Air−Water Exchange of Brominated Anisoles in the Northern Baltic Sea

Terry F. Bidleman,*,[†] Kathleen Agosta,[‡] Agneta Andersson,[§] Peter Haglund,[†] Olle Nygren,[†] Matyas Ripszam,[†] and Mats Tysklind[†]

[†]Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden
[‡]Altflora Designs, Helena Elisabeth väg 2, SE-903 42 Umeå, Sweden
[§]Department of Ecology and Environmental Science, Umeå University, SE-901 87 Umeå, Sweden

S *Supporting Information*

ABSTRACT: Bromophenols produced by marine algae undergo O-methylation to form bromoanisoles (BAs), which are exchanged between water and air. BAs were determined in surface water of the northern Baltic Sea (Gulf of Bothnia, consisting of Bothnian Bay and Bothnian Sea) during 2011−2013 and on a transect of the entire Baltic in September 2013. The abundance decreased in the following order: 2,4,6-tribromoanisole (2,4,6-TBA) > 2,4-dibromoanisole (2,4-DBA) ≫ 2,6-dibromoanisole (2,6-DBA). Concentrations of 2,4-DBA and 2,4,6-TBA in September were higher in the southern than in the northern Baltic and correlated well with the higher salinity in the south. This suggests south-to-north advection and dilution with fresh riverine water enroute, and/or lower production in the north. The abundance in air over the northern Baltic also decreased in the following order: 2,4,6-TBA > 2,4-DBA. However, 2,6-DBA was estimated as a lower limit due to breakthrough from polyurethane foam traps used for sampling. Water/air fugacity ratios ranged from 3.4 to 7.6 for 2,4-DBA and from 18 to 94 for 2,4,6-TBA, indicating net volatilization. Flux estimates using the two-film model suggested that volatilization removes 980−1360 kg of total BAs from Bothnian Bay (38000 km^2) between May and September. The release of bromine from outgassing of BAs could be up to 4−6% of bromine fluxes from previously reported volatilization of bromomethanes and bromochloromethanes.
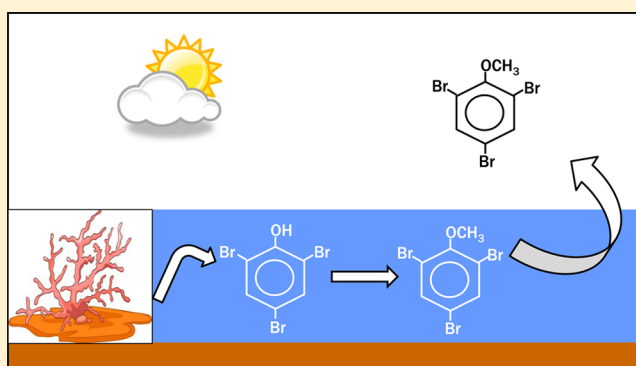
INTRODUCTION

Biogenesis of halogenated organic compounds occurs worldwide, mainly in the oceans but also in the terrestrial environment.[1,2] Volatile compounds include chloro-, bromo-, and iodomethanes and mixed halomethanes. These carry halogens into the atmosphere, and air concentrations are often elevated in highly productive marine areas.[3−6] Many higher-molecular weight organohalogens are also synthesized by marine algae, sponges, corals, and worms.[2,7−10] Formation of bromophenols (BPs) from substrates phenol, 4-hydroxybenzoic acid, and 4-hydroxybenzyl alcohol is catalyzed by bromoperoxidase.[11,12] BPs also have anthropogenic sources such as water chlorination[13] and production as industrial compounds.[7] BPs undergo O-methylation to brominated anisoles (BAs),[14] and both BAs and BPs have been reported in Baltic algae and mussels[15] and in mussels, fish, and seabirds from Norway.[16] BPs were prominent in human blood plasma collected in a Swedish hospital,[17] and they displayed weak binding to the estrogen receptor in human breast cancer cell line MCF-7.[18] Binding to the human thyroid hormone transport protein transthyretin (TTR) has been demonstrated for 2,4,6-tribromophenol (2,4,6-TBP), isolated from house dust.[19]

2,4,6-TBP accumulated in the zebra fish (*Danio rerio*) from its diet, and 25−30% was converted to the corresponding anisole (2,4,6-TBA) over a 6 week exposure.[20] Fertilization success was reduced and gonad morphology disrupted by the TBP exposure.[20] BAs and BPs are "taste and odor" compounds that impart a characteristic and desirable taste to seafood but can cause off-flavors if levels are too high.[21−24] They have been responsible for tainting foods[22] and wine.[25] Mixed chloro-bromoanisoles and phenols were identified in an episode of "swampy, musty" odor in Swedish tap water.[26]

BPs undergo bromoperoxidase-catalyzed coupling to form polybrominated dibenzo-*p*-dioxins (PBDD),[27] which contribute to human exposure to total dioxin-type equivalents (TEQs).[28] Levels of PBDDs in seafood from the Swedish west coast and Baltic Proper are close to or exceed the European Union maximal residue limits in food for anthropogenic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).[29]
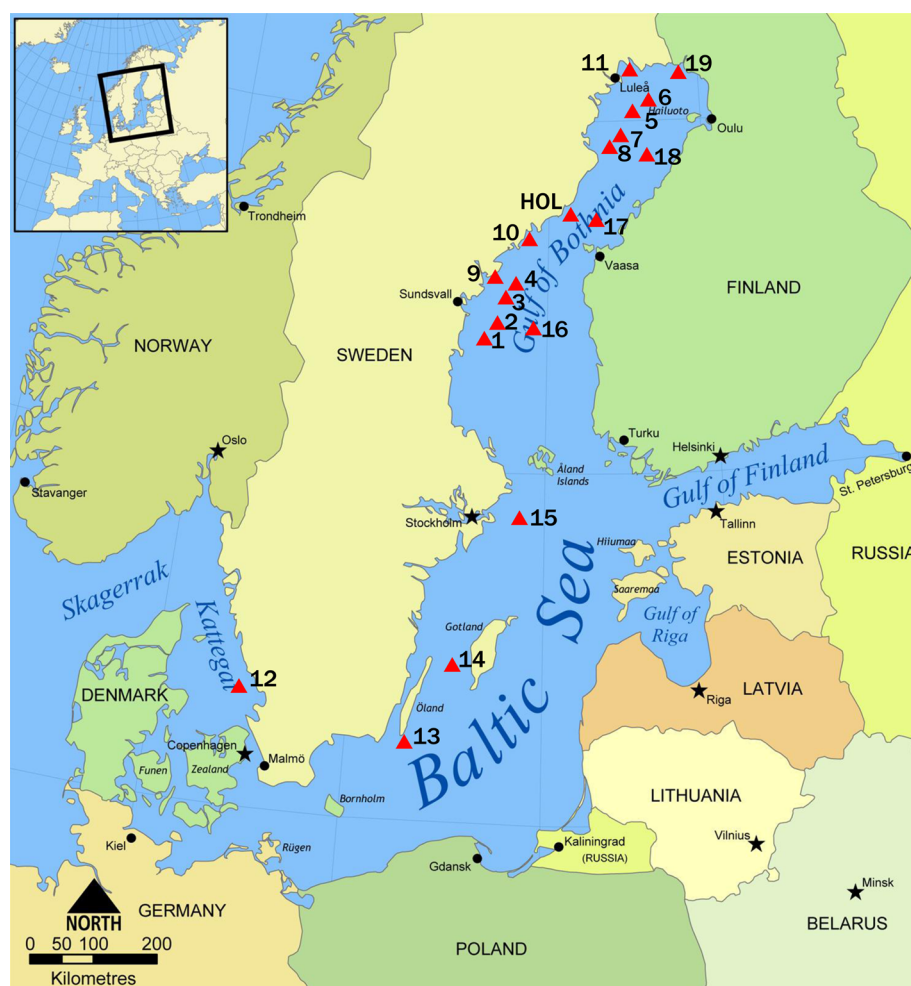
Figure 1. Sampling locations in the Baltic Sea in 2011−2013. See Table S1 of the Supporting Information for coordinates. Map by Norman Einstein, Wikimedia Commons (http://en.wikipedia.org/wiki/File:Baltic_Sea_map.png#file).

