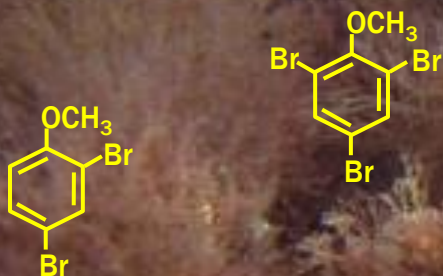


Atmospheric Transport and Deposition of Bromoanisoles In Temperate and Arctic Fennoscandia

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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, others¹⁻⁴



*Saccoglossus
bromophenolosus*



*Dysidea
granulosa*



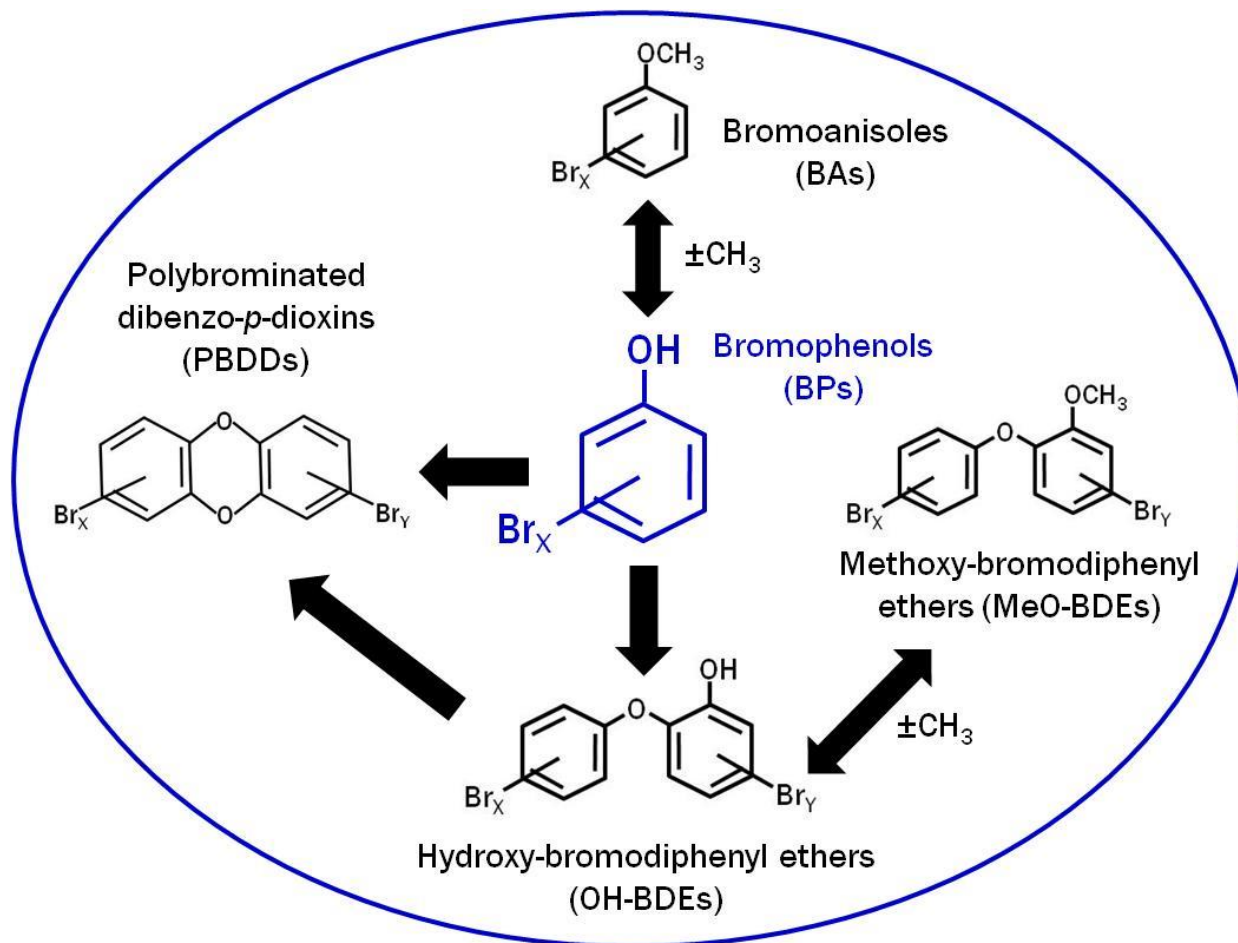
*Ceramium
tenuicorne*



*Nodularia
spumigena*

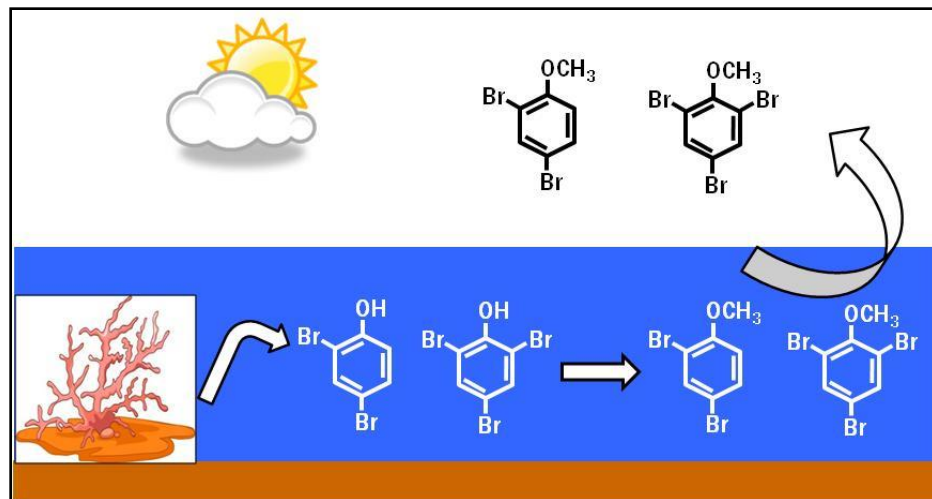
1. Agarwal V et al. 2017. *Nature Chem Biol* 13, 537-543.
2. Dahlgren E et al. 2015. *Environ Sci Pollut Res* 22, 18107-18114.
3. Hauler C, Vetter W. 2015. *Rapid Commun Mass Spectrom* 29, 619-628.
