The role and significance of the Arctic for the cycling and fate of Persistent Organic Pollutants (ARCPOP)

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Introduction

Polar environments are particularly vulnerable to contamination by semi-volatile organic compounds due to the ability of these chemicals to undergo long range transport (in air and ocean currents) and accumulate in compartments such as surface ocean waters, snow/ice, tundra soils and biota. The cold conditions, coupled to low biological productivity and periods of darkness all serve to promote chemical longevity in this environment.
ARCPOP is a NERC-funded project that is part of the International Polar Year (2007-09) (IPY) to investigate the geochemical cycling of organic pollutants between the atmosphere, snow & ice-surfaces and ocean waters. ARCPOP is organized into the OASIS (Ocean-Air Sea-Ice Snowpack) cluster of IPY projects and is aimed at investigating two key areas:

- Transfer of pollutants between the air and surface ocean waters and investigating biologically-mediated transport to deeper waters and air-water exchange.
- The role of snow in storing and delivering atmospherically-derived pollutants to arctic surfaces;

Both these science areas will involve ship-based campaigns as part of the IPY programs and involve collaborative efforts with a group of international partners.

Materials and Method

Recent fieldwork has been undertaken in conjunction with the Circumpolar Flaw-Lead System Study (CFL), utilizing the Canadian ice-breaker CCGS 'Amundsen' in the Canadian Arctic during the International Polar Year (IPY). From March to June 2008, researchers from Lancaster University joined the 'Amundsen' located in the eastern part of the Beaufort Sea near Banks Island. Measurements of air, sea-ice snow and seawater have been conducted for a range of persistent organic pollutants (POPs) and emerging compounds, such as polybrominated diphenyl ethers (PBDEs) and PFCs (perfluorinated compounds). In addition, fieldwork trips are also being planned to UNIS on Svalbard (Figure 1b) in conjunction with Dr Roland Kallenborn.
Whenever possible, integrated sampling was conducted combining air, snow, ice and seawater sampling at various CFL stations. Due to the diversity of target analytes, separate sampling equipment and strategies where adopted. These were roughly distributed between 'large volume' techniques for legacy POPs, and 'low volume' sampling methods/techniques for PFCs.

Air Sampling

A high-volume (Hi-Vol) air sampler was used to collect aerosol and gas phase on a glass fibre filter (GGF) and on a Polyurethane Foam (PUF), respectively. 36-48 h samples were taken for 'legacy' POPs, with the sampler deployed both on the ice (Figure 2), approximately 50 m upwind of the ship and on the roof of the wheel-house/bridge. In addition, 10 air samples using a 25g PUF/XAD/PUF vapour trap were taken for PFAS.
Passive air samplers (PUF-disk samplers) were deployed at different locations on the ship, both indoor and outdoor, to assess ship-based contamination, particularly for polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Elevated levels of these compounds have been found in many marine research vessels and deployment of PUF-disk samplers will serve as a useful quality control for the contaminant group as a whole. PUF-disk samplers (3) were located on the meteorological mast at different heights at the bow of the ship (Figure 3a) and on the top bridge (2) (Figure 3b). These may reflect true contaminant levels in the Arctic marine boundary layer and will be compared to indoor samplers deployed within the laboratory and covered deck of the stern of the ship.

Seawater samples

Large volume seawater samples were collected for POPs using a dedicated onboard Teflon-lined seawater line.

Seawater proceeding from the well-mixed surface layer (~7 m depth) passed through an in-line GFF filter and XAD-cartridge system (Figure 4), which operationally collect the respective particle-bound and dissolved fractions of POPs. Due to some problems encountered with the seawater-line (notably rust-like deposits) seawater samples comprising of volumes of <500 L were collected and will be analysed for OC pesticides. 4 large volumes seawater samples were collected with Infiltrex system directly from the ice.
Low-volume samples (2-4 L) for particulate and dissolved phase were taken at different stations for PFAS. After drilling a hole in the ice, water was collected using a Teflon-free Niskin Bottle from beneath the sea-ice and 5 m below the ice edge. Filtered water was loaded on SPE cartridge in the ship lab (Figure 5). Filters and cartridges were frozen to successive extraction and analysis at Lancaster lab.

Snow & ice samples
Three 50L gas-tight snow sampling cans (Figure 6) were deployed at different stations to collect sea-ice snow samples for OC pesticides. After snow melt into the can, water was filtered through a GFF filter and XAD column to separate particle from dissolved phase (Figure 7).
Snow-cans were also used to collect and melt sea-ice cores and low volume (2-4 L) snow samples to determine PFAS contaminant levels.

The following contaminants classes will be examined with the help of international collaborators.

- POPs i.e. OC pesticides, PCBs and PBDEs will be analyzed at Lancaster laboratory by gas chromatography/electronic impact–mass spectrometry (GC/EI–MS)[1].
- PFAS in air: i.e. fluorotelomer alcohols (FTOHs) as well as fluorinated sulfonamides and sulfonamidoethanols (FOSAs/FOSEs) will be analyzed at Lancaster University and at Environmental Canada in Toronto. Analytical methods for volatile PFAS[2] include gas chromatography/chemical ionization–mass spectrometry (GC/CI–MS).
- PFAS in water: i.e. perfluorinated carboxylic acid (PFCAs) and perfluorooctane sulfonate (PFOS) will be analyzed in collaboration with Dr Ralf Ebinghaus at GKKS in Germany by liquid chromatography/mass spectrometry (LC–MS).

