cruise legs and possible stereoisomeric differences between syn- and antiDP were known. The deposition rates of DP to the Arctic and Antarctica should be studied by analysis of snowpack/ice(-cores) from the Arctic/Antarctic to examine current and previous deposition rates of DP into remote regions.

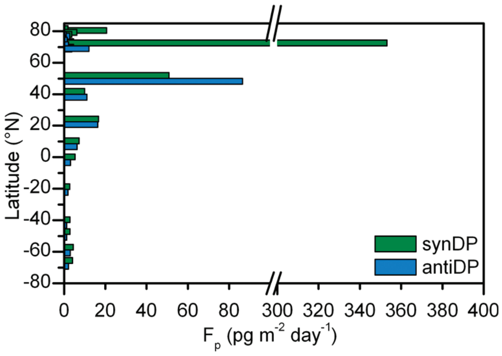

FIGURE 6. Dry deposition flux as a function of latitude.

Implications. This study has shown the occurrence of DP in air and seawater in the East Greenland Sea and in the Northern and Southern Atlantic Ocean, as a result of particle-associated LRAT. Western Europe was found to be a source of DP in the marine environment, but there is no information on the Canadian Arctic or the Pacific Ocean which might be influenced by, possibly higher, emissions from Northern America or China. There remains the question of the environmental fate of DP once deposited in seawater which needs to be studied using marine samples including seawater, biota and sediment.

The stereoisomeric profile showed synDP to be stable in the atmosphere leading to a stereoselection during LRAT and therewith to a different bioavailability of the isomers in the marine environment. Besides photodegradation, there seem to be further mechanisms leading to (1) an alteration of the profile and (2) formation of DP degradates. More research is needed to investigate the transport pathways and stereoselection of the DP isomers in the (marine) environment.

Acknowledgments

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Supporting Information Available

A detailed description of the sampling sites, individual DP concentrations and f_{syn} values in air and seawater, blank values, MDLs, and plots of air mass back trajectories for each sampling station. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Large–scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica

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10 pages

6 tables

2 figures

TABLE S1. Detailed information on air sampling and individual concentrations of syn– and antiDP in the gaseous (gas.) and particulate (part.) phase (pg m^{-3}). Latitude and longitude are mean sampling stations. Air temperature represents the mean air temperature during sampling. The distance covered during sampling represents an estimated value.

	Date	Latitude	Longitude	Distance	Volume	Air temperature	synDP		antiDP	
		(°N)	(°E)	(km)	(m^3)	(°C)	gas.	part.	gas.	part.
					ARK–XXIV/3					
A1	7–9/8/09	70.539	–16.223	500	743	6.5	0.71	0.1	0.22	0.04
A2	9–13/8/09	71.675	–21.110	300	1935	5.2	0.06	0.05	0.03	0.05
A3	13–16/8/09	71.536	–20.514	500	1331	3.9	n.d.	0.04	n.d.	0.05
A4	16–21/8/09	78.722	–10.924	1000	966	–0.3	n.d.	0.24	n.d.	0.03
A5	21–25/8/09	79.913	–1.377	400	1649	1.0	0.09	0.02	0.08	0.01
A6	25–31/8/09	76.045	7.170	300	2678	3.6	n.d.	0.01	n.d.	0.01
A7	31/8–6/9/09	77.483	–10.848	1100	2625	0.7	n.d.	0.07	n.d.	0.07
A8	6–9/9/09	76.183	6.736	500	1060	6.0	n.d.	0.04	n.d.	0.02
A9	9–14/9/09	73.325	–14.176	800	2101	2.0	n.d.	0.02	0.02	0.02
A10	14–20/9/09	70.826	–17.432	500	1339	0.8	—[a]	4.1	—[a]	0.14
					ANT–XXV/1+2					
A11	2–4/11/08	50.120	–2.184	500	687	11.5	0.01	0.59	0.01	1.0
A12	7–9/11/08	40.008	–12.511	700	640	16.5	0.01	0.12	n.d.	0.13
A13	12–15/11/08	22.500	–20.499	1000	1101	21.3	0.02	0.19	n.d.	0.19
A14	16–20/11/08	8.503	–19.452	1500	968	28.6	0.04	0.08	0.01	0.07
A15	20–23/11/08	–1.624	–10.699	1200	877	25.5	0.02	0.06	n.d.	0.04
A16	27–29/11/08	–20.506	5.607	900	522	18.9	0.01	0.03	n.d.	0.02
A17	6–8/12/08	–41.492	9.476	1100	602	19.3	n.d.	0.03	n.d.	0.01
A18	8–10/12/08	–49.011	2.834	1000	516	11.2	0.05	0.03	0.03	0.01
A19	10–12/12/08	–58.910	0.131	1100	573	3.6	0.05	0.05	0.02	0.03
A20	12–15/12/08	–67.354	–2.064	1000	934	–2.5	n.d.	0.05	n.d.	0.03

[a] only the particulate phase of sample A10 was analyzed

TABLE S2. Detailed information on water sampling. Latitude and longitude are mean sampling stations. Water temperature and salinity represent the mean values during sampling.

	Date	Latitude (°N)	Longitude (°E)	Volume (L)	Water temperature (°C)	Salinity (PSU)
			ARK–XXIV/3			
W1	7/8/09	69.461	–15.590	1000	6.8	34.7
W2	9/8/09	72.157	–23.144	733	4.8	33.4
W3	14/8/09	71.111	–18.642	1000	4.4	32.4
W4	16/8/09	73.741	–19.147	1000	1.2	29.0
W5	17/8/09	76.797	–13.492	692	–0.2	28.9
W6	19/8/09	79.815	–13.202	832	–0.9	30.2
W7	21/8/09	80.095	–3.447	1280	–1.5	30.9
W8	23/8/09	79.831	–0.867	1000	–1.6	32.1
W9	25/8/09	77.893	–2.898	987	2.4	32.6
W10	27/8/09	75.902	8.215	1000	7.5	35.0
W11	29/8/09	77.415	–0.057	1000	5.5	34.4
W12	31/8/09	80.461	–10.633	1000	–0.8	29.3
W13	9/9/09	73.754	–3.830	1000	5.2	34.3
W14	11/9/09	73.524	–14.086	1000	1.8	32.4
W15	13/9/09	72.078	–16.397	1000	2.3	32.9
W16	16/9/09	71.497	–20.329	1000	1.6	31.7
			ANT–XXV/1+2			
W17	2/11/08	50.923	1.311	409	13.8	35.1
W18	4/11/08	47.723	–6.758	1000	12.4	35.4
W19	6/11/08	43.854	–10.516	1073	15.4	35.7
W20	7/11/08	38.438	–12.979	1088	15.9	35.9
W21	8/11/08	31.175	–14.866	835	17.2	36.4
W22	12/11/08	25.196	–17.858	1296	21.0	36.8
W23	14/11/08	16.861	–20.861	950	22.5	36.8
W24	17/11/08	9.608	–19.830	1041	28.6	35.2
W25	19/11/08	4.109	–15.606	925	29.1	34.6
W26	21/11/08	–1.613	–10.708	935	26.1	36.1
W27	23/11/08	–7.106	–6.061	1000	25.5	36.2
W28	25/11/08	–13.414	–0.651	1000	22.9	36.2
W29	29/11/08	–24.301	9.070	1000	19.1	35.5
W30	7/12/08	–37.836	13.198	311	22.3	35.5
W31	10/12/08	–52.941	10.836	804	4.6	33.9
W32	14/12/08	–67.275	–1.949	771	–1.6	34.0

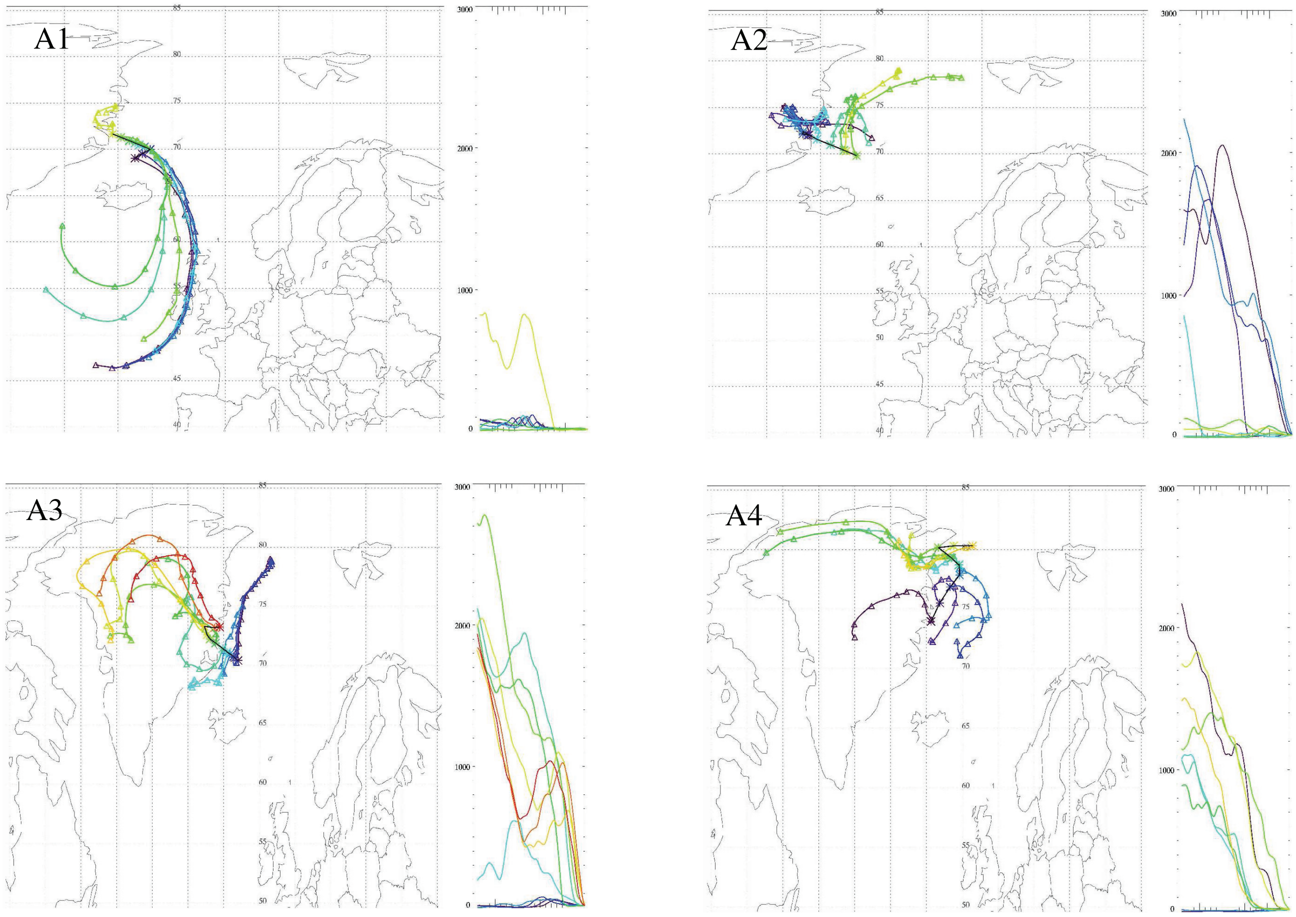
TABLE S3. Mean field blank values for ARK–XXIV/3 in pg.

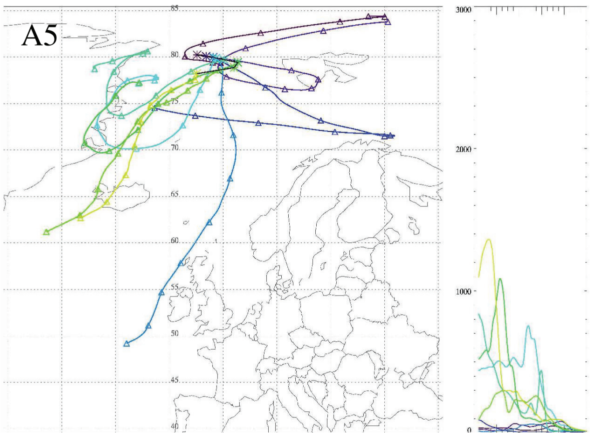
	air column	air filter	water column	water filter
synDP	46 ± 19	0.6 ± 0.3	2.9 ± 3.0	1.1 ± 0.5
antiDP	19 ± 5	0.2 ± 0.1	0.7 ± 0.9	0.8 ± 0.4

TABLE S4. Method detection limits for ARK–XXIV/3 and ANT–XXV/1+2 (in pg m^{-3} for air samples and pg L^{-1} for water samples, n.d. = not detected). MDLs for synDP and antiDP were calculated from mean field blank values plus three times the standard deviation for ARK–XXIV/3 and based on instrumental S/N ratios of 3 for ANT–XXV/1+2. For $aCl_{11}DP$ and $aCl_{10}DP$, the MDLs were calculated based on instrumental S/N ratios of 3, too. Mean sample volumes of 1500 m^3 and 1000 m^3 were estimated for air samples of ANT–XXIV/3 and ANT–XXV/1+2, respectively, and a mean volume of 1000 L was estimated for water samples.

	air		water	
	gaseous	particulate	dissolved	particulate
synDP	0.07/0.005[a]	0.0009/0.005[a]	0.01/0.005[a]	0.002/0.005[a]
antiDP	0.02/0.006[a]	0.0004/0.006[a]	0.003/0.006[a]	0.002/0.006[a]
$aCl_{11}DP$	n.d.	n.d.	0.0009	0.0007
$aCl_{10}DP$	n.d.	n.d.	n.d.	0.0005

[a] (ARK–XXIV/3)/(ANT–XXV/1+2)

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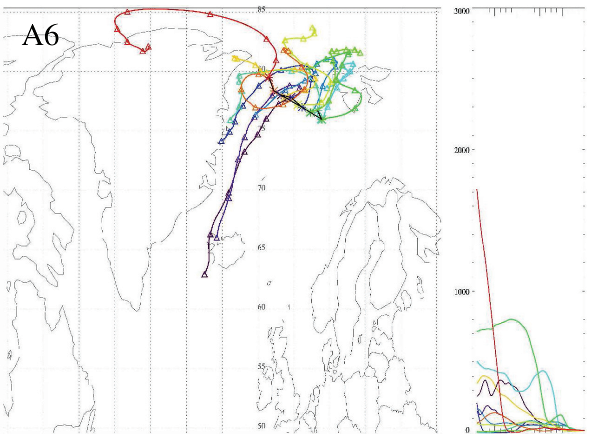
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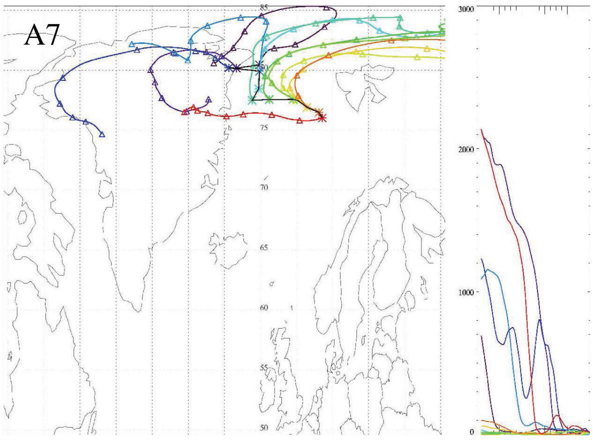
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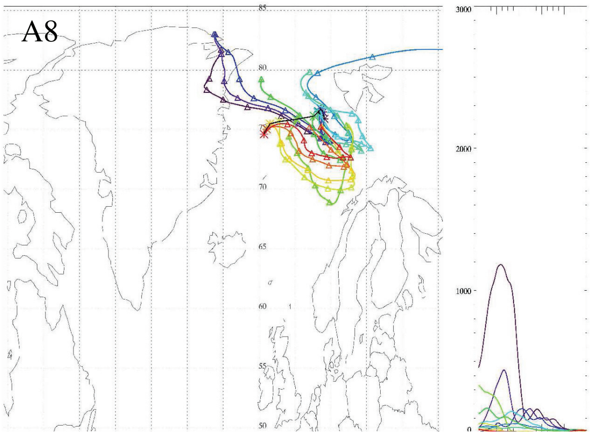
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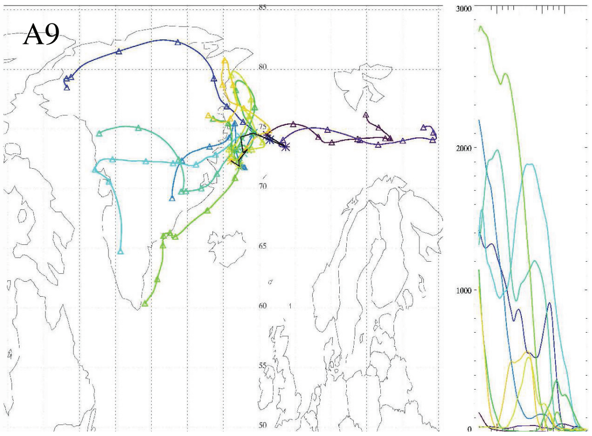
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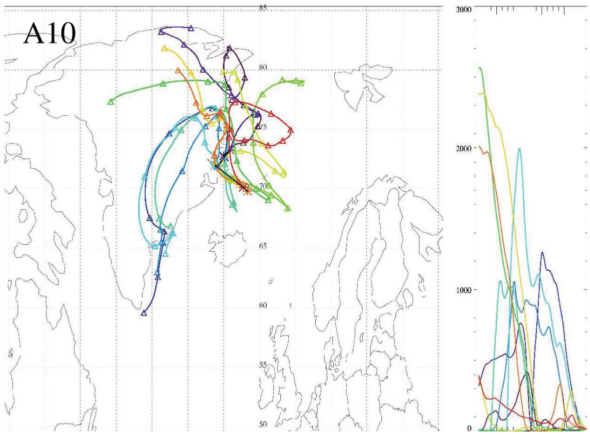
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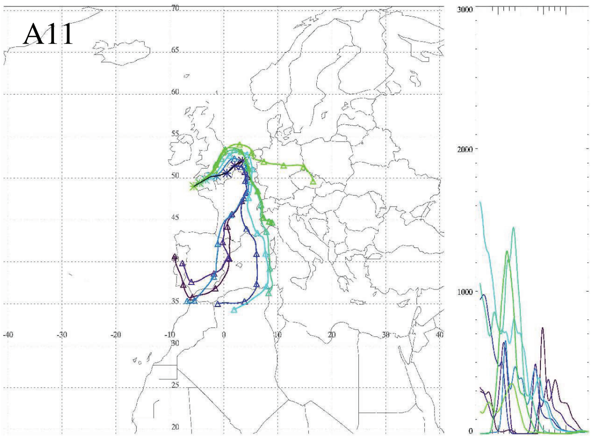
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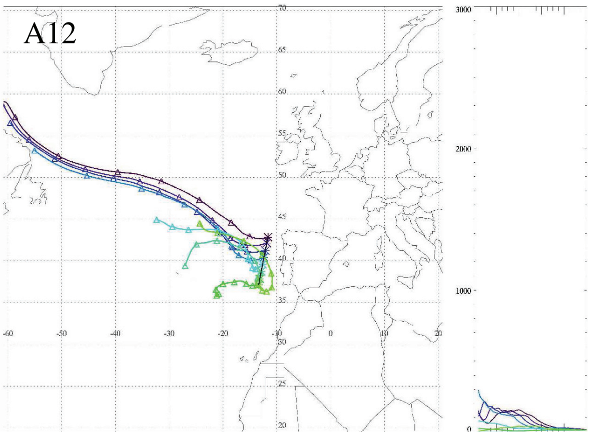
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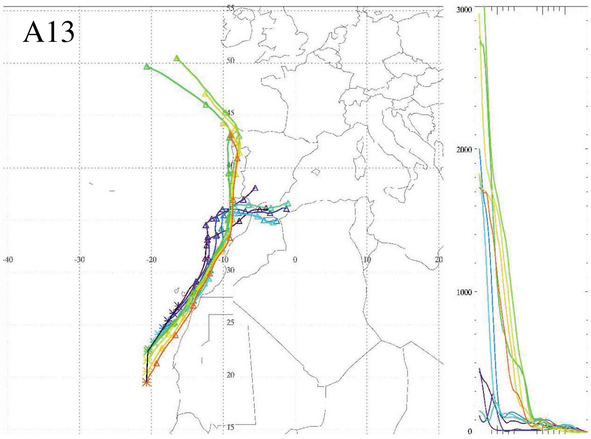
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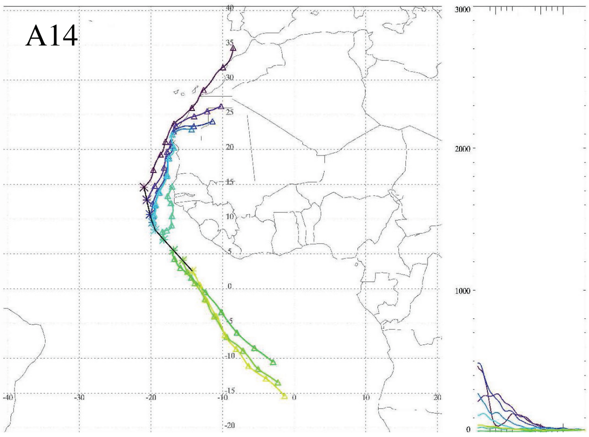
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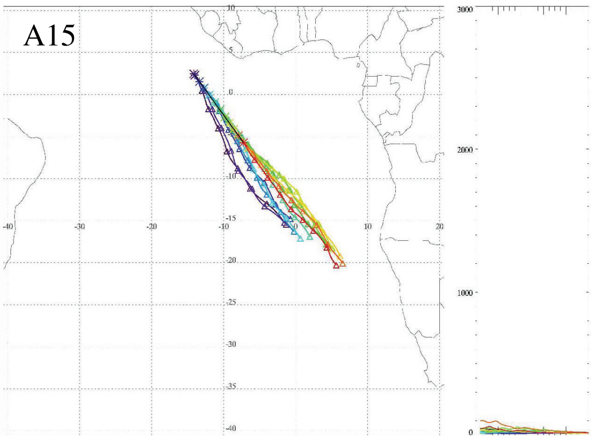
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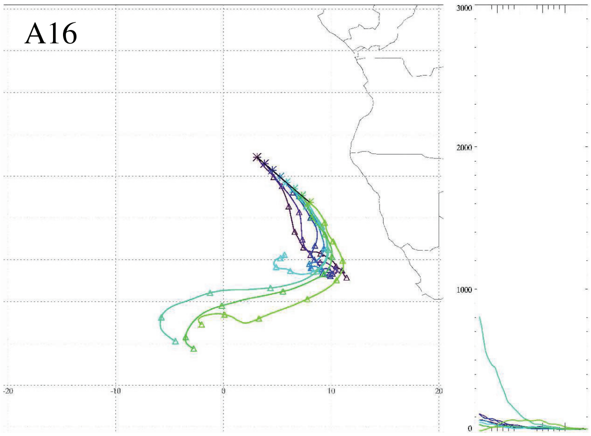
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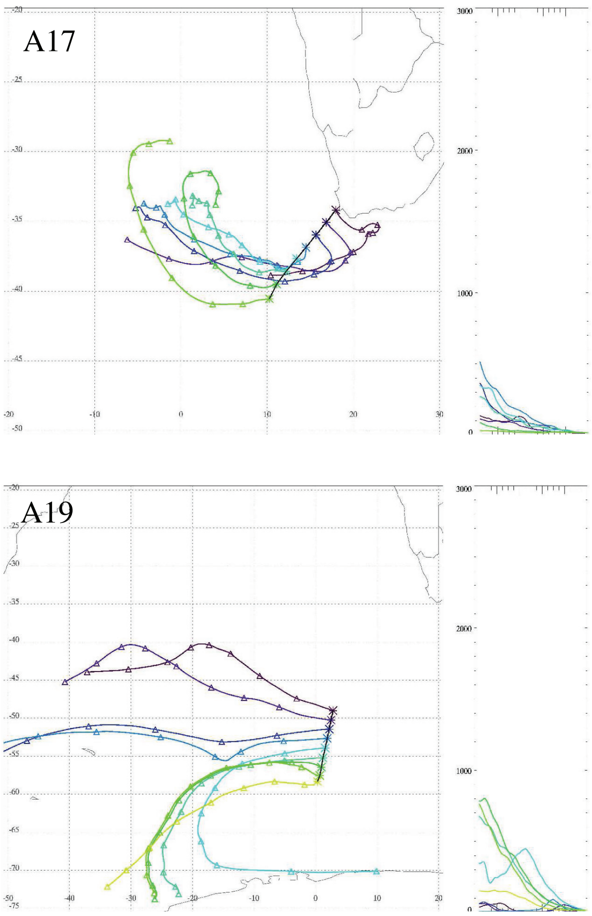

FIGURE S1. 96 h air mass back trajectories (6 h steps) and altitudinal profiles of the air mass parcels for the cruises ARK–XXIV/3 (A1–A10) and ANT–XXV/1+2 (A11–A20). For samples longer than 72 h, only every second BT was plotted. The black line indicates the cruise leg.

TABLE S5. Individual DP concentrations in the dissolved (diss.) and particulate (part.) phase (in pg L^{-1}) and f_{syn} values (diss. + part.) in seawater

	synDP		**antiDP**		**f_{syn}**
	diss.	**part.**	**diss.**	**part.**	
			ARK–XXIV/3		
W1	n.d.	0.01	0.01	0.007	0.38
W2	n.d.	0.02	n.d.	0.01	0.63
W3	n.d.	0.006	0.007	n.d.	0.46
W4	n.d.	0.003	n.d.	n.d.	S
W5	n.d.	0.38	n.d.	0.20	0.66
W6	0.03	0.06	0.03	0.13	0.35
W7	0.04	0.86	0.02	0.38	0.70
W8	n.d.	0.01	n.d.	0.01	0.52
W9	n.d.	0.005	n.d.	0.003	0.65
W10	n.d.	n.d.	n.d.	0.003	A
W11	n.d.	n.d.	n.d.	0.003	A
W12	n.d.	n.d.	n.d.	n.d.	n.d.
W13	n.d.	0.007	n.d.	0.01	0.41
W14	n.d.	n.d.	n.d.	n.d.	n.d.
W15	n.d.	0.006	n.d.	0.004	0.57
W16	n.d.	n.d.	n.d.	n.d.	n.d.
			ANT–XXV/1+2		
W17	0.20	0.15	0.18	0.13	0.53
W18	0.06	0.05	0.009	0.03	0.63
W19	0.008	0.07	n.d.	0.03	0.74
W20	0.006	0.03	n.d.	0.02	0.70
W21	0.006	—[a]	n.d.	—[a]	S
W22	0.03	0.03	0.02	0.02	0.62
W23	0.01	0.03	0.008	0.02	0.63
W24	0.009	0.01	n.d.	n.d.	S
W25	0.01	0.02	0.006	0.009	0.67
W26	0.007	0.08	n.d.	0.06	0.58
W27	n.d.	n.d.	n.d.	n.d.	n.d.
W28	n.d.	0.01	n.d.	0.006	0.67
W29	n.d.	0.009	n.d.	n.d.	S
W30	0.06	0.08	0.05	0.03	0.63
W31	0.01	0.02	n.d.	0.007	0.79
W32	0.008	0.007	n.d.	n.d.	S

[a] only the dissolved phase was analyzed
S/A = only the syn–/anti– isomer was detected
n.d. = not detected

TABLE S6. Concentrations of $aCl_{11}DP$ and $aCL_{10}DP$ in seawater from East Greenland Sea for the dissolved (diss.) and particulate (part.) phase in pg L^{-1}

	$aCl_{10}DP$		**$aCl_{11}DP$**	
	diss.	**part.**	**diss.**	**part.**
W1	0.002	n.d.	n.d.	n.d.
W2	n.d.	n.d.	n.d.	<0.001
W3	n.d.	n.d.	n.d.	<0.001
W4	n.d.	n.d.	n.d.	<0.001
W5	n.d.	0.004	n.d.	0.013
W6	n.d.	0.005	n.d.	<0.001
W7	0.001	0.007	n.d.	0.02
W8	n.d.	n.d.	n.d.	0.002
W9	n.d.	n.d.	n.d.	n.d.
W10	n.d.	n.d.	n.d.	n.d.
W11	n.d.	n.d.	n.d.	n.d.
W12	n.d.	n.d.	n.d.	<0.001
W13	n.d.	n.d.	n.d.	0.074
W14	n.d.	n.d.	n.d.	n.d.
W15	n.d.	n.d.	n.d.	0.003
W16	n.d.	n.d.	n.d.	n.d.

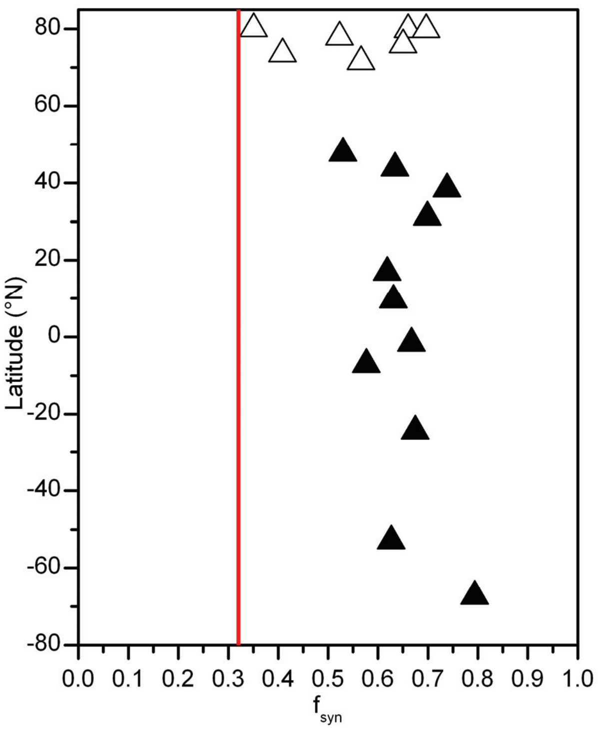

FIGURE S2. The f_{syn} value in seawater from East Greenland Sea (white triangle) and along the Atlantic Transect (black triangle) as a function of latitude. The red line of f_{syn} = 0.32 represents the mean commercial f_{syn} value reported by Wang et al. *(1).*

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(1) Wang, D.-G.; Yang, M.; Qi, H.; Sverko, E.; Ma, W.-L.; Li, Y.-F.; Alaee, M.; Reiner, E. J.; Shen, L. An Asia-specific source of Dechlorane Plus: Concentration, isomer profiles, and other related compounds. *Environ. Sci. Technol.* **2010**, *44*, 6608–6613.

Paper II

Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic

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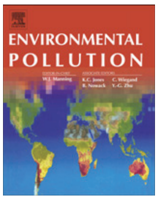

Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic

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Alternative flame retardants hexabromobenzene (HBB) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) undergo long-range atmospheric transport to the Arctic.

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ABSTRACT

The spatial distribution of polybrominated diphenyl ethers (PBDEs) and several alternative non-PBDE, non-regulated brominated flame retardants (BFRs) in air and seawater and the air–seawater exchange was investigated in East Greenland Sea using high-volume air and water samples. Total PBDE concentrations (Ó$_{10}$PBDEs) ranged from 0.09 to 1.8 pg m^{-3} in the atmosphere and from 0.03 to 0.64 pg L^{-1} in seawater. Two alternative BFRs, Hexabromobenzene (HBB) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), showed similar concentrations and spatial trends as PBDEs. The air–seawater gas exchange was dominated by deposition with fluxes up to −492 and −1044 pg m^{-2} day^{-1} for BDE-47 and DPTE, respectively. This study shows the first occurrence of HBB, DPTE and other alternative flame retardants (e.g., pentabromotoluene (PBT)) in the Arctic atmosphere and seawater indicating that they have a similar long-range atmospheric transport potential (LRAT) as the banned PBDEs.

1. Introduction

Brominated flame retardants (BFRs), in particular polybrominated diphenyl ethers (PBDEs), have been used for several decades as additives in industrial and consumer products to reduce their inflammability. PBDEs are persistent as well as bioaccumulative and some are known to induce adverse health effects (Birnbaum and Staskal, 2004). They are ubiquitous in various environmental matrices, presumably as a result from PBDE-treated products, with increasing temporal trends, even in the remote areas of the Arctic and Antarctica (Hites, 2004; Borghesi et al., 2008; de Wit et al., 2010). The Arctic has been shown to be exposed to several legacy Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls, organochlorine pesticides and polychlorinated dibenzodioxins and furans (PCDD/DFs) (Hung et al., 2010; Verreault et al., 2010). One important medium transporting POPs from source regions to remote areas within a relatively short period of time is the atmosphere (Wania, 2003). Models suggested that PBDEs have an adequate LRAT potential to reach the Arctic (Wania and Dugani, 2003), including the completely brominated non-volatile BDE-209 which was shown to undergo particle-bound LRAT (Wang et al., 2005; Breivik et al., 2006).

In response to their known adverse properties, the production and usage of the technical Penta- and OctaBDE mixtures in the European Union (EU) was banned by 2004 and the production in the United States (U.S.) was voluntarily phased out by the end of 2004. The exemption of the technical DecaBDE from the EU restriction was subsequently annulated in 2008 because of the possible environmental and healthy risks (European Court of Justice, 2008). In the U.S., the usage of DecaBDE is already banned by some states and a phase out is expected for 2013 (Hess, 2010). Recently, the Penta- and OctaBDE mixtures were officially classified as POPs and included in Annex A (elimination of production and use of all intentionally produced POPs) of the Stockholm Convention on POPs at the 4th meeting of the parties (Stockholm Convention Secretariat, 2009).

This resulted in an industrial shift towards alternative non-regulated, non-PBDE flame retardants. 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) was developed to replace the OctaBDE mixture (Hoh et al., 2005) while 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) were applied in Firemaster 550 replacing the PentaBDE mixture (Stapleton et al.,

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2008). Even though some non-PBDE BFRs have been used for several decades and have been firstly observed in the environment in the 1970/1980s (Mattsson et al., 1975; Watanabe et al., 1986; Qiu et al., 2007), they have received only little public and scientific attention until the banishment of PBDEs and the increasing demand of replacement compounds in the past decade. An increasing number of publications on non-PBDE BFRs has been published within the last years, including first findings in the Arctic region, e.g., hexabromobenzene (HBB), pentabromotoluene (PBT), BTBPE and pentabromoethylbenzene (PBEB) in seabird eggs from the Norwegian Arctic (Verreault et al., 2007) and BTBPE in seabird eggs from the Faroe Islands (Karlsson et al., 2006) indicating that they can undergo LRAT to remote areas. Nevertheless, only BTBPE was reported in the abiotic Arctic environment in an ice core from Svalbard (Norway) (Hermanson et al., 2010) while data on the atmosphere are lacking.

In this study, marine boundary layer air as well as seawater samples were simultaneously taken from East Greenland Sea. The samples were analyzed for 10 PBDE congeners and several non-PBDE BFRs in order to (i) compare levels of banned PBDEs with their alternatives, (ii) investigate their spatial distribution and (iii) estimate direction and fluxes of air–seawater exchange and dry deposition fluxes.

2. Materials and methods

2.1. Sampling cruise

Air and seawater samples were simultaneously taken aboard the German research vessel *R/V Polarstern* during the expedition cruise ARK-XXIV/3 in East Greenland Sea in August and September 2009 (69–80.5 °N). Details on sampling are given in Möller et al. (2010). Ten high-volume air samples (700–2700 m^3) using glass fibre filters (GFF) combined with a glass column packed with PUF/Amberlite® XAD-2 were taken at the upper deck. 16 seawater samples ($\sim$1000 L) were collected via the ship intake system using a GFF and a glass column packed with Serdolit® PAD-2 (SERVA Electrophoresis). Sampling parameters such as latitude, longitude, air and water temperature and salinity are included in Tables S1 and S2 in the Supporting information (SI).

2.2. Extraction and analysis

Extraction and analysis of the samples are described more in detail in Möller et al. (2010). Briefly, the samples were spiked with ^{13}C-BDE-77 and ^{13}C-BDE-138 (Wellington Laboratories) as surrogate standards, extracted in a Soxhlet apparatus and further cleaned on a silica column (10% water deactivated) topped on 3 g anhydrous granulated sodium sulphate. Finally, 1 ng ^{13}C-HCB (Cambridge Isotope Laboratories) was added as a recovery standard prior to injection. Samples were analyzed for 10 PBDE congeners (−28, −47, −66, −85, −99, −100, −153, −154, −183, −209), and PBT, PBEB, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB, BTBPE, octabromotrimethylphenylindane (OBIND) and TBPH (all obtained from Wellington Laboratories). ^{13}C-BDE-77 was used as surrogate for BDE-28, -47, -66, -85, -99, -100, PBT, PBEB, DPTE and HBB, and ^{13}C-BDE-138 was used for BDE-153, -154, -183, -209, BTBPE, OBIND and TBPH. Analysis was done by a GC/MS-system (6890 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI).

2.3. QA/QC

Breakthrough of the target compounds was checked for both seawater and air samples using tandem columns during the present cruise and the cruise ANT-XXV/1+2 reported in our recent study (Möller et al., 2010). No target compounds were observed above the method detection limits (MDLs) in the lower columns. Three field blanks were taken for each sample type resulting in blank values maximum in the one to two digit absolute pg range (see Table S3 for individual blank values). MDLs were derived from mean blank values plus three times the standard deviation or, for those BFRs showing no blank values, from the instrumental detection limits at signal-to-noise (*S*/*N*) ratios of three. MDLs ranged from 0.0001 pg m^{-3} for PBT (air filter) to 0.24 pg L^{-1} for BDE-209 (water column) (see Table S4 for individual MDLs). The method recovery was examined by spike tests resulting in recoveries of 69 ± 10% for PBDEs and 73 ± 12% for non-PBDE BFRs.

2.4. Air mass back trajectories

Air mass origins were calculated for the air samples using NOAA's HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php). Back trajectories (BTs) were calculated for each sample in 6 h steps along the sampling cruise. BTs were traced back for 120 h with the sampling height as arrival height (see Fig. S1 for individual BTs).

3. Results and discussion

3.1. Atmospheric concentrations

In East Greenland Sea atmosphere, all investigated PBDE congeners were detected with a total PBDEs concentration (defined as Σ_{10}PBDEs hereafter) ranging from 0.06 to 1.6 pg m^{-3} and from 0.03 to 0.46 pg m^{-3} in the gaseous and particulate phase, respectively (see Table S5 for individual BFR concentrations). The individual concentration of the dominating congener BDE-47 ranged from 0.07 to 1.0 pg m^{-3} (gaseous + particulate phase). Following the increasing logK_{OA} of PBDEs with increasing degree of bromination (9.5 for BDE-28, 11.96 for BDE-183 at 25 °C (Harner and Shoeib, 2002)), the particulate associated fraction of PBDEs consequently increased from 7 ± 12% for BDE-28 (a tri-BDE) to 100% for BDE-183 (a hepta-BDE) and BDE-209. The PBDE congener profile was dominated by the main congeners which have been used in the commercial PentaBDE mixture – BDE-47 > BDE-99 > BDE-100 – contributing 89 ± 8% of Σ_{10}PBDEs (see Fig. 1). BDE-209 was detected at three stations at concentrations <0.1 pg m^{-3}.

Bossi et al. (2008) observed similar concentrations in Nuuk, South-West Greenland, between 0.14 and 3.26 pg m^{-3} for Σ_{11}PBDEs with a dominance of the PentaBDE congeners, too, while Pozo et al. (2006) reported a Σ_{17}PBDEs concentration of 5.3 pg m^{-3} on Svalbard. Wang et al. (2005) investigated particle-bound PBDEs during their expedition cruise in the Arctic from the Bohai Sea towards the Canadian Arctic ranging from <2.58 to 60.9 pg m^{-3} for Σ_{11}PBDEs, which is several times higher than the concentrations from East Greenland Sea.

Among the non-PBDE BFRs, HBB and DPTE were detected in all samples, mainly in the gaseous phase (1 ± 1% and 28 ± 31% in the particulate phase, respectively). The concentrations ranged between 0.001 and 0.66 pg m^{-3} for HBB and between 0.009 and 1.7 pg m^{-3} for DPTE (gaseous + particulate phase), respectively, which are similar to those of the dominating PBDE congeners. DPTE was produced in the 1970/1980s by the Chemische Fabrik Kalk asthe main compound in the commercial flame retardant Bromkal 73-5 PE while no other manufacturer reported its production

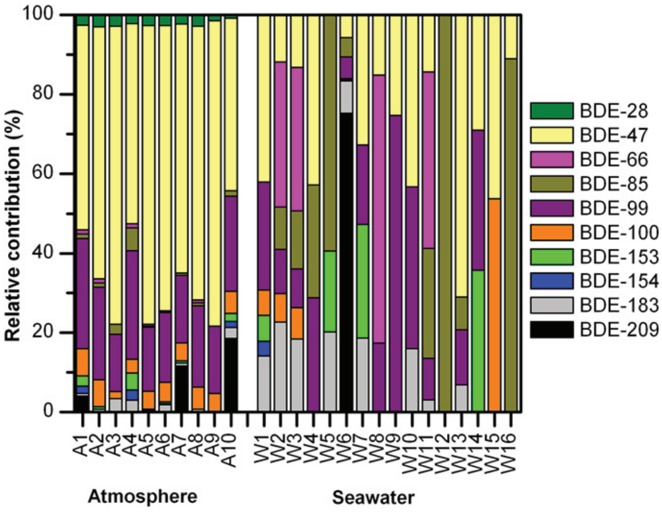

Fig. 1. Relative contribution of individual PBDEs from Σ_{10}PBDEs in the atmosphere and seawater of East Greenland Sea.

(de Kok et al., 1979; von der Recke and Vetter, 2007). Environmental data on DPTE are rare. It was firstly reported in 1997 in sewer slime from Germany. (Sauer et al., 1997) and Arend et al. (2002) detected DPTE in fish from the Northern Pacific from 0.3 to 5.6 ng g^{-1} lipid weight (lw). Interestingly, von der Recke and Vetter (2007) observed concentrations from 322 to 470 ng g^{-1} wet weight (ww) and from 130 to 340 ng g^{-1} ww in blubber and brain from harp seals (*Phoca groenlandica*) from East Greenland Sea sampled in 1991, respectively. PBDE concentrations in ringed seal blubber (*Phoca hispida*) from Greenland Sea are reported to be one order of magnitude lower, e.g. from 21 to 74 ng g^{-1} lw for Σ_{42}PBDEs in 2001 (Vorkamp et al., 2004). Furthermore, the enrichment of DPTE in brain was found to be 5–30 fold higher compared to PBDEs (von der Recke and Vetter, 2007). This, together with the findings of DPTE and PBDEs in the atmosphere and seawater in this study, shows that DPTE might be emitted into the environment and transported to remote areas in equal or higher extents as PBDEs in the present and recent decades.

Hexabromobenzene (HBB) was widely used as an additive flame retardant in Japan and is still produced in low volumes in Japan (Watanabe and Sakai, 2003) and additionally in China, while no production is reported for the EU (Verreault et al., 2007). Atmospheric concentrations of HBB reported in recent studies were in the range of 0.02–0.09 pg m^{-3} in the Great Lakes atmosphere (Gouteux et al., 2008), 0.3–6.5 pg m^{-3} in East China (Qiu et al., 2010) and up to 610 pg m^{-3} in Japanese air (Ministry of Japan, 2006). In 2007, Verreault et al. (2007) reported HBB for the first time in Arctic biota showing the third highest concentrations after PBDEs and hexabromocyclododecane (HBCD).

PBT, BTBPE and TBPH were detected in comparably low concentrations in the Arctic atmosphere which are summarized in Table 1. PBT and BTBPE have recently been reported in Arctic biota (Verreault et al., 2007) and BTBPE in an ice core (Hermanson et al., 2010) while this study shows the first occurrence of these BFRs in the Arctic atmosphere. Venier and Hites (2008) reported BTBPE concentrations from 0.5 to 1.2 pg m^{-3} in the atmosphere of the Great Lakes and Qiu et al. (2010) reported an annual mean concentration of 0.73 pg m^{-3} in East China. TBPH was detected in house dust from 1.5 to 10630 ng g^{-1} (Stapleton et al., 2008) and Lam et al. (2009) reported its first occurrence in marine mammals from Hong Kong (<0.04–3859 ng g^{-1} lw).

3.2. *Seawater concentrations*

The Σ_{10}PBDEs concentration in seawater ranged from 0.005 to 0.64 pg L^{-1}. The congener pattern was generally dominated by BDE-47 (n.d.–0.06 pg L^{-1}) and BDE-99 (n.d.–0.04 pg L^{-1}) while the pattern was less clear than in the atmosphere (see Fig. 1, and Table S6 for individual BFR concentrations). Interestingly, BDE-66, BDE-85 and BDE-183 were detected in comparably high concentrations while at station W12, BDE-85 was even the only detected PBDE (see Fig. 1). BDE-183 was the main congener of the technical OctaBDE mixture while BDE-66 and -85 were used only in minor percentages in the PentaBDE mixture (La Guardia et al., 2006). Several studies reported a high relative abundance of BDE-66 in biota possibly resulted from metabolism of higher brominated PBDEs (Meng et al., 2008; Wang et al., 2008) while both congeners might also originate from photodegradation of BDE-209 (Bezares-Cruz et al., 2004; Zeng et al., 2008) during LRAT to the Arctic. BDE-209 was detected only at one station at a relatively high concentration of 0.48 pg L^{-1}. Similar to the Arctic atmosphere, the fraction of particulate associated PBDEs increased with increasing degree of bromination from 0% and 6 ± 24% for BDE-66 and -47, respectively, to 57 ± 51% for BDE-183.

Table 1
Non-PBDE BFRs in the atmosphere (pg m^{-3}) and seawater (pg L^{-1}). The value in brackets represents the detection frequency in %. n.d. = not detected.

	Atmosphere	
	Gaseous	Particulate
DPTE	n.d.–1.7 (89)	0.005–0.05 (100)
HBB	0.04–0.66 (100)	0.001–0.005 (100)
PBT	0.001–0.02 (100)	n.d.–0.001 (20)
TBPH	n.d.	n.d.–0.08 (40)
BTBPE	n.d.–0.06 (22)	n.d.–0.02 (70)
	Seawater	
	Dissolved	Particulate
DPTE	n.d.–0.3 (81)	n.d.
HBB	n.d.–0.003 (13)	n.d.–0.002 (19)
PBT	n.d.	n.d.
TBPH	n.d.–1.3 (25)	n.d.–0.12 (6)
BTBPE	n.d.	n.d.–0.002 (6)

There are very limited data on PBDEs in (sea-) water in the literature. Coastal concentrations of 1, 0.5 and 0.1 pg L^{-1} were reported for BDE-47, -99 and −153 in the North Sea (Booij et al., 2002), respectively, which are 1–2 orders of magnitude higher than in the present study. In the San Francisco Estuary, Σ_{22}PBDEs ranged from 3 to 513 pg L^{-1} (Oros et al., 2005) and concentrations in the Izmir Bay, Turkey, ranged from 87 ± 57 pg L^{-1} in the dissolved phase to 479 ± 340 pg L^{-1} in the particulate phase for Σ_7PBDEs (Cetin and Odabasi, 2007). Concentrations in Lake Michigan were 18 and 3.1 pg L^{-1} (Σ_6PBDEs) in the dissolved and particulate phase, respectively (Streets et al., 2006). Carroll et al. (2008) reported concentrations between 1.8 and 10.8 pg L^{-1} (Σ_{43}PBDEs) in the Rivers Ob and Yenisei and their estuaries discharging into the Arctic Ocean and contributing to the PBDE contamination of the Arctic.

Regarding the non-PBDE BFRs, similar to the East Greenland Sea atmosphere DPTE was found to be the dominating non-PBDE BFR in seawater in dissolved concentrations from <MDL to 0.41 pg L^{-1} (it was not detected in the particulate phase). Concentrations of non-PBDE BFRs are included in Table 1. There are currently no data on DPTE in the water environment available, but, as mentioned in Section 3.1, relatively high DPTE concentrations in seals (*P. groenlandica*) from this region (von der Recke and Vetter, 2007) indicate LRAT of DPTE to East Greenland Sea, as proved in this study, followed by deposition to seawater and bioaccumulation and possibly biomagnification in marine organisms. Even though HBB was detected in the atmosphere in concentrations similar to PBDEs, it was detected in only five seawater samples slightly above the MDL (maximum 0.003 pg L^{-1}). HBB was recently observed in a pond close to an e-waste recycling site in China at 0.52 ± 0.04 ng L^{-1} (Wu et al., 2010). In the 1980s, Watanabe and Sakai (2003) reported HBB concentrations between 5.6 and 60 ng g^{-1} dry weight (dw) in Osaka sediment and Guerra et al. (2010) reported a maximum concentration of 2.4 ng g^{-1} dw in Llobregat River sediment. While PBT was not detected in any seawater samples, TBPH and BTBPE were observed at four and one stations, respectively (see Table 1).

3.3. *Spatial trends and possible sources*

The highest atmospheric concentrations for PBDEs as well as HBB, DPTE, BTBPE and TBPH were observed at station A1 which originated from continental air masses passing Ireland and the northern United Kingdom (U.K.) indicating that Western Europe might be a source region of these compounds in the European Arctic (see Fig. 2 for the spatial distribution of atmospheric BFRs). Since the congener pattern was dominated by the PentaBDE congeners (see above) which were significantly correlated in the atmosphere ($p < 0.01$), the PBDEs in the Arctic atmosphere can be related to the formerly widespread usage of the technical PBDE mixtures. Gioia et al. (2006) reported several times higher PBDE concentrations in the UK than in Norway resulting from their production and usage in the UK. Sources of HBB in the Arctic atmosphere might be (1) the emission from products containing HBB as additive flame retardant as known for additive BFRs (Alaee et al., 2003), (2) formation by the pyrolysis of the widely used BDE-209 (Thoma and Hutzinger, 1987) or (3) emission from polymeric BFRs (Gouteux et al., 2008). The remaining atmospheric samples originated from rather diverse air masses leading to a mixing of oceanic, continental (Greenland) and Arctic air masses resulting in no clear spatial concentration trends in East Greenland Sea atmosphere.

The PentaBDE congeners (BDE-47, -99, -100), HBB and DPTE were significantly correlated in the atmosphere East Greenland Sea ($p < 0.01/0.05$) indicating that they have similar sources and a similar LRAT potential. A similar spatial trend has been additionally observed for Dechlorane Plus (DP), a highly chlorinated flame retardant, as published in our recent study on DP (Möller et al., 2010) showing that PBDEs as well as several alternative halogenated flame retardants were transported from Western Europe to the European Arctic. Harju et al. (2009) placed HBB in the transition area between single and multiple hopper within the global transport model of POPs developed by Wania (2003, 2006). Thus, HBB has a high LRAT potential to the Arctic compared to those of established POPs. So far, DPTE and HBB have not been reported in continental air from Europe which is needed in order to estimate the emission of HBB and DPTE in source regions to the (marine) environment while long-term studies are needed to verify the influence of possible source regions such as Western Europe on BFR levels in the (European) Arctic.

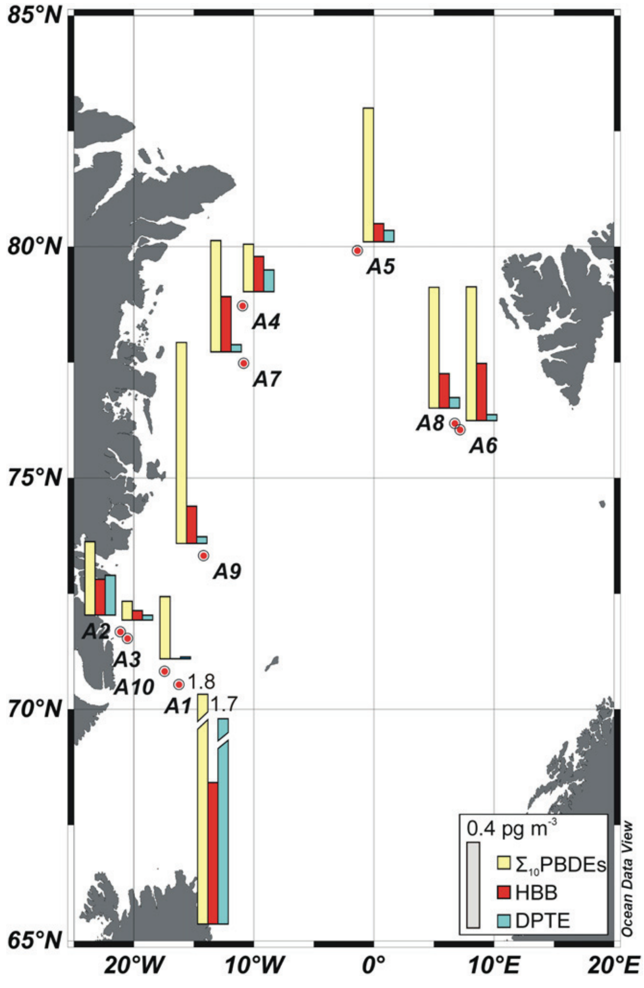

Fig. 2. Map showing the concentrations of Σ$_{10}$PBDEs, HBB and DPTE in the East Greenland Sea atmosphere. The stations represent mean stations since samples were taken continuously along the cruise leg. NOTE: For station A10 only the particulate phase was analyzed.

In seawater, the highest PBDE and DPTE concentrations were generally observed at stations close to the Eastern coast of Greenland while values at stations in the open ocean were lower (see Fig. 3). This can be explained by the East Greenland current transporting Arctic Ocean water masses, and >90% of the seaice from the Arctic Ocean southwards along the Eastern coastline of Greenland (Woodgate et al., 1999). POPs are known to accumulate in ice-/snowpacks (Gustafsson et al., 2005) while they might be released to seawater during ice melt periods. In ice cores from the Arctic Ocean, concentrations between 0.5 and 2.3 pg L^{-1} for BDE-47 and -99 were reported (Lacorte et al., 2009) which are approximately one order of magnitude higher than the observed seawater concentrations. In addition, glacier meltwater from Greenland might transport relatively high fluxes of BFRs into East Greenland Sea, too. However, the samples were taken continuously along the cruise leg what might lead to a mixing of different water masses such as Atlantic water, Arctic water, seaice meltwater and glacier meltwater. Interestingly, TBPH was observed at station W6 at a concentration of 1.3 g L^{-1}, where the highest BDE-209 and DPTE

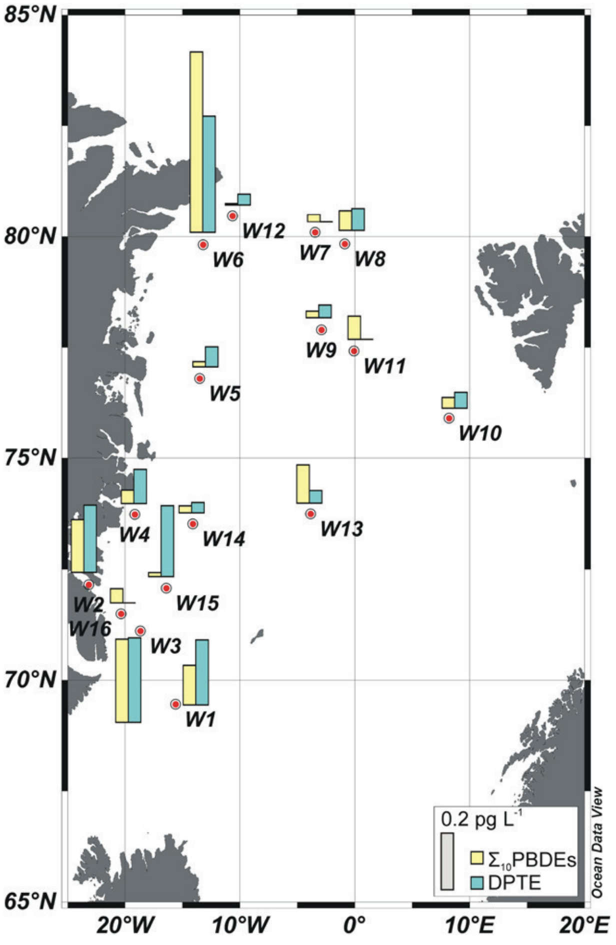

Fig. 3. Map showing the concentrations of Σ$_{10}$PBDEs and DPTE in seawater from East Greenland Sea.

concentrations were observed, too. This shows that they might have similar sources in East Greenland Sea.

3.4. Air–seawater exchange

The air–seawater exchange direction was predicted for BDE-47, BDE-99 and DPTE by calculating the fugacity ratio between both phases using equation (1)

$$\frac{f_W}{f_A} = \frac{C_W H}{C_A R T_A} \tag{1}$$

where f_W and f_A are the fugacities in water and air, respectively, C_W and C_A are the dissolved and gaseous concentrations in water and air (pg m^{-3}), respectively, H is the Henry's Law constant at the given water temperature and corrected by the salinity according to Schwarzenbach et al. (2003) (Pa m^3 mol^{-1}), R is the gas constant (8.31 Pa m^3 K^{-1} mol^{-1}) and T_A is the air temperature. The Henry's Law constant of BDE-47 and -99 and their temperature dependence was taken from Cetin and Odabasi (2005). Since there is no measured or predicted Henry's Law constant for DPTE available, we estimated it to be 0.0478 Pa m^3 mol^{-1} using EPI Suite 4.0 developed by US EPA (US EPA, 2010) and the temperature dependence was estimated to be similar to BDE-47. A fugacity quotient <1 and >1 indicates net dry gaseous deposition and volatilization, respectively, while $f_W/f_A = 1$ indicates thermodynamic equilibrium. The error associated with the fugacity was propagated from the estimated relative standard deviations of the water and air concentrations (±20%) and the Henry's Law constant (<13% for PBDEs (Cetin and Odabasi, 2005)), and the air temperature during sampling (±5%) resulting in a total uncertainty of ±32%. Since no measured Henry's Law constant of DPTE is available, we assumed an uncertainty of a factor of at least three for the fugacity ratio. The calculations derived fugacity ratios for BDE-47 and -99 below 0.1 suggesting a net deposition from the atmosphere to seawater, while the ratios of DPTE ranged from <0.01 to 1.5 suggesting that DPTE might show dry gaseous deposition, equilibrium conditions and possibly volatilization within East Greenland Sea.

The net air–seawater gas exchange flux was calculated based on the modified version of the Whitman two-film resistance model (Liss and Slater, 1974; Bidleman and McConnell, 1995) which has extensively been used to determine the air–water exchange of POPs, also in the Arctic (e.g., Xie et al., 2007; Zhang and Lohmann, 2010). The net flux (F_{AW}, pg m^{-2} day^{-1}) is defined by equation (2):

$$F_{AW} = K_{OL}\left(C_W - \frac{C_A}{H'_{\text{salt},T}}\right) \tag{2}$$

where H' is the dimensionless temperature and salinity corrected Henry's Law constant and K_{OL} (m day^{-1}) is the gas phase overall mass transfer coefficient compromising the resistances to mass transfer in both water (K_W) and air (K_A):

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'_{\text{salt},T}} \tag{3}$$

Details on the calculation F_{AW} are given in the SI. The estimated air–seawater gas fluxes are presented in Fig. 4. The overall propagated uncertainty of BDE-47 and -99 was ±51% based on an uncertainty of ±40% for K_{OL} taken from Cetin and Odabasi (2007). Since the Henry's Law constant of DPTE was estimated, K_{OL} and consequently F_{AW} will have higher uncertainties which were estimated to be at least ± 500% for F_{AW}. The gas exchange process of BDE-47 and -99 was dominated by atmospheric dry gaseous deposition with net fluxes ranging from −13 to −492 pg m^{-2} day^{-1} and from −7 to −272 pg m^{-2} day^{-1}, respectively. DPTE showed net dry gaseous deposition fluxes up to −1044 pg m^{-2} day^{-1}. The highest dry gaseous deposition fluxes were observed at station W1 as a result of BFRs atmospherically transported from Western Europe to East Greenland Sea (see above) suggesting that air–seawater gas exchange is a significant process for the transport of BFRs to the Arctic. Several stations showed DPTE (and BDE-47 and -99) nearly at air–seawater equilibrium while stations W3 even showed a slight net volatilization of DPTE of 3 pg m^{-2} day^{-1}, respectively. This might be a result of BFRs emitted into East Greenland Sea, e.g., by glacier meltwater leading to a change of the air–seawater gas exchange flux direction and to a further atmospheric transport of BFRs within the Arctic.

