

ACCUMULATED ORGANIC CONTAMINANTS IN ICE CORES FROM SVALBARD: CONSIDERATIONS OF A FUTURE SOURCE TO THE ENVIRONMENT

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ABSTRACT

Since 1998 we have analyzed various persistent organic contaminants in ice cores collected from three ice caps and glaciers on Svalbard, including Holtedahlfonna (2005) to the west, Austfonna (1998) to the east, about 220 km apart, and Lomonosovfonna (2009) between them. All contaminants observed have been delivered to the sites by long-range atmospheric transport.

We selected the most highly accumulated contaminants (in ng cm⁻²) in each of five compound classes (brominated flame retardants, polychlorinated biphenyls, legacy pesticides, current-use pesticides (CUPs), and industrial halobenzenes (HBs). Compounds from these groups cover vapor pressures (VP) ranging over >11 orders of magnitude (231 Pa to 6.23 x 10⁻¹⁰ Pa), and include compounds considered to be too volatile to be deposited (1,4-dichlorobenzene) and others once thought to be too non-volatile for long-range transport (decabromodiphenyl ether, BDE-209). Chlorpyrifos, the most abundant CUP, has OH[•] reaction rate suggesting atmospheric lifetime ~5 hours which is too short for long-range transport.

The relative burdens of these compounds is uncorrelated to physical-chemical properties vapor pressure (VP) or OH[•] reaction rate. Other factors are contributing to the accumulated burdens of these compounds and likely include emissions, and efficiency and geography of transport.

These results show that a wide range of organic contaminants needs to be analyzed when considering what compounds are accumulating in the polar regions and which will be released when polar ice eventually melts.

Keywords: Svalbard, ice cores, long-range atmospheric transport, pesticides, flame retardants, chlorinated biphenyls, halobenzenes, vapor pressure, hydroxyl radicals

1. Introduction

The Arctic is a region characterised by low summer air temperatures, long periods of continuous darkness, long periods of continuous light, dry air, and low precipitation. It is also a region of few sustainable human resources. The combined physical characteristics result in low levels of human population. Because of low human population, no agriculture, and few industrial bases, the presence of contaminants in the Arctic is expected to be low.

Contaminants that are found in remote sites in the Arctic are assumed to have reached there through long-range atmospheric transport (LRAT). Historically, the process was thought to involve vaporization of contaminants into the gas phase at source areas (agricultural or industrial) with later condensation in colder climates from which they would never again vaporize, leading to net accumulation (Wania & Mackay 1996). In addition, it is thought that decomposition processes are slower in the Arctic because of low air temperatures and seasons with no atmospheric photolysis or oxidation. As recently as 2003 it was assumed that low-volatility chemicals associated with particles would not be subject to long-range transport to remote areas (Wania & Dugani, 2003).

2. Methods

Beginning in 1998, we drilled ice cores from three sites on Svalbard (Figure 1). Holtedahlfonna, on the west, was sampled in 2005 at 1150 meters above sea level (m.a.s.l.). Austfonna, about 220 km east-northeast from Holtedahlfonna, was sampled in 1998 at ~750 m.a.s.l. Lomonosovfonna, between these two sites was sampled in 2009 at 1200 m.a.s.l.



Figure 1: Map of Svalbard showing the three ice core drilling sites at Holtedahlfonna (2005), Lomonosovfonna (2009) and Austfonna (1998).

Core segments were shipped frozen to the laboratory where they were melted and pumped through an absorbent which was extracted in solvents and analysed for contaminants in five general categories, including halobenzenes (HB) (15 compounds), polychlorinated biphenyls (PCBs) (209 compounds), brominated flame retardants (BFRs) (15 compounds) and legacy and current use pesticides (CUPs) (64 compounds). Details of the analytical methods appear in Garmash *et al.*, 2013, Hermanson *et al.*, 2010, Ruggirello, *et al.*, 2010, and Hermanson *et al.*, 2005.

