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HYDROCARBON FUEL SPILL DISPERSION ON WATER: LITERATURE REVIEW

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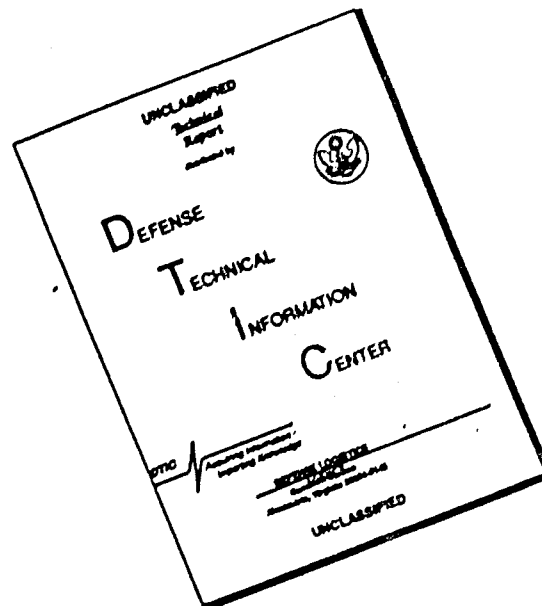
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The literature concerning the fate of light hydrocarbon fuel spills on water is reviewed. The review focuses on jet fuels and contains some discussion of gasoline, diesel, marine, and kerosene fuel spills. The two major fates of light hydrocarbon spill on water are evaporation and dissolution, although biodegradation, photooxidation, and adsorption onto suspended sediments can also be of some importance.					
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PREFACE

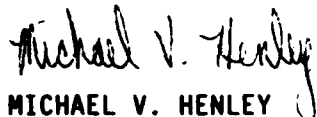
This review was part of an ongoing effort to study the dispersion of a hydrocarbon fuel spill on water. The work was conducted by Battelle Columbus Division, 505 King Avenue, Columbus OH 43201, under Task Order Contract F08635-85-C-0122, Subtask 1.02 for the Engineering and Services Laboratory of the Air Force Engineering and Services Center.

This work was conducted from May 1986 through September 1986. The HQ AFESC/RDVC project officer was Mr Michael V. Henley.

This interim report covers the literature review of hydrocarbon fuel/water interactions.

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

This report has been reviewed and is approved for publication.



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SECTION I

INTRODUCTION

The environmental impact of Air Force-specific fuels and chemicals is of great concern to the United States Air Force. This report presents the results of a literature search on the characterization of the fate of hydrocarbon fuels in the aquatic environment.

A. OBJECTIVE

The objective of this work was to review the literature on the dispersion, evaporation, dissolution and degradation of light hydrocarbon fuels on water, and to summarize all data on fuel/water interactions. In addition, applicable experimental techniques are reviewed for the design of laboratory studies to determine the kinetics of fuel distribution following a spill. The literature study focuses on Air Force aircraft fuels, JP-4, JP-5, JP-8, and gasoline, diesel, marine, and kerosene fuels.

B. BACKGROUND

The dispersion process for fuels accidentally spilled on water is physically and chemically complex, involving such elementary processes as:

1. Physical spreading of the fuel layer
2. Evaporation and dispersion of the more volatile fuel components into the atmosphere.
3. Partitioning of fuel components between the fuel and water phases.
4. Mixing and transport of dissolved fuel components.
5. Adsorption of fuel components on suspended particulate matter.
6. Chemical and/or biological interactions within each phase.

The complexity of the problem is compounded because both the equilibrium states in each phase and the dynamics of approach to equilibrium are influenced by temperature, turbulence (air and water), and composition (fuel and water). An understanding of the overall process is critical in assessing environmental impact and preventing contamination.

C. GENERAL APPROACH

A literature review of fuel/water interactions and spill studies was conducted to assemble and evaluate information relevant to hydrocarbon fuel dispersion on water. The general approach was to first conduct a search of the literature for relevant abstracts. A computerized search of several applicable data bases was completed and papers and articles relating to the above objective were retrieved. References cited in these reports and articles were then screened for additional citations that had been missed in the computer search. Finally, manual searches were conducted in the most recent literature for articles by key authors of the papers identified earlier.

