

## Phthalic acid esters in the marine environment

by

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**Abstract:** The waters, particulate matter and sediments of the lower Mississippi River and the adjacent Gulf of Mexico were examined for their concentrations of phthalic acid ester plasticizers and nutrients. The nutrient content of the water remained almost constant in the river, but decreased rapidly upon entrance into the Gulf of Mexico. The phthalic acid ester concentrations, on the other hand, gradually increased from New Orleans downriver to Head of the Passes. But like the nutrients their concentrations also decreased rapidly into the Gulf of Mexico.

The predominant phthalic acid ester (PAE) was di-(2-ethyl hexyl) phthalate, a plasticizer commonly used in resins and synthetic rubber. The cumulative concentration of the PAE's was from 1-2 ppb with the greatest concentration in the water. Particulate matter has about half the concentration, while the PAE's were almost absent in the sediment. Laboratory experiments have indicated that there is a great loss of phthalic acid ester due to hydrolytic activity. This may possibly explain the low concentration in the sediments.

During the spring of 1970, samples of water, suspended matter and sediment were collected from the Mississippi River and northeast Gulf of Mexico for the determination of chlorinated hydrocarbon concentrations. When hexane extracts of these samples had gone through a cleanup procedure and analyzed by gas chromatography using an electron capture detector, the chromatograms showed two large well-defined peaks with retention times beyond the pesticide range. Because these peaks represented much higher concentrations than the pesticides, we became interested in their identification. After a great deal of investigation we found these peaks to be due to phthalic acid esters. About this same time, Jaeger and Rubin (1970) published an article indicating that blood can extract the phthalic acid esters from polyvinyl chloride plastic. Because blood and seawater are similar in many ways and are of similar ionic strength, our interest in their presence in the environment grew. Our interest was especially piqued when they (Jaeger and Rubin, 1973) speculated on the role of phthalic acid esters (PAE's) in the occurrence of shock lung, a condition characterized by an impeded circulation of blood in the lungs. Very few studies on the possible hazardous effects of the esters have been done, but these few gave indications of possible mutagenic and teratogenic effects.

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In the fall of 1975 we again visited the Mississippi River area. This time, with the specific purpose of determining the distribution and concentration of various common phthalic acid esters. It is the results from this cruise that we are going to discuss.

### MATERIAL AND METHODS

Water, particulate and sediment samples were collected from the Mississippi River and Gulf of Mexico (Fig. 1). A total of 17 sites were sampled: 11 within the Mississippi River system itself; 3 just off the major Mississippi River outlets to the Gulf of Mexico; and 3 stations just off three major ports on the eastern Gulf coast. At each station, water samples were taken at the surface, at mid-depth and close to the bottom, using an all metal Niskin-type water sampler. The all-metal water sampler was used to avoid any possible PAE interference or masking by the plasticizers used in the PVC polymer of the standard plastic Niskin sampler.

Immediately after collection, a one liter volume of water was drawn from the sampler and filtered through a pre-weighed, pre-ignited Whatman GF-C, glass fiber filter. Dissolved organics were removed from the filtered water by passing it through a 130mm x 4mm XAD-2 resin (20-60 mesh) column. The extraction procedure was a minor modification by Junk *et al* (1974) and has a recovery rate of about 98% with respect to the various simple diesters of phthalic acid. The XAD-2 resin was stored prior to, during, and after use in a 150mm x 6mm O.D. thin-walled glass tube and capped at both ends with metal Swagelok\* with teflon seals. The glass fiber filter pads (containing the particular material) were stored, frozen, in glass scintillation vials sealed with foil-lined plastic caps. After drawing off water for PAE analysis, samples were collected for routine nutrient analysis, salinity and dissolved oxygen. Protected reversing thermometers were used to obtain *in situ* temperatures. Sediment samples were collected with a standard 2' gravity corer using an aluminum core liner.

The extracted organics were eluted from the XAD-2 columns with 30 ml of spectral grade diethyl ether. This ether was then dried with anhydrous sodium sulfate and reduced in volume to about 1 ml on a steam bath using a Kunderna-Danish evaporative condenser. About 10 ml of hexane was added to the ether extract and the mixture again reduced to a volume of 2 ml. The ether and its hexane azeotropes are lost early in this volume reduction step. This hexane extract was again dried with anhydrous sodium sulfate and analyzed for its phthalic acid ester concentration on a Tracor, Model 222 gas chromatograph having a  $^{63}\text{Ni}$  electron capture detector. The chromatographic column used was a non-polar 1.95% SP2250, 1.5% SP2401 on a 100/120 Supelcon support.