4. Gribble GW. 2010. *Prog Chem Org Nat Prod*, 91, 613 pp.

Bromophenolic HNPs¹



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 Baltic¹



$$\text{Fugacity Ratio} = f_W/f_A = C_W H / C_A R T_A$$

FR = 1 Steady state, no net flux

FR > 1 Net volatilization

FR < 1 Net deposition

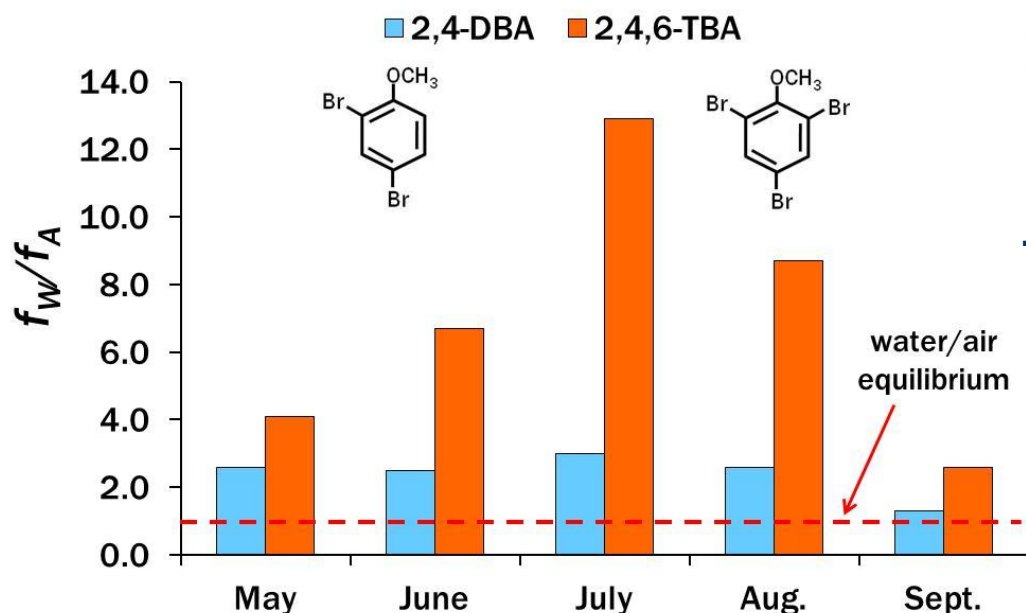
C_W = dissolved water concentration.

C_A = gaseous air concentration.

H = Henry's law constant, $\text{Pa m}^3 \text{mol}^{-1}$ at the water temperature¹.

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

T_A = air temperature, K.



