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Volatile Organic Pollutants in Biota and Sediments of Lake Pontchartrain

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For several decades now our inland and coastal aquatic ecosystems have been the recipients of a multitude of man-made and naturally-occuring chemical substances. This is a natural consequence of our ever-increasing population and the concomitant growth of industrial and agricultural activity. Each year many new chemical species are produced by industry for our use. Many of these materials, the by-products of their production, and degradation products ultimately find their way into our aquatic environment as pollutants. The extent to which these pollutants impact the environment and its inhabitants depends largely on the quantity and nature of these pollutants.

As part of our continuing studies to characterize and identify chemical pollutants in natural bodies of water (Laska et al. 1976, Laseter et al. 1978, McFall et al. 1979, Laseter and Ledet, 1979, Overton and Laseter 1980, Overton et al. 1980, and Laseter et al. 1981) and as part of a preliminary study of the nutrient and toxic substances chemistry for the three passes into Lake Pontchartrain, we have screened biota and sediment samples from the lake for volatile organic pollutants. What follows is a report of our findings.

Lake Pontchartrain (New Orleans, Louisiana) is a shallow, oligohaline, 1631 km^2 estuary located in the deltaic plain of the Mississippi River. Three passes, The Rigolets, the Chef Menteur Pass, and the Inner Harbor Navigation Canal (IHNC) provide an indirect, restricted connection to the Gulf of Mexico. The Rigolets accounts for 44 percent of water transport in and out of the lake; the Chef Menteur Pass and the IHNC, for 32 and 6 percent, respectively. Other inputs include rivers, bayous, municipal and agricultural run-off and the overflow from the Mississippi River during times of potential flooding. The lake serves an adjacent metropolitan area of over 1.5 million people as a major recreational area and as a source of substantial quantities of crabs, shrimp, and other aquatic foods (McFall et al. 1979 and Stone 1980).

MATERIALS AND METHODS

Samples of oysters (Crassostrea virginica), clams (Rangia cuneata), and sediments were collected in May-June, 1980, from the mouths of the Inner Harbor Navigation Canal (IHNC), the Chef Menteur Pass, and The Rigolets, at Lake Pontchartrain. All samples were immediately packed in ice, then frozen and kept at -5°C until analysis.

All samples were processed for analysis using methodology based on a highly modified version of the National Bureau of Standards procedure for petroleum hydrocarbons (Chesler et al. 1976). All critical parameters (i.e., sample size, purge time, flow rate, etc.) were empirically determined and subsequently optimized to achieve the sensitivity necessary for detection of low level contamination in environmental samples. Briefly, the procedure is as follows:

Four grams of tissue (oyster or clam) were accurately weighed and immediately spiked with one hundred nanograms each of a three component recovery standard (bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane). The samples were then mechanically and ultrasonically disrupted with a Brinkman Polytron tissue homogenizer; the homogenizer blades were subsequently rinsed with pre-purged water (3 x 50 mls) and the washings combined with the original tissue homogenate. The tissue/water homogenate was transferred to a purge vessel containing 350 ml of prepurged water and purged. Sediment samples (approximately 13 grams) were weighed while frozen, transferred to a purge vessel containing 500 ml of pre-purged water, spiked with 100 ng each of the three component internal standard and purged. All sample manipulations, except for the purge itself, were conducted inside a desk-top coldroom maintained at 4°C. The purge vessels containing the pre-purged water were assembled while still hot and held under positive pressure until the introduction of the sample and initiation of the purge period. Six purge and trap assemblies (including 4 samples, 1 system blank, and 1 calibration standard) all spiked with the recovery standards were run simultaneously to insure constant conditions and maintain sufficient quality control. All samples were purged with pre-purified nitrogen at a flow of 37 mL/min for two hours at 25°C, followed by two hours as 70°C, while constantly being stirred. The volatile organics were swept out of the purge vessel into a Tenax/silica gel trap (16mm x 105 mm stainless steel tube packed with 80% Tenax-GC and 20% silica gel) maintained at 2°C. At completion of the purge and trap procedure, the traps were securely capped and stored at -5°C until analysis.

