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Organics at the Air-Water Interface of Lake Pontchartrain

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Many kinds of organic compounds are supplied to rivers, lakes, and estuaries by industrial wastes, domestic sewerage, atmospheric fallout, and agricultural runoff. Since the amount of these compounds increases day by day, it is important to obtain a detailed knowledge of the identity and concentration of the specific pollutants and their sources.

The lack of information concerning organics at the air-water interface, is due, in part, to the chemical complexities of the layer and the technical difficulties of collecting a representative sample of the layer. GOERING and MENZEL (1965) found that the surface water had a mean dissolved organic carbon content greater than that of the underlying water. GARRETT (1967) found that the quantity and distribution of fatty acids and alcohols at the sea surface differed from those found at 20 cm below. BIDLEMAN and OLNEY (1974) and HARVEY et al. (1973) found that the highest concentrations of chlorinated hydrocarbons, pesticides, and polychlorinated biphenyls were associated with the surface microlayer (150 µm) of the Sargasso Sea and North Atlantic. DUCE et al. (1972) analyzed samples from Narragansett Bay and reported similar results. These studies and others (LEDET and LASETER 1974) suggest that there is the selective accumulation of certain types of organic molecules at the air-water interface. It has been suggested that these organics can affect the physical properties of the surface layer of major bodies of water (GARRETT 1972).

As part of our continuing studies to characterize the organics found at the air-water interface of natural bodies of water we are now investigating the more polar components. Three separate samples were collected, one each month, during the Spring 1976 from the surface of Lake Pontchartrain (New Orleans, Louisiana). This lake is a major body of brackish water (40.3 KM x 51.5 KM) that opens onto the Gulf of Mexico via Lake Borne. Several small tributaries empty into the lake at various points as well as the overflow from the Mississippi River during periods of potential flooding. A metropolitan area of over 1.5 million people is adjacent to the lake and it is used as a major recreational area and substantial quantities of crabs, shrimp, and other foods are produced in the lake.

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MATERIALS AND METHODS

An aluminum backed teflon disc was employed for sample collection. Details of construction and the sampling procedure using the teflon disc are discussed elsewhere (MIGET *et al*. 1974, MCFALL 1977). The residues collected were fractionated by using a silica gel column (10 grams silica gel for every 25 mg of lipid) with alumina on top of the silica gel. First, the alkanes were eluted with 50 ml of *n*-hexane and then the more polar compounds were eluted with 50 ml of benzene. The benzene was removed at 30°C under reduced pressure in a rotary evaporator. The residue was dissolved in 250 μl of benzene and further resolved by gas chromatography.

Due to the complexity of separating the organic mixture, a portion of the benzene fraction was refractionated on a silica gel column. The following fractions were obtained: 10% benzene in *n*-hexane (30 ml), benzene (50 ml), and methylene chloride (50 ml). Each of these fractions was further analyzed by employing glass capillary gas chromatography. A splitless method of sample injection described by GROB (1975) was used. The gas chromatograph utilized was a Hewlett-Packard (H.P.) Model 5711A equipped with a flame ionization detector and a H.P. Model 18740A glass capillary inlet system. Analog data were displayed on a strip chart recorder and digitized into "area slice" data and transmitted to a H.P. 3354 central laboratory data system (OVERTON *et al*. 1978).

The glass capillary column used in all analyses was made in this laboratory according to the $BaCO_3$ treatment outlined by GROB and GROB (1976). The column utilized was 28 m long by 0.3 mm I.D. and was coated with SE-52. The temperature program was 90°C to 240°C at 2°C/min. The flow rate of the helium carrier gas was 1.9 ml/min. The injection port and detector were maintained at 250°C and 300°C, respectively.

Identification of individual components in each fraction was based on the low and high resolution mass spectral data collected from a Varian MAT 311A high resolution mass spectrometer. Samples were introduced to the mass spectrometer via a glass capillary gas chromatograph equipped with a Grob type splitless injector. Chromatographic conditions were the same as those described for gas chromatography. Sample ionization was by electron impact at 70 eV. The accelerating potential of the 311A was 3 KV and the source temperature was 250°C. For routine sample runs, the resolution of the mass spectrometer was 1000 (M/M at 10% valley) and the mass range scanned was from 35 to 600 AMU. All mass spectral data were acquired in digital form by a Varian Spectrosystem 100 MS data system.

RESULTS AND DISCUSSION

Branched alkanes, alkyl benzenes, and polychlorinated biphenyls (PCB's) were found to be the predominant classes of compounds in the 10% benzene in n-hexane eluate (Figure 1A). Numerous isomers of alkyl benzenes were present in this fraction such that an unresolved hump was produced in the GC chromatogram. In addition to BHT (2,6-ditertiarybutyl-4-methyl phenol), polynuclear aromatic hydrocarbons (PAH's) and substituted phenols were the main components of the benzene eluate (Figure 1B). Both substituted and unsubstituted polynuclear aromatic hydrocarbons were detected among the PAH's. The number of isomers of the phenolic compounds was also large and therefore produced a similar unresolved hump like the alkyl benzenes. The primary components of the methylene chloride fraction were the long-chain alcohols and fatty acids (Figure 1C). Both methyl branched free fatty acids and straight chain methyl, ethyl, and butyl fatty acid esters were detected. The presence of pesticides such as nonachlor and chlordane (Figure 1B) in the surface microlayer of Lake Pontchartrain appears to be quite evident, but the quantity of these compounds is low in comparison with PCB's and PAH's. Table 1 identifies the compounds in the air-water interface of Lake Pontchartrain (Figure 1).