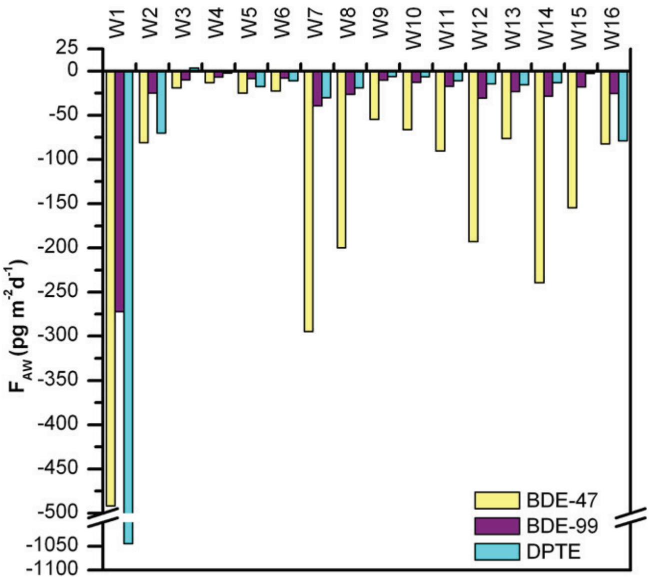

Fig. 4. Air–sea gas exchange fluxes of BDE-47, -99 and DPTE in East Greenland Sea. Negative flux indicates net dry gaseous deposition into the water column.

3.5. Dry particle-bound deposition

Besides air–seawater gas exchange, dry particle-bound deposition is an important deposition process of POPs into the global oceans and remote areas (Duce, 1990; Dachs et al., 2002), especially for highly hydrophobic POPs such as BDE-209 (Wang et al., 2005; Gouin et al., 2006). On the other hand, dry deposition of POPs leads to a removal from the atmosphere and to a limitation of the LRAT potential of non-volatile POPs (Wania, 2003). The dry particle-bound deposition flux (F_d, pg m^{-2} day^{-1}) was calculated for PBDEs and DPTE using equation (4):

$$F_d = V_d C_p \tag{4}$$

where V_d is the deposition velocity (m d^{-1}) and C_p is the concentration in the particulate phase (pg m^{-3}). The deposition velocity strongly depends on meteorological parameters (e.g., wind speed) and physicochemical parameters of the particle and the pollutant (Franz et al., 1998). Therefore, we estimated an uncertainty of a factor of 3 for the deposition velocity. There are no measured velocities for BFRs for open ocean conditions available. Based on recent studies on the dry deposition of POPs (Castro-Jiménez et al., 2010; Jurado et al., 2004; Del Vento and Dachs, 2007), we used a constant velocity of 0.1 cm s^{-1} (86.4 m d^{-1}) for the open sea conditions in this study. Since the dry deposition was calculated based on a constant deposition velocity, the differences in the

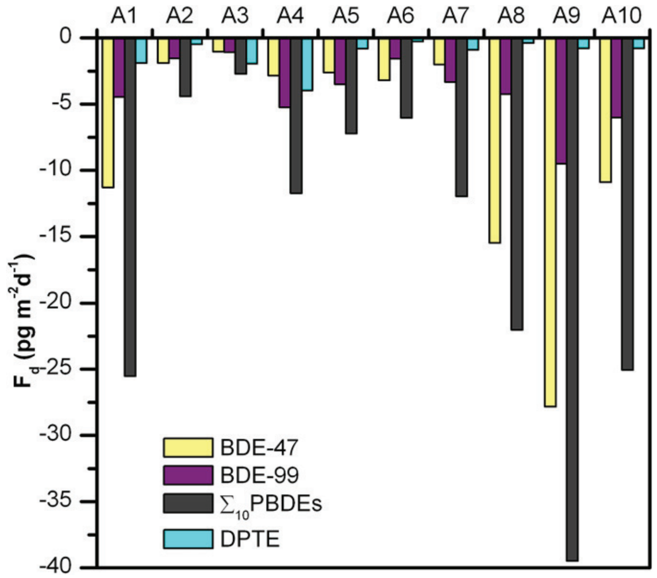

Fig. 5. Dry particle-bound deposition fluxes of BDE-47, -99, Σ_{10}PBDEs and DPTE in East Greenland Sea. Negative (−) flux indicates net deposition into the water column.

fluxes resulted only from the differences in the particulate concentrations and higher differences are expected if the velocities for the individual BFRs were known. The dry deposition fluxes are shown in Fig. 5. The dry particle-bound deposition flux for Σ_{10}PBDEs ranged from −2.7 to −39.5 pg m^{-2} day^{-1} with individual fluxes from −1.1 to −27.8 pg m^{-2} day^{-1} for BDE-47, -1.1 to −9.5 pg m^{-2} day^{-1} for BDE-99, -0.4 to −4.0 pg m^{-2} day^{-1} for DPTE. Compared to the air–seawater gas fluxes, dry particle-bound deposition fluxes are about one order of magnitude lower as a result of continuous dry deposition along atmospheric transport from the source region to the Arctic. This shows that air–seawater gas exchange is the dominating deposition pathway of BFRs into East Greenland Sea. Nevertheless, there might be other input pathways such as riverine discharge and wet deposition, which need to be investigated to estimate the flux of PBDEs to East Greenland Sea and, in general, to the Arctic.

4. Conclusions

The investigation of PBDEs and alternative brominated flame retardants showed the dominance of the common PentaBDE congeners BDE-47 -99, and, interestingly, two non-PBDE BFRs: HBB and DPTE. Even though both have been produced for several decades, they were detected for the first time in the Arctic atmosphere and seawater. The concentrations and spatial trends were similar to PBDEs as a result of similar sources and of an apparently similar LRAT potential as the known POPs BDE-47 and -99. Thereby, the origin of HBB needs to be investigated in future research since it might be a degradation product of BDE-209 which is still being produced and used, e.g., in the U.S. and in China. Both air–seawater gas transfer and dry particle-bound deposition contribute do the input of BFRs into East Greenland Sea. Besides, PBT, BTBPT and TBPH were detected in the Arctic atmosphere for the first times which need to be included in further studies on non-PBDE BFRs in the Arctic environment.

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Appendix. Supporting information

Supporting information associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.02.054.

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Supporting Information

Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic

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Air–water exchange

The air–seawater gas exchange was calculated based on the modified version of the Whitman two–film resistance model (Liss and Slater, 1974; Bidleman and McConnell, 1995):

$$F_{AW} = K_{OL}\left(C_W - \frac{C_A}{H'_{salt,T}}\right) \tag{A1}$$

where $H'_{salt,T}$ is the dimensionless temperature and salinity corrected Henry's Law constant defined as $H' = H/RT$ (R = gas constant, T = Temperature). If C_A or C_W were below detection limit, half of the MDL was estimated for the calculation. The dimensionless Henry's Law constant was corrected by the temperature and salinity using (Schwarzenbach et al., 2003):

$$H'_{salt,T} = H' \times 10^{K_S C_S} \tag{A2}$$

where C_S is the salt concentration (mol L^{-1}) and K_S is the Setschenow constant (L mol^{-1}) which was taken from Cetin and Odabasi (2007) for BDE-47 and -99, respectively. For DPTE, K_S was calculated by the method described by Ni and Yalkowsky (2003) based on a $\log K_{OW}$ of 6.34 calculated using EPI Suite 4.0 (US EPA, 2010). K_{OL} (m h^{-1}) is the gas phase overall mass transfer coefficient compromising the resistances to mass transfer in both water (K_W, m h^{-1}) and air (K_A, m h^{-1}) and is defined by:

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'} \tag{A3}$$

where (Hornbuckle et al., 1994):

$$k_A = (0.2U_{10} + 0.3) \times \left(\frac{D_{i,air}}{D_{H_2O,air}}\right)^{0.61} \times 36 \tag{A4}$$

$$k_W = (0.45 U_{10}^{1.64}) \times \left(\frac{Sc_i}{Sc_{CO_2}}\right)^{-0.5} \times 0.01 \tag{A5}$$

D_{air} is the diffusity in air, U_{10} is the wind speed at 10 m height above sea level (m s^{-1}), and Sc is the Schmidt number which was set to 1395 for CO_2 a mean temperature of 5°C during the cruise (Schwarzenbach et al., 2003). D_{air} was calculated using the method described by Fuller et al. (1966) and *Sc* for the BFRs was calculated using the method described by Hayduk and Laudi (1974).

TABLE S1. Detailed information on air sampling. Latitude and longitude are mean sampling stations. Air temperature represents the mean air temperature during sampling. The distance covered during sampling represents an estimated value.

	Date	**Latitude**	**Longitude**	**Distance**	**Volume**	**Air temperature**
		(°N)	**(°E)**	**(km)**	**(m^3)**	**(°C)**
A1	7–9/8/09	70.539	-16.223	500	743	6.5
A2	9–13/8/09	71.675	-21.110	300	1935	5.2
A3	13–16/8/09	71.536	-20.514	500	1331	3.9
A4	16–21/8/09	78.722	-10.924	1000	966	-0.3
A5	21–25/8/09	79.913	-1.377	400	1649	1.0
A6	25–31/8/09	76.045	7.170	300	2678	3.6
A7	31/8–6/9/09	77.483	-10.848	1100	2625	0.7
A8	6–9/9/09	76.183	6.736	500	1060	6.0
A9	9–14/9/09	73.325	-14.176	800	2101	2.0
A10	14–20/9/09	70.826	-17.432	500	1339	0.8

[a] only the particulate phase of sample A10 was analyzed

TABLE S2. Detailed information on water sampling. Latitude and longitude are mean sampling stations. Water temperature (T_W), salinity and wind speed represent the mean values during sampling.

	Date	Latitude (°N)	Longitude (°E)	Volume (L)	T_W (°C)	Salinity (PSU)	Wind speed (m/s)	Corresponding air sample
W1	7/8/09	69.461	-15.590	1000	6.8	34.7	7.7	A1
W2	9/8/09	72.157	-23.144	733	4.8	33.4	4.9	A2
W3	14/8/09	71.111	-18.642	1000	4.4	32.4	4.5	A3
W4	16/8/09	73.741	-19.147	1000	1.2	29.0	2.3	A3
W5	17/8/09	76.797	-13.492	692	-0.2	28.9	3.4	A4
W6	19/8/09	79.815	-13.202	832	-0.9	30.2	3.0	A4
W7	21/8/09	80.095	-3.447	1280	-1.5	30.9	8.7	A5
W8	23/8/09	79.831	-0.867	1000	-1.6	32.1	5.4	A5
W9	25/8/09	77.893	-2.898	987	2.4	32.6	2.7	A6
W10	27/8/09	75.902	8.215	1000	7.5	35.0	3.6	A6
W11	29/8/09	77.415	-0.057	1000	5.5	34.4	5.5	A6
W12	31/8/09	80.461	-10.633	1000	-0.8	29.3	8.2	A7
W13	9/9/09	73.754	-3.830	1000	5.2	34.3	4.1	A8
W14	11/9/09	73.524	-14.086	1000	1.8	32.4	7.6	A9
W15	13/9/09	72.078	-16.397	1000	2.3	32.9	4.4	A9
W16	16/9/09	71.497	-20.329	1000	1.6	31.7	4.9	A2

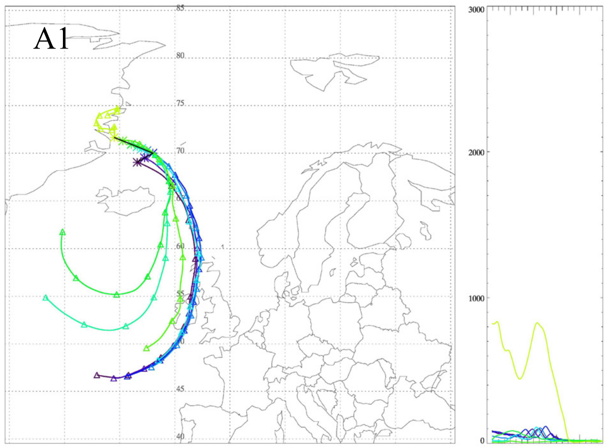
TABLE S3. Mean field blank values in pg, and pg m^{-3} for air samples or pg L^{-1} for seawater samples (values in brackets). Mean sample volumes of 1500 m^3 and 1000 m^3 were estimated for air and water samples, respectively.

	air column	**air filter**	**water column**	**water filter**
BDE-28	n.d.	n.d.	n.d.	0.4 ± 0.1 (0.0004 ± 0.0001)
BDE-47	13 ± 4 (0.09 ± 0.003)	0.7 ± 0.3 (0.0005 ± 0.0002)	1 ± 1 (0.001 ± 0.001)	5 ± 4 (0.005 ± 0.004)
BDE-66	n.d.	n.d.	4 ± 3 (0.004 ± 0.003)	0.3 ± 0.4 (0.0003 ± 0.0004)
BDE-85	1 ± 0.3 (0.001 ± 0.0002)	1 ± 0.2 (0.001 ± 0.0001)	3 ± 1 (0.003 ± 0.001)	2 ± 1 (0.002 ± 0.001)
BDE-99	33 ± 7 (0.02 ± 0.005)	1 ± 0.3 (0.001 ± 0.0002)	2 ± 1 (0.002 ± 0.001)	10 ± 5 (0.01 ± 0.005)
BDE-100	5 ± 2 (0.003 ± 0.001)	n.d.	n.d.	2 ± 1 (0.002 ± 0.001)
BDE-153	14 ± 5 (0.009 ± 0.003)	n.d.	n.d.	0.4 ± 0.4 (0.0004 ± 0.0004)
BDE-154	5 ± 2 (0.003 ± 0.001)	n.d.	n.d.	0.1 ± 0.1 (0.0001 ± 0.0001)
BDE-183	80 ± 24 (0.05 ± 0.02)	n.d.	1 ± 2 (0.001 ± 0.002)	1 ± 0.3 (0.001 ± 0.0003)
BDE-209	36 ± 32 (0.02 ± 0.02)	n.d.	59 ± 59 (0.06 ± 0.06)	n.d.
BTBPE	13 ± 6 (0.009 ± 0.004)	n.d.	3 ± 6 (0.003 ± 0.006)	n.d.
DPTE	12 ± 6 (0.008 ± 0.004)	3 ± 0.3 (0.002 ± 0.0002)	12 ± 5 (0.012 ± 0.005)	19 ± 19 (0.02 ± 0.02)
HBB	1 ± 0.3 (0.007 ± 0.0002)	0.1 ± 0.1 (0.0001 ± 0.0001)	n.d.	0.3 ± 0.2 (0.0003 ± 0.0002)
PBT	n.d.	0.02 ± 0.04 (0.00001 ± 0.00003)	0.1 ± 0.2 (0.0001 ± 0.0002)	0.2 ± 0.03 (0.0002 ± 0.0003)
TBPH	n.d.	n.d.	n.d.	n.d.
OBIND	n.d.	n.d.	n.d.	n.d.

TABLE S4. Method detection limits (in pg m^{-3} for air samples and pg L^{-1} for water samples, n.d. = not detected). MDLs were calculated from mean field blank values plus three times the standard deviation or based on instrumental S/N ratios of 3 if no blank was detected. Mean sample volumes of 1500 m^3 and 1000 m^3 were estimated for air and water samples, respectively.

	air		**water**	
	gaseous	**particulate**	**dissolved**	**particulate**
BDE-28	0.001[1]	0.001[1]	0.002[1]	0.002[1]
BDE-47	0.016	0.001	0.005	0.016
BDE-66	0.005[1]	0.005[1]	0.014	0.002
BDE-85	0.002	0.001	0.005	0.004
BDE-99	0.037	0.001	0.005	0.026
BDE-100	0.007	0.0002[1]	0.0003[1]	0.006
BDE-153	0.02	0.0002[1]	0.0003[1]	0.002
BDE-154	0.008	0.0005[1]	0.0007[1]	0.001
BDE-183	0.10	0.0009[1]	0.006	0.002
BDE-209	0.088	0.028[1]	0.24	0.042[1]
BTBPE	0.019	0.0005[1]	0.021	0.0007[1]
DPTE	0.021	0.002	0.028	0.076
HBB	0.001	0.0002	0.0002[1]	0.001
PBT	0.0005[1]	0.0001	0.0007[1]	0.0007[1]
TBPH	0009[1]	0.009[1]	0.013[1]	0.013[1]
OBIND	0.007[1]	0.007[1]	0.011[1]	0.011[1]

[1] calucated based on an instrumental S/N ratio of 3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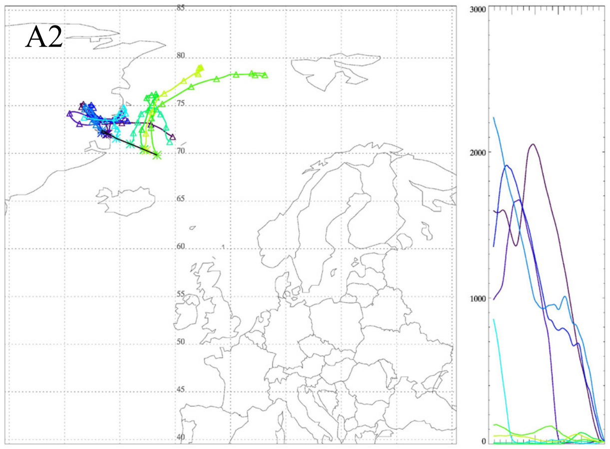
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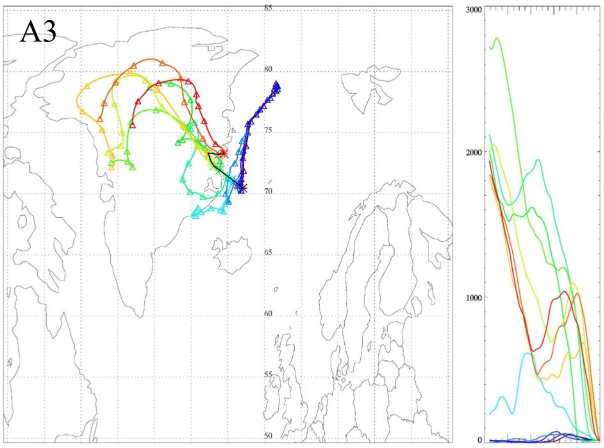
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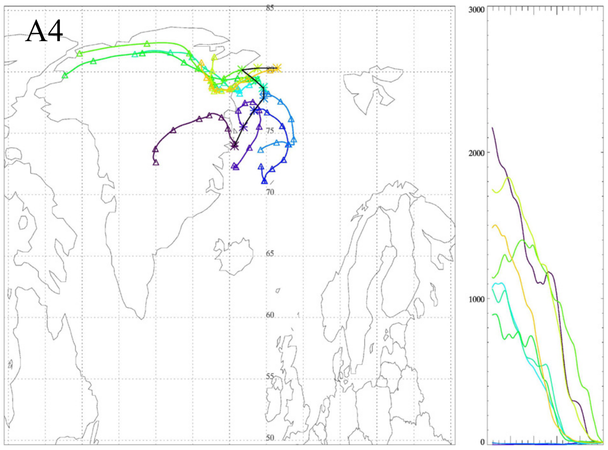
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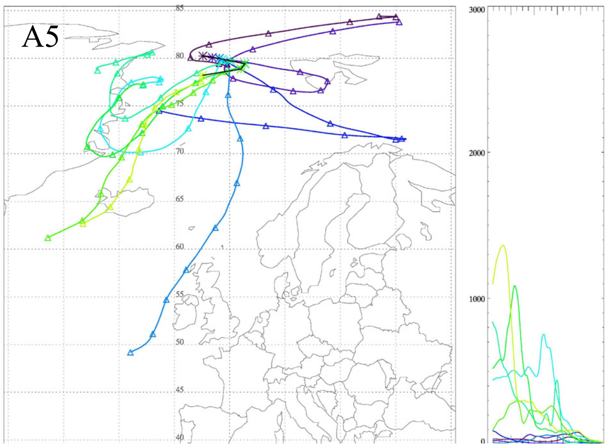
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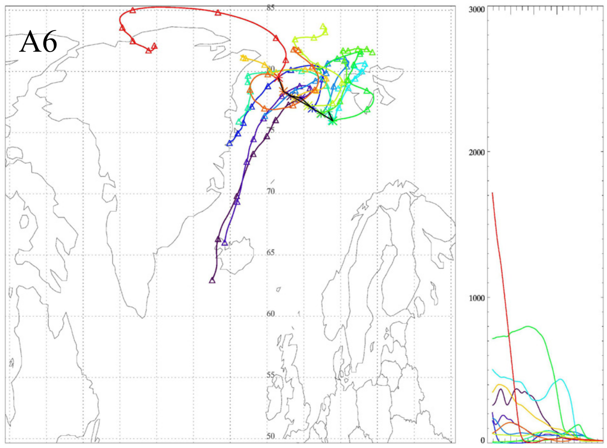
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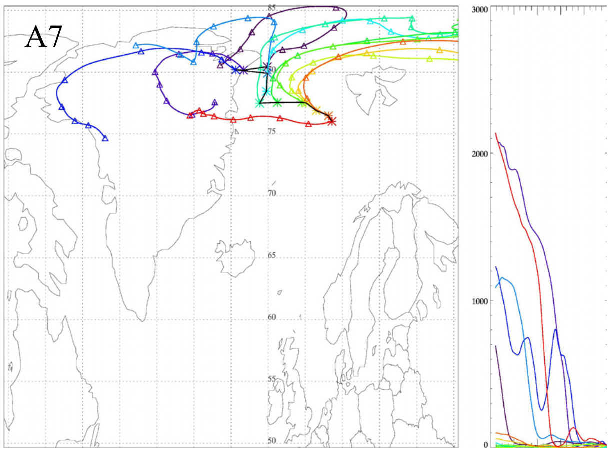
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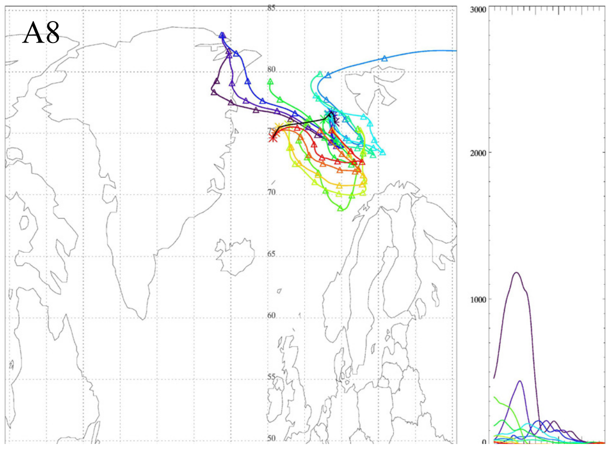
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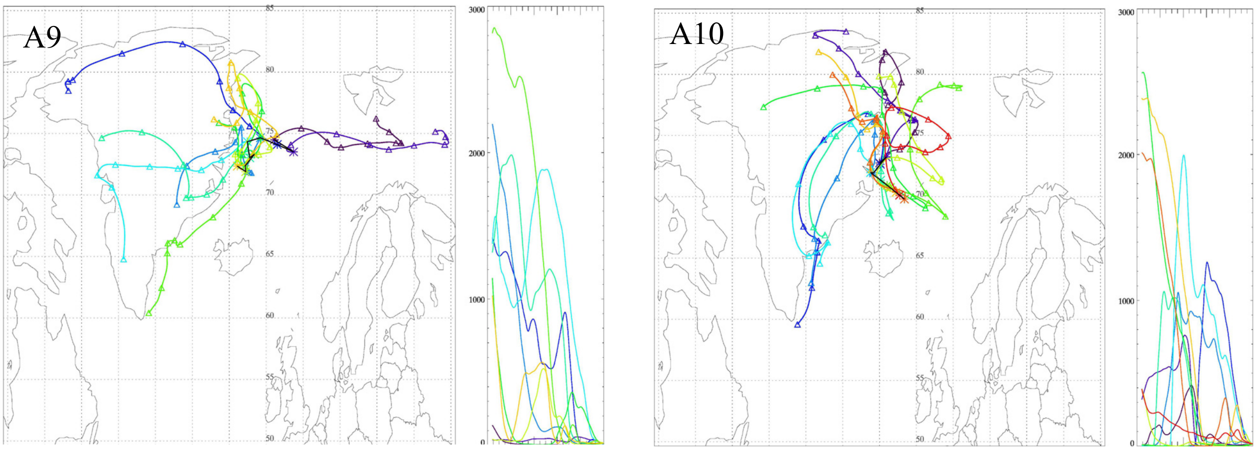

FIGURE S1. 96 h air mass back trajectories (6 h steps) and altitudinal profiles of the air mass parcels. For samples longer than 72 h, only every second BT was plotted. The black line indicates the cruise leg.

TABLE S5. Individual BFR concentrations in the gaseous (gas.) and particulate (part.) phase of the atmosphere (in pg m^{-3})

		A1	A2	A3	A4	A5	A6	A7	A8	A9	A10[a]
BDE-28	**gas.**	0.04	0.01	0.003	0.005	0.02	0.007	0.01	0.01	0.0133	—
	part.	0.004	0.0006	n.d.	n.d.	n.d.	0.001	n.d.	0.006	n.d.	0.002
BDE-47	**gas.**	0.82	0.19	0.05	0.08	0.44	0.20	0.30	0.21	0.4011	—
	part.	0.13	0.02	0.01	0.03	0.03	0.04	0.02	0.18	0.3222	0.13
BDE-66	**gas.**	0.02	0.004	n.d.	0.002	0.003	n.d.	n.d.	n.d.	n.d.	—
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.
BDE-85	**gas.**	0.02	0.002	n.d.	n.d.	0.002	n.d.	n.d.	0.002	n.d.	—
	part.	0.003	0.002	0.002	0.01	n.d.	0.001	0.003	0.002	n.d.	0.004
BDE-99	**gas.**	0.46	0.06	n.d.	n.d.	0.06	0.04	0.05	0.07	0.0488	—
	part.	0.05	0.02	0.01	0.06	0.04	0.02	0.04	0.05	0.1101	0.07
BDE-100	**gas.**	0.11	0.02	n.d.	n.d.	0.02	0.01	0.02	0.02	0.0188	—
	part.	0.01	0.004	0.002	0.008	0.008	0.004	0.007	0.02	0.0249	0.02
BDE-153	**gas.**	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—
	part.	0.006	0.002	n.d.	0.01	0.002	0.002	0.003	n.d.	n.d.	0.006
BDE-154	**gas.**	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—
	part.	0.003	n.d.	n.d.	0.006	n.d.	0.001	n.d.	n.d.	n.d.	0.004
BDE-183	**gas.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—
	part.	0.01	0.003	0.003	0.007	0.002	0.006	0.004	0.004	n.d.	0.008
BDE-209	**gas.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—
	part.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	0.05
DPTE	**gas.**	1.7	0.18	n.d.	0.06	0.04	0.02	0.02	0.04	0.0233	—
	part.	0.02	0.006	0.02	0.05	0.01	0.003	0.01	0.005	0.0091	0.01
HBB	**gas.**	0.66	0.17	0.04	0.16	0.08	0.27	0.26	0.16	0.1699	—
	part.	0.002	0.002	0.001	0.005	0.001	0.001	0.001	0.002	0.0041	0.001
PBT	**gas.**	0.01	0.016	0.004	0.008	0.001	0.007	0.01	0.02	0.0080	—
	part.	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	n.d.	n.d.	n.d.	0.0003
TBPH	**gas.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—
	part.	0.08	0.01	0.04	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
BTBPE	**gas.**	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	—
	part.	0.02	0.003	0.004	0.006	0.005	n.d.	n.d.	0.01	n.d.	0.009

[a] only the particulate phase was analyzed

n.d. = not detected

TABLE S6. Individual BFR concentrations in the dissolved (diss.) and particulate (part.) phase in seawater (in pg L^{-1})

		W1	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**
BDE-28	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-47	**diss.**	0.06	0.02	0.04	0.02	n.d.	0.04	0.008	0.01	0.006	0.02
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-66	**diss.**	n.d.	0.07	0.11	n.d.	n.d.	n.d.	n.d.	0.05	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-85	**diss.**	n.d.	0.02	0.04	0.01	0.01	0.03	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-99	**diss.**	0.04	0.02	0.03	0.01	n.d.	0.04	0.005	0.01	0.02	0.02
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-100	**diss.**	0.009	0.01	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-153	**diss.**	0.009	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	0.004	0.003	0.007	n.d.	n.d.	n.d.
BDE-154	**diss.**	0.005	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	n.d.	n.d.
BDE-183	**diss.**	0.02	0.04	0.05	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	0.004	n.d.	n.d.	0.004	0.003	0.005	n.d.	n.d.	0.006
BDE-209	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	0.37	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.
DPTE	**diss.**	0.23	0.24	0.30	0.12	0.07	0.41	n.d.	0.08	0.04	0.06
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HBB	**diss.**	0.003	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	n.d.
PBT	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TBPH	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	1.29	0.13	n.d.	n.d.	0.21
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BTBPE	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002	n.d.	n.d.	n.d.

n.d. = not detected

Continuation of Table S6

		W11	W12	W13	W14	W15	W16
BDE-28	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-47	**diss.**	0.01	n.d.	0.01	0.007	0.007	0.005
	par.	n.d.	n.d.	0.08	n.d.	n.d.	n.d.
BDE-66	**diss.**	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-85	**diss.**	0.01	0.005	n.d.	n.d.	n.d.	n.d.
	par.	0.009	n.d.	0.01	n.d.	n.d.	0.04
BDE-99	**diss.**	0.009	n.d.	0.02	0.009	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-100	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	0.008	n.d.
BDE-153	**diss.**	n.d.	n.d.	n.d.	0.009	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-154	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-183	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	0.003	n.d.	0.009	n.d.	n.d.	n.d.
BDE-209	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DPTE	**diss.**	n.d.	0.04	0.04	0.04	0.250	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HBB	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	0.001	n.d.	n.d.	0.002	n.d.
PBT	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TBPH	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	0.15
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12
BTBPE	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	par.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

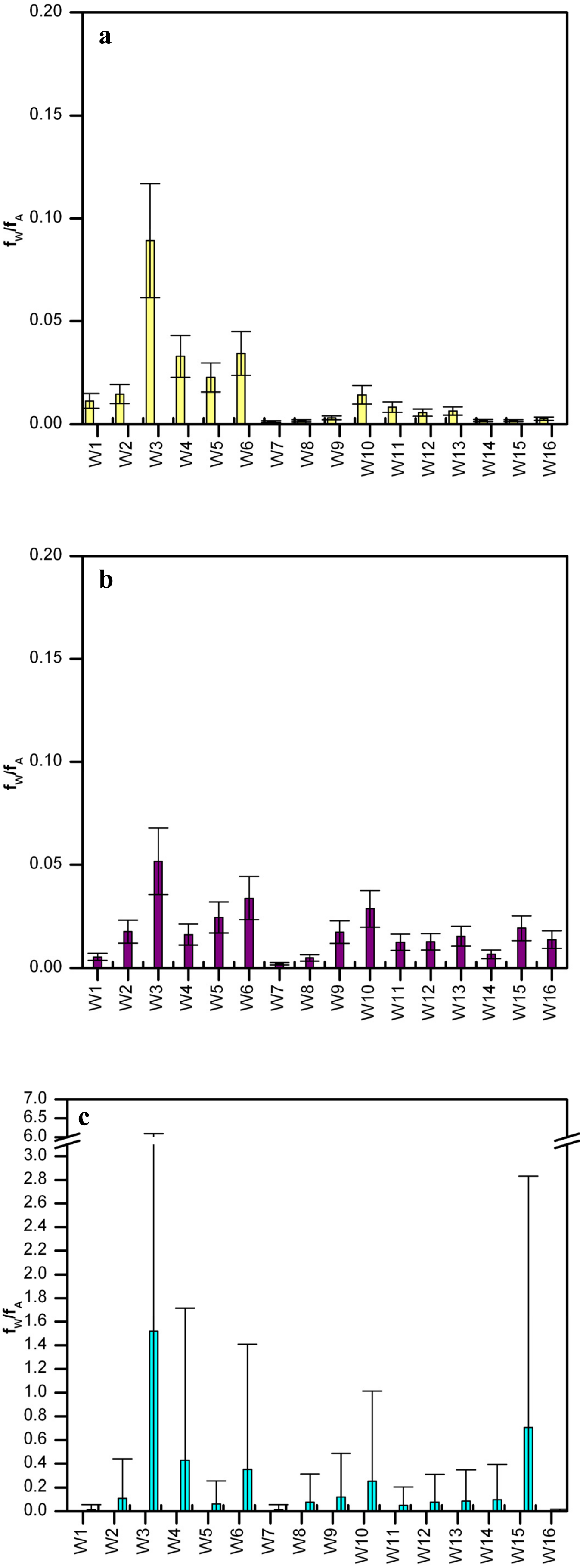

FIGURE S2. Fugacity ratios of BDE–47 (a), –99 (b) and DPTE (c) in East Greenland Sea

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Paper III

Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean

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Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean

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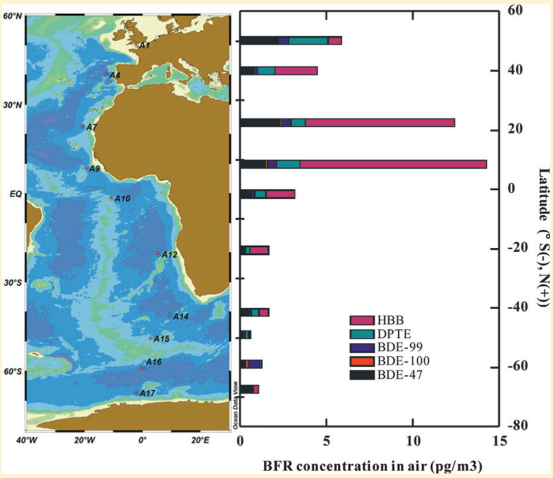
Ⓢ *Supporting Information*



ABSTRACT: Seawater and air samples were collected aboard the FS *Polarstern* during the cruises ANT-XXV/1 + 2 in the Atlantic and Southern Ocean in 2008. The particulate and dissolved phase in water and particulate and gaseous phase in air were analyzed separately for nine polybrominated diphenyl ethers (PBDEs) and six non-PBDE brominated flame retardants (BFRs). Air concentrations of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and hexabromobenzene (HBB) in the gaseous and particulate phase (median = 0.56 pg m^{-3} for DPTE and 0.92 pg m^{-3} for HBB) were comparable to $\sum_9$PBDEs (1.0 pg m^{-3}). Pentabromotoluene (PBT) was detectable in $\sim$30% of the gaseous phase samples, whereas concentration of 2,4,6-tribromophenyl allylether (ATE), hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO) and 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTBB) were below their method detection limits. DPTE, and PBDEs were also found in seawater at low pg per liter levels. Elevated seawater concentrations of PBDEs and DPTE were measured in the English Channel and close to South African coast. Concentrations of DPTE, BDE-47, and BDE-99 in the atmosphere generally decreased from Europe toward the Southern Ocean, whereas no latitudinal trend was observed in seawater. Air−water exchange gradients suggested net deposition dominates for all selected substances. The medians of net deposition fluxes for the air−water gas exchange were 83, 21, 69, 20, and 781 pg m^{-2} day^{-1} for BDE-47, BDE-100, BDE-99, DPTE, and HBB, whereas medians of dry deposition fluxes were 2.0, 0.3, 1.2, 1.0, and 0.5 pg m^{-2} day^{-1} for BDE-47, BDE-100, BDE-99, DPTE, and HBB. Overall, these results highlight the important role of the long-range atmospheric transport of PBDE and non-PBDE BFRs to remote regions.

INTRODUCTION

Brominated flame retardants (BFRs) have been used in a variety of commercial application to prevent fire. The ubiquitous distribution of BFRs in the environment and their potential risk for animals and humans has become an increasing concern for the scientific community.[1] As a result, the technical penta- and octa-brominated diphenyl ether (BDE) mixtures were banned in the European Union (EU) in 2004 and were recently included in the Stockholm Convention of Persistent Organic Pollutants (POPs).[1,2] In addition, deca-BDE has been implemented in the EU Directive on the restriction of use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) and was banned in Europe by July 2008.[2] Therefore, there is increasing demand and production of nonregulated flame retardants including non-PBDE BFRs.[3] For example, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) is the main constituent of the BFR Bromkal 73-5 PE (Chemische Fabrik Kalk), which was used in extrusion material for polypropylene (PP) and as an additive to acrylonitril-butadine-styrene copolymers.[4] In the environment, DPTE can be transformed to 2,4,6-tribromophenyl allylether (ATE) under anaerobic condition .[4] Hexabromobenzene (HBB) and pentabromotoluene (PBT) have been used as a flame retardant in polymers, plastics textiles, wood, and paper. Octa- and deca-BDEs and hexabromobiphenyl were also identified in a thermal decomposition product. Recently, non-PBDE BFRs, such as DPTE, HBB, and PBT, have been determined in environmental and biological samples of North America, Europe, and Asia.[3−7] HBB and PBT have been detected in Herring Gull (*Larus smithsonianus*) eggs in the Great Lakes basin[8] and in plasma of male Glaucous Gulls (*Larus hyperboreus*) from the Norwegian Arctic,[9] while there is very limited data available for hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO) and 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTBB) in the environment.[10]

Occurrences of PBDEs and non-PBDE BFRs in the biota in remote oceans suggested the BFRs are subject to long-range transport via atmosphere or ocean current.[11−13] The interaction of air−water exchange and process within the ocean are critical to the global fate and behavior of POPs.[14] Among the BFRs, only

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PBDEs have been extensively monitored in ambient air in Asia, Europe, North America, Indian Ocean, Pacific Ocean, and in the Arctic region.[15−20] Despite the importance of oceans for biological exposure and the global burden of many POPs,[21] BFRs have been investigated less frequently in seawater.[22,23] A study of PBDEs in Izmir Bay has shown that atmospheric deposition is the major process controlling air−water exchange fluxes.[24] Simultaneously, atmospheric reactions with OH radicals will deplete PBDEs during their long-range transport. Once BFRs are deposited to the ocean via dry and wet deposition,[25] BFRs may be subject to the accumulation in the marine food chain and degradation and deposition into the deep sea.[26] Microbial degradation of organic matter can also result in the cometabolism of OH-BDEs.[15]

The aim of this study was to examine atmospheric and surface water concentrations of PBDEs, and non-PBDE BFRs in the Atlantic and Southern Ocean. The cruises ANT-XXV/1 + 2 aboard the FS *Polarstern* was carried out along the European and African coast and in the Southern Ocean (50° N−67° S). The specific objectives of this study include (i) to investigate the spatial distribution and pattern of PBDEs and non-PBDE BFRs in the northern and Southern Hemisphere, and (ii) to estimate the air−water gas exchange fluxes and particle dry deposition fluxes of BFRs in the Atlantic and the Southern Ocean.

EXPERIMENTAL SECTION

Sampling Campaign. Seawater and air samples were collected onboard the FS *Polarstern* in the Atlantic and Southern Ocean (50° N−67° S) in November and December 2008. Sampling locations, dates, and general sampling conditions were recorded aboard from PODAS (Polarstern Data System) and are summarized in Supporting Information (SI) Tables SI1 and SI2, respectively. Detail sampling process has been described by Moeller et al.[27] Briefly, seawater samples were collected from the ship's intake system located in the keel (depth: 11 m) using a combination of PAD-2 resins (Polystyrene-DVB-copolymer resin, SERVA GmbH, Heidelberg, Germany) and glass fiber filters (GFF). Air samples were collected using GFF filters combined with a glass column packed with PUF/PAD-2 at the upper deck (Altitude: 20 m) (See SI Figure SI 1). Water and air samples were stored at −4 °C and −20 °C, respectively.

Chemicals and Materials. The analytical standards were obtained from Wellington Laboratories and included nine PBDEs (i.e., BDE-MXF including BDE-28, -47, -66, -85, -99, -100, -153, -154, -183), six non-PBDE BFRs (i.e., 2,4,6-tribromophenyl allylether (ATE), DPTE, PBT, HBB, EHTBB, HCDBCO), and an internal standard (IS) mixture (i.e., ^{13}C labeled BDE-77 and BDE-138) (for details see SI Table SI3). All solvents used for the extraction and cleanup procedure were residue-analysis grade and were distilled with full glass unit in the clean-lab prior to use. Glass vials, GFF filters and silica gel were baked out at 450 °C. PUF/PAD-2 and PAD-2 columns were cleaned using modified Soxhlet extractor with acetone/methanol (50/50, v/v), hexane/acetone (50/50, v/v), DCM and acetone in turn for 96 h. After cleaning, PAD-2 columns were conditioned with purified Milli-Q water, and PUF/PAD-2 columns were dried with nitrogen (purity 99.999%) for sampling.

Sample Processing and Instrumental Analysis. Detailed sample processing and analysis methods have been described in.[27] In brief, analysis was performed using gas chromatography (Agilent 6890; Agilent Technologies) − mass spectrometry (Agilent 5973; Agilent Technologies) (GC/MS) in selective ion monitoring (SIM) mode using negative chemical ionization (NCI). The following masses were monitored: m/z 79, 81, and 485.7 for PBT, m/z 79, 551.6, and 473.7 for HBB, m/z, 358.8, 79, and 81 for EHTBB, m/z 79, 81, and 159.8 for DPTE, m/z 79, 81, and 291.9 for ATE, m/z 79 and 81 for PBDEs and internal standard BDE-77 L (SI Figure SI2). The response factors were derived from the calibration curves (6-points) made for response ratio between targets compounds (0.1−10 ng mL^{-1}) and IS (1 ng mL^{-1}).

QA/QC. Breakthrough of target compounds for both water and air sampling has been checked with tandem columns aboard FS *Polarstern* (an example for air sample given in SI Figure SI 3). In general, all target compounds were not detectable in the lower column. The mean recoveries from spiked columns and filters (n = 3) were 90 ± 8% for PBDEs and 80 ± 10% for non-PBDE BFRs. The instrumental limit of detection (LOD) was determined by the signal-to-noise ratio ($S/N = 3$), which ranged within 0.02−0.05 pg for PBDEs, ATE, DPTE, PBT, HBB, and 0.15 pg for EHTBB. Method detection limits (MDLs) were derived from three times standard deviation (3σ) of field blanks, which were 0.005−0.02 pg L^{-1} and 0.005−0.02 pg m^{-3} for PBDEs and non-PBDEs in seawater and air samples, respectively. Necessary modifications have been made for the laboratory equipment to eliminate contamination during sample preparation. Due to the high percent recoveries (70−110%) and low blank values (e.g., BDE-47 <25 pg, BDE-99 < 50 pg and DPTE < 80pg pro sample, see SI Table SI 4 for detail), it was not necessary to recovery and blank correct the BFR concentrations.

Air Mass Back Trajectories. Air mass origins were calculated for the air samples using NOAA's HYSPLIT model (http://www.arl.noaa.gov/HYSPLIT_info.php). Back trajectories (BTs) were calculated for each sample in 6 h steps along the sampling cruise. BTs were traced back for 120 h with the sampling height as arrival height (SI Figure SI 4).

RESULTS AND DISCUSSION

PBDEs in Air. PBDEs were found in the atmosphere in both gas and particle phases (Figure 1A and Table 1; for detail see SI Table SI5). Among the PBDEs measured in this study, BDE-47 and BDE-99 were the major congeners, which were detected in all air samples; whereas BDE-153, -154, -183, -100, -85, -66, and -28 were only present in a few gaseous or particle samples. The gaseous and particle concentrations of total PBDEs ($\sum_9$PBDE) ranged from 0.31−2.85 pg m^{-3} and from <0.04−2.16 pg m^{-3}, with average concentrations of 1.12 and 0.33 pg m^{-3}, respectively. High PBDE concentrations were observed in the Northern Hemisphere (0.95−3.30 pg m^{-3} for the $\sum_9$PBDE of gaseous and particle phases, locations A1−A10) where the air masses originated from European and Northwestern Africa continents (SI Figure SI4). In the Southern Hemisphere, from the equator toward the Antarctic, the concentrations of PBDEs were fairly constant ranging from 0.40−1.33 pg m^{-3} for the $\sum_9$PBDE (locations A11−A17) which may represent an oceanic background level. It has been shown in previous studies that ambient air concentrations of $\sum$PBDEs were 5.8 ± 0.4 pg m^{-3} in remote site of the Great Lakes,[19] 0.2−5.0 pg m^{-3} in Mace Head, Ireland,[28] 0.8−1.6 pg m^{-3} in Norwegian costal sites,[29] 1.5−16 pg m^{-3} in the Indian Ocean,[20] and 0.40−47 pg m^{-3} in the Canadian Arctic (Alert, Nunavut).[18] In general, the concentrations measured in this study were in the range to those background levels of remote sites.

PBDEs in Seawater. Among the measured 9 PBDEs, BDE-47 and BDE-99 were present in both dissolved and particulate phases (SI Table SI6). BDE-153, -154, -183, -100, −-5 were only detectable in a few seawater samples, whereas BDE-28 and BDE-66 were below the MDLs in both dissolved and particulate phases

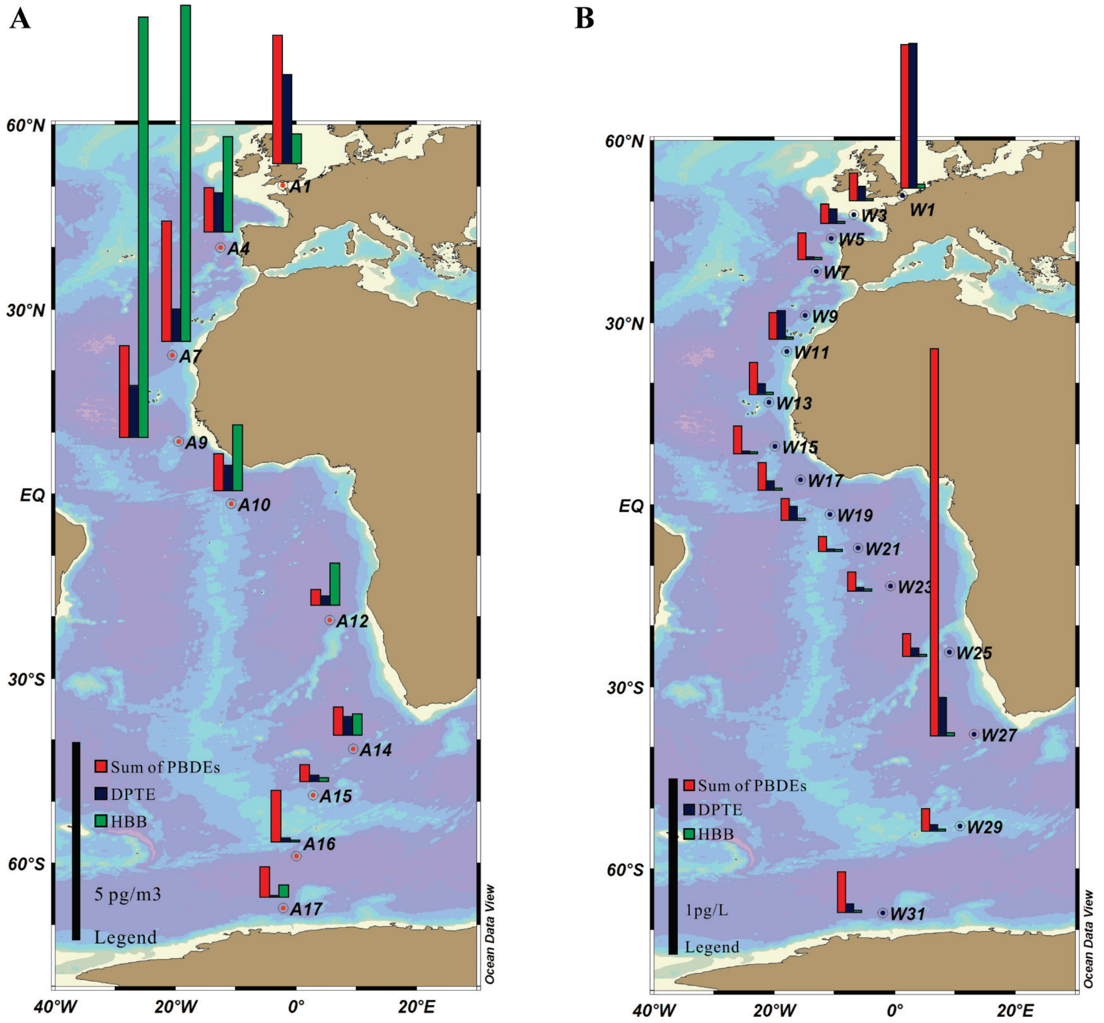

Figure 1. Concentrations of $\sum$PBDE, DPTE, and HBB in air (A) and seawater (B) of the Atlantic and Southern Ocean.

Table 1. Concentrations of PBDEs and non-PBDE BFRs in air and seawater of the Atlantic and Southern Ocean[a]

compound	sea water (pg L^{-1})			air (pg m^{-3})		
	dissolved	TSM	median of sum	vapor	particle	median of sum
PBDEs						
BDE-47	0.02−1.05	nd−0.10	0.06	0.16−2.27	0.008−1.121	0.59
BDE-100	nd−0.11	nd−0.023	nd	nd−0.14	nd−0.02	0.048
BDE-99	0.01−0.53	nd−0.10	0.03	0.015−0.53	nd−0.51	0.2
BDE-85	nd−0.03	nd	nd	nd−0.02	nd	0.008
BDE-154	nd−0.11	nd	nd	nd−0.03	nd−0.12	0.013
BDE-153	nd−0.05	nd−0.029	nd	nd−0.04	nd−0.03	0.008
BDE-183	nd−0.075	nd−0.066	0.01	nd−0.064	nd−0.21	0.013
Non-PBDE BFRs						
PBT	nd	nd	nd	nd−0.04	nd	0.01
DPTE	nd−0.77	nd−0.04	0.05	0.03−1.89	0.01−0.40	0.56
HBB	nd−0.02	nd	nd	0.04−10.8	nd−0.12	0.92

[a] nd = Not detected. BDE-28, BDE-66, ATE, HCDBCO, and EHTBB were not detected in air and seawater samples.

(<0.004 pg L^{-1}). The highest concentrations of $\sum_9$PBDEs were present in the English Channel (0.81 pg L^{-1}, location W1) and close to the South Africa coast (2.19 pg L^{-1}), respectively. Except from these two peak concentrations, the levels of PBDEs through the north to south Atlantic transect were relatively constant with $\sum_9$PBDEs ranging from 0.09−0.23 pg L^{-1} (Figure 1B and Table 1).

Literature data of PBDEs in seawater of oceans are rare. Recently, PBDEs in coastal waters have been reported in a few studies.[22−24] BDE-47 and BDE-99 in the English Channel and at the African coast were similar to those reported in the Kara Sea (BDE-47: 1.6 pg L^{-1}, BDE-99: 1.9 pg L^{-1})[22] and in the Dutch coast (BDE-47: 1 pg L^{-1}, BDE-99: 0.5 pg L^{-1}),[30] and were 1−3 orders magnitude lower than those in the San Francisco estuary (3−513 pg L^{-1}),[31] Hong Kong ($\sum$PBDEs: 31.1−118.8 pg L^{-1})[23] and in Izmir Bay ($\sum$PBDEs: 212 ± 65 and 87 ± 57 pg L^{-1} in summer and winter).[24] Oros et al. reported that the PBDEs were mostly partitioned in the total suspended matter (TSM) fraction in the San Francisco Estuary with the relative composition of 78−93% of $\sum$PBDE concentrations.[31] However, the seawater samples for this study were collected in open ocean and the TSM fractions of BDE-47 and BDE-99 ranged from 3−35% (median: 9%) and 6−43% (median: 22%), respectively. The lower particulate fraction in this study could be that the concentrations had reached equilibrium in the open ocean water and/or different composition of the TSM (e.g., particle size, organic matter) which can influence the adsorption capacity of the particles.

Non-PBDE BFRs in Air. DPTE and HBB were determined in all gaseous phase samples, PBT was detectable in ∼30% of the gaseous phase samples. ATE, HCDBCO and EHTBB were below their MDLs (0.003, 0.014, and 0.016 pg m^{-3}, respectively) in all air samples. Data on non-PBDE BFRs in the open ocean are limited. Air concentrations of HBB were reported from land-based measurements with 610 pg m^{-3} in Japan,[32] and 0.02−0.09 pg m^{-3} in Egbert, Great Lakes.[5]

Between 50° N and 35° S, the total concentrations of HBB were higher than those of $\sum$PBDEs (locations A1−A12), whereas a reversed trend was observed in the Southern Ocean with higher concentrations of the $\sum$PBDEs. HBB is being used for fabrication of textiles, thermosetting resins and thermoplastic resins under several trade names in United States and Japan.[3] Though production of HBB is considered low (5−230 t y^{-1} in U.S. from 1986 to 1998), whereas the e-waste burning in Africa may directly release HBB into the atmosphere being transported to the Atlantic Ocean, and thus leads to elevated concentrations in this region of the Atlantic. Moreover, HBB in tropic/subtropics air may partly result from degradation of high molecular PBDEs (e.g., BDE-209), either in the environment or during e-waste burning.[33] As environmental data and physicochemical properties for non-PBDE BFRs are very limited, we estimated their physicochemical properties with EPI Suite Program (SI Table SI3). The atmospheric half-life time was estimated to be 934 days for HBB, which is almost 1−2 orders of magnitude higher than those of PBDEs (e.g., 11 days for BDE-47 and 19 days for BDE-99). The DPTE atmospheric half-life time was estimated to be 2.7 days which is less stable than PBDEs. Nevertheless, the presence of HBB and DPTE in the Southern Ocean has shown that these non-PBDE BFRs are subject to long-range transport via the atmosphere (Figure 1A, Table 1).

Non-PBDE BFRs in Seawater. Dissolved DPTE was detected in most samples with concentrations ranging from 0.008−0.77 pg L^{-1} (SI Table SI6). Although HBB has shown high concentrations in air, it was only detectable in three water samples with concentrations slightly higher than the MDL (<0.006−0.02 pg L^{-1},). In particulate phase, only DPTE was found in two water samples (W1: 0.04 pg L^{-1}, W19: 0.03 pg L^{-1}), whereas the other non-PBDE BFRs were below their MDLs (Figure 1B, Table 1).

DPTE has been first identified in sewer slime from German urban residential zones, with the concentrations from 50−1940 μg kg^{-1}.[34] Von der Recke and Vetter have reported that DPTE was the dominating BFR in blubber and brain of hooded seals (*Cystophora cristata*) and harp seals (*Pagophilus groenlandicus*) from the Barents and Greenland Seas (130−470 μg/kg wet weight), which concentrations were 1 order of magnitude higher than for the PBDEs.[4] Our finding may further prove that DPTE is a dominating BFR in ocean water.

Latitudinal Trends of North−South Transect. The concentrations and patterns of individual BFRs in the Atlantic Ocean atmosphere were highly variable. As shown in Figure 5 in the SI, BDE-47 and DPTE concentrations showed good correlation with the latitudes (67° S−50° N, R^2 = 0.477 and 0.714, respectively), whereas no clear latitudinal trend was observed for BDE-100 and BDE-99. HBB showed highest air concentrations in the tropic/subtropics region at the West Coast of Africa (locations A7 and A9). Global source emission inventories and passive sampling net works (GAPS) identified Europe and North America as the most significant source regions of PBDEs.[35,36] This can explain the positive correlation of BDE-47 and DPTE with the latitude in the Atlantic and Southern Ocean. No trend was observed for BDE-100, BDE-99, and HBB, which may be caused by atmospheric degradation of these compounds during the long-range transport .[37] Overall, the latitudinal trends of BFRs present in this study are comparable to those reported for PCBs and PAHs in the Atlantic Ocean.[38,39]

Elevated Air Concentrations off the West Coast of Africa. GAPS net work and regional monitoring identified Asia, Europe, and North America as the most important source regions of PBDE.[29,40] Elevated BFR levels off the West Coast of Africa indicate that the African continent acts as a source for BFRs and they were subsequent transported to the Atlantic Ocean atmosphere. BTs and the observation of large quantities of Saharan yellow dust on the GFF confirm that the air masses from the samples collected along the African coast (locations A7 and A9) originated from Africa. Besides, African countries receive great amount of electronic waste from Europe and United States. For example, according to the European Environment Agency (EEA) more than 15 000 tonnes of color television sets were exported from the EU to African countries in 2005. On average 35 tonnes, or more than 1000 units of used television sets, arrive every day in Ghana, Nigeria, and Egypt.[41] Obviously, the occurrence of BFRs in ambient air may result from increased emissions from the growing industry for recycling of electronic goods. In the rural area, open-hearth domestic fires, using a variety of fuels, are often used to dispose domestic waste which may contain large proportions of PBDEs and non-PBDE BFRs.[28] In Ghana and Nigeria, the electronic wastes, which were produced in the inland and imported from western countries, are deposed by combustion or open-hearth domestic fire after recycling.[41] The emissions from these kinds of diffuse sources may become a significant concern for the local environment and are subject to long-range atmospheric transport.

Air−Water Gas Exchange Fluxes. Air−water gas exchange fluxes were estimated using the modified equation of Whitman two-film resistance model

$$F = K_{OL}\left(C_w - \frac{C_a}{H'}\right) \qquad (1)$$

where F is the flux (pg m^{-2} day^{-1}), ($C_w - C_a/H'$) describes the concentration gradient (pg m^{-3}), H' is the dimensionless Henry's law constant and K_{OL} (m day^{-1}) ($1/K_{OL} = 1/K_w + 1/K_aH'$) is the mass transfer coefficient comprising resistances to mass transfer in both water (k_w) and air (k_a). H' values of BDE-47, −100, −99 were taken from Cetin and Odabasi,[24] H' of HBB was taken from

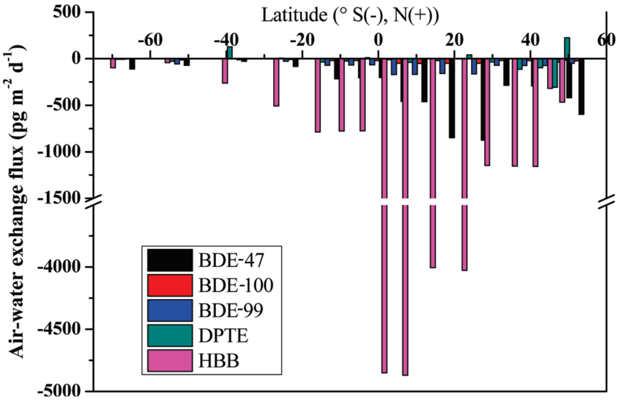

Figure 2. Air−water exchange fluxes for BDE-47, -100, -99, DPTE and HBB in the Atlantic and Southern Ocean, minus value means net deposition, and plus value means volatilization.

Tittlemier et al.,[42] and DPTE value was estimated using the EPIWEB program (see SI for details of the parameter). H' values were corrected with mean water temperatures (T, K) and averaged salt concentrations (C_s, 0.5 mol L^{-1}). Overall, the propagated error for F was 51% for PBDEs and HBB which is deduced from a propagation of error analysis derived from previous study for PBDEs.[24] DPTE may have higher uncertainty due to the estimated H'.

The latitudinal variation of air−water gas exchange fluxes of BDE-47, BDE-99, BDE-100, DPTE, and HBB are shown in Figure 2. The net deposition fluxes ranged from 28−875 pg m^{-2} day^{-1} for BDE-47, 2−50 pg m^{-2} day^{-1} for BDE-100, 3−170 pg m^{-2} day^{-1} for BDE-99, and 96−4870 pg m^{-2} day^{-1} for HBB. Volatilization fluxes of DPTE from water to air have also been observed in three samples (5−225 pg m^{-2} day^{-1}), which were collected from Western European coast and South Africa coast, whereas net deposition flux dominated in most cases (12−308 pg m^{-2} day^{-1}). Because of elevated HBB concentrations in the gaseous phase from the tropic/subtropics region, the net deposition fluxes of HBB are 1−2 orders of magnitude higher than those of PBDEs and DPTE. The median values of the net deposition fluxes of BDE-47, BDE-99, BDE-100 are 1−2 orders of magnitude lower in comparison to those estimated in Izmir Bay, Turkey,[24] and Taihu Lake of China.[7] To our knowledge, this is the first report for air−water gas exchange fluxes of HBB and DPTE. Further studies on the calculation of the Henry's law constants for BFRs are required to improve the understanding of their air−water exchange processes.

Particle Dry Deposition Fluxes. The dry deposition fluxes of organic compounds associated with particles can be estimated using an overall dry deposition velocity (V_p) and particle air concentration (C_p):

$$F_p = V_p C_p \qquad (2)$$

In general, the V_p for various POPs range beween 0.4 and 6.7 cm s^{-1}. Cetin and Odabasi measured the V_p for PBDEs at an urban site in Izmir, Turkey, which were 3.9 for BDE-47, 6.4 of BDE-100 and 3.1 for BDE-99.[24] No estimates have been adequately developed for PBDEs for oceanic application, and therefore we used a constant velocity of 0.1 cm s^{-1} (86.4 m d^{-1}) for the Open Sea conditions,[43] which may give an uncertainty of a factor of ∼3 for the estimation of F_p for BFRs.

