

Atmospheric Transport and Deposition of Bromoanisoles Along a Temperate to Arctic Gradient

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Introduction

Among the thousands of halogenated natural products (HNPs) in the world's oceans and seas are bromophenols (BPs) and compounds derived from them: bromoanisoles (BAs), hydroxylated and methoxylated bromodiphenyl ethers (OH-BDEs, MeO-BDEs), and polybrominated dibenzo-*p*-dioxins (PBDDs). These bromophenolic HNPs are produced by bacteria, algae, sponges and other invertebrates [1-5]. Some bromophenolic HNPs have toxic properties. Reproductive effects in the zebrafish (*Danio rerio*) have been demonstrated for 2,4,6-TriBP and the accumulated phenol was partly transformed to 2,4,6-TriBA [6]. OH-BDEs uncouple oxidative phosphorylation [7], and MeO-BDEs disrupt hormonal synthesis or activity [8]. PBDDs have been assigned toxic equivalency factors (TEFs) similar to their anthropogenic chlorinated PCDDs analogs [9]. HNPs are listed among the "Chemicals of Emerging Arctic Concern" in an Arctic Monitoring and Assessment (AMAP) report [10].

BAs in seawater arise from O-methylation of bromophenols [3]. They volatilize from surface water and are found in air over oceans and seas [3,11-13], including the Arctic Ocean [14,15]. Only once have BAs been reported inland, at a site 60 km from the northern Baltic Sea [12]. Here we compare BAs in air on a gradient from the Swedish west coast, the northern Baltic region, and arctic Finland. BAs in precipitation were measured at the west coast and arctic sites. Implications for BA transport, deposition and contamination of inland streams and lakes are discussed.

Materials and methods

Air and bulk atmospheric deposition samples were collected at the European Monitoring and Evaluation Program (EMEP) station Råö on the Swedish west coast (57.39 N, 11.91 E) and at the EMEP/AMAP station Pallas in the interior of arctic Finland (68.00 N, 24.23 E). Sites are described in [16] and shown in Figure 1, along with northern Baltic locations Holmön, Krycklan, and Haparanda Sandskär, where we measured BAs in an earlier project [12]. The Råö and Pallas samples were originally collected for persistent organic pollutants (POPs) and their temporal trends in air have been reported [16,17]. After determination of POPs, sample extracts were archived until used for analysis of BAs in this project. Air extracts were available from Råö for years 2004, 2006, 2012, 2014 and 2015; and from Pallas for years 2002, 2004, 2006, 2010, 2012, 2014 and 2015. Extracts of deposition samples were analysed from Råö in 2012, 2014 and 2015 and from Pallas in 2012 and 2015.

Air sampling was done with a glass fiber filter (GFF) followed by a polyurethane foam (PUF) trap. One GFF-PUF assembly was used for each week, sampling approximately 3000 – 5000 m³ air. Extracts from weekly samplings at Råö were combined for analysis: 2 weeks in 2004 and 2006, and 4-5 weeks in 2012, 2014 and 2015. A single weekly sample was taken during each month at Pallas during 2002, 2004 and 2006, while sampling was done each week and pooled in sets of 4-5 in subsequent years. BAs at the northern Baltic stations were collected by integrated passive sampling over 3-4 month periods or short-term active sampling with a GFF-PUF train [12].

Bulk atmospheric deposition was collected over 22-35 day periods at Råö and Pallas with a 1-m² aluminum funnel coated with polytetrafluoroethylene [18]. Precipitation passed through a PUF trap in the deposition sampler and

was not collected. Temperature and precipitation data for Råö were obtained at nearby Nidingen (57.30 N, 11.91 E) or Onsala (57.38 N, 11.97 E), by the Swedish Meteorological and Hydrological Institute (SMHI). The Finnish Meteorological Institute (FMI) provided similar data at Kittilä Kentärova (67.99 N, 24.24 E) for Pallas. We assumed the same precipitation collection efficiency for our deposition samplers. At the end of sampling, the funnel was wiped with GFFs wetted with ethanol and the PUF trap and GFFs were analysed together.

Sample extraction and analysis for POPs were conducted at the Swedish Environmental Research Institute (IVL) [16]. At Umeå University, we obtained cleaned-up fractions containing polychlorinated biphenyls (PCBs), chlorinated pesticides, polybrominated diphenyl ethers (PBDEs) and BAs. After addition of PCB-54 internal standard, BAs were determined by capillary gas chromatography– electron impact quadrupole mass spectrometry (GC-MSD, Agilent Technologies, Santa Clara, CA) and selected ion monitoring. The column was J&W DB-5MS, 30 m × 0.25 mm i.d., 0.25 µm film (Agilent) or equivalent. The oven program was 85 °C (1 min), 1 °C/min to 125 °C, 10 °C/min to 250 °C (10 min). Inlet and transfer line temperatures were 250 °C; source and quadrupole temperatures were 230 °C and 150 °C. Target compounds were 2,4-, 2,5-, 2,6- and 3,5-dibromoanisoles (DiBAs) and 2,4,6-tribromoanisole (2,4,6-TriBA). Ions monitored (quantifying in bold) were **266**, 264 (DiBAs) and **344**, 346 (2,4,6-TriBA). The internal standard PCB-54 was quantified with ion 290.

