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# CONTAMINANTS OF EMERGING CONCERN IN THE ARCTIC: AN ASSESSMENT OF HALOGENATED NATURAL PRODUCTS

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## Introduction:

Halogenated natural products (HNPs) are organic compounds containing bromine, chlorine, iodine, and sometimes fluorine. Many HNPs are biosynthesized by marine bacteria, phytoplankton, macroalgae, tunicates, corals, worms, sponges and other organisms. Over 4000 HNP compounds have been discovered in environmental biota[1]. Natural and anthropogenic halocarbons have received much attention as regulators of ozone in the atmosphere and a detailed assessment has recently been conducted by the World Meteorological Organization[2]. Many natural halocarbons are "very short-lived substances" (VSLS) which typically have atmospheric lifetimes < 0.5 y and may account for 10-40 % of stratospheric bromine[2]. Higher molecular weight and bioaccumulating compounds include bromophenols and anisoles (BPs, BAs), hydroxylated and methoxylated polybrominated diphenyl ethers (OH-BDEs and MeO-BDEs), brominated dibenzo-p-dioxins (PBDDs), polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles (PDBPs), (1R,2S,4R,5R,1'E)-2-bromo-1-bromomethyl-1,4-dichloro-5-(2-chloroethenyl)-5-methylcyclohexane (MHC-1) and others.

This review is part of a 2016 assessment of contaminants of emerging concern in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP). Chapter 2.16 of this AMAP assessment summarizes the occurrence HNPs in the arctic physical environment and accumulation in arctic biota. The chapter is divided into two main sections, 2.16.1. Halocarbons and 2.16.2. Higher molecular weight compounds. Each contains subsections on: a) physical-chemical properties, b) sources, production, use and emissions, c) transformation processes, d) modeling studies, e) environmental concentrations, and f) spatial and temporal trends. Information is presented by compound class and generally in order of increasing molecular weight, as most information on halocarbons relates to air/water media while higher molecular weight compounds are generally reported in biota. Except for halocarbons, there have been few investigations of HNPs in polar environments. Discussions of HNP formation processes and occurrence in temperate and antarctic ecosystems are occasionally included to provide context. An overview of reported HNP occurrences in arctic-subarctic media is shown in Table 1 and compound formulas or abbreviations are given in Table 2. Figures (1-6) from the AMAP HNP chapter are shown below. References are minimized here.

Conclusions to this HNP assessment chapter are intended to be forward-looking and identify knowledge gaps.

- The role of largely natural VSLS halocarbons in ozone regulation has come into prominence.
- Future trends of halocarbons in the Arctic Ocean could be affected by changes in river runoff, precipitation and loss of ice cover, forcing primary production, species composition, circulation patterns, formation of halocline water and air-sea exchange.
- A multitude of biosynthetic and transformation pathways have been identified for higher molecular weight HNPs. Little is known about the operation of these in arctic ecosystems, but relevant factors are likely to be similar to those for halocarbons.
- Only two studies have reported trophic magnification of HNPs in arctic food webs. Temporal/ spatial trends are poorly known relative to anthropogenic POPs. There have been some studies of metabolic transformations, e.g. for MeO-BDEs, OH-BDEs and PBDEs, but not for other compounds.

Measurements of higher molecular weight HNPs in abiotic compartments are sparse or lacking altogether.
• The relative contribution of HNP biosynthesis within the Arctic versus delivery by atmospheric and oceanic currents is unknown.

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**References:**
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**Table 1. Reported occurrence of HNPs in arctic-subarctic media**

| | Atmosphere | | Terrestrial | | Freshwater | | | Marine | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Air | Snow | Soil | Biota | Water | Sediment | Biota | Water | Sediment | Biota |
| Halocarbons | X | X | X | | X | | | X | | |
| BPs | X | | | X | | | | | X | X |
| BAs | X | | | | | | | X | | X |
| OH-BDEs | | | | | | | | | | X |
| MeO-BDEs | | | | | | | X | | | X |
| PDBPs | | | | | | | | | X | X |
| MHC-1 | | | | | | | | | | X |

a) See Figure 1 for structures of some high molecular weight HNPs.