The on-line databases searched included NTIS, Compendex, Geoarchive, Energyline, Georef, Ei Meetings, P/E News, Chemical Abstracts, Water Resources and Aerospace Abstracts. On-line retrieval of 97 abstracts revealed approximately 23 papers and reports relevant to modeling the process of fuel dispersion on water. Those reports were then ordered.

References from the reports revealed another 30-40 papers of interest. A manual search through NTIS and Chemical Abstracts of very recent literature found approximately another dozen potentially relevant papers. A total of approximately 75 papers and reports were reviewed for relevancy to the Air Force objective of modeling the process of fuel dispersion on water. The papers and reports were organized by topic and those papers addressing the same topic were simultaneously reviewed.

D. ORGANIZATION OF THE REPORT

This report is organized by the subjects which address fuel/water interactions and experimental methodology for conducting laboratory studies of the kinetics of fuel spills on water. The relevant topics covered by the papers and reports compiled in the literature search concerning jet fuels are:

1. Chemical and Physical Properties
2. Evaporation from water
3. Dissolution in water

4. Biodegradation in aquatic communities
5. Dispersion and surface effects of fuel evaporation and degradation
6. Adsorption onto suspended sediments in water
7. Photooxidation on water
8. Experimental methodology for determining dissolution and volatilization of jet fuels on water

Potentially relevant findings from the literature search will be organized by topic. Section II reviews the literature search, broken out into the eight topics listed above.

SECTION II

RESULTS AND DISCUSSION OF THE LITERATURE REVIEW

A. PHYSICAL AND CHEMICAL PROPERTIES OF JET FUEL

The dispersion of hydrocarbon fuels on water is very dependent upon the physical and chemical properties of the fuel. The composition of jet fuels may vary from one refinery to another. Major components of JP-4,5 and 8 have been assessed (Reference 1). Recently, a study was conducted to determine the variability of major and minor chemical components of Air Force distillate fuels, including reference, petroleum-derived, and shale-derived fuels (Reference 2). Significant differences were found between the three types of water-equilibrated fuels. The total concentration of water-soluble components in the reference JP-5 fuel was only 20 percent of that in the reference JP-4 fuels. The concentration of water solubles in the shale-derived JP-4 was 40 percent of that in the petroleum-derived JP-4 fuel. The reference JP-4 fuel was shown to be a good qualitative standard for the petroleum-derived JP-4 fuels. However, while most major features of the Reference JP-4 fuel showed coefficients of variation of only about 10 percent, the major features of the 50 petroleum derived JP-4 fuels showed deviations generally greater than 50 percent. Tables 1-3 summarize the neat fuel, water, and vapor phase concentrations of the JP-4 reference fuel from these studies.

Important properties in modeling the dispersion of fuel spills on water include fuel solubility, volatility, rate of dissolution and weathering, and rate of spreading or surface tension. While these data may exist in chemical handbooks for pure components, properties of mixtures are not always well characterized. Properties such as density and viscosity for jet fuels as a category have been measured (Reference 3). Some of the physical properties of JP-4 and JP-8 are shown in Tables 4-11 (Reference 1). Data are available for specific gravity and latent heat of vaporization for JP-4 (Reference 4). Solubility data can be found in the literature (References 1, 5,6,7,8) for fractions of jet fuels and for diesel fuels (References 9,10,11). Some surface tension data for jet fuels are also available (Reference 12). The relevancy of these physical properties of the fuels will be discussed and data will be presented in the following sections.

TABLE 1. NEAT FUEL FEATURE CONCENTRATIONS FOR SELECTED COMPOUNDS (REFERENCE 2)

COMPOUND	JP-4 REFERENCE FUEL			DATABASE OF 54 JP-4 PETROLEUM-DERIVED FUELS		
	AVERAGE CONC. (mg/ml)	% REL.	STD. DEV.	AVERAGE CONC. (mg/ml)	% REL.	STD. DEV.
benzene	3.64		7.85	4.1		100
n-heptane	25.1		4.21	24.3		42.6
toluene	8.51		4.15	13.8		60.0
naphthalene	2.66		12.3	2.2		54.8
total concentration	607		4.13	601		11.7