For this study, we calculated the abundance of each compound in the core, identified as a “burden” expressed in ng cm^{-2} a measure of the total mass of contaminant in the core, normalized to the cross sectional core area (there was some variability in core diameters). The most abundant compound in each category was selected for discussion here, along with the least and most chlorinated PCBs. For CUPs and BFRs the two most abundant were selected. For each category, the selected contaminants are 1,4-dichlorobenzene (1,4-DCB) for HBs, PCB-1, PCB-70 and PCB-209 for PCBs, Chlorpyrifos and α -Endosulfan (CUPs), Dieldrin (legacy pesticide), and hexabromocyclododecane (HBCD) and BDE-209 for the BFRs.

Here we compare the relative abundances of these selected compounds to vapor pressure and OH \cdot reaction rate, two factors thought to play large roles in identifying compounds expected to reach and accumulate in the Arctic (Wania & Mackay, 1996).

3. Volatility and oh \cdot reaction rates of selected contaminants

The VP values for each of our nine compounds is shown in Figure 2, and range from 232 Pa for 1,4-DCB to a low of 6.23×10^{-10} Pa for BDE-209. In general, 1,4-DCB would be considered to have no deposition anywhere, while BDE-209 would be considered to have low mobility because of its low VP and apparent association with atmospheric particles. HBCD, α -endosulfan and PCB-209 would also be considered to have low mobility (Wania & Mackay, 1996).

The OH \cdot reaction rates are shown in Figure 3. Chlorpyrifos has a rate 1 order of magnitude higher than any other compound, and has an atmospheric lifetime <5 hours (Ruggirello *et al.* 2010).

Dieldrin and a-Endosulfan have lifetimes 42 and 48 hours, respectively. These compounds would theoretically oxidize before reaching the Arctic. HBCD is expected to be similar. PCB-70 and 1,4-DCB are expected to have lifetimes 500 hours or longer, while PCB-1 would be estimated ~250 hours. Finally, PCB-209 and BDE-209 would have very long lifetimes, in part because particle-associated compounds are expected to have extremely low OH[•] reaction rates. During the dark season, all of these compounds would have long lifetimes because of no chemical reaction from UV radiation (including OH[•] Production) and could reach the Arctic, however, pesticides are not used during the dark season so the effect on Chlorpyrifos, Dieldrin and a-Endosulfan would be negligible.

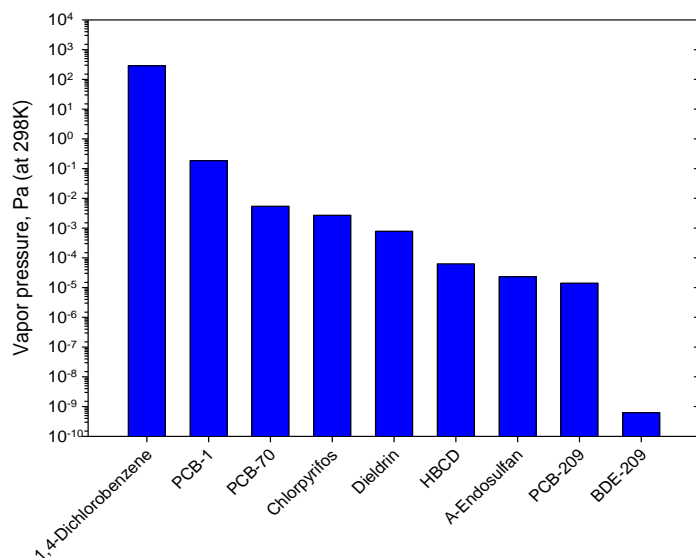


Figure 2: VP values for nine compounds found on Svalbard.

