
Reports

1-26-1982

Hydrocarbon fuel chemistry : sediment water interaction

William G. MacIntyre
Virginia Institute of Marine Science

C. L. Smith
Virginia Institute of Marine Science

P. O. deFur
Virginia Institute of Marine Science

C. W. Su
Virginia Institute of Marine Science

Follow this and additional works at: <https://scholarworks.wm.edu/reports>



Part of the [Environmental Chemistry Commons](#)

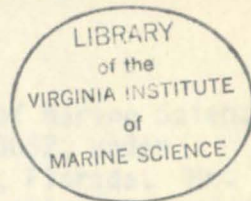
Recommended Citation

MacIntyre, W. G., Smith, C. L., deFur, P. O., & Su, C. W. (1982) Hydrocarbon fuel chemistry : sediment water interaction. Virginia Institute of Marine Science, William & Mary. <https://scholarworks.wm.edu/reports/2354>

This Report is brought to you for free and open access by W&M ScholarWorks. It has been accepted for inclusion in Reports by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.

VIMS
GC
380.2
074 M32
1981

JUL 17 1982



HYDROCARBON FUEL CHEMISTRY
SEDIMENT WATER INTERACTION

Prepared by:

W. G. MacIntyre, C. L. Smith, P. O. deFur and C. W. Su

Virginia Institute of Marine Science
College of William and Mary
Gloucester Point, Virginia 23062

Dated: January 26, 1982

Final Report on USAF/AFESC
Contract No. F08635-81-C-0019

VIMS

QD

341

H9M3

PREFACE

This program was conducted by the Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, Virginia 23062, under Contract No. F08635-81-C-0019 with AFESC/RDVC, Tyndall AFB, Florida. Mr. Thomas B. Stauffer managed the program for AFESC. Work on this program was done in the period from December 1, 1980 to December 1, 1981.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

2.	ADSORPTION CONSTANTS AT 20°C AND NATURAL pH	17
3.	DISCUSSION OF ADSORPTION CONSTANTS AS APPLIED TO HYDROCARBON MIXTURES	26
4.	ADSORPTION CONSTANTS AT OTHER pH AND TEMPERATURE VALUES	39
5.	VARIATION OF ADSORPTION CONSTANTS WITH AQUEOUS ORGANIC CONTENT	44
6.	REVERSIBILITY OF ADSORPTION	48
7.	MODEL PHE SPILL EXPERIMENTS	49
IV	CONCLUSIONS	51
V	RECOMMENDATIONS	62
VI	REFERENCES	63
VII	APPENDIX	
	Microfilm of Figures	

TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
I	INTRODUCTION.	1
II	MATERIALS AND METHODS	9
III	RESULTS AND DISCUSSION.	16
	1. ISOTHERM MEASUREMENTS	16
	2. ADSORPTION CONSTANTS AT 20°C AND NATURAL pH	17
	3. DISCUSSION OF ADSORPTION CONSTANTS AS APPLIED TO HYDROCARBON MIXTURES	36
	4. ADSORPTION CONSTANTS AT OTHER pH AND TEMPERATURE VALUES.	39
	5. VARIATION OF ADSORPTION CONSTANTS WITH ADSORBENT ORGANIC CONTENT	44
	6. REVERSIBILITY OF ADSORPTION	48
	7. MODEL FUEL SPILL EXPERIMENTS.	48
IV	CONCLUSIONS	51
V	RECOMMENDATIONS	52
VI	REFERENCES.	53
VII	APPENDIX.	
	Microfilm of Isotherms.	

LIST OF FIGURES

<u>Figures</u>	<u>Title</u>	<u>Page</u>
1	Solubility of Compounds from Fuel Mixtures vs Adsorption Constants of these Compounds on Marsh Sediment in Distilled Water.	8
2	Apparatus for Preparation of Aqueous Solutions of Hydrocarbons	11
3	Spurge and Trap Apparatus for Collection of Volatile Hydrocarbons from Water Solution	13
4	Selected Isotherms with Corresponding r^2 Values.	18
5	OPS Simulation Mixture in Distilled Water	27
6	OPS Simulation Mixture in Salt Water.	28
7	OPS Simulation Mixture in Distilled Water	29
8	OPS Simulation Mixture in Salt Water.	30
9	OPS Simulation Mixture in Distilled Water	31
10	OPS Simulation Mixture in Salt Water.	32
11	OPS Simulation Mixture in Distilled Water	33
12	OPS Simulation Mixture in Salt Water.	34
13	Absorption Constants for Dinitrofluorobenzene at 25°C and Natural pH Measured in Different Fuel Mixtures at 1-2 %/cc and 0-25 %/cc	38
14	Absorption Constants for Dinitrofluorobenzene at 25°C and Natural pH Measured in Different Fuel Mixtures at 1-2 %/cc and 1-25 %/cc	39
15	OPS in Distilled and Salt Water	40
16	High Density Fuels in Distilled Water	41
17	Effect of pH and Temperature on OPS Simulation Mixture.	42
18	Effect of pH and Temperature on OPS Simulation Mixture.	43
19	Effects of Reduction in Organic Carbon Content.	46
20	Comparison of Adsorption and Desorption K Values.	49

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Composition of Synthetic Fuel Mixtures.	2
2	Composition of High Density Fuels	5
3	Natural Sediment Characteristics.	10
4	JP4 Shale Simulation Mixture in Distilled Water	24
5	JP4 Petroleum Simulation Mixture in Distilled Water	25
6	JP4 Petroleum Simulation Mixture in Salt Water.	26
7	JP5 Simulation Mixture in Distilled Water	27
8	JP5 Simulation Mixture in Salt Water.	28
9	JP8 Simulation Mixture in Distilled Water	29
10	JP8 Simulation Mixture in Salt Water.	30
11	MF2 Simulation Mixture in Distilled Water	31
12	MF2 Simulation Mixture in Salt Water.	32
13	Adsorption Constants for 2-Methylnaphthalene at 20°C and Natural pH Measured in Different Fuel Mixtures at S=0 ‰ and S=35 ‰	34
14	Adsorption Constants for Dimethylnaphthalenes at 20°C and Natural pH Measured in Different Fuel Mixtures at S=0 ‰ and S=35 ‰.	35
15	JP9 in Distilled and Salt Water	37
16	High Density Fuels in Distilled Water	38
17	Effect of pH and Temperature on JP5 Simulation Mixture.	40
18	Effect of pH and Temperature on JP8 Simulation Mixture.	42
19	Effects of Reduction in Organic Carbon Content.	46
20	Comparison of Adsorption and Desorption K Values.	49

SECTION I
INTRODUCTION

The objective of this program was to determine the effect of sediments on aqueous solutions of selected United States Air Force (USAF) hydrocarbon fuels. Effects of sediment type, organic carbon content, pH, temperature and salinity on interaction of dissolved hydrocarbons with sediment were studied. The results of this work can be used to estimate the role of sediment-hydrocarbon interaction terms in fate models of aqueous systems, such as the Environmental Protection Agency "EXAMS" model.

Adsorption of hydrocarbons on sediments was the major interaction studied, and the possible formation of chemical reaction products due to oxidation, photolysis, or surface catalysis was investigated. AF distillate fuels (JP-4 shale, JP-4 petroleum, JP-5, JP-8 and DMF2) and high density fuels (JP-9, JP-10, RJ-5 and RJ-6) were used in this program. Since the distillate fuels are extremely complex mixtures which are not completely separable for analysis, 15 component hydrocarbon mixtures were used to simulate these fuels. Particular components were selected spanning the boiling range of the real fuel. These components occur in the real fuel and represent the hydrocarbon compound classes. Compositions of simulated fuel mixtures are given in Table 1, which also shows water solubility of each compound determined at a hydrocarbon mixture to water ratio of 1:1000.

The high density fuels are simple mixtures of a few aliphatic hydrocarbons, and complete fuels were used in all experiments. Composition of the high density fuels is shown in Table 2. Three sediments and three clays were taken as adsorbents. Clays were included because they are major mineral constituents of sediments, and they provide reference materials available for further studies of aqueous solutions of hydrocarbons with sediments.

There has been little previous study of the interaction of aqueous hydrocarbon solutions with clays and sediments. In reviews by Theng (1974) and Van Olphen (1977), these interactions are mentioned, but most work has been done with polar organic molecules such as pesticides, herbicides, and humates which are important to agricultural chemists. Enough literature exists to establish that sediments and clays do interact with hydrocarbon solutions, but interactions with hydrocarbon mixtures in water solutions have not been studied. The most significant publications on interaction of hydrocarbons with sediments are by Means et al. (1980a, 1980b) and Karickhoff et al. (1979). Rogers et al. (1980) studied the interaction of benzene with montmorillonite clay. The information obtained in the present work on

TABLE 1. COMPOSITION OF SYNTHETIC FUEL MIXTURES.

JP4 Petroleum		
<u>Component</u>	<u>Wt % in Mixture</u>	<u>Solubility (mg/l)</u>
n-Hexane	5.4	undetermined
Cyclohexane	6.4	0.89
n-Heptane	5.6	0.036
Methylcyclohexane	6.3	0.32
Toluene	7.1	14.01
n-Octane	5.8	undetermined
Ethylcyclohexane	6.5	undetermined
p-Xylene	7.1	5.16
Isopropylbenzene	7.1	2.55
1,3,5-Trimethylbenzene	7.1	2.84
Indan	7.9	9.14
Naphthalene	6.6	11.40
2-Methylnaphthalene	8.2	3.02
n-Tetradecane	6.3	<.001
2,3-Dimethylnaphthalene	6.7	undetermined

JP4 Shale		
<u>Component</u>	<u>Wt % in Mixture</u>	<u>Solubility (mg/l)</u>
2-Methylpentane	5.5	0.68
Benzene	7.3	53.0
n-Heptane	5.7	0.074
2,2,4-Trimethylpentane	5.8	0.136
n-Octane	5.9	0.085
Ethylcyclohexane	6.6	0.233
Ethylbenzene	7.2	14.4
m-Xylene	7.3	14.0
n-Butylbenzene	7.2	0.87
1,2,4,5-Tetramethylbenzene	6.4	1.54
Tetralin	8.1	6.49
n-Dodecane	6.3	<0.001
2-Methylnaphthalene	8.3	2.60
Biphenyl	6.2	5.13
2,6-Dimethylnaphthalene	6.3	0.37

N.D. = below detection limit (0.005 mg/l)

TABLE 1. COMPOSITION OF SYNTHETIC FUEL MIXTURES (CONTINUED).

JP5		
<u>Component</u>	<u>Wt % in Mixture</u>	<u>Solubility (mg/l)</u>
1,3,5-Trimethylbenzene	7.0	2.72
n-Decane	5.9	N.D.
cis-Decalin	3.6	N.D.
Trans-Decalin	3.5	N.D.
n-Undecane	6.0	N.D.
1,2,4,5-Tetramethylbenzene	6.5	1.24
1,2,3,4-Tetramethylbenzene	7.3	1.84
Tetralin	7.9	3.27
Naphthalene	6.5	6.21
n-Dodecane	6.1	N.D.
2-Methylnaphthalene	6.1	1.58
n-Tridecane	6.1	N.D.
Biphenyl	6.5	1.15
2,6-Dimethylnaphthalene	6.4	0.37
2,3-Dimethylnaphthalene	6.5	0.42
n-Pentadecane	6.2	N.D.

N.D. = below detection limit (0.005 mg/l)

JP8		
<u>Component</u>	<u>Wt % in Mixture</u>	<u>Solubility (mg/l)</u>
p-Ethyltoluene	6.7	3.12
1,2,4-Trimethylbenzene	6.9	3.47
Indan	7.5	6.93
n-Undecane	5.8	N.D.
n-Dodecane	5.8	N.D.
1-3,5-Triethylbenzene	6.8	0.14
2-Methylnaphthalene	6.3	1.53
1-Methylnaphthalene	7.8	2.03
Phenylcyclohexane	7.4	0.19
1,3,5-Triisopropylbenzene	6.6	N.D.
2-Ethyl naphthalene	7.8	0.53
n-Tetradecane	6.0	N.D.
2,3-Dimethylnaphthalene	6.3	0.45
4-Methylbiphenyl	6.3	0.33
n-Pentadecane	6.0	N.D.

N.D. = below detection limit (0.005 mg/l)

TABLE 1. COMPOSITION OF SYNTHETIC FUEL MIXTURES (CONTINUED).

Component	MF2	
	Wt % in Mixture	Solubility (mg/l)
n-Undecane	6.3	N.D.
1,2,3,4-Tetramethylbenzene	7.7	2.49
Tetralin	8.3	4.03
n-Dodecane	6.4	N.D.
1-Methylnaphthalene	8.6	3.14
Biphenyl	4.3	1.07
n-Tetradecane	6.5	N.D.
1,3-Dimethylnaphthalene	8.6	0.82
2,3-Dimethylnaphthalene	4.3	0.43
n-Pentadecane	6.6	N.D.
2,3,5-Trimethylnaphthalene	8.6	0.30
Fluorene	4.4	0.55
3,3'-Dimethylbiphenyl	8.5	0.16
n-Heptadecane	6.6	N.D.
Phenanthrene	4.3	0.21

N.D. = below detection limit (0.005 mg/l)

Component	Wt % in Mixture	Solubility (mg/l)
Tetrahydro-2H-pyridine	46.2	1.85
Dehydro-THP	14.1	1.13
THP	16.4	1.82
THP	24.3	1.04

THP = Hexahydro-2H-pyridine
 Dehydro-THP = Hexahydro-2H-pyridine
 Dehydro-THP = THP-2H

TABLE 2. COMPOSITION OF HIGH DENSITY FUELS.

JP10

<u>Component</u>	<u>Wt % in Original Fuel</u>	<u>Solubility (mg/l)</u>
Tetrahydrodicyclopentadiene	100	1.85

RJ5

<u>Component</u>	<u>Wt % in Original Fuel</u>	<u>Solubility (mg/l)</u>
Dehydro-HNN	8.4	.015
HXX	15.1	.028
HNN	71.4	.135

JP9

<u>Component</u>	<u>Wt % in Original Fuel</u>	<u>Solubility (mg/l)</u>
Tetrahydrodicyclopentadiene	58.4	1.45
HNN	28.5	0.038

RJ6

<u>Component</u>	<u>Wt % in Original Fuel</u>	<u>Solubility (mg/l)</u>
Tetrahydrodicyclopentadiene	46.2	.85
Dehydro-HNN	14.1	.015
HXX	15.4	.022
HNN	24.3	.045

HXX = Hexacyclic-exo-exo-dihydrodinorbornadiene
HNN = Hexacyclic-endo-endo-dihydrodinorbornadiene
Dehydro-HNN = HNN-2H

hydrocarbon fuel component mixtures is new and can only be compared in broad outline with published results.

Physical adsorption on the solid is the major interaction between hydrocarbon fuel components and clays or sediments in water. Chemisorption, in which a solute forms chemical bonds with the surface, is unlikely because the hydrocarbons do not have charges or directed bonding orbitals for strong bond formations. It is probable that London-van der Waals forces and hydrocarbon-water interactions cause the adsorption of hydrocarbons by clays and sediments. Aromatic hydrocarbons may form some association of the delocalized π electrons with mineral surfaces, but strong bonds should not be formed.

Reactions of hydrocarbons from USAF fuels such as decomposition or oxidation on the surface of sediments are not expected to be significant over short-time intervals without enzymatic catalysis (bacterial degradation). However, it is possible that some highly strained cyclic compounds may oxidize quite rapidly.

Adsorption of hydrocarbons from aqueous solution is a complex process whose equilibrium thermodynamics is described by Stumm and Morgan (1981). There are actually two molecules adsorbing on the particular mineral surface, the hydrocarbon and water, which compete for adsorption sites. In solution, the hydrocarbon molecules are surrounded in a somewhat ice-like cage of water molecules.