The filters were weighed, Soxhlet extracted for two hours with acetone, followed by a two-hour Soxhlet extraction with hexane, air dried, and weighed again. The particulate weight was obtained by difference. The two solvent extracts were combined and the acetone removed by repeated washings with a 2% (W/V) sodium sulfate in water solution. The hexane extract was dried with sodium sulfate and reduced in volume to about 0.5 ml using a Kunderna-Danish evaporative condenser. Interfering compounds, such as chlorinated pesticides, were chromatographically removed by using a Florosil clean-up procedure (Corcoran,

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1973; Giam *et al.*, 1975). The phthalic acid esters were quantitatively eluted from the Florosil column with a 50% (V/V) diethyl ether in hexane solution. This ether fraction was then reduced in volume, mixed with 10 ml of hexane and again reduced to a volume of 2 ml. The extract was then analyzed in the same manner as described earlier. Sediment samples (5 gr) were extracted and analyzed in the same manner as the particulate samples.

All glassware and aluminum foil used were pre-cleaned with Liqui-Nox\* and water, rinsed with distilled water and finally heated to 600 C for one hour. The glass fiber filters were heated to 500 C for three hours prior to weighing, then wrapped with heat-treated aluminum foil. No detectable levels of organic compounds were observed when equipment cleaned in this manner were extracted and the extracts analyzed by gas chromatography.

## RESULTS AND DISCUSSION

The salinity of the Mississippi River remains relatively constant (about 0.15‰) from Station 9 (near New Orleans) to Station 3 located in Head of Passes. From this point the salinity of the river water increases rapidly as it flows toward the Gulf of Mexico. At Head of the Passes (Station 3) the unidirectional flow of the river is interrupted and flows into the Gulf of Mexico through a number of shallow passes (Stations 1, 2, 10, 11). In the past, the principal flow of the river to the Gulf was through Main Pass and Pass a Loutre. The U.S. Army Corps of Engineers, has changed the principal flow of the river so that it now flows through Southwest and South Passes. This flow pattern is maintained by continual dredging of the main shipping channels and by maintaining the sills constructed in other passes leading to the Gulf. A well-defined salt wedge was observed in Southwest Pass and South Pass extending from the Gulf almost to the Head of the Passes.

The river temperature was lowest (21 C) near New Orleans and increased steadily to the 25 C Gulf waters. Surface temperatures were always higher than those of the bottom waters. At three river locations (Stations 9, 6, 3) a small but significant increase in temperature, was observed. This observation was not found in the salinity data. Thus, we have a strong indication of a large input of warm water not significantly different from that of the river.

Our nutrient data showed that their concentrations were inversely related to salinity. In general, the nitrate, nitrite and phosphate concentrations in the river water were relatively high (as compared to the concentrations in the Gulf of Mexico) and were relatively constant from Station 9 (New Orleans) to Station 3 (Head of the Passes). The nutrient concentration in the water decreased sharply from Station 3 to Station 1 (off Southwest Pass), and remained a nominally low level at all the Gulf Stations.

The observed concentration of nitrate varied by only a small amount around a mean concentration of 40  $\mu\text{M}$  with a maximum variation of less than 5  $\mu\text{M}$ . The concentration of nitrate found at all stations in the Gulf of Mexico were an order of magnitude less. Nitrite too, was high in comparison to the Gulf (2  $\mu\text{M}$  versus 0.1  $\mu\text{M}$ ) and again did not show any significant variation among river stations. Orthophosphate had a mean river value of 4.5  $\mu\text{M}$ . The phosphate data show increased levels at three stations (8, 5, and 2). Each of these stations was just south of those where elevated temperatures were observed. Concentration increases were

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\* Alconox, Inc., New York, N. Y. 10003.

also in the nitrate and nitrite data. Unfortunately, the increases in these two parameters were less than two times the analytical precision, and, as a result, cannot be used as supportive data.

Water collected from each of the 17 stations was analyzed for 5 phthalic acid esters. These esters were the diisobutyl (DIBP), dibutyl (DBP), butyl glycol butyl (BGBP), butyl benzyl (BBP), and diethyl hexyl (DEHP) esters of phthalic acid. The concentrations of each of these esters found in a particular water sample were totaled and are reported graphically in Figure 2. The most prevalent ester, almost without exception, was the diethyl hexyl ester (DEHP). In general, this was the only ester found in the sediments collected at each station. Butylglycol butyl phthalic (BGBP) acid ester was not generally found in water, particulate or sediment.