Results and discussion
The CFL study system represents a unique opportunity to study arctic marine ecosystem in the Beaufort See. Samples collected during CFL campaign will be analyzed throughout the rest of 2008. Understanding the physical transport and biogeochemical cycling of organic is of particular importance to assess the impact of persistent bioaccumlative toxins in arctic foodwebs, with subsequent biomagnification in arctic fauna[3].
Contaminants concentrations in snow will be related to snow physical properties as well as concentrations observed in air and underlying seawater. Inter-compartmental transfer and chemistry of this class of contaminants will be examined to evaluate air-snow-sea ice-seawater-biota interactions.
Collaboration with Drs Tom Harner and Mahiba Shoeib from Environment Canada will provide an extended data set for PFCs in air to study the presence of perfluoroalkyl substances, particularly in remote regions of the world. Time series for those chemicals covers winter, spring and summer embracing different ice cover and meteorological conditions. Air data in conjunction with water results might help to shed light on origin and transport pathway of PFCAs into the Arctic Ocean. Both the atmospheric oxidation of volatile precursor compounds, such as the FTOHs, and the long-range oceanic transport of directly emitted PFCAs are considered to be responsible of the bulk of the PFCA input to the Arctic[4,5].

Future fieldwork campaign at Svalbard will provide useful data set to compare arctic regions influenced by different air masses and water circulations.

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References
1.Gioia R., Nizzetto L., Lohmann R.,Dachs J., Temme C. and Jones, K. C. *Environ. Sci. Technol*. 2007; 42: 1426-1422
2. Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C. *Journal of Environmental Monitoring* 2007 ; 9:530-541
3.Tomy G. T., Budakowski W., Halldorson T., Helm P. A., Stern G. A., Friesen K., Pepper K., Tittlemier S. A. and Fisk A. T. *Environ. Sci. Technol*. 2004; 38: 6475-6481
4.Jahnke A., Berger U. Ebinghaus R., Temme, C. *Environ. Sci. Technol.* 2007; *41*, 3055-3061.
5. Simcik M. F. *Journal of Environmental Monitoring* 200; 57: 759-763

Figure 1: Banks Island and Amundsen Gulf in the Beaufort See (a) and Svalbard Island (b)

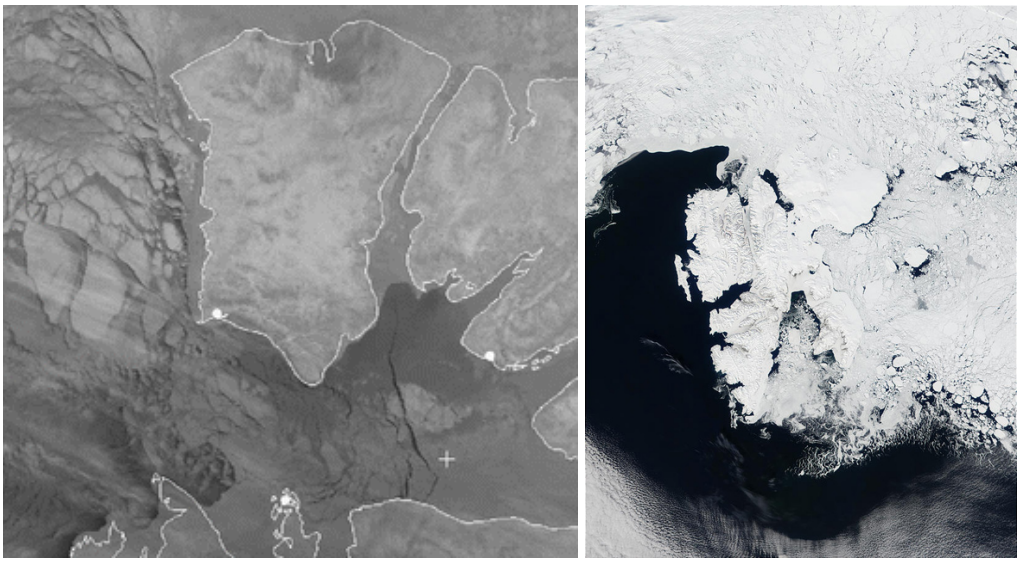

Figure 2: Hi-vol air sampler deployed on the ice

Figure 3: PUF disk on the meteorological mast (a) and on the top bridge (b)

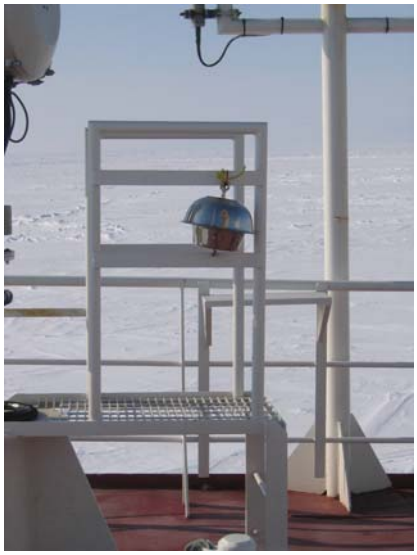

Figure 4: Onboard seawater sampling line.

Figure 5: Extraction system for PFCs.

Figure 6: Snow-cans deployed on the ice

Figure 7: Snow-can melt-water extraction