Original Research

Halomethoxybenzenes in air of the Nordic region

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A B S T R A C T

Halomethoxybenzenes (HMBs) are a group of compounds with natural and anthropogenic origins. Here we extend a 2002–2015 survey of bromoanisoles (BAs) in the air and precipitation at Råo on the Swedish west coast and Pallas in Subarctic Finland. New BAs data are reported for 2018 and 2019 and chlorinated HMBs are included for these and some previous years: drosophilin A methyl ether (DAME: 1,2,4,5-tetrachloro-3,6-dimethoxybenzene), tetrachloroveratrole (TeCV: 1,2,3,4-tetrachloro-5,6-dimethoxybenzene), and pentachloroanisole (PeCA). The order of abundance of HMBs at Råo was ∑BAs > ∑DAME > TeCV > PeCA, whereas at Pallas the order of abundance was DAME > ∑BAs > TeCV > PeCA. The lower abundance of BAs at Pallas reflects its inland location, away from direct marine influence. Clausius-Clapeyron (CC) plots of log partial pressure (Pp)/Pa versus 1/T suggested distant transport at both sites for PeCA and local exchange for DAME and TeCV. BAs were dominated by distant transport at Pallas and by both local and distant sources at Råo. Relationships between air and precipitation concentrations were examined by scavenging ratios, SR = (ng m⁻³)precip∕(ng m⁻³)air. SRs were higher at Pallas than Råo due to greater Henry’s law partitioning of gaseous compounds into precipitation at colder temperatures. DAME is produced by terrestrial fungi. We screened 19 fungal species from Swedish forests and found seven of them contained 0.01–3.8 mg DAME per kg fresh weight. We suggest that the volatilization of DAME from fungi and forest litter containing fungal mycelia may contribute to atmospheric levels at both sites.

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1. Introduction

Halomethoxybenzenes (HMBs: anisoles, veratroles, and related compounds), a group of compounds with natural and anthropogenic origins [1,2], are found in the air worldwide from the southern and northern hemispheres, over oceans and in polar regions [1–6,8–13]. Typical HMBs in the atmosphere are chloro-, bromo- and mixed chlorobromo-anisoles, and halogenated dimethoxy compounds [1,2,10].

Bromophenols (BPs) have well-known natural production by marine bacteria, phytoplankton, macroalgae, invertebrates [7,14–16] and multiple anthropogenic sources [17,18]. O-methylation of BPs produces bromoanisoles (BAs) [19]. Chloroanisoles (CAs) are thought to be mainly anthropogenic [2], although structurally related “chlorinated anisyl metabolites” and other chlorinated organic compounds are synthesized by terrestrial fungi [20–22]. Pentachloroanisole (PeCA) is a metabolite of the wood preservative pentachlorophenol (PeCP) [23] and is common in the air [1–4,8–12,24,25]; however, continent-wide spatial patterns of PeCA and PeCP in pine needles suggest separate origins [26]. CAs and BAs are “taste and odor” compounds arising from the disinfection of drinking water containing halogens [27], infamous for causing “cork taint” in wines [28,29], and mustiness in packaged food [30] and water [31].

Dimethoxylated HMBs reported in air are trichloro- and tetrachloroveratroles (TriCV: 1,2,3-trichloro-5,6-dimethoxybenzene; TeCV: 1,2,3,4-tetrachloro-5,6-dimethoxybenzene), and drosophilin A methyl ether (DAME: 1,2,4,5-tetrachloro-3,6-dimethoxybenzene), an isomer of TeCV. The CVs are O-methylation products of chloroguaiacols found in bleached Kraft mill effluent [31,32] from chlorine bleaching of lignin, while DAME, its precursor drosophilin A (DA:...
2. Materials and methods

Air and deposition locations at Råö and Pallas and sampling methods are described in Supplementary Material (SM1-1) and [5]. Briefly, the air was drawn through a glass fiber filter (GFF) followed by a polyurethane foam (PUF) trap. Bulk deposition (wet + dry) was collected in a funnel drained through a GFF-PUF trap. Råö and Pallas are European Monitoring and Evaluation Program (EMEP) stations, and Pallas is in the Arctic Monitoring and Assessment Program (AMAP) network. Sample processing and analysis for 12 polycyclic aromatic hydrocarbons ($\Sigma_{12}$PAHs, see SM1-2), other persistent organic pollutants (POPs, not reported here) surrogates, and internal standards were done at the Swedish Environmental Research Institute (IVL) as previously described [42], and HMBs in cleaned extracts were determined at Umeå University (UmU).