Atmospheric dry deposition fluxes of BDE-47, -100, -99, DPTE, and HBB are shown in Figure 3. The median values were estimated to be 2.0, 0.3, 1.2, 1.0, and 0.5 pg m^{-2} day^{-1} for BDE-47, BDE-100, BDE-99, DPTE, and HBB, respectively. Atmospheric dry deposition fluxes of BDE-47, BDE-100, BDE-99 estimated in this work are 3 orders of magnitude lower than those estimated in Izmir, Turkey.[24] This may be due to different particle-bound concentrations of PBDEs and different V_p values used for the estimation. Atmospheric dry deposition fluxes accounted for less than 5% of the total air and particle deposition fluxes for BFRs. Except for BDE-100, atmospheric dry deposition fluxes of BDE-47, BDE-99, DPTE, and HBB were lower in the tropical/subtropical latitudes, and increased from the equator toward north and south high latitudes.

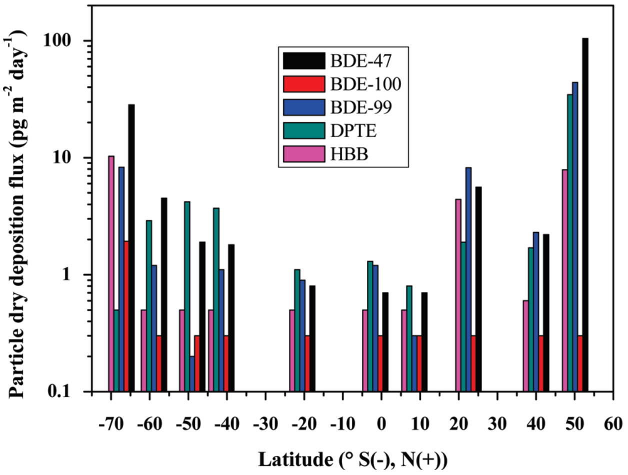

Figure 3. Atmospheric particle dry deposition fluxes for BDE-47, -100, -99, DPTE, and HBB in the Atlantic and Southern Ocean.

Implications. The data suggest that there was a net deposition of BFRs to the Atlantic and Southern Ocean during November and December 2008. The decreasing latitudinal gradients (50° N−67° S) for atmospheric BDE-47, DPTE and HBB implies ongoing atmospheric releases of these compounds from Europe and Africa. However, the patterns of PBDEs, DPTE and HBB changed depending on the latitude and distance to source regions (i.e., Europe and Africa) which suggest multiple processes causing these contrasting profiles. Atmospheric concentrations of PBDEs were mostly comparable to those from remote regions and European background levels, but can be changed by varying air-mass origins from Europe, Africa or open ocean. Elevated concentrations of BFRs along the western African coast of the Atlantic Ocean may originate from Southern Europe and Africa. Although the ban and regulation on the application of certain PBDEs were effective in the manufacture of electronic products, the input of BFRs to the atmosphere can be expanded by the increasing e-waste recycling industry in Asia and Africa and by the using of non-PBDE BFRs as replacement products of PBDEs. Consequently, more field investigations for BFRs in different oceans are necessary to understand the global transport of BFRs from source to remote region.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean

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Figure SI 1. High-volume air sampling on board *F/S Polarstern*. Picture A shows the entire operation system; picture B shows the stainless steel filter plate with a GFF filter; picture C is the glass column (Length: 16 cm, O.D. 6.0 cm, I.D.5.2 cm) packed with 30 g of PAD-2 resins (Particle size: 0.3-1 mm, Surface area: 450 m^2/g) and a slice of polyurethane form (2.5cm x 5 cm); picture D shows sampling with two columns for breakthrough check. The column is always wrapped with aluminum film during sampling to prevent from sunlight.

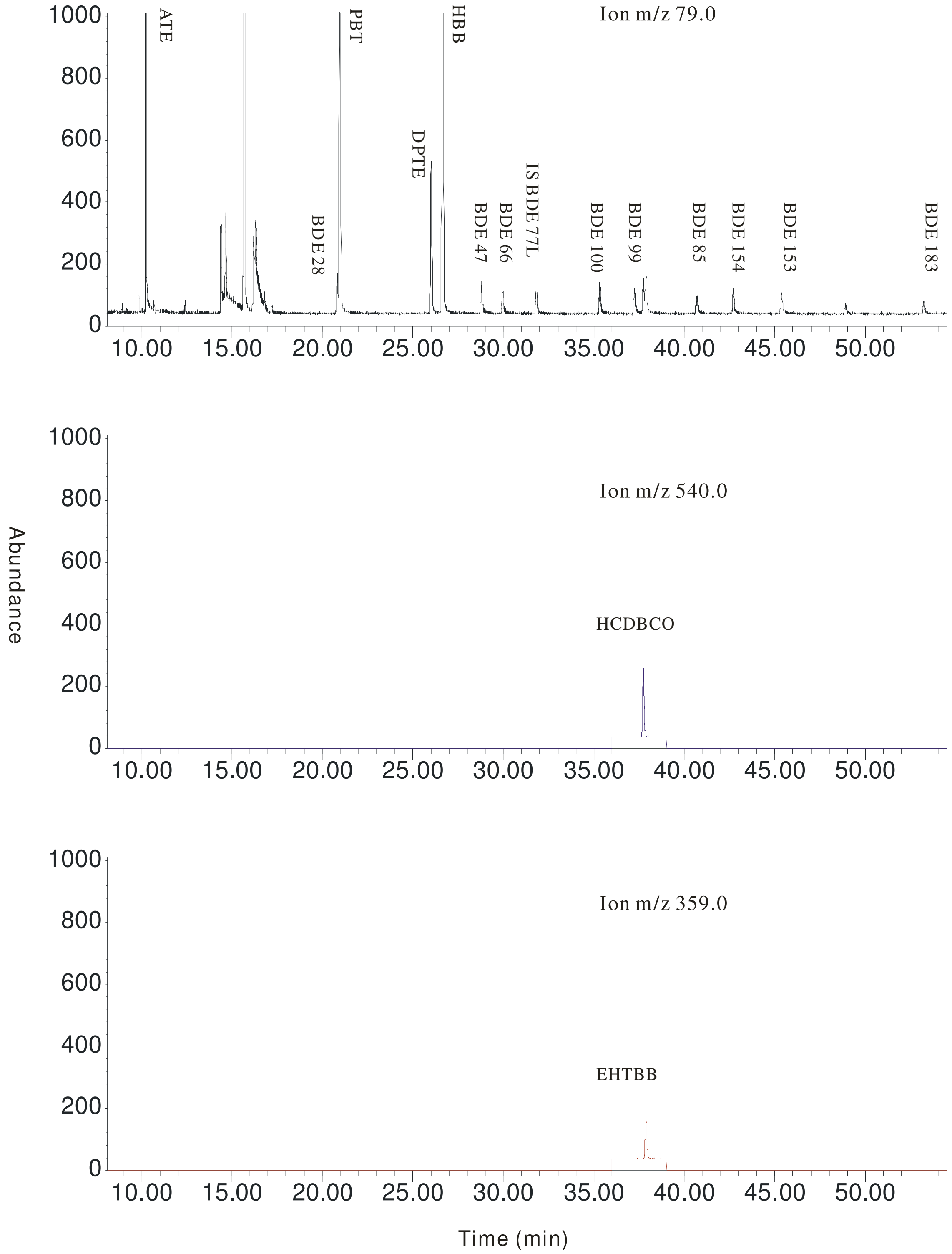


Figure SI 2. Extracted ion chromatogram of PBDEs (1ng mL^{-1} in hexane) and non-PBDE BFRs (50 ng mL^{-1} in hexane) obtained using GC-MS-NCI.

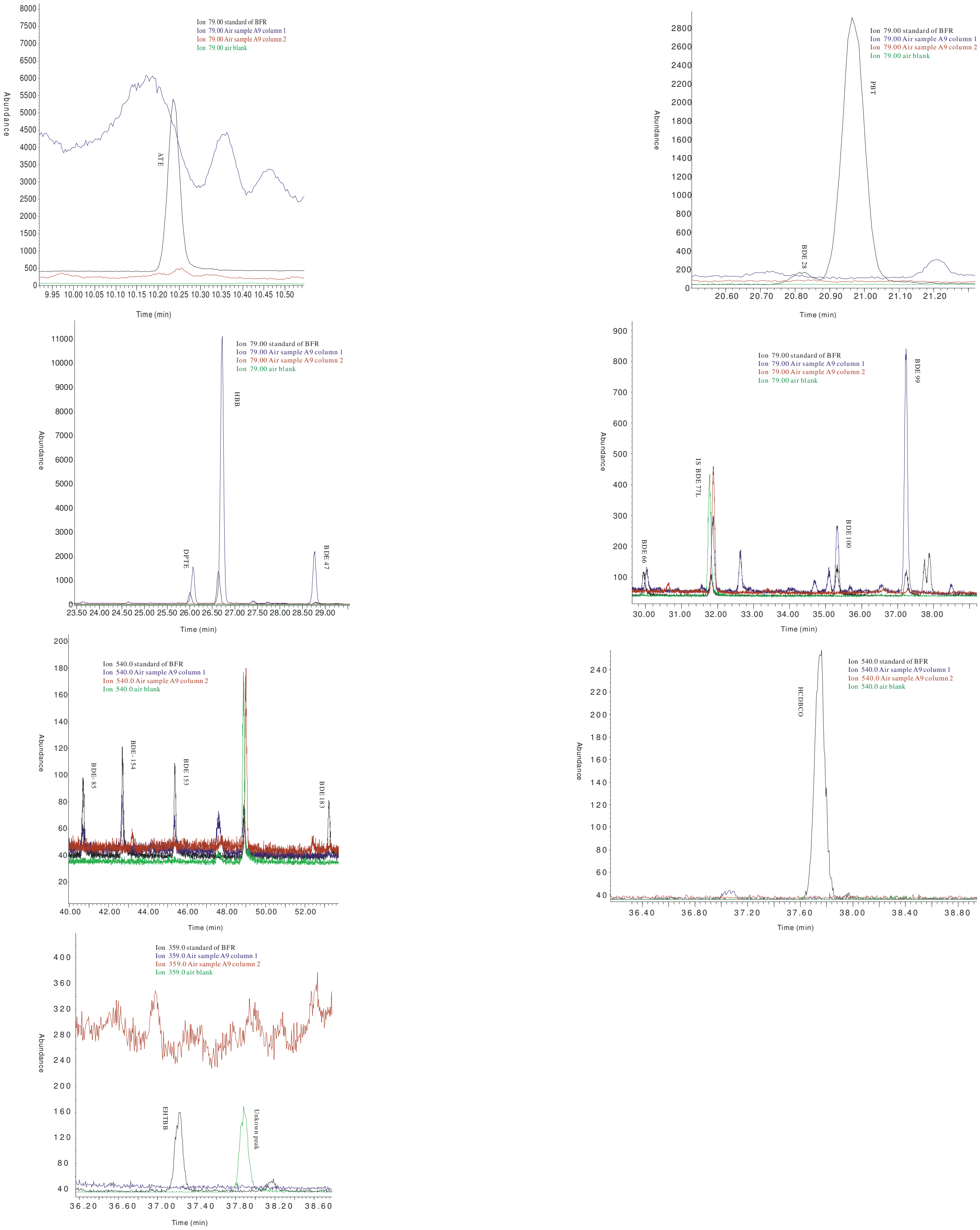
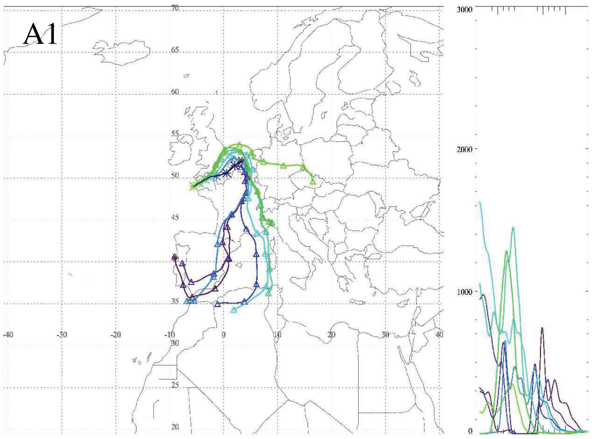
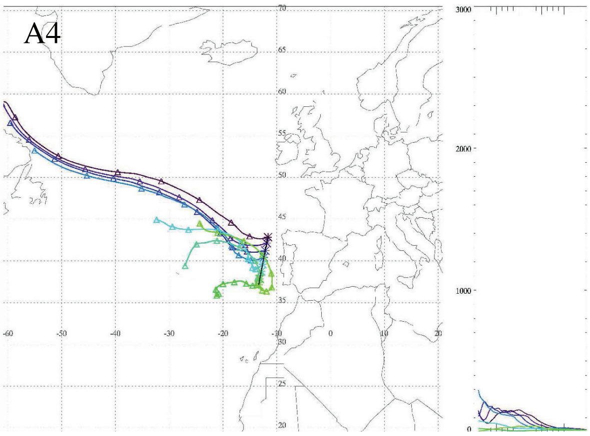


Figure SI 3. Extracted ion chromatogram of PBDEs and non-PBDE BFRs in air sample A9 (C1 is the upper sample and C2 is the lower column for breakthrough control), air blank, and in standard mixture solution (PBDEs, 1ng mL^{-1} and non-PBDE BFR, 50 ng mL^{-1} in hexane).

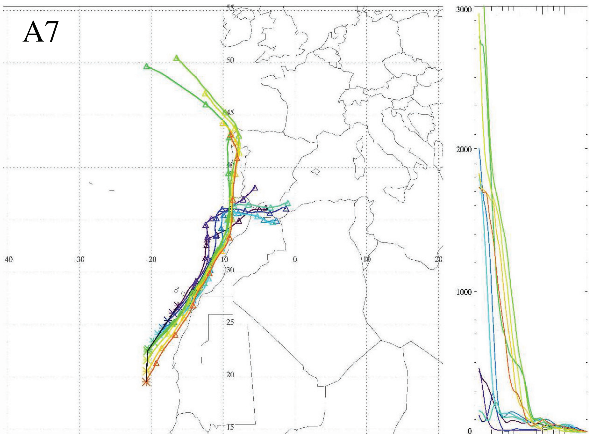
A1



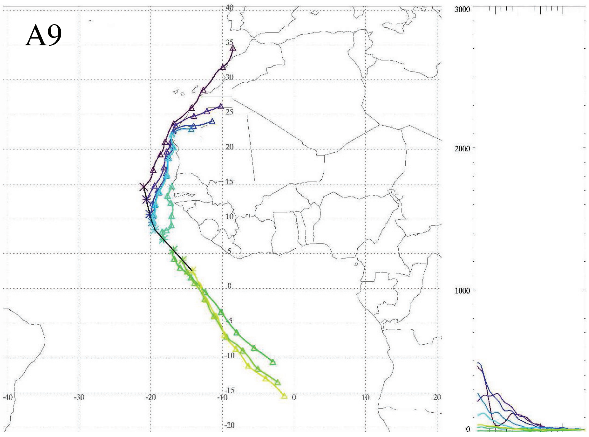
A4



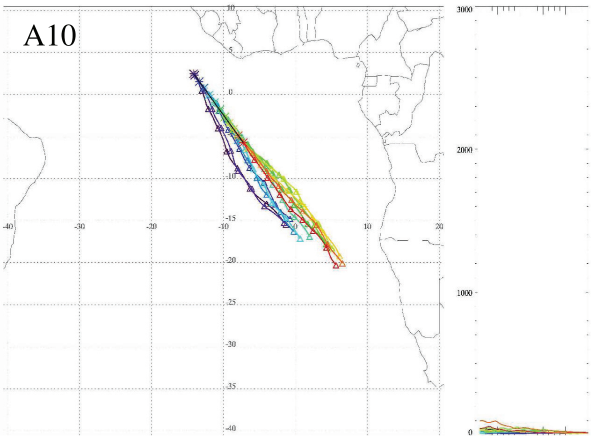
A7



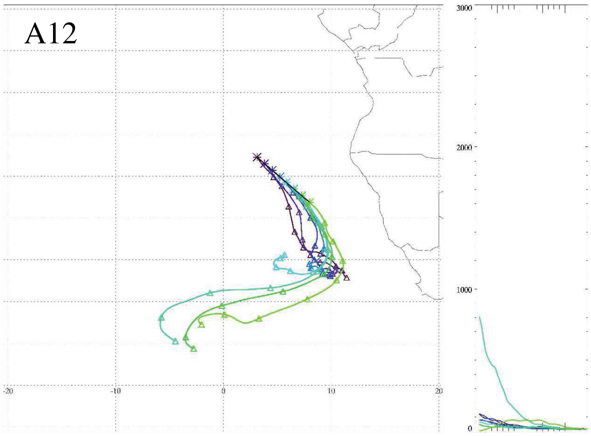
A9



A10



A12



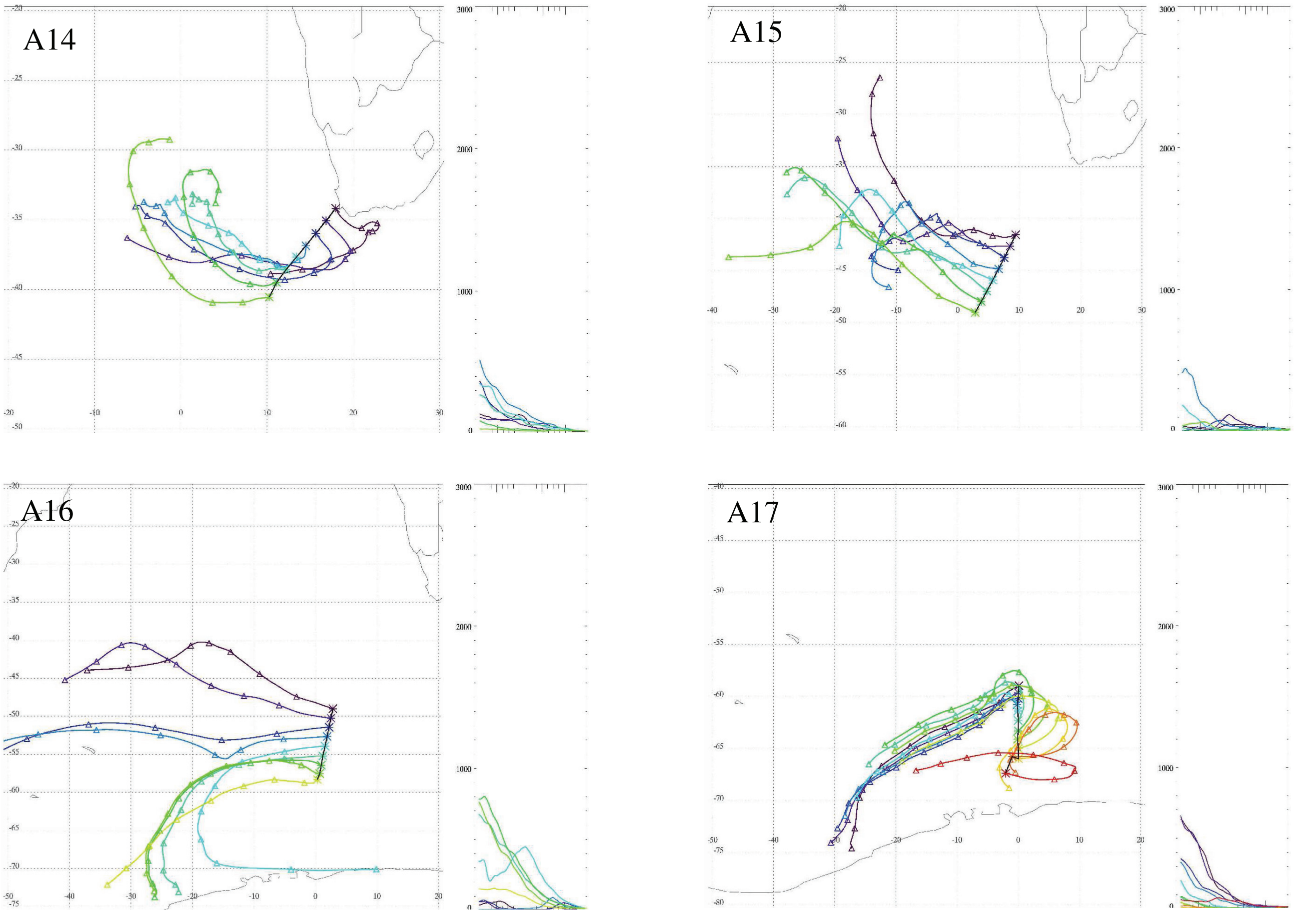


Figure SI 4. 96 h air mass back trajectories (6 h steps) and altitudinal profiles of the air mass parcels for the cruises ANT-XXV/1+2 (A1-A17). For samples longer than 72 hours, only every second BT was plotted. The black line indicates the cruise leg.

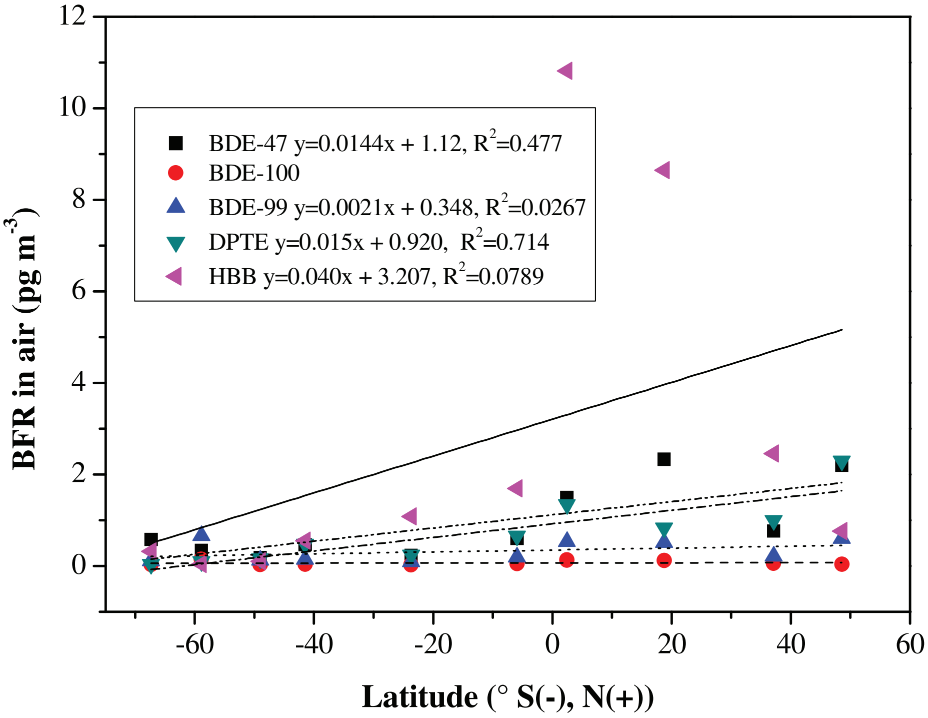


Figure SI 5. Latitude distribution of BDE-47, 99, 100, DPTE and HBB from 50 °N to 67 °S.

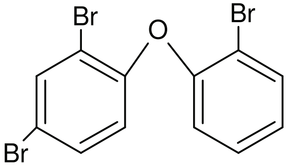
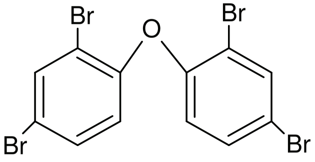
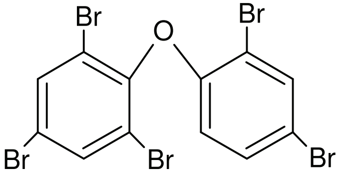
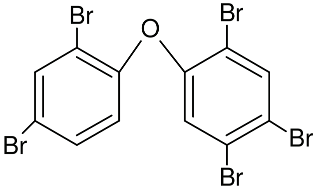
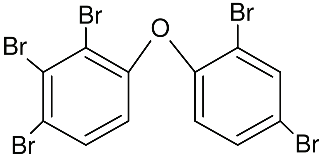
Table SI 1. Detailed information on air sampling during ANT-XXV/1+2. Latitude and longitude are mean sampling stations. Air temperature represents the mean air temperature during sampling. Air sample distance means the moving space from start to the end of each air sample.

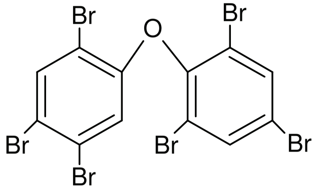
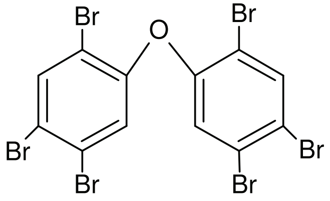
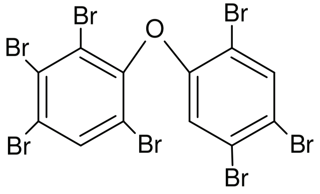
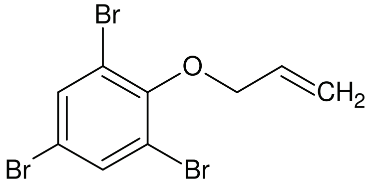
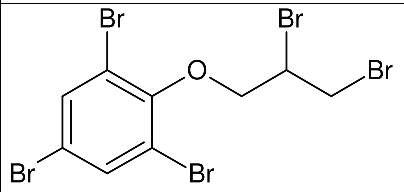
	Date	Latitude (°N)	Longitude (°E)	Distance (km)	Volume (m^3)	Air temperature (°C)	Wind speed $m\ s^{-1}$
A1	2-4/11/08	50.120	-2.184	500	687	11.5	6
A4	7-9/11/08	40.008	-12.511	700	640	16.5	9
A7	12-15/11/08	22.500	-20.499	1000	1101	21.3	10.6
A9	16-20/11/08	8.503	-19.452	1500	968	28.6	8.3
A10	20-23/11/08	-1.624	-10.699	1200	877	25.5	6.9
A12	27-29/11/08	-20.506	5.607	900	522	18.9	5.5
A14	6-8/12/08	-41.492	9.476	1100	602	19.3	18.9
A15	8-10/12/08	-49.011	2.834	1000	516	11.2	7.4
A16	10-12/12/08	-58.910	0.131	1100	573	3.6	12.3
A17	12-15/12/08	-67.354	-2.064	1000	934	-2.5	8.4

Table SI 2. Detailed information on water sampling during ANT-XXV/1+2. Latitude and longitude are mean sampling stations. Water temperature and salinity represent the mean values during sampling.

	Date	Latitude (°N)	Longitude (°E)	Volume (L)	Water temperature (°C)	Salinity (PSU)
W1	2/11/08	50.923	1.311	409	13.8	35.1
W3	4/11/08	47.723	-6.758	1000	12.4	35.4
W5	6/11/08	43.854	-10.516	1073	15.4	35.7
W7	7/11/08	38.438	-12.979	1088	15.87	35.9
W9	8/11/08	31.175	-14.866	835	17.23	36.4
W11	12/11/08	25.196	-17.858	1296	21.03	36.8
W13	14/11/08	16.861	-20.861	950	22.54	36.8
W15	17/11/08	9.608	-19.830	1041	28.6	35.2
W17	19/11/08	4.109	-15.606	925	29.13	34.6
W19	21/11/08	-1.613	-10.708	935	26.1	36.1
W21	23/11/08	-7.106	-6.061	1000	25.48	36.2
W23	25/11/08	-13.414	-0.651	1000	22.91	36.2
W25	29/11/08	-24.301	9.070	1000	19.05	35.5
W27	7/12/08	-37.836	13.198	311	22.3	35.5
W29	10/12/08	-52.941	10.836	804	4.6	33.9
W31	14/12/08	-67.275	-1.949	771	-1.57	34.0

Table SI 3. PBDEs and non-PBDE Brominated flame retardants selected in this study

Abbreviation	Name	CAS number	Henry' law constant Pa m^{-3} mol^{-1}	Atmospheric half-life days	Structure
BDE-28	**2,2´,4-tribromodiphenyl ether**	41318-75-6		7.570	
BDE-47	**2,2´,4, 4´-tetrabromodiphenyl ether**	5436-43-1	0.85	10.661	
BDE-100	**2,2´,4, 4´,6-pentabromodiphenyl ether**	189084-64-8	0.24	-	
BDE-99	**2,2´,4, 4´,5-pentabromodiphenyl ether**	60348-60-9	0.60	19.439	
BDE-66	**2,3´,4, 4´-Tetrabromodiphenyl ether**	189084-61-5	355.2	93.62	
BDE-85	**2,2´,3,4, 4´-pentabromodiphenyl ether**	182346-21-0	23.37	19.439	

BDE-154	2,2´,4,4´,5,6´-hexabromodiphenyl ether	189084-64-8			
BDE-153	2,2´,4,4´,5,5´-hexabromodiphenyl ether	60348-60-9	206.4	19.439	
BDE-183	2,2´,3,4,4´,5´,6-heptabromodiphenyl ether	68928-80-3	147	35.512	
ATE	2,4,6-tribromophenyl allylether	3278-89-5	64.1	0.33	
DPTE	2,3-dibromopropyl-2,4,6-tribromophenyl ether	35109-60-5	25.12	2.650	

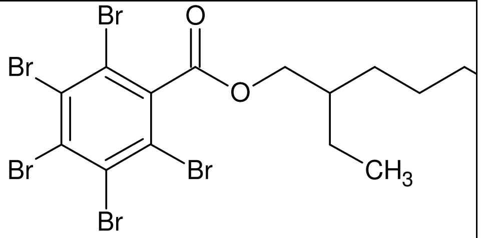
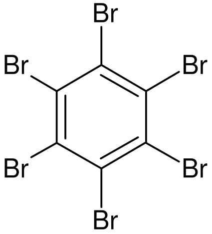
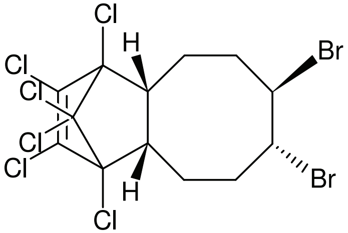
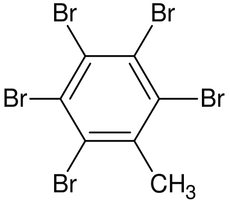
EHTBB	2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate	183658-27-7	-	-	
HBB	Hexabromobenzene	87-82-1	0.14	933.944	
HCDBCO	Hexachlorocyclopentadienyl-dibromocyclooctane	51936-55-1	112.7	0.816	
PBT	Pentabromotoluoene	87-83-2	10.1	57.822	

Table SI 4. Mean field blank values in pg.

	air column	**air filter**	**water column**	**water filter**
BDE–47	13 ± 4	0.7 ± 0.3	1 ± 1	5 ± 4
BDE–99	33 ± 7	1 ± 0.3	2 ± 1	10 ± 5
BDE–100	5 ± 2	n.d.	n.d.	2 ± 1
BDE–153	14 ± 5	n.d.	n.d.	0.4 ± 0.4
BDE–154	5 ± 2	n.d.	n.d.	0.1 ± 0.1
DPTE	12 ± 6	3 ± 0.3	12 ± 5	19 ± 19
HBB	1 ± 0.3	0.1 ± 0.1	n.d.	0.3 ± 0.2
PBT	n.d.	0.02 ± 0.04	0.1 ± 0.2	0.2 ± 0.03

*BDE-28, BDE-66, BDE-85, BDE-183, ATE, HCDBCO, and EHTBB were not detected in column and filter blanks

Table SI 5. Individual PBDE and non-PBDE BFR concentrations and the particle associated proportion in the atmosphere of the Atlantic and Southern Ocean

Compound	BDE28	BDE-47	BDE66	BDE 100	BDE99	BDE 85	BDE 154	BDE 153	BDE 183	∑PBDEs)	ATE	PBT	DPTE	HBB	HCDBCO	EHTBB
MDL (pg m^{-3})	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.04	0.003	0.003	0.008	0.006	0.012	0.016
Vapor (pg m^{-3})																
A1	0.004	0.99	0.004	0.038	0.088	0.004	0.004	0.004	0.006	1.14	0.003	0.003	1.89	0.67	0.012	0.016
A4	0.050	0.73	0.018	0.052	0.178	0.004	0.008	0.004	0.006	1.05	0.003	0.02	0.98	2.44	0.02	0.00
A7	0.004	2.27	0.010	0.12	0.422	0.004	0.016	0.008	0.008	2.85	0.003	0.01	0.81	8.60	0.012	0.016
A9	0.062	1.48	0.050	0.13	0.525	0.016	0.030	0.018	0.006	2.32	0.003	0.04	1.33	10.8	0.012	0.016
A10	0.034	0.59	0.004	0.050	0.190	0.004	0.012	0.004	0.006	0.90	0.003	0.01	0.63	1.69	0.012	0.016
A12	0.018	0.22	0.004	0.021	0.075	0.004	0.004	0.004	0.006	0.35	0.003	0.003	0.23	1.08	0.012	0.016
A14	0.030	0.44	0.004	0.039	0.132	0.004	0.004	0.004	0.006	0.66	0.003	0.003	0.44	0.54	0.012	0.016
A15	0.035	0.16	0.006	0.030	0.130	0.004	0.004	0.004	0.006	0.38	0.003	0.003	0.11	0.09	0.012	0.016
A16	0.009	0.28	0.004	0.14	0.649	0.020	0.026	0.040	0.064	1.23	0.003	0.003	0.07	0.04	0.012	0.016
A17	0.021	0.25	0.004	0.004	0.015	0.004	0.004	0.004	0.006	0.31	0.003	0.01	0.03	0.20	0.012	0.016
mean	0.027	0.741	0.011	0.062	0.240	0.007	0.011	0.009	0.012	1.12	0.003	0.012	0.653	2.6	0.012	0.014
Median	0.025	0.516	0.004	0.044	0.155	0.004	0.006	0.004	0.006	0.98	0.003	0.007	0.536	0.87	0.012	0.016
Particle (pg m^{-3})																
A1	0.004	1.21	0.004	0.004	0.51	0.004	0.12	0.10	0.21	2.16	0.003	0.003	0.40	0.09	0.012	0.016
A4	0.004	0.026	0.004	0.004	0.03	0.004	0.004	0.004	0.006	0.082	0.003	0.003	0.02	0.007	0.012	0.016
A7	0.004	0.065	0.004	0.004	0.09	0.004	0.015	0.03	0.03	0.24	0.003	0.003	0.02	0.051	0.012	0.016
A9	0.004	0.008	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.042	0.003	0.003	0.01	0.006	0.012	0.016
A10	0.004	0.008	0.004	0.004	0.013	0.004	0.004	0.004	0.006	0.051	0.003	0.003	0.01	0.006	0.012	0.016
A12	0.004	0.009	0.004	0.004	0.010	0.004	0.004	0.004	0.006	0.048	0.003	0.003	0.01	0.006	0.012	0.016
A14	0.004	0.021	0.004	0.004	0.013	0.004	0.004	0.004	0.006	0.064	0.003	0.003	0.04	0.006	0.012	0.016
A15	0.004	0.022	0.004	0.004	0.003	0.004	0.004	0.004	0.006	0.054	0.003	0.003	0.05	0.006	0.012	0.016
A16	0.004	0.052	0.004	0.004	0.014	0.004	0.004	0.004	0.006	0.10	0.003	0.003	0.03	0.006	0.012	0.016

A17	0.004	0.33	0.004	0.02	0.10	0.004	0.004	0.004	0.006	0.47	0.003	0.003	0.01	0.12	0.012	0.016
mean	0.004	0.175	0.004	0.005	0.078	0.004	0.017	0.016	0.028	0.33	0.003	0.003	0.061	0.030	0.012	0.016
Median	0.004	0.024	0.004	0.004	0.014	0.004	0.004	0.004	0.006	0.07	0.003	0.003	0.021	0.006	0.012	0.016
Vapor+Particle																
(pg m^{-3})																
A1	0.01	2.20	0.01	0.04	0.60	0.01	0.13	0.10	0.21	3.30	0.01	0.01	2.29	0.76	0.02	0.03
A4	0.05	0.76	0.02	0.06	0.21	0.01	0.01	0.01	0.01	1.13	0.01	0.03	1.00	2.45	0.03	0.02
A7	0.01	2.33	0.01	0.12	0.52	0.01	0.03	0.03	0.03	3.10	0.01	0.02	0.83	8.65	0.02	0.03
A9	0.07	1.49	0.05	0.13	0.53	0.02	0.03	0.02	0.01	2.36	0.01	0.05	1.34	10.82	0.02	0.03
A10	0.04	0.60	0.01	0.05	0.20	0.01	0.02	0.01	0.01	0.95	0.01	0.01	0.65	1.69	0.02	0.03
A12	0.02	0.23	0.01	0.02	0.09	0.01	0.01	0.01	0.01	0.40	0.01	0.01	0.24	1.08	0.02	0.03
A14	0.03	0.46	0.01	0.04	0.14	0.01	0.01	0.01	0.01	0.73	0.01	0.01	0.48	0.55	0.02	0.03
A15	0.04	0.18	0.01	0.03	0.13	0.01	0.01	0.01	0.01	0.43	0.01	0.01	0.16	0.10	0.02	0.03
A16	0.01	0.34	0.01	0.14	0.66	0.02	0.03	0.04	0.07	1.33	0.01	0.01	0.10	0.04	0.02	0.03
A17	0.02	0.58	0.01	0.03	0.11	0.01	0.01	0.01	0.01	0.78	0.01	0.02	0.04	0.32	0.02	0.03
mean	0.030	0.915	0.015	0.067	0.319	0.011	0.027	0.025	0.041	1.45	0.006	0.015	0.714	2.646	0.024	0.030
Median	0.029	0.589	0.009	0.048	0.204	0.008	0.013	0.008	0.013	1.04	0.006	0.010	0.565	0.922	0.024	0.031
Cp/(Ca+Cp)*100%																
A1	50	55	50	8	85	50	97	96	97		50	54	17	12	50	50
A4	7	3	20	6	13	50	32	46	50		50	12	2	0	40	83
A7	50	3	31	3	18	50	49	76	77		50	20	3	1	50	50
A9	6	1	8	3	1	21	11	18	50		50	7	1	0	50	50
A10	10	1	50	7	7	48	23	50	50		50	23	2	0	50	50
A12	17	4	50	14	12	50	50	50	50		50	54	5	1	50	50
A14	11	5	50	8	9	50	50	50	50		50	54	9	1	50	50
A15	10	12	43	10	2	50	50	50	50		50	54	30	6	50	50

A16	30	15	50	3	2	17	12	9	9	50	54	33	13	50	50
A17	16	57	50	86	87	50	50	50	50	50	20	15	38	50	50
mean	13	19	29	8	25	38	60	62	70	50	22	9	1	49	52
Median	13	4	50	7	7	50	26	48	50	50	32	4	1	50	50

Table SI 6. Individual PBDE and non-PBDE BFR concentrations and the particle associated proportion in sea water of the Atlantic and Southern Ocean

Compound	BDE28	BDE-47	BDE66	BDE 100	BDE99	BDE 85	BDE 154	BDE 153	BDE 183	∑PBDEs)	ATE	PBT	DPTE	HBB	HCDBCO	EHTBB
MDL (pg L^{-1})	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.040	0.003	0.003	0.008	0.006	0.012	0.016
Dissolved (pg L^{-1})																
W1	0.004	0.32	0.004	0.03	0.12	0.004	0.11	0.04	0.075	0.70	0.003	0.003	0.77	0.02	0.02	0.02
W3	0.004	0.05	0.004	0.004	0.02	0.004	0.004	0.03	0.006	0.13	0.003	0.003	0.08	0.006	0.012	0.01
W5	0.004	0.03	0.004	0.004	0.02	0.004	0.004	0.004	0.006	0.082	0.003	0.003	0.07	0.006	0.012	0.01
W7	0.004	0.07	0.004	0.004	0.02	0.004	0.004	0.004	0.006	0.12	0.003	0.003	0.008	0.006	0.012	0.01
W11	0.004	0.05	0.004	0.004	0.03	0.004	0.004	0.004	0.008	0.12	0.003	0.003	0.15	0.006	0.012	0.00
W13	0.004	0.07	0.004	0.01	0.04	0.004	0.004	0.01	0.009	0.15	0.003	0.003	0.05	0.01	0.012	0.01
W15	0.004	0.06	0.004	0.004	0.04	0.004	0.004	0.01	0.006	0.13	0.003	0.003	0.008	0.006	0.012	0.01
W17	0.004	0.03	0.004	0.004	0.02	0.004	0.004	0.04	0.009	0.13	0.003	0.003	0.04	0.006	0.012	0.00
W19	0.004	0.02	0.004	0.004	0.01	0.004	0.004	0.004	0.006	0.067	0.003	0.003	0.05	0.006	0.012	0.00
W21	0.004	0.02	0.004	0.004	0.01	0.004	0.004	0.004	0.009	0.069	0.003	0.003	0.008	0.006	0.012	0.01
W23	0.004	0.03	0.004	0.004	0.01	0.004	0.004	0.004	0.006	0.074	0.003	0.003	0.008	0.006	0.012	0.01
W25	0.004	0.04	0.004	0.004	0.02	0.004	0.004	0.02	0.006	0.10	0.003	0.003	0.04	0.006	0.012	0.00
W27	0.004	1.05	0.004	0.11	0.53	0.03	0.02	0.05	0.055	1.85	0.003	0.003	0.20	0.01	0.012	0.02
W29	0.004	0.03	0.004	0.004	0.04	0.004	0.004	0.01	0.006	0.10	0.003	0.003	0.03	0.006	0.012	0.01
W31	0.004	0.11	0.004	0.01	0.05	0.004	0.004	0.01	0.012	0.21	0.003	0.003	0.04	0.006	0.012	0.01
Mean	0.004	0.13	0.004	0.01	0.06	0.01	0.01	0.015	0.015	0.26	0.003	0.003	0.10	0.01	0.01	0.01
Median	0.004	0.05	0.004	0.004	0.02	0.004	0.004	0.008	0.006	0.12	0.003	0.003	0.05	0.01	0.01	0.01
Total suspended matter (TSM)																
(pg L^{-1})																
W1	0.004	0.032	0.004	0.008	0.031	0.001	0.007	0.000	0.020	0.11	0.003	0.003	0.04	0.006	0.012	0.016
W3	0.004	0.004	0.004	0.004	0.005	0.000	0.000	0.000	0.007	0.029	0.003	0.003	0.01	0.006	0.012	0.016
W5	0.004	0.007	0.004	0.004	0.008	0.000	0.000	0.000	0.001	0.028	0.003	0.003	0.008	0.006	0.012	0.016

W7	0.004	0.004	0.004	0.004	0.004	0.000	0.000	0.000	0.005	0.027	0.003	0.003	0.01	0.006	0.012	0.016
W11	0.004	0.004	0.004	0.004	0.008	0.000	0.000	0.002	0.007	0.033	0.003	0.003	0.01	0.006	0.012	0.016
W13	0.004	0.004	0.004	0.004	0.009	0.000	0.000	0.000	0.001	0.027	0.003	0.003	0.01	0.006	0.012	0.016
W15	0.004	0.004	0.004	0.004	0.004	0.001	0.001	0.001	0.001	0.023	0.003	0.003	0.008	0.006	0.012	0.016
W17	0.004	0.004	0.004	0.004	0.011	0.000	0.000	0.000	0.000	0.029	0.003	0.003	0.01	0.006	0.012	0.016
W19	0.004	0.013	0.004	0.004	0.010	0.008	0.001	0.001	0.011	0.056	0.003	0.003	0.03	0.006	0.012	0.016
W21	0.004	0.001	0.004	0.004	0.001	0.000	0.000	0.000	0.001	0.016	0.003	0.003	0.01	0.006	0.012	0.016
W23	0.004	0.007	0.004	0.004	0.014	0.000	0.000	0.000	0.000	0.034	0.003	0.003	0.01	0.006	0.012	0.016
W25	0.004	0.004	0.004	0.004	0.004	0.000	0.000	0.004	0.003	0.028	0.003	0.003	0.01	0.006	0.012	0.016
W27	0.004	0.099	0.004	0.023	0.099	0.001	0.010	0.029	0.066	0.34	0.003	0.003	0.02	0.006	0.012	0.016
W29	0.004	0.004	0.004	0.004	0.006	0.000	0.000	0.000	0.001	0.024	0.003	0.003	0.01	0.006	0.012	0.016
W31	0.004	0.004	0.004	0.004	0.003	0.000	0.000	0.000	0.002	0.022	0.003	0.003	0.01	0.006	0.012	0.016
Mean	0.004	0.013	0.004	0.005	0.015	0.001	0.001	0.003	0.008	0.054	0.003	0.003	0.013	0.006	0.012	0.016
Median	0.004	0.004	0.004	0.004	0.008	0.000	0.000	0.000	0.002	0.028	0.003	0.003	0.009	0.006	0.012	0.016
Dissolved+TSM																
(pg L^{-1})																
W1	0.01	0.35	0.01	0.04	0.15	0.00	0.12	0.04	0.10	0.81	0.01	0.01	0.82	0.02	0.03	0.03
W3	0.01	0.06	0.01	0.01	0.02	0.00	0.00	0.03	0.01	0.16	0.01	0.01	0.08	0.01	0.02	0.02
W5	0.01	0.04	0.01	0.01	0.03	0.00	0.00	0.00	0.01	0.11	0.01	0.01	0.08	0.01	0.02	0.02
W7	0.01	0.07	0.01	0.01	0.03	0.00	0.00	0.01	0.01	0.15	0.01	0.01	0.02	0.01	0.02	0.03
W11	0.01	0.06	0.01	0.01	0.04	0.00	0.00	0.01	0.01	0.15	0.01	0.01	0.16	0.01	0.02	0.02
W13	0.01	0.07	0.01	0.01	0.05	0.00	0.00	0.01	0.01	0.18	0.01	0.01	0.06	0.01	0.02	0.02
W15	0.01	0.06	0.01	0.01	0.04	0.00	0.00	0.01	0.01	0.16	0.01	0.01	0.02	0.01	0.02	0.02
W17	0.01	0.04	0.01	0.01	0.03	0.00	0.00	0.04	0.01	0.16	0.01	0.01	0.05	0.01	0.02	0.02
W19	0.01	0.04	0.01	0.01	0.02	0.01	0.00	0.00	0.02	0.12	0.01	0.01	0.08	0.01	0.02	0.02
W21	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.09	0.01	0.01	0.01	0.01	0.02	0.02

W23	0.01	0.04	0.01	0.01	0.03	0.00	0.00	0.00	0.01	0.11	0.01	0.01	0.02	0.01	0.02	0.02
W25	0.01	0.04	0.01	0.01	0.02	0.00	0.00	0.02	0.01	0.13	0.01	0.01	0.05	0.01	0.02	0.02
W27	0.01	1.15	0.01	0.13	0.63	0.03	0.03	0.08	0.12	2.19	0.01	0.01	0.22	0.02	0.02	0.03
W29	0.01	0.04	0.01	0.01	0.04	0.00	0.00	0.01	0.01	0.13	0.01	0.01	0.04	0.01	0.02	0.02
W31	0.01	0.11	0.01	0.02	0.05	0.00	0.00	0.01	0.01	0.23	0.01	0.01	0.05	0.01	0.02	0.02
Mean	0.01	0.15	0.01	0.02	0.08	0.01	0.01	0.02	0.02	0.32	0.01	0.01	0.12	0.01	0.02	0.02
Median	0.01	0.06	0.01	0.01	0.03	0.00	0.00	0.01	0.01	0.15	0.01	0.01	0.05	0.01	0.02	0.02
$C_{TMS}/(C_{diss}+C_{TMS})*100\%$																
W1	50	9	50	21	21	11	6	1	21		50	50	5	26	42	47
W3	50	8	50	50	19	11	11	1	51		50	50	7	50	50	65
W5	50	18	50	50	29	10	10	10	10		50	50	9	50	50	67
W7	50	6	50	50	16	11	11	8	35		50	50	50	50	50	54
W11	50	8	50	50	19	4	4	33	48		50	50	5	50	50	79
W13	50	6	50	29	19	7	7	3	6		50	50	16	45	50	75
W15	50	7	50	50	9	13	13	4	13		50	50	187	50	50	72
W17	50	12	50	50	35	6	6	1	4		50	50	11	50	50	80
W19	50	35	50	50	43	65	17	17	65		50	50	16	50	50	81
W21	50	4	50	50	6	10	10	10	8		50	50	52	50	50	74
W23	50	11	50	50	15	5	5	109	42		50	50	100	50	50	65
W25	50	10	50	50	18	5	5	19	31		50	50	22	50	50	87
W27	50	9	50	17	16	2	33	37	55		50	50	3	32	50	51
W29	50	11	50	50	15	8	8	4	8		50	50	36	50	50	64
W31	50	3	50	21	6	4	4	2	17		50	50	18	50	50	65
mean	50	9	50	28	18	13	11	14	35		50	50	11	45	49	67
Median	50	8	50	50	24	10	10	5	26		50	50	17	50	50	67

Paper IV

Occurrence and air-seawater exchange of brominated flame retardants and Dechlorane Plus in the North Sea

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ABSTRACT

The occurrence, spatial and seasonal concentration variations in air and seawater and the air–seawater exchange of polybrominated diphenyl ethers (PBDEs), alternate brominated flame retardants (BFRs) and Dechlorane Plus (DP) were studied in the German part of the North Sea in 2010. BDE–209 and DP were found to be the dominating compounds, both in the atmosphere and in seawater. Sum PBDEs ($\sum_{10}$PBDEs) ranged from 0.31 to 10.7 pg m^{-3} in the atmosphere and from not detected (n.d.) to 10.5 pg L^{-1} in seawater, respectively. DP ranged from 0.13 to 22.3 pg m^{-3} and from 0.10 to 17.7 pg L^{-1} in air and seawater, respectively. Besides, four other BFRs including hexabromobenzene (HBB) and pentabromobenzene (PBBz) were detected. Elevated atmospheric concentrations were observed in continentally influenced air masses while highest seawater concentrations were observed at sampling stations close to the coast influenced by riverine discharge. The ratio of the two DP stereoisomers both in air and water was found to be close to the technical mixture at high concentrations but changed at lower concentrations giving first evidence for the alteration within the aquatic environment. Both dry air-seawater gas exchange and dry deposition are input pathways of BFRs and DP in the North Sea besides riverine discharge.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), which have been applied as flame retardants for several decades, were banned for production and usage in the European Union (EU) by 2004 due to their adverse effects on the environment. Initially, the technical DecaBDE mixture with its main congener BDE–209 was excluded from the EU restriction, but this exception was withdrawn in 2008 (European Court of Justice, 2008). But, the restriction of DecaBDE in the EU still only includes the usage in electrical and electronic products. The volume of DecaBDE sold within Europe was reported with 6648 metric tons in 2010 (VECAP, 2010). Some PBDEs are known to be bioaccumulative and persistent and can undergo long range atmospheric transport (LRAT) (Darnerud, 2008; Wania and Dugani, 2003). They are meanwhile ubiquitous in the global environment (de Wit et al., 2010; Hites, 2004; Law et al., 2008). In a further banishment step, congeners of the technical Penta– and OctaBDE mixtures were recently officially classified as Persistent Organic Pollutants (POPs) by their inclusion in the Stockholm Convention (SCOP, 2009).

Despite its highly hydrophobic character, BDE–209 has been shown to be subject to LRAT, too (de Wit et al., 2010; Gouin et al., 2006), and possible direct (Lee et al., 2010a) and indirect toxic effects by in-situ metabolism (Huwe and Smith, 2007) are still being discussed. In addition, BDE–209 can undergo phototransformation (Söderström et al., 2003) to more toxic lower brominated congeners leading to an ongoing need for research of its environmental fate and impact. Discussions on alternatives for DecaBDE to be applied in electronics and other commercial products include non-PBDE brominated flame retardants (BFRs), chlorinated FRs, organophosphorus FRs as well as inorganic FRs. 27 alternatives were listed by the European Commission (European Comission, 2007), including as well the highly halogenated flame retardant Dechlorane Plus (DP), which has received increasing scientific interest in the last five years. DP is produced in the United States (U.S.) (Hoh et al., 2006) and in China (Wang et al., 2010) and was, despite its decade-long production, first detected in the environment in 2006 (Hoh et al., 2006). Elevated environmental DP concentrations were reported close to production and e-waste sites in the U.S. and China (Chen et al., 2011; Hoh et al., 2006; Wang et al., 2010). First studies reported DP in the European (de la Torre et al., 2011; Möller et al., 2010;

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Qiu and Hites, 2008) and even global remote environment (Möller et al., 2010; Sverko et al., 2010) showing that DP is more than a local pollutant. Besides PBDEs and DP, other non-PBDE BFRs (e.g., hexabromobenzene (HBB), pentabromotoluene (PBT), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)) have been recently investigated in the environment. Several alternatives have been detected in source-near environments, but also in the marine and even Arctic environment (Covaci et al., 2011; de Wit et al., 2010).

In the present study, we investigated PBDEs, non-PBDE BFRs and DP in the atmosphere and seawater from the German part of the North Sea during three sampling cruises in 2010, and additionally in surface water from the rivers Elbe and Weser in 2011 which discharge into the North Sea. The flame retardants were analyzed in order to determine the current levels and composition of FRs in the Western European remote environment, possible seasonal and source related variations as well as air–seawater exchange fluxes.

2. Material and methods

2.1. Sampling

In 2010, 20 air samples (~300 m^3) and 36 seawater samples (~150 L) from the German part of the North Sea were taken during three cruises of the German research vessel *Heincke* (cruise H319 in March: 6 air samples and 11 seawater samples; cruise H325 in May: 7 air samples and 12 seawater samples; cruise H331 in July: 7 air samples and 13 seawater samples). The pollution of the North Sea is on the one hand influenced by atmospheric as well as riverine emissions from the surrounding industrialized Western European countries including Germany, the Netherlands and the United Kingdom (U.K.). But, it is relatively open towards the North/Northwest leading to the influence of non-continental and even Arctic air during northerly winds. Sampling followed the procedure described in Möller et al. (2010) and is given in detail in the SI. Eight surface water samples (5 L) from the rivers Elbe and Weser and their estuaries were additionally taken aboard the research vessel *Ludwig Prandtl* in February 2011. Air columns and filter samples were stored at −20 °C and water columns were stored at 4 °C until extraction, respectively. Detailed information on the sampling stations is included in Tables S1–S3 of the supplementary information (SI).

2.2. Extraction, clean-up and analysis

The extraction followed the method described in Möller et al. (2010). Chemicals and suppliers are included in the SI. Briefly, the samples were spiked with 200 pg of ^{13}C–HBB, ^{13}C–BDE–77, ^{13}C–BDE–138 and ^{13}C–synDP, and 2000 pg ^{13}C–BDE–209 as surrogates prior to extraction. Columns and filters were Soxhlet extracted for 16 h using DCM. The extracts were purified on a 2.5 g 10% water deactivated silica gel column. Finally, ten ng ^{13}C–HCB was added as injection standard. Analysis was done by an Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer (GC–MS) in electron capture negative chemical ionization mode (ECNCI). Samples were analyzed for 10 PBDEs, 8 non-PBDE BFRs, DP and the one- and twofold dechlorinated DP species (see SI).

2.3. Air mass back trajectories

Air mass origins were calculated for the air samples using NOAA's HYSPLIT model (Draxler and Rolph, 2003). Back trajectories (BTs) were calculated for each sample in 4 h steps along the sampling cruises. BTs were traced back for 120 h with the sampling height as arrival height (see Figure S1 for individual BTs).

2.4. QC/QA

Breakthrough of the target compounds was checked using tandem columns during the cruises. No target compounds were observed above the method detection limits (MDLs) in the lower column. Field blank values taken for all different kind of samples for each cruise were in the low absolute one- to two-digit pg range (see Table S4 and S5 for individual blanks). MDLs were derived from mean blank values plus three times the standard deviation or, for those compounds showing no blanks, from the instrumental detection limits at a signal-to-noise (*S*/*N*) ratio of three. MDLs ranged from 0.002 to 2.4 pg m^{-3} for atmospheric samples, from 0.004 to 0.66 pg L^{-1} in seawater, and from 0.12 to 79.7 pg L^{-1} in riverine surface water (see Table S6 and S7 for individual MDLs). Mean recoveries of the surrogates ranged from 75 ± 19% for

Table 1
Concentration ranges (and median in brackets) of investigated flame retardants in the atmosphere (gaseous + particulate phase, pg m^{-3}) and seawater (dissolved + particulate phase, pg L^{-1}) of the North Sea and the f_{syn} values (f_{syn} = [synDP]/[synDP]+[antiDP]) during the three cruises. For compounds which were detected in <50% of the samples no median value is reported (–).

	H319, March		H325, May		H331, July	
	Air	Seawater	Air	Seawater	Air	Seawater
BDE–47	0.20–0.73 (0.24)	n.d.–0.28 (0.15)	0.10–0.79 (0.21)	n.d.–0.32 (0.10)	0.14–0.40 (0.30)	n.d.–1.1 (0.12)
BDE–99	0.09–0.29 (0.13)	n.d.–0.30 (0.09)	0.07–0.39 (0.10)	n.d.–0.15 (0.04)	0.09–0.22 (0.13)	n.d.–1.1 (0.07)
BDE–100	n.d.–0.06 (0.01)	n.d.–0.03 (–)	n.d.–0.10 (–)	n.d.	n.d.–0.04 (0.02)	n.d.–0.18 (–)
BDE–153	n.d.–0.04 (–)	n.d.–0.40 (–)	n.d.	n.d.	n.d.	n.d.–0.06 (–)
BDE–183	0.02–0.19 (0.04)	n.d.–0.18 (–)	n.d.–0.10 (–)	n.d.	n.d.–0.32 (0.03)	n.d.–0.20 (–)
BDE–209	n.d.–9.4 (0.42)	n.d.–9.3 (1.6)	0.21–2.2 (0.55)	n.d.–1.7 (0.63)	0.30–5.7 (1.7)	n.d.–4.3 (1.2)
∑PBDEs	0.31–10.7 (0.89)	0.20–10.5 2.1	0.37–3.4 (0.96)	n.d.–2.1 (0.76)	0.83–6.1 (2.4)	n.d.–6.9 (1.3)
PBBz	0.14–0.37 (0.31)	n.d.	n.d.–0.24 (0.04)	n.d.	n.d.–0.81 (0.23)	n.d.
PBT	0.06–0.08 (0.07)	n.d.	n.d.–0.09 (0.03)	n.d.	n.d.–0.24 (0.08)	n.d.
DPTE	0.52–2.1 (0.91)	0.31–1.5 (0.46)	0.16–1.7 (0.29)	0.18–1.0 (0.27)	n.d.–2.5 (0.29)	n.d.–5.7 (0.32)
HBB	2.8–6.3 (4.49)	n.d.–0.06 (–)	0.09–1.2 (0.20)	n.d. 0.02 (–)	0.10–2.81 (0.36)	n.d.–0.08 (–)
synDP	0.16–1.8 (0.39)	0.09–1.2 (0.38)	0.07–6.8 (0.17)	0.22–16.9 (0.52)	0.13–1.5 (0.59)	0.13–7.0 (0.47)
antiDP	0.03–1.5 (0.08)	0.01–0.55 (0.12)	0.05–15.5 (0.06)	n.d.–0.79 (0.08)	0.05–1.0 (0.49)	0.06–1.6 (0.16)
f_{syn}	0.40–0.89 (0.77)	0.51–0.95 (0.66)	0.30–0.86 (0.71)	0.54-S (0.89)	0.49–0.75 (0.61)	0.64–0.87 (0.72)

n.d.: not detected.
S: only the syn-isomer was detected.

^{13}C–synDP to 98 ± 35% for ^{13}C–BDE–77. All concentrations were recovery corrected.

3. Results and discussion

3.1. Atmospheric concentrations

Among the investigated flame retardants, six PBDE congeners (BDE–47, –99, –100, –153, –183, –209), four non-PBDE BFRs (pentabromobenzene (PBBz), PBT, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), HBB) and the two DP stereoisomers – synDP and antiDP – were detected. Four other analyzed non-PBDE BFRs – pentabromoethyl benzene (PBEB), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), BTBPE and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) – as well the one- and twofold dechlorinated DP species were not detected within this study. The individual concentration ranges are included in Table 1 (see Table S8 for individual concentrations). Atmospheric PBDEs (as sum of gaseous and particulate phase; also in the following discussion) ranged from 0.20 to 10.7 pg m^{-3} ($\sum_{10}$PBDEs) with BDE–47, –99 and –209 being the predominant congeners contributing 96 ± 5% to $\sum_{10}$PBDEs (see Figure S2 for the composition of analyzed FRs). The observed PBDE concentrations are within the lower range of European PBDE levels given in the literature (see Figure S3), mainly representing European non-source related background concentrations. It should be noted that the majority of studies did not include BDE–209, which is shown to be meanwhile the dominating congener of the European atmosphere in this study.

