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IDENTIFICATION AND FATE OF ORGANIC COMPOUNDS EMITTED FROM OUTBOARD MOTOR SUBSURFACE EXHAUSTS

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Progress Report for Division of Water Pollution Control,
Massachusetts Water Resources Commission.
Contract Number 15-51451.

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ENVIRONMENTAL ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF MASSACHUSETTS
AMHERST, MASSACHUSETTS

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Environmental Engineering Program
Department of Civil Engineering
University of Massachusetts
Amherst, Massachusetts

PREFACE

This progress report is the third in a series of detailed progress reports prepared for the Division of Water Pollution Control, Massachusetts Water Resources Commission, Contract Number 15-51451, "Effect of outboard motor exhausts on water quality and associated biota of small lakes."

This report is presented in two separate and complete sections. Section ONE focuses on the identification of organic compounds emitted into water through subsurface exhausts from outboard motors. Section TWO of this report presents information on the fate of organic compounds emitted into water through the subsurface exhausts of outboard motors. In total, it represents a portion of the research performed by the authors during the period from January, 1972 to April, 1973. The authors are respectively, assistant professor and graduate research assistants, Department of Civil Engineering, University of Massachusetts at Amherst.

This report will be brought to the attention of various agencies, organizations, companies, industries, and individuals interested in the preservation of our natural resources.

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SECTION ONE

The Identification of Organic Compounds Emitted from Outboard Motor Subsurface Exhausts

ABSTRACT

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The major hydrocarbon compounds present in outboard motor fuel and OMSE-water were evaluated by the techniques of gas chromatography and mass spectroscopy.

The major hydrocarbon compounds found in OMSE-water ranged from C_7 to C_{12} and a majority of these compounds were alkyl-benzenes; whereas, the major hydrocarbons present in the raw fuel mixture varied from C_5 to C_{12} and contained approximately the same number of alkyl-benzene compounds as aliphatic compounds. The similarity in composition, retention time, and peak shape of the hydrocarbon compounds in the raw fuel mixture and OMSE-water suggested that the hydrocarbons in OMSE-water were derived from the passage of a portion of the unburned raw fuel mixture into receiving waters.

INTRODUCTION

INTRODUCTION

A variety of hydrocarbon compounds may be present in outboard motor subsurface exhaust (OMSE)-water. The five-day biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrogen, and total carbon analyses all have been used successfully to describe the degree (concentration) and oxidizability of organic substances in the aquatic environment. These analyses do not serve as tools to identify or measure any specific organic compound present in water.

In addition to the gases (water vapor, the oxides of carbon, nitrogen, sulfur, and others) from the combustion chamber, hydrocarbons and lead compounds in the unburned fuel mixture, complexed particulate lead compounds, hydrocarbons derived from rearrangement (cracking or synthesizing reactions), and partial oxidation products all can be expected to be discharged below the water surface by outboard motors. With the exception of research on the percent of raw fuel passing through an outboard engine, a minimal amount of work has been done on qualifying and quantifying the compounds present in OMSE-water. Considerable achievement has been made in the identification of compounds emitted from four-cycle engines and it is expected that some of these same compounds are present in OMSE-water.

This particular experimentation consisted of the laboratory investigation of various factors involved with the outboard motor pollution problem. The specific scientific objectives of this investigation were:

1. The identification of the major hydrocarbon components in OMSE-waters. Integral to this objective is an investigation of the techniques of gas chromatography and mass spectroscopy for outboard motor derived hydrocarbon separation and identification.

LITERATURE REVIEW

LITERATURE REVIEW

Sources of Outboard Motor Engine Emissions

Aside from the fuel spills that might occur during fueling operations, it would appear that there are two sites for compound emissions into receiving waters from two-stroke cycle engines. The first site is the cylinder itself. Within the cylinder, intake and exhuast are accomplished in the same stroke. Even with deflectors some portion of the incoming fuel vapors may be mixed into the exhaust gases which are vented into the receiving waters. The second site of emissions is the crankcase where the drainage of an excess gasoline/oil mixture is directed into the receiving waters in most older model engines. Some researchers agree that the major source of engine emissions is derived from the crankcase drainage (1,2)* with the amount of unburned fuel passing through the cylinder being only a small percentage of the total quantity of emissions discharged into receiving waters.

It has been shown by numerous investigators (1,3,4,5,6,7,8,9) that various compounds can pass through an outboard engine and into receiving waters without being burned within the cylinder. Various engine liquid and solid (in the form of particulate matter) emissions, along with exhaust gases are passed into the receiving waters in the vicinity of the propeller. The propeller's mixing action rapidly disperses these materials throughout the receiving waters. The quantity of these substances discharged is dependent upon several variables and also upon conditions which are prescribed by the manufacturer. These variables and conditions

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*Numbers in parentheses refer to equivalent reference article.

have been thoroughly reviewed by Jackivicz and Kuzminski (10) and the reader is referred to their publication for a detailed treatment of this particular topic.

Outboard Motor Fuel Composition

All substances emitted by outboard motors are derived from the fuel mixture which consists of gasoline with or without its additives and lubricating oil. Gasoline with a boiling point range from 40°C to 180°C contains mainly hydrocarbons from the C_6 to C_{10} range. Over 100 compounds have been identified in gasoline and these include normal and branched alkanes, cycloalkanes, and alkylbenzenes (11,12,13). Under normal conditions of compression with air and explosive combustion in the engine, these hydrocarbons are converted largely to water vapor, carbon dioxide, and carbon monoxide.

Lubricant oils for four-stroke engines vary in the number of carbon atoms from 26 to 38 (12) with a boiling point range of from 405°C to 515°C, and contain metals such as zinc, sulfur, and phosphorus (14). The lubricating oil most commonly used in two-cycle outboard motors is different in detergent composition from oils utilized by four cycle engines. Outboard motor oils employ organic detergents which are biodegradable while four-cycle oils employ metallic detergents which are not biodegradable. Since the boiling point of motor oils (405°C to 515°C) is considerably higher than that of gasoline (40°C to 180° C), the gasoline will volatilize more readily in the crankcase of two-stroke cycle engines.

Compounds Emitted During Operation of Outboard Motors

Various investigators (8,15,16,17,18) have reported values for the volatile and non-volatile fractions of oil, phenols, lead, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in OMSE-water and their findings appear in Table 1. A BOD value for the main component of outboard motor fuels (gasoline was found to be of 0.078 grams per gallon (19). Mention of the various hydrocarbons in gasoline included normal and branched alkanes, cycloalkanes and alkylbenzenes (11,12,13). Zajic, et al (20) examined specific hydrocarbons (several found in gasoline) for 5-day BOD values and found that n-hexane and n-heptane gave a 5-day BOD of zero ppm. As the length of the paraffinic hydrocarbon chain increased, the BOD increased up to the longest-chained hydrocarbon compound tested by the researchers, n-heptadecane, whose 5-day BOD was 60 ppm.

In addition to the COD values (2.5 to 114 mg/l) reported (8,15,16) for OMSE-water, the engine condensates for some engines used by the military have a reported COD value of 900 to 2000 ppm (21). It should be noted that all COD values presented in Table 1 are not a true representation of all the hydrocarbon compounds present in OMSE-water because the aromatic and straight chained aliphatic compounds in gasoline, OMSE-water, and engine condensates are not oxidized in the standard COD test (22).

Of the one billion gallons of gasoline consumed annually by outboard motors it has been estimated that 100 to 160 million gallons of fuel are wasted into receiving waters (23). In a recent reconnaissance study by Shuster (7) it was reported that if a discharge of 400 ml of exhaust products per 30 minutes of outboard motor operation is typical of an average day operation, this may be transformed into a wastewater burden in terms of population equivalent. Assuming that the products contain 85 percent biodegradable carbon, the discharge based on one engine-day would be equivalent to a population of 400 people. The estimates for fuel wasted annually and the 24 hour organic carbon population equivalent have both been questioned as to validity (24).

Table 1. Various Compounds Found in Outboard Motor Subsurface Exhausted Water (8,15,16,17,18)

			Compound (g/l of fuel consumed)				
Author	Oil/Gasoline Ratio	Non-volatile Oil	Volatile Oil	Lead	Phenol	BOD	COD
Kempf, et al (44)	1:25	5-7				-	110
	1:50	2.5-3.5	2-3	0.03-0.05	0.16-0.20	-	60
	1:100	2-3				-	60
English, et al (45)	1:16	28	15.0	0.14	0.16	42*	114
Vogel (46)	1:20-1:25	8-10	-	-	-	-	-
Eberan-Eberhorst (47)	1:24	9-23	-	-	-	-	-
	1:50	4-11	-	-	-	-	-
Environmental Engineering, Inc. (33)	Oil/Gas Ratio	Hours of Operation					
	1:50	1	-	-	-	1.05**	2.5
	1:50	4	-	-	-	4.20**	11.5
	1:50	8	-	-	-	9.00**	19

*Ultimate BOD - Seed was settled river water.

**Assumed as 5-day BOD results - Seed unknown.

Many organic compounds have been reported in automobile (four stroke engine) exhaust gases. Since these compounds could be found in outboard motor exhausts (because of the similarity in two-stroke and four-stroke engine fuels) some mention will be made of them. The separation and identification of hydrocarbons in automobile exhaust gases has been accomplished by numerous investigators (25,26,27,28,29,30,31,32). Their findings indicate that literally a hundred or more hydrocarbon compounds can be emitted in the exhausts of internal combustion engines. Many of these will not persist for a long period of time in water due to their immiscibility, volatility, biodegradability, and the effects of weathering; but on the other hand, others may persist for extended periods of time.

Of all the possible oxidation products that could be formed from the partial oxidation of gasoline in both two-stroke and four-stroke engines, perhaps the phenolic family has been the most troublesome from the pollution standpoint (32,33,34). English, et al (16) and Kempf, et al (15) were able to measure in OME-water 0.16 and 0.16 to 0. 2 grams of phenol per liter of fuel consumed; respectively. In addition to phenols other compounds found in the partial oxidation products in automotive exhausts include alcohols, aldehydes, esters, ketones, and acid derivatives (35). DesRosiers (21) reported concentrations of 10 to 15 milligrams per liter of formaldehyde (CH_2O) in the condensates from military engines.

Perhaps the earliest attempt to identify the various compounds in OMSE-water was that of English, et al (16,36). These workers were able to measure volatile and non-volatile oil in OME-water by extraction with chloroform followed by measurement of the oil fractions using a pycnometer. In addition to the oil analysis, phenol and COD determinations were also conducted on OME-water. The techniques of infrared spectroscopy were utilized to evaluate any alteration in lubricating oil after passage through an outboard engine. The original outboard motor lubricating oil was found to contain mainly straight chain aliphatic hydrocarbons; however, after passage through the outboard motor engine, carbonyl groups, indicating oxidation, appeared in addition to the straight chain aliphatic hydrocarbons.

In a series of field experiments, English, et al (36) were able to recover organic material by adsorption onto activated carbon from dilute solutions of OME-water in a motor pond and motor lake, and from water in a control pond. The hydrocarbon bearing carbon was air dried and extracted with chloroform. After evaporating the chloroform, the extract was weighed and then separated into aliphatic, aromatic and oxygenated hydrocarbons on silica gel. Iso-octane was used to desorb aliphatic hydrocarbons, benzene for aromatic hydrocarbons, and a chloroform-methanol mixture for the oxygenated compounds. Bottom muds from the same ponds were also analyzed for hydrocarbons. The muds were dried at room temperature and extracted in a soxhlet extractor with chloroform. Only the aliphatic fraction was separated by chromatography on silica gel.

Investigations on the effects of outboard motor exhausts on Lake X water quality included the use of gas chromatography to measure the quantity of organic compounds present after the lake water had been contaminated with outboard motor exhaust products (8). A one gallon OME-water sample was extracted with chloroform and then injected into a gas chromatograph. To obtain a reference solution for identification of hydrocarbon peaks a 10 horsepower motor was allowed to operate for four hours in a 50 gallon drum but the amount of fuel consumed during this time was not presented. A one gallon sample from this drum was extracted with chloroform, injected into a gas chromatograph, and approximately 16 "fingerprint peaks" were revealed in the resulting chromatogram. Identification of the various hydrocarbon peaks was not attempted and the temperature program rate for the temperature programmed chromatogram or temperature hold times were not presented with the instrumental parameters.

The determination of hydrocarbon emissions from four-stroke cycle engines has been the object of numerous investigators (27,27,30,32,37,38). The raw fuel used in both four-stroke cycle and two-stroke cycle engines are identical in nature except for the lubricating oil added to outboard motor engines for purposes of lubrication; therefore, the exhaust products may be similar in composition. With this in mind, it was thought that the methods employed for the identification of four-stroke cycle emissions would be applicable to the analysis of two-stroke emissions and was so utilized. For an in-depth discussion of these methods, the reader is referred to the above-referenced articles.

MATERIALS AND METHODS

MATERIALS AND METHODS

Chemical analysis was confined to the identification of the various hydrocarbon components of raw water, raw fuel (gasoline/oil mixture), and OMSE-water.

Outboard motor. A 7 1/2 horsepower, Merc 75[1] outboard motor having an engine bore of 2 inches, a 1 3/4 inch stroke, and a total piston displacement of 11.0 cubic inches was used to generate the OMSE-water. The speed of the engine operating within the test water was monitored with a tachometer.

Test fuel. The test fuel was a commercial leaded gasoline[2], plus commercial outboard motor lubricating oil[3] recommended by the manufacturer. A fuel to oil ratio of fifty to one was employed throughout the experiment as recommended by the outboar motor manufacturer (39). The test fuel mixture was blended in graduated cylinders to insure proper volume measurement as follows: a total of one gallon of fuel was prepared for each run by mixing 74 ml of lubricating oil with 3711 ml of gasoline to yield a ratio of 50/1 and a total volume of 3785 ml (one U.S. gallon). The prepared fuel mixture was then stored in a three-gallon storage tank ffom which it was siphoned to the outboard engine for combustion. At no time did this storage period exceed two hours.

Test water. For hydrocarbon identification OMSE-water was generated by exhausting one gallon of fuel into a known volume of Amherst tap water. This tap water is mainly surface waters held in local reservoirs and supplemented with ground water.

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[1] Manufactured by Kiekhaefer Mercury, Fond du Lac, Wisconsin

[2] Gulf regular gasoline

[3] Quicksilver-Formula 50 outboard motor oil manufactured by Kiekhaefer Mercury, Fond du Lac, Wisconsin.

The composition of test water (Amherst tap water) prior to outboard motor operation must be known before any conclusion can be drawn on the contribution of various compounds by outboard motors. To assure that the water to be exhausted did not interfere with the measurement of hydrocarbon compounds it was characterized intermittently for the duration of the laboratory testing for the following quality parameters:

1. Turbidity
2. Total solids
3. Dissolved solids
4. Suspended solids
5. Color
6. pH
7. Alkalinity, phenolphthalein
8. Alkalinity, total
9. Hardness, total
10. Hardness, non-carbonate
11. Temperature
12. Copper
13. Organic material
14. Chlorine

These analyses were done using wet chemical techniques as described in Standard Methods (22). The quantity of organic material present in the test waters was measured as total carbon with a total organic carbon analyser[1].

Outboard motor testing area. Two test tanks, each 4 ft deep x 4 ft wide x 6 ft long, were fabricated from 26 gage-type 304 stainless steel sheets, reinforced with 3/4 in. plywood and braced by 2 in x 4 in wood supports. To prevent loss of test water due to splashing and allow for the operation of the test motors at high engine speeds (full throttle), 1 ft long stainless steel deflector shields were pop-riveted to the body of the stainless steel tank. The seams of the test tanks were

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[1] Beckman Model 915 Total Organic Carbon Analyser manufactured by Beckman Instruments, Incorporated, Fullerton, California.

double rolled and soldered with a 60/40 solder (60 percdnt lead and 40 percent tin) to assure water tightness. To prevent the test water from coming in contact with the solder and possibly altering the test water characteristics, the inside tank seams were caulked with General Electric Silicone Seal. Each tank was equipped with a set of two semi-steel rigid casters and four semi-steel swivel casters with plain bearings so that each tank could be readily moved. Motor mounts, which enabled the outboard motors to be raised and lowered into the test tanks, were permanently bolted to the wooden test tank structure.

The gases formed upon the combustion of the fuel mixture were vented below the water's surface where they were either absorbed or escaped into the atmosphere above the test tank. For safety reasons, an exhaust system was constructed to vent these gases during motor operation outside the building which housed the test tanks.

The Amherst tap water was directed into the test tanks through a rubber hose. Each test tank had a drain system made of 2 in polyvinyl chloride (PVC) pipe and was regulated by 2 in globe valves. The tank drainage network discharged into a floor drain.

Generation of OMSE-water. OMSE-water was generated by combusting one gallon of fuel mixture in a 7 1/2 horsepower outboard engine operating at 1700 ± 100 rpm and allowing the exhaust products to discharge into 400 gallons of Amherst tap water. This resulted in a OMSE-water which was termed a 'stock solution' and represented a 400/1 test mixture (400 gallons of recipient dilution water to one gallon of exhausted fuel). This stock solution served as a source of OMSE-water for hydrocarbon identification.

Amherst tap water was directed into a stainless steel tank to a depth corresponding to a volume of 400 gallons of water. This water was held in the test tank for varying periods of time ao allow for temperature adjustment between the laboratory temperature and water temperature and for dissipation of any chlorine residual. The tap water was allowed to adjust near ambient so that a relatively uniform receiving water temperature could be maintained during the entire experimentation period. It was felt that this would allow for a uniform gas absorption coefficient for all experiments.

After this brief holding period, the outboard motor was started andallowed to run until it utilized one gallon of fuel. During this OMSE-water generation period, the exhaust gases were removed from the atmosphere just above the water's surface by an exhaust fan. The engine speed was checked at the beginning of the experiment and adjusted to 1700 ± 100 rpm for the duration of motor operation. Approximately three hours of motor operation at this engine speed were required to consume one gallon of fuel. Upon consumption of this quantity of fuel a portion of the OMSE-water was then removed for the experiments of choice.

Hydrocarbon Analysis Procedure. The identification of hydrocarbons was to be accomplished for three specific samples; raw water (Amherst tap), raw fuel (gasoline/oil at a 50/1 ratio), and OMSE-water (stock solution-ratio of 400/1 gallons of dilution water to fuel consumed). The identification of the various hydrocarbons in OMSE-water progressed in four steps; concentration, extraction, separation, and identification.

Concentration was accomplished on an activated carbon column and extraction of hydrocarbons off the activated carbon was achieved with chloroform. Separation of the various hydrocarbon compound components in the different samples was achieved by gas chromatography and subsequent identification occurred with the us[illegible] of a mass spectrometer coupled with gas chromatography retention time data.

A flow diagram of the entire process involved for the preparation and identificat of hydrocarbons in OMSE-water is presented in Figure 1. The same procedure occurred for the raw water except that the raw water was brought directly to the activated carbon column and was not pumped from the stainless steel test tank. Concentration and extraction of the raw fuel was not necessary; however, separation on a gas chromatograph and subsequent identification as outlined in Figure 1 was required.

OMSE-water extract preparation for hydrocarbon analysis. The hydrocarbons present in both raw water and OMSE-water were concentrated so that an adequate quantity of sample would be available for detection by the hydrogen flame-ionization detector of the gas chromatography units utilized in the separation and identification phases of this portion of the experiments. Concentration of organic compounds onto activated carbon was chosen as the method for concentration because of its widespread use and success as reported by various investigators (22,40,41,42,43,44,45,46,47). An organic sampler[1] similar to those used in the Environmental Protection Agency's water pollution surveillance system was used to adsorb the hydrocarbons from raw-water and OMSE-water (22).

The organics sampler was located in an area free from vibration to insure that the volumetric measuring system would operate accurately. The volumetric measuring

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[1] Model LF-2 Organics Sampler manufactured by TriCraft Specialty Company, Cincinnati, Ohio.

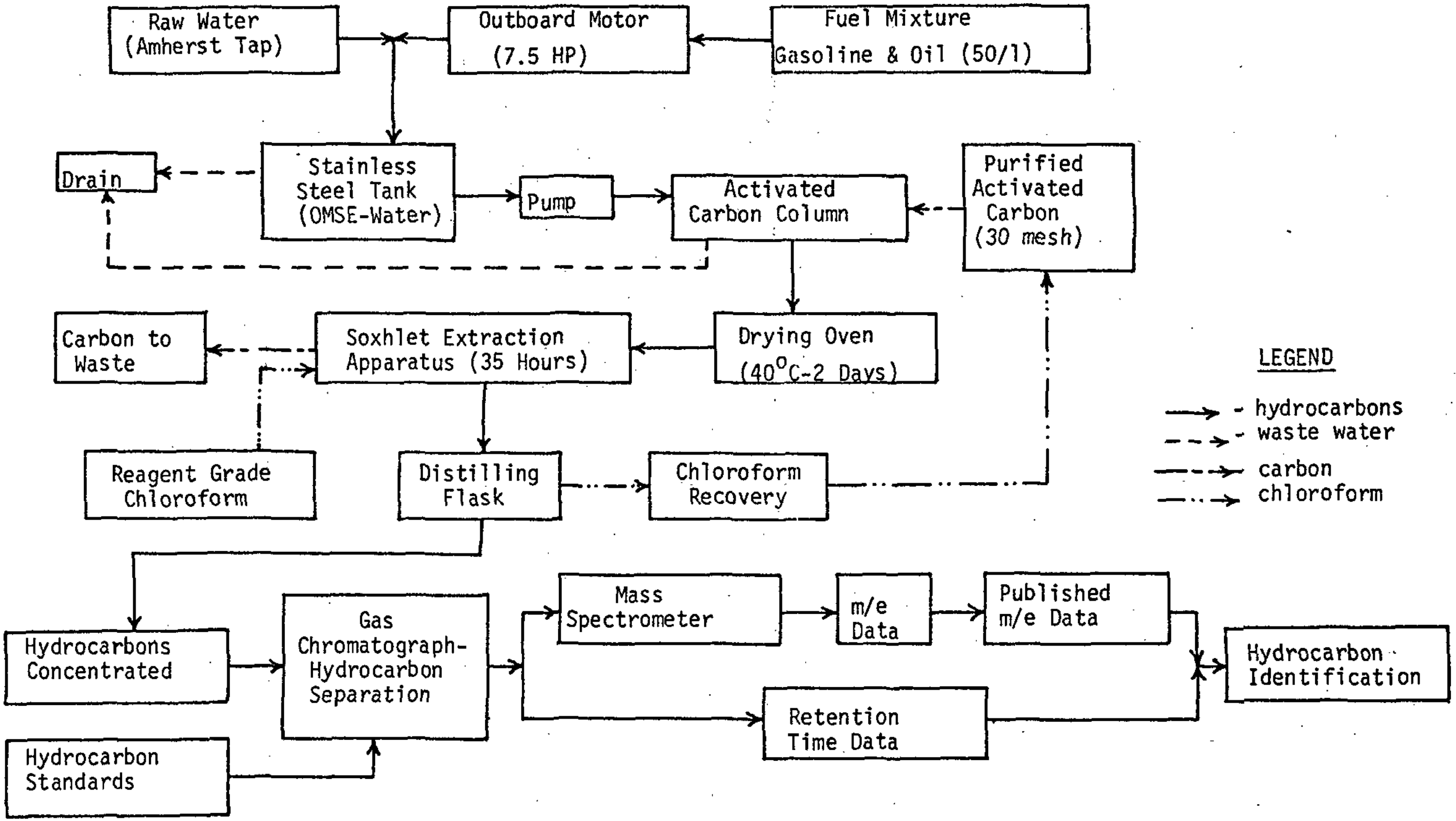

Figure 1. Flow Diagram of Preparation, Concentration, Extraction, Separation, and Identification of Hydrocarbons in OMSE-Water.

tank was calibrated to hold exactly one liter of test water. The 'all fine' activated carbon column was packed with 30 mesh activated carbon[1] previously extracted with chloroform.

The OMSE-water was continuously pumped thorugh the activated carbon column at a rate of approximately 8 to 12 liters per hour. The total quantity of OMSE-water passed through the column varied from 200 to 275 gallons. Raw-water passed through the activated column ranged from 150 to 250 gallons and was also passed through the column at a rate of between 8 to 12 liters per hour. The exact flow for OMSE-water and raw-water for each individual sampling run was metered and recorded. The hydrocarbon-bearing activated carbon was then removed from the glass adsorption column and prepared for extraction.

The procedure used for extraction of the hydrocarbons of raw-water and OMSE-water from the activated carbon with chloroform (or other appropriate solvent/solvents is described by Standard Methods (22) and other investigators (41,47) and a detailed explanation of the procedure can be found in these references. However, a brief summary of the extraction procedure will be presented herein.

Prior to extraction with chloroform, the activated carbon was oven-dried at 40^{o}C on stainless steel trays for two days to remove any excess water. Following drying, the carbon was placed into an extraction column which had been prepacked with approximately 2 to 3 inches of chloroform melted glass wool which prevented any carbon fines from passing into the boiling flask.

Extraction of the hydrocarbon sample adsorbed to the activated carbon was accomplished inside a Soxhlet extraction apparatus. This was performed for a 35 hour period using reagent grade chloroform as the solvent. Upon completion

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[1] Nuchar C-190+30 Mesh Activated Carbon manufactured by Westvaco Corporation, Covington, Virginia.

of the extraction, the remainder of the chloroform in the extraction apparatus was siphoned over into the boiling flask by adding fresh chloroform to the extraction chamber until a shiponing action was created by the flow of chloroform from the chamber into the boiling flask. Glass beads were always used in the boiling flask to avoid localized heating.

