Toxaphene Quantitation: Improvements and Application to Ambient Atmospheric Samples

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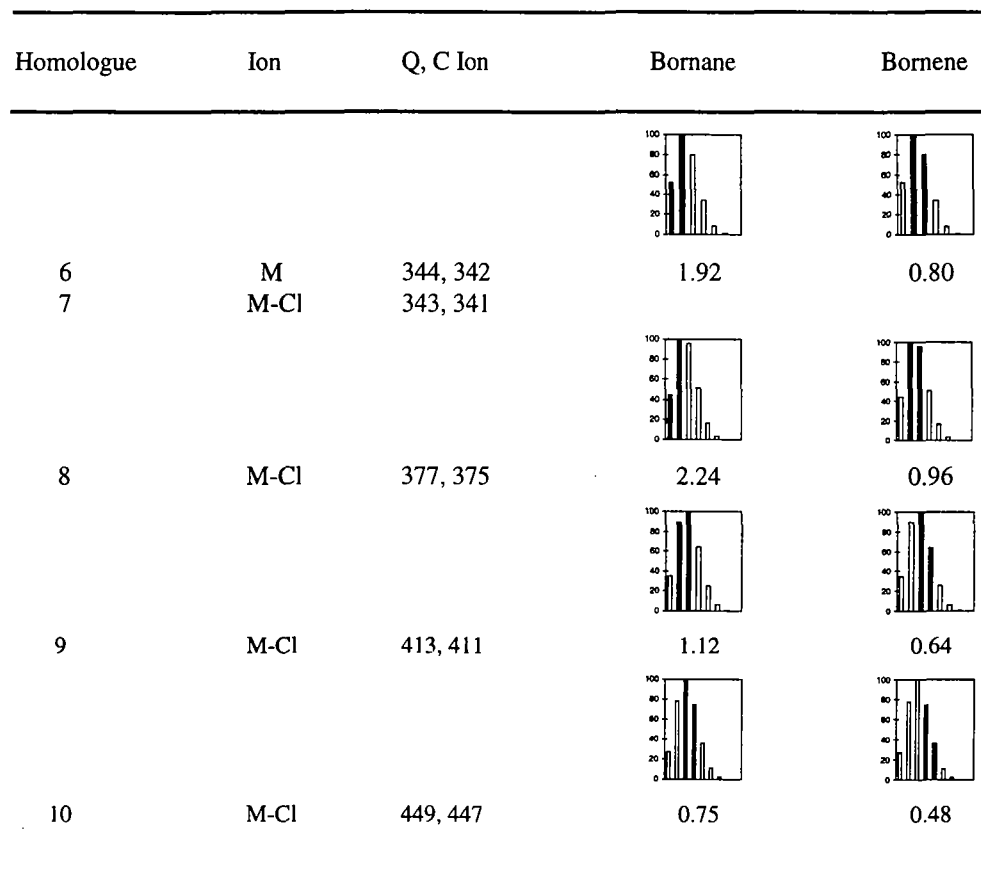*Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, L7R 4A6,
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Introduction

In the late 1940's, the Hercules Company introduced toxaphene in the United States as an insecticide (1). Since chlorination of camphene can take place to varying degrees and on various carbon atoms, there are thousands of theoretically possible congeners (2), of which more than 600 have been found in commercial toxaphene (3). Due to the complexity of the mixture, less than 30 of these congeners have been isolated and structurally identified (4).

Like PCBs and other heavily used organochlorines, toxaphene is ubiquitous in the environment. The U. S. EPA canceled the registrations for most of toxaphene's uses in 1982, but allowed the existing stocks to be used in limited circumstances until 1986 (5). Toxaphene has not been registered in Canada since 1983 (6). In addition to the United States and Canada, toxaphene's use has been banned in England, Sweden, Finland, Denmark, France, Germany, Switzerland, Hungary, Italy, Egypt, India, China, and Algeria (7).

Toxaphene's complex nature makes accurate quantitation difficult. Quantitation methods using mass spectrometry can be categorized into three types: (a) those that include only a handful of peaks in each sample; (b) those that sum all of the peaks in a particular mass to charge range; and (c) those that compare the ratio of the quantitation to the confirmation ion to determine if a peak is indeed toxaphene. The first two methods tend to under- and overestimate the amount of toxaphene in a sample, respectively, and do not give accurate homologue distributions, while the third method is time consuming and subject to human error. As an alternative, we have developed a QBASIC computer program that performs the isotopic ion ratio comparison, thus decreasing the time required for analysis while maintaining accurate and precise quantitation. Figure 1 illustrates the isotopic ratios of each of the toxaphene homologues; in each figure, the first dark line is the quantitation ion, while the second is the confirmation ion. The ratio of the confirmation to quantitation ion used in the QBASIC program

Figure 1. Isotopic ratios of toxaphene homologues.

