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Fatty Acids and Hydrocarbons in the Surface Waters of the York River

John G. Windsor College of William and Mary - Virginia Institute of Marine Science

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FATTY ACIDS AND HYDROCARBONS IN THE SURFACE WATERS OF THE YORK RIVER

A Thesis

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Presented to

Virginia Institute of Marine Science The College of William and Mary in Virginia

In Partial Fulfillment Of the Requirements for the Degree of Master of Arts in Marine Science

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John Golay Windsor, Jr.

1972

APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Arts in Marine Science

If- *l l J m d a M .* **^ John G. Windsor,**

Approved, May 1972

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TAELE OF CONTENTS

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ABSTRACT

The surface waters (approximately 60μ layer) of the York River, from the mouth to West Point, were sampled over a twenty-two month period with a rotating stainless steel cylinder. Samples were filtered, solvent extracted and were subjected to thin-layer and gas chromatographic techniques to chemically analyze for hydrocarbons, as indicators of petroleum oil slicks, and fatty acids, as indicators of slicks **of** biological origin.

Percent composition and concentration values were reported for free fatty acids ranging from ${\tt C10:0}$ to ${\tt C23:0}$ and normal alkanes from C $_{10}$ to C $_{24}$. $\,$ C $_{14:0}$, C $_{16:0}$, C $_{16:1}$, $C_{18:0}$ and $C_{18:1}$ were the predominant fatty acids. Neither odd nor even numbered hydrocarbons predominated. Petroleum oil slicks and slicks of biological origin were not able to be chemically distinguished. Concentrations of organic material in surface films seems to bear no relation to the description of the slick or the area in which the sample was taken. Surface fatty acid concentrations are dependent upon surface films in the area.

FATTY ACIDS AND HYDROCARBONS IN THE SURFACE WATERS OF THE YORK RIVER

INTRODUCTION

The first recorded application of the methods by which insoluble monomolocular layers were studied seems to be a 4000 year old cuneiform inscription found in ancient Babylon (Trurnit, 1954). A priest dropped sesame oil in a flat wooden bowl filled with water and looked at the surface against the rising sun, The colors and movement of the oil film were thought to indicate the course of future events.

The *fact that* vegetable oils are effective in calming waves was known to the Egyptians. Benjamin Franklin described experiments he conducted on a pond near Clapham, England. He was greatly impressed by the visible speed and force of the spreading oil. He observed that on a windy day, a teaspoon of oil was sufficient to smooth half an acre of water. Trurnit (1954) noted that this corresponds to 20 A for the thickness of the oil film, which is the correct order of magnitude for a menomolecular layer.

Surface films of organic material, very often monolayers, can be found over most of the lakes, estuaries and oceans of the world. These slicks are associated primarily with bigh productivity areas according to Dietz and LaFond (1950), who observed very *few* or no surface films on the Great Salt Lake in Utah and over deep oceanic waters, which

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are both thought to be low in biological productivity. Surface films occur when wind speeds are less than ten knots, and become mixed with subsurface water at higher wind speeds. The capillary wave dampening effect of slick material, which produces the "calm" area, allows them to be seen. These surface films move under the influence of surface currents, tidal action and winds.

The films are composed of relatively non-polar, water insoluble, organic compounds of many varieties. There is not a great deal of information available on the aging of marine surface, films, Such aging studies have been made only on various types of fuel, oils. According to Smith and MacIntyre (19/1), fuel oils break down initially by evaporation and dissolution.

Surface films originate from several sources. Petroleum slicks consist predominantly of hydrocarbons. These sometimes arise through natural fissures, as off the Santa Barbara channel. Oil spills also result from the poor design of equipment, or the improper operation for handling the oil, according to the First Report of the President*'s* Panel on Oil Spills (1970).

Other surface films are of biological origin. Dietz and LaFond (1950) displaced tale on distilled water with crushed kelp, fish, zooplankton and phytoplankton. The phytop1ankton, consisting mainly of diatoms, produced the strongest reaction. This is not surprising for diatoms are known to synthesize droplets of oil in their cells as a

food reserve and a flotation mechanism. (Sverdrup, Johnson, and. Fleming, 1942) . Clark and Mazur (1941) showed in diatom lipids the abundant presence of fatty acids and other substances that are potential slick producers, Unless observation or sampling of the slick material occurs soon after its generation, the surface film will be a partially decomposed mixture of hydrocarbon, biological and locally extracted material (Garrett, 1967), composed of hydrocarboas from crude and refined oils and biologically derived decarboxylation products of fatty acids, *fatty* acids, alcohols and esters, and other lipid material.