Travel blanks (PUFs taken to and from the field) and extraction blanks (PUFs in the laboratory) were analysed. No chromatographic peaks were found at the retention times of target compounds, and baseline “noise” was integrated to estimate the instrumental detection limits (IDL). The mean noise level corresponded to 51 ± 22 pg for 2,4-DiBA and 65 ± 40 pg for 2,4,6-TriBA, and the limits of detection (LOD = mean IDL + 3xSD) were 116 and 186 pg for the two compounds. For statistical evaluations, ½ the LOD was substituted in cases of non-detection.

Results and discussion

The large air volumes sampled at Råö and Pallas resulted in extensive breakthrough of BAs from the PUF trap in most cases. We assumed PUF/air equilibrium and calculated air concentrations using temperature-dependent PUF/air partition coefficients, K_{PA} [19]. PUF/air equilibrium was not attained during cold periods and in these situations we evaluated the collection efficiency from frontal chromatography theory [20].

Mean and geometric mean (GM) concentrations of 2,4-DiBA and 2,4,6-TriBA at Råö, Pallas and northern Baltic stations are summarized in Table 1 and 2012-2015 means are shown in Figure 1. 2,6-DiBA was present at about 10% of 2,4-DiBA in some samples, but was unquantifiable in others. 2,6-DiBA is more volatile than the other DiBAs and its K_{PA} has not been determined. Other DiBAs were not found. GM concentrations of ΣBAs (2,4-DiBA + 2,4,6-TriBA, pg m⁻³) in 2012-2015 were Råö (79) > Holmön (51) ~ Krycklan (50) > Sandskär (29) > Pallas (19). GMs increased significantly at Pallas between 2002-2015 for 2,4-DiBA (p = 0.041), but not for 2,4,6-TriBA. The abundance of 2,4,6-TriBA was greater than 2,4-DiBA at Råö and Holmön, approximately the same at Sandskär and Pallas, and reversed at Krycklan (Figure 1), which might reflect contributions from different sources. Relationships of BA partial pressure (p , Pa) to temperature were examined by plotting $\log p/\text{Pa}$ versus $1/T$ (K). Regressions were significant (p < 0.0001) at Råö, with slopes of -2018 for 2,4-DiBA and -2375 for 2,4,6-TriBA (Figure 2). The similarity to slopes of Henry's law constants ($\log H/\text{Pa m}^3 \text{ mol}^{-1} = m/T + b$) for 2,4-DiBA ($m = -2418$) and 2,4,6-TriBA ($m = -1980$) [11] indicates sea-air exchange at this site. In contrast, variation in $\log p/\text{Pa}$ with reciprocal temperature at inland Pallas was less for 2,4-DiBA (slope = -1212, p = 0.003) and not significant for 2,4,6-TriBA.

Mean and (GM) fluxes of 2,4-DiBA and 2,4,6-TriBA were 80 ± 45 (68) and 74 ± 38 (60) pg m⁻² day⁻¹ at Råö; 77 ± 98 (41) and 38 ± 23 (33) pg m⁻² day⁻¹ at Pallas. Mean concentrations of 2,4-DiBA and 2,4,6-TriBA in precipitation were 35 ± 16 and 38 ± 22 pg L⁻¹ at Råö; 30 ± 32 and 18 ± 9.9 pg L⁻¹ at Pallas. These are 9-41% of northern Baltic surface water concentrations measured in 2011-2013 [11]. BAs are deposited mainly by Henry's law controlled scavenging of gaseous species, and washout ratios ($WR = C_{precip}/C_{air}$) were higher for 2,4-DiBA than 2,4,6-TriBA [18]. Although air concentrations were higher at Råö, WR were higher at Pallas due to colder air temperatures.

Implications

This study and our previous work in the northern Baltic region [11,12] are the first reports that BAs can be transported inland from marine areas. It is likely that deposited BAs find their way into streams, rivers and lakes, through direct atmospheric deposition and runoff over and through soils. Bothnian Bay, the northernmost basin of the Baltic Sea, has an area of 36,800 km² and a catchment seven times larger (260,375 km²). Riverine delivery of BAs deposited on land may be an unexpected source to the bay, especially in northern estuaries, augmenting their natural production in the sea. By analogy to chlorinated anisoles [21,22], BAs could be O-demethylated in soil to release free BPs, which are precursors to formation of OH-BDEs, MeO-BDEs and PBDDs. MeO-BDEs have been found in fish from Swedish inland lakes [23,24] and eggs of white-tailed sea eagles (*Haliaeetus albicilla*) [24] from inland areas. Atmospherically deposited BAs may indirectly contribute to MeO-BDEs in these ecosystems.

