

ARE PULP AND PAPER MILLS SOURCES OF TOXAPHENE TO LAKE SUPERIOR AND NORTHERN LAKE MICHIGAN?

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Introduction

Toxaphene is transported through the atmosphere to the U.S. Great Lakes, where it contaminates fish. Toxaphene concentrations in both lake trout and smelt from the Great Lakes seem to have responded to its ban in 1982 (Glassmeyer et al., 1997). For example, the toxaphene concentrations in trout from Lake Ontario decreased by about a factor of about 10 between 1982 and 1992. There are, however, two important yet puzzling exceptions: In Lake Superior and in northern Lake Michigan, the levels of toxaphene in trout and smelt have not changed over the last 10-15 years (Glassmeyer et al., 1997). Why are fish from these two locations not showing the expected decline in toxaphene concentrations such as that observed in the other Great Lakes? There are two hypotheses: (a) The water in Lake Superior and northern Lake Michigan is colder than in the other Great Lakes, resulting in reduced air-water exchange and reduced degradation of toxaphene. (b) Toxaphene is being supplied to Lake Superior and northern Lake Michigan by non-atmospheric sources. This paper addresses this second hypothesis.

There are two non-atmospheric sources that could be delivering toxaphene to the Great Lakes: First, although toxaphene's use in the Midwest was slight, it is possible that farming the soil on which it had once been applied brings contaminated soil to the surface, and this process re-releases toxaphene into the environment. Second, it is possible that toxaphene-like compounds are produced and released by pulp and paper mills, which are numerous in the Great Lakes Basin. This second idea requires some chemical elaboration.

Toxaphene is produced by the photochlorination of camphene, an isomerization product of α -pinene. Both camphene and α -pinene are present in the softwood pulp from which paper is made. In fact, a typical pulp and paper mill has a "turpentine stream" of the water insoluble components coming from the pulping process. This stream contains terpenes that could act as potential precursors of toxaphene-like compounds (Kringstad and Lindstrom, 1984). Of course, pulp and paper mills are intensive users of chlorine-based bleaching agents. On average, pulp and paper mills use 60-70 kg of chlorine per metric ton of pulp (Kringstad and Lindstrom, 1984). Thus, pulp and paper mills have all the necessary ingredients for the inadvertent production of toxaphene-like compounds. If produced, these chlorinated by-products could be discharged into the mill's receiving stream and eventually make their way to the Great Lakes.

There is some literature to support the inadvertent production of toxaphene from the bleaching of paper. A study by Jarnuzi et al. (1992) found 90 ng/L and 80 ng/g of "toxaphene-like" compounds in water effluent and striped mullet fish, respectively, that had been collected near pulp and paper mills. Laboratory studies have also verified that camphene can be chlorinated under conditions ranging from complete darkness to simulated and real sunlight and at pHs of 2 and 8 (Larson and Marley, 1986).

To determine if these laboratory studies can be extrapolated to the real world and to determine if pulp and paper mills are potential sources of toxaphene-like compounds to the Great Lakes, we measured toxaphene in sediment collected upstream and downstream from the dis-

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charge points of seven pulp and paper mills, most of which now use chlorine dioxide in their bleaching processes (Schwartz, 1998). If the mills were discharging toxaphene, we should observe relatively elevated concentrations downstream from the mills. As controls, we also measured toxaphene near locations where it may have been used for agricultural purposes and at pristine locations where toxaphene should only have been delivered by the atmosphere.

Experimental Methods

Sampling. Sediment samples were collected in March and July of 1997 in conjunction with the US EPA. The locations of the sampling sites are listed in Table 1 and shown in Figure 1. For the pulp and paper mill sites, six samples (in close proximity to one another) were collected above and below each mill. The Wisconsin River site was sampled at three locations because there were three mills discharging their effluent into the same river. The lower two mills shared a common effluent discharge source. Samples were taken between the two discharge points as well as above and below them. The sediment collected from all sites was divided and duplicates were given to the mill where we had sampled. Distances from the mills to where the samples were collected were all less than 0.4 km.

Table 1. Sample Locations and descriptions.