PREVIOUS WORK

Studies of dissolved organic matter in the open ocean (Menzel, 1967; Duursna, 1961) showed surface concentrations to be 0.2-2.7 milligrams D.O.M. per liter. Landlocked areas ware found to have higher values, 3.3-8.0 milligrams per liter (Duursma, 1961) .

Slowey, Jeffrey and Hood (1962) studied vertical distributicns of fatty acids in the seawater of the Gulf of Mexico, Concentrations of 0.5 milligrams per liter were reported for the 10 meter samples. $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, and $C_{18:1}$ fatty acids predominated in these samples. The fatty acid composition of phytoplankton, zooplankton and mullet from Galveston Bay were also reported and found to be similar to the fatty acid analysis of seawater.

Fatty acids of the waters of the Straits of Georgia, Juan *do* Fuca, and the adjacent Pacific Ocean waters were determined by Williams (1965). He reported individual fatty acid concentrations ranging from 1-9 micrograms per liter of seawater which passed through a 2.0 micron glass fiber filter. Williams also reported fatty acid concentrations for algae, zooplankton and hake, obtaining resails similar to those of Slowey, Jeffrey and Hood (1962) for the zooplankton, phytoplankton, and mullet of the Galveston Bay. $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, and $C_{18:1}$ were

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also the predominant fatty acids in some seaweeds (Cheucas and Riley, 1966).

Stauffer (1969) reported fatty acid data for the James River, the lower Chesapeake Bay and the nearby Atlantic Ocean. Values of 3.25 - 82 micrograms per liter were obtained for samples which were taken at the two meter depth, Most values ranged between 10 and 25 micrograms per liter. These values seem to be somewhat low in comparison to other published reports.

The fatty acids of 20 marine animals, primarily fishes and crustaceans, were determined by gas-liquid chromatography by Lewis (1967). The fatty acids that predominated were the same as those reported by Slowey, Jeffrey and Hood (1962) for Galveston Bay samples. These results would seem to indicate that fatty acid analysis of seawater or any marine organism sample would yield even numbered fatty acids, either completely saturated or singly unsaturated.

Garrett (1965) was the first to attempt to use screens to sample thin films (0.15 mm) . Prior to this time, all surface samples were taken with buckets or bottles . Estimates of total lipid material were $0.2 - 1.0$ milligrams per liter (Garrett, 1967). One hydrocarbon was identified and the existence of fatty acids was reported at eight sampling stations. Garrett's work was primarily concerned with the total dissolved organic material that could be extracted from seawater with chloroform. The analyses were

not quantitative for individual lipid compounds. Although the screen samples the 0.15 mm layer effectively, it may contaminate samples with subsurface particulate matter and it requires an impractically long time to collect a large volume of the continually changing surface layer,

Jarvis (1967) and Jarvis, et al, (1967) speculated that films of surface active material at the sea surface are primarily mixtures of saturated and unsaturated fatty acids and their esters, with lesser amounts of proteins, carbohydrates and hydroearbons. No chemical analyses were na.de .

Jeffrey (1966) used solvent extraction, column, thin-1ayer and gas chromatography with infrared and ultraviolet absorption, techniques to reveal a complex mixture of alkanes, alkenes, fatty acids, steroids, phospholipids and many unidentified materials from seawater. Twenty to thirth alkanes were detected and saturated and unsaturated fatty acids were present varying in carbon chain length from $14 - 22$ carbons.

Gas chromatographic analysis of gasoline in water and mineral oil in water were, carried out successfully by Jeltes (1967, 1969). By means of relatively simple gas chromatographic methods, he was able to quantitatively analyze components of mineral oil. with boiling points up to 300° C.

Smith and MacIntyre (1971), using temperature programmed gas chromatography, reported the various components of fuel oils (No. 2, 4, and 6) after initial aging on the sea. The following results were obtained six hours after the generation of a No. 2 fuel oil slick, with winds at 18 knots and the seawater temperature 5° C:

To date, qualitative analyses have been carried out on samples taken with bottles and screens. The only quantitative work on surface water has been done on bottle samples. No analyses have been carried out on surface samples taken in Virginia waters.

A quantitative study of the individual organic constituents was needed. Surface concentrations of organic material may be related to biological communities and industrial or municipal effluents in the area. Surface concentrations of hydrocarbons and fatty acids may be indicators of slick type. The source and eventual fate of this lipid material and the present concentrations are useful in determining the ecological significance of marine fatty acids and hydrocarbon films.

