

(iii) the freezing-in of the field, which, during departure, inhibits ( $d\phi/dt$ ) and therefore depresses the recorded voltage, meanwhile extending the record well outside the region where the pole-piece field had ceased to affect the pickup coil in the Textolite disk.

If, in the case of the curve for Al, the encounter part of the curve is rotated 180° and superimposed on the departure part, the integrated difference between the encounter and departure curves gives the anomalous flux not accounted for by the magnet and by back electromotive force.

The decay of the frozen flux is approximately exponential, vanishing after about 10 msec. To assess the exponential character of the decay, a semi-logarithmic plot was made of the data in Fig. 1. The linear region of this plot has a slope indicative of a decay time constant of 0.0052 second. This

is in good agreement with the theory, which predicts a decay time constant of about 0.003 second.

The general conclusion for sunspot theory is that the frozen-in magnetic field is in fact a valid starting point, once a high-conductivity plasma is assumed to constitute the photosphere. Near a sunspot, the decay time constant [if we assume a conductivity of 100 ohm-m (4)] would be about 10<sup>20</sup> seconds.

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## Microparticulates: Isolation from Water and Identification of Associated Chlorinated Pesticides

*Abstract. Microparticulates suspended in lake water were collected by continuous centrifugation and either examined directly or placed on a linear sucrose gradient. Total residue as well as fractions of the centrifuged gradient were extracted with hexane and examined by gas chromatography for the presence of chlorinated hydrocarbon pesticides. Hexane extracts of total residues were also examined by thin-layer chromatography. Lindane and endrin were shown, by gas-liquid chromatography and thin-layer chromatography, to be associated with microparticles. These and other pesticides appeared to be selectively associated with microparticles of different densities, when gas-liquid chromatography was used, although concentrations were below the detection limits required for confirmation by thin-layer chromatography. Samples taken at different times from different locations in Lake Erie revealed different associations with hexane-soluble electron-capturing compounds.*

The ubiquity of pesticides and the significance of their presence in the aquatic habitat has been established. Techniques for identification of pesticides in natural water usually involve extraction from water by adsorption on activated carbon. This particular method has been included in the 1962 USPHS drinking water standards as the method for the determination of organic substances in water (1). In this procedure, up to 5,000 gallons (about 19,000 liters) of water are passed through a column of activated carbon 18 by 3 inches (45.7 by 7.6 cm). The column is extracted with chloroform to remove adsorbed pesticides, and the extract is analyzed by gas chromatography. It is possible to obtain analyses by extraction of small volumes of water (for example, 1 liter) where

concentrations of pesticides are high enough to cause a detector response at that level. Water samples containing pesticide concentrations below limits of detection are usually extracted by a countercurrent batch process or by liquid-liquid extraction processes to increase sensitivity of the method (2). Combinations of these methods have been useful for detection of extremely small amounts of contaminants but are quite time-consuming.

We have investigated the association of chlorinated hydrocarbon pesticides with microscopic particles suspended in Lake Erie. Water was collected in the vicinity of the Bass Islands in the western basin of Lake Erie from 15 feet (4.6 m) below the surface. A 5-gallon sample was centrifuged in a Sorvall RC-2B Szent-Györgyi and Blum con-

tinuous flow centrifuge at 27,000g at a flow rate of 11 ml/min. The particulates from this fraction (0.15  $\mu$ m in diameter and above) were placed on top of a preformed linear gradient of sucrose (0 to 65 percent) and centrifuged at 1500g for 60 minutes. The tube was divided into four fractions, each of which was extracted with hexane. Raw water samples (2 liters) have been extracted by using the liquid-liquid extraction procedure. No detectable chlorinated pesticides were found. Analysis of the hexane extracts for presence of chlorinated hydrocarbon pesticides was made by using an Aerograph 200 gas chromatograph equipped with an electron-capture detector [250 mc of titanium tritride, column temperature 190°C, detector 200°C, injector port 230°C, 5-foot glass, 1/8 inch (internal diameter) column packed with Chromosorb W 60/80 mesh, coated with 5 percent Dow silicone SE-30, high-purity N<sub>2</sub> carrier gas 60 ml/min].

Because gas-liquid chromatography (GLC) retention time and reinforcement of peaks are analytically inadequate for identification purposes, the presence of specific pesticides must be regarded as presumptive. The data suggested, however, that concentrations of specific pesticides associated with individual particulate fractions were below the level of detection by thin-layer chromatography (TLC) (3). Therefore, the use of confirmatory TLC on particulates from larger water samples was employed. For this purpose, a 20-gallon water sample was centrifuged as previously described. The total particulate residue was extracted with hexane and concentrated to 0.5 ml by evaporation. Aliquots (2  $\mu$ l) were injected into the gas chromatograph and the remaining volume was added as a single spot onto Eastman Chromogram 6061 TLC sheets. The TLC sheets were preconditioned and developed by the methods of Kovacs (4), and sprayed with 0.05 percent Rhodamine B (3); 5- $\mu$ g and 50- $\mu$ g spots of control pesticides were chromatographed on the same TLC sheet.

The TLC sheets indicated the presence of spots with  $R_F$  values identical to lindane and endrin. The GLC recordings verified the presence of lindane and endrin as well as several additional peaks from this particular sample.

Pesticides which have been tentatively identified from GLC recordings taken from particulate fractions are lindane, heptachlor, aldrin, and endrin; there were also several unidentified peaks.

