

20 Years of Air-Water Gas Exchange Observations for Pesticides in the Western Arctic Ocean

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Introduction

Persistent Organic Pollutants are transported to the Arctic by air and ocean currents.

Sampling in the Western Arctic has been done at land based stations and on cruises from 1993-2013 by the same team.

Target compounds are pesticides, legacy and current use.

Here we report the time trends and air-water exchange of pesticides in the western Arctic.

Rationale

Understanding the processes and current state of air-surface exchange helps to interpret environmental exposure and evaluate the effectiveness of international protocols and provides insights for the environmental fate of new and emerging chemicals.

Sampling Techniques



air sampler

submersible water sampler

rosette water sampler

Target Compounds: OPEs

• Legacy Pesticides

• Chlordanes (TC, CC), Nonachlors (TN, CN), Dieldrin (DIEL), Heptachlor epoxide (HEPX), Toxaphene (Σ CHBs).

• Trifluralin (TFN), Dacthal (DAC), Chlorothalonil (CHT), Endosulfan (ENDO-I, ENDO-II, ENDO-SUL), Chlorpyrifos (CPF) and Pentachloronitrobenzene (PCNB and its metabolite pentachloroanisole (PCTA)).

Materials and Methods

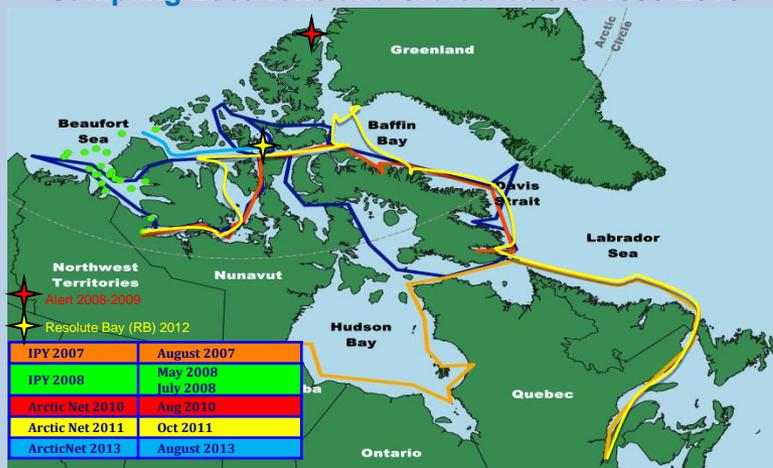
• Water: 40-100 L were processed through a glass-fiber filter followed by XAD-2 resin, pesticides are mainly dissolved.

• Air: 400-1500 m³ were sampled with a glass fiber filter – PUF/XAD cartridge, pesticides are mainly found in the gas phase.

• Pesticides were determined by capillary GC using a DB-5 column, with detection by ECNI-MS mode.

• Labelled surrogates (¹³C and deuterated) were added to each sample to monitor recoveries (range from 67-109%).

Sampling Locations and Cruise Tracks 1999-2013



Resolute Bay (RB) 2012

IPY 2007 August 2007

IPY 2008 May 2008

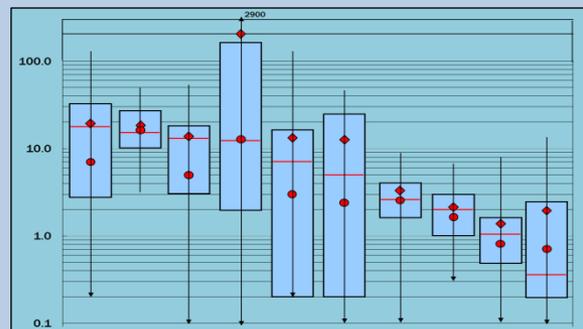
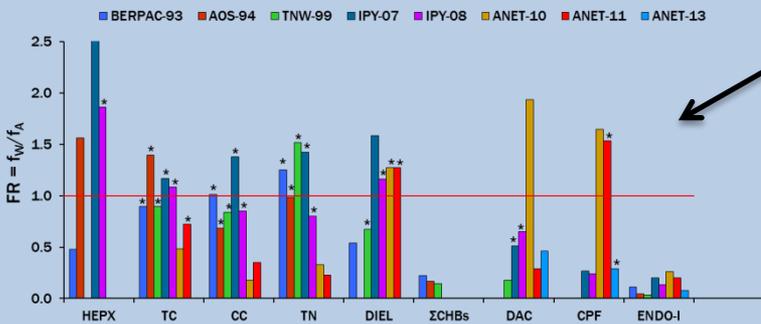
Arctic Net 2010 July 2010

Arctic Net 2011 Oct 2011

Arctic Net 2013 August 2013

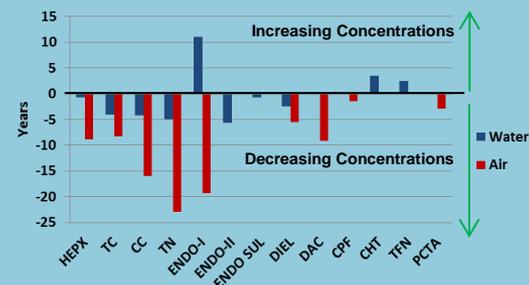
Results and Discussion

- Concentrations of legacy pesticides have declined in surface water
- Some current use pesticides increased (ENDO-I, CHT, and TFN) or showed no significant change (CPF and DAC) in surface water
- Most pesticides declined or had no significant change in air.
- The rate of change in air concentrations is slower than changes in water, probably do to continuing secondary sources to the air.
- Water-air fugacity ratios indicated net volatilization ($FR > 1.0$) or near equilibrium (FR not significantly different from 1.0) for most legacy compounds but net deposition ($FR < 1.0$) for Σ CHBs. Net deposition was shown for ENDO-I on all expeditions, while the net exchange direction of other CUPs varied.



Box-and-whisker plots of legacy and current use pesticides in arctic surface water; arranged by median concentrations (red bars). Red diamonds and dots are arithmetic means and geometric means, respectively. Vertical bounds of boxes indicate 25th and 75th percentile, whiskers indicate the range, with lower arrows for samples below the IDL.

50% Change in Concentration ($t_{0.5, y}$)



The length of time required for a 50% change in pesticide concentrations in water and air ($t_{0.5, y}$). Positive numbers are increases in concentration, where negative are declines in concentration. Missing values indicate no significant change in air or water concentrations.

Water/air fugacity ratios, $FR = f_w/f_a$, of pesticides on arctic expeditions. Bars without asterisks (*) indicate significant ($p < 0.05$) net volatilization ($FR > 1$) or deposition ($FR < 1$), while those with asterisks indicate exchanges not significantly different from equilibrium ($FR = 1$).

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