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OBJECTIVE

The objective of this work was to develop analytical techniques in the laboratory to differentiate between a slick of biological origin and a petroleum oil slick. This objective was unable to be carried out. The analytical results were to have been coordinated with remote sensing data in such a fashion as to develop a system for differentiating slick types with remote sensors. From these results an attempt was to be made to remote sense sea slicks and determine the slick type. The remote sensing was not carried out due to unavailability of the aircraft.

A second, objective was to determine the effectiveness of the drum sampling device in the sampling of thin films on sea surfaces.

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MATERIALS AND METHODS

Samples were taken along the York River, from the mouth to *West* Point (see Figs. 1, 2, 3). Dates, positions, and descriptions of samples taken are given in the Appendix, Table I.

The Sampling Drum

Ries and Gabor (1966) showed that monomolecular layers on water surfaces can be transferred quantitatively to a rotating stainless steel cylinder. By rotating the cylinder in opposition to the water flow (Fig. 4) and by changing the depth of immersion and rotation speed, it was shown by Ries (1968) and Ries and Gabor (1966) that the removal of thin films from the surface of the water was optimized.

Under laboratory conditions, Ries and Grutsch (1968) showed that the maximum amount of contaminant removed by the method of a single rotating cylinder was two percent of the liquid. To maximize the recovery of oil, a dual drum system was adopted, with the two drums rotating in opposite directions. The first drum concentrated the surface contaminant and the second collected the surface sample, with as high as 98% of the collected material being oil $(\text{Fig. 4}).$

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Fig. 1. Sampling sites on the York River.

Fig. 2. Sampling sites on the York River.

Fig. 3. Sampling sites on the York River.

Fig. 4. Direction of cylinder rotation for thick and thin- \mathtt{films} .

Harvey (1966) reported using a rotating cylinder to collect subrnillimeter thickness surface water samples. He used a 60 x 38 cm stainless steel drum coated with a ceramic material to prevent oxidation. Studies to determine effective methods of collection and observation resulted in improvements that saved time, reduced the problem of deterioration or alteration of the slick during sampling, and allowed the collection of a 60 μ m layer, with *a* minimum of vertical mixing. Samples obtained by the •methods of Harvey indicate larger amounts of organic material in the thin surface layer of the sea than in the water at a depth of ten centimeters. These organic materials include living nannoplankton organisms, structural components of disintegrated organisms, surface active substances, chlorophyll, and carotenoid pigments. Ho chemical analyses were conducted on these samples to determine dissolved organic material.

The stainless steel drum was coated with Solaramic S3210-2C (Solar Company, San Diego, California). Specifications of the coating material are given in the Appendix, Table VII. The coating material was used primarily to prevent oxidation of the stainless steel. The drum is approximately five feet long by two feet in diameter,

The drum was supported three feet in front of the bow of a Cheyenne Model Thunderbird (Fig. 5). The apparatus was raised and lowered by an electrically operated winch. When not in use the weight was supported by a small boom

Fig. 5. Drum-skimmer device.

on the bow. Within the tubular aluminum supporting structure, a stainless steel trough with a teflon blade was mounted in such a fashion as to scrape the rotating cylinder. The drum was driven by an electric motor at between eight and ten revolutions per minute, a slightly faster rate than a wheel on the boat would be turning at the boat's speed. After being scraped from the drum and being deposited in the trough, the sample was drawn by vacuum through one-quarter inch teflon tubing into a chemically clean glass carboy. The entire system was rinsed just prior to collecting a laboratory sample with some of the sample.

Analytica'i Procedures

Immediately upon return to the laboratory, the samples were gravity filtered through Geiman Type A, 0.45 micron, glass fiber filters. Although vacuum filtration offers speed, ruptured cells would have contaminated samples with lipid material. The pH of the filtrate was then adjusted to 2.0 to 2.5 with 12 HC1, so that the salts of the fatty acids would be converted to the free fatty acids. At this point 50 ml of chloroform were added to retard bacterial degradation of the sample. This step was necessary since it took three to four hours to extract each sample and sometimes it was several days before all the samples could be extracted.

According to Jeffrey and Hood (1958), solvent extraction appeared to be most effective of the six common

methods for isolating organic material from seawater. However, in that study and in more recent work by Jeffrey (1968), efficiencies of solvent extraction with chloroform ranged from $5 - 15\%$.

A seawater-chloroform ratio of $12:1$ was chosen. A continuous extraction device (Fig. 6) was built and an optimum extraction time of four hours was selected, since longer periods of time resulted in a serious loss of chloroform due to evaporation. The 1500 ml of chloroform was then removed and reduced in volume by vacuum rotary evaporator.

The extract was subjected to preparative thin-layer chromatography according to the methods of Stahl (1969).