The free energy of adsorption of a hydrocarbon is given by:

$$\Delta G_{\text{abs}}^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ} - \Delta G_{\text{Solv}}^{\circ}$$

Where $\Delta G^{\circ}_{\text{Solv}}$ is the free energy of hydration of the hydrocarbon molecule in solution, ΔG_1° is the free energy of adsorption of unhydrated hydrocarbon and ΔG_2° is the free energy of hydration of the hydrocarbon molecule on the solid adsorbent. Hydrocarbons which are less soluble in water tend to adsorb more strongly because they are less easily hydrated. These generalizations do not indicate detailed mechanics of the process of adsorption of a hydrocarbon from water solution on a mineral surface. Details of interactions between a clay and a single hydrocarbon compound in water are not known. The clay minerals contain many different surface sites and include many organic and inorganic impurities. Hydration of the mineral surface and the nature of hydrocarbon adsorption sites is unknown. The situation becomes even more complex when real sediments are used as adsorbents for several hydrocarbons from water. Determination of the mechanism of adsorption in this situation cannot be done by existing methods.

In order to obtain information to describe adsorption of hydrocarbons by sediments following fuel releases, an empirical approach based on equilibrium thermodynamic analysis is used. The object of this analysis is determination of an adsorption isotherm which relates the concentration of single hydrocarbon in the water phase with the amount of the hydrocarbon adsorbed on the sediment at constant temperature. Each point on an adsorption isotherm is defined by an equilibration of a particular system containing a measured

amount of hydrocarbon, water and sediment. Without other information on the mechanism of adsorption, the shape of the isotherm provides only a general description of the adsorption process.

Adsorption isotherms can also be determined with multicomponent hydrocarbon solutions used in place of single hydrocarbon solutes. Since there is no possibility of elucidating mechanics of these complex systems, it is assumed here that all isotherms are linear and obey an equation of the form $C_s/C_w = K_p$, which is a special case of the Freundlich isotherm with K_p having an exponent of unity. Greenland and Hayes (1981) refer to this as a "C type" isotherm. The use of this equation is common to the limited literature on hydrocarbon adsorption, and it holds for adsorption from aqueous solution of several other nonpolar compounds by several adsorbent materials.

In this and earlier works, deviation from linearity of isotherms have been noted in some cases. We have chosen not to fit other isotherm equations in such cases because mechanisms cannot be obtained to justify isotherms, and an exercise in curve fitting is the only product. In all isotherms, a least square line is fitted to the data points and a K_p value calculated. This K_p value has been referred to in the literature as a Freundlich constant, a partition coefficient, and an adsorption constant. The latter term is used in this report.

Measurement of C_w , the solution concentration of hydrocarbons, is direct and described later in this report. C_s , the weight of hydrocarbon per unit weight of adsorbent, was measured indirectly because of difficulties in extraction of volatile hydrocarbon from adsorbent and in separation of all aqueous phase from the adsorbent. The weight of hydrocarbon adsorbed is calculated from the difference between the initial solution concentration and that measured at equilibrium with the adsorbent. This technique has been used by Karickhoff et al. (1979) and many others.

In this work, complete adsorption isotherms were run in both fresh and ocean salinity water at 20°C and natural pH of each adsorbent used. K_p 's at other temperatures and pH values were calculated from single equilibration experiments, assuming isotherm linearity, with the origin being the other point used to establish the slope K_p of the isotherm. Such single data points are sufficient for comparison with the isotherms at 20°C and natural pH.

There is a dependence between solubility of a neutral organic sorbate and its adsorption constant on a substrate, which is often expressed as Traube's rule. In general, K is higher for compounds of low solubility. Figure 1 shows this general relation for the compounds in fuel mixtures used in this program and demonstrates that the relation is only approximate due to apparent specific structural interactions.

K
Marsh

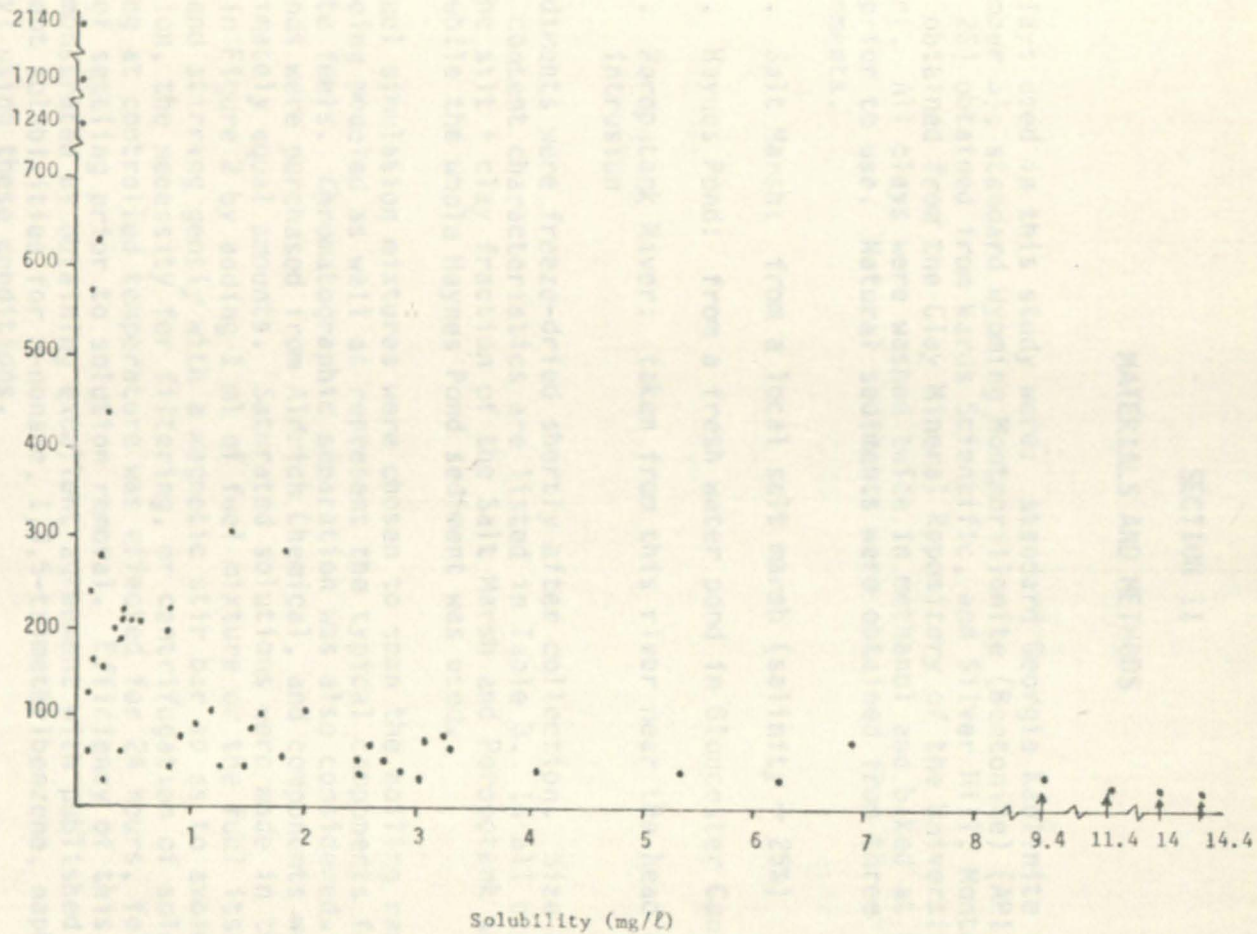


Figure 1. Solubility of Compounds from Fuel Mixture vs Adsorption Constants of these Compounds on Marsh Sediment in Distilled Water.

TABLE 3. NATURAL SEDIMENT CHARACTERISTICS.

SECTION II

MATERIALS AND METHODS

Clays used in this study were: standard Georgia Kaolinite (API Project 49, Number 3); standard Wyoming Montmorillonite (Bentonite) (API Project 49, Number 26) obtained from Wards Scientific, and Silver Hill, Montana; standard Illite obtained from the Clay Mineral Repository of the University of Missouri. All clays were washed twice in methanol and baked at 60°C for 12 hours prior to use. Natural sediments were obtained from three local aquatic environments.

1. Salt Marsh: from a local salt marsh (salinity ~ 25%)
2. Haynes Pond: from a fresh water pond in Gloucester County, Virginia
3. Poropotank River: taken from this river near the head of the salt intrusion

All sediments were freeze-dried shortly after collection. Size and organic carbon content characteristics are listed in Table 3. In all experiments, only the silt + clay fraction of the Salt Marsh and Poropotank sediments were used, while the whole Haynes Pond sediment was used.

Fuel simulation mixtures were chosen to span the boiling range of the fuel being modeled as well as represent the typical components found in the complete fuels. Chromatographic separation was also considered. Standard compounds were purchased from Aldrich Chemical, and components were added in approximately equal amounts. Saturated solutions were made in the apparatus shown in Figure 2 by adding 1 ml of fuel mixture or the fuel itself to 1 g of water and stirring gently with a magnetic stir bar so as to avoid droplet formation, the necessity for filtering, or centrifugation of solutions. Stirring at controlled temperature was effected for 24 hours, followed by 24 hours of settling prior to solution removal. Efficiency of this technique was demonstrated by obtaining excellent agreement with published single component solubilities for n-nonane, 1,3,5-trimethylbenzene, naphthalene and biphenyl using these conditions.

Solutions were delivered into 25 ml Corex centrifuge tubes containing weighed amounts of clay or sediment and the tubes were immediately closed with aluminum foil-lined caps. Volumes of solutions were determined by weighing the tubes before and after solution addition, and all tubes were filled as full as possible to avoid head space loss of the more volatile components. For each isotherm of natural sediments, five different weights of sediment were used, and a control with no sediment was run to obtain

TABLE 3. NATURAL SEDIMENT CHARACTERISTICS.

<u>Sediment</u>	<u>% Gravel</u>	<u>% Sand</u>	<u>% Silt</u>	<u>% Clay</u>
Salt Marsh	.6	81.3	9.8	8.3
Haynes Pond	.7	60.4	18.5	20.4
Poropotank River	.1	82.7	8.5	8.7

	<u>% Organic Carbon Whole Sediment</u>	<u>% Organic Carbon Silt-Clay Fraction</u>
Salt Marsh	0.53	1.83
Haynes Pond	0.59	0.51
Poropotank River	0.67	2.74
Oxidized Salt Marsh		0.42

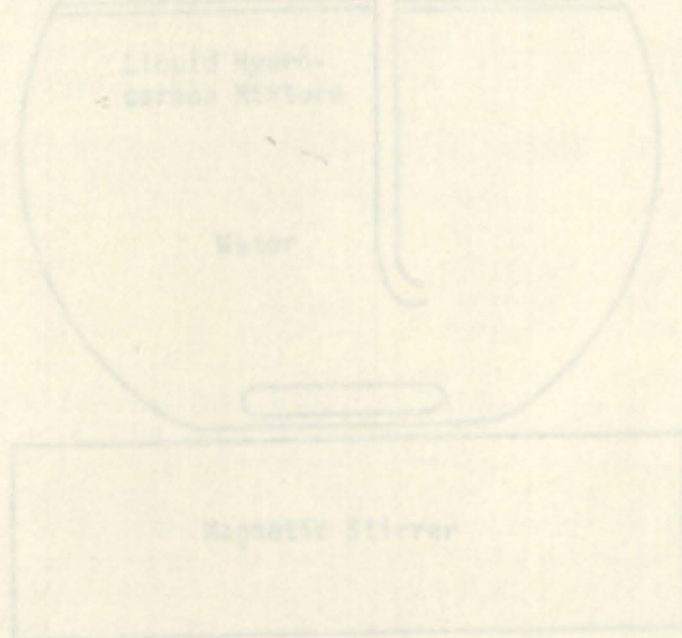


Figure 2. Apparatus for Preparation of Aqueous Solutions of Hydrocarbons.

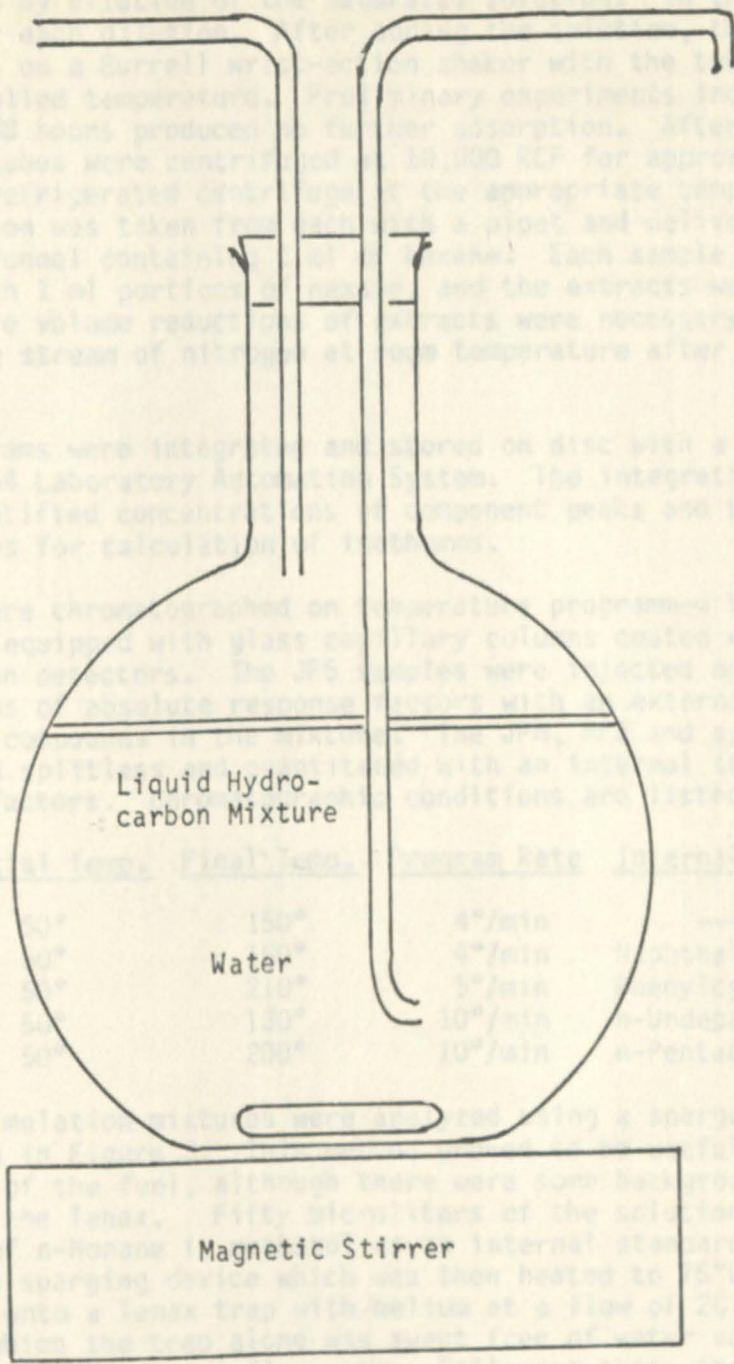


Figure 2. Apparatus for Preparation of Aqueous Solutions of Hydrocarbons.

initial concentrations. The individual clays showed low adsorption even with the maximum possible amount of clay, and, consequently, the concentration of solution was varied by dilution of the saturated solution. In this case, a control was run for each dilution. After adding the solution, the tubes were shaken for 16 hours on a Burrell wrist-action shaker with the tubes inside an incubator at controlled temperature. Preliminary experiments indicated that shaking for 24 to 48 hours produced no further adsorption. After shaking, the equilibration tubes were centrifuged at 10,000 RCF for approximately 30 minutes in an IEC refrigerated centrifuge at the appropriate temperature. Twenty ml of solution was taken from each with a pipet and delivered directly into a separatory funnel containing 1 ml of hexane. Each sample was extracted twice with 1 ml portions of hexane, and the extracts were combined for analysis. Where volume reductions of extracts were necessary, they were done under a gentle stream of nitrogen at room temperature after internal standard addition.

