Organophosphate Esters in the Canadian Arctic Air - Conclusions from Seven Years of Observations

Roxana Sühring [1,2], Miriam L. Diamond [1], Martin Scheringer [3], Fiona Wong[4], Monika Pucko [5], Gary Stern [5], Hayley Hung [4], Phil Fellin[6], Henrik Li[6], Liisa M. Jantunen [4]

[1]University of Toronto, [2]Cefas, [3]ETH Zürich, [4]Environment and Climate Change Canada, [5]University of Manitoba, [6]AirZOne
Contact: Liisa Jantunen: liisa.jantunen@canada.ca

Conclusions

- Concentrations of organophosphate esters (OPEs) in the Canadian Arctic air exceed those of the brominated flame retardants (BFRs) by orders of magnitudes
- Chlorinated OPEs (Cl-OPEs) in air seem to be primarily transported via the water-phase (rivers/oceanic currents)
- TnBP and EHDPP in air seem to have local sources
- TPhP air concentrations are increasing significantly

Introduction

- The Canadian Arctic is under pressure from climate change, industrial/oil/gas exploitation, destruction of habitats and chemical pollution
- OPEs have previously been reported in samples from the European Arctic even though they have been deemed "non-persistent"
- OPEs are used in various consumer products and are proposed as "environmentally friendly" alternatives for restricted BFRs including PBDEs

Figure 1: Air sampler on the bow of the CCGS Amundsen

Objectives

Through the observation of OPEs over several years and the comparison of land- and ship-based sampling results, we aimed to identify geographic and temporal trends, as well as indications of the processes determining the observed OPE patterns

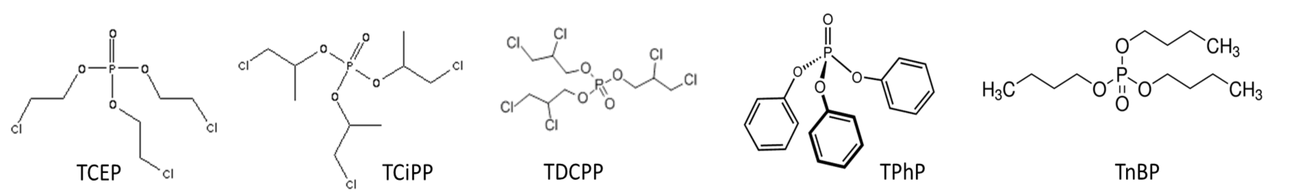

Figure 2: The most frequently detected OPEs

Methods

- 117 active air samples (glass-fibre filter fraction) from ship and 2 land-based sampling stations
- 7 years of sampling (2007-2013)
- Soxhlet extraction overnight with dichloromethane – no further cleanup required
- Instrumental analysis using GC-EI-MSD, GC-ECNI-MSD (DB 5 column, 30 m, 0.25 mm i.d., 0.25 µm)
- Deuterated and ^{13}C isotope labelled standards; recoveries 79 – 116%

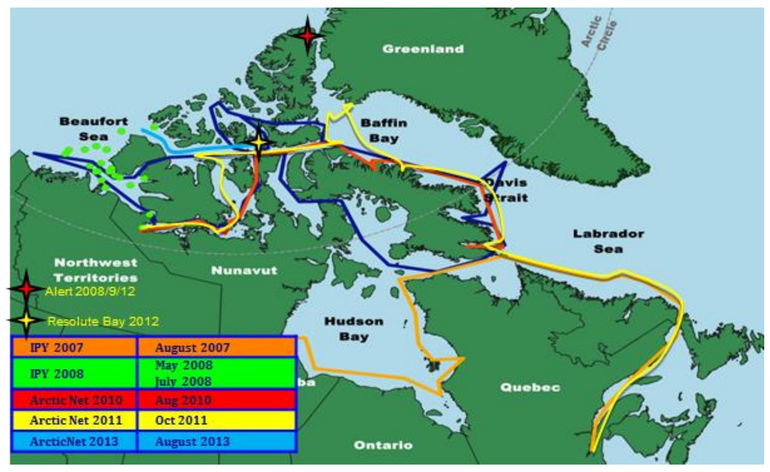

Figure 3: Cruise tracks between 2007-2013.

