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Occurrence and concentrations of halogenated natural products derived from seven years of passive water sampling (2007–2013) at Normanby Island, Great Barrier Reef, Australia

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ABSTRACT

Polydimethylsiloxane (PDMS) based passive water samplers deployed at Normanby Island, Great Barrier Reef (Australia) from 2007 to 2013 were analyzed for halogenated natural products (HNPs). Altogether, 38 samples, typically deployed for 30 days, were studied. Five HNPs (Q1, 2′-MeO-BDE 68, BC-10, 2,4-dibromoanisole and 2,4,6-tribromoanisole) were detected in all samples. Most samples (> 90%) featured 2,2′-diMeO-BB 80, 6-MeO-BDE 47, 2′,6-diMeO-BDE 68 and 2,4-dibromophenol. In addition, tetrabromo-*N*-methylpyrrole (TBMP) was detected in ~80% and Cl_6-DBP in ~30% of the samples. Estimated time weighted maximum water concentrations were > 150 pg Q1 and 60 pg 2′-MeO-BDE 68 per L seawater. Typically, the concentrations were varying from year to year. Moreover, time weighted average water concentration estimates did not reveal consistent maximum trend levels within a given year. Additional screening analysis via GC/MS indicated the presence of several polyhalogenated 1′-methyl-1,2′-bipyrroles (PMBPs), 1,1′-dimethyl-2,2′-bipyrroles (PDBPs), and 1-methylpyrroles (PMPs) along with four brominated *N*-methylindoles and several other polyhalogenated compounds at Normanby Island.

1. Introduction

Halogenated natural products (HNPs) is a summarizing term for organohalogen compounds which are naturally produced by algae, sponges and other marine organisms. More than 5,000 structurally different HNPs have been discovered so far, mainly in marine environments (Gribble, 2010, 2012). Several of these HNPs have the potential to bioaccumulate in higher organisms, similarly to anthropogenic persistent organic pollutants (POPs) (Vetter, 2006). Occasionally, concentrations of such HNPs in marine organisms were comparable to or even higher than those of POPs (Vetter et al., 2001; Haraguchi et al., 2006; Stapleton et al., 2006; Alonso et al., 2014). The risks associated with exposure to HNPs are currently not elucidated, though studies suggest that some HNPs have toxic properties similar to polybrominated diphenyl ethers (PBDEs) and other POPs (Tittlemier et al., 2003; Wiseman et al., 2011). Likewise, sources and routes of entrance into the marine food web are sparsely known. For instance, HNPs have been repeatedly detected in marine mammals but it is unlikely that the mammals are directly consuming the natural producers of HNPs (Vetter et al., 2002). Hence, release of HNPs into the water phase and “conventional” food chain enrichment similarly to POPs seems to be the most plausible route of exposure. However, both substance classes enter the environment in a different way. While POPs are mainly released into ocean water via atmospheric deposition and discharge of contaminated river water, HNPs are released into water wherever the natural producers are found. Hence, annual air concentration profiles are different from that of anthropogenic POPs (Melcher et al., 2008). However, the global and even local distribution of HNPs is currently poorly understood. First analyses of passive water samplers deployed at the Great Barrier Reef (Australia) showed that many of the relatively hydrophobic HNPs accumulate in semi-permeable membrane devices (SPMDs) (Vetter et al., 2009; Gaul et al., 2011). Deployed for a given period, passive water samplers not only accumulate (and concentrate) hydrophobic compounds; they also provide time weighted information on their concentration in the water phase during the deployment time of the samplers (Huckins et al., 1999; Allan et al., 2009). Yet, transfer of analyte concentration into concentrations in water requires an understanding of the sampling kinetics which is

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usually obtained in controlled calibration experiments assessing uptake and/or clearance of the chemicals (Rusina et al., 2010). Due to the lack of calibration data for HNPs with passive samplers at the time, however, the partly high mass accumulation of selected HNPs observed in samplers at 15 time points in the Great Barrier Reef, could not be translated into water concentration estimates (Vetter et al., 2009). Since then, such calibration of HNPs in passive water samplers based on polydimethylsiloxane (PDMS) and SPMD samplers (these samplers are among the most frequently used for organic contaminants with log $K_{ow} > 3$) has been achieved (Kaserzon et al., 2014).