TABLE 2. WATER SOLUBLE FEATURE CONCENTRATIONS FOR SELECTED COMPOUNDS (REFERENCE 2)

COMPOUND	JP-4 REFERENCE FUEL			DATABASE OF 54 JP-4 PETROLEUM-DERIVED FUELS		
	AVERAGE CONC. (mg/ml)	% REL.	STD. DEV.	AVERAGE CONC. (mg/ml)	% REL.	STD. DEV.
benzene	1.34x10(4)		9.39	1.61x10(4)		89.6
n-heptane	157		11.2	132		43.7
toluene	9.48x10(3)		10.6	1.62x10(4)		64.0
naphthalene	ND		-	328		63.9
total concentration	3.64x10(4)		9.29	5.03x10(4)		48.1

TABLE 3. VAPOR PHASE FEATURE CONCENTRATIONS FOR SELECTED COMPOUNDS (REFERENCE 3)

COMPOUND	JP-4 REFERENCE FUEL			DATABASE OF 55 JP-4 PETROLEUM-DERIVED FUELS		
	AVERAGE CONC. ($\mu\text{g/l}$)	% REL. STD. DEV.		AVERAGE CONC. ($\mu\text{g/l}$)	% REL. STD. DEV.	
benzene	4.68x10(3)	8.46		6.18x10(3)	116	
n-heptane	1.20x10(4)	14.1		1.18x10(4)	44.8	
toluene	2.96x10(3)	16.0		4.80x10(3)	62.1	
naphthalene	9.51	32.6		20.0	192	
total concentration	31.2x10(4)	10.7		33.3x10(4)	25.5	

TABLE 4. PHYSICAL PROPERTIES OF JP-4 (REFERENCE 1)

SAMPLE	<u>FUEL 1A GEC-145-400-792033 (JP-4)</u>	
Viscosity (cSt)	-30°F (SFQLA)	2.46
	-20°F	2.206
	32°F	1.288
	70°F	0.9546
	100°F	0.7864
Surface Tension (dyne/cm)	-20°F	27.52 *extrapolated
	32°F	25.05
	70°F	23.28
	100°F	21.73
Density (g/CC)	-20°F	0.7957
	32°F	0.7957
	70°F	0.7557
	100°F	0.7423
Gravity (60/60) D287/Calc SFQLA	54.3°API	0.7616 Specific
Freezing Pt. SFQLA	-64°C	-83°F

TABLE 5. PHYSICAL PROPERTIES OF JP-4 (REFERENCE 1)

SAMPLE FUEL 1A GEC-145-400-792033 (JP-4)

Color D156	+20
Acidity (mg KOH/g) D3242	0.002
Copper Strip (2 hrs at 212°F) D130	1A
Existent Gum (mg/100 ml) D381	0.8
Particulates (mg/l) D2276	0.1
Filtration Time D2276	17 min at 27"
Water Reaction, Vol. Change (ml) D1094	0.0
Ratings D1094	No. 1 No. 1
WSIM, Minisonic	96
Additives	
Anti-icing (Vol %)	07

TABLE 6. PHYSICAL PROPERTIES OF JP-4 (REFERENCE 1)

Sample	Fuel 1A GEC-145-400-792033 (JP-4)		79-F-2270
			79-F-245
			45
Composition			45A
			09
	Vol %		
	Mass spec		
	MRC	SFQLA	
1. Paraffins	61.2		
2. Monocycloparaffins	24.2		
3. Dicycloparaffins	4.9		
4. Alkylbenzenes	8.2		
5. Indans and Tetralins	1.1		
6. Indenes and Dihydronaphthalenes	---		
7. Naphthalenes	0.4		
Aromatics (4 + 5 + 6 + 7) D1319	9.7	12.3	
Olefine D1319		1.5	
Total Paraffins (1+2+3)/D1319(100%-A-0)	90.3	86.2	

Hydrogen Content (wt %)			
POSF - D3701 / SFQLA - D3343	14.48	14.46	
Sulfur, Mercaptan (wt %) D1219-61		0.0004	
Total (wt %) D2622-67		3.03	
Net Heat of Combustion (BTU/lb)			
(MRC-D240/SFQLA-D3338)	18767	18747	
Luminometer Number D1740		77	
Smoke Pt. (SFQLA-Calc/SFQLA-D1322)	28	25.0	