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

Locations and Methods

➤ Air sampling

- Holmön¹: PUF passive, hi-vol 2011-15
- Krycklan¹, Sandskär¹: PUF passive 2011-12
- Råö (PUF hi-vol, 2004, 06, 12, 14, 15)
- Pallas (PUF hi-vol, 2002, 04, 06, 10, 12, 14, 15)

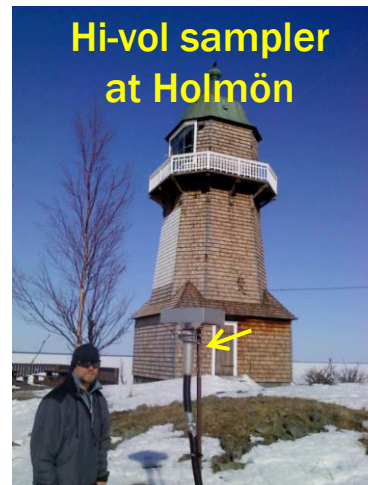
➤ Bulk deposition (funnel, PUF)

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

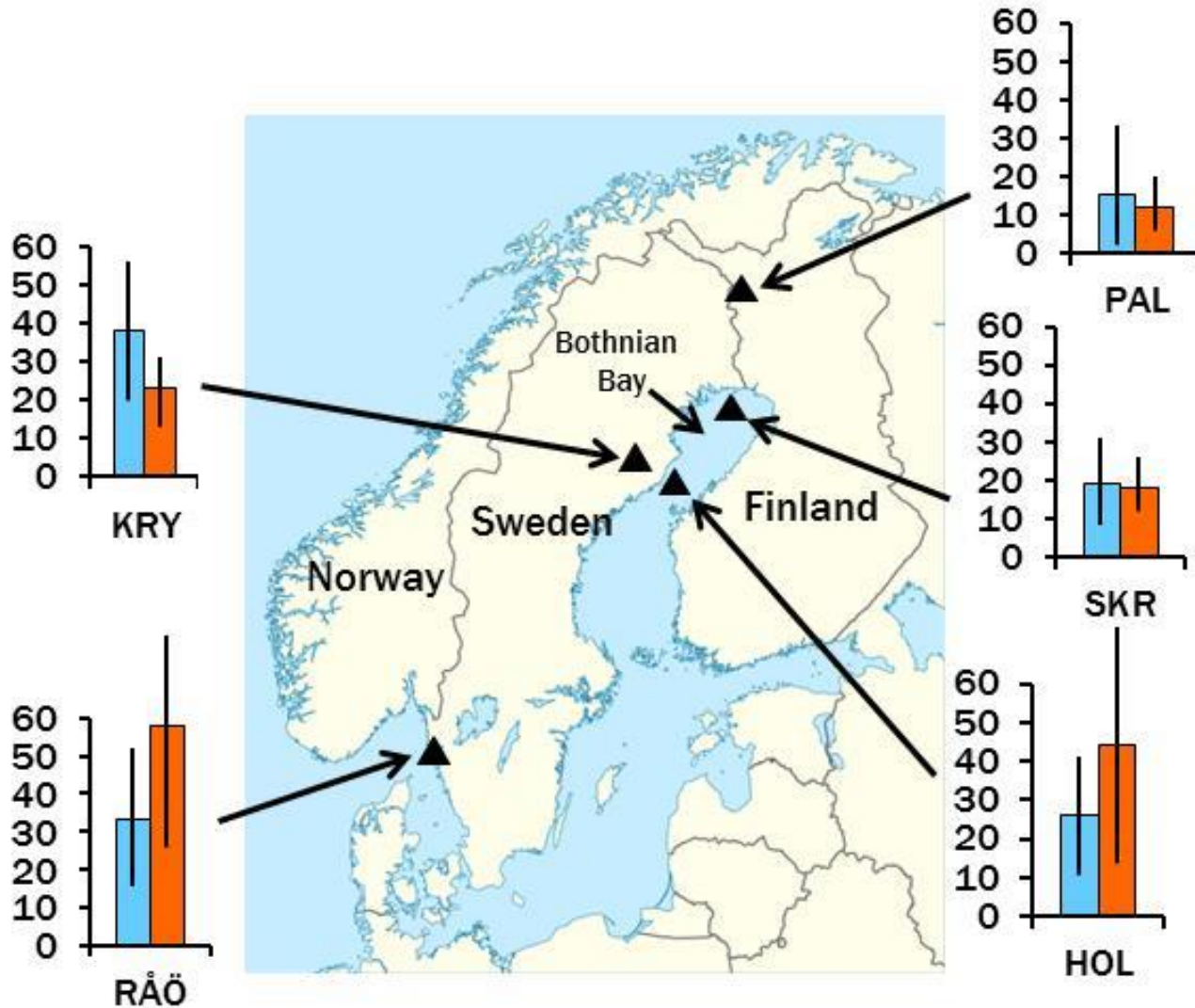
➤ River water (GF filter, SPE cartridges), spring, 2017