The total ester concentration in the water (Station 9) to Head of Passes (Station 3) then decreases rapidly toward the Gulf of Mexico. As observed in the hydrological data, we saw a sharp spike in the total ester concentrations at Stations 8, 5, and 2. Closer examination of the data shows the total esters are about equally distributed between the water and particulate material. There is no indication of any transfer between these two phases.

Further, the distribution and concentration of the esters of phthalic acid in the sediments appear to be independent of the distribution and concentration found in the overlying water. We always observed that the concentrations of all esters found in surface sediments decrease rapidly with depth, disappearing completely, less than 0.50 m from the sediment surface. The lighter esters (DIBP, DBP) generally are not found in sedimentary material. The probability of finding any particular ester in the sediment increased markedly with molecular weight. This observed independence of sediment ester concentrations is more than likely a reflection of the rapid rate at which water passes through the river delta, as well as the relatively small release of the suspended sediment. The decrease in concentration with depth of burial is the direct result of degradation by anaerobic bacteria (Taylor, 1975) and hydrolysis of the ester linkage (Giam *et al.*, 1978).

The steadily increasing downstream concentration of the esters in the water is the result of a number of factors. First there are a large number of municipal and industrial sewage outfalls as well as surface runoff of industrial waste throughout the length of the river as far south as Venice, Louisiana. The major areas of input being near Venice (Station 5), Port Sulfur (Station 7) and Belle Chasse (Station 8). Beyond Head of Passes (Station 3) the data show a sharp decline in the concentration of the various esters. This decline results from mixing of riverwater with the Gulf water of the saltwedge discussed earlier, dropping of the suspended load as the river slows, aerobic bacterial degradation (Taylor, 1975) and finally a complete lack of municipal and industrial sewage input.

## CONCLUSIONS

In the past twenty years, the use of plasticizers has increased from about 200 million kg/year to about 675 million/kg year. A few years ago, PAE's alone have gone from about 100 million to well over 500 million kg, while polychlorinated biphenyls (PCB) have kept at a constant of about 15 million kg, and are now decreasing.

Figuring an average flow of 600,000 ft<sup>3</sup>/sec, and a constant concentration of PAE in the water, we find about 1/10 of 1% of the total diethyl hexyl phthalate

manufactured and the most commonly used phthalic acid ester actually enters the Gulf of Mexico. An additional amount (or about 1/2) enter on the Gulf absorbed to particulate, but just how toxic are these PAE's? Unfortunately, most of the experimental work has been done on the effect of diethyl hexyl phthalate on higher forms of life and non-marine animals. Those experiments that have been performed on aquatic organisms indicate that the lower alkyl homologs are more toxic. A few experiments by Stalling's group (Mayer *et al.*, 1972) have shown a 96-hour LC50 for scuds, crayfish and other invertebrates were about 10 ppb, while only 3 ppb were required to reduce reproduction of *Daphnia amazona* by 60%.

The lower alkyl homologs are more toxic, but are also more susceptible to decomposition by bacteria and hydrolysis. The toxicity of the group may be due to hydrolysis, as two moles of toxic alcohol are formed.

Although the precise biological implications of plastics and plasticizers in the environment are not known, the ubiquitous and increased rise of these substances in packaging materials for food intended for human consumption demand a heightened awareness about the biochemical and toxicological role of phthalate ester plasticizers; and how these compounds are recycled through the complex marine foodweb of which man is a significant recipient. More important, the Mississippi River is used throughout its length, as a primary source of potable water for a large number of river municipalities. Water treatment processes presently used are not very effective in removing these compounds. River communities, as a result, are jeopardizing their citizens to an as yet unknown health hazard.

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#### RESUMEN

Se examinó las aguas, las partículas en suspensión y los sedimentos de la parte baja del Río Mississippi y partes adyacentes del Golfo de México para averiguar las concentraciones de plastificantes de ésteres de ácido ftálico y nutrientes. El contenido de nutrientes en el agua permaneció casi constante en el río pero disminuyó rápidamente al entrar en el Golfo. Las concentraciones de ésteres de ácido ftálico, por el contrario, aumentaron gradualmente desde Nueva Orleans aguas abajo hasta Head of the Passes, pero al igual que en los nutrientes, sus concentraciones disminuyeron rápidamente al entrar en el Golfo.

