Atmospheric Transport and Deposition of Bromoanisoles In Temperate and Arctic Fennoscandia

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Halogenated Natural Products (HNPs) – thousands!

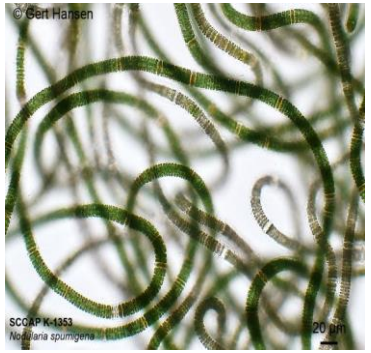
- Halocarbons ($CHBr_3$, CH_2Br_2, $CHClBr_2$, CHI_3, etc.).
- More complex compounds containing Br, Cl, I.

Produced by marine phytoplankton, bacteria, sponges, soft corals, worms, sea slugs, others[1-4]

Saccoglossus bromophenolosus

Dysidea granulosa

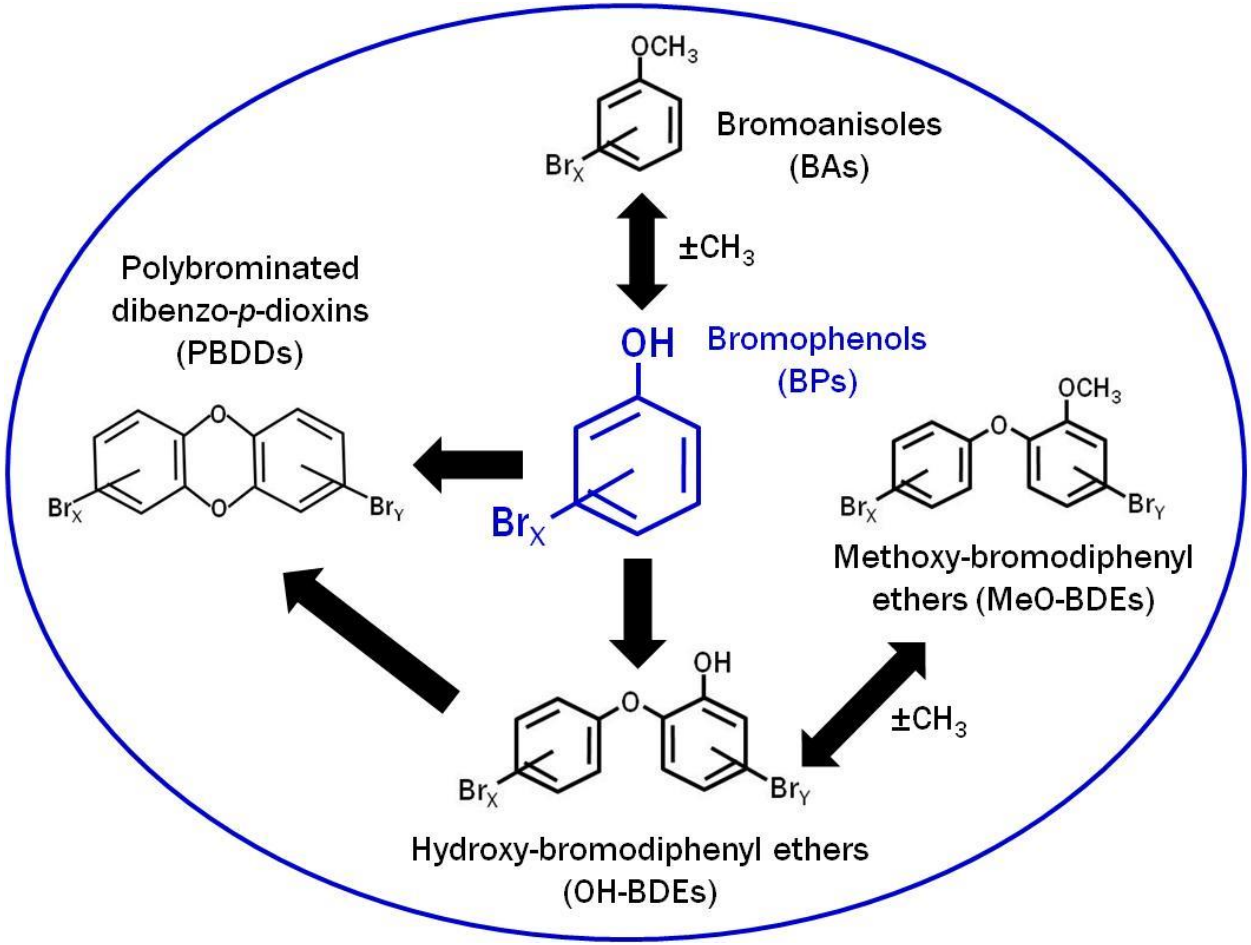
Ceramium tenuicorne



Nodularia spumigena

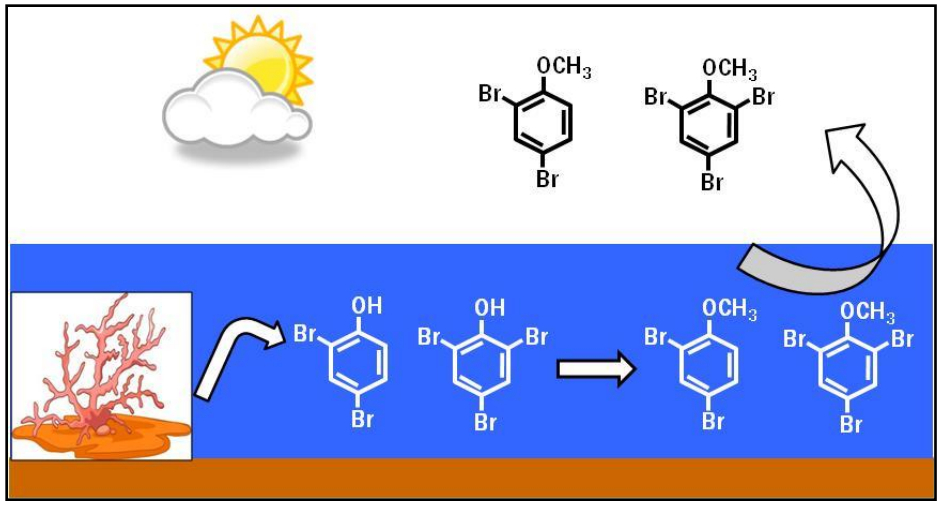
1. Agarwal V et al. 2017. *Nature Chem Biol 13*, 537-543.
2. Dahlgren E et al. 2015. *Environ Sci Pollut Res 22*, 18107-18114.
3. Hauler C, Vetter W. 2015. *Rapid Commun Mass Spectrom 29*, 619-628.