➤ Analysis: GC-MSD-SIM

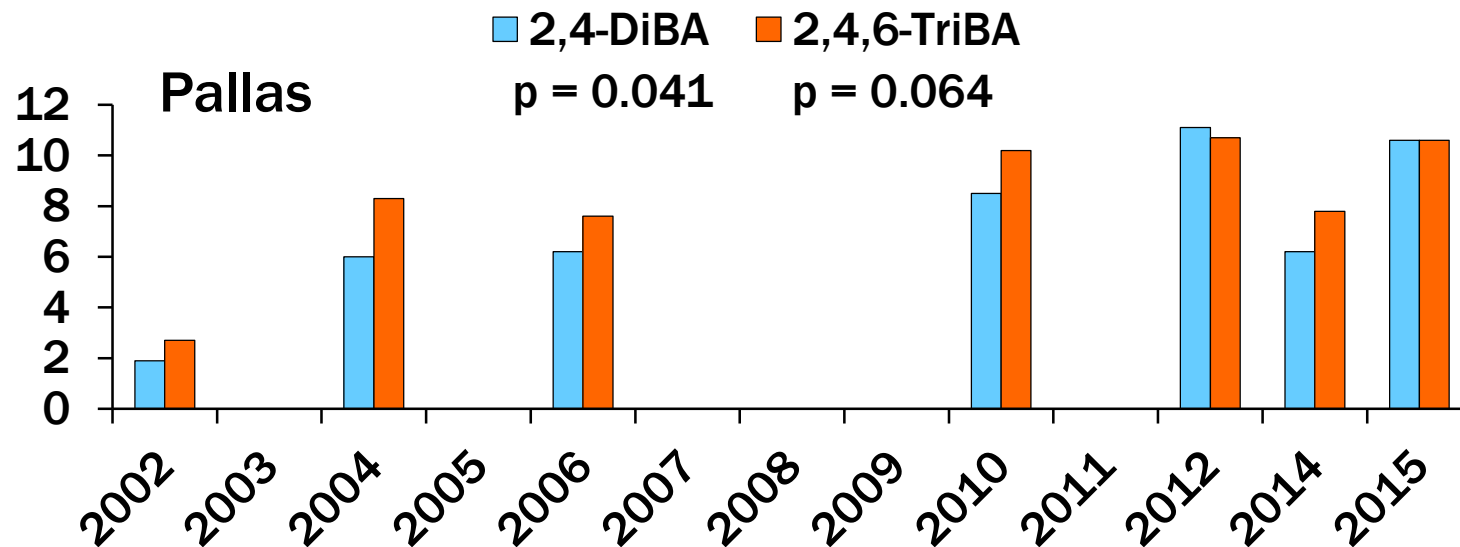
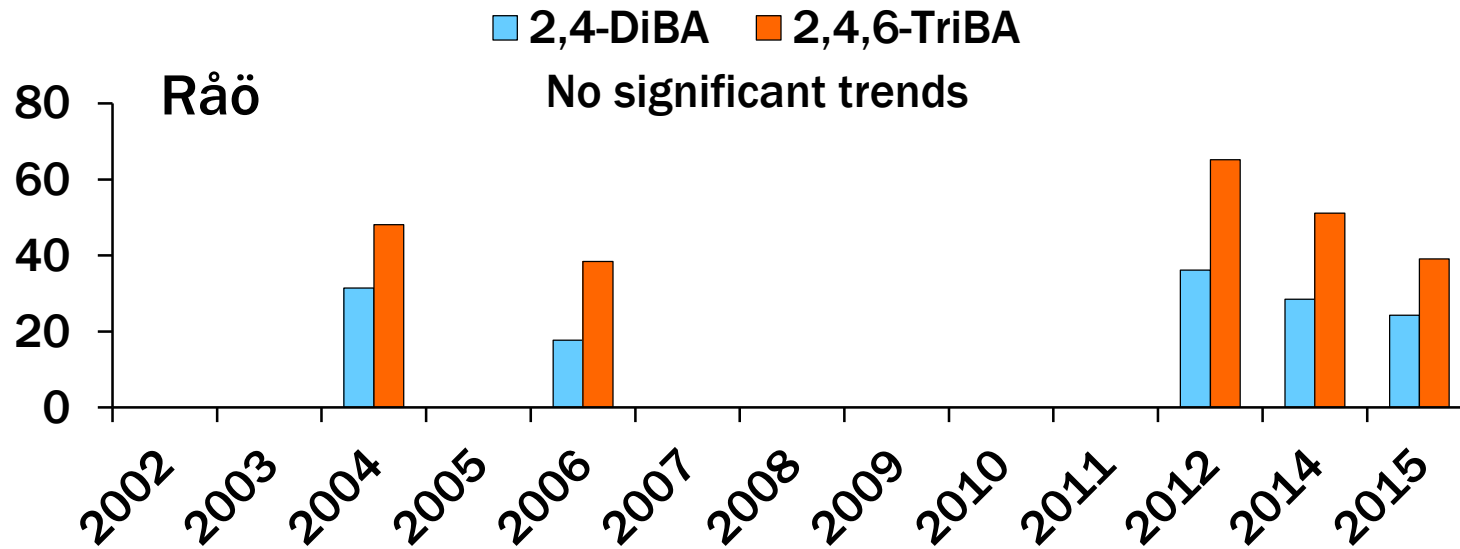
1. Bidleman TF et al. 2017.
Environ Pollut 225, 381-389.



