

Sources and Air-Water Gas Exchange of Toxaphene to Lake Superior

Liisa Jantunen, Tom Harner, Terry Bidleman, Janine Wideman Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4, Canada; William Parkhurst Tennessee Valley Authority, Muscle Shoals, Alabama, USA.

Abstract

Air samples were taken in Alabama in 1996 and South Carolina in 1994-95, to determine the seasonal atmospheric cycling of toxaphene and other OC pesticides. To complement this, soil samples were collected to determine the residues of toxaphene and estimate the potential atmospheric source. Toxaphene levels in Alabama air increased from an average of 120 pg/m³ in winter to 406 pg/m³ in the summer. No seasonal variation was evident in South Carolina where toxaphene averaged 189 pg/m³ from August to January. Toxaphene was the highest OC residue in Alabama soils, ranging 3-2832 ng/g dry wt. with a geometric mean of 149 ng/g. A soil fugacity model predicted volatilization of toxaphene from soils. Air and water samples were collected during August 1996 in Lake Superior to determine the fugacity ratio and net flux of OCs including toxaphene. Concentrations of toxaphene in air ranged from 17-41 pg/m³, an order of magnitude lower than those found in the southern U.S. Toxaphene concentrations in the water ranged from 0.56-1.4 ng/L. The fugacity ratio (f_w/f_a) of toxaphene in Lake Superior was >1.0 implying volatilization from water to air.

Introduction

Toxaphene is a complex mixture of several hundred compounds that results from the chlorination of camphene to yield mostly chlorinated bornanes². Toxaphene was heavily used in the U.S. during the 1960s and 1970s, mainly in the southern states on cotton and soyabeans. The peak usage of toxaphene was 25×10^6 kg/yr in 1972³. Most registrations of toxaphene were cancelled in 1982, but remaining stocks were applied through 1986. Like other semi-volatile organic pesticides, toxaphene continues to evaporate from soils and is atmospherically transported to non-source regions where it undergoes air-water gas exchange and wet and dry deposition onto land and water. The Great Lakes have been sinks for these compounds because they have large surfaces areas and are cold. Evidence from peak cores⁴ and sediments⁵ in the Great Lakes region indicates that atmospheric deposition of toxaphene peaked in the mid-1970s and declined into the 1980s. Despite the decrease of atmospheric loadings, toxaphene is still prevalent in Great Lake fish, particularly in Lake Superior where 69% of the fish consumption advisories are due to toxaphene contamination⁶. Toxaphene levels in fish from Superior are approximately two times higher than those in the lower Great Lakes⁷. In this study, the air-water gas exchange of toxaphene in Lake Superior was determined. We also examined potential sources of toxaphene to Lake Superior by measuring air and soil concentrations in the southern U.S. where large quantities of toxaphene had been used in the past.

Dioxin '97, Indianapolis, Indiana, USA

Experimental Methods

Air samples were collected in two southeastern U.S. locations, the city of Columbia, South Carolina (August 1994 to January 1995) and outside the town of Muscle Shoals, Alabama (December 1995 to June 1996). Sampling of air and water was carried out on a cruise of the CSS Limnos in Lake Superior, August 1996 (Figure 1). Air was drawn through a glass fiber filter followed by a polyurethane foam (PUF) trap. A submersible pump was used to take surface water on board ship. The water samples were stored in stainless steel cans, then passed through a glass fiber filter and a column of XAD-2 resin. Details of sampling and procedures for cleaning PUFs and XAD-2 resin are given elsewhere^{8,9,10}. Sample volumes were ~350-800 m³ for air and 80 L for water. Filter, PUFs and XAD-2 resin were soxhlet extracted with organic solvents and the extracts were cleaned up and fractionated on an alumina-silicic acid column to separate PCBs from the chlorinated pesticides, using published methods^{8,11}. Cleaned up extracts of air and water samples were transferred into isoctane and adjusted to ~200 µL for analysis by nitrogen blowdown. Mirex was added as an internal standard.

