



Sea-air exchange of bromoanisoles and methoxylated bromodiphenyl ethers in the Northern Baltic



Terry F. Bidleman^{a,*}, Kathleen Agosta^a, Agneta Andersson^b, Peter Haglund^a, Per Liljelind^a, Alyse Hegmans^c, Liisa M. Jantunen^d, Olle Nygren^a, Justen Poole^e, Matyas Ripszám^a, Mats Tysklind^a

^a Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

^b Department of Ecology and Environmental Science, Umeå University, SE-901 87 Umeå, Sweden

^c Department of Environmental Science, Royal Roads University, Victoria, BC, V9B 5Y2, Canada

^d Air Quality Processes Research Section, Environment and Climate Change Canada, 6248 Eighth Line, Egbert, ON L0L 1N0, Canada

^e Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada

ARTICLE INFO

Article history:

Received 13 May 2016

Received in revised form 11 August 2016

Accepted 18 August 2016

Available online 27 August 2016

Keywords:

Halogenated natural products

Bromoanisoles

Methoxylated bromodiphenyl ethers

Air-water exchange

Baltic Sea

ABSTRACT

Halogenated natural products in biota of the Baltic Sea include bromoanisoles (BAs) and methoxylated bromodiphenyl ethers (MeO-BDEs). We identified biogenic 6-MeO-BDE47 and 2'-MeO-BDE68 in Baltic water and air for the first time using gas chromatography – high resolution mass spectrometry. Partial pressures in air were related to temperature by: $\log p/\text{Pa} = m/T(K) + b$. We determined Henry's law constants (HLCs) of 2,4-dibromoanisole (2,4-DiBA) and 2,4,6-tribromoanisole (2,4,6-TriBA) from 5 to 30 °C and revised our assessment of gas exchange in the northern Baltic. The new water/air fugacity ratios (*FRs*) were lower, but still indicated net volatilization in May–June for 2,4-DiBA and May – September for 2,4,6-TriBA. The net flux (negative) of BAs from Bothnian Bay (38,000 km²) between May – September was revised from –1319 to –532 kg. *FRs* of MeO-BDEs were >1, suggesting volatilization, although this is tentative due to uncertainties in their HLCs and binding to dissolved organic carbon.

Crown Copyright © 2016 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Halogenated natural products are synthesized by marine organisms worldwide and thousands of compounds have been identified (Gribble, 2010; Vetter and Gribble, 2007). Prominent among these are bromophenolic compounds, including parent bromophenols (BPs) and their transformation products bromoanisoles (BAs), hydroxylated and methoxylated bromodiphenyl ethers (OH-BDEs, MeO-BDEs), and polybrominated dibenzo-*p*-dioxins (PBDDs).

MeO-BDEs and OH-BDEs arise from surface-catalyzed or enzymatic coupling of precursor BPs (Lin et al., 2014a, 2014b) and are synthesized by marine bacteria and sponges (Agarwal et al., 2014, 2015). The two compound classes are interconverted by methylation-demethylation reactions (Wiseman et al., 2011; Zhang et al., 2012). OH-BDEs and MeO-BDEs are also transformation products of polybrominated diphenyl ether (PBDE) flame retardants (Wiseman et al., 2011), and substitution patterns give clues to natural versus anthropogenic origins (Agarwal et al., 2015; Marsh et al., 2004; Wiseman et al., 2011). Natural origin of the more abundant MeO-BDEs has been confirmed by ¹⁴C dating (Guitart et al., 2011; Teuten et al., 2005) and by their presence in

historical specimens: archived whale oil from the pre-industrial period (Teuten and Reddy, 2007) and a sea eagle egg laid in 1941 in the Baltic region (Nordlöf et al., 2012). They occur in deep layers of ocean sediments (Fan et al., 2014a, 2014b). Worldwide, MeO-BDEs in marine mammals often exceed concentrations of PBDEs (Alonso et al., 2014; Rotander et al., 2012).

Although they are natural, some HNPs have toxic properties. OH-BDEs interrupt oxidative phosphorylation (Legradi et al., 2014) and bind to the thyroid hormone receptor (Wiseman et al., 2011). OH-BDEs and MeO-BDEs affect endocrine hormone activity or synthesis (Hu et al., 2011; Wiseman et al., 2011). Photolysis of OH-BDEs (Erickson et al., 2012) and MeO-BDEs (Arnoldsson et al., 2012a) and enzymatic coupling of BPs (Arnoldsson et al., 2012b) yield PBDDs, which have toxic equivalence factors similar to those of anthropogenic PCDDs (Haglund et al., 2007; van der Berg et al., 2013).