Other brominated phenolic compounds include hydroxylated and methoxylated brominated diphenyl ethers (OH-BDEs and MeO-BDEs) which are transformation products of PBDE flame retardants[30,31] and also formed naturally[32,33] The possibility of OH-BDEs being produced from BPs in aquatic systems was shown in a suspension of manganese dioxide (δ-MnO$_2$), a common constituent of sediments.[34] Simulated sunlight irradiation of 2,4-DBP in an aqueous solution produced 2′-OH-BDE68.[35] OH-BDEs and/or MeO-BDEs occur in algae, mussels, sponge, and fish of the Baltic Sea[15,29,36−41] and in marine biota worldwide.[42−44] Interconversion of OH-BDEs and MeO-BDEs occurs by methylation and demethylation in marine sediments.[45] Toxic effects have been documented for OH-BDEs in fish[46] and via interference with thyroid hormone metabolism and transport[47] and human placental aromatase.[48]

Although much research has been devoted to understanding global cycles of volatile halocarbons and many papers have appeared recently on bromophenolic compounds in biota, less attention has been given to the occurrence, transport, and cycling of BPs and BAs in the physical environment. Such knowledge is needed to predict the influence of climate change factors on the production and distribution of natural brominated compounds. BPs and bromoindoles were found in water and sediment of the North Sea and southern Baltic.[49] The only other report of BPs in Nordic waters is from a laboratory study in which BPs and OH-BDEs were determined in water for algal cultivation, taken from the Swedish west coast and the Baltic Proper.[50] Sources of BPs in marine and riverine water and sediment in Korea were natural but also associated with chlorination of cooling water from a nuclear power plant.[13] BPs, BAs, OH-BDEs, and other natural halogenated compounds were determined semiquantitatively in water of the Great Barrier Reef using passive semipermeable membrane devices,[9] and BAs were quantified in seawater of the Canadian Arctic[51] and the North and South Atlantic Ocean.[52] O-methylation of BPs converts them to the more volatile BAs, which provides a loss mechanism from marine waters. A Level I fugacity model predicted >80% partitioning of 2,4-dibromo-anisole (2,4-DBA), 2,6-DBA, and 2,4,6-TBA into air, with the remainder in water, soil, and sediment.[53] BAs and bromo-chloroanisoles were first measured in the North Pacific atmosphere[54] and subsequently over the Atlantic and Indian oceans[52,55,56] and in the Canadian Arctic.[51] BAs were determined in air samples collected at Lista, Norway, while the corresponding BPs were also identified but not quantified.[57]

Here we report for the first time (a) measurements of BAs in Baltic air and water, (b) estimates of the gas exchange of BAs in the northern Baltic, and (c) Br fluxes from BA volatilization with respect to the release of Br from bromomethanes and bromochloromethanes in the southern Baltic.[4]

■ EXPERIMENTAL PROCEDURES

Air and Water Sampling Locations and Methods. The study focused on the Gulf of Bothnia in the northern Baltic Sea, which is divided into the upper Bothnian Bay and the lower Bothnian Sea. Most water samples were collected from the upper 5 m in PVC Niskin bottles from shipboard in the Gulf in July 2011 and May 2012. Water column depths ranged from 13 to 210 m (Table S1 of the Supporting Information). The water was transferred to 20 or 40 L stainless steel cans. A transect from the south to north Baltic was made in September 2013. Water was drawn through the ship's FerryBox line at a depth of 7 m while the ship was enroute (http://www.ferrybox.org/routes/baltic_sea/index.html.en) and delivered into glass bottles. Two surface water samples were obtained in July 2012 from a small boat approximately 300 m west of Bergudden Light on Holmön, a group of islands in the "Quark" or nexus between the Bothnian Bay and Bothnian Sea (water column depth of 25 m). Collections were done through the ice in Sörsundet, a strait between the two islands of Holmön and Ängesön (3 m depth where samples were taken) in January 2013 and off Bergudden Light in April 2013. Sampling was done by dipping 20 L cans just below the surface. Coordinates are given in Table S1 of the Supporting Information and shown in Figure 1.

The water was passed through a glass fiber filter (GFF/F, nominal porosity of 0.7 μm, Whatman, Maidstone, England). In most cases, BAs and organochlorine pesticides (to be reported elsewhere) were concentrated from 40 L of water with a column of XAD-2 resin (70 mL, 20−60 mesh, Supelco, Bellefonte, PA), at flow rates of 120−150 mL min^{-1}. The September samples were processed for BAs only using 200 mg ENV+ solid phase extraction cartridges (Biotage, Uppsala, Sweden) at a flow rate of 40 mL min^{-1}. Procedures were slight modifications of those reported previously.[58] Before extraction, water samples were spiked with labeled surrogate recovery compounds [$^{13}C_6$]-γ-hexachlorocyclohexane ([$^{13}C_6$]-γ-HCH, 18 ng) for XAD-2 or 2,4,6-TBA-d_5 (0.9−1.8 ng) for ENV+.

Air sampling was done at the base of Bergudden Light on the coast of Holmön approximately 30 m.a.s.l. during 14 dates between May 2012 and September 2013, and from the ship during the May 2012 expedition in the Gulf. Air was drawn at a rate of 0.5 m^3 min^{-1} through a 20 cm × 26 cm GFF (Whatman EPM 2000) followed by two traps of polyether-type polyurethane foam (PUF), each 7.6 cm in diameter and 7.5 cm in thickness, density of 0.021 g cm^{-3} (PacWill Environmental, Beamsville, ON).[58] Collection times were mostly restricted to ~60−150 m^3, with exceptions (Table S2 of the Supporting Information), to minimize breakthrough of BAs.

XAD-2 resin was cleaned before use by Soxhlet extraction (24 h each, in order) with acetone, dichloromethane, and acetone and stored under deionized water. ENV+ cartridges were cleaned via elution with methanol followed by deionized water. PUF traps were cleaned by being washed with water and subjected to Soxhlet extraction with acetone followed by hexane (24 h each) and dried under a stream of clean nitrogen. GFFs were wrapped loosely in aluminum foil and baked at 400 °C.

Extraction and Cleanup. BAs are relatively soluble and volatile compounds[53] that are likely to be mainly dissolved in water and gaseous in air. Considering this, water and air GFFs were not analyzed. XAD-2 columns were eluted with 50 mL of acetone followed by 300 mL of dichloromethane. Deionized

water (150 mL) was added, and the mixture was shaken. The phases were separated, and the water−acetone layer was extracted with an additional 50 mL of dichloromethane. The dichloromethane extracts were pooled and dried over granular anhydrous sodium sulfate. Hexane (20 mL) was added, and the extract was concentrated to 5 mL by rotary evaporation and further to 1−2 mL by being blown down with a gentle stream of nitrogen. ENV+ cartridges were eluted with 10 mL of dichloromethane; 3 mL of hexane was added, and the extract was blown down to 1−2 mL. PUF traps of air samples were spiked with 2,4,6-TBA-d_5 (93 ng) and/or [$^{13}C_6$]-γ-HCH (18 ng) and subjected to Soxhlet extraction for 12−18 h with hexane, and the extracts were concentrated to 1−2 mL, as described above.

Extracts of water and air samples were cleaned with a 0.5 g column of Florisil (baked at 400 °C and deactivated by adding 5% deionized water) in a Pasteur pipet, topped with 1 cm of granular anhydrous sodium sulfate. The column was eluted with 12 mL of a 2:1 dichloromethane/hexane mixture. The eluate was concentrated, and the solvent was exchanged with isooctane by being blown down to 100−200 μL. A labeled polychlorinated biphenyl ([$^{13}C_{12}$]PCB-105, 1.6 ng) was added as an internal standard.