Fruiting bodies of terrestrial fungi and forest litter/underlying humus were collected in Västerbotten and Gävleborg counties, Sweden, in 2021. Homogenized fruiting bodies and litter/humus (0.5–2 g) were extracted by soaking them in ethyl acetate. Extracts were spiked with an internal standard and analyzed without cleanup. Details are given in the SM1-2.

Samples at UmU were analyzed by capillary gas chromatography—electron impact quadrupole mass spectrometry (GC-MSD) with selected ion monitoring, using methods similar to those for BAs [5]. The column, conditions, monitored ions, and quality control are given in the SM1-2.

HMBs are relatively volatile and suffer losses during air sampling on PUF due to breakthroughs. We corrected for this by considering the collection efficiency of a PUF trap as a function of compound volatility (octanol-air and PUF-air partition coefficients, $K_{OA}$ and $K_{PUF}$) and the number of theoretical plates in the PUF cartridge [5,43]. Details are given in the SM3.

3. Results and discussion

3.1. HMB concentrations in air

The range, mean ± SD, and geometric mean concentrations of HMBs in the air at Råö and Pallas over 2002–2019 are listed in Table 1, with annual results in Fig. 1 and Tables S1–S3. The data set for BAs include results previously obtained [5], with a reanalysis of some samples. New results for BAs are from the years 2002, 2018,

| Table 1 | Halomethoxybenzenes in the air during 2002–2019 (pg m$^{-3}$). |
|---------|------------------|
| Råö     |                  |
| 2,4-diBA| 0.4–95           |
| 2,4,6-triBA| 1.6–138       |
| DAME    | 1.9–214          |
| TeCV    | 0.6–40           |
| PeCA    | ND–7             |
| 2002    |                  |
| 2004    |                  |
| 2006    |                  |
| 2010    |                  |
| 2012    |                  |
| 2014    |                  |
| 2015    |                  |
| 2018    |                  |
| 2019    |                  |
| All     |                  |
| Pallas  |                  |
| 2,4-diBA| ND–89            |
| 2,4,6-triBA| 0.03–37        |
| DAME    | 1.4–244          |
| TeCV    | ND–64            |
| PeCA    | ND–4.7           |

Statistics are reported in Tables S2 and S3.

2,3,5,6-tetrachloro-4-methoxyphenol) and related "chlorinated hydroquinone metabolites" are synthesized by terrestrial fungi [20,33–36]. DA has been reported in the meat of wild boar (Sus scrofa), apparently due to consuming fungi [37]. Both DAME and DA have antibacterial properties [34,38]. Threshold toxic concentrations were spiked with an internal standard and analyzed without cleanup. Details are given in the SM1-2.

Crystals of DAME were discovered in a mesquite (Prosopis juliflora) log decayed by the basiomycete Phellinus radius and the authors suggested that DAME could be released into the atmosphere through biomass burning [33]. Nontarget screening qualitatively revealed chlorinated anisoles and dimethoxybenzenes in Arctic air [39] and DA in Moscow snow [40]. TeCV and PeCA were quantitatively detected in Arctic air [8,11] and air and deposition at Lake Victoria, Africa [3].

