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INTERIM TECHNICAL REPORT I

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MISSISSIPPI-ALABAMA SEA GRANT CONSORTIUM



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Pollutant Transport in Mississippi Sound

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Prepared for

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ANNUAL SUMMARY

Introduction

Recent legislative approval of the "Superfund" to rehabilitate communities devasted by chemical wastes reflects the concern and knowledge shown now both by the government and the public for pollution throughout the United States. A study was initiated in 1979 to address the issue of pollution in the coastal areas of Mississippi. Pollution in this area has received minimal attention in the past and has been tolerated as a necessary by-product of progressive growth in the area. The levels of pollutants quite probably are not as profound as found in areas such as the Love Canal in the New York area, but with so little scientific data, the status of pollution in coastal Mississippi has remained essentially unknown. This study was conceived to characterize the pollutants of Mississippi Sound, clarify those processes responsible for pollutant movement and develop criteria that will be required for a more responsible coastal management than that used in the past. In 1979 the study area was the region influenced by the Pascagoula River in the eastern Mississippi Sound.

Sampling

Because of delays in the contractual core sampling program, we designed a surface sediment sampling program to provide some needed insight into the transport of pollutants associated with the paper mill and other industries on the Escatawpa River, a tributary of the Pascagoula River. This area was an area of almost unrestrained waste disposal between 1960 and 1970 and has been unofficially designated by the Environmental Protection Agency, EPA, as having the highest pollution probability



Figure 1. Core sampling sites chosen for 1979. The surface samples in the Escatawpa River were located in the vicinity of the area labeled Paper Mill.

in the Mississippi Sound. Sixteen stations sampled in July and August, 1979 were located along a five mile stretch extending both up and down river from the suspected pollutant sources.

Sampling and analysis have been aimed primarily at sediments collected as surface and core samples. Sediments show tremendous tenacity for the majority of estuarine pollutants and tend to trap them. Sediments also reflect averaged levels of pollution whereas water and biota retain only an instantaneous image of pollution in the area. Surface samples were collected to map surface pollution. Sediment cores were included in the sampling scheme to observe the history of pollution in the Sound and to acquire data useful in making dredging impact decisions. The coring program was designed to cover a larger area of the eastern Sound than was surveyed in the surface samples collected in the Escatawpa River. Figure 1 depicts the core sampling sites chosen for 1979. The surface samples in the Escatawpa River were located in the vicinity of the area labeled Paper Mill.

In November, 1979 cores were collected at 15 sites using a vibracore and specially cleaned aluminum coring tubes. Core sizes were 10-foot x 4 inch which was considered sufficient to reach down into the sediment column to the layers deposited prior to industrialization. The actual coring operation is shown in Figure 2.

Analysis Preparation

Because core sediment profiles were to be used to document specific depositional periods of pollutants, precautions were required to prevent re-working of sediment material in the extrusion process. X-ray analysis was investigated as a possible means of locating geological boundaries that could be used as sectioning points on the sediment core. Preliminary



Figure 2. Vibracore operation. Core sizes 10 ft. x 4 in. were taken. These are considered sufficient to penetrate the sediment column to the layers deposited prior to industrialization.

studies indicated that the x-ray procedure created no significant alteration of the chemical constituents of the sediment. However, the escalating cost of x-ray film prevented use of this technique. A special trough and saw was designed to cut through just the core pipe along its length leaving the contents intact with no contact with contamination sources. This technique has been quite successful, and though the pipes are of aluminum construction, the central core materials can still be sampled for heavy metal analysis by this extrusion technique. Our staff geologist is on-hand during these extrusions to make subsample boundary decisions based on geologic characteristics. Decisions of parameters to be included in the analytical scheme were based on National Pollutant Discharge Elimination Systems (NPDES) permits in effect in 1978-79, the industrial and municipal developments, both present and proposed; and probable or confirmed pollution incidents affecting coastal Mississippi. Some consideration was also given to compounds that could be useful tracers of pollutant movements and to geological parameters that would aid in the interpretation of sediment pollution. Based on these criteria, cores are appropriately sectioned and processed to be analyzed for hydrocarbons, priority pollutants (a "catch-all" coined by the Environmental Protection Agency for select pollutants of various types that pose the most eminent threat to the environment), phenols, trace metals, organic carbon, organic nitrogen, clay mineralogy, grain size, and phenolic aldehydes.