El éster dominante fue el ftalato de di-(2 etil hexilo), un plastificante usado comúnmente en resinas y en el hule sintético. La concentración acumulada de ésteres de ácido ftálico fue de 1-2 ppm estando la mayor concentración en el agua. Aproximadamente la mitad de esta concentración está compuesta por materias en suspensión mientras que los ésteres casi no se encuentran en el sedimento. Experimentalmente se comprobó que hay una gran pérdida de ésteres de ácido ftálico debido a la actividad hidrolítica, lo que posiblemente explica su baja concentración en los sedimentos.

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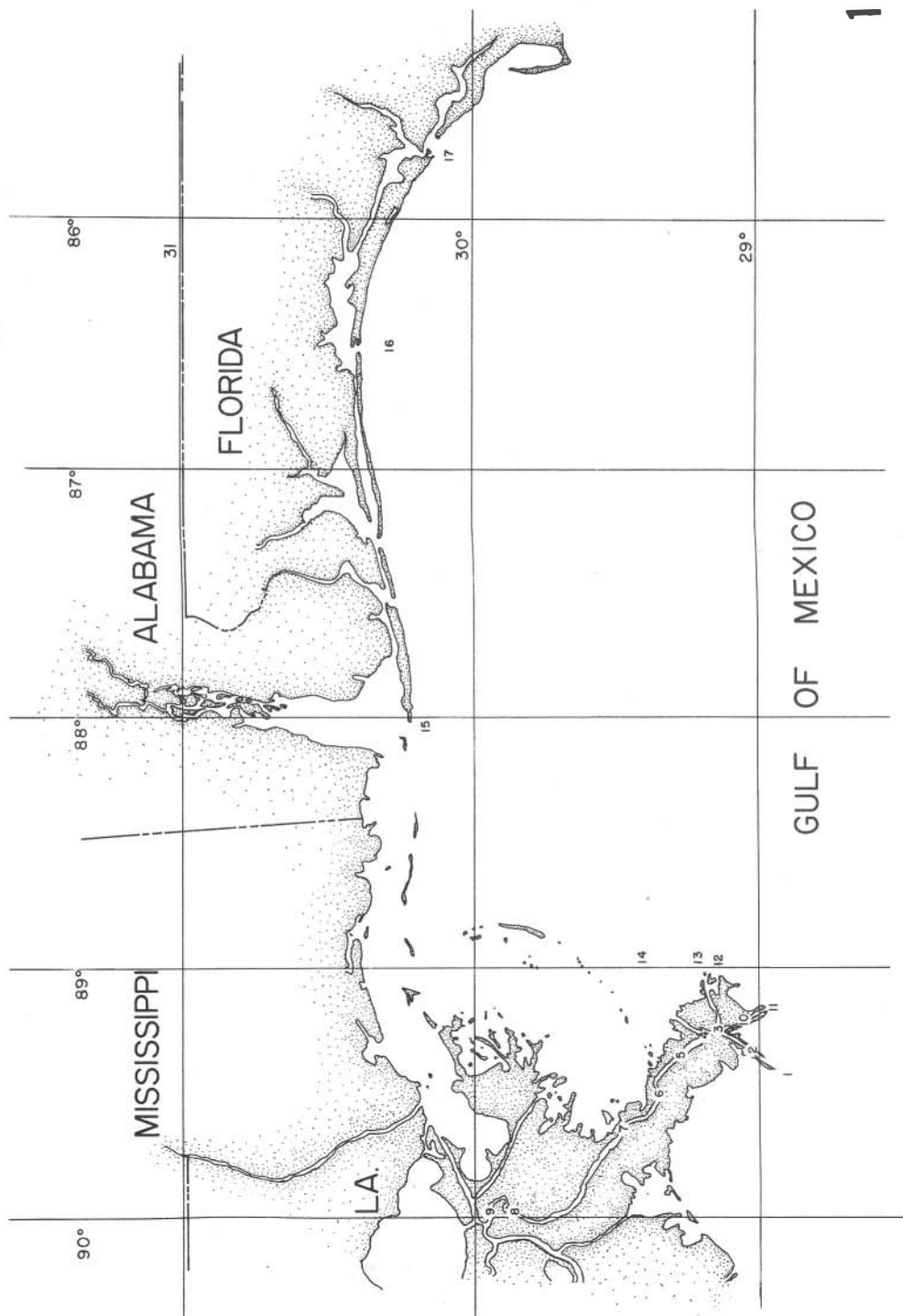


Fig. 2. The total (soluble plus particulate) phthalate acid esters found at each station.