All chromatograms were integrated and stored on disc with a Hewlett-Packard 3354 Laboratory Automation System. The integration program identified and quantified concentrations of component peaks and stored processed data files for calculation of isotherms.

All samples were chromatographed on temperature programmed Varian 3700 gas chromatographs equipped with glass capillary columns coated with SE-52 and flame ionization detectors. The JP5 samples were injected on-column and quantitated by means of absolute response factors with an external standard containing all the compounds in the mixture. The JP8, MF2 and synthetic fuels were injected splitless and quantitated with an internal standard using relative response factors. Chromatographic conditions are listed below.

<u>Fuel Mixture</u>	<u>Initial Temp.</u>	<u>Final Temp.</u>	<u>Program Rate</u>	<u>Internal Standard</u>
JP5	50°	150°	4°/min	---
JP8	50°	150°	4°/min	Naphthalene
MF2	50°	210°	5°/min	Phenylcyclohexane
JP10	50°	130°	10°/min	n-Undecane
RJ5	50°	200°	10°/min	n-Pentadecane

The two JP4 simulation mixtures were analyzed using a sparge and trap technique, as shown in Figure 3. This method proved to be useful for the full boiling range of the fuel, although there were some background interferences from the Tenax. Fifty microliters of the solution to be analyzed and 1 ml of n-Nonane in methanol as an internal standard were injected in a glass sparging device which was then heated to 75°C. The sample was sparged onto a Tenax trap with helium at a flow of 20 ml/min for 10 minutes, after which the trap alone was swept free of water vapor for an additional 10 minutes at the same flow rate. Following this, the trap was inserted in the Gas Chromatograph injector, heated to 240°C and desorbed onto the capillary column, which was cooled to -45°C with liquid nitrogen. After a 10-minute desorption, the oven was rapidly heated to 0°C and then temperature programmed to 160°C at 6°/min.

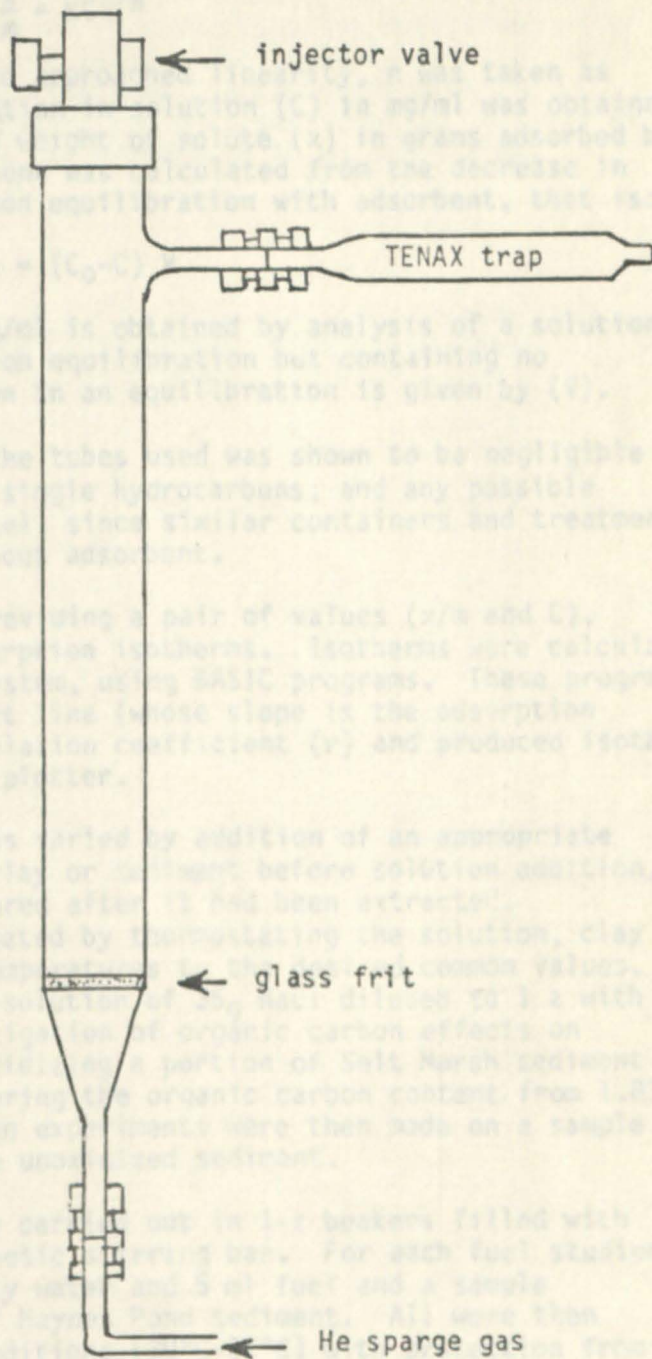


Figure 3. Sparge and Trap Apparatus for Collection of Volatile Hydrocarbons from Water Solution.

Calculation of isotherms was based on the Freundlich adsorption isotherm, which often describes adsorption from solution (Bikerman, 1970), and can be expressed as:

$$\frac{x}{m} = KC^{1/n}$$

Since most isotherms obtained approached linearity, n was taken as unity. The equilibrium concentration in solution (C) in mg/ml was obtained by analysis described above. The weight of solute (x) in grams adsorbed by a dry weight (m) in grams of adsorbent was calculated from the decrease in solute concentration occurring upon equilibration with adsorbent, that is:

$$x = (C_0 - C) V$$

The concentration (C_0) in mg/ml is obtained by analysis of a solution treated similarly to the adsorption equilibration but containing no adsorbent. Volume of the solution in an equilibration is given by (V).

Adsorption on the walls of the tubes used was shown to be negligible by test with saturated solutions of single hydrocarbons; and any possible container adsorption effects cancel, since similar containers and treatments are given solutions with and without adsorbent.

Five equilibrations, each providing a pair of values (x/m and C), provided data for five-point adsorption isotherms. Isotherms were calculated with the laboratory automation system, using BASIC programs. These programs also calculated a least square fit line (whose slope is the adsorption constant K), calculated the correlation coefficient (r) and produced isotherm plots on a Tektronix Model 4662 plotter.

Acidity of equilibrations was varied by addition of an appropriate volume of 1N NaOH or HCl to the clay or sediment before solution addition, and the pH of the water was measured after it had been extracted. Temperature effects were investigated by thermostating the solution, clay equilibration and centrifuging temperatures to the desired common values. For salt water equilibrations, a solution of 35g NaCl diluted to 1 l with distilled water was used. Investigation of organic carbon effects on adsorption was accomplished by oxidizing a portion of Salt Marsh sediment with 30% H₂O₂ for six hours, lowering the organic carbon content from 1.83% to 0.43%. Single point adsorption experiments were then made on a sample of this sediment and compared to the unoxidized sediment.

Model spill experiments were carried out in 1-l beakers filled with distilled water containing a magnetic stirring bar. For each fuel studied there was a sample containing only water and 5 ml fuel and a sample containing water, fuel and 5 g of Haynes Pond sediment. All were then stirred under ambient outdoor conditions (20°C-35°C) with protection from rain and sampled weekly for three weeks.

The reversibility of the adsorption process was investigated by calculating adsorption and desorption constants and comparing them. If the two values are the same, within error limits, then the process can be assumed

to be reversible. For each of four replicates, the same amount of marsh sediment was equilibrated with saturated MF2 solution for 16 hours, and single-point constants were calculated. The solution in the tubes was then replaced with clean water and equilibrated for another 16 hours, thus approaching sediment-water equilibrium from the opposite direction. The initial amount of hydrocarbons on the sediment was calculated from the adsorption constant values and water volumes. After correction for hydrocarbons in residual water, this value, plus the solution analysis after desorption, enabled a constant for the desorption to be calculated.

1.1. ISOTHERM MEASUREMENTS

The isotherms whose adsorption constants are reported here are each based on five points for conditions of (1) 20°C, salinity 0 ‰ and natural pH of adsorbent, and (2) 20°C, salinity 20 ‰ and natural pH of adsorbent. Many isotherms have been produced and adsorption constants for each are reported in this section. The isotherm plots for each of these are presented in a microfilm appendix to this report at page-size reproduction is impractical. Five-point isotherms were selected as adequately defining K values with reasonable effort and expense.

Single-point adsorption equilibrations were done with variations in one of the variables, temperature, pH or total organic content. Results of these equilibrations were compared with isotherm data at 20°C, salinity 0 ‰ and natural pH in order to estimate effect of changes in the above variables of the adsorption constant. In order to obtain adsorption constants corresponding to single-point equilibrations, the slope of the line from the origin to the single point was calculated, yielding an adsorption constant. This procedure is necessarily less accurate than determining constants from a many-point isotherm, but is sufficient for comparison purposes. Differences between adsorption constants under two sets of experimental conditions are used to measure the effect of a variable alteration on fuel adsorption.

Soil-to-water ratios in isotherm measurements varied from 1:6 to 1:60. Ratios were chosen to produce sufficient change in concentration of the hydrocarbons during equilibration to permit accurate analysis and to provide sufficient water volume in the centrifuge tubes used for analysis. Since hydrocarbons from fuels are not strongly adsorbed, the amounts of sediment were generally as large as possible. This permits best measurement of adsorption coefficients of the various number of simulated fuel components. Natural conditions of a fuel release might involve different soil-to-water ratios than used here, but the adsorption constants apply to equilibrium with any soil-to-water ratio.

In order to measure adsorption constants accurately, saturated solutions of fuel components were used in many equilibrations. When very effective adsorbents were tested or strongly adsorbing fuels, dilutions of these saturated solutions were used. Saturation as used here implies equilibration of a multi-component hydrocarbon mixture with water, and the concentrations of dissolved hydrocarbons differ from those found in saturated solutions of single hydrocarbons in water. Equilibrium concentrations of hydrocarbons in

SECTION III

RESULTS AND DISCUSSION

1. ISOTHERM MEASUREMENTS

The isotherms whose adsorption constants are reported here are each based on five points for conditions of (1) 20°C, salinity 0 ‰ and natural pH of adsorbent, and (2) 20°C, salinity 35 ‰ and natural pH of adsorbent. Many isotherms have been produced and adsorption constants for each are reported in this section. The isotherm plots for each of these are presented in a microfilm appendix to this report as page size reproduction is impractical. Five-point isotherms were selected to adequately define K values with reasonable effort and expense.

Single-point adsorption equilibrations were done with variations in one of the variables, temperature, pH or total organic content. Results of these equilibrations were compared with isotherm data at 20°C, salinity 0 ‰ and natural pH in order to estimate effect of changes in the above variables on the adsorption constant. In order to obtain adsorption constants corresponding to single-point equilibrations, the slope of the line from the origin to the single point was calculated, yielding an adsorption constant. This procedure is necessarily less accurate than determining constants from a many-point isotherm, but is sufficient for comparison purposes. Differences between adsorption constants under two sets of experimental conditions are used to measure the effect of a variable alteration on fuel adsorption.

Soil-to-water ratios in isotherm measurements varied from 1:6 to 1:60. Ratios were chosen to produce sufficient change in concentration of the hydrocarbons during equilibration to permit accurate analysis and to provide sufficient water volume in the centrifuge tubes used for analysis. Since hydrocarbons from fuels are not strongly adsorbed, the amounts of sediment were generally as large as possible. This permits best measurement of adsorption coefficients of the maximum number of simulated fuel components. Natural conditions of a fuel release might involve different soil-to-water ratios than used here, but the adsorption constants apply to equilibrium with any soil-to-water ratio.

In order to measure adsorption constants accurately, saturated solutions of fuel components were used in many equilibrations. When very effective adsorbents were tested on strongly adsorbing fuels, dilutions of these saturated solutions were used. Saturation as used here implies equilibration of a multicomponent hydrocarbon mixture with water, and the concentrations of dissolved hydrocarbons differ from those found in saturated solutions of single hydrocarbons in water. Equilibrium concentrations of hydrocarbons in

multicomponent solutions are given approximately by the product of their mole fractions and single compound solubilities. The hydrocarbon concentrations obtained have been found to depend on the relative amounts of hydrocarbon and water phases. In this work a ratio of 1:1000 was used. More research is needed on the aqueous behavior of hydrocarbon mixtures in aqueous solution (Stumm and Morgan, 1981), but the hydrocarbon mixture solution preparation methods used here provide suitable solute mixtures to serve as sorbates simulating dissolved fuel oils in adsorption measurements.

Adsorption coefficients are presented along with values of the square of the correlation coefficient (r^2) calculated from the isotherm lines. The r^2 value is a measure of the scatter of points or of deviation from a linear Freundlich isotherm. Figure 4 shows isotherms with several different r^2 values; an r^2 greater than 0.70 indicates satisfactory agreement with a linear adsorption isotherm. The square of the correlation coefficient was used rather than the coefficient, because it is more sensitive to the scatter of the isotherm data. The use of r^2 is consistent with that of Means et al. (1980a), who studied adsorption of higher molecular weight PAH on sediments.

Sediments and clays used in this program have unknown mineral composition, organic composition, amorphous oxide content and surface properties. Adsorption constants obtained on these materials are representative of sediments from different environments and of clays that are sediment components, but constants cannot be related to detailed properties of adsorbent surface.

Sediments were sieved through a 64 micron screen to assure uniformity of particle size and homogeneity of samples. Trial isotherms showed regular behavior for all sieved sediments except Haynes Pond. The cause of irregularity for sieved Haynes Pond sediment is not known. Regular isotherms were obtained with unsieved samples, which were used in this study. The exclusion of large sediment particles makes little difference in adsorption measurements, because this fraction is mostly quartz sand which does not adsorb hydrocarbons as shown in some trial equilibrations in this program. Adsorption on the sieved sediment can be converted approximately to adsorption on the whole sediment by correcting for the sand content of the sediment which is given in Table 3.

