Science of the Total Environment 409 (2011) 792–799

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Modeling toxaphene behavior in the Great Lakes

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ARTICLE INFO

Article history:
Received 26 June 2010
Received in revised form 24 October 2010
Accepted 28 October 2010
Available online 9 December 2010

Keywords:
Toxaphene
Bioaccumulation
Great Lakes
Fish
Modeling

ABSTRACT

Chlorinated camphenes, toxaphene, are persistent organic pollutants of concern in the Great Lakes since elevated concentrations are found in various media throughout the system. While concentrations have decreased since their peak values in the 1970s and 80s, recent measurements have shown that the rate of this decline in Lake Superior has decreased significantly. This modeling study focused on toxaphene cycling in the Great Lakes and was performed primarily to determine if elevated water and fish concentrations in Lake Superior can be explained by physical differences among the lakes. Specifically, the coastal zone model for persistent organic pollutants (CoZMo-POP), a fugacity-based multimedia fate model, was used to calculate toxaphene concentrations in the atmosphere, water, soil, sediment, and biota. The performance of the model was evaluated by comparing calculated and reported concentrations in these compartments. In general, simulated and observed concentrations agree within one order of magnitude. Both model results and observed values indicate that toxaphene concentrations have declined in water and biota since the 1980s primarily as the result of decreased atmospheric deposition rates. Overall the model results suggest that the CoZMo-POP2 model does a reasonable job in simulating toxaphene variations in the Great Lakes basin. The results suggest that the recent findings of higher toxaphene concentrations in Lake Superior can be explained by differences in the physical properties of the lake (primarily large volume, large residence time and cold temperatures) compared to the lower lakes and increased recent inputs are not needed to explain the measured values.

1. Introduction

Toxaphene is a pesticide mixture made up of chlorinated bornanes and chlorinated bornenes. It was introduced in the United States by the Hercules Company in the late 1940s and was heavily used in the southern United States (Li, 2001a,b) on cotton fields after DDT was banned in 1972. Toxaphene is considered to be carcinogenic (Saleh, 1991) and is assumed to present a significant risk to human health through occupational exposure and the consumption of contaminated fish (ATSDR, 1996). Once applied, toxaphene can volatilize into the air where it can be transported to and deposited in regions where it was not originally used. Because of its persistence and toxicity, the U.S. Environmental Protection Agency canceled the registration of toxaphene in 1982.

Toxaphene is ubiquitous in the Great Lakes region. It has been and continues to be detected in the air, rain, water, sediment, and fish in the Great Lakes (De Vault, 1985; De Vault et al., 1986, 1996; Swackhamer et al., 1998; Glassmeyer et al., 1997; James and Hites, 2002; Jantunen and Bidleman, 2003; Hickey et al., 2006; Carlson and Swackhamer, 2006). High toxaphene air concentrations of 1 to 100 pg m^{-3} were found over the Great Lakes region in the late 1990s (Swackhamer et al., 1998). Glassmeyer et al. (1997) also found that toxaphene concentrations in Lake Superior lake trout were still significantly higher than lake trout in the other Great Lakes. Although elevated concentrations of toxaphene were observed in the Great Lakes, direct application of toxaphene in the Great Lakes basin was estimated at only 1–4% of the total U.S. consumption (De Geus et al., 1999; Rice et al., 1986). The minimal direct usage of toxaphene suggests that elevated Great Lakes levels is caused by atmospheric transport instead of local use (Ma et al., 2005a,b). Studies show that the southern United States was the largest user of toxaphene in the world before the mid-1980s suggesting soils in those states are likely major previous and current reservoirs of toxaphene transported the Great Lake basin (Ma et al., 2005a,b; James and Hites, 2002).

The lack of emission (application) data makes it difficult to define a starting point to understand the fate of toxaphene in the Great Lakes. MacLeod et al. (2002) estimated the total use of toxaphene in the Great Lakes basin and made the assumption that the primary emissions of toxaphene were distributed 70% into the soil, 25% into air, and 5% into fresh water to simulate toxaphene in the whole Great Lakes region. However, based solely on those data, it is difficult to explain why the concentration of toxaphene in Lake Superior is the

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doi:10.1016/j.scitotenv.2010.10.051

highest among the five lakes since there were minimal agricultural applications in this region.

According to Wania and Mackay (1993), the global distribution of toxaphene is affected primarily by temperature. Their modeled results show toxaphene water concentrations increased with latitude suggesting toxaphene evaporates in warm areas and condenses in cold regions leading to elevated concentrations (i.e. global distillation). This possible explanation supports the decreasing rate of toxaphene concentration decline in Lake Superior relative to the other Great Lakes. Specifically, this modeling study of toxaphene cycling in the Great Lakes was performed primarily to address whether the elevated water and fish concentrations in Lake Superior can be explained by physical differences among the lakes. Toxaphene usage in the Great Lakes watershed was estimated and the coastal zone model for persistent organic pollutants (CoZMo-POP2) was used to predict the concentration of toxaphene in air, water, and sediment compartments of the five lakes as well as top predator fish (lake trout). Sensitivity analysis was also performed to illustrate the potential effect input parameter uncertainties on model results.