Analysis. The main target compounds were 2,4-DBA, 2,6-DBA, and 2,4,6-TBA, which are the most abundant BAs reported in air and water.[51,52,55,57] We also screened for 2,3-DBA, 2,5-DBA, and 3,5-DBA. Tetra- and pentabromoanisoles have previously been reported in marine air[52,55] but were not determined here. BPs were not included because they would be partially or fully dissociated in pH 7.8−8.2 Baltic seawater (pK_a values of 2,4-DBA and 2,4,6-TBA of 7.79 and 6.08, respectively[7]) and may not be efficiently extracted by the sampling media. Samples were analyzed by capillary gas chromatography and mass spectrometry using an Agilent 6890 chromatograph-5775 mass selective detector (Agilent Technologies, Santa Clara, CA). The column was an RTx5 column [30 m × 0.25 mm (inside diameter), 0.25 μm film (Restek Corp., Bellefonte, PA)]. Injection of 2 μL was done in a splitless manner (split opened after 1 min) with the column at 75 °C. The oven program was as follows: 10 °C min^{-1} to 85 °C, 1 °C min^{-1} to 115 °C, 20 °C min^{-1} to 220 °C (5 min), and 20 °C min^{-1} to 250 °C (5 min). The elution order was as follows: 2,6-, 3,5-, 2,5-, 2,3-, 2,4-DBA, 2,4,6-TBA-d_5, and 2,4,6-TBA. Quantification of most compounds was done in electron impact mode by monitoring quantitative/qualitative ions 266/264 for DBAs and 344/346 for 2,4,6-TBA. The surrogate compound 2,4,6-TBA-d_5 was determined using ion 351, while [$^{13}C_6$]-γ-HCH was determined by electron capture negative ion mass spectrometry using ion 261 (Quality Control). Compounds were quantified versus the labeled PCB-105 internal standard using solutions of BAs in isooctane. BA standards were obtained from AccuStandard (New Haven, CT). Mass-labeled PCB-105 and γ-HCH were from Cambridge Isotope Laboratories (Andover, MA), and labeled 2,4,6-TBA was from CDN Isotopes (Pointe-Claire, QC).

Water for dissolved organic carbon (DOC) analysis was acidified and purged to remove volatile organic carbon and carbonates. Nonpurgable DOC was oxidized to CO_2 over platinized aluminum at 680 °C; the gas stream was dried, and CO_2 was determined by a nondispersive infrared gas analyzer.[59]

Quality Control. Quality control procedures consisted of spiking with mass-labeled surrogate compounds to check recoveries, analysis of sorbent resin blanks, monitoring

quantifying/qualifying ion ratios in GC—MSD analysis, and checking for breakthrough of BAs from front to back PUF traps during air sample collection. Recoveries of $[^{13}C_6]$-γ-HCH with XAD-2 and 2,4,6-TBA-d_5 with ENV+ averaged 60 ± 14 and 96 ± 11%, respectively. Recoveries of 2,4,6-TBA-d_5 and $[^{13}C_6]$-γ-HCH from PUF traps averaged 96 ± 28 and 96 ± 14%, respectively. Samples were corrected for surrogate recoveries on an individual basis. XAD-2 limits of detection (LOD) for water samples collected with XAD-2 resin were 0.4, 0.8, and 2.6 pg L^{-1} for 2,6-DBA, 2,4-DBA, and 2,4,6-TBA, respectively ($n = 3$), based on the mean blank + 3 × the standard deviation (SD) and assuming 40 L of water sampled. LODs for 5 L of water sampled with ENV+ cartridges were 4.0, 4.0, and 10 pg L^{-1} for 2,6-DBA, 2,4-DBA, and 2,4,6-TBA, respectively ($n = 2$). The LODs (picograms per cubic meter) for BAs in PUF traps, assuming 100 m^3 of air sampled, were 0.44 for 2,6-DBA, 0.41 for 2,4-DBA, and 0.34 for 2,4,6-TBA ($n = 5$). All water and air samples were well above these limits for 2,4-DBA and 2,4,6-TBA. Further description of quality control procedures is given in the Supporting Information.

■ RESULTS AND DISCUSSION

BAs in Water: Distribution and Influencing Factors. Concentrations of BAs at each station are listed in Table S2 of the Supporting Information and averaged by basin in Table 1. Overall means were 86 ± 51 pg L^{-1} for 2,4-DBA and 199 ±

Table 1. Bromoanisoles in Surface Water and Air

water	picograms per liter		
	2,6-DBA	2,4-DBA	2,4,6-TBA
all locations			
range	<4−29	30−205	64−637
mean ± SD	14 ± 7	86 ± 51	199 ± 150
N	12[a]	21	21
Bothnian Bay and Sea			
May			
range	9.4−29	82−171	100−368
mean ± SD	17 ± 11	115 ± 31	176 ± 101
N	3[a]	6	6
July			
range		38−98	172−637
mean ± SD	10	71 ± 25	353 ± 197
N	1[a]	5	5
September			
range	<4−15	30−42	72−89
mean ± SD	10 ± 5.5	36 ± 4.9	78 ± 7.5
N	4	4	4

air	picograms per cubic meter		
	2,6-DBA[b]	2,4-DBA	2,4,6-TBA
April to September			
range	>0.4−>6.9	2.1−37	5.5−116
mean ± SD	>3.4	18 ± 13	40 ± 33
N	13	13	13
May to September			
range	>0.5−>6.9	7.9−37	25−116
mean ± SD	>4.4	23 ± 10	50 ± 31
N	10	10	10

[a]Some samples for 2,6-DBA were not included if they could not be quantified because of chromatographic interference (Table S1 of the Supporting Information). [b]Lower limits because of the breakthrough on PUF traps (Supporting Information).
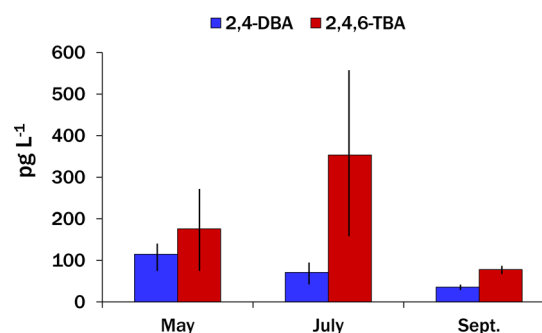
150 pg L^{-1} for 2,4,6-TBA. The mean for 2,6-DBA was 14 ± 7 pg L^{-1}, assuming half the LOD for samples below. Other targeted compounds (2,3-DBA, 2,5-DBA, and 3,5-DBA) were not detected. Few comparisons are available. The ranges of concentrations (mean ± SD) in surface water of the Canadian Archipelago and Labrador Sea in 2007−2008 were 8.5−38 (19 ± 6.9) pg L^{-1} for 2,4-DBA and 4.7−163 (54 ± 11) pg L^{-1} for 2,4,6-TBA.[51] Ranges (mean ± SD) at four stations on a cruise from Germany to South Africa in 1999−2000 were 2.8−5.3 (4.2 ± 1.0) pg L^{-1} for 2,6-DBA, 22−192 (72 ± 80) pg L^{-1} for 2,4-DBA, and 44−200 (128 ± 64) pg L^{-1} for 2,4,6-TBA, and monobromo- and pentabromoanisoles were also found.[52] A mean 2,4,6-TBA concentration of 540 pg L^{-1} was estimated on the Great Barrier Reef.[9]

A simple comparison of means in Table 1 does not adequately convey the spatial and temporal variability. In particular, collections were made in the Baltic Proper and Kattegat only in late September, whereas the rest of the basins were sampled in May and July as well as September. The Quark (off Holmön and in Sörsundet between islands) was sampled once in July and September and twice more through ice cover in January and April. Figure 2 shows the May, July, and

Figure 2. Concentrations of 2,4-DBA and 2,4,6-TBA in surface water (means ± SD). Data are listed in Table 1 and Table S1 of the Supporting Information.

September trends for the Bothnian Bay−Bothnian Sea region (including the Quark), compiling results from all years. The highest concentrations of 2,4,6-TBA occurred in July and of 2,4-DBA in May, and both BAs fell off in September. Concentrations of BAs were lowest in April when sampling through ice off Holmön but were higher in Sörsundet in January, also collected during ice cover (Table S1 of the Supporting Information). The April samples were from at a site with a water depth of 25 m; the January site was only 3 m deep, and macroalgae could be seen.