After cooling to room temperature, the boiling flask was removed from the extraction system and the chloroform/hydrocarbon mixture was placed in a distillation flask. The extract was next concentrated by distilling the chloroform at 62°C from approximately 2 to 3 liters to a volume of approximately 200 ml. In the preliminary experiments this 200 ml volume was further concentrated by evaporating the solvent to about 20 ml on a steam bath. This 20 ml volume was filtered through solvent-washed filter paper to remove any carbon fines, transferred to glass vials, and stored at 4°C until analysis.

The response of the flame-ionization detector of the gas chromatograph indicated that concentration of the hydrocarbons to a 20 ml volume was more than adequate for distinct peaks to occur even at high attenuations. Chromatograms of the pre-evaporated (but distilled)sample (200 ml volume) provided distinct peaks at lower attenuations (more sensitivity) and for the remainder of the testing the 200 ml volume, after filtering through a solvent-washed filter paper and refrigeration at 4°C, served as the hydrocarbon-containing extract which would be utilized for gas chromatography and mass spectroscopy.

This extraction procedure provided extracts of raw-water and OMSE-water which contained hydrocarbon compounds with boiling points higher than that of the solvent chloroform which was distilled from the samples. The loss of hydrocarbons with boiling points less than 62°C was anticipated for all samples extracted by the carbon-chloroform technique.

Instrumental analysis of hydrocarbons. Separation of the various hydrocarbon compounds in raw-water extract, raw fuel, and OMSE-extract was necessary for two reasons: first, to provide retention time data and therefore, preliminary identification of each individual major peak and secondly, to provide adequate component separation enabling a single hydrocarbon component scan by mass spectroscopy. Hydrocarbons in the exhaust emissions of automobile engines (26,27,30, 32,37,38), straight chain alkyl benzenes (48), hydrocarbons in gasoline (25,28,29), and hydrocarbons in OME-water (8) have been successfully separated by gas chromatography.

Once the hydrocarbons were concentrated by means of adsorption and extraction, they were injected into various gas chromatography units for separation on selected analytical columns[1]. The column specifications for the two open tubular (packed) columns, two wall-coated open tubular (capillary) and support-cated open tubular (SCOT) column used during the experimentation appear in Table 2.

To aid in the identification of hydrocarbons in the various samples, a mixture of gas chromatographic quality known hydrocarbons[2] were blended into a reference standard. This reference standard contains many of the major hydrocarbon compounds found in gasoline (11,12,13), automotive exhaust emissions (26,30,37) and they cover the same boiling point range of hydrocarbons present in Table 3 and were used for the tentative identification of hydrocarbons based upon retention time data.

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[1] All analytical columns supplied by Perkin-Elmer Corporation, Norwalk, Connecticut

[2] Purchased from Chemical Samples, Company, Columbus, Ohio

Table 2. Specifications of Various Gas Chromatography Columns Used in Hydrocarbon Separation

	Open Tubular (Packed)		Wall-Coated Open Tubular (Capilliary)		Support-Coated Open Tubular (SCOT)
Specification	Vers F-50*	DC-200*	Vers F-50*	OV-101***	SF-85****
Metal tubing	SS[δ]	SS[δ]	SS[δ]	SS[δ]	SS[δ]
Length (ft)	12	12	150	150	50
I.D. (in)	--	--	0.01	0.01	0.02
O.D. (in)	0.125	0.125	--	--	--
Liquid phase	Versilube F-50 5%	DC-200 20%	Versilube F-50	OV-101 Silicone	SF-85 Dimethyl Silicone Oil
Solid Phase	Chrom W[+] 80/100 M[++]	Chrom W[+] HMDS 60/80M[++]	--	--	--
Max.temp.(°C)	approx. 150	approx. 200	160	250	170

*Versilube F-50 - methyl chloro-phenyl siloxane.

**DC-200-Dimethyl polysiloxane.

***OV-101-Dimethyl polysiloxane but polychain is larger than that of DC-200.

****SF-85 - Dimethyl silicone oil.

δ - Stainless steel.

\+ - Chromosorb W - white, flux calcined diatomite.

++ - Numbers such as 80/100 M refer to the standard sieve size through which the support particles will and will not pass, respectively. Number 60 mesh corresponds to 250 microns opening, number 80 to 177, and number 100 to 149 microns ~~(109)~~.

Table 3. *Hydrocarbon Composition of Reference Mixture in Ascending Boiling Point Order.*

Order	Compound	Boiling Point in ^{o}C
1	2-Methylpentane	60.271
2	3-Methylpentane	63.282
3	2,4-Dimethylpentane	80.5
4	3-Methylhexane	92.0
5	Heptane	98.42
6	2,2,3-Trimethylpentane	109.841
7	Methylbenzene	110.6
8	Octane	125.66
9	Ethylbenzene	136.2
10	1,4-Dimethylbenzene	138.35
11	1,3-Dimethylbenzene	139.1
12	1,2-Dimethylbenzene	144.4
13	Nonane	150.798
14	1,2,4-Trimethylbenzene	169.35
15	Decane	174.1
16	Undecane	195.9
17	Dodecane	216.3
18	Tridecane	235.4
19	Pentadecane	270.63

Preliminary retention time data for various hydrocarbons presentin the reference standard, raw fuel, raw water extract, and OMSE-water extract was obtained on a gas chromatograph equipped with a hydrogen flame-ionization detector. Two open-tubular packed columns were used during the preliminary stages for tentative separatinn and were chosen because of their reported success in hydrocarbon separation by various investigators (26,27,30,37). In addition to obtaining preliminary retention time data, the open-tubular column packed with Chrom W 80/100 M and coated with Versiluble F-50 (basically dimethyl polysiloxane) was used for hydrocarbon separation prior to analysis by a mass spectrometer[2]. The use of this packed column with the Model RMU-7A mass spectrometer[2] was necessitated for two reasons: first, the gas chromatograph[3] preceeding the Model RMU-6A mass spectrometer could not accommodate a capillary column and, secondly, the minimum carrier gas flow rate of 20 cc/min as necessitated by the available separator[4] could not provide adequate hydrocarbon separation on a capillary column.

The packed open-tubular columns supplied valuable information during the preliminary stages of experimentation; however, the slight variations in gas flow rates through the columns and the relative distance between individual hydrocarbon peaks made its success, with regards to collection of reliable retention time data quite limited. For the collection of dependable retention time data, two wall coated open-tubular (capillary) columns were used for the duration of the experiments. The columns of choice were 150 in length x

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[1] Perkin-Elmer Model 990 Gas Chromatograph with temperature programmer, manufactured by Perkin-Elmer Corporation, Norwalk, Connecticut

[2] Hitachi Perkin-Elmer, RMU-6A, Mass Spectrometer manufactured by Perkin-Elmer, Corporation, Norwalk, Connecticut

[3] Varian Aerograph Series 1200 Gas Chromatograph manufactured by Varian Techtron, Palo Alto, California

[4] Biemann-Watson Separator supplied by Perkin-Elmer Corporation, Norwalk, Connecticut

0.01 in I.D. coated with Versilube F-50 for one column and OV-101, dimethyl polysiloxane, in the other column.

For all gas chromatographic work conducted during this investigation the detector air contained zero hydrocarbons and the carrier gases (nitrogen and helium) were prepurified. The carrier gas flow rates for the capillary and SCOT columns was measured with a bubble meter, and for the packed columns with a calibrated rotometer[1]. A split ratio for the combined sample and carrier gas flows of 170/1 was used on the gas chromatographs whenever a capillary or SCOT column was employed. All samples were injected into the gas chromatographs with a solvent cleaned syringe[2]. Raw fuel mixture and the reference misture were injected directly into the gas chromatographs and did not require a concentration step as did the raw-water and OMSE-water samples.

For all gas chromatographic analyses the following parameters were recorded:

Column type
Column length
Column inside diameter (I.D.)
Column packing and/or coating
Injection temperature
Manifold temperature
Column temperature (isothermal)
Column temperature range
Column temperature program rate
Column tempera ture hold time (initial and final)
Hydrogen gas pressure or flow rate
Air pressure or flow rate
Carrier gas
Carrier gas pressure or flow rate
Chart speed
Attentuation
Sample type
Sample size
Sample split ratio

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[1] Brooks E-C Meter manufactured by Emerson Electric Company, Hatfield, Pennsylvania

[2] Hamilton 7101 N Syringe manufactured by Hamilton Company, Whittier, California

The identification of the various hydrocarbon components in raw water extract, raw fuel, and OMSE-water extract was accomplished by comparing mass charge to 'electron ratio' (m/e) and relative intensity data collected on a mass spectrometer for individual hydrocarbon compounds to mass spectrometer data for specific hydrocarbon compounds as published by the American Petroleum Institute (API) and Mass Spectrometry Data Centre (MSDC) (49,50). In instances where more than one hydrocarbon standard exhibited mass spectroscopy data similar to the data of the unknown hydrocarbon compound, retention time data from a gas chromatograph was utilized to supplement the mass spectrometry data and narrow down the possibilities to one or more specific hydrocarbon compounds.

Preliminary mass spectrometer analysis of hydrocarbons in the various samples was conducted on a Hitachi Perkin-Elmer, RMU-6A mass spectrometer whose scan time for a mass range from 12 to 180 was five seconds. The Model RMU-6A mass spectrometer operated at an accelerating voltage of 2 1/2 kilovolts and an electron multiplier voltage of 1500 volts. For reasons previously discussed, this mass spectrometer could only be operated when coupled with a gas chromatograph utilizing a packed column. The effluent from this packed column was split with 50 percent going to a hydrogen flame-ionization detector and the remainder being sent to the ion source within the mass spectrometer.

Inadequate hydrocarbon peak separation on the packed column with the gas chromatograph and the lengthy five second scan time of the Model RMU-6A mass spectrometer used to collect preliminary m/e data necessitated the use of a gas chromatograph and column which would yield better hydrocarbon peak separation and a mass spectrometer with a briefer scan time. The combination of a SCOT column coated with SF-85 operated in a gas chromatograph[1] capable of handling capillary columns and a Hitachi Perkin-Elmer RMU-6L mass spectrometer with a scan time of 3.1 seconds for a mass spectra range of 15 to 200 provided m/e data which was more meaningful than that previously obtained from the preliminary Model RMU-6A mass spectrometer equipment. The operating conditions for the Model RMU-6L mass spectrometer were: ionizing voltage, 70 ev; accelerating voltage 100 ev; and total pressure, 1×10^{-5} torr.

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[1] Perkin-Elmer Model 990 Gas Chromatograph manufactured by Perkin-Elmer Corporation, Norwalk, Connecticut

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Identification of Hydrocarbon Compounds in OMSE-water. In order to identify the various hydrocarbon compounds emitted by outboard motors into receiving waters, the major hydrocarbon compounds originally present in the receiving waters must also be identified. Hydrocarbons added to the receiving waters as the result of outboard motor operation will appear as new compounds or as an increase in the quantity of hydrocarbon compounds originally present in receiving waters. The major hydrocarbons present in the raw fuel mixture were to be identified and compared against the hydrocarbons present in OMSE-water. This comparison was intended to show whether the hydrocarbon compounds emitted into receiving waters were altered either by oxidation, rearrangement, cracking, etc., or remain unaltered and pass through the engine as unburned (raw) fuel.

Preliminary gas chromatographic separation of hydrocarbons. Direct injection of Amherst tap (raw water and stock OMSE-water (400 parts dilution water to one part spent full) into a Perkin-Elmer Model 990 gas chromatograph was attempted to ascertain if the concentration of hydrocarbons present in these samples was sufficient for detection by the hydrogen flame-ionization detector. Two gas chromatography columns were used to verify if the hydrocarbons present in raw water and stock OMSE-water would require concentration prior to gas chromatography separation. The first column tested was an open tubular (packed) Versilube F-50 column in which 1.0 μl of raw water and stock OMSE-water were injected. At a very sensitive instrument attenuation of 20, there was no significant detector response to either sample but some very slight recorder pen movements were noted. A second wall-coated open tubular (capillary) OV-101 column was utilized after modifications to physically accommodate a capillary column were made to the injector and manifold of the Perkin-Elmer Model 990 gas chromatograph. A volume of 1.0 µl of raw water and OMSE-water was injected into the capillary column and then split internally with 1 part going through the column and then to a flame-ionization detector, while another 170 parts were vented into the atmosphere. This split of 170/1 is recommended by the manufacturer of the gas chromatograph At a high sensitivity (attenuation of 20) only a slight response to OMSE-water was noted and no recorder response was observed for the raw water sample.

Based on this preliminary work, it was decided that the quantity of hydrocarbons present in raw water and OMSE-water was virtually immeasurable with the instrumentation available and that a means of concentrating the hydrocarbons to a measurable level would have to be utilized for subsequent experimentation. The instrumental parameters employed during the attempted preliminary gas chromatographic analysis and separation of raw water and OMSE-water samples can be found in the Appendix, Table A-1.

The method chosen for the concentration of hydrocarbons in raw water and OMSE-water was activated carbon adsorption followed by solvent extraction. The procedure utilized during the experimentation has previously been outlined. After the concentration step, the concentrated hydrocarbons of each sample were designated as extracts (eg. raw-water extract and OMSE-water extract). The total quantity of OMSE-water extracted usually ranged from 200 to 275 gallons and was concentrated to a volume of approximately 200 to 250 ml. Using these figures the concentration factor for OMSE-water extract was calculated to be between 3000 to 5000 times by volume. Approximately 150 to 250 gallons of raw water were concentrated to about 200 to 250 ml, yielding a concentration factor of between 2300 to 4700.

Principal gas chromatographic separation of hydrocarbons.

(a) Packed column experimentation. Gas chromatograms were obtained on isothermally operated Versilube F-50 open tubular packed column for the raw-water extract, OMSE-water extract, and raw fuel mixture. The instrumental parameters used and the hydrocarbon retention time data collected for the three samples is presented in the Appendix, Table A-2. The isothermal separation of hydrocarbons revealed that only one major hydrocarbon peak other than chloroform was present in the sample of raw-water extract. The chromatograms of the raw fuel mixture and OMSE-water extract each contained 16 major hydrocarbon peaks with nearly identical retention times indicating that the hydrocarbons present in OMSE-water may be similar in composition to those in the raw fuel mixture. Under these specified (Appendix, Table A-2) operating conditions hydrocarbon peak separation did not appear to be adequate as far as yield of different kinds of compounds (26,27,30, 32,37,38) and also for joint use with a mass spectrometer. Isothermal operation of an open tubular packed column for use in hydrocarbon separation and identification was abandoned but other operational parameters were explored which would provide adequate hydrocarbon separation in all three samples.

To achieve a better separation of the various major hydrocarbon compounds in the three samples, the compounds would have to be retained within the gas chromatography column for a longer period of time. This could be accomplished in either/or a combination of three ways; use of a longer gas chromatography column decrease of the carrier gas flow rate, or elimination of isothermal operation and temperature program the column up to the maximum desired temperature. Sample volumes of 0.5 μl each of OMSE-water extract and raw fuel mixture at an attenuation of 3200 were injected into the Versilube F-50 open tubular packed column (column specifications and gas flow rates and pressures same as those in Appendix, A Table A-1) and temperature programmed from 50° to 200°C at a rate of 4°C/min and held at 200°C for 24 minutes. Under these operating conditions both sample chromatograph were completed in less than 35 minutes.

A total of 63 hydrocarbon peaks (Figure 2) were present in the chromatogram of the raw fuel mixture, whereas, 36 hydrocarbon peaks (Figure 3) were discernible in the OMSE-water extract chromatogram. Each of the 36 hydrocarbon peaks present in the OMSE-water extract chromatogram seemed to have a corresponding peak in both shape and retention time in the raw fuel chromatogram, indicating that some of the hydrocarbons present in OSME-water were derived from the raw fuel mixture. This suggests that the raw fuel mixture may be passing unburned into the receiving waters.

Separation of the various hydrocarbons on a Versilube F-50 open tubular packed column appeared to be adequate to attempt the identification of the hydrocarbon peaks on a Hitachi Perkin-Elmer Model RMU-6A mass spectrometer. However, even under these instrumental parameters many of the hydrocarbon peaks were relatively close to each other so that precise retention time data for each hydrocarbon peak was difficult to obtain. Consequently, in order to obtain reliable hydrocarbon retention time data it became necessary to utilize capillary columns of 150 ft length operating at decreased carrier gas flow rates which would provide for better hydrocarbon peak separation.

(b) Capillary column experimentation. To aid in the identification of the hydrocarbon compounds in the various samples, a reference mixture was prepared with known chromatographic quality hydrocarbons previously listed in Table 3. This reference mixture and its individual components was also used to 'spike'

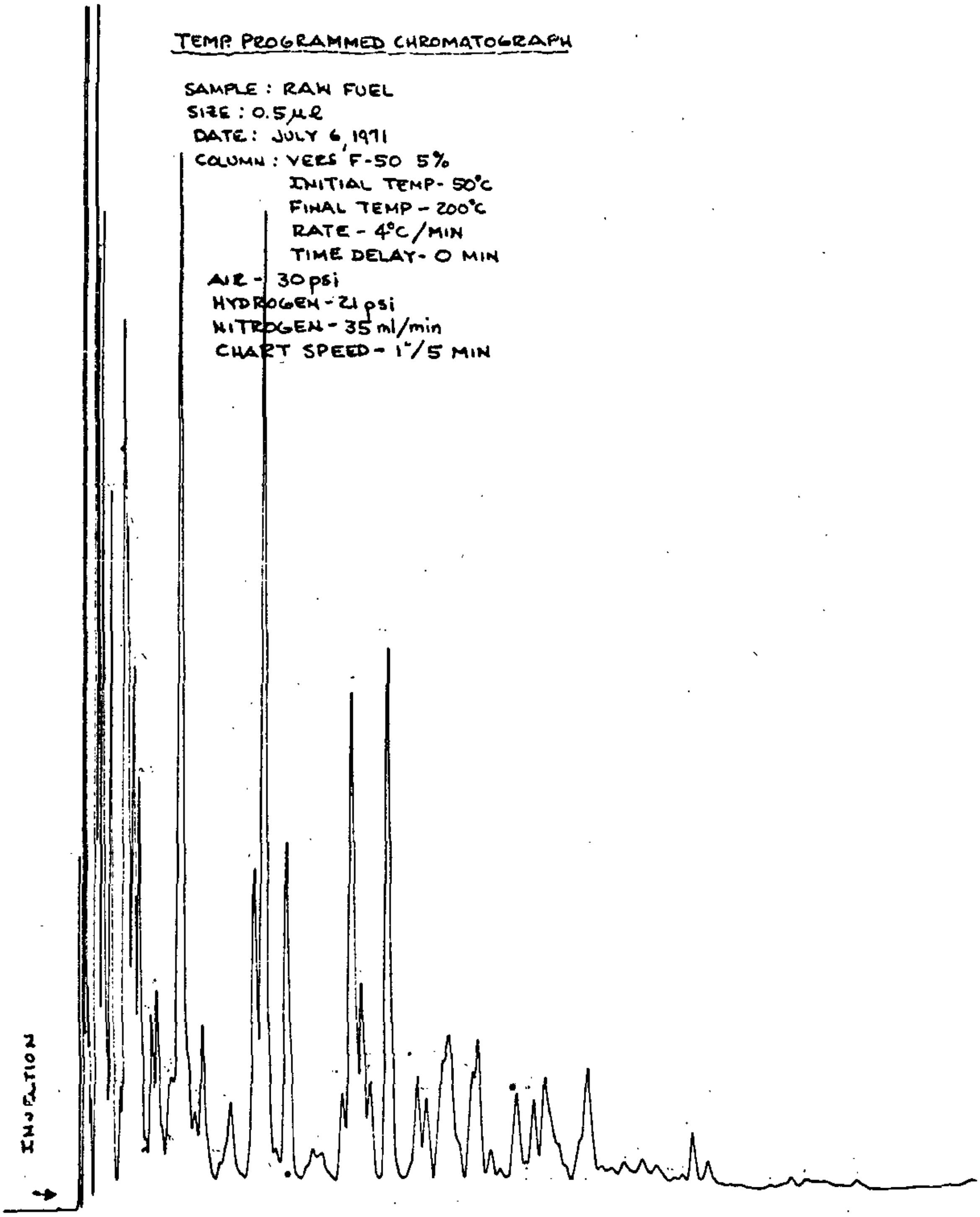

Figure 2. Picture of Raw Fuel Mixture Gas Chromatogram Obtained on a Packed Versilube F-50 Column.

the various sample extracts for peak shape and retention time verification.

Gas chromatograms of the three samples of interest were obtained from two different wall-coated open tubular (capillary) columns; the specifications of which were previously outlined in Table 2. The chromatograms obtained from both capillary columns for OMSE-water extract and the raw fuel mixture, revealed that over 100 hydrocarbon compounds were present in each of the samples. Many of the peaks were well defined with appreciable area under them which indicated that their concentration with respect to other hydrocarbon compounds present was considerable. Peaks having these qualifications were considered to be of major importance and were termed major hydrocarbon peaks; whereas, the other peaks were considered to be minor or of negligible concern to this particular study. The instrumental parameters used with the Versilube F-50 and OV-101 capillary columns for the separation of hydrocarbon compounds in raw-water extract, OMSE-water extract, raw fuel mixture, and the reference standard are given in the Appendix, Table A-3. With the use of a capillary column coated with OV-101 (higher temperature capability than Versilube F-50) 46, 33, and 5 major hydrocarbon peaks (Figure 4) were found in the raw fuel mixture, OMSE-water extract, and raw-water extract, respectively. A comparison of retention times of the reference standard with components separated from the raw fuel mixture, OMSE-water extract, and raw-water extract on the OV-101 capillary column is presented in Table 4. Based on these retention times, it appeared as though the major hydrocarbons present in the raw fuel mixture seemed to be in the C_6 to C_{11} range and were chromatogrammed under the specified instrumental parameters (Appendix, Table A-3) in less than 45 minutes. The majority of the major hydrocarbons present in OMSE-water extract seemed to be in the C_7 to C_{13} range which suggested that some

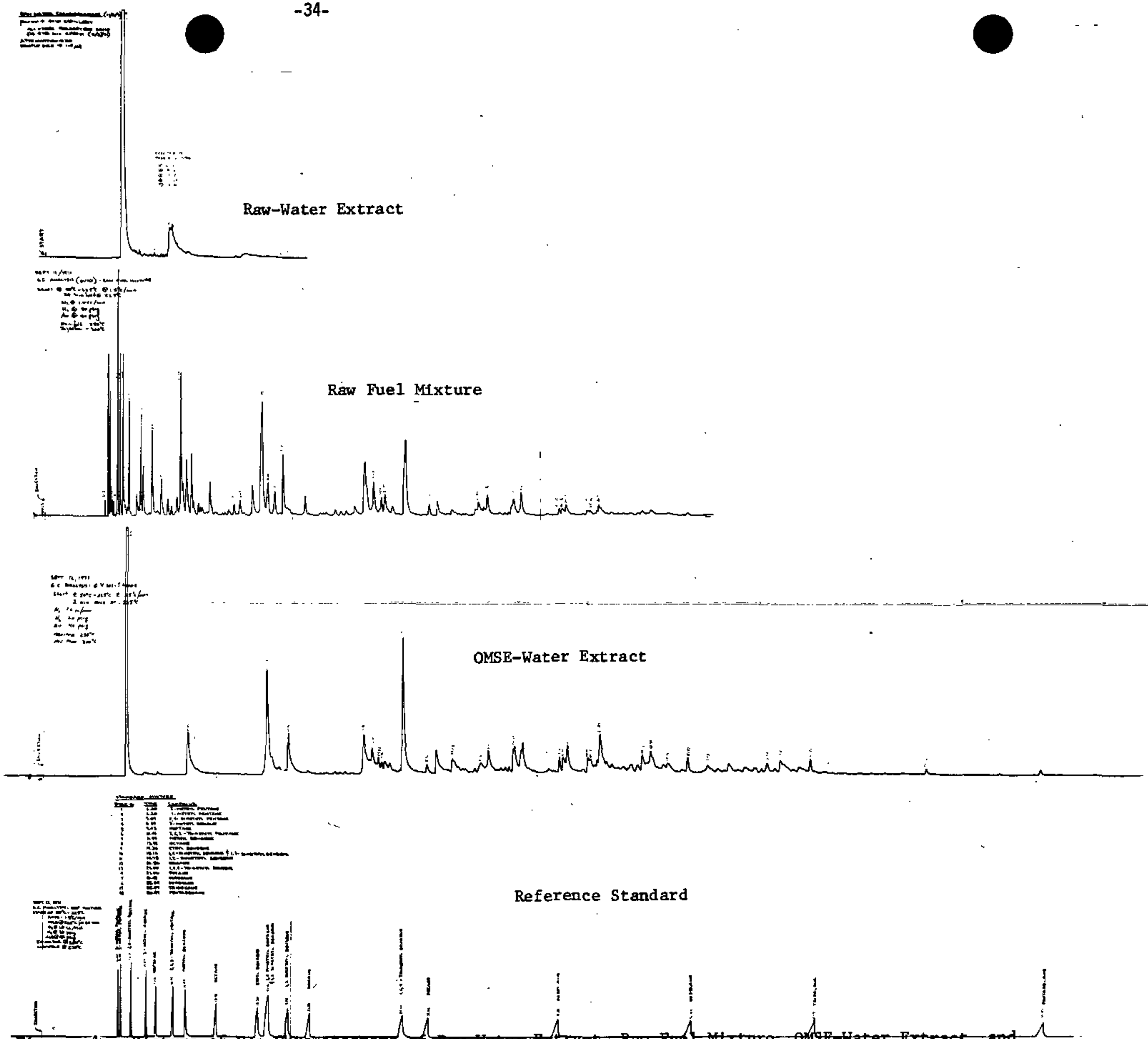

Figure 4. Picture of Gas Chromatograms of Raw-Water Extract, Raw Fuel Mixture, OMSE-Water Extract, and Standard Mixture Obtained on an OV-101 Capillary Column.