The thin-layer $(0.25 \text{ millimeters})$ was composed of Silica Gel G (Merck, Darmstadt, Germany) and applied rapidly (the calcium sulfate binder sets up rapidly) to a 20×20 centimeter glass plate by means of a spreading device (Brinkmann Instruments, Westbury, New York). The plate was then air dried for thirty minutes and activated at 110°C for another thirty minutes. Plates were stored in a desiccator until ready for use.

The evaporated sample was spotted on the thin-layer plate with a micropipette. The plate was developed with 90:10:1 hexane, diethyl ether, and acetic acid as recommended by Mullins (1970) , who developed the procedures used here for thin-layer chromatography. The hydrocarbon band migrated to the solvent front while the fatty acid

Fig. 6. Continuous extraction apparatus.

band was less than halfway up the plate.

The hands of organic material were made visible by a 0.354 nannometer light. The hydrocarbon and fatty acid bands were both vacuumed off the plate with a spot collecting device. The silica gel was washed with methanol to remove the organic material. At this point the hydrocarbon and fatty acid portions of the samples were separated to prepare them for gas chromatography.

The methanolic hydrocarbon solution was reduced to a very small volume and then extracted with hexane to remove the hydrocarbons from the methanol. This micro-extraction was necessary to remove the methanol soluble calcium sulfate binder. The hexane solution of hydrocarbons was reduced in volume to dryness and redissolved in a known volume of hexane just prior to injection in the gas chromatogx aph.

Gas chromatographic analyses were carried out on a Perkin-Elmer Model 900 Gas Chromatograph equipped with dual columns and dual flame ionization detectors, being operated under dual column compensated conditions.

For the hydrocarbon work, 6 ft. x $1/8$ in. 0.D. copper columns were used. They were packed with 10% SE-30 (Dow) on a non-acid, washed Chromosorb P (Mesh 60/80) both from Applied Science, State College, Pa. A temperature program was used with an initial temperature of 100°C for two minutes and a final temperature of 280°C for twelve minutes. The program rate was set at 4°C per minute with the

injectors at 320°C and the manifold at 290°C. Zero grade helium was used as a carrier gas, with breathing quality air and hydrogen, all from Air Products. Average injection volumes were from 5 to 10 microliters.

The methanolic fatty acid solution was taken to dryness by air evaporation. The fatty acids were converted to their methyl esters for gas chromatographic analysis according to the esterification method of Metcalfe and Schmidtz (1961). To the dried sample several ml of 15% (by wr .) boron trifluoride in methanol were added. The samples were then sealed in vials and placed in boiling water for ten minutes. After cooling and adding one ml of water, three extractions, each using two ml of hexane were used three times to isolate the methyl esters of the fatty acids. The hexane extract was washed with water and dried over sodium sulfate for 30 minutes. The extract was then filtered through hexane-washed glass wool to remove the sodium sulfate crystals and then evaporated to dryness. The sample was then redissolved in a known amount of hexane and was now ready for gas chromatography.

The fatty acid methyl esters were run with a program similar to the hydrocarbon program. The initial temperature was 1.00°C for two minutes while the final temperature was 250 $^{\circ}$ C for eight minutes. The program rate was 4 $^{\circ}$ C per minute. The injector temperature was set at 300°C and the manifold was set at 275°C. Glass columns $(1/4" \times 6")$ were packed with 5% SE-30 on Chromosorb G (AW-DMCS, 80/100 Mesh)

prepared by Perkin-Eimer (lot #3, 8-18-70). The rest of the procedure was the same for hydrocarbon analyses.

Peaks were identified by comparison of retention times with those of a series of standards purchased from Applied Science, State College, Pa. The areas under the peaks were determined since they are directly proportional to concentration when F.I.D, is used. Duplicate runs were made on the standards daily. Blanks were run to determine contaminants of the system. A volume of chloroform (1500 ml) was evaporated to near dryness and subjected to all analytical techniques described in the methods section. This was conducted three times on each lot of solvent purchased. The contaminants were then identified on gas chromatograms and were subtracted from the peaks present. Known concentrations of fatty acids and hydrocarbons were added to distilled water to determine the efficiency of recovery of organic material.
RESULTS

Hyrirocarbon*&*

Percent composition and concentration data for hydrocarbons are recorded in Table II. Due to improperly functioning injection ports, the hydrocarbon concentrations for the first eleven samples were not determined. However, the percent composition of these samples was calculable.