TABLE 7. PHYSICAL PROPERTIES OF JP-4 (REFERENCE 1)

Vol % Recovered	Fuel Volatility					
	Sample		FUEL 1A GEC-145-400-792033 (JP-4)			
	JP-4	JP-8	SFQLA 2887 oC	MRC 2887 oC	SFQLA Deg oC	SFQLA Deg oF
IBP (0.5%)	*	*	28	25	60	140
1				34		
5			72	72		
10	*	**	89	93	97	206
15			97			
20	**	*	104	108	110	230
25			115			
30			119	123		
35			126			
40			137	141		
45			144			
50	**	*	155	160	146	295
55			166			
60			176	180		
65			188			
70			197	199		

TABLE 7. PHYSICAL PROPERTIES OF JP-4 (REFERENCE 1) (CONCLUDED)

Vol % Recovered	JP-4	JP-8	SFQLA		MRC	SFQLA	
			2887 oC			Deg oC	Deg oF
75			208				
80			217		218		
85			228				
90	**	*	237		237	224	435
95			253		254		
99					273		
FBP (99.5%)	**	**	283		281	248	478
Residue	**	**					1.0
Loss (%)	**	**					1.0
Recovery at 400oF (%) (204.4%)							82.0
Vapor Pressure (1b Acid)	**					2.5	
Flash pt (oC)		**	D56 (Tag closed)		D93 (Pensky-Martens)	D3243 (Setflash)	
True Vapor Pressure			-70oF		+37oF	+70oF	100oC

TABLE 8. PHYSICAL PROPERTIES OF JP-8 (REFERENCE 1)

SAMPLE	<u>FUEL 2A GEC-140-800-792033 (JP-8)</u>		
Viscosity (cSt) MRC	-30°F (SFQLA)		
	-20°F	9.101	
	32°F	3.526	
	70°F	2.233	
	100°F	1.665	
Surface Tension (dyne/cm) MRC	-20°F	31.17	*extrapolated
	32°F	28.78	
	70°F	27.08	
	100°F	25.69	
Density (g/CC) MRC	-20°F	0.8460	
	32°F	0.8252	
	70°F	0.8096	
	100°F	0.7977	
Gravity (60/60) D287/Calc SFQLA		42.3°API	0.8142 Specific
Freezing Pt. SFQLA		-8°C	-47°F

TABLE 9. PHYSICAL PROPERTIES OF JP-8 (REFERENCE 1)

SAMPLE FUEL 2A GFC-140-800-792033 (JP-8)

Color D156		+20
Acidity (mg KOH/g) D3242		0.002
Copper Strip (2 hrs at 212°F) D130		1A
Existent Gum (mg/100 ml) D381		0.0
Particulates (mg/l) D2276		0.5
Filtration Time D2276		11 min at 27"
Water Reaction, Vol. Change (ml) D1094		0.0
Ratings D1094	No. 1	No. 1
WSIM, Minisonic		65
Additives		
Anti-icing (Vol %)		0.14

TABLE 10. PHYSICAL PROPERTIES OF JP-8 (REFERENCE 1)

Sample	Fuel 2A GEC-140-800-792033 (JP-8)		79-F-2270
			79-F-245
			45
Composition			45
			09
	Vol %		
	Mass spec		
	MRC	SFQLA	
1. Paraffins	44.4		
2. Monocycloparaffins	41.4		
3. Dicycloparaffins	2.6		
4. Alkylbenzenes	6.7		
5. Indans and Tetralins	3.4		
6. Indenes and Dihydronaphthalenes	---		
7. Naphthalenes	1.5		
Aromatics (4 + 5 + 6 + 7) D1319	11.6	16.8	
Olefine D1319		2.1	
Total Paraffins (1+2+3)/D1319(100%-A-0)	88.4	81.1	

Hydrogen Content (wt %)			
POSF - D3701 / SFQLA - D3343	13.94	13.78	
Sulfur, Mercaptan (wt %) D1219-61		0.0004	
Total (wt %) D2622-67		0.12	
Net Heat of Combustion (BTU/lb)			
(MRC-D240/SFQLA-D3338)	18576	18591	
Luminometer Number D1740		48	
Smoke Pt. (SFQLA-Calc/SFQLA-D1322)	22	26.0	