Table 4. Comparison of Retention Times of the Reference Standard with Components Separated from Raw Fuel Mixture, OMSE-Water Extract, and Raw-Water Extract on the OV-101 Capillary Column.**

Standard Compound			Possible Related Compound					
			Raw Fuel		OMSE-Water Extract		Raw Water Extract	
Peak No. ***	Name	Ret. Time (Min.)	Peak No. **	Ret. Time (Min.)	Peak No. **	Ret. Time (Min.)	Peak No. **	Ret. Time (Min.)
1	2-Methylpentane	6.00	1	4.79				
			2	5.03				
			3	5.20				
			4	5.34				
			5	5.47				
			6	5.76				
			7	5.97				
2	3-Methylpentane	6.20	8	6.20	1	6.60	1	6.38
			9	6.70				
3	2,4-Dimethylpentane	7.09	10	7.29				
			11	7.61				
4	3-Methylhexane	8.27	12	7.82			2	8.01
			13	8.30				
5	Heptane	9.03	14	9.30			3	9.02
6	2,2,3-Trimethylpentane	10.41	15	10.52			4	10.24
			16	10.84			5	10.40
7	Methylbenzene	11.44	17	11.01	2	11.51		
			18	11.21				
			19	11.71				
8	Octane	13.92	20	13.22				
			21	15.20				
			22	15.68				
9	Ethylbenzene	17.30	23	16.70				
			24	17.49				
10	1,4-Dimethylbenzene & 1,3-Dimethylbenzene	18.16	25	18.00	3	17.96		
			26	18.51				
11	1,2-Dimethylbenzene	19.78	27	19.20	4	19.70		
12	Nonane	21.56	28	21.01				
13	1,2,4-Trimethylbenzene	29.00	29	25.96	5	25.91		
			30	26.63	6	26.62		
			31	27.23	7	27.22		
			32	27.51	8	27.40		
			33	29.19	9	29.08		
14	Decane	31.06	34	31.06	10	31.00		
			35	31.70	11	31.74		
			36	32.35	12	33.05		
			37	35.00	13	35.30		
			38	35.71	14	35.91		
15	Undecane	41.41	39	37.83	15	38.00		
			40	38.40	16	38.60		
			41	44.50	17	41.62		
			42	41.70	18	41.92		
			43	42.08	19	42.23		
			44	43.80	20	44.00		
			45	44.06	21	44.20		
			46	44.71	22	44.37		
16	Dodecane	52.09			23	48.31		
					24	48.99		
					25	50.31		
					26	51.82		
					27	53.53		
					28	55.21		
17	Tridecane	62.07			29	58.34		
					30	59.40		
					31	61.86		
					32	71.26		
18	Pentadecane	80.47			33	80.38		

**Peak numbers refer to corresponding numbered peaks in Figure 4.

of these hydrocarbons may be present as unburned fuel, while others may be partial oxidation products or even fragments of higher carbon number hydrocarbon compounds either in gasoline or in the lubricating oil. The total time elapsed for the separation of hydrocarbons present in OMSE-water extract was less than 85 minutes. Raw-water extract contained only five major hydrocarbon peaks; however, the chloroform present in both the extracts peaked at between 6.40 to 6.60 minutes under the specified instrumental parameters. Therefore, only 32 and 4 peaks could be attributed to major hydrocarbon compounds present before the extraction with chloroform of OMSE-water and raw water, respectively.

Approximately the same number of major hydrocarbon peaks were found for the raw fuel mixture, OMSE-water extract, and raw-water extract (Figure 5) when separated on the Versilube F-50 capillary column operating under the parameters listed in the Appendix, Table A-3. Retention times for the individual peaks and total time for sample separation were comparable to those obtained on the OV-101 capillary column which appear in Table 4. Since both capillary columns gave similar separations of the hydrocarbons present in the various samples the OV-101 capillary column was utilized because of its higher temperature range (250^{0}C vs 160^{0}C) for the collection of retention time data to verify the mass spectrometer data of suspect hydrocarbon compounds.

From the separation of the reference mixture of standard hydrocarbons and the various major peaks in the three samples, a tentative classification based on molecular structure and boiling points was made and is presented in Table 4. As an example of this classification, major hydrocarbon compounds numbered 34 thru 38 in the raw fuel mixture were presumed, because of similar retention times, to be more closely related to the structure and boiling point of decane than

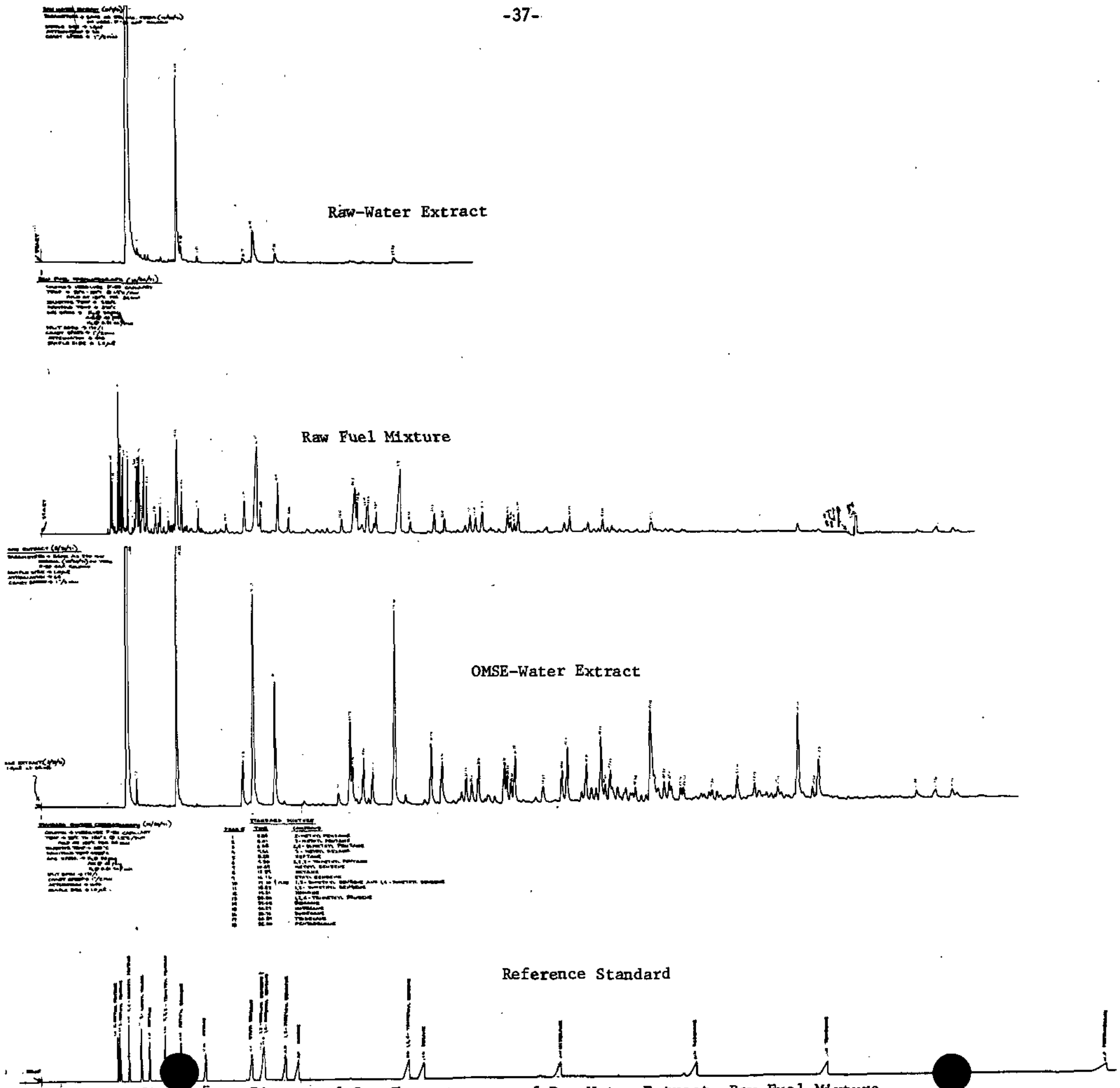

Figure 5. Picture of Gas Chromatograms of Raw-Water Extract, Raw Fuel Mixture, OMSE Water Extract, and Standard Mixture Obtained on a Versilube

these hydrocarbon compounds would be to 1,2,4-trimethylbenzene, undecane, or any of the other hydrocarbon standards. Similar reasoning was applied to the major hydrocarbon peaks numbered 10 thru 14 of the OMSE-water extract.

(c) SCOT column experimentation. The Hitachi Perkin-Elmer Model RMU-6L mass spectrometer used during the experimentation was capable of analyzing the effluent from a capillary or SCOT column. To insure that a sufficient quantity of sample was available for the model RMU-6L mass spectrometer to scan, it was decided to use the SF-85 SCOT column whose specifications appear earlier in Table 2 which was capable of accommodating a larger sample than either of the two capillary columns.

The chromatograms obtained on a SF-85 SCOT column for the reference hydrocarbon standards, raw fuel mixture, and OMSE-water extract which appear in Figure 6 indicated that adequate separation of the major hydrocarbon compounds in the samples had been accomplished on this particular column. Accordingly, the possibility of obtaining discrete mass spectrum data for each hydrocarbon compound scanned by the model RMU-6L mass spectrometer was enhanced. The operational parameters used in obtaining the gas chromatograms in Figure 6 are presented in the Appendix, Table A-4.

The reference standard whose chromatogram appears in Figure 6 was a mixture of the previous reference standard mentioned earlier in Table 3 and additional similar quality hydrocarbons which appear in Table 5. These new hydrocarbons were added to the original reference standard as a further aid in identification substantiation of hydrocarbon compounds in the raw fuel mixture.

The chromatograms of the raw fuel mixture and OMSE-water extract in Figure 6 are very similar to those obtained for similar samples on capillary columns coated with OV-101 (Figure 4) and Versilube F-50 (Figure 5). The major hydrocarbon

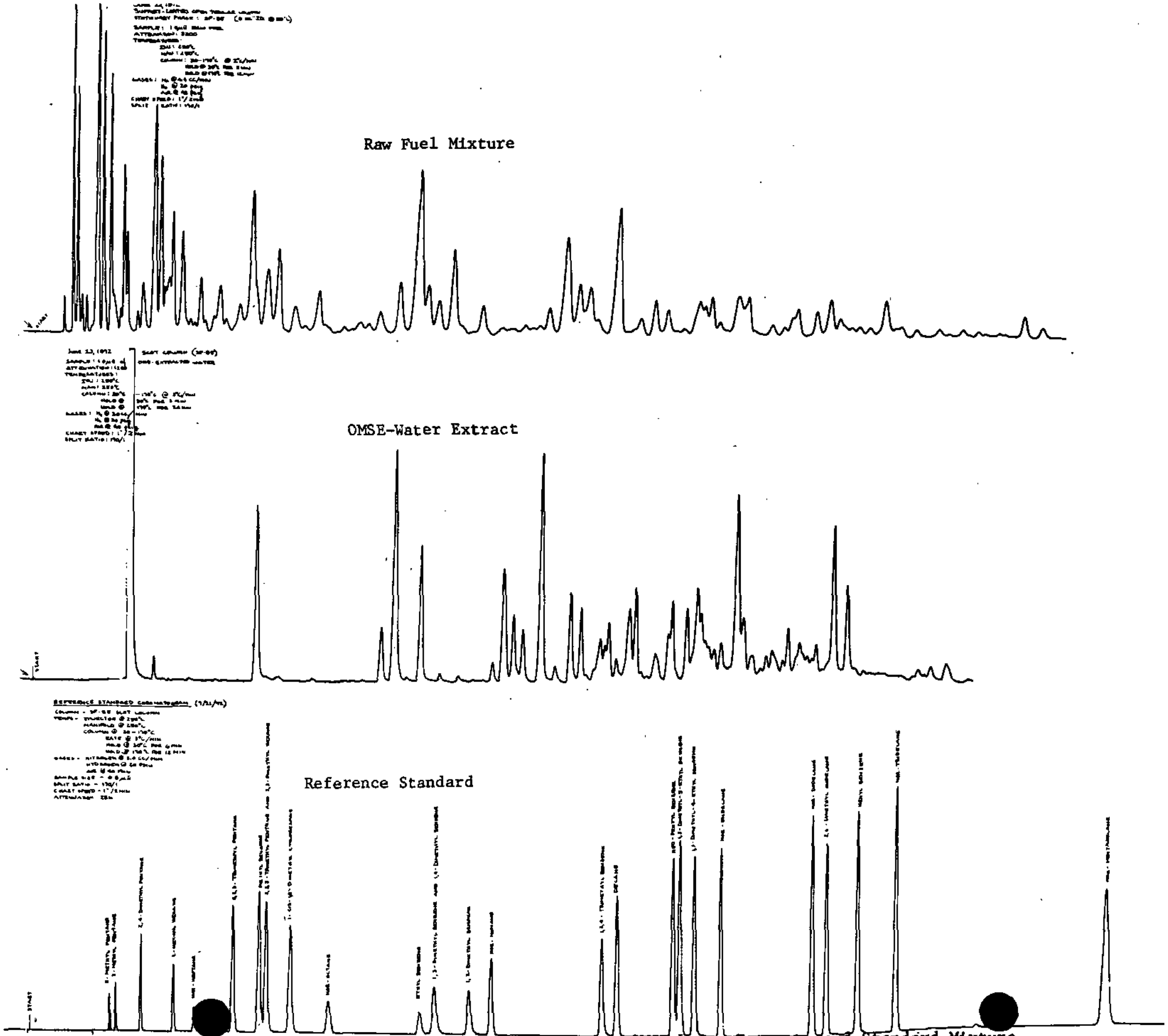

Figure 6. Picture of Gas Chromatograms of the Raw Fuel Mixture, OMSE-Water Extract, and Standard Mixture

Table 5. Additional Hydrocarbon Compounds Added to the Reference Mixture in Ascending Boiling Point Order.

Order	Compound	Boiling Point in °C
1	2,3,3-Trimethylpentane	109.84
2	2,3-Dimethylhexane	115.6
3	1-Cis-1,3 Dimethylcyclohexane	120.1
4	1,3-Dimethyl-5-ethylbenzene	183.75
5	neo-Pentylbenzene	205.4
6	Hexylbenzene	227
7	1,3-Dimethyl-4-ethylbenzene	N.A.
8	2,6-Dimethylundecane	N.A.

compounds in the raw fuel mixture have retention times similar to the C_5 to C_{11} hydrocarbons in the reference standard; similarly, the major hydrocarbon compounds in OMSE-water extract have retention times similar to the C_7 to C_{13} hydrocarbons in the reference standard.

Hydrocarbon analysis by a model RMU-6A mass spectrometer. In mass spectrometry. ions are produced from a compound by bombarding the molecules of the compound with a mono-energetic beam of electrons. The mass spectrometer then separates the ions according to their mass to charge rations (m/e) and measures the relative abundances of each species with a given m/e value. This information on mass and the abundance ratios of ions was used in the interpretation of molecular structure and when coupled with gas chromatography retention time data yielded the exact chemical composition of compounds.

A Hitachi Perkin-Elmer Model RMU-6A mass spectrometer was available for use through the Food Science and Technology Depatment of the University of Massachusetts in Amherst. Separation of the major hydrocarbon compounds in the various samples prior to mass spectrum analysis was accomplished on a Varian Aerograph Series 1200 gas chromatograph. The effluent gas flow from the Series 1200 gas chromatograph was split by a Biemann-Watson Separator with 50 percent going to a hydrogen flame-ionization detector and the remainder being sent to the ion source within the mass spectrometer.

This model RMU-6A mass spectrometer has a minimum carrier gas flow requirement of 10 cc/min and coupled with the separator ratio, a minimum carrier gas flow rate of 20 cc/min was imposed upon the gas chromatography column. This virtually eliminated the use of a capillary column at these flow rates and dictated the use of an open-tubular (packed) column. The Versilube F-50 open tubular column was chosen for hydrocarbon separation of the raw fuel mixture and OMSE-water extract samples. Various instrumental parameters were evaluated to provide the best separation between subsequent hydrocarbon peaks in order to meet the mass spectrometer's peak scan time requirement of five seconds. The optimum operating conditions found for the gas chromatographic separation of hydrocarbon present in the two samples using the Versilube F-50 open tubular column are presented in the Appendix, Table A-5 and were used for the generation of the gas chromatograms of the raw fuel mixture and OMSE-water which appear in Figure 7. The total number of major hydrocarbon peaks present in these gas chromatograms of the raw fuel mixture and OMSE-water were 45 and 24, respectively.

With the model RMU-6A mass spectrometer operating at an acceleration voltage of 2 1/2 kilovolts and an electron multiplier voltage of 1500 volts, a number of these major hydrocarbon peaks were scanned to obtain m/e and relative intensity data. Not all the major hydrocarbon peaks were evaluated because of the rapid exit of the compounds from the gas chromatography unit (less than five seconds between distinct consecutive peaks as monitored on the model RMU-6A mass spectrometer's electron multiplier). The mass spectrum data for the major hydrocarbon peaks scanned was analyzed for specific ions and the relative abundance of these ions. A typical mass spectrum of a major hydrocarbon peak is represented in Figure 8. The ten most abundant ions, as a function of m/e peak height, for the mass spectrum presented in Figure 8 were tabulated in order of their abundance and compared against published mass spectrum data (49,50) for pure hydrocarbon compounds. The tabulated data for the hydrocarbon peak in Figure 8 and its corresponding published pure hydrocarbon mass spectrum abundance data are presented in Table 6. For each major hydrocarbon peak scanned, m/e and relative intensity data were derived and are presented along with other model RMU-6L mass spectrometer data in the Appendix A, Tables A-7 and A-8. The reference number

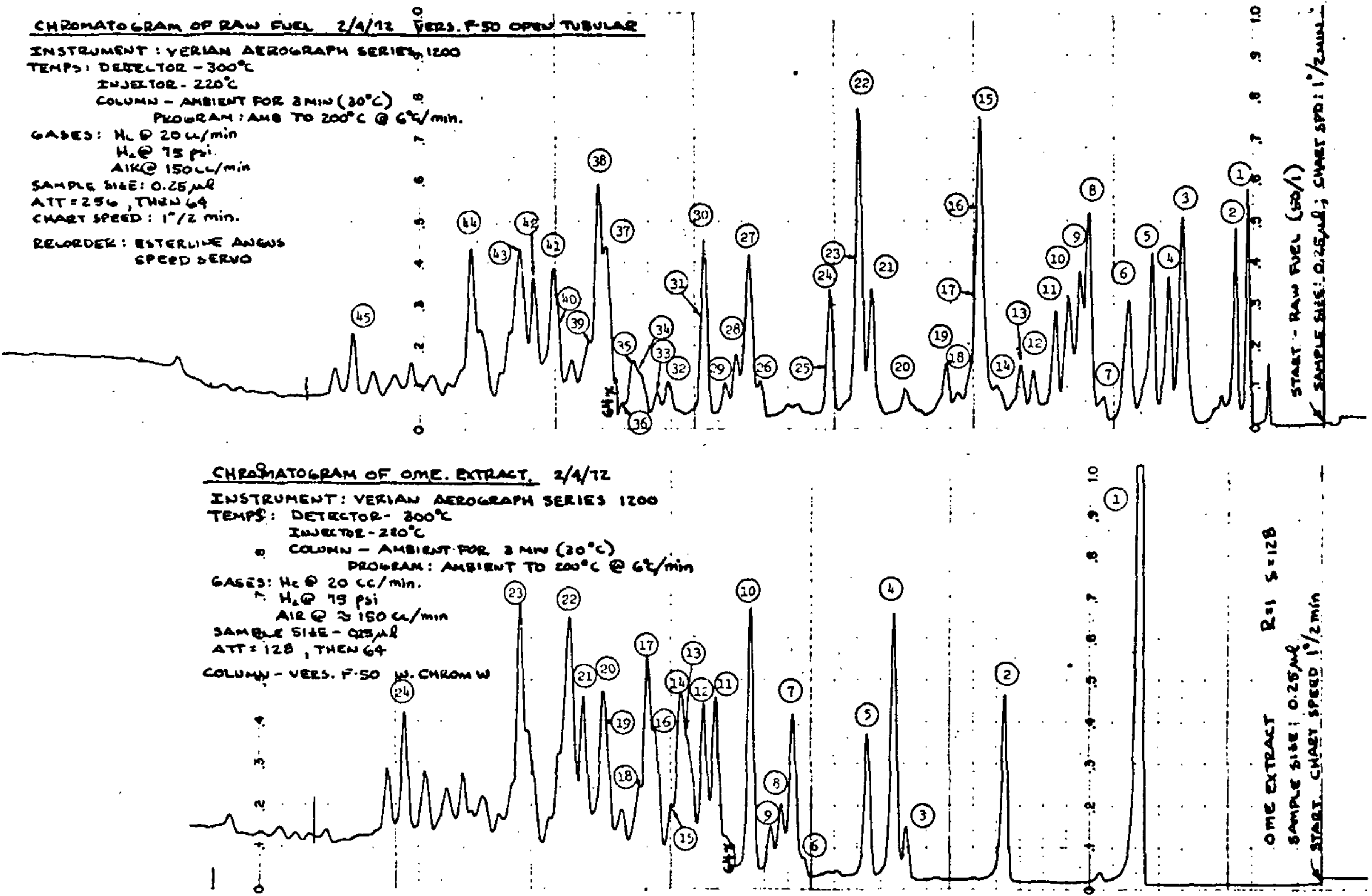

Figure 7. Chromatograms of the Raw Fuel Mixture and OMSE-Water Extract Used in Conjunction with Model RMU-6A Mass Spectrometer Analysis of Hydrocarbon Compounds.

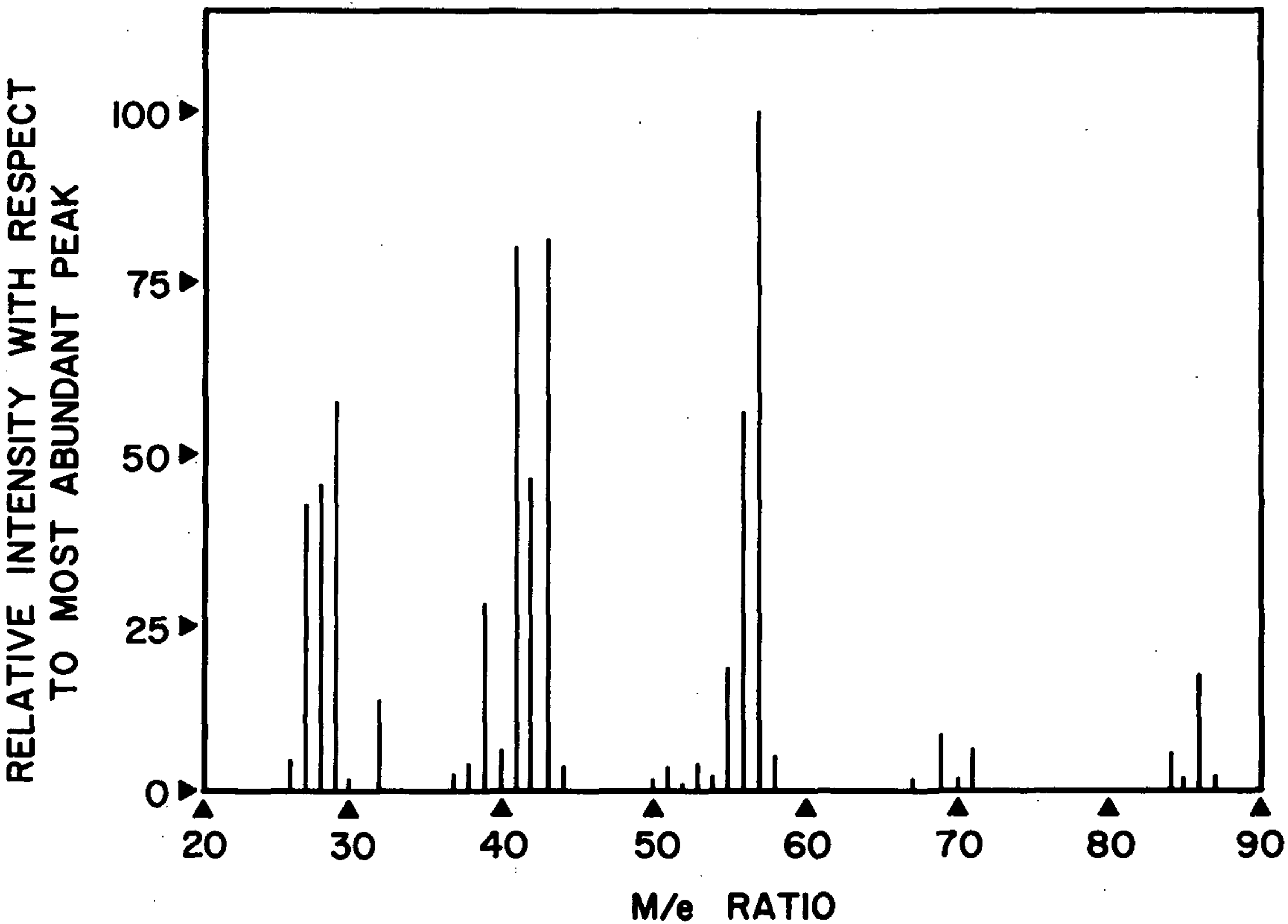

Figure 8. Plot of Relative Intensity *versus* Mass Charge to Electron Ratio for Hydrocarbon Peak Number Five of the Raw Fuel Mixture (Figure 7).