The spatial distribution for the entire Baltic was examined in September 2013 on a transect from Kattegat to Bothnian Bay (Table S1 of the Supporting Information). Levels of 2,4-DBA and 2,4,6-TBA were highest in Kattegat, intermediate in the Baltic Proper, and lowest in the Bothnian Sea and Bothnian Bay. Figure 3 shows the positive correlation with salinity for 2,4-DBA ($r^2 = 0.98$; $p < 10^{-5}$) and 2,4,6-TBA ($r^2 = 0.95$; $p < 10^{-4}$). Significant correlations were also obtained for the Baltic Proper and northern basins (removing the Kattegat sample): 2,4-DBA ($r^2 = 0.86$; $p = 0.0027$) and 2,4,6-TBA ($r^2 = 0.73$; $p = 0.014$). Concentrations of 2,6-DBA were much lower and not correlated with salinity, with or without the Kattegat sample ($r^2 = 0.18$, and $p = 0.33$; $r^2 = 0.50$, and $p = 0.12$, respectively). Reasons for why 2,6-DBA was not related to salinity are not
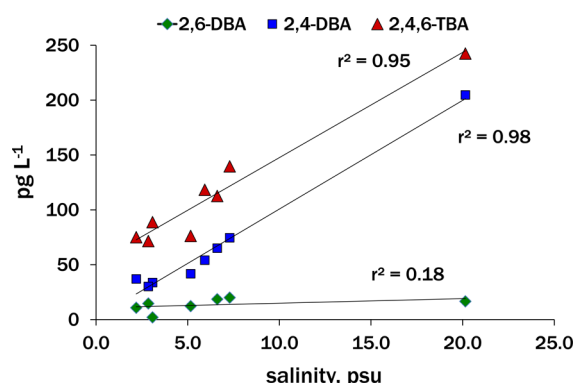
Figure 3. Correlations of BA concentrations in surface water vs salinity in September 2013. Data are listed in Table S1 of the Supporting Information. For 2,4,6-TBA $r^2 = 0.95$ ($p < 10^{-4}$). For 2,4-DBA $r^2 = 0.98$ ($p < 10^{-5}$). Without the highest sample (Kattegat), for 2,4-DBA $r^2 = 0.86$ ($p = 0.0027$) and for 2,4,6-TBA $r^2 = 0.73$ ($p = 0.014$). 2,6-DBA was not significantly correlated with salinity ($p = 0.33$ and 0.12).

known. The 2,6-DBA/(2,6-DBA + 2,4,6-TBA) mean fraction in September was 0.12 ± 0.05 in the Baltic Proper, Bothnian Sea, and Bothnian Bay and 0.06 in Kattegat, while the 2,4-DBA/(2,4-DBA + 2,4,6-TBA) mean fraction averaged 0.33 ± 0.03 in the former three regions and was 0.46 in Kattegat (Table S1 of the Supporting Information). A higher 2,4-DBA/(2,4-DBA + 2,4,6-TBA) fraction was also found in air passing over the North Atlantic and sampled on the Norwegian coast[57] (see below). This suggests that algal species may contribute differing proportions of the three BAs, as was reported for BPs among Australian red, brown, and green algae.[10]

The BP content of algae is known to vary with season and location. In Australia, higher concentrations in the green alga *Ulva lactuca* were found in summer than in winter.[60] BPs in three species of brown algae (*Padina arborescens*, *Sargassum siliquastrum*, and *Lobophora variegate*) sampled in Hong Kong were relatively low in summer compared to other seasons, which may have been caused by dieback of the algae due to overheating and strong solar radiation.[61] OH-BDEs in blue mussels (*Mytilus edulis*) from the Stockholm Archipelago (Baltic Proper) peaked strongly in June, with substantially lower levels in May, August, and October, while most MeO-BDEs displayed similar though less dramatic seasonality.[39] Highest concentrations of OH- and MeO-BDEs in red alga (*Ceramium tenuicorne*) of the Archipelago occurred in July, while 2,4,6-TBP increased in June, reached a maximum in July and August, and declined sharply by September.[50] Our results for 2,4,6-TBA are consistent with these trends.

The BA levels in water are likely to depend on the spatial distribution and density of producers and environmental conditions. Baltic species known to contain BP, BA, and/or more brominated compounds include red (*C. tenuicorne*) and brown (*Dictyosiphon foenicolaceus*) algae, cyanobacteria (*Aphanizomenon flosaquae* and *Nodularia spumigena*),[15,29,36,37,50] and the freshwater sponge *Ephydatia fluviatilis*.[41] Phytoplankton primary production is 10-fold higher in the southern Baltic than in the north.[62]

Production of 2,4,6-TBP in female *C. tenuicorne* was stimulated by light intensity, grazing by the isopod *Idotea baltica*, and salinity in the range of 5−7‰.[50] The growth length of female *C. tenuicorne* is influenced by salinity, light intensity, and temperature, and effects of these variables were different depending on whether the test clone originated from 7‰

(Baltic Proper) or 20‰ (Swedish west coast) salinity.[63] Nevertheless, the species is found worldwide at salinities ranging from 1 to 32‰.[63] An unexplored effect of salinity on the production of BPs by Baltic algae is the availability of bromide (0.8 mM in 35‰ seawater). The bromoperoxidase production and release of hypobromite (HOBr) in the arctic diatom *Porosira glacialis* at pH 6.5 increased from nearly zero at 0.3 mM KBr and 0.24 mM H_2O_2 and reached a plateau above 0.9 mM KBr.[64] Assuming constant seawater ion ratios, the concentration of bromide at Baltic salinities of 2−7‰ (Table S2 of the Supporting Information) is only 0.045−0.16 mM. Thus, several factors may contribute to the correlation of lower BA concentrations with lower salinity found on the September expedition (Figure 3): higher phytoplankton productivity in the southern Baltic,[62] advection and dilution by fresh riverine water during transport northward, and a lack of sufficient bromide in the northern Baltic for the efficient production of BPs.

BAs in Air. BA concentrations in air are summarized in Table 1 and reported by sample in Table S2 of the Supporting Information. Ranges (means ± SD) for the entire study were 2.1−37 (18 ± 13) pg m^{-3} for 2,4-DBA and 5.5−116 (40 ± 33) pg m^{-3} for 2,4,6-TBA. The mean for 2,6-DBA was >3.4 pg m^{-3}, given as a lower limit because of breakthrough during sampling. As for water, 2,3-DBA, 2,5-DBA, and 3,5-DBA were not detected. Distinct seasonal trends from May to September were not apparent with the few samples collected, though concentrations of all BAs were substantially lower in early April, when Bothnian Bay was covered with ice. 2,4-DBA/(2,4-DBA + 2,4,6-TBA) fractions averaged 0.33 ± 0.15 between May and September. Better coverage is needed to relate air concentrations to monthly patterns of algae growth and yearly variations. Annual mean air concentrations at Lista, Norway (58.10N, 63.66E, 14 m.a.s.l.), in 2003 were 19 ± 12 pg m^{-3} for 2,4-DBA and 13 ± 9 pg m^{-3} for 2,4,6-TBA,[57] and the 2,4-DBA/(2,4-DBA + 2,4,6-TBA) fraction was 0.59 based on these averages. Thus, 2,4,6-TBA was more abundant in the northern Baltic atmosphere, whereas 2,4-DBA dominated in air off the North Atlantic. Total BAs in air at Lista, Norway, were 5−20 pg m^{-3} from January to mid-April, increased to 40 pg m^{-3} by mid-May, peaked at 65 pg m^{-3} at the end of July, and remained at 25−50 pg m^{-3} through the end of the year.[57] Ranges of BAs measured in air on transects of North and South Atlantic Ocean from Germany to South Africa in 1993[55] and 1999−2000[52] were 0.4−3.6 pg m^{-3} for 2,6-DBA, 0.4−17 pg m^{-3} for 2,4-DBA, and 0.5−69 pg m^{-3} for 2,4,6-TBA. Mono-, tetra-, and pentabrominated species were also occasionally found in these studies, and the higher BA levels were associated with productive upwelling regions off Africa.[55] Earlier measurements found 2,4,6-TBA in the range of 8−30 (15 ± 7) pg m^{-3} at Réunion, South Indian Ocean.[56] BA concentrations in air of the Canadian Arctic in 2007−2009 were 4.6−25 (16 ± 6.7) pg m^{-3} for 2,4-DBA and 6.4−39 (23 ± 7.3) pg m^{-3} for 2,4,6-TBA.[51] Our Baltic measurements are at the high end of those reported in other studies.