The last nine samples were contaminated by a recently purchased lot of chloroform. This contaminant obscured peaks and prevented determination of C_{17} and the C_{18} for the last nine hydrocarbon samples. An approximate correction factor was determined from the first twenty samples and applied to the last nine. These corrected values for the total hydrocarbons per sample are compiled in Table IV,

Hydrocarbon values ranged from $0.16 - 1.20$ mg/1, with most values in the $0.20 - 0.60$ mg/l range. The average value for the unidentifiable material was 31.10% with nearly all values falling in the $20 - 40\%$ range,

Samples #21 through #29 *were* taken with the intention of comparing methods of sampling. The results are compiled in Table V for the hydrocarbons.

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Fatty Acids

The per cent composition and concentration data for the fatty acids is recorded in Table III in the Appendix. Sample #7 was lost due to spillage.

The last nine samples were contaminated by the solvent. Approximate correction factors were determined from other data. This was not quite as serious as it could have been, since blanks were run through the entire system. The last nine samples were also compared to one another. The corrected values are compiled in Table VI.

Fatty acid concentration values were reported from $0.40 - 8.0$ mg/l with most samples of surface films falling in the $1.0 - 4.0$ mg/1 range (Table IV). The average value for unidentified material was 9.10% .

SOURCES OF ERROR

Before discussing the results, it is necessary to examine, the analytical procedures adopted for sources of error.

The drum, sampling device performed satisfactorily, but the trough had to be kept level to avoid spilling sample over the side. It was necessary to keep the vessel as level as possible and to try and avoid wakes of passing boats « The trough also had to be kept empty so that the samples collected would be as uniform as possible. Some organic moterial was probably lost due to adsorption onto the stainless steel surface of the collecting trough.

While being pumped to the sample collecting bottle, little or no organic material was lost due to adsorption on the teflon tubing. The sample bottle was rinsed with some of the sample prior to collecting the laboratory sample, but some organic material probably was lost due to adsorption to the glass surface. Similar losses could be predicted in the filtration process, where glass fiber filter pads were used.

Extraction efficiency was predicted to be on the order of 5 - 15% efficient. This loss and the loss experienced during filtration account for most of: the loss of organic

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material during the analytical procedures. When this extract was reduced in volume, some of the more volatile, lower molecular weight components were probably lost.

Thin-layer chromatography was helpful in separating the classes of compounds from one another as well as contamiriants present. Some losses could be experienced in the vacuum spot collecting technique and the washing of the silica gel with methanol.

At this point, fatty acids were esterified. A series of standard fatty acids were esterified with boron trifluoride methanol. The results indicated there was no preferential esterification of fatty acids by this technique.

Up to this point in the analytical procedure, it was difficult to determine any sort of preferential loss or quantify sources of error. Standard mixtures of hydrocarbons and esterified fatty acids were run daily and were found to be reproducible within $\pm 5\%$ (Table VII). This is a measure of the reproducibility of injection techniques, column and detector response of the PE-900 Gas Chromatograph. The PE-900 Gas Chromatograph is sensitive to organic material of 5 x 10^{-12} gm carbon/sec.

DISCUSSION

The original intent for this investigation was to differentiate between predominantly hydrocarbon (petroleum slicks) and fatty acid (recent organic generation) slicks. The results of the first twenty samples showed that chemical differentiation would be extremely difficult.

Sample #12 was taken at the mouth of the York River. It was a very light slick with no foam or particulate natter noticeable. Sample #14, taken just upriver on the same day, was reported to be heavy with foam and particulate matter. This slick also contained hundreds of dead jellyfish. These two samples were analyzed and found to have the same concentrations of fatty acids and hydrocarbons. The light slick sample (#12) shewed slightly larger concentrations of fatty acids and hydrocarbons.

Samples #16 and #17 showed relatively large amounts of hydrocarbons. They were taken in the area of the Naval Weapons Station dock in Yorktown. Higher amounts of hydrocarbons would be expected in this area since there is usually a slick being generated from the dock area.

In general, the results showed that the fatty acid and hydrocarbon content of the samples taken seemed to bear no relation to the area in which the sample was taken or the

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particular appearance of the slick. Samples taken off the Amoco (Yorktown) Refinery pier showed no exceptionally large concentrations of hydrocarbons even though there is always a slick present around the terminal. There is little industrialization and light ship traffic on the York River but higher concentrations of hydrocarbons would be expected in the areas of the Naval Weapons Station and the Amoco Refinery in Yorktown.

The results obtained for the last nine samples indicated that the drum skimmer device is effective in sampling surface films. In all cases, the surface film samples contained more dissolved fatty acids than samples taken just outside the slick with the drum skimmer. Bottle samples taken just under the slick had lower amounts of fatty acids than any of the slick samples taken, indicating this to be a poor method of sampling surface films.