2. ADSORPTION CONSTANTS AT 20°C AND NATURAL pH

Results of adsorption isotherms run in fresh and salt water are given in Tables 4-12. Adsorption constants (K) were calculated and reported for each fuel component, and adsorption constants for the overall mixture (reported last in each table) were calculated from the total amount of hydrocarbon adsorbed. In general, montmorillonite adsorbed more than kaolinite and illite. K values near unity produced poorly defined isotherms, as indicated by their r^2 values. For some fuels, adsorption on kaolinite or illite was very small. For JP4 mixtures, adsorption constants for kaolinite and illite were not significant, and since adsorption was so low, some isotherms were not produced. Montmorillonite produced measurable adsorption for all fuel mixtures. Negative K values are not considered to have physical reality and

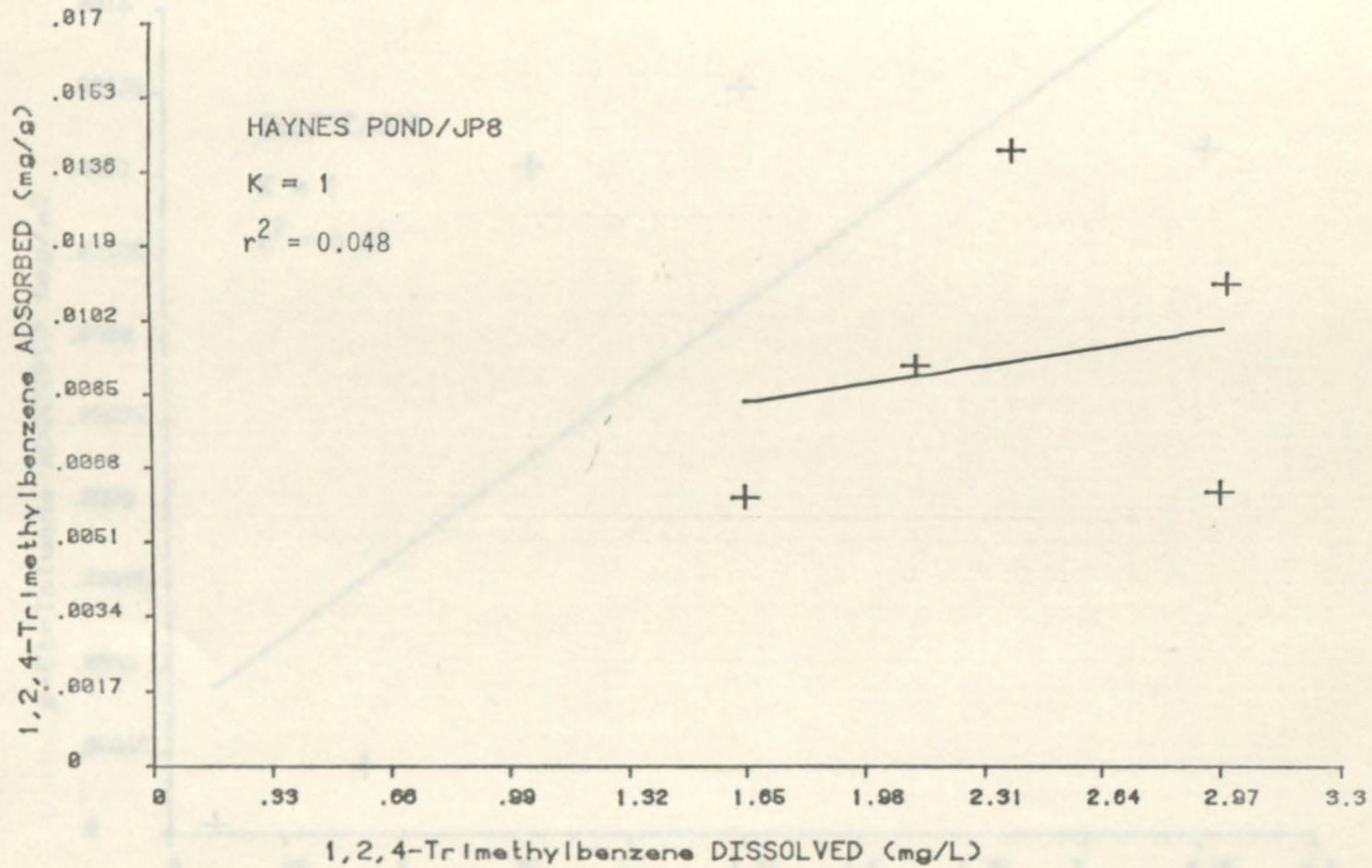


Figure 4. Selected Isotherms with Corresponding r^2 Values.

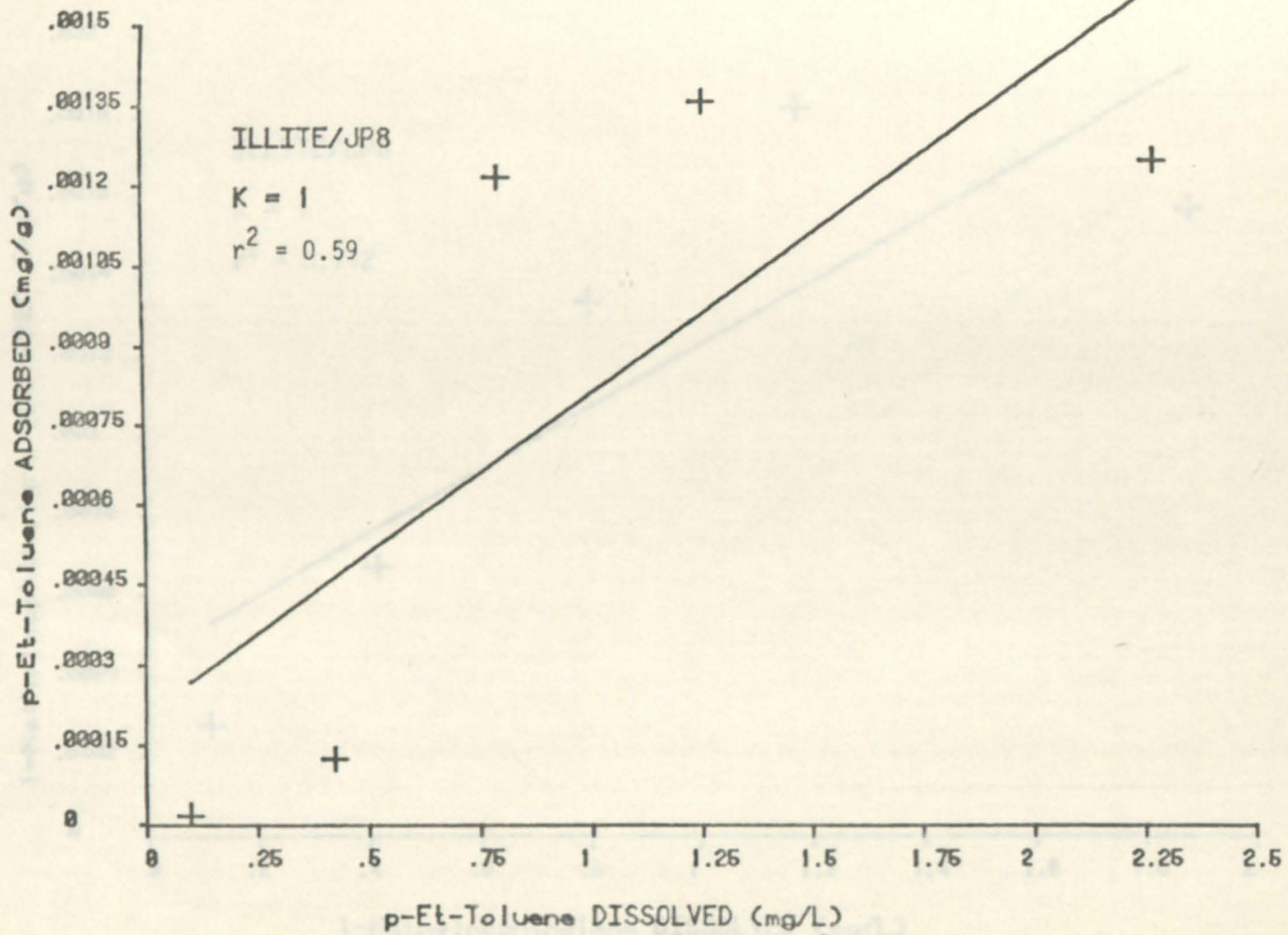


Figure 4. Selected Isotherms with Corresponding r^2 Values (Continued).

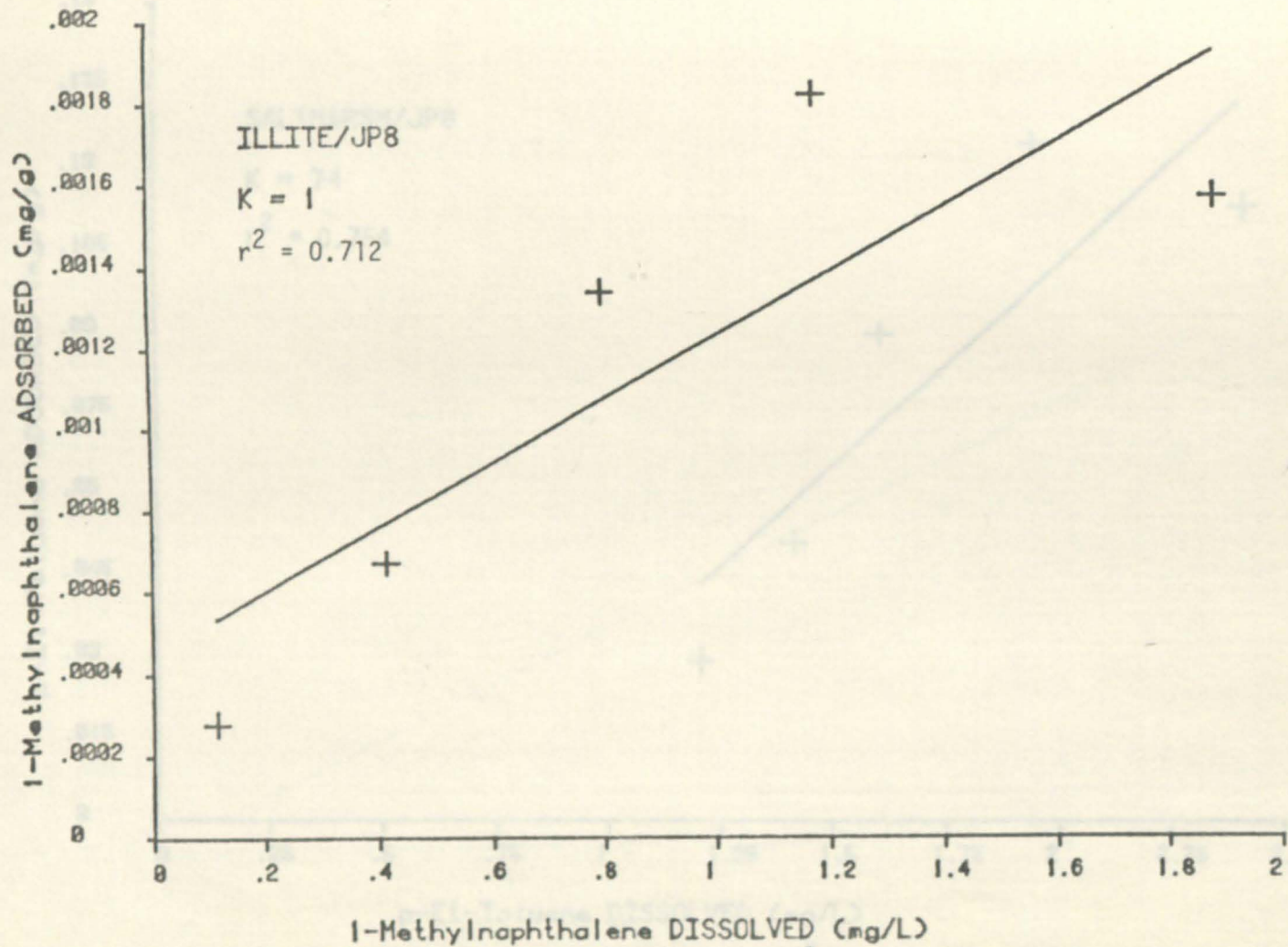


Figure 4. Selected Isotherms with Corresponding r^2 Values (Continued).

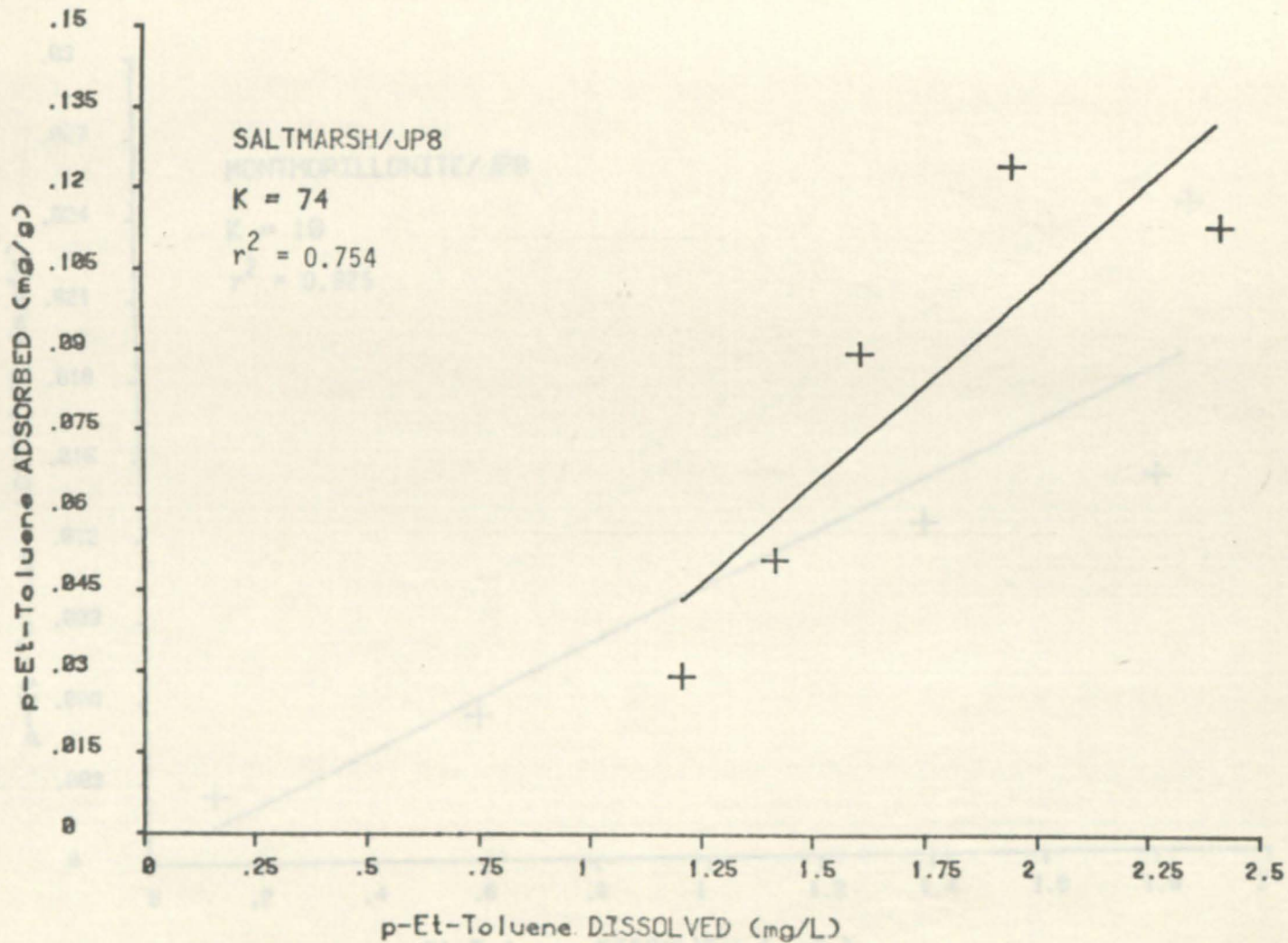


Figure 4. Selected Isotherms with Corresponding r^2 Values (Continued).