Air−Water Exchange. Fugacities (f, Pa) of BAs were estimated from concentrations of dissolved BAs in water (C_W, mol m^{-3}), gaseous BAs in air (C_A, mol m^{-3}), and the Henry's law constant at the water temperature (H, Pa m^3 mol^{-1}):[58,65]

$$f_W = C_W H \tag{1}$$

$$f_A = C_A R T_A \tag{2}$$

$$f_W/f_A = C_W H / C_A R T_A \qquad (3)$$

where T_A (K) is the air temperature and $R = 8.31$ Pa m^3 mol^{-1} K^{-1}. Henry's law constants for the BAs were those reported at 25 °C[53] and were adjusted for temperature by the procedure described in the Supporting Information. The water/air fugacity ratio (f_W/f_A) indicates the net direction of exchange: volatilization at >1, deposition at <1, and equilibrium at 1.[51,58,65,66] C_A was calculated from quantities found on PUF traps. The XAD-2 and ENV+ resins may have collected both freely dissolved BAs and BAs bound to dissolved organic carbon (DOC). The percent freely dissolved was estimated from

$$\% \text{ free} = 100[1/(1 + K_{DOC}C_{DOC})] \qquad (4)$$

K_{DOC} (L kg^{-1}) was determined for a suite of nonpolar and polar organic compounds by kinetic solid phase micro-extraction (SPME) using Nordic Reference Fulvic Acid.[67] Log K_{DOC} values of 3.74 for 2,4-DBA and 4.17 for 2,4,6-TBA were estimated from their log octanol−water partition coefficients (log K_{OW} values of 3.75 and 4.44, respectively),[53] using a correlation of log K_{DOC} versus log K_{OW} for other low-polarity compounds. C_{DOC} was measured on the September cruise and averaged 4.8 ± 1.7 mg L^{-1}. The estimated freely dissolved percentages were 97% for 2,4-DBA and 93% for 2,4,6-TBA.

C_W values for 2,4-DBA and 2,4,6-TBA were monthly means for May, July, and September (Table 1 and Figure 2), and C_W values for June and August were estimated as averages of the bracketing monthly means. C_A values for 2,4-DBA and 2,4,6-TBA were assumed to be constant over the five-month period, averaging 23 ± 10 and 50 ± 31 pg m^{-3}, respectively (Table 1). The fugacity ratio was not calculated for 2,6-DBA because of possible underestimation of C_A due to breakthrough from PUF traps (Quality Control and Supporting Information).

Fugacity ratios ranged from 3.4 to 7.6 for 2,4-DBA and from 18 to 94 for 2,4,6-TBA, with peak values in July (Figure 4). These indicate oversaturation in water and net volatilization, especially for 2,4,6-TBA. Similarly, fugacity ratios of BAs were 10−70 in the North and South Atlantic between Germany and South Africa,[52] indicating large-scale outgassing from oceanic regions.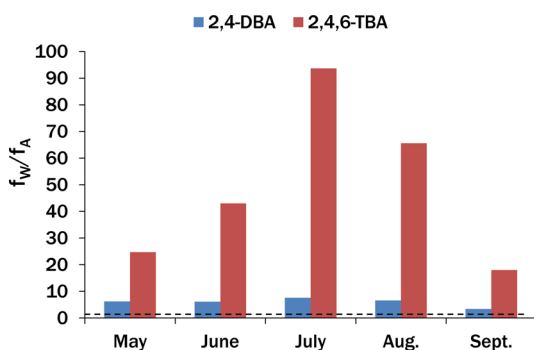 Exchange of BAs in the Canadian Arctic varied from net deposition, near equilibrium, and net volatilization.[51] Uncertainties in fugacity ratios and their 95% confidence intervals were estimated by propagation of errors in eq 3,[66] considering the relative uncertainties in C_W, C_A, and H. The relative standard deviations (RSDs) for C_W in May, July, and September were 14−35% for 2,4-DBA and 10−57% for 2,4,6-TBA, while RSDs for C_A from May to September were 43−62% (Table 1). RSDs for experimentally determined Henry's law constants of chlorinated pesticides are generally 20−30%.[68] With these uncertainties, the fugacity ratios estimated here indicated significant net volatilization of 2,4-DBA and 2,4,6-TBA. However, uncertainties introduced by assuming temperature slopes for the BA Henry's law constants could not be established (Henry's law constants and Supporting Information).

Gas exchange fluxes were estimated using the two-film model with fugacity parameters.[65,66] Volatilization (negative), deposition (positive), and net fluxes (F, mol m^{-2} d^{-1}) were calculated with mass transfer coefficients (MTCs) as functions of wind speed at a 10 m height (U_{10}, m s^{-1})[65,66,69] and (1) liquid phase MTCs derived from a quadratic−cubic relationship to long-term (monthly) average U_{10} and (2) weighted MTCs based on a cubic relationship to short-term (3 h) average U_{10}. Discussion, parameters, and relevant equations are given in the Supporting Information. Fluxes were estimated with the mean C_W and C_A values used for fugacity calculations (see above). Only the volatilization flux was calculated for 2,6-DBA with an overall mean C_W of 14 pg L^{-1} (Table S1 of the Supporting Information).

Fluxes and loadings (kilograms per month) to Bothnian Bay (38000 km^2) are listed in Table 2. Weighted MTCs derived from 3 h averaged U_{10} and corresponding fluxes/loadings were 20−50% higher than those estimated from monthly averaged U_{10}. Total volatilization loadings using the two sets of MTCs were −42 and −56 kg for 2,6-DBA, −164 and −214 kg for 2,4-DBA, and −780 and −1095 kg for 2,4,6-TBA. Deposition loadings were much smaller: 28 and 36 kg for 2,4-DBA and 19 and 26 kg for 2,4,6-TBA. Deposition fluxes and loadings could not be calculated for 2,6-DBA because air concentrations were only estimated as lower limits.

■ IMPLICATIONS

Volatilization of BAs may be an important loss pathway from the Bay. The depth profiles of BAs have not been determined, but if the concentration of total BAs [mean of 300 pg L^{-1} (Table S1 of the Supporting Information)] is uniform with depth, the 1 m^2 water column in Bothnian Bay (average depth of 40 m) contains 1.2×10^4 ng. The average volatilization flux of total BAs is −169 to −234 ng m^{-2} day^{-1} (Table 2). If this is the dominant loss process, the estimated water residence time is 51−71 days.

Cyanobacteria in the Baltic Proper produce volatile halo-methanes containing Cl, Br, and I,[3] which are important carriers of ozone-depleting bromine in the atmosphere.[4−6] Bromine from volatilized BAs may contribute to this pool. The mean flux of bromine from May to September from outgassing of the three BAs in Bothnian Bay was −1.4 to −2.0 nmol m^{-2} day^{-1}. This is 2−3% of the mean flux of −67 nmol m^{-2} day^{-1} for Br over the same months due to volatilization of bromomethanes and bromochloromethanes in the southern Baltic.[4] From the September 2013 transect, the mean concentration of total BAs in the Baltic Proper and Kattegat region was twice as high as in the Bothnian Bay and Bothnian Sea (Table S1 of the

Figure 4. Water/air fugacity ratios (f_W/f_A, mean $\pm$ SD) of 2,4-DBA and 2,4,6-TBA. Water concentrations were those measured in May, July, and September (Table 1 and Table S1 of the Supporting Information) and estimated as averages of the bracketing months for June and July. Air concentrations were assumed to be constant over the five months (Table 1 and Table S2 of the Supporting Information). Mean fugacity ratios are above the equilibrium $f_W/f_A = 1$ at $p < 0.05$, indicating net volatilization (Supporting Information).