TABLE 11. PHYSICAL PROPERTIES OF JP-8 (REFERENCE 1)

Vol % Recovered	Sample	Fuel Volatility					
		FUEL 2A GEC-140-800-792033 (JP-8)					
		JP-4	JP-8	SFQLA 2887 oC	MRC 2887 oC	SFQLA	
						Deg oC	Deg oF
IBP (0.5%)	*	*		144	128	183	361
1					144		
5				175	176		
10	*	**		188	190	202	396
15				195			
20	**	*		200	203	208	406
25				205			
30				210	214		
35				215			
40				218	222		
45				221			
50	**	*		226	231	221	429
55				230			
60				234			
65				237			
70				242	249		

TABLE 11. PHYSICAL PROPERTIES OF JP-8 (REFERENCE 1) (CONCLUDED)

Vol % Recovered	JP-4	JP-8	SFQLA		MRC	SFQLA	
			2887	oC		Deg oC	Deg oF
75			248				
80			253		259		
85			251				
90	**	*	264		272	248	478
95			272		282		
99					300		
FBP (99.5%)	**	**	296		306	267	512
Residue	**	**					1.0
Loss (%)	**	**					1.0
Recovery at 400oF (%) (204.4%)							
Vapor Pressure (lb Acid)	**						
Flash pt (oC)		**	D56 (Tag closed)		093 (Pensky-Martens)	D3243 (Setflash)	
					54		
True Vapor Pressure			-70oF		+37oF	+70oF	100oC

3. EVAPORATION OF JET FUELS FROM WATER

Many studies have been conducted to determine the volatilization rates of major water-soluble fuel components (References 1, 11,13-22). These studies have generally approached the problem from the perspective of the volatilization of dissolved hydrocarbons at a water/air interface, a formulation related to but slightly different from that of the volatilization of fuel components from an unmixed fuel layer, such as that of an undissolved fuel spill on water.

The model generally used for estimating mass transfer of light hydrocarbon fuel spills is a specialized case of the classical two-film model (References 23, 24), with negligible resistance in the liquid phase, in the case of a thin film, and all the resistance in the gas phase. The classical two-film model is generally presented as the starting point for the theoretical development of the volatilization of hydrocarbon fuel components, although fugacity models have also been developed (References 25,26,27). The two-film model is used most frequently to describe the flux of gases across an air/water interface. The main body of each phase is well-mixed, and resistance to transport occurs at both a gaseous and a liquid interfacial layer. In this case, the flux, F , of a liquid component of concentration C_l , into the gaseous phase is described as:

$$F = -k\Delta C \quad (1)$$

where ΔC is the concentration difference across the interface and k is the exchange constant:

$$k = D/z \quad (2)$$

where D is the coefficient of molecular diffusion, and z is the boundary layer thickness. In the two-film model, the resistance to any exchange of gas is due to a combination of a gas phase and a liquid phase resistance. In steady state, the fluxes at the interface are equal, and applying Henry's law, the flux, written in terms of the liquid-phase resistance K_l , is:

$$F = K_l (C_g/H - C_l) \quad (3)$$

and
$$K_1 = \left(1/k_1 + 1/(Hk_g) \right)^{-1} \quad (4)$$

and where H is Henry's constant and k_1 and k_g are the mass transfer coefficients for the gas and liquid phases, respectively, and c_g is the gas phase concentration. Henry's constants for selected hydrocarbons in jet fuels are given in many references (References 28,29,30,31,32). Tables 12-14 show recently determined experimental values for Henry's law constants and other properties for common hydrocarbons (Reference 32). The two-film model is useful for determining the volatilization rates of dissolved hydrocarbons. For high-volatility, well-mixed hydrocarbons, the resistance is usually dominated by a liquid-phase resistance.