Homologue	Ion	Q, C Ion	Bornane	Bornene
6	M	344, 342	1.92	0.80
7	M-Cl	343, 341		
8	M-Cl	377, 375	2.24	0.96
9	M-Cl	413, 411	1.12	0.64
10	M-Cl	449, 447	0.75	0.48

Table I. Vapor phase concentrations (pg/m^3)

Month	Average	Literature[11]
September	42	50
October	18	14
November	2.4	18
December	4.1	2.2
January	1.0	0.39
February	16	0.08
March	3.3	7.6
April	6.0	11
May	8.9	15

is given below each figure. To test the program, we have examined the atmospheric concentrations of toxaphene near Lake Superior.

Material and Methods

Sample Collection. Samples were taken at Eagle Harbor, located on Michigan's Keweenaw peninsula, which extends into Lake Superior. The high volume air samplers (Graseby GMW, modified Hi Volume Sampler, Cleves, OH) were calibrated quarterly, and the air flow rate was set at 34 m^3/hr. The vapor phase constituents were collected on XAD-2 resin, while the particle bound fraction was collected on quartz fiber filters (QFF). Samples for this project were taken every twelve days, from September 9, 1996 until December 31, 1997.

Sample Preparation. The analytical method employed in this project is based on that of Swackhamer *et al.* (8). Samples were Soxhlet extracted for 24 hours in 50% acetone in hexane; due to the low concentration of particle bound toxaphene, the quartz fiber filters (QFF) were composited monthly, and extracted as one sample. With every batch, at least one of three categories of a blank sample was prepared. Procedural blanks consisted solely of a glass thimble plugged with glass wool. XAD and QFF blanks consisted of fresh media. The primary samples and blanks were spiked with a known mass of the internal standards, $^{37}Cl_6$-*trans*-nonachlor (EPA Repository, Research Triangle Park, NC) and $^{13}C_1$-chlordane (Cambridge Isotope Laboratories, Andover, MA). With every other batch, a procedural-blank spike was also extracted. This sample consisted of a glass thimble plugged with glass wool and spiked with a known amount of toxaphene (Hercules, Wilmington, DE). Interferences and contaminants were removed using silica column chromatography with three solvents: hexane, 80% dichloromethane in hexane, and dichloromethane. The last two fractions were combined, solvent exchanged to hexane, and reduced for analysis.

Analysis by Electron Capture Gas Chromatographic Mass Spectrometry. A Hewlett Packard 5989A mass spectrometer was used to analyze the samples. The samples were injected into a Hewlett Packard 5890 Series II gas chromatograph containing a 30 m DB-5MS™ column (0.25 µm film thickness, 250 µm i.d., J&W Scientific). The temperature and pressure parameters have been published previously. (9).

The EC GCMS analysis procedure was developed by Swackhamer *et al.* (8) and modified by Myers (10). The M^- or $(M-Cl)^-$ of the hexa- to decachlorinated norbornanes and norbornenes were monitored in the selected ion monitoring (SIM) mode. Four time windows, each monitoring a subset of the ions, were used to increase sensitivity relative to monitoring all of the ions through the entire run.

Results and Discussion

The monthly average of the vapor phase concentration of toxaphene in each sample is presented in Table I. While two internal standards were spiked onto each sample, the $^{13}C_1$-chlordane demonstrated better recovery with the Procedural Blank Spikes, and was thus chosen for quantitation. For comparison, toxaphene concentrations measured on Lake Ontario in

1988 and 1989 are also presented in Table I. With the exception of the extraordinarily high February value, the values agree well, indicating that toxaphene deposition across the Great Lakes basin is uniform. The particle phase concentrations of the monthly composites were all very close to the procedural blank levels, indicating that toxaphene resides primarily in the vapor phase, at least at this location.

A modified Clausius-Clapeyron plot of the toxaphene concentrations is shown in Figure 2. The correlation between temperature and concentration ($r^2 = 0.55$) suggests a long-range atmospheric source of toxaphene into the Lake Superior area; a local source would likely give a constant concentration, regardless of the season.

The homologue composition of the vapor phase samples tended to skew towards the lower chlorinated homologue groups as compared to a toxaphene standard. This trend was expected; the more highly chlorinated congeners are generally less volatile than the lesser-chlorinated components; thus, they would either not be transported from the source regions, or they would become associated with the particles.

Acknowledgments

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Figure 2. Logarithm of the air concentration of toxaphene versus the inverse of the mean air temperature during each sampling period.