The trapped organics were thermally desorbed at 200°C directly into a Hewlett-Packard 5700A gas chromatograph which was interfaced to a Dupont 21-491B mass spectrometer. The GC oven was maintained at -50°C for the duration of the 10 minute desorption period effectively trapping the volatiles at the head of the column. Following desorption, the column temperature was rapidly increased to 0°C, then programmed at 2°C/minute to facilitate separation. The gas chromatographic separations were achieved on 50 m x 0.4 mm WCOT SF-96 column prepared by the method of Grob and Grob (1976). The column effluent was subsequently introduced into the ion source of the mass spectrometer via a heated transfer line. Sample ionization was by electron-impact at 70 eV. The mass range was scanned repetitively from 35 to 350 amu under computer control by a Finnigan INCOS 2000 data system. GC/MS data analysis was performed on the Finnigan data system by means of user prepared routines for EPA priority pollutant volatile organics and a general search for other volatiles.

RESULTS AND DISCUSSION

The results of the analysis of oyster samples from the IHNC and of clam samples from the Chef Menteur Pass and The Rigolets are presented in Tables 1 and 2. The oysters from the IHNC population contained thirteen specific EPA priority pollutants, of which ten were identified as halogenated with the remainder being benzene and two of its derivatives. The mean concentrations ranged from 0.04 ng/gram (ppb) wet weight for chlorobenzene to 310 ng/gram (ppb) wet weight for 1,1,1-trichloroethane. The clam samples from the Chef Menteur Pass and The Rigolets populations contained eight and seven specific priority pollutants, respectively, with the majority being halogenated. The concentrations of compounds found in the Chef Menteur clam population ranged from 0.6 ng/gram (ppb) wet weight for chlorobenzene to 260 ng/gram (ppb) wet weight for benzene. The concentrations of compounds found in The Rigolets clam population ranged from 0.8 ng/gram (ppb) wet weight for trichloroethylene to 39 ng/gram (ppb) wet weight for 1,1,1-trichloroethane.

The general search of the GC/MS data developed for oyster and clam samples from the three passes revealed 83 distinct non-priority pollutant compounds which were identified, at least to chemical class. The chemical

Table 1. Volatile Organic Priority Pollutants Detected in Biota Samples from Lake Pontchartrain at Passes

COMPOUND	nanogram/gram (ppb) wet weight		
	IHNC Oysters[a]	Chef Menteur Clams[b]	Rigolets Clams[b]
Chloroethane	7.6	-[c]	-
Dichloromethane	7.8	27	4.5
1,1-Dichloroethylene	-	-	4.4
Carbon tetrachloride	1.3	-	3.9
1,1-Dichloroethane	33	-	-
1,2-Dichloroethane	95	1.0	1.5
1,1,1-Tichloroethane	310	160	39
Trichloroethylene	2.2	5.7	0.8
Benzene	220	260	-
Tetrachloroethylene	10	3.3	-
Toluene	3.4	18	11
Chlorobenzene	0.04	0.6	-
Ethylbenzene	0.8	-	-

[a]Mean of five samples.
[b]Results are of composite samples.
[c]"-" means not detected.

classes represented in the suite of non-priority pollutant compounds identified in the biota samples include alkanes, alkenes, aromatics, aldehydes, alcohols, phenols, and furans.

The results of the analysis for volatile organic pollutants in sediment samples from the three passes are given in Tables 3 and 4. Thirteen specific priority pollutants were identified in these analyses, with the IHNC samples showing the largest number of pollutants. Most of the priority pollutants identified are halogenated, with the remaining compounds being benzene and toluene. The concentrations of priority pollutants identified in the IHNC sediment samples ranged from < 0.01 ng/gram (ppb) wet weight for 1,2-dichloroethane to 8.0 ng/gram (ppb) wet weight for benzene. The concentration of the priority pollutants identified in the Chef Menteur and The Rigolets sediment samples ranged from 0.1 ng/gram (ppb) wet weight for trichlorofluoromethane, 1,2-dichloroethane, and trichloroethylene, to 21 ng/gram (ppb) wet weight for benzene.