Previously we reported 2,4-dibromoanisole (DiBA) and 2,4,6-tribromoanisole (TriBA) in the air and deposition on the Atlantic coast of southern Sweden (Råö, 57.39° N, 11.91° E), inland Subarctic Finland (Pallas, 68.00° N, 24.23° E) (Fig. 1), air [5,6] and air-sea exchange [41] in the northern Baltic. Sampling locations are shown on maps in these publications. Air concentrations were in the order Råö > northern Baltic > Pallas and were typical of those in other marine regions of the world [7]. Proportions of TriBA/DiBA decreased inland and northward. BAs were also determined in other marine regions of the world [7]. Proportions of TriBA/DiBA was conducted to gain insight into the sources and transport pathways of the chlorinated versus brominated compounds. Considering that fungal sources of DAME are likely, we screened fungi specimens and samples of forest litter.

2. Results and discussion

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and 2019 at Rå and 2018 and 2019 at Pallas. DAME, TeCV, and PeCA were determined for the years 2002, 2004, 2014, 2018, and 2019.

The order of abundance of HMBs at Rå was \( \Sigma \)BAs (DiBa + TriBa) > DAME > TeCV > PeCA, whereas at Pallas the order was DAME > \( \Sigma \)BAs > TeCV > PeCA. The lower abundance of BAs at Pallas reflects its inland location, away from direct marine influence [5].

Concentrations of DAME at Rå and Pallas were similar, whereas TeCV and PeCA at Pallas were lower than at Rå. The proportion of DAME/TeCV was lower at Pallas than at Rå (Fig. 1) for unknown reasons. Correlations among compounds are summarized in Table S4 and Fig. 2 for Rå and Table S5 and Fig. 3 for Pallas. At both stations, correlations were positive and significant \((p < 0.05)\) among \( \Sigma \)BAs, DAME, TeCV, and PeCA.

At Rå, \( \Sigma \)BAs, DAME, and TeCV were negatively and significantly correlated with \( \Sigma \)PAHs, with no significant association for PeCA. None of the HMBs was significantly correlated with \( \Sigma \)PAHs at Pallas. Negative or no association of HMBs, particularly DAME, with \( \Sigma \)PAHs; DAME showed a negative correlation with BaP at Rå and an insignificant correlation at Pallas (Tables S4 and S5). However, the [33] hypothesis is not necessarily refuted because biomass burning may not be the dominant source of PAHs at these sites. The higher DAME concentrations occur in the warm periods when PAHs are low (Fig. 2, see below) and are likely caused by non-combustive volatilization.

Comparisons of chlorinated HMBs at Rå and Pallas to air concentrations reported previously are shown in Fig. 4. Many of those measurements were made decades ago. Concentrations of DAME at Rå and Pallas are within the range of those reported at Lake Victoria, Africa. PeCA concentrations at Rå and Pallas tend to be below the other reported values.

3.2. Temperature relationships and trends

Clausius-Clapeyron (CC) plots of log partial pressure in air \((P_{\text{air}}/\text{Pa})\) versus reciprocal temperature are shown in Fig. 5 for BAs, DAME, TeCV, and PeCA. The CC data analysis is summarized in Table S7, where apparent enthalpies of surface-air exchange \(\Delta_{SAH}\) (kJ mol\(^{-1}\)) and octanol-air partition coefficients \(K_{OA}\) imply local air-surface exchange, whereas more shallow slopes reflect a greater contribution from distant transport [45, 46]. Physicochemical properties for compounds examined here and two POPs of similar molecular mass (pentachlorobenzene and hexachlorobenzene) are given in Table S6.

DAME, TeCV, and PeCA. Regression statistics are given in Table S5. The BAs dataset consists of measurements reported earlier [5] plus new results reported here (see above). CC slopes at both sites were significant for DiBa, TriBa, DAME, and TeCV, but not for PeCA.

Site-specific CC slopes which are similar to those for liquid-phase vapor pressures \((P_v, \text{Pa})\), Henry’s law constants \((H, \text{Pa} \cdot \text{m}^3 \text{ mol}^{-1})\) or octanol-air partition coefficients \(K_{OA}\) imply local air-surface exchange, whereas more shallow slopes reflect a greater contribution from distant transport [45, 46]. Physicochemical properties for compounds examined here and two POPs of similar molecular mass (pentachlorobenzene and hexachlorobenzene) are given in Table S6.

