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SEA GRANT PROJECT R/E-8

MONITORING HYDROCARBONS ON AND IN SEA WATER

FINAL REPORT

November 1, 1977

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INTRODUCTION

The objectives of this project were the following:

- a) To determine seasonal variations in surface films and dissolved petroleum pollutants in sea water.
- b) To determine the variations in surface films and dissolved petroleum pollutants in pleasure craft and commercial harbors, and along the Rhode Island coast.
- c) To determine those components of petroleum that dissolve in sea water or are otherwise removed during weathering.
- d) To explore new methods for identifying the source of petroleum on sea water.

The first two objectives were accomplished through a field program in which over 300 water and 27 beach sand samples were analyzed. The latter two objectives (c and d) were accomplished through a laboratory investigation; however, actual field samples were used to test the methods. In addition to the objectives listed above, a new method was tested for detecting and identifying chemicals directly in water.

RESULTS AND DISCUSSION

I. Field Investigation of Hydrocarbons

a) Water Column

One liter water samples were collected from Wickford (R.I.) Harbor weekly for two years from 4/73 to 4/75, and samples were collected daily for a one week period during the middle of each season of the year. Over 250 samples were analyzed for total organics and for specific chemicals (1).

The objective of this study was to determine the effect of pleasure craft on the organic content of sea water. Definite evidence of petroleum pollution was found occasionally within the harbor; both lubricating and fuel (diesel or No. 2 fuels) were identified, but their appearance could not be correlated with the use of the harbor by pleasure craft. On the other hand, significant amounts of phthalic acid esters (phthalates) were detected during the study. The relative amounts of phthalates are plotted in Figure 1. Since this chemical class was not identified until the end of the study, we do not have exact concentration data, and we have plotted the relative amounts. However, we estimate that the values given in the graph are in parts per billion.

There are two significant features on the graph in Figure 1. From the first to the second year of the investigation the minimum amount of phthalates increased almost 5-fold. Furthermore, there seems to be a direct correlation between the relative amounts and the time of the year. Values of zero (non-detectable) were observed during the Spring of each year, i.e., during May and June of the first year, during March of the second year, and during April at the end of the investigation. Moreover, peak values were observed during December for both years.

Phthalates are used as plasticizers in many plastic (polymeric) products and they can be leached from these materials. During this investigation we found larger amounts of phthalates in laboratory experiments when petroleum was added to sea water. It was suggested (2) that these compounds could be formed from the

microbial degradation of certain chemicals in petroleum, e.g., naphthalene and o-xylene. We added small amounts of each chemical to aerated sea water and observed the formation of phthalates within 24 hours (3). Thus, the exact source of phthalates in Wickford Harbor is unclear, i.e., they could come from plastics or petroleum.

There is an additional problem with the source of petroleum and other chemicals found in Wickford Harbor. They may not have originated in or near the Harbor, but rather they could enter the Harbor during the tidal change. In an attempt to provide an answer to this problem we undertook an extensive study of 7 other Narragansett Bay sites during the summer of 1975. The sites are shown on the map in Figure 2 (a - g). Three were in the upper Bay, three in the lower Bay and one on the ocean. Water samples from these sites were collected bi-weekly at 6 times during the summer.

Again, petroleum was found occasionally at 3 of the sites: Seekonk River, Providence River and Jamestown. Phthalates were found at all of the sites in varying amounts; however, the largest amount (having a maximum value of ~ 5 mg/liter) was always found in the Seekonk River, and the amounts decreased in going down the Bay toward the Ocean, where negligible amounts were found at Pt. Judith.

The latter investigation does suggest that some of the phthalates found in Wickford Harbor could have originated in the upper Bay area.

b) Beach Sands

Beach sands from nine locations along the R.I. ocean shore and lower Narragansett Bay were analyzed for petroleum hydrocarbons (1); the sites for this study are also shown in Figure 2 (sites 1 - 9). Three samples were collected from each site at 7 month intervals between 11/1/73 and 1/1/75. The extracted samples were analyzed by infrared spectroscopy and gas chromatography. Very small amounts of n-paraffins with a distribution similar to petroleum were found in the gas chromatograms of samples taken from Charlestown and Moonstone (sites 1 and 2); the others

had non-detectable amounts. Varying amounts of aromatic hydrocarbons were identified in the infrared spectra of all samples collected from lower Narragansett Bay (sites 4 - 9), and there was a 10-fold increase from site 4 to site 9. These aromatics were highly substituted or of the polynuclear type and their infrared fingerprints were similar to heavy, residual petroleum. The hydrocarbons in all samples collected at each site during the three sampling periods were identical in type and quantity, i.e., they did not change during the time period of this study.

