

AIR-WATER EXCHANGE OF METHOXYLATED BROMODIPHENYL ETHERS
IN THE NORTHERN BALTIC SEABidleman TF^{1*}, Agosta K¹, Andersson A², Haglund P¹, Nygren O¹, Ripszam M¹, Tysklind, M¹.¹Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden; ²Department of Ecology and Environmental Sciences, Umeå University, SE-901 87 Umeå, Sweden**Introduction:**

Thousands of halogenated compounds are naturally produced in the world's oceans^{1,2}. Prominent among these are hydroxylated and methoxylated bromodiphenyl ethers (OH-BDEs, MeO-BDEs), which arise from coupling of precursor bromophenols (BPs)^{3,4} or are biosynthesized by marine bacteria⁵. These compounds are also transformation products of polybrominated diphenyl ether (PBDE) flame retardants, and substitution patterns give clues to natural vs. anthropogenic origins⁶. Natural origin of the more abundant MeO-BDEs has been confirmed by ¹⁴C dating^{7,8}, and by their occurrence in archived whale oil from the pre-industrial period⁹, and in deep layers of ocean sediments¹⁰. OH-BDEs and MeO-BDEs are widespread in macroalgae, fish, mussels and seals of the Baltic Sea¹¹⁻¹⁷, and MeO-BDEs in marine mammals worldwide often exceed concentrations of PBDEs^{18,19}. OH-BDEs interrupt oxidative phosphorylation^{6,20} and bind to the thyroid hormone receptor⁶, and both compound classes are endocrine disruptors^{6,21}. Photolysis of OH-BDEs²² and MeO-BDEs²³ and enzymatic coupling of bromophenols²⁴ yields polybrominated dibenzo-*p*-dioxins (PBDDs), which have toxic properties similar to those of anthropogenic PCDDs²⁵. PBDDs are widespread in the Baltic Sea and the Swedish west coast^{12,13,26}, where levels can exceed European Union guidelines for dioxin-type toxic equivalents²⁶.

There are few reports of OH-BDEs and MeO-BDEs in water and air. Both compound classes were found in river water, air, soil and vegetation of Busan, South Korea²⁷, and OH-BDEs in snow, rain and lake water in Ontario, Canada²⁸. MeO-BDEs and other halogenated natural products were estimated from passive sampling of seawater on the Great Barrier Reef, Australia²⁹. Bromoanisoles (BAs), produced by O-methylation of BPs, are also present in Baltic organisms^{10,15,16} and seawater³⁰ and undergo net volatilization^{30,31}. Here we report the first measurements of MeO-BDEs in Baltic water and air, and consider their potential for gas exchange.

Materials and methods:

Seawater samples were passed through glass fibre filters (GFFs) and analytes were extracted using XAD-2 resin (40 L) or ENV+ cartridges (5 L). Air samples of 50-120 m³ for BAs and 600-1700 m³ for chlorinated pesticides were filtered through GFFs then through polyurethane foam (PUF). Collection methods, sample extraction, cleanup using Florisil columns and analysis by gas chromatography – low-resolution mass spectrometry in electron impact or electron capture negative ion modes (GC-EI-LRMS or GC-ECNI-LRMS) for these compound classes have been previously reported^{30,31}. Selected sample extracts were combined to represent water volumes of 20-120 L and air volumes of 1300-2200 m³ for MeO-BDEs. Analysis was carried out by capillary GC with detection by EI-high resolution mass spectrometry (HRMS) or ECNI-LRMS, monitoring the ions in Table 1. Analytical standards of tetrabrominated 2'-MeO-BDE68 and 6-MeO-BDE47, pentabrominated 6-MeO-BDE85, 6-MeO-BDE90, 6-MeO-BDE99, and 2-MeO-BDE123, and hexabrominated 6-MeO-BDE137 were obtained from Dr. Lillemor Asplund, Stockholm University. ¹³C₁₂-PCB-105 was added as an internal standard. Recoveries of MeO-BDEs from water and air samples were estimated by adding ¹³C-labelled organochlorine pesticides or ²H₅-tribromoanisole^{30,31}. Recoveries averaged 61±27% for water and 101±27% for air.