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

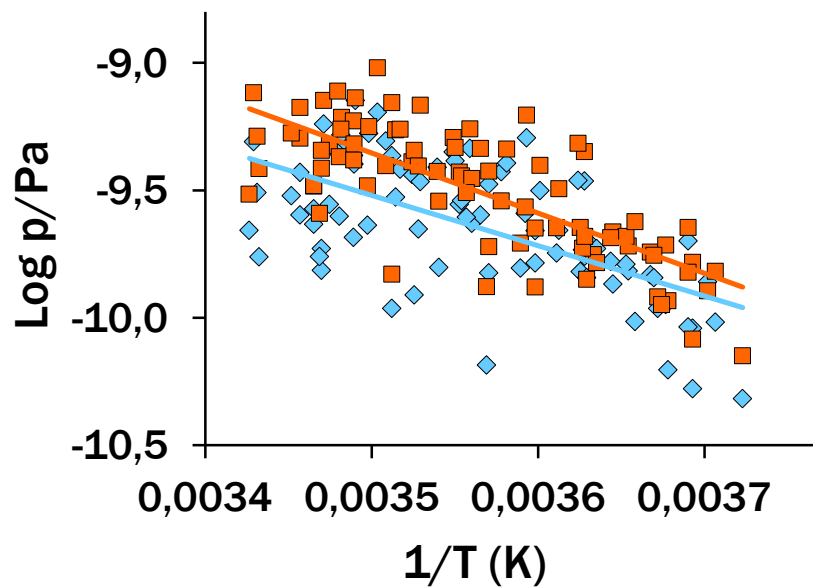
Råö

$r^2 = 0.39$

$r^2 = 0.58$

◆ 2,4-DiBA

■ 2,4,6-TriBA



