Spatial Variations in the Seasonality of Organochlorine Pesticides (OC) in Arctic Air

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Introduction

Under the Canadian-managed Northern Contaminants Program (NCP), air samples were collected at three Canadian Arctic sites, namely Alert, Nunavut (1992-ongoing); Tagish, Yukon (Dec 1992 – Mar 1995) and Kinngait, Nunavut (Mar 1994 – Feb 1996, Oct 2000 – Sep 2002), as well as Dunai Island, Russia (Apr 1993 – May 1995) and Amderma, Russia (1999-2001) to assess the levels, transport pathways and potential sources of persistent organic pollutants (POPs) in the Arctic. A simultaneous sampling period exists between March 1994 and April 1995 at Alert, Tagish, Kinngait and Dunai Island. Spatial comparisons of organochlorine pesticide (OC) seasonality from this concurrent sampling period is presented in this study.

Materials and Methods

Weekly air samples were collected with a high volume air sampler at each site. Sampler operation, sample extraction, cleanup and analysis have been described elsewhere.[1] Briefly, ~13000 m^3 of air was aspirated through a glass fibre filter and two polyurethane foam plugs (PUFs) to collect the respective particle and vapour phases. All weekly samples were analyzed individually except for 1994-1995 samples from Kinngait. Weekly air samples were taken at this site but only 19 samples were analyzed individually as weekly extracts while the rest were analyzed as four-week composites.

Results and Discussions

Among the four sites, Alert is the only location where continuous long-term air monitoring has been conducted. Figure 1 shows time series of the vapour phase air concentrations, expressed as the natural log of partial pressure, *P*, of γ-HCH, *t*-chlordane and endosulfan I measured at Alert from 1993 to 1999. The time trends and seasonal cycles were developed using the digital filtration technique. This technique has been successfully used to derive long-term trends for polychlorinated biphenyls (PCBs) and OCs measured at Alert. Details of this technique are given elsewhere.[2,3] From Figure 1, it can be seen that elevated air concentrations were generally observed before and after the warmest time of the year. This phenomenon was noted not only for the current-used pesticides, such as lindane (γ-HCH) and endosulfan, but also for banned pesticides, such as the chlordanes. To determine whether this is a unique phenomenon observed at Alert, OC gas phase air concentrations from Alert, Tagish, Dunai and Kinngait measured during the 1994-1995 co-sampling period are plotted against months of the year for comparisons. As an example, Figure 2 shows the box-and-whisker plots of *t*-chlordane air concentrations at Alert, Tagish and Dunai (left panel). For Alert, data from 8th March, 1993 to 24th April, 1995 (same as sampling period at Dunai) are used in the plots. Since there are very few data for Kinngait during this co-sampling period, as most samples were analyzed as four-week composites, a scatter plot of all data is given in Figure 2d. Also shown on Figure 2 are the box-and-whisker plots of the weekly averaged temperatures at the sites (right panel). For Kinngait, the temperatures are weekly averaged when 7-day samples were taken and four-weekly averaged when four-week composites were analyzed.

Similar to *t*-chlordane (Figure 2 left panel), many OCs showed elevated air concentrations in April and May at Alert, Tagish and Dunai. At Kinngait, this "Spring Maximum Event" usually occurred slightly earlier, beginning in March and ending in May. Spring peaks occurred for air concentrations of *c*-chlordane and endosulfan I at Alert, Kinngait and Dunai but not at Tagish; *t*-nonachlor at Kinngait and Dunai only; *o,p*'-DDE at Alert only; *o,p*'- and *p,p*'-DDT at Alert and Dunai only; octachlorostyrene at Dunai only; and tetrachloroveratrole at Alert and Tagish only. Most transformation/ metabolites of parent pesticides, i.e. oxychlordane, heptachlor epoxide and dieldrin, generally do not show spring peaks. Rather, they followed the seasonal temperature cycles and reached highest air concentrations in Arctic air in the summer.