The general search of the GC/MS data for the sediment samples from the three passes revealed a total of 25

Table 2. Other Volatile Organic Non-Priority Pollutants Detected in Biota Samples from Lake Pontchartrain at Passes

COMPOUND	nanogram/gram (ppb) wet weight		
	IHNC Oysters[a]	Chef Menteur Clams[b]	Rigolets Clams[b]
Pentadiene	3.2	-[d]	1.4
Hexadienal	35	7.5	-
Unknown alkane	8.0	0.8	1.5
Methylcyclohexane	1.3	-	0.9
Ethylcyclopentane	3.9	2.2	-
Methylpropenamine	0.1	-	-
Dihydromethylfuran	3.5	-	-
Trimethylpentane	0.2	-	1.3
Branched alkane	-	1.5	-
Ethylmethylhexane	2.5	0.7	-
Ethyldimethylpentane	1.0	-	0.2
Dimethylcyclohexane	-	-	-
Dimethylheptane	-	11	8.0
Octane	22	-	-
Branched alkane	-	0.9	10
Octene	0.8	-	-
Methylheptadiene	27	-	2.8
Methylheptane	-		-
Branched alkane	-	32	-
Unknown alkane	0.27	0.9	1.1
Unknown alkane	-	1.0	-
Ethylpentene	8.0	-	-
Trimethyl hexene	0.2	-	-
Branched alkane	-	-	4.3
Trimethylheptane	-	3.2	-
Xylene	16	-	-
Unknown alkane	0.4	-	-
Branched alkane	1.0	-	-
Unknown alkane	3.9	-	-
Methylpentylcyclopropane	6.0	-	-
Nonene	0.5	1.6	-
Unknown alkane	-	6.7	-
Nonane	25	-	24
Ethylphenol	1.4	-	-
Branched alkane	2.0	5.5	-
Methylnonane	5.5	-	-
Unknown alkane	-	1.3	-
Branched alkane	-	14	-
Methylethylbenzene	3.1	-	-
Unknown alkene	0.7	-	-
Methyloctanol	-	2.4	-
Dimethyloctanol	-	3.7	-

Table 2. (continued)

COMPOUND	IHNC Oysters[a]	Chef Menteur Clams[b]	Rigolets Clams[b]
	nanogram/gram (ppb) wet weight		
Dimethyloctane	-	-	0.1
Ethylmethylpentanol	-	2.5	-
Unknown alkane	0.2	-	-
Unknown alkane	6.4	-	-
Branched alkane	1.5	-	1.5
Methylpropylpentanol	-	2.2	1.5
Unknown alkane	17	-	-
Unknown alkane	4.9	-	-
Unknown alkane	9.8	-	-
Unknown alkane	2.9	-	-
Branched alkane	1.9	-	-
Methyldecane	-	-	24
Decane	21	-	2.5
Tetramethylhexene	4.2	-	-
Unknown alkane	15	2.9	-
Unknown alkane	4.2	-	16
Dimethyloctane	8.7	-	-
Branched alkane	3.3	-	-
Decanol	-	4.0	-
Unknown alkane	4.3	0.4	-
Unknown alkane	-	-	4.0
Branched alkane	17	-	-
Branched alcohol	-	-	5.7
Undecane	10	-	-
Unknown alkene	-	-	1.9
Branched alkane	3.7	-	-
C_{12}-Branched alkane	5.3	-	-
Decadiene	2.8	-	-
Branched alkane	3.8	-	-
Methylpropylpentanol	5.5	-	-
Branched alkane	3.8	-	-
Unknown alkane	3.9	-	-
Unknown cycloalkane	0.8	-	-
Unknown alkane	0.	-	-
Unknown alkane	5.8	-	-
Trimetylcyclohexane	0.9	-	-
Unknown alkane	1.7	-	-
Unknown cycloalkane	0.04	-	-
Unknown alkane	0.4	-	-
Unknown alkane	0.2	-	-
Unknown alkane	0.3	-	-

[a]Expressed as equivalents of 2-bromo-1-chloropropane.
[b]Mean of five samples.
[c]Results are of composite samples.
[d]"-" means not detected.