PBBz, PBT, DPTE and HBB, which were detected in almost all samples, ranged from n.d. to 0.81 pg m^{-3}, n.d. to 0.24 pg m^{-3}, n.d. to 2.5 pg m^{-3} and from 0.09 to 6.3 pg m^{-3}, respectively, which are, especially for HBB and DPTE, similar or higher than BDE–47 and –99. DP was detected in all air samples within a range from 0.13 to 22.3 pg m^{-3} ($\sum$synDP + antiDP).

There are only a few data on non-PBDE BFRs in the abiotic outdoor environment available, especially on the European environment. HBB and DPTE were recently detected in similar or lower concentrations in the Atlantic Ocean and East Greenland Sea (Möller et al., 2011; Xie et al., 2011). Similar HBB concentrations were observed in the Great Lakes area and East China, too (Gouteux et al., 2008; Qiu et al., 2010) and Arp et al. (2011) detected HBB in airborne particles in Norway at relatively high concentrations of 4.3 ± 5.3 pg/m^3. PBT was detected <0.05 pg m^{-3} in the Atlantic Ocean, East Greenland Sea and the Great Lakes region (Gouteux et al., 2008; Möller et al., 2011; Xie et al., 2011). The global occurrence of PBBz in the atmosphere was qualitatively reported by Lee et al. (2010b). After its first report in 2006, the occurrence of DP in the atmosphere was mainly investigated in source-near or urbanized and industrialized regions in the U.S and China with source-elevated concentrations up to the ng m^{-3} range (Hoh et al., 2006; Ren et al., 2008; Wang et al., 2010), while concentrations comparable to the present study were observed in non-source sites in the U.S. and China (Ren et al., 2008; Venier and Hites, 2008), and also in the East Greenland Sea atmosphere (Möller et al., 2010) and Sweden (Kaj et al., 2010).

Only very little or no information on production, import and usage and consequently possible sources of other BFRs and DP, especially for Europe, are available. DP is listed as Low Production Volume chemical (LPV) being produced/imported to the EU by a German company (ESIS). PBT is listed as LPV, too (ESIS), being imported/produced the Netherlands but no information on production/import and usage on the other BFRs observed in this study are available. However, since HBB and PBT are known to be produced in other regions such as the U.S. and China (Covaci et al., 2011), they are likely been imported into Europe within manufactured products leading to emissions into the European environment. In addition to production and usage, PBT, HBB and PBBz might also originate from degradation of higher brominated FRs or polymeric BFRs (Buser, 1986; Gouteux et al., 2008) both during production or product finishing, during waste treatment such as burning processes or possibly also during transport within the environment.

DPTE is a flame retardants which has been produced in Germany until the 1980s, but since then no other company reported its production (von der Recke and Vetter, 2007), but it is obviously still somehow emitted into the (European) environment and even transported into remote regions as recently shown (Möller et al., 2011).

3.2. Seawater and riverine concentrations

In seawater, $\sum_{10}$PBDEs ranged from n.d. to 10.5 pg L^{-1} (sum of dissolved and particulate phases; also in the following discussion; see Table 1 for details and Table S9 for individual concentrations) with BDE–209 being the dominating congener ranging from n.d. to 9.3 pg L^{-1} (see Figure S4 for the seawater composition of analyzed FRs). BDE–47 and –99 remained below 1 pg L^{-1} in almost all samples (maximum 1.1 pg L^{-1}) and BDE–153 and –183 were detected only in 14% and 11% of all samples, respectively. Among the non-PBDE BFRs, only DPTE and HBB, and DP were detected in concentrations from n.d. to 5.7 pg L^{-1} for DPTE and from 0.10 to 17.7 pg L^{-1} for DP, respectively, while HBB remained <0.1 pg L^{-1} in all samples (see Table S9 for individual concentrations).

According to the predominating analytes found in the seawater samples, the additional riverine samples from the rivers Elbe and Weser and their estuaries were analyzed only for PBDEs, DPTE and DP. $\sum_{10}$PBDEs ranged from 99.3 to 6792 pg L^{-1}, dominated again by BDE–209 with a mean contribution of 98 ± 2%. DP ranged from 11.8 to 105 pg L^{-1} and DPTE was detected from n.d. to 69.8 pg L^{-1} (see Table S10 for individual concentrations).

PBDEs in seawater from the Dutch coast of the North Sea and from the River Scheldt estuary ranged from 0.1 to 5 pg L^{-1} which is similar to the seawater concentrations in the present study, while the BDE–209 concentrations in the estuary of the rivers Elbe and Weser are much higher than in the river Scheldt estuary (Booij et al., 2002). This might be a result of the different sampling equipment since Booij et al. (2002) used semipermeable membrane devices which usually sample only dissolved residues and BDE–209 is mainly distributed into the particulate phase (78 ± 28% in the present study). PBDE concentrations in the open oceans of the Atlantic and East Greenland Sea were <1 pg L^{-1} at most sites (Möller et al., 2011; Xie et al., 2011) which is similar or lower to the offshore seawater stations in this study. BDE–209 concentrations similar to the riverine samples were found in Izmir Bay, Turkey (Cetin and Odabasi, 2007) while the concentrations of other lower brominated congeners in Izmir Bay were clearly higher (e.g., 34 ± 7 pg L^{-1} and 11 ± 5 pg L^{-1} for BDE–47 in the dissolved and particulate phase in winter, respectively). Higher PBDE concentrations of all congeners were found in the Pearl River Delta, China (2.69–19.1 ng L^{-1} for $\sum_{17}$PBDEs) (Guan et al., 2007). DPTE and HBB were detected in similar concentrations in the Arctic and the Atlantic Ocean (Möller et al., 2011; Xie et al., 2011) while a source-elevated HBB concentration of 520 ± 40 pg L^{-1} was reported in China (Wu et al., 2010). In this study DPTE was observed in riverine surface water for the first time. DP was found in oceanic seawater in maximum concentrations of 1.3 pg L^{-1} (Möller et al., 2010) which is similar to the offshore stations in the present study. Concentrations of 0.54 ± 0.49 ng L^{-1} and 1.2 ± 1.1 ng L^{-1} were recently reported for coastal seawater from the Bohai and Huanghai Sea shore area in Northern China (Jia et al., 2011) which are about 10–100 times higher than in the present study, both for the seawater and riverine samples, and, surprisingly, even higher than those in a freshwater pond near an e-waste recycling site (Wu et al., 2010). Jia et al. (2011) stated that the source of their observed elevated DP seawater concentrations is unknown. However, the seawater concentrations in the present study seem to be more representative for DP levels in the marine (coastal) environment. Riverine DP concentrations similar to the present study were found in rural areas of China, while concentrations in urbanized regions ranged up to 2.4 ng L^{-1} (Qi et al., 2010).

3.3. Temporal and spatial trends

3.3.1. Atmosphere

The spatial distribution of the dominating compounds in the atmosphere in shown in Fig. 1. In general, correlation analyses showed no seasonal, temperature depended atmospheric concentration trends. A long term monitoring would be necessary to identify possible seasonality of BFRs and DP in the North Sea's atmosphere. But, as expected, a temperature dependence of the particle−vapour partitioning was observed for BDE−47, −99, −100 with a significant decrease ($p < 0.01$) of the particulate associated fraction with increasing air temperature from 46 ± 31%, 63 ± 13% and 78 ± 19% in March, respectively, down to 2 ± 5%, 17 ± 18% and 0% in July, respectively. While the more volatile compounds − PBBz, PBT and HBB − where detected during all three cruises almost exclusively in the gaseous phase, the highly hydrophobic BDE−209 and DP were detected mainly in the particulate phase.

In general, the cruises H319 and H325 were dominated by northerly, northwesterly and northeasterly winds which partially passed the Scandinavian countries or northern Germany, but not the heavily industrialized regions such as the Rhine-Ruhr metropolitan region in Germany or other highly populated and industrialized regions. In contrast, samples taken during H331 where mainly dominated by southerly and southwesterly continental air masses passing the industrialized Western European countries including Germany, the Netherlands and the U.K. Elevated peak atmospheric concentrations were observed during all three cruises when continental air masses were sampled what has been earlier reported for PBDEs for other regions (Jaward et al., 2004; Shen et al., 2006) including the marine environment (Wurl et al., 2006; Xie et al., 2011). Especially BDE−209 and DP showed relatively high concentration peaks indicating regional sources while concentrations of the Penta− and OctaBDE congeners − BDE−47 and −99 − were only slightly elevated. This can be explained by the banishment the PentaBDE mixture from usage and production while, in contrast, DecaBDE and DP are allowed to be used and are imported to Europe. Overall, the median concentrations of BDE−209 and DP were generally but not significantly higher during H331 than during H319 and H325 what is likely be resulted by the different wind directions (southerly/southwesterly vs. northerly) and transport of these two current use flame retardants at southerly wind directions from the adjacent countries towards the North Sea. But, it needs to be noted that, on the other hand, the higher air temperatures during H331 in summer might lead to an increased photodegradation rate during atmospheric transport which might counterbalance possible higher emissions and, therefore, possible higher concentrations.

The lowest concentrations during all cruises were observed in samples dominated by oceanic or even Arctic air masses (e.g., H325 A4). Interestingly, BDE−47 (and BDE−99) was the predominant PBDE congener in these samples rather than BDE−209 which dominated the peak concentrations at continental air mass origin. This shows that BDE−209 and DP are emitted from the Western European countries into the North Sea environment mainly during southerly and southwesterly wind directions while, in contrast, remote air masses without continental influence are dominated by the traditional congeners BDE−47 and BDE−99 which are much more persistent and show higher LRAT potential than BDE−209 (Wania and Dugani, 2003). No clear explanation of the elevated concentrations at station H319 A2 can be given, while station H325

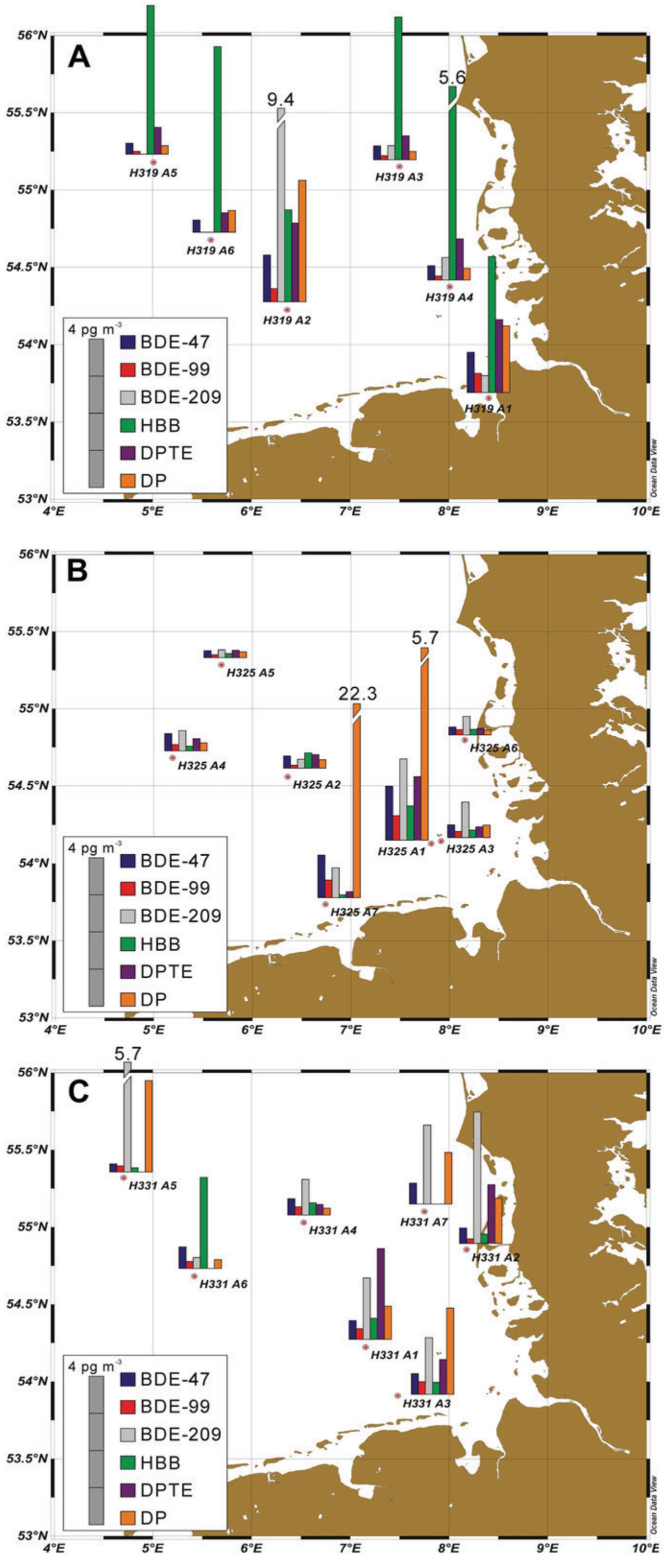

Fig. 1. Spatial distribution of the major BFRs and DP in the atmosphere of the North Sea during H319 (A), H325 (B) and H331 (C).

A1 was taken partly in the estuary of the river Weser and was influenced by air masses passing parts of Germany, the Netherlands and Belgium. The highest DP concentration of 22.3 pg m^{-3} at station H325 A7 was influenced by air masses from Northern Germany and Scandinavia and was taken relatively close to the coast. Interestingly, the ratio of the DP stereoisomers was close to the technical mixture, possibly indicating the influence of a specific point source (see Section 3.4 for discussion).

3.3.2. Comment on elevated atmospheric HBB concentrations during H319

Interestingly, HBB showed comparably high atmospheric concentrations at all stations of H319 which were about ten times higher than during H325 and H331. Thereby, both the gaseous as well as the particle-bound concentrations were elevated. Lee et al. (2004) observed elevated PBDE concentrations in the UK in winter and proposed combustion events during winter time as possible sources. The air masses sampled during H319 originated mainly from Scandinavia, where of course combustion events such as burning of wood, but also waste and fuel, for heating of houses could take place especially during winter. HBB was shown to be formed by thermal reaction of higher brominated PBDEs such as BDE−209 (Buser, 1986), and possibly by other highly brominated FRs, too, and might also be released from polymeric BFRs (Gouteux et al., 2008) what could lead to an additional release of HBB during burning. Arp et al. (2011) reported HBB in the City of Drammen located in the South of Norway at 4.3 ± 5.3 pg m^{-3} in atmospheric particles. Since HBB is known to be mainly distributed into the gaseous phase (e.g., particle-bound fraction of 5 ± 5% in the present study), the total atmospheric concentrations are expected to be substantially higher. This gives at least an indication that the Nordic countries could contribute significantly to the HBB pollution of the North Sea at northerly wind conditions in winter time as observed during H319. The results of this study shows that the sources, possible formation in the environment and environmental fate need future research since it seems to be meanwhile a dominating BFR in the (European) environment as we recently proved even for the Arctic (Möller et al., 2011).

3.3.3. Seawater and discharging rivers

The spatial seawater distribution of the major BFRs and DP is shown exemplarily for H331 in Fig. 2 (see Figures S5 and S6 for H319 and H325). In general, the highest concentrations were observed in the coast-near stations, again, especially for BDE−209 and DP. A significant inverse correlation with the salinity was observed only during H331 indicating a freshwater influence from the discharging rivers. But, it should be noted that the samples represent integrated seawater samples taken for several hours during the ships movement leading to sampling of different water masses including riverine discharges and North Atlantic waters. In addition, the coastal area of the North Sea is in general a highly dynamic system and heavily influenced by the tides what might lead to no significant trends.

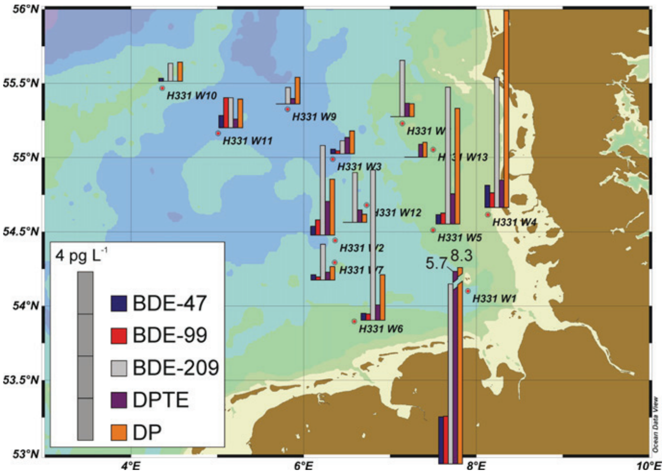

Fig. 2. Spatial distribution of major BFRs and DP in seawater of the North Sea during H331.

However, since the spatial distributions clearly indicate riverine influences, we analyzed samples from the rivers Elbe and Weser and their estuaries. The latitudinal profile is displayed in Fig. 3 showing a strong decrease of all compounds towards the estuaries as a result of mixing with lower polluted seawater. The riverine concentrations are 10–100 times higher than the seawater concentrations. The increase of BDE−209 and DP at station E3 can not be clarified within this study, but possible sources could be the discharge of waste water treatment plants or industrial emissions by chemical factories which are located in this area. However, the riverine concentrations clearly show a riverine influence on BFRs and DP in the North Sea whose extent, including possible sedimentation processes in the estuaries, and consequently their benthic occurrence, especially of BDE−209 and DP, need future research.

3.4. DP stereoisomer ratio

In terms of the environmental fate of DP, the ratio (f_{syn} = synDP/[synDP]+[antiDP]) of the two stereoisomers has been frequently discussed. The value in the industrial mixture ranges from 0.20 to 0.41 (Wang et al., 2010), while it might also vary between the production lots or with time of production (Hoh et al., 2006). The f_{syn} values in air and seawater of the present study are included in Table 1. We could not observe any temperature or seasonal related trend, but we observed a significant decrease of f_{syn} with increasing atmospheric DP concentrations ($p < 0.05$, Pearson correlation, decadic logarithm of DP concentration) which has been observed by Hoh et al. (2006) with increasing distance to the source, too, that emphasis the theory of stereoselective depletion during LRAT (see Figure S7). However, a specific source of DP could not be identified within this study. It was shown that f_{syn} might undergo alteration (i.e., increase of f_{syn} with increasing distance from the source) during atmospheric transport by stereospecific depletion of the anti-isomer by UV–sunlight (Hoh et al., 2006; Möller et al., 2010; Sverko et al., 2008). Analytically related influences such as a dirty injector liner (Sverko et al., 2008) and behaviour differences during storage (de la Torre et al., 2011) which might influence the analyzed ratio in real samples were reported. However, the liner was frequently changed, no degradation products were detected and the responses of the isomers in standard mixtures were similar and constant before and after the sample measurement indicating no analytical shift of f_{syn}.

Median f_{syn} values in seawater were 0.66 ± 0.14, 0.89 ± 0.14 and 0.72 ± 0.08 during the three cruises. Interestingly, the riverine and estuarine values ranged from 0.18 to 0.54 with a median of 0.29 which is close to the commercial mixture. Similar to the atmosphere, the f_{syn} value in riverine and seawater decreased significantly ($p < 0.01$, Pearson correlation, decadic logarithm of DP concentration) with increasing concentration. This gives evidence for a change of f_{syn} with travelling time in the (sea–) water phase and, consequently, with increasing distance from the source. Possible mechanisms influencing the alteration could be differences of the isomers in their (1) biodegradation, (2) photodegradation, (3) hydrolysis and (4) sedimentation behaviour which need to be investigated to understand the fate of DP in the (marine) environment. Besides processes within the aquatic environment, atmospheric deposition fluxes of already altered DP into seawater

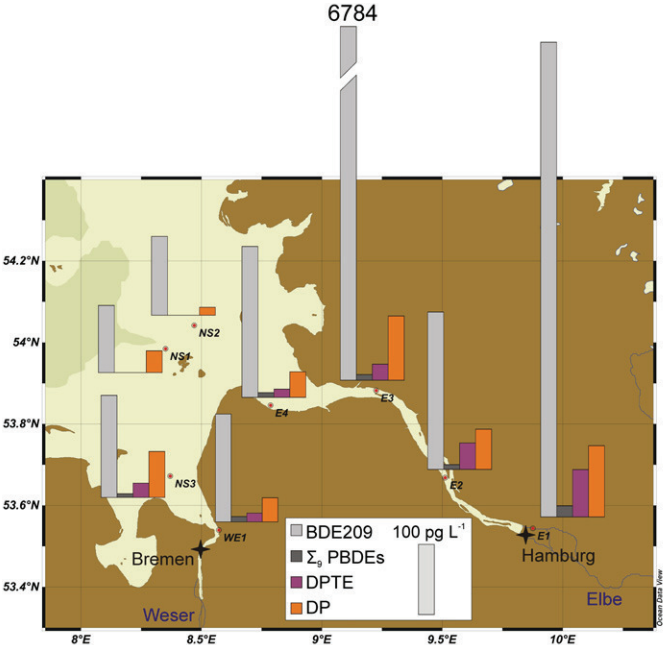

Fig. 3. Spatial distribution of BDE–209, sum of the nine remaining PBDEs, DPTE and DP in the surface water of the rivers Elbe and Weser and their estuaries. Note that for station E4 only the particulate phase was analyzed.

might influence the ratio in seawater, especially in open oceans without any riverine inputs. In addition to that, the isomer ratio of DP used and imported to Europe, the sources and possible hotspots need to be known and studied.

3.5. *Air-seawater gas exchange and dry deposition*

The air–seawater gas exchange calculation of BDE–47, –99 and DPTE, which were detected in almost all gaseous and dissolved samples, was done based on the modified version of the Whitman two-film resistance model (Liss and Slater, 1974; see SI for details). The results for the three cruises are shown in Fig. 4. During all cruises, the air–seawater exchange was obviously dominated by net deposition into the North Sea with fluxes from 42 pg m^{-2} d^{-1} (volatilization) to –229 pg m^{-2} d^{-1} (deposition), 29 to –81 pg m^{-2} d^{-1} and –30 to –1608 pg m^{-2} d^{-1} for BDE–47, –99 and DPTE, respectively. The BDE–47 and –99 fluxes are, compared to DPTE, relatively close to equilibrium and low compared to those reported for the Izmir Bay, Turkey (Cetin and Odabasi, 2007). Elevated DPTE deposition fluxes were observed especially for stations during H319 and for DPTE, BDE–47 and –99 during H325 at temporally high atmospheric concentrations resulting from continental air mass origins. This shows the strong coupling of the air-seawater gas exchange with the wind directions within the North Sea. In general, lowest fluxes were observed in May, possible resulting from relatively low atmospheric concentrations of due to mainly northwesterly winds, while higher BDE–47 and –99 fluxes were observed in July what might be a result of a decreased particle binding and higher partitioning into the gaseous phase of these compounds in summer. Volatilization from the seawater was observed for BDE–47 and BDE–99 at only one coastal station during H331 which showed high dissolved aquatic concentrations, and for BDE–99 at another offshore station. Especially the volatilization at the coastal station shows that riverine influence might lead to a change of the flux direction coastal areas and to re-emissions and further atmospheric transport what need to be confirmed by the analysis of estuarine samples.

Since the predominating compounds BDE–209 and DP are mainly attached to airborne particles, we estimated the particle-bound dry deposition using a deposition velocity of 0.2 cm s^{-1} (172.8 m d^{-1}) which was proposed by Castro-Jiménez et al. (2010) for offshore marine aerosols influenced by continental sources (see SI for details of the calculation). The dry deposition fluxes are shown in Fig. 5. As shown for the concentrations, the dry deposition flux, especially of BDE–209 and DP showed peaks during continentally influenced air masses mainly during H331 with a sum flux up to 1738 pg m^{-2} d^{-1}. Caused by the temperature dependence of the partitioning of BFRs between the gaseous and particulate phase,

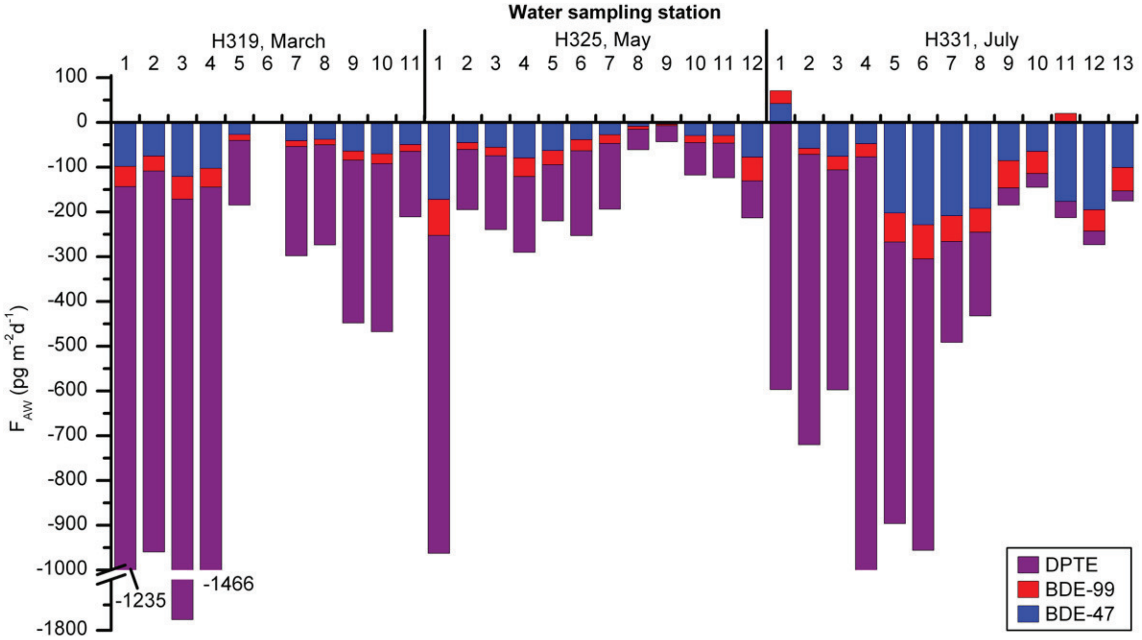

Fig. 4. Air–seawater gas exchange flux of BDE–47, –99 and DPTE in the North Sea. Negative (–) flux indicates deposition into the water column. For station H319 W6 no dissolved phase was analysed.

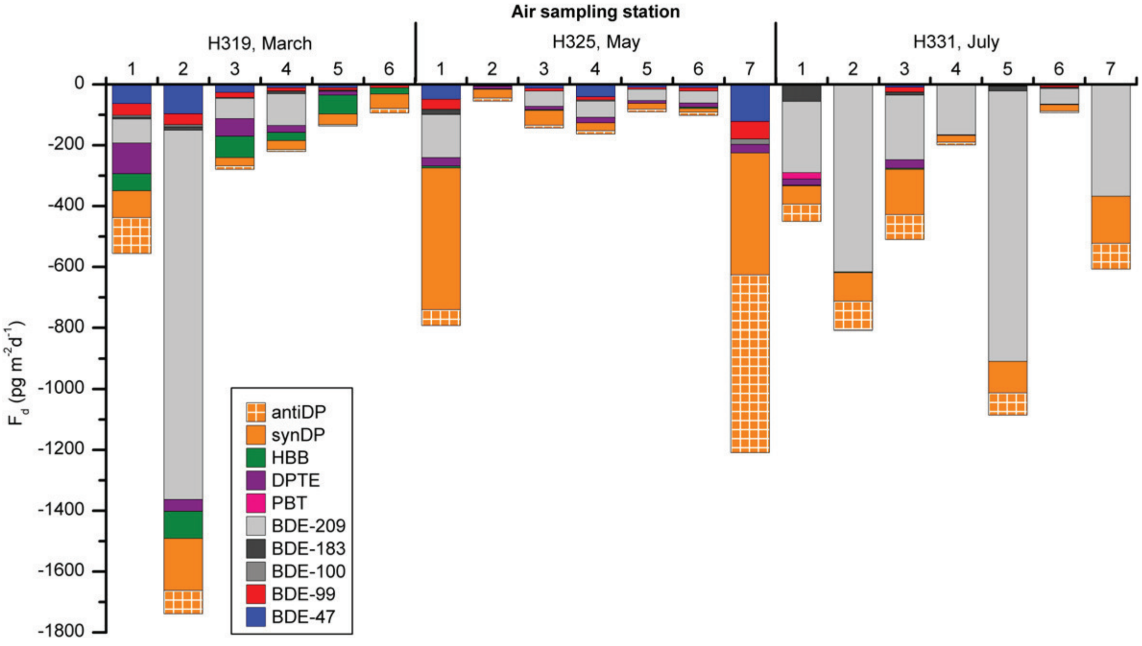

Fig. 5. Dry deposition fluxes of BFRs and DP into the North Sea.

the dry deposition fluxes of the Penta– and OctaBDE congers as well as DPTE and HBB decreased in summer, while the net gaseous deposition increased. Overall, several BFRs, especially DPTE and BDE–209, as well as DP are emitted into the North Sea both via gas exchange as well as via dry deposition.

4. Conclusions

The present study in the North Sea showed the emissions of PBDEs, several other BFRs and DP into the North Sea via the atmosphere as well as via riverine discharge. Especially the particle-bound BDE–209 and DP are deposited into the North Sea during southerly and southwesterly wind directions transporting continental air masses. In addition, HBB was found in highest concentrations in winter time during northerly wind directions leading to the question of the sources and origin of HBB which is an important question for future research on BFRs. The already known stereoisomeric differences of DP during atmospheric transport was confirmed within this study, while this study gives the first evidence for the alteration and the increase of f_{syn} within the aquatic environment which is important for possible bioaccumulation or sedimentation in the marine environment. The air-seawater gas exchange was shown to be dominated by net deposition into the North Sea, while a strong dependence on the wind directions was observed.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2011.09.055.

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Supplementary information

Occurrence and air-seawater exchange of brominated flame retardants and Dechlorane Plus in the North Sea

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Additional Information on materials and method

Sampling. Integrated one day air samples (~300 m^3) were taken in the front of the ship's most upper deck (Altitude: 12 m) using a high–volume pump passing the air through a glass fiber filter ([GFF], GF/F, pore size: 0.7 µm) to trap the airborne particles followed by a glass column packed with PUF/Amberlite® XAD–2 resin. Seawater samples were taken via the ship's seawater intake system (Depth: 5.5 m) and the seawater was passed through a GFF (GF/C, 1.2 µm) for the suspended particulate matter followed by a glass column packed with Serdolit® PAD–2 (SERVA Electrophoresis). For riverine and estuarine samples, 5 L water was filtered (GFF, MN GF 1, 0.7 µm) and then passed through a glass column packed with Serdolit® PAD–3 (SERVA Electrophoresis).

Chemicals. A BDE–Mix (BDE–MXF; including BDE–28, –47, –66, –85, –99, –100, –153, –154, –183), BDE–209, pentabromobenzene (PBBz), pentabromotoluene (PBT), 2,3–dibromopropyl–2,4,6–tribromophenyl ether (DPTE), hexabromobenzene (HBB), pentabromoethyl benzene (PBEB), 2–ethylhexyl 2,3,4,5–tetrabromobenzoate (EHTBB), 1,2–bis(2,4,6–tribromophenoxy)ethane (BTBPE), bis–(2–ethylhexyl)–tetrabromophthalate (TBPH), the one– and twofold dechlorinated DP species (aCl11DP, aCl10DP), and the two DP stereoisomers (synDP, antiDP) were purchased from Wellington Laboratories. Mass labelled standards were purchased from Wellington Laboratories (^{13}C–HBB, ^{13}C–BDE–77, ^{13}C–BDE–138, ^{13}C–BDE–209) and from Cambridge Isotope Laboratories (^{13}C–synDP), respectively. ^{13}C–Hexachlorobenzene (^{13}C–HCB) was obtained from Cambridge Isotope Laboratories. Acetone, hexane and dichloromethane (DCM) were pico grade (PromoChem) and silica gel (0.063–0.200 mm) was purchased from Merck.

Table S1. Detailed information on air sampling. Latitude and longitude are mean sampling stations. Air temperature (T_a) and wind speed represent the mean values during sampling.

Sample I.D.	Volume (m^3)	Date	Latitude (°N)	Longitude (°E)	Wind speed (m/s)	T_A (°C)
H319 A1	320	4–5/3/10	54.847	7.981	6.6	1.2
H319 A2	294	5–6/3/10	53.928	7.494	11.5	0.5
H319 A3	322	6–7/3/10	54.378	6.351	4.6	0.6
H319 A4	249	8–9/3/10	55.199	7.283	3.3	0.8
H319 A5	399	9–10/3/10	55.427	4.400	6.2	2.5
H319 A6	119	10/3/10	54.681	6.609	3.0	1.6
H325 A1	86	1–2/5/10	54.129	7.814	5.9	7.8
H325 A2	307	2–3/5/10	54.558	6.357	8.1	7.0
H325 A3	349	3–4/5/10	54.145	7.914	8.4	8.0
H325 A4	267	4–5/5/10	54.682	5.191	7.7	6.3
H325 A5	324	5–6/5/10	55.284	5.686	4.3	6.7
H325 A6	348	6–7/5/10	54.796	8.155	10.3	7.7
H325 A7	127	7/5/10	53.735	6.740	13.7	6.6
H331 A1	314	13–14/7/10	54.223	7.155	4.3	18.8
H331 A2	331	14–15/7/10	54.854	8.177	9.8	20.4
H331 A3	272	15–16/7/10	53.908	7.480	9.3	18.9
H331 A4	243	16–17/7/10	55.029	6.529	8.7	17.3
H331 A5	322	17–18/7/10	55.319	4.704	8.8	15.4
H331 A6	311	18–19/7/10	54.682	5.420	8.2	17.0
H331 A7	42	19–19/7/10	55.101	7.751	3.9	19.0

Table S2. Detailed information on seawater sampling. Latitude and longitude are mean sampling stations. Water temperature (T_W), air temperature (T_A), wind speed and salinity represent the mean values during sampling.

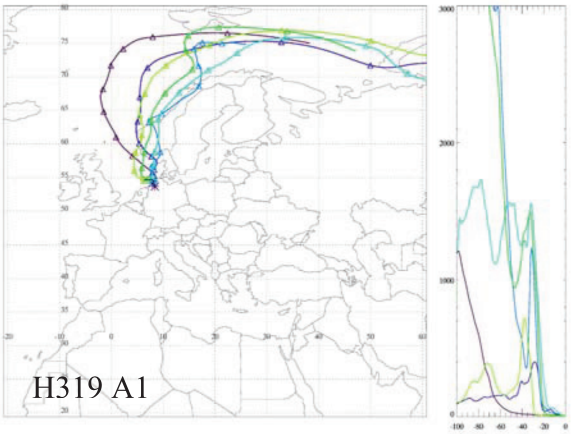
Sample I.D.	Volume (L)	Date	Latitude (°N)	Longitude (°E)	Wind speed (m/s)	T_W (°C)	T_A (°C)	Salinity (psu)
H319 W1	105	4/3/10	54.235	8.248	10.1	1.0	0.5	30.1
H319 W2	192	5/3/10	54.440	6.371	7.5	3.5	2.6	34.1
H319 W3	152	5/3/10	53.977	6.599	10.9	2.5	2.3	32.6
H319 W4	214	6/3/10	55.004	7.502	8.7	2.1	–0.7	34.1
H319 W5	196	6/3/10	55.052	6.701	5.3	3.4	0.8	34.5
H319 W6	100	7/3/10	54.205	8.256	6.0	1.0	0.8	30.0
H319 W7	106	8/3/10	54.718	8.128	2.2	0.4	–2.9	30.9
H319 W8	205	8/3/10	55.146	7.531	1.9	1.9	0.7	33.9
H319 W9	226	9/3/10	55.396	4.558	6.7	3.9	3.3	34.5
H319 W10	201	9/3/10	55.745	3.832	7.0	3.4	3.5	34.5
H319 W11	217	10/3/10	54.679	6.278	2.6	3.6	1.5	34.4
H325 W1	94	1/5/10	54.095	7.910	5.3	7.7	7.4	31.9
H325 W2	144	2/5/10	54.226	7.088	4.9	7.9	6.8	32.5
H325 W3	209	2/5/10	54.343	6.360	6.3	7.7	6.9	33.5
H325 W4	202	3/5/10	54.451	7.496	9.4	7.7	8.3	31.7
H325 W5	167	3/5/10	54.145	7.914	6.6	8.4	8.5	30.1
H325 W6	212	4/5/10	54.679	6.324	10.6	7.0	6.1	33.9
H325 W7	138	4/5/10	54.681	5.232	7.9	7.1	6.9	34.5
H325 W8	189	5/5/10	55.399	4.490	3.0	7.4	6.0	34.5
H325 W9	184	5/5/10	55.155	5.053	2.1	8.2	6.5	34.6
H325 W10	164	6/5/10	55.128	7.662	8.9	7.8	6.8	n.a.
H325 W11	146	6/5/10	55.052	8.251	9.6	9.2	8.5	n.a.
H325 W12	65	7/5/10	53.771	7.030	14.1	9.1	6.6	32.1
H331 W1	100	13/7/10	54.101	7.903	2.4	18.6	18.3	31.0
H331 W2	124	14/7/10	54.442	6.365	2.6	18.2	18.5	33.0
H331 W3	185	14/7/10	54.990	6.337	3.1	18.6	19.2	33.5
H331 W4	127	15/7/10	54.615	8.133	10.8	20.0	18.7	30.2

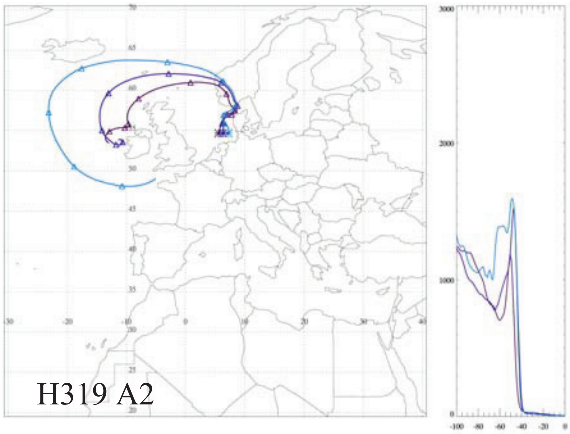
H331 W5	148	15/7/10	54.512	7.499	10.5	18.4	19.1	30.6
H331 W6	126	16/7/10	53.897	6.587	10.8	18.0	19.7	31.9
H331 W7	204	16/7/10	54.294	6.359	10.2	16.8	17.5	33.0
H331 W8	164	17/7/10	55.230	7.143	8.2	16.5	17.2	33.1
H331 W9	196	17/7/10	55.326	5.814	9.2	16.2	15.3	34.1
H331 W10	185	18/7/10	55.468	4.362	7.1	15.3	15.3	34.3
H331 W11	194	18/7/10	55.164	5.011	8.8	15.9	16.2	34.2
H331 W12	153	19/7/10	54.680	6.730	7.1	17.2	18.0	32.4
H331 W13	169	19/7/10	55.054	7.501	5.0	17.6	18.5	31.2

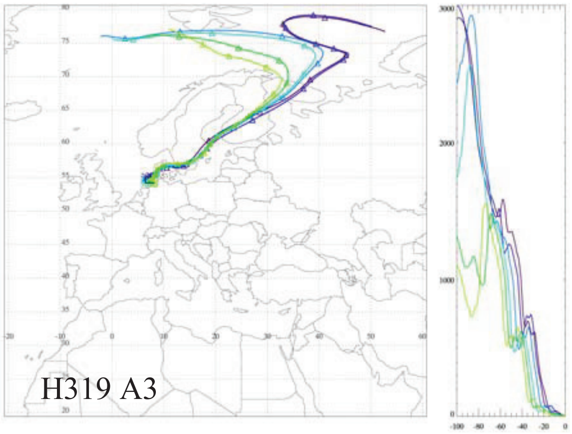
n.a. = not available

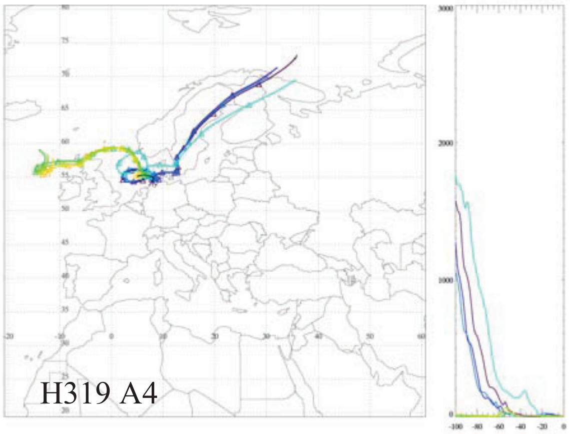
Table S2. Detailed information on water sampling in the rivers Elbe and Weser and their estuaries.

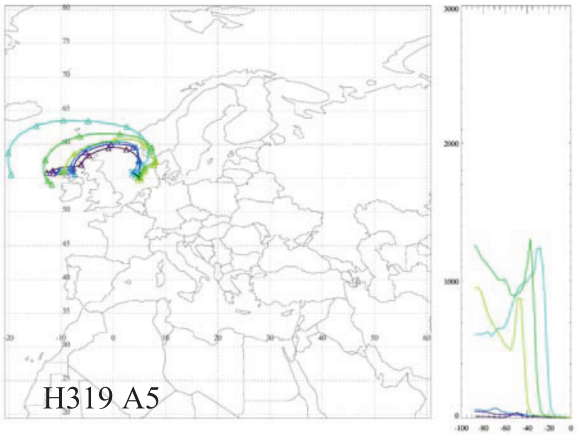
Sample I.D.	Watersystem	Date	Latitude (°N)	Longitude (°E)
E1	Elbe	22/2/11	53.544	9.876
E2	Elbe	22/2/11	53.668	9.512
E3	Elbe	22/2/11	53.882	9.225
E4	Elbe mouth	22/2/11	53.846	8.787
NS1	North Sea	23/2/11	53.985	8.351
NS2	North Sea	24/2/11	54.042	8.470
NS3	Weser mouth	23/2/11	53.538	8.583
WE1	Weser	24/2/11	53.540	8.572











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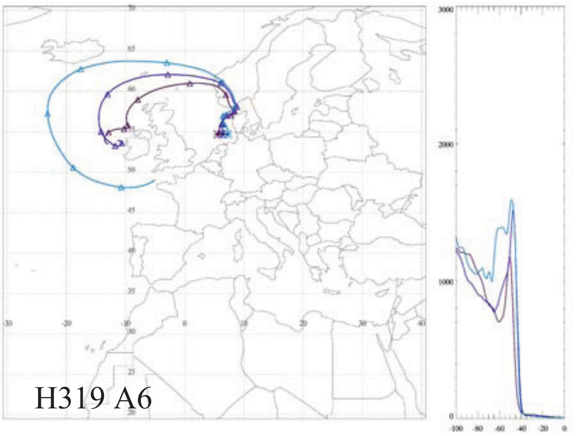

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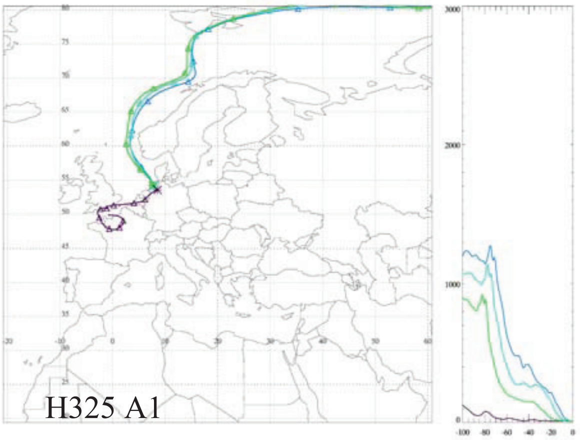

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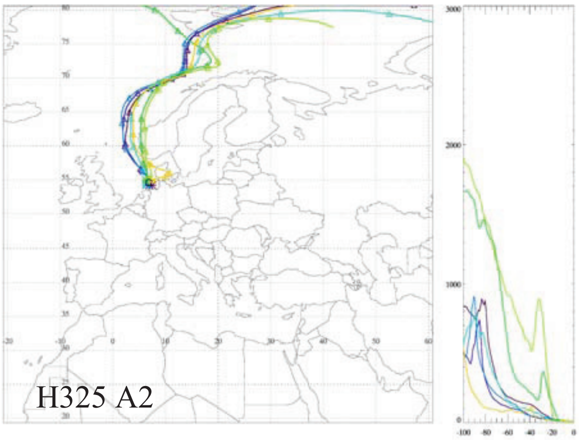

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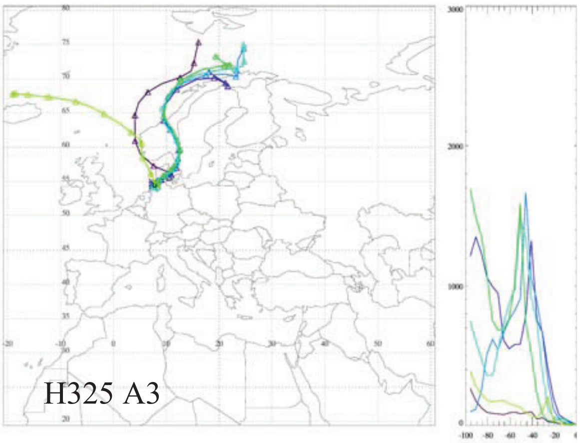

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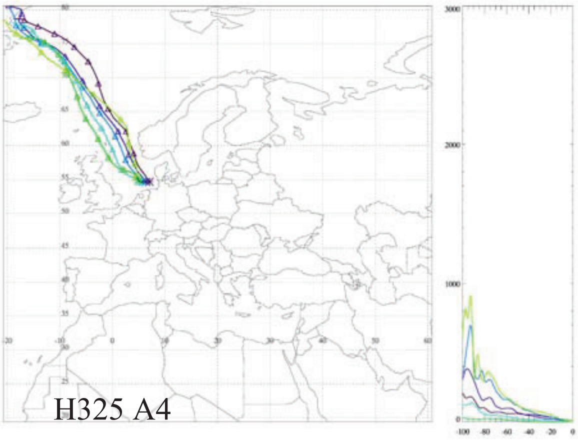

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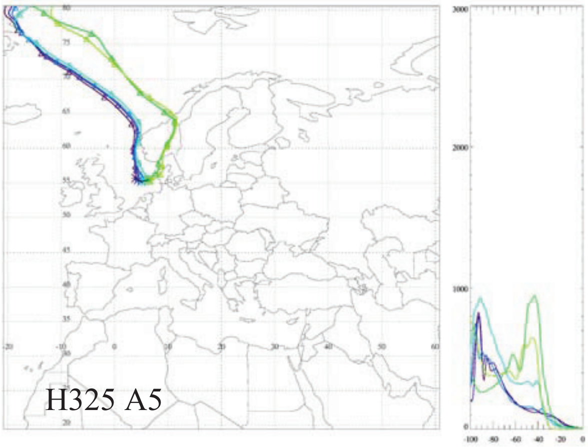

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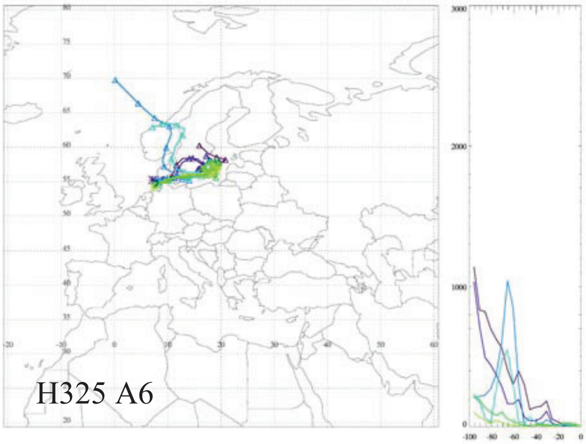

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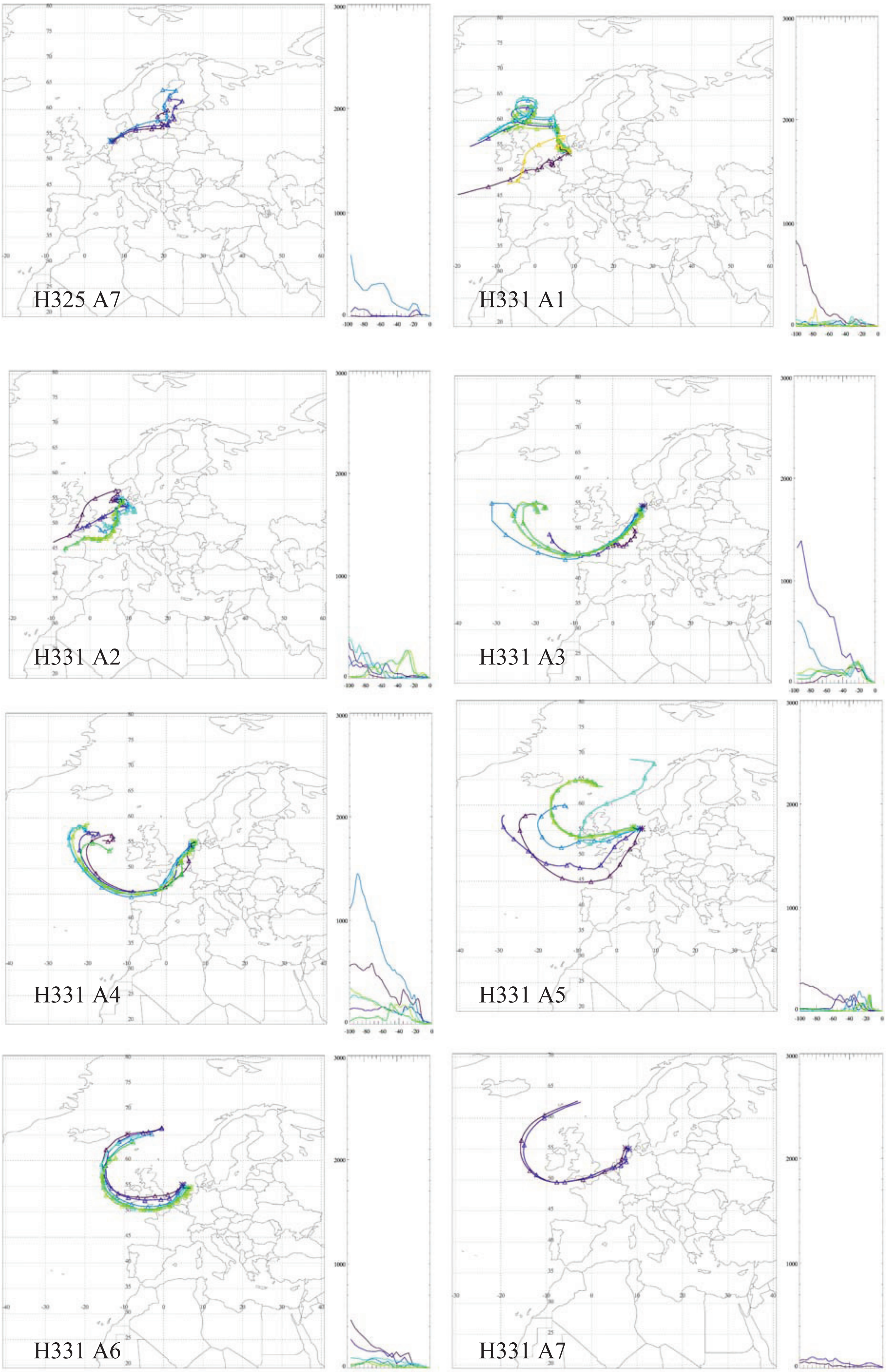

Figure S1. 120 h air mass back trajectories (4 h steps) and altitudinal profiles of the air mass parcels for the cruises H319, H325 and H331. The black line indicates the cruise leg.

Table S4. Individual blank values in air and seawater in pg absolute.

	H319				H325				H331			
	air		water		air		water		air		water	
	column	filter	column	filter	column	filter	column	filter	column	filter	column	filter
BDE–47	3.9 ± 0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.7 ± 0.2	n.d.	n.d.	n.d.
BDE–99	3.9 ± 2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5 ± 1.4	n.d.	n.d.	n.d.
BDE–209	231 ± 158	70 ± 7	60 ± 5	46 ± 2	34 ± 8	27 ± 6	36 ± 14	51 ± 16	30 ± 11	22 ± 17	25 ± 8	17 ± 2
DPTE	20 ± 11	17 ± 2	19 ± 4	9.3 ± 1.7	16 ± 6	10±2	14 ± 5	13 ± 5	27 ± 13	15 ± 2	10 ± 1	27 ± 4
HBB	4.8 ± 4.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
synDP	8.3 ± 9.3	2.0 ± 0.9	n.d.	n.d.	16 ± 26	0.9 ± 0.4	3.5 ± 1.9	n.d.	2.0 ± 2.2	1.1 ± 0.2	2.6 ± 2.4	4.1 ± 2.9
antiDP	5.0 ± 5.0	n.d.	n.d.	n.d.	4.5 ± 6.1	1.0 ± 0.3	n.d.	n.d.	1.1 ± 0.3	0.8 ± 0.3	0.3 ± 0.5	1.0 ± 0.5

BDE–28, –66, –85, –100, –153, –154, –183, PBBz, PBT, PBEB, TBPH, EHTBB, BTBPE, aCl10DP and aCl11DP were not detected in any blanks

Table S5. Individual blank values in surface water in pg L^{-1}.

	column	filter
BDE–47	0.77 ± 0.14	n.d.
BDE–99	0.57 ± 0.49	0.34 ± 0.48
BDE–209	11 ± 19	26 ± 18
DPTE	6.5 ± 1.9	1.5 ± 0.9

BDE–28, –66, –85, –100, –153, –154, –183, synDP and antiDP were not detected in any blanks

Table S6. Method detection limits (in pg m^{-3} for air samples and pg L^{-1} for seawater samples). MDLs were calculated from mean field blank values plus three times the standard deviation or based on instrumental S/N ratios of 3 if no blank was detected. Mean sample volumes of 300 m³ and 150 L were estimated for air and seawater samples, respectively.

	H319				H325				H331			
	air		water		air		water		air		water	
	column	filter	column	filter	column	filter	column	filter	column	filter	column	filter
BDE–28	0.04[a]	0.04[a]	0.08[a]	0.08[a]	0.04[a]	0.04[a]	0.08[a]	0.08[a]	0.04[a]	0.04[a]	0.08[a]	0.08[a]
BDE–47	0.02	0.04[a]	0.07[a]	0.07[a]	0.04[a]	0.04[a]	0.07[a]	0.07[a]	0.01	0.04[a]	0.07[a]	0.07[a]
BDE–66	0.06[a]	0.06[a]	0.12[a]	0.12[a]	0.06[a]	0.06[a]	0.12[a]	0.12[a]	0.06[a]	0.06[a]	0.12[a]	0.12[a]
BDE–85	0.05[a]	0.05[a]	0.1[a]	0.1[a]	0.05[a]	0.05[a]	0.1[a]	0.1[a]	0.05[a]	0.05[a]	0.1[a]	0.1[a]
BDE–99	0.04	0.02[a]	0.04[a]	0.04[a]	0.02[a]	0.02[a]	0.04[a]	0.04[a]	0.02	0.02[a]	0.04[a]	0.04[a]
BDE–100	0.01[a]	0.01[a]	0.03[a]	0.03[a]	0.01[a]	0.01[a]	0.03[a]	0.03[a]	0.01[a]	0.01[a]	0.03[a]	0.03[a]
BDE–153	0.03[a]	0.03[a]	0.05[a]	0.05[a]	0.03[a]	0.03[a]	0.05[a]	0.05[a]	0.03[a]	0.03[a]	0.05[a]	0.05[a]
BDE–154	0.01[a]	0.01[a]	0.03[a]	0.03[a]	0.01[a]	0.01[a]	0.03[a]	0.03[a]	0.01[a]	0.01[a]	0.03[a]	0.03[a]
BDE–183	0.02[a]	0.02[a]	0.04[a]	0.04[a]	0.02[a]	0.02[a]	0.04[a]	0.04[a]	0.02[a]	0.02[a]	0.04[a]	0.04[a]
BDE–209	2.4	0.3	0.5	0.35	0.19	0.15	0.52	0.66	0.20	0.25	0.34	0.14
PBBz	0.004[a]	0.004[a]	0.008[a]	0.008[a]	0.004[a]	0.004[a]	0.008[a]	0.008[a]	0.004[a]	0.004[a]	0.008[a]	0.008[a]
PBT	0.007[a]	0.007[a]	0.014[a]	0.014[a]	0.007[a]	0.007[a]	0.014[a]	0.014[a]	0.007[a]	0.007[a]	0.014[a]	0.014[a]
PBEB	0.005[a]	0.005[a]	0.01[a]	0.01[a]	0.005[a]	0.005[a]	0.01[a]	0.01[a]	0.005[a]	0.005[a]	0.01[a]	0.01[a]
DPTE	0.18	0.08	0.21	0.095	0.12	0.05	0.20	0.18	0.22	0.06	0.08	0.25
HBB	0.06	0.005[a]	0.01[a]	0.01[a]	0.005[a]	0.005[a]	0.01[a]	0.01[a]	0.005[a]	0.005[a]	0.01[a]	0.01[a]
TBPH	0.15[a]	0.15[a]	0.30[a]	0.30[a]	0.15[a]	0.15[a]	0.30[a]	0.30[a]	0.15[a]	0.15[a]	0.30[a]	0.30[a]
EHTBB	0.04[a]	0.04[a]	0.08[a]	0.08[a]	0.04[a]	0.04[a]	0.08[a]	0.08[a]	0.04[a]	0.04[a]	0.08[a]	0.08[a]
BTBPE	0.2[a]	0.2[a]	0.4[a]	0.4[a]	0.2[a]	0.2[a]	0.4[a]	0.4[a]	0.2[a]	0.2[a]	0.4[a]	0.4[a]
aCl10DP	0.002[a]	0.002[a]	0.004[a]	0.04[a]	0.002[a]	0.002[a]	0.004[a]	0.04[a]	0.002[a]	0.002[a]	0.004[a]	0.04[a]
aCl11DP	0.008[a]	0.008[a]	0.016[a]	0.016[a]	0.008[a]	0.008[a]	0.016[a]	0.016[a]	0.008[a]	0.008[a]	0.016[a]	0.016[a]
synDP	0.12	0.005	0.01[a]	0.01[a]	0.3	0.007	0.06	0.01[a]	0.03	0.005	0.07	0.09
antiDP	0.02	0.005[a]	0.01[a]	0.01[a]	0.08	0.005	0.01[a]	0.01[a]	0.007	0.006	0.01	0.02

[a] calculated via instrumental limits at a S/N–ratio of 3

Table S7. Method detection limits in pg L^{-1} for riverine and estuarine surface water samples. MDLs were calculated from mean field blank values plus three times the standard deviation or based on instrumental S/N ratios of 3 if no blank was detected.

	column	filter
BDE–47	1.2	1.7[a]
BDE–66	2.4[a]	2.4[a]
BDE–85	2.4[a]	2.4[a]
BDE–99	2.0	1.8
BDE–100	0.8[a]	0.8[a]
BDE–153	1.6[a]	1.6[a]
BDE–154	1.1[a]	1.1[a]
BDE–183	1.3[a]	1.3[a]
BDE–209	68.2	79.7
DPTE	12.1	4.2
synDP	0.13[a]	0.13[a]
antiDP	0.12[a]	0.12[a]

[a]calculated via instrumental limits at a S/N–ratio of 3

Table S8. Individual concentrations of PBDEs, other BFRs and DP in pg m^{-3} and f_{syn} value in the atmosphere. gas. = gaseous phase, part. = particulate phase. Concentrations <MDL were treated as not detected (n.d.).