Site	Abbr. ^a	Location	Mill	Type
Rainy River	RA	Internat'l Falls, MN	Boise Cascade	Pulp/paper
Menominee River	ME	Quinnesec, MI	Champion Paper	Pulp/paper
Escanaba River	ES	Escanaba, MI	Mead Paper	Pulp/paper
Peshtigo River	PE	Peshtigo, WI	Badger Paper	Pulp/paper
Wisconsin River	WI	Port Edwards, WI	Consolidated Paper	Pulp/paper
Wisconsin River	WI	Nekoosa, WI	Port Edwards and Nekoosa Paper ^b	Pulp/paper
Fish Lake	FL	Stark, MN		Background
Mississippi River	MN	Bemidji, MN		Background
Saginaw River	SA	Saginaw, MI		Previous use
Sheboygan River	SH	Sheboygan Falls, WI		Previous use
Root River	R	Racine, WI		Previous use
Grand River	G	Grand Haven, MI		Previous use
Sand Lake	SN	Scandia, MN		Previous use

^asee Figure 1 for locations; ^boperated by Georgia-Pacific Corp.

Sediments (three replicates in close proximity to one another) were also collected from rivers that drain areas where the US EPA indicated that toxaphene had been used as a pesticide. Sand Lake, a known toxaphene use location, was sampled once to give a deep piston core, which was sub-divided into 13 sub-samples. Background samples (also three replicates) were collected from pristine lakes and rivers that were assumed to be free of any input of toxaphene other than from atmospheric deposition.

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Samples were collected using three different methods depending on location, accessibility, and the nature of the sediment. In March 1997, the cores were collected with a 5 cm diameter gravity corer. In July 1997, the cores were collected with a 5 cm diameter commercial sediment

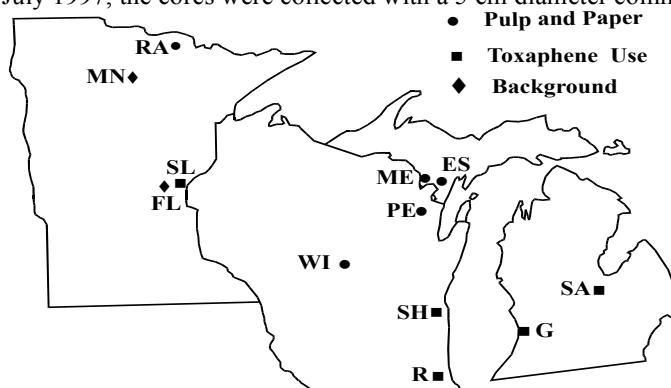


Figure 1. Map of sampling sites; see Table 1 for the sampling site codes.

corer. When sediment conditions would not allow the use of corers on the July sampling trip, sediment was collected with an Eckman dredge sampler. Samples were collected by wading or from a boat or bridge depending on the accessibility of the site. Sediment from core tubes was extruded, and the top 5 to 10 cm was retained for analysis. Samples from the dredge sampler were directly transferred into collection jars. A single 65-cm deep sediment core was collected from Sand Lake, a previous toxaphene use area. This core was sectioned every 5 cm. After being filled, the sample jars were placed in coolers with ice, shipped back to the laboratory, and stored at 4 °C until they were warmed to room temperature for extraction.

Extraction and Analysis. Sample preparation, extraction, clean up, and other details have been described elsewhere (Howdeshell and Hites, 1996). The one exception to this published method was our use of $^{13}\text{Cl}_1$ -chlordane (Cambridge Isotope Laboratories, Cambridge, MA) as the internal standard. In summary, toxaphene was quantitated by gas chromatographic mass spectrometry (Hewlett Packard 5989A or 5973) operated in the electron capture, negative ionization mode with methane as the reagent gas. The ion source temperature was 125 °C. The instruments were equipped with 30 m, DB-5MS columns. Data were acquired using the selected ion monitoring method based on ions suggested by Swackhamer et al. (1987). A relative response factor standard of Hercules toxaphene was run every 5 samples. Quantitation used a software system recently described by Glassmeyer et al. (1999).

Loss-on-ignition. LOI was determined for all samples. Sediment samples were weighed, placed in crucibles, and dried at 105 °C for 24 hours to remove water. Samples were then re-weighed and heated in a muffle furnace at 525 °C for 24 hours and weighed again. Total organic carbon was estimated by dividing the LOI by 1.724 (Howard and Howard, 1990).

