RECENT FINDINGS OF ATMOSPHERIC POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND ORGANOCHLORINE PESTICIDES (OCPs) UNDER THE ARCTIC MONITORING AND ASSESSMENT PROGRAMME (AMAP)

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Abstract

The multi-year measurements of organic contaminants at Alert, Nunavut, Canada showed different inter-annual variations in the Arctic atmosphere: increasing tendencies for polybrominated diphenyl ethers, which were widely used as flame retardants; very slow decrease for currently-used pesticide endosulfan I; and continuous decline for legacy chlordane-related compounds. This suggests that global usage/emissions and their subsequent transport routes to the Arctic likely differ for various contaminant groups. Comparison of air measurements among different Arctic stations may provide insights into global emissions and atmospheric transport of these contaminants to the Arctic. Air measurements of organochlorine pesticides (OCPs) were available for 2000-2003 at six Arctic stations, namely Alert, Kinngait and Little Fox Lake in Canada; Point Barrow in Alaska, US; Valkarkai in Russia; and Zeppelin in Norway. As these stations cover a large area of the Arctic, the multi-year dataset provides a circumpolar perspective of atmospheric OCPs. Endosulfan I showed homogeneous behaviour in November-May, whereas large spatial divergence was found in June-October, which coincided with application seasons in the south. On the other hand, homogeneous behaviour of chlordane-related compounds indicated that influence of primary emissions on Arctic air was less important in 2000-2003. Chlordane currently observed in Arctic air is mainly from secondary emissions.

Introduction

Air monitoring of organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons, and polychlorinated biphenyls (PCBs) are being continuously conducted at Alert (Nunavut) since 1992 under the Northern Contaminants Program, as part of the Arctic Monitoring and Assessment Programme (AMAP).[1] Starting in 2002, polybrominated diphenyl ethers (PBDEs) are being analyzed in all air samples at Alert. One primary goal for the monitoring program at Alert is to derive long-term trends of organic contaminants in Arctic air. This dataset may further help to track potential sources of organic contaminants and changes in emissions,[2] since air concentrations in the Arctic reflect global usage/emissions.[3] Emissions of organic contaminants differ around the world and their influence on the Arctic varies. It is necessary to understand spatial variations and seasonality of these chemicals in the circumpolar atmosphere. By studying spatial distributions, global emissions of these chemicals and their subsequent influences on the Arctic could be better understood: homogeneous spatiality may indicate lack of primary emissions worldwide, whereas large spatial divergence suggest ongoing emissions in source regions and their different influences on various Arctic sites.[4] Atmospheric measurements of organic contaminants have been conducted at several Arctic stations over different time periods since the 1990s.[1] In 2000-2003, air measurements of OCPs were available at five Arctic stations in addition to Alert. This unique dataset provides information for a more recent assessment of their spatial distributions compared to previous work.[4] This current study presents inter-annual variations of PBDEs in 2002-2004 and long-term trends of two selected OCPs from 1993-2001 observed at Alert. Spatial/seasonal variations and their potential emission sources of the OCPs are then discussed.

Materials and Methods

Six Arctic sampling stations are shown in Figure 1: Alert (ALT), Little Fox Lake (LFL), Kinngait (KNG) in Canada; Point Barrow (PTB) in USA; Valkarkai (VKK) in Russia; and Zeppelin (ZPN) in Norway. Weekly high volume samples representing ~13000 m^3 of air were taken over seven days at five sites, except for ZPN, where 48-h sampling collected ~1000 m^3 of air every week. Each sample set consisted of one glass fiber filter (GFF) and two polyurethane foam (PUF) plugs. Samples were prepared and extracted by AirZone One for ALT, KNG, LFL, and PTB, while VKK samples were treated by the Typhoon Laboratory in Russia. Extracts of the five sites were analyzed by Freshwater Institute, Canada. The samples at ZPN were collected, treated, and analyzed by the Norwegian Institute for Air Research (NILU). GFF and PUF blanks were taken once every four weeks at all stations. Detailed description of field sites, sampling processes, analytical methods and detailed QA/QC procedures can be found elsewhere.[2, 4,5]