		BDE-47	BDE-99	BDE-100	BDE-153	BDE-183	BDE-209	$\sum_{10}$PBDEs	PBBz	PBT	DPTE	HBB	synDP	antiDP	ΣDP	f_{syn}
H319 A1	**gas.**	0.15	0.07	0.02	n.d.	n.d.	n.d.	0.23	0.37	0.06	1.4	3.9	0.21	0.40	0.61	0.34
	part.	0.36	0.22	0.04	n.d.	0.04	0.46	1.1	n.d.	n.d.	0.59	0.32	0.51	0.68	1.2	0.43
H319 A2	**gas.**	0.17	0.07	0.02	0.04	0.13	2.4	2.8	0.14	0.06	1.9	2.3	0.84	1.00	1.8	0.46
	part.	0.56	0.20	0.04	n.d.	0.06	7.0	7.9	n.d.	n.d.	0.22	0.52	0.99	0.45	1.4	0.69
H319 A3	**gas.**	0.07	0.03	n.d.	n.d.	n.d.	n.d.	0.11	0.28	0.06	0.31	4.1	n.d.	n.d.	n.d.	n.d.
	part.	0.15	0.09	0.02	n.d.	n.d.	0.38	0.65	n.d.	n.d.	0.34	0.41	0.16	0.07	0.23	0.69
H319 A4	**gas.**	0.18	0.06	n.d.	n.d.	n.d.	n.d.	0.24	0.35	0.07	0.97	6.2	0.10	n.d.	0.10	S
	part.	0.06	0.06	n.d.	n.d.	0.05	0.60	0.78	n.d.	n.d.	0.13	0.15	0.17	0.04	0.21	0.83
H319 A5	**gas.**	0.14	0.04	n.d.	n.d.	n.d.	n.d.	0.18	0.21	0.08	0.65	4.1	n.d.	n.d.	n.d.	n.d.
	part.	0.06	0.04	n.d.	n.d.	0.02	n.d.	0.13	n.d.	n.d.	0.07	0.36	0.20	0.03	0.23	0.87
H319 A6	**gas.**	0.20	0.06	n.d.	n.d.	0.09	n.d.	0.34	0.36	0.08	0.52	5.5	0.23	n.d.	0.23	S
	part.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	0.12	0.27	0.08	0.36	0.77
H325 A1	**gas.**	0.44	0.19	0.06	n.d.	n.d.	1.4	2.0	0.24	0.09	1.5	1.1	2.2	0.47	2.7	0.82
	part.	0.28	0.19	n.d.	n.d.	0.10	0.82	1.4	n.d.	n.d.	0.16	0.04	2.7	0.30	3.0	0.90
H325 A2	**gas.**	0.13	0.04	n.d.	n.d.	n.d.	0.24	0.41	0.05	0.03	0.31	0.48	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	0.06	0.01	0.17	0.06	0.23	0.74
H325 A3	**gas.**	0.14	0.06	n.d.	n.d.	0.10	0.65	0.95	0.08	0.05	0.23	0.24	n.d.	n.d.	n.d.	n.d.
	part.	0.07	0.05	n.d.	n.d.	n.d.	0.29	0.42	n.d.	n.d.	0.06	0.01	0.29	0.05	0.34	0.85
H325 A4	**gas.**	0.06	0.03	n.d.	n.d.	n.d.	0.24	0.33	n.d.	n.d.	0.23	0.15	n.d.	n.d.	n.d.	n.d.
	part.	0.23	0.07	0.02	n.d.	n.d.	0.31	0.63	n.d.	n.d.	0.10	n.d.	0.16	0.06	0.22	0.71
H325 A5	**gas.**	0.04	0.03	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	0.02	0.15	0.12	n.d.	n.d.	n.d.	n.d.
	part.	0.05	0.04	n.d.	n.d.	n.d.	0.21	0.31	n.d.	n.d.	0.05	n.d.	0.11	0.05	0.16	0.69
H325 A6	**gas.**	0.06	0.03	n.d.	n.d.	n.d.	0.27	0.35	n.d.	0.06	0.10	0.18	n.d.	n.d.	n.d.	n.d.
	part.	0.06	0.06	n.d.	n.d.	n.d.	0.23	0.35	n.d.	n.d.	0.08	0.03	0.07	0.06	0.13	0.54
H325 A7	**gas.**	0.08	0.05	0.00	n.d.	n.d.	0.80	0.94	0.04	0.02	n.d.	0.09	4.4	12.1	16.6	0.27
	part.	0.70	0.33	0.10	n.d.	n.d.	n.d.	1.1	n.d.	n.d.	0.16	n.d.	2.3	3.4	5.7	0.41
H331 A1	**gas.**	0.30	0.13	0.04	n.d.	n.d.	0.30	0.76	0.19	0.12	2.3	0.65	0.15	0.06	0.21	0.70
	part.	n.d.	n.d.	n.d.	n.d.	0.32	1.4	1.7	n.d.	0.12	0.12	0.01	0.35	0.33	0.68	0.51
H331 A1	**gas.**	0.30	0.12	0.03	n.d.	n.d.	n.d.	0.45	0.81	0.06	1.6	0.30	0.06	0.07	0.13	0.44
	part.	0.00	0.02	n.d.	n.d.	n.d.	3.5	3.6	n.d.	n.d.	n.d.	0.02	0.54	0.55	1.1	0.50
H331 A2	**gas.**	0.35	0.13	0.03	n.d.	n.d.	0.30	0.80	0.42	0.09	0.78	0.34	0.49	0.50	0.99	0.50
	part.	0.05	0.10	n.d.	n.d.	0.06	1.2	1.4	n.d.	n.d.	0.16	0.02	0.86	0.47	1.3	0.65
H331 A3	**gas.**	0.32	0.09	0.02	n.d.	n.d.	n.d.	0.43	0.23	0.08	0.29	0.39	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.96	0.96	n.d.	n.d.	n.d.	0.01	0.13	0.05	0.18	0.72
H331 A4	**gas.**	0.14	0.09	0.02	n.d.	n.d.	0.55	0.80	n.d.	0.02	n.d.	0.13	0.91	0.53	1.4	0.63
	part.	n.d.	0.03	n.d.	n.d.	0.10	5.1	5.3	n.d.	n.d.	n.d.	n.d.	0.60	0.42	1.0	0.59
H331 A5	**gas.**	0.09	n.d.	n.d.	n.d.	n.d.	0.30	0.39	0.09	n.d.	2.8	n.d.	0.03	0.09	0.68	0.68
	part.	n.d.	0.05	n.d.	n.d.	0.03	0.30	0.38	n.d.	n.d.	n.d.	0.01	0.12	0.03	0.15	0.79
H331 A6	**gas.**	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	2.1	n.d.	n.d.	n.d.	n.d.	0.90	0.49	1.4	0.65

n.d. = not detected
S = only synDP detected

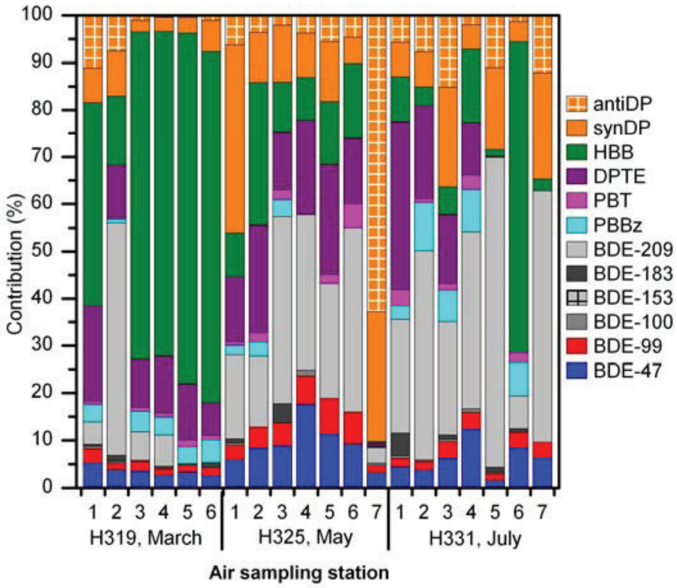

Figure S2. Composition profile of PBDEs, other BFRs and DP in the atmosphere.

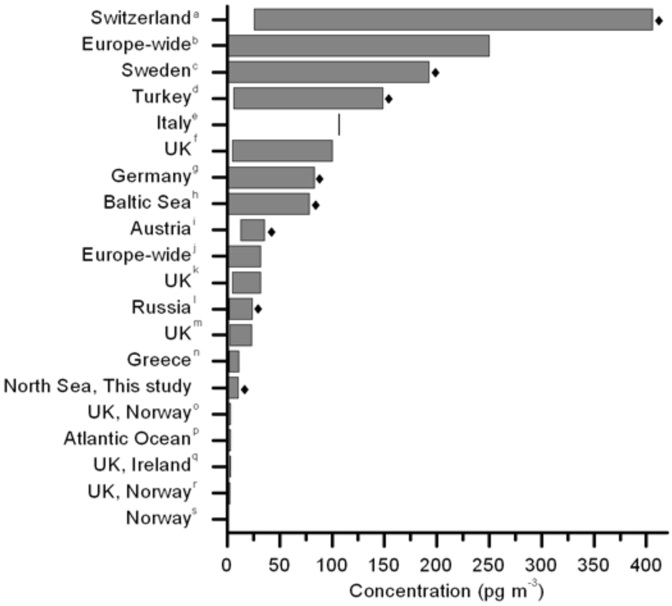

Figure S3. ∑PBDEs concentration ranges in the European outdoor atmosphere given in the literature (excluding the European Arctic) in pg m^{-3}. Bars marked with a diamond include the congener BDE–209, the other bars not. [a]Bogdal et al., 2010; [b]Jaward et al., 2004a; [c]Agrell et al., 2004 (only urban reference site); [d]Cetin and Odabasi, 2008; [e]Mariani et al., 2008; [f]Farrar et al., 2004 (including a cobustion event); [g]Knoth et al., 2010; [h]ter Schure et al., 2004; [i]Gans et al., 2007; [j]Pozo et al., 2008; [k]Moeckel et al., 2008; [l]Chernyak et al., 2008 (excluding the Arctic station); [m]Harrad and Hunter, 2006; [n]Iacovidou et al., 2009 (only gaseous phase); [o]Gioia et al., 2006; [p]Xie et al., 2011 (only North Atlantic stations); [q]Lee et al., 2004; [r]Jaward et al., 2004b; [s]Rossland et al., 2006 (only particulate phase)

Table S9. Individual concentrations of PBDEs, other BFRs and DP in pg L^{-1} and f_{syn} value in seawater. diss. = dissolved phase, part. = particulate phase. Concentrations <MDL were treated as not detected (n.d.).

		BDE-47	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-183**	**BDE-209**	**$\sum_{10}$PBDEs**	**DPTE**	**HBB**	**synDP**	**antiDP**	**ΣDP**	**f_{syn}**
H319 W1	**diss.**	0.24	0.14	0.00	n.d.	n.d.	0.85	1.2	1.3	0.06	0.95	0.16	1.1	0.85
	part.	n.d.	0.07	n.d.	n.d.	n.d.	1.4	1.5	0.25	n.d.	0.27	0.14	0.41	0.67
H319 W2	**diss.**	0.20	0.18	0.03	0.09	0.18	0.83	1.5	0.84	0.03	0.63	0.12	0.75	0.84
	part.	0.08	0.09	n.d.	0.13	n.d.	2.2	2.5	0.13	n.d.	0.31	0.22	0.54	0.58
H319 W3	**diss.**	0.17	0.11	n.d.	0.10	0.08	1.2	1.6	0.63	0.02	0.43	0.27	0.70	0.62
	part.	0.11	0.17	n.d.	0.30	n.d.	8.1	8.7	0.15	n.d.	0.43	0.18	0.61	0.71
H319 W4	**diss.**	0.12	0.09	n.d.	n.d.	n.d.	0.47	0.69	0.39	0.01	0.34	0.18	0.52	0.65
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.2	n.d.	n.d.	0.04	0.05	0.09	0.45
H319 W5	**diss.**	0.12	0.11	0.03	0.04	0.10	0.54	0.93	0.36	0.01	0.09	0.01	0.10	0.86
	part.	0.06	0.19	n.d.	0.05	n.d.	0.46	0.76	0.11	n.d.	n.d.	n.d.	n.d.	n.d.
H319 W6	**diss.**[a]													
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	6.2	6.2	n.d.	n.d.	0.21	0.12	0.32	0.64
H319 W7	**diss.**	0.15	0.07	n.d.	n.d.	n.d.	n.d.	0.22	0.66	n.d.	0.43	0.16	0.59	0.73
	part.	n.d.	0.07	n.d.	0.09	n.d.	4.3	4.4	0.15	n.d.	0.15	0.40	0.55	0.28
H319 W8	**diss.**	0.09	0.05	n.d.	n.d.	n.d.	n.d.	0.13	0.44	n.d.	0.13	0.02	0.16	0.85
	part.[a]													
H319 W9	**diss.**	0.16	0.09	n.d.	n.d.	n.d.	n.d.	0.25	0.31	n.d.	0.07	0.02	0.10	0.75
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.45	n.d.	n.d.	0.09	0.06	0.15	0.60
H319 W10	**diss.**	0.10	0.03	n.d.	n.d.	n.d.	n.d.	0.13	0.26	n.d.	0.05	n.d.	0.05	S
	part.	n.d.	0.03	n.d.	n.d.	n.d.	0.59	0.62	0.07	n.d.	0.41	0.03	0.44	0.94
H319 W11	**diss.**	0.09	0.06	n.d.	n.d.	n.d.	n.d.	0.15	0.26	n.d.	0.05	0.01	0.07	0.80
	part.	n.d.	0.03	n.d.	n.d.	n.d.	0.53	0.57	0.08	n.d.	0.09	0.10	0.18	0.47
H325 W1	**diss.**	0.32	0.12	n.d.	n.d.	n.d.	n.d.	0.44	1.0	0.02	0.41	0.06	0.47	0.88
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7	1.7	n.d.	n.d.	0.68	0.07	0.75	0.90
H325 W2	**diss.**	0.16	0.06	n.d.	n.d.	n.d.	n.d.	0.23	0.61	n.d.	2.1	0.16	2.3	0.93
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.8	0.63	15.4	0.96
H325 W3	**diss.**	0.15	0.06	n.d.	n.d.	n.d.	0.65	0.86	0.38	n.d.	1.7	0.17	1.9	0.91
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.36	0.07	0.43	0.83
H325 W4	**diss.**	0.16	0.07	n.d.	n.d.	n.d.	n.d.	0.23	0.40	n.d.	0.30	0.05	0.35	0.87
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	0.04	0.26	0.85
H325 W5	**diss.**	0.11	0.05	n.d.	n.d.	n.d.	n.d.	0.15	0.35	n.d.	0.33	0.03	0.37	0.91
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.80	0.80	n.d.	n.d.	0.22	0.04	0.26	0.86
H325 W6	**diss.**	0.07	n.d.	n.d.	n.d.	n.d.	0.50	0.58	0.19	n.d.	0.18	0.02	0.20	0.89
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.54	0.54	n.d.	n.d.	0.45	0.41	0.86	0.52
H325 W7	**diss.**	0.09	n.d.	n.d.	n.d.	n.d.	0.62	0.71	0.21	n.d.	0.33	0.03	0.36	0.91
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	0.02	0.22	0.90
H325 W8	**diss.**	0.08	0.04	n.d.	n.d.	n.d.	n.d.	0.12	0.19	n.d.	0.12	0.01	0.13	0.89
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	0.07	0.20	0.68
H325 W9	**diss.**	0.13	0.15	n.d.	n.d.	n.d.	n.d.	0.29	0.18	n.d.	0.34	0.02	0.36	0.95
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	0.01	0.05	0.77
H325 W10	**diss.**	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.22	n.d.	0.23	0.02	0.25	0.91
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.73	0.73	n.d.	n.d.	0.08	0.02	0.10	0.77
H325 W11	**diss.**	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	0.21	n.d.	0.11	0.01	0.13	0.90
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	1.4	n.d.	n.d.	0.11	0.17	0.28	0.38
H325 W12	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.33	n.d.	0.31	n.d.	0.31	S
	part.[a]													
H331 W1	**diss.**	1.1	1.1	0.18	0.06	0.20	1.1	3.8	5.7	0.08	5.7	0.53	6.2	0.92
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	3.1	3.1	n.d.	n.d.	1.4	0.70	2.1	0.66
H331 W2	**diss.**	0.21	0.36	n.d.	n.d.	n.d.	0.63	1.2	0.80	0.02	0.77	0.06	0.82	0.93
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	1.5	n.d.	n.d.	0.33	0.17	0.50	0.66
H331 W3	**diss.**	0.11	0.07	n.d.	n.d.	n.d.	n.d.	0.18	0.39	n.d.	0.31	0.03	0.33	0.92
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.31	0.31	n.d.	n.d.	0.16	0.05	0.21	0.78
H331 W4	**diss.**	0.52	0.34	n.d.	n.d.	n.d.	0.53	1.4	0.64	n.d.	2.3	0.12	2.4	0.95
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	2.5	2.5	n.d.	n.d.	0.76	1.5	2.3	0.33
H331 W5	**diss.**	0.22	0.20	0.04	n.d.	n.d.	0.93	1.4	0.71	n.d.	0.72	0.09	0.81	0.89
	part.	n.d.	0.05	n.d.	n.d.	n.d.	2.3	2.4	n.d.	n.d.	1.2	0.74	1.9	0.62
H331 W6	**diss.**	0.16	0.15	n.d.	n.d.	n.d.	0.51	0.81	0.36	n.d.	0.46	0.04	0.50	0.91
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	3.1	3.1	n.d.	n.d.	0.46	0.11	0.57	0.80
H331 W7	**diss.**	0.12	0.07	n.d.	n.d.	n.d.	0.26	0.46	0.19	n.d.	0.07	n.d.	0.07	S
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.58	0.58	n.d.	n.d.	0.13	0.11	0.25	0.54
H331 W8	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	0.53	0.53	0.32	n.d.	0.10	n.d.	0.10	S
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.80	0.80	n.d.	n.d.	0.12	0.08	0.20	0.58
H331 W9	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	0.36	0.03	0.39	0.93
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.39	0.39	n.d.	n.d.	0.08	0.16	0.24	0.35
H331 W10	**diss.**	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	0.21	0.02	0.23	0.93
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	0.42	n.d.	n.d.	0.13	0.09	0.22	0.57
H331 W11	**diss.**	0.29	0.71	0.11	n.d.	n.d.	0.29	1.4	0.11	n.d.	0.15	0.04	0.19	0.79
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	0.42	0.09	n.d.	0.32	0.17	0.49	0.65
H331 W12	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.19	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.2	0.11	n.d.	0.13	0.06	0.19	0.70
H331 W13	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	0.29	0.06	0.35	0.84
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

S = only synDP detected

[a] not analyzed

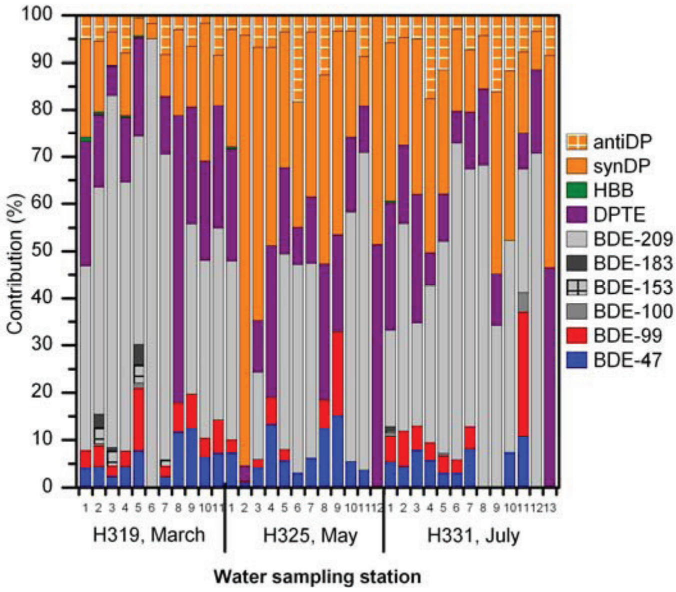

Figure S4. Composition profile of PBDEs, other BFRs and DP in seawater.

Table S10. Individual concentrations of PBDEs, DPTE and DP in pg L^{-1} and f_{syn} value in surface water of the rivers Elbe and Weser and their estuaries. diss. = dissolved phase, part. = particulate phase. Concentrations <MDL were treated as not detected (n.d.).

		BDE-47	BDE-99	BDE-100	BDE-183	BDE-209	$\sum_{10}$PBDEs	DPTE	synDP	antiDP	$\sum$DP	f_{syn}
E1	**diss.**	n.d.	3.3	n.d.	n.d.	n.d.	3.3	22.0	1.1	1.6	2.7	0.41
	part.	3.3	6.9	0.94	1.6	701	714	47.8	55.3	47.3	103	0.54
E2	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18.5	0.97	4.4	5.4	0.18
	part.	2.4	4.6	n.d.	n.d.	233	240	20.7	16.0	38.1	54.1	0.30
E3	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.52	1.0	1.5	0.34
	part.	2.8	4.7	n.d.	n.d.	6785	6792	23.8	17.0	76.4	93.4	0.18
E4	**diss.**[a]											
	part.	2.3	3.6	n.d.	n.d.	223	229	11.9	10.5	27.2	37.7	0.28
NS1	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.70	0.8	1.5	0.46
	part.	n.d.	n.d.	n.d.	n.d.	99.2	99	n.d.	7.2	23.5	30.7	0.24
NS2	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.64	1.3	1.9	0.34
	part.	n.d.	n.d.	n.d.	n.d.	116	116	n.d.	3.5	6.4	9.9	0.36
NS3	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13.1	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	2.4	n.d.	1.4	151	155	8.0	20.7	47.2	67.9	0.30
WE1	**diss.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	1.6	2.8	0.42
	part.	2.3	3.8	n.d.	n.d.	159	165	12.8	10.1	22.7	32.8	0.31

n.d. = not detected

[a] not analyzed

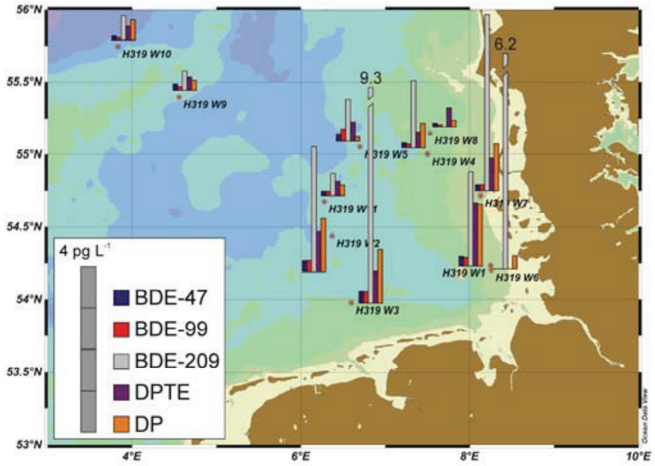

Figure S5. Spatial distribution of major BFRs and DP in seawater during H319. Note that for station H319 W6 only the particulate and for station H319 W8 only the dissolved phase was analyzed.

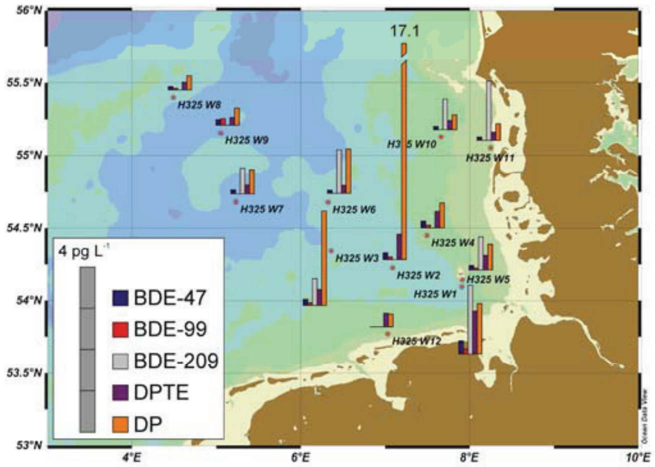

Figure S6. Spatial distribution of major BFRs and DP in seawater during H325. Note that for station H325 W12 only the dissolved phase was analyzed.

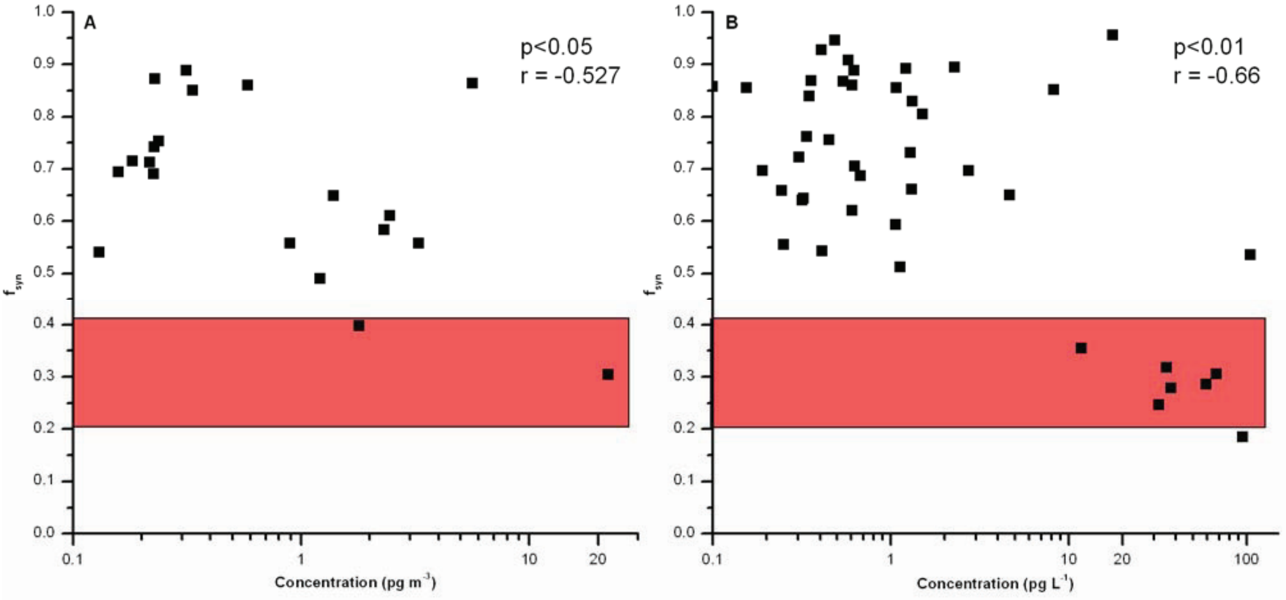

Figure S7. The f_{syn} value in the atmosphere (A) and seawater and riverine water (B) of the North Sea and the rivers Elbe and Weser and their estuaries as a function of ∑DP concentration. The red box shows the reported range of technical f_{syn} values (Wang et al., 2010).

Comment on the calculation of the air–seawater gas exchange

The air seawater exchange was calculated based on following eq S1 (Bidleman and McConnell, 1995; Liss and Slater, 1974)

$$F_{AW} = K_{OL}\left(C_W - \frac{C_A}{H'_{salt,T}} \right) \tag{S1}$$

where C_W and C_A are the dissolved and gaseous concentrations in water and air (pg m^{-3}), respectively, $H'_{salt,T}$ is the dimensionless Henry's Law constant defined as $H' = H/RT$ (R = gas constant, T = Temperature) at the given water temperature. The dimensionless Henry's Law constant was corrected by the salinity using eq S2 (Schwarzenbach et al., 2003)

$$H'_{salt,T} = H' \times 10^{K_S C_S} \tag{S2}$$

where C_S is the salt concentration (mol L^{-1}) and K_S is the Setschenow constant (L mol^{-1}) which was taken from Cetin and Odabasi (2005) for BDE–47 and –99, respectively, and calculated for DPTE following eq S3 (Ni and Yalkowsky, 2003)

$$K_S = 0.04 \log K_{OW} + 0.114 \tag{S3}$$

and corrected by the salinity according to Schwarzenbach et al. (2003). The Henry's Law constant of BDE–47 and –99 and their temperature dependence was taken from Cetin and Odabasi, 2005 and the Henry's Law constant. Since there are no measured or predicted Henry's Law constant for DPTE available, we estimated it to be 0.0478 Pa m^3 mol^{-1} using EPI Suite 4.0 developed by U.S EPA (U.S. EPA, 2010) and the temperature dependence was estimated to be similar to BDE–47. If C_A or C_W were not available, 2/3 of the MDL was used.

K_{OL} (m h^{-1}) is the gas phase overall mass transfer coefficient compromising the resistances to mass transfer in both water (K_W, m h^{-1}) and air (K_A, m h^{-1}) and is defined by:

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'} \tag{S4}$$

where (Hornbuckle et al., 1994):

$$k_A = (0.2U_{10} + 0.3) \times \left(\frac{D_{i,air}}{D_{H_2O,air}} \right)^{0.61} \times 36 \tag{S5}$$

$$k_W = (0.45{U_{10}}^{1.64}) \times \left(\frac{Sc_i}{Sc_{CO_2}} \right)^{-0.5} \times 0.01 \tag{S6}$$

D_{air} is the diffusity in air, U_{10} is the wind speed at 10 m height above sea level (m s^{-1}), and Sc is the water phase Schmidt number which was taken from Schwarzenbach et al. (2003) for CO_2. D_{air} was calculated using the method described by Fuller et al. (1966) and Sc for the BFRs was calculated using the method described by Hayduk and Laudi (1974). The molar volume of BDE–47, –99 which is needed for the calculation of $D_{i,air}$ was taken from Mackay et al. (2006) or calculated following Abraham and McGowan, (1987) for DPTE. The overall uncertainty of BDE–47, –99 was calculated with ± 51% based on an uncertainty of ± 40 % for K_{OL} (Cetin and Odabasi, 2005). The uncertainty of DPTE has to be estimated to be at least ± 500% since the uncertainties of both H' and K_{OL} are not known.

Comment on the calculation of the dry deposition

The dry particle–bound deposition flux F_d (F_d, pg m^{-2} day^{-1}) was calculated using eq S8

$$F_d = V_d C_p \tag{S8}$$

where V_d is the deposition velocity (m d^{-1}) and C_p is the concentration in the particulate phase (pg m^{-3}). The deposition velocity strongly depends on both meteorological parameter, size and physicochemical parameters of the airborne particle and of the pollutant itself *(16)*, especially for air masses transporting particles originating from urbanized and industrialized regions. For the investigated area no measured deposition velocities of the analyzed compounds are available. Castro–Jiménez et al. (2010) used a velocity of 0.2 cm s^{-1} for PCDD/Fs, representing marine aerosols influenced by continental sources in the Open Mediterranean Sea. Since the North Sea is influenced by continental sources, too, we used the value of 0.2 cm s^{-1} as deposition velocity. However, the differences in the dry particle–bound deposition velocities are still mainly resulted by the differences in the particulate concentrations of the analyzed BFRs and DP. Higher differences are to be expected if the differences of the deposition velocities, both spatially and between the different compounds would be know. Therefore, we estimate an uncertainty of a factor of 3 for the velocity, and consequently for the dry particle–bound deposition flux.

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Paper V

Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic

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Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic

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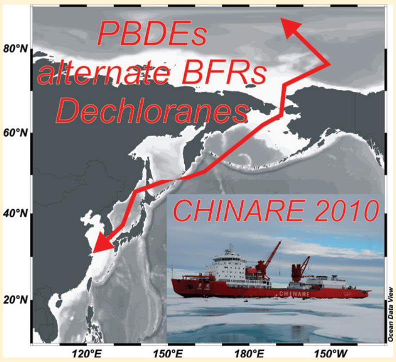
S *Supporting Information*



ABSTRACT: Marine boundary layer air and seawater samples taken during a polar expedition cruise from East China Sea to the Arctic were analyzed in order to compare the occurrence, distribution, and fate of the banned polybrominated diphenyl ethers (PBDEs) with their brominated alternatives as well as the chlorinated Dechloranes. The sum of PBDEs (Σ_{10}PBDEs) in the atmosphere ranged from 0.07 to 8.1 pg m^{-3} with BDE−209 being the dominating congener and from not detected (n.d.) to 0.6 pg L^{-1} in seawater. Alternate brominated flame retardants (BFRs), especially hexabromobenzene (HBB), (2,3−dibromopropyl−2,4,6−tribromophenyl ether (DPTE), pentabromotoluene (PBT), 2−ethylhexyl 2,3,4,5−tetrabromobenzoate (EHTBB), bis−(2−ethylhexyl)−tetrabromophthalate (TBPH), were detected in higher concentrations than PBDEs, even in the high Arctic (0.6 to 15.4 pg m^{-3} for sum of alternate BFRs), indicating the change of PBDEs toward alternate BFRs in the environmental predominance. In addition, Dechlorane Plus (DP) as well as Dechlorane 602, 603, and 604 were detected both in the atmosphere and in seawater. The highest concentrations as well as the highest compound variability were observed in East Asian samples suggesting the Asian continent as source of these compounds in the marine environment. The air−seawater exchange indicates strong deposition, especially of alternate BFRs, as well as dry particle−bound deposition of BDE−209 into the ocean.

INTRODUCTION

Halogenated, mainly brominated flame retardants (BFRs) have been applied in electronics, (building) foams, and furnishing since the 1960s.[1] Thereby, the polybrominated diphenyl ethers (PBDEs) have been the most scientifically, politically, and publicly focused group in the 2000s and are still the dominating species in terms of environmental research on halogenated flame retardants (HFRs). PBDEs are known to be harmful for the environment caused by their bioaccumulation potential, toxicity, persistence, and potential for atmospheric transport over (very) long distances[2,3] leading to "flame−proofing" of remote regions such as the Arctic environment.[4] Since the early 2000s, the production and usage of PBDEs has been strictly regulated and partly banned, i.e., voluntary production phase−out of Penta− and OctaBDE in 2004[5] and expected production phase−out of DecaBDE by 2012[6] in the United States (U.S.), and ban of Penta−, Octa− (2004), and DecaBDE (2008, only in electrical and electronic equipment) in the European Union (EU).[7] Finally, components of the Penta− and OctaBDE mixtures were included in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009 (www.pops.int).

Nevertheless, a global annual HFR production increase of ∼5% was reported[8] which can be traced back to increasing usage in Asia, in particular China,[9] with an annual increase of the BFR demand of 8% in 2005.[10] Non−PBDE BFRs include both BFRs which have been (only recently) developed as substitutes for the banned PBDEs (e.g., 2−ethylhexyl 2,3,4,5−tetrabromobenzoate (EHTBB), bis−(2−ethylhexyl)−tetrabromophthalate (TBPH)) as well as traditional non−PBDE BFRs such as hexabromobenzene (HBB) and pentabromotoluene (PBT) which have been produced and used similar to PBDEs for several decades. There is very little knowledge on their behavior in terms of persistence and long−range atmospheric transport (LRAT) in the environment which are important criteria for POPs, but models assessed a sufficient POP potential of some new BFRs to reach remote regions[11,12] or they were prioritized for further research in the (remote) environment.[13]

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Several non−PBDE BFRs have been investigated and detected in the environment, primarily in source regions such as urban areas or the indoor environment (e.g., 1,2−bis(2,4,6−tribromophenoxy) ethane (BTBPE),[14] TBPH,[15] HBB[16]), but also in non−source outdoor regions and even remote areas such as the Arctic and Antarctica,[2,17] again, indicating their LRAT potential. Another HFR, the highly chlorinated flame retardant Dechlorane Plus (DP), has been produced and likely unnoticed emitted into the environment for more than forty years. Since its first detection in the environment in 2006,[18] reports on DP in the environment increased rapidly, and it has been recently observed in the remote regions of the Arctic and Antarctica.[19] Nevertheless, data on the occurrence and environmental fate on non−PBDE BFRs and Dechloranes, in particular in remote regions, are still lacking.

In the present study, marine boundary layer air samples and seawater samples were taken during a polar expedition of the Chinese research vessel *Xuelong* from East China Sea to the high Arctic in 2010. The samples were analyzed for PBDEs, non−PBDEs BFRs, Dechlorane Plus and its transformation products, and the Dechloranes 602, 603, and 604 in order to investigate their occurrence and latitudinal distribution, and air−sea exchange including air−seawater gas exchange and dry particle−bound deposition, both with special consideration of the non−PBDEs HFRs compared to the banned PBDEs.

MATERIALS AND METHODS

Sampling Cruise. Onboard the Arctic expedition CHINARE2010 of the research ice−breaker *R/V Xuelong (Snow Dragon)* of the Polar Research Institute of China from June to September 2010, air and seawater samples were taken from the East China Sea to the high Arctic (33.23−84.5°N). Air samples (1−2 days, 17 samples) were taken via a high−volume air sampler placed in the front of the ship's upper deck. About 500 m^3 air was passed through a glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) to trap airborne particles followed by a self−packed PUF/Amberlite XAD−2 glass column. Both air column and filters were stored at −20 °C until analysis. Seawater samples (12−24 h, 18 samples) were taken by passing 176−1120 L seawater obtained by the ship's intake system through a GFF (GF/C, pore size: 1.2 μm) following self−packed Serdolit PAD−3 glass column. Seawater filter and columns were stored at −20 and 4 °C, respectively. Sampling parameters including date, position, temperature, and wind speed are included in Tables S1 and S2 in the Supporting Information (SI).

Extraction, Analysis, QC/QA. Extraction, clean−up, and analysis of the samples was done based on our previously published method[19,20] and is described in more detail in the SI. Three field blanks were run for each sample type, while blanks showed very low HFR values which were generally in the one− to two−digit absolute pg range (see Table S4 in the SI). Method detection limits (MDLs) ranged from 0.002 to 0.27 pg m^{-3} for atmospheric samples and from 0.001 to 0.17 pg L^{-1} for seawater samples, respectively (see Table S5 for details). Recoveries of the surrogate standards ^{13}C−HBB, ^{13}C−BDE−77, ^{13}C−BDE−138, ^{13}C−BDE−209, and ^{13}C−synDP ranged from 78 ± 32% (^{13}C−BDE−77) to 95 ± 57% (^{13}C−BDE−209), and spiked recoveries of the analyzed HFRs were in the same range.[17,19,20] Samples were analyzed for 10 PBDE congeners, 8 alternate BFRs, DP, the one− and 2-fold dechlorinated DP species ($aCl_{11}DP$ [-1Cl+1H], $aCl_{10}DP$ [-2Cl+2H]), and Dechlorane 602, 603, and 604 by GC−MS in electron capture negative chemical ionization mode (ECNCI) (see Table S6 for the chemical structures). The total estimated method uncertainty according to Eurachem guidelines [21] ranged from 9.8% (PBT) to 45.3% (EHTBB) with a median uncertainty of the detected analytes of 16 ± 19%.

Air Mass Back Trajectories. Air mass origins along the cruise segments of the individual air samples were calculated using NOAA's HYSPLIT model.[22] Air mass back trajectories (BTs) were calculated in 6 h steps tracing back the air masses for 5 days using the sampling height as arrival height (see Figure S1 for individual BTs).

RESULTS AND DISCUSSION

Polybrominated Diphenyl Ethers (PBDEs). Among the investigated PBDEs, the common Penta−, Octa−, and DecaBDE congeners − BDE−47, −99, and −209 − were detected in almost all atmospheric samples within a concentration range for Σ_{10}PBDEs from 0.07 pg m^{-3} to 8.1 pg m^{-3} (gaseous+particulate, see Table S7 for individual concentrations of all analytes). BDE−209 was found to be the dominating congener with a median contribution of 72 ± 25% of Σ_{10}PBDEs and individual concentrations from not detected (n.d.) to 4 pg m^{-3}, while it was found mainly in the particulate phase with a mean particle−bound fraction of 74 ± 35% (median 100%). BDE−47 and −99 were detected from 0.02 to 0.8 pg m^{-3} and from 0.04 to 1.0 pg m^{-3} contributing 8 ± 9% and 13 ± 17% to Σ_{10}PBDEs, respectively. Among the other congeners, BDE−100, −153, −154, and −183 were detected in 41%, 18%, 17% and 18% of the air samples. In 2005, Wang et al. reported particle−bound PBDEs along the same sampling transect in concentrations which are several times higher with median concentrations for Σ_{11}PBDEs of 47.5 pg m^{-3} in Far East Asia and 15.2 pg m^{-3} in the Arctic.[23] The elevated concentrations in East Asia were traced back to continental air masses which were not observed within this study (see chapter *Latitudinal trends*). High concentrations in the Arctic were supposed to be caused by impact from North America where PBDEs were still produced at this time.[23] The production phase−out in the U.S may have led to decreasing concentrations in the Arctic as reflected by the lower Arctic concentrations in this study, while, in addition, no continental air masses from Northern America were sampled in the Arctic during this study. Concentrations in the Canadian Arctic were 0.78−48 pg m^{-3} for Σ_{15}PDBEs in 2002−2003[24] which are, again, significantly higher than in the present study. Jaward et al.[25] reported concentrations in the East Asian terrestrial atmosphere mainly in the low pg m^{-3} range which are similar to the concentrations observed in the East Asian samples in this study. The observed concentrations in the Arctic are similar to those recently observed in Greenland and East Greenland Sea[20,26] and the Southern Ocean[17] representing remote concentrations derived from LRAT.

Total seawater concentrations ranged from n.d. to 0.8 pg L^{-1} for Σ_{10}PBDEs (dissolved+particulate) with BDE−47 and −99 being the dominating congeners with individual concentrations from n.d. to 0.3 pg L^{-1} and n.d. to 0.2 pg L^{-1}, respectively, which were mainly distributed in the dissolved phase (see Table S8 for individual concentrations). In contrast to the atmosphere, BDE−209 was detected at five stations only, with concentrations from 0.1 to 0.2 pg L^{-1}. The observed concentrations are similar to those observed in East Greenland Sea[20] and in the Atlantic and

Southern Ocean.[17] Guan et al.[27] reported concentrations for Σ_{17}PBDEs from 2.69 to 19.1 pg L^{-1} in the Pearl River Delta, China, which are at least 2 orders of magnitude higher indicating that riverine discharge might contribute significantly to the PBDE pollution of the (coastal) marine Asian environment.

Alternate Brominated Flame Retardants. Among the non−PBDE BFRs, 7 different compounds were observed in the atmosphere: PBBz, PBT, DPTE, HBB, EHTBB, BTBPE, and TBPH. The most dominant compounds were PBBz, PBT, HBB, and DPTE which were detected at all stations mainly in the gaseous phase and ranged from 0.09 to 2 pg m^{-3}, 0.1 to 4.5 pg m^{-3}, 0.10 to 5.9 pg m^{-3}, and 0.1 to 2.5 pg m^{-3}, respectively, which are mostly higher than the dominating PBDE congeners. EHTBB, BTBPE, and TBPH were detected at a few stations only but with maximum concentrations of 8.9, 1.6, and 3.4 pg m^{-3}, respectively.

Data on new BFRs, especially in the atmosphere, are extremely limited. Lee et al. reported PBBz within their Global Atmospheric Passive Sampling (GAPS) network, but concentrations are not given.[28] It was found in human tissue from Japan[29] and in Danish and Finnish breast milk and placentas,[30] while it was shown to be produced by in−situ debromination of HBB in rats.[31] PBT was detected in Canada from <0.01−0.02 pg m^{-3} [32] and only recently in the Atlantic Ocean and in East Greenland Sea in concentrations <0.05 pg m^{-3},[17,20] which are several times lower to the concentrations observed in this study, both for the East Asian samples (0.36−4.53 pg m^{-3}) as well as for the North Pacific and Arctic stations (0.12−0.79 pg m^{-3}). HBB has been reported in concentrations from 0.3−6.5 pg m^{-3} and up to 610 pg m^{-3} in East China[33] and Japan,[34] respectively. Concentrations of HBB and DPTE similar to the present study were observed in the marine environment of the Atlantic and Southern Ocean and East Greenland Sea,[17,20] too. We recently reported BTBPE and TBPH for the first time in the Arctic atmosphere,[20] while the concentrations were clearly lower than in the present study. High atmospheric concentrations of BTBPE were observed in the U.S. (4−70 pg m^{-3} [14]) and in Guangzhou, China (3.8−67 pg m^{-3} [35]). EHTBB was first reported in house dust from the U.S.,[15] and Lee et al. reported qualitatively their worldwide occurrence within the GAPS Network.[28]

In seawater, PBT, DPTE, and HBB were the most frequently detected compounds (78%, 56%, and 100% detection frequency, respectively) with concentrations from n.d.−0.4, n.d.−1.6, and 0.006−0.1 pg L^{-1}. Besides, PPBz, BTBPE, and TBPH were detected at four, two, and one station, respectively, with a maximum concentration of 0.2 pg L^{-1} for TBPH, while PBBz and BTBPE remained below 0.1 pg L^{-1} at all stations. Only a few data on new BFRs in (sea)−water have been published so far. PBT was detected in the Western Scheldt from <0.1−2.4 ng L^{-1} and HBB in a Chinese source−near pond at 0.52 ± 0.04 ng L^{-1}.[36] DPTE, HBB, TBPH, and BTBPE were recently reported for the first times in (remote) seawater in comparable concentrations to the present study.[17,20]

Dechloranes. DP, consisting of the syn− and anti−stereoisomer, was detected in all air samples mainly in the particulate phase from 0.01 to 1.4 pg m^{-3}. Seawater concentrations ranged from 0.006 to 0.4 pg L^{-1}. In addition, the onefold dechlorinated species aCl_{11}DP was observed in five air samples at concentrations <0.1 pg m^{-3}. In addition, we observed the Dechloranes 602, 603, and 604 in the atmosphere in concentrations of 0.01−0.2 pg m^{-3}, 0.4 pg m^{-3}, and 0.03−0.05 pg m^{-3}, respectively, while they were also present in a few seawater samples in concentrations of 0.2 pg L^{-1}, 0.007−0.2 pg L^{-1}, and 0.02−0.05 pg L^{-1}, respectively. The atmospheric DP concentrations are similar to those observed in the marine Arctic and Atlantic environment,[19] U.S. non−source sites[18,37] and Chinese rural sites.[38] The mean atmospheric fractional abundance of the syn−isomer (f_{syn}) was 0.64 ± 0.12 without any spatial trends from East Asia toward higher latitudes. The mean seawater f_{syn} value was comparable with 0.61 ± 0.11. Recent studies showed an increase of f_{syn} value during atmospheric transport caused by stereoselective depletion of the anti-isomer.[14,19] Since the air masses, even in the Korean Strait close to coastline, in the present study were rather oceanic than directly source−related, the present study emphasizes this conclusion. In addition, sampling took place in summer at high temperatures in East Asia above 25 °C with a high sun−irradiation which might lead to a quite fast alteration of f_{syn}. Dechlorane 602, 603, and 604 were first reported in sediment and fish of the Great Lakes and their tributaries.[39,40] Wang et al. reported Dechlorane 602 in soil and air in eastern China close to a production facility with atmospheric concentrations of ∼5 pg m^{-3},[41] and Jia et al. observed Dechlorane 602 and 603 in marine coastal sediment and oysters from China Sea indicating emissions of these compounds into the marine environment.[42] This is the first finding of these Dechloranes in the marine atmosphere.

Composition Profile of HFRs. The composition profiles of all HFRs in air and seawater are shown in Figure 1. The atmospheric composition profile was dominated by PBT, BDE−209, HBB, PBBz, and DPTE with median contributions of 25 ± 11%, 15 ± 16%, 12 ± 7%, 10 ± 5%, and 9 ± 8%, respectively. In seawater, DPTE, BDE−47, PBT, and HBB generally dominated with median percentages of 11 ± 19%, 9 ± 16%, 8 ± 10%, and 5 ± 9%, respectively, while the profile differed since a number of HFRs were detected at a few stations only but then with a relatively high contribution. No significant latitudinal trends were observed between East Asia and the Arctic. Comparing PBDEs to their brominated and chlorinated alternates, PBDEs accounted only for 27 ± 15% and 38 ± 27% (median values), while the non-PBDE BFRs dominated with 65 ± 16% and 48 ± 25% in air and seawater, respectively. This shows that non-PBDE BFRs are (meanwhile) the dominating HFRs in the marine atmosphere and seawater in East Asia and, at least in the studied part, also in the Arctic. Especially the samples in the Korean Straight and the Sea of Japan (stations A1, A2, A16, and A17) showed a wide range of HFRs, including both highly−brominated BFRs (i.e., BTBPE, EHTBB, TBPH) which are substitutes for the banned BDE−mixtures as well as the more volatile BFRs (i.e., HBB, PBT) which have been used as BFRs for several decades and Dechloranes.

The predomination of BDE−209 among the PBDEs is a result of DecaBDE being the mostly used (and produced) BDE−mixture in the Asian countries.[43] HBB was widely used in Japan with about 350 tons/year (2001)[44] and is additionally produced in China with 600 tons/year.[9] PBT is produced by the same factory with 600 tons/year, too, while the total global production volume ranges between 1000−5000 tons/year.[9] BTBPE, EHTBB, and TBPH are known to be produced in the U.S.,[14,15] while it can be assumed that they are produced in Asian countries, too, caused by the increasing demand of flame retardants. Dechlorane Plus is produced in Huai'an, China, with an annual production of 300−1000 tons.[41] Besides these production sites located in Eastern China which might be primary sources, the general usage of HFRs in consumer and industrial

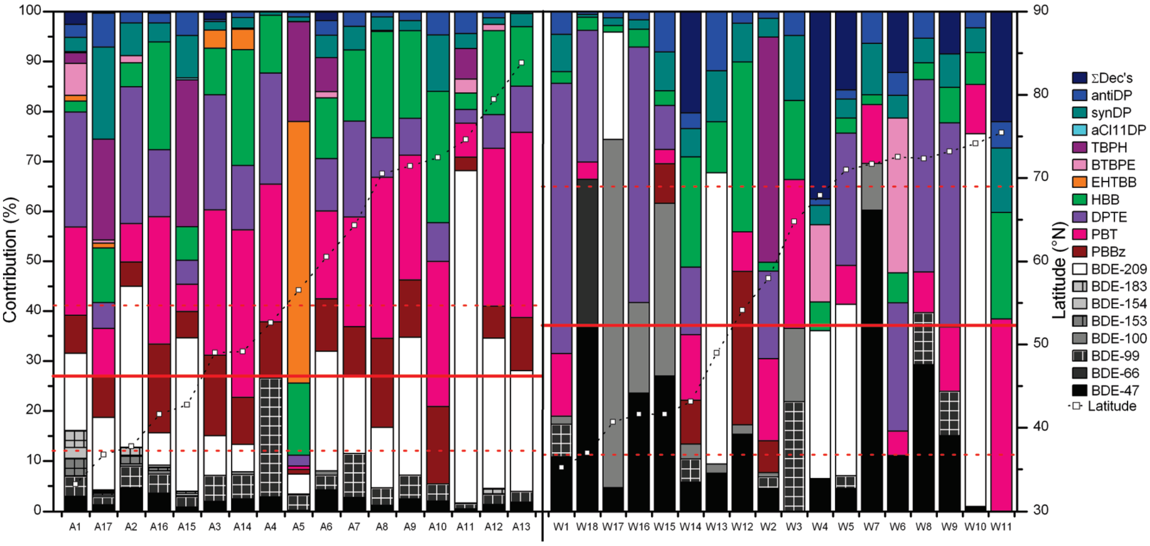

Figure 1. Composition profile of HFRs in the atmosphere (left) and seawater (right) along the sampling transect. The red line indicates the median Σ_{10}PBDEs contribution (the red dashed line shows the median plus/minus one SD). Note that for station A4 only the gaseous phase and for stations W1, W2, W16, and W18 only the dissolved phase was analyzed. Σ_3Dec's = Dechlorane 602 + 603 + 604. The black dotted line indicates the latitude (°N).

products and subsequently the emission of HFRs from products into the environment, especially in urbanized and industrialized regions, and e−waste disposals, which are known to be important sources of PBDEs in the (Asian) environment,[45] contribute to the HFR pollution of the (marine) environment. Another possible source, especially of HBB, PBBz, and PBT, could be the release from polymeric BFRs or highly brominated FRs such as BDE−209.[32,46,47] Arp et al. proposed the possible breakdown of decabromodiphenyl ethane (DBDPE), a substitute of DecaBDE, to PBT[48] which needs to be experimentally confirmed in future research. DPTE is currently not known to be produced, but its occurrence in air, seawater,[17,20] and marine mammals,[49,50] both in the Pacific, Atlantic, and Southern Ocean and the Arctic in concentrations similar or higher to PBDEs, indicates that it still might be somehow emitted into or formed in the environment.

Latitudinal Trends. The latitudinal distribution of PBDEs, other BFRs, DP, and other Dechloranes in air and seawater along the sampling transect is shown in Figure 2. The latitudinal trend of the individual compounds in the atmosphere is additionally shown in Figure S2. The highest concentrations, both in air and in seawater, were generally observed in the Korean Straight and the Sea of Japan where the most different compounds were observed (see chapter *Composition profile of HFRs*) as a result of East Asia as source region of HFRs in the environment. But, the air mass back trajectories (BT) analysis showed only a slight influence of the air samples in Korea Straight and the Sea of Japan by continental (Asian) air masses, while the traveling times over the ocean mostly accounted for several days before being sampled. Highly elevated concentrations can be expected if samples would have been dominated by continental, source−related air masses as observed by Wang et al.[23]

Peak concentrations were observed for HBB, EHTBB, and TBPH at station A5 in the North Pacific, while also BDE−99 showed slightly higher concentrations and BDE−153 and −183 were detected above the MDLs, too. Interestingly, TBPH was found in the corresponding seawater station (W2), too. Another elevated concentration was observed for BDE−209 at station A11 in the Arctic, where BTBPE and TBPH were detected, too. The BT analysis showed no clear explanations for the observed peaks. In contrast to stations A4 and A6, station A5 was influenced by air masses passing part of Eastern Russia where local sources such as waste burning could be located. The origin of the elevated concentrations in the Arctic as well as the general sources of alternate BFRs and Dechloranes in the Arctic, which can be assumed to be the LRAT both from the Eurasian and the American continent, need further global long−term study.

The atmospheric concentrations of most BFRs decreased rapidly from the source region toward the North Pacific and the Artic where they remained relatively stable. The Pacific and Arctic air samples were dominated by oceanic or even Arctic air masses representing remote concentrations of HFRs being influenced by deposition and/or degradation during LRAT. Significant correlations ($p < 0.05$ and 0.01, respectively; see Table S9) were observed for several PBDEs as well as for PBBz, PBT, DPTE, and DP indicating similar source regions and comparable LRAT behavior. Even BDE−209 was significantly correlated with other PBDE congeners (except BDE−100) and other HFRs, although it has been shown to undergo photochemical degradation.[51] But, the degradation behavior of BDE−209 attached to airborne particles is not yet studied, while this paper emphasizes the particle−bound LRAT of BDE−209 into remote areas.[20,23,52]

The seawater concentrations were found to be the highest in the samples in the Korea Straight, too, with a strong latitudinal decrease toward the Pacific Ocean (see Figure S3 for the latitudinal trends of the individual compounds). Again, significant correlations were observed between several PBDEs and their alternates ($p < 0.05$ and 0.01, respectively; see Table S10). The high seawater concentrations could be resulted either by aquatic discharges from coastal sources of HFRs in Asia, as shown for e.g., the Korean coast[53] and the Pearl River,[27] or by atmospheric deposition processes as observed in coastal areas of Korea[54] and shown in chapter *Atmospheric depositions*. However, the riverine discharge into the investigated region is not known and needs to be studied to evaluate the influence of the different sources.

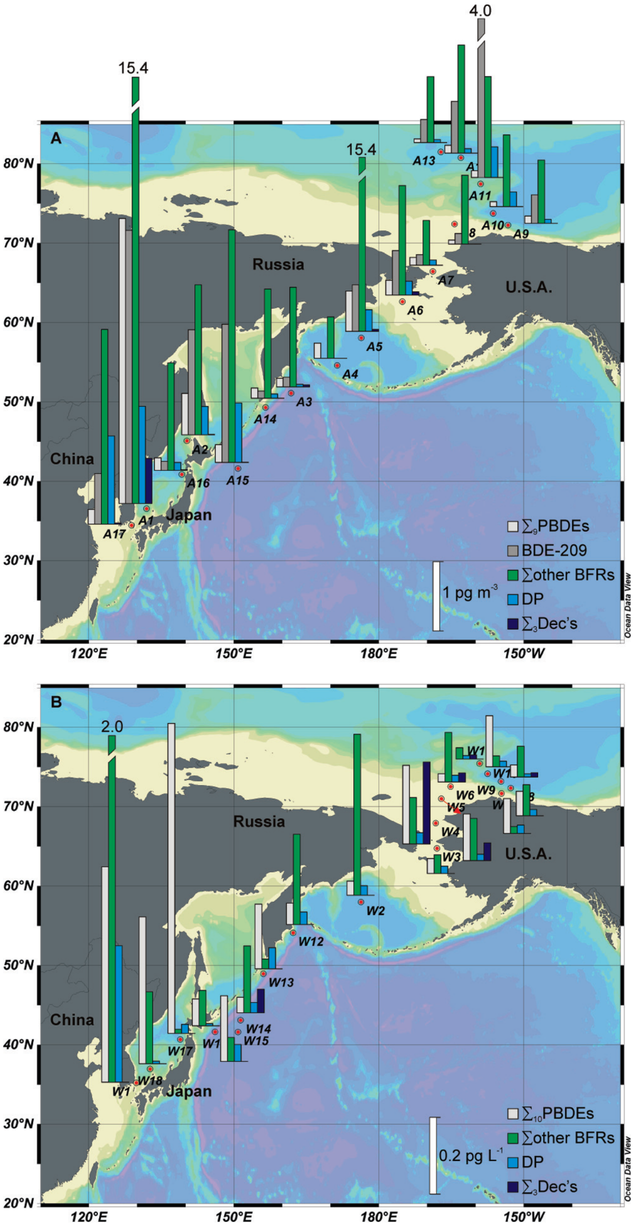

Figure 2. Concentrations of PBDEs, other BFRs, DP (synDP + antiDP), and sum of Dechlorane 602, 603, and 604 in the atmosphere (A) and seawater (B) along the sampling cruise. Note that for station A4 only the gaseous phase and for stations W1, W2, W16, and W18 only the dissolved phase was analyzed.

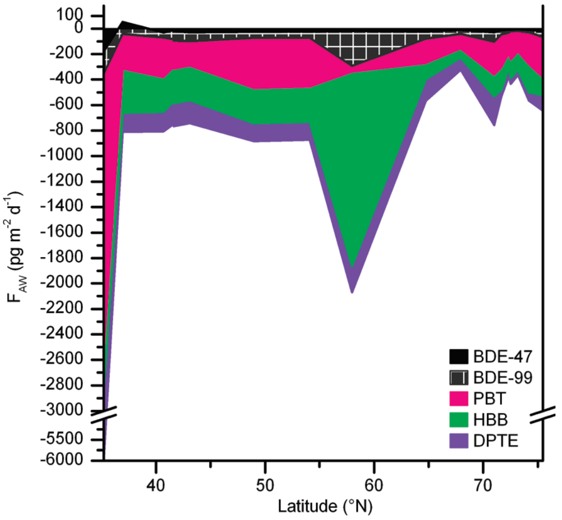

Figure 3. Air−sea gas exchange fluxes (F_{AW}) of BDE−47, −99, PBT, HBB, and DPTE vs latitude along the sampling transect. Negative (−) flux indicates deposition into the water column.

Atmospheric Depositions. In order to estimate the influence of air−seawater coupling and the atmospheric input of HFRs into the ocean, we calculated the air−seawater gas exchange and estimated the particle−bound dry deposition flux of HFRs into the ocean. To estimate the direction (or equilibrium status) of the gas exchange, we calculated the fugacity ratio f_W/f_A of the dominating BFRs (see the SI for details of the calculation; see Figure S4 for plots of the ratios for the individual BFRs). In general, the ratios were <1 within the uncertainty suggesting net deposition at almost all sites for all compounds along the entire transect indicating the atmosphere as a source of BFRs in the ocean. The net air−seawater gas exchange was calculated for BDE−47 and −99, PBT, HBB, and DPTE based on the modified version of the Whitman two−film resistance model.[55,56] The calculation for BFRs has been described elsewhere[20] and is described in detail in the SI. The estimated air−seawater gas exchange fluxes are shown in Figure 3. The net flux was generally dominated by net deposition, while the highest deposition flux was observed in the Korea Straight with individual deposition fluxes from 180 pg m^{-2} day^{-1} for BDE−47 to 3100 pg m^{-2} day^{-1} for DPTE driven by the relatively high atmospheric concentrations apparently resulting from emissions by the East Asian countries. The non−PBDEs showed generally higher fluxes than the PBDEs which were lower than 50 pg m^{-2} day^{-1} at most stations or showed even slight volatilization (BDE−47 at station W18). This shows that atmospheric transport and deposition is an important source of non−PBDEs BFRs in the (coastal) marine environment, while the gaseous atmospheric input of PBDEs is comparably low. In the Pacific Ocean and the Arctic, the flux was relatively constant in the 2 to 3−digit pg m^{-2} day^{-1} range, while a higher deposition flux of 1500 pg m^{-2} day^{-1} was calculated for station W2 in the Pacific which might be influenced by Russian air masses.