4. Gribble GW. 2010. *Prog Chem Org Nat Prod, 91*, 613 pp.

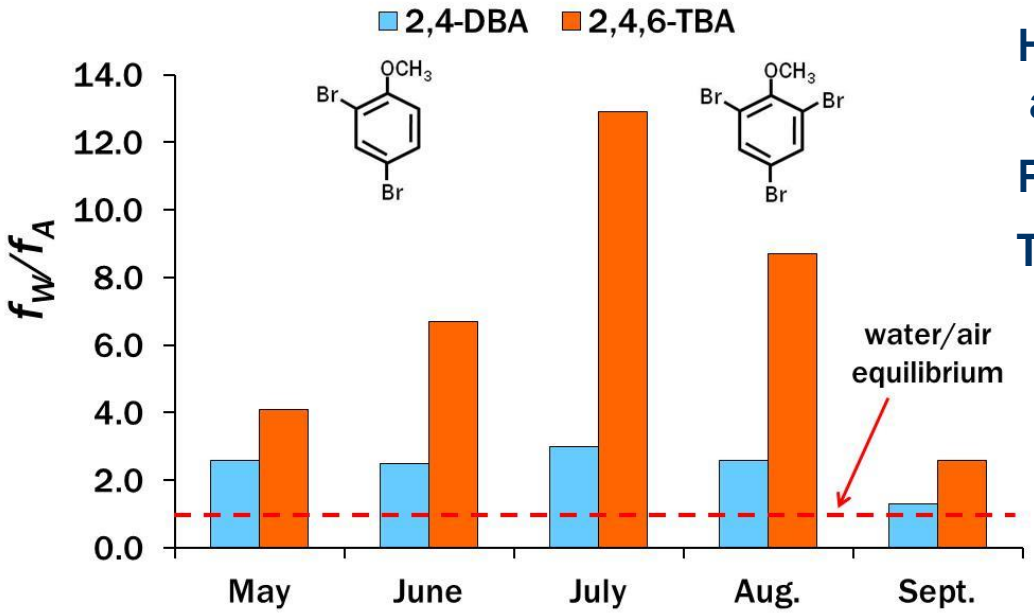
Bromophenolic HNPs[1]



1. Transformation pathways identified by Arnoldsson K et al. 2012. *ES&T 46*, 7239-7244; *Ibid*. 7567-7574; Lin K et al. 2014, *ES&T 48*, 263-271; *Ibid.* 11977-11983; Erickson PR et al. 2012. *ES&T 46*, 8174-8180; Zhao H et al. 2015. *ES&T 49*, 14120-14128.

Net volatilization of BAs from the northern Baltic[1]





Fugacity Ratio = $f_W/f_A = C_W H/C_A RT_A$

FR = 1 Steady state, no net flux

FR > 1 Net volatilization

FR < 1 Net deposition

C_W = dissolved water concentration.

C_A = gaseous air concentration.

H = Henry's law constant, Pa m^3 mol^{-1} at the water temperature[1].

R = 8.31 Pa m^3 mol^{-1} K^{-1}.

T_A = air temperature, K.