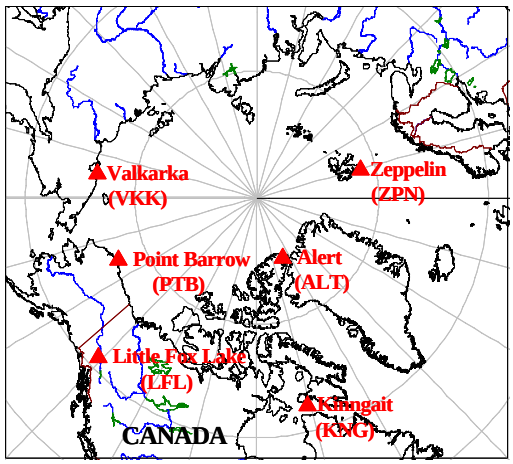

Figure 1. Map of stations.

Results and Discussion

PBDEs are flame retardants applied to commercial products, such as polyurethane foam, textile and plastics,[6] and can be gradually released to the environment. Their presence in various environmental media in remote areas, such as the Arctic, has raised international concern as they may exert persistent-organic-pollutant-like (POP-like) characteristics. Measurements in 2002-2004 show that BDE-28/33, 47, 99, 100, 153, 154, 183, and 209 were frequently detected, suggesting that PBDEs in Alert air were likely influenced by usage of "penta-BDE" and "deca-BDE" technical mixtures worldwide. Apparent seasonality in summer time may indicate that less brominated PBDEs could originate from volatilization emissions in a local and/or regional scale. Long-range transport inputs were also likely to be important in winter time when episodically elevated concentrations of PBDEs were observed. Long-term trends were previously developed for atmospheric OCPs and PCBs observed at Alert using a digital filtration (DF) technique.[2] Temporal trends and seasonal cycles of BDE-47, 99 and 154 (2002-2004) developed by DF are shown in Figure 2. An apparent first order halflife, $t_{1/2}$, can be estimated by dividing ln 2 with the negative value of the linear regression slope of the trend line. Results show that concentrations of 8 major PBDEs (i.e., BDE-28/33, 47, 99, 100, 153, 154, and 209) increased inter-annually in 2002-2004 with doubling times of 2-6 years. The doubling times of PBDEs observed in Arctic air are similar to the growth rates found previously in biotic samples. [7] It indicates that global emissions of PBDEs and their consequent influences on the Arctic were increasing. This highlights the potential risk that this group of chemicals posed on the Arctic ecosystems. Note that the doubling times are derived from the 3-year measurements in this current study, and should be regarded as a first and general indication of increasing tendencies of PBDEs in Arctic air. Air monitoring of PBDEs is currently ongoing, and long-term trends of PBDEs can be studied after additional years of air measurements become available at Alert.

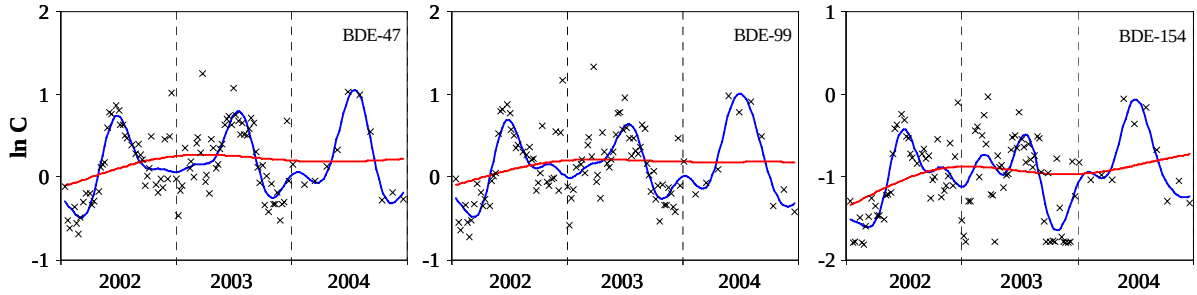

Figure 2. Seasonal cycles, inter-annual trends, and measurements for atmospheric BDE-47, 99 and 154 at Alert.