In this study we aimed to investigate the temporal concentration profiles of several HNPs in archived PDMS samplers from a unique set of 38 samples deployed at Normanby Island on the Great Barrier Reef, over a period of seven years (2007–2013). The Great Barrier Reef in Australia stretches for about 2500 km along the northern coastline of eastern Australia and is home to a rich and diverse ecosystem and a known source of HNP production (Kennedy et al., 2012). Normanby Island was chosen since HNPs were previously identified in marine biota samples collected from around the Island which was recognized as a prime area for potential HNP biosynthesis (Vetter et al., 2009). Moreover, the sample number was sufficiently high for long term evaluation. Purified sample extracts were analyzed by gas chromatography coupled with high resolution electron ionization mass spectrometry (GC/EI-HRMS) in a targeted approach on several HNPs previously detected in samples from the Great Barrier Reef. Concentrations in the passive water samplers were converted into water concentrations and studied for time trends for the individual HNPs. In addition, qualitative data was collected for several homologs of major compound classes of HNPs.

2. Materials and methods

2.1. HNP standards

2,4-Dibromophenol (2,4-DBP), 2,4,6-tribromoanisole (2,4,6-TBA) and 2,4,6-tribromophenol (2,4,6-TBP) were obtained from Sigma Aldrich (Steinheim/Taufkirchen, Germany), 2,6-dibromophenol (2,6-DBP) was from Lancaster Synthesis (Frankfurt, Germany), and 2,4-dibromoanisole (2,4-DBA) was from Alfa Aesar (Karlsruhe, Germany). 2,3,4,5-Tetrabromomethylpyrrole (TBMP) was synthesized by Gaul et al. (2011). 2,3,3′,4,4′,5,5′-heptachloro-1′-methyl-1,2′-bipyrrole (Q1) was synthesized according to Wu et al. (2002), 1,1′-dimethyl-3,3′,4,4′-5,5′-hexachloro-2,2′-bipyrrole (Cl_6-DBP) was synthesized by Martin et al. (2011), 2,2′-dimethoxy-3,3′,5,5′-tetrabromobiphenyl (2,2′-diMeO-BB 80 or BC-1) and 3,5-dibromo-2-(3′,5′-dibromo-2′-methoxy)phenoxyanisole, (2′,6-diMeO-BDE 68 or BC-11) were synthesized according to Marsh et al. (2005), 4,6-dibromo-2-(2′,4′-dibromo)phenoxyanisole (2′-MeO-BDE 68 or BC-2) was synthesized by Vetter and Wu (2003), 3,5-dibromo-2-(2′,4′-dibromo)phenoxyanisole (6-MeO-BDE 47 or BC-3) was synthesized according to Marsh et al. (2003), 5,5′-dichloro-1,1′-dimethyl-3,3′,4,4′-tetrabromo-2,2′-bipyrrole (BC-10) was synthesized according to Gribble et al. (1999). 2,7-Dibromo-4a-bromomethyl-1,1-dimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (TriBHD) and 2,5,7-tribromo-4a-bromomethyl-1,1-dimethyl-2,3,4,4a,9,9a-hexahydro-1H-xanthene (TetraBHD) were isolated and identified by Garson et al. (1989) and a quantitative solution was prepared by Melcher et al. (2007). Perdeuterated α-HCH (α-PDHCH) was synthesized by Vetter and Luckas (1995) and 6′-methoxy-2,3′,4,4′-tetrabromodiphenylether (BCIS) was synthesized by Vetter et al. (2011).

2.2. GC/EI-HRMS analysis

Quantitation of HNPs was performed with a TRACE 1310 gas chromatograph interfaced to a DFS high resolution magnetic sector mass spectrometer equipped with a Tri Plus auto sampler (Thermo, Bremen, Germany). Helium (5.0 quality, BOC Gases, Sydney, Australia) was used as the carrier gas at a flow rate of 1.0 mL/min. The transfer line and ion source temperatures were set to 280 °C and 300 °C. Injections (1 μL) were conducted in splitless mode at an injection temperature of 250 °C. Separations were performed with a 30 m × 0.25 mm i.d., 0.25 μm film thickness DB-multi residue column (Zebron, ZB1-MS, Phenomenex, Torrance, Ca, USA). The GC oven temperature program started 1 min isothermal at 50 °C. Then, the oven was heated at 10 °C/min to 300 °C which was held for 5 min. Samples were analyzed at a resolution of $R = 10,000$, in selected ion monitoring (SIM) mode. For each compound two intense and high molecular mass fragments were selected for analysis. Generally, the most intense isotope peak served as a quantitation ion and the second most intense isotope peak as a verification ion. A compound was considered identified, if (i) the retention time did not deviate from the standard by > 0.02 s, (ii) both ions were detected and (iii) the ratio of both ions did not differ from the theoretical ratio by > 20%. Each time window included a lock mass and a calibration mass from perfluorotributylamine (PFTBA).

