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Chlorinated pesticides and natural brominated anisoles in air at three northern Baltic stations☆

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ABSTRACT

Polyurethane foam (PUF) disk passive samplers were deployed at one inland and two island locations in the Bothnian Bay region of the northern Baltic Sea. Uptake was linear over 81–147 d and a temperature range of −2.6 to 14.2 °C for organochlorine pesticides (OCPs) and current-use pesticides (CUPs) having log $K_{OA} \geq 9$ at ambient temperatures. Partial saturation of the PUF disks occurred for the more volatile OCPs hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB), and for bromoanisoles (BAs), which are products of bromophenols released by natural and anthropogenic sources. Correction for nonlinear uptake of these was made using experimentally measured PUF-air partition coefficients. Passive-derived air concentrations of pesticides were uniform over the bay and agreed within a factor of 2 or better with levels determined by active (pumped) sampling at one of the island stations. Levels of OCPs were similar to those reported at background sites in the European and Canadian Arctic and at monitoring stations in the central Baltic and southern Scandinavia, indicating long-range transport. The insecticide chlorpyrifos was 10 times lower at bay stations than in the Canadian Arctic. Insight to sources and processes was gained by examining compound profiles. Fractions F_{alpha} = α-HCH/(α-HCH + γ-HCH) and F_{TC} = *trans*-chlordane/(*trans*-chlordane + *cis*-chlordane) at bay stations were higher than in the Norwegian and Finnish Arctic and similar to those at the southern monitoring stations. Volatilization of chlordanes from Baltic seawater may also modify F_{TC}. Higher F_{TriBA} = 2,4,6-TriBA/(2,4,6-TriBA + 2,4-DiBA) distinguished local volatilization from the Baltic Sea versus lower F_{TriBA} found at the inland site and reported in air on the Norwegian coast, suggesting westerly transport from the Atlantic across Norway and Sweden.

1. Introduction

Atmospheric transport delivers persistent organic chemicals to the northern Baltic Sea and other Nordic ecosystems. Long-term measurements are being made at Pallas, Finland (68.00°N, 24.23°E) and Andøya, Norway (69.28°N, 16.01°E), two stations operating under the Arctic Monitoring and Assessment Program (AMAP) and European Monitoring and Evaluation Program (EMEP) (Anttila et al., 2016; Bohlin-Nizzetto et al., 2015; Hung et al., 2016). We are investigating atmospheric transport and deposition to Bothnian Bay in the northern Baltic (Fig. 1), about 300–600 km from Pallas and Andøya. The populations of larger cities on the Swedish and Finnish sides of the bay totaled >580 000 in 2013. The 38,000 km^2 bay and its seven-fold larger catchment area receive atmospheric loadings of organochlorine pesticides (OCPs) and current-use pesticides (CUPs) from precipitation and dry particle deposition (Bidleman et al., 2015a; Newton et al., 2014). Other anthropogenic compounds deposited in the bay region are polychlorinated biphenyls (PCBs) (Agrell et al., 1999; Bergknut et al., 2011; Newton et al., 2014), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Assefa et al., 2014; Bergknut et al., 2011) and halogenated flame retardants (Newton et al., 2014). These may come from urban and industrial areas around the bay and from background atmospheric transport. The bay also influences the regional atmosphere through air-sea gas exchange of synthetic compounds (Bidleman et al., 2015a) and natural brominated compounds produced within the bay itself (Bidleman et al.,

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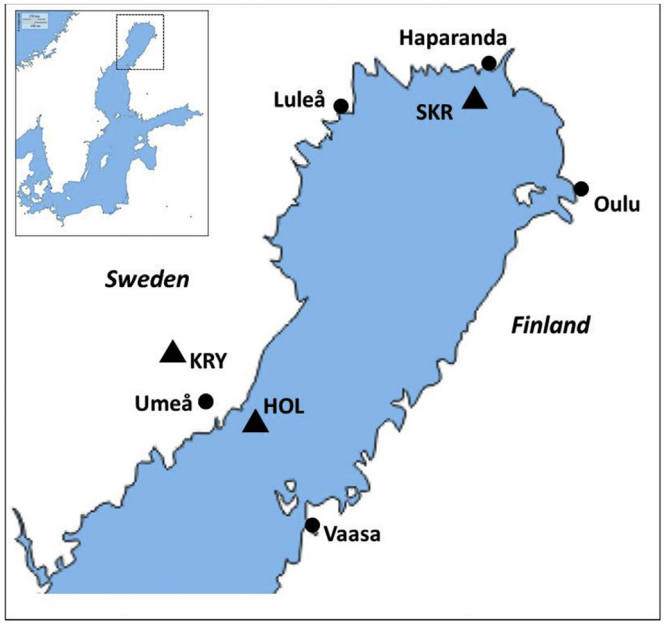

Fig. 1. Passive air sampler locations in the Bothnian Bay region. Island stations at Holmön (HOL) and Haparanda Sandskär (SKR) and the forest station Svartberget in Krycklan Catchment (KRY). Active (pumped) air samples were also collected at HOL (Bidleman et al., 2014, 2015a, 2016a). Coordinates are given in the text.

2014, 2015a, 2016a,b). For these reasons, the more northern monitoring stations may not adequately represent the air concentrations and processes in the bay and its catchment.