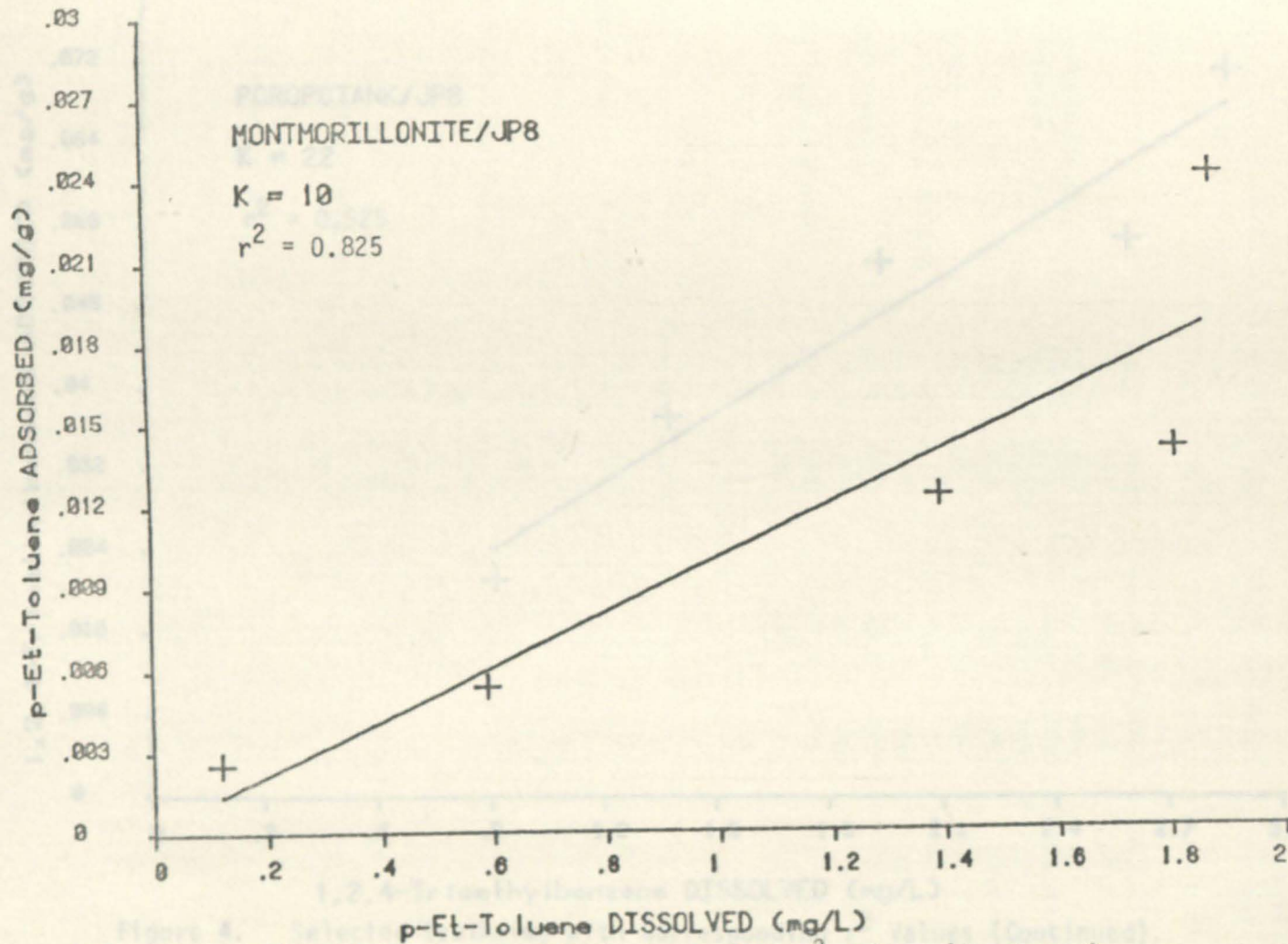


Figure 4. Selected Isotherms with Corresponding r^2 Values (Continued).

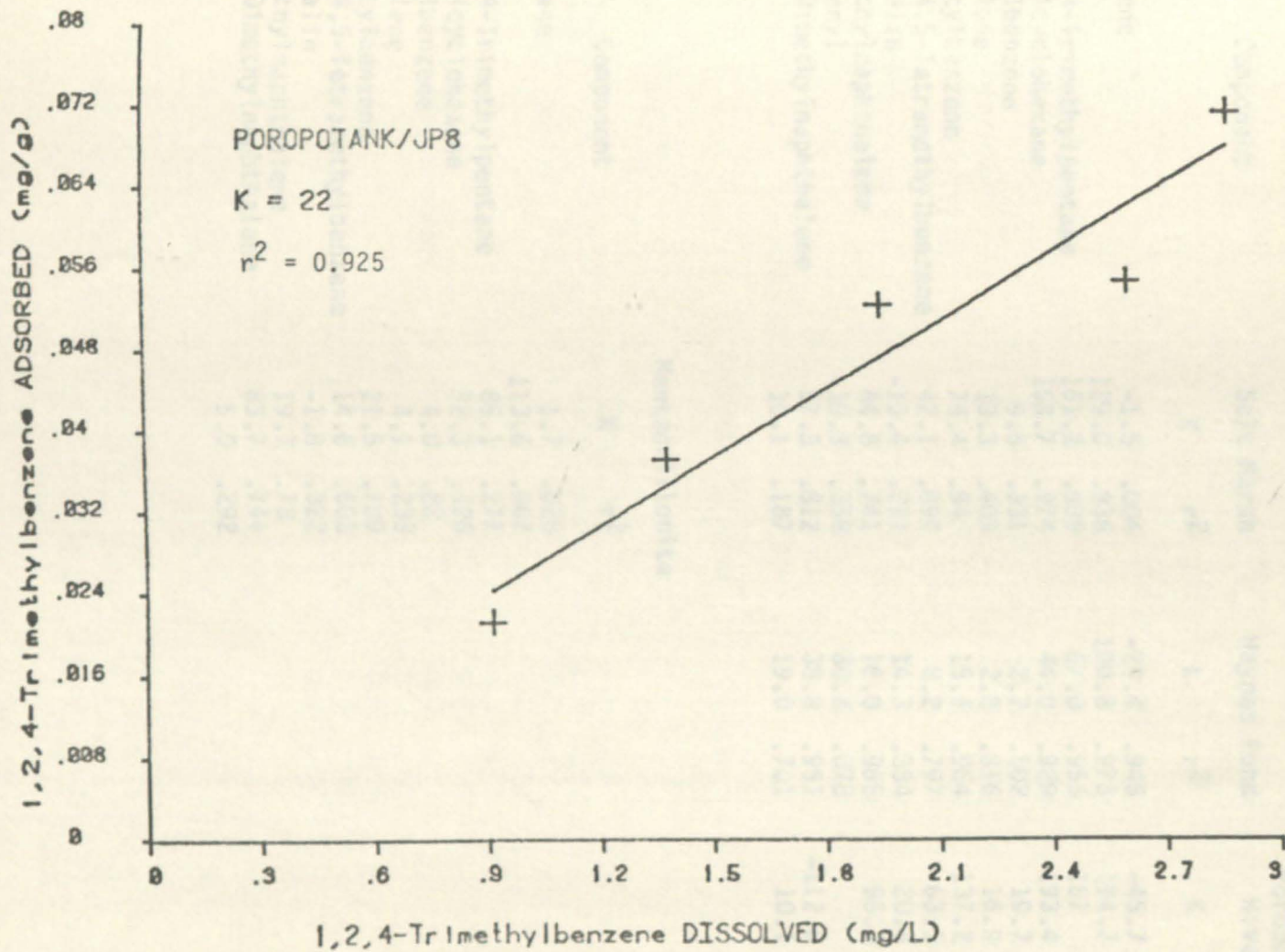


Figure 4. Selected Isotherms with Corresponding r^2 Values (Continued).

TABLE 4. JP4 SHALE SIMULATION MIXTURE IN DISTILLED WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
Benzene	-1.5	.004	-29.4	.946	-45.7	.539
n-C7	129.0	.936	100.8	.973	194.3	.671
2,2,4-Trimethylpentane	161.2	.989	67.0	.955	167	.832
Ethylcyclohexane	158.7	.974	44.0	.929	193.4	.902
Ethylbenzene	9.5	.331	2.7	.502	19.7	.32
m-Xylene	13.3	.409	2.8	.816	16.9	.367
n-Butylbenzene	75.4	.94	15.6	.964	137.2	.97
1,2,4,5-Tetramethylbenzene	42.1	.894	8.2	.797	63.5	.886
Tetralin	-13.4	.221	14.3	.354	20.8	.284
2-Methylnaphthalene	64.8	.741	16.0	.965	98.3	.998
Biphenyl	-19.3	.358	30.2	.078		
2,6-Dimethylnaphthalene	57.3	.812	38.8	.951	-112.6	.771
JP4	10.1	.187	19.0	.701	10.1	.171

Component	Montmorillonite		Illite	
	K	r ²	K	r ²
Benzene	1.7	.028	3.2	.6
n-C7	113.6	.967	1.2	.062
2,2,4-Trimethylpentane	85.1	.277	7.1	.077
Ethylcyclohexane	52.3	.426	0.2	.137
Ethylbenzene	4.0	.22	0.3	.321
m-Xylene	4.1	.233	0	.001
n-Butylbenzene	21.5	.709	0.4	.096
1,2,4,5-Tetramethylbenzene	14.6	.605	1.3	.322
Tetralin	-1.8	.322	0.2	.172
2-Methylnaphthalene	19.7	.78		
2,6-Dimethylnaphthalene	83.7	.744		
JP4	5.0	.292		

TABLE 5. JP4 PETROLEUM SIMULATION MIXTURE IN DISTILLED WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
Cyclohexane	41.7	.751	61.1	.996	13.0	.522
n-Heptane	66.5	.704	259	.908	-172.2	.073
Methylcyclohexane	35.2	.993	67.4	.292	55.0	.811
Toluene	58.4	.575	-14.2	.553	-236.1	.488
p-Xylene	33.8	.883	94.9	.485	75.1	.839
Isopropylbenzene	38.6	.972	85.9	.652	86.1	.889
1,3,5-Trimethylbenzene	38.2	.994	85.6	.712	99.2	.906
Indan	26.0	.99	72.7	.608	72.9	.898
Naphthalene	16.6	.914	20.1	.809	29.9	.958
2-Methylnaphthalene	29.4	.959	-6.6	.293	19.4	.481
JP4	31.4	.976	-68.9	.153	72.9	.967

Component	Montmorillonite		Illite	
	K	r ²	K	r ²
Cyclohexane	20.8	.503	.6	.15
n-Heptane	54.6	.897	4.2	.273
Methylcyclohexane	16.5	.918	3.2	.6
Toluene	2.8	.696	-.2	.062
p-Xylene	3.3	.786	-.1	.077
Isopropylbenzene	5.3	.898	0.2	.187
1,3,5-Trimethylbenzene	4.6	.82	0.3	.371
Indan	1.5	.208	0	.001
Naphthalene	2.6	.246	0.4	.096
2-Methylnaphthalene	8.6	.718	1.3	.322
JP4	3.3	.687	0.2	.172

TABLE 6. JP4 PETROLEUM SIMULATION MIXTURE IN SALT WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
Cyclohexane	57.8	.634	8.4	.461	95.2	.864
n-Heptane	94.5	.927	1.4	.02	251	.991
Methylcyclohexane	27.5	.311	29.5	.943	118.3	.81
Toluene	49.7	.582	-14.2	.483	122.4	.252
p-Xylene	26.4	.251	14.2	.599	63.9	.637
Isopropylbenzene	36.5	.664	10.5	.799	70.7	.877
1,3,5-Trimethylbenzene	54.8	.728	8.4	.756	72.4	.921
Indan	32.0	.34	1.4	.182	63.6	.782
Naphthalene	54.7	.773	6.3	.545	69.0	.965
2-Methylnaphthalene	93.4	.831	22.7	.749	122.9	.992
JP4	41.6	.633	22.7	.201	90.3	.85

Montmorillonite

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
Cyclohexane	7.6	.763	0.4	.02	1.0	.08
n-Heptane	98.0	.717	0.4	.02	0.3	.02
Methylcyclohexane	22.1	.917	0.2	.01	0.3	.02
Toluene	3.8	.728	0.2	.01	0.7	.07
p-Xylene	1.3	.229	0.5	.04	2.3	.22
Isopropylbenzene	2.2	.528	0.6	.05	4.7	.46
1,3,5-Trimethylbenzene	4.7	.88	1.7	.16	5.0	.49
Indan	0.4	.025	1.7	.16	11.5	.11
Naphthalene	4.2	.788	0.3	.03	1.4	.14
2-Methylnaphthalene	18.1	.99				
JP4	3.9	.896				

TABLE 7. JP4 SIMULATION MIXTURE IN DISTILLED WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
1,3,5-Trimethylbenzene	45.8	.827	-6.3	.933	19.5	.643
1,2,4,5-Tetramethylbenzene	51.9	.849	3.2	.539	45.4	.874
1,2,3,4-Tetramethylbenzene	40.5	.566	1.7	.332	35.6	.853
Tetralin	65.7	.658	0	0	27.9	.777
Naphthalene	27.4	.332	-1.6	.582	24.1	.774
2-Methylnaphthalene	84.0	.936	5.8	.901	65.5	.954
Biphenyl	99.6	.952	10.0	.955	82.6	.967
2,6-Dimethylnaphthalene	197.3	.986	22.3	.985	148.6	.971
2,3-Dimethylnaphthalene	191.9	.979	17.6	.988	112.3	.977
Total JP5	59.0	.813	1.3	.249	35.3	.824

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
1,3,5-Trimethylbenzene	15.6	.743	0	.03	1.0	.821
1,2,4,5-Tetramethylbenzene	24.0	.856	0.4	.725	0.4	.114
1,2,3,4-Tetramethylbenzene	21.2	.83	0.4	.684	0.5	.258
Tetralin	17.9	.8	0.2	.524	0.3	.103
Naphthalene	15.0	.778	0.2	.556	0.7	.617
2-Methylnaphthalene	30.5	.946	0.5	.93	2.3	.92
Biphenyl	21.8	.706	0.6	.96	4.7	.906
2,6-Dimethylnaphthalene	38.6	.834	1.7	.986	5.0	.92
2,3-Dimethylnaphthalene	35.4	.94	1.7	.987	11.5	.857
Total JP5	19.3	.853	0.3	.729	1.2	.855

TABLE 8. JP5 SIMULATION MIXTURE IN SALT WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
1,3,5-Trimethylbenzene	33.0	.629	22.7	.755	78.3	.704
1,2,4,5-Tetramethylbenzene	50.4	.92	27.5	.916	110.1	.836
1,2,3,4-Tetramethylbenzene	58.6	.828	25.5	.911	95.4	.799
Tetralin	49.0	.679	22.7	.868	87.1	.71
Naphthalene	31.5	.543	19.3	.819	70.1	.696
2-Methylnaphthalene	95.8	.87	30.6	.962	145.7	.922
Biphenyl	87.6	.757	39.0	.97	122.6	.934
2,6-Dimethylnaphthalene	252.9	.947	70.3	.989	390.3	.907
2,3-Dimethylnaphthalene	223.7	.96	68.0	.985	265.0	.973
Total JP5	56.3	.733	26.6	.884	94.9	.778

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
1,3,5-Trimethylbenzene	8.9	.802	1.5	.876	2.1	.871
1,2,4,5-Tetramethylbenzene	17.7	.989	1.8	.829	2.3	.878
1,2,3,4-Tetramethylbenzene	13.6	.967	1.8	.911	2.1	.856
Tetralin	10.8	.936	2.1	.875	1.8	.826
Naphthalene	7.1	.921	1.6	.842	1.6	.763
2-Methylnaphthalene	24.4	.991	1.9	.768	2.3	.834
Biphenyl	42.5	.983	3.1	.837	3.5	.839
2,6-Dimethylnaphthalene	59.8	.994	3.1	.94	3.1	.862
2,3-Dimethylnaphthalene	59.0	.988	3.1	.862	4.9	.889
Total JP5	13.3	.938	1.9	.887	2.0	.836

TABLE 9. JP8 SIMULATION MIXTURE IN DISTILLED WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
p-Et-Toluene	74.3	.754	0.2	.002	21.0	.908
1,2,4-Trimethylbenzene	72.2	.832	1.2	.048	22.2	.925
Indan	74.8	.748	1.2	.034	17.5	.871
1,3,5-Triethylbenzene	239.0	.979	30.3	.965	163.2	.993
2-Methylnaphthalene	97.4	.968	8.3	.81	66.0	.988
1-Methylnaphthalene	105.6	.978	8.7	.844	63.2	.987
Phenylcyclohexane	273.7	.976	35.0	.984	202.5	.996
2-Ethyl-naphthalene	204.9	.982	23.6	.974	158.7	.998
2,3-Dimethylnaphthalene	218.3	.973	25.3	.972	176.2	.997
Total JP8	101.7	.927	6.0	.588	40.9	.967

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
p-Et-Toluene	9.8	.825	0.6	.59	-.1	.027
1,2,4-Trimethylbenzene	8.6	.98	0.5	.826	-.1	.039
Indan	7.8	.908	0.5	.64	-.2	.078
1,3,5-Triethylbenzene	58.7	.981	1.8	.96	2.5	.912
2-Methylnaphthalene	23.6	.951	0.8	.672	0.3	.112
1-Methylnaphthalene	19.9	.968	0.7	.712	0.2	.084
Phenylcyclohexane	77.8	.973	1.5	.895	2.5	.862
2-Ethyl-naphthalene	55.5	.972	1.3	.599	1.4	.656
2,3-Dimethylnaphthalene	64.2	.948	2.1	.726	3.6	.974
Total JP8	13.6	.917	0.6	.747	0	.001