One of the dominant organics at the air-water interface was BHT. BHT has been identified in the wastewater effluents of a tire manufacturing plant (JUNGCLAUS et al. 1976) and is used by a host of other industries as an antioxidant (MERRILL 1965). BHT which has practically no systemic toxicity is approved for food use and is used as a preservative for foods (STECHER 1972). Phenols have also been found in the effluent of tire manufacturing plants (JUNGCLAUS et al. 1976) and have been identified in rivers (KAWAHARA 1971, MATSUMOTO et al. 1977). Phenols are used in the preparation of lubricating oil additives, resins, plasticizers, and surface-active agents (HERBES 1977). The detection of phenols is of interest because many substituted phenols have been found to be harmful to fish and other aquatic life forms (CHRISWELL et al. 1975).

The aromatic hydrocarbons associated with the air-water interface are derived from petroleum related sources. However, alkyl benzenes have been found in the wastewaters of tire manufacturing plants (JUNGCLAUS et al. 1976) and are used extensively as solvents for greases, rubber, resins, and numerous other applications in industry (MERRILL 1965). PAH's constitute a homologous series of fused-ring compounds which have been identified in many natural waters (HITES 1970, ISHIWATARI and HANYA 1974). Although found in both road runoff and domestic wastewaters, primary contributors of PAH's are effluents from industrial high-temperature pyrolysis operations such as coke production (HITES and BIEMAN 1972). The occurrence of PAH's are of concern since a number of PAH's are known to induce or promote cancer development. In aquatic systems high levels of PAH's in water and sediment have been implicated in tumor development in fish (BROWN et al. 1973). Also of concern is the fact that PAH's may be altered photochemically by natural sunlight to give products which in some cases may be more toxic and harmful than the original compounds introduced into the

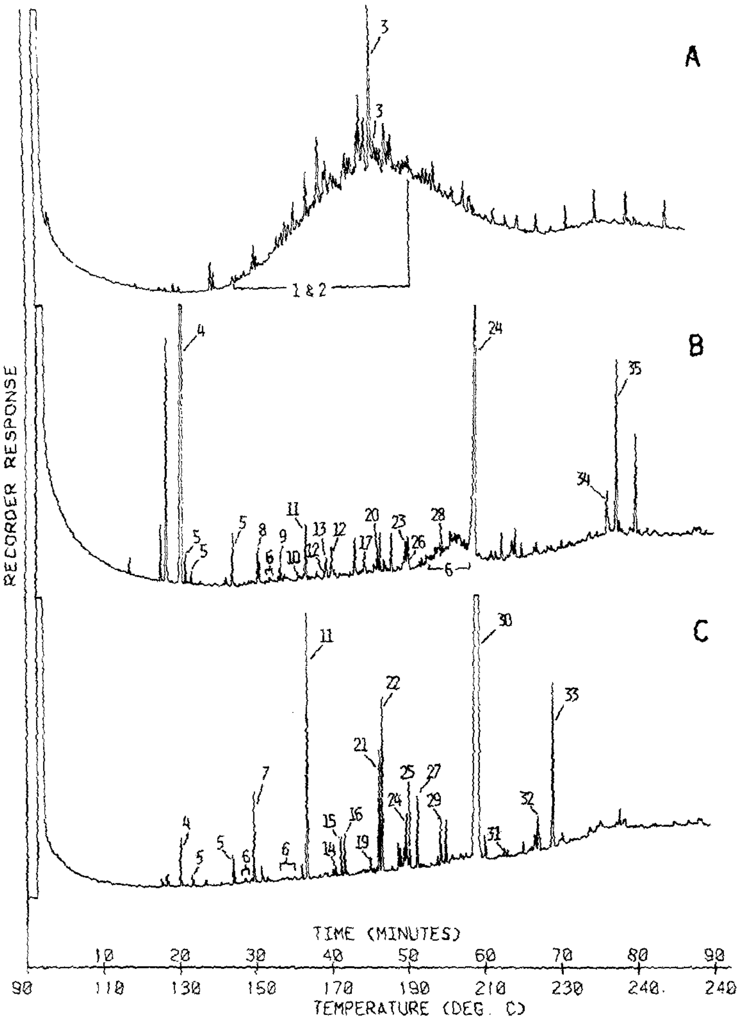

Figure 1: Gas chromatographic separation of the organics at the air-water interface of Lake Pontchartrain in the 10% benzene in n-hexane (A), benzene (B), and methylene chloride (C) fractions after refractionation of the original benzene fraction.

