TEMPORAL TRENDS OF ORGANOCHLORINE PESTICIDES (OCS) IN THE ARCTIC ENVIRONMENT (1993-1997)

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Introduction

There has been growing concern about the contamination of the arctic environment by organochlorine pesticides (OCs) due to their environmental persistence and diversity of physical chemical properties, which influence their fate. Although the use of some, e.g. DDT, chlordane and technical HCH, has been banned or restricted in western countries, these compounds are still widely produced and used in Asia. Pesticides currently used in industrialized countries, such as Europe and North America, include lindane (γ-HCH), endosulfan and trifluralin.[1,2] Under the Northern Contaminants Program, multi-year systematic air sampling has been implemented to assess the levels, transport pathways and potential sources of persistent organic pollutants (POPs), such as the organochlorine (OCs) pesticides, in the Arctic region. In this study, the temporal patterns of OC atmospheric levels at one of the stations, namely Alert, in the Canadian Arctic from 1993 to 1997 will be examined.

Materials and Methods

Weekly air samples were collected with a high volume air sampler at Alert, NT (82.5 °N, 62.3 °W) in the Canadian high arctic. Sampler operation, sample extraction, cleanup and analysis have been described elsewhere.[3] Briefly, ~13000 m^3 of air was aspirated through a glass fibre filter and two polyurethane foam plugs (PUFs) to collect operationally defined particle and vapour fractions, respectively. Method detection limits (MDLs) were determined from monthly field blanks.

Results and Discussion

OC Pesticide Levels. Mean annual concentrations (filter + PUFs) of selected OCs are given in Figure 1. α- and γ-HCHs, being the lightest of all the selected OCs, attained the highest concentration in all five years. β-HCH, heptachlor, c-nonachlor, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, trifluralin, were detected at very low levels. The atmospheric concentrations were greatest in the following order during the first three years: ΣHCHs > Σchlordanes > endosulfan> dieldrin> ΣDDTs > trifluralin. After 1996, endosulfan concentrations became higher than that of Σchlordanes. While the average concentrations of endosulfan did not change significantly during the five years of sampling, that of Σchlordanes apparently decreased from 1994-1997. Although chlordane has been deregistered in most European countries and North America since the 1980s,[4] its sole producer, Velsicol, has only permanently ceased production in May 1997.[5] U.S. custom records have shown that between 1991 and 1994, at least 2028 metric tonnes of chlordane and

2584 metric tonnes of heptachlor were exported.[5] A decrease in emissions of these compounds has not been reflected in the Arctic atmospheric levels until recently. Dieldrin, as an insecticide and the epoxidation product of aldrin, did not show much change in atmospheric concentration in the Arctic, although both aldrin and dieldrin were banned in Europe and North America before 1990 and world production ceased in 1991.[6]

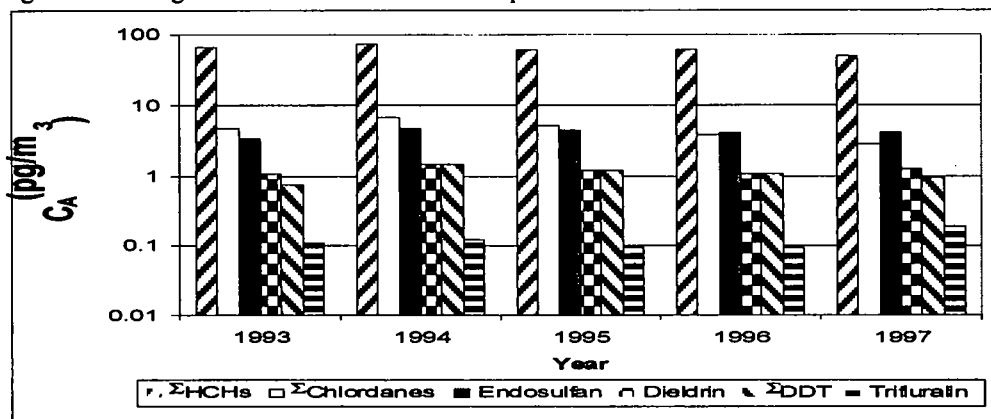Figure 1. Average annual concentrations of OC pesticides at Alert