Table 6. Mass Spectral Abundance Data for Major Hydrocarbon Peak Number Five of the Raw Fuel Mixture and Published Mass Spectrum Distribution of n-Hexane (49,50)

Raw Fuel Mixture Hydrocarbon Peak Number 5		A.P.I. Standards (49)		Eight Peak Index (50)	
M/e	Relative Intensity	M/e	Relative Intensity	M/e	Relative Intensity
57	100	57	100	57	100
43	81	43	81.3	43	82
41	80	41	75.4	41	78
29	57	29	63.2	56	52
56	55	27	50.5	29	50
42	46	56	44.7	42	39
27	42	42	41.0	27	32
39	27	39	22.8	39	18
55	18	86	14.1		
86	17	28	13.3		

designated for the various major hydrocarbon peaks in the raw fuel mixture and OMSE-water extract appear in Figure 7 and are referred to in the RMU-6A mass spectrometer data presented in the Appendix A, Tables A-7 and A-8.

The mass to charge ratio and relative intensity data for the major hydrocarbon compounds present in the raw fuel mixture and OMSE-water extract were compared against published mass spectrometer data for pure hydrocarbon compounds. Many of the hydrocarbon peaks with short retention times (lower boiling points) could be readily identified. As the gas chromatography retention time for the peaks increased, the number of possibilities for each peak also increased and this was attributed to the increased number of possible isomers for a certain carbon number compound.

Many major hydrocarbon peaks were not scanned because the time of exit between consecutive peaks did not meet the model RMU-6A mass spectrometer's minimum scan time requirement of five seconds between consecutive peaks. Other peaks which were scanned by the RMU-6A mass spectrometer yielded data which could not be identified by comparison with published data. Two possible reasons exist for not being able to 'key' out such data; thecompound had not been scanned previously by other researchers, or lastly, interference from either or both of the two adjacent hydrocarbon peaks had occurred. The latter possiblity appeared to be the most probable, since m/e and relative intensity data for nearly every hydrocarbon compound through C_{12} or even higher has been published.

Hydrocarbon analysis by a model RMU-6L mass spectrometer. To overcome these difficulties the use of a Hitachi Perkin-Elmer Model RMU-6L mass spectrometer with a shorter mass spectrum scan time of 3.1 seconds, and the capability of receiving the effluent from a capillary or SCOT column (better major hydrocarbon peak separation) appeared to be warranted. The model RMU-6L mass spectrometer was made available by the Chemistry Department at Boston University. The Perkin-Elmer Model 990 gas chromatograph preceeding the model RMU-6L mass spectrometer was capable of accommodating a SCOT column coated with SF-85.

Raw fuel mixture, raw-water extract, and OMSE-water extract samples were injected into the model 990 gas chromatograph with the entire column effluent going directly to the RMU-6L mass spectrometer. This was necessitated because of the model RMU-6L mass spectrometer's relatively high vacuum pressure of 10^{-5} torr. As a result, hydrocarbon compounds entering the model RMU-6L mass spectrometer could only be monitored on a total ion recorder and corresponding gas chromatograms were not obtained. However, the total ion recorder's hydrocarbon peak plots could readily be matched with the major hydrocarbon peaks in the gas chromatograms presented in Figure 7.

The operational parameters for the model RMU-6L mass spectrometer were presented earlier; and the concommitant operational parameters for the model 990 gas chromatograph are presented in the Appendix, Table A-6. The m/e and relative intensity data obtained by the model RMU-6L mass spectrometer for many of the major hydrocarbon compounds appears jointly with model RMU-6A mass spectrometer data in the Appendix, Table A-7, A-8, and A-9.

As a result of SCOT column gas chromatographic and subsequent mass spectroscopic analysis, the possible hydrocarbon compounds associated with the major hydrocarbon peaks in the raw fuel mixture and OMSE-water extract are presented in Tables 7 and 8, respectively. The author was unable to establish the identity of any of the few hydrocarbon peaks in raw-water extract because the m/e and relative intensity data corresponding to these peaks (Appendix Table A-9) could

Table 7. Possible Hydrocarbon Compounds Present in the Raw Fuel Mixture Based on Combined Model RMU-6A and RMU-6L Mass Spectrometer Analysis.

Reference Peak Number	Possibility Number 1	Possibility Number 2	Possibility Number 3	Possibility Number 4	Possibility Number 5	Possibility Number 6	Probable Compound
1	2-Metnylbutane	n-Pentane					
2	2-Methylbutane	n-Pentane					
3	2,3-Dimethylbutane						2,3-Dimethylbutane
4	3-Methylpentane						3,-Methlypentane*
5	n-Hexane						n-Hexane
6	2,3-Dimethylpentane						2,3-Dimethylbutane
7	Unknown						Unknown
8	2,4-Dimethylpentane						2,4-Dimethlypentane
9	2,6-Dimethylheptane	2-Methyloctane	2,4-Dimethylpentane	3,4-Dimethylheptane	n-Heptane		
10	2,2,3-Trimethylbutane						2,2,3-Trimethylbutane
11	n-Heptane						n-Heptane
12	2,2-Dimethyl-Cis-3-Hexane	1-Methyl-Cis-3-Ethylcyclopentane	2-Methyl-3-Ethyl-1-Pentene				
13	3-Methylheptane		2,5-Dimethylhexane				
14	3-Ethylpentane		2-Methyl-1-Pentanol	2,3,3-Trimethylpentane			
15	Toluene						Toluene
16	2,7-Dimethyloctane	2,6-Dimethylhexane	2-Methylheptane				
17	2,6-Dimethylheptane	n-Nonane	2-Methyloctane	2,4-Dimethylpentane	3,4-Dimethylpentane	2-Methylheptane	
18	2,2-Dimethylheptane	2,2,3-Trimethylpentane	2,2-Dimethyl-3-Ethylpentane	2,2,3-Trimethylhexane			
19	n-Octane	2,4-Dimethylhexane					
20	n-Nonane	2-Methyloctane	4-Ethylheptane	2,6-Dimethylheptane	3,4-Dimethylheptane		
21	Ethylbenzene						Ethylbenzene*
22	m-Xylene	p-Xylene					m & p-Xylene*
							Unknown
23	3-Ethylheptane	2,5-Dimethylheptane	3-Methyloctane	3,3-Diethylpentane	4-Isopropylheptane	4-Nor-Propylheptane	
24	o-Xylene						o-Xylene*
	2,7-Dimethyloctane	n-Nonane	n-Decane	n-Undecane	2-Methylnonane	2,5-Dimethylhexane	n-Nonane*
25	3,4-Dimethylheptane	2-Methyldecane	4-Ethylheptane				n-Propylbenzene
26	n-Propylbenzene						
27	Isopropylbenzene	1-Methly-4-ethylbenzene	1-Methyl-4-ethylbenzene	1-Methyl-3-ethylbenzene	Ethyltoluene		
28	Isopropylbenzene	1-Methly-4-ethylbenzene	1-Methyl-4-ethylbenzene	1-Methyl-3-ethylbenzene	Ethyltoluene		
29	Isopropylbenzene	1-Methly-4-ethylbenzene	1-Methyl-4-ethylbenzene	1-Methyl-3-ethylbenzene	Ethyltoluene		
30	1,2,3-Trimethylbenzene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene				
	n-Decane	n-Undecane	2,7-Dimethyloctane	n-Nonane			
31	2-Methyldecane	4-Ethylheptane			2-Methylnonane	3,4-Dimethylheptane	n-Decane*
32	1,2,3-Trimethylbenzene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene				
33	2,6-Dimethyloctane	2-Methyl-4-Ethylhexane	3-Ethylheptane	2,2,3,3-Tetramethylpentane	2,5-Dimethyloctane	4-Methyl-nonane	
34	1,2-Diethylbenzene	Sec-Butylbenzene	1-Methyl-2-Nor-Propylbenzene	1-Methyl-3-Nor-Propylbenzene	1-Methyl-4-Nor-Propylbenzene	O-Nor-Propyltoluene	
35	Sec-Butylbenzene	1-Methyl-3-Nor-Propylbenzene	o-Nor-Propyltoluene	1-Methyl-4-Nor-Propylbenzene			
36	Nor-Dodecane	2,2,3,3-Tetramethylpentane	2,6-Dimethyloctane				
	1,3-Dimethyl-5-Ethylbenzene	1,4-Dimethyl-2-Ethylbenzene	1,3-Dimethyl-4-Ethylbenzene	1,3-Dimethyl-2-Ethylbenzene	1,2-Dimethyl-3-Ethylbenzene	1,2-Dimethly-4-Ethylbenzene	
37	1-Methyl-3-Isopropylbenzene	1-Methyl-4-Isopropylbenzene	1-Methyl-2-Isopropylbenzene	1-Isopropyl-2-Methylbenzene	m-Nor-Propyltoluene	5-Ethyl-m-Xylene	1,3-Dimethyl-4-Ethylbenz
38	Methallylbenzene	P-Ethylstyrene	m-Ethylstyrene				
39	5-Methyldecane	2,6-Dimethyloctane	2,3-Dimethyl-3-Ethylpentane	2,2,3,3-Tetramethylhexane	n-Dodecane	n-Undecane	n-Undecane*
40	1,2,3,4-Tetramethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene				
41	1,2,3,4-Tetramethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene				
42	Unknown						Unknown
43	Unknown						Unknown
44	Naphthalene						Naphthalene
45	1-Methylnaphtahlaene	2-Methylnaphthalene					

*Indicates confirmation with gas chromatography retention time data

Table 8. Possible Hydrocarbon Compounds Present in OMSE-Water Extract Based on Combined Model RMU-6A and RMU-6L Mass Spectrometer Analysis.

Reference Peak Number	Possibility Number 1	Possibility Number 2	Possibility Number 3	Possibility Number 4	Possiblity Number 5	Possibility Number 6	Probable Compound
1	Chloroform						Chloroform
2	Toluene						Toluene
3	Ethylbenzene						Ethylbenzene
4	m-Xylene	p-Xylene					m & p-Xylene
5	o-Xylene						o-Xylene
6	n-Propylbenzene						n-Propylbenzene
7	Isopropylbenzene	1-Methyl-4-Ethylbenzene	1-Methyl-3-Ethylbenzene	1-Methyl-2-Ethylbenzene	Ethyltoluene		
8	Isopropylbenzene	1-Methyl-4-Ethylbenzene	1-Methyl-3-Ethylbenzene	1-Methyl-2-Ethylbenzene	Ethyltoluene		
9	Isopropylbenzene	1-Methyl-4-Ethylbenzene	1-Methyl-3-Ethylbenzene	1-Methyl-2-Ethylbenzene	Ethyltoluene		
10	1,2,3-Trimethylbenzene	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene				
11	1,2,3-Trimethylbenzene	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene				
12	2,6-Dimethyloctane	2-Methyl-4-Ethylhexane	3-Ethylheptane	2,2,3,3-Tetramethylpentane	2,5-Dimethyloctane	4-Methylnonane	
13	1,2-Diethylbenzene	Sec-butylbenzene	1-Methyl-2-Nor-Propylbenzene	1-Methyl-3-Nor-Propylbenzene	1-Methyl-4-Nor-Propylbenzene	o-Nor-Propyltoluene	
14	Sec-Butylbenzene	1-Methyl-3-Nor-Propylbenzene	o-Nor-Propyltoluene	1-Methyl-4-Nor-Propylbenzene			
15	Nor-Dodecane	2,2,3,3-Tetramethylpentane	2,6-Dimethyloctane				
	1,3-Dimethyl-5-Ethylbenzene	1,4-Dimethyl-2-Ethylbenzene	1,3-Dimethyl-4-Ethylbenzene	1,3-Dimethyl-2-Ethylbenzene	1,2-Dimethyl-4-Ethylbenzene		
16	1-Methyl-3-Isopropylbenzene	1-Methly-4-Isopropylbenzene	1-Methyl-2-Isopropylbenzene	1-Isopropyl-2-Methylbenzene	5-Ethyl-m-Xylene		
17	Methallybenzene	P-Ethylstyrene	m-Ethylstyrene				
18	5-Methyldecane	Nor-Dodecane	2,6-DImethyloctane	2,3-Dimethyl-3-Ethylpentane			
19	1,2,3,4-Tetramethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene				
20	1,2,3,4-Tetramethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene				
21	Unknown						Unknown
22	Unknown						Unknown
23	Napthalene						Naphthalene
24	1-Methylnaphthalene	2-Methylnaphthalene					

not be found in any available published mass spectrum data (49,50). This could be attributed to the possibility that these compounds had never been scanned before or to the greater likelihood that these peaks were overlapped by neighboring peaks and a mixture of compounds was represented by the mass spectrum data. Since the m/e and relative intensity data for these unidentified peaks in raw-water extract did not correspond to any m/e or relative intensity data for the major hydrocarbon peaks in the OMSE-water extract, it was assumed that interference from these unidentified peaks would not be a factor in the identification of the major hydrocarbon compounds in OMSE-water extract. From the OV-101 capillary column data presented in Table 4 it was concluded that these unidentified hydrocarbon peaks in the raw-water extract were similar in composition to C_7 and C_8 hydrocarbons.

The major hydrocarbon peaks present in the raw fuel mixture through reference peak number 20 (Table 4) appear to be either straight-chained ranging from possibly pentane to nonane or branched alkanes varying from possibly methylbutane to 2-Methyloctane, while higher numbered reference peaks are mainly alkyl-substituted benzene derivatives ranging from toluene to 2-Methylnapthalene with a mixture of some alkanes and branched alkanes. Almost all the major hydrocarbon peaks in OMSE-water extract (Table 8) are alkyl substituted benzene derivatives ranging from toluene to 2-Methylnapthalene with the exception of a few straight-chained and branched alkanes. The absence of lower boiling point hydrocarbons (such as those up to reference peak number 20 of the raw fuel mixture) in OMSE-water extract may be attributed to: the complete or nearly complete combustion of these products within the cylinder or crankcase of the outboard engine, their volatility in receiving waters, their possible insolubility in water, the possible inability of the solvent to extract them off the activated carbon column, their possible loss during the distillation step in the carbon-chloroform extraction of OMSE-water, and finally, possible compound alteration while retained within the activated carbon column.

There is a noticeable absence of oxygenated hydrocarbon compounds in OMSE-water. This lack of oxygenated hydrocarbon compounds was also noted by the authors in the literature (26,27,30,31,37,38) of hydrocarbon exhaust products found in automotive exhaust emissions. This absence may be attributed to several factors; the complete oxidation of hydrocarbons within the engine, their presence in OMSE-water in extremely minute (eg. undetectable) quantities; and finally, extreme volatility and/or biodegradability when present in OMSE-water. In addition perhaps if any partial oxidation products were present in OMSE-water, they were not extracted by the carbon/chloroform concentration technique and a wet chemical analysis specific for partial oxidation products may be required for their determination.

Hydrocarbon compound verification with gas chromatography retention time data. The extract identification of each major hydrocarbon compound in the raw fuel mixture and OMSE-water may be accomplished by comparing the retention times for each possible hydrocarbon peak obtained to the retention time of the specific major hydrocarbon peak of interest on at least two different gas chromatography columns. This additional procedure coupled with a more detailed analysis of the specific ions formed while collecting mass spectrum data should be sufficient to identify each major hydrocarbon compound.

Gas chromatograms of the raw fuel mixture, reference standards, and sample comprised of a mixture of 10 parts raw fuel mixture and three parts of reference standard (eg. 'spiked' raw fuel mixture) were obtained on a SF-85 SCOT column to assist in the verification of the hydrocarbon compounds present in Table 7 for the raw fuel mixture. The chromatograms for these three samples are presented in Figure 9. The instrumental parameters for the separation of the hydrocarbon compounds in these three samples on the SF-85 SCOT column functioning within a Perkin-Elmer Model 990 gas chromatograph are presented in the Appendix, Table A-10.

The 'spiked' raw fuel mixture chromatogram from Figure 9 indicated that several of the hydrocarbon compounds present in the raw fuel mixture had corresponding retention times as some of the hydrocarbons in the reference mixture. These compounds with similar retention times were then checked against the tabulation of possible hydrocarbon compounds (Table 8) to determine the most probable hydrocarbon compound as indicated with an asterisk in the probable compound column for the designated peak number.

This same type of analysis could be applied to the OMSE-water extract so that many of the hydrocarbon compound possibilities for a given peak would be reduced to a single hydrocarbon compound. An analysis of this nature for the different hydrocarbon possibilities in both the raw fuel mixture and OMSE-water extract would require additional gas chromatographic quality known hydrocarbons before a complete analysis of the hydrocarbon compounds could be achieved.

A comparison of hydrocarbon peak characteristics for the raw fuel mixture and OMSE-water from Figure 7 coupled with the various hydrocarbon possibilities for these peaks from Tables 7 and 8 suggested that the major hydrocarbon compounds present in OMSE-water are derived from the direct passage of the raw fuel mixture through the outboard engine and into the receiving waters. Several examples of this were reference peaks 26, 27, 28, and 29 of the raw fuel mixture and reference peaks 6, 7, 8, and 9 of the OMSE-water extract chromatograms in Figure 7. Many of the other peaks in both gas chromatograms were found to exhibit this same pattern.

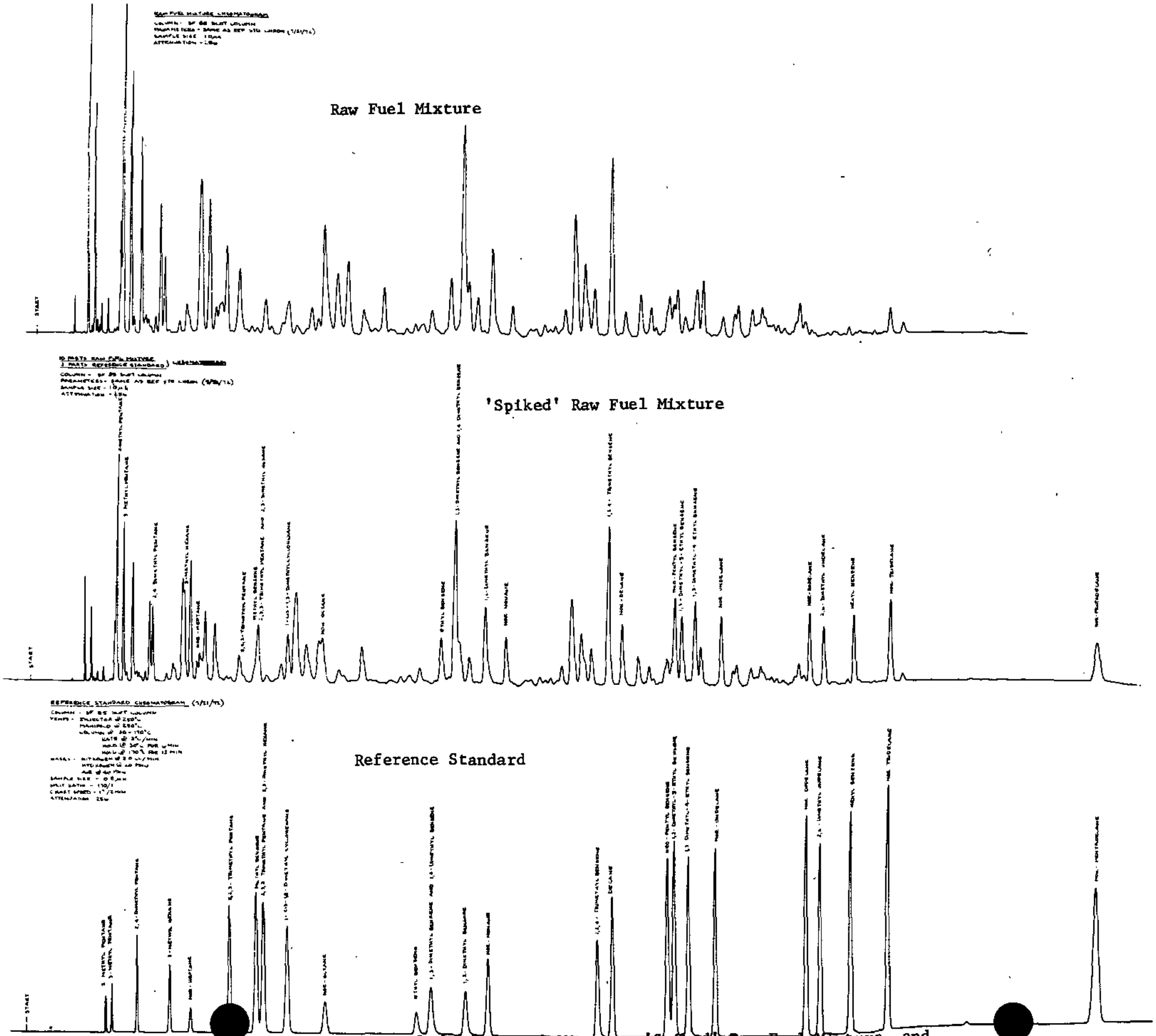

Figure 9. Picture of Gas Chromatograms of the Raw Fuel Mixture, 'Spiked' Raw Fuel Mixture, and Standard Mixture Obtained on a SF-85 SCOT Column.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The techniques of gas chromatography and mass spectroscopy which have been used successfully for the identification of hydrocarbon compounds in automotive exhaust emissions can be readily adapted for the measurement and identification of certain hydrocarbon compounds in water.
2. There are 45 major hydrocarbon compounds in the raw fuel mixture used to generate OMSE-water. Most of these hydrocarbon compounds have between five to twelve carbon atoms in their structure and there are approximately the same number of alkyl-benzene compounds as there are aliphatic compounds.
3. There are 23 major hydrocarbon compounds present in OMSE-water. Many of these hydrocarbon compounds have between 7 to 12 carbons atoms in their structure and the majority of the hydrocarbons are alkyl-benzene compounds.
4. The similarity of the major hydrocarbon compounds in OMSE-water in composition, peak shape, and retention time, to other major hydrocarbon compounds in the raw fuel mixture suggested that the hydrocarbons in OMSE-water are derived from the passage of a portion of the unburned raw fuel mixture through the outboard engine and into receiving waters.
5. The absence of the lower boiling point aliphatic compounds (carbon atom numbers of 6 and lower) in OMSE-water which were present in the raw fuel mixture suggested that they possibly were combusted into products undetected by techniques used in this investigation or possibly were lost by the carbon adsorption method followed by chloroform extraction-concentration technique used in the preparation of the OMSE-water extract.

6. The use of the standard carbon adsorption method followed by chloroform extraction could be applied to the majority of hydrocarbon compounds present in OMSE-water but was not an effective method for the determination of low boiling point hydrocarbons with carbon atom number of 6 or less which may have been present in OMSE-water.
7. The major hydrocarbon compounds present in raw water did not interfere with the analysis of hydrocarbon compounds present in OMSE-water.
8. The absence of oxygenated compounds in OMSE-water was attributed to limitations inherent in the technique and materials selected for use in the experimentation and their possible presence in immeasurable quantities in OMSE-water.

RECOMMENDATIONS

1. A study be conducted to determine the quantity of each of the major hydrocarbon compounds herein found to be present in OMSE-water under laboratory conditions.
2. Various gas chromatography column coatings and packing be investigated to find a suitable column which will allow for the identification of oxygenated-hydrocarbon compounds in OMSE-water.
3. Field studies be conducted to evaluate the quality and quantity of hydrocarbon compounds present in OMSE-water with time under natural conditions.
4. Investigate the outboard motor parameters of engine horsepower rating and speed of operation on the quality and quantity of OMSE-compounds discharged into receiving waters.
5. Determine the efficiency of crankcase recycling devices with respect to their capability of altering the quality and quantity of OMSE-compounds in receiving waters.
6. Investigate the technique of freeze concentration of hydrocarbons in OMSE-water as a substitute for the concentration process of carbon adsorption followed by extraction with chloroform which may have chemically altered the hydrocarbons or resulted in a loss of the lower boiling point hydrocarbons during the distillation step.
7. A study be conducted to assess the effect of OMSE-emissions upon the air quality above receiving waters.

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LITERATURE CITED

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Appendix A - Gas Chromatography and Mass Spectroscopy Data

Table A-1. Instrumental Parameters for the Preliminary Gas Chromatographic Separation of Hydrocarbon Compounds in Raw Water and OMSE-Water.