Endosulfan is a widely used insecticide and its presence is found in various environmental media, for example,

atmosphere and seawater.[8] Technical endosulfan is composed of endosulfan I (Endos I) and II. Application of endosulfan has raised environmental concerns because of its bioaccumulation potential, high toxicity,[9] and potential for LRT.[5] Temporal trends and seasonal cycles of Endos I (1993-2001) are developed by DF and shown in Figure 3A. An apparent first order halflife $t_{1/2}$ of 62 yr was estimated for Endos I during 1993-2001, indicating that air concentrations of Endos I were declining very slowly or remain stable in the Arctic. This likely reflects the current usage of technical endosulfan in mid-latitudes which sustained its level in Arctic air. Figure 3B shows the monthly concentrations of Endos I at five Arctic stations. It is apparent that Endos I is generally evenly distributed throughout the circumpolar atmosphere between November and May. Monthly air concentrations of Endos I varied approximately by a factor of 2 among the five sites during this period of time (except for February), indicating that primary emissions were likely less important during this period. However, large spatial divergence appeared between June and October (dashed box in Figure 3B). This is not surprising since endosulfan is a current-use OCP. Technical endosulfan is usually applied in summer time, and relatively high concentrations of Endos I were previously reported in source regions and nearby areas.[9] Large spatial differences in the circumpolar atmosphere in June-October could be attributed to applications of Endos I in source regions followed by transport to the Arctic. A recent study indicates that Endos I was subjected to net deposition potential from air to seawater in the Arctic,[6] suggesting that influences of primary emissions were still important for Endos I in the circumpolar atmosphere. The median concentration of endosulfan I was 3.2 pg·m^{-3} in the circumpolar atmosphere (n=245).

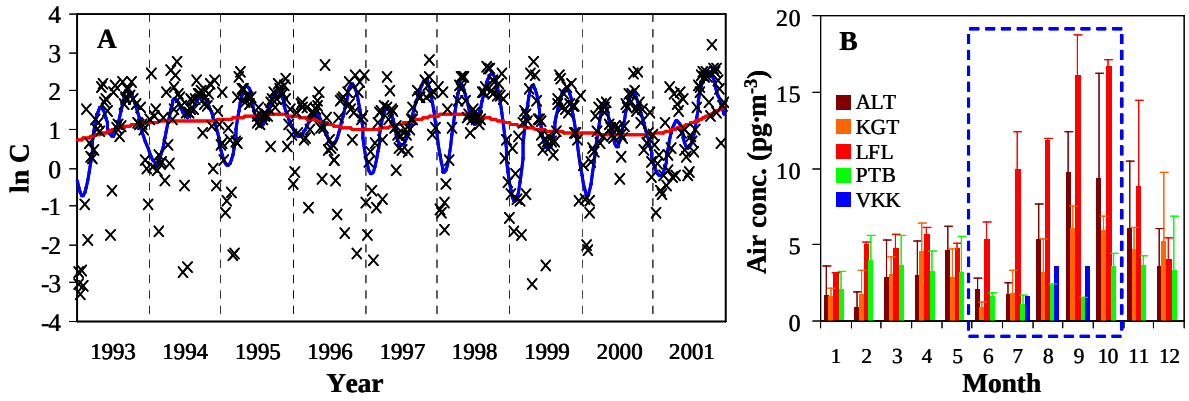

Figure 3. Seasonal cycles, inter-annual trends, and measurements for atmospheric Endos I at ALT (A), and monthly average air concentrations of Endos I at 5 Arctic stations (B).