To investigate the particle−bound deposition flux of highly hydrophobic HFRs, we estimated the dry particle−bound using deposition velocities of 0.3 cm s^{-1} and 0.1 cm s^{-1} for the East Asian and the Pacific Ocean and the Arctic, respectively (see the SI for details). The dry deposition flux is shown in Figure 4. Similar to the gaseous deposition, the particle−bound deposition was highest in the East Asian stations with a total flux of 2900 pg m^{-2} day^{-1} which was dominated by BDE−209 but also several other highly brominated FRs as well as Dechloranes are deposited into the ocean. Excluding station A11, the dry deposition in the Arctic was relatively constant ranging from 12 to 99 pg m^{-2} day^{-1}, while, again, BDE−209 dominated. The dry particle−bound flux of BDE−209 is comparable to the gaseous deposition of the lower brominated FRs, while the particle−bound flux of BDE−47 and BDE−99 is negligible. In any case, BDE−209, DP, and alternate BFRs are emitted into the atmosphere by East Asian countries and further deposited into the ocean, especially into coastal areas. The sources of those alternate BFRs and

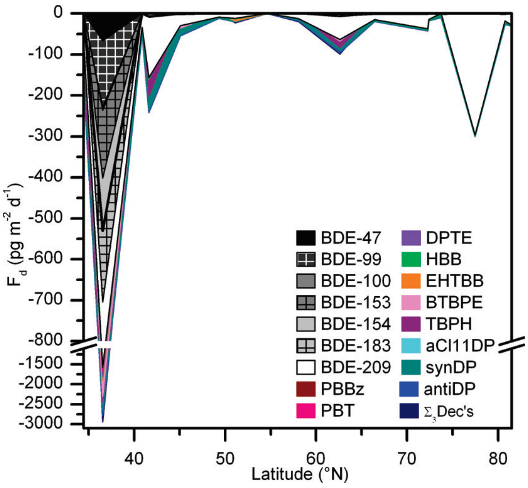

Figure 4. Dry particle–bound deposition fluxes (F_d) of HFRs vs latitude along the sampling transect.

Dechloranes in the environment of the East Asian countries as well as their atmospheric and aqueous emissions into the ocean, especially into the coastal areas such as the Bohai Bay, require future research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables on the sampling sites, *m*/*z* values, blanks, MDLs, chemical structures, BTs, individual concentrations, latitudinal trends, correlations, method description, and a description of the air–seawater exchange calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Polybrominated diphenyl ethers vs. alternate brominated flame retardants and Dechloranes from East Asia to the Arctic

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9 tables

4 figures

Additional information on materials and methods

Chemicals. All solvents were residue grade and additionally distilled in a full glass unit prior to use. The samples were analyzed for the following HFRs: A BDE–Mix (BDE–MXF; including BDE–28, –47, –99, –100, –153, –154, –183), BDE–209, pentabromobenzene (PBBz), pentabromotoluene (PBT), 2,3–dibromopropyl–2,4,6–tribromophenyl ether (DPTE), hexabromobenzene (HBB), pentabromoethyl benzene (PBEB), 2–ethylhexyl 2,3,4,5–tetrabromobenzoate (EHTBB), 1,2–bis(2,4,6–tribromophenoxy) ethane (BTBPE), bis–(2–ethylhexyl)–tetrabromophthalate (TBPH), the one– and twofold dechlorinated DP species (aCl$_{11}$DP, aCl$_{10}$DP), and the two DP stereoisomers (synDP, antiDP) which were purchased from Wellington Laboratories. The Dechloranes 602, 603 and 604 were purchased from Toronto Research Chemicals.

Mass labeled standards used as surrogates were purchased from Wellington Laboratories (^{13}C–HBB, ^{13}C–BDE–77, ^{13}C–BDE–138, ^{13}C–BDE–209) and from Cambridge Isotope Laboratories (^{13}C–synDP), respectively. ^{13}C–Hexachlorobenzene (used as injection standard) was obtained from Cambridge Isotope Laboratories.

Extraction and clean–up. Extraction and clean–up of the samples was done in a clean laboratory class 10 000. All solvents were residue–analysis grade and were distilled prior to use. Samples were spiked with 200 pg of the surrogates (2000 pg for ^{13}C–BDE–209) prior to extraction. Columns and filters were Soxhlet extracted using dichloromethane for 16 h. The extracts were evaporated to 1–2 mL while the solvent was exchanged to hexane. They were further cleaned on a 2.5 g silica column (10 % water deactivated) topped on 3 g anhydrous granulated sodium sulfate. The extracts were purified by eluting with 20 mL hexane, and evaporated to the final volume of 30 µL. 1 ng ^{13}C–HCB was added as recovery standard before injection.

Analysis. Analyses were done by a GC/MS–system (6890 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI) with methane as ionization gas fitted with a HP–5MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness, J&W Scientific). More details are given in ref (1). m/z values used for quantification and quality control are included in Table S3.

QA/QC. The air columns were protected against UV–sunlight during sampling using aluminum foil in order to avoid degradation of the target compounds on the column. All air columns were precleaned with solvents of different polarity and GFFs were baked at 450 °C for 12 h prior to their usage. All used glass ware was baked at 250 °C for 10 h and rinsed with solvent and silica gel was cleaned with acetone for 12 h and baked at 450 °C for 12 h prior to usage. Breakthrough of the target compounds was checked for both seawater and air samples using tandem columns during previous sampling cruises *(1–3)*. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (σ) (for compounds showing no blanks the instrumental limits at a signal–to–noise ratio of three were used).

TABLE S1. Detailed information on air sampling. Latitude and longitude represent the mean sampling station. Air temperature and wind speed are mean values.

	Date	Latitude (°N)	Longitude (°E)	Volume (L)	Wind speed (m s^{-1})	T_A (°C)
A1	4.–5.7.2010	36.55	131.97	300	3.0	24.4
A2	5.–7.7.2010	45.09	140.30	505	6.7	15.9
A3	8.–10.7.2010	51.10	161.86	500	6.4	7.2
A4	10.–12.7.2010	54.59	171.41	500	5.5	7.7
A5	12.–15.7.2010	58.07	176.39	500	7.3	7.4
A6	15.–17.7.2010	62.64	–175.12	500	8.8	7.3
A7	19.–20.7.2010	66.43	–168.81	500	9.6	5.8
A8	23.–25.7.2010	72.40	–164.32	500	6.7	4.0
A9	25.–27.7.2010	72.27	–153.28	500	5.2	3.5
A10	27.–29.7.2010	73.75	–156.32	500	6.5	2.4
A11	29.–31.7.2010	77.47	–158.93	500	16.7	–0.4
A12	1.–3.8.2010	80.76	–163.00	500	9.5	–0.1
A13	23.–25.8.2010	81.50	–167.14	500	11.6	0.0
A14	5.–6.9.2010	49.31	156.58	500	7[a]	7[a]
A15	7.–9.9.2010	41.60	150.89	500	7[a]	20[a]
A16	9.–11.9.2010	40.86	139.26	500	7[a]	20[a]
A17	11.–12.9.2010	34.45	128.83	500	7[a]	25[a]

[a] estimated values since no measured data were available

TABLE S2. Detailed information on water sampling. Latitude and longitude represent the mean sampling station. Air temperature represents the mean air temperature during sampling. The water temperature was assumed to be similar to the air temperature since no measured data is available.

	Corresponding air sample	Date	Latitude (°N)	Longitude (°E)	Volume (L)	Wind speed (m/s)	T_A (°C)	T_W[a] (°C)
W1	A1	4.07.2010	35.21	129.83	176	7.0	21.9	22
W2	A5	11.–14.7.2010	57.98	176.32	613.5	6.8	7.4	7
W3	A7	19.–20.7.2010	64.76	–167.96	1020	11.5	5.5	5
W4	A7	20.–21.7.2010	67.94	–168.20	707.5	5.8	7.4	7
W5	A7	21.–22.7.2010	71.02	–167.04	932.5	15.8	6.2	6
W6	A8	24.07.2010	72.54	–165.14	893.5	6.1	3.2	3
W7	A9	25.–26.7.2010	71.68	–154.59	946.5	8.2	5.1	5
W8	A9	26.–27.7.2010	72.35	–152.69	899.5	4.5	3.4	3
W9	A10	27.–28.7.2010	73.19	–154.71	639	4.4	4.1	4
W10	A10	28.–29.7.2010	74.16	–157.48	1006.5	7.6	0.6	0
W11	A11	29.–30.7.2010	75.46	–159.14	1066.5	9.4	0.2	0
W12	A14	4.–5.9.2010	54.11	162.27	786	7[a]	7[a]	7
W13	A14	5.–6.9.2010	48.95	156.12	737.5	7[a]	12[a]	12
W14	A15	6.–7.9.2010	43.10	151.41	662.5	7[a]	17[a]	17
W15	A15	7.–8.9.2010	41.61	150.87	1112	7[a]	20[a]	20
W16	A15	8.–9.9.2010	41.62	146.14	725	7[a]	20[a]	20
W17	A16	9.–10.9.2010	40.67	138.94	1119.5	7[a]	20[a]	20
W18	A17	10.–11.9.2010	36.94	132.68	1327	7[a]	25[a]	25

[a] estimated values since no measured data were available

TABLE S3. m/z values used for quantification and quality control of HFRs in ECNCI–(SIM)–mode

	Q	Q1	Q2	Q3
^{13}C–HCB	289.8	255.8		
^{13}C–HBB	559.6	479.6		
^{13}C–BDE–77	79	81		
^{13}C–BDE–138	79	81		
^{13}C–BDE–209	494.6	413.8		
^{13}C–synDP	667.8	633.8		
BDE–28	79	81	161	327
BDE–47	79	81	161	
BDE–66	79	81	161	
BDE–85	79	81	161	
BDE–99	79	81	161	
BDE–100	79	81	161	
BDE–153	79	81		
BDE–154	79	81	563.7	482.8
BDE–183	79	81		
BDE–209	486.5			
PBBz	79	81	472	474
PBT	79	81	485.7	
PBEB	79	81	499.7	421.6
DPTE	79	81	159.8	
HBB	549.5	473.7		
EHTBB	356.7	79	81	470.9
BTBPE	79	81	251.8	
TBPH	384	464		
aCl$_{10}$DP	583.8	549.9	513.8	
aCl$_{11}$DP	617.8	583.7	547.7	
synDP	653.8	617.9	583.9	
antiDP	653.8	617.9	583.9	
Dec 602	613.7	340.8		
Dec 603	637.7	601.7		
Dec 604	79	81		

TABLE S4. Mean absolute blank values of HFRs in pg.

	air		water	
	column	**filter**	**column**	**filter**
BDE–47	1.0 ± 1.1	n.d.	n.d.	n.d.
BDE–99	1.4 ± 1.3	n.d.	n.d.	n.d.
BDE–209	43 ± 30	38 ± 4	25 ± 44	38 ± 4
PBBz	1.1 ± 0.6	n.d.	n.d.	n.d.
PBT	n.d.	6.4 ± 5.8	n.d.	6.4 ± 5.8
DPTE	11 ± 6	46 ± 20	4.3 ± 7.5	46 ± 20
Dec 602	0.3 ± 0.5	1.7 ± 1.4	1.5 ± 1.7	1.7 ± 1.4
Dec 603	12 ± 4	6.8 ± 8.6	0.7 ± 1.2	6.8 ± 8.6

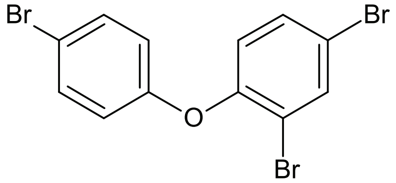
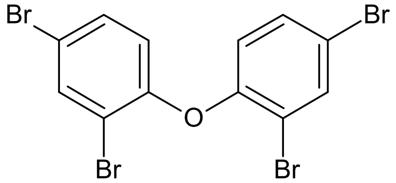
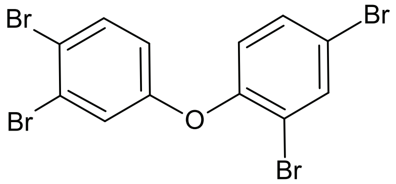
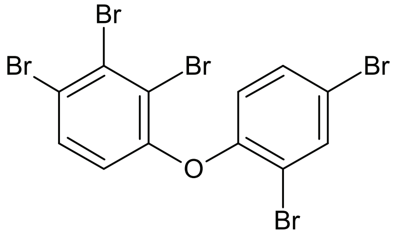
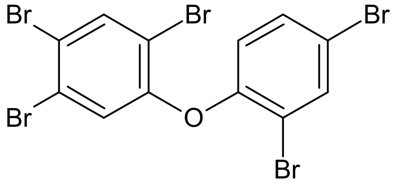
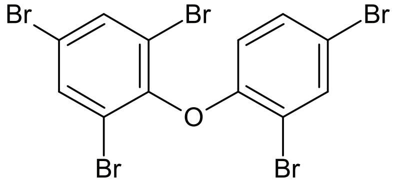
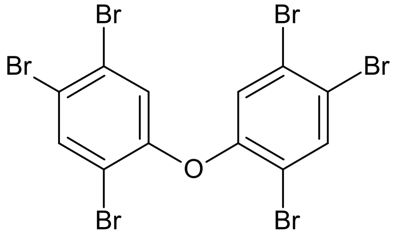
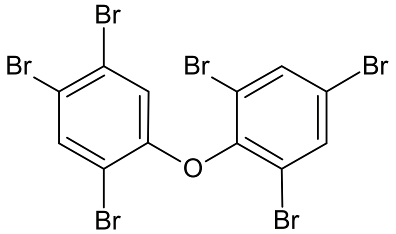
BDE–28, –66, –85, –100, –153, –154, –183, PBEB, HBB, TBPH, EHTBB, BTBPE, Dec 604, aCl10DP, aCl11DP, synDP and antiDP were not detected in any blanks

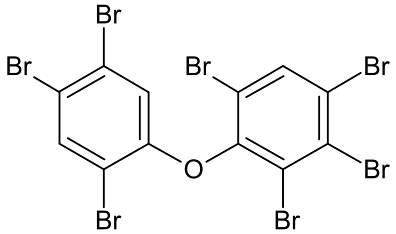
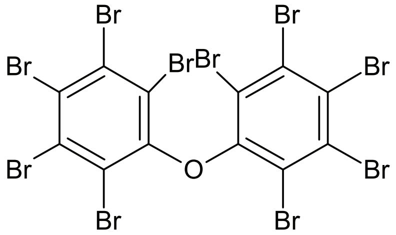
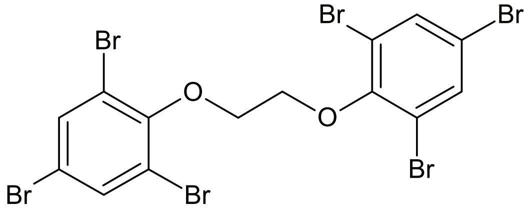
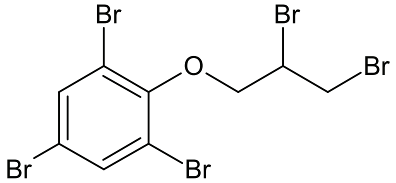
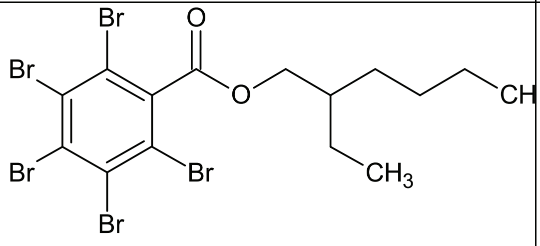
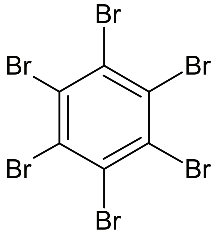
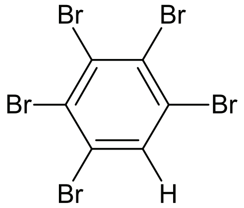
TABLE S5. MDLs for HFRs in pg m^{-3} and pg L^{-1} for the atmosphere and seawater, respectively. MDLs were calculated from mean field blank values plus three times the standard deviation or, if no blank values detected, based on instrumental S/N ratios of 3. Mean sample volumes of 500 m^{3} and 900 L were estimated for air and seawater samples, respectively.

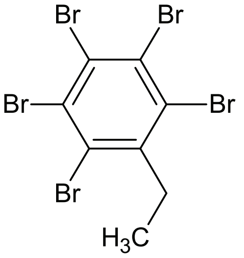
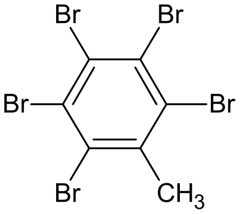
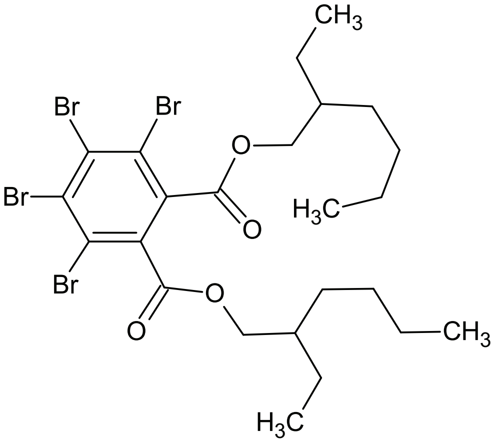
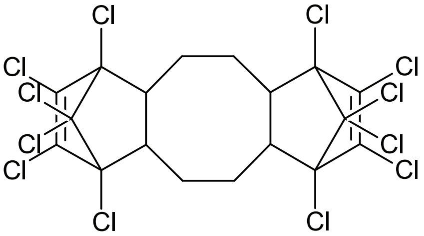
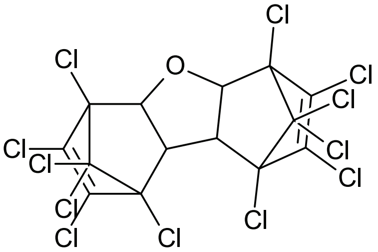
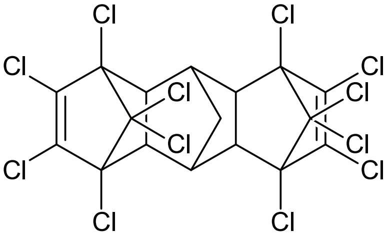
	air		water	
	column	**filter**	**column**	**filter**
BDE–28	0.006[a]	0.006[a]	0.003[a]	0.003[a]
BDE–47	0.008	0.008[a]	0.004[a]	0.004[a]
BDE–66	0.011[a]	0.011[a]	0.006[a]	0.006[a]
BDE–85	0.015[a]	0.015[a]	0.008[a]	0.008[a]
BDE–99	0.011	0.009[a]	0.005[a]	0.005[a]
BDE–100	0.004[a]	0.004[a]	0.002[a]	0.002[a]
BDE–153	0.013[a]	0.013[a]	0.007[a]	0.007[a]
BDE–154	0.006[a]	0.006[a]	0.004[a]	0.004[a]
BDE–183	0.014[a]	0.014[a]	0.008[a]	0.008[a]
BDE–209	0.27	0.10	0.17	0.092
PBBz	0.006	0.002[a]	0.001[a]	0.001[a]
PBT	0.002[a]	0.047	0.001[a]	0.026
PBEB	0.001[a]	0.001[a]	0.0004[a]	0.0004[a]
DPTE	0.06	0.21	0.03	0.12
HBB	0.002[a]	0.002[a]	0.001[a]	0.001[a]
TBPH	0.16[a]	0.16[a]	0.089[a]	0.089[a]
EHTBB	0.042[a]	0.042[a]	0.023[a]	0.023[a]
BTBPE	0.031[a]	0.031[a]	0.017[a]	0.017[a]
aCl10DP	0.002[a]	0.002[a]	0.001[a]	0.001[a]
aCl11DP	0.002[a]	0.002[a]	0.001[a]	0.001[a]
synDP	0.002[a]	0.002[a]	0.001[a]	0.001[a]
antiDP	0.003[a]	0.003[a]	0.002[a]	0.003[a]
Dec 602	0.003	0.011	0.007	0.006
Dec 603	0.047	0.065	0.005	0.036
Dec 604	0.008[a]	0.008[a]	0.005[a]	0.005[a]

[a] calculated based on an instrumental S/N ratio of 3

TABLE S6. Abbreviation, chemical structure and CAS-number of PBDEs, non-PBDE BFRs and Dechloranes investigated in this study

Abbreviation	Structure	CAS
PBDEs		
BDE-28		41318-75-6
BDE-47		5436-43-1
BDE-66		189084-61-5
BDE-85		182346-21-0
BDE-99		60348-60-9
BDE-100		189084-64-8
BDE-153		68631-49-2
BDE-154		207122-15-4

BDE-183		207122-16-5
BDE-209		1163-19-5
non-PBDE BFRs		
BTBPE		37853-59-1
DPTE		35109-60-5
EHTBB		183658-27-7
HBB		87-82-1
PBBz		608-90-2

PBEB		85-22-3
PBT		87-83-2
TBPH		26040-51-7
Dechloranes		
DP		13560-89-9
Dec 602		31107-44-5
Dec 603		13560-92-4

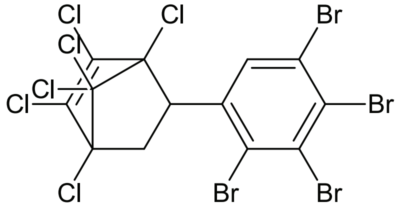
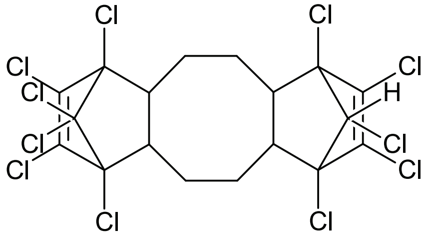
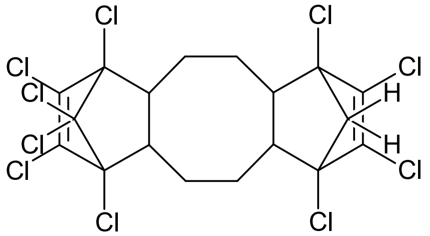
Dec 604		34571-16-9
aCl$_{11}$DP		n.a.
aCl$_{10}$DP		n.a.

TABLE S7. Individual concentrations of HFRs in the gaseous (gas.) and particulate (part.) phase of the atmosphere in pg m^{-3}. BDE–28, –66, –85, PBEB and aCl10DP were not detected in any sample.

		BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209	PBBz	PBT	DPTE	HBB	EHTBB	BTBPE	TBPH	aCl11DP	synDP	antiDP	fysn	Dec602	Dec603	Dec604
A1	gas.	0.50	0.38	n.d.	0.26	0.05	0.21	0.57	1.9	4.2	5.4	0.45	n.d.	0.06	n.d.	0.01	0.10	0.07	0.58	0.02	n.d.	n.d.
	part.	0.26	0.62	0.03	0.64	0.50	0.67	3.37	0.03	0.29	0.51	0.13	0.29	1.57	0.54	0.05	0.63	0.6	0.51	0.18	0.44	n.d.
A2	gas.	0.20	0.19	0.02	0.07	0.01	0.07	1.2	0.23	0.36	1.29	0.23	n.d.	n.d.	n.d.	n.d.	0.13	0.06	0.70	0.005	n.d.	n.d.
	part.	0.01	0.01	n.d.	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	0.18	0.05	0.80	n.d.	n.d.	n.d.
A3	gas.	0.04	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	0.28	0.52	0.41	0.15	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	S	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	0.01	0.06	n.d.	n.d.	n.d.	0.01	0.01	0.64	n.d.	n.d.	0.03
A4	gas.	0.02	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.23	0.18	0.1	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	S	n.d.	n.d.	n.d.
	part.[a]																					
A5	gas.	0.04	0.51	n.d.	0.02	n.d.	0.02	0.53	0.15	0.12	0.37	2.45	8.92	n.d.	3.4	0.01	0.13	0.13	0.48	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.02	0.57	n.d.	n.d.	0.03
A6	gas.	0.08	0.04	0.01	n.d.	n.d.	n.d.	n.d.	0.28	0.47	0.28	0.31	n.d.	n.d.	n.d.	n.d.	0.04	0.02	0.62	n.d.	n.d.	n.d.
	part.	0.03	0.04	0.02	n.d.	n.d.	n.d.	0.64	n.d.	n.d.	n.d.	0.01	n.d.	0.03	0.18	n.d.	0.08	0.05	0.60	n.d.	n.d.	0.05
A7	gas.	0.03	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	0.22	0.19	0.13	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.63	n.d.	n.d.	n.d.
	part.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.03	0.02	0.60	n.d.	n.d.	n.d.
A8	gas.	0.02	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.22	0.41	0.1	0.25	n.d.	n.d.	n.d.	0.003	0.02	0.005	0.77	n.d.	n.d.	n.d.
	part.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.67	n.d.	n.d.	n.d.
A9	gas.	0.03	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	0.37	0.11	0.24	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.70	n.d.	n.d.	n.d.
	part.	0.01	0.01	n.d.	n.d.	n.d.	n.d.	0.41	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	0.02	0.02	0.44	n.d.	n.d.	n.d.
A10	gas.	0.02	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	0.38	0.1	0.33	n.d.	n.d.	n.d.	n.d.	0.09	0.04	0.68	n.d.	n.d.	n.d.
	part.	0.01	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	0.06	0.02	0.76	n.d.	n.d.	n.d.
A11	gas.	0.03	0.06	0.004	n.d.	n.d.	n.d.	0.54	0.16	0.41	0.16	0.17	n.d.	0.17	0.36	n.d.	0.17	0.25	0.41	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.43	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.48	n.d.	n.d.	n.d.
A12	gas.	0.02	0.04	0.004	n.d.	n.d.	0.03	0.56	0.16	0.79	0.17	0.40	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.56	n.d.	n.d.	n.d.
	part.	0.01	0.01	n.d.	n.d.	n.d.	n.d.	0.19	n.d.	n.d.	n.d.	0.02	n.d.	0.03	n.d.	n.d.	0.02	0.02	0.50	n.d.	n.d.	n.d.
A13	gas.	0.03	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	0.51	0.13	0.16	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	S	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.33	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.79	n.d.	n.d.	n.d.
A14	gas.	0.05	0.09	0.01	n.d.	n.d.	n.d.	n.d.	0.18	0.64	0.24	0.43	0.08	n.d.	n.d.	0.005	0.02	0.01	0.6	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	0.02	0.01	0.69	n.d.	n.d.	n.d.
A15	gas.	0.06	0.13	0.01	n.d.	n.d.	0.03	1.42	0.34	0.36	0.31	0.43	n.d.	n.d.	1.75	0.02	0.43	0.28	0.61	0.004	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	0.58	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.16	n.d.	0.12	0.03	0.80	n.d.	n.d.	n.d.
A16	gas.	0.07	0.07	0.01	0.01	0.01	n.d.	n.d.	0.35	0.51	0.27	0.43	n.d.	n.d.	n.d.	n.d.	0.04	0.01	0.72	0.01	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	0.02	0.61	n.d.	n.d.	n.d.
A17	gas.	0.07	0.08	0.02	0.02	0.01	0.02	0.47	0.41	0.49	0.26	0.54	0.05	0.03	0.84	n.d.	0.79	0.27	0.75	0.02	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.26	n.d.	n.d.	n.d.	0.01	n.d.	n.d.	0.18	n.d.	0.14	0.08	0.64	n.d.	n.d.	n.d.

[a] not analyzed

S = only synDP detected

n.d. = not detected

TABLE S8. Individual concentrations of HFRs in the dissolved (diss.) and particulate (part.) phase in seawater in pg L^{-1}. BDE–28, –85, PBEB, aCl10DP and aCl11DP were not detected in any sample.

		BDE 47	BDE 66	BDE 99	BDE 100	BDE209	PBBz	PBT	DPTE	HBB	BTBPE	TBPH	synDP	antiDP	fsyn	Dec602	Dec603	Dec604
W1	diss.	0.32	n.d.	0.19	0.048	n.d.	n.d.	0.37	1.6	0.070	n.d.	n.d.	0.22	0.14	0.62	n.d.	n.d.	n.d.
	part.[a]																	
W2	diss.	0.022	n.d.	0.011	0.004	n.d.	0.031	0.079	0.084	0.009	n.d.	0.22	0.018	0.007	0.74	n.d.	n.d.	n.d.
	part.[a]																	
W3	diss.	n.d.	n.d.	0.023	0.016	n.d.	n.d.	0.030	n.d.	0.017	n.d.	n.d.	0.010	0.005	0.67	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	S	n.d.	n.d.	n.d.
W4	diss.	0.037	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.020	0.088	n.d.	0.011	n.d.	S	0.021	0.192	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	0.012	n.d.	n.d.	0.011	0.007	0.60	n.d.	n.d.	n.d.
W5	diss.	0.013	n.d.	0.007	n.d.	n.d.	n.d.	0.023	0.078	0.009	n.d.	n.d.	0.006	0.005	0.53	n.d.	n.d.	0.046
	part.	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.005	n.d.	S	n.d.	n.d.	n.d.
W6	diss.	0.021	n.d.	n.d.	n.d.	n.d.	n.d.	0.009	0.049	0.008	0.059	n.d.	0.007	0.009	0.45	n.d.	0.007	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	0.002	n.d.	S	n.d.	n.d.	0.016
W7	diss.	0.070	n.d.	n.d.	0.012	n.d.	n.d.	0.015	n.d.	n.d.	n.d.	n.d.	0.011	0.008	0.58	n.d.	n.d.	n.d.
	part.	0.008	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	0.002	n.d.	S	n.d.	n.d.	n.d.
W8	diss.	0.021	n.d.	0.017	n.d.	n.d.	n.d.	0.013	0.062	0.005	n.d.	n.d.	0.004	0.005	0.47	n.d.	n.d.	n.d.
	part.	0.026	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	0.004	0.49	n.d.	n.d.	n.d.
W9	diss.	0.016	n.d.	0.012	n.d.	n.d.	n.d.	0.017	0.054	0.006	n.d.	n.d.	0.004	n.d.	S	n.d.	0.011	n.d.
	part.	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	0.005	n.d.	S	n.d.	n.d.	n.d.
W10	diss.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.017	n.d.	0.008	n.d.	n.d.	0.003	0.002	0.60	n.d.	n.d.	n.d.
	part.	0.002	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	0.005	0.003	0.61	n.d.	n.d.	n.d.
W11	diss.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.019	n.d.	0.007	n.d.	n.d.	0.003	0.003	0.57	n.d.	0.011	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	0.003	n.d.	S	n.d.	n.d.	n.d.
W12	diss.	0.050	n.d.	n.d.	0.006	n.d.	0.089	0.025	n.d.	0.098	n.d.	n.d.	0.021	0.008	0.74	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.010	n.d.	n.d.	0.012	n.d.	n.d.	0.004	n.d.	S	n.d.	n.d.	n.d.
W13	diss.	0.019	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	n.d.	0.016	n.d.	n.d.	0.020	0.026	0.44	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	0.009	n.d.	n.d.	0.006	0.004	0.59	n.d.	n.d.	n.d.
W14	diss.	0.017	n.d.	0.014	0.009	n.d.	0.027	0.040	0.041	0.063	n.d.	n.d.	0.014	0.010	0.60	0.015	0.046	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	0.003	n.d.	S	n.d.	n.d.	n.d.
W15	diss.	0.075	n.d.	n.d.	0.096	n.d.	0.022	0.008	0.024	0.008	n.d.	n.d.	0.022	0.022	0.49	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	nd.d	n.d.	n.d.	n.d.
W16	diss.	0.040	n.d.	n.d.	0.030	n.d.	n.d.	n.d.	0.086	0.006	n.d.	n.d.	0.003	0.003	0.54	n.d.	n.d.	n.d.
	part.[a]																	
W17	diss.	0.037	n.d.	n.d.	0.59	0.18	n.d.	n.d.	n.d.	0.010	n.d.	n.d.	0.012	0.011	0.52	n.d.	n.d.	n.d.
	part.	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	n.d.	n.d.	0.001	n.d.	S	n.d.	n.d.	n.d.
W18	diss.	0.21	0.17	n.d.	n.d.	n.d.	n.d.	0.020	0.15	0.015	n.d.	n.d.	0.003	0.003	0.46	n.d.	n.d.	n.d.
	part.[a]																	

[a] not analyzed

S = only synDP detected

n.d. = not detected

TABLE S9. Correlations (calculated as Pearson correlation) of major HFRs in the atmosphere.

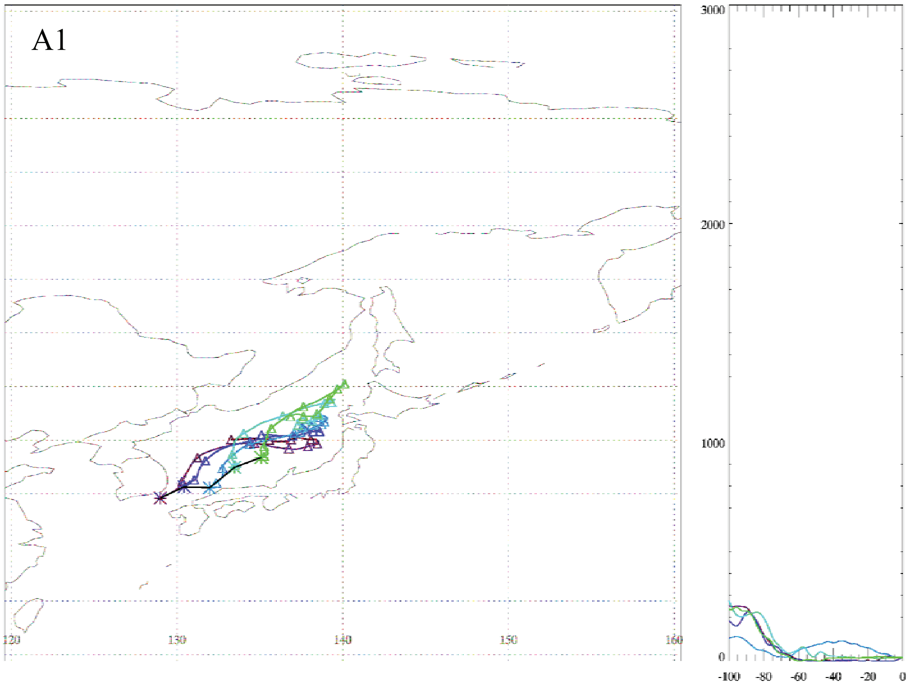
		BDE–47	**BDE–99**	**BDE–100**	**BDE–153**	**BDE–154**	**BDE–183**	**BDE–209**	**PBBz**	**PBT**	**DPTE**	**HBB**	**DP**
BDE–47	Correlation		.880**	.804**	.986**	.971**	.984**	.625*	.960**	.951**	.992**	.029	.660**
	Significance		.000	.009	.002	.006	.000	.013	.000	.000	.000	.914	.005
	N		16	9	5	5	7	15	16	16	16	16	16
BDE–99	Correlation	.880**		.736*	.886*	.991**	.890**	.564*	.859**	.837**	.906**	.468	.613*
	Significance	.000		.024	.045	.001	.007	.029	.000	.000	.000	.068	.012
	N	16		9	5	5	7	15	16	16	16	16	16
BDE–100	Correlation	.804**	.736*		.892	.845	.783	.211	.721*	.630	.750*	.296	.537
	Significance	.009	.024		.108	.072	.066	.586	.028	.069	.020	.440	.136
	N	9	9		4	5	6	9	9	9	9	9	9
BDE–153	Correlation	.986**	.886*	.892		.998**	1.000**	.962**	.987**	.995**	.993**	–.197	.661
	Significance	.002	.045	.108		.002	.000	.009	.002	.000	.001	.751	.224
	N	5	5	4		4	5	5	5	5	5	5	5
BDE–154	Correlation	.971**	.991**	.845	.998**		.996**	.884*	.996**	.998**	.980**	.538	.610
	Significance	.006	.001	.072	.002		.000	.047	.000	.000	.003	.350	.275
	N	5	5	5	4		5	5	5	5	5	5	5
BDE–183	Correlation	.984**	.890**	.783	1.000**	.996**		.898**	.982**	.988**	.992**	–.109	.619
	Significance	.000	.007	.066	.000	.000		.006	.000	.000	.000	.815	.138
	N	7	7	6	5	5		7	7	7	7	7	7
BDE–209	Correlation	.625*	.564*	.211	.962**	.884*	.898**		.601*	.594*	.630*	–.015	.650**
	Significance	.013	.029	.586	.009	.047	.006		.018	.019	.012	.957	.009
	N	15	15	9	5	5	7		15	15	15	15	15
PBBz	Correlation	.960**	.859**	.721*	.987**	.996**	.982**	.601*		.975**	.967**	.036	.716**
	Significance	.000	.000	.028	.002	.000	.000	.018		.000	.000	.896	.002
	N	16	16	9	5	5	7	15		16	16	16	16
PBT	Correlation	.951**	.837**	.630	.995**	.998**	.988**	.594*	.975**		.965**	–.014	.610*
	Significance	.000	.000	.069	.000	.000	.000	.019	.000		.000	.959	.012
	N	16	16	9	5	5	7	15	16		16	16	16
DPTE	Correlation	.992**	.906**	.750*	.993**	.980**	.992**	.630*	.967**	.965**		.062	.649**
	Significance	.000	.000	.020	.001	.003	.000	.012	.000	.000		.819	.007
	N	16	16	9	5	5	7	15	16	16		16	16
HBB	Correlation	.029	.468	.296	–.197	.538	–.109	–.015	.036	–.014	.062		.145
	Significance	.914	.068	.440	.751	.350	.815	.957	.896	.959	.819		.591
	N	16	16	9	5	5	7	15	16	16	16		16
DP	Correlation	.660**	.613*	.537	.661	.610	.619	.650**	.716**	.610*	.649**	.145	
	Significance	.005	.012	.136	.224	.275	.138	.009	.002	.012	.007	.591	
	N	16	16	9	5	5	7	15	16	16	16	16	

**<0.01
*<0.05
N=number of values used for correlation analyses

TABLE S10. Correlations (calculated as Pearson correlation) of major HFRs in seawater.

		BDE–47	BDE–99	BDE–100	BDE–209	PBBz	PBT	DPTE	HBB	DP
BDE–47	correlation		.998**	–.070	.812	.137	.770**	.842**	.285	.780**
	significance		.000	.859	.095	.863	.003	.002	.286	.000
	N		6	9	5	4	12	10	16	16
BDE–99	correlation	.998**		.984*			.981**	.998**	.672	.996**
	significance	.000		.016			.000	.000	.098	.000
	N	6		4			7	6	7	7
BDE–100	correlation	–.070	.984*			–.418	.174	.134	–.236	–.076
	significance	.859	.016			.582	.709	.829	.512	.835
	N	9	4			4	7	5	10	10
BDE–209	correlation	.812							.430	.273
	significance	.095							.470	.657
	N	5							5	5
PBBz	correlation	.137	–1.000**	–.418			–.184	.954	.831	–.039
	significance	.863	.	.582			.816	.194	.169	.961
	N	4	2	4			4	3	4	4
PBT	correlation	.770**	.981**	.174		–.184		.982**	.417	.978**
	significance	.003	.000	.709		.816		.000	.138	.000
	N	12	7	7		4		9	14	14
DPTE	correlation	.842**	.998**	.134		.954	.982**		.675*	.987**
	significance	.002	.000	.829		.194	.000		.032	.000
	N	10	6	5		3	9		10	10
HBB	correlation	.285	.672	–.236	.430	.831	.417	.675*		.444
	significance	.286	.098	.512	.470	.169	.138	.032		.065
	N	16	7	10	5	4	14	10		18
DP	correlation	.780**	.996**	–.076	.273	–.039	.978**	.987**	.444	
	significance	.000	.000	.835	.657	.961	.000	.000	.065	
	N	16	7	10	5	4	14	10	18	

**<0.01
*<0.05
N=number of values used for correlation analyses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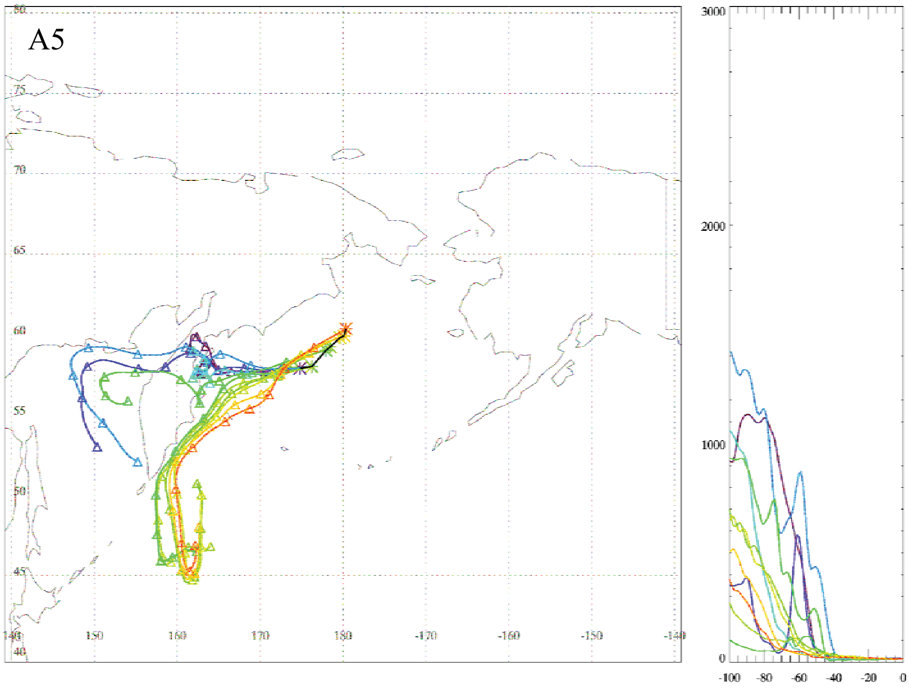
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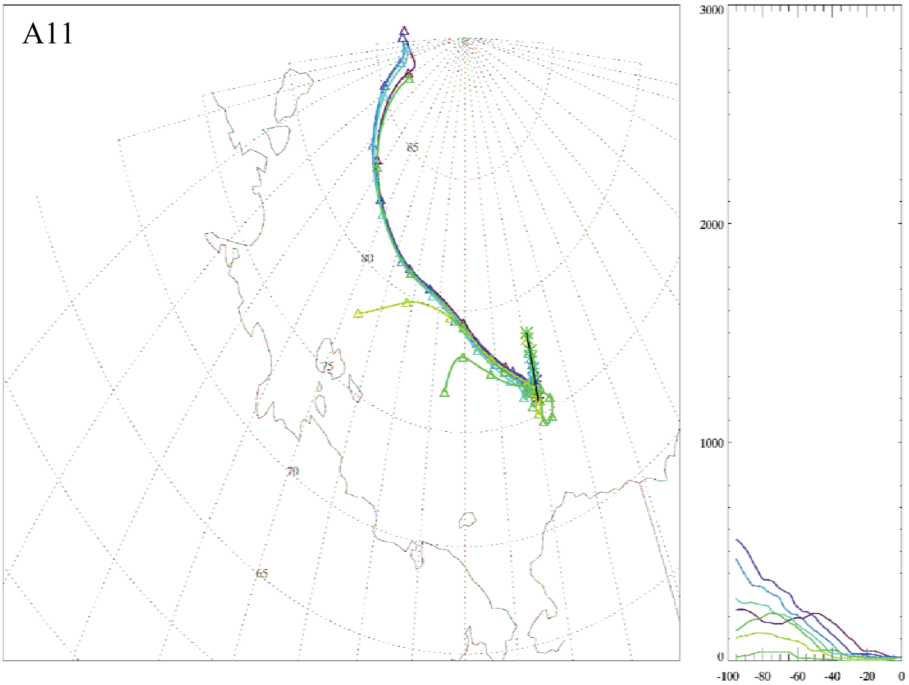
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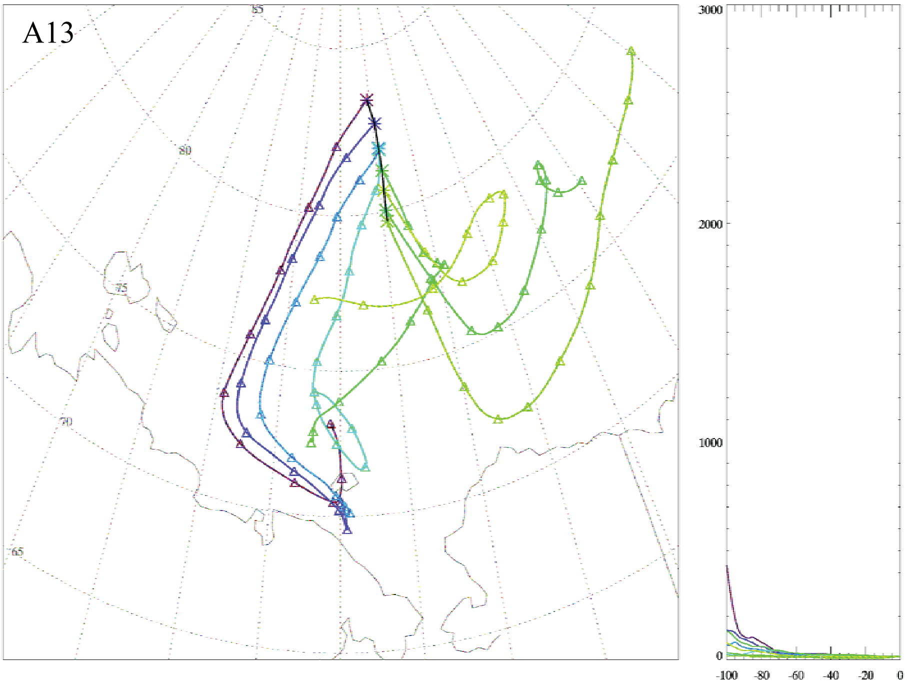
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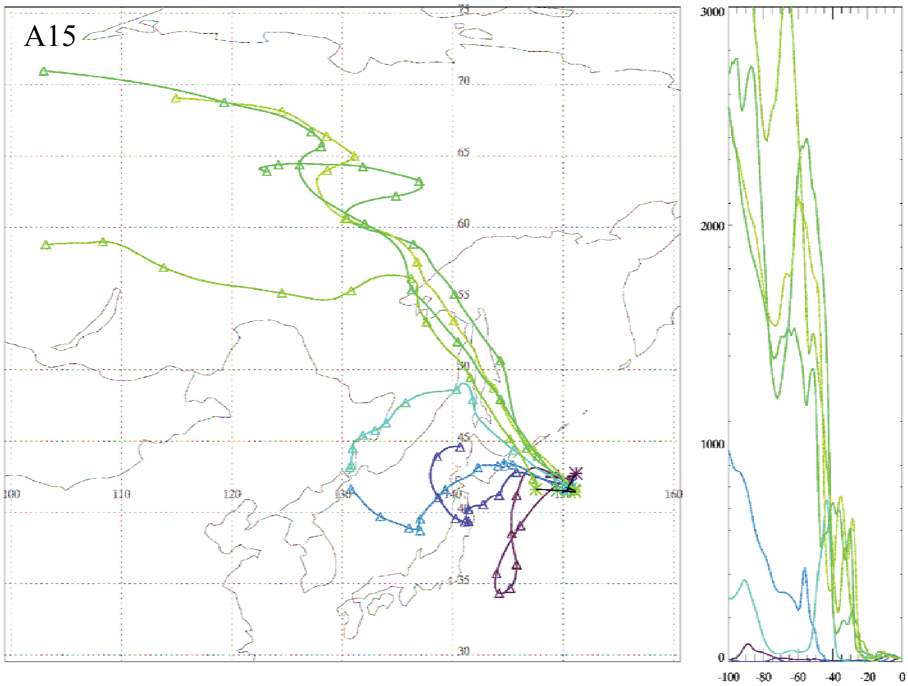

FIGURE S1. Plots of air mass back trajectories and altiduninal profile traced back for 120 h (96 h for A11) for the samples A1, A5, A11, A13 and A15. The black line indicates the ships cruise leg during sampling.

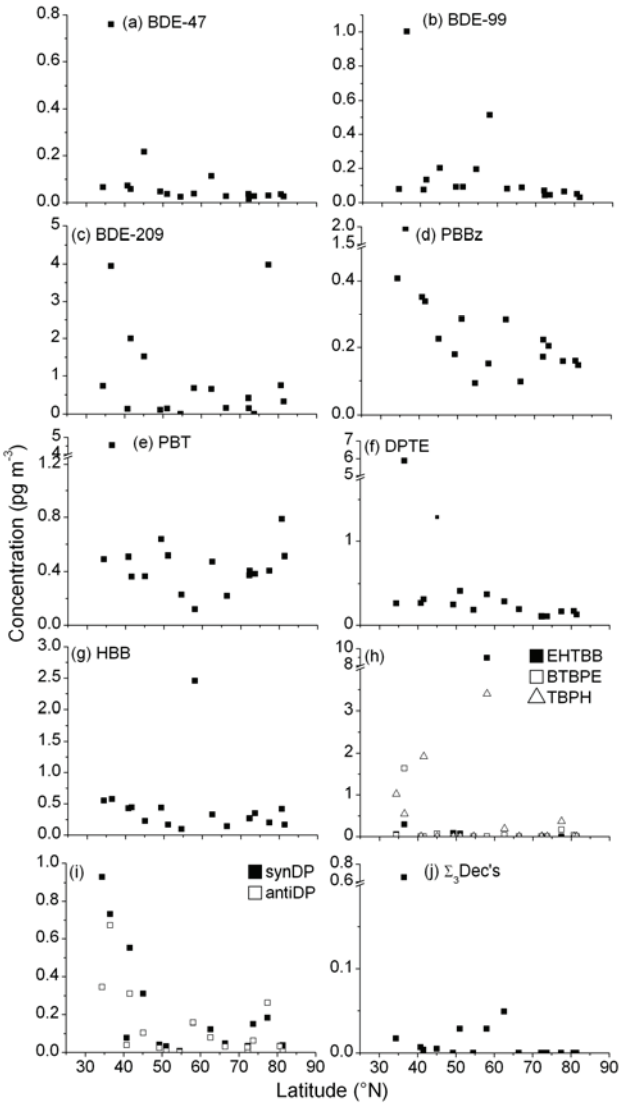

FIGURE S2. Latitudinal trends of individual HFRs in the atmosphere. Note that for station A4 only the gaseous phase was analyzed.

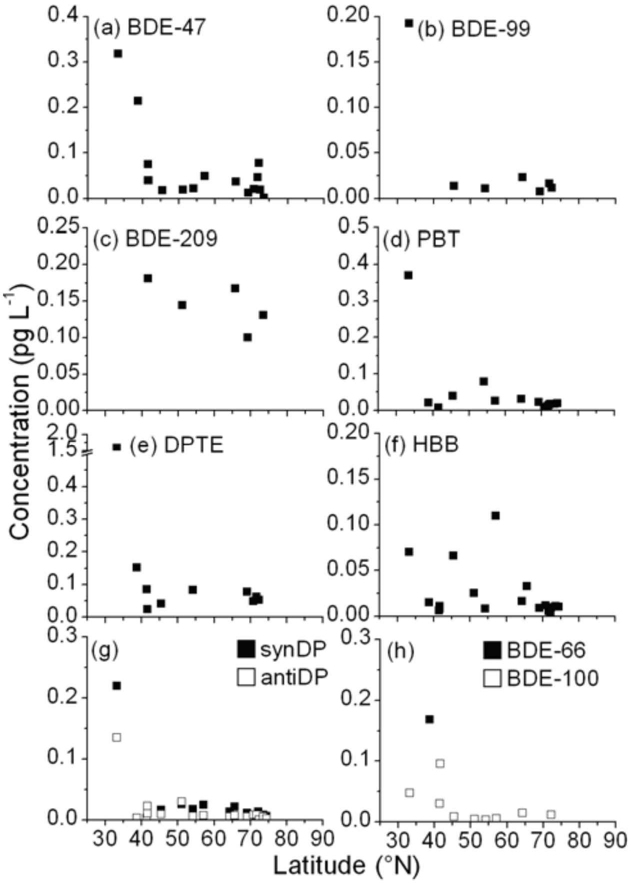

FIGURE S3. Latitudinal trends of individual HFRs in seawater. Note that for station W1, W2, W16 and W18 only the dissolved phase was analyzed.

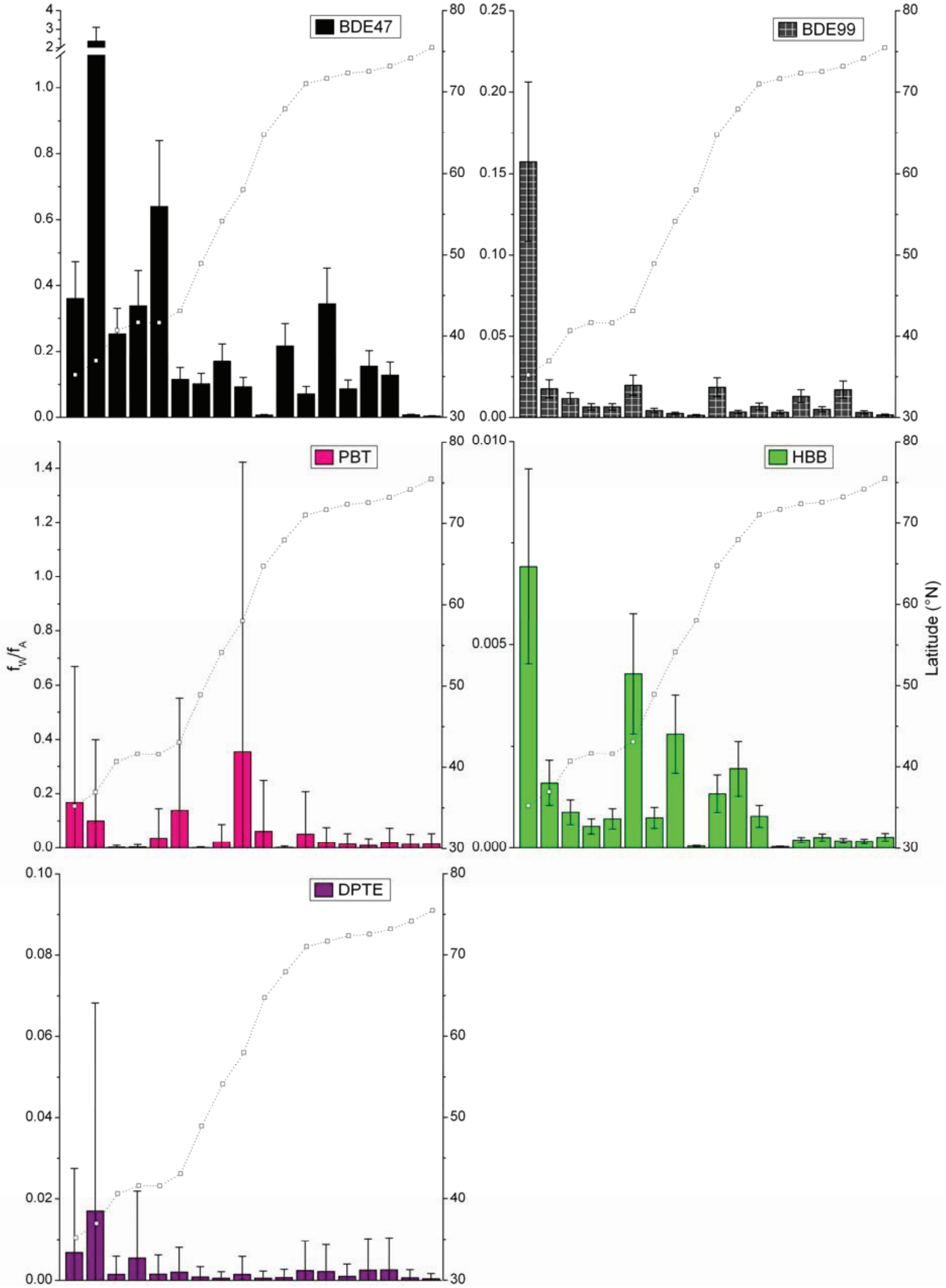

FIGURE S4. f_W/f_A ratios of individual HFRs. The Latitude is included as dotted line.

Comment on the calculation of the fugacity ratios, air–seawater gas exchange and dry particle bound deposition

Fugacity ratios. The fugacity ratio was calculated using eq S1

$$\frac{f_W}{f_A} = \frac{C_W H}{C_A R T_A} \tag{S1}$$

where f_W and f_A are the fugacities in water and air, respectively, C_W and C_A are the dissolved and gaseous concentrations in water and air (pg m^{-3}), respectively, H is the Henry's Law constant (Pa m^3 mol^{-1}) at the given water temperature and corrected by the salinity according to ref *(4)*, R is the gas constant (8.31 Pa m^3 K^{-1} mol^{-1}) and T_A is the air temperature (K). The Henry's Law constant of BDE–47 and –99 and their temperature dependence was taken from Cetin and Odabasi *(5)* and the Henry's Law constant of HBB was taken from Tittlemier et al. *(6)*. Since there are no measured or predicted Henry's Law constant for DPTE and PBT available, we estimated it to be 0.0478 Pa m^3 mol^{-1} and 6.05 Pa m^{-3} $mole^{-1}$ using EPI Suite 4.0 developed by US EPA *(7)* and the temperature dependence was estimated to be similar to BDE–47 (for HBB, too). If C_A or C_W were not available, 2/3 of the MDL was used. A fugacity quotient <1 and >1 indicates net dry gaseous deposition and volatilization, respectively, and $f_W/f_A = 1$ indicates thermodynamic equilibrium. The total uncertainty of the fugacity was propagated from the estimated relative standard deviations of the water and air concentrations (± 20 %) and the Henry's Law constant (<13% for PBDEs *(5)*; estimated to be 20% for HBB), and the air temperature during sampling (± 10%) resulting in a total uncertainty of ± 32% and ± 35% for HBB. Since no measured Henry's Law constant of DPTE and PBT is available, we assumed an uncertainty of a factor of at least three for the fugacity ratio.

Air–seawater gas exchange. The air seawater exchange was calculated based on following eq S2 *(8, 9)*

$$F_{AW} = K_{OL}\left(C_W - \frac{C_A}{H'_{salt,T}} \right) \tag{S2}$$

where $H'_{salt,T}$ is the dimensionless temperature and salinity corrected Henry's Law constant defined as $H' = H/RT$ (R = gas constant, T = Temperature). The dimensionless Henry's Law constant was corrected by the salinity using eq S3 *(4)*

$$H'_{salt,T} = H' \times 10^{K_S C_S} \tag{S3}$$

where C_S is the salt concentration (mol L^{-1}) and K_S is the Setschenow constant (L mol^{-1}) which was taken from ref *(5)* for BDE–47 and –99, respectively, and calculated for HBB, DPTE and PBT following eq S4 *(10)*

$$K_S = 0.04 \log K_{OW} + 0.114 \tag{S4}$$

K_{OL} (m h^{-1}) is the gas phase overall mass transfer coefficient compromising the resistances to mass transfer in both water (K_W, m h^{-1}) and air (K_A, m h^{-1}) and is defined by:

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_A H'} \tag{S5}$$

where *(11)*:

$$k_A = (0.2U_{10} + 0.3) \times \left(\frac{D_{i,air}}{D_{H_2O,air}} \right)^{0.61} \times 36 \tag{S6}$$

$$k_W = (0.45 U_{10}^{\;1.64}) \times \left(\frac{Sc_i}{Sc_{CO_2}} \right)^{-0.5} \times 0.01 \tag{S7}$$

D_{air} is the diffusity in air, U_{10} is the wind speed at 10 m height above sea level (m s^{-1}), and Sc is the water phase Schmidt number which was taken from ref *(4)* for CO_2. D_{air} was calculated using the method described by Fuller et al. *(12)* and Sc for the BFRs was calculated using the method described by Hayduk and Laudi *(13)*. The molar volume of BDE–47, –99 and HBB, which is needed for the calculation of $D_{i,air}$ was taken from ref *(14)* or calculated following ref *(15)* for PBT and DPTE. The overall uncertainty of BDE–47, –99 and HBB was calculated with ± 51% and ± 55% based on an uncertainty of ± 40 % for K_{OL} *(5)*. The uncertainty of DPTE and PBT has to be estimated to be at least ± 500% since the uncertainties of both H' and K_{OL} are not known.

