Organohalogen Compounds, Volume 61, Pages 409-412 (2003)

ATMOSPHERIC MEASUREMENTS OF TOXAPHENE AND COPLANAR PCBS AT A CANADIAN IADN SITE

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Introduction

The Integrated Atmospheric Deposition Network (IADN) has been in operation since 1990. This bi-national network located around the Great Lakes is devoted to the monitoring and surveillance of persistent organic pollutants. Master stations are sited on each of the five Great Lakes and from atmospheric and precipitation data, loadings estimates are calculated every two-years for a suite of POPs. The stations are also being used for several research projects. At the Canadian IADN station of Point Petre on Lake Ontario, dedicated samples have been collected for the measurement of toxaphene and coplanar PCBs since the mid nineties. Although toxaphene use as a pesticide was banned in the early 1980s, it has been found throughout the Great Lakes basin in air, water, sediments and biota. Coplanar PCBs have been extensively studied in biota due to their toxicity, however atmospheric measurements in the Great Lakes basin are limited. In this paper, air concentrations of these two groups of compounds are presented with implications related to temporal trends and fate.

Methods and Materials

Sample collection and chemical analysis for toxaphene have been presented elsewhere. [1,2]
Briefly air volumes of 1700 m^3 for 1992 and 1000 m^3 for 1995-2000 were collected using a Hi-vol PS1 sampler equipped with GFF, PUF and subsequently XAD-2 (in 1996). Samples were extracted (hex/DCM), cleaned-up (Florisil) and analyzed using GC-ECNIMS. Co-planar PCBs were quantified using a similar method. It is worth noting that non-ortho coplanar PCBs have enhanced response characteristics compared to any co-eluting non-coplanars (of higher homologue), which significantly decreases the possibility of response interference.

Results and Discussion

a) Toxaphene

Figure 1 shows the airborne vapor-phase concentrations for toxaphene components T2 (7Cl), T2 (8Cl), T12B (9Cl) and total toxaphene at Point Petre for the 1992 and 1995-2000 sampling periods. The individual components track the total toxaphene pattern remarkably well although their contribution is only of the order of 10%. The strong seasonality is expected given previous investigations[1,3,4] in the Great Lakes basin where the Clausius-Clapeyron equation has been used to describe the relationship between toxaphene and temperature. Also shown in Figure 1, total toxaphene levels for air samples collected at Eagle Harbor on Lake Superior from September 1996 to May 1997 (analyzed at MSC) as well as values obtained by James and Hites[4] for Lake Michigan. The concentrations for both studies are similar to those observed at Point Petre, suggesting that a significant spatial variability does not exist for toxaphene in the Great Lakes background air.

In order to investigate the trend of atmospheric toxaphene at Point Petre a statistical time series analysis technique (digital filtration, DF) was employed to smooth any seasonality in the air data (Nakazawa et al., 1997). This technique has been successfully used in determining the trends of