1. Bidleman TF et al. 2016. *Marine Pollut Bull 112*, 58-64.

Locations and Methods

Air sampling

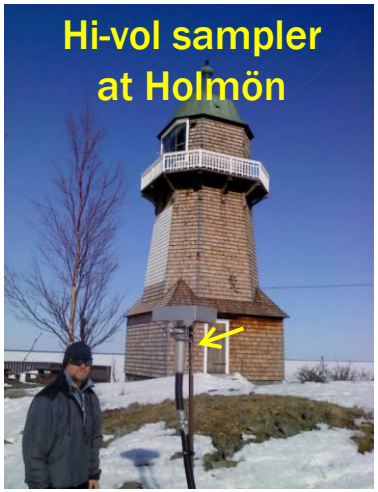
- Holmön[1]: PUF passive, hi-vol 2011-15
- Krycklan[1], Sandskär[1]: PUF passive 2011-12
- Råö (PUF hi-vol, 2004, 06, 12, 14, 15)
- Pallas (PUF hi-vol, 2002, 04, 06, 10, 12, 14, 15)

Bulk deposition (funnel, PUF)

- Råö (2012, 2014, 2015)
- Pallas (2012, 2015)

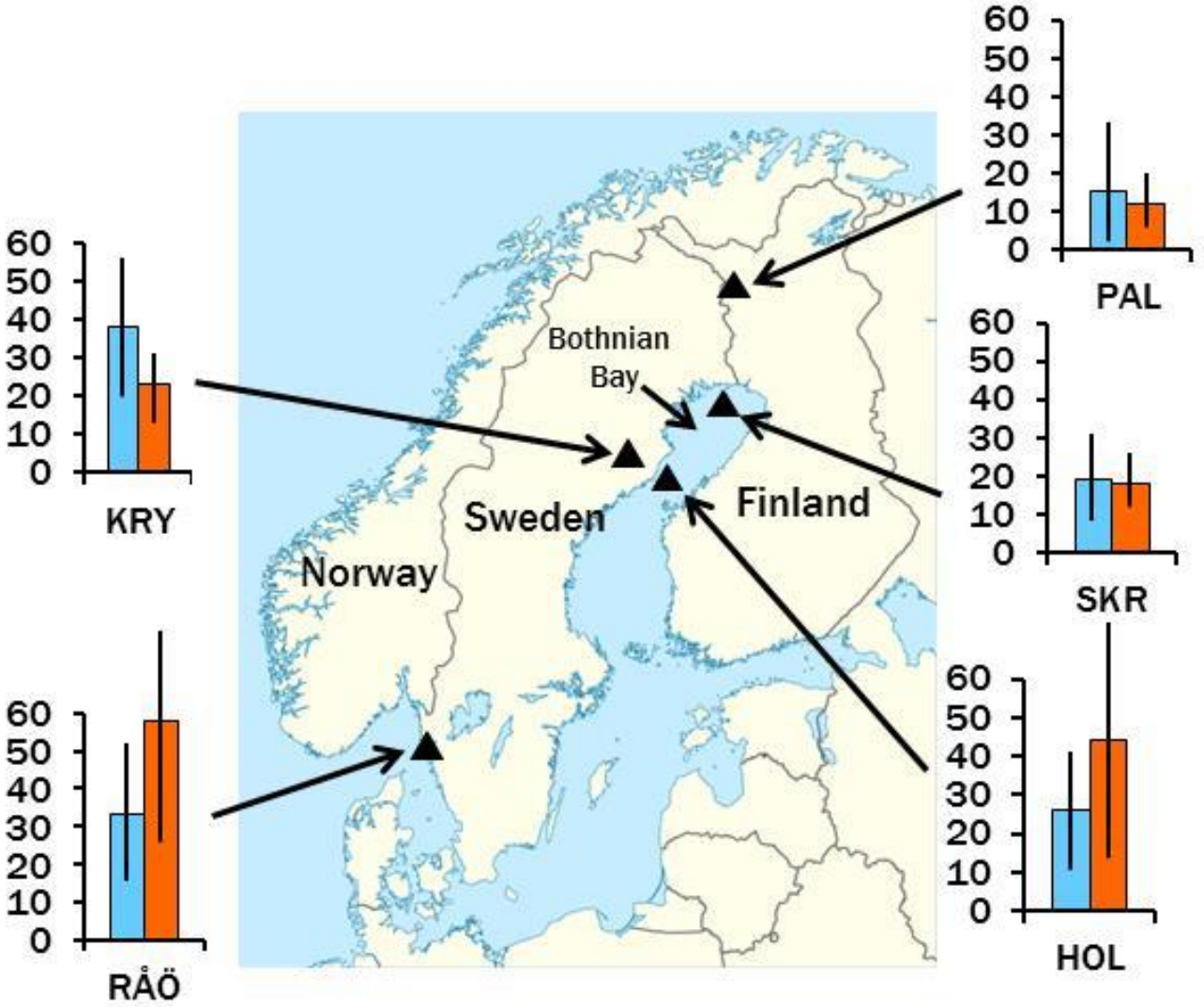
River water (GF filter, SPE cartridges), spring, 2017

