Polychlorinated biphenyls (PCBs) and Organochlorine pesticides (OCs) in the Arctic Atmosphere

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Abstract

Atmospheric PCBs and OC pesticides have been routinely sampled (weekly) at three locations in the Canadian and Russian Arctic over several years. Mean annual ΣPCB concentrations ranged from 17 - 34 pg/m^3 for 1993. No temporal pattern was observed in ΣPCB concentrations, however, changes in the homologue group profile with temperature were apparent. The trichlorinated congeners dominated the profile on an annual basis, with greater contributions of the more chlorinated congeners occurring during the months of May to August, most notably at the Russian site. Selected OC pesticides showed little spatial variation between the sites, atmospheric concentrations being greatest in the order of HCHs>chlordanes>endosulfan~toxaphene>DDTs. Seasonal variation was evident for some of the compounds and related to either seasonal changes in temperature and/or long range atmospheric transport. Assuming equilibrium for PCBs, between the atmosphere and arctic surfaces, Clapeyron-Clausius plots of partial pressure (ln P) vs. 1/T for selected congeners, revealed weak correlations, the slope of the lines being far lower than those reported from temperate regions. Given that temperatures can reach as high as 20°C at the southern most sample site, suggests that re-volatilisation off arctic surfaces plays a minor role in driving the atmospheric concentrations.

Introduction

As part of the Canadian commitment to assessing the sources, levels and pathways of persistent organic pollutants (POPs) to the Arctic region, a muti-year systematic air sampling programme has been established as part of the Northern Contaminants Programme[1-3]. To date, a large database has been generated from three sites operating in both the Canadian and Russian Arctic. The database has been divided into the respective compound classes with separate vapour and particle concentrations of PCBs and OC pesticides now being available for the years 1992-1995. In this paper temporal and spatial patterns in concentrations and profiles are examined, and discussed with reference to seasonal temperature change and long range atmospheric transport.

Experimental Methods

High volume air samplers were located at three sites: Alert in the North West Territories (82°30'N, 62° 20'W), Tagish in the Yukon (60°20'N, 134°12'W) and Dunai Island in eastern Siberia (74°6'N, 124°30'E). On a weekly basis ~11,000 m^3 of air were aspirated in order to achieve detectable concentrations of selected pesticides, PCBs and PAHs. Each sample consisted of a glass fibre filter and polyurethane foam plugs (PUFs) to collect the respective particle and vapour fractions. Sampler operation, sample extraction and clean-up/analysis have been described in detail elsewhere[1]. Minimum detection limits for the respective sampling years were determined from routine field blanks, other qualtiy controls included the development of a flagging system to highlight sample breakthrough or artifacts in the sampling process.

Results and Discussion

PCBs. Tables 1 presents monthly mean ΣPCB concentrations (where Σ=90 congeners) for the three arctic sites during 1993. Annual mean concentrations (1993) of SPCB were 27.4, 17.0 and 34.0 pg/m3 for Alert, Tagish and Dunai respectively. Lack of sesonal variability of ΣPCB concentrations agreed with a similar study carried out at Ny Alesund on Svalbard[4].

Table 1. Monthly ΣPCB concentrations (pg/m^3) for 1993 (vap.+part.)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Alert	14.0	40.4	21.9	23.6	27.2	9.9	64.1	27.8	15.2	20.5	22.8	16.2
Tagish	26.3	17.8	21.5	16.2	18.7	14.8	12.7	15.9	14.7	13.3	14.4	18.9
Dunai	NA	NA	55.4	51.7	31.9	30.7	32.3	26.9	NA	NA	23.8	21.4

NA = not available

Although changes in total air concentrations with temperature were not apparent, changes in homologue profile did occur. On an annual basis the trichlorinated congeners made the largest single contribution to the atmospheric ΣPCB concentrations, however, this contribution declined with the onset of the warmer months. This was clearly evident at the Siberian site of Dunai, where the contribution of the pentachlorinated congeners matched or exceeded that of the trichlorinated congeners during May, June and July of 1993. A similar phenomenon was observed at Tagish and Alert, but not to the same degree, and was largely dependent on air mass direction. That is, for those sample weeks where the air flow could be assigned from the Eurasian side of the Arctic, then the contribution by the heavier homologues increased. This would indicate that a site's proximity to source regions, where different PCB mixtures and quantities have been used, as well as air mass movement play a key role in determining the atmospheric profile during the warmer months. During the winter months, however, the profile at all of the sites was dominated by the trichlorinated congeners irrespective of air mass origin.

OC pesticides. Mean annual concentrations of selected OCs are presented in Figure 1. For comparison, data for 1993 from Ny Ålesund have also been included. On an annual basis large spatial differences between the sites were not evident. Seasonality in air concentrations was apparent for many of the compounds, but not to the degree found in temperate studies. Furthermore, the summer months did not always possess the highest

concentrations, for example, levels of α– and γ-HCH tended peak during the months of April and May, rather than July and August. This is believed to be the result of agricultural use of either Lindane (γ-HCH) (Europe) or technical HCH (Russia/Asia) during the spring. This was most marked at Tagish and Dunai rather than at the high Arctic sites of Alert and Ny Ålesund, although at Alert, fresh 'pulses' of γ-HCH were clearly evident during May of 1993 and 1994.

