Continuous Analysis of Chlorinated Hydrocarbon Pesticides in the Lower Mississippi River

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A 1970 survey (USPHS, 1970) of 26 water supplies in the New Orleans Standard Metropolitan Statistical area was undertaken to assess the drinking water quality in the area. This survey was a cooperative effort of the Division of Sanitary Engineering, Louisiana State Board of Health, and the Bureau of Water Hygiene (Region VII), USPHS, as part of a nationwide study (USPHS, 1970).

A portion of this study involved the analysis of 1-gallon grab samples of potable waters for chlorinated hydrocarbon pesticides. The results (Table I) indicated that only a trace amount ($<$ 0.1 ppb) of DDT could be found in the East Jefferson Waterworks District No. 1 finished water supply and that no chlorinated hydrocarbon pesticides were found in the West Jefferson Waterworks District No. 2 finished water supply.

It was our belief that the zero concentrations for several other chlorinated hydrocarbon pesticides listed in Table I indicated simply that a more effective sampling method was needed to determine if ug/l (ppb) or ng/l (ppt) amounts of these materials could be found in the source of supply for these two water districts, i.e., the Mississippi River.

For this reason we used a continuous liquid/liquid extraction apparatus (LLM) as described by Kahn & Wayman (1964) to monitor ng/l levels of eight chlorinated hydrocarbon pesticides in the Mississippi River at the Jefferson Parish (East Jefferson) Waterworks, District No. 1.

The raw water intake of this plant is located at river mile 105.2 AHP.** This location is approximately one river mile above the intakes for the City of New Orleans water purification facility.

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TABLE I Pesticides Analysis on Surface Water Supplies *

(Data in ug/l)

	East Jefferson Waterworks District No. 1	West Jefferson Waterworks District No. 2
Aldrin	0	0
γ-Chlordane	0	0
DDT	<0.1	0
Dieldrin	0	0
Endrin	0	0
Heptachlor	0	0
Heptachlor Epoxide	0	0
Lindane	0	0
Methoxychlor	0	0
Toxaphene	0	0

EXPERIMENTAL

Sample periods were 7 days each. The average raw water flow rate through the extraction apparatus was 36 ml/min., average sample volume was 367 l. The sample rate was approximately twice as fast as that reported by Kahn & Wayman (1964). The high turbidity of the sample stream necessitated this increased flow rate to prevent plugging of the outlet tube on the extraction apparatus.

At the end of the 7 day sample period extracts from the 3 flasks were combined and concentrated to 25 ml. This concentrated extract was then cleaned up by column chromatography and, if necessary, by thin layer chromatography (TLC) prior to gas-liquid chromatography analysis (GLC).

The 300 mm L x 20 mm I.D. chromatographic tubes were packed with a 120 mm column of Florisil (activated at 130°C) and a 15 mm topping of anhydrous sodium sulfate. After wetting the column with 35 - 40 ml of hexane (which was discarded) the extract was placed on the Florisil column. The pesticides were then eluted first with 200 ml of 6% ethyl ether/petroleum ether solution (v/v) and then 200 ml of 15% ethyl ether/petroleum ether solution (v/v). Dieldrin and endrin were eluted by the second solution.

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*USPHS, Community Water Supply Study, August, 1970.

**Above Head of Passes

The 15% eluant required further cleanup on a MgO-Celite column. The 6% eluant was ready for GLC after evaporative concentration on a steam bath using a 3-ball Snyder column attached to a 500 ml flask.

The MgO (Fisher Sea-Sorb 43) was slurried with distilled water, heated on a steam bath for 30 minutes, filtered, and dried overnight at 130°C. The dried filtrate was pulverized in a blender and then mixed in a 1:1 ratio with Celite 545 (Johns-Manville).

A plug of glass wool topped by 10 gms of the MgO-Celite mix was used in the 300 mm L x 20 mm I.D. chromatographic column. The mix was packed into the column under full vacuum (approximately 640 mm Hg). The vacuum line was then bled to set a elution rate of 15 - 20 ml/min for a 35 - 40 ml petroleum ether prewash (not necessary to discard). The 15% eluant was first evaporated by refluxing to 10 ml and then applied to the MgO-Celite columns under partial vacuum. Dieldrin and endrin were then eluted with 100 ml of petroleum ether. After concentration to 15 ml this fraction was also ready for GLC analysis.