For a liquid spill, however, the evaporation is from a fuel layer itself, and not a well-mixed aqueous phase. In this case, the volume fuel fraction evaporated, after time t , f_v (dimensionless), is:

$$f_v = H (k_g t / L) \quad (5)$$

where L is the depth of the fuel layer. For complex hydrocarbon mixtures, such as those found in jet fuels, Henry's constant must be expressed as a function of the flux itself, as the more volatile compounds vaporize. There has been some theoretical work concerning the calculation of H as a function of F (Reference 33), however the enthalpy of vaporization for the fuel mixtures must be accurately known and this data is not always available. Where the spreading of the fuel over the water is rapid, and the fuel layer is thin, the resistance is entirely in the air phase since the material does not have to diffuse through a liquid phase. From Equations (1) and (2), the flux can be expressed as:

$$F = -(D \Delta C) / z \quad (6)$$

and the mass flow rate, $\dot{m}$ is

$$\dot{m} = -A (D \Delta C) / z \quad (7)$$

where A is the area of the spill. For turbulent conditions, the mass transfer coefficient $k_g (=D/z)$ is a function of the transport conditions in the

TABLE 12. HENRY'S CONSTANT FOR SOLUTES USED IN
VOLATILIZATION EXPERIMENTS (REFERENCE 32)

	Small Scale Apparatus	Wind Wave Tank	H at 25°C atm m ³ /mol
Carbon Tetrachloride	✓	✓	1.6×10^{-2}
Toluene	✓	✓	6.7×10^{-3}
Benzene	✓	✓	5.5×10^{-3}
Chorobenzene	✓	✓	3.7×10^{-3}
1,2-dichloropropane	✓	✓	2.1×10^{-3}
0-dichlorobenzene	✓		1.9×10^{-3}
Bromobenzene	✓		2.1×10^{-3}
1-Choro-2-Methylpropane	✓		1.2×10^{-3}
1,2-dibromoethane	✓	✓	6.3×10^{-4}
Bromoform	✓		6.2×10^{-4}
1,3-dibromopropane	✓		3.2×10^{-4}
3-heptanone	✓		1.5×10^{-5}
2-heptanone	✓	✓	1.0×10^{-4}
4-methyl-2-pentanone	✓		3.1×10^{-5}
2-butanone	✓		4.3×10^{-5}
2-pentanone	✓	✓	3.7×10^{-5}
2-butanol	✓		3.9×10^{-5}
1-pentanol	✓	✓	1.5×10^{-5}
Acetophenone	✓		1.1×10^{-5}
Cyclohexanol	✓		8.7×10^{-6}
2-methyl-1-propanol		✓	5.6×10^{-5}
1-butanol		✓	1.1×10^{-5}

TABLE 13a. PROPERTIES OF SOLUTES (REFERENCE 32)
PROPERTIES OF THE SOLUTES USED IN THIS STUDY

ESTIMATED VALUES ARE DESIGNATED WITH AN ASTERISK*

Compound	Molecular Weight	Vapor Pressure (atm)	Aqueous Solubility mol/m	Solubility of water in solute at 25°C (mol frn)	Henry's Law Constant atm m ³ /mol.
		20°C	20°C		20°C
		25°C	25°C		25°C
Benzene	78.11	0.100	22.4	7x10 ⁻⁴	4.39x10 ⁻³
Toluene	92.13	0.029	5.39	5x10 ⁻⁴	5.18x10 ⁻³
Chlorobenzene	112.56	0.012	4.44	2x10 ⁻³	3.72x10 ⁻³
Bromobenzene	157.02	0.056	2.61	2x10 ⁻³	2.08x10 ⁻³
o-Dichlorobenzene	147.01	0.00132	0.68	4x10 ⁻⁴	1.8x10 ⁻³
Carbon-tetrachloride	153.84	0.118	5.20	7x10 ⁻⁴	1.95x10 ⁻³
1,2-Dichloro-propane	113.0	0.052	25.0	2x10 ⁻³	2.27x10 ⁻²
1-Chloro-2-methyl propane	92.57	0.119	99.0	4x10 ⁻³	2.07x10 ⁻³
1,2-Dibromoethane	187.9	0.0144	23.0	4x10 ⁻³	1.2x10 ⁻³
1,3-Dibromo-propane	201.9	0.0027	8.4	2x10 ⁻³	6.32x10 ⁻⁴
Bromoform	252.7	0.0060	12.0	1x10 ⁻³	3.18x10 ⁻⁴
1-Butanol	74.12	0.0058	1040	0.5	6.15x10 ⁻⁴
2-Butanol	74.12	0.0158	1686	0.76	1.65x10 ⁻⁵
1-Pentanol	88.15	0.0034	307 (22°)	0.33	7x10 ⁻⁶
2-Methyl-1-propanol	74.12	0.0079	1280	0.51	8x10 ⁻⁶
Cyclohexanol	100.16	0.00112	1260	0.58	1.0x10 ⁻⁵
2-Pentanone	86.14	0.016	500	0.14	2.5x10 ⁻⁶
2-Heptanone	114.18	0.0034	38.0	0.11	3.67x10 ⁻⁵
					1.01x10 ⁻⁴