Table 2. Bromoanisole Fluxes (nanograms per square meter per day) and Loadings (kilograms per month) to Bothnian Bay[a]

		May	June	July	August	September
2,6-DBA flux						
	V	−7.7	−6.3	−7.1	−6.4	−8.4
		−9.4	−8.6	−10	−9.2	−11
	D	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
		NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
	N	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
		NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
2,6-DBA loading						
	V	−9.1	−7.2	−8.4	−7.5	−10
		−11	−9.8	−12	−11	−13
	D	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
		NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
	N	NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
		NA[b]	NA[b]	NA[b]	NA[b]	NA[b]
2,4-DBA flux						
	V	−43	−31	−29	−21	−17
		−52	−41	−41	−29	−21
	D	6.9	5.1	3.9	3.2	5.0
		8.4	6.7	5.4	4.4	6.4
	N	−36	−26	−25	−18	−12
		−44	−34	−35	−24	−15
2,4-DBA loading						
	V	−51	−35	−35	−24	−19
		−61	−47	−48	−34	−24
	D	8.1	5.8	4.5	3.7	5.7
		9.9	7.6	6.4	5.1	7.3
	N	−43	−30	−30	−21	−13
		−51	−38	−41	−29	−17
2,4,6-TBA flux						
	V	−140	−150	−210	−110	−57
		−170	−210	−310	−160	−76
	D	5.7	3.5	2.2	1.7	3.2
		7.0	4.9	3.3	2.5	4.2
	N	−130	−150	−210	−110	−54
		−170	−210	−310	−160	−72
2,4,6-TBA loading						
	V	−170	−170	−240	−130	−65
		−200	−240	−370	−190	−87
	D	6.7	4.0	2.6	2.0	3.7
		8.2	5.6	3.9	3.0	4.8
	N	−160	−170	−240	−130	−62
		−200	−240	−360	−190	−83

[a]V, D, and N indicate volatilization, deposition, and net fluxes, respectively, estimated using mass transfer coefficients derived from monthly average wind speeds (U_{10}) (top) and 3-h averaged U_{10} (bottom). [b]NA, not available, uncertain air concentrations due to breakthrough during sampling (Supporting Information).

Supporting Information). If this holds for other months, it is reasonable to expect the bromine flux from BA volatilization in the southern Baltic to be correspondingly higher, 4−6% of that due to the lighter bromine carriers.

Physical impacts of climate change on the Baltic Sea include increasing water temperature and fresh water input and reduction in ice cover and salinity.[70] A shift is anticipated from a phytoplankton-based to microbially based food web in the northern Baltic coupled with increasing river runoff,[70] and phytoplankton production in the south is expected to increase in certain scenarios of rising temperature and nutrient loading.[71] Greater discharge of fresh water and brown-colored DOM in the northern Baltic may reduce bromide availability, phytoplankton production,[70] and consequently BPs and BAs. On the other hand, volatile halocarbons are produced by reaction of HOBr with DOM.[64] How will BPs and BAs respond to the opposing changes in HOBr (lower) and DOM (higher)? Predicting the influence of these climate-driven factors on BPs, BAs, and other natural brominated compounds requires a better understanding of their production and biogeochemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Quality control information, description of the procedure for adjusting Henry's law constants for water temperature, discussion, parameters, and equations for estimating gas exchange fluxes from the two-film model, tables of station locations, BA concentrations in water and air, parameters for temperature adjustment of Henry's law constants, diffusive transport properties and mass transfer coefficients of BAs, and a figure showing the frequency distribution of wind speeds at Holmön. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: terry.bidleman@chem.umu.se. Phone: +46-70-627-1254.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Ballschmiter, K. Review: Pattern and sources of naturally produced organohalogens in the marine environment: Biogenic formation of organohalogens. *Chemosphere* **2003**, *52*, 313−324.
(2) Gribble, G. W. The diversity of naturally produced organohalogens. *Chemosphere* **2003**, *52*, 289−297.
(3) Karlsson, A.; Auer, N.; Schulz-Bull, D. E.; Abrahamsson, K. Cyanobacteria blooms in the Baltic: A source of volatile halocarbons. *Mar. Chem.* **2008**, *110*, 129−139.
(4) Orlikowska, A.; Schulz-Bull, D. E. Seasonal variations of volatile organic compounds in the coastal Baltic sea. *Environ. Chem.* **2009**, *6*, 495−507.
(5) Quack, B.; Wallace, D. W. R. Air-sea flux of bromoform: Controls, rates and implications. *Global Biogeochem. Cycles* **2003**, *17*, 1023.
(6) Ziska, F.; Quack, B.; Abrahamsson, K.; Archer, S. D.; Atlas, E.; Bell, T.; Butler, J. H.; Carpenter, L. J.; Jones, C. E.; Harris, N. R. P.; Hepach, H.; Heumann, K. G.; Hughes, C.; Kuss, J.; Krüger, K.; Liss, P.;

Moore, R. M.; Orlikowska, A.; Raimund, S.; Reeves, C. E.; Reifenhäuser, W.; Robinson, A. D.; Schall, C.; Tanhua, T.; Tegtmeier, S.; Turner, S.; Wang, L.; Wallace, D.; Williams, J.; Yamamoto, H.; Yvon-Lewis, S.; Yokouchi, Y. Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide. *Atmos. Chem. Phys.* **2013**, *13*, 8915−8934.

(7) Howe, P. D.; Dobson, S.; Malcolm, H. M. 2,4,6-Tribromophenol and Other Simple Phenols. Concise International Chemical Assessment Document 66; World Health Organization: Geneva, 2005; pp 47 (http://www.who.int/ipcs/publications/cicad/cicad_66_web_version.pdf) (accessed April 18, 2014).

(8) Vetter, W. Marine halogenated natural products of environmental relevance. *Rev. Environ. Contam. Toxicol.* **2006**, *188*, 1−57.

(9) Vetter, W.; Hasse-Aschoff, P.; Rosenfelder, N.; Komarova, T.; Müller, J. F. Determination of halogenated natural products in passive samplers deployed along the Great Barrier Reef, Queensland/Australia. *Environ. Sci. Technol.* **2009**, *43*, 6133−6137.

(10) Whitfield, F. B.; Helidoniotis, F.; Shaw, K. J.; Svoronos, D. Distribution of bromophenols in species of algae from eastern Australia. *J. Agric. Food Chem.* **1999**, *47*, 2367−2373.

(11) Flodin, C.; Whitfield, F. B. 4-Hydroxybenzoic acid: A likely precursor of 2,4,6-tribromophenol in *Ulva lactuca*. *Phytochemistry* **1999**, *51*, 249−255.

(12) Nielson, A. H. Biological effects and biosynthesis of brominated metabolites. In *Organic Bromine and Iodine Compounds*; Nielson, A. H., Ed.; Springer-Verlag: Berlin, 2003; pp 5−204.

(13) Sim, W.-J.; Lee, S.-H.; Lee, I.-S.; Choi, S.-D.; Oh, J.-E. Distribution and formation of chlorophenols and bromophenols in marine and riverine environments. *Chemosphere* **2009**, *77*, 552−558.

(14) Flodin, C.; Whitfield, F. B. Brominated anisoles and cresols in the red alga *Polysiphonia sphaerocarpa*. *Phytochemistry* **2000**, *53*, 77−80.

(15) Löfstrand, K.; Malmvärn, A.; Haglund, P.; Bignert, A.; Bergman, Å.; Asplund, L. Brominated phenols, anisoles, and dioxins present in blue mussels from the Swedish coastline. *Environ. Sci. Pollut. Res.* **2010**, *17*, 1460−1468.

(16) Vetter, W.; von der Recke, R.; Hetzke, D.; Nygård, T. Natural and man-made organobromine compounds in marine biota from central Norway. *Environ. Int.* **2007**, *17*, 17−26.

(17) Hovander, L.; Malmberg, T.; Athanasiadou, M.; Athanassiadis, I.; Rahm, S.; Bergman, Å.; Wehler, E. K. Identification of hydroxylated PCB metabolites and other phenolic halogenated pollutants in human blood plasma. *Arch. Environ. Contam. Toxicol.* **2002**, *42*, 105−117.

(18) Olsen, C. M.; Meussen.Elholm, E. T. M.; Holme, J. A.; Hongslo, J. K. Brominated phenols: Characterization of estrogen-like activity in the human breast cancer cell-line MCF-7. *Toxicol. Lett.* **2002**, *129*, 55−63.