**Table 2. HNPs of relevance to the arctic-subarctic environment.**

| Compound | | Compound | |
|---|---|---|---|
| methyl chloride (chloromethane) | $CH_3Cl$ | 2,4,6-tribromophenol | 2,4,6-TriBP |
| dichloromethane | $CH_2Cl_2$ | 2,4-dibromoanisole | 2,4-DiBA |
| methyl bromide (bromomethane) | $CH_3Br$ | 2,6-dibromoanisole | 2,6-DiBA |
| dibromomethane | $CH_2Br_2$ | 2,4,6-tribromoanisole | 2,4,6-TriBA |
| bromoform (tribromomethane) | $CHBr_3$ | methoxylated polybrominated diphenyl ethers | MeO-BDEs |
| bromochloromethane | $CH_2BrCl$ | hydroxylated polybrominated diphenyl ethers | OH-BDEs |
| bromodichloromethane | $CHBrCl_2$ | polybrominated dibenzo-*p*-dioxins | PBDDs |
| dibromochloromethane | $CHBr_2Cl$ | polybrominated dibenzofurans | PBDFs |
| ethyl bromide (bromoethane) | $C_2H_5Br$ | polyhalogenated 1'-methyl-1,2'-bipyrroles | PMBPs |
| methyl iodide (iodomethane) | $CH_3I$ | polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles | PDBPs |
| diiodomethane | $CH_2I_2$ | polyhalogenated N-methylpyrroles | PMPs |
| iodoform (triiodomethane) | $CHI_3$ | polyhalogenated N'methylindoles | PMIs |
| iodochloromethane | $CH_2ICl$ | bromoheptyl- and bromooctyl pyrroles | BHPs, BOPs |
| ethyl iodide (iodoethane) | $C_2H_5I$ | polybrominated hexahydroxanthene derivatives | PBHDs |
| trifluoroacetic acid (acetate) | TFA | bromovinyl phenols | BVPs |
| 2,4-dibromophenol | 2,4-DiBP | bromocoumarates | BCUs |
| 2,6-dibromophenol | 2,6-DiBP | 1R,2S,4R,5R,1'E)-2-bromo-1-bromomethyl-1,4-dichloro-5-(2-chloroethenyl)-5-methylcyclohexane | MHC-1 |

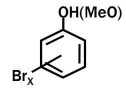
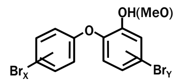
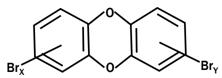
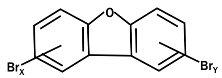
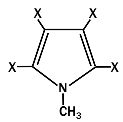
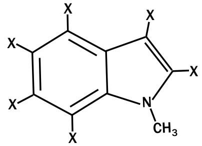
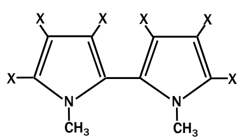
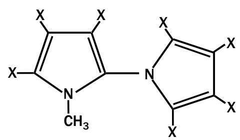
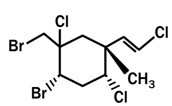
| | |
|---|---|
| BPs, BAs |  |
| OH-BDEs, MeO-BDEs (only *ortho*- position shown) |  |
| PBDDs |  |
| PBDFs |  |
| PMPs (X = Br or Cl) |  |
| PMIs (X = Br or H) |  |
| PDBPs (X = Cl, Br or H) |  |
| PMBPs (X = Br or H) |  |
| MHC-1 |  |