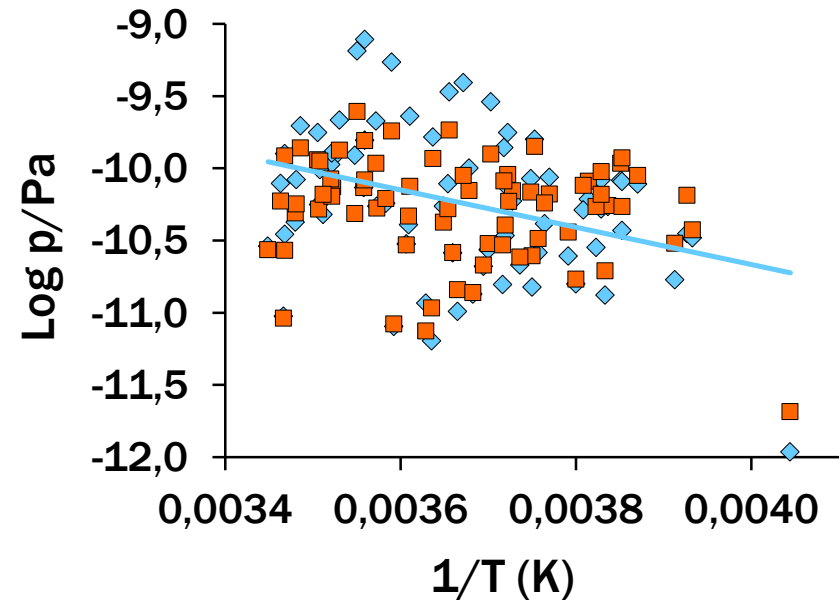
Pallas

$r^2 = 0.13$

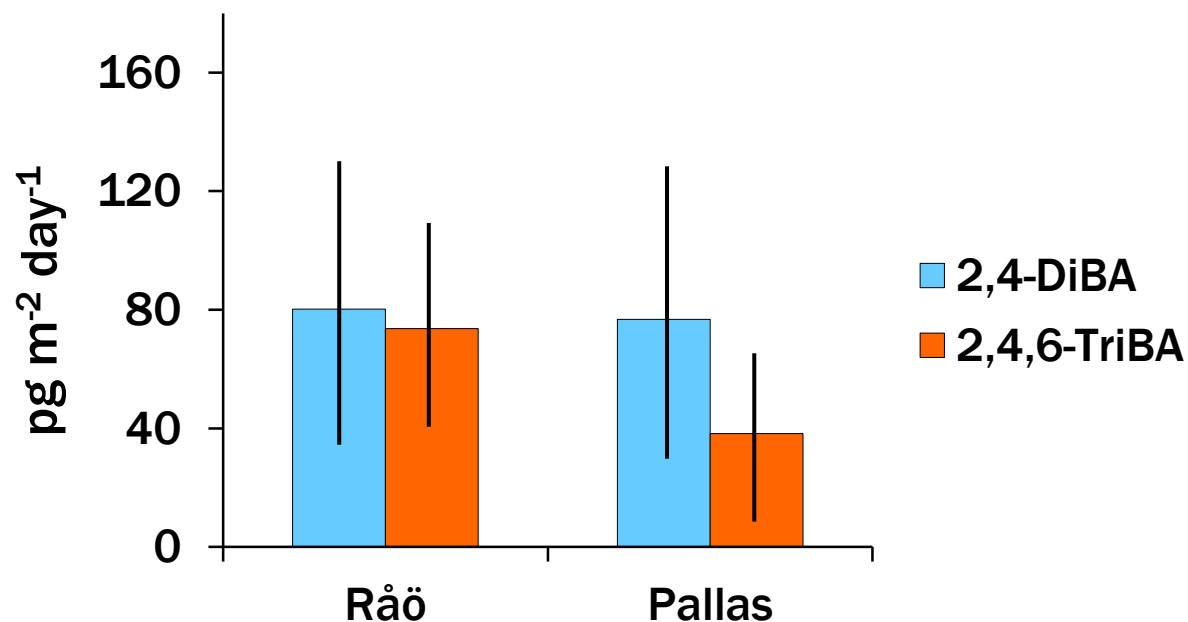
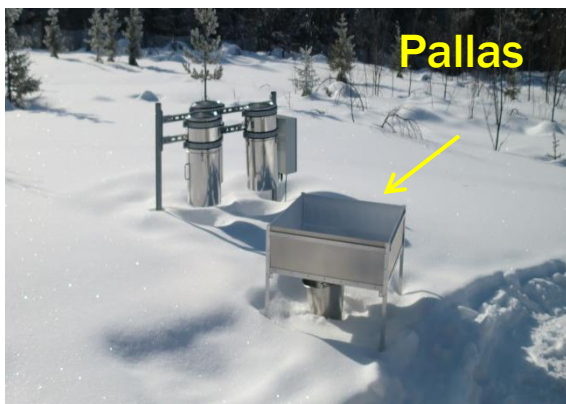
not significant