TABLE 10. JP8 SIMULATION MIXTURE IN SALT WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
p-Et-Toluene	-12.1	.172	11.4	.471	-5.9	.277
1,2,4-Trimethylbenzene	-6.6	.06	14.0	.52	5.8	.445
Indan	-27.1	.418	10.4	.432	4.7	.872
1,3,5-Triethylbenzene	190.7	.622	79.7	.99	562.9	.977
2-Methylnaphthalene	55.0	.978	22.9	.971	124.9	.991
1-Methylnaphthalene	52.3	.97	22.4	.967	127.5	.98
Phenylcyclohexane	228.2	.724	84.9	.994	404.4	.995
2-Ethyl-naphthalene	185.5	.936	54.4	.986	373.2	.979
2,3-Dimethylnaphthalene	201.1	.94	58.9	.985	475.3	.96
Total JP8	13.6	.338	19.5	.767	32.7	.972

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
p-Et-Toluene	-4.2	.422	0.4	.385	0.4	.211
1,2,4-Trimethylbenzene	1.1	.03	0.3	.262	0.3	.113
Indan	-1.9	.042	0.3	.196	0	.009
1,3,5-Triethylbenzene	66.2	.995	1.5	.862	6.9	.887
2-Methylnaphthalene	19.9	.952	0.6	.709	1.0	.472
1-Methylnaphthalene	17.6	.943	0.5	.545	0.8	.328
Phenylcyclohexane	91.3	.997	8.3	.692	5.4	.878
2-Ethyl-naphthalene	58.3	.999	1.1	.803	2.9	.747
2,3-Dimethylnaphthalene	93.9	.961	1.9	.912	4.8	.809
Total JP8	10.9	.668	0.5	.416	0.5	.228

TABLE 11. MF2 SIMULATION MIXTURE DISTILLED WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
1,2,3,4-Tetramethylbenzene	46.0	.63	15.1	.918	54.5	.967
Tetralin	37.2	.506	15.0	.905	46.5	.957
1-Methylnaphthalene	73.3	.742	24.5	.971	93.6	.973
Biphenyl	91.1	.818	32.2	.954	131.4	.984
1,3-Dimethylnaphthalene	191.8	.898	52.0	.967	244.8	.988
2,3-Dimethylnaphthalene	203.9	.903	59.7	.944	249.1	.986
2,3,5-/Trimethylnaphthalene	434.6	.964	111.1	.969	521.9	.99
Fluorene	206.1	.892	63.4	.933	277.2	.98
3,3'-Dimethylbiphenyl	575.5	.974	147.0	.982	735.5	.971
Phenanthrene	627.4	.97	182.3	.944	924.1	.983
Total DMF2	99.7	.802	33.6	.977	106.0	.953

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
1,2,3,4-Tetramethylbenzene	39.4	.289	-.2	.039	0.9	.122
Tetralin	33.7	.225	-.2	.045	0.5	.062
1-Methylnaphthalene	49.9	.476	-.3	.089	1.0	.165
Biphenyl	167.1	.589	-.2	.068	2.2	.305
1,3-Dimethylnaphthalene	92.6	.81	0	0	4.1	.484
2,3-Dimethylnaphthalene	252.8	.641	0	.001	6.4	.549
2,3,5-Trimethylnaphthalene	269.8	.888	0.8	.334	10.6	.607
Fluorene	258.1	.608	-.1	.023	5.6	.538
3,3'-Dimethylbiphenyl	195.3	.969	0.4	.069	9.1	.56
Phenanthrene	550.0	.714	2.6	.752	6.6	.074
Total MF2	81.2	.534	-.1	.028	1.4	.246

TABLE 12. MF2 SIMULATION MIXTURE IN SALT WATER.

Component	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
1,2,3,4-Tetramethylbenzene	100.0	.631	15.3	.859	193.9	.884
Tetralin	90.0	.557	13.1	.775	180.1	.847
1-Methylnaphthalene	99.4	.765	17.8	.886	226.2	.934
Biphenyl	107.0	.812	24.5	.96	271.9	.96
1,3-Dimethylnaphthalene	196.3	.924	46.7	.964	476.3	.971
2,3-Dimethylnaphthalene	187.1	.908	46.3	.94	474.0	.969
2,3,5-/Trimethylnaphthalene	356.6	.941	95.7	.961	921.7	.987
Fluorene	148.1	.794	47.3	.878	443.3	.975
3,3'-Dimethylbiphenyl	432.4	.892	140.9	.879	1133.2	.985
Phenanthrene	382.1	.891	146.8	.689	1290.5	.972
Total DMF2	124.8	.774	25.8	.879	264	.913

Component	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
1,2,3,4-Tetramethylbenzene	77.9	.596	0.4	.049	2.2	.519
Tetralin	82.9	.561	0.1	.007	2.1	.556
1-Methylnaphthalene	59.2	.602	0.6	.107	2.4	.632
Biphenyl	274.4	.49	1.4	.308	4.3	.74
1,3-Dimethylnaphthalene	92.6	.794	3.2	.517	5.7	.68
2,3-Dimethylnaphthalene	356.4	.458	3.0	.477	7.3	.693
2,3,5-Trimethylnaphthalene	284.8	.806	7.1	.546	13.6	.695
Fluorene	347.6	.38	3.0	.53	6.5	.768
3,3'-Diphenylbiphenyl	196.2	.967	6.2	.361.1	11.1	.522
Phenanthrene	629.1	.321	9.6	.718	18.8	.732
Total DMF2	126.7	.614	0.8	.147	3.0	.642

generally have corresponding low r^2 values. In cases where r^2 is low, the sign and magnitude of K is highly variable and not significant.

The reliability of calculated K values (which are estimates of the strength of association of each fuel component with an adsorbent) is dependent upon the accuracy of gas chromatographic analyses of solution concentrations in a set of equilibrations of a fuel mixture solution with an adsorbent which define an isotherm. The accuracy and precision of solution analyses was better than $\pm 5\%$ from replicate analyses of known mixtures. The value of K, derived from five separate equilibrations, has a less directly measurable error. Uncertainty of each point defining the isotherm depends on the relative magnitudes of the error in solution analysis and the percent loss of dissolved compounds due to adsorption. This uncertainty is minimized at fifty percent or greater adsorption, a condition that was sought in these experiments. Limits of the adsorbent-water system and of hydrocarbon solubilities from the fuel mixtures prevented attainment of this condition. This occurred in particular for experiments with high equilibrium concentrations of a dissolved hydrocarbon. Limits of GC methods prevented analysis of very dilute solutions.

The reliability of K values is best estimated by the corresponding coefficients of determination (r^2). Those K values with coefficients less than 0.7 have extensive scatter or nonlinearity, which are not separable factors. The precision of K values depends upon the magnitude of K and the composition of the fuel mixture. A single value of error cannot be applied to all K values obtained in this work. Another estimate of the precision of each K could be obtained from three or more repeats of each adsorption isotherm, but this procedure involves great expense and produces little new information.

Comparisons among the above tables between K values for distilled and salt water indicate that the effect of salinity on fuel component adsorption is not large or completely uniform. The general tendency is for higher K values with higher salinity, with this effect being most pronounced for Poropotank sediments. Separation of the effect of salinity on K into relative solubility and relative adsorption factors of fuel components cannot be done. However, the variability of salt effects on the same fuel mixture by different sediments suggest that the salt concentrations near or on the adsorbent may alter the adsorbent surface characteristics and consequent equilibrium behavior.

Tables 13 and 14 demonstrate the effect of salinity on adsorption for sediments used and montmorillonite. In these tables, means and standard deviations of K values are given separately for fresh and salt water, for 2-methylnaphthalene and for dimethylnaphthalene. These compounds were common to most fuel mixtures, so the variation of K between fuel mixtures for a compound can be observed at salinities 0 ‰ and 35 ‰. Since the fuel mixtures are different, the statistics reported refer to variation of K with fuel type, and do not estimate error in K determination. The K values for both 2,6-dimethylnaphthalene and 2,3-dimethylnaphthalene were treated in this table as if they were a single compound. Some mixtures contained only one of the compounds, and the use of data from either compound was justified by the

TABLE 13. ADSORPTION CONSTANTS FOR 2 METHYLNAPHTHALENE AT 20°C AND NATURAL pH MEASURED IN DIFFERENT FUEL MIXTURES AT S= 0‰ and S=35 ‰.

	<u>Salt Marsh</u>	<u>Haynes Pond</u>	<u>Poropotank River</u>	<u>Montmorilite</u>
		0 ‰		
JP4 Shale	64.8	16.0	--	19.7
JP4 Petroleum	29.4	--	--	8.6
JP5	84.0	17.6	65.5	30.5
JP8	97.4	8.3	66.0	23.6
MF2	<u>73</u>	<u>24.5</u>	<u>93.6</u>	--
\bar{m}	69.7	16.6	75.0	20.6
σ	25.6	6.6	16.0	9.6
		35 ‰		
JP4 Petroleum	93.4	22.7	122.9	18.1
JP5	95.8	30.6	145.7	24.4
JP8	55.0	22.9	124.9	19.9
MF2	<u>99.4</u>	<u>17.8</u>	<u>226.2</u>	--
\bar{m}	85.9	23.5	154.9	20.8
σ	20.7	5.3	48.6	3.2

TABLE 14. ADSORPTION CONSTANTS FOR DIMETHYLNAPHTHALENES AT 20°C AND NATURAL pH MEASURED IN DIFFERENT FUEL MIXTURES AT S=0 ‰ and S=35 ‰.

	<u>Salt Marsh</u>	<u>Haynes Pond</u>	<u>Poropotank River</u>	<u>Montmorilite</u>
	0 ‰			
JP4 Shale	57.3	38.8	--	83.7
JP5	197.3	22.3	148.6	38.6
JP8	218.3	25.3	176.2	64.2
MF2	<u>203.9</u>	<u>59.7</u>	<u>249.1</u>	<u>92.6</u>
\bar{m}	169.2	36.5	191.1	69.8
σ	65.0	14.7	42.4	20.7
	35 ‰			
JP5	252.9	70.3	340.3	59.8
JP8	201.1	58.1	475.3	93.9
MF2	<u>187.1</u>	<u>46.3</u>	<u>474.0</u>	<u>92.6</u>
\bar{m}	213.7	48.2	429.8	82.1
σ	28.3	9.8	63.3	15.8

observation that K for methyl substituted aromatics in a particular fuel mixture is almost independent of the location of the substitutes.

Inspection of this table shows a rather small variation of K values among fuel mixtures and an effect of salinity on adsorption with Poropotank sediment and a weaker effect with Haynes Pond sediment. From this, it appears that somewhat approximate Ks for individual compounds can be used for individual components of a released fuel, without major influences due to overall fuel composition, within the limits of fuel composition studied here. JP4 mixtures show the largest change in K for the compounds selected. The data supports the general conclusion that K values are slightly higher in salt than fresh water. This is in agreement with the observation of Karickhoff et al. (1978), who found that K values for pyrene on a Georgia sediment were approximately 15% higher in 20 ‰ NaCl than in distilled water.

The polycyclic aliphatic synthetic fuels have a similar effect of salinity on K values for both the JP10 and RJ5 components, as shown in Tables 15 and 16.

3. DISCUSSION OF ADSORPTION CONSTANTS AS APPLIED TO HYDROCARBON MIXTURES

K values for systems of a single hydrocarbon with water and adsorbent cannot be derived from K values obtained using hydrocarbon mixtures. However, K values from mixtures approximate single compound K values for hydrocarbons used in this study. This is supported by the relative invariance of K with fuel mixture composition and by the existing literature for single compound K values. Karickhoff et al. (1979) report K for naphthalene is 39 and K for 2-methylnaphthalene is 255 on North Georgia sediments. Karickhoff (1980) gives K for naphthalene as 20 and K for phenanthrene as 250 on a Mississippi River sediment. The results are in general agreement with the data obtained from mixtures in this study, and differences are probably due to the adsorbents used. It would be interesting to produce isotherms of selected single hydrocarbons on the sediments studied here and use these to better define differences between K values from single compounds and from mixtures.

It is possible that the relative insensitivity of K for a compound on an adsorbent to presence of other hydrocarbons in solution is a consequence of adsorption being site independent and of sorbate-sorbent binding forces that are similar for most hydrocarbons. Thus, each molecule of a sorbate species interacts with the available area of the adsorbent surface to establish an equilibrium for that species that is, to a degree, independent of other hydrocarbon species present.

The K values obtained here are, as expected, small with respect to values for the higher PAH on midwest sediments reported by Means et al. (1980a).

Relations between K values for the various compounds in the synthetic fuel mixtures can be considered in terms of structure, solubility and size differences between the various sorbate molecules. Such comparisons would be

TABLE 15. JP9 IN DISTILLED AND SALT WATER.

JP9 IN DISTILLED WATER

	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
JP10 Component	306	.916	59	.970	513	.995
RJ5 Component	888	.982	436	.972	1866	.959
	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
JP10 Component	21	.537	12	.851	11	.995
RJ5 Component	70	.839	22	.818	74	.996

JP9 IN SALT WATER

	Salt Marsh		Haynes Pond		Poropotank River	
	K	r ²	K	r ²	K	r ²
JP10 Component	418	.991	57	.949	651	.984
RJ5 Component	1240	.994	375	.989	3907	.998
	Montmorillonite		Illite		Kaolinite	
	K	r ²	K	r ²	K	r ²
JP10 Component	145	.921	7	.978	9	.971
RJ5 Component	658	.997	52	.965	47	.995

TABLE 16. HIGH DENSITY FUELS IN DISTILLED WATER.

	Salt Marsh		Haynes Pond		Poropotank River		Montmorilite	
	K	r ²	K	r ²	K	r ²	K	r ²
<u>JP10</u>	280	.856	70	.972	573	.786	73	.985
<u>RJ5</u>								
Dehydro-HNN	1928	.62	464	.885	1881	.975	195	.872
HXX	1939	.958	268	.707	2214	.979	160	.768
HNN	2135	.974	368	.883	1980	.995	178	.823
Total RJ5	2120	.958	360	.867	2011	.993	177	.819
<u>RJ6</u>								
JP10 Component	214	.983	237	.793	449	.987	93	.965
RJ5 Component	1752	.993	327	.772	2462	.995	429	.985

better made using data from isotherms obtained with single hydrocarbon solutions on adsorbents of more defined and uniform surface structure than the sediments used in this study. The generalizations that arise from the present data are:

1. K values are relatively invariant for a substituted aromatic ring system with a given total number of aliphatic carbon atoms in substituents, regardless of the position of substitution.
2. K values increase with substitution along an aromatic series.
3. For similar solubility compounds, K values are greater for aromatics than for aliphatics.
4. For similar solubility compounds, K values are considerably greater for high density fuel components than for distillate fuel aliphatic or aromatic components.
5. For unsubstituted aromatic ring systems, K values increase with the increasing number of fused rings.

The observations are consistent with the general description of hydrocarbon adsorption described above. In particular, the cage structures of high density fuel components can be expected to behave quite differently than distillate aliphatic or aromatic molecules in solution and on adsorbent surfaces.

4. ADSORPTION CONSTANTS AT OTHER pH AND TEMPERATURE VALUES

The effect of altering pH and temperature on the adsorption of fuels was investigated by comparing K values from single equilibration experiments at selected temperatures and pH with K values from isotherms at 20°C, salinity 0 ‰ and natural pH. This procedure is adequate to detect major pH or temperature effects. A more sensitive comparison could be made if complete isotherms were done at the various pH and temperature conditions, but the results reported here do not justify this expenditure of time and effort.

All adsorbents except kaolinite and Poropotank River sediment were originally basic, and two acidified solutions were tested. Kaolinite forms acidic solutions, so two more basic solutions were tested. The Poropotank sediment was near neutral; adjustments were made to produce both higher and lower pH values. pH was generally kept in the range of 4-10, which includes possible environmental values. The practical difficulties in measuring sediment pH relate to sediment particle effects on reference cell liquid junction potentials. All measurements here were made with both electrodes in the supernatant liquid above the centrifuged sediment.