**Figure 1.** Some high molecular weight HNPs of arctic relevance.

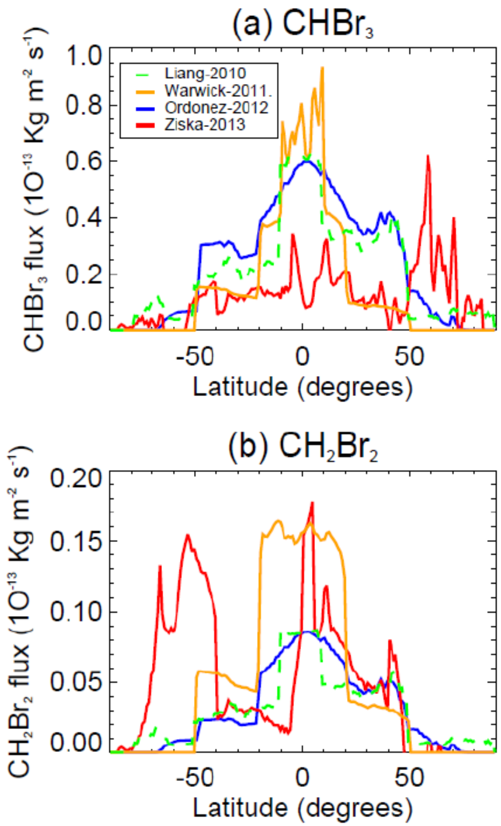



**Figure 2.** Model estimates[3] of zonally averaged emission source strengths for (a) $CHBr_3$ and (b) $CH_2Br_2$.

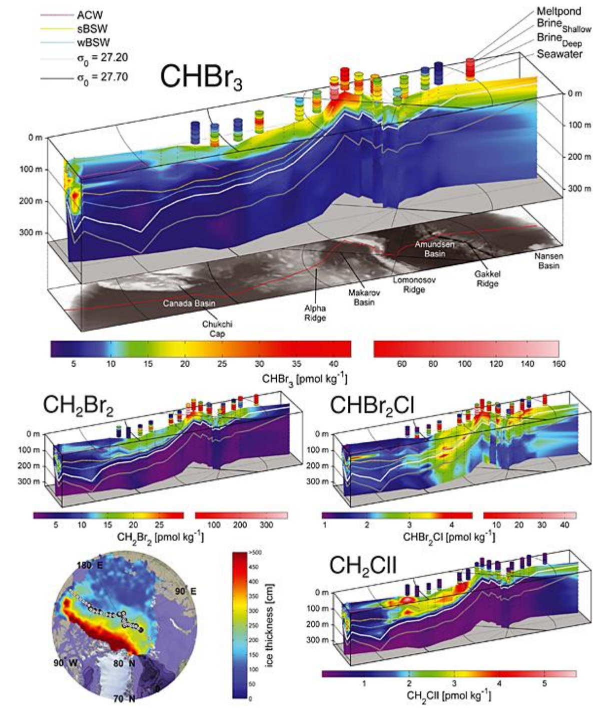



**Figure 3.** Horizontal and depth distribution of $CHBr_3$, $CH_2Br_2$, $CHBr_2Cl$, and $CH_2ClI$ in the upper 320 m of the Arctic Ocean between Barrow, Alaska and Svalbard[4].