2. CoZMo-POP2 model structure

The CoZMo-POP2 model is a non-steady state, multimedia mass balance model for describing the long term fate of persistent organic pollutants in a coastal environment. It was developed by Wania et al. (2006) based on the CoZMo-POP model. The CoZMo-POP2 model consists of 19 compartments that are linked by 69 transport processes. The compartments include forest, soil, water body, sediment, and atmosphere compartments. Key processes are the two-directional exchange of persistent organic pollutants between the atmosphere and aquatic and terrestrial surfaces, and the uni-directional run-off of chemical from soil to fresh water and further to the oceans. Other important processes include loss of chemical during the transport in atmosphere and water, i.e. degradation and deposition in the atmosphere, and degradation, net sedimentation to sediments and volatilization from the water body. The air–water exchange is calculated based on the standard two-film theory invoking two MTCs in series. Diffusive gas exchange between atmosphere and fresh water ceases when the terrestrial air temperature drops below −2 °C, based on the assumption that an impenetrable ice cover is formed. The water–sediment exchange is based on the approach by Mackay and Yuen (1983) and Mackay et al. (1992). All of the mass balance equations of the contaminants are formulated in terms of fugacity including Z values mol/(Pa m^3) which describe phase partitioning and D-values mol/(Pa h) which describe contaminant fate processes. These equations take the generic form as follows:

$$\frac{d(V_x{*}BZ_x{*}f_x)}{dt} = E_x + \sum_Y D_{YX}f_Y - \left(\sum_Y D_{XY} + D_{RX}\right)f_X$$

where V_X, BZ_X, f_X are the volume, bulk Z-value and fugacity of compartment X, respectively. D_{XY} and D_{YX} are the D-values describing the transport processes moving a contaminant from compartment Y to compartment X, and vice versa. E_X is the emission rate into compartment X in mol/h. D_{RX} is the D-value describing the degradation loss in compartment X. The set of mass balance equations are solved using a stepwise approach of 12 h for simulation and 8760 h for result storage, with a finite difference approximation. In this study, the model was parameterized to represent the Great Lakes basin to simulate the fate of toxaphene in this region (Table 1).

3. Physical and chemical properties of toxaphene

The physical and chemical properties of individual toxaphene congeners vary considerably. Molecular weights vary from 345 for $C_{10}H_{12}Cl_6$ to 483 for $C_{10}H_8Cl_{10}$. The average molecular weight is usually assumed to be 414 for $C_{10}H_{10}Cl_8$. Vapor pressures range from 3.41×10^{-3} Pa to 2.53×10^{-5} Pa for hepta- and nonachlorobornanes (Bidleman et al., 2003). Log K_{ow} values range from 2.47 to 5 according to the toxicological profile prepared by U.S. Department of Health and Human Services (ATSDR, 1996). Fisk et al. (1999) measured the octanol–water partition coefficients for technical toxaphene and different congeners using a slow stripping method, and found that log K_{ow} values range from 4.77 to 6.64 and are a function of chlorine position and the structure of the carbon skeleton. The average value of log K_{ow} is typically assumed to be 5.5 (Isnard and Lambert, 1988). Jantunen and Bidleman (2000) found that Henry's law constant of a technical standard and temperature can be related using the following equation:

$$\log H = m / T + b$$

where $m = -3029$ and $b = 10.42$. In this study, the average physicochemical properties for this mixture (Table 1) were used to model toxaphene as if it were a pseudo single chemical compound.

The half-life of toxaphene in different environmental compartments (Table 2) was obtained from various sources. In the Lake Michigan Lake Wide Management Plan (LaMP, 2000), the half-life of toxaphene in water was reported to be more than 200 days. The half-life in soil was reported to be from 1 to 14 years. According to Macleod et al. (2002), the half-life of toxaphene in air and vegetation is 170 h each, in freshwater, coastal water, soil and sediment it is 6.3 years. Mackay et al. (2006) reported the half-life of toxaphene in air was 4–5 days, more than 7 h in surface water, approximately 0.8 years in soil, and 15.6 days in fruit tree leaves. Since the half-life in vegetation is rather uncertain, it was assumed to be 170 h equal to that in air based on Cousins and Mackay (2001). The half lives in other modeling departments were estimated bases on Citra's estimated program (Monte Carlo based multimedia fate model for the Great Lakes Ecosystem).

It is assumed in the CoZMo-POP 2 model that the gas-phase reaction of the modeled chemical with hydroxyl radicals is the only significant degradation pathway. Since there are no directly measured data for toxaphene, an estimated value was used. Atkinson and Arey (2003) provides the rate constant for the gas-phase reactions of hydroxyl radical with camphene at room temperature. Using a structure reactivity

Table 1
Compartment dimensions and the properties of the model (www.epa.gov/greatlakes/atlas).

	Lake Superior	Lake Michigan	Lake Erie	Lake Ontario	Lake Huron
Surface area (m^2)	2.09E+11	1.76E+11	1.04E+11	8.30E+10	1.94E+11
Water area (m^2)	8.21E+10	5.78E+10	2.57E+10	1.89E+10	5.96E+10
Fraction covered by lakes	0.39	0.33	0.25	0.23	0.31
Fraction covered by uncultivated soils	0.1	0.1	0.1	0.1	0.1
Fraction covered by forest	0.91	0.41	0.21	0.49	0.68
Fraction of coniferous trees	0.53	0.5	0.5	0.5	0.5
Average water depth	147	85	19	86	59
Rain rate	30.52	32.18	35.04	35.35	32.18
Total loading (kg)	3700000	3100000	1890000	1480000	3370000