Analysis: GC-MSD-SIM

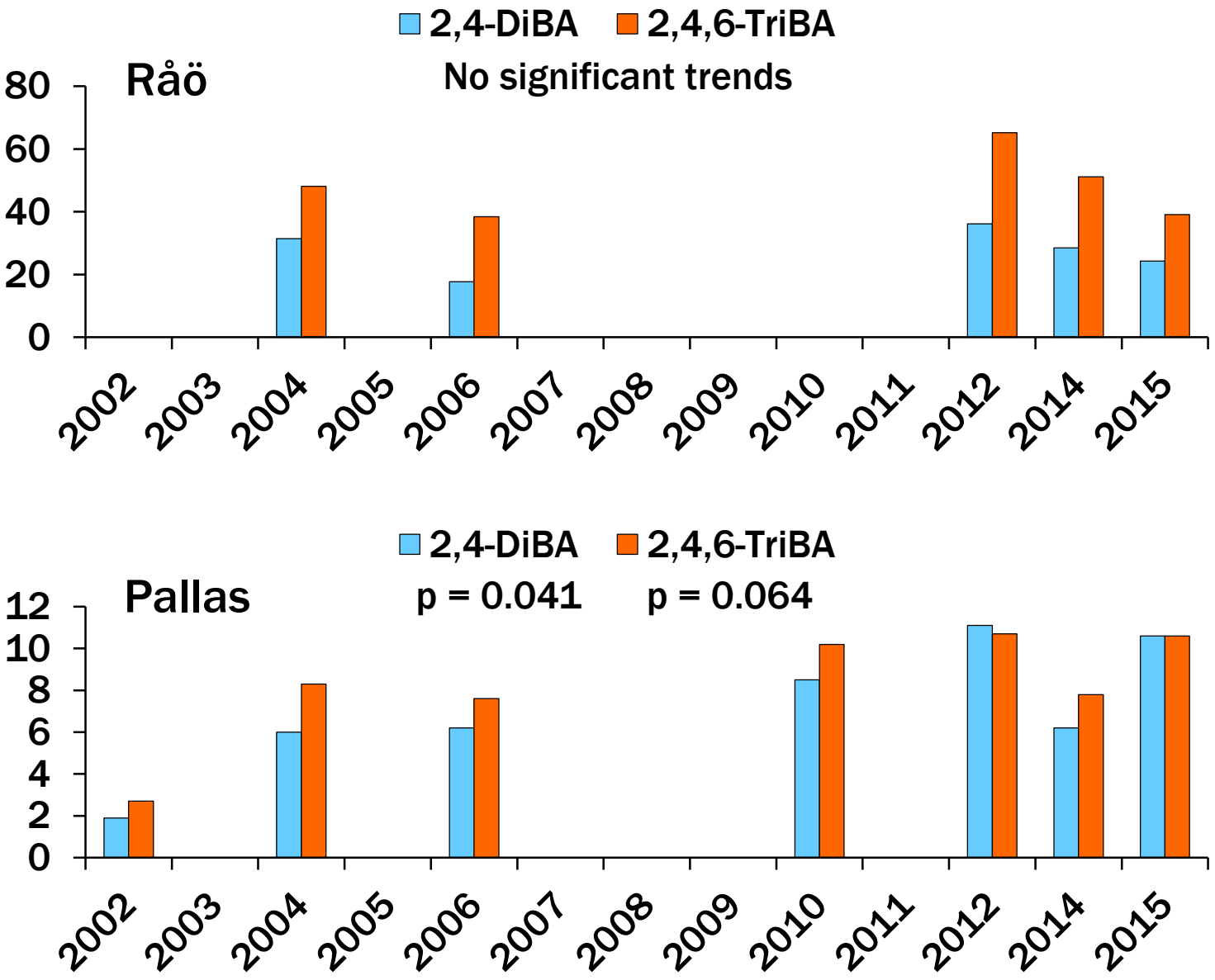


1. Bidleman TF et al. 2017. *Environ Pollut 225*, 381-389.

BAs in air from temperate to arctic regions 2012-2015 (pg m^{-3})