Results and Discussion

The results of this study are summarized in Table 2. While there were considerable variations within the six (or three) replicates, we have simply reported an arithmetic average and standard error of the non-zero concentrations. Using these average statistics and paired Student's *t*-tests, we find that the concentrations of toxaphene found downstream from each mill's effluent

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discharge point are not significantly different (at the 90% confidence level) from those found upstream. On average, the concentrations of toxaphene found upstream from the mills ranged from 1.4 to 8.3 ng/g, and downstream from the mills, the concentrations ranged from 1.5 to 8.7 ng/g. From these data, we conclude that these pulp and paper mills are probably not now sources of toxaphene to the Great Lakes.

Table 2. Summary toxaphene concentrations and standard errors.

Mill	Abbr.	Location	ng/g dry sediment	ng/g organic carbon
Boise Cascade	RA	Upstream	1.4 ± 0.5	11 ± 3
		Downstream	1.5 ± 0.6	44 ± 18
Champion Paper	ME	Upstream	7.5 ± 4.6	10 ± 200
		Downstream	8.7 ± 3.6	230 ± 80
Mead Paper	ES	Upstream	8.3 ± 6.6	460 ± 430
		Downstream	6.3 ± 5.0	140 ± 36
Badger Paper	PE	Upstream	1.9 ± 0.4	170 ± 100
		Downstream	4.6 ± 3.1	490 ± 240
Consolidated Paper	WI	Upstream	2.0 ± 1.1	490 ± 390
Port Edwards and	WI	Middle	9.0 ± 4.7	190 ± 70
Nekoosa Paper	WI	Downstream	7.3 ± 2.7	2100 ± 1200

With the exception of the Sand Lake site, the average concentration of toxaphene in the sediment samples collected from rivers that drain previous toxaphene use areas ranged from 6.0 to 43 ng/g. These concentrations were somewhat higher than those found in the samples collected near the pulp and paper mills. The average toxaphene concentrations at the two background sites were 0.3 and 0.5 ng/g, values much lower than those observed at all of the other sites. The samples from Sand Lake were in the form of a chronologically segmented core. In this case, the 6 upper sections had higher toxaphene concentrations (0.2-3.6 ng/g) as compared to the lower sections (not detected-1.0 ng/g). The upper sections are comparable to the previous toxaphene use samples, and the lower sections are comparable to the background sites. The elevated concentrations in previous use areas compared to the background sites suggests that some of these areas could be releasing toxaphene back into the environment, where it could make its way into the Great Lakes. However, we cannot estimate how much toxaphene this process might be contributing to Lake Superior or to northern Lake Michigan.

Our measurements of toxaphene in these samples are compared to some previously reported measurements in Table 3. The previously reported toxaphene concentrations in Lake Ontario, Michigan, and Superior sediments range from 3 to 45 ng/g, values which are similar to the concentrations reported here for sediment in rivers near pulp and paper mills and near sites of previous toxaphene use, which range from 1.4 to 43 ng/g. Previously reported toxaphene concentrations at other background locations range from 0.6 to 9 ng/g, values which are somewhat higher than our measurements of 0.3 and 0.5 ng/g at our background locations. Averaging the samples from Sand Lake over the entire core gave a toxaphene concentration of 1 ng/g, a value comparable with other background locations. Total toxaphene concentrations were also normalized to organic

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carbon (see the last column of Table 2. Like the dry weight normalized data, these organic carbon normalized data did not show significantly higher toxaphene concentrations downstream from the pulp and paper mills either. These comparisons support our conclusion that pulp and paper mills are probably not now sources of toxaphene to Lake Superior or to northern Lake Michigan.

Table 3. Toxaphene concentrations in selected sediments.

Site	Conc. (ng/g dry wgt.)
Rivers near pulp and paper mills	1.4-9.0
Rivers near previous usage sites	6.0-43
Lake Ontario ^b	15
Lake Ontario ^c	10-20
Lake Michigan ^b	15-45
Lake Superior ^a	3-15
Lake Superior ^b	15
Sand Lake	1
Siskiwit Lake ^a	9
Outer Island ^a	4
Apostle Islands ^b	4-9
Lake Nipigon ^d	0.6-3
Mississippi River	0.3
Fish Lake	0.5

^aPearson et al. (1997); ^bSwackhamer et al. (1996); ^cHowdeshell et al. (1996); ^dStern and Muir (unpublished data)