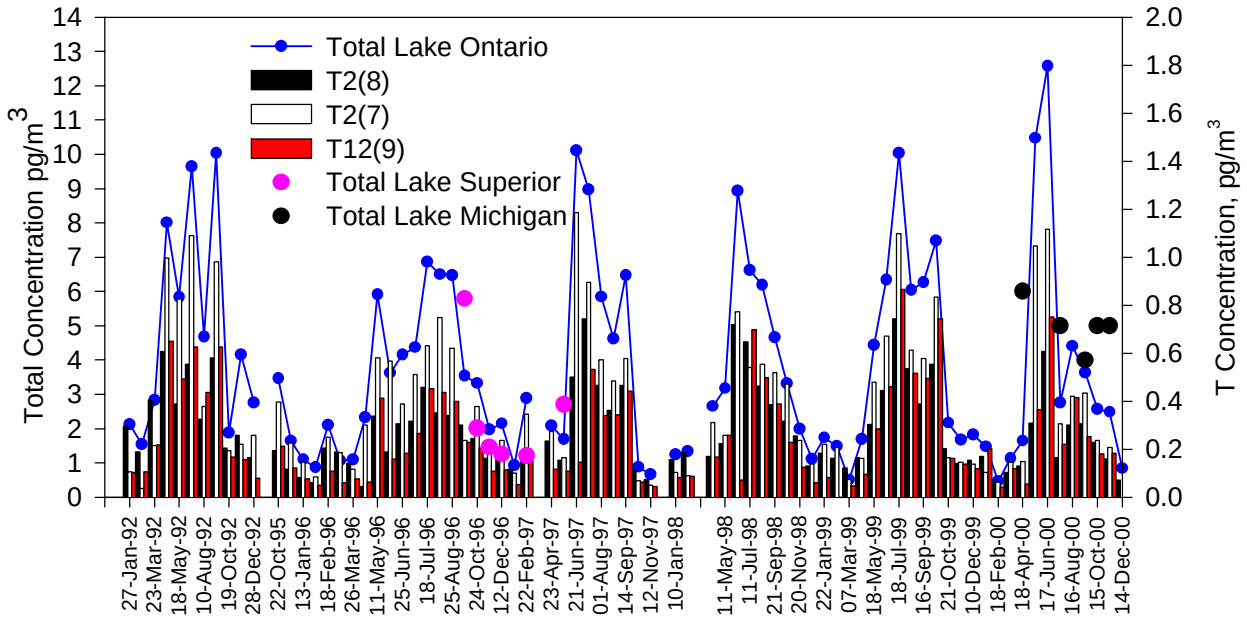

Figure 1. Vapor-phase airborne toxaphene concentration at Point Petre during 1992 and 1995-2000.

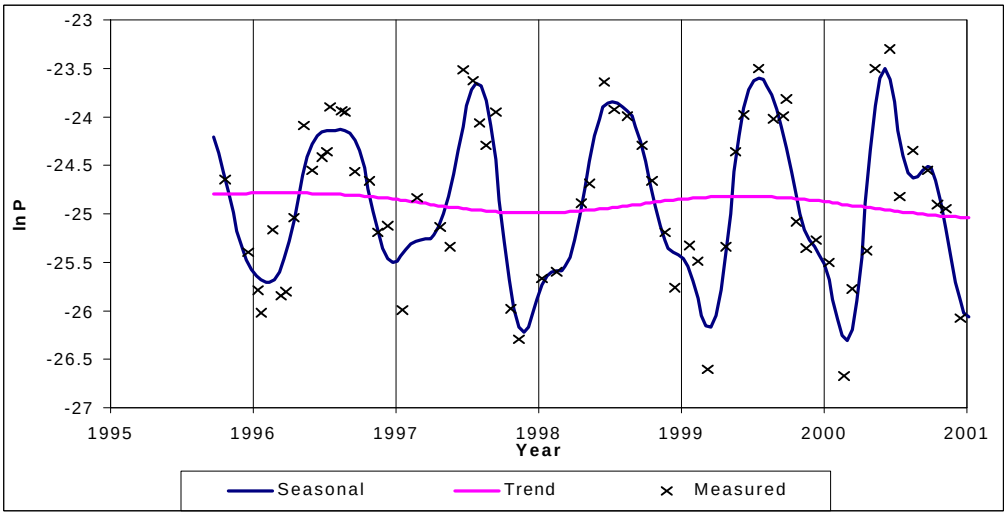

Figure 2. Trend and seasonal cycle derived using the digital filtration technique for total Toxaphene at Point Petre.

Organochlorines[5] in Arctic air. For total toxaphene long- and short-term variations of the trend and the seasonal cycle were extracted using iterative digital filters with two cut-off periods: a short term cut-off period, set to 4 months, and a long term cut-off period, set to 24 months. Results of the DF technique are presented in Figure 2. No significant trend was observed for toxaphene at Point Petre between 1995 and 2000. To access the relative decline rate of toxaphene, an apparent first-order half-life, $t_{1/2}$, was estimated by dividing ln 2 by the regression slope of the trend line. The half-life for toxaphene at Point Petre using data between 1995 and 2000 was found to be 26 years. Although this is a much longer half-life than 4-10 years obtained by James and Hites[4] for the Great Lakes region, it could be the result of the shorter time series employed here. The lack of trend for atmospheric toxaphene at Point Petre in recent years and the spatial similarity of concentrations to other background areas of the Great Lakes basin are consistent with observations in biota which have remained relatively constant over the last 10 years[6].

b) Coplanar PCBs

Several non- and mono-ortho substituted PCBs have been measured in the Great Lakes biota[7]. These PCB may account for 95% of the "dioxin-like" toxic activity in some species e.g. terns. Specifically congeners 77 and 126 have great toxicological significance in Lake Ontario salmonids. Non-ortho PCB 77 has been measured in air samples at Point Petre since 1995, both in the particulate phase and in the vapour phase. Results of these measurements are presented in Figure 3 where PCB 77 is plotted along with di-ortho PCB 110. A strong seasonality is seen whereby colder winter temperatures result in an enhancement of the percentage of PCB 77 in the particulate phase. This tendency for non-ortho PCBs to sorb to particles has been shown before in urban samples[8] and attributed to vapor pressure and dihedral angle between biphenyl rings. The partitioning to aerosol for the background site of Point Petre is significant as it will affect the dry and wet deposition of these toxicologically important species to Lake Ontario.