Table 1. Regression results of ln P (Pa) versus $1/T$ (1/K)

OCs	m	b	r^2	ΔH_{SA} kJ/mol	OCs	M	b	r^2	ΔH_{SA} kJ/mol
α-HCH	**227**	**-22.7**	**4.6×10⁻³**	**-1.9**	heptachlor	**592**	**-31.7**	**0.03**	**-4.9**
γ-HCH	**-27**	**-23.6**	**4.5×10⁻⁵**	**0.22**	hep. epox.	-3107	-14.2	0.31	26
dieldrin	-2943	-14.7	0.30	24	*p,p'*-DDE	**1594**	**-33.6**	**0.10**	**-13**
t-chlordane	-854	-23.9	0.04	7	*p,p'*-DDD	**-600**	**-26.8**	**0.03**	**5.0**
c-chlordane	-1930	-19.0	0.17	16	*p,p'*-DDT	**-1055**	**-24.2**	**0.06**	**8.8**
t-nonachlor	-2870	-15.4	0.35	24	endosulfan	**1102**	**-15.7**	**0.08**	**-9.2**
c-nonachlor	-3919	-13.6	0.54	33	trifluralin	**-507**	**-26.4**	**0.08**	**4.2**
oxychl.	-2195	-18.1	0.24	18					

Underline indicates that slopes are not significant at the $p = 0.01$ level.
Bold type indicates compounds that were negatively correlated with temperature.

Air-surface equilibrium. If equilibrium has been reached between the air and arctic surfaces, the relationship between temperature, T (K), and air concentration, represented by partial pressure, P (Pa), can be expressed according to the Clausius-Clapeyron equation:

$$\ln P = m/T + b \qquad (1)$$

where m and b are compound-specific constants. m is, in fact, $-\Delta H_{SA}/R$, where ΔH_{SA} is the enthalpy of phase change between surface and air.[7] Regression results for the various OCs are given in Table 1. Significant correlation was observed for most of the compounds ($p < 0.01$). The slopes obtained for all compounds were lower than those calculated using only 1992-94 data and were considerably lower than those obtained in temperate regions.[8] The conclusions drawn are generally the same as those described by Halsall *et al.*.[8] In summary, major current-use pesticides, such as the HCHs, DDTs, endosulfan and trifluralin have lower correlation with temperature due to fresh atmospheric inputs. Metabolites, such as *c*-chlordane, oxychlordane and heptachlor

epoxide, showed higher correlation with temperature ($p < 0.001$) indicating revolatilization from arctic surfaces.

Seasonality and Time-Series Analysis. Seasonality of atmospheric levels was apparent for many of the OCs analyzed. The seasonal cycle and trend lines (shown in Figure 2 for *c*-chlordane) were determined using a digital filter technique described by Nakazawa *et al.*.[9] Both *t*- and *c*-chlordanes peak around May-Jun and again around Nov-Dec. For both α- and γ-HCHs, peaks were observed around Feb and Aug during all five years. Elevated concentrations around February probably resulted from spring spraying of technical HCHs and/or lindane in Asia. Back trajectory analysis has indicated that, in February, Alert was strongly influenced by air from Eurasia.[10] Although most of the DDT-related compounds were observed at very low levels, *p,p'*-DDE, the most abundant of all DDT-related compounds in air, showed distinct seasonal peaks. *p,p'*-DDE level usually peaked from Oct-Dec, then decreased slightly and peaked again around Mar-May, followed by a summer minimum. In India, elevated levels of *p,p'*-DDE have been recorded during the dry season of Jan-May, probably due to oxidative dehydrochlorination of DDT to DDE in dry paddy soil.[11] This may account for the elevated level in spring at Alert. Not all the OCs showed concentration peaks during the warmest months. As mentioned above, levels of *p,p'*-DDE, *t*- and *c*-chlordanes soared during winter (~Oct-Dec). Cyclonic movement of air flow during the winter causes air, originating from the strong Siberian anticyclone, to curve eastwards around the Arctic region.[4] This makes pollutant dissipation difficult in winter. Besides, slow degradation rates at low temperatures and the lack of photodegration, due to the low levels of solar radiation, may result in elevated levels of certain compounds, such as *t*- and *c*-chlordanes, in winter.

