Seasonal variation of organochlorine pesticides at two arctic sites

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Introduction

Weekly high volume air samples were collected between July 2002 and July 2003 at Little Fox Lake (LFL) (61.35° N/135.63°W, 1128 m above sea level or m.a.s.l.), Yukon, Canada and between March 2002 and April 2003 at Point Barrow (PB) (71.32°N/156.60°W, 11 m.a.s.l.), Alaska, USA. The two sampling periods overlapped and all samples were analyzed in the same laboratory, i.e., Freshwater Institute, Canada, thus it is possible to study spatial variation of some organochlorine pesticides (OCs) without considering inter-laboratory correction. Comparison of various compounds can provide insight into their potential sources (e.g., long-range transport (LRT) or local secondary emissions) and environmental pathways at the two sites. Preliminary data analysis focuses on selected OCs, i.e., α-HCH, γ-HCH, dieldrin, pentachloroanisole (PCA), endosulfan I, and chlordanes. These compounds show significantly different air concentrations and seasonality at the two sites.

Materials and Methods

A high volume sampler was operated on a weekly basis at each site. Approximately 13000 m^3 of air was aspirated through a glass fibre filter (GFF) and two polyurethane foam plugs (PUFs) to sample the particle and vapour phase, respectively. Weekly GFF and PUFs were extracted separately using Soxhlet. Sampler operation, sample extraction, and cleanup are described in detail elsewhere.[1] GFF samples from PB were analyzed individually to obtain weekly particle-bound concentrations; whereas front and back PUF extracts were combined to provide weekly gaseous concentrations at this site. At LFL, extracts from two weekly samples (GFF and PUFs) were combined prior to instrumental analysis to obtain biweekly particle-bound and gaseous concentrations. Again, analytical methods can be found in ref. 1.

Results and Discussion

Particle-bound phase accounted for only a minor fraction of total concentration for most OCs at the two sites. Gaseous and particle-bound concentrations were combined for individual OCs in the current data analysis in order to circumvent seasonal temperature effect on gaseous/particle partitioning of some OCs. To illustrate the difference in seasonality of OC air concentrations, monthly average concentrations were calculated by averaging all samples collected in the same month (not necessarily from the same year). The monthly average concentrations were then normalized by the total concentration over the whole sampling period to enhance the seasonal profiles. Several OCs, namely, α-HCH, γ-HCH, dieldrin, PCA, endosulfan I and isomer ratios of HCHs and chlordanes are presented in Figure 1 to illustrate the difference between the two sampling sites.

Fig. 2A and 2B show monthly average temperature and monthly precipitation rate recorded at the meteorological stations of Whitehorse and Barrow (averages from 1961 to 1990), which are the closest meteorological stations to LFL and PB, respectively. Monthly rain rate, snow rate, and snow coverage at LFL are shown in Fig. 2C. In Fig. 2A, the monthly average temperature was approximately 10 °C higher at LFL (or Whitehorse) than at PB (or Barrow). Fig. 2B indicates that the annual precipitation rate at LFL was 2.4 times that of PB. Further examination of Fig. 2C reveals that the precipitation at LFL was mostly from snow between October and April, and mainly from rain between May and September when temperature was generally above freezing, whereas all precipitation was from snow at PB throughout the year. It is noteworthy that snow accumulated between November and March at LFL, and to a lesser

extent in April and October (Fig. 2C, "+" indicates snow cover in cm). However, there was usually no snow coverage from May till September.