Bromophenolic compounds are widespread in Baltic algae, invertebrates, fish, birds and seals (Table 1). Moreover, PBDDs in mussels (Haglund et al., 2007) and OH-BDEs in herring (Dahlberg et al., 2016a) appear to be increasing recently. Data for abiotic compartments are sparse (Table 1). In previous papers, we estimated the exchange of BAs between Baltic surface water and air from measurements in 2011–2013 (Bidleman et al., 2014, 2015). The net direction of exchange was volatilization, based on fugacity calculations using the Henry's law

* Corresponding author.

E-mail address: terry.bidleman@umu.se (T.F. Bidleman).

Table 1
Reports of bromophenolic compounds in the Baltic ecosystem^{a,b}.

| Medium | BPs | BAs | OH-BDEs | MeO-BDEs | PBDDs |
|---------------|---------|--------------------|------------------|----------------------------------|-----------------|
| Water | | This work, 1, 2 | | This work | |
| Air | | This work, 1, 2 | | This work | |
| Sediment | | | | | 3 |
| Macroalgae | 4, 5, 6 | 4, 5, 6 | 4, 5, 6, 7, 8, 9 | 4, 5, 6, 7, 8, 9 | 4, 9, 10 |
| Cyanobacteria | | | 9 | 9 | 9 |
| Sponge | | | | | 11 |
| Amphipods | 6 | 6 | 6 | 6 | |
| Mussels | 4, 12 | 4, 12, 13 | 4, 7, 12, 14 | 4, 7, 12, 13, 14 | 3, 4, 8, 10, 14 |
| Fish | 6, 15 | 6, 15 | 6, 15, 16 | 6, 10, 15, 16, 17, 18, 19, 20 | 3, 10, 17, 21 |
| Birds | 12 | 12 | 12 | 12, 22 | |
| Seal | | | 23 | 20 | |

a) BPs: bromophenols, BAs: bromoanisoles, OH-BDEs: hydroxylated bromodiphenyl ethers, MeO-BDEs: methoxylated bromodiphenyl ethers, PBDDs: polybrominated dibenzo-*p*-dioxins.

b) References: 1. Bidleman et al., 2014; 2. Bidleman et al., 2015; 3. Haglund, 2010; 4. Löfstrand et al., 2010; 5. Dahlgren et al., 2015; 6. Dahlgren et al., 2016; 7. Malmvärn et al., 2005a; 8. Malmvärn et al., 2005b; 9. Malmvärn et al., 2008; 10. Haglund et al., 2007; 11. Unger et al., 2009; 12. Dahlberg et al., 2016b; 13. Hauler et al., 2014; 14. Löfstrand et al., 2011; 15. Dahlberg et al., 2016a; 16. Marsh et al., 2004; 17. Haglund et al., 2010; 18. Kierkegaard et al., 2004; 19. Sinkkonen et al., 2004; 20. Haglund et al., 1997; 21. Zacs et al., 2013; 22. Nordlöf et al., 2010; 23. Routti et al., 2009.

constants (HLCs) of BAs reported by Pfeifer et al. (2001). These were calculated from the ratio of vapour pressure to water solubility at 25 °C, and assumptions were made to adjust the HLCs to Baltic water temperatures. In this paper we report direct HLC measurements for BAs as functions of temperature and update previous gas exchange estimates of BAs in the northern Baltic. We also report the first identification of two biogenic MeO-BDEs in Baltic water and air and assess their potential for air-sea exchange.