SIM method 1: 5.0–12.3 min (2,4-/2,6-DBP, 2,4-DBA): *m/z* 242.98508 (*lock mass*), *m/z* 249.86290, *m/z* 251.86090, *m/z* 263.87850, *m/z* 265.87650, *m/z* 268.98189 (*calibration mass*); 12.3–21.9 min (2,4,6-TBP, 2,4,6-TBA): *m/z* 230.98508 (*lock mass*), *m/z* 329.77140, *m/z* 331.76930, *m/z* 342.97869 (*calibration mass*), *m/z* 343.78700, *m/z* 345.78490; 21.9–25.0 min (TriBHD, 2′-MeO-BDE 68/6-MeO-BDE 47, 2,2′-diMeO-BB 80, 2′,6-diMeO-BDE 68): *m/z* 454.97231 (*lock mass*), *m/z* 465.89650, *m/z* 467.89450, *m/z* 513.72380, *m/z* 515.72170, *m/z* 527.73940, *m/z* 529.73730, *m/z* 543.73430, *m/z* 545.73220, *m/z* 554.96592 (*calibration mass*); 25.0–31.0 min (TetraBHD): *m/z* 530.96592 (*lock mass*), *m/z* 543.80710, *m/z* 545.80500, *m/z* 554.96592 (*calibration mass*).

SIM method 2 (α-PDHCH): 5.0–14.0 min: *m/z* 218.98508 (*lock mass*), *m/z* 221.94590, *m/z* 223.94300, *m/z* 230.98508 (*calibration mass*); 14.0–16.5 min (DPTE, TBMP): *m/z* 354.97869 (*lock mass*), *m/z* 369.80260, *m/z* 371.80060, *m/z* 394.69690, *m/z* 396.69400, *m/z* 404.97550 (*calibration mass*) 16.5–21.0 min (Q1, ATE/BATE, Cl_6-DBP): *m/z* 304.98189 (*lock mass*), *m/z* 315.87090, *m/z* 317.86800, *m/z* 329.77140, *m/z* 331.76930, *m/z* 365.86330, *m/z* 367.86030, *m/z* 380.97550 (*calibration mass*); 21.0 – 31.0 min (BCIS, BC-10, Br_5Cl-DBP, Br_6-DBP): *m/z* 492.96911 (*lock mass*), *m/z* 513.72380, *m/z* 515.72170, *m/z* 543.65820, *m/z* 545.65530, *m/z* 587.60770, *m/z* 589.60480, *m/z* 631.55900, *m/z* 633.55700, *m/z* 642.95953 (*calibration mass*). Using these conditions 2′-MeO-BDE 68 and 2,2′-diMeO-BB 80 were coeluting but they were resolved by monitoring different SIM masses (2′-MeO-BDE 68: *m/z* 513.72374/515.72169; 2,2′-diMeO-BB 80: *m/z* 527.73939/529.73734).

2.3. GC/ECNI-MS analysis

Homolog patterns of three classes of polyhalogenated alkaloids (polyhalogenated 1′-methyl-1,2′-bipyrroles – PMBPs, polyhalogenated 1,1′-dimethyl-2,2′-bipyrroles – PDBPs, and polyhalogenated 1-methylpyrroles - PMPs) were studied by means of a 6890/5975 GC/MS system operated in the electron capture negative ion (ECNI) mode using the setup of Hauler et al. (2013). Heptahalogenated PMBPs exist in a theoretical variety of 78 congeners which differ in number and positions of chlorine and/or bromine substituents (Vetter, 2012). Likewise, hexahalogenated PDBPs and tetrahalogenated PMPs exist in a variety of 36 congeners, respectively (Vetter, 2012). Since the discovery of these substance classes in environmental samples (Tittlemier et al., 1999; Vetter et al., 2001; Gaul et al., 2011), different PMBPs, PDBPs and PMPs were detected in the environment (Tittlemier et al., 1999; Vetter et al., 2007; Pangallo et al., 2008; Hauler et al., 2013, Hauler and Vetter, 2017; Alonso et al., 2017) These HNPs were not available as standards, but previous protocols indicated the GC elution range (Hauler et al., 2013; Hauler and Vetter, 2017), and the two most abundant isotope

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