Potential factors that may be responsible for spring OC concentration maxima in Arctic air include:

1) Spring application of current-use pesticides, e.g. lindane (γ-HCH). However, elevated spring air concentrations were also observed for banned pesticides, e.g. chlordanes, and industrial by-products, e.g. octachlorostyrene and tetrachloroveratrole.
2) "Spring pulse" which is defined as the springtime revolatilization of chemicals trapped in snowpack during winter as a result of snowmelt, rendering elevated spring air concentrations.[4] However, from Figure 2, it can be seen that local ice/snowmelt (T>0 °C with T= 0 °C indicated by the solid line on each plots) did not occur until May in Kinngait and June in Alert and Dunai, not coinciding with the spring OC concentration peaks. The only exception is at Tagish where the temperature reaches 0 °C in March. However, chemicals released from snowpacks at southern latitudes during snowmelt might be transported to the Arctic resulting in higher Arctic air concentrations.
3) Increased atmospheric removal in late spring/summer. After polar sunrise around April, removal rates of OCs by photodegradation and depletion reactions with OH radicals would increase, resulting in a decrease in air concentrations during the summertime. Yet, if this was the only reason for the seemingly high air concentrations in spring, the 'spring maximum event' should occur at all sites, not just some sites for some compounds.
4) Scavenging of OCs by forests along the transport pathway to the Arctic during the growing season. At leaf burst in late spring, the waxy cuticle on the new leaves would adsorb semivolatile organic compounds in air in the vicinity of forests. This process would reduce the

amount of chemicals in air available for transport to the Arctic, resulting in a decrease in Arctic air concentrations in late spring/summer.

It is currently not possible to explain why only certain OCs showed elevated concentrations in spring and only at some sites but not others. This is probably the result of a combination of the above factors. Spring is a sensitive time of the year when various activities resume in the Arctic as well as at southern latitudes. To determine the influence of each of the abovementioned factors on the 'spring maximum event' of different OCs at different locations, further investigation in the atmospheric flow pattern in spring, which controls the movement of pollutants into, through and out of the Arctic, is required.

Acknowledgement

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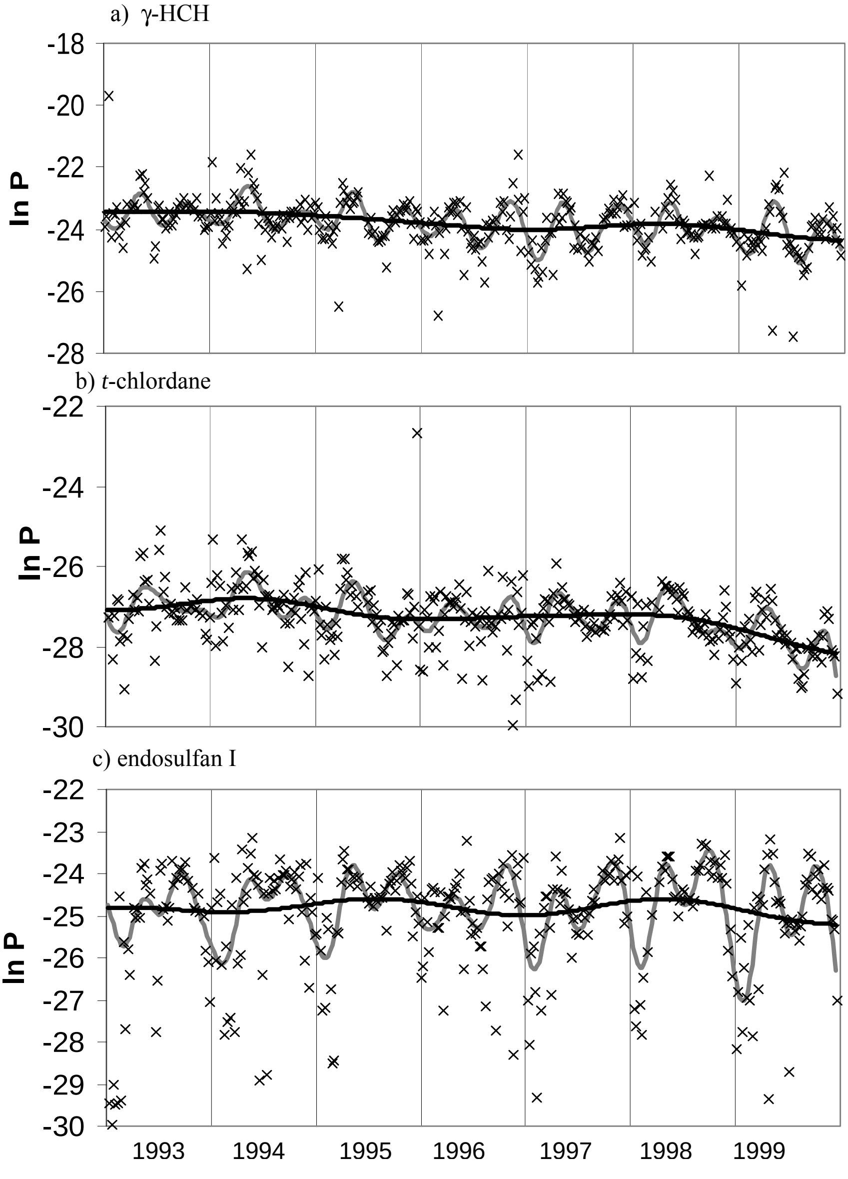