Fig. 3. Correlations of air concentrations at Pallas: a. DAME vs. \( \Sigma \)PAHs; b. DAME vs. \( \Sigma \)BAs; c. TeCV vs. DAME; d. PeCA vs. DAME. The trendline for DAME vs. \( \Sigma \)PAHs (a) is shown, but the regression is not significant \((p > 0.05)\). Regressions of DAME vs. \( \Sigma \)BAs (b), TeCV vs. DAME (c), and PeCA vs. DAME (d) are significant at \( p < 0.05 \). Statistics are given in Table S5.

DAME, TeCV, and PeCA concentrations reported previously are shown in Fig. 4. Many of those measurements were made decades ago. Concentrations of DAME at Rå and Pallas are within the range of those reported at Lake Victoria, Africa. PeCA concentrations at Rå and Pallas tend to be below the other reported values.

Clausius-Clapeyron (CC) plots of log partial pressure in air \((P_{\text{air}}/\text{Pa})\) versus reciprocal temperature are shown in Fig. 5 for BAs, DAME, TeCV, and PeCA. The CC data analysis is summarized in Table S7, where apparent enthalpies of surface-air exchange \(\Delta_{SAH}\) (kJ mol\(^{-1}\)) and octanol-air partition coefficients \(K_{OA}\) imply local air-surface exchange, whereas more shallow slopes reflect a greater contribution from distant transport [45, 46]. Physicochemical properties for compounds examined here and two POPs of similar molecular mass (pentachlorobenzene and hexachlorobenzene) are given in Table S6.

The CC data analysis is summarized in Table S7, where apparent enthalpies of surface-air exchange \(\Delta_{SAH}\) (kJ mol\(^{-1}\)) = – slope \(\times R \times 2.303/1000\) are compared to enthalpies of liquid-phase vapor pressure \(\Delta_{VLPH}\), Henry’s law constant \(H\), and octanol-air partition coefficient \(K_{OA}\). The \(H\) of DiBa was outside the \(\pm 2\) SD limit, implying local exchange of TriBa and more distant (over the open ocean) transport of DiBa. The difference between the two BAs may relate to the enrichment of TriBa in macroalgae along the Swedish and Norwegian coasts, in which the fraction TriBa/TriBa + DiBa is 0.75 ± 0.15 [15].

Temperature-dependent properties for DAME and TeCV have not been reported. Their apparent \(\Delta_{SAH}\) values were compared to thermodynamically consistent “final adjusted values” (FAVs) \(\Delta_{VLPH}\),
Halomethoxybenzenes in precipitation, Råo (2014, 2018, and 2019) and Pallas (2018 and 2019).

3.3. HMBs in precipitation

Rain and snow meltwater were processed by draining through a GFF-PUF trap, and the water volume was not measured. Bulk precipitation fluxes (pg m⁻² d⁻¹) of particulate and gaseous species were determined by analysis of the GFF-PUF trap, and concentrations (pg L⁻¹) were estimated from precipitation volumes.

Table 2

Halomethoxybenzenes in precipitation, Råo (2014, 2018, and 2019) and Pallas (2018 and 2019).