Table 3. Volatile Organic Priority Pollutants Detected in Sediment Samples from Lake Pontchartrain at Passes

COMPOUND	nanogram/gram (ppb) wet weight		
	IHNC[a]	Chef Menteur[b]	Rigolets[b]
Trichlorofluoromethane	1.5	0.1	3.3
Chloroethane	0.2	–[c]	–
Dichloromethane	1.5	3.2	–
Chloroform	3.1	18	1.7
Carbon tetrachloride	–	–	0.3
1,2-Dichloroethane	<0.01	–	0.1
1,1,1-Trichloroethane	0.01	–	–
1,2-Dichloropropane	0.2	–	0.4
Trichloroethylene	0.2	–	0.1
Benzene	8.0	21	–
Tetrachloroethylene	0.3	–	–
Toluene	0.7	–	–
Chlorobenzene	0.03	0.7	–

[a]Mean of five samples.
[b]Results are of composite samples.
[c]"–" means not detected.

individual compounds which were identified at least to chemical class in the volatile organic fraction. The chemical classes represented in the data derived from the general search for the sediments include alkanes, alkenes, aromatics, and alcohols.

While the volatile organic priority pollutants found in the biota and sediment samples are of obvious anthropogenic origin, the majority of the other compounds identified are probably biogenic. The presence of the benzene series, including benzene, toluene, C_2- and C_3-benzene, along with the cyclo- and branched-alkanes, are indicative of petroleum hyrocarbon residues. These findings are not unusual since small recreational craft and commercial vessels serving several industries traffic through these waterways.

The volatile EPA priority pollutants identified in the biota and sediment have quite variable physical, chemical, and toxicological properties allowing a variety of commercial and industrial applications. These chemicals are used extensively as solvents, chemical intermediates, dewaxing agents, aerosol propellants, blowing agents, pharmaceuticals, etc. (Clayton and Clayton 1981 and Verschueren 1977).

Table 4. Other Volatile Organic Non-Priority Pollutants Detected in Sediment Samples from Lake Pontchartrain at Passes

	nanogram/gram (ppb) wet weight[a]		
COMPOUND	IHNC[b]	Chef Menteur[c]	Rigolets[c]
Unknown alkane	4.7	-[d]	-
Methylpentene	1.2	2.4	-
Unknown alkane	0.2	-	-
Unknown alkane	0.3	-	-
Methylcyclohexane	-	0.01	0.5
Unknown alkane	0.06	-	0.3
Unknown alkane	<0.01	-	0.1
Octane	0.07	-	0.2
Ethylcyclohexane	0.04	-	-
Unknown alkane	0.1	0.2	0.07
Unknown cycloalkane	0.04	-	-
Trimethylheptane	3.0	-	4.5
Unknown alkane	0.9	-	-
Ethylmethylheptane	3.6	-	0.1
Nonane	0.07	-	-
Unknown alkane	0.06	-	-
Dimethyloctane	1.0	-	-
Ethylmethylheptane	0.07	-	-
Unknown alkane	1.8	-	0.3
Unknown alkane	0.2	-	0.8
Unknown alkane	2.7	-	0.4
Branched alcohol	0.08	-	-
Unknown alkane	0.6	-	-
Dimethylethylbenzene	0.7	-	0.2
Unknown alkane	-	0.2	-

[a]Expressed as equivalents of 2-bromo-1-chloropropane.
[b]Mean of five samples.
[c]Results are of composite samples.
[d]"-"means not detected.

All the volatile EPA priority pollutants identified have possible adverse human health effects including central nervous system depression, narcosis, and various renal and hepatotoxic effects (Christensen et al. 1975). At the present time maximum permissible tissue concentrations for aquatic organisms are not available. However, carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethylene, trichloroethylene and benzene are suspected carcinogens in humans and as such no safe exposure limit can rationally be established based on the non-threshold assumption (EPA 1980). Since these compounds tend to concentrate in biological systems due to their high lipid solubility, their accumulation in the food chain could have possible adverse health effects due to chronic low level consumption. In addition, biomagnification in higher trophic levels is probable since the fishes of Lake Pontchartrain feed primarily on benthic or planktonic-nektonic food webs.

The data which have been developed in this study show the presence of a significant number of volatile organic priority pollutants and other volatile organics of petrogenic and biogenic origin in benthic organisms and sediment samples from Lake Pontchartrain. The extent to which these pollutants affect the ecology of Lake Pontchartrain is unknown and cannot be assessed until more detailed studies are conducted.

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