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Airborne Concentration of Toxaphene Congeners at Point Petre Ontario using Gas Chromatography-Electron Capture Negative Ion Mass Spectrometry (GC-ECNIMS) and Multidimensional Gas Chromatography-Electron Capture Detection MDGC-ECC)

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Toxaphene is a complex mixture of chlorinated camphene derivatives (polychlorinated camphenes, PCCs), primarily bornanes and bornenes containing 6 to 10 chlorines. It has been extensively used as a pesticide in the United States and many other parts of the world. Due to its environmental persistence and toxicity, the use and production of toxaphene was banned in 1982 by the U.S. Environmental Protection Agency. However, manufacture and use of toxaphene continues elsewhere in the world and residues can be identified in the environment in locations far removed from sites of application

The analysis of toxaphene residues in environmental samples is important to understand the sources, transport and bioaccumulation of these compounds. However, the compositional complexity of technical toxaphene introduces considerable difficulties in quantification: the possible presence of more than 670 individual PCCs (congeners) has been proposed. Furthermore, environmental samples do not typically display the technical toxaphene pattern due to selective weathering, degradation and bioaccumulation processes. This introduces additional complications to the analysis, with the possibility of substantial bias to the results in the absence of reliable congener-specific standards matching the species identified in the actual samples. Recently, a limited number of individual toxaphene congeners have become available commercially, aiding investigations of the response behavior of these compounds on both GC-ECD and GC-ECNIMS. Based upon results obtained using these pure toxaphene congeners (bornanes with 7 to 10 chlorines, the response factors for GC-ECD show reasonable consistency with a relative standard deviation (RSD) of 13%. In contrast, for GC-ECNIMS selective-ion mode, the response factors were highly variable with a RSD of 177%. This difference in response behavior for the two techniques introduces difficulties in the comparison of the respective chromatograms obtained using a technical toxaphene standard. Furthermore, these findings clearly indicate that the conventional use of technical toxaphene as an analytical standard for GC-ECNIMS, combined with the calculation of a "single" response factor (I), could introduce significant errors into the quantitation for environmental samples possessing a different distribution of toxaphene components.

Over the past two years, work at the Atmospheric Environment Service has resulted in the development of a reliable in-house analytical method using GC-ECNIMS for the determination of individual toxaphene congeners in air samples collected as part of the Integrated Atmospheric Deposition Network (IADN) operations. For comparability with previous data reported by Muir and co-workers us-

ing GC-ECD, the approach has focussed upon the identification and quantitation of specific peaks or clusters ("T" species) typically observed in environmental samples. The identifications of the "T" species in technical toxaphene congeners were transferred from the GC-ECD chromatogram to the GC-ECNIMS chromatogram using a correlation of the Relative Retention Index (RRI) values obtained for the pure toxaphene congeners on both systems. A similar correlation has been established using known PCBs and tested for PCBs not used in the correlation: the calculated and experimental values of retention times for PCBs have been found to agree within 0.005 min. The assumption of equivalent ECD response factors (amount/area) for all toxaphene species allowed the assignments of concentrations to the major peaks and peak clusters of concern in a technical toxaphene standard. This standard has been used as the basis for the calibration of the GC-ECNIMS system. Further refinements have been made using observed Florisil fractionation of technical toxaphene and information on chlorination from the mass spectrometric analysis to resolve certain of these peak clusters into multiple components. The concentrations assigned for some congeners have been compared with those calculated by calibration against the available individual standards using GC-ECNIMS and MDGC-ECD and typically agree within $\pm 15\%$, which provides further confidence in the adequacy of the developed calibration approach. The resulting calibration table for the method comprises over 40 assignments covering nearly all well-defined responses observed in typical air samples with each assignment possessing a unique response factor.

Air samples were collected at a rural site (Point Petre) on the northern shoreline of Lake Ontario: this site is an important component of the Integrated Atmospheric Deposition Network (IADN). A PS1 high-volume sampler was used, with the sample head employing a glass fiber filter (GFF) for particle collection followed by a polyurethane foam (PUF) plug for vapor absorption. Multi-day sampling has been necessary to satisfy the detection limit restrictions, with collected air volumes of approximately 1000 m^3 (over 4 day integration periods) in 1992 and about 1200 m^3 (using 5-day integration periods) in 1995/6. GFF and PUF were extracted and subjected Florisil column chromatography for clean up and fractionation of PCBs and organochlorine pesticides, including toxaphene. The GC-ECNIMS methodology has been applied to the measurement of toxaphene in the Florisil fractions. An MDGC-ECD procedure has been used for examination of the technical toxaphene standard and individual toxaphene congeners, as well as for some of the air sample fractions, for further confirmation of the results. Airborne concentrations between 1992 and 1996 appear to have undergone little change, where the total concentrations (defined as the sum of the calibrated components) range from 1.8 pg/m^3 to 11.9 pg/m^3 in 1992 and from 1.1 pg/m^3 to 8.1 pg/m^3 in 1995/6. However, a clear seasonality has been observed, with a summer to winter ratio of about 4. In a typical air sample, the homologue distribution of the total mass is octachlorobornane 48%, heptachlorobornane 45%, and nonachlorobornane 7%. The chlorobornanes, T2 and T12 were found in all air samples but contribute only about 10% of the total toxaphene in air. T_{sed} was the dominant heptachlorobornane accounting typically for 25% of this homologue. In addition to T2, the peaks named AES1, T8 (Parlar #39), T9, T10 (Parlar #42) and AES2 constitute the major octachlorobornane congeners in air samples. T12 represents almost the only nonachlorobornane observed in all analyzed air samples from 1992 to 1995/6.

- (1) Swackhamer, D. Charles, M. J. and Hites, R. A. 1987 Quantitation of toxaphene in environmental samples using negative ion chemical ionization mass spectrometry, *Anal. Chem.*, **59**, 913-917.