A Hewlett-Packard 5750 gas chromatograph equipped with two tritium electron capture detectors was used for all GLC work. Both columns were Pyrex glass, 1.83 m L by 0.32 cm I.D. Column A was packed with 5% DC-200 on 80/100 Chromosorb W-DCMS. Carrier flow rate (5% methane in argon) through Column A was 80 ml/min. Column B was packed with 1.5% OV-17 and 1.95% QF-1 on 80/100 Chromosorb W-DCMS. Carrier flow rate (5% methane argon) through this column was 50 ml/min. No additional purge gas was used at either detector. Both pairs of injectors, columns and detectors were operated at, respectively, 212°C, 184°C, and 204°C.

Qualitative interpretations of the chromatograms of river water extracts were made by comparison of relative retention times of peaks in the unknown to known peaks on chromatograms obtained by injection of calibration mixtures of analytical standard grade pesticides. These pesticide standards were obtained from the Pesticides and Toxic Substances Laboratory of the U. S. Environmental Protection Agency.

Quantitative data was obtained by the comparison of identified and confirmed peak heights in the unknown to those of the standards calibration mix.

Identification of all pesticides was confirmed by the use of two columns with liquid phases of different polarity as indicated. Additionally, some samples were further confirmed by TLC (Breidenbach, et al, 1968) and subsequent elution of resolved spots on the thin layer chromatogram. The silica gel was then picked up and washed with petroleum ether. This extract was then concentrated and a 5 ul aliquot injected into the GLC again.

Recovery rates shown in Table II were obtained by spiking petroleum ether aliquots with known weights of the pesticides and carrying the ether solutions through the entire cleanup and GLC procedure.

TABLE II.Recovery Rates for Pesticides: Cleanup and GLC Procedure

	% Recovered
γ-Chlordane	95.2
Lindane	92.2
Heptachlor	83.8
Heptachlor Epoxide	96.8
Dieldrin	95.6
Endrin	97.5
p,p'-DDD	91.5
p,p'-DDT	85.8

RESULTS AND DISCUSSION

Data for eight chlorinated hydrocarbon pesticides found in the Mississippi River are plotted in Figure 1. The data points represent monthly averages (N = 4 except April, November and December where N = 3) and are in ng/l.

At first glance there would appear to be some correlation between observed values for some of the related compounds (i.e., metabolites, etc.) such as heptachlor—heptachlor epoxide, dieldrin—endrin, and p,p'-DDD—p,p'-DDT.

The possible significance of these correlations was checked statistically by computing the correlation coefficient, "r", using the formula (Bailey, 1959):