In our previous study (Bidleman et al., 2015a), OCPs and CUPs in air were measured at the island station Holmön (HOL) using a combination of active (pumped) sampling and passive sampling with polyurethane foam (PUF) disks. Passive samples were also collected 60 km inland at Krycklan Catchment (KRY), a watershed where research is conducted on water quality, hydrology and aquatic ecology. The stations are shown in Fig. 1. Bromoanisoles (BAs) were collected by active sampling at HOL (Bidleman et al., 2014, 2015a, 2016a,b). BAs are thought to arise from O-methylation of bromophenols (Flodin and Whitfield, 2000), which are produced by marine algae and other organisms (Howe et al., 2005). Bromophenols also have anthropogenic sources as industrial intermediates, through water chlorination and combustion of leaded gasoline and waste (Howe et al., 2005). BAs are among the "Halogenated Natural Products" listed as "Chemicals of Emerging Concern" in a forthcoming Arctic Monitoring Assessment Program report of that title (AMAP, 2017). Here we report results from passive sampling at a second island station, Haparanda Sandskär National Park (SKR), located in the far north of Bothnian Bay (Fig. 1). We also include an additional sampling period at the HOL and KRY stations. Air concentrations of pesticides and BAs at all three stations are re-evaluated using common criteria for estimating passive air sampling rates and we show that the choice of physicochemical properties is critical in deriving these rates for the more volatile compounds. Insight to sources and processes is gained by comparing compound profiles at our stations to those at more northern and southern sites.

2. Experimental methods

2.1. Sample collection

Collection and analytical methods have been reported previously (Bidleman et al., 2014, 2015a, 2016a) and are briefly described here. Air concentrations of pesticides and BAs were monitored between July 2011 and January 2013 by deploying duplicate passive samplers of the type and dimensions reported by Pozo et al. (2004) in forest clearings on two islands in Bothnian Bay: HOL (63.792°N, 20.839°E) and SKR (65.573°N, 23.753°E), and at a forest clearing 60 km inland at the Krycklan Svartberget Field Station (KRY) (64.233°N, 19.767°E). PUF disks were polyether type, 14 cm diameter x 1.3 cm thick, surface area 365 cm^2 (top, bottom and edge), density 0.021 g cm^{-3} (PacWill Environmental, Beamsville ON, Canada). Daily mean temperatures were obtained from the Swedish Meteorological and Hydrological Institute (SMHI). Passive sampling locations are shown in Fig. 1, and Table 1 gives dates and a temperature summary.

Active air samples were collected from shipboard in the northern Baltic (May, 2012), and at Bergudden Lighthouse on HOL by pumping air through a 20 × 25-cm glass fiber filter (Whatman EPM, 2000, baked at 450 °C) followed by two PUF plugs, each 7.5 cm diameter x 7.5 cm thick. Flow rates were 0.45–0.57 m^3 min^{-1}. Short samples of 2–4 h were taken for BAs and hexachlorobenzene (HCB) to avoid breakthrough and longer ones of 24–72 h for other pesticides. Samples collected for pesticides and BAs from May to August 2012 are reported in Bidleman et al. (2015a). Additional samples were taken for OCPs and BAs in April 2013, HCB, HCHs and BAs in September 2013, and HCB and BAs in April 2015. Active samples were not taken at a sufficient frequency to calibrate PUF disk sampling rates, but were intended to provide an alternative measure of air concentrations over the study.

PUF disks and plugs were cleaned by Soxhlet extraction for 12 h with acetone followed by 12 h with hexane and dried in a vacuum desiccator. PUF disks were spiked before deployment with four depuration compounds (DCs), PCB congeners not present or <1% in Aroclor fluids (Frame et al., 1996): PCB19 (2,2′,6-trichlorobiphenyl), PCB54 (2,2′,6,6'-tetrachlorobiphenyl), PCB103 (2,2′,4,5′,6-pentachlorobiphenyl) and PCB147 (2,2′,3,4′,5,6-hexachlorobiphe-nyl). The PUFs were sealed in glass jars with aluminum foil-lined caps for shipment to and from the field sites and collected samples were frozen until analysis.

2.2. Analysis

PUFs were extracted with hexane followed by cleanup on Florisil. Glass fiber filters from the active samples were not analyzed. After volume adjustment and addition of internal standard ($^{13}C_{12}$-PCB105), analysis was conducted by capillary gas chromatography – quadrupole mass spectrometry (Agilent 6890N chromatograph-5975 mass selective detector (Agilent Technologies, Santa Clara, CA) and selected ion monitoring. Electron impact was used for 2,4-dibromoanisole (2,4-DiBA), 2,4,6-tribromoanisole (2,4,6-TriBA) and the PCB DCs, while pesticides were determined in the electron capture negative ion mode. The column was RTx5 (30 m × 0.25 mm i.d., 0.25 μm film, Restek Corp., Bellefonte, PA) or equivalent. Target OCPs were α-HCH, γ-HCH, HCB, heptachlor *exo*-epoxide (HEPX), *trans*- and *cis*-chlordane (TC, CC), *trans*- and *cis*-nonachlor (TN, CN), *p,p'*-DDE (DDE), dieldrin (DIEL), endosulfans I, II and endosulfan sulfate (ENDO-I, ENDO-II, ESUL). Three CUPs were included: insecticides endosulfan (ENDO) and chlorpyrifos (CPF), and herbicide dacthal (DAC). Ions monitored for BAs and pesticides are reported by Bidleman et al. (2015a). Those for DC PCBs 19, 54, 103 and 147 were 256, 292, 326 and 360, respectively; 338 was monitored for the $^{13}C_{12}$-PCB105 internal standard.