Results and Discussion

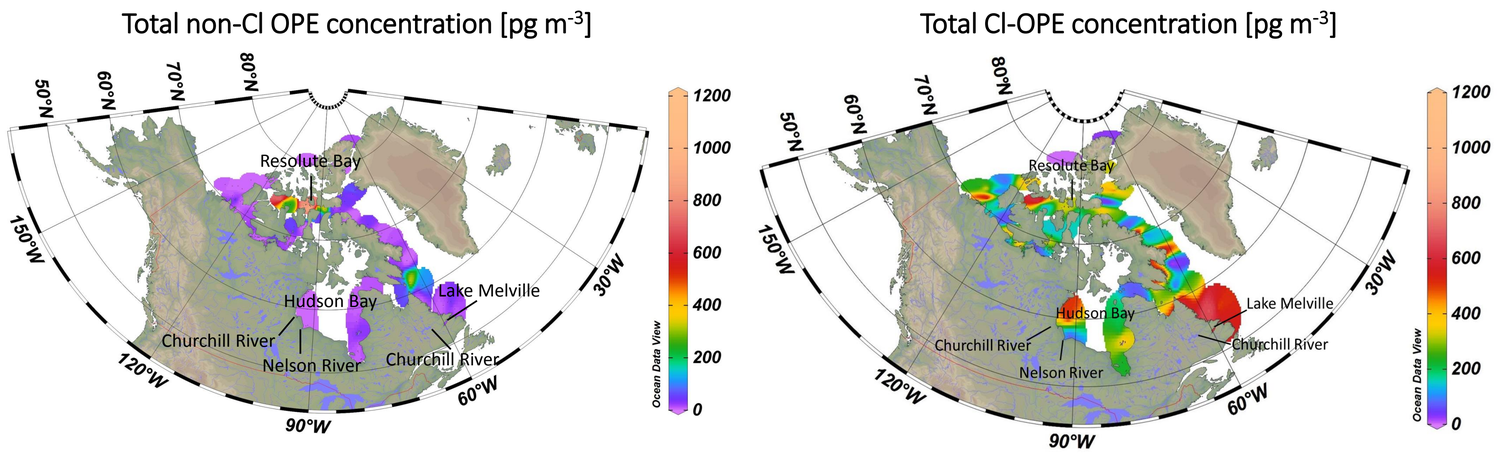

Figure 4: Concentration of total non-Cl-OPEs [pg m^{-3}] (left) and total Cl-OPEs [pg m^{-3}] (right) in the Canadian Arctic

Geographic Distribution

- Non-Cl OPEs: no geographic trend (Figure 4)
  - Local sources for TnBP, EHDPP
  - All others: diffuse sources
- Cl-OPEs: significant negative correlation with increasing latitude
  - Sources close to population areas
  - Hotspots around river mouths (Figure 4)

Driving Factors for OPE Patterns and Temporal Trends

- **Non-Cl OPEs**
  - Local sources for TnBP and EHDPP, in case of TnBP likely from the use in aircraft fuel at the Resolute Bay airport
  - All other non-Cl OPEs seem to have diffuse sources likely from atmospheric transport
  - TPhP was only OPE with a significant temporal trend: increase of >100% per year
- **Cl-OPEs**
  - Negative correlations with latitude and positive correlations with temperature suggest population areas such as Quebec City as sources
  - Hotspots around the river mouths of the Nelson and Churchill rivers suggest water-based transport, this is congruent with the higher persistence (P_{OV}) in water and therefore higher characteristic travel distance (CTD) in water of Cl-OPEs compared to non-CL OPEs (Table 1)
  - Cl-OPE concentrations seemed to be constant or decreasing, however that could be an artefact of dilution due to increased river discharge

Table 1: Estimated characteristic travel distance (CTD) and persistence (P_{OV}) in air and water for Cl-OPEs (top) and non-Cl OPEs (bottom) by the OECD P_{OV} and LRTP Screening Tool

	CTD air [km]	CTD water [km]	P_{OV} air [h]	P_{OV} water [h]
TCIPP	135	523	28	305
TDCPP	107	445	239	259
TCEP	173	300	51	174
TTBPP	2861	1	161	0.60
TPPP	2857	1	90	0.60
TDMPP	2808	1	83	0.60
TEHP	2601	24	23	16
EHDPP	1363	80	36	46
TCP	734	93	6.4	0.60
TPhP	434	70	6.8	41
TnBP	67	21	0.38	12
TBEP	41	73	36	42

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