Source: <http://www.srcinc.com/what-we-do/environmental/scientific-databases.html>

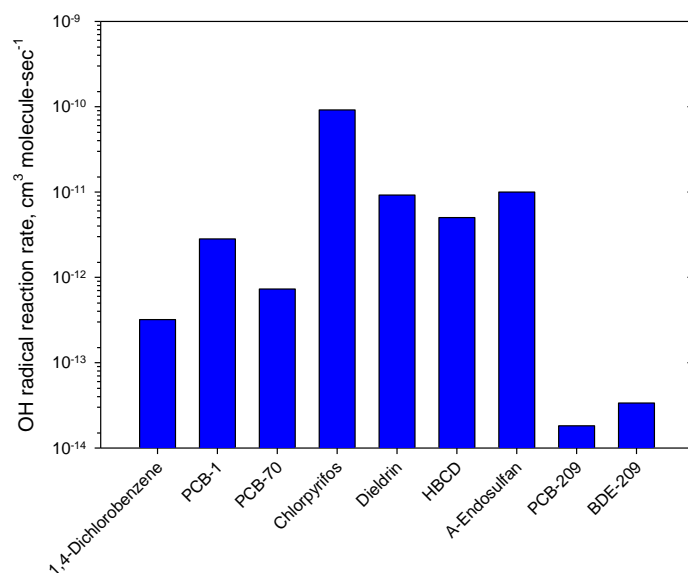


Figure 3: OH[•] Radical reaction rates for nine compounds found on Svalbard.

Source: <http://www.srcinc.com/what-we-do/environmental/scientific-databases.html>

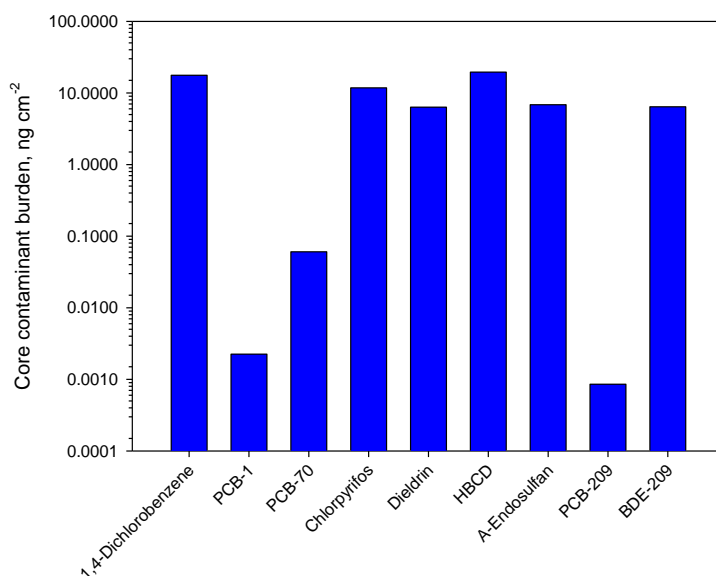


Figure 4: Maximum burdens of contaminants from ice cores on Svalbard.

Source: references Garmash *et al.*, 2013, Hermanson *et al.*, 2005, 2010, Rugirrello *et al.*, 2010.

4. Abundances (burdens) of nine selected compounds on svalbard

The ice-core burdens of our nine selected compounds are shown in Figure 4. The results show clearly that four of the most abundant compounds (1,4-DCB, Chlorpyrifos, HBCD and BDE-209) should not be found at all either because they are too volatile (1,4-DCB), associated with particles (HBCD and BDE-209) or too reactive with OH[·] (Chlorpyrifos). In fact, there is a weak and not significant correlation between burden and VP ($r = 0.5096$, $\rho = 0.16$) and between burden and OH[·] reaction rate ($r = 0.2269$, $\rho = 0.56$) showing that for these contaminants in Svalbard ice cores, the conventional interpretations and assumptions about movement to the Arctic and accumulation there are not valid.

5. Conclusions

The weak relationship between accumulated burdens of different classes of contaminants in ice cores on Svalbard with vapor pressure and OH[·] reaction rate indicates that other factors involving these compounds are apparently more important in identifying them as being subject to transport, persistence and accumulation in the Arctic. Among them are likely to be magnitude of emissions (and use) and effectiveness of air mass transport. The locations of the emissions and transport geography are important considerations.

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