The bulk of core analysis was postponed until 1980 because cores were not obtained until the end of the 1979 year. Analytical efforts were devoted to procedure development, technique refinements and closer analytical scrutiny of the Escatawpa River surface sediments. Included in methods development were: construction of apparatus for microdetermination of phenolic compounds, updating of the gas chromatographic data systems, development of statistical analysis packages for pollutant detection, modification of procedures for micro-Kjeldahl organic nitrogen determinations, improvements in dissolved-particulate organic carbon determinations and full utilization of fluorescence spectra for aromatic hydrocarbon scanning.

Tracer Compounds

Certain industries release compounds in their effluent which are not necessarily toxic but are unique to the effluent and can be easily

distinguished from naturally occurring compounds in the sediments and water. These compounds, when found in sediments and if sufficiently stable and easily analyzed, may serve three purposes: (1) delineate the extent and source of certain pollutant materials; (2) provide an "event marker" which can be useful in dating the core sections; and (3) give information valuable in assessing transport mechanisms of pollutants. The area in the lower Escatawpa River is of considerable interest because of the virtual lack of life in this area until the early 1970's. A paper mill and former lumber yards in the area utilizing mostly pines should be amenable to tracer studies using phenolic aldehydes as the tracer compounds. These compounds present in all plant material exist in very characteristic distributions in pine which enables pine detrital material to be distinguished from the more typical marsh vegetation predominant along the Escatawpa. Procedures are being developed to identify phenolic aldehydes to be used as tracers of pollutant movement in the eastern Mississippi Sound. Fatty acids have been used in the past with limited success as tracers near paper mills. They were analyzed initially to establish the need to try a more sophisticated approach, i.e. phenolic aldehydes. A very large PCP spill in 1980 near the western end of the Sound is being followed closely using PCP as a possible tracer of sediment transport in that part of the Sound.

Broad Spectrum Analysis

In order to give this program a broader scope in terms of identifying the key pollutant compounds, non-selective screening of pollutants of representative sediments are being conducted.

December meetings with Dr. Han Tai, director, EPA chemical Laboratory at NSTL; Dr. Rick Kutz, branch chief, Survey and Analysis EPA Washington; Mr. Martin Halper, division director, Survey and Analysis EPA Washington; and Ms. Sam Wastler EPA Specialist Washington resulted in a working agreement with the EPA Priority Pollutant Program at Bay St. Louis. The agreement includes select numbers of samples to be processed through the gas chromatograph-mass spectrometer housed at the EPA Bay St. Louis facility in exchange for the pollutant data and other input from our program efforts that are relevant to EPA concerns.

Pollution Target Areas

Initial results in the Escatawpa River tributary of the East Pascagoula River have served to label this as a prime pollution trouble spot. Grossly elevated organic matter levels were seen at several locales. Aliphatic and aromatic hydrocarbons are extremely variable in this region. Even at the two closest sampling stations, in a canal facing a paper mill, the distributions of aliphatics are completely different as shown in Figures 3 and 4. In Figure 3, most hydrocarbon material lies between C9 and C15, whereas in Figure 4, not only the low molecular weight (C9 - C15) hydrocarbons are present, but also a large concentration of high molecular weight hydrocarbons reflecting natural plant input.

Figure 5 portrays a few of the gravimetric values for stations above the industrial area, in the industrial area and below the industrial area. The three parameters typically are enriched in areas subject to serious organic waste pollution. All three zones exceed values that would be considered normal for this region but this is especially so in the industrial zone. When certain parameters indicative of oil pollution were applied to the aliphatic and aromatic hydrocarbon chromatographic data it appears that the hydrocarbons in sediments from above the industrial zone are of natural input, coming from higher plant sources whereas, the



A comparison of Figures 3 and 4 illustrates a completely different distribution of aliphatics even at these two closest sampling stations.



industrial area is a region clearly of petrogenic waste disposal. Natural variability can account for much of the differences in hydrocarbon concentrations but cannot be offered as an explanation of the tremendous differences seen in levels of specific hydrocarbons found in this river. These differences amply document the contribution of man-made wastes to the sedimentary basin.