Table 1. Nanograms of chlorinated hydrocarbon pesticides per liter of lake water associated with each fraction of particulates. Samples 79 and 75 show the qualitative presence or absence of chlorinated pesticides in each extracted fraction of two other samples taken at different times of the year.

Pesticide	Gradient fraction			
	1	2	3	4
	<i>Sample 86</i>			
Lindane	0.53	4.6	3.2	16.5
Heptachlor	0.69	0	1.7	2.1
Aldrin	14.7	2.0	1.0	1.3
Endrin	9.6	0	0	0
DDT: metabolic products or isomers	0	0	0	0
	<i>Sample 79</i>			
<i>p,p'</i> -DDD	+	+		+
Lindane	+		+	
Heptachlor	+	+	+	+
<i>p,p'</i> -DDT	+		+	
<i>o,p'</i> -DDT		+		
Endrin		+		+
<i>o,p'</i> -DDD			+	
	<i>Sample 75</i>			
<i>o,p'</i> -DDD	+	+	+	
<i>p,p'</i> -DDD	+	+	+	+
<i>o,p'</i> -DDT	+	+	+	+
<i>p,p'</i> -DDT		+	+	+
Lindane		+		+
Heptachlor		+	+	+
Endrin			+	

Pesticides were tentatively identified by comparison of retention times to those of control samples of known purity (dieldrin, aldrin, endrin, 99+ percent, Shell Chemical Co.; DDT and isomers, 99+ percent, USPHS pesticide repository; lindane, heptachlor, 99+ percent, City Chemical Corp.), and also by reinforcement of peaks by addition of known compounds. The distribution pattern of pesticides with different particulate fractions illustrates that various chlorinated hydrocarbons have an affinity for particulates separable by density-gradient centrifugation (that is, different particles). The distribution of these pesticides demonstrates their association with the particulate components suspended in the water. The utility of the collection and fractionation procedures is verified by the variety of pesticide separations obtained through its use.

Table 1 is a compilation of pesticide distribution and concentration in the particulate fractions of three separate lake water samples taken at different times, based upon GLC data without TLC confirmation, since the concentration of pesticide in gradient fractions is below the limit of TLC detection.

Evidence from this study suggests that there is a quantitative as well as qualitative distribution of pesticides associating with varied particulate com-

ponents in natural waters. Pesticides that were determined were attached to particles of 0.15  $\mu\text{m}$  or larger in size, and different pesticides were shown to be associated individually with particles of different density. For example, in sample 86, lindane was found in greater concentration in fraction 4, the inorganic portion of the particulate material (5), while aldrin and endrin were associated with less dense upper fractions 1, 2, and 3, which consist primarily of organics, detritus, and microorganisms. The presence of various chlorinated pesticides associated with different particulate components suggests a complex involvement of these compounds with components of the environment. These compounds could be present in the environment as either molecular aggregates in aqueous solution (4.1 nm or less) or in suspension (up to 0.11  $\mu\text{m}$ ) (6). In our system, particulates below 0.15  $\mu\text{m}$  were not included, so that the presence of pesticides is indicative of some kind of true pesticide-particulate association. The particles could be cell, detritus, or inorganic materials (for example, clay minerals).

Different chlorinated hydrocarbons are present in different water samples. For example, samples 70 and 75 suggest the presence of DDT, its isomers, and metabolic breakdown products, whereas no DDT-group compounds were detected in sample 86. The lack of detection of DDT or isomers in this sample may be a reflection of the possibility of the specific association of such compounds with specific particulates, or, of course, it may be that these compounds were below the level of detection in the quantity of particulate used for the extraction.

In analyses where activated carbon filters have been used (for example, U.S. Public Health Service Water Pollution Surveillance Program) levels (0.05 ng to 0.05  $\mu\text{g/liter}$ ) of pesticides are detected. This technique has made use of 30-mesh high-grade carbon or layered 30-mesh and 4- by 10-mesh carbon which has been preextracted to remove organic material. It seems likely that chlorinated hydrocarbons associated with particles that have the general size of 0.15  $\mu\text{m}$  could pass through coarse carbon filters and remain undetected in the water sample. Evidence from our study suggests that removal and analysis of particulates may need to be included to give more adequate estimates of pesticides in aquatic environments. In an environ-

ment such as Lake Erie, where the shallow water is so easily disturbed by wind action, the turnover and accumulation of pesticides in bottom sediments may be significant.

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#### Pulsar Test of a Variation of the Speed of Light with Frequency

Abstract. *The sharply defined optical and radio pulses from pulsars make possible a test of the variation of the speed of light with frequency, and of the possible existence of a photon mass. The data indicate that the mass of a real photon is less than  $10^{-44}$  gram. Detection of extragalactic pulsars could allow a substantial improvement of this limit.*

The conventional description of light as a stream of massless particles implies that the speed of light in a vacuum is independent of its frequency. Direct tests of this independence have been made on earth by comparing the speed of radio waves with that of visible light (1). These speeds agree to about one part in  $10^6$ . With the detection of the sharply defined radio and optical pulses from the pulsars, a substantial improvement of this comparison has become possible, both for visible light and for radio waves. This is done by comparing the arrival times of pulses at different frequencies, which presumably left the pulsar within one period of pulsation. An observed variation of