Table 2. Linear regression of calculated OC trends, on ln *P* (Pa) versus time series (year) plots, using digital filter technique

OCs	Trends[*] Slope	r^2	OCs	Trends[*] Slope	r^2	OCs	Trends[*] Slope	r^2
α-HCH	-0.0410	0.79	*t*-nonachlor	-0.112	0.71	*p,p'*-DDE	-0.0366	0.054
γ-HCH	-0.142	0.88	*c*-nonachlor	-0.0878	0.28	*p,p'*-DDD	0.0385	0.54
dieldrin	0.0134	0.021	oxychl.	-0.200	0.84	*p,p'*-DDT	0.107	0.41
t-chl.	-0.0834	0.48	heptachlor	0.0899	0.10	endo.	0.134	0.25
c-chl.	-0.169	0.84	hep. epox.	-0.110	0.72	trifl.	-0.0925	0.36

[*]Linear regression of trends calculated by digital filter technique.

Table 2 summarizes regression results of the calculated trends. Most of the compounds showed decreasing trends from 1993 to 1997. γ-HCH was declining at a faster rate than α-HCH. This might be caused by photo-transformation of γ- to α-HCH during transport or past/present use of technical HCH, in which ~70 % is α-HCH.[8] Although dieldrin showed a positive trend (despite its low r^2), close examination of its seasonality showed that the amplitudes of the seasonal cycle decreased by about 50 % from 1993 to 1997. The average growth rate had decreased from 0.2 pg/m^3 per year in 1993 to 0.08 pg/m^3 per year in 1997, with negative average growth rates in 1995 and 1996. Thus, from this analysis, a significant decline in dieldrin atmospheric concentrations is likely within the next few years despite its almost constant level from 1993 to 1997. All chlordane-related compounds showed significant decreasing trends, except heptachlor. This is probably an artifact of its extremely low concentrations in the Arctic. However, its degradation

product heptachlor epoxide showed a significant negative slope as expected, since heptachlor has been restricted/banned in most countries during the 1970-80s. Endosulfan, as a current-use pesticide, showed an increase in concentrations from early to mid-1993. Then, an almost steady level was maintained through the end of 1997.

Some of the OCs manifested similar trends in a study on male Pangnirtung beluga blubber.[12] In some cases, the trends may even be magnified in mammals since most of these compounds are hydrophobic. For instance, endosulfan concentrations in beluga blubber increased by a factor of 2.1 from 1982 to 1997 in the eastern Arctic. Future studies may focus on investigating the connection between the concentration trends in different arctic media.
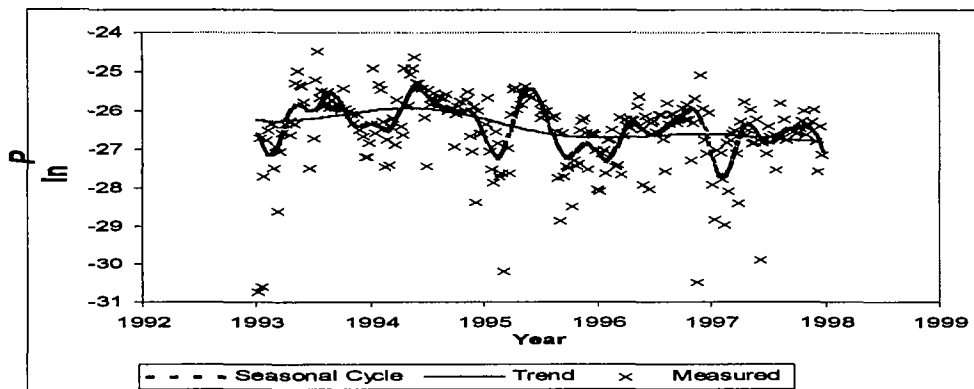

Figure 2. ln P of c-chlordane measured from January 1993 to December 1997 at Alert. Seasonal cycle and trend were calculated using digital filter technique.[9]

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