	Samples-Raw Water and OMSE-Water	
	Column	
Parameter	Open Tubular(Packed)	Wall-Coated Open Tubular(Capillary)
Column length (ft)	12	150
Column I.D. (in)	1/8	0.01
Column-liquid phase	Versilube F-50 5%	OV-101 Silicone
Column-solid phase	Chrom W 80/100 M	-
Injector Temp. (°C)	200	300
Manifold Temp. (°C)	220	250
Column Temp (Isothermal) (°C)	200	-
Column Temp. range (°C)	-	50-200
Column Temp. Program Rate (°C/min.)	-	1.5
Column Temp. Hold Time (min)	-	None
Hydrogen (psig)	20	20
Air (psig)	30	40
Carrier gas	Nitrogen	Nitrogen
Carrier gas flow rate (cc/min)	35	1.0
Chart speed	1"/5 min	1"/2 min
Attenuation	20	20
Sample Size (μl)	1.0	1.0
Sample Split Ratio	None	170/1

Table A-2. Instrumental Parameters and Retention Time Data for the Isothermal Gas Chromatographic Separation of Raw-Water Extract, OMSE-Water Extract, and Raw Fuel.

	Sample Retention Times (Seconds)		
	Raw Water Extract*	Raw Fuel*	OMSE-Water Extract*
Peak No.	Att = 640 Sample Size = 0.1μl	Att = 6400 Sample Size = 0.1μl	Att = 640 Sample Size = 0.1μl
1	62	62	62
2	78	69	70
3	-	76	76
4	-	85	86
5	-	90	90
6	-	98	98
7	-	104	104
8	-	114	114
9	-	123	123
10	-	133	132
11	-	140	140
12	-	155	155
13	-	161	161
14	-	170	169
15	-	183	183
16	-	192	192

*Instrumental Parmeters Same as Those for Open-Tubular Packed Column of Table C-1, Except for the Sample Size and Attenuation as Noted in this Table.

Note: Chloroform retention time is 62 seconds.

Table A-3. Instrumental Parameters for the Gas Chromatographic Separation of Compounds Present in Raw-Water Extract, OMSE-Water Extract, Raw Fuel Mixture, and the Reference Standard on Two Capillary Columns.

	Capillary Column	
Parameter	Vers F-50	OV-101
Column length (ft)	150	150
Column I.D. (in.)	0.01	0.01
Column-liquid phase	Versilube F-50	OV-101 Silicone
Injector Temp.($^{\circ}$C)	250	250
Manifold Temp. ($^{\circ}$C)	270	270
Column Temp. range ($^{\circ}$C)	50-150	50-225
Column Temp. Program Rate ($^{\circ}$C/min)	1.5	1.5
Column Temp. Hold Time (min)	24 (at 150°C)	24 (at 225°C)
Hydrogen (psig)	20	20
Air (psig)	40	40
Carrier gas	Nitrogen	Nitrogen
Carrier gas flow rate (cc/min)	0.81	1.00
Chart speed	1"/2 min	1"/2 min
Attenuation-Ref.Standard	1600	1600
-OME-Water Ext.	64	128
-Raw-Water Ext.	20	20
-Raw-Fuel	400	400
Sample Size-Ref.Standard (μl)	1.0	1.0
-OME-Water Ext.	1.0	1.0
-Raw Water Ext.	1.0	1.0
-Raw Fuel	1.0	1.0
Sample Split Ratio	170/1	170/1

Table A-4. Instrumental Parameters for the Gas Chromatographic Separation on a SF-85 SCOT Column of Compounds Present in the Reference Standard, Raw Fuel Mixture, and OMSE-Water Extract

Parameter	Sample		
	Reference Standard	Raw Fuel Mixture	OMSE-Water Extract
Column length (ft)	50	50	50
Column I.D. (in)	0.02	0.2	0.02
Column-liquid phase	SF-85	SF-85	SF-85
Column-solid phase	None	None	None
Injector Temp. (°C)	250	250	250
Manifold Temp. (°C)	250	250	250
Column Temp. range(°C)	30-170	30-170	30-170
Column program rate	3°C/min	2°C/min	3°C/min
Column temp. hold time (min)	6 min 2 30°C 12 min @ 170°C	3 min @ 30°C 12 min @ 170°C	3 min @ 30°C 24 min @ 170°C
Hydrogen (psig)	20	20	20
Air (psig)	40	40	40
Carrier gas	Nitrogen	Nitrogen	Nitrogen
Carrier gas flow rate (cc/min)	3.0	4.4	3.0
Chart speed	1"/2 min	1"/2 min	1"/2 min
Attenuation	256	3200	1280
Sample size (µl)	0.8	1.0	1.0
Sample split ratio	170/1	170/0	170/1

Table A-5. Instrumental Parameters for the Gas Chromatographic Separation of Compounds Present in Raw Fuel Mixture, and OMSE-Water Extract in Conjunction with RMU-6A Mass Spectrometer Analysis.

Parameter	Open Tubular Column - Versilube F-50
Column length (ft)	12
Column I.D. (in.)	1/8
Column-liquid phase	Versilube F-50 5%
Column-solid phase	Chrom W 80/100 M
Injector Temp. (^{o}C)	220
Manifold Temp. (^{o}C)	300
Column Temp. range (^{o}C)	Ambient (30^{o}C)-200
Column program rate	6^{o}C/min
Column temp. hold time (min)	3 (at ambient)
Hydrogen (psig)	75
Air (cc/min)	$\cong$150
Carrier gas	Helium
Carrier gas flow rate (cc/min)	20
Chart speed	1"/2 min
Attenuation	128 and 64
Sample size (μl)	0.25
Sample split ratio	None

Table A-6. Instrumental Parameters for the Gas Chromatographic Separation of Compounds Present in Raw Fuel Mixture, Raw-Water Extract, and OMSE-Water Extract in Conjunction with RMU-6L Mass Spectrometer Analysis

Parameter	Sample		
	Raw-Water Extract	Raw Fuel Mixture	OMSE-Water Extract
Column length (ft)	50	50	50
Column I.D. (in)	0.02	0.02	0.02
Column-liquid phase	SF-85	SF-85	SF-85
Column-solid phase	None	None	None
Injector Temp. (^{o}C)	250	250	250
Manifold Temp. (^{o}C)	250	250	250
Column temp. range (^{o}C)	50-170	40-170	40-170
Column program rate (step)	5^{o}C/min	5^{o}C/2 min	5^{o}C/min
Column Temp. hold time(min)	3 min @ 50^{o}C	5 min @ 40^{o}C	3 min @ 40^{o}C 15 min @ 170^{o}C
Hydrogen (psig)	40	40	40
Air (psig)	40	40	40
Carrier gas	Helium	Helium	Helium
Carrier gas flow rate (cc/min)	1.5	1.5	1.5
Chart speed	N.A.	N.A.	N.A.
Attenuation	N.A.	N.A.	N.A.
Sample size (μl)	0.2	0.15	0.1
Sample split ratio	170/1	170/1	170/1

Table A-7. Mass to Charge Ratio and Relative Intensity of the Major Hydrocarbon Compounds in the Raw Fuel Mixture Subjected to RMU-6A and RMU-6L Mass Spectrometer Analysis.

Table A-7. Sample: Raw Fuel

Peak No: 1
Ref: RMU-6L

m/e	R.I.
43	100
42	94
41	77
29	62
57	56
44	32
56	23
39	17
55	18
72	7

Peak No: 2
Ref: RMU-6L

m/e	R.I.
43	100
42	76
29	70
41	57
44	39
39	20
57	18
55	16
72	10
40	8

Peak No: 3
Ref: RMU-6A

m/e	R.I.
43	100
42	80
71	43
41	40
70	20
39	20
29	19
55	19
27	13
86	13

Peak No: 4
Ref: RMU-6L

m/e	R.I.
57	100
56	89
41	81
29	62
43	48
39	16
42	16
44	13
55	11
71	9

Peak No: 5
Ref: RMU-6A

m/e	R.I.
57	100
43	81
41	80
29	57
56	55
42	46
27	42
39	27
55	18
86	17

Peak No: 6
Ref: RMU-6A

m/e	R.I.
56	100
41	68
43	48
57	40
69	34
42	28
55	25
27	23
39	23
84	19

Peak No: 7
Ref: RMU-6L

m/e	R.I.
43	100
29	87
78	79
44	68
71	44
41	44
55	31
39	29
56	23
77	21

Peak No: 8
Ref: RMU-6A

m/e	R.I.
43	100
41	47
85	45
58	42
57	41
42	39
78	33
39	22
29	22
27	20

Table A-7. Sample: Raw Fuel, Continued

Peak No: 9
Ref: RMU-6L

m/e	R.I.
43	100
57	54
41	53
71	47
56	42
70	41
29	41
56	16
39	15
42	13

Peak No: 10
Ref: RMU-6A

m/e	R.I.
57	100
56	68
41	49
43	40
70	32
55	28
29	19
39	18
27	17
42	12

Peak No: 11
Ref: RMU-6A

m/e	R.I.
43	100
41	75
57	59
71	45
56	42
29	39
27	38
39	25
70	25
42	24

Peak No: 12
Ref: RMU-6L

m/e	R.I.
55	100
83	76
41	72
56	59
29	54
42	44
70	38
40	38
57	37
98	35

Peak No: 13
Ref: RMU-6A

m/e	R.I.
43	100
57	85
41	62
56	40
29	31
85	31
42	31
55	29
70	27
27	26

Peak No: 14
Ref: RMU-6L

m/e	R.I.
43	100
71	48
70	39
29	30
41	25
55	20
44	17
57	17
39	10
81	10

Peak No: 15
Ref: RMU-6L

m/e	R.I.
91	100
92	73
43	39
70	23
39	19
71	19
65	18
41	14
29	13
44	11

Peak No: 16
Ref: RMU-6L

m/e	R.I.
43	100
57	92
42	46
41	42
29	32
70	27
71	21
55	18
99	9
39	9

Table A-7. Sample: Raw Fuel, Continued

Peak No: 17
Ref: RMU-6L

m/e	R.I.
43	100
57	62
41	51
29	40
85	37
56	37
84	26
55	18
70	14
39	12

Peak No: 18
Ref: RMU-6L

m/e	R.I.
57	100
56	55
41	49
55	45
29	40
43	27
44	25
83	21
71	20
70	18

Peak No: 19
Ref: RMU-6A

m/e	R.I.
43	100
41	57
57	41
85	36
55	34
29	34
56	30
71	26
27	25
70	23

Peak No: 20
Ref: RMU-6A

m/e	R.I.
43	100
57	55
41	49
55	37
85	32
56	29
27	28
71	27
29	24
70	24

Peak No: 21
Ref: RMU-6L

m/e	R.I.
91	100
106	30
29	18
51	17
44	17
39	15
65	14
55	12
41	12
77	10

Peak No: 22
Ref: RMU-6L

m/e	R.I.
91	100
106	77
105	36
43	35
39	26
51	21
77	20
79	15
41	14
57	13

Peak No: 23
Ref: RMU-6L

m/e	R.I.
57	100
43	37
41	35
29	29
56	27
55	14
98	11
44	11
71	9
99	7

Peak No: 24
Ref: RMU-6L

m/e	R.I.
91	100
106	50
105	21
39	19
55	17
77	16
51	16
41	13
29	13
57	12

Table A-7. Sample: Raw Fuel, Continued

Peak No: 25
Ref: RMU-6L

m/e	R.I.
43	100
57	71
41	39
29	37
71	26
56	17
85	16
44	15
70	15
55	14

Peak No: 26
Ref: RMU-6L

m/e	R.I.
91	100
29	32
120	22
44	22
41	20
65	16
57	16
43	16
39	16
55	16

Peak No: 27
Ref: RMU-6A

m/e	R.I.
105	100
120	28
57	27
43	20
91	14
41	14
39	12
77	12
106	10
97	9

Peak No: 28
Ref: RMU-6L

m/e	R.I.
105	100
57	62
120	50
44	45
43	34
41	30
29	29
71	29
56	23
77	21

Peak No: 29
Ref: RMU-6L

m/e	R.I.
105	100
44	38
120	30
57	21
29	20
79	18
77	17
91	17
39	15
41	15

Peak No: 30
Ref: RMU-6L

m/e	R.I.
105	100
120	59
77	20
39	18
119	17
79	16
91	15
41	15
51	14
106	13

Peak No: 31
Ref: RMU-6L

m/e	R.I.
43	100
57	90
29	44
41	42
71	35
44	30
55	25
56	22
85	17
70	16

Peak No: 32
Ref: RMU-6L

m/e	R.I.
105	100
120	48
29	26
57	25
43	20
44	20
41	19
119	17
39	15
77	15

Table A-7. Sample: Raw Fuel, Continued

Peak No: 33
Ref: RMU-6L

m/e	R.I.
57	100
43	78
29	61
41	49
71	47
117	46
44	40
56	33
118	28
55	26

Peak No: 34
Ref: RMU-6L

m/e	R.I.
105	100
57	54
29	43
119	39
43	38
134	33
41	31
44	30
71	28
91	19

Peak No: 35
Ref: RMU-6A

m/e	R.I.
105	100
134	25
57	18
91	16
106	16
119	16
77	13
43	13
41	12
39	10

Peak No: 36
Ref: RMU-6L

m/e	R.I.
57	100
43	74
71	53
29	48
41	43
44	40
105	38
56	32
55	23
70	20

Peak No: 37
Ref: RMU-6A

m/e	R.I.
119	100
134	27
91	20
117	17
105	15
41	12
77	12
120	12
39	12
115	10

Peak No: 38
Ref: RMU-6L

m/e	R.I.
117	100
44	45
119	35
115	33
132	33
91	27
57	27
29	27
41	24
55	22

Peak No: 39
Ref: RMU-6L

m/e	R.I.
57	100
43	94
29	45
41	44
71	41
119	30
44	25
55	24
56	18
85	18

Peak No: 40
Ref: RMU-6L

m/e	R.I.
119	100
134	51
57	45
29	45
44	41
41	36
43	35
91	31
71	22
39	18

Table A-7. Sample: Raw Fuel

Peak No: 41
Ref: RMU-6A

m/e	R.I.
119	100
134	52
57	20
41	18
91	17
43	14
39	13
120	12
33	11
77	11

Peak No: 42
Ref: RMU-6L

m/e	R.I.
117	100
57	78
29	78
44	71
43	51
41	46
91	46
119	41
131	41
132	41

Peak No: 43
Ref: RMU-6L

m/e	R.I.
117	100
105	71
106	58
91	45
44	45
29	41
57	38
132	35
43	30
119	30

Peak No: 44
Ref: RMU-6L

m/e	R.I.
128	100
29	26
44	25
51	21
57	20
127	16
43	16
64	14
129	14
131	14

Peak No: 45
Ref: RMU-6L

m/e	R.I.
142	100
141	89
44	76
29	72
57	57
43	43
71	37
41	35
115	33
55	26

Peak No: 46
Ref:

m/e	R.I.

Peak No: 47
Ref:

m/e	R.I.

Peak No: 48
Ref:

m/e	R.I.

Table A-8. Mass to Charge Ratio and Relative Intensity of the Major Hydrocarbon Compounds in OMSE-Water Extract Subjected to RMU-6A and RMU-6L Mass Spectrometer Analysis.

Table A-8. Sample: OMSE-Water

Peak No: 1
Ref: RMU-6L

m/e	R.I.
Chloroform	

Peak No: 2
Ref: RMU-6A

m/e	R.I.
91	100
92	69
39	16
65	14
63	10
51	9
50	6

Peak No: 3
Ref: RMU-6A

m/e	R.I.
91	100
106	67
57	61
41	59
39	47
51	44
43	43
71	40
65	32
42	30

Peak No: 4
Ref: RMU-6A

m/e	R.I.
91	100
106	54
105	26
77	15
39	14
51	13
65	8
78	8
79	8
63	7

Peak No: 5
Ref: RMU-6L

m/e	R.I.
91	100
106	59
44	33
105	26
77	17
39	16
51	16
79	13
29	13
27	11

Peak No: 6
Ref: RMU-6L

m/e	R.I.
91	100
29	32
120	22
44	20
41	20
65	16
57	16
43	16
39	16
55	16

Peak No: 7
Ref: RMU-6A

m/e	R.I.
105	100
120	26
57	21
43	18
77	15
39	14
91	13
41	12
79	11
106	10

Peak No: 8
Ref: RMU-6L

m/e	R.I.
105	100
57	62
120	50
44	45
43	34
41	30
29	29
71	29
56	23
77	21

Table A-8. Sample: OMSE-Water, Continued

Peak No: 9
Ref: RMU-6L

m/e	R.I.
105	100
44	38
120	30
57	21
29	20
79	18
77	17
91	17
39	15
41	15

Peak No: 10
Ref: RMU-6A

m/e	R.I.
105	100
120	52
119	16
77	14
91	11
39	11
106	11
57	9
43	9
41	9

Peak No: 11
Ref: RMU-6A

m/e	R.I.
105	100
57	57
120	44
43	37
41	35
71	29
39	26
55	23
57	23
27	21

Peak No: 12
Ref: RMU-6L

m/e	R.I.
57	100
44	91
117	50
43	48
29	47
71	44
41	42
56	37
55	35
118	29

Peak No: 13
Ref: RMU-6L

m/e	R.I.
105	100
44	33
134	30
57	21
106	20
77	17
91	16
41	16
29	16
79	15

Peak No: 14
Ref: RMU-6A

m/e	R.I.
105	100
134	25
57	20
43	17
91	17
116	15
119	15
77	14
41	14
39	13

Peak No: 15
Ref: RMU-6L

m/e	R.I.
57	100
105	76
43	67
71	53
41	42
44	38
56	31
29	29
55	24
85	24

Peak No: 16
Ref: RMU-6A

m/e	R.I.
119	100
117	36
134	29
91	25
41	15
115	14
132	13
105	13
39	13
77	13

Table A-8. Sample: OMSE-Water, Continued

Peak No: 17
Ref: RMU-6L

m/e	R.I.
117	100
44	45
119	35
115	33
132	33
91	27
57	27
29	27
41	24
55	22

Peak No: 18
Ref: RMU-6A

m/e	R.I.
43	100
57	100
41	64
71	45
55	37
119	35
105	34
56	25
39	25
85	24

Peak No: 19
Ref: RMU-6L

m/e	R.I.
119	100
134	51
57	45
29	45
44	41
41	36
43	35
91	31
71	22
39	18

Peak No: 20
Ref: RMU-6A

m/e	R.I.
119	100
134	51
57	26
41	21
91	19
43	19
39	14
71	13
120	11
77	10

Peak No: 21
Ref: RMU-6L

m/e	R.I.
117	100
119	51
132	43
131	34
91	34
115	34
44	34
57	30
41	20
55	18

Peak No: 22
Ref: RMU-6L

m/e	R.I.
117	100
119	58
57	54
132	44
91	40
115	36
44	36
43	35
71	27
105	27

Peak No: 23
Ref: RMU-6L

m/e	R.I.
128	100
133	53
57	51
131	49
43	44
44	38
71	33
41	29
91	21
51	20

Peak No: 24
Ref: RMU-6L

m/e	R.I.
142	100
141	82
44	48
115	34
57	31
71	25
29	23
43	21
41	16
55	15

Table A-9. Mass to Charge Ratio and Relative Intensity of Major Hydrocarbon Compounds in Raw-Water Subjected to RMU-6A and RMU-6L Mass Spectrometer Analysis.

Table A-9. Sample: Raw-Water

Peak No: 1		Peak No: 4		Peak No: 5		Peak No: 6	
Ref:		Ref: RMU-6L		Ref: RMU-6L		Ref: RMU-6L	
m/e	R.I.	m/e	R.I.	m/e	R.I.	m/e	R.I.
Chloroform		44	100	44	100	44	100
		57	77	29	75	29	64
		29	59	57	59	57	61
		43	53	43	49	43	39
		71	39	41	37	41	38
		41	39	71	33	71	30
		55	31	55	27	55	23
		85	28	85	16	56	20
		69	24	69	16	69	18
		56	20	39	14	85	18

Table A-10. Instrumental Parameters for the Gas Chromatographic Separation of Compounds Present in the Raw Fuel Mixture, Reference Standard, and 'Spiked' Raw Fuel Sample on a SCOT Column.

Parameter	SCOT Column
Column length (ft)	50
Column I.D. (in)	0.02
Column-liquid phase	SF-85
Column-solid phase	None
Injector Temp. (°C)	250
Manifold Temp. (°C)	250
Column Temp. range (°C)	30-170
Column program rate	3°C/min
Column Temp. hold time (min)	30°C for 6 min 170°C for 12 min
Hydrogen (psig)	20
Air (psig)	40
Carrier gas	Nitrogen
Carrier gas flow rate (cc/min)	3.0 cc/min
Chart speed	1"/2 min
Attenuation	256
Sample size-Reference Standard (μl)	0.8
- Raw Fuel Mixture	1.0
- 'Spiked'Raw Fuel Mixture	1.0
Sample split ratio	170/1

SECTION TWO

The Fate of Organic Compounds Emitted from Outboard Motor Subsurface Exhausts

ABSTRACT

ABSTRACT

Various questions have been proposed concerning the effects of outboard motors on the aquatic environment. It was the purpose of this study to determine the fate of organic compounds released to a natural body of water as a result of simulated heavy outboard motor usage. The Carbon Adsorption Method (CAM) was utilized in an attempt to quantify toluene and n-dodecane, representative of aromatic and aliphatic hydrocarbons found in outboard motor subsurface exhaust recipient water (OMSE recipient water). Preliminary investigations in the laboratory yielded efficiency of recoveries of toluene and n-dodecane from activated carbon of 54.7 and 18.7%, respectively.

At several points within the field test area, samples were obtained at various depths below the surface over a period of time for Total Organic Carbon (TOC) and turibidty analysis. The results showed that the highest concentrations of emitted organic compounds are found at the surface of the water and at the depth of the outboard motor propeller. It was also discovered that TOC levels returned to normal 12 days after the outboard motor operation and that turbidity measurements closely parallel the decline in TOC concentration with time.

Because of the rapid disappearance of the organic compounds from the recipient water, the CAM was not successful in field quantification of toluene and n-dodecane. Gas chromatographic analysis of CAM chloroform extracts showed that only one organic compound demonstrated any appreciable persistence in OMSE-water under field conditions.

INTRODUCTION

INTRODUCTION

The question has been raised by various agencies, industries, and concerned individuals as to whether the operation of outboard motors on the nation's waterways has a detrimental effect on water quality and associated aquatic biota. Although studies on the question of outboard motor discharges have been sponsored by various State and Federal agencies, many questions remain unresolved. Due to the complexity of this issue, several differing points of view can be expected. As an example, it has been reported that oil slicks and unpleasant odors originate in waters commonly used for regular outboard motor operation (1)*, while others claim that the issue of outboard motor pollution is one of speculation and therefore merits further scientific investigation (2).

Studies have been undertaken which investigated the actual organic compounds released to the aquatic environment as a result of outboard motor operation. English, et al (3) quantified total aliphatic, aromatic and oxygenated compounds present in a test lake after outboard motor usage. Shuster (4) conducted studies on variations in organic compound concentration with pool depth and on persistence of these compounds with time. Investigations by Jackivicz (5) resulted in the positive identification of numerous organic compounds recovered from OMSE-water under controlled laboratory conditions, while tests were performed by Environmental Engineering, Incorporated (6) in order to determine whether compounds characteristic of OMSE-water could be detected under field conditions.

Based on the information presented thus far, certain questions may be asked: What is the fate or organic compounds emitted by outboard motor subsurface exhausts in a natural environment? What segment of the recipient water might the hydrocarbons

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*numbers in parentheses refer to equivalent referenced article.

accumulate in? Does the aromatic or aliphatic nature of the hydrocarbons produce a preferential tendency of accumulation in the recipient water? With these questions in mind, the objectives of this project were:

1. To attempt to quantify individual hydrocarbons representative of both aromatic and aliphatic compounds found in OMSE-water under field conditions.
2. To determine the locational fate of emitted hydrocarbons in a natural body or water under conditions simulating heavy outboard motor usage.
3. To determine the persistence of these hydrocarbons with time in a natural body of water.

LITERATURE REVIEW

LITERATURE REVIEW

The principal means of detecting small quantities of organic compounds in a waterway is by the Carbon Adsorption Method (CAM), developed by the United States Public Health Service in 1951, whereby water containing organic contaminants is passed through a column of activated carbon, resulting in removal of the organics by adsorption onto the carbon granules. This process is advantageous in that large quantities of water may be sampled in order to concentrate organic pollutants for ease of subsequent detection and measurement. Accepted procedure called for the passage of 5,000 gallons of water at a rate of 0.25 gpm through a column containing 4.5 inches of each of 4 x 10 mesh, 30 mesh, and 4 x 10 mesh activated carbon. The carbon is then extracted with chloroform followed by evaporation to a residue (7).

Various investigators have been concerned about the actual types and quantities of organic compounds emitted to the receiving water as a result of outboard motor operation. Shuster (4) varied engine rpm and the quantity of fuel consumed in an effort to determine fuel wastage percentages under laboratory conditions. The receiving water was sampled at various pool depths and subjected to total carbon and total organic carbon analyses. Samples were also obtained at different depths over a period of six days for the purpose of determining variations in carbon concentration with time. The results obtained were extremely erratic and generally inconclusive. One notable observation that could be made from the presented data is that, irregardless of the quantity of fuel utilized, the organic carbon concentration in the receiving water remained relatively low and constant. Shuster attributed high total carbon concentrations obtained entirely to dissolved carbon dioxide. No explanation was given by Shuster as to why the organic carbon content remained virtually constant over the entire six day sampling period.