Soil samples were collected from the top 10 cm at agricultural research stations and private farms in Alabama and background samples were collected in cemeteries. Replicate cores from fields were pooled to obtain a representative sample. The soils were sieved to remove stones and plant material. The moisture content was determined by drying a weighed portion at 40°C. A 5-10 g portion of soil was mixed with anhydrous sodium sulfate soxhlet extracted with dichloromethane for 12 h and cleaned up using a 0.5 g column of neutral alumina containing 6% water.

Total toxaphene and Parlar congeners P26 and P50 were determined by capillary GC on a DB-5 column with detection by negative ion mass spectrometry. Chromatographic conditions are described elsewhere¹². Recovery of toxaphene from spiked PUFs averaged 96±3% (n=3). Spikes recoveries for the soils averaged 102% (n=4). The spike recovery for water ranged 81-88% and the blank was 4.51 ng.

Results and Discussion

Toxaphene in Air

Vapor-phase toxaphene concentrations in air over Lake Superior in August 1996 ranged from 17-41 pg/m³. Toxaphene in Alabama showed a strong seasonal variability. The lowest concentration was found in January (8 pg/m³) and the highest in June (612 pg/m³), with average winter and summer concentrations of 120 pg/m³ and 406 pg/m³, (Figure 2). Toxaphene in Columbia, SC averaged 189±107 pg/m³, with little seasonal trend over the six month study. P26 and P50 were enriched in air samples relative to their percentages in technical toxaphene, concentrations ranged 0.17-0.41 pg/m³ for P26 and 0.88-1.8 pg/m³ for P50.

Toxaphene in Alabama Soil

Concentrations of toxaphene in soil were quite variable in different parts of Alabama. The highest concentrations were found in the experimental farms (150-2800 ng/g dry wt) whereas soils from the Blackbelt (8-80 ng/g) and Gulf Coast Stations (18-88 ng/g) contained lower levels. Toxaphene in random grab samples from the northwest part of the state ranged from 3-455 ng/g. Two of the three cemetery samples contained measurable levels of toxaphene (10-67 ng/g). The

TRANSPORT AND FATE

fugacity ratio of soil to air (f_s/f_a) was estimated from ¹³).

$$f_a = C_a RT_a \quad (1)$$

$$f_s = C_s H / K_{oc} f_{oc} \quad (2)$$

where C_a and C_s are the concentrations in the air and soil, H is the Henry's law constant (see below), $K_{oc} = 0.41 \times$ octanol-water coefficient ($K_{ow}=3.16 \times 10^5$) and f_{oc} is the fraction of organic carbon in the soil (assumed to be 0.01). A fugacity ratio (f_s/f_a) >1.0 implies volatilization. In the winter $f_s/f_a = 31$ and in June $f_s/f_a = 8$. Thus, even when ambient air concentrations are high the fugacity ratio predicts that toxaphene is still volatilizing from the soil in Alabama.

Air/Water Exchange of Toxaphene in Lake Superior

Concentrations of toxaphene in Lake Superior surface water ranged from 0.54-1.4 ng/L, (Figure 3). To estimate the air-water gas exchange direction and flux of toxaphene, the Henry's Law constant (Pa m³/mol) of technical toxaphene was determined by the gas stripping technique, over a temperature range of 10 - 35°C, by the method described by Kucklick et al.¹⁴). HPLC grade water was spiked 1.0 mL of acetone containing technical toxaphene, giving initial concentration of 58 µg/L. This toxaphene concentration is at least an order of magnitude below its solubility. Toxaphene vapors were purged with UHP nitrogen, at a flow rate of 0.025 m³/h. The nitrogen was pre-saturated with HPLC grade water at the same temperature as the apparatus. The relationship of the Henry's Law constant to temperature is shown in Figure 4. The resulting equation is:

$$\log H = 10.48 - 3206/T \quad (3)$$

The net gas exchange direction was estimated from the water/air fugacity ratio, where a fugacity ratio >1.0 implies volatilization and <1.0 implies deposition:

$$f_w/f_a = C_w H / C_a RT_a \quad (4)$$

f_w and f_a are the fugacity in water and air, C_w and C_a are the dissolved concentration in water and vapor-phase concentration in air, H is the Henry's Law constant at the temperature of the water, $R = 8.31$ Pa m³/mol K and T_a is the temperature of the air. Temperatures ranged from 13 - 17°C (air) and 3.5 - 15°C (water). The net flux (N) was estimated from:

$$N \text{ (ng /m}^2 \text{ d}^1) = D_{aw} (f_w - f_a) \quad (5)$$

where

$$D_{aw} \text{ (mol/ m}^2 \text{ d}^1 \text{ Pa}^1) = 86400k_a/RT \quad (6)$$

Since the exchange of toxaphene is gas-phase controlled, the mass transfer coefficient for air ($k_a = 0.0044$ at a wind speed of 5 m/s) is used in equation (6). Further discussion of gas exchange and equations 4-6 are given in Bidleman and McConnell¹⁵). The fugacity ratio ranged from 1.5-4.2 for Lake Superior and the net flux was 0.5-16 ng/ m² d into the air.

Toxaphene was last used in the U.S. over a decade ago, but large reservoirs still persist in the

Dioxin '97, Indianapolis, Indiana, USA

soils and are continuously evaporating. This leads to the potential of atmospheric transport to the Great Lakes. Lake Superior has accumulated vast quantities of toxaphene over the years and today toxaphene is volatilizing during the summer months.

Acknowledgements

We would like to thank the technical operators and crew of the CSS Limnos for sampling help.

Literature Cited

- (1) Hoff, R.; Muir, D.C.G.; Grift, N.P.; Brice, K.A. *Chemosphere* **1993**, 27, 2057-2062.
- (2) Hainzl, D.; Burhenne, J.; Parlar, H. *Chemosphere* **1994**, 14, 593.
- (3) Voldner, E.C.; Schroeder, W. H. *Atmos. Environ.*, **1989**, 23, 1949-1961.
- (4) Rapaport, R.A.; Eisenreich, S.J. *Atmos. Env.* **1986**, 20, 2367-2379.
- (5) Howdeshall, M.J.; Hites, R.A. *Environ. Sci. Technol.* **1996**, 30, 220-224.
- (6) Guide to Eating Ontario Sport Fish: 1997-98, 19th ed., Queens printer for Ontario, 1997, p11.
- (7) Glassmeyer, S.T.; De Vault, D.S.; Myer, T.R.; Hites, R.S. *Environ. Sci. Technol.* **1997**, 31, 84-88.
- (8) Kucklick, J.R.; Bildeman, T.F.; McConnell, L.L.; Walla, M.D.; Ivanov, G.P. *Environ. Sci. Technol.* **1994**, 34, 197-209.
- (9) Capel, P.D.; Eisenreich, S.J. *J. Great Lakes Res.* **1985**, 11, 447-461.
- (10) Billings W.N.; Bidleman, T.F. *Environ. Sci. Technol.* **1980**, 14, 679-683.
- (11) Keller, C.D.; Bidleman, T.F. *Atmos. Environ.* **1984**, 18, 837-845.
- (12) Bidleman, T.F.; Alegria, H.; Ngabe, B.; Green, C. *Atmos. Environ.* **1997**, submitted.
- (13) Mackay, D. *Multimedia Environmental Models: Fugacity Approach*; Lewis, Chelsea, MI, **1991**.
- (14) Kucklick, J.R.; Hinckley, D.A.; Bidleman, T.F. *Mar. Chem* **1991**, 34, 197-209.
- (15) Bidleman, T.F.; McConnell, L.L. *Sci. Tot. Environ.* **1995** 159, 101-117.