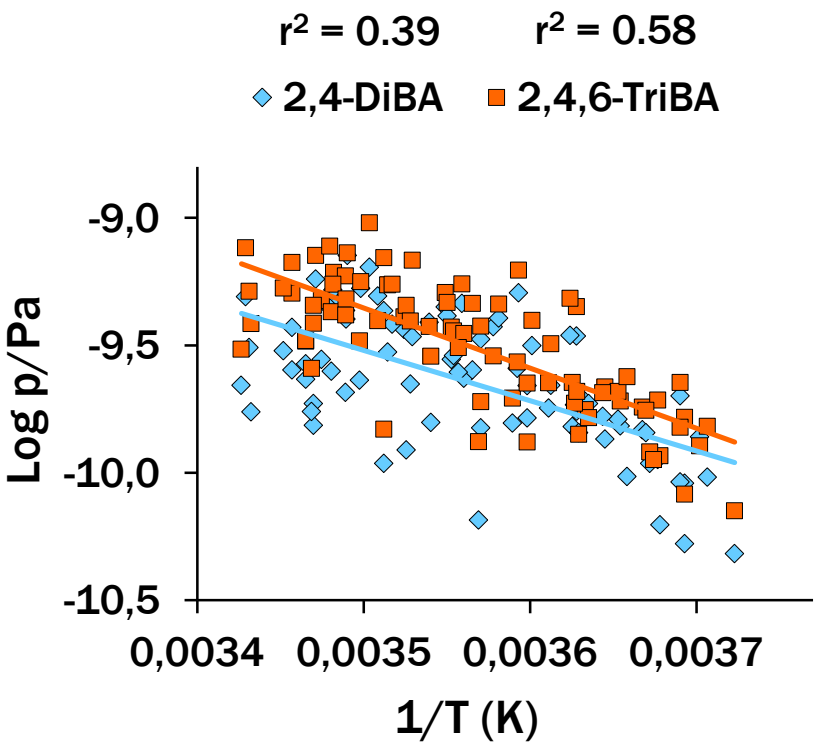


Annual geometric mean concentrations of BAs, pg m^{-3}

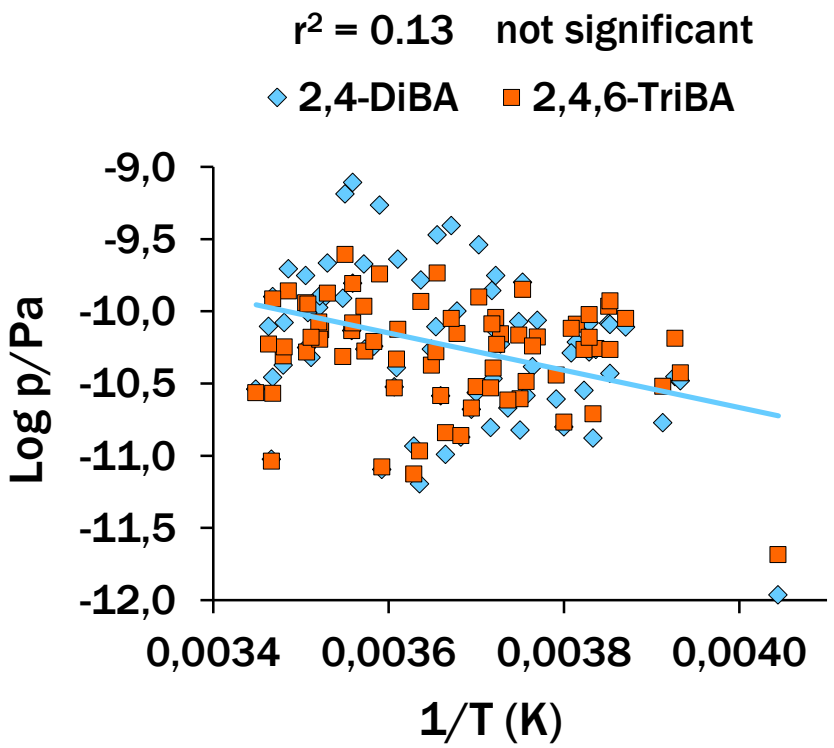


Relationships of air partial pressures to temperature

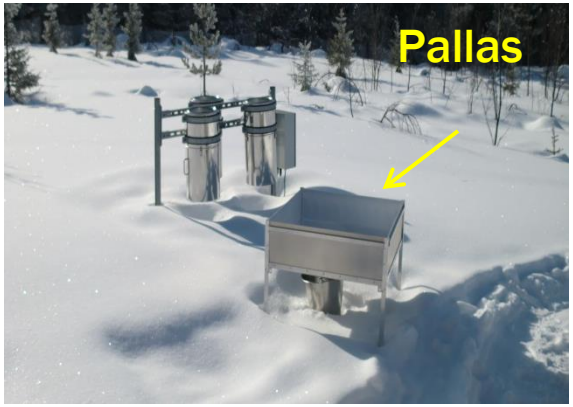
Råö

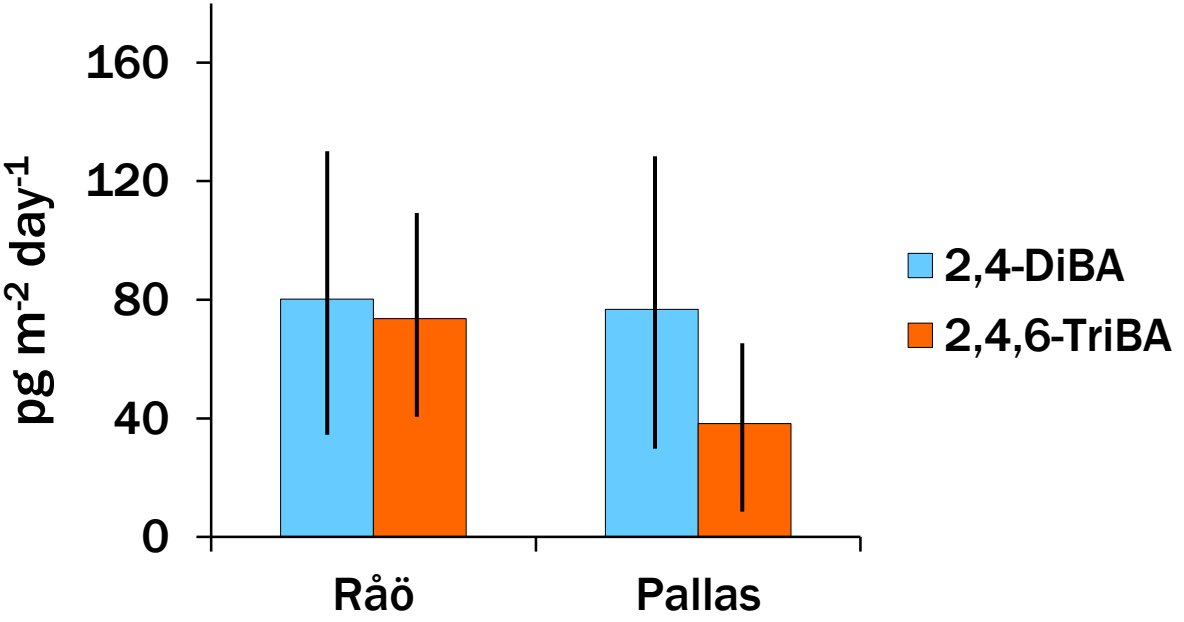


Pallas



BAs in bulk atmospheric deposition





- Rain and snowmelt run through a PUF trap.
- Precipitation volumes from SMHI and FMI.
- Similar fluxes at Råö and Pallas, despite higher air concentrations at Råö. Colder temperatures at Pallas.