Environmental Engineering, Incorporated (6) performed gas chromatographic analysis on one gallon water samples obtained from a test lake. These samples had been extracted with chloroform to concentrate any suspended or dissolved organic compounds present in the water. The chromatograms obtained were compared to a standard chromatogram of OMSE-water produced in the laboratory. The laboratory OMSE-water was prepared by operating a 10 hp outboard motor in a 50 gallon drum for a total of four hours. One gallon of this water was extracted with chloroform to be followed by injection into a gas chromatograph. The absence of characteristic peaks in the sample chromatograms served as conclusive evidence to these investigators that no detrimental organic compounds existed in the test lake. Although this study demomstrated the feasibility of utilizing gas chromatography in OMSE-water analysis, a one gallon sample column would not, under most circumstances, contain a sufficient quantity of organic compounds originating from outboard motor operation that would be readily detectable by a gas chromatograph. It is quite possible that an organic compound concentration considerably less than that found in the one gallon samples from the test lake used by Environmental Engineering, Incorporated may be detrimental to members of the aquatic biota (8,9). Therefore, the use of a larger sample volume with a concentration technique is in order.

The actual identification of compounds present in OMSE-water was accomplished in research conducted by Jacivicz (5). Utilizing the CAM, the chloroform extract was subjected to gas chromatographic-mass spectrophotometric analysis. Numerous organic compounds were positively identified by this procedure (see Section One of this Progress Report).

Quantitative measurements of groups of compounds originating from outboard motor usage was reported by English, *et al.* (3). Four outboard motors of various horsepower rating and year of manufacture were operated on a 1.7 million gallon motor pond. These outboard motors were fitted with special propellers to allow operation at 4,100 to 4,200 rpm without violent agitation of the test water. The CAM was followed utilizing a flow rate of 0.25 gpm with a total flow through of 2,000 gallons. The CCE was weighed and separated into aliphatic, aromatic, and oxygenated hydrocarbons by column chromatography on silica gel. A motor pond blank yielded approximately 0.5 mg/l CCE residue. After peak operation, the residue was measured to be approximately 1.0 mg/l. Although persistence studies were not originally intended in this research, it was observed from presented data that a lull in outboard motor operation of approximately 18 days allowed the motor pond to recover, by natural purification, to the original 0.5 mg/l CCE residue level.

EXPERIMENTAL METHODOLOGY

EXPERIMENTAL METHODOLOGY

The technique used in the attempt to quantify toluene and n-dodecane, representative of aromatic and aliphatic compounds present in OMSE-water, was essentially the same as appears in the tentative low flow rate CAM procedure found in Standard Methods (7). A specified quantity of water containing hydrocarbon was passed thorugh a model 1F-2 Low Flow Rate Organics Sampler. The carbon containing the adsorbed organics was air-dried and extracted with chloroform to yield a Carbon-Chloroform-Extract (CCE). At this point, the CCE was concentrated by low heat evaporation and then analyzed by gas chromatography, rather than the usual gravimetric procedure normally employed for the CCE in Standard Methods (7).

Preliminary Trials to Ascertain the Efficiency of Recoveries for Toluene and n-Dodecane by the CAM.

In order to quantify toluene and n-dodecane in OMSE-water, it was necessary to first obtain recovery efficiencies for the two compounds using the CAM in the laboratory. A two cubic foot glass tank sealed with a silicone sealant was filled with 50 liters of water. It was desired to disperse 0.1 ml of each compound, resulting in a concentration of 1.58 mg carbon/l for the toluene series and 1.27 mg carbon/l for the n-dodecane series of trials. Although acetic acid is commonly used as a solubilizing agent for organic compounds in aqueous systems, it has been reported that a reduction of the pH of a solution leads to an increase in adsorption efficiency onto activated carbon (10). Therefore, as in the study by Eichelberger and Lichtenberg (11), 3 ml of acetone proved to be a suitable substitute. The contents of the tank were gently stirred for one minute, covered to suppress evaporation of organics to the atmosphere, and passed through the organics sampler for concentration of the organic compounds onto previously extracted activated carbon.

Preparation of the CCE

After passage of the water through the activated carbon column, the carbon was dried in stainless steel trays at 40°C for approximately two days. A large capacity Soxhlet extractor, with a pre-extracted glass wool plug in the bottom, was filled with the dried carbon which was then extracted with two cylinder volumes (approximately 3 l) of redistilled chloroform for 35 hours at a rate of one cylinder volume per hour. The CCE was distilled to a volume of 200 ml and then passed through a 0.45 micron membrane filter to remove any particles of carbon which may have syphoned over from the reaction flask. The CCE was slowly evaporated, by heating to approximately 50°C, to a volume of 20 ml prior to injection of a 1.0 μl aliquot of the concentrate into a Perkin-Elmer Model 990 Gas Chromatograph. This gas chromatograph was equipped with a stainless steel capillary column* in which the stationary phase was 5% Versilube F-50 (methyl-chloro-phenylsiloxane). The operational parameters were as follows:

Temperatures:

injection port - 300°C
manifold - 250°C
column: initial - 50°C
final - 170°C
program rate = 3°C/min
Column length = 150 ft.
Column I.D. - 0.01 in
Attenuation - 320x
Chart Speed - 1 min/in

Gases:

Detector: air, zero hydrocarbons - 40 psig
Carrier gas: N_2 = 1 cc/min flow rate

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*Obtained from Perkin-Elmer Corporation, Norwalk, Connecticut

The concentration of each compound was determined by peak area triangulation and compared to calibration curves of peak area vs. concentration for each compound (Figures 1 and 2).

Preparation of Field Test Site

A field test site was selected in order to perform studies dealing with the locational fate and persistence of organic compounds resulting from outboard motor operation on a natural body of water. A small cove on a portion of the University Campus Pond was chosen because of its close proximity to the laboratory and to a source of power. The cove was isolated from the rest of the pond by a galvanized iron mesh fence covered with a polyethylene sheet material, weighted down along the pond bottom to provide a seal sufficient for the purposes of this study.

The test facility consisted of a pier with provision made for the simultaneous operation of three outboard motors and for the housing of the organics sampler during performance of the CAM. A 1/12 hp submersible centrifugal pump was used to supply head to the activated carbon column. A control volume within the test area was also constructed next to the pier for the purpose of maintaining initial water quality throughout the experimental period. The test volume was calculated to be 57,800 gallons by surface area survey and extensive depth gauging. The reader is referred to the following pages for an overview diagram (Figure 3) and photographs of the experimental area (Figures 4a and 4b).

Field Study Operational Procedure

Prior to any outboard motor operation, 1,000 l of pond water were passed through the organics sampler, extracted with chloroform, and injected into the gas chromatograph for the purpose of obtaining a raw water chromatogram. Water

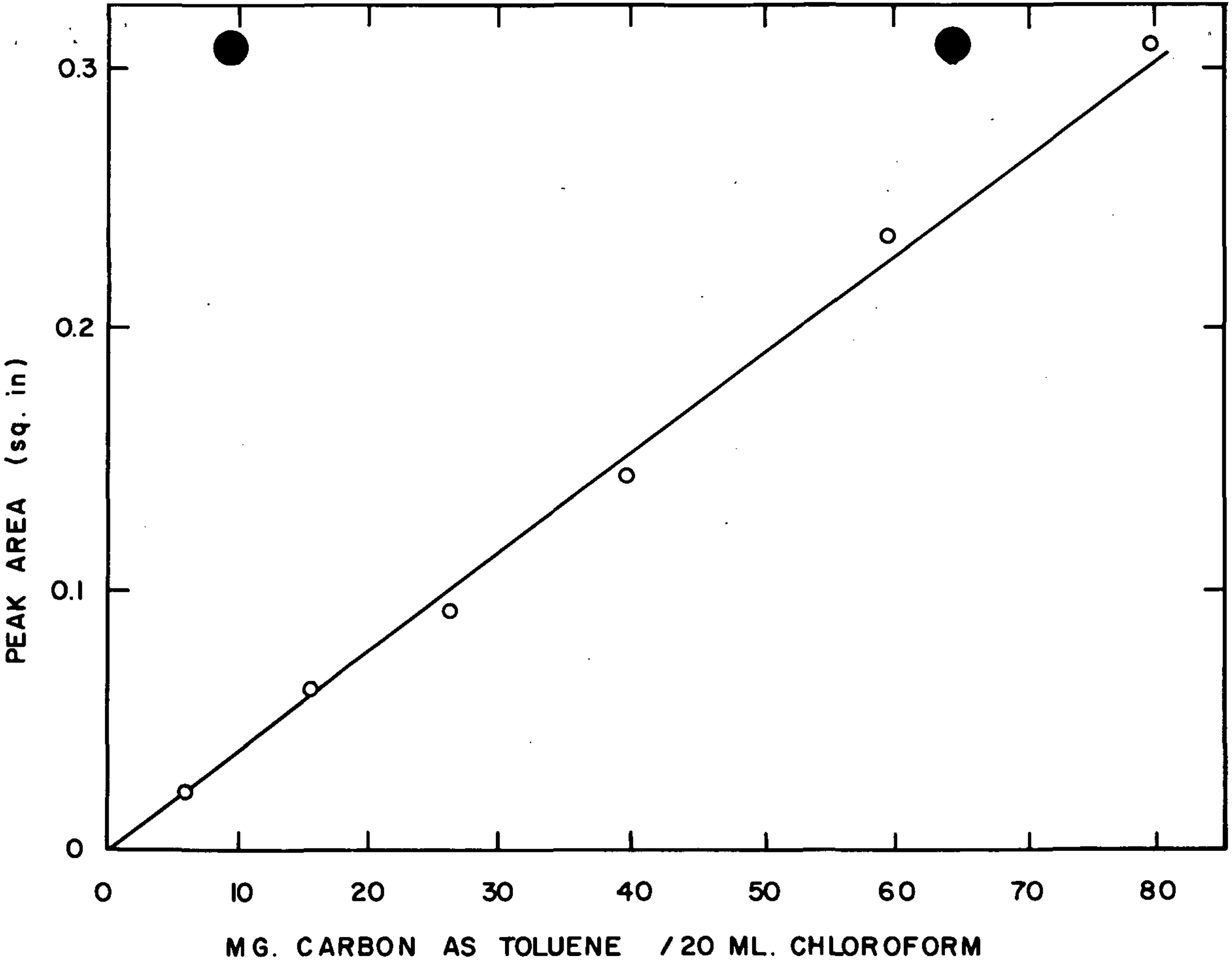


Figure I. Calibration Curve for Toluene by Gas Chromatographic Analysis.

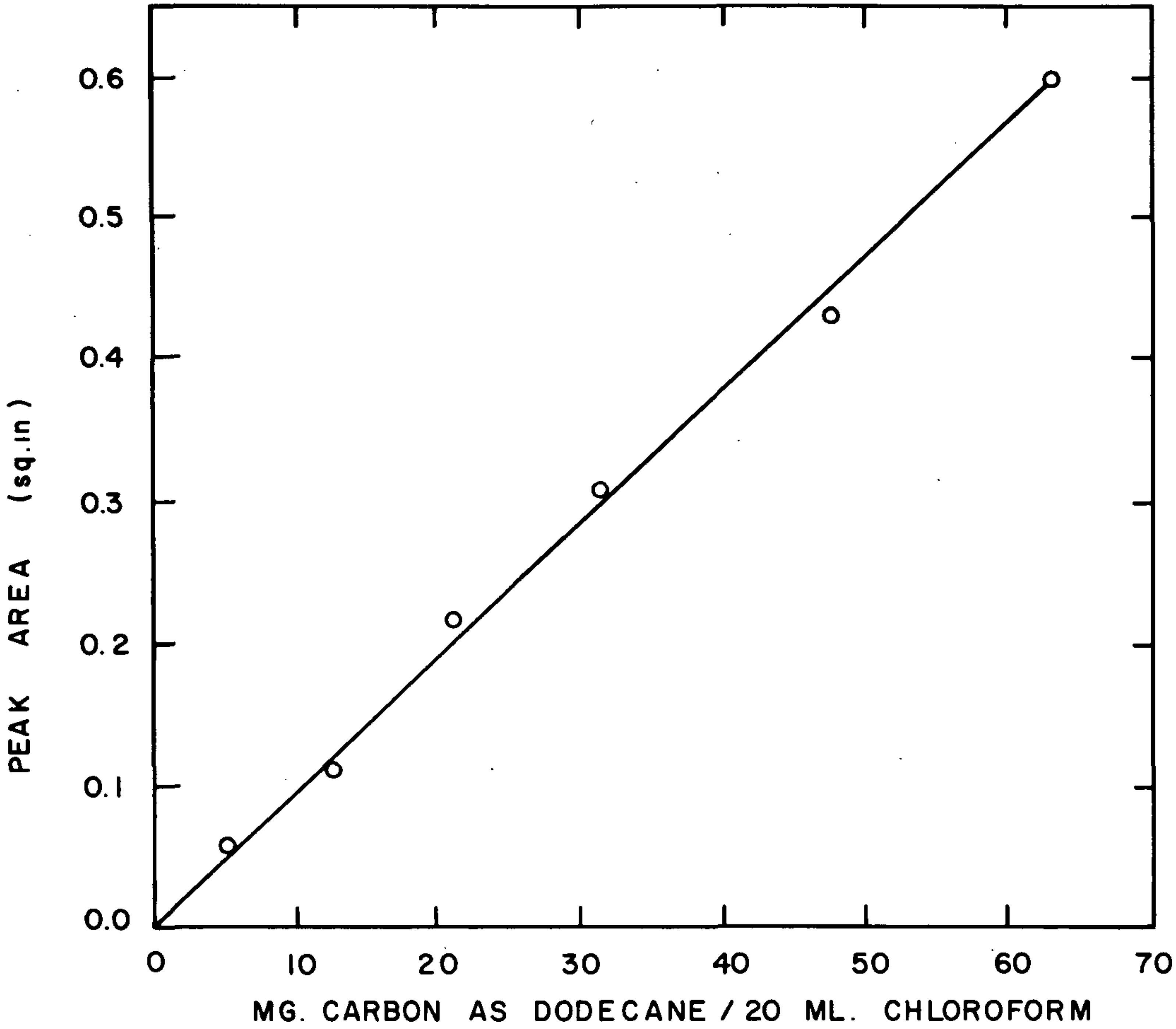


Figure 2. Calibration Curve for n-Dodecane by Gas Chromatographic Analysis.

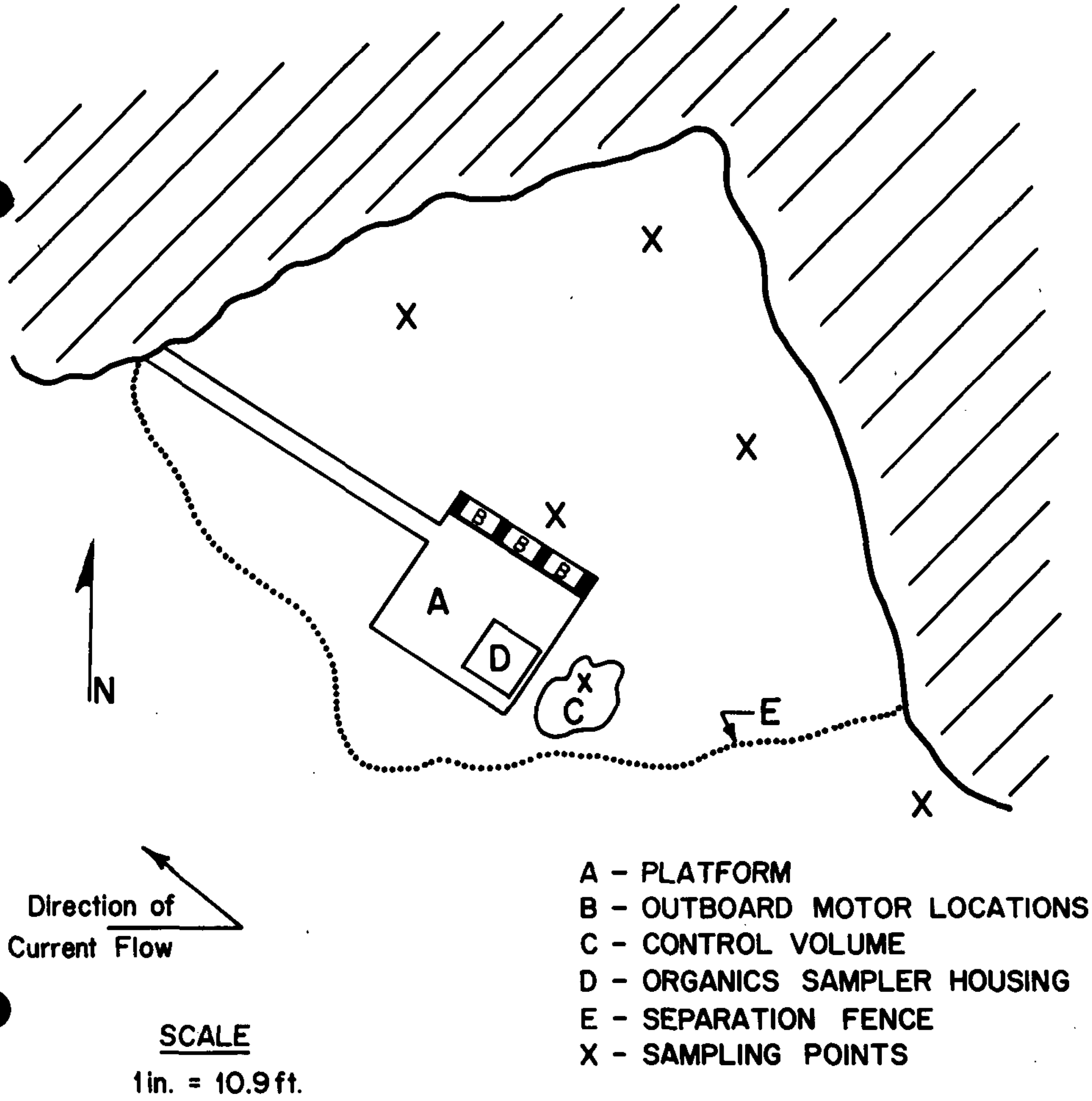
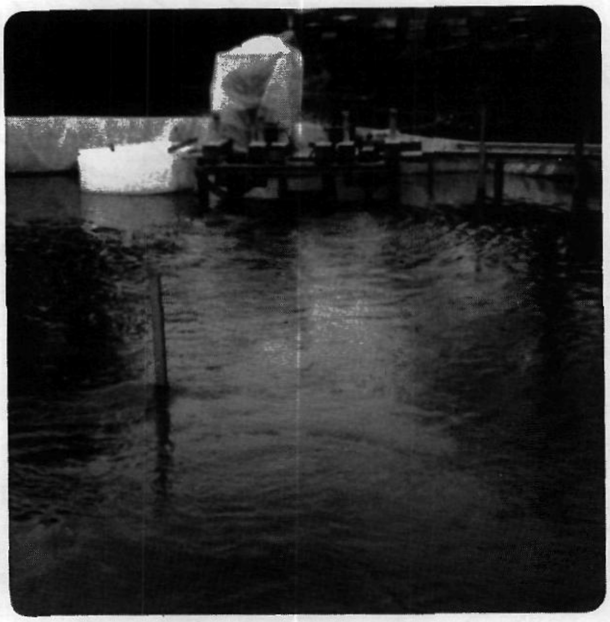
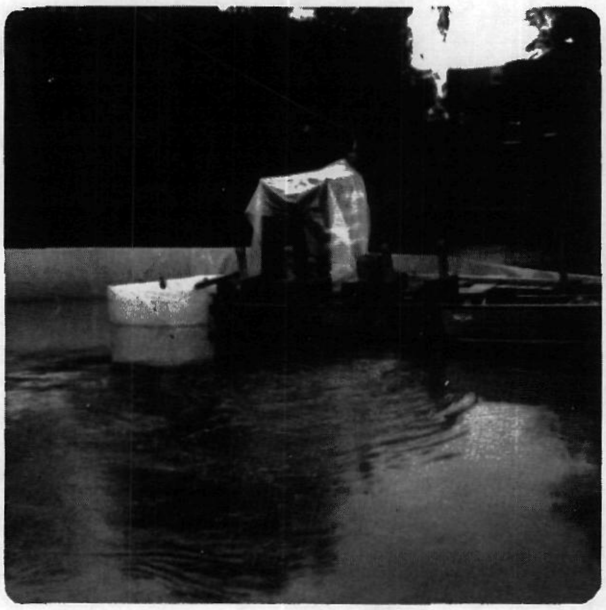


Figure 3. Overview Diagram of Field Test Site.





Figures 4a and 4b. Photographs Depicting Various Features of the Field Test Site.

samples were obtained at five locations and at various depths within the test area, including the control volume, for Total Organic Carbon (TOC) evaluation on a Beckman Model 915 Total Organic Carbon Analyzer. Triplicate 20μl samples were each injected into the Total Carbon and Total Inorganic Carbon channels and results were recorded on a strip chart recorder. The peak heights were measured and referred to the calibration curves for Total Carbon and Total Inorganic Carbon. The TOC was obtained by the difference between the Total Carbon and Total Inorganic Carbon values.

On two separate trial runs, 9 gallons of Gulf regular grade gasoline, mixed in a 50/1 ratio of gasoline to an outboard motor oil recommended by the engine manufacturer (Quicksilver Formula-50), were combusted in two Mercury outboard motors: 4.0 and 7.5 hp 1970 models. On each occasion, after complete fuel utilization by the engines, two 1,000 l volumes of OMSE-water were passed through the organics sampler over a period of 12 consecutive days. As with the raw water extract, the OMSE-water CCE was concentrated to 200 ml (point of distillation vapor temperature increase signifying the loss of organic compounds, in addition to the solvent, through distillation) and injected into the gas chromatograph for analysis. The resulting chromatogram was compared to a standard chromatogram which was prepared in the laboratory by combusting one gallon of fuel into a stainless steel tank containing 200 gallons of water followed by the performance of the CAM to obtain an extract suitable for gas chromatographic analysis. The operational parameters of the gas chromatograph for field CAM samples were the same as those previously described with the exception that the column temperature program rate was 0.5°C/min and the recorder chart speed was maintained at 5 min/in.

Water samples were obtained from specified depths at each sampling site for both trial runs in order to evaluate TOC variations with depth and time. The sampling sites are depicted in Figure 3 and the sampling depths at each site were as follows:

Trial I	Trial II
TOP	TOP
6"	6"
18"	12"
48"	18"
	48"

Samples were alos collected after Trial II for turbidity analysis by a Hach Model 2100A turbidimeter for the purpose of evaluating whether any correlation existed between TOC and turbidity values in the OMSE-recipient water.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Preliminary Trials to Ascertain the Efficiency of Recoveries for Toluene and n-Dodecane by the CAM

A summary of recovery efficiencies, which are combined adsorption and desorption efficiencies for toluene and n-dodecane, as determined by the CAM, are presented in Table 1. By referral to the calibration curves for toluene and n-dodecane (Figures 1 and 2, respectively), the milligram of each compound recovered can be determined. The efficiency of recovery by CCE from the activated carbon is computed to be the ratio of the amount obtained to the actual theoretical quantity actually passed through the organics sampler. On the basis of five extractions for each compound, average results showed that the recovery efficiency was 54.7% for toluene and only 18.7% for n-dodecane with standard deviations of 10.9% and 6.5%, respectively.

As previously stated, 3 ml of acetone were used as a solubilizing agent for the toluene trials. This quantity of acetone was increased continuously for the n-dodecane trials in order to determine whether overloading of a single activated carbon column might occur for large amounts of organics in the water. This would result in a steadily decreasing recovery for n-dodecane. Two identical carbon columns were connected in series and a known volume of water from the 2 cu.ft. glass tank was passed through the newly modified organics sampler. Assuming that all of the n-dodecane which was passed through the organics sampler was adsorbed by the two columns in series, results from Table 2 show that significant increases of organics in solution failed to overload the first carbon column and that 81.7% of the total weight of n-dodecane recovered was extracted from the first column. It was felt that the high concentrations of acetone used would surpass expected concentrations of organic carbon resulting from outboard motor usage. Therefore,

Table 1. Summary of Recovery Efficiency Studies by CAM for Toluene and n-Dodecane

CONC. (mg carbon/l)	VOLUME TESTED BY CAM (liters)	WT. OF CARBON TESTED BY CAM (mg)	GC PEAK AREA (Sq.in.)	WT. OF CARBON EXTRACTED BY CCE (mg)	EFFICIENCY OF RECOVERY (%)
TOLUENE					
1.58	47.4	74.9	0.21	55.5	74.2
1.58	46.0	72.7	0.182	47.8	65.7
1.58	47.5	75.1	0.142	37.4	49.8
1.58	45.6	72.1	0.105	27.7	38.4
1.58	47.1	74.5	0.128	33.8	45.4
				AVE.	54.7
n-DODECANE					
1.27	43.4	55.0	0.052	5.5	10.0
1.27	44.6	56.6	0.105	11.0	19.4
1.27	40.1	50.9	0.071	7.4	14.6
1.27	43.5	55.2	0.120	12.8	23.2
1.27	44.5	56.5	0.142	14.9	26.4
				AVE.	18.7

Table 2. Laboratory Adsorption Capacity Determination for CAM

TRIAL NUMBER	VOLUME ACETONE SOLVENT	CONC. ACETONE SOLVENT (mg carbon/l)	WT. OF n-DODECANE RECOVERED ON COL. 1 (mg carbon/l)	WT. OF n-DODECANE RECOVERED ON COL. 2 (mg carbon/l)	% OF TOTAL WEIGHT RECOVERED ON COL. 1
1	3.0	29.3	5.5	1.3	80.9
2	10.0	97.6	11.0	0.17	98.5
3	20.0	195	7.4	4.2	64.0
4	30.0	293	12.8	3.4	78.7
5	60.0	586	14.9	2.4	86.2
				AVE.	81.7

the use of a single column was considered to be saitsfactory and would not result in column overloading under field conditions.