Results and discussion:*MeO-BDEs in water and air*

Two prominent tetrabrominated MeO-BDEs were identified in water and air, 2'-MeO-BDE68 and 6-MeO-BDE47 at RTs 33.14 and 33.91, respectively (Figure 1). Their concentrations are reported in Table 2. An unidentified tetrabromo-MeO-BDE compound at RT 32.14 was found in air, based on agreement of monitored ion ratios with those of the tetrabromo- standards. It was only minor in water (Figure 1). Two unidentified

tribromo-MeO-BDEs were prominent in air at RTs 24.93 and 26.73 and several minor compounds were also found (Figure 1). The compound at 26.72 was also abundant in water, while the one at 24.93 was minor. Pentabromo- and hexabromo-MeO-BDEs were either not found or their peaks were too small to be quantified.

Only the gaseous (PUF) fraction of air samples was analysed, while in some cases both the dissolved (XAD-2 or ENV+) and particulate (GFF) fractions were analysed for water samples. The particulate fraction averaged $8.0 \pm 4.9\%$ (n=5). Average dissolved concentrations were $8.2 \pm 5.9 \text{ pg L}^{-1}$ (n=11) for 2'-MeO-BDE68 and $25 \pm 17 \text{ pg L}^{-1}$ for 6-MeO-BDE47 (n=11). Corresponding gaseous concentrations in air averaged $0.023 \pm 0.016 \text{ pg m}^{-3}$ (n=7) and $0.021 \pm 0.012 \text{ pg m}^{-3}$ (n=7) between May-September, but were below detection in early April 2013, when the northern Baltic was covered with ice.

Table 1. Ions monitored for GC-EI-HRMS analysis of MeO-BDEs

Tribromo-MeO-BDEs	433.8147	Hexabromo-MeO-BDEs	671.5422
	435.8127		673.5402
	437.8107		675.5402
Tetrabromo-MeO-BDEs	513.7238	$^{13}\text{C}_{12}$ -PCB-105 (I.S.)	337.9207
	515.7128		339.9718
	517.7198		
Pentabromo-MeO-BDEs	591.6337		
	593.6337		
	595.6207		

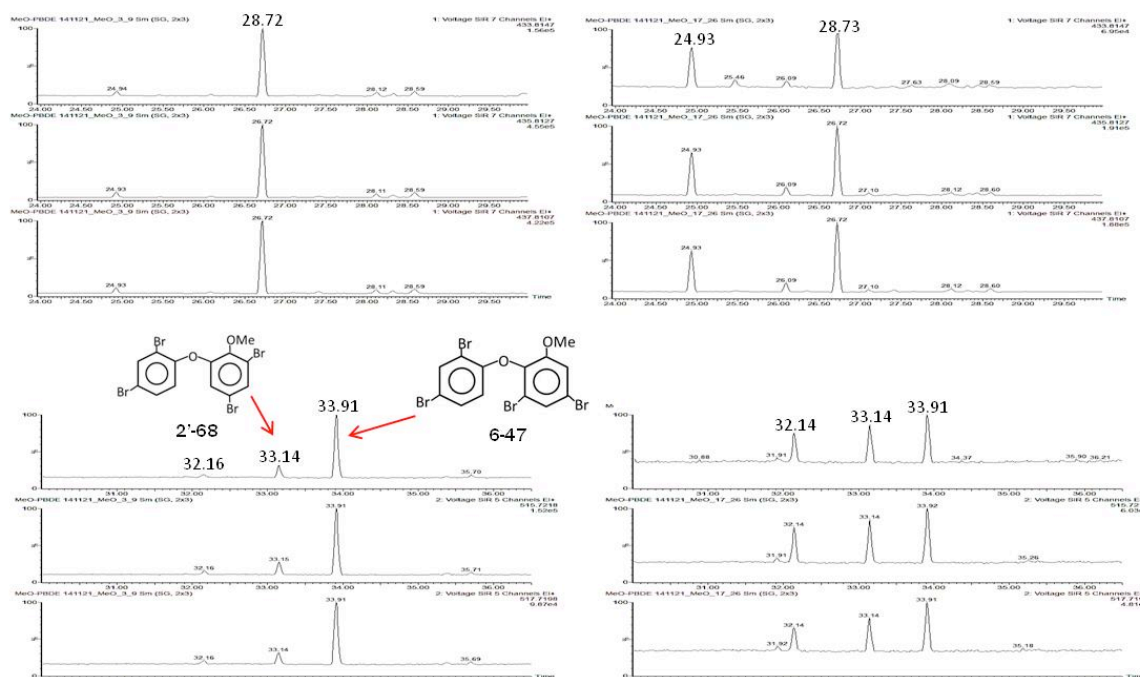
Table 2. Tetrabrominated MeO-BDEs in Baltic water (pg L^{-1}) and air (pg m^{-3})