Figure 1.Trends and seasonal cycles of a) γ-HCH, b) t-chlordane and c) endosulfan I measured at Alert (1993-1999)

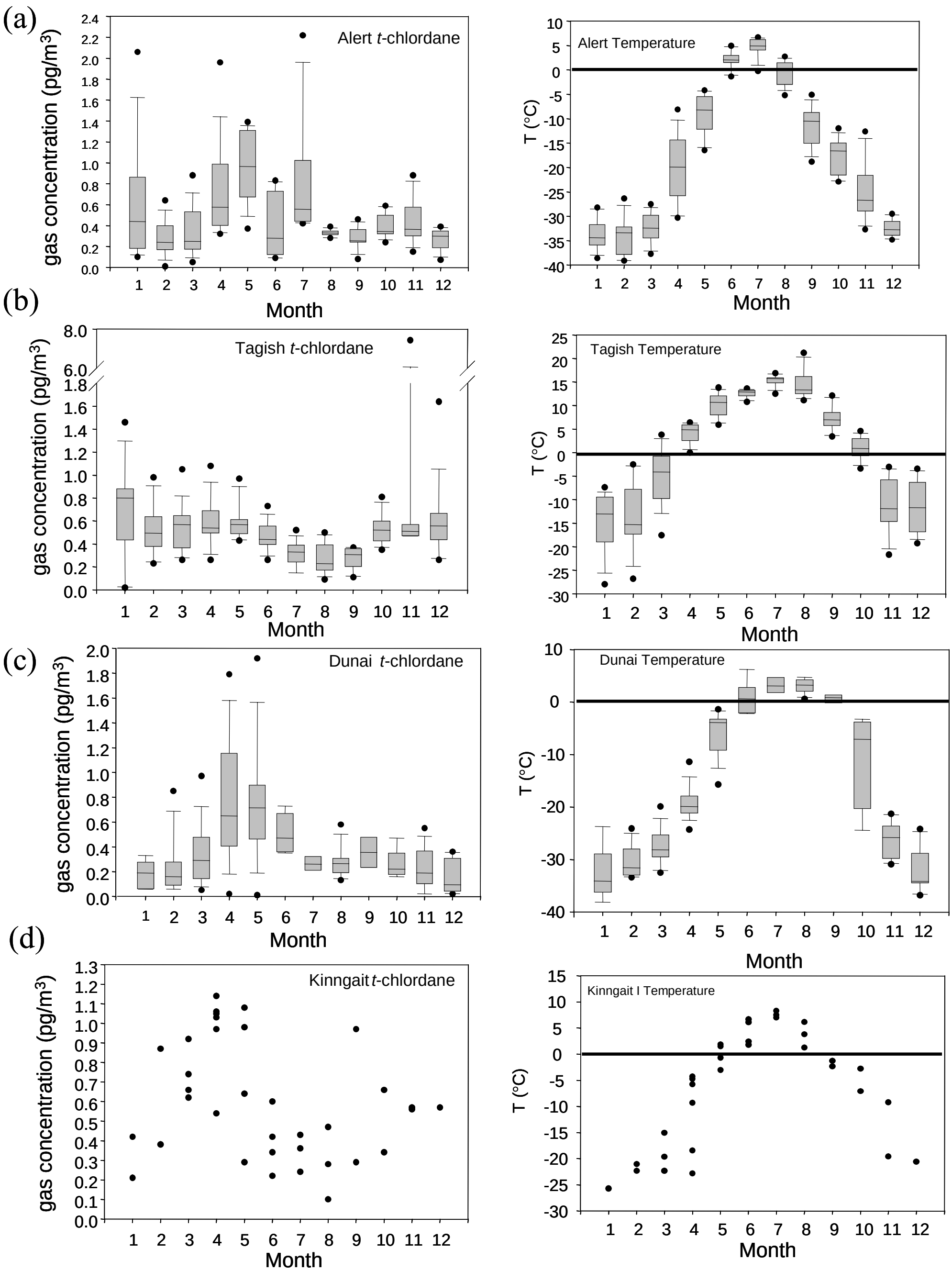

Figure 2. *t*-chlordane seasonality and temperature at (a) Alert, (b) Tagish, (c) Dunai and (d) Kinngait.

Centre box of box-and –whisker plots, is bounded by the 25th and 75th percentile with the horizontal line representing the median. Outliers (≥1.5 × interquartile range) are represesnted by a ●.