Seasonal elevations in air concentrations, typically marked by increased levels during the warmer months of June July and August, were observed for endosulfan (I and II), *cis/trans*-nonachlor and several of the chlordane metabolites, oxychlordane and heptachlor epoxide. Levels of both *cis*- and *trans*- chlordane tended to be higher during April, May and June. Concentrations of the less stable *trans*- isomer were generally lower than the *cis*- isomer, an indicator of atmospheric 'ageing' due to the remoteness of the arctic region. To highlight this, the ratio of *trans/cis*-chlordane at Tagish ranged from 0.6 to 0.2, the lowest values occurring during the summer as a result of increased photolytic degradation. Similarly, with the DDT group, levels of the metabolite *p,p*-DDE were greater than those of the parent compound, *p,p*-DDT. Little evidence of seasonality was found in the concentrations of *p,p*-DDT, however, *p,p*-DDE displayed elevated levels in January, February and March of 1993/4, at both Tagish and Alert. Reasons for these winter episodes are at present unclear, but imply that an increase in OC concentrations are not always related to a seasonal rise in temperature.

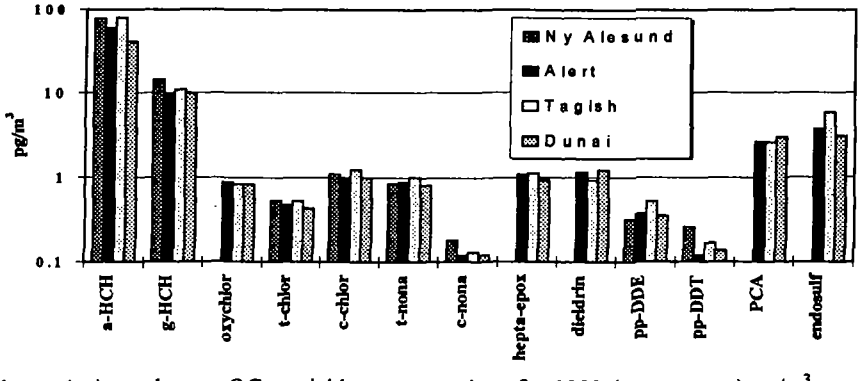

Figure 1. Annual mean OC pesticide concentrations for 1993 (vap. + part.) pg/m^3. Data for Ny Ålesund taken from Oehme *et al.*[4]

Seasonal patterns in OC air concentrations were blurred to some extent by episodes associated with long range transport events, these often occured during the winter months and were particularly marked at Tagish. The elevation of this site (~1500 m) and its location close to the Pacific resulted in several weeks when calculated air mass back trajectories revealed air flow from China and S.E. Asia, these weeks showed notable increases in pesticide levels.

Air-surface exchange equilibrium. Assuming equilibrium between air and arctic surfaces for a range of PCB congeners, then the vapour component in the atmosphere, expressed

as partial pressure, can be considered to be dependent on temperature according to the Clapeyron-Clausius equation:

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

where ln P is the natural log of partial pressure (calculated from the observed vapour-phase air concentrations) and m and b are compound-specific constants. Plots of ln P versus 1/T, for 52 weekly samples (1993) revealed correlations ranging from $r^2 = 0.03$ ($p>0.01$) for the lighter trichlorinated congeners, to $r^2 = 0.56$ ($p<0.01$) for the heavier heptachlorinated congeners. Slopes of the line, m, progressively increased with degree of chlorination, representing an increase in the enthalpy of phase change (air/surface) for these heavier congeners. Values of m and b, derived for six congeners observed at the most northerly site (Alert), are presented in Table 2 along with corresponding values from a temperate study carried out in southern Ontario[5].

Table 2. Values of m and b for selected PCB congeners at Alert (high Arctic) and S. Ontario, Canada[5]

	Alert			S. Ontario		
PCB	**m**	**b**	r^2	**m**	**b**	r^2
28	-178	0.687	0.03*	-3550	13.5	0.39
52	-285	1.181	0.06	-3750	14.2	0.51
101	-595	1.985	0.12	-3420	12.6	0.40
153	-1900	6.708	0.54	-3740	13.4	0.37
138	-1645	5.529	0.45	NA	NA	NA
180	-2240	7.769	0.56	**187** -3970	13.9	0.38

NB. To allow direct comparison, values of m and b for the Alert samples were generated using $\log_{10}$ vapour concentrations, rather than ln P, in line with the earlier Ontario study.
* not significant at the p = 0.01 level.

Clearly the values of m and b are significantly lower at Alert, poor correlations being observed for the lighter congeners in contrast to the temperate study. It has been suggested that temperatures in the high Arctic during the summer months (ranging between -1 to 6°C) are not high enough to promote significant re-volatilisation and hence provide a seasonal increase in air concentrations [4]. However, plots of ln P versus 1/T for the same congeners measured at Tagish, the southern most site, where temperatures during the summer are markedly higher (15-20°C), yielded similar correlations and values of m and b comparable to Alert. This would suggest that even with temperatures well above 0°C (Tagish summer), atmospheric PCB concentrations are not significantly enhanced, providing evidence that arctic surfaces play a minor role in driving the atmospheric concentrations.

Acknowledgements

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