Tracking Toxaphene in the North American Great Lakes Basin

S. Venkatesh and J. Ma Air Quality Research Branch Meteorological Service of Canada Toronto, Canada

GOES-8 satellite imagery and toxaphene air concentration on Sept 10 2000

Why toxaphene?

- One of the most heavily used organochlorine pesticides, U.S. has been the largest user of toxaphene in the world
- One of "Dirty Dozen" toxics on the list of the Stockholm Convention on persistent organic pollutants
- One of 16 Tier II toxic substances listed by GLWQA
- One of Level I pesticides affecting human heath and environment listed by USEPA
- Still a major contaminant in the Great Lakes fish after the compound was banned in early 1980s in North America
- Major sources of toxaphene affecting the GL ecosystem are still not well understood
- Good toxaphene emission inventory in MSC

Half life of Toxaphene in soil	10 yrs		
Half life in air	A few days		

A schematic illustration of pesticides transport



Ma et al, ES&T, 2003, 2004; Harner et al, Environ. Toxicol. Chem. 2001





Maximum: 143 t at grid (142,40) in Alabama

Li et al, JGR, 2001



Model domain, grids, and regions for modeling scenarios

Numerical Experiments setup: six scenarios

Scenario 1. With all toxaphene sources in the U.S Scenario 2. sources in the southeast U.S. only Scenario 3. sources in the northeast U.S. only Scenario 4. sources in the northwest U.S. only Scenario 5. sources in the southwest U.S. only Scenario 6. sources in the west-Coast U.S. only

- Model run: from January 1st 2000 to December 31th 2000 Initial condition:
- Toxaphene soil residues on 1st Jan. 2000 were assumed to be in the Reservoir Layer, as legacies from past application.
- No Initial background air concentration.

Meteorology: GEM objective analyzed winds and temperature, and predicted precipitation

Toxaphene is treated as a single chemical compound with averaged physical-chemical properties for the mixture



Modeled monthly mean daily air concentration (All Sources of toxaphene)



Toxaphene - Monthly averaged daily air concentration over each lake (pg m⁻³) in 2000



Monthly dry, wet and total depositions (kg month⁻¹) to all five lakes



Modeled annual dry, wet and total (dry + wet) depositions (kg yr⁻¹) to each lake in 2000

Annual total deposition

Superior

Model: 1.5 kg in 2000 Measured: 19 kg (mid-1990s)

Michigan

Model: 5.8 kg in 2000 Measured: 13.6 kg (mid-1990s)

Ontario

Model: 3.3 kg in 2000 Measure: 5 kg (mid-1990s)

Measured by Swackhamer et al *ES&T*, 1999.



Monthly contribution of southeast (major) and northeast U.S. (Near the Great Lakes) toxaphene sources to the toxaphene budget over the Great Lakes: Southeast sources (strong emissions) made a larger contribution in spring and fall than in summer, whereas the contribution from northeast sources (weak emission) is maximum in the summer. The negative correlation is associated with atmospheric circulation patterns



Model calculated toxaphene soil/air fugacity ratio (fs/fa) at model source grids (142, 39) in Alabama with soil residue at 135 t cell⁻¹, and (155, 100) in southern Michigan with soil residue at 0.12 t cell⁻¹. Soil fugacity was taken at reservoir layer (1-10 cm below the surface) and air fugacity was taken at 1.5 m height.





The September Event

Episodic long-range/trans-boundary transport September event

- Nature of source of pollutants
- Atmospheric flows with minimal dispersion
- Limited chemical destruction (no chemical or photochemical degradation, long-enough half-life in air)





A schematic view of a shearing deformation wind field consists basically of an area of flat pressure between two opposing highs and two opposing lows. The axis of deformation flow is an area where strong convergence occurs.

Flow deformation acts to increase the horizontal temperature gradient and convergence, leading to a frontogenesis (initial formation of a front through an increase in the horizontal gradient of temperature)



Vector winds at 1200 m height on Sept 11 2000









Cross-section/vertical profile of air concentration indicating northward transport of toxaphene



NOAA Geostationary Satellite (GOES-8) visible image



Warm and humid air was also transported from southern U.S. / Gulf of Mexico to the Great Lakes, resulting in heavy rain and wet deposition to the lakes.

> GEM predicted total precipitation (mm) accumulated over 9-12 September



GOES-8 visible satellite imagery on 10 September at 18:15 UTC and daily toxaphene air concentration at 1200 m on 10 September 2000





Wet deposition to the lakes (kg day⁻¹)



September event: A memory in soil



Soil concentration (µg kg⁻¹) in buffer layer (0.1-1 cm below ground surface)

Summary

- 1. The southeast U.S. is a dominant source contributing to toxaphene levels in the atmosphere over the Great Lakes basin and depositions to the lake waters.
- 2. In spring and autumn, relative contributions of SE sources to GL basin are higher than those of NE sources, but of similar magnitudes in summer
 - primarily due to the inter-seasonal changes in atmospheric circulation systems
- 3. Episodic long-range transport is a major pathway for moving toxaphene from its sources in the southern U.S. to the Great Lakes
 - During the *September event*, *d*eformation flow and convergent winds formed a conveyer belt for toxaphene transport from the southeast U.S. to the Great Lakes.

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LRT of Organochlorine pesticides Info Table July 2005

	Lindane	Endosulfan	Toxaphene	HCB	BaP	Atrazine	DDT
Strategy substance	II		Ι	I	Ι		Ι
(Level I or II)							
LRT potential	$\mathrm{H}^{1,2}$	M^2	H^1	$\mathrm{H}^{1,2}$	Н	L	$H^{1,2}$
NA Emis Inv (Grid	1/4°x1/6°	1/4°x1/6°	1/4°x1/6°	Under	Under	1/4°x1/6°	
0 Lon x 0 Lat)				development	development		
Global Emis Inv	1°x1°	1°x1°					l°x1°
(Grid ⁰ Lon x ⁰ Lat)	(incomplete)	(incomplete)					
Estimated Current	370 (usage	850 (usage in	740 $(2005)^3$	1.6 ¹¹		35500 (usage	$470(2004)^3$
emissions – NA	$(in 2001)^3$	$(2002)^3$				$in 2002)^3$	
(tonnes)							
Estimated Current	1300 (usage	11,000 (usage		10-100 ¹²			$3000(2002)^3$
emissions – Global	$(in 2001)^3$	$in 2002)^3$					
(tonnes)							
Half life in air (days)	4-90 ⁴	3 ⁷	5-7 ⁹	700^{6}	$3.5 - 10^6$	0.6^{15}	$5-7^{16, 17}$
Half life in soil	24 5	1.7^{7}	70-120 ⁶	$36-72^{6,13}$	0.1-23 ⁶	$2-10^{15}$	24-120 ^{16, 17}
(months)							
logK _{oa} at 25°C	7.92^{6}	6.0^{8}	9.3 ¹⁰	6.78 ⁶	10.77^{6}	9.68 ⁶	9.21 ⁸
$log K_{ow}$ at 25°C	3.7 ⁶	3.62 ⁸	5.5 ¹⁰	5.5 ⁶	6.04 ⁶	2.75 ⁶	6.19 ⁸
Henry's Law const**	1318	10.23^{8}	0.29^{10}	17.6^{14}	0.012^{14}	0.0003^{15}	2.36^{8}
$at 25^{\circ}C (Pa m^{-3} mol^{-1})$							

** Higher the Henry's law constant, greater the propensity for the chemical to move from Water/soil to air