In contrast, the hydrocarbon concentrations reported for samples $#21$, $#24$, and $#27$ were lower than other hydrocarbon samples. These are slick samples taken with the drum skimmer. The corresponding samples for just outside the slick reported higher concentrations of hydrocarbons, The bottle samples taken just under the slick also vere reported to contain higher concentrations of hydrocarbons, The concentration of hydrocarbons in non-slick surface samples was higher than the bottle samples. This may be explained by the relative surface pressures of the hydrocarbons and fatty acids. The relatively' polar

fatty acid material may force the non-polar hydrocarbons outside the main body of the slick. Due to the differing orientations of the hydrocarbon and fatty acid molecules at the air-sea interface, the hydrocarbon film would be much thinner and less easily seen. This does not explain the higher concentrations of hydrocarbons in the samples taken with bottles.

The last nine samples offer interesting results (related to wind velocity). The water temperature and other conditions were fairly constant during the sample period. When sampling first started, wind was very light. As the day progressed, wind velocity increased somewhat and there was considerable mixing of surface and subsurface water, as indicated by the results, even though the wind velocity was only $8 - 10$ knots. The concentrations of fatty acids in slick and non-slick samples were more similar when slick concentration values become diluted, while the non-slick samples and bottle samples changed less drastically.

This was not true for hydrocarbons, however. As the winds increased, concentration values Increased for slick, non-slick and bottle samples. The slick sample was still the least concentrated with the non-slick samples being of greatest concentration.

Samples taken on the same day showed various total concentrations but were very similar in their per cent composition. The last nine samples did not agree with this completely. The fatty acid concentrations of samples #21, #24, #27, contained large percentages of $C_{17:0}$ and $C_{18:0}$. These values were lower for non-slick and bottle samples,

A monomolecular layer is on the order of magnitude of 50 A, Calculations show that the slick material in a sample, assuming the drum picks up a 100 micron layer, represents approximately 0.005% of the sample by volume. An eighteen liter slick sample consequently would contain about nine-tenths of a gram of slick derived organic material. This amount of material was not recovered in part due to adsorption in the filtering process, low extraction efficiency and low sampling efficiency. A layer of organic material on the water does increase the amount of organic material dissolved in the water just under the slick according to Le Chatelier's principle.

The non-slick samples and bottle samples had total concentration values for fatty acids of 0.3 to 0.7 mg/1. Slowey, Jeffrey, and Hood (1962) reported subsurface concentration values for fatty acids of the Gulf of Mexico to be 0,5 mg/I. Landlocked bodies of water were reported to have values of 3.3 to 8.0 mg/I of dissolved organic matter (Duursma, 1961). Since only part of the D.O.M. Is fatty acid, these figures do not seem in conflict.

The fatty acids from seawater most often mentioned in the literature were the $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, and $C_{18:1}$ fatty acids (Slowey, Jeffrey, and Hood, 1962; Williams, 1965; Cheucas and Riley, 1966; Lewis, 1967;

Stauffer, 1969). The data, reported by this author are basically in agreement with other published reports. The three slick samples taken on November 3, 1971, added $C_{17:0}$ to this list but the non-slick samples contained little of this fatty acid.

In samples #21 through #29, fatty acids are shown to be more concentrated in slicked over areas than non-slick areas. This is somewhat in disagreement with the work of Garrett (1967), who stated that surface *fatty* acid concentration was independent of slicks in the area. However, his slick samples were taken at sea with screens. The samples taken for this study were from an area of extremely high biological productivity. This may account for the difference in results.

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RECOMMENDATIONS FOR FURTHER WORK

This author feels that the drum skimmer device is an efficient device for taking large volume surface samples. It is recommended, however, that in the future the device be constructed in such a fashion that It be independent of the main body of a vessel. It should either be towed behind on pontoons, such as Harvey's (1965), or be able to be removed from the water and stored in the research vessel. In this manner, research operation could be carried out at sea or in areas that might be potentially dangerous to a small craft.

In this study the drum skimmer was compared to the bottle sampling technique used for sampling surface water. The differences in non-slick samples, slick samples, and bottle samples were noted in the discussion section. It may be of interest to compare the drum skimmer technique to the screen technique developed by Garrett (1965) .

A complete temporal and spatial examination of organic materials in a body of water may be of interest. By coordinating these data with particulate analysis and species known in the area it may be possible to facilitate the study of a food chain, especially when higher molecular weight fatty acids and hydrocarbons that are not metabolized

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are studied. By having background information available of this type, statements having to do with quantities of oil in the ecosystem or concentration of pesticides in surface films could be more firmly supported by fact.