(19) Suzuki, G.; Takigami, H.; Watanabe, M.; Takahashi, S.; Nose, K.; Asari, M.; Sakai, S.-I. Identification of chlorinated and brominated phenols as potential thyroid-disrupting compounds in indoor dusts. *Environ. Sci. Technol.* **2008**, *42*, 1794−1800.

(20) Haldén, A. N.; Nyholm, J. R.; Andersson, P. L.; Holbech, H.; Norrgren, L. Oral exposure of adult zebrafish (*Danio rerio*) to 2,4,6-tribromophenol affects reproduction. *Aquat. Toxicol.* **2010**, *100*, 30−37.

(21) Whitfield, F. B.; Last, J. H.; Shaw, K. J.; Tindale, C. R. 2,6-Dibromophenol: The cause of an iodoform-like off-flavour in some Australian crustacea. *J. Sci. Food Agric.* **1988**, *46*, 29−42.

(22) Whitfield, F. B.; Hill, J. L.; Shaw, K. J. 2,4,6-Tribromoanisole: A potential cause of mustiness in packaged food. *J. Agric. Food Chem.* **1997**, *45*, 889−893.

(23) Chung, H. Y.; Ma, W. C. J.; Kim, J.-S. Seasonal distribution of bromophenols in selected Hong Kong seafood. *J. Agric. Food Chem.* **2003**, *51*, 6752−6760.

(24) Da Silva, V. M.; Lopes, W. A.; de Andrade, J. B.; da Cuena Veloso, M. C.; dos Santos, G. V.; Oliveira, A. S. Brominated phenols as key flavor compounds found in marine organisms. *Quim. Nova* **2007**, *30*, 629−635.

(25) Chatonnet, P.; Bonnet, S.; Boutou, S.; Labadie, M. D. Identification and responsibility of 2,4,6-tribromoanisole in musty, corked odors in wine. *J. Agric. Food Chem.* **2004**, *52*, 1255−1262.

(26) Corbi, E.; Benanou, D.; Cantet, J.; Tabet, J. C. Identification of new odorous compounds in Swedish water: Mixed haloanisoles and phenolic precursors. *Water Sci. Technol.* **2007**, *55*, 185−193.

(27) Arnoldsson, K.; Andersson, P. L.; Haglund, P. Formation of environmentally relevant brominated dioxins from 2,4,6-tribromophenol via bromoperoxidase-catalyzed dimerization. *Environ. Sci. Technol.* **2012**, *46*, 7239−7244.

(28) van der Berg, M.; Denison, M. S.; Birnbaum, L. S.; DeVito, M. J.; Fiedler, H.; Falandysz, J.; Rose, M.; Schrenk, D.; Safe, S.; Tohyama, C.; Tritscher, A.; Tysklind, M.; Peterson, P. E. PBDD/Fs and PBBs: Inclusion in the toxicity equivalency factor concept for dioxin-like compounds. *Toxicol. Sci.* **2013**, *133*, 197−208.

(29) Haglund, P.; Malmvärn, A.; Bergek, S.; Bignert, A.; Lautsky, L.; Nakano, T.; Wiberg, K.; Asplund, L. Brominated dibenzo-*p*-dioxins: A new class of marine toxins? *Environ. Sci. Technol.* **2007**, *41*, 3069−3074.

(30) Stapleton, H. M.; Kelly, S. M.; Pei, R.; Letcher, R. J.; Gunsch, C. Metabolism of polybrominated diphenyl ethers (PBDEs) by human hepatocytes *in vitro*. *Environ. Health Perspect.* **2009**, *117*, 197−202.

(31) Ueno, D.; Darling, C.; Alaee, M.; Pacepavicius, G.; Teixeira, C.; Campbell, L.; Letcher, R. J.; Bergman, A.; Marsh, G.; Muir, D. Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) in the abiotic environment: Surface water and precipitation from Ontario, Canada. *Environ. Sci. Technol.* **2008**, *42*, 1657−1664.

(32) Teuten, E. L.; Xu, L.; Reddy, C. M. Two abundant bioaccumulated halogenated compounds are natural products. *Science* **2005**, *307*, 917−920.

(33) Guitart, C.; Slattery, M.; Ankisetty, S.; Radwan, M.; Ross, S. J.; Letcher, R. J.; Reddy, C. M. Contemporary C-14 radiocarbon levels of oxygenated polybrominated diphenyl ethers (O-PBDEs) isolated in sponge-cyanobacteria associations. *Mar. Pollut. Bull.* **2011**, *62*, 631−636.

(34) Lin, K.; Yan, C.; Gan, J. Production of hydroxylated polybrominated diphenyl ethers (OH-PBDEs) from bromophenols by manganese dioxide. *Environ. Sci. Technol.* **2014**, *48*, 263−271.

(35) Liu, H.; Zhao, H.; Quan, X.; Zhang, Y.; Chen, S.; Zhao, H. Formation of 2′-hydroxy-2,3′,4,5′-tetrabromodiphenyl ether (2′-OH-BDE68) from 2,4-dibromophenol in aqueous solution under simulated sunlight irradiation. *Chemosphere* **2011**, *84*, 512−518.

(36) Malmvärn, A.; Marsh, G.; Kautsky, L.; Athanasiadou, M.; Bergman, Å; Asplund, L. Hydroxylated and methoxylated brominated diphenyl ethers in the red algae *Ceramium tenuicorne* and blue mussels from the Baltic Sea. *Environ. Sci. Technol.* **2005**, *39*, 2990−2997.

(37) Malmvärn, A.; Zebühr, Y.; Kautsky, L.; Bergman, Å.; Asplund, L. Hydroxylated and methoxylated polybrominated diphenyl ethers and polybrominated dibenzo-*p*-dioxins in red alga and cyanobacteria living in the Baltic Sea. *Chemosphere* **2008**, *72*, 910−916.

(38) Haglund, P.; Löfstrand, K.; Malmvärn, A.; Bignert, A.; Asplund, L. Temporal variations of polybrominated dibenzo-*p*-dioxin and methoxylated diphenyl ether concentrations in fish revealing large differences in exposure and metabolic stability. *Environ. Sci. Technol.* **2010**, *44*, 2466−2473.

(39) Löfstrand, K.; Liu, X.; Lindqvist, D.; Jensen, S.; Asplund, L. Seasonal variations of hydroxylated and methoxylated brominated diphenyl ethers in blue mussels from the Baltic Sea. *Chemosphere* **2011**, *84*, 527−532.

(40) Marsh, G.; Athanasiadou, M.; Bergman, Å.; Asplund, L. Identification of hydroxylated and methoxylated polybrominated diphenyl ethers in Baltic Sea salmon (*Salmo salar*) blood. *Environ. Sci. Technol.* **2004**, *38*, 10−18.

(41) Unger, M.; Asplund, L.; Haglund, P.; Malmvärn, A.; Arnoldsson, K.; Gustafsson, Ö. Aquatic sponge: A producer of brominated dioxins in the Baltic. *Environ. Sci. Technol.* **2009**, *43*, 8245−8250.

(42) Melcher, J.; Olbrich, D.; Marsh, G.; Nikiforov, V.; Gaus, C.; Gaul, S.; Vetter, W. Tetra- and tribromophenoxyanisoles in marine samples from Oceania. *Environ. Sci. Technol.* **2005**, *39*, 7784−7789.

(43) McKinney, M.; De Guise, S.; Martineau, D.; Beland, P.; Lebeuf, M.; Letcher, R. J. Organohalogen contaminants and metabolites in beluga whale (*Delphinapterus leucas*) from two Canadian populations. *Environ. Toxicol. Chem.* **2006**, *25*, 1246−1257.

(44) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Gobas, F. A. P. C. Hydroxylated and methoxylated polybrominated diphenyl ethers in a Canadian Arctic marine food web. *Environ. Sci. Technol.* **2008**, *42*, 7069−7077.

(45) Zhang, K.; Wan, Y.; Jones, P. D.; Wiseman, S.; Giesy, J. P.; Hu, J. Occurrence and fates of hydroxylated polybrominated diphenyl ethers in marine sediments in relation to trophodynamics. *Environ. Sci. Technol.* **2012**, *46*, 2148−2155.