II. Laboratory Investigations

a) Petroleum Hydrocarbons in Sea Water

Four petroleum oils (No. 2 fuel, Bunker C, Kuwait Crude, and So. La. Crude) were mixed with sea water (2% oil added) with strong agitation for 24 hours. The water was separated from the oil and the hydrocarbons extracted. The objective of these experiments was to determine qualitatively those components that enter the water. We found that the amount of aromatic hydrocarbons entering the water column was related to their concentrations in the oils, but there did not appear to be a direct relationship between the amount of paraffins in the oils and those found in the water. In three of the extracts we found another major component. The concentrations of this component in the extracts was related to the concentration of aromatic hydrocarbons and sulfur content of the oil, and it was identified by infrared spectroscopy as an aromatic sulfonyl compound. We have never detected this chemical in field samples, but this may be accounted for by the use of low sulfur fuels in New England. Furthermore, it is possible that the compound can be found only in the immediate vicinity of a spill since it is so soluble.

b) Analysis of Hazardous Chemicals in Water by Laser-Raman Spectroscopy

The major difficulty and limitation of analyzing chemicals in sea water is the necessity to remove the chemical or chemicals from the water. This requires extracting and separation techniques that may take several days to perform. To al-

leviate this difficulty, we have explored the use of a technique called laser-Raman spectroscopy to do both qualitative and quantitative analysis in situ, i.e. without removing the chemicals from the water. The latter feature makes it possible to do the analysis directly at the site of interest, e.g., on a boat or on shore.

In laser-Raman spectroscopy a sample of any chemical in any physical state (solid, liquid or gas) is subjected to an intense, monochromatic (single wavelength) laser radiation. The sample scatters the light spherically at the same wavelength, but also at shorter and longer wavelengths. The latter wavelengths are referred to as Stokes-Raman scattering, and these wavelengths reflect the molecular composition of the chemical and, the amount of light scattered, the concentration of the chemical.

Water is a very weak Raman scatterer and it is possible to identify other chemicals in water at low concentrations. Previously, we (4) showed that inorganic anions could be detected at concentrations of 10 - 100 ppm (parts per million). We were limited in going to lower concentrations by the Raman spectrum of water. The 10 - 100 ppm range is of little use in pollution monitoring; the 10 - 100 ppb range is more desirable.

In the present program we explored a new approach to lowering the detection and identification limits. Normal Raman scattering is obtained from chemicals that do not absorb (i.e., do not have an absorption band) the laser radiation. If, however, the molecules are excited in or near an absorption band, a resonance effect takes place. This is called resonance or pre-resonance Raman spectroscopy, and it can enhance the amount of scattering by up to 10^6 times. Thus, it would be possible to lower the detection/identification limits by as many orders of magnitude.

Our laser has two strong lasing lines; one in the blue at 480.0 nm, and the other in the green at 514.5 nm. Thus, to test the resonance-Raman approach we chose a series of red industrial dyes that absorb in the blue-green region of the electromagnetic spectrum. Four dyes were tested and their detection/identification levels in distilled water are given in Table I (5). All four could be detected at

<55 ppb and identified at <175 ppb. The detection levels using visible spectrophotometry with the samples contained in a 5 cm cell are also given in the table; the detection levels with resonance-Raman are as good as the visible, and the dyes can also be identified. One of the dyes, Superlitefast Rubine, was added to river and sea water. We could identify the dye in river water at a concentration of 288 ppb and in sea water at 444 ppb.

As an additional test for the resonance-Raman method we studied six pesticides/fungicides (6). These chemicals have absorption bands in the uv-region. In this case we used a weaker laser line at 457.9 nm for excitation. The pesticides/fungicides, their absorption band maxima, the levels of detection and the observed Raman bands are listed in Table II. In all but one case the detection level was below 1 ppm. The reason for the higher level of detectability was due to the use of a weaker laser line and to the fact that the laser line was not at the center of the absorption band (this is really pre-resonance Raman); however, this study does suggest that pesticides/fungicides can be detected at much lower levels by using appropriate laser excitation in the uv-region.