Particle–bound dry deposition. The dry particle–bound deposition flux F_d (F_d, pg m^{-2} day^{-1}) was calculated using eq S8

$$F_d = V_d C_p \tag{S8}$$

where V_d is the deposition velocity (m d^{-1}) and C_p is the concentration in the particulate phase (pg m^{-3}). The deposition velocity strongly depends on both meteorological parameter, size and physicochemical parameters of the airborne particle and of the pollutant itself *(16)*, especially for air masses transporting particles originating from urbanized and industrialized regions. For the studied area (i.e., East China Sea and Sea of Japan, North Pacific, Arctic) no measured deposition velocities of the analyzed compounds are available. Castro–Jiménez et al. *(17)* used a velocity of 0.2 cm s^{-1} for PCDD/Fs, representing marine aerosols influenced by continental sources. Li et al. *(18)* measured deposition velocities betwenn 0.16 and 0.32 cm s^{-1} for PBDEs in Guangzhou, China and Hong Kong *(18)*. Therefore, we used a value of 0.3 cm s^{-1} for sampling stations in East Asia (A1, A15, A16, A17). Based on recent studies on dry deposition fluxes for open Sea conditions *(19, 20)*, we used an value of 0.1 cm s^{-1} for the stations in the North Pacific and in the Arctic. However, the differences in the dry particle–bound deposition velocities are still mainly resulted by the differences in the particulate concentrations of the analyzed HFRs. Higher differences are to be expected if the differences of the deposition velocities, both spatially and between the different compounds would be know. Therefore, we estimate an uncertainty of a factor of 3 for the velocity, and consequently for the dry particle–bound deposition flux.

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Paper VI

Brominated Flame Retardants and Dechlorane Plus in the Marine Atmosphere from Southeast Asia toward Antarctica

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Brominated Flame Retardants and Dechlorane Plus in the Marine Atmosphere from Southeast Asia toward Antarctica

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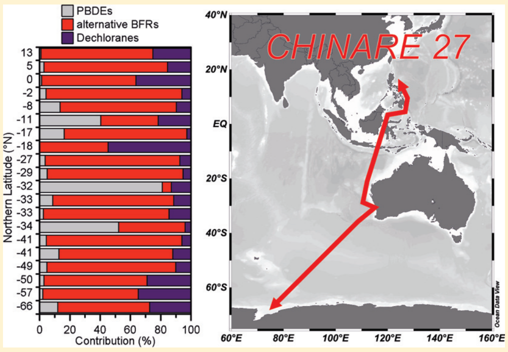
Ⓢ *Supporting Information*



ABSTRACT: The occurrence, distribution, and temperature dependence in the marine atmosphere of several alternative brominated flame retardants (BFRs), Dechlorane Plus (DP) and polybrominated diphenyl ethers (PBDEs) were investigated during a sampling cruise from the East Indian Archipelago toward the Indian Ocean and further to the Southern Ocean. Elevated concentrations were observed over the East Indian Archipelago, especially of the non-PBDE BFR hexabromobenzene (HBB) with concentrations up to 26 pg m^{-3} which were found to be related to continental air masses from the East Indian Archipelago. Other alternative BFRs— pentabromotoulene (PBT), pentabromobenzene (PBBz), and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE)—were elevated, too, with concentrations up to 2.8, 4.3, and 2.3 pg m^{-3}, respectively. DP was detected from 0.26 to 11 pg m^{-3} and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) ranged from not detected (nd) to 2.8 pg m^{-3}, respectively. PBDEs ranged from nd to 6.6 pg m^{-3} (Σ_{10}PBDEs) with the highest individual concentrations for BDE-209. The approach of Clausius–Clapeyron (CC) plots indicates that HBB is dominated by long-range atmospheric transport at lower temperatures over the Indian and Southern Ocean, while volatilization processes and additional atmospheric emissions dominate at higher temperatures. In contrast, BDE-28 and -47 are dominated by long-range transport without fresh emissions over the entire cruise transect and temperature range, indicating limited fresh emissions of the meanwhile classic PBDEs.

INTRODUCTION

Halogenated flame retardants (HFRs) are applied to reduce the flammability of many consumer products such as electrical and electronic products (E&E), textiles, and furnishings in order to protect humans from outbreak and spread of fires. They have been industrial chemicals of growing worldwide environmental and political concern in the 1990s and 2000s, and are still an emerging class of chemicals. Polybrominated diphenyl ethers (PBDEs) were the most produced and used brominated flame retardants (BFRs) in the 1990s and early 2000s. They are known to be harmful for the environment and humans because of their toxicity, bioaccumulation potential, and persistence in the environment, as well as their potential to be atmospherically transported from source regions over very long distances toward remote regions.[1] Meanwhile, the production and use of two traditional industrial PBDE mixtures—Penta- and OctaBDE—has been restricted worldwide and they were included into the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009 (www.pops.int). The third technical PBDE mixture—DecaBDE—is still being produced, even though its application is partly restricted (e.g., in E&E equipment in the European Union (EU)[2]) and production phase-outs have been announced (e.g., for 2012 in the United States[3]).

PBDEs have been detected worldwide in various environmental compartments[4,5] including remote regions such as the Arctic[6] and Antarctic.[7] In recent years, an increasing number of studies focused on the Asian environment due to (a) the growing (BFR) industry in Asian countries, in particular in China, and (b) the treatment of electronic waste (e-waste) which is being shipped mainly from Europe and Northern America to Asia, again predominantly to China, and recycled rather primitively (e.g., burning in open fires).[8−11] In addition to PBDEs, alternative aromatic BFRs such as 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) have received emerging concern due to their application as PBDE-replacements. Even more alarming, some alternative BFRs have been used similar to PBDEs for several decades (e.g., hexabromobenzene (HBB),

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pentabromotoluene (PBT)[12]) but have been omitted from most environmental investigations on BFRs during that time. Besides, another highly chlorinated flame retardant with annual production volumes of several thousand tons—Dechlorane Plus (DP)—has been frequently investigated since its first report in the environment in 2006,[13] but its production and usage had already started already back in the 1970s.[13] Several alternative BFRs and DP have been detected on different continents as summarized in recent reviews.[6,14,15] Nevertheless, knowledge on their possible adverse effects, bioaccumulation potential and occurrence, distribution, and transport in the environment is still very limited.

Because PBDEs and several alternative BFRs can be classified as semivolatile chemicals they can be transported in the gas phase over long ranges from source regions toward the Polar Regions, or, as shown for the extremely hydrophobic nonvolatile HFRs such as BDE-209 and DP, be transported attached to airborne particles over similar ranges.[16,17] Thereby, they travel over the global oceans and can interact with the oceans surface including deposition processes. These are important sources for the open oceans, besides riverine inputs which mainly influence coastal environments. Once deposited into the ocean, they become bioavailable for marine organisms and are subject to further transport via ocean currents. In addition, they can revolatilize into the atmosphere or deposit in sediments. Besides PBDEs, several non-PBDE BFRs, namely HBB, PBT, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), and DP, have been recently detected during sampling cruises in the European Arctic, the Northern and Southern Atlantic Ocean toward Antarctica, and the Northern Pacific Ocean toward the high Arctic in similar or even higher concentrations.[17−20] Obviously, they share the property of long-range atmospheric transport (LRAT) potential with PBDEs but this still needs to be investigated for further oceanic regions.

In the present study, we investigated the occurrence and spatial distribution of PBDEs and several alternative BFRs as well as dechloranes in the atmosphere during a sampling cruise through the East Indian Archipelago (EIA) toward the west coast of Australia, and further to the Southern Ocean toward Antarctica, with respect to possible source regions and temperature dependence, especially of alternative BFRs to further improve the understanding of the global atmospheric transport of (alternative) BFRs and DP.

■ MATERIALS AND METHODS

Sampling Cruise. Atmospheric boundary layer air samples were taken aboard the Chinese research ice-breaker R/V *Xuelong (Snow Dragon)* of the Polar Research Institute of China during the 27th Chinese National Antarctic Expedition (CHINARE 27) from November 2010 to March 2011. Twenty high-volume air samples (1−2 days, ~500 m^3) were taken along the following transect: Sulu Sea (6.93° N, 120.28° E)−Fremantle (Australia)−Antarctica (−68.11° N, 75.64° E)−Fremantle (Australia)−Philippine Sea (16.25° N, 127.17°E). Samples were taken by a high-volume air pump placed on a platform used for air sampling purposes only in the front of the ship's most upper deck ~20 m above sea level. The sampler generally consisted of a high-volume air pump connected to a filter head in which a glass fiber filter (grade GF/F, pore size: 0.7 μm) was fixed to trap airborne particles, followed by a glass column packed with PUF/Amberlite XAD-2 to trap gaseous compounds. Filters and columns were stored at −20 °C until extraction. Sampling parameters such as latitude, longitude, and air temperature are included in Table S1 in the Supporting Information (SI).

Extraction, Cleanup, and Analysis. Extraction, cleanup, and analysis of the samples followed the method described in Möller et al.[17] Air columns and filters were extracted separately while only half of the filter was used for extraction. Briefly, the samples were spiked with 200 pg of each ^{13}C−HBB, ^{13}C−BDE-77, ^{13}C−BDE-138 (Wellington Laboratories), and ^{13}C−synDP (Cambridge Isotope Laboratories) and with 2000 pg ^{13}C−BDE-209 (Wellington Laboratories) as surrogates, extracted by dichloromethane in a Soxhlet apparatus and further cleaned on a silica column (2.5 g, 10% water deactivated) topped on anhydrous granulated sodium sulfate. After volume reduction to 30 μL, 500 pg of CB-207 (Dr. Ehrenstorfer GmbH) was added as a recovery standard prior to injection. Analysis was done by a GC/MS-system (Agilent 6890 GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI). The analytes were separated on a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific) except BDE-209 which was separated using a DB5-MS column (15 m × 0.25 mm i.d. × 0.10 μm film thickness, J&W Scientific). Samples were analyzed for 10 PBDE congeners (-28, -47, -66, -85, -99, -100, -153, -154, -183, -209), 8 alternative BFRs (pentabromobenzene (PBBz), HBB, PBT, pentabromoethylbenzene (PBEB), DPTE, BTBPE, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and TBPH (all obtained from Wellington Laboratories)), synDP and antiDP and the 1- and 2-fold dechlorinated DP species ($aCl_{11}DP$ [−1Cl + 1H], $aCl_{10}DP$ [−2Cl + 2H]; Wellington Laboratories), and Dechlorane 602, 603, and 604 (Toronto Research Chemicals).

QA/QC. As described elsewhere, good care was taken to avoid sample contamination before sampling, during sampling, and during extraction and further treatment.[17,19] By sampling in the front of the most upper deck and sampling during good wind conditions only, which means no sampling during backwinds which might transport exhaust gas to the sampler, the risk of possible contamination by the ship itself was limited as much as possible. In addition, sampling was stopped at wind speeds <3 m s^{-1} to prevent sample contamination by possible diffuse emissions from the ship. In addition, spatial trends from source regions toward the open ocean and air mass related trends (see Spatial Distribution) would not have been observed if contamination by the ship had occurred which would rather lead to constantly high concentrations along the entire cruise leg. Nevertheless, similar to land-based sampling of organic pollutants in remote regions, the prevention from local contamination can not be completely ensured. Breakthrough of the target compounds was checked during earlier sampling cruises.[17,19] Both air filter and column blanks were taken. Blank values were in the one- to three-digit absolute pg range (see Table S2 for individual blank values). Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation or, for the BFRs showing no blank values, from the instrumental detection limits at signal-to-noise (*S*/*N*) ratios of three. Based on a mean sampling volume of 500 m^3 and 250 m^3 for the air columns and filters, respectively, MDLs ranged from 0.002 to 1.2 pg m^{-3} except BDE-209 which had a higher MDL of 3.4 pg m^{-3} (see Table S3 for individual MDLs). However, since the sampling volume varied from 190 to 770 m^3, concentrations below the MDLs were excluded based on absolute MDLs. Recovery spike tests were run in parallel to the samples for both air columns and filters showing

Table 1. Atmospheric Concentrations (in pg m^{-3}, Sum of Gaseous and Particulate Phases) of PBDEs, HBB, PBT, DPTE and DP over the Global Oceans and Their Marginal Seas (na = Not Analyzed, nd = Not Detected)

	year[a]	BDE-47	BDE-209	ΣPBDEs	HBB	PBT	DPTE	DP	ref
Atlantic Ocean	2008	0.57−8.3	na	0.86−6.4	na	na	na	na	ref49
Atlantic Ocean	2008	0.18−2.3	na	0.43−3.3	0.10−11	0.01−0.05	0.10−2.3	0.05−1.6	ref17,20
Atlantic Ocean (North Sea)	2010	0.10−0.79	nd−9.4	0.31−10.7	0.09−6.3	nd−0.24	nd−2.5	0.13−22	ref23
Pacific Ocean	2010	0.04−0.11	nd−2.0	0.22−2.3	0.10−2.5	0.12−0.64	0.18−0.41	0.01−0.86	ref18
Pacific Ocean[b]	2003	0.88−17	<0.5−27	1.4−37	na	na	na	na	ref22
Pacific Ocean (East Asian Seas)	2010	0.07−0.76	0.13−3.9	0.31−8.1	0.26−5.9	0.36−4.53	0.26−5.9	0.52−0.75	ref18
Pacific Ocean (East Asian Seas)[b]	2003	<0.16−112	<0.50−29	2.3−199	na	na	na	na	ref22
Pacific Ocean (East and South China Seas)	2008	0.41−13	na	2.9−29	na	na	na	na	ref49
Pacific Ocean (East Indian Archipelago and Philippine Sea)	2010/11	0.14−0.32	nd−4.0	0.14−4.6	3.7−19	0.71−2.2	0.44−2.3	1.7−11	this study
Indian Ocean	2008	0.57−8.3	na	1.15−13	na	na	na	na	ref49
Indian Ocean	2004/05	<3.4−13	<0.6	1.5−16	na	na	na	na	ref39
Indian Ocean	2010/11	nd−0.49	nd−6.5	nd−6.6	0.15−26	nd−2.8	nd−1.1	0.26−2.1	this study
Arctic Ocean	2010	0.03−0.04	nd−4.0	0.07−4.1	0.16−0.42	0.22−0.79	0.10−0.19	0.05−0.44	ref18
Arctic Ocean[b]	2003	<0.16-31	<0.50−41	<2.58−61	na	na	na	na	ref22
Arctic Ocean (Greenland Sea)	2009	0.06−0.95	nd−0.07	0.09−1.8	0.08−0.66	nd−0.02	0.01−1.7	0.02−4.2	ref17,19
Southern Ocean	2008	0.58	na	0.78	0.32	0.02	0.04	0.07	ref17,20
Southern Ocean	2010/11	0.08	nd	0.13	0.12	nd	nd	0.31	this study

[a] Year of sampling. [b] Only aerosols.

recoveries of the target analytes of 86 ± 19% and relative recoveries corrected by the surrogates of 101 ± 16%.

Air Mass Back Trajectories. For each sample, air mass back trajectories (BTs) were calculated using NOAA's HYSPLIT model.[21] BTs were calculated for arrival times in 6-h steps at the corresponding position of the ship along the cruise leg. BTs were traced back for 120 h with the sampling height as arrival height (see Figure S1 for individual BTs).

RESULTS AND DISCUSSION

Concentration Levels of PBDEs. In the present paper, the concentrations are given as sum of gaseous and particulate phase if not stated otherwise. Individual concentrations of all investigated HFRs for each sample and phase are given in Table S4. Σ_{10}PBDEs refers to the sum of all ten PBDE congeners analyzed in this study.

The Σ_{10}PBDEs concentrations ranged from not detected (nd) to 6.6 pg m^{-3} with a median concentration of 0.24 ± 2.2 pg m^{-3}. Thereby, the common PentaBDE congener BDE-47 was the most frequently detected congener, followed by BDE-28 and BDE-99 and BDE-209. Four other congeners—BDE-100, -153, -154, and -183—were detected only sporadically, while BDE-66 and -85 were not detected. BDE-47 ranged from nd to 0.49 pg m^{-3} while the highest individual concentrations among the detected congeners were observed for BDE-209 ranging from nd to 6.5 pg m^{-3}. It needs to be noted that the MDL of BDE-209 was higher than that for the lower brominated congeners which might lead to some nondetections of BDE-209 whereas BDE-47 was detected in almost all samples.

The observed concentrations are in the range of typical atmospheric PBDE concentrations over the global oceans. To the best of our knowledge, all available data on PBDE concentrations in the atmosphere over the global oceans, including their marginal seas, are summarized in Table 1 (please note that only ship-based studies are summarized and coastal land studies were not included). PBDE concentrations over the global oceans are generally in the three-digit fg m^{-3} to one-digit pg m^{-3} range. Thereby, they underlie regional differences such as the distance to possible source regions and the related emissions. In addition, environmental parameters such as wind direction and wind speed during sampling and temperature-related effects influence PBDE levels. These individual regional differences and influences are discussed for the different regions in the references given in Table 1. Due to the individual influences as described above, it is not useful to compare these given PBDEs concentrations over the different oceans. Atmospheric PBDEs over the Pacific, Atlantic, and Indian Oceans generally represent, at least over the open oceans, global background concentrations. Within the oceans, the highest concentrations were generally observed in the marginal seas such as East China Sea for the Pacific Ocean[18,22] or the North Sea for the Atlantic Ocean,[23] primarily during land breeze where BFRs are transported from the source region toward the ocean.

Comparing the Southern and Arctic Ocean, relatively lower concentrations were observed over the Southern Ocean. This can be explained by the relatively close adjacency to the (former) production and use regions (i.e., Europe, Northern America, Asia) of the Arctic Ocean compared to the Southern Ocean. Nevertheless, PBDEs have been detected in Antarctic organisms[7,24−26] showing that even if atmospheric concentrations are comparably low and transport toward Antarctica were/is limited, they are still sufficient to force accumulation of PBDEs, and possibly other HFRs, into the Antarctic food web after deposition into the Southern Ocean and Antarctica.

Concentration Levels of Alternative BFRs and Dechloranes. Besides PBDEs, several alternative BFRs—PBBz, HBB, PBT, DPTE, EHTBB, and TBPH—were detected. Thereby, the "traditional" non-PBDEs BFRs—HBB, PBT—and PBBz dominated with individual concentrations from 0.12 to 26 pg m^{-3}, nd−2.8 pg m^{-3}, and nd−4.3 pg m^{-3}, respectively, which were predominantly distributed into the gaseous phase (particle-bound fractions of 6 ± 5% for HBB, 0% for PBT and PBBz). DPTE and TBPH were detected in 85% and 90% of samples with concentrations of nd−2.3 and nd−2.8 pg m^{-3}, respectively. EHTBB was detected in only 20% of samples with maximum concentrations of 0.21 and 0.40 pg m^{-3}, respectively.

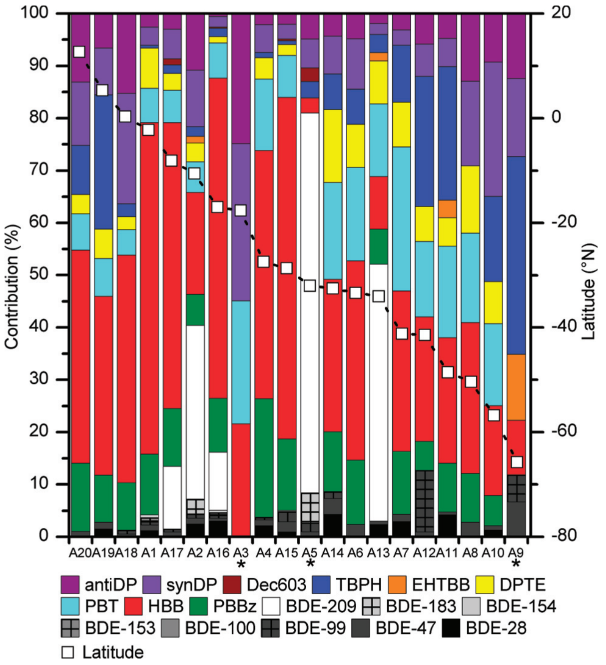

Figure 1. Contribution of individual HFRs in the atmosphere. For samples marked with an asterisk only the particulate phase was analyzed.

In Figure 1, the relative contribution of all investigated HFRs is plotted. Here it becomes evident that HBB is the predominating compound between 20° N and −35° N with a mean contribution of 42 ± 17% (excluding stations A3 and A5 where only the particulate phase was analyzed). Against the background that PBDEs, especially BDE-47, have traditionally been the dominating and most frequently investigated and detected BFRs in the global atmospheric environment,[5,6,27,28] this might be surprising. But taking the most recent literature on PBDEs vs alternative BFRs into account, it is not. Concentrations of HBB over the global oceans are summarized in Table 1, showing concentrations similar to or higher than those of PBDEs, both in marginal seas which are directly influenced by continental emissions as well as far from possible source regions such as in the Arctic. The HBB concentrations observed in this study are the highest reported atmospheric HBB concentrations over the marine environment so far. Regarding continental air levels, Arp et al.[12] reported HBB in Norway at 4.3 ± 5.3 pg m^{-3} attached to airborne particles only, which reflects a total atmospheric HBB concentration of ∼100 pg m^{-3} assuming a particle-bound fraction of ≤5% (calculated from U.S. EPA EPI Suite V 4[29]). Interestingly, in the Great Lakes atmosphere the highest HBB concentrations were detected at a rural site (Sturgeon Point) at 6.4 ± 0.9 pg m^{-3} which is 80% of the ΣPBDEs concentration (in the gas phase), and even ∼5 times higher than the BDE-47 concentrations of 1.4 ± 0.2 pg m^{-3} at this sampling site.[30] In contrast, HBB was much lower than PBDEs at urbanized sites. In the North Sea atmosphere (marginal sea of the Atlantic Ocean), HBB was found about 10 times higher than BDE-47 during winter time and to be influenced by Scandinavian or even Arctic air masses.[23] This indicates that the occurrence and distribution of HBB in the global atmosphere seems to be related to more complex mechanisms than PBDEs, which are generally strongly correlated with point sources, the degree of urbanization or simply the distance to source regions.[20,31,32] In any case, a persistence and LRAT potential of HBB similar to known POPs was estimated for HBB.[33] This shows that HBB is a chemical compound of (increasing) global concern and a possible POP candidate, what is further demonstrated by this study.

The PBT, PBBz, and DPTE concentrations are present at a range similar to that observed for the Pacific Ocean,[18] both for the investigated marginal seas (EIA vs East Asian Seas) and for the open ocean and remote regions (Indian Ocean toward Antarctica vs Northern Pacific Ocean toward the Arctic) indicating similar concentrations over the oceans in the Northern and Southern Hemisphere. Noticeably, the concentrations of PBT are somewhat higher in the Pacific Ocean and the American/Russian Arctic than in the Atlantic Ocean and the European Arctic. This might be related to the production (and probably usage) of PBT primarily in the U.S. and China (see ref 15 for information on production). Because PBT might be also a breakdown product of higher brominated FRs (such as decabromodiphenyl ethane as shown by Grause et al.[34]), the distribution of PBT in the global atmosphere might be also related to the production, use, and emission of other BFRs. It needs to be noted that ship-based samples represent instantaneous samples while concentrations might vary over time.

Among the dechloranes, DP was detected in all samples from 0.26 to 11 pg m^{-3} (as sum of the two stereoisomers). Dechlorane 603 was observed in only 20% of samples at a maximum concentration of 0.40 pg m^{-3}. Again, the DP concentrations are in the range of previously reported DP concentrations in the marine atmosphere (see Table 1), while the highest concentrations in this study were detected over the EIA and are in the range of those detected in the North Sea, Atlantic Ocean[23] representing coastal marine environments with continental influence. Sverko et al.[35] reported DP from continental air sampling stations of Southeast Asian archipelagic states and from Australia within the Global Atmospheric Passive Sampling (GAPS) program. Concentrations were generally in a range similar to that observed in this study, while unexpected high concentrations up to 79 pg m^{-3} were observed at a background site in Tasmania possibly resulting from local sources. On a global scale, the highest DP concentrations were generally detected in the U.S and China, with concentrations up to several ng m^{-3} close to the known production sites or e-waste treatment facilities.[14] The observed Dechlorane 603 concentrations are similar to those observed over the Sea of Japan,[18] but further data on Dechlorane 603 in the global atmosphere are lacking.

The fractional abundance of the synDP isomer (f_{syn} = synDP/synDP + antiDP) ranged from 0.48 to 0.80 with a mean abundance of 0.59 ± 0.09 which is higher than the ratio of the technical mixture (f_{syn} = 0.20−0.41).[36] We could not observe any correlation of f_{syn} with the latitude, temperature, or total DP concentration. As a conclusion, DP has already been subject to stereoselective depletion of the anti isomer during atmospheric transport as first noticed by Hoh et al.[13] and further confirmed in other studies on DP.[17,23,37,38] A similar ratio has also been observed during a sampling cruise over the Northern Pacific Ocean toward the Arctic.[18] Sverko et al.[14] proposed izomerization from syn- to antiDP as a second mechanism for the alteration of f_{syn}. In addition, the ratio could have been altered before emission into the environment. However, the mechanisms and parameters which might strengthen stereoselective differences such as solar radiation or air temperature are still not understood and need further experimental studies as well as environmental monitoring.

Spatial Distribution. The spatial distribution of Σ_{10}PBDEs, HBB, PBBz, PBT, DPTE, TBPH, and DP is shown in Figure 2, individual plots for the dominating HFRs vs the northern latitude are given in Figure S2. The highest concentrations, especially for HBB, PBBz, and PBT were observed over the EIA toward the West coast of Australia and are more than 10 times higher than over the open Indian Ocean. Slightly higher concentrations were observed for BDE-28, -47 and -99, too, but not in an extent similar to the alternative BFRs, whereas BDE-209 did not show any clear spatial distribution due to the nondetects caused by the higher MDL (as mentioned above). The peak concentration of DP (11 pg m^{-3}) was detected in this region, too, also in the gaseous phase. Over the EIA, samples were taken in relatively close proximity to land (i.e., the Indonesian islands) and the BT plots show continentally influenced air masses (see Figure S1). A similar trend has been observed by Wurl et al. who reported the highest atmospheric PBDE concentrations over the Indian Ocean in proximity to the Indonesian islands, too.[39] Even if, to the best of our knowledge, production sites of BFRs in the Archipelagic states are not known, the elevated concentrations can be explained by the high population density in this region, with Indonesia being the world's fourth most populated country (population ~240 million), and the associated industry, including electronic industry, and general use and emissions of HFRs.

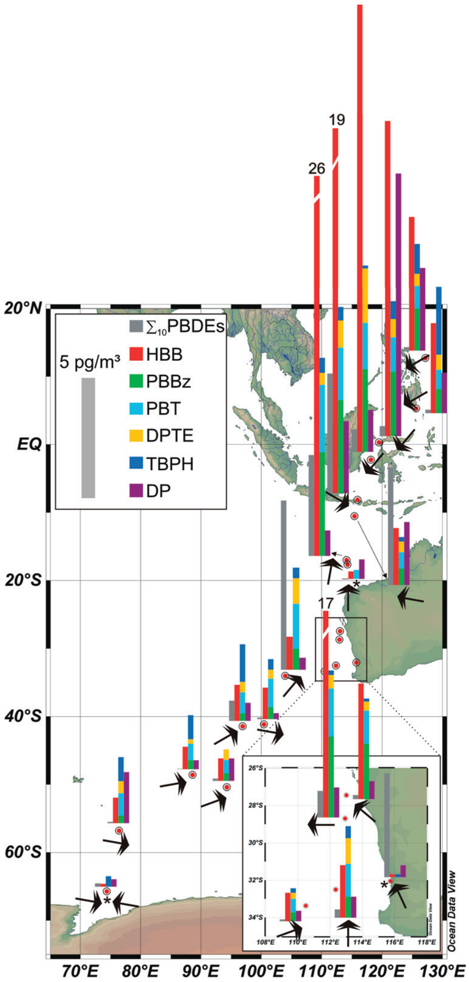

Figure 2. Spatial distribution of the dominating HFRs. For samples marked with an asterisk only the particulate phase was analyzed. The black arrow indicates the mean wind direction during sampling (see Figure S1 for detailed BT plots).

Besides, the treatment of e-waste might be an important source of HFRs in the environment as shown for several sites in China.[8,11] China receives 70% of all global exported e-waste;[40] the remaining amount also ends up in other Southeast Asian countries.[41] Considering HBB, PBT, and PBBz might also be emitted by degradation of higher brominated flame retardants or polymeric flame retardants,[34,42−44] the emissions from e-waste treatment might be even higher for these compounds than from the production, which takes place in China and Japan (HBB)[45] and U.S. and China (PBT),[15] and from their use. Very strikingly, Xie et al.[20] reported elevated HBB concentrations over the Atlantic Ocean up to 11 pg m^{-3} off the West coast of Africa which are in the range of the elevated concentrations over the EIA. They likely resulted from emissions from Africa (with the source possibly being the treatment of e-waste) followed by atmospheric transport toward the Atlantic Ocean.[20] Therefore, source regions of BFRs over the global oceans, and especially HBB, are not necessarily those where they are produced, but those where they end up. Interestingly, elevated concentrations were also observed in two samples taken south of the EIA toward Australia with limited air mass influence from Southeast Asia, but with influence from Australia. However, the influences and transport of BFRs, especially of HBB, toward the ocean from different possible source regions need to be investigated by more detailed long-term studies in theses regions.

Samples in the Philippine Sea (A19 and A20) were dominated mainly by easterly air masses from the Pacific Ocean, resulting in ~5 times reduced concentrations than over the EIA. From Western Australia over the Indian Ocean toward the Southern Ocean, samples were dominated exclusively by oceanic air masses with traveling times over the ocean of several days. This resulted in concentrations generally ≤1 pg m^{-3} derived from long-range atmospheric transport without continental influence and fresh emissions, both for PBDEs and alternative BFRs and dechloranes. TBPH, which was detected in almost all samples, did not show any clear distribution pattern as observed for the other alternate BFRs. In contrast to those HFRs showing elevated concentrations in the EIA, TBPH was detected only in the particulate phase showing that they might have different sources and are subject to different transport and degradation mechanisms in the environment. However, only very little data on TBPH in the global atmosphere are available and more detailed studies are needed to further draw hypothesis on the distribution of TBPH.

Temperature Dependence. The usage of Clausius–Clapeyron (CC) plots is a common approach to investigate possible temperature dependence of gaseous POPs in the atmosphere which is based on[46]

$$\ln P = -\frac{\Delta H}{RT} + c \tag{1}$$

where P (atm) is the partial pressure of the chemical, ΔH (kJ mol^{-1}) is the transition energy between two phases, e.g., from the terrestrial or aquatic environment into the atmosphere, R is the gas constant, and T (K) is the air temperature. In theory, plotting $\ln P$ as function of the inverse air temperature will result in a slope which mimics the heat of the phase transfer. It needs to be noted that the CC equation theoretically refers to a closed, ideal system which is not given in the investigated environment. In the environment, this approach can be generally used for well resolved stationary long-term measurement, ideally with constant wind directions. Nevertheless, we used this approach for analyzing possible temperature-related effects for our nonstationary and relatively short sampling campaign since our major task was to compare the possible temperature dependence of the different BFRs, especially of alternative BFRs vs PBDEs. The resulting CC plots might be influenced by differences in location which can not be resolved in this study. Therefore, they certainly need to be confirmed by future long-term single point measurements for individual regions in future studies.

In the CC plot, a slope flatter than the theoretical ΔH value indicates the POP to originate from LRAT rather than volatilization processes.[46] We generated CC plots for the dominating BFRs in the gas phase—BDE-28, BDE-47, PBBz, PBT, HBB, and DPTE—which are shown in Figure 3. With the exemption of DPTE, statistically significant correlations ($p < 0.01$ or <0.05) were observed with linear correlations (R^2) ranging from weak correlations for PBT (0.29) to good correlations for PBBz (0.70), indicating a relationship of the gaseous air concentration with the ambient air temperature. Taking a more detailed look into the plots, especially the temperature dependence of the slope and comparison of the BFRs, important differences in the temperature dependence are evident. The slopes of BDE-28 and -47 do not show any shift with the temperature. The calculated ΔH values of the two congeners of 41 ± 13 kJ mol^{-1} ($n = 11$) and 55 ± 9 kJ mol^{-1} ($n = 18$) are lower than those for the energy of vaporization of the subcooled liquid (78 and 95 kJ mol^{-1}, respectively)[47] but close to the energy for the air–water transfer (59 and 58 kJ mol^{-1}, respectively).[48] This indicates that BDE-28 and -47 in the atmosphere are probably not or very little influenced by fresh atmospheric emissions over the entire temperature range, even over the EIA, and also over the entire cruise leg. Therefore, atmospheric concentrations are likely driven by long-range atmospheric transport, which is temperature independent,[46] as well air–seawater exchange processes.

Interestingly, the CC plots of HBB and PPBz show a change in the slope which flattens toward lower temperatures. This type of pattern has been described as a "hockey stick diagram" by Hoff et al.[46] To investigate in more detail, we simply divided the plot into two sections as indicated by the arrows in Figure 3: (a) $1/T < 0.0034$ and (b) $1/T > 0.0034$. Due to the limited number of samples the linear correlations become non-significant. Nevertheless, this approach gives information on the temperature dependence but this trend has to be confirmed by a larger data set. In the lower temperature range, the resulting slope of HBB is much flatter and the ΔH of HBB of 19 ± 7 kJ mol^{-1} ($n = 8$) is much lower than the energy of vaporization of the subcooled liquid of 85 kJ mol^{-1}[47] and presumably also of the air–water exchange which is not known. This indicates that long-range atmospheric transport is the process which dominates atmospheric HBB in this temperature range. The same is evident for PBBz with a ΔH of 29 ± 15 kJ mol^{-1} ($n = 8$) in the cold temperature range, even though no transition energies are reported in the literature but they can be assumed to be somewhat lower than for HBB.

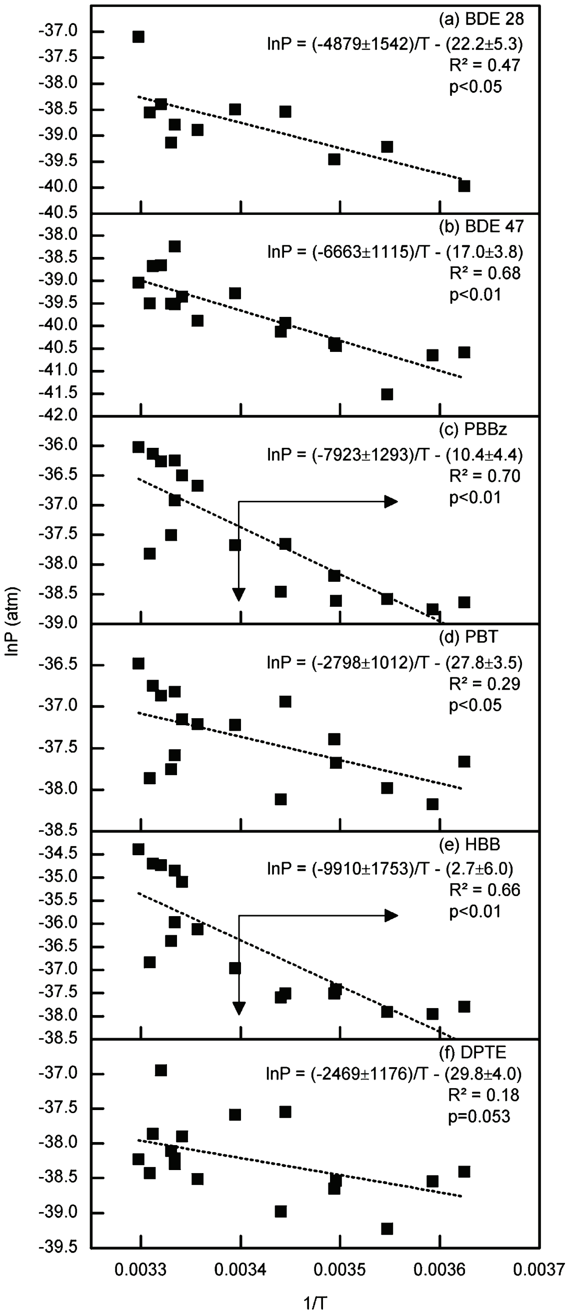

Figure 3. CC plots for BDE-28, BDE-47, PBBz, PBT, HBB, and DPTE. The range to the right and below the arrow indicates the "hockey-stick" where the slope flattens out and the temperature range was cut into two sections.

In the higher temperature range, the calculated ΔH value of HBB is 161 ± 84 kJ mol^{-1} ($n = 10$) which is almost twice as high as the energy of vaporization of the subcooled liquid. This implies that atmospheric HBB concentrations at higher temperatures are enhanced by atmospheric emissions besides volatilization from surfaces. The ΔH value of PBBz increased to 84 ± 65 kJ mol^{-1} ($n = 10$). One reasonable source of atmospheric emissions of HBB (and also PBBz) resulting in the steeper slope at higher temperatures is the degradation of higher brominated FRs to HBB (see Spatial Distribution), both before or during their emission or within the environment, which will depend on air temperature and solar radiation and might lead to high atmospheric HBB concentrations around the equator as observed in this study and over the Atlantic Ocean.[20] Certainly, the observed temperature dependence is valid only for the described cruise. Nevertheless, this study indicates that HBB is increasingly emitted into the atmosphere, or possibly formed within the atmosphere, with increasing ambient air temperature, combined with continental air masses. In contrast, the former dominating BFR in the atmosphere —BDE-47—is not. This needs to be further studied by lab experiments and by long-term stationary environmental monitoring in order to examine the individual influences of the air mass origins and air temperature, together with possible regional and seasonal differences. In any case, this study shows that HBB is a dominating BFR in the global atmosphere and necessarily has to be included in future research on HFRs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables on the sampling sites, blank values, MDLs, individual concentrations, plots of individual concentrations vs the latitude, and BT plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information

Brominated flame retardants and Dechlorane Plus in the marine atmosphere from Southeast Asia toward Antarctica