◆ 2,4-DiBA

■ 2,4,6-TriBA



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

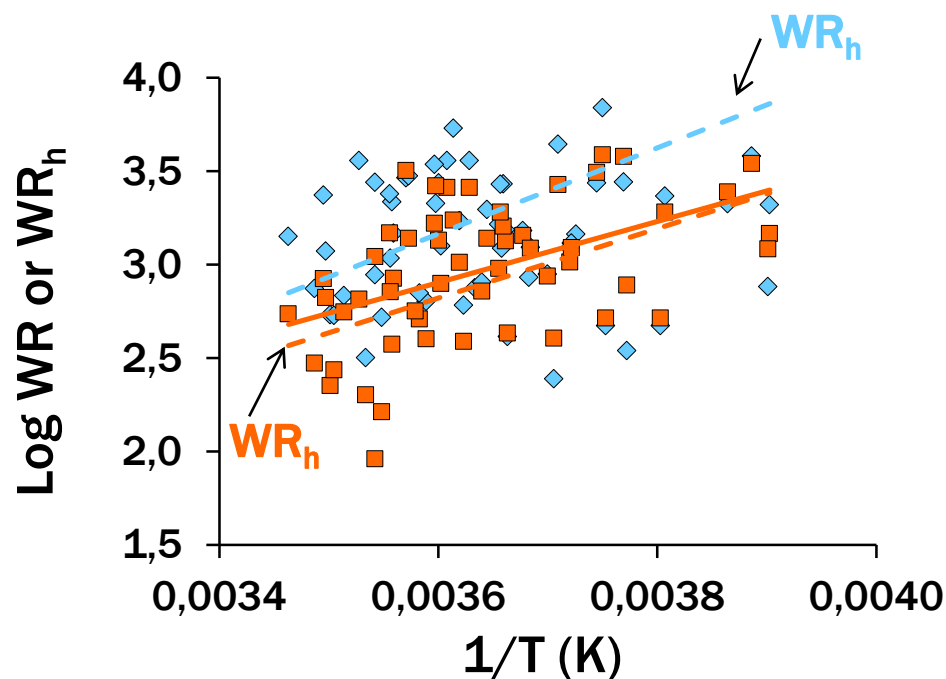


Observed washout ratio
♦ 2,4-DiBA ■ 2,4,6-TriBA

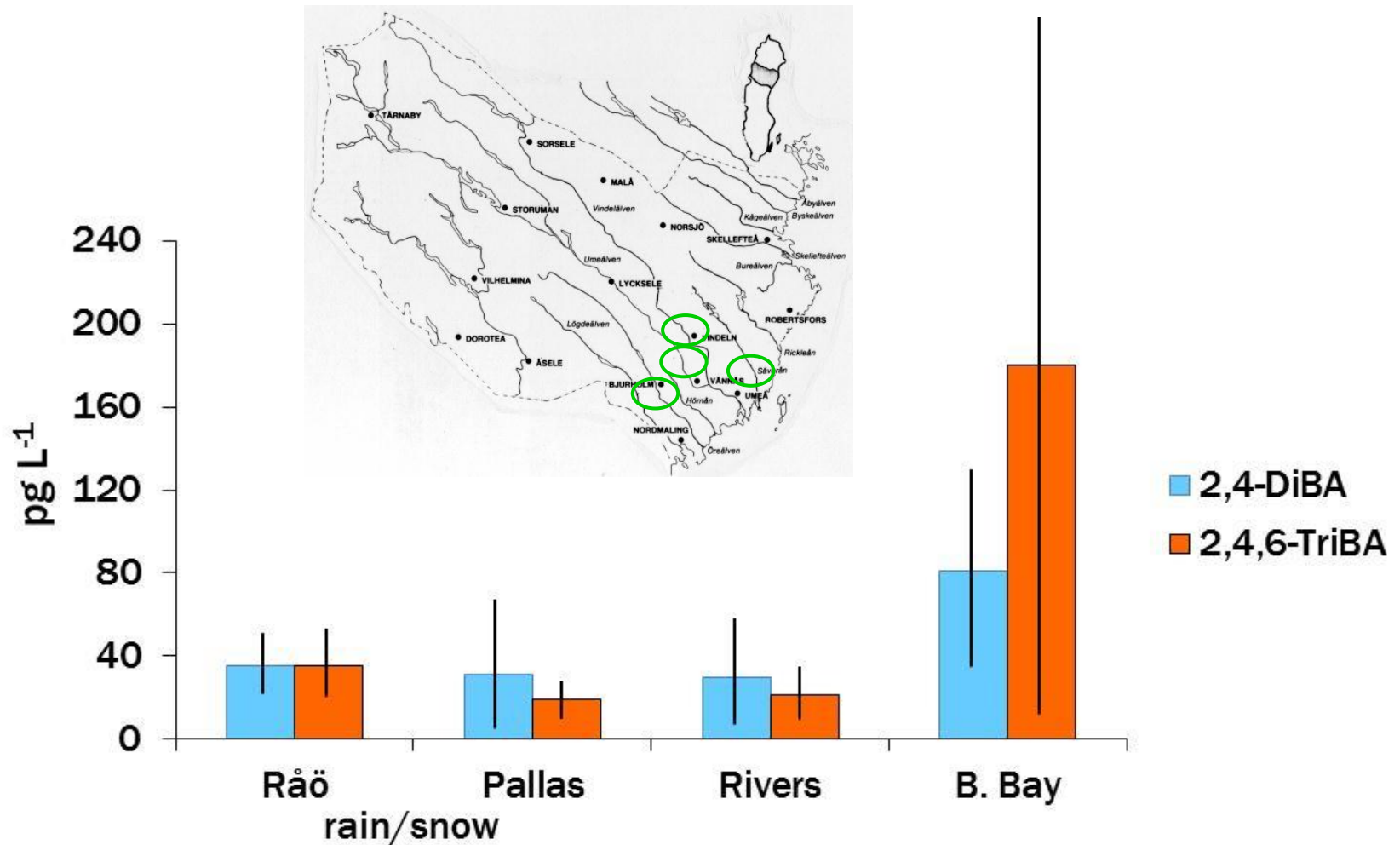
$$WR = \frac{C_{precip}}{C_{air}}$$

Henry's law scavenging (dotted): $WR_h = RT/H$
 H (Pa m³ mol⁻¹) from [1]; $R = 8.31$ Pa m³ mol⁻¹ K⁻¹.