K values for components of JP5 and JP8 simulation mixtures at various pH values are presented in Tables 17 and 18. The probable error of these constants, from single equilibrations, is greater than that from five-point isotherms, but the results show no systematic effect of change in pH. This observation is reasonable because physical adsorption of nonpolar sorbates

TABLE 17. EFFECT OF pH AND TEMPERATURE ON JP5 SIMULATION MIXTURE.

Salt Marsh

	Dist.*					
	<u>5.46/20°</u>	<u>6.61/20°</u>	<u>8.05/20°</u>	<u>8.05/20°</u>	<u>7.95/5°</u>	<u>7.95/30°</u>
1,3,5-TriMebenz.	30.0	16.9	46.0	46.0	26.2	25.2
1,2,4,5-TetraMebenz.	38.7	37.4	41.0	41.0	38.0	44.6
1,2,3,4-TetraMebenz.	40.6	32.5	52.0	52.0	39.4	41.4
Tetralin	37.1	25.9	66.0	66.0	32.8	32.4
Naphthalene	46.0	21.5	27.0	27.0	27.8	25.8
2-Methylnaphthalene	73.2	55.9	84.0	84.0	153.3	70.1
Biphenyl	71.1	60.3	100.0	100.0	34.1	108.5
2,6-DiMe naphth.	161.6	177.2	197.0	197.0	413.0	382.9
2,3-DiMe naphth.	153.5	172.3	192.0	192.0	274.7	405.6
Total JP5	46.7	31.7	59.0	59.0	34.7	39.8

Haynes Pond

	Dist.*					
	<u>5.71/20°</u>	<u>7.01/20°</u>	<u>7.82/20°</u>	<u>7.82/20°</u>	<u>7.82/5°</u>	<u>7.82/30°</u>
1,3,5-TriMebenz.	4.3	5.2	-	-	5.1	3.1
1,2,4,5-TetraMebenz.	8.5	10.5	3.0	3.0	8.6	6.5
1,2,3,4-TetraMebenz.	7.1	9.1	2.0	2.0	8.2	6.0
Tetralin	6.0	7.2	.02	.02	7.3	4.5
Naphthalene	5.2	6.0	-	-	6.9	3.3
2-Methylnaphthalene	13.4	16.4	6.0	6.0	14.8	9.9
Biphenyl	14.9	17.4	10.0	10.0	11.0	11.0
2,6-DiMe naphth.	36.0	51.5	22.0	22.0	31.9	30.0
2,3-DiMe naphth.	31.0	46.6	18.0	18.0	21.3	28.4
Total JP5	6.7	8.0	1.0	1.0	7.6	5.3

Poropotank

	Dist.*					
	<u>4.90/20°</u>	<u>8.29/20°</u>	<u>7.50/20°</u>	<u>7.50/20°</u>	<u>7.50/5°</u>	<u>7.50/30°</u>
1,3,5-TriMebenz.	11.3	33.3	20.0	20.0	3503.4	15.5
1,2,4,5-TetraMebenz.	21.1	63.0	45.0	45.0	36.6	31.4
1,2,3,4-TetraMebenz.	20.8	55.5	36.0	36.0	30.2	27.9
Tetralin	16.1	45.5	28.0	28.0	24.5	20.4
Naphthalene	21.1	42.1	24.0	24.0	25.7	17.4
2-Methylnaphthalene	50.7	103.8	66.0	66.0	70.3	56.0
Biphenyl	47.2	185.7	83.0	83.0	90.1	77.1
2,6-DiMe naphth.	126.9	339.9	149.0	149.0	125.6	255.9
2,3-DiMe naphth.	135.7	262.4	112.0	112.0	65.7	234.3
Total JP5	22.7	51.3	35.0	35.0	40.0	26.0

* Natural pH

TABLE 17. EFFECT OF pH AND TEMPERATURE ON JP5 SIMULATION MIXTURE (CONTINUED).

Montmorillonite

	Dist.*					
	4.28/20°	6.94/20°	9.61/20°	9.61/20°	9.61/5°	9.61/30°
1,3,5-TriMe benz.	28.3	17.9	16.0	16.0	13.5	7.1
1,2,4,5-TetraMe benz.	34.6	26.3	24.0	24.0	14.0	12.8
1,2,3,4-TetraMe benz.	33.3	22.9	21.0	21.0	13.2	11.7
Tetralin	30.9	19.2	18.0	18.0	11.8	10.0
Naphthalene	31.7	19.4	15.0	15.0	10.5	7.0
2-Methylnaphthalene	54.7	38.4	31.0	31.0	16.0	18.3
Biphenyl	68.6	51.0	22.0	22.0	20.0	27.9
2,6-DiMe naphth.	61.4	49.8	39.0	39.0	17.2	54.9
2,3-DiMe naphth.	74.7	65.3	35.0	35.0	15.5	44.2
Total JP5	35.2	23.1	19.0	19.0	12.7	11.3

Illite

	Dist.*					
	6.02/20°	7.25/20°	8.85/20°	8.85/20°	8.85/5°	8.85/30°
1,3,5-TriMe benz.	0.4	0.2	0.1	0.1	0.8	-
1,2,4,5-TetraMe benz.	0.4	0.4	0.5	0.5	0.9	0.3
1,2,3,4-TetraMe benz.	0.4	0.5	0.4	0.4	1.0	0.4
Tetralin	0.4	0.4	0.3	0.3	0.9	0.3
Naphthalene	0.3	0.4	0.2	0.2	0.9	0.2
2-Methylnaphthalene	0.7	0.7	1.0	1.0	0.7	0.6
Biphenyl	0.8	0.9	1.0	1.0	0.9	0.5
2,6-DiMe naphth.	1.7	1.0	2.0	2.0	-	1.6
2,3-DiMe naphth.	0.8	0.8	2.0	2.0	-	1.7
Total JP5	0.4	0.4	0.4	0.4	0.8	0.4

Kaolinite

	Dist.*					
	5.47/20°	6.51/20°	8.94/20°	5.47/20°	5.47/30°	5.47/5°
1,3,5-TriMe benz.	1.0	-	0.3	1.0	0.1	0.8
1,2,4,5-TetraMe benz.	0.4	0.1	0.2	0.4	0.7	1.0
1,2,3,4-TetraMe benz.	1.0	0.1	0.6	1.0	0.7	0.9
Tetralin	0.3	0.1	0.3	0.3	0.5	0.8
Naphthalene	1.0	0.1	0.9	1.0	0.2	0.7
2-Methylnaphthalene	2.0	0.7	1.4	2.0	1.0	0.8
Biphenyl	5.0	1.9	2.0	5.0	2.3	1.4
2,6-DiMe naphth.	5.0	1.7	2.5	5.0	2.8	-
2,3-DiMe naphth.	12.0	3.8	2.9	12.0	5.6	0.6
Total JP5	1.0	0.4	0.8	1.0	0.7	0.8

TABLE 18. EFFECT OF pH AND TEMPERATURE ON JP8 SIMULATION MIXTURE.

Salt Marsh

	*					
	<u>3.72/20°</u>	<u>7.3/20°</u>	<u>8.0/20°</u>	<u>8.0/20°</u>	<u>8.0/30°</u>	<u>8.0/5°</u>
P-Et Toluene	86.0	19.4	74.0	74.0	47.0	29.0
1,2,4-TriMebenz.	65.0	18.8	72.0	72.0	50.0	30.0
Indan	83.0	13.0	75.0	75.0	37.0	24.0
1,3,5-TriEtbenz.	198.0	185.0	239.0	239.0	264.0	167.0
2-Methylnaphthalene	100.0	54.0	97.0	97.0	80.0	90.0
1-Methylnaphthalene	95.0	48.0	106.0	106.0	75.0	85.0
Phenylcyclohexane	241.0	210.0	274.0	274.0	263.0	231.0
2-Ethyl naphthalene	180.0	161.0	205.0	205.0	169.0	198.0
2,3-DiMe naphth.	185.0	171.0	218.0	218.0	180.0	237.0
Total JP8	86.0	23.0	102.0	102.0	56.0	36.0

Haynes Pond

	*					
	<u>5.13/20°</u>	<u>7.39/20°</u>	<u>7.8/20°</u>	<u>7.8/20°</u>	<u>7.8/30°</u>	<u>7.8/5°</u>
P-Et Toluene	7.7	2.1	0.3	0.3	2.8	2.9
1,2,4-TriMebenz.	7.4	2.5	1.0	1.0	3.3	3.3
Indan	5.9	1.6	1.0	1.0	2.2	2.8
1,3,5-TriEtbenz.	37.0	34.0	30.0	30.0	29.0	30.0
2-Methylnaphthalene	16.2	11.0	8.0	8.0	9.5	16.2
1-Methylnaphthalene	15.3	9.7	9.0	9.0	9.0	14.2
Phenylcyclohexane	49.0	39.0	35.0	35.0	35.0	41.0
2-Ethyl naphthalene	38.0	32.0	24.0	24.0	24.0	47.0
2,3-DiMe naphth.	40.0	35.0	25.0	25.0	25.0	70.0
Total JP8	8.7	3.4	6.0	6.0	4.6	4.2

Poropotank

	*					
	<u>4.61/20°</u>	<u>7.5/20°</u>	<u>7.88/20°</u>	<u>7.5/20°</u>	<u>7.5/30°</u>	<u>7.5/5°</u>
P-Et Toluene	27.0	21.0	35.0	21.0	27.0	28.0
1,2,4-TriMebenz.	30.0	22.0	37.0	22.0	40.0	30.0
Indan	24.0	18.0	27.0	18.0	18.2	22.0
1,3,5-TriEtbenz.	208.0	163.0	298.0	163.0	173.0	184.0
2-Methylnaphthalene	109.0	66.0	127.0	66.0	66.0	156.0
1-Methylnaphthalene	101.0	63.0	114.0	63.0	60.0	142.0
Phenylcyclohexane	276.0	203.0	361.0	203.0	153.0	313.0
2-Ethyl naphthalene	26.8	159.0	315.0	159.0	142.0	379.0
2,3-DiMe naphth.	344.0	176.0	348.0	176.0	171.0	492.0
Total JP8	39.0	41.0	42.0	41.0	35.0	34.0

* Natural pH

TABLE 18. EFFECT OF pH AND TEMPERATURE ON JP8 SIMULATION MIXTURE (CONTINUED).

Montmorillonite

	*					
	<u>4.37/20°</u>	<u>7.32/20°</u>	<u>9.6/20°</u>	<u>9.6/20°</u>	<u>9.6/30°</u>	<u>9.6/5°</u>
P-Et Toluene	4.0	5.3	10.0	10.0	14.5	10.7
1,2,4-TriMe benz.	4.6	5.0	9.0	9.0	13.9	10.5
Indan	2.3	2.8	8.0	8.0	11.8	8.8
1,3,5-TriEt benz.	60.0	67.0	59.0	59.0	84.0	39.0
2-Methylnaphthalene	20.0	23.0	24.0	24.0	32.0	22.0
1-Methylnaphthalene	16.8	19.0	20.0	20.0	28.0	21.0
Phenylcyclohexane	96.0	92.0	78.0	78.0	90.0	57.0
2-Ethyl naphthalene	61.0	67.0	56.0	56.0	75.0	48.0
2,3-DiMe naphth.	87.0	90.0	64.0	64.0	77.0	47.0
Total JP8	6.6	7.5	14.0	14.0	18.8	12.2

Illite

	*					
	<u>4.91/20°</u>	<u>7.49/20°</u>	<u>8.85/20°</u>	<u>8.85/20°</u>	<u>8.85/30°</u>	<u>8.85/5°</u>
P-Et Toluene	2.5	0.7	1.0	1.0	0.4	0.7
1,2,4-TriMe benz.	1.9	0.6	1.0	1.0	0.5	0.8
Indan	1.7	0.5	1.0	1.0	0.4	0.8
1,3,5-TriEt benz.	1.7	0.8	2.0	2.0	0.9	1.2
2-Methylnaphthalene	1.2	1.2	1.0	1.0	0.5	1.1
1-Methylnaphthalene	1.2	1.1	1.0	1.0	0.5	1.1
Phenylcyclohexane	2.0	1.9	2.0	2.0	1.1	1.2
2-Ethyl naphthalene	2.0	2.0	1.0	1.0	0.9	1.5
2,3-DiMe naphth.	2.8	2.3	2.0	2.0	1.6	2.8
Total JP8	1.8	0.8	1.0	1.0	0.5	0.9

Kaolinite

	*					
	<u>5.5/20°</u>	<u>7.05/20°</u>	<u>10.10/20°</u>	<u>5.5/20°</u>	<u>5.5/30°</u>	<u>5.5/5°</u>
P-Et Toluene	-0.1	2.8	1.2	-0.1	1.0	1.0
1,2,4-TriMe benz.	-0.1	2.6	1.1	-0.1	1.0	1.0
Indan	-0.2	2.3	1.0	-0.2	0.8	0.9
1,3,5-TriEt benz.	3.0	6.9	-	3.0	4.0	3.2
2-Methylnaphthalene	0.3	3.2	0.7	0.3	1.2	1.4
1-Methylnaphthalene	0.3	3.0	0.8	0.3	1.1	1.3
Phenylcyclohexane	3.0	7.4	0.6	3.0	4.2	3.2
2-Ethyl naphthalene	1.0	5.1	0.7	1.0	2.3	2.4
2,3-DiMe naphth.	4.0	6.1	0.5	4.0	4.1	5.2
Total JP8	0.03	2.8	1.0	0.0	1.2	1.1

* Natural pH

should not be highly dependent on adsorbent surface charge. The differences between K values at different pH are probably caused by experimental error rather than pH change. It is possible that pH-sensitive adsorption would be observed if the pH was adjusted outside the range used, thereby causing rapid major structural alteration of the adsorbent aluminosilicate framework. Such considerations are probably irrelevant here because the natural pH of sediment suspensions encountered during fuel exposures will usually be between 6.0 and 8.5.

Table 17 and 18 show K values obtained at natural pH in distilled water for temperatures of 5°C and 30°C; each is based on a single equilibration. When these results were compared with those from five-point isotherms at natural pH and 20°C in distilled water, a situation similar to that for pH variation was found. K values of fuel components showed no discernible trend with temperature, and large changes in K values with temperature were not observed. Since the mechanism of hydrocarbon uptake by the adsorbent from mixtures is unknown, it is not possible to justify the observed temperature effects by any theoretical consideration.

5. VARIATION OF ADSORPTION CONSTANTS WITH ADSORBENT ORGANIC CONTENT

The effect of organic matter content of sediments on adsorption of non-polar organic compounds has been the subject of considerable research, but satisfactory and generally applicable conclusions have not been reached. Several workers have proposed equations relating sediment total organic content with K values. Karickhoff et al. (1979) proposed K_{oc} values for sediment fine particles, where K_{oc} equals the experimentally measured K multiplied by the sediment organic content. They stated that, for a particular sediment type, the adsorption constants on each sample of that sediment were solely a function of the organic carbon content of that sample. It was concluded that differences in adsorption are mainly related to sediment organic content. Chiou et al. (1979) proposed that adsorption of nonpolar chlorinated hydrocarbons by soils is governed by partitioning between the water solution and the soil organic matter. They assumed organic matter is the principal adsorbent and presented some data to support their argument. Means (1980a) found a correlation between his measured adsorption constants and sediment total organic carbon. There is now a tendency to assume that a functional relation between organic content of a clay, soil or sediment sample and adsorption constants holds without exception.