Both α- and γ-HCH exhibited much higher concentrations at LFL than at PB, specifically in the summer time (Fig. 1A, 1C). Moreover, stronger seasonal variation of the two HCH isomers was observed at LFL (Fig. 1B, 1D). Usage of technical HCH products (generally containing 5 stable isomers of HCHs, a: 55–80 %, b: 5–14 %, g: 8–15 %, d: 2–16 %, ε: 3–5%) was banned in the US and Canada in the 1970s [2] and air concentration of α-HCH is expected to be more or less uniformly distributed among different locations. [3] Relatively low air concentrations of α- and γ-HCH with less seasonal variation at PB are consistent with this fact. However, elevated concentrations of α- and γ-HCH and strong seasonal variation at LFL suggest that secondary emissions of HCHs were important in this region. Global usage of technical HCH peaked in 1970s and significantly declined in 1980s and 1990s [2] ; therefore, direct application of technical HCH is less important in the global environment currently. However, historically when the technical mixture was widely used, these compounds can be transported via LRT and deposited in the Arctic environment. HCHs can be effectively scavenged by both snow and rain and further deposited to soils. During this period of time, there was net deposition from the atmosphere to soils since air concentrations of HCHs were relatively high. However, after primary emissions of HCHs have ceased, HCH transfer between the atmosphere and soil reversed from net deposition to net evaporation as air concentrations of HCHs decreased. Fresh snow above soils could act as an effective barrier, reducing evaporation of HCHs from occurring during the cold period. When the temperature rises above freezing (i.e., from May to September), evaporation of HCHs from soils becomes significant at LFL. This process can lead to observed elevated atmospheric concentration of α-HCH in this area. γ-HCH shows slightly different seasonal profile at LFL: γ-HCH concentration greatly increased in July compared to June. The elevated concentration of γ-HCH could be from source regions via LRT. In contrast, atmospheric scavenging of OCs at PB is expected to be less efficient than at LFL. LFL is at a higher elevation (1128 m.a.s.l.) and generally experience more precipitation (Fig. 2B) than PB. [4] Therefore, historical deposition of HCHs at PB can be expected to be less than that at LFL. Moreover, PB is covered by snow nearly year round which acts as a barrier for HCH evaporation from soil. The observed low concentrations of α- and γ-HCH reflect background air concentrations in this region. Ratio of α-HCH to γ-HCH is calculated for both sites, which is in the range of 9–21 (mean 15) at LFL and 5–15 (mean 8) at PB (Fig. 1K). The α/γ ratio of HCH technical mixture is typically between 4 and 7. The α/γ ratio at the both sites, specifically at LFL, is much higher than previous observations in the Arctic. [5,6] The surprisingly high α/γ ratio could be from: 1) secondary re-emission of previously applied HCHs with high percentage of α-HCH; 2) declined usage of γ-HCH or lindane.

Dieldrin is used as an insecticide and could also be a breakdown product of aldrin. Air concentrations of dieldrin at PB were consistently higher than that at LFL, and the difference in concentration was up to a factor of 5–6 during the summer time (Fig. 1E). Temperature at PB was typically 10 °C lower than at LFL; therefore, both biotic and abiotic transformation should be less important at PB than at LFL. The higher dieldrin concentration at PB may also be related to different source regions as a result of LRT. More work is required to illustrate this aspect, for example, tracking major source areas using Lagrangian back-trajectory calculation. Seasonal variation of dieldrin is apparent at both sites: concentration is elevated at high temperature, whereas levels decline when temperature drops (Fig. 1F).

Endosulfan I differed in both concentration and seasonal profile at the two sites. Concentration of endosulfan I was comparable during winter and early spring (cold time), but there was significant difference during the warm time at the two sites (Fig. 1G). At PB, endosulfan I was depleted during the summer time. As mentioned above, secondary emission of OCs from soils was probably less important at PB because of snow cover; therefore, observed endosulfan I could be from the result of LRT. During the warm time, less amount of endosulfan I may survive LRT to this remote area because of rapid degradation at relatively high ambient temperatures en route. However, at LFL, higher concentration of endosulfan I occurred during the warm time (i.e., summer and fall) and lower concentrations during cold time (i.e., winter and early spring), which could be a result of seasonal re-emission of secondary sources: due to elevated temperature and exposed soil with no snow cover. Variation of sources led to different seasonal profiles at the two sites, which showed nearly opposite trends (Fig. 1H).

PCA is one of several OCs which are detected in all samples at the two sites. Generally speaking, higher PCA concentration was observed during fall and winter at both sites relative to that in spring and early summer. However, during three summer months (i.e., June, July, and August), considerably higher concentration of PCA was recorded at PB (Fig. 1I, 1J). Interestingly, the temperature in this location was above 0 °C only during these three months. It is believed that PCA is an environmental metabolite of pentachlorophenol (PCP), which is restrictedly used as a pesticide and a wood preservative. Elevated PCA at PB could be from usage of PCP-treated wood or building

material at this site and subsequent transformation. PB is fairly close to the sea and increased evaporation from open water could also lead to higher air concentration of PCA during these three months. However, more study is required to illustrate this issue.

Ratio of *trans*-chlordane (TC) and *cis*-chlordane (CC) (i.e., TC/CC) can provide extra information on whether the presence of these compounds in Arctic air is due to fresh usage or previous application. Technical products of chlordane (TC/CC ~ 1.16) were banned for use in North America many years ago. The observed TC/CC ratios were normally below 1 in arctic air, which is a reflection of aged chlordane.[5] The TC/CC ratios at the two sites were fairly low. The annual average was 0.30 at LFL and yearly average of TC/CC ratio was 0.63 at PB. Seasonal profile suggests reduced TC/CC ratio during the summer and fall time (Fig. 1L). It is believed that *trans*-chlordane is more susceptible to bio-degradation.[7] Considering 10 °C higher temperature at LFL than at PB, it is understandable that bio-degradation is faster in this location, which could lead to overall lower TC/CC ratio at LFL provided that the two sites have similar emission source (e.g., LRT input). Elevated TC/CC was observed during March and May at PB. This is probably related a difference in source region influence.