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Table 1: Bromoanisoles in Råö and Pallas Air, pg m^{-3} .

Site and Year	2,4-DiBA			2,4,6-TriBA		
	Mean \pm SD	GM ^a	N	Mean \pm SD	GM	N
Råö						
2004	35 \pm 16	31	25	55 \pm 27	48	25
2006	20 \pm 9.1	18	25	44 \pm 22	38	25
2012	41 \pm 20	36	11	74 \pm 36	65	11
2014	33 \pm 20	29	11	57 \pm 26	51	11
2015	26 \pm 11	24	12	43 \pm 20	39	12
Pallas						
2002	3.7 \pm 4.4	1.9	10	4.9 \pm 5.5	2.7	10
2004	9.1 \pm 8.2	6.0	12	10 \pm 5.9	8.3	12
2006	9.0 \pm 7.6	6.2	11	9.0 \pm 4.5	7.6	11
2010	10 \pm 7.0	8.5	10	12 \pm 5.3	10	10
2012	17 \pm 19	11	12	12 \pm 6.4	11	12
2014	7.1 \pm 3.5	6.2	8	8.3 \pm 2.8	7.8	8
2015	20 \pm 23	11	10	14 \pm 12	11	10
Northern Baltic^b						
Holmön, 2011-2015	23 \pm 17	16	21	43 \pm 30	34	21
Krycklan, 2011-2012	38 \pm 19	30	4	23 \pm 8.9	21	4
Sandskär, 2011-2012	19 \pm 13	14	4	18 \pm 7.9	15	4

a) GM: geometric mean b) Bidleman et al., 2017a

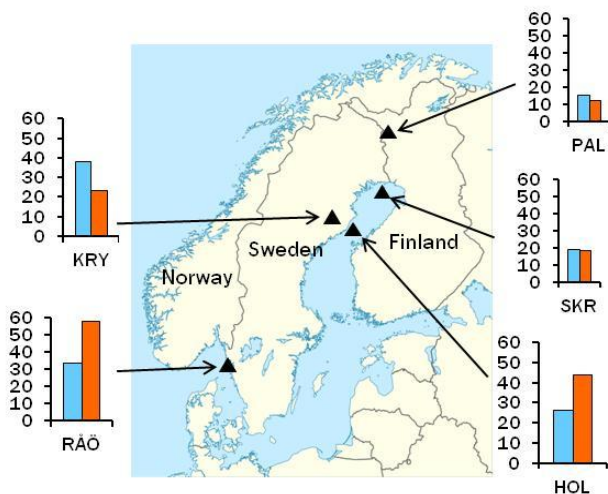


Figure 1. Locations for air sampling and mean concentrations from 2012-2015 (pg m^{-3}) of 2,4-DiBA (blue) and 2,4,6-TriBA (red). Råö (RÅÖ) and Pallas (PAL) (this study), Holmön (HOL), Krycklan (KRY) and Haparanda Sandskär (SKR) [12].

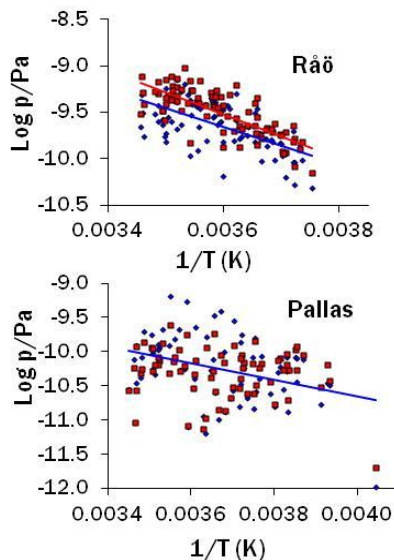


Figure 2. Temperature variation in partial pressures (p , Pa) of BAs. Top, Råö: $\text{Log } p/\text{Pa} = -2041/T - 2.42$ ($r^2 = 0.39$, $p < 0.0001$) for 2,4-DiBA (blue) and $-2365/T - 1.12$ ($r^2 = 0.58$, $p < 0.0001$) for 2,4,6-TriBA (red). Bottom, Pallas: $\text{Log } p/\text{Pa} = -1212/T - 5.81$ ($r^2 = 0.12$, $p = 0.0031$) for 2,4-DiBA, not significant for 2,4,6-TriBA.