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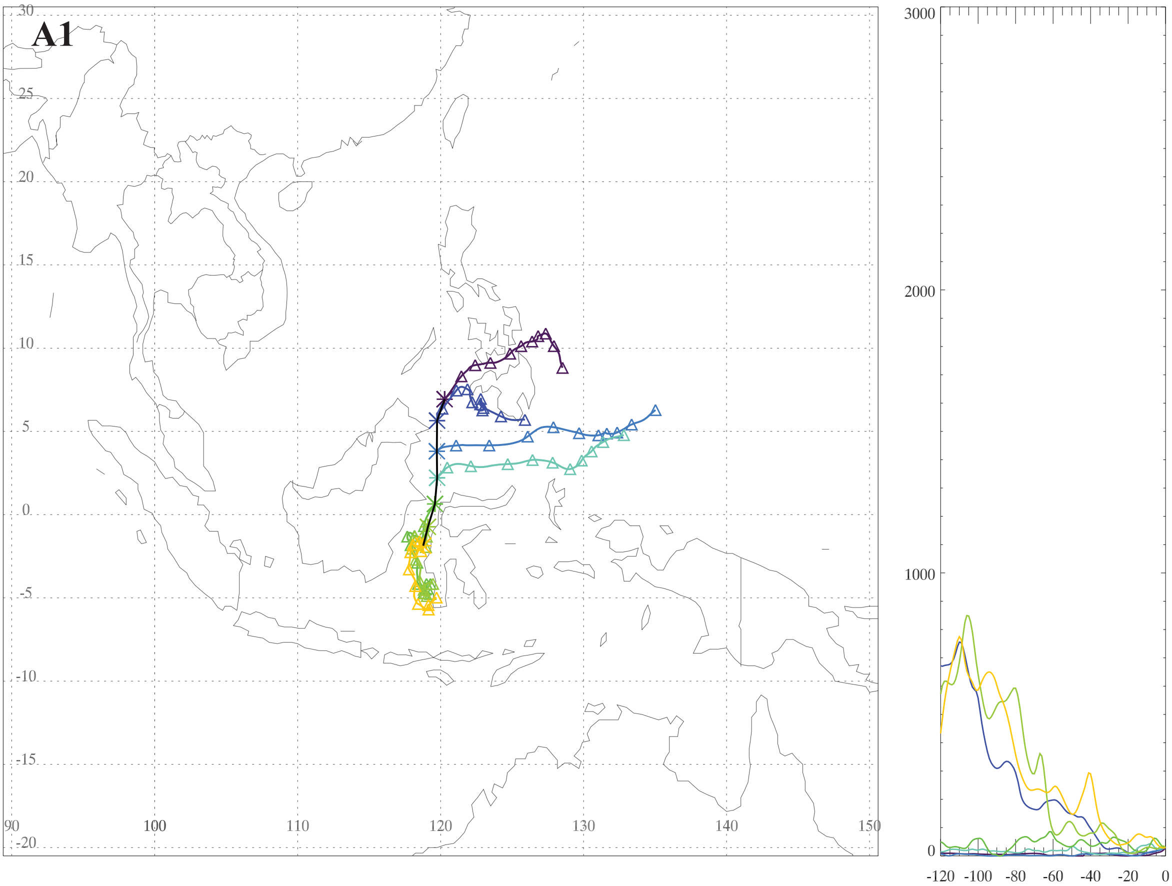
2 figures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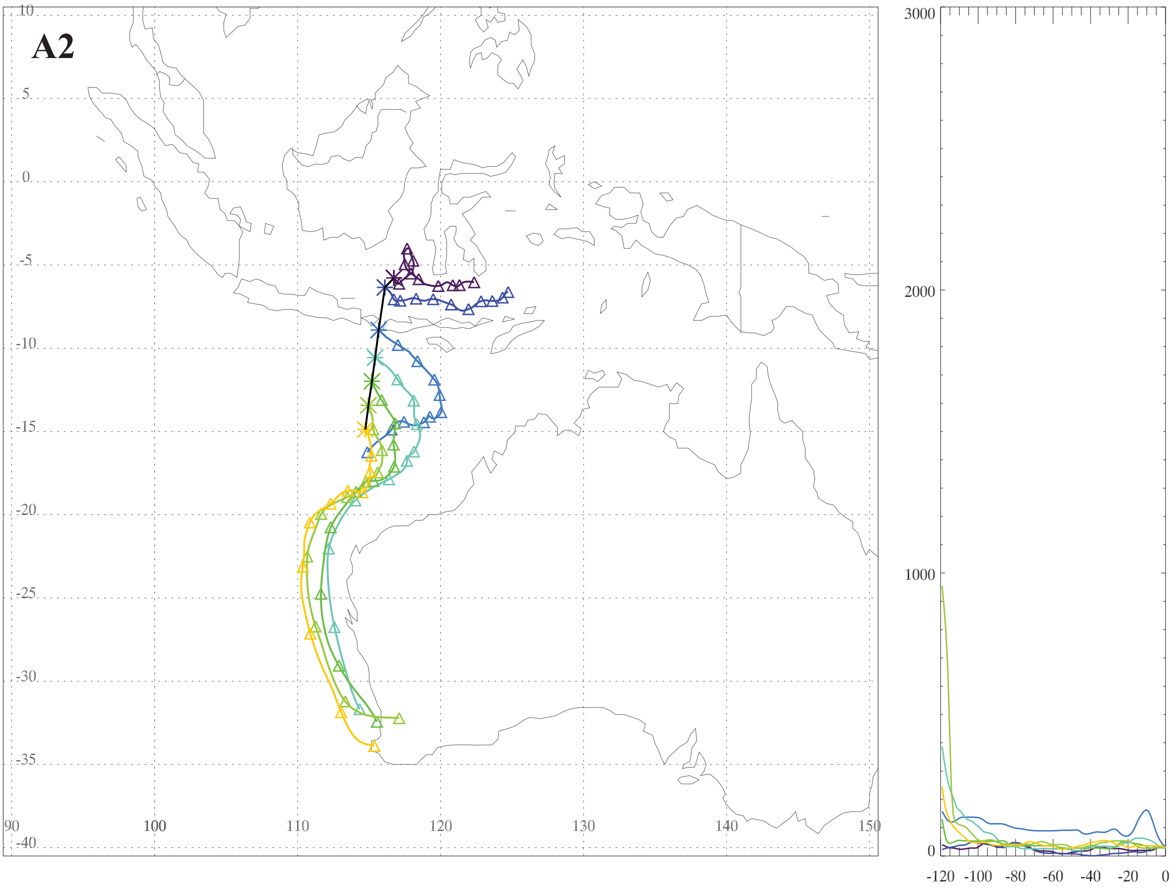
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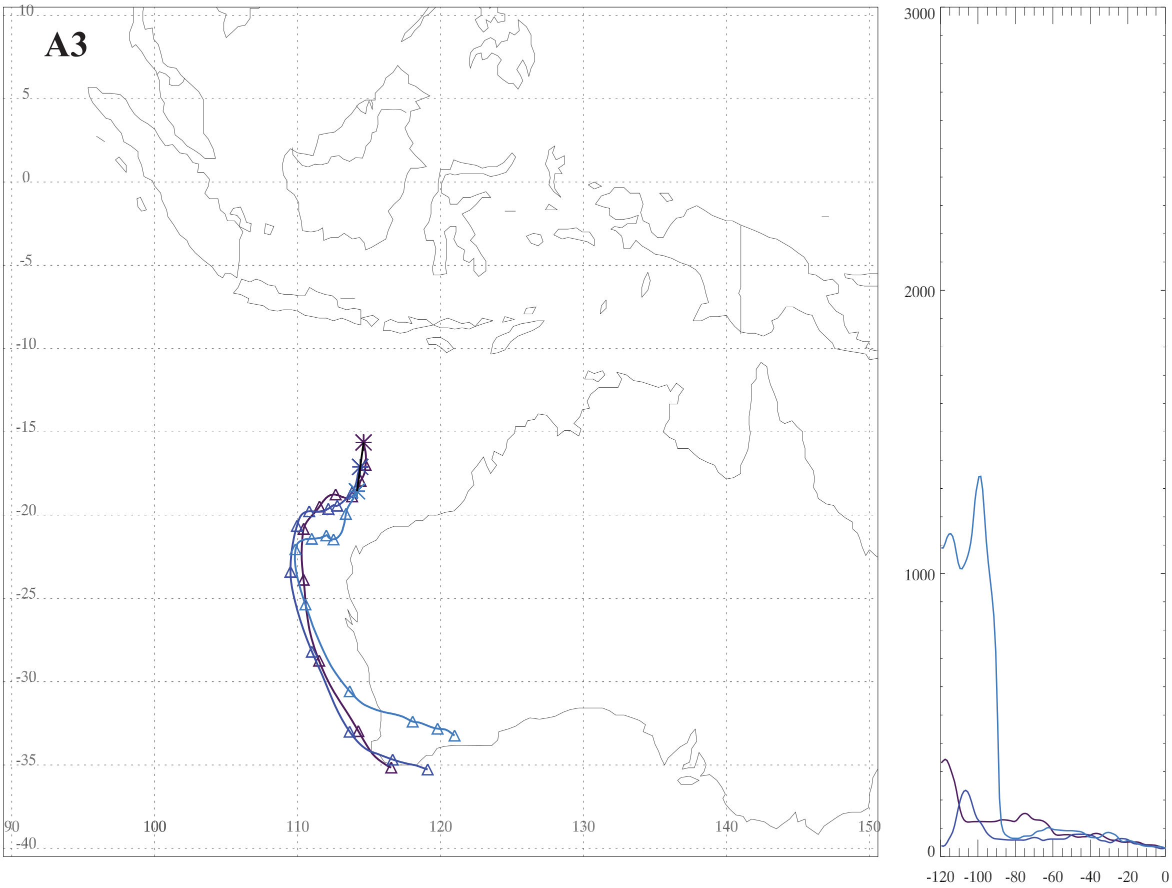
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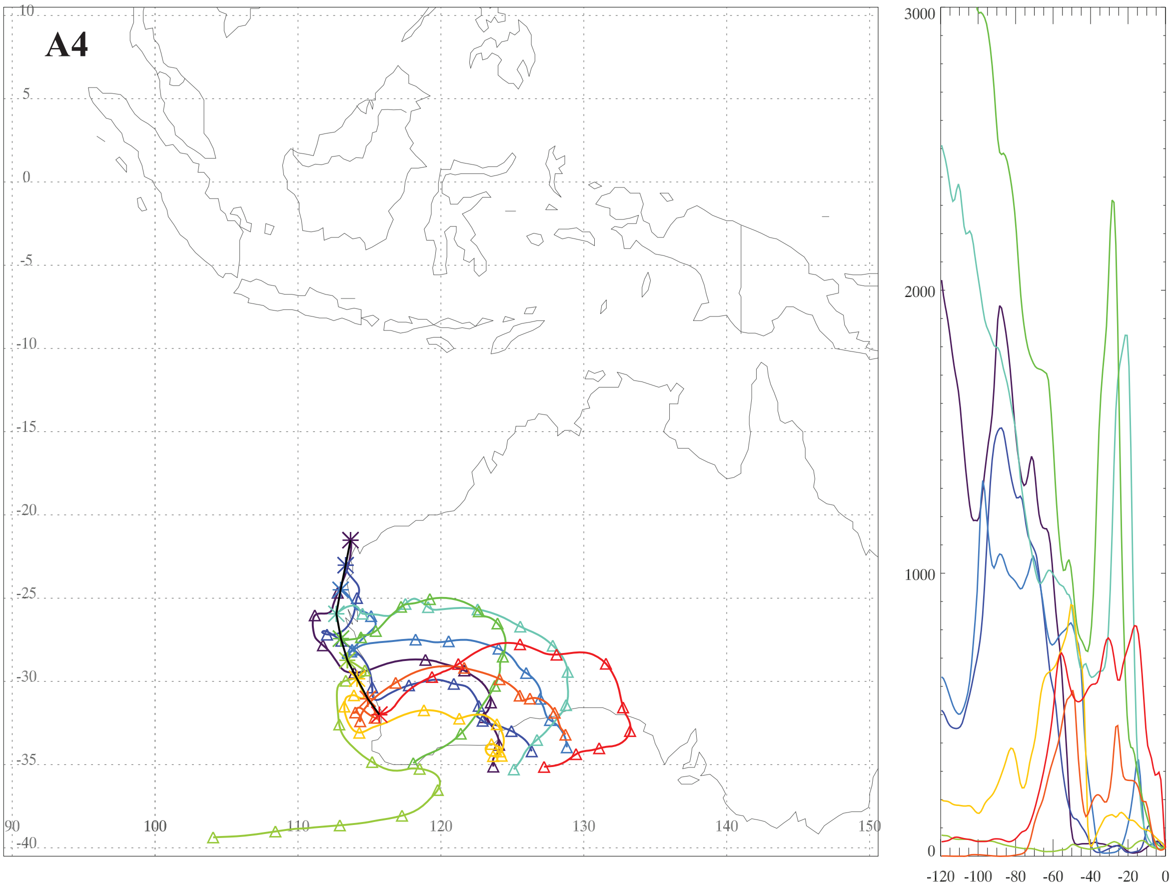
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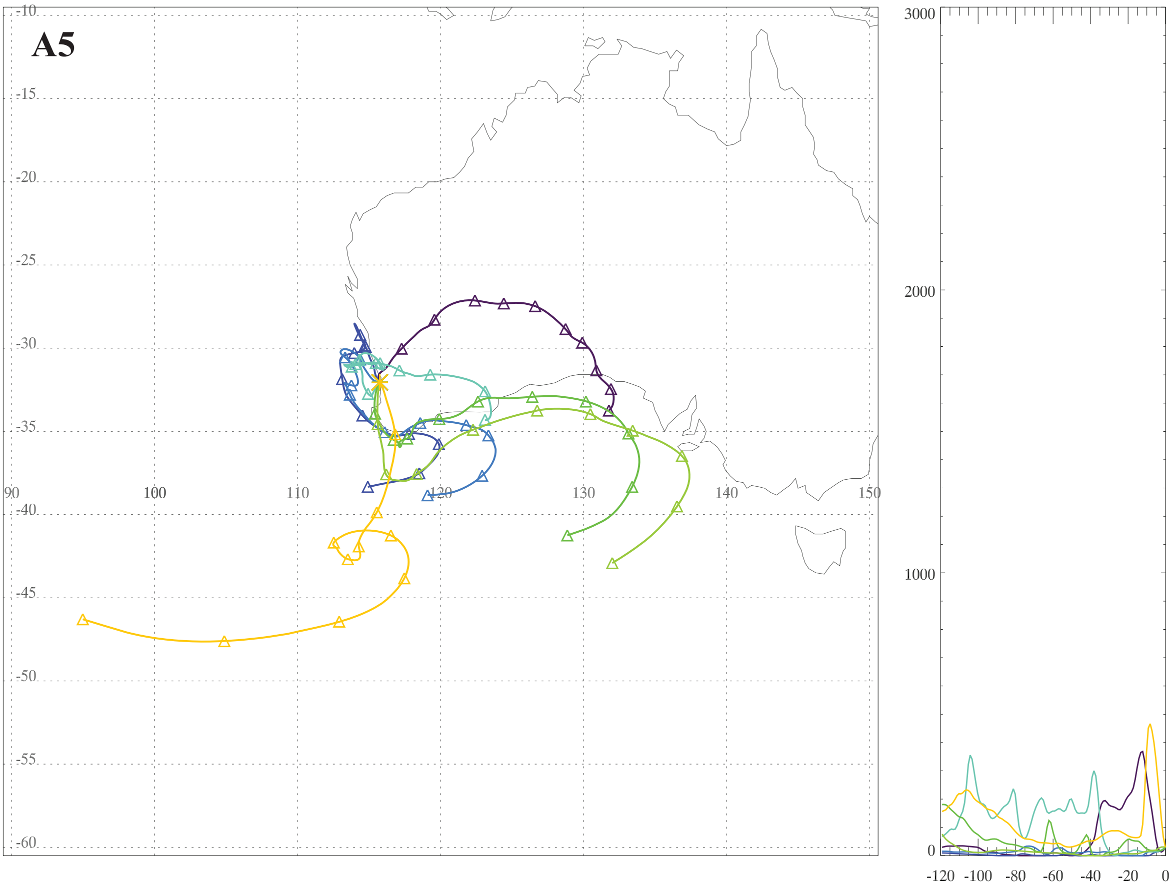
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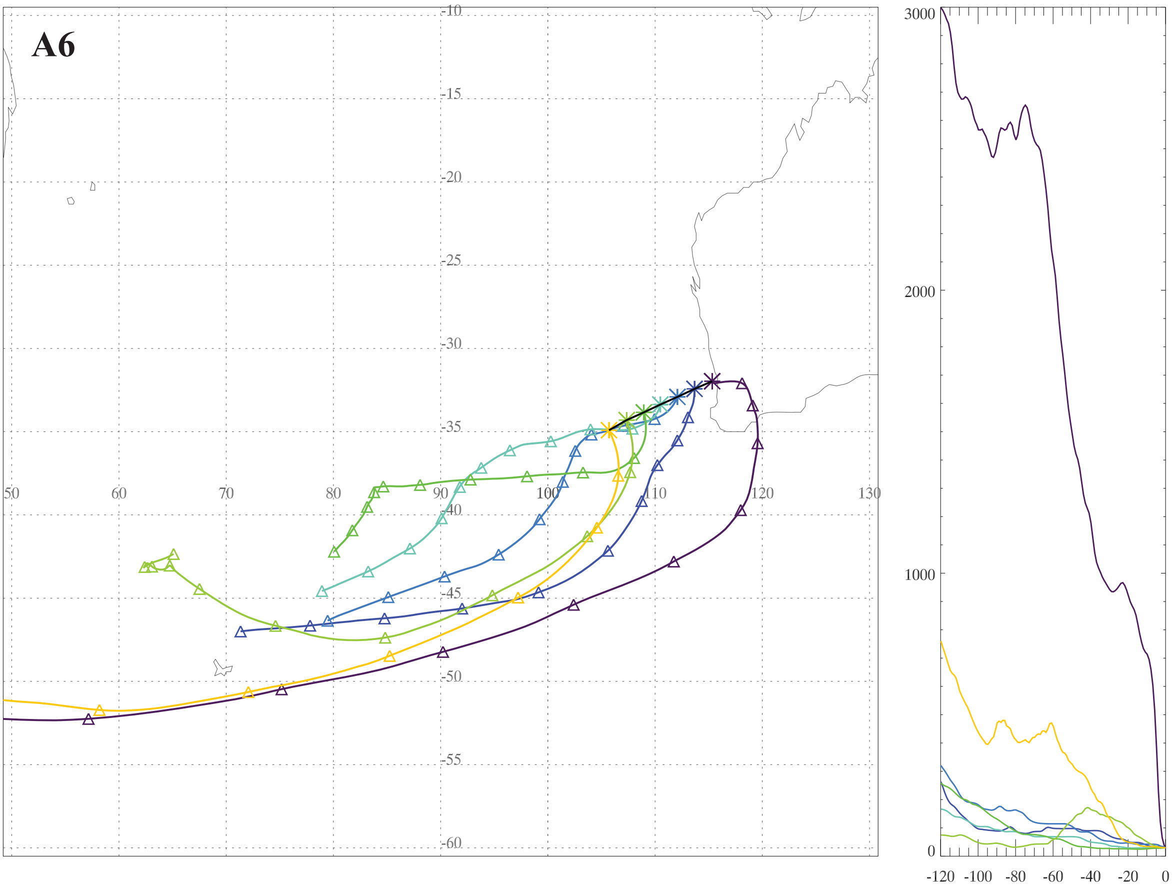
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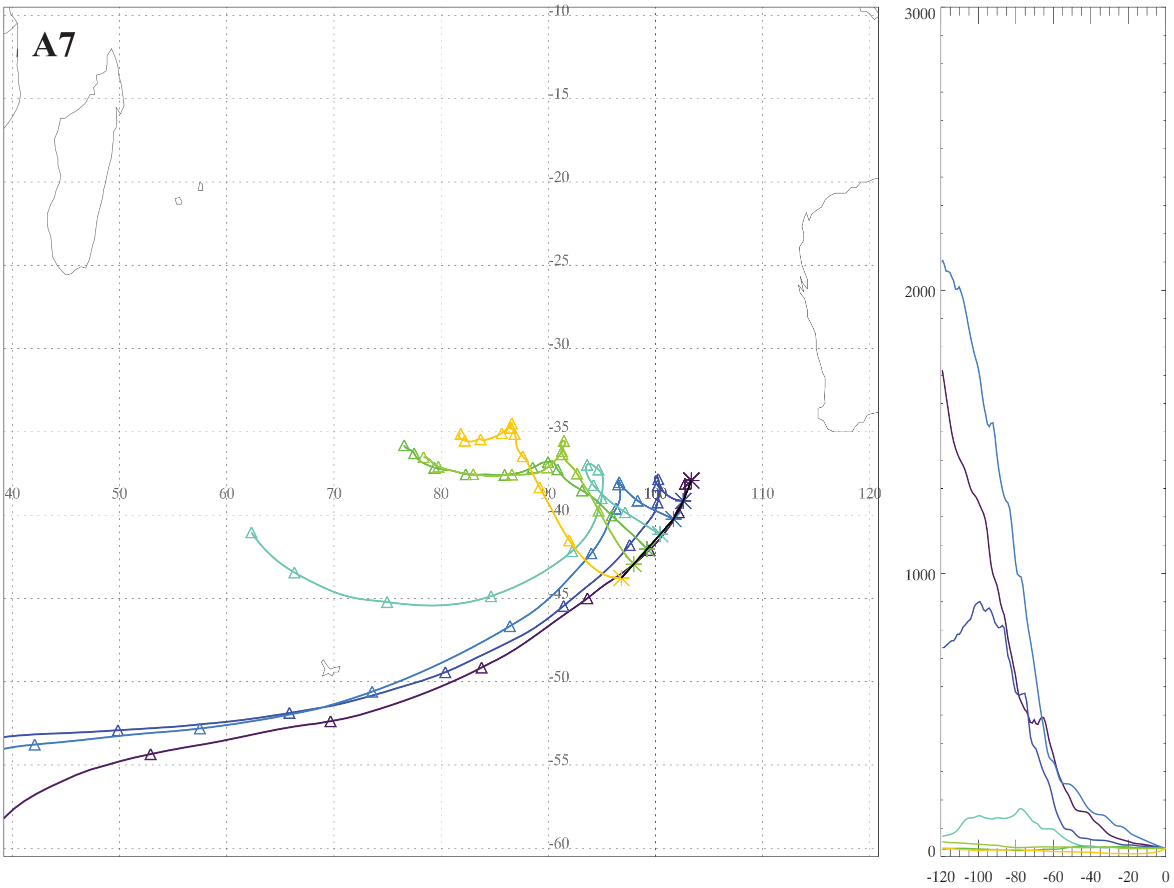
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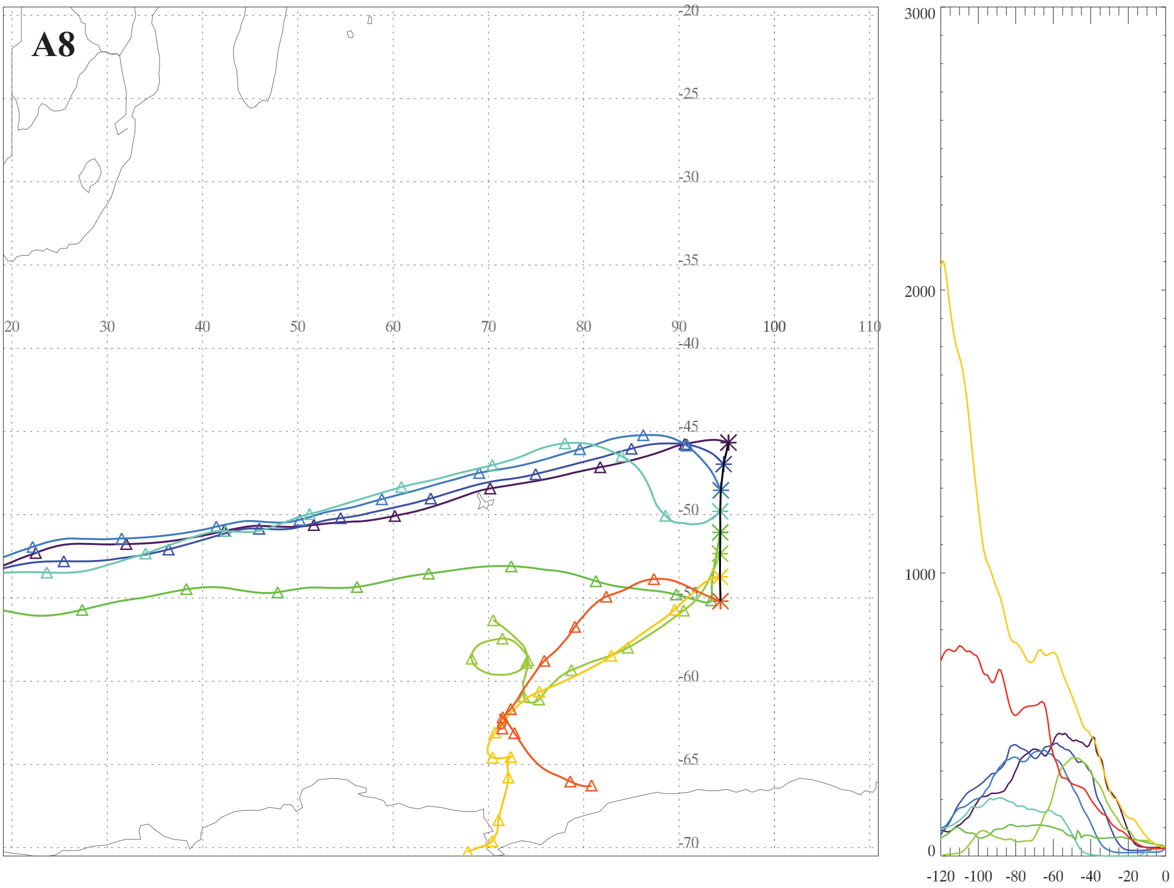
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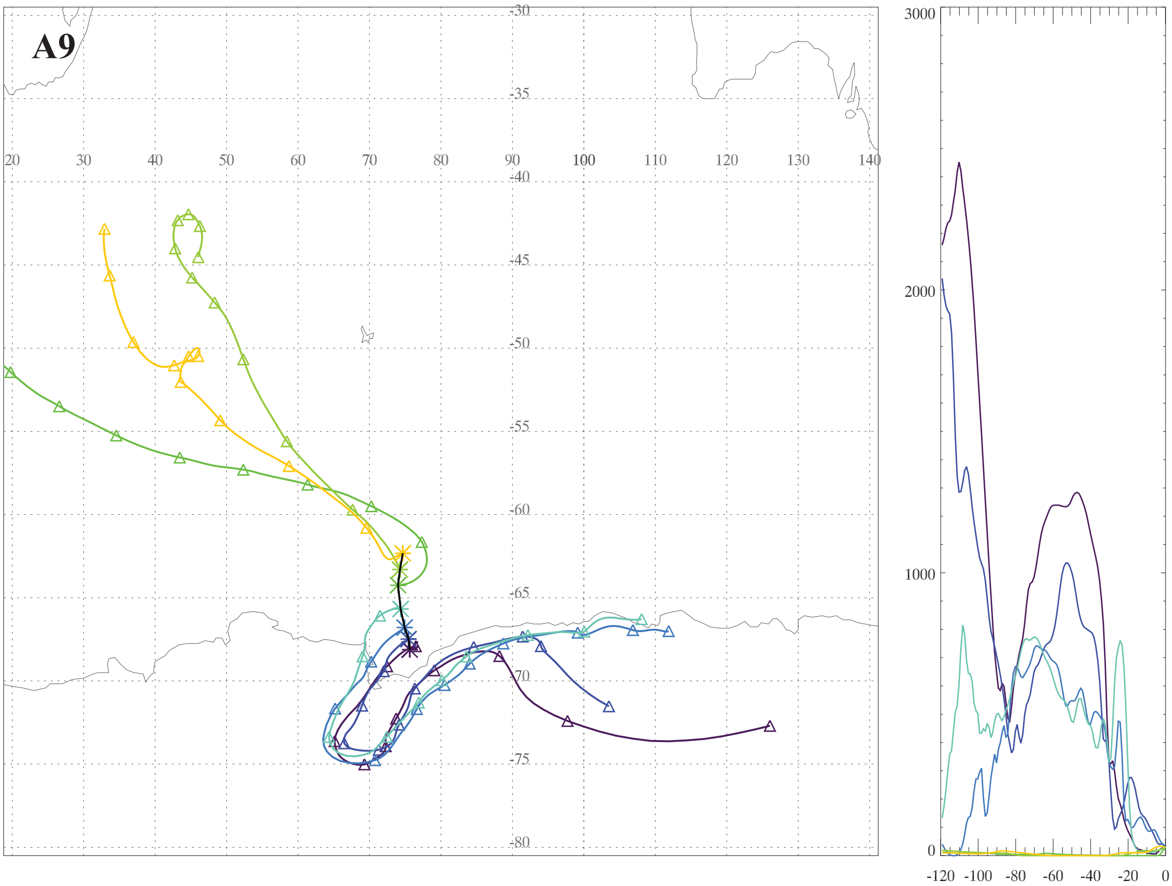
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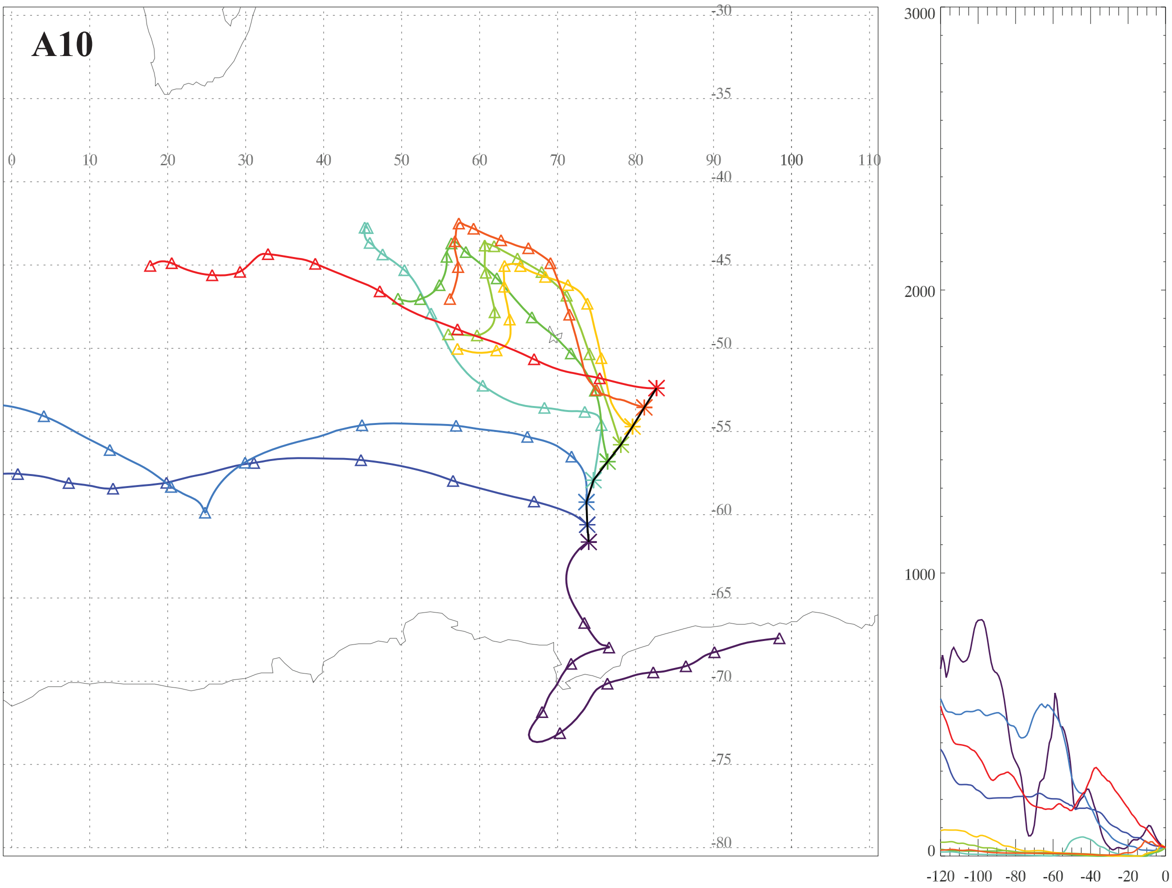
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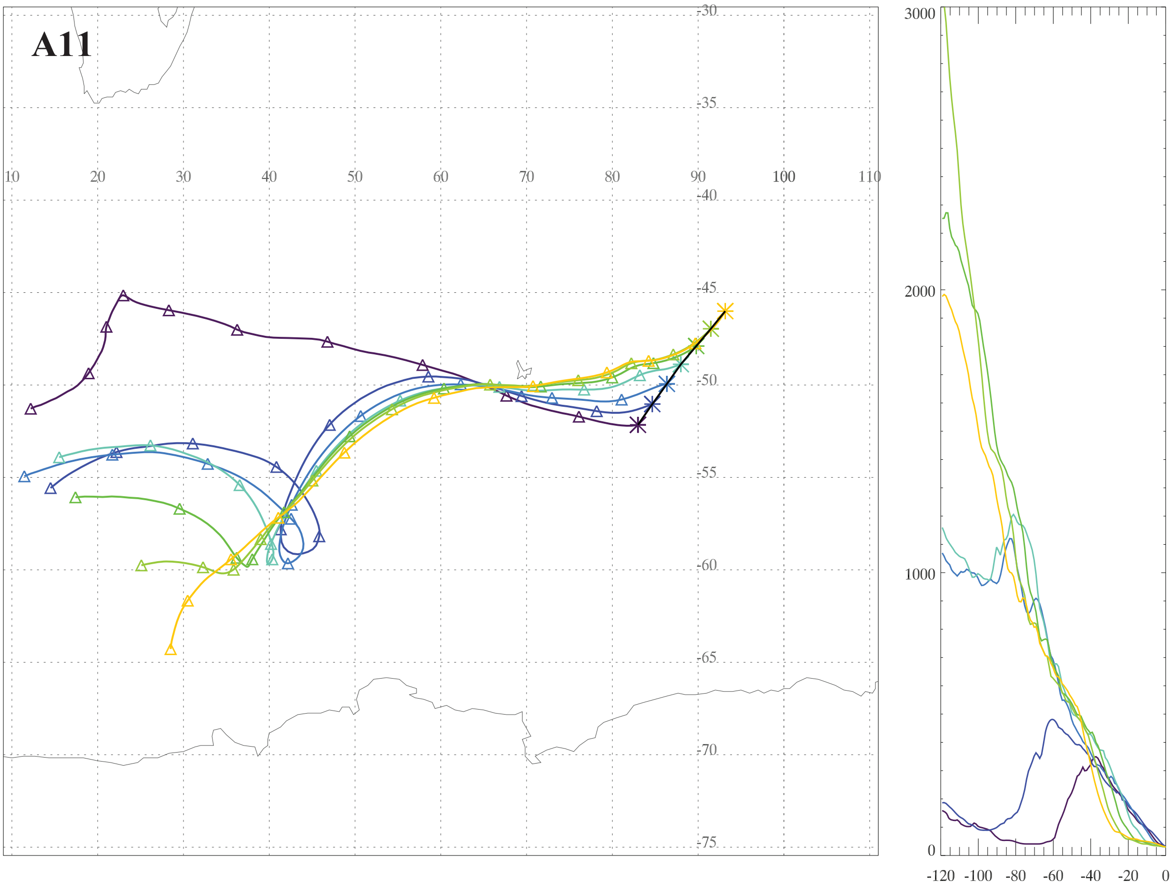
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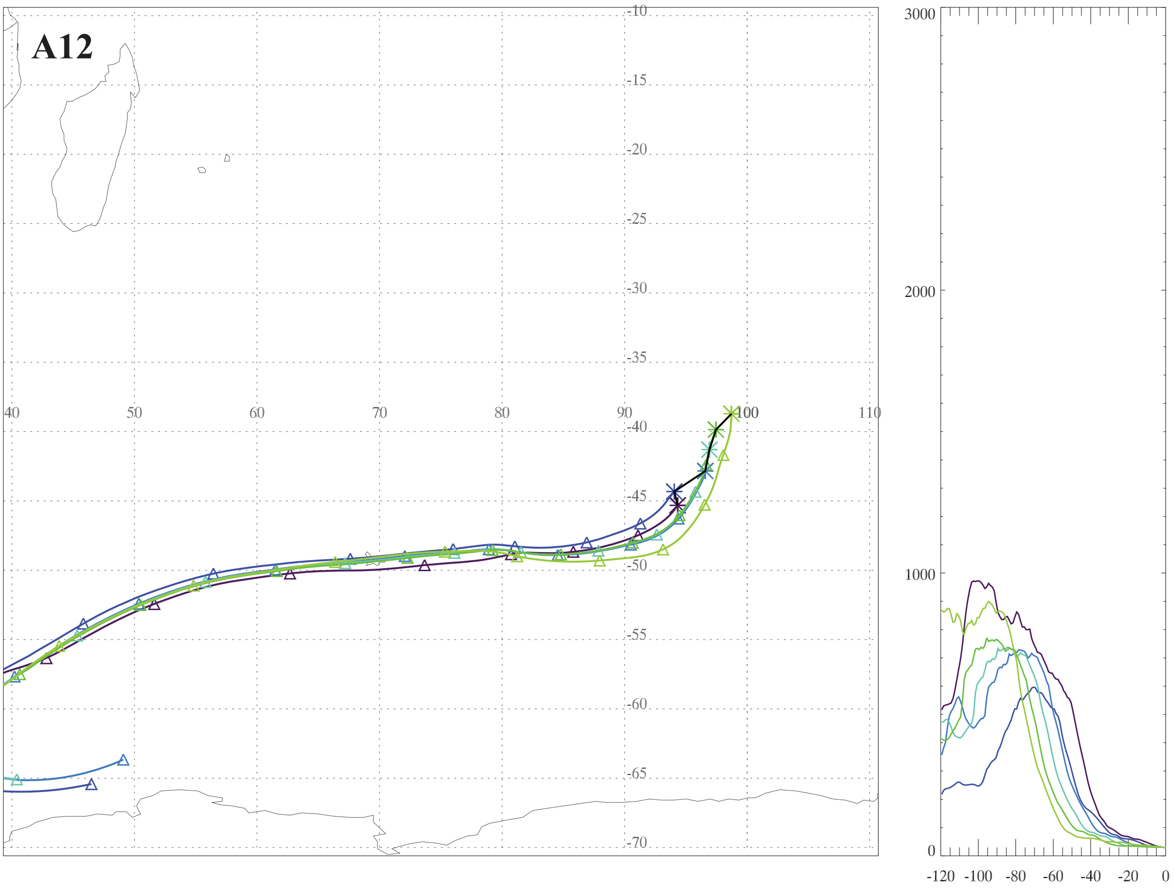
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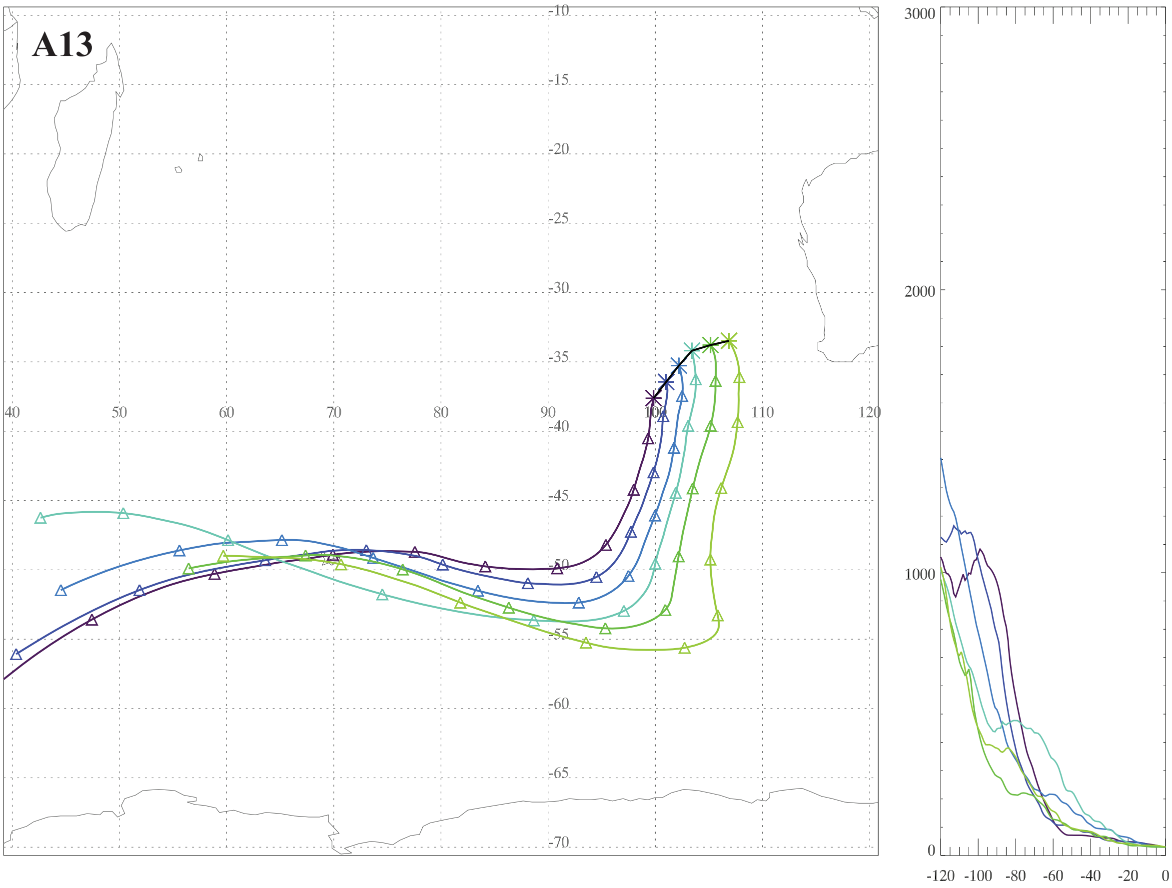
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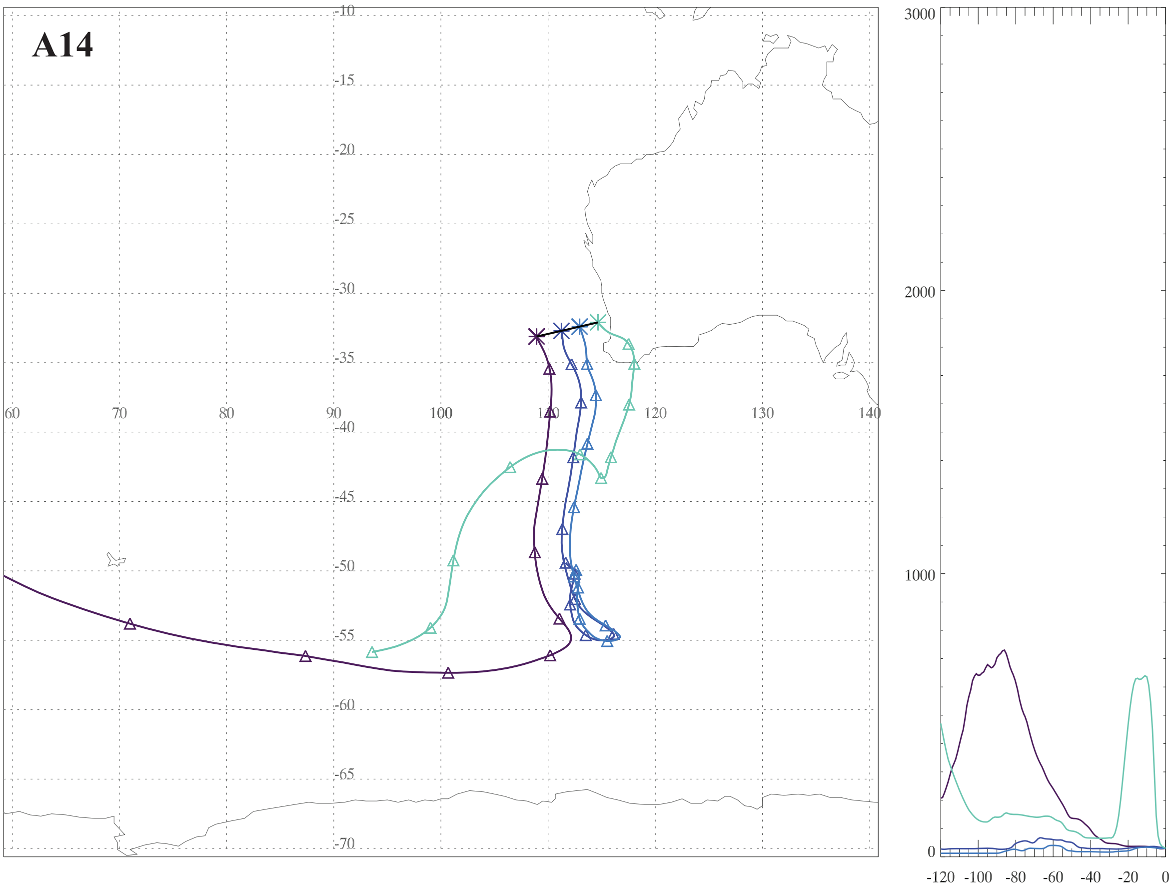
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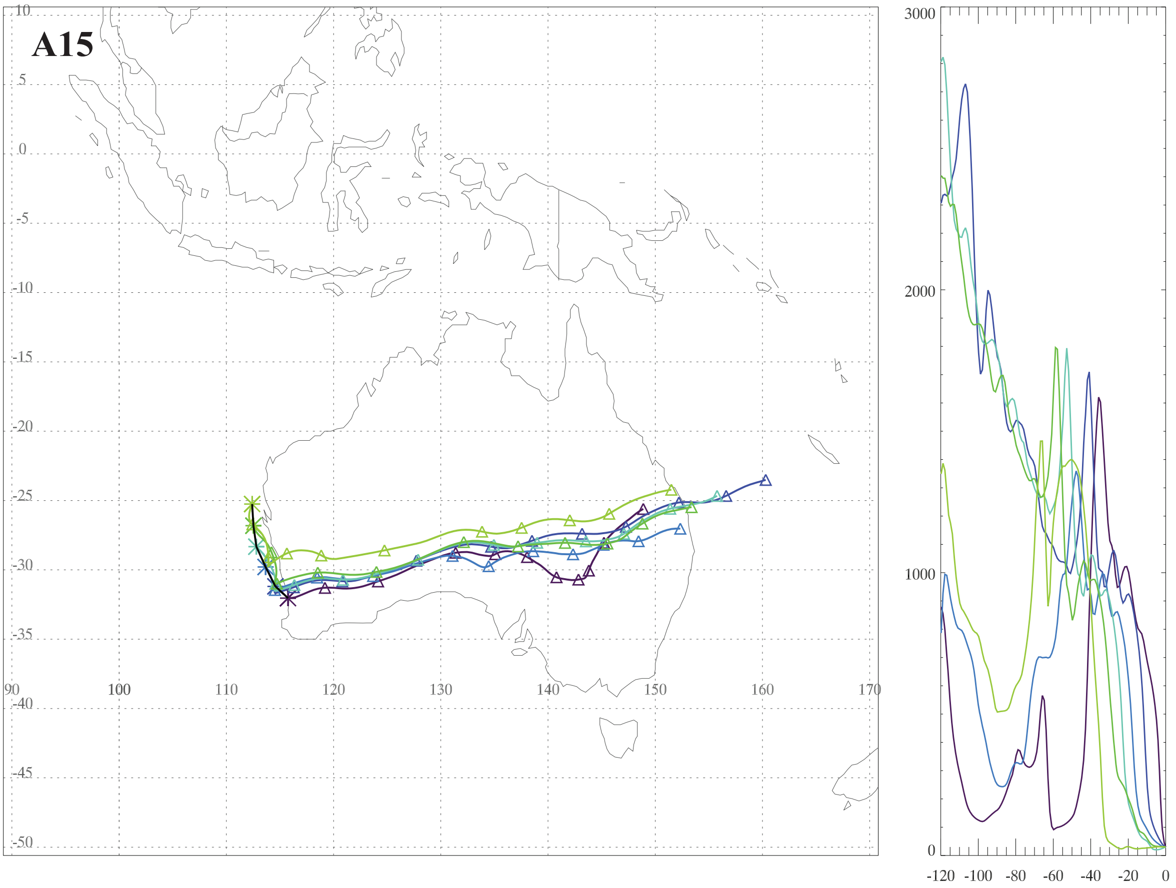
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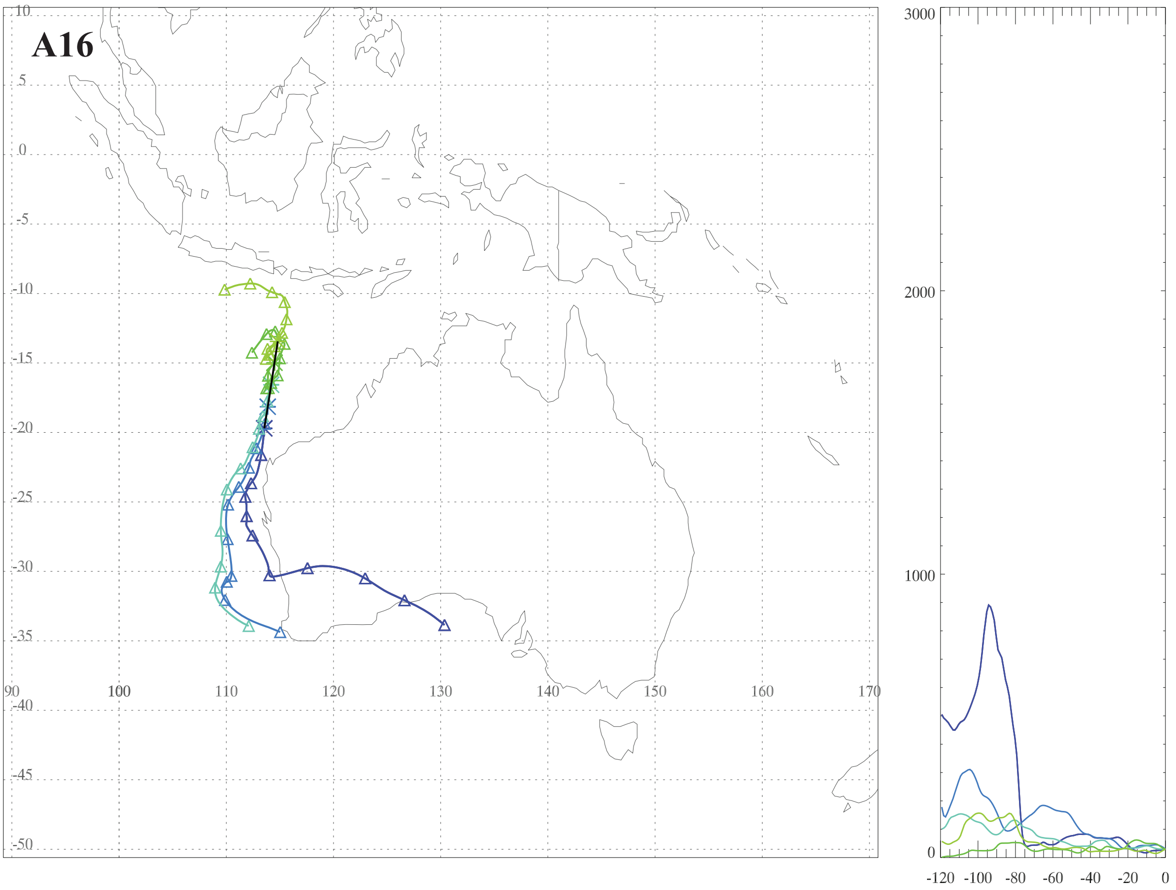
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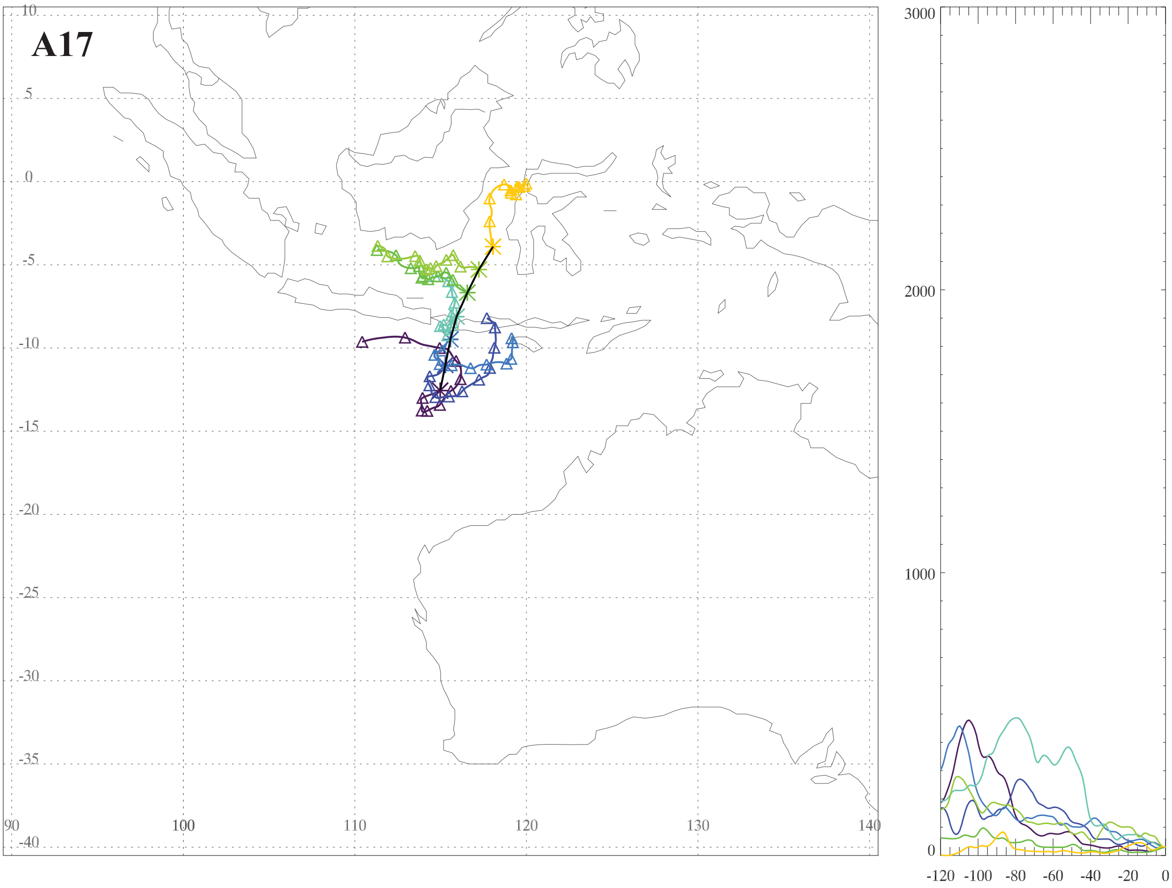
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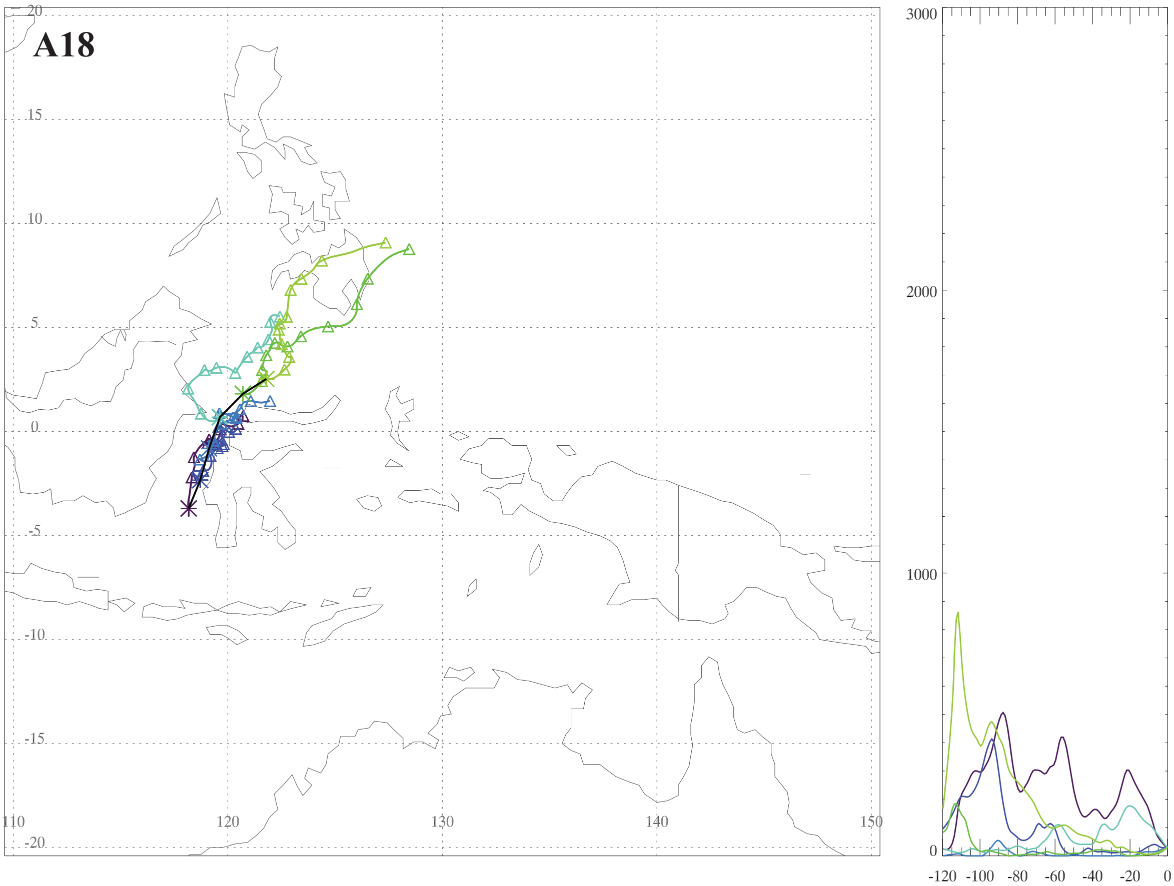
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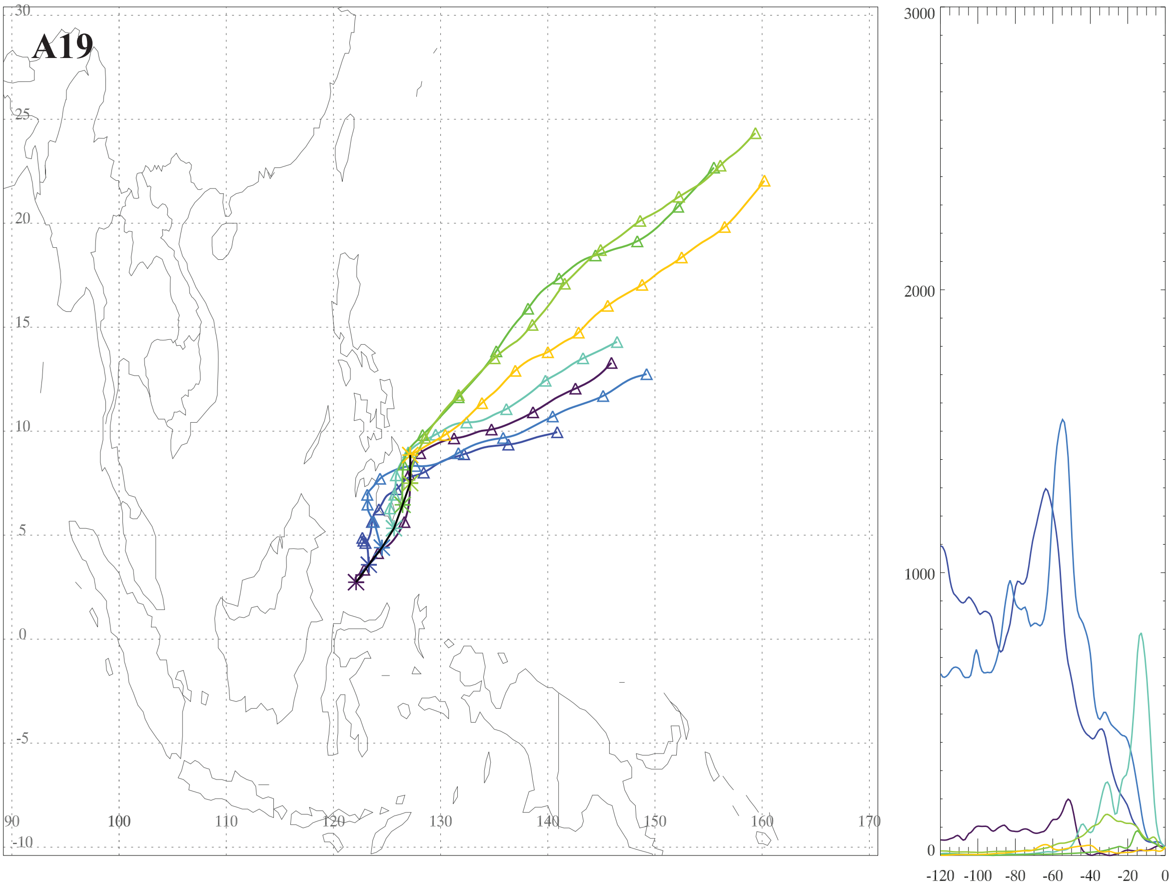
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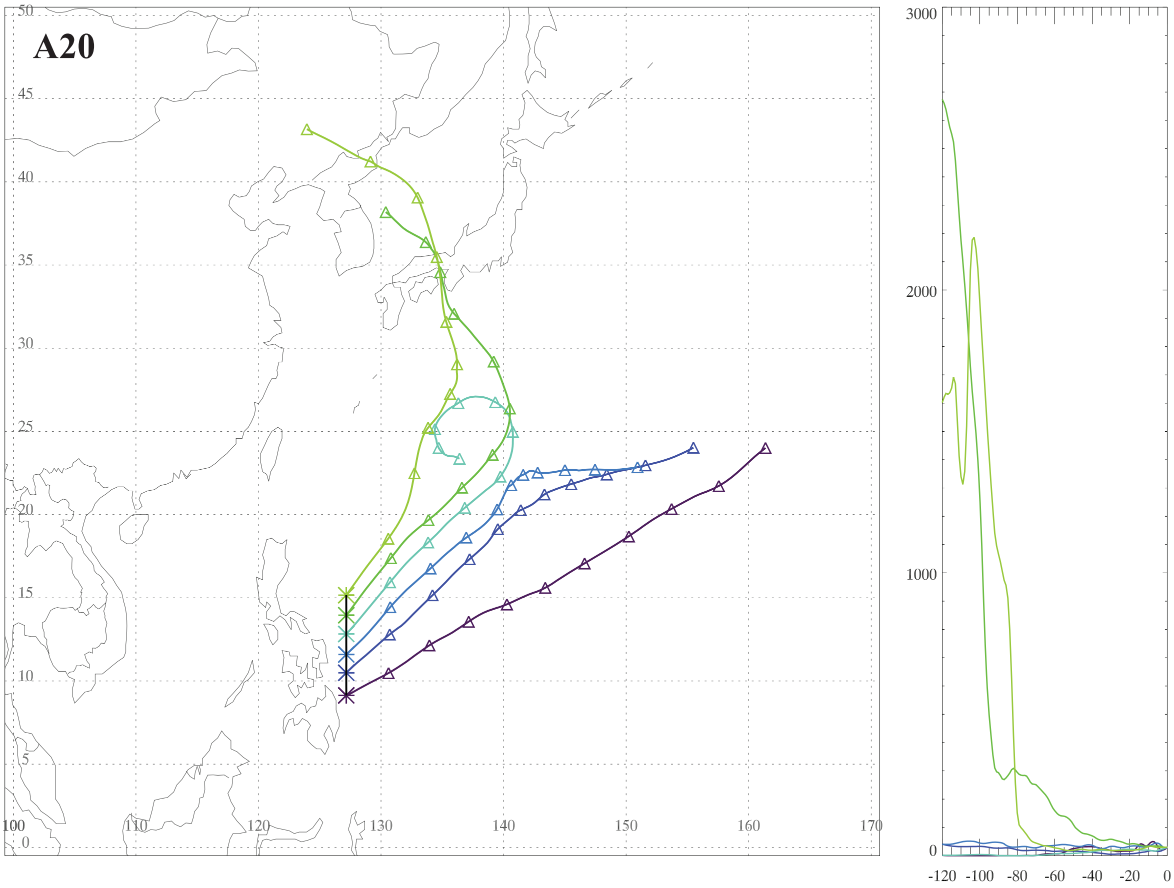
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Figure S1. Plots of 120h air mass back trajectories (left) and altitudinal profiles in meters (right). (BTs) were calculated using NOAA's HYSPLIT model. BTs were calculated for arrival times in 6 h steps at the corresponding position of the ship along the cruise leg. The black line indicates the ships cruise leg during sampling.

TABLE S1. Detailed information on air sampling. Latitude and longitude represent the mean sampling station. Air temperature and wind speed are mean values.

	Date	Latitude (°N)	Longitude (°E)	Volume (m³)	Wind speed (m s^{-1})	T_A (°C)
A1	14.-15.11.2010	-2.22	118.15	485.3	3.5	28.0
A2	16.-17.11.2010	-10.54	115.43	513.9	7.3	29.1
A3	18.11.2010	-17.64	114.26	191.0	7.8	27.7
A4	19.-21.11.2010	-27.45	113.01	769.6	10.9	24.7
A5	21.-22.11.2010	-32.05	115.74	591.8	12.0	17.4
A6	24.-25.11.2010	-33.37	110.49	499.4	11.9	17.5
A7	26.-27.11.2010	-41.15	100.44	536.0	9.2	13.0
A8	28.-29.11.2010	-50.38	94.27	533.9	13.2	5.2
A9	26.-28.2.2011	-65.73	74.38	521.0	8.7	4.0
A10	28.2.-2.3.2011	-56.80	76.42	706.3	13.4	2.7
A11	2.-4.3.2011	-48.57	88.58	629.2	9.5	8.8
A12	4.-5.3.2011	-41.43	96.90	458.8	8.6	12.9
A13	5.-7.3.2011	-34.02	103.96	486.6	10.7	17.1
A14	7.-8.3.2011	-32.50	112.35	389.7	17.1	21.4
A15	17.-18.3.2011	-28.70	112.93	511.5	7.9	26.8
A16	19.-20.3.2011	-16.98	114.10	485	4.2	30.1
A17	20.-21.3.2011	-8.12	115.93	506.8	4.7	28.8
A18	21.-23.3.2011	0.33	119.47	378.1	6.7	26.1
A19	23.-24.3.2011	5.32	125.64	472.2	9.4	27.1
A20	24.-26.3.2011	12.72	127.16	490.7	19.2	26.8

TABLE S2. Mean absolute blank values of HFRs deteced in the blanks (pg). Other HFRs were not detected in any blanks. n.d. = not detected; n.a. = not analyzed

	Air column	Air filter
BDE-99	13 ± 12	n.d.
BDE-183	130 ± 29	n.d.
BDE-209	n.a.	210 ± 190
PBBz	n.d.	3.0 ± 6.6
DPTE	66 ± 5.4	66 ± 3.2
HBB	92 ± 110	n.d.
Dec602	25 ± 29	8.2 ± 11
TBPH	120 ± 160	n.d.
synDP	30 ± 6.0	n.d.
antiDP	34 ± 2.7	n.d.

TABLE S3. MDLs of HFRs in pg m^{-3}. MDLs were calculated from mean field blank values plus three times the standard deviation or, if no blank values detected, based on instrumental S/N ratios of 3. Mean sample volumes of 500 m³ for air columns and 250m³ for air filters were assumed. n.a. = not analyzed.

	air	
	column	**filter**
BDE–28	0.008[a]	0.015[a]
BDE–47	0.015[a]	0.030[a]
BDE–66	0.015[a]	0.031[a]
BDE–85	0.016[a]	0032[a]
BDE–99	0.096	0.022[a]
BDE–100	0.013[a]	0.026[a]
BDE–153	0.013[a]	0.026[a]
BDE–154	0.009[a]	0.018[a]
BDE–183	0.43	0.029[a]
BDE–209	n.a.	3.4
PBBz	0.002[a]	0.092
PBT	0.003[a]	0.007[a]
PBEB	0.003[a]	0.005[a]
DPTE	0.17	0.30
HBB	0.84	0.006[a]
TBPH	1.2	0.025[a]
EHTBB	0.008[a]	0.015[a]
BTBPE	0.023[a]	0.046[a]
aCl10DP	0.001[a]	0.002[a]
aCl11DP	0.001[a]	0.003[a]
synDP	0.096	0.003[a]
antiDP	0.084	0.003[a]
Dec 602	0.22	0.17
Dec 603	0.002[a]	0.004[a]
Dec 604	0.018[a]	0.035[a]

[a] calculated based on instrumental S/N ratios

TABLE S4. Individual concentrations of HFRs detected in the gaseous (gas.) and particulate (part.) phase of the atmosphere in pg m^{-3}. Other analyzed HFRs were not detected

		BDE-28	BDE-47	BDE-99	BDE-100	BDE-154	BDE-153	BDE-183	BDE-209[a]
A1	gas.	0.35	0.32	0.20	0.02	0.16	0.18	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A2	gas.	0.30	0.14	0.10	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34	4.0
A3	gas.[b]								
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A4	gas.	0.21	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	0.02	0.05	n.d.	n.d.	n.d.	n.d.	n.d.
A5	gas.[b]				n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	0.05	0.09	n.d.	n.d.	n.d.	0.29	3.7
A6	gas.	n.d.	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A7	gas.	0.13	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A8	gas.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A9	gas.[b]				n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	0.08	0.06	n.d.	n.d.	n.d.	n.d.	n.d.
A10	gas.	0.08	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A11	gas.	0.16	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A12	gas.	n.d.	0.06	0.73	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A13	gas.	0.31	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.5
A14	gas.	0.32	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	0.05	0.10	n.d.	n.d.	n.d.	n.d.	n.d.
A15	gas.	0.24	0.49	0.45	0.06	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.
A16	gas.	1.3	0.22	0.26	0.04	0.18	0.18	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.7
A17	gas.	n.d.	0.31	0.22	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.2
A18	gas.	n.d.	0.16	0.23	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A19	gas.	0.17	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
A20	gas.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] for BDE-209, only the particulate phase was analyzed

[b] not analyzed

n.d. = not detected

Continuation of Table S4

		PBBz	PBT	DPTE	HBB	EHTBB	TBPH	synDP	antiDP	Dec603
A1	gas.	3.4	1.9	1.9	18.3	n.d.	n.d.	0.71	0.57	n.d.
	part.	n.d.	n.d.	0.32	0.21	n.d.	0.16	0.30	0.19	n.d.
A2	gas.	0.72	0.71	0.44	2.2	n.d.	n.d.	0.68	0.13	n.d.
	part.	n.d.	n.d.	n.d.	0.13	0.15	0.22	0.63	1.2	n.d.
A3	gas.[b]									
	part.	n.d.	0.36	n.d.	0.33	n.d.	n.d.	0.46	0.38	n.d.
A4	gas.	2.3	1.4	0.41	4.7	n.d.	n.d.	0.29	0.07	n.d.
	part.	n.d.	n.d.	n.d.	0.12	n.d.	0.10	0.24	0.14	n.d.
A5	gas.[b]									
	part.	n.d.	n.d.	n.d.	0.14	n.d.	0.16	0.28	0.24	0.13
A6	gas.	0.39	0.57	0.26	1.1	n.d.	n.d.	0.14	0.00	n.d.
	part.	n.d.	n.d.	n.d.	0.13	n.d.	0.21	0.16	0.15	n.d.
A7	gas.	0.52	1.2	0.37	1.2	n.d.	n.d.	n.d.	n.d.	n.d.
	part.	n.d.	n.d.	n.d.	0.12	n.d.	0.47	0.13	0.14	n.d.
A8	gas.	0.31	0.56	0.42	0.79	n.d.	n.d.	0.27	0.24	n.d.
	part.	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	0.26	0.18	n.d.
A9	gas.[b]									
	part.	n.d.	n.d.	n.d.	0.12	0.14	0.43	0.17	0.14	n.d.
A10	gas.	0.35	0.95	0.49	0.94	n.d.	n.d.			n.d.
	part.	n.d.	n.d.	n.d.	0.10	n.d.	0.98	1.6	0.56	n.d.
A11	gas.	0.36	0.67	0.21	0.82	n.d.	n.d.	0.08	0.07	n.d.
	part.	n.d.	n.d.	n.d.	0.11	0.13	0.98	0.12	0.12	n.d.
A12	gas.	0.34	0.90	0.41	1.3	n.d.	n.d.	0.20	0.20	n.d.
	part.	n.d.	n.d.	n.d.	0.16	n.d.	1.5	0.19	0.17	n.d.
A13	gas.	0.88	1.8	1.1	1.2	n.d.	n.d.	0.11	0.10	n.d.
	part.	n.d.	n.d.	n.d.	0.16	0.21	0.46	0.17	0.16	n.d.
A14	gas.	0.85	1.4	1.0	2.0	n.d.	n.d.	0.24	0.13	n.d.
	part.	n.d.	n.d.	n.d.	0.16	n.d.	0.51	0.29	0.19	n.d.
A15	gas.	3.5	2.0	0.54	16.4	n.d.	n.d.	0.38	0.28	0.08
	part.	n.d.	n.d.	n.d.	0.18	n.d.	0.17	0.33	0.24	n.d.
A16	gas.	4.3	2.8	0.53	25.7	n.d.	n.d.	0.87	0.22	0.08
	part.	n.d.	n.d.	n.d.	n.d.	n.d.	0.66	n.d.	n.d.	n.d.
A17	gas.	3.9	2.2	0.77	18.9	n.d.	n.d.	1.1	0.37	0.13
	part.	n.d.	n.d.	0.34	0.14	n.d.	0.58	0.90	0.66	0.26
A18	gas.	2.7	1.4	0.75	12.9	n.d.	n.d.	5.8	4.4	n.d.
	part.	n.d.	n.d.	n.d.	0.16	n.d.	0.75	0.51	0.21	n.d.
A19	gas.	0.98	0.79	0.61	3.6	n.d.	n.d.	0.69	0.53	n.d.
	part.	n.d.	n.d.	n.d.	0.16	n.d.	2.8	0.28	0.19	n.d.
A20	gas.	1.8	0.94	0.50	5.4	n.d.	n.d.	1.5	1.5	n.d.
	part.	n.d.	n.d.	n.d.	0.13	n.d.	1.3	0.18	0.32	n.d.

[b] not analyzed

n.d. = not detected

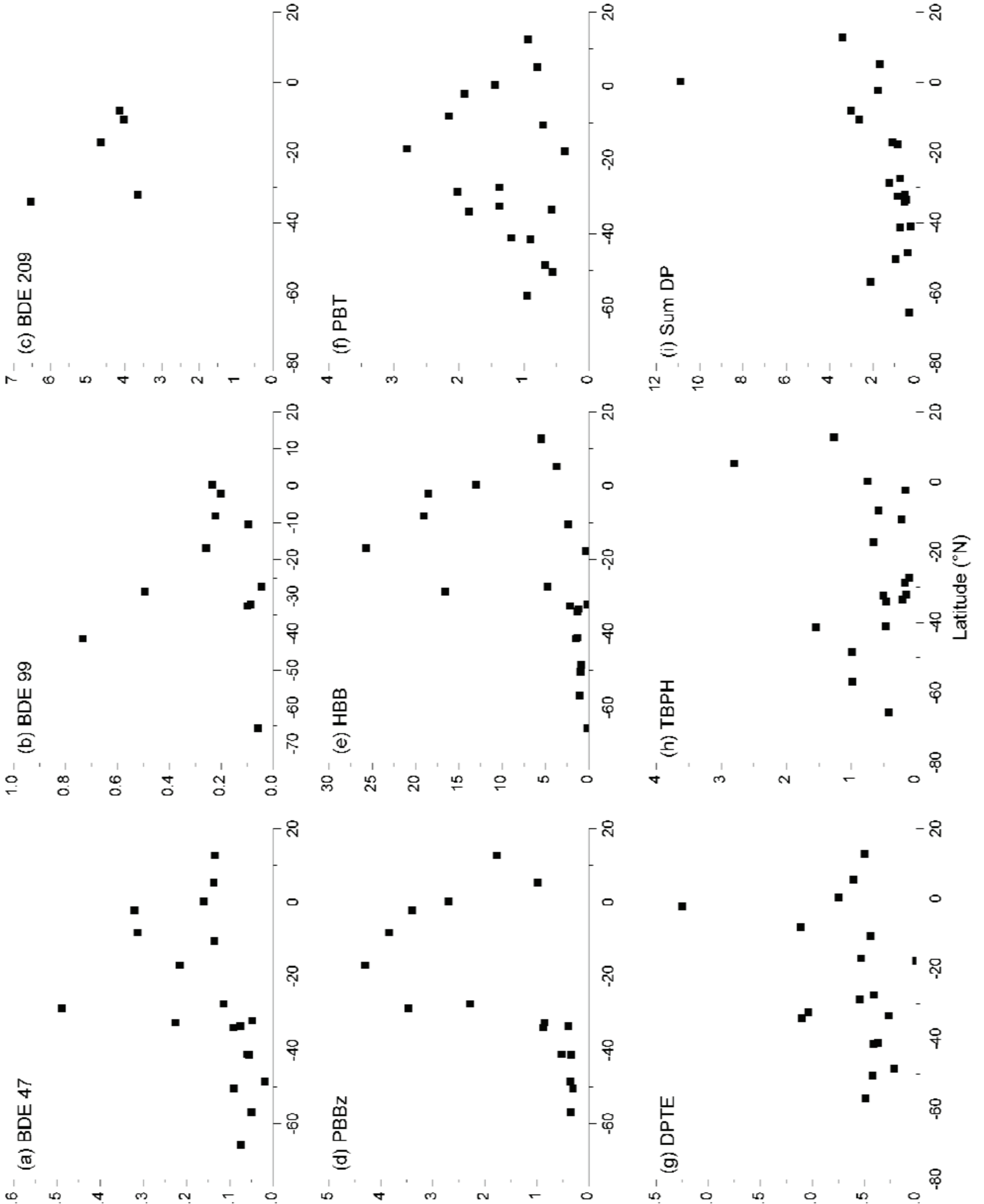

Figure S2. Concentrations of the major individual HFRs vs. the northern Latitude.

List of publications

Included in this thesis

Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-scale distribution of Dechlorane Plus in air and seawater from the Arctic to Antarctica. Environ. Sci. Technol. **2010**, *44 (23)*, 8977-8982

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Sühring, R.; **Möller, A.**; Freese, M.; Pohlmann, J.-D.; Wolschke, H.; Sturm, R.; Xie, Z.; Hanel, R.; Ebinghaus, R. Brominated flame retardants and dechloranes in eels from German Rivers. Chemosphere **2012** (in press).

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Presentations and poster (only as presenting author)

Möller, A.; Xie, Z.; Sturm, R.; Wolschke, H.; Gandraß, J.; Ebinghaus, R. (2012): Non-PBDE halogenated and non-halogenated flame retardants: Replacements following the track of the banned PBDEs through the global oceans toward the Polar Regions. NORMAN workshop "Sampling and Analysis of Emerging Contaminants in the Aquatic Environment: Current and Future Challenges"

Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. (2011): Occurrence, distribution and transport of (alternative) brominated flame retardants and Dechlorane Plus in the global abiotic marine environment. SETAC North America 32nd Annual Meeting, Boston (poster)

Möller, A., Xie, Z.; Cai, M.; Zhong, G.; Huang, P.; Cai, M.; Sturm, R.; He, J.; Ebinghaus, R. (2011): Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic. 31st International Symposium on Halogenated Persistent Organic Pollutants (POPs) – Dioxin 2011, Brussels

Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. (2011): Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. 31st International Symposium on Halogenated Persistent Organic Pollutants (POPs) – Dioxin 2011, Brussels

Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. (2011): Brominated flame retardants and Dechlorane Plus in air and seawater from the German Bight, North Sea. SETAC Europe 21st Annual Meeting, Milan

Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. (2010): Large-scale distribution and transport of Dechlorane Plus in air and seawater of the Northern and Southern Atlantic Ocean. 30th International Symposium on Halogenated Persistent Organic Pollutants (POPs) – Dioxin 2010, San Antonio

Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. (2010): Levels and Transport of PBDEs and alternative brominated flame retardants in air and seawater from the Arctic to Antarctica. 30th International Symposium on Halogenated Persistent Organic Pollutants (POPs) – Dioxin 2010, San Antonio (poster)

Möller, A.; Xie, Z.; Busch, J.; Sturm, R.; Ebinghaus, R. (2010): Non-PBDE brominated flame retardants and Dechlorane Plus in air and seawater of the Arctic. International Polar Year – Oslo Science Conference, Oslo (poster)

Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. (2010): Riverine Transport and Sources of Polyfluoroalkyl Compounds (PFCs) along the Rivers Elbe and Rhine. 38th IAD Conference, Dresden (poster)

Möller, A.; Xie, Z.; Busch, J.; Sturm, R.; Ebinghaus, R. (2010) Non-PBDE brominated flame retardants and Dechlorane Plus in air and seawater of the Arctic. SETAC Europe 20th Annual Meeting, Sevilla (poster)

Möller, A.; Xie, Z.; Busch, J.; Sturm, R.; Ebinghaus, R. (2010): Non-PBDE brominated flame retardants and Dechlorane Plus in air and seawater of the Arctic. BFR 2010, Kyoto (poster)

Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. (2009): Poly- and perfluoroalkyl compounds (PFCs) in surface water along the River Rhine. SETAC Europe 19th Annual Meeting, Göteborg (poster)

Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. (2009): Polyfluoroalkyl compounds (PFCs) in surface water along the River Rhine. Workshop Water Framework Directive and Emerging Pollutants. Measures to minimize river contamination by WWTP discharges, EU-Projekt Neptune, Koblenz (poster)

Curriculum Vitae

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Ausbildung

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03/2005 – 05/2009	Fachhochschule Lübeck, Chemieingenieurwesen Studienschwerpunkt: Instrumentelle Analytik Abschluss: Diplom-Ingenieur (FH), Gesamtnote 1.3
10/2004 – 02/2005	Technische Universität Hamburg-Harburg, Bauingenieurwesen und Umwelttechnik
10/2003 – 09/2004	Universität Lüneburg, Umweltwissenschaften
1994 – 2003	Gymnasium am Mühlenberg, Bad Schwartau Abschluss: Abitur, Note 2.1

Expeditionen

10/2011 + 09/2012	Forschungsaufenthalt auf der AWIPEV Station, Ny Alesund (Spitzbergen)
11/2010-02/2011	Polarsternfahrt ANT-XXVII/2 Kapstadt – Neumayer Station – Punta Arenas
2008-2012	Forschungsfahrten auf der FS Heincke und FS Ludwig Prandtl (Nordsee, Elbe, Weser)

Auszeichnungen

Förderpreis der Possehl-Stiftung Lübeck für Diplomarbeit, Lübeck, November 2010 (1500 €)

Review Aktivitäten

Reviewer für folgende wissenschaftliche Zeitschriften:

- Environmental Science and Technology
- Chemosphere
- Environmental Pollution
- Water Research
- Analytical and Bioanalytical Chemistry
- Science of the Total Environment
- Atmospheric Pollution Research
- Journal of Hazardous Materials
- Atmospheric Environment
- Environment International