Chlordane was mainly used in agriculture, gardening, and home building for insect and termite control before it was banned worldwide. Technical chlordane consists of *trans*-chlordane (TC), *cis*-chlordane (CC), and *trans*-nonachlor (TN); and trace amounts of heptachlor (HEPT), *cis*-nonachlor (CN), and other species.[10] Technical HEPT was also used independently and contains some TC and CC isomers.[10] Figure 4A shows temporal trends and seasonal cycles for TC in 1993-2001, a component of past-use pesticide technical chlordane. An apparent first order halflife $t_{1/2}$ of 4.9 years was estimated for TC. Similar halflives were also found for other chlordane-related compounds. In contrast to increasing tendencies of PBDEs and steady trends of Endos I, continuous declining concentrations of chlordane-related compounds were found in Arctic air. Comparison among the 6 Arctic sites shows homogeneous behaviour of chlordane-related compounds in the Arctic atmosphere. Seasonality of chlordane-related compounds was generally weak considering the variations in the dataset: monthly averages varied within a factor of 5 between January-December at five sites (excluding VKK). Figure 4B shows a box-and-whisker plot of the sum of four chlordane isomers (i.e., TC, CC, TN, and CN) (Σ_4CLD) at the six stations. Mean and median concentrations of Σ_4CLD were nearly identical among ALT, KNG, LFL, and PTB, and slightly higher concentrations of Σ_4CLD were observed at VKK and ZPN. Concentrations of Σ_4CLD appear to follow the normal distribution in the circumpolar atmosphere with mean of 1.3±0.63 pg·m^{-3} (n=413). Air concentrations of individual chlordane-related compounds are normally distributed as well. Mean concentrations (pg·m^{-3}) of TC, CC, TN, OXY, and HEPX were 0.25±0.17 (n=413), 0.59±0.26 (n=413), 0.46±0.23 (n=413), 0.31±0.15 (n=245), and 0.56±0.28 (n=244), respectively, in the circumpolar atmosphere. The

homogeneous behaviour of chlordane-related compounds in the circumpolar atmosphere is consistent with the fact that chlordane currently observed in air is mainly from secondary emissions.[11] It also indicates the effectiveness of the global emission control initiatives of technical chlordane.

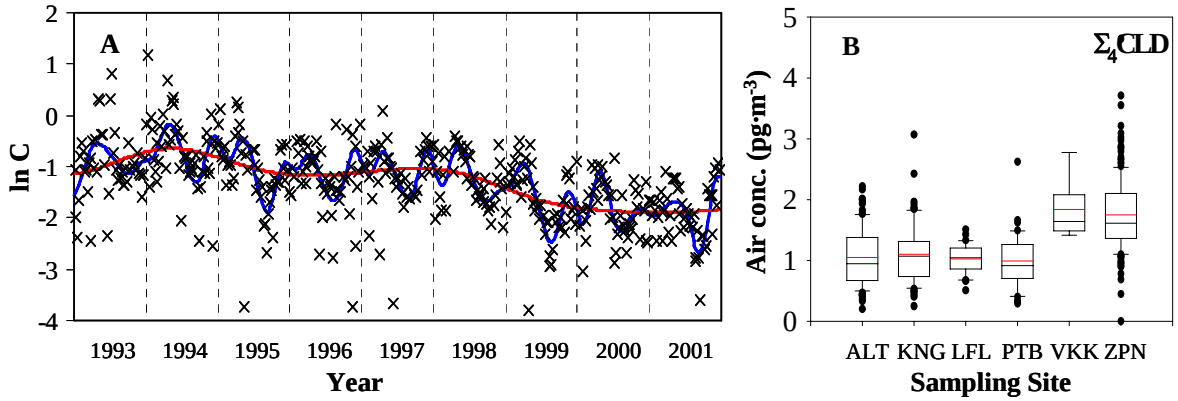

Figure 4. Seasonal cycles, inter-annual trends, and measurements for atmospheric TC at ALT (A), and Box-and-whisker plot of $\sum_4$CLD at 6 Arctic stations (B). The centre box is bounded by the 25th and 75th percentiles, and whiskers indicate the 10th and 90th percentiles. Dots are outliers of the 10th and 90th percentiles. Black and red horizontal lines represent median and arithmetic mean, respectively.

Acknowledgements
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