(46) van Boxtel, A. L.; Kamstra, J. H.; Cenijn, P. H.; Pieterse, B.; Wagner, M. J.; Antink, M.; Krab, K.; van der Burg, B.; Marsh, G.; Brouwer, A.; Legler, J. Microarray analysis reveals a mechanism of phenolic polybrominated diphenyl ether toxicity in zebra fish. *Environ. Sci. Technol.* **2008**, *42*, 1773−1779.

(47) Meerts, I. A. T. M.; Letcher, R. J.; Hoving, S.; Marsh, G.; Bergman, Å.; Lemmen, J. G.; van der Burg, B.; Brouwer, A. *In vitro* estrogenicity of polybrominated diphenyl ethers, hydroxylated PBDEs, and polybrominated bisphenol A compounds. *Environ. Health Perspect.* **2001**, *109*, 399−407.

(48) Canton, R. F.; Scholten, D. E. A.; Marsh, G.; de Jong, P. C.; van den Berg, M. Inhibition of human placental aromatase activity by hydroxylated polybrominated diphenyl ethers (OH-PBDEs). *Toxicol. Appl. Pharmacol.* **2008**, *227*, 68−75.

(49) Reineke, N.; Biselli, S.; Franke, S.; Francke, W.; Heinzel, N.; Hühnerfuss, H.; Iznaguen, H.; Kammann, U.; Theobald, N.; Vobach, M.; Wosnick, W. Brominated indoles and phenols in marine sediment and water extracts from the North and Baltic seas: Concentrations and effects. *Arch. Environ. Contam. Toxicol.* **2006**, *51*, 186−196.

(50) Enhus, C.; Boalt, E.; Lindqvist, D.; Eklund, B.; Asplund, L. Natural production of brominated aromatic compounds in the red alga Ceramium tenuicorne. Technical Report 2:2012; Swedish Museum of Natural History: Stockholm, 2012; pp 14 (http://www.nrm.se/download/18.551d33ba13a8a19ad042336/1367705040683/2_2012+Nnatural+production+of+brominated+aromatic+compounds+in+C.+tenuicorne.pdf) (accessed April 18, 2014).

(51) Wong, F.; Jantunen, L. M.; Pućko, M.; Papakyriakou, T.; Stern, G. A.; Bidleman, T. F. Air-water exchange of anthropogenic and natural organohalogens on International Polar Year (IPY) expeditions in the Canadian Arctic. *Environ. Sci. Technol.* **2011**, *45*, 876−881.

(52) Pfeifer, O.; Ballschmiter, K. Halogenated methyl-phenyl ethers (HMPE; halogenated anisoles) in the marine troposphere and in the surface water of the Atlantic Ocean: An indicator of the global load of anthropogenic and biogenic halophenols. *Organohalogen Compd.* **2002**, *57*, 483−486.

(53) Pfeifer, O.; Lohmann, U.; Ballschmiter, K. Halogenated methyl-phenyl ethers (anisoles) in the environment: Determination of vapor pressures, aqueous solubilities, Henry's law constants, and gas/water (K_{gw}), n-octanol/water (K_{ow}) and gas/n-octanol (K_{go}) partition coefficients. *Fresenius' J. Anal. Chem.* **2001**, *371*, 598−606.

(54) Atlas, E.; Sullivan, K.; Giam, C. S. Widespread occurrence of polyhalogenated aromatic ethers in the marine atmosphere. *Atmos. Environ.* **1986**, *20*, 1217−1220.

(55) Führer, U.; Ballschmiter, K. Bromochloromethoxybenzenes in the marine troposphere of the Atlantic Ocean: A group of organohalogens with mixed biogenic and anthropogenic origin. *Environ. Sci. Technol.* **1998**, *32*, 2208−2215.

(56) Wittlinger, R.; Ballschmiter, K. Studies of the global baseline pollution XIII. C_6-C_{14} organohalogens (*α*- and *γ*.HCH, HCB, PCB, 4,4′-DDT, 4,4′-DDE, *cis*- and *trans*-chlordane, *trans*-nonachlor, anisoles) in the lower atmosphere of the southern Indian Ocean. *Fresenius' J. Anal. Chem.* **1990**, *336*, 193−200.

(57) Melcher, J.; Schlabach, M.; Andersen, M. S.; Vetter, W. Contrasting the seasonal variation of halogenated natural products and anthropogenic hexachlorocyclohexanes in the southern Norwegian atmosphere. *Arch. Environ. Contam. Toxicol.* **2008**, *55*, 547−557.

(58) Jantunen, L. M.; Kylin, H.; Bidleman, T. F. Air−water gas exchange of *α*-hexachlorocyclohexane enantiomers in the South Atlantic Ocean and Antarctica. *Deep Sea Res., Part II* **2004**, *51*, 2661−2672.

(59) *Water Analysis Guidelines for the Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)*; ISO-CEN EN 1484:1998, ICS 13.060.30; European Committee for Standardization: Brussels, 1998; pp 3−4.

(60) Flodin, C.; Helidoniotis, F.; Whitfield, F. B. Seasonal variation in bromophenol content and bromoperoxidase activity in *Ulva lactuca*. *Phytochemistry* **1999**, *51*, 135−138.

(61) Chung, H. Y.; Ma, W. C.; Ang, P. O., Jr.; Kim, J.-S.; Chen, F. Seasonal variations of bromophenol in brown algae (*Padina arborescens*, *Sargassum siliquastrum*, and *Lobophora variegata*) collected in Hong Kong. *J. Agric. Food Chem.* **2003**, *51*, 2619−2624.

(62) Samuelsson, K.; Berglund, J.; Andersson, A. Factors structuring the heterotrophic flagellate and cilate community along a brackish water primary production gradient. *J. Plankton Res.* **2006**, *28*, 345−359.

(63) Eklund, B. Development of a growth inhibition test with the marine and brackish water red alga *Ceramium tenuicorne*. *Mar. Pollut. Bull.* **2005**, *50*, 921−930.

(64) Hill, V. L.; Manley, S. L. Release of reactive bromine and iodine from diatoms and its possible role in halogen transfer in polar and tropical oceans. *Limnol. Oceanogr.* **2009**, *54*, 812−822.

(65) Bidleman, T. F.; McConnell, L. L. A review of field experiments to determine air-water gas exchange of persistent organic pollutants. *Sci. Total Environ.* **1995**, *159*, 101−117.

(66) Jantunen, L. M.; Bidleman, T. F. Air-water gas exchange of toxaphene in Lake Superior. *Environ. Toxicol. Chem.* **2003**, *22*, 1229−1237.

(67) Ripszam, M.; Haglund, P. Automated method for determination of dissolved organic carbon − water partitioning constants of structurally diverse pollutants using pre-equilibrium solid phase microextraction − gas chromatography − mass spectrometry. Manuscript submitted for publication.

(68) Cetin, B.; Ozer, S.; Sofuoglu, A.; Odabasi, M. Determination of Henry's law constants of organochlorine pesticides in deionized and saline water as a function of temperature. *Atmos. Environ.* **2006**, *40*, 4538−4546.

(69) Wanninkhof, R.; Asher, W. E.; Ho, D. T.; Sweeney, C.; McGillis, W. R. Advances in quantifying air-sea gas exchange and environmental forcing. *Annu. Rev. Mar. Sci.* **2009**, *1*, 213−244.

(70) Climate change in the Baltic Sea Area: HELCOM Thematic Assessment in 2013. *Baltic Sea Environment Proceedings No. 137*; Baltic Marine Environment Protection Commission-Helsinki Commission: Helsinki, 2012; pp 65.

(71) Meier, H. E. M.; Müller-Karulis, B.; Andersson, H. C.; Dieterich, C.; Eilola, K.; Gustafsson, B. G.; Höglund, A.; Hordoir, R.; Kuznetsov, I.; Neumann, T.; Ranjbar, Z.; Savchuk, O. P.; Schimanke, S. Impact of climate change on ecological quality indicators and biogeochemical fluxes in the Baltic Sea: A multi-model ensemble study. *Ambio* **2012**, *41*, 558−573.