| Year | Location | Concentration (pg L⁻¹)ᵃ | Flux (pg m⁻² d⁻¹)ᵇ | Scavenging ratio, SRᶜ |
|------|----------|--------------------------|---------------------|----------------------|
| 2014 | Råo      | DiBA 44 | 214 | 52 | 115 | 1289 | 862 | 1964 | 1659 |
|      |          | TriBA 18 | 31 | 24 | 40 | 34 | 26 | 195 | 137 |
|      |          | Geomean 37 | 213 | 44 | 72 | 80 | 416 | 84 |
|      |          | N 11 | 12 | 11 | 11 | 11 | 12 | 12 |
| 2018 | Råo      | DiBA 21 | 52 | 30 | 27 | 23 | 44 | 54 | 27 |
|      |          | TriBA 14 | 22 | 18 | 27 | 18 | 32 | 27 | 14 |
|      |          | Geomean 17 | 43 | 22 | 21 | 18 | 36 | 46 | 24 |
|      |          | N 11 | 11 | 11 | 11 | 11 | 11 | 11 |
| 2019 | Råo      | DiBA 18 | 22 | 14 | 28 | 46 | 59 | 45 | 28 |
|      |          | TriBA 11 | 11 | 26 | 25 | 45 | 45 | 54 | 25 |
|      |          | Geomean 12 | 15 | 11 | 11 | 39 | 46 | 26 | 20 |
|      |          | N 7 | 9 | 10 | 8 | 9 | 12 | 10 |
| 2018 | Pallas   | DiBA 8.6 | 51 | 4.6 | 16 | 19 | 105 | 7.6 |
|      |          | TriBA 5.7 | 44 | 2.5 | 13 | 9.1 | 108 | 3.0 |
|      |          | Geomean 6.7 | 37 | 4.2 | 14 | 14 | 61 | 7.1 |
|      |          | N 8 | 11 | 12 | 10 | 8 | 11 | 12 | 10 |

ᵃ Concentrations and fluxes were calculated with substitution of 1/2×LOD for samples < LOD.
ᵇ SR = (pg m⁻² d⁻¹)₂SD/(pg m⁻² d⁻¹)₁SD, calculated for events with both precipitation and air > LOD.
ᶜ Scavenging ratio, SR = (pg m⁻² d⁻¹)₂SD/(pg m⁻² d⁻¹)₁SD, calculated for events with both precipitation and air > LOD.
measured at a nearby station, as in our previous study [5]. Annually averaged precipitation concentrations and fluxes of BAs, DAME, and TeCV at Råo (2014, 2018, and 2019) and Pallas (2018 and 2019) are summarized in Table 2. BAs in precipitation from 2002 to 2015 have been reported previously [5]; Råo 2014 is repeated here because the chlorinated HMBs were also determined for that year. PeCA was generally below the detection limit in precipitation and not reported.

Geometric mean (GM) fluxes of DiBA and TriBA at Råo in combined years 2018–2019 were 24 and 40 pg m$^{-2}$ d$^{-1}$. GM fluxes at Råo of 68 and 60 pg m$^{-2}$ d$^{-1}$ were reported for the two BAs in 2012, 2014, and 2015 [5]. The lower fluxes in 2018–2019 might be due partly to reduced monthly precipitation in these years (4.9 ± 2.5 cm) compared to 7.0 ± 3.2 cm in the earlier years. GM fluxes of DiBA and TriBA at Pallas in 2018–2019 were 18 and 18 pg m$^{-2}$ d$^{-1}$, while 41 pg m$^{-2}$ d$^{-1}$ for DiBA and 33 pg m$^{-2}$ d$^{-1}$ for TriBA were reported for combined 2012–2015 [5]. Monthly precipitation at Pallas in 2018–2019 (4.9 ± 2.9 cm) was only slightly lower than in 2012 and 2015 (5.6 ± 2.6 cm) and unlikely to account for the lower fluxes in recent years. GM fluxes of DAME and TeCV at Råo (2018–2019) were 34 and 22 pg m$^{-2}$ d$^{-1}$ and at Pallas (2018–2019) 73 and 8.2 pg m$^{-2}$ d$^{-1}$.

Scavenging ratios (SR = (pg m$^{-3}$)precip/(pg m$^{-3}$)air) were estimated from monthly precipitation and air concentrations. GM SRs of DiBA and TriBA at Råo in 2018–2019 were 540 and 791 and at Pallas 1052 and 1650. In our earlier study [5], GM SRs for DiBA and TriBA were 1140 and 642 at Råo, and 1760 and 1490 at Pallas. Precipitation scavenging of gaseous compounds increases at lower temperatures due to greater Henry's law partitioning into rain (SR = RT/HC and sorption to snow surfaces [48,49]). This is shown by the significant (p < 0.0001) trend of log SR versus 1/T (K) for the combined Råo–Pallas TriBA data set in 2018–2019 (Fig. 6) and also in our earlier study [5]. In both data sets, the SRs of DiBA were also suggestive of an increasing trend at lower temperatures, but the regressions were not significant. The trendline for TriBA agrees well with the theoretical log SR versus 1/T, estimated from its Henry’s law constant (Table S6).