Acknowledgements

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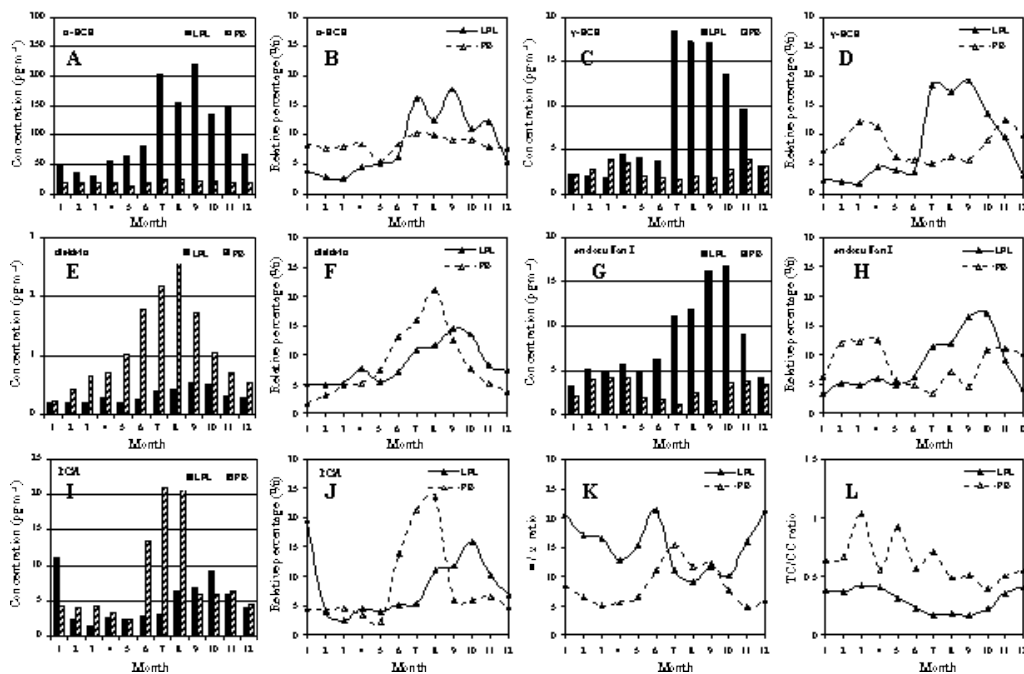7. Beeman, R.W., F. Matsumura. (1981) *J. Agric. Food Chem.* 29, 84-89.

Figure 1. Monthly concentrations and seasonal variations of α-HCH, γ-HCH, dieldrin, endosulfan I, and PCA at LFL and PB.
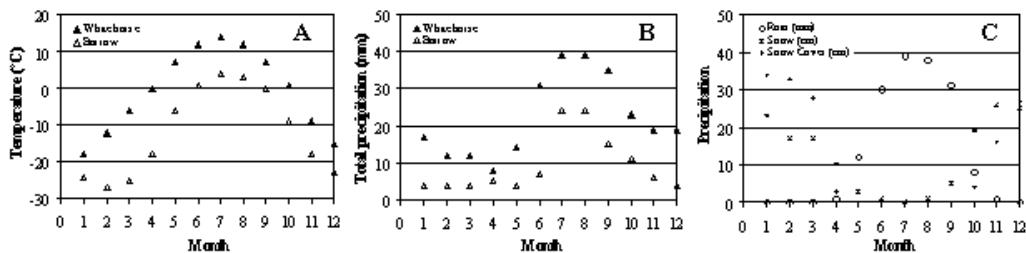

Figure 2. Monthly temperature (°C) and total precipitation (mm) are shown in A and B for both Whitehorse (60.43° N/135.04°W, 703 m above sea level) (http://www.theweathernetwork.com/weather/stats/pages/C02142.htm? CAYT0019) and Barrow (71.18°N/156.47°W, 9 m above sea level) (http://www.theweathernetwork.com/weather/stats/pages/C01873.htm). Monthly rain rate (mm), snow rate (cm), and snow cover (cm) at Whitehorse are indicated in C.