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Project Summary

Atmospheric Transport of Toxaphene to Lake Michigan

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Atmospheric levels of toxaphene were monitored during the summer and fall of 1981 at four locations: Greenville, Mississippi, St. Louis, Missouri, Bridgman, Michigan, and Beaver Island, Michigan. Each collection was conducted by continuously sampling air during the first two weeks of the months of August, September, October, and November. The collected toxaphene was analyzed on a capillary equipped electron capture gas chromatograph. The average concentrations over the entire sampling period for each site were 7.39 ng/m³ in Greenville, 1.18 ng/m³ in St. Louis, and 0.27 ng/m³ for Lake Michigan (Bridgman and Beaver Island combined). The summer versus fall fluctuations in amount of toxaphene at each site was 0.44 ng/m³ versus 0.26 ng/m³ for Bridgman; 1.73 ng/m³ versus 0.63 ng/m³ for St. Louis; and 9.05 ng/m³ versus 4.34 ng/m³ for Greenville. The maximum monthly average occurred in September for all of these collections. Diagnostic modeling to describe possible air transport of toxaphene showed that at all receptor locations the air transport corridor for toxaphene was associated with southerly winds. The strength of this corridor increased from northern to southern measurement sites. A flux estimate for toxaphene deposition to the lake surface ranged from 3,360 to 6,720 kg/yr.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

For this study, atmospheric levels of toxaphene were monitored simultaneously during the summer and fall of 1981 at four locations: Greenville, Mississippi; St. Louis, Missouri; Bridgman, Michigan; and Beaver Island, Michigan.

The sampling intervals at each site were adjusted to occur simultaneously in an attempt to determine possible atmospheric links between the sites and a southern input source for toxaphene. Backward air trajectories were constructed for each location during the sample-collection periods. These trajectories, coupled with the observed atmospheric concentrations of toxaphene, were used to construct probability contours for the likeliest toxaphene delivery corridors into each of the sites.

Collection was conducted by continuously sampling air during the first two weeks of each of the following months of 1981: August, September, October, and November. Beaver Island samples were collected only during the second and third time interval. Samples were collected using both high- and low-volume air samplers. The high-volume sampler employed a General Metals suction pump drawing air at a rate of 0.6 to 1.1 m³/min through a sampling train having a glass fiber filter followed by two to three polyurethane foam plugs (9 cm diam. x 6.5 cm long). The high-volume system was used in St. Louis, Bridgman, and Beaver Island and operated for periods of 2 to 4 days for each sample collection. Three samples were collected for each 2-week period. The low-volume air sampler consisted of a low-volume suction pump (flow rates of 7 to 10 L/min) which was connected to a series of 2 to 3

polyurethane foam plugs (3.5 cm diam. x 10.5 cm long). The low-volume system was used at the Greenville sampling site. During this study, one sampler was operated continuously over the entire 4-month period to secure an integrated collection.

The collected toxaphene was removed from the plugs and filters using Soxhlet extraction with petroleum ether. The toxaphene was analyzed on a fused silica capillary equipped electron capture gas chromatograph. Sample extracts were subjected to a minimum of cleanup and fractionation prior to analysis in order to avoid changes in the chromatographic appearance of the toxaphene mixtures. The extracts were treated with sulfuric acid for cleanup and then injected directly into the gas chromatograph. Individual peaks in the samples were compared to peaks in a standard of toxaphene obtained from EPA. The peak matching method was relative retention time using either p,p'-DDE or octachloronapthalene as the reference standard. To avoid misidentification of peaks, a narrow window for peak matching was selected, and peak regions suspected of interferences, e.g., PCBs and chlordanes, were not included in the matching routine.

With the capillary column selected and the sensitivity provided by the instrument, between 26 to 60 peaks were selected for matching against the samples. Although approximately 200 peaks were identified in the standard, many were screened out for various reasons, e.g., poor baseline resolution, low detector response, or inteference from PCBs or chlordanes.

A percentage of the number of peaks matched versus the number of peaks sought was calculated. This provided an estimate of the similarity of the material measured to the standard used. The mean percent matches for each of the sampled regions were 36% for Lake Michigan, 38% for St. Louis, and 51% for Greenville. One interpretation of the results posited that the composition of toxaphene nearest the source would have the best match; Greenville, located in an area of high toxaphene usage, seemed to fit this concept.

While most of the toxaphene was recovered from the foam plugs, less than 5% was on the filters, indicating little or no particulate-phase toxaphene in the air. The average concentrations over the entire sampling period for each site were 7.39 ng/m^3 in Greenville, 1.18 ng/m^3 in St. Louis, and 0.27 ng/m^3 for Lake Michigan (Bridgman and Beaver Island combined). These results indicate a definite decline in concentration of toxaphene moving from south to north. Also, the amount of toxaphene at each site varied seasonally, i.e., the levels measured higher in the two summer collections than in the two fall collections. For Bridgman, these values were 0.44 ng/m^3 for the summer and 0.26 ng/m^3 for the fall; for St. Louis these respective values were 1.73 ng/m^3 versus 0.63 ng/m^3; and for Greenville they were 9.05 ng/m^3 versus 4.34 ng/m^3. The maximum average level of toxaphene for all sites was measured in the second 1981 sampling period (25 August through 3 September). The changing pattern for toxaphene in air over the sampling period appears to be one of an initial increase in early August to a maximum in early September, and then a gradual decrease in October and November. This cycle agrees with similar observations of changing levels of toxaphene in air measured in the Mississippi delta by other researchers in 1974.

Diagnostic modeling to describe possible air transport of toxaphene showed that at all receptor locations the air transport corridors for toxaphene were associated with southerly winds. The preferred corridors of transport of higher concentrations increased from northern to southern measurement sites, presumably in response to the larger range of concentrations in the south. This analysis does not prove which source region(s) contributed to the observed concentrations, partly because so little is known about the magnitude of the source strenghts. However, the methodology developed for this analysis can identify the probable corridors of transport delivering the material to the receptor. The methodology is well suited for analysis of data which, because of low concentrations in the atmosphere, must be collected over long time periods (longer than a day). With a sufficient number of samples, intra-period fluctuations in contribution to the sample will be removed and meaningful transport characteristics will be discerned.

A flux estimate for toxaphene deposition to Lake Michigan was calculated. An event rain sample collected at Beaver Island during one of the 1981 air collection periods was used in this calculation. The toxaphene measured in this sample gave a washout coefficient of 1,355 for this sample. This was higher than the range of values (16 - 861) reported in 1981 by other researchers; therefore, the current study used values of 500 to 1,000 for the wet flux estimate. For the air concentration for this flux calculation, this study used measured values an assumed that the Beaver Island result represented northern Lake Michigan an that the Bridgman site represented south ern Lake Michigan. To estimate winte levels, the summer average was reduce by one-fourth. This resulted in an esti mate of the year-round level of toxaphen in air over Lake Michigan to be 0.1 ng/m^3. The wet flux, which was calcu lated using the above derived values ranged from 3,000 to 6,000 kg of toxa phene per year. To derive a dry flu estimate, we chose a deposition velocit range of 0.12 to 0.24 cm/sec and use our measured whole lake air concentra tion. Using these values, the calculate dry flux was 360 to 720 kg of toxaphen deposited per year. Together, these ac counted for a total estimate of 3,360 t 6,720 kg/yr for toxaphene flux to Lak Michigan in 1981.

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The complete report, entitled "Atmospheric Transport of Toxaphene to Lake Michigan," (Order No. PB 85-121 143; Cost: $10.00, subject to change) will be available only from:
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