TABLE 13a. PROPERTIES OF SOLUTES (REFERENCE 32)

Compound	Molecular Weight	Vapor Pressure (atm)		Aqueous Solubility mol/m ³		Solubility of water in solute at 25°C (mol frn)	Henry's Law Constant atm m/mol.	
		20°C	25°C	20°C	25°C		20°C	25°C
3-Heptanone	114.18		0.00184	125.2		0.047	2.0×10^{-4}	
4-Methyl-2-pentanone	100.16	0.0079	0.0095	190		0.097	4.60×10^{-5}	
Acetophenone	120.16		4.87×10^{-4}		45.8	0.01		1.06×10^{-5}
2-Butanone	72.12	0.102	0.129	3702	3134	0.055	2.92×10^{-5}	4.35×10^{-5}
(Methyl ethyl ketone)				3328			3.23×10^{-5}	
Oxygen	32.0	-	-	-	-	-	-	-
Water	18.0	-	-	-	-	-	-	-
Air	29	-	-	-	-	-	-	-
Carbon dioxide	44	-	-	-	-	-	-	-
Radon								

TABLE 13b. PROPERTIES OF SOLUTES (REFERENCE 32)

PROPERTIES OF THE SOLUTES USED IN THIS STUDY

ESTIMATED VALUES ARE DESIGNATED WITH AN ASTERISK*

Compound	Diffusivities (cm^2/s)			Schmidt Numbers		Molar Volume at $N. B.P.$ cm^3/mol
	in air 20°C	in air 25°C	in water $\times 10^6$ 20°C	in air 25°C	in water 25°C	
Benzene	0.0797	0.0817	9.57	1.892	1.898	96
Toluene	0.0732	0.0751	8.45	2.060	2.065	118.2
Chlorobenzene	0.0705	0.0724	8.05	2.139	2.142	116.9
Bromobenzene	0.0691	0.0709	7.95	2.182	2.187	119.3
o-Dichlorobenzene	0.0643	0.0659	7.704	2.345	2.353	137.8
Carbon-tetrachloride	0.0695	0.0713	8.22	2.169	2.175	112.8
1,2-Dichloro-propane	0.0716	0.0734	8.09	2.106	2.113	115.8
1-Chloro-2-methyl propane	0.0719	0.0739	8.04	2.097	2.104	117.1
1,2-Dibromethane	0.0724	0.0742	8.92	2.083	2.090	98.4
1,3-Dibromo-propane	0.0663	0.0680	7.9	2.275	2.281	120.6
Bromoform	0.0710	0.0728	8.87	2.125	2.130	99.5
1-Butanol	0.0778	0.0798	8.65	1.938	1.943	103.6
2-Butanol	0.0778	0.0798	8.65	1.938	1.943	103.6
1-Pentanol	0.0703	0.0721	7.70	2.145	2.151	125.8
2-Methyl-1-propanol	0.0778	0.0798	8.65	1.938	1.943	103.6
Cyclohexanol	0.0693	0.0711	7.71	2.176	2.181	125.6
2-Pentanone	0.0723	0.0741	7.99	2.086	2.093	118.4
2-Heptanone	0.0591	0.0606	6.26	2.552	2.559	177.6

TABLE 13b. PROPERTIES OF SOLUTES (REFERENCE 32)