Observed and predicted washout ratios of BAs

Observed washout ratio

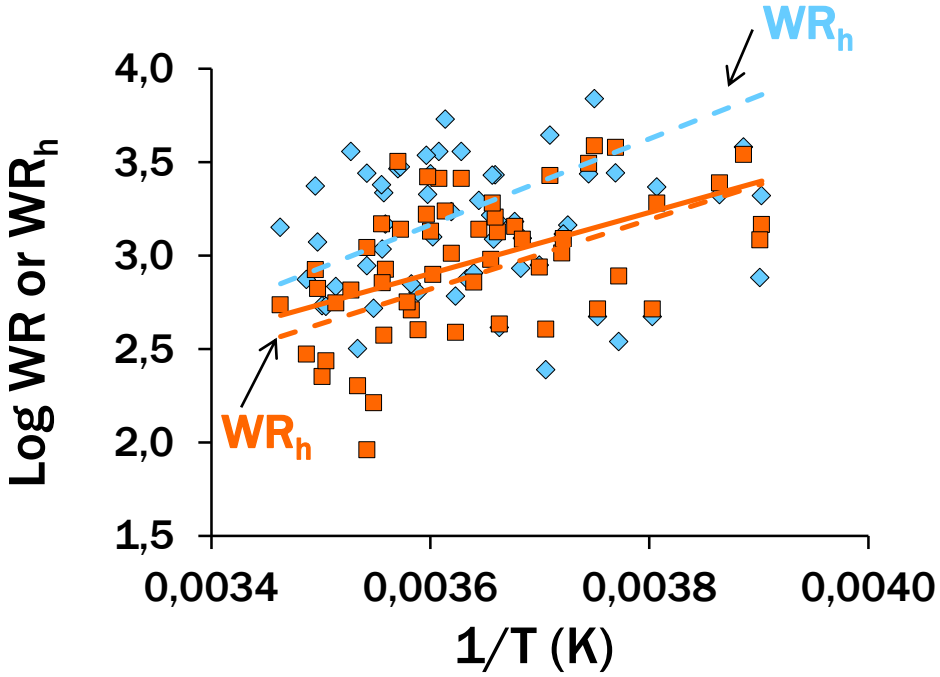
◆ 2,4-DiBA ■ 2,4,6-TriBA

$$WR = \frac{C_{precip}}{C_{air}}$$

Henry's law scavenging (dotted): $WR_h = RT/H$

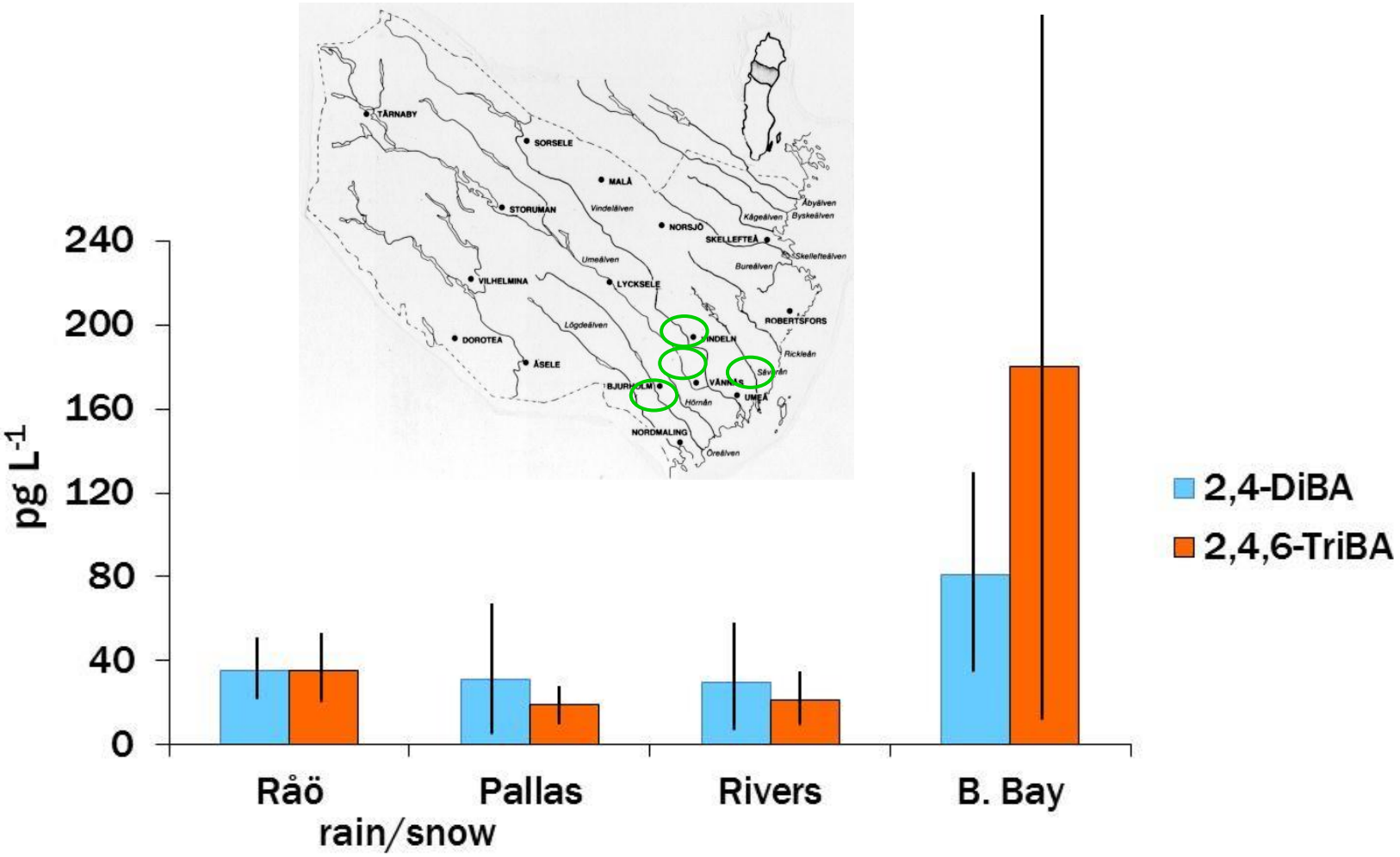
H (Pa m^3 mol^{-1}) from [1]; *R* = 8.31 Pa m^3 mol^{-1} K^{-1}.

- WR and WR_h were higher for 2,4-DiBA than 2,4,6-TriBA.
- WR of 2,4,6-TriBA was correlated with 1/T (r^2 = 0.24, p = 0.0002).
- More scatter for 2,4-DiBA; correlation was not significant