In normal Raman spectroscopy the intensity of the Raman bands is directly proportional to the concentration of the chemical. We investigated the intensity vs concentration dependence for resonance-Raman spectra and found that it is not linear (7, 8). In a sample of finite size the amount of light scattered by the molecules e.g., at the center of the sample is proportional to concentration; however, some of this scattered light will be absorbed by other molecules before it leaves the sample. Thus, there is a combination of two effects; a linear scattering dependence and an exponential absorption (Beer's law $I = I_0 e^{-abc}$, where a is the inherent absorptivity of the chemical, b the pathlength and c the concentration). The intensity of the Raman bands will depend upon the exciting (laser) frequency, the frequencies of the Raman bands, and the pathlength of the cell. Therefore, the intensity vs concentration dependence has to be determined for each chemical.

Since Raman and resonance Raman spectra can be measured in situ without prior treatment, we explored the feasibility of measuring spectra with a "flow-through" system (8, 9). The idea of this method is to be able to pump water from a natural source (river, ocean, etc.) and monitor that source for pollution. We investigated various cell designs (cylindrical and square cross sections, filtered vs unfiltered), pumping speeds, and sensitivity to continuous and instantaneous changes in concentration. Square cross sectional cells used without a filter produced the best results. Continuous changes could be detected below 100 ppb. Instantaneous changes could also be detected, if their duration was long enough, e.g., if the changes were for a very short period of time, the chemical might be too dilute by the time it reached the laser beam. Of course this depends upon the pumping system and the distance to the polluted source.

In summary, those chemical exhibiting resonance Raman scattering can be detected and identified in both distilled and natural waters. By using an appropriate laser that excites within the absorption band of the chemical, it is possible to detect molecules in the 10 - 100 ppb range. Since most hazardous chemicals do not absorb in the visible region of the electromagnetic spectrum, we were limited in the present study by the wavelength of our laser. However, lasers emitting in the uv region are commercially available, and these can extend the method to most of the hazardous chemicals.

c) New Methods for Identifying the Source of Petroleum.

Two new methods for identifying the source of petroleum were developed and tested during this project. The first method was based on the method of infrared fingerprints which we had developed earlier (10); however, in this case, the infrared fingerprints were measured with the petroleum samples at sub-ambient temperatures of 80 or 20°K (11). The fingerprints were considerably different at the lower temperatures; thus, they provided an entirely new set of data for identifying the oil. The method was applied to two actual spills; one in New Haven, Conn. and

the other in Pawtucket, R.I. In the first case, spectra measured at room temperature identified the wrong suspect and, in the second case, the match was ambiguous at room temperature. However, the correct suspects were identified unambiguously with spectra measured at 80°K.

A second method for identifying the source of petroleum based on Raman spectroscopy was also developed and tested (12). Previously, it was not possible to measure Raman spectra of petroleum because of interference from fluorescence. However, we found that fluorescing compounds could be removed from light oils (lubricating, kerosenes, No. 2 and diesel fuels) by mixing the oil with pentane to reduce its viscosity and adding a small amount of coconut charcoal. After removing the charcoal and pentane, very characteristic Raman fingerprints could be obtained. Using the method, the correct suspect in a spill case from New York Harbor was correctly identified.

CONCLUSIONS

The field studies show that water in a pleasure craft harbor was probably uneffected by boating in the harbor. Although petroleum was found on occasions, it did not persist and was probably due to a limited spill. The major chemical found in the water samples was phthalates, but their amounts could not be correlated with the use of the harbor since the largest amounts were found in the winter. The field studies also showed that beach sands along Narragansett Bay contained residual petroleum from previous oil spills whereas the R.I. ocean beaches were relatively free of petroleum.

Two new methods were developed for identifying the source of spilled petroleum, and these were tested on actual spills. Finally, a new method was developed for detecting and identifying hazardous chemicals without removing them from water. This method appears to be very promising for analysis of water samples since it completely eliminates the time consuming extraction and separation processes.

Table I

Minimal detection and identification levels*

Dye Name	Raman		Visible Spectrophotometry
	Detection	Identification	
Superlitefast Rubine	35	75	66
Procion Red	30	140	30
Lyrazol Fast Red	45	160	40
Direct Red 83	55	175	50

*All values in parts per billion (ppb)

TABLE 11
Pesticides, absorption wavelength, and minimum detectable concentration by Raman.