Fatty acids were analyzed to be used as tracer compounds because other investigators have reported that a certain ratio of unique fatty acids was indicative of the presence of wood pulp. However, the area has such a variety of other anthropogenic wastes (menhaden fertilizer plants, chemical plant, ship building firms and sewage treatment input) that the fatty acid distributions were highly variable and proved to be all but useless in tracing organic waste movements. Archived samples will be analyzed in 1980 for phenolic aldehydes which should be more source-specific to investigate the use of tracers in the eastern Mississippi Sound. Some of the more pertinent facts gathered about pollution in the eastern Mississippi Sound, specifically the Pascagoula River are:

- Organic matter (<u>ca</u>. 2x organic C values) in the sediments is <u>extremely</u> high - 40% or more at several locations even in regions that we had tentatively designated as control sites (see Fig. 5).
- 2. Because there are so many sources of organic pollutants in this area, it is difficult to trace one specific source of pollution. Tracers finding success in previous studies have served only to present additional problems of interpretation. At this time, we are seeking those "unique" tracer compounds to help us follow the transport of specific pollutant sources.



the industrial area and below the industrial area.

- 3. Very low concentrations or no phenols were found in the water column near the industrial area. Other workers have also expressed surprise at finding low phenol levels in water and sediments near known sources of phenol waste disposal. The ease of phenol oxidation to quinones has prompted us to take a look at these compounds that may essentially conceal large quantities of phenolic materials in sediments and may under suitable environmental conditions be converted back to the more toxic phenolic form.
- 4. Aliphatic and aromatic hydrocarbons in these sediment samples show anomalously high variability as stated earlier reflecting the variety of wastes dumped in this region and also clearly evidencing a need to abandon the approach taken in pollutant survey sampling presently done by the U.S. Geological Survey and EPA. These agencies and other well meaning groups have relied too heavily on one or two random sediment samples to depict the chemical make-up of a large region. Our documentation of enormous spatial variability of sediment pollutants no longer permits use of this collection scheme.

Meetings Attended

Both co-principal investigators attended the 1979 Oil Spill Conference (EPA/API/USCG) March 19-22 in Los Angeles, California. Latest techniques for measuring and monitoring hydrocarbon pollution were reviewed at this meeting. State of the art techniques have not changed in the past year, but weathering of oil under extreme environmental conditions and subsequent measurements of hydrocarbons have been studied in more detail. We had anticipated more studies involving transport or migration of hydrocarbons, in particular, aromatic hydrocarbons. Indications are, based on the papers presented, that this area of research is still an area that is slighted, most likely because of the need for a greater understanding of the depositional processes, estuarine circulation, and biological and chemical interactions that affect movements of pollutants. Evaluation of these processes are difficult and modeling concepts not always adaptable to the real events. However, the meeting was helpful for exchange of . ideas. Many papers were presented on "effects" of hydrocarbons on the biota and organisms in the environment. Techniques for testing toxicities are now much better defined and can better be compared from laboratory to laboratory.

Public Awareness

An essential educational objective of this pollution transport study has been to let the public know how pollution affects the Mississippi Sound, what we are doing to resolve this situation and what they as private individuals can do to support corrective measures aimed at combating pollution. We have given talks and slide presentations to two Rotary Clubs, to numerous high school and college groups; to the National Science Foundation (NSF) Sea Grant Eco Systems' principal investigators who met at the laboratory in January, 1980; to the Mississippi Academy of Sciences Annual meeting in Biloxi in two papers presented on March 3, 1980, one by Julia Lytle and the other by Tom Lytle, and to groups that tour our laboratory. Newspaper, telephone and radio interviews have also been beneficial in promoting greater public reaction to pollution. We also worked with an elementary student from Moss Point who presented "Pollution in the Pascagoula River" at a Science Fair exhibit. In April, 1980, both Julia Lytle and Thomas Lytle presented a seminar outlining our research and giving some results to the Biology Department at the University of Southern Mississippi in Hattiesburg.

Agency Interactions

The successful utilization of the data and research findings of this study depends to a great extent on promoting a market for the research. A number of state and federal agencies have been contacted and several have expressed an interest in using the data if appropriate formats could be developed to present the data in a useful fashion. The Corps of Engineers, Mobile Branch, the EPA Priority Pollutant Program at Bay St. Louis and the Mississippi Air and Water Pollution Control Commission are among those soliciting our data. Their special needs are known, and data formats have been devised to assure maximum utilization of this programs results and to generate a feeling of confidence in the efforts being spent to protect the aquatic environment of Mississippi.