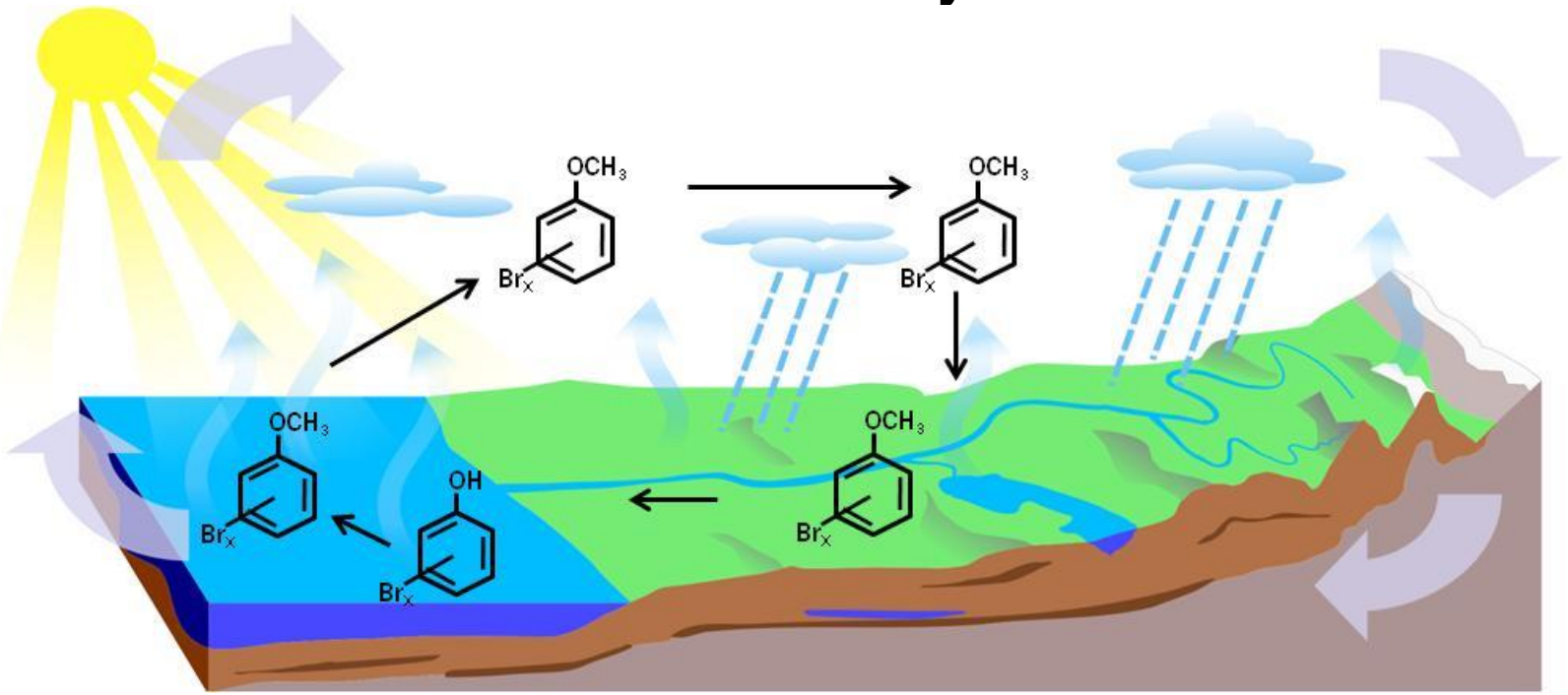


1. Bidleman TF et al. 2016. *Marine Pollut Bull 112*, 58-64.

BA concentrations in precipitation and rivers are about 10-40% of those in Bothnian Bay.

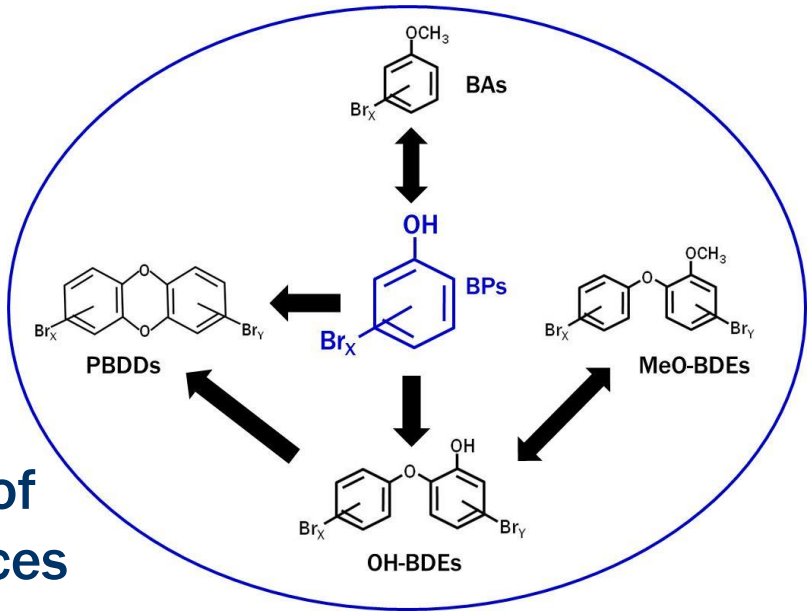


”What Goes Around Comes Around” the sea-land-sea cycle of BAs



- The catchment area of Bothnian Bay (280 000 km^2) is 7 times larger than the bay itself (38 000 km^2)
- Riverine drainage is an unexpected source to BB estuaries, especially for 2,4-DiBA.

Beyond BAs? A Hypothesis…



- MeO-BDEs are reported in fish[1-3] and eggs of white-tailed sea eagle (*Haliaeetus albicilla*)[3] from inland regions of subarctic Sweden.
- They do not appear to be metabolites of PBDE flame retardants, but their sources have not been identified.
- By analogy to chlorinated anisoles[4], deposited BAs may be O-demethylated to free BPs in soils, streams and lakes.
- Could coupling of these BPs could produce more complex HNPs?

1. Kierkegaard A et al., 2004. *Environ Pollut 130*, 187-198. 2. Asplund, L. et al., 2010. *Organohalogen Cpds 72*, 1197-1200; 3. Nordlöf U et al., 2010. *Sci Total Environ 409*, 238-246. 4. Campoy S et al., 2009. *Environ Microbiol 11*, 99-110.

EcoChange
Ecosystem Dynamics in the Baltic Sea

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Johannes Tiwari
Paulina Viteri