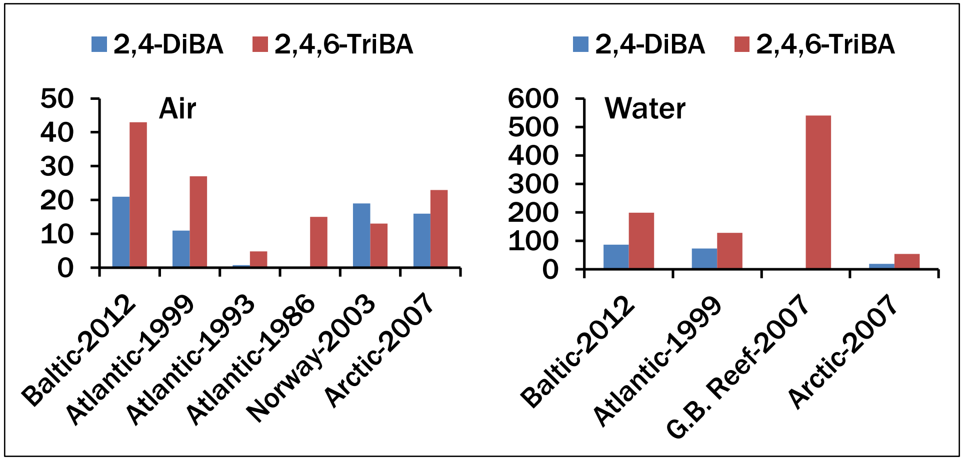



**Figure 4.** Bromoanisoles in ocean surface water (pg $L^{-1}$) and arctic air[5] (pg $m^{-3}$) compared to other studies.

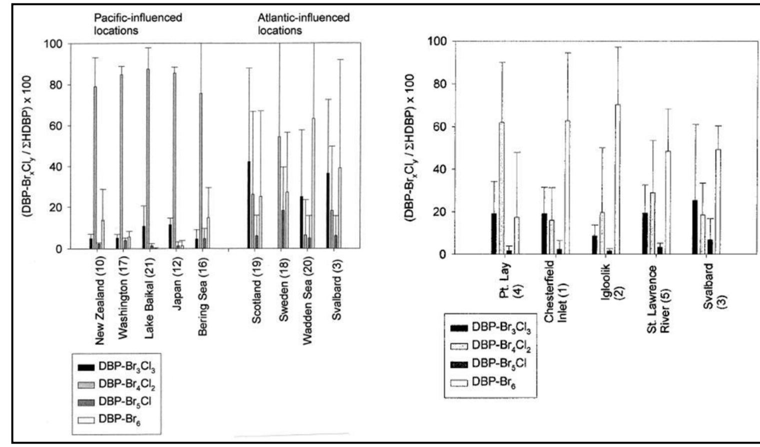



**Figure 5.** PDBP congener profiles (expressed as percentages of $\Sigma_4$PDBPs) in marine mammals living in waters influenced by Pacific versus Atlantic Ocean transport. Left: seals (excluding ringed seals); right: beluga[6].

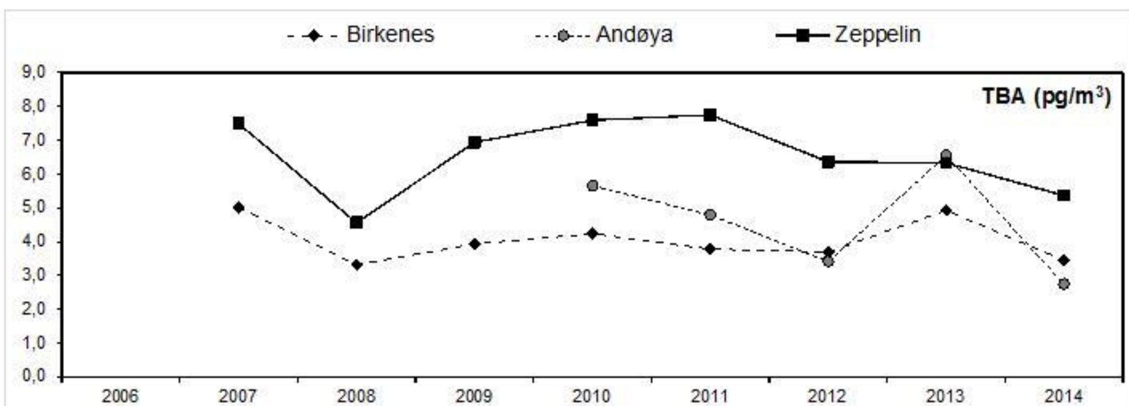



**Figure 6.** Annual mean concentrations of 2,4,6-TriBA (pg $m^{-3}$) in air[7].