Water ^a	Medium ^b	2'-MeO-BDE68	6-MeO-BDE47	Method ^c
July 2011, 1-4	D	13.4	25.6	ECNI
July 2011, 5-8	D	1.7	5.9	ECNI, HR
May 2012, B3	D	17.2	52.1	ECNI, HR
May 2012, B3	P	0.7	3.5	ECNI, HR
May 2012, C14+GA1	D	12.6	47.1	ECNI, HR
May 2012, C14+GA1	P	0.8	4.5	ECNI
May 2012, A5+A13	D	7.2	34.2	ECNI, HR
May 2012, A5+A13	P	<0.3	0.7	ECNI
May 2012, RA2	D	15.6	34.2	ECNI
May 2012, RA2	P	2.2	8.5	HR
July 2012, HOL	D	5.0	15.9	ECNI
January 2013, HOL	D	9.2	29.2	ECNI, HR
January 2013, HOL	P	0.7	1.3	HR
April 2013, HOL	D	5.4	20.9	ECNI, HR
September 2013, 1,3,4,6	D	0.8	2.1	ECNI, HR
September 2013, 9,11,13,15	D	1.4	4.5	ECNI, HR
Air ^a	Medium ^b	2'-MeO-BDE68	6-MeO-BDE47	Method ^c
May 2012, 1	G	0.010	0.010	ECNI, HR
May 2012, 2	G	0.010	0.012	ECNI, HR
May 2012, 3	G	0.010	0.020	HR
June 2012	G	0.029	0.015	ECNI, HR
July 2012	G	0.020	0.018	ECNI
August 2012, 1	G	0.054	0.044	ECNI, HR
August 2012, 2	G	0.026	0.029	ECNI, HR
April 2013	G	<0.004	<0.004	HR

a) Data and internal lab sample designations. b) D = dissolved (XAD-2 or ENV+), P = particulate (GFF)
 c) ECNI = electron capture negative ion low-resolution mass spectrometry, HR = electron impact high-resolution mass spectrometry.

Few data are available for comparison. Estimates from passive water sampling on the Great Barrier Reef²⁹ averaged 41 pg L⁻¹ for 2'-MeO-BDE68 and 58 pg L⁻¹ for 6-MeO-BDE47. The Σ_6 tetrabromo-MeO-BDEs reported in Busan, Korea²⁷ were 2 orders of magnitude higher, averaging 5500 pg L⁻¹ in river water and 6.9 pg m⁻³ in air.

Figure 1. Tribromo- (top) and tetrabromo- (bottom) MeO-BDEs in the Baltic



Water-air gas exchange

The potential for MeO-BDEs to volatilize from water was estimated from the water/air fugacity ratio, $FR = C_W/H/C_A RT_A$, where C_W and C_A are the dissolved and gas-phase concentrations (pg m⁻³), H is the Henry's law constant (Pa m³ mol⁻¹) at the surface water temperature, $R = 8.31$ Pa m³ mol⁻¹ K⁻¹ and T_A is air temperature (K). $FR = 1$, <1 and >1 imply steady state (no net exchange), net deposition and net volatilization, respectively^{30,31}. Henry's law constants for MeO-BDEs have not been measured, and were estimated tetrabromo-MeO-BDEs using the reported Henry's law constant and temperature adjustment factors for PBDE-47 and the relationship between $\log H$ and molar volume³². The resulting equation was $\log H/\text{Pa}$ (tetrabromo-MeO-BDEs) = $10.06 - 3194/T$. Using average dissolved and gaseous MeO-BDE concentrations (see above), the FR s at water and air temperatures of 15°C were 13 for 2'-MeO-BDE68 and 46 for 6-MeO-BDE47. However, the measured "dissolved" MeO-BDEs may be associated with dissolved organic carbon (DOC), as is common in the Baltic for other compounds^{33,34}. A correction was made for binding to DOC using the relationship between $\log K_{DOC}$ and $\log K_{OW}$ for hydrophobic compounds³³, using $\log K_{OW} = 7.0$, the average of reported values^{35,36} for 6-MeO-BDE47 and a DOC concentration in Baltic water of 4×10^{-6} kg L⁻¹. This results in only about 10% of the MeO-BDEs being "truly dissolved", which lowers FR to 1.3-4.6. Thus, tetrabromo-MeO-BDEs may be volatilizing or close to water-air equilibrium. Further improvements in gas exchange estimates require more accurate Henry's law constants and estimates of binding to DOC. Similar calculations for BAs estimated net volatilization, based on older^{30,31} or recently measured³⁷ Henry's law constants.

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