Rappe et al. (1998) analyzed the duplicate samples we provided to the Georgia Pacific Co., and in most cases, these authors found less than about 0.2 ng/g dry weight of total toxaphene. These values seem unusually low, being about 1-5% of the concentrations we found in the same samples, about 1% of the concentrations found in Great Lakes sediments, and about 10-20% of the concentrations found in sediments from the background sites. These authors did not observe any significant differences in toxaphene levels between upstream and downstream samples. The difference in these results between our two laboratories may indicate a possible bias inherent in one or both of the toxaphene analytical methods. We should point out that all of the data in Table 3 were obtained with the Swackhamer et al. (1987) method while the Rappe et al. (1998) data were obtained with another method. It is possible that the differences between the two data sets for the Georgia Pacific samples are due to differences in the two methods. It is important to note, however, that neither laboratory finds that concentrations below the pulp and paper mills were significantly higher than those found above the mills.

There is considerable variability in the toxaphene concentrations, in the losses-on-ignition (LOI), and in the homologue profiles among the replicate samples taken at the same locations because of problems associated with sampling sediment in rivers. Sediment in rivers can vary dramatically over small spatial regions. In addition, the location of sediment deposition zones in a river can shift because of day-to-day and seasonal flow variations, because of the presence of ice,

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and because of human influences (such as damming of the rivers and motor boat use). Sediment focusing and defocusing in rivers may also be a major problem, and historic information on the presence of toxaphene could be lost if sediment defocusing were significant. Despite these problems, we are convinced that our sediment samples from these rivers were sufficiently high in organic carbon to retain toxaphene. We reach this conclusion for two reasons: First, the toxaphene concentrations we have measured in these river sediments are similar to those measured in lakes, particularly the Great Lakes. Second, the LOI values, and by extension the total organic carbon values, are typical of those for sediments known to accumulate pollutants (Simcik et al., 1996).

Although our results do not indict the pulp and paper industry as a current toxaphene source, we should point out that things may have been different in the past, and they may be different in the future. Additional toxaphene measurements of mills' effluent streams and of their various paper products would be helpful.

Acknowledgments

We thank D. DeVault, H. Wiegner, P. King, L. Lins, and P. Novak, Jr. for their assistance in sampling, S. Kendall for technical assistance, and the U.S. Environmental Protection Agency for funding (Grant X985360). A full version of this paper has been published in the *J. Great Lakes Research*.

References

- Glassmeyer, S. T., De Vault, D. S., Myers, T. R., and Hites, R. A. 1997. *Environ. Sci. Technol.* 31:84-88.
- Glassmeyer, S. T., Shanks, K. E., and Hites, R. A. 1999. *Anal. Chem.* 71:1448-1453.
- Howard, P. J. A., and Howard, D. M. 1990. *Biol. Fertil. Soils.* 9:306-310.
- Howdeshell, M. J., and Hites, R. A. 1996. *Environ. Sci. Technol.* 30:220-224.
- Jarnuzi, G., Matsuda, M., and Wakimoto, T. 1992. *Kankyo Kagaku.* 2:364-365.
- Kringstad, K. P., and Lindstrom, K. 1984. *Environ. Sci. Technol.* 18:236A-248A.
- Larson, R. A., and Marley, K. A. 1986. *Formation of Toxaphene-Like Contaminants During Simulated Paper Pulp Bleaching*. Water Resource Center, University of Illinois, Urbana, IL. WRC 205.
- Pearson, R. F., Swackhamer, D. T., Eisenreich, S. J., and Long, D. T. 1997. *Environ. Sci. Technol.* 31:3523-3529.
- Rappe, C., Haglund, P., Anderson, R., and Buser, H. 1998. *Organohalogen Compounds* 35:291-294.
- Schwartz, J. 1998. American Forest & Paper Assoc. Personal communication.
- Simcik, M. F., Eisenreich, S. J., Golden, K. A., Liu, S. Lipiatou, E., Swackhamer, D. L., and Long, D. T. 1996. *Environ. Sci. Technol.* 30:3039-3046.
- Swackhamer, D. L., Charles, M. J., and Hites, R. A. 1987. *Anal. Chem.* 59:913-917.
- Swackhamer, D. L., Eisenreich, S. J., and Long, D. T. 1996. Report to the U.S. EPA and the Great Lakes Protection Fund.