Compound Name (a)	λ_a (b) (nm)	E_a (c)	E_o (d)	Minimum Detect- able Concentra- tion (ppm)	Raman Bands Observed (cm ⁻¹)
2-nitrophenol	414	1.43×10^3	7.85×10^2	0.8	824, 881, 1083, 1255, 1338
2,4-dinitrophenol	357	1.02×10^4	9.81×10^2	0.7	801, 964, 1318, 1350
2-methyl-4,6-dinitrophenol (DNOC) (DITROSOL)	366	7.29×10^3	1.43×10^3	0.9	1279, 1330
0,0-dimethyl-0-4-nitrophenyl phosphorothioate (METHYL PARATHION)	278	2.86×10^3	3.74×10^1	7.0	1361
2,6-dichloro-4-nitroaniline (DICHLORAN)	364	1.19×10^4	2.42×10^2	0.4	1338
4,6-dinitro-2-sec-butylphenol (DINOSEB) (DNBP)	376	1.45×10^4	4.15×10^3	0.5	943, 1272, 1327

(a) Some trade names are given in parenthesis.

(b) λ_a = position of absorption band maximum.

(c) E_a = molar absorptivity at band maximum.

(d) E_o = molar absorptivity at excitation wavelength, 457.9 nm.

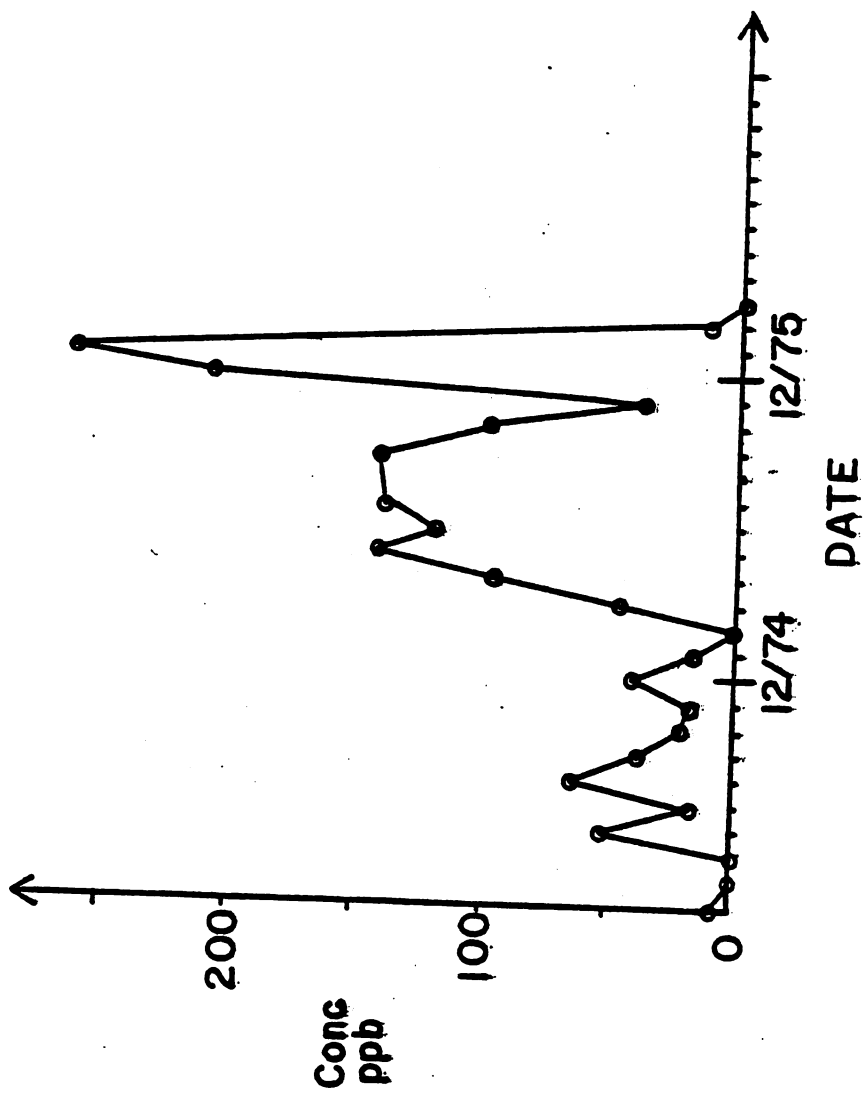


Figure 1

Relative concentration of phthalates in water samples from Wickford Harbor by month. The concentrations are estimated to be ppb units.



Figure 2

Sites for collecting water samples in Narragansett Bay; a - g.
Sites for collecting beach sand samples along R.I. shores; 1 - 9.

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THESIS

1. "Hydrocarbon Analysis of Surface Seawater and Beach Sands by Infrared Absorption Methods", W.-p. T. Lee, Ph.D., University of R.I. (1976).

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