TABLE 1. COMPOUNDS IDENTIFIED AT THE AIR-WATER INTERFACE OF LAKE PONTCHARTRAIN BY GC-MS TECHNIQUES

PEAK NUMBER		COMPOUND
1		Alkyl benzenes (R=C_{10} to C_{15})
2	*	Polychlorinated biphenyls (contains 3 to 5 chlorines)
3		C_{10} indene
4		BHT
5		BHT isomer
6	*	Phenolic compounds
7		Dodecanol
8		1,1,3-trimethyl-3-phenyl-2,3-dihydroindane
9	*	Anthracene or phenanthrene
10		Dimethyl fluorene
11		Methyl tridecanoic acid
12		Methyl phenanthrene
13		Diphenyl benzene
14		Alkyl nitrile (C_{12}-CN)
15		Alkyl nitrile (C_{13}-CN)
16		Methyl palmitate
17		Dimethyl phenanthrene
18		C_{14} nitrile + dimethyl phenanthrene
19		Ethyl palmitate
20	*	Pyrene
21		Branched nitrile (C_{16}-CN)
22		Methyl pentadecanoic acid
23		Chlordane
24		Long chain alcohol
25		Alkyl nitrile
26		Nonachlor
27		Methyl stearate
28		C_9 indene
29		Ethyl stearate
30		C_{18} alcohol
31		Butyl stearate
32		C_{22} alcohol
33	*	Di-octyl phthalate
34		Phenyl alcohol
35		1,2 bis (ditertiary hydroxy phenyl) ethane

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*Compounds on the EPA Priority Pollutant List water. For example, polynuclear aromatic hydrocarbons may be photooxidized to arene oxides (DOWTY *et al*. 1974) which have been implicated as causative agents in necrosis and carcinogenic activity induced by aromatic compounds (JERINA and DALY 1974, LEVIN *et al*. 1976, BOYD *et al*. 1976).

Phthalic acid esters are widely used as plasticizers and often have been found in natural waters (HITES 1970, MAYER *et al*. 1972, HITES and BIEMAN 1972, MORITA *et al*. 1974). Di-octyl phthalate was identified in the surface water of Lake Pontchartrain. The source of phthalate esters is of interest because of their unusual ubiquity and their possible teratogenicity (BOWER *et al*. 1970, HITES 1970, ISHIWATARI and HANYA 1974). Likely routes of contamination for phthalate esters are the atmosphere, domestic sewerage, and factory wastewater.

Chlorinated hydrocarbons (pesticides and PCB's) have been widely detected throughout the world's aquatic environments. They are accumulated by aquatic organisms and so present concern not only for their acute and chronic toxic effects but also because of the probability of their transmission in food chains. This is of more concern for PCB's which are more persitent than pesticides and essentially nonalterable by microbial or physiochemical activities (CROBSY and MOILANEN 1973). Chlordane which we have identified is often used for structural pest control and, to a lesser extent, as a soil insecticide for agricultural purposes. Chlordane has also been identified in the Sargasso Sea, in Hawaiian rainwater, and in Texas dust (BEVENUE *et al*. 1972, BIDLEMAN and OLNEY 1974). Rivers are a potential source of PCB's along with agricultural runoff. PCB's are used in a variety of industries as fire retardants, protective coatings, plasticizers, sealers, and dielectrics and are often discharged into sewers and may enter natural waters with sewer sludge (HOLDEN 1970). PCB's can also be produced photochemically in the vapor phase from DDT and its derivatives (MAUGH 1973). Polychlorinated biphenyls (tri-, tetra-, and penta-chlorobiphenyls) have also been identified in the surface microlayer of the Sargasso Sea (BIDLEMAN and OLNEY 1974).

Long chain alcohols and free fatty acids and fatty acid esters were also identified in the lake surface microlayer. Branched-chain (2 and 3 methyl) fatty acids have been detected in many organisms in small amounts with bacteria containing larger quantities of branched-chain fatty acids than other organisms (KANEDA 1967). Only a few studies involving the detection of fatty acid methyl esters have been reported (LASETER *et al*. 1968, LEDET 1972) and we have found no reference to the occurrence of ethyl and butyl esters. Long chain alcohols have been used for years as evaporation supressants and as dispersants for petroleum in natural waters. Although these compounds are considered nontoxic, they encourage bacterial growth and produce noticeable changes in algae populations and shore vegetation (PARKER and BARSOM 1970).

A wide variety of organics have been characterized by GC-MS in our samples collected from the air-water interface of Lake Pontchartrain. These include chlorinated hydrocarbons, aromatic hydrocarbons, fatty acids, alcohols, phenolic compounds, and phthalic acid esters. Although some are clearly biological in origin, a large number of the organic compounds present are of industrial origin that enter the lake from industrial effluents, domestic sewerage, atmospheric fallout, and agricultural runoff. These organics potentially have an effect on the biological processes in the environment. Therefore many of the organic compounds appear on the USEPA Priority Pollutant List and can be toxic to the aquatic organisms present and can also affect the health and well-being of humans deriving food products from Lake Pontchartrain. Studies are presently underway to determine the origin of these organics. Additionally, investigations into the nature of the primary uncharacterized organics are being carried out.

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