Identification of Toluene and n-Dodecane in OMSE-water. It was first necessary to determine whether toluene and n-dodecane were present in OMSE-water extract and whether the peaks obtained on the chromatogram could be satisfactorily resolved. From analysis of retention times, the chloroform solvent appeared as the first major peak, to be followed by toluene on the chromatogram. Because of the large number of peaks obtained from the OMSE-water extract chromatogram, positive identification of n-dodecane was accomplished by spiking a portion of the OMSE-water extract with re-distilled n-dodecane. The resulting chromatogram yielded the location of the actual OMSE-water n-dodecane peak (Figure 5).

Analysis of Raw Water CCE Obtained from the Test Site. As evidenced by the raw water extract chromatogram (Figure 6), there is essentially only one peak in the area of interest up to and including the n-dodecane peak. This peak is presumably toluene by comparison of the spiked and unspiked raw water extract chromatograms (Figure 7). There are some high boiling organic compounds present in the original extract chromatogram that are of no import for the purposes of this study. That portion of the chromatogram was not included.

OMSE-Water Extract Analysis. One of the objectives of this study was to quantify two compounds which typify aromatic and aliphatic hydrocarbons found in OMSE-water. However, the chromatograms representing the first and second 1,000 l CCE indicate that the amount of organics originally released to the water from the outboard motor operation had diminished to the point where only the compounds initially present in the greatest quantity were detectable after the first six day CAM procedure (Figure 8). It is quite evident that both toluene and n-dodecane are non-existent in OMSE-water after six days under natural field conditions.

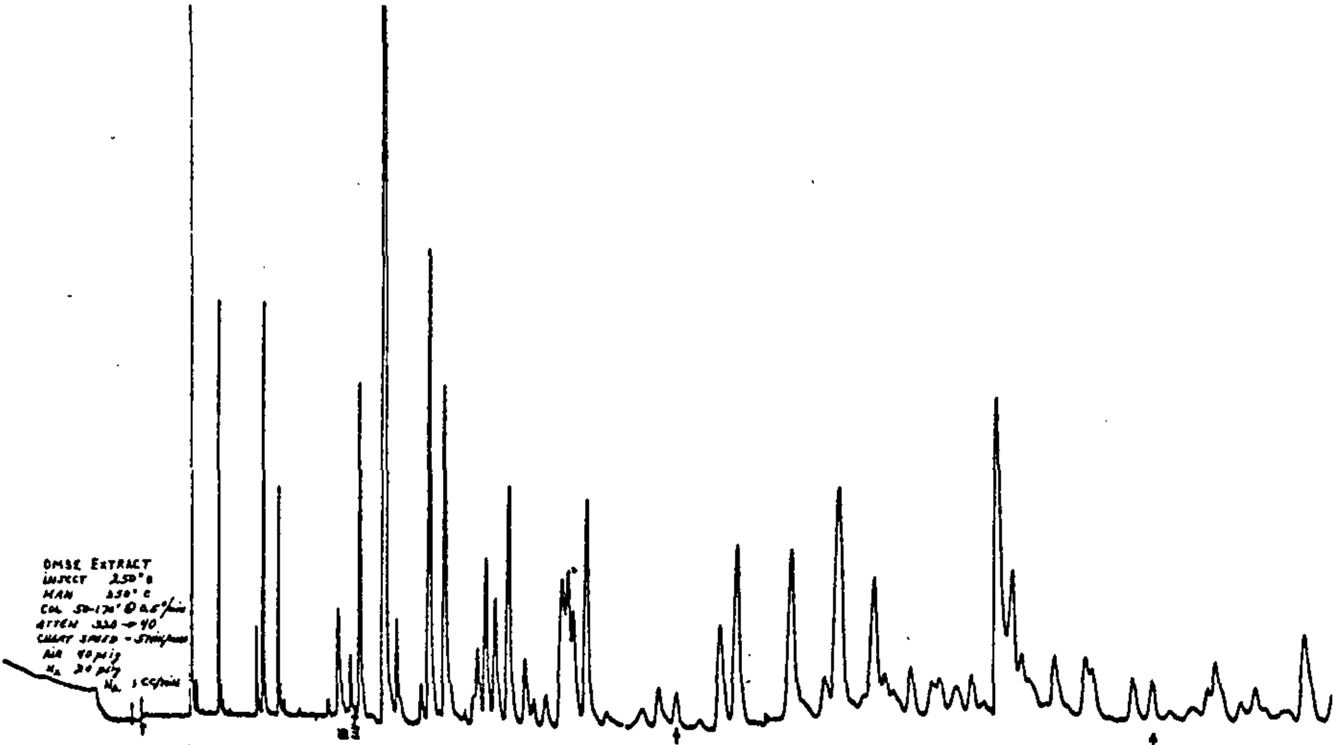
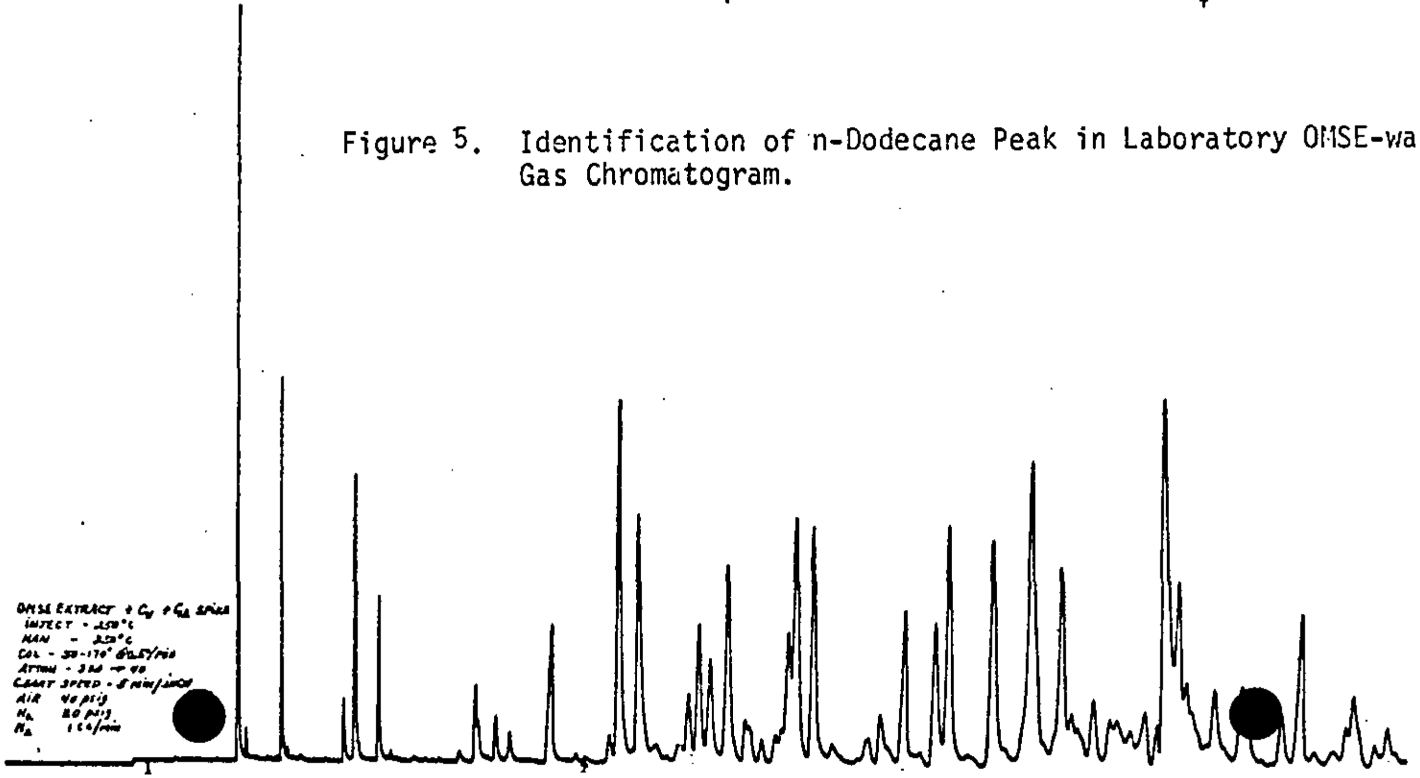


Figure 5. Identification of n-Dodecane Peak in Laboratory OMSE-water Gas Chromatogram.



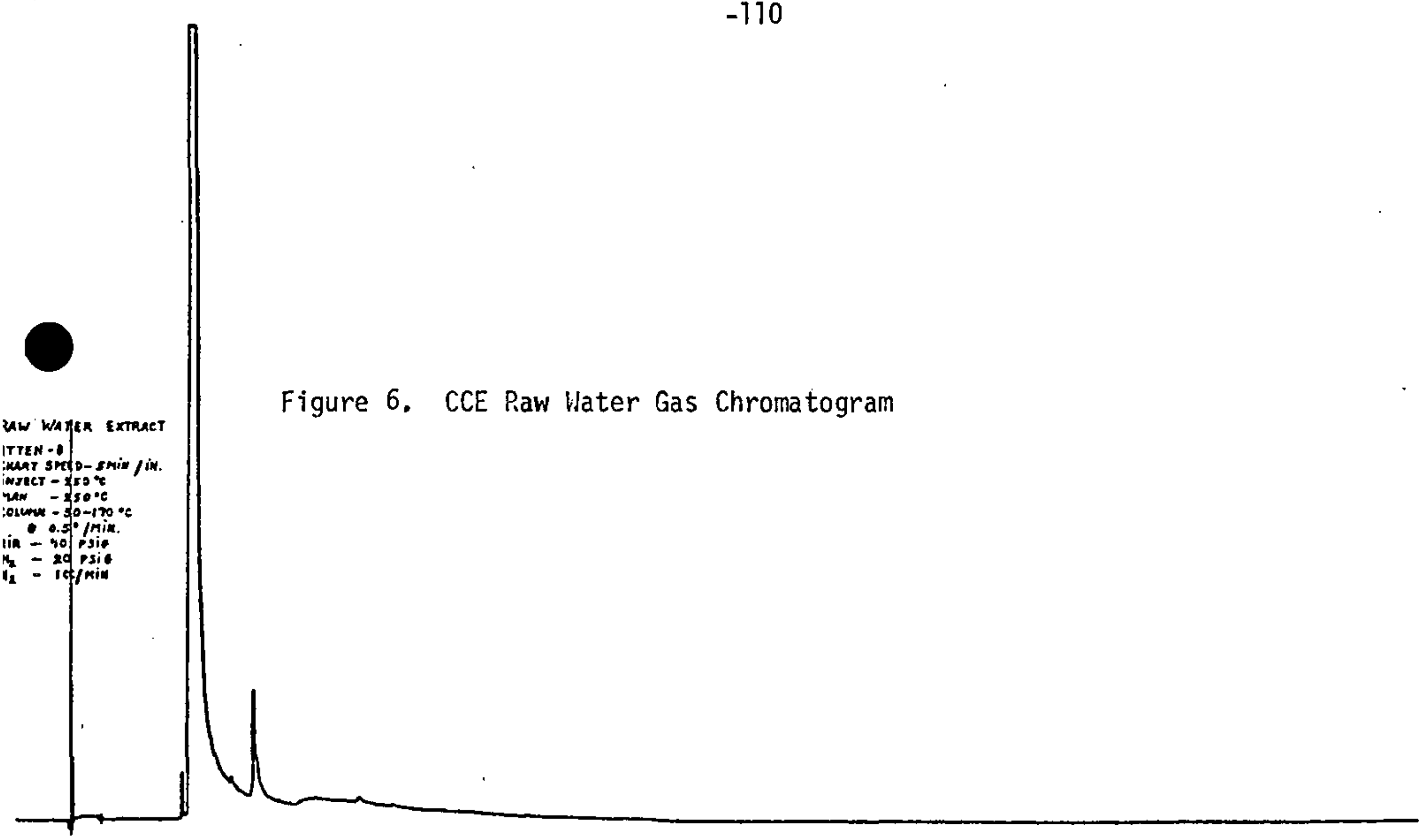


Figure 6. CCE Raw Water Gas Chromatogram

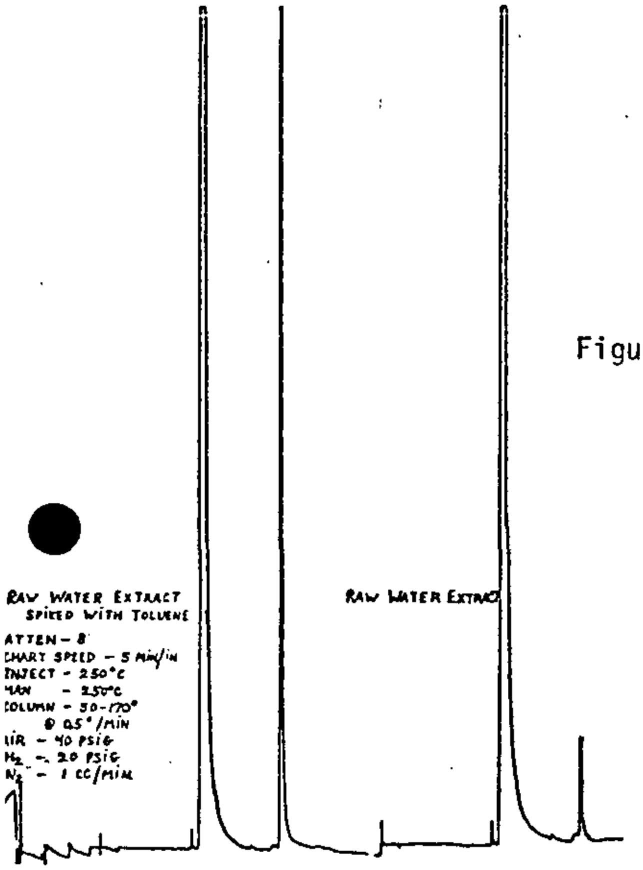


Figure 7. Identification of Toluene in Raw Water by Comparison of Spiked and Unspiked CCE Gas Chromatograms.

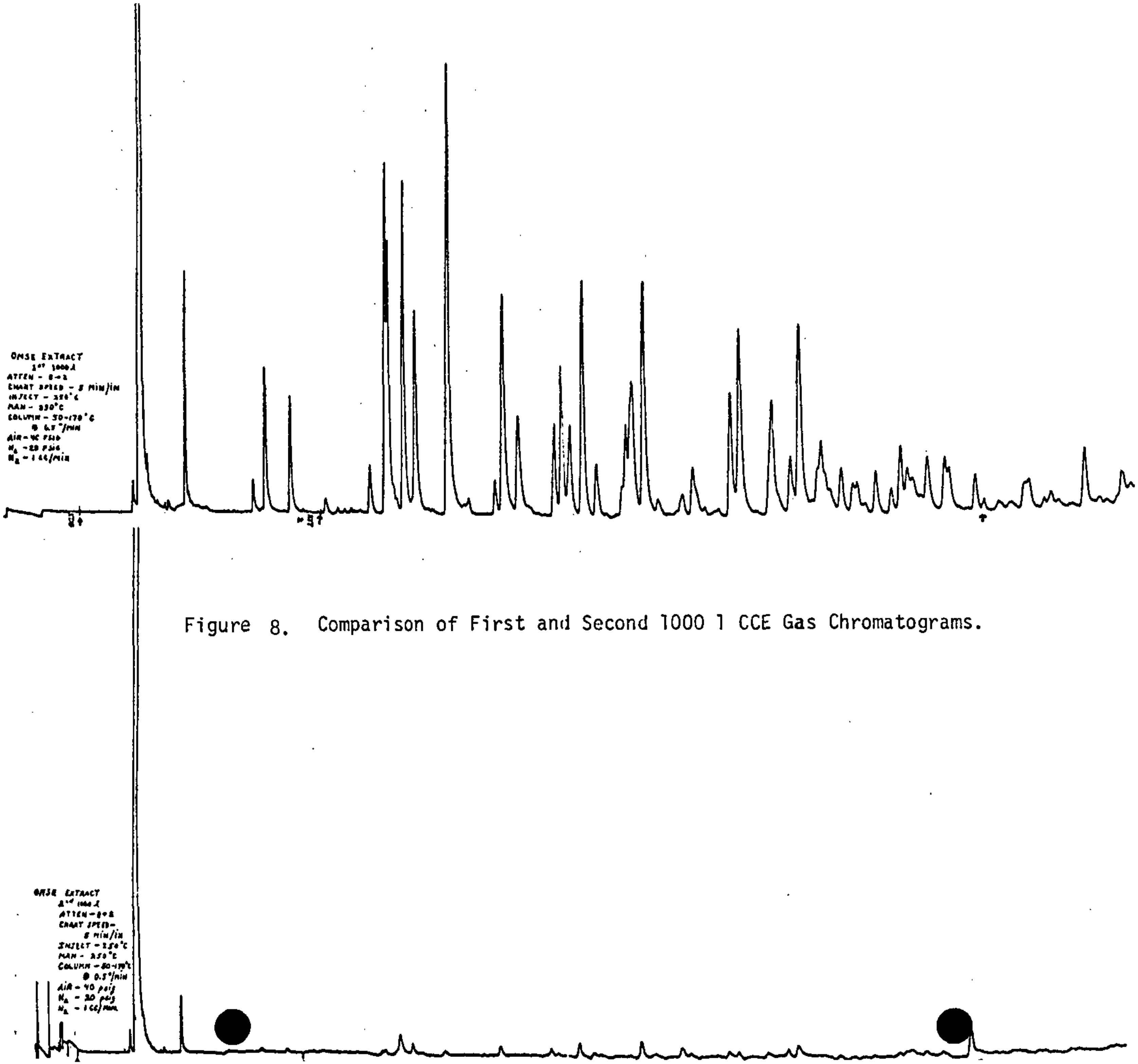


Figure 8. Comparison of First and Second 1000 l CCE Gas Chromatograms.

Because of the rapidly diminishing concentrations of organics in the water, it would be presumptive to attempt to determine initial amounts of toluene and n-dodecane resulting from outboard motor usage. The toluene peak area present in the second 1,000 l OMSE-water extract is nearly equivalent to that found in the raw water extract chromatogram and it is also concluded that little toluene remained after six days.

One striking result observable from comparison of the two OMSE-water extract chromatograms is the persistence of the compound immediately preceeding the n-dodecane peak. Although the unknown compound is initially present in relatively small amounts, its concentration in the OMSE-water has been reduced only slightly throughout the 12 day CAM procedure. Since it is the only compound present that has not been altered appreciably by natural purification, it appears that the stability of organic compounds in aqueous systems is not merely due to the aromatic or aliphatic nature of the compound, but also due to the specific physical properties of that compound, i.e. the affinity for a polar solvent such as water. It is suspected that the mechanism for the reduction in concentration of the organics released as a result of outboard motor operation lies in the knowledge that the majority of the organic compounds present in OMSE-water have densities less than water and are either slightly soluble or insoluble in water. It is therefore postulated that the compounds rapidly rise to the surface and are removed by evaporation, aided by wind initiated surface turbulence.

Fate of Organic Carbon Resulting from Outboard Motor Operation in the Field Test Area.

Water samples for Trial I were obtained at each of four test sites and the control volume designated by "x" on Figure 3. The water was sampled at depths of 1/4, 6, 18 and 48 inches below the surface on six occasions over a period of 12 days and evaluated for Total Organic Carbon. The results are summarized in Table 3,

Table 3. OMSE Hydrocarbon Persistence Data at Various Sampling Depths for Trial I.

DAY	TOP		6"		18"		48"		CONTROL	
	mg carbon/l		mg carbon/l		mg carbon/l		mg carbon/l		mg carbon/l	
	TC	TOC	TC	TOC	TC	TOC	TC	TOC	TC	TOC
0	20.5	10.2	21.4	11.0	20.9	11.2	21.0	10.5	26	16
1	26.0	17.0	25.0	16.0	25.7	15.8	26.5	15.5	--	--
3	25.5	15.2	25.7	13.0	25.7	15.0	25.3	12.0	26	14
6	25.3	12.4	24.7	11.5	24.0	12.2	23.7	10.8	21	11
9	26.0	13.0	23.7	10.0	23.0	10.3	22.5	9.3	21	11
12	23.0	11.0	22.7	9.8	23.0	11.0	23.0	10.2	23	15

and represent average values obtained from the four experimental test sites. The fact that the TOC values have returned to normal levels at all depths by the end of the 12 day sampling period is clearly demonstrated in Figure 9. As shown in Figure 10, surface TOC values were consistently greater than or equal to any other depth. This tends to support the assumption that the majority of hydrocarbons emitted as a result of outboard motor operation, being lighter than water, rapidly rise to the surface. It should be pointed out that the control volume did not prove to be watertight and control results were thereby somewhat invalidated. The control values reported were those of the motor pond outside of the test area.

One distinct result can be seen from Figure 10 whereby the TOC at 18 inches is consistently greater than the 6 and 48 inch TOC values. This is approximately the depth of the outboard motor propeller during normal operation at the test site. It is also possible that the action of the propellers on the organic compounds released to the water could to some degree, have resulted in an emulsified subsurface region. This would lead to a slower rate of separation from the receiving water at the 18 inch depth.

The results of Trial II are summarized in Table 4 and presented graphically in Figures 11 and 12. Once again, it is plainly evident that TOC concentrations have returned to initial levels after 12 days. Analysis of Figure 12 also shows that, after 7 days, an increase in TOC values occurs in the 12 and 18 inch depth region and that the surface TOC value becomes greater than those obtained at all depths below the surface. It is also evident that the water samples obtained on day 1 showed the greatest TOC concentration in the 12 and 18 inch depth region. This further supports the contention that the organic compounds released below the surface are suspended, in part, at the depth of the outboard motor propeller.

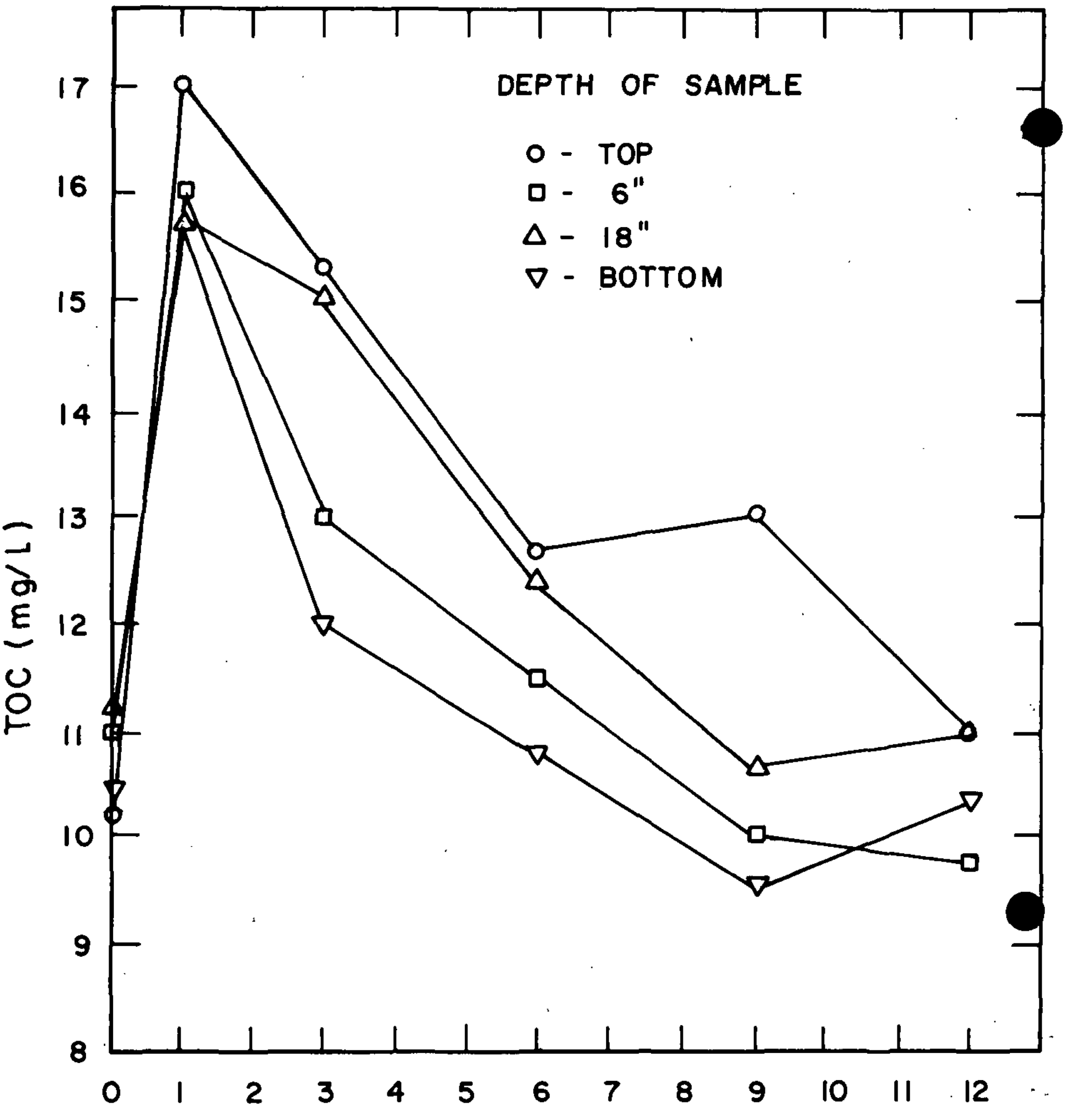


Figure 9. Changes in TOC with Time in OSME-Water Field Studies: Trial I.