Acknowledgements

Financial support for this work was provided by the Environment Canada Great Lakes 2000 Program. P. Blanchard would like to thank H. Hung for help with the DF model.

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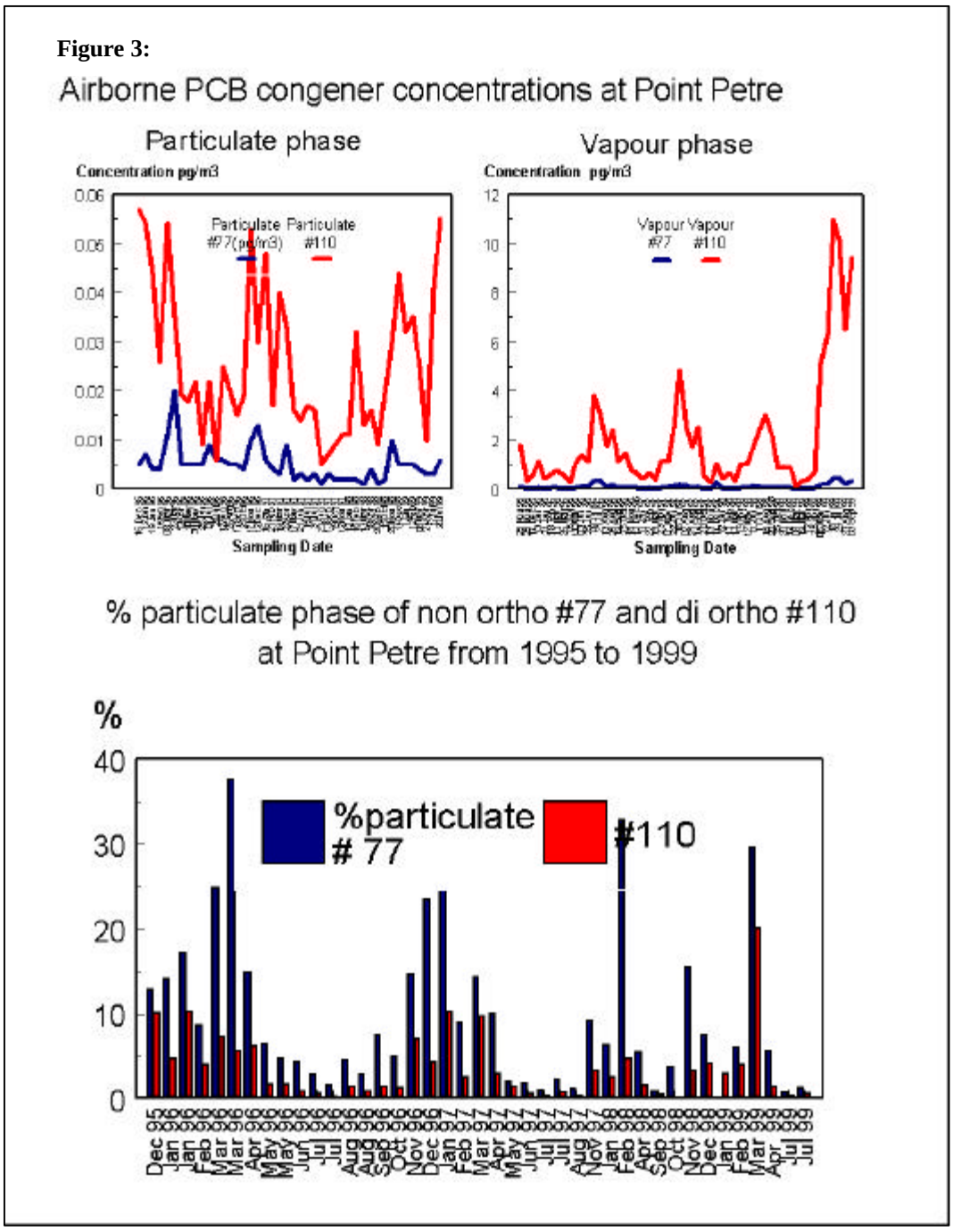
Figure 3:


Airborne PCB congener concentrations at Point Petre
Particulate phase
Concentration pg/m3
Particulate #77(pg/m3)
Particulate #110
Sampling Date
Vapour phase
Concentration pg/m3
Vapour #77
Vapour #110
Sampling Date
% particulate phase of non ortho #77 and di ortho #110 at Point Petre from 1995 to 1999
%
%particulate # 77
#110