GM SRs at Råo (2014, 2018, and 2019) were 1219 for DAME and 1623 for TeCV, and 2543 for DAME and 4503 for TeCV at Pallas. Regressions of log SR versus 1/T (K) for the combined data sets were significant for both species, p = 0.007 for DAME and p = 0.0006 for TeCV (Fig. 6). Theoretical SRs for gas-phase DAME and TeCV were assumed to be the same and were estimated from Henry’s law constant of TeCV at 25 °C and the estimated CC slope for Henry’s law constant of hexachlorobenzene (Table S6). Fig. 6 shows that measured SRs tend to be about a factor of 3 or less above the theoretical estimates, which assume only gaseous dissolution into precipitation. Elevated SRs can result from the scavenging of particulate species, surface adsorption at the air-water interface [49] and on snow crystals [48].

3.4. HMBs in terrestrial fungi and forest litter

Fruiting bodies of terrestrial fungi (19) and litter/humus samples (6) were screened for DAME and TeCV. Our method has a limit of detection (LOD, see SM) of about 0.0015 mg kg$^{-1}$. DAME in four species ranged from 0.8 to 3.7 mg kg$^{-1}$ fresh weight (fw): Microphale perforans (a saprotroph), Stereum hirsutum (a white rot), Thelephora terrestris (an ectomycorrhiza), and Hydnellum mirabile (an ectomycorrhiza). Three others, i.e., Stereum subomentosum (a white rot), Cladonia stellaris (a lichen), and Jackrogersella multifornis (a soft rot, intermediate between white and brown rot), contained 0.011–0.049 mg kg$^{-1}$ fw. The litter/humus samples, presumably permeated with fungal mycelia, contained 0.006–1.5 mg kg$^{-1}$ fw. Thus, in accordance with earlier work [20,34], we found DAME in fungi representing a range of nutritional strategies. Only a few samples contained detectable levels of TeCV, 0.0033 and 0.042 mg kg$^{-1}$ in M. perforans and T. terrestris, respectively, and 0.0033–0.016 mg kg$^{-1}$ in litter/humus (n = 3). The general lack of TeCV in fungi and litter is surprising, given its abundance in air and precipitation; however, we note that the number of fungal species screened here is small compared to their diversity. BAs and PeCA were not detected in fungi nor litter/humus.

4. Conclusions

This study adds to the growing body of knowledge concerning natural halogenated compounds in the air and deposition and is the first report of DAME in Arctic air. BAs follow the previously established trend of higher levels near the coast (Råo) versus inland (Pallas), in agreement with the known production of BAs in the marine environment. Local versus distant sources of TriBA versus DiBA at Råo may be related to the high proportion of TriBA/DiBA in coastal macroalgae. Inferred local sources of DAME at the two sites suggest volatilization from the terrestrial environment. In support of this, DAME was quantified in several species of fungi and forest
litter. Sea-air exchange may also contribute at Råo since DAME has been reported in seawater. DAME in air showed negative or no correlation with $\Sigma_2$ PAHs, in apparent contradiction to a hypothesis that biomass burning would release DAME into the atmosphere [33]. However, this hypothesis is not refuted, as biomass burning may not be the main source of PAHs at our sites. TeCV has been associated with the pulp and paper industry, but its close association with DAME in this study also suggests natural sources. PeCA was found in the air at levels lower than reported in the past, and we can report nothing further about its sources now. Deposition of HMBS by rain and snowfall increased at colder temperatures and was reasonably described by gas-phase scavenging according to Henry's Law.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Terry Bidleman reports equipment, drugs, or supplies was provided by IVL Swedish Environmental Research Institute.

Appendix A. Supplementary data

Supplementary data can be found online at https://doi.org/10.1016/j.jes.2022.102029.

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