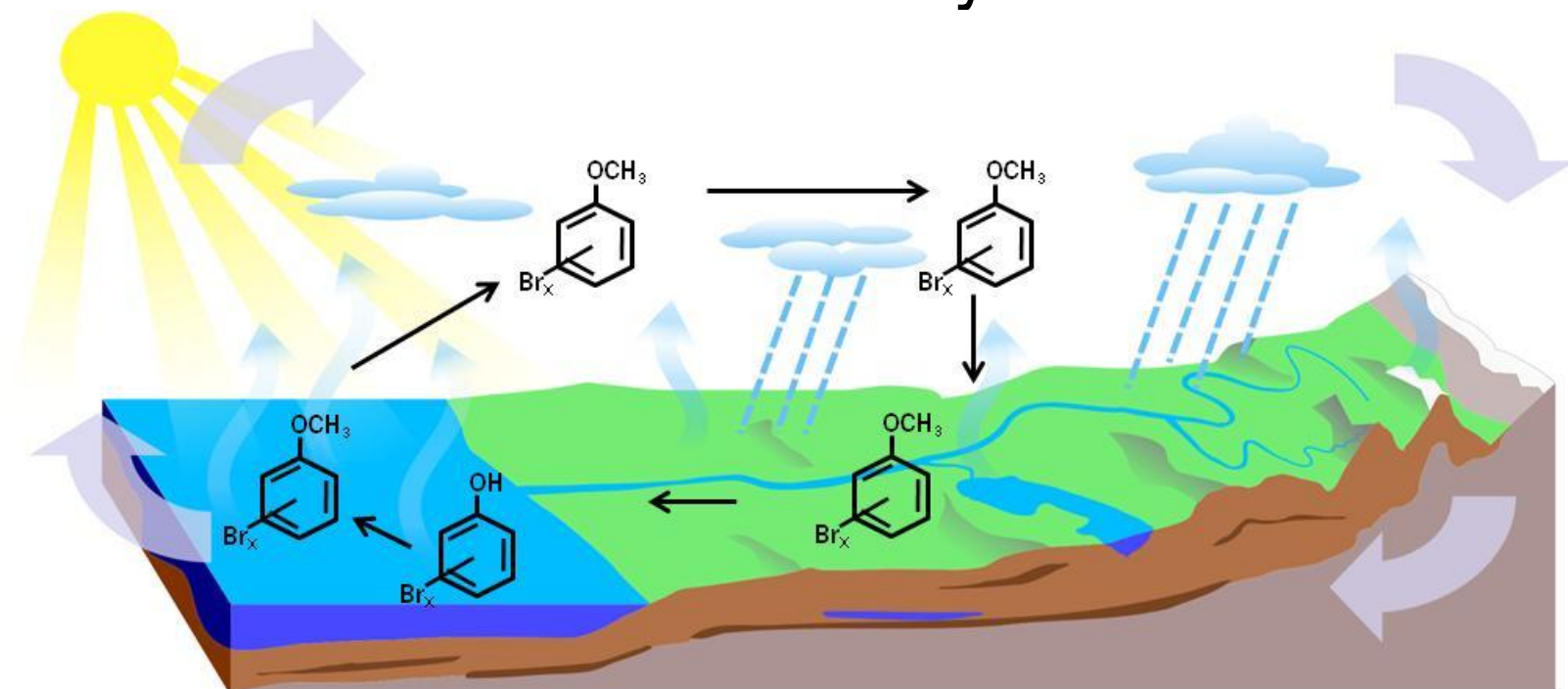
- ❖ WR and WR_h were higher for 2,4-DiBA than 2,4,6-TriBA.
- ❖ WR of 2,4,6-TriBA was correlated with $1/T$ ($r^2 = 0.24$, $p = 0.0002$).
- ❖ More scatter for 2,4-DiBA; correlation was not significant



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



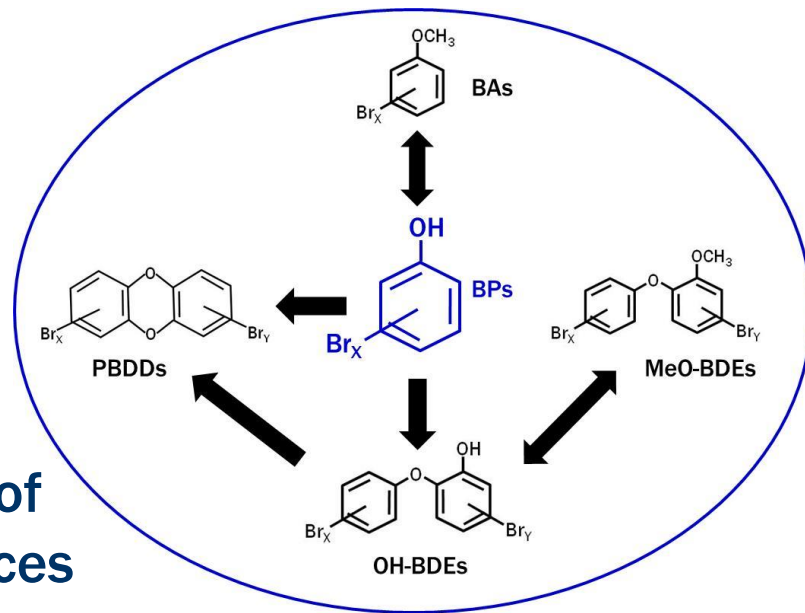
"What Goes Around Comes Around" the sea-land-sea cycle of BAs



- ❖ The catchment area of Bothnian Bay (280 000 km²) is 7 times larger than the bay itself (38 000 km²)
- ❖ Riverine drainage is an unexpected source to BB estuaries, especially for 2,4-DiBA.

Beyond BAs? A Hypothesis...

- ❖ MeO-BDEs are reported in fish¹⁻³ 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 anisoles⁴, 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 Cmps* 72, 1197-1200; 3. Nordl f U et al., 2010. *Sci Total Environ* 409, 238-246. 4. Campoy S et al., 2009. *Environ Microbiol* 11, 99-110.

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Finnish Meteorological Institute

River sampling:

Kathleen Agosta

Kenichi Shimizu

Johannes Tiwari

Paulina Viteri