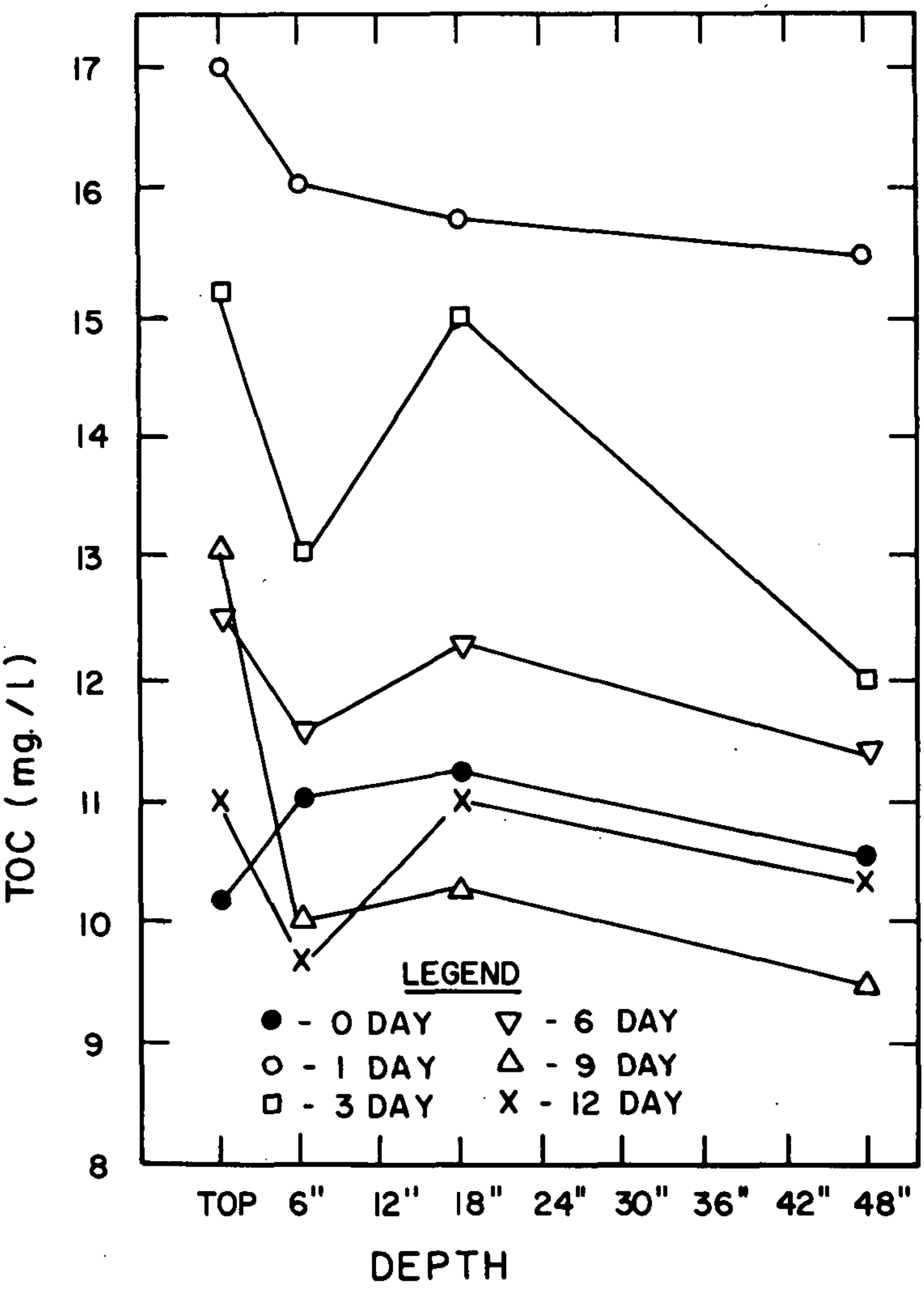


Figure 10. Variation of TOC with Depth in OSME-Water Field Studies: Trial I.

Table 4. OMSE Hydrocarbon Persistence Data at Various Sampling Depths for Trial II.

DAY	TOP		6"		12"		18"		48"		CONTROL	
	mg carbon/l		mg carbon/l		mg carbon/l		mg carbon/l		mg carbon/l		mg carbon/l	
	TC	TOC	TC	TOC	TC	TOC	TC	TOC	TC	TOC	TC	TOC
0	23.0	10.0	21.0	10.0	22.0	9.5	23.0	9.0	22.0	9.0	--	--
1	29.0	15.5	31.0	16.5	31.7	16.8	31.7	16.8	31.3	16.0	24	12
3	30.5	15.5	29.7	15.7	29.5	15.0	29.5	14.5	29.7	14.0	25	15
7	27.5	12.5	26.5	11.8	26.5	12.1	26.7	12.0	26.5	12.0	24	13
11	25.7	10.8	24.5	9.8	24.7	10.3	25.0	10.3	24.3	9.8	23	13

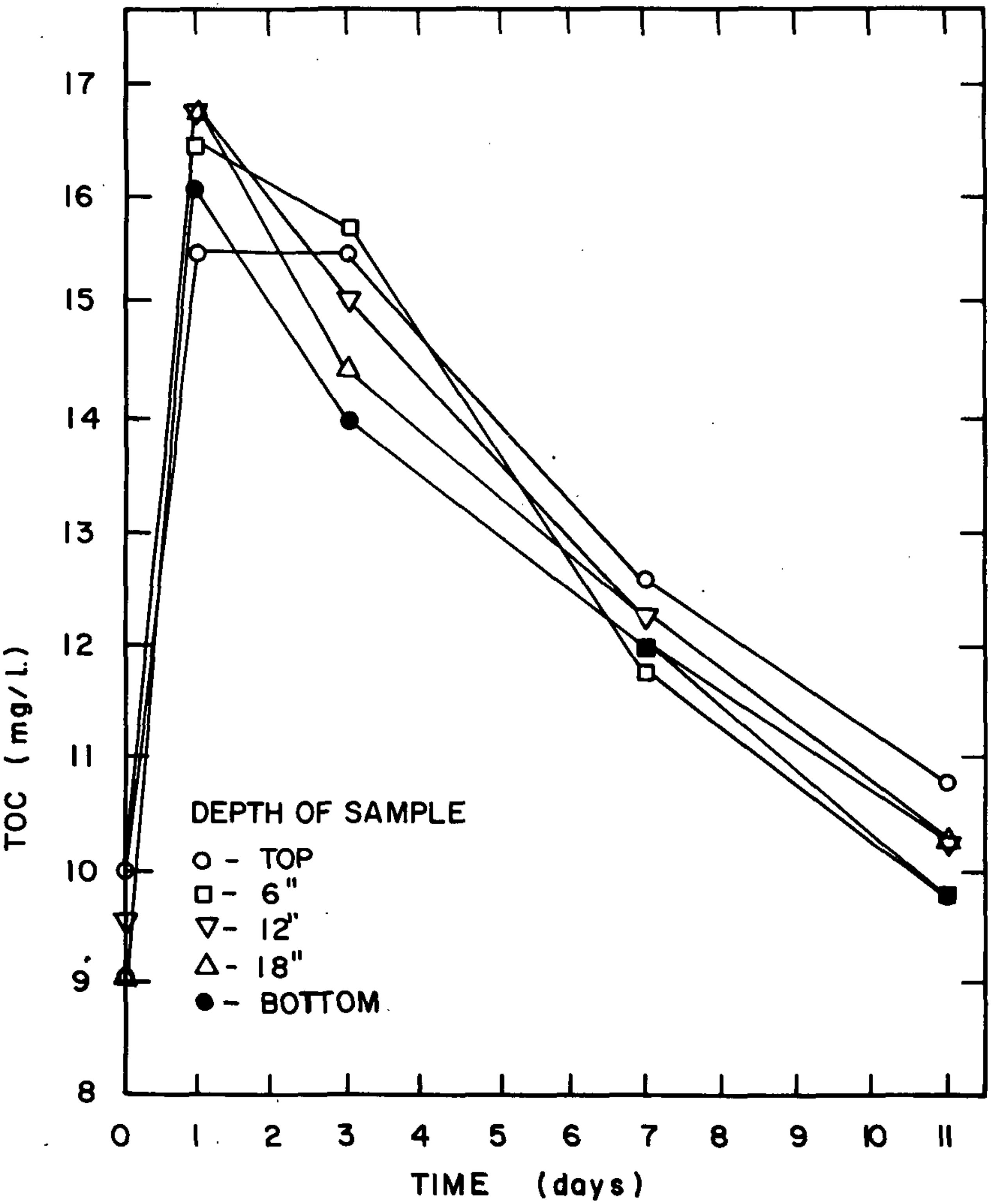


Figure 11. Changes in TOC with Time in OSME-Water Field Studies: Trial II.

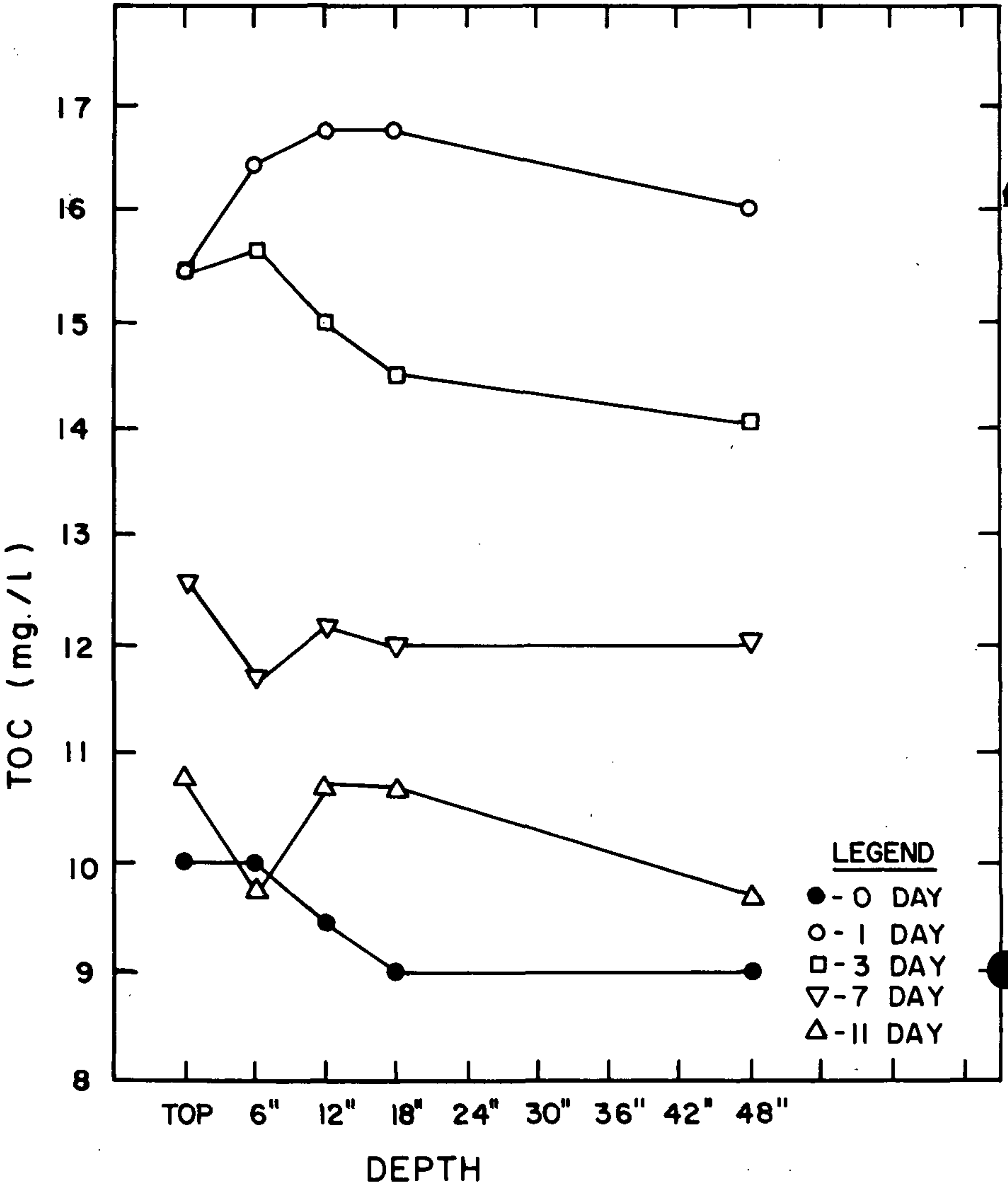


Figure 12. Variation of TOC with Depth in OSME-Water Field Studies: Trial II.

These same Trial II OMSE-water samples were analyzed for turibidity as shown by Table 5 and Figure 13 and 14. Curves of the same characteristic shape as those obtained by TOC analysis resulted, demonstrating a direct correlation between TOC and turbidity in the operation of outboard motors. One notable difference is the rapid initial decrease in turbidity within the first three days after outboard motor operation, is shown in Figure 13. This is probably due to the settling of bottom sediments that had been suspended as a result of propeller turbulence. After the third day, a linear reduction in turbidity occurs, paralleling that of Trial II TOC results. This turbidity is considered, therefore, to be solely due to organic compounds in the OMSE-water.

Table 5. Analysis of Turbidity in OMSE-Water

DEPTH	0 DAY	1 DAY	3 DAY	7 DAY	11 DAY
TOP	38	101	78	74	68
6 inches	39	115	84	68	52
18 inches	38	115	92	77	62
48 inches	38	116	92	68	54

*Jackson Turbidity Units

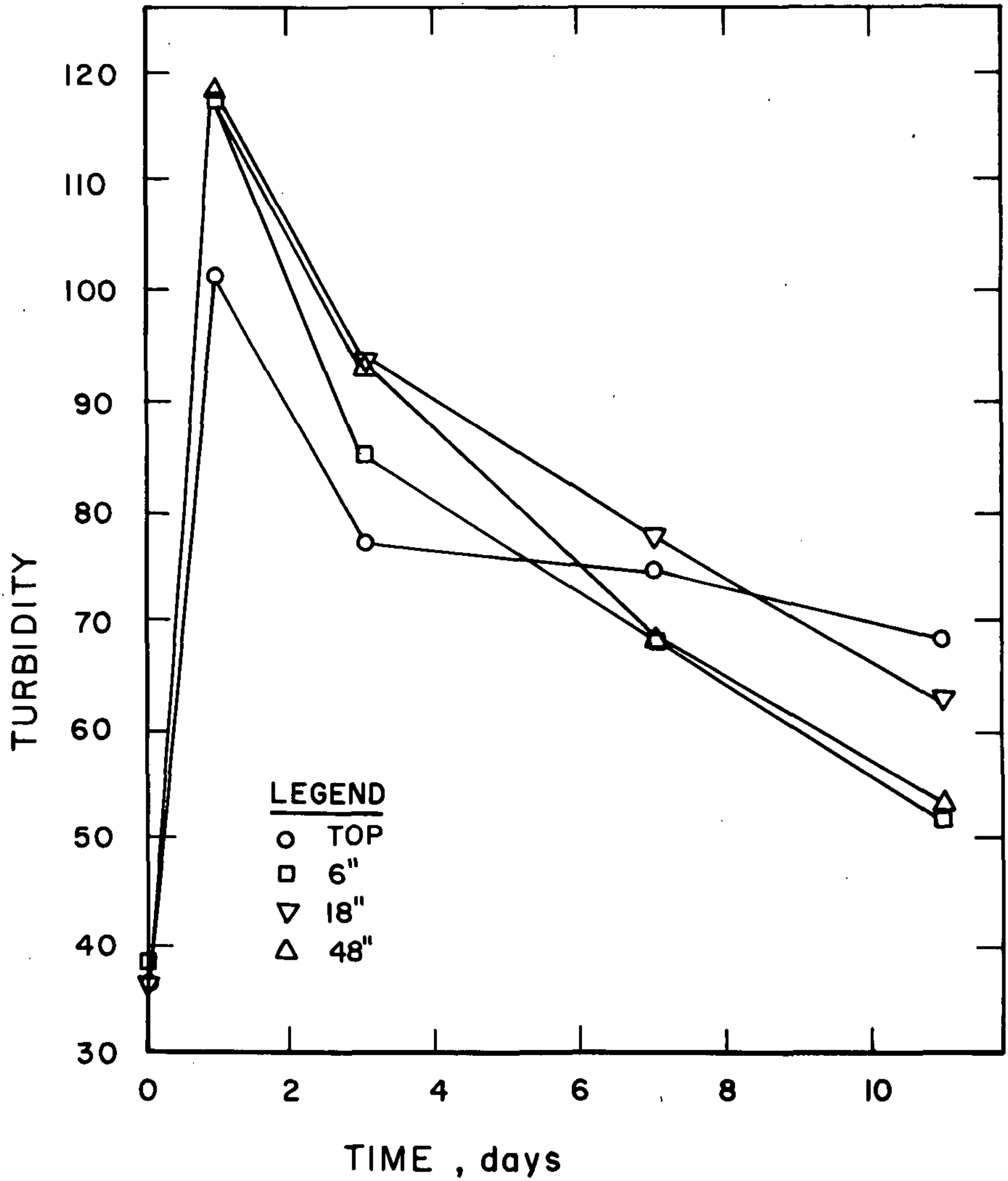


Figure 13. Changes in Turbidity with Time in OSME-Water Field Studies.

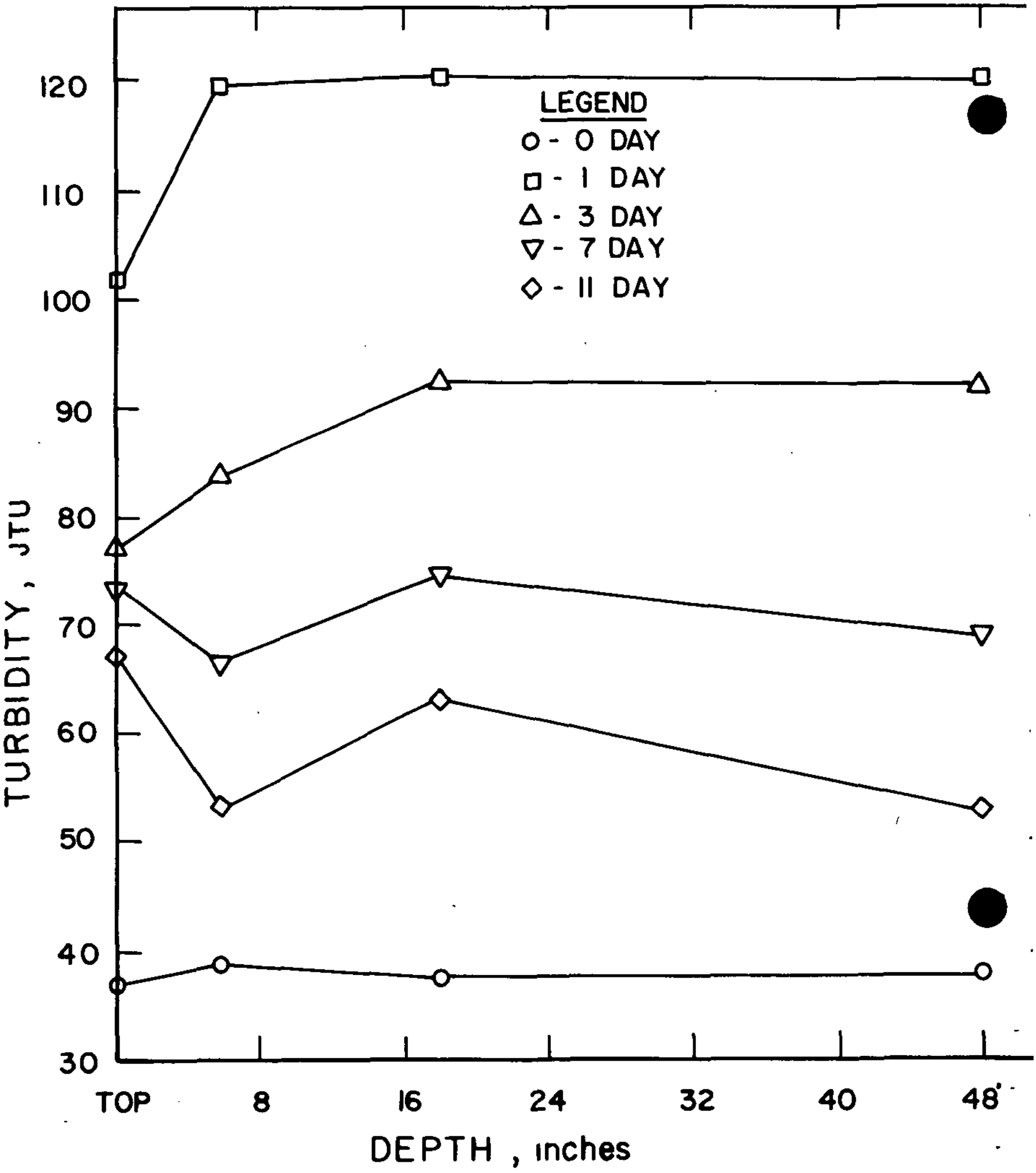


Figure 14. Variation of Turbidity with Sampling Depth in OSME-Water Field Studies.

GENERAL DISCUSSION

From calculation of the volume of the tank employed by Shuster (4), maximum and minimum dilution volumes of water/fuel combusted were 14,400/l to 5,570/l respectively. The ratio of water to gasoline volumes used in this study was 6,420/l. One would expect, therefore, comparable TOC values between the two studies. Such was not the case. Shuster reports that, irregardless of the quantity of fuel combusted, the TOC values remained relatively constant. This does not seem reasonable since one would expect a larger TOC concentration with increased outboard motor usage. This relatively constant TOC value, reported to be approximately 4 mg carbon/l, was only one-half as great as the TOC increase reported by this study, although dilution volumes were comparable in most cases.

Another point of interest is the high inorganic carbon concentration reported by the Shuster study, values which were approximately 75-80% of the Total Carbon concentrations obtained. The study by Kuzminski, et al. (9) demonstrates Total Inorganic Carbon increase of approximately 4 mg carbon/l using a water to gasoline dilution ratio of 400/l. In this study, Total Inorganic Carbon values increased approximately 3 mg carbon/l while TOC values increased 7-8 mg carbon/l. Therefore, results from this study and that of Kuzminski, et al. (9) show that from 70-90% of the Total Carbon increase is due to organic compounds present in OMSE-water rather than inorganic compounds such as CO_2.

As mentioned previously, English, et al. (3) performed several CCE determinations as a means of measurement of organics resulting from outboard motor operation. While persistence studies of these hydrocarbons in OMSE-water were not intended in the objectives of the paper by English, et al., it was observed from reported data that if operation of the motors were halted for approximately 18 days, the pond would return to its original state. Because it takes nearly six days to complete the CAM procedure, it is apparent that after a 12 day lull in operation, little, if any, organic compounds remained in the motor pond. Otherwise, the 12 to 18 day period would have yielded some measurable CCE increase above the 0.5 mg carbon/l base level. It was also noted that the CCE of both this study and that of English, *et al*. had an odor resembling musty, decaying vegetation. This odor was discovered in both the raw water and OMSE-water extracts.

CONCLUSIONS

CONCLUSIONS

1. The efficiency of recovery for toluene and n-dodecane utilizing the CAM were 54.3% and 18.7%, respectively, under the conditions of this experiment.
2. Due to the rapid disappearance of organic compounds from OMSE-water under field conditions, it was neither possible to quantify toluene and n-dodecane nor determine the relative persistence of aromatic vs. aliphatic compounds in a natural body of water.
3. The selective accumulation of an organic compound in OMSE-water is not entirely dependent upon the aliphatic or aromatic nature of that compound, as illustrated by the persistence of only one compound in the CCE chromatograms.
4. The field test site required 12 days to return to initial TOC levels after extremely heavy outboard motor usage.
5. Surface (1/4 inch depth) TOC values were generally greater than sub-surface values, indicating that the disappearance of the organic compounds emitted to the recipient water was due to the fact that these compounds are relatively insoluble in and less dense than water.
6. There is definite evidence that organic compounds are partially suspended in OMSE-water at the depth of the outboard motor propeller.
7. Analysis of water samples for turbidity showed a sharp initial decrease, presumably due to the settling of suspended bottom sediments, followed by a gradual linear decrease which closely parallels decline in TOC with time.

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LITERATURE CITED

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