In examination of surface films, it has come to this author's attention that it would be most helpful to have the thickness of the surface film being sampled as a known factor. Perhaps it may someday be possible to get estimates of film thickness from a physical measurement.

Finally., the other classes of compounds present in the surface film samples should be examined. Since surface films are so common in the biologically rich areas, it would be interesting to see if these materials serve any function in the ecosystem.

TABLES

TABLE I

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

Long. 76°32'5" Water Temp. 28.0°C Lat. $37^{\circ}15^{\prime}33^{\prime\prime}$ Ambient Temp. 27°

The slick extended from the Yorktown Naval Weapons Station (N.W.S.) to about 1/2 mile northeast of the N.W.S. dock. The slick also extended to mid-channel. Light slick material, no particulate matter and no foam were noted.

Long. 76°28'37"
Water Temp. 28° Lat. $37^{\circ}14$ '30" Ambient Temp. 27 $^{\circ}$ C

The slick was about 2 miles long and 40 feet wide in the vicinity of the Coleman Bridge, Little particulate material, no foam and heavy damping of capillary waves was reported. Increasing winds were also experienced.

SAMPLE $#3$ August 18, 1970 1215 hrs.

Long $76^{\circ} 28^{\prime} 37^{\prime\prime}$ Lat. $37^{\circ} 15^{\prime} 29^{\prime\prime}$ Water Temp. 29.5 $^{\circ}$ C \qquad Ambient Temp. 30 $^{\circ}$ C

Due to Increasing winds, this sample was taken in the Sarah's Creek inlet. The slick was reported as very light with some particulate material and very little foam. Sampling was discontinued at this time due to extreme weather conditions.

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

August 28, 1970 1430 hrs. $SAMPLE$ #8 Long. 76°321571 * Lat. 37°16?37" Water Temp. 29°C Ambient Temp. 29°C A very large slick was reported to contain much particulate material and foam. It extended up and down river for several miles with a width about 50 yards. SAMPLE #9 September 24, 1970 1030 hrs. Long. 76° 26' 39"
Water Temp. 27°C Lat. $37^{\circ}13^{\dagger}34^{\dagger}$
Ambient Temp. 24°C A slick was reported off the Amoco (Yorktown) pier. It was light with some foam and particulate matter. SAMPLE #10 September 24, 1970 1145 hrs. Long, 76°30'18"
Water Temp. 27°C Lat. 37°14'30"
Ambient Temp. 24°C This sample was taken under the Coleman Bridge. It was reported as light with no

SAMPLE #11 September 24, 1970 1300 hrs. Long. $76°32"7"$
Water Temp. $27°$ C Lat. 37°15'34"
Ambient Temp. 25°C

> This slick was also light with some foam and little particulate matter. The sample was taken in the area of the N.W.S., Yorktown.

foam and little particulate material.

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

SAMPLE $#12$ May 15, 1971 0915 hrs. Lat. 37°14'20"
Ambient Temp. 20°C Long. 76°23'
Water Temp. 18°C The sample was taken at the mouth of the York River near the Chesapeake Bay. The slick was very light with no foam or particulate material. 0945 hrs. $SAMPI.E. #13$ May 15, 1971 Long. $76^{\circ}25^{\circ}$ $\mathtt{Lat.}$ 37°13'55" Water Temp. $18\,^{\circ}$ C Ambient Temp. 20 $^{\circ}$ C Down river from the Amoco (Yorktown) Refinery a slick was noted. There was some foam and particulate material but the. slick was light. SAMPLE #14 May 15, 1971 1015 hrs. Long. $76^{\circ}26'33''$ Lat. $37^{\circ}13'32$ Water Temp. $18\,^{\circ}$ C Ambient Temp. $21\,^{\circ}$ G **A** very heavy, foamy slick was reported just west of the Amoco Refinery pier. Hundreds of dead jellyfish were noted in the slick. SAMPLE $\#15$ May 15, 1971 1050 hrs. Long. $76^{\circ}29'25''$ Lat. $37^{\circ}14'17''$
Water Temp. 18° C Ambient Temp. 21° C Water Temp. 18°C A slick was noted close to the Virginia Institute of Marine Science pier. It was light with some foam and particulate matter. Winds were increasing.

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

SAMPLING SITE LOCATIONS , DATES, AND DESCRIPTIONS

Taken just after a very heavy storm. Absolute calm with very slight capillary waves. Slick was either a monolayer or very close to it. Very light with no foam and no particulate matter.

Sample was taken with drum skimmer outside the slick. Conditions were the same as #21.

SAMPLE $#23$ November 3, 1971 1315 hrs.