The results presented in Tables 17 and 18 do not support a universal correlation between organic content and K, even for a particular sediment "type." In the author's opinion, it is not possible to obtain two sediment samples of the same "type" with differing organic contents. Some prior work should be considered before discussing detailed results from this program. Greenland and Hayes (1981) observed that the binding of a compound to a soil may be correlated with organic matter in one soil, but not in another, due to differences in humification, effect of cations or structural differences in soil organic material. They treat the correlation between soil organics and K values as empirical and only applicable to some soils. Goring and Hamaker (1972) propose that, in some cases, mineral phases of soils make a significant contribution to adsorption of neutral molecules, and that there

is a significant adsorption of many compounds after removal of soil organic carbon by H_2O_2 wet oxidation. Adsorptive sites other than soil organic matter are implicated in this argument. Means et al. (1980b) encountered difficulty with the above correlation and noted that a sediment with very low carbon content gave a high K value. They suggest that this is caused by the presence of montmorillonite clay, thereby introducing a new sediment variable, clay mineral content. Another sediment had high organic content but gave a low adsorption that is "difficult to explain." Such exceptions to a correlation and the unsatisfying exclusion of clean mineral surfaces from the descriptive picture of hydrocarbon adsorption by soils and sediments cast doubt on the correlation's generality. If the correlation holds, sediments with organic matter removed should not significantly adsorb hydrocarbons from water. Adsorption on clay minerals should be more dependent on organic content of the (necessarily impure) mineral source bed than on the structure of the particular clays. Finally, adsorption of hydrocarbon fuel components by the sediments used should occur in amounts directly dependent on the total organic contents of the sediments.

Table 19 presents K values for oxidized (wet H_2O_2) and unoxidized sieved marsh sediment for the fuel mixtures used in this program. This oxidation lowered the sediment total organic carbon content from 1.83% to 0.43%, and the small amount remaining was probably quite refractive and altered from original composition. Differences between oxidized and not oxidized condition K values were generally small for total fuel components of each fuel. For the lighter fuel components of each fuel with low K values, adsorption often increased after oxidation, while for heavier fuel components K values decreased after oxidation. The reason for this behavior is unknown. In general, the high density fuels were similar to heavier components of distillate fuel mixtures in their response to sediment oxidation.

The results obtained here indicate that organic carbon content cannot be used to predict hydrocarbon adsorption. Also, doubts are cast on the proposed partitioning of Chiou et al. (1979). Adsorption on the montmorillonite, with little organic carbon, closely approached the adsorption measured on the natural sediments in many cases. This would be impossible if adsorption only occurs on organic material in sediments.

Correlation of adsorption with total organic matter appears simplistic when the complexity of the adsorbent is considered. A sorbate hydrocarbon molecule encounters clay mineral surfaces, amorphous metal oxide surfaces, humic acid (unresolved but variable in composition), recent biogenic molecules and polymers (composition dependent on local flora and fauna), indigenous microorganisms, along with many other silicate minerals. A correlation may sometimes be found, but no mechanistic predictions or generalization to other sediments should be made. One also finds a good correlation between sediment montmorillonite content and hydrocarbon adsorption. It does not follow that montmorillonite is necessary for hydrocarbon adsorption.

Since the validity of an organic carbon content correlation with fuel component adsorption is in doubt, the exercise has not been done with sediments and fuels used here. The general order of fuel adsorption strength

TABLE 19. EFFECTS OF REDUCTION IN ORGANIC CARBON CONTENT.

JP4 Shale

<u>Component</u>	<u>K (not oxidized)</u>	<u>K (oxidized)</u>
Benzene	-	6
n-Heptane	242	163
2,2,4-Trimethylpentane	120	114
Ethylcyclohexane	122	73
Ethylbenzene	3	9
n-Butylbenzene	45	30
1,2,4,5-Tetramethylbenzene	30	18
Tetralin	35	24
2-Methylnaphthalene	43	30
2,6-Dimethylnaphthalene	88	73
Total JP4	4	10

JP5

<u>Component</u>	<u>K (not oxidized)</u>	<u>K (oxidized)</u>
1,3,5-Trimethylbenzene	12	41
1,2,4,5-Tetramethylbenzene	28	36
1,2,3,4-Tetramethylbenzene	25	37
Tetralin	20	54
Naphthalene	15	59
2-Methylnaphthalene	43	73
Biphenyl	48	40
2,6-Dimethylnaphthalene	127	115
2,3-Dimethylnaphthalene	110	101
Total JP5	22	52

JP8

<u>Component</u>	<u>K (not oxidized)</u>	<u>K (oxidized)</u>
p-Ethyltoluene	31	32
1,2,4-Trimethylbenzene	32	44
Indan	22	33
1,3,5-Triethylbenzene	338	103
2-Methylnaphthalene	86	44
1-Methylnaphthalene	80	41
Phenylcyclohexane	343	85
2-Ethyl-naphthalene	220	74
2,3-Dimethylnaphthalene	237	83
Total JP8	41	40

TABLE 19. EFFECTS OF REDUCTION IN ORGANIC CARBON CONTENT (CONTINUED).

		MF2	
MF2	Component	K (not oxidized)	K (oxidized)
	1,2,3,4-Tetramethylbenzene	29	29
	Tetralin	23	44
	1-Methylnaphthalene	41	48
	Biphenyl	53	39
	1,3-Dimethylnaphthalene	105	74
	2,3,-Dimethylnaphthalene	106	70
	2,3,5-Trimethylnaphthalene	206	113
	Fluorene	92	49
	3,3'-Dimethylbiphenyl	243	123
	Phenanthrene	236	137
	Total MF2	38	45
JP10	Tetrahydrocyclopentadiene	253	337
RJ5	Dehydro-HNN	1071	1600
	HXX	1172	1895
	HNN	1234	1851
	Total RJ5	1223	1821
JP9	Tetrahydrocyclopentadiene	232	894
	HNN	1871	
RJ6	Tetrahydrocyclopentadiene	248	171
	Total RJ5 Components	1422	281

by sediments is Poropotank River > Salt Marsh > Haynes Pond. This order is in agreement with the sediment organic contents, but this is considered a point of interest rather than elucidation of an adsorption mechanism. It is not recommended that sediment organic carbon content be used to predict the behavior of fuel releases.

6. REVERSIBILITY OF ADSORPTION

Reversibility of adsorption was determined by altering an adsorption equilibrium by decanting the aqueous solution and replacing with clean water. A new adsorption equilibrium was then attained. Single equilibration K values were calculated for adsorption equilibrium before and after dilution. Reversibility is indicated if differences between the two K values are small. These K values are shown in Table 20 for simulated MF2 components and marsh sediment. It is apparent that two K values are quite similar and the standard deviations overlap. The adsorption of fuel components thus occurs reversibly, and the slight differences in K values are attributed to errors in single equilibration K values rather than irreversible adsorption.

Reversible adsorption can be anticipated for hydrocarbon fuels used here, because chemisorption (strong bonding between sorbate and sorbent) does not occur with light hydrocarbons. Strong evidence that equilibrium was reached in the adsorption experiments reported here is provided by the fact that approach to equilibrium from adsorption and desorption produced similar K values.

7. MODEL FUEL SPILL EXPERIMENTS

A series of model fuel spill experiments were conducted to determine whether sediments affect the behavior and fate of fuel components in a situation of exposure to weather and natural sunlight, and of free exchange between the liquid phases and the atmosphere. Protection from rain was provided. These experiments allowed vapor losses of fuel components to occur and were conducted with JP4, JP8 and JP9 complete fuels. JP4 and JP8 were selected because they contain most hydrocarbons in the range of this study, and JP9 was selected because it contains a mixture of dicyclopentadiene and dinorbornadiene fuels and represents JP10 and RJ5 satisfactorily.

Model fuel spills were done with and without Haynes Pond sediment, and concentrations of dissolved fuel components in the aqueous layer in each spill experiment were determined. Differences in concentrations between spill experiments for a particular fuel with and without sediment, if present, would indicate the effect of sediment on the model spill. If new compounds were created in either the sediment or no sediment case, they would be detected in water phase analyses, assuming significant concentrations. In the design of these experiments, concentrations of dissolved fuel components approaching 1 mg/l were considered significant. Each model oil spill was sampled after three hours of equilibration and then sampled weekly for two more weeks.

In the experiments with petroleum derived JP4, total dissolved hydrocarbon concentrations initially were about 1 mg/l in systems with and

TABLE 20. COMPARISON OF ADSORPTION AND DESORPTION K VALUES.

	Mean K* (Adsorption)	Mean K* (Desorption)
1,2,3,4-Tetramethylbenzene	47.8 ± 10.5	58.4 ± 6.5
Tetralin	39.8 ± 9.1	50.0 ± 5.3
1-Methylnaphthalene	66.5 ± 13.8	71.0 ± 6.1
Biphenyl	88.0 ± 18.7	91.0 ± 9.3
1,3-Dimethylnaphthalene	171.0 ± 28.5	160.0 ± 19.8
2,3-Dimethylnaphthalene	171.0 ± 30.3	161.0 ± 21.4
2,3,5-Trimethylnaphthalene	314.0 ± 50.4	269.0 ± 46.7
Fluorene	175.0 ± 28.6	162.0 ± 24.1
3,3'-Dimethylbiphenyl	407.0 ± 77.7	321.0 ± 93.1
Phenanthrene	594.0 ± 193.8	421.0 ± 99.4
Total MF2	60.0 ± 12.2	71.7 ± 6.0

* Mean and standard deviation of four determinations

without sediment. Subsequent samples at one and two weeks contained no fuel components at more than 0.005 mg/l because of the high volatility of the fuel. The JP8 experiments showed similar results, with total initial concentrations of about 0.4 mg/l, which declined to less than 0.005 mg/l after one week.

The JP10 and RJ5 components of JP9 were present in the water phase of spill experiments at initial concentrations which were lower than previously measured saturation levels. This was probably due to the short equilibration time and the small surface area of the fuel water interface. The fuel components then separated, with JP10 floating and RJ5 sinking to form small droplets at the surface and bottom of the liquid in the beaker. After four days, the JP10 phase had evaporated, and dissolved JP10 concentrations were only 0.04 mg/l. RJ5 remained, and concentrations of HNN, the primary compound in RJ5, had risen to 0.27 mg/l with sediment and 0.08 mg/l without sediment. Over the next 25 days, HNN concentrations maintained a level of 0.08 mg/l without sediment and 0.14 mg/l with sediment present. The slightly higher concentrations in the presence of sediments are believed due to collection of some coated sediment particles in water samples, which were incompletely removed by centrifugation. This was unavoidable because sediment and RJ5 were in direct contact on the bottom of the container, a situation that did not occur for other fuels. HXX and dehydro HNN components of RJ5 were present at 0.003 and 0.002 mg/l respectively.

After four days, a group of new compounds was detected, which eluted later from G.C. columns than any of the RJ5 components. Several compounds were present at levels over 0.01 mg/l, but one compound predominated at a concentration of 0.82 mg/l and remained at this value throughout the experiment. The minor peaks increased in number and concentration until day seven, after which they remained constant. There were about 30 compounds present at more than 0.01 mg/l, but aside from the predominant one, no other was at more than 0.3 mg/l. The total concentration of these compounds was 2.2 mg/l in experiments with and without sediment, although there were small differences in the relative concentrations of minor components in the two experiments.

Mass spectra of the primary compound arising in these JP9 model fuel spill experiments showed that it had a molecular ion 16 amu. higher than HNN, but was of similar structure. It appears to be an oxidation product of HNN with one oxygen atom added, but the location of the oxygen atom could not be derived from the mass spectral data. Similar oxidation products were also identified for HXX and dehydro-HNN. There was at least one other (unidentified) oxidation product of dehydro-HNN. The other compounds produced in the JP9 experiments were present at levels which were too low for mass spectral analysis.

Oxidation products of RJ5 did not occur in adsorption measurements because the equilibration time was too short and contact with the atmosphere was minimized. These oxidation products should be considered in modeling the fate of high density fuel spills involving an RJ5 fuel or fuel fraction, because RJ5 sinks readily and does not vaporize rapidly, as is the case for most of other compounds in Air Force fuels.

SECTION IV

CONCLUSIONS

1. In general, equilibrium adsorption constants of hydrocarbon components of Air Force jet fuels dissolved in water on natural sediments and clays are small when compared with those of more polar organic compounds.
2. The magnitude of the adsorption constant on a given sediment is highly dependent on the size and complexity of the dissolved hydrocarbon, and bears an inverse relationship to the aqueous solubility of the hydrocarbon. Hydrocarbons of a similar structure (e.g. isomeric dimethylnaphthalenes) have similar adsorption constants.
3. The nature of the sediment has a considerable influence on the extent of adsorption of dissolved hydrocarbons. Non-swelling clays (illite and kaolinite) are poorly adsorbing substrates compared with montmorillonite or natural sediments. The organic carbon content of natural sediments has only a casual relationship to its adsorbent ability, and does not appear to be the sole causation of hydrocarbon adsorption.
4. Temperature does not have a strong effect on hydrocarbon adsorption over the range of temperatures occurring in natural aquatic environments.
5. The pH of the solution is not an important factor in the adsorption of dissolved hydrocarbons on sediments over the pH range occurring in natural aquatic environments.
6. Suspended sediments produce no measurable effect on the weathering of Air Force jet fuels with respect to the dissolved hydrocarbon components and their reaction products.
7. Increasing the salinity of the dissolved hydrocarbon solution from fresh to oceanic salinity produces a small, but rather consistent, increase in hydrocarbon adsorption by clays and sediments.

SECTION V

RECOMMENDATIONS

Although adsorption of dissolved jet fuel components on suspended sediments does not appear to be the major environmental fate in fuel spills on water, there is certainly a measurable effect. Since equilibrium adsorption constants determined for individual hydrocarbons in mixtures are rather independent of the fuel mixture, and since the adsorption constants for classes of hydrocarbon types are similar, it is possible to use these adsorption constants in combination with other information on jet fuel composition and hydrocarbon solubilities to calculate all aspects of sediment interaction with a jet fuel spill. These interactions should be incorporated in spill modeling studies.

Further investigation is also warranted on the interactive effects of hydrocarbons in mixtures on their aqueous solubilities. Anomalous effects were observed during this study, including deviations from ideality of hydrocarbon solubility, and, to a lesser extent, adsorption caused by qualitative differences in the makeup of the hydrocarbon mixture.

REFERENCES

- Bikerman, J. J. Physical Surfaces. New York: Academic Press, 1970.
- Chiou, C. T.; Peters, L. J.; and Freed, V. H. "A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds," Science 206, 16, 831-832, 1979.
- Goring, C. A. I., and Hamaker, J. W., eds. "Adsorption," in Organic Chemicals in the Soil Environment, Vol. 1. New York: Marcel Dekker, Inc., 1972.
- Greenland, D. J., and Hayes, M. H. B., eds. "The Chemistry of Soil Processes," Adsorption, pp. 221-400. New York: John Wiley and Sons, 1981.
- Karickhoff, S. W. "Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments," Contaminants and Sediments, Vol. 2, Chapter 11. R. A. Baker, ed. Ann Arbor Science Press, Ann Arbor Michigan, 1980.
- Karickhoff, S. W.; Brown, D. S.; and Scott, T. A. "Sorption of Hydrophobic Pollutants on Natural Sediments," Water Research, 13, 12, 241-248, 1979.
- Means, J. C.; Hassett, J. J.; Wood, S. G.; Banwart, S. Ali; and Khan, A. "Sorption Properties of Polynuclear Aromatic Hydrocarbons and Sediments: Heterocyclic and Substituted Compounds," Polynuclear Aromatic Hydrocarbons - Chemical and Biological Effects, 4th International Symposium. Columbus, Ohio: Battelle Press, 1980b.
- Means, J. C.; Wood, S. G.; Hassett, J. J.; and Banwart, W. L. "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils," Environ. Sci. Tech., 14, 12, 1524-1528, 1980a.
- Rogers, R. D.; McFarlane, J. C.; and Cross, A. J. "Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay," Environ. Sci. Tech., 14, 4, 457-460, 1980.
- Stumm, W., and J. J. Morgan. Aquatic Chemistry. New York: John Wiley and Sons, 1981.
- Theng, B. K. G. The Chemistry of Clay-Organic Interactions. New York: John Wiley and Sons, 1974.
- van Olphen, H. An Introduction to Clay Colloid Chemistry, 2nd ed. New York: John Wiley and Sons, 1977.