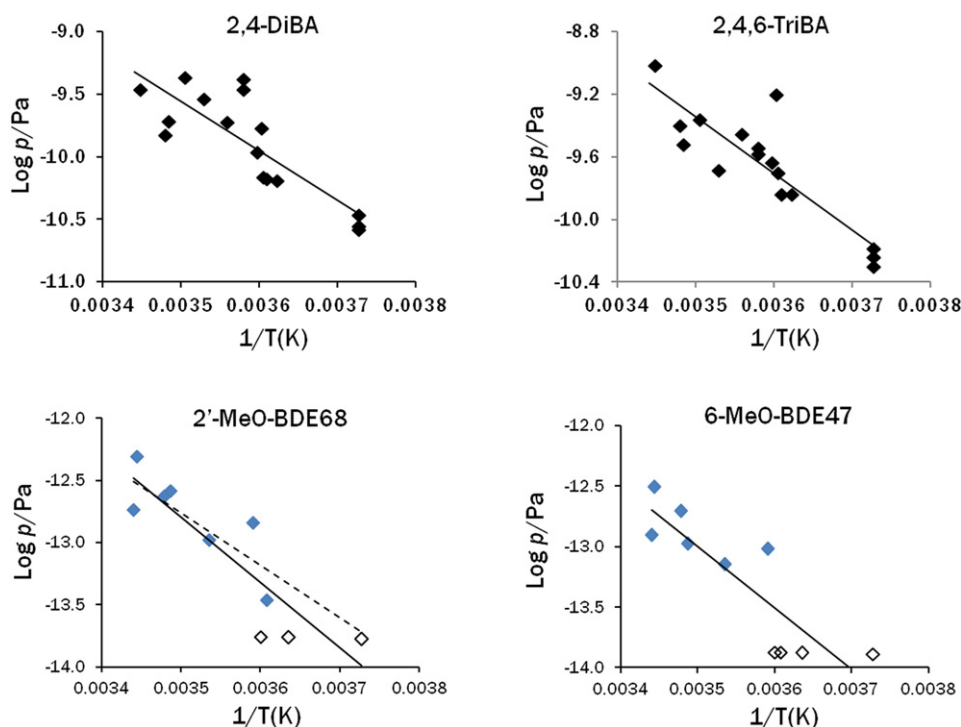


Fig. 1. Relationships of $\log p/\text{Pa}$ to $1/T(\text{K})$ for BAs (Bidleman et al., 2016a, 2016b) and MeO-BDEs. Open diamonds for MeO-BDEs indicate substitution of $1/2$ LOD for ND values. 2,4-DiBA: $Y = -3948/T + 4.26$ ($r^2 = 0.684$, $p = 8 \times 10^{-5}$); 2,4,6-TriBA: $Y = -3607/T + 3.28$ ($r^2 = 0.758$, $p = 1 \times 10^{-5}$); 2'-MeO-BDE68 including NDs: $Y = -5234/T + 5.52$ ($r^2 = 0.774$, $p = 8 \times 10^{-4}$), excluding NDs (dashed line): $Y = -4227/T + 2.04$ ($r^2 = 0.774$, $p = 0.029$); 6-MeO-BDE47 including NDs: $Y = -5047/T + 4.66$ ($r^2 = 0.750$, $p = 0.001$), excluding NDs: not significant, line not shown.

2. Experimental methods

2.1. Sampling and analysis

Water samples were collected mainly in the Gulf of Bothnia, northern Baltic Sea in 2011–2012, with one expedition to the southern Baltic in 2013. Air samples were taken on the island Holmön. Locations are shown in Fig. 1 of Bidleman et al. (2014) and dates are reported here in Tables 2 and 3. Surface seawater (40 L) was passed through stacked Whatman D and F glass fibre filters followed by a column of XAD-2 resin. In a few cases 5 L of filtered seawater was extracted with ENV + cartridges. Extracts representing 20–80 L were combined for analysis of MeO-BDEs. Air volumes of 60–150 m³ for BAs and 1300–3300 m³ for MeO-BDEs were pumped through a Whatman EPM 2000 filter followed by two plugs of polyether-type polyurethane foam (PUF), each 7.6 cm diameter \times 7.5 cm thick. Sampling times and air volumes were adjusted according to ambient temperature to avoid breakthrough losses of the BAs (Bidleman et al., 2014, 2015, 2016a, 2016b). Samples were extracted with organic solvents, cleaned up on Florisil and blown down with nitrogen into 100–200 μL iso-octane for chromatographic analysis. These procedures were developed for BAs and organochlorine pesticides. Further details are given in other papers (Bidleman et al., 2014, 2015, 2016a, 2016b). Additional cleanup before MeO-BDE determination was done by diluting the iso-octane extract to 1–2 mL, shaking with 18 M sulfuric acid, and concentrating the cleaned iso-octane layer to 100 μL .

Analysis was done by capillary gas chromatography with low- or high-resolution mass spectrometry (GC-LRMS, GC-HRMS). Target compounds were 2,4-DiBA, 2,6-DiBA, 2,4,6-TriBA, 2'-MeO-BDE68, 6-MeO-BDE47, 6-MeO-BDE90 and 6-MeO-BDE99 (Fig. S1). BAs were determined by GC-LRMS in the electron impact mode using an Agilent 6890 N chromatograph-5975 mass selective detector (MSD) (Agilent Technologies, Santa Clara, CA). MeO-BDEs were determined by electron impact GC-HRMS (Autospec Ultima NT, Waters Corporation, Milford, MA, USA) or GC-LRMS with electron capture negative ion (ECNI)

Download English Version:

<https://daneshyari.com/en/article/5757988>

Download Persian Version:

<https://daneshyari.com/article/5757988>

[Daneshyari.com](https://daneshyari.com)