Compound	Diffusivities (cm^2/s)				Schmidt Numbers		Molar Volume at N.B.P. (cm^3/mol)
	in air 20°C	in air 25°C	in water 20°C	$\times 10^6$ 25°C	in air 25°C	in water 20°C	
3-Heptanone	0.0591	0.0606	6.26	7.54	2.559	1604	177.6
4-Methyl-2-pentanone	0.0661	0.0678	7.21	8.68	2.287	1393	140.6
Acetophenone	0.0649	0.0666	7.21	8.683	2.329	1393	140.4
2-Butanone (Methyl ethyl ketone)	0.0805	0.0825	9.05	10.9	1.880	1109	96.2
Oxygen			18.0			558	25.6
Water					0.77		18.9
Air			18.0		0.60		29.9
Carbon dioxide			17.7			570	34.0
Radon							

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32)

Compound	Literature Data	Experimental		Sorbent Concentration g/m ³
		Henry's Law Constants		
		Water	Water + Sorbent	
Naphthalene	MW=128.2	4.40x10 ⁻⁴		
	P ^S = 1.08x10 ⁻⁴ atm	4.43x10 ⁻⁴	3.73x10 ⁻⁴	28.6 FA
	C ^S =31.7g/m ³	4.31x10 ⁻⁴	4.24x10 ⁻⁴	10.0 FA
	=0.247mol/m ³	4.38x10 ⁻⁴	3.93x10 ⁻⁴	14.3 FA
	H =4.37x10 ⁻⁴ atm m ³ /mol	4.66x10 ⁻⁴	4.18x10 ⁻⁴	28.6 FA
	H =4.83x10 ⁻⁴ atm m ³ /mol (28)	4.13x10 ⁻⁴	4.18x10 ⁻⁴	14 HA
		4.47x10 ⁻⁴	3.70x10 ⁻⁴	14 HA
		4.38x10 ⁻⁴	3.87x10 ⁻⁴	28 HA
		4.18x10 ⁻⁴	3.58x10 ⁻⁴	7.7HA
		4.42x10 ⁻⁴	4.35x10 ⁻⁴	19.14HA
		4.68x10 ⁻⁴	4.63x10 ⁻⁴	22.3 HA
		4.56x10 ⁻⁴	4.24x10 ⁻⁴	36.7 HA
		4.44x10 ⁻⁴	4.22x10 ⁻⁴	54.1 HA
		4.50x10 ⁻⁴	4.28x10 ⁻⁴	20 B
		4.85x10 ⁻⁴	4.49x10 ⁻⁴	100 B
		4.34x10 ⁻⁴	4.18x10 ⁻⁴	50 B

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32)

Compound	Literature Data	Experimental		Sorbent Concentration g/m ³
		Henry's Law Constants		
		Water	Water + Sorbent	
Naphthalene	MW=128.2	4.40x10 ⁻⁴		
	P ^S = 1.08x10 ⁻⁴ atm	4.43x10 ⁻⁴	3.73x10 ⁻⁴	28.6 FA
	C ^S =31.7g/m ³	4.31x10 ⁻⁴	4.24x10 ⁻⁴	10.0 FA
	=0.247mol/m ³	4.38x10 ⁻⁴	3.93x10 ⁻⁴	14.3 FA
	H =4.37x10 ⁻⁴ atm m ³ /mol	4.66x10 ⁻⁴	4.18x10 ⁻⁴	28.6 FA
	H =4.83x10 ⁻⁴ atm m ³ /mol (28)	4.13x10 ⁻⁴	4.18x10 ⁻⁴	14 HA
		4.47x10 ⁻⁴	3.70x10 ⁻⁴	14 HA
		4.38x10 ⁻⁴	3.87x10 ⁻⁴	28 HA
		4.18x10 ⁻⁴	3.58x10 ⁻⁴	7.71HA
		4.42x10 ⁻⁴	4.35x10 ⁻⁴	19.14HA
		4.68x10 ⁻⁴	4.63x10 ⁻⁴	22.3 HA
		4.56x10 ⁻⁴	4.24x10 ⁻⁴	36.7 HA
		4.44x10 ⁻⁴	4.22x10 ⁻⁴	54.1 HA
		4.50x10 ⁻⁴	4.28x10 ⁻⁴	20 B
		4.85x10 ⁻⁴	4.49x10 ⁻