 $\rm{Long.}~~76^{\circ}29^{\prime}42^{\prime\prime}.$ Water Temp. $18\,^{\circ}$ C Lat. 37°14 *39" $\mathop{\rm Ambien}\nolimits$ t T $\mathop{\rm emp}\nolimits$. 20 $^{\circ}$ C

Sample taken by dipping a large mouth glass bottle under the slick. Conditions were the same as samples $#21$ and $#22$.

SAMPLE $#24$ November 3, 1971 1415 hrs. Long. $76°36'$ Water Temp. 18°C Lat. $37^{\circ}17'48''$ Ambient Temp. 20° C

> Winds are increasing but this sample was taken on the western shore, of the York River near Queen's Creek. A great deal of detrital material and foam was flowing out in a heavy sliek. IhIs s1ick was *d*escribed *as* a semi-permanent variety by Lake (1972).

SAMPLING SITE LOCATIONS, DATES, AND DESCRIPTIONS

SAMPLE $#25$ November 3, 1971 1440 hrs. Long. $76°36'10''$ Lat. $37°17'36''$
Water Temp. $18°C$ Ambient Temp. Ambient Temp. 19°C Conditions were the same as $#24$. The sample was taken with a drum skimmer out of the slide, SAMPLE $#26$ November 3, 1971 1430 hrs. Long. $76°36'$ Lat. $37°17'48'$ Water Temp. 18°C Ambient Temp. 19°C Sample taken by dipping large mouth bottle under slick sample #24. SAMPI $#27$ November 3, 1971 1545 hrs. Long. $76°30'$ Lat. $37°14'46'$ Water Temp. 18° C - - - - Ambient Temp. 17°C ' Winds increasing in a slick that is light and has some particulate matter and no foam. Sample taken just off VIMS pier, SAMPLE $\#28$ November 3, 1971 1630 hrs. Long. $76^{\circ}30^{\circ}5^{\prime\prime}$ Lat. $37^{\circ}14^{\circ}48^{\prime\prime}$
Water Temp. 18° C Ambient Temp. 17° C Water Temp. $18°C$ Sample taken with the drum skimmer outside the slick area, Conditions similar to $#27$. SAMPLE $\#29$ November 3, 1971 1600 hrs. Long. $76°30'$ Lat. $37°14'46'$ Water Temp. $13\degree{\rm C}$. Ambient Temp. $17\degree{\rm C}$ Sample taken by dipping bottle under the slick. Conditions the same as $\#27$ and $\#28$.

TABLE II

HYDEOCAAEON SAMPLE CONCENTRATION AND COMPOSITION

 $\mathrm{\star}\,$ Concentration val **Sample lost due $_{\rm a}$ lues una to spil available. lags.

HYDROCARBON SAMPLE CONCENTRATION AND COMPOSITION

*Concentration values unavailable.

HYDROCARBON SAMPLE CONCENTRATION AND COMPOSITION

*Concentration values unavailable.

TABI.fi II (Continued)

TABIiE **Ii (Continued)**

TABLE 111

FATTY ACID SAMPLE CONCENTRATION AND COMPOSITION

*No concentrations available.

TABLE III (Continued)

FATTY ACID SAMPLE CONCENTRATION AND COMPOSITION

TABLE III (Continued)

FATTY ACID SAMPLE CONCENTRATION AND COMPOSITION

TABLE III (Continued)

FATTY ACID SAMPLE CONCENTRATION AND COMPOSITION

TABLE IV

TOTAL FATTY ACIDS AND HYDROCARBONS DISSOLVED IN SAMPLES

TABLE V $\frac{1}{2}$

COMPARISON OF HYDROCARBON SAMPLES TAKEN IN AND OUT OF SLICKS WITH

TABLE VI

COMPARISON OF FATTY ACID SAMPLES TAKEN IN AND OUT OF SLICK WITH

TABLE VII

SOLARAMIC S5210-C DATA SHEET

Dated: 6/4/59

Revised: 10/12/66

Purpose of Coating

To prevent oxidation, carburization, etc., of chromium containing steels ,

Specifications

Properties

Salt spray resistance (200 hr test):

Excellent

Source for Coating Application

Sol $\operatorname{ar},$ a Division of International Harvester, San Diego, California

REPRODUCIBILITY DATA* FOR STANDARD INJECTIONS

FATEV ACTA STANDADDS

*Unitless values are proportional to concentration

TABLE VIII (Continued)

REPRODUCIBILITY DATA* FOR STANDARD INJECTIONS

HYDROCARSON STANDARDS

*Unitless values are proportional to concentration

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