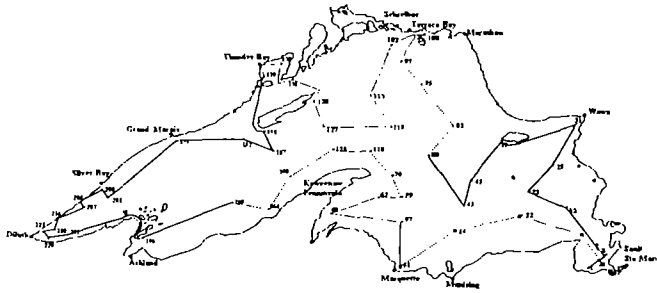


Figure 1: Lake Superior cruise track, August 1996, Lines refer to air samples and numbers indicate water stations.

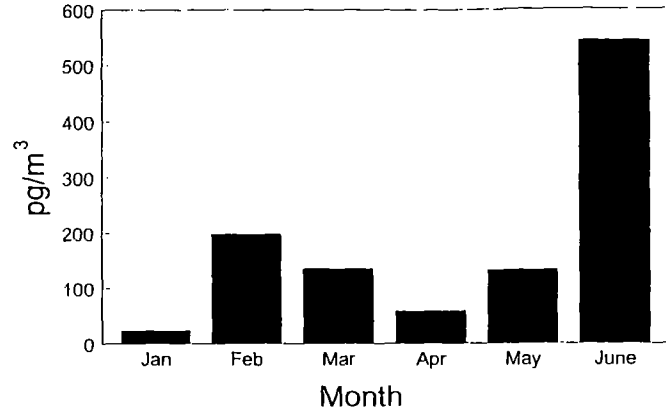


Figure 2: Toxaphene in Alabama Air

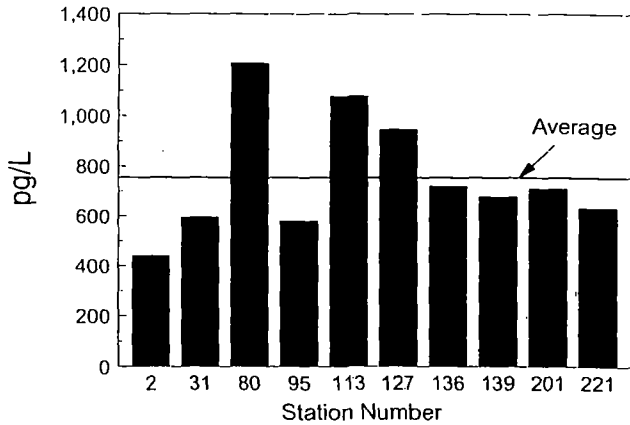


Figure 3: Toxaphene in Lake Superior Water

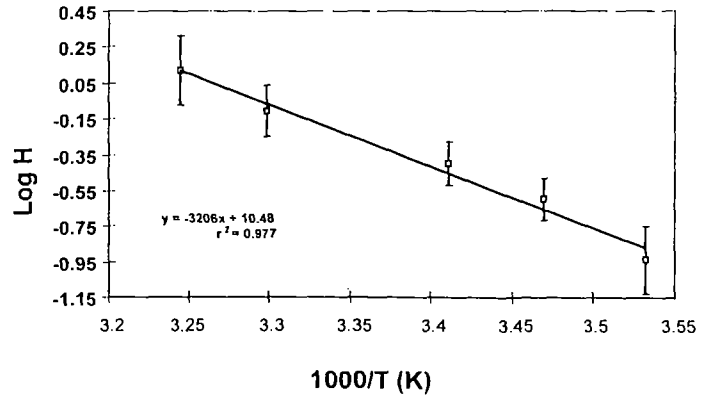


Figure 4: Temperature Dependence of the Henry's law constant for technical toxaphene