$$r = \frac{\Sigma(x-\bar{x})\,(y-\bar{y})}{\sqrt{\Sigma(x-x)^2(y-y)^2}}$$

PESTICIDE CONCENTRATIONS IN THE MISSISSIPPI RIVER AT MILE 105.2 AHP

FIGURE 1-A

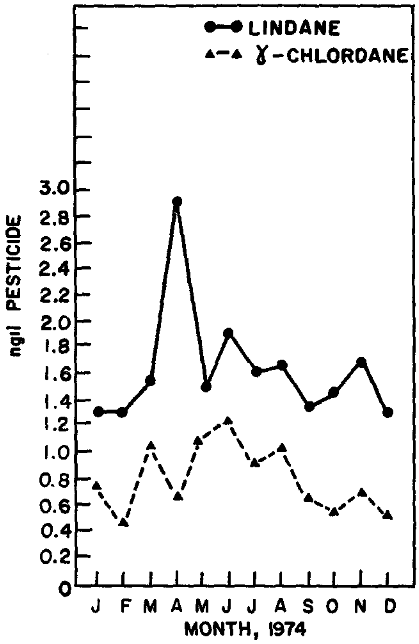


FIGURE 1-B

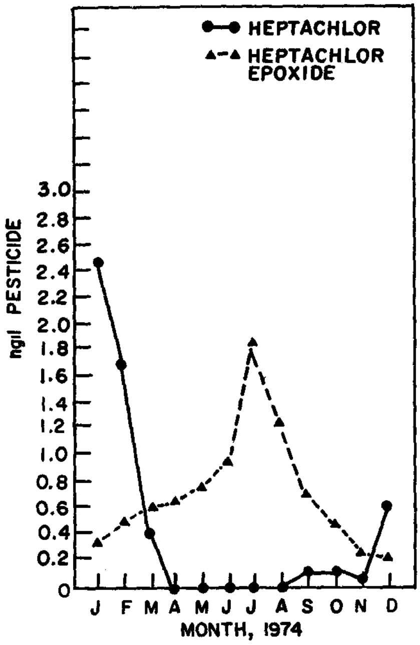


FIGURE 1-C

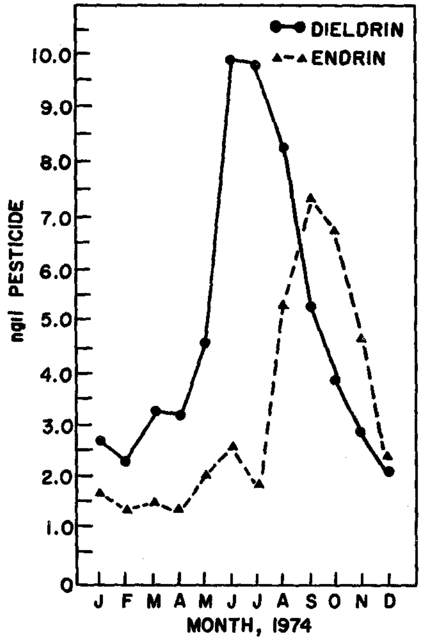
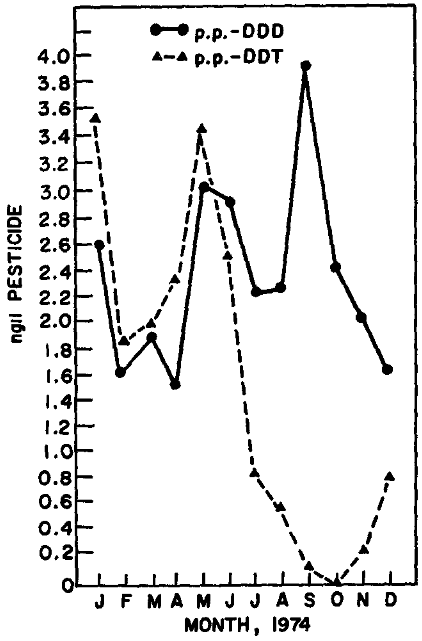


FIGURE 1-D



As can be seen in the following list the only possibly significant correlation in the pesticide "pairs" was a negative correlation between the concentration of heptachlor and heptachlor epoxide.

	r	Critical r Value @ P = 0.05 (42 DF)
Heptachlor—Hept. Epoxide	-0.310	0.304
Dieldrin—Endrin	+0.106	0.304
p,p'-DDD—p,p'-DDT	+0.113	0.304

Although each of the eight pesticides studied occurred in the ng/l range, it is interesting to note that the calculated total load of these compounds introduced annually to the Gulf of Mexico by the Mississippi River is quite high.

In order to determine this total annual load the sum of the annual average concentrations of the eight pesticides (15.53 ng/l) was multiplied by the average discharge volume of the Mississippi River (l/sec) at Tarbert Landing, a U. S. Army Corps of Engineers river monitoring station. This station is located approximately 200 river miles above the sampling point used for this study. However, no other influents or outfalls exist in the span of the river between the two points.

The results of these calculations indicate that a minimum of 49.7 lbs. of the eight pesticides (combined weight) is introduced to the Gulf of Mexico each day. On an annual basis this figure equates to a weight of a minimum of 9 tons/year.

In summary eight chlorinated hydrocarbon pesticides (Figure I) occur almost continuously in the Mississippi River near the point of discharge into the Gulf of Mexico. Quantitative data indicate that the concentrations of the pesticides are in the ng/l range for all compounds studied.

ACKNOWLEDGEMENT

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REFERENCES

BAILEY, N.T.J.: Statistical Methods in Biology. English Universities Press, Ltd., London, England (1959).

BREIDENBACH, A., LICHTENBERG, J., HENKE, C. F., SMITH, D. J., EICHELBERGER, J. W. and STIERLI, H.: The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters. U. S. Government Printing Office: 1968-0-315-824.

KAHN, L. and WAYMAN, C. H.: Anal. Chem. 36, 1340 (1964).

U. S. PUBLIC HEALTH SERVICE (REGION VII): Community Water Supply Study, New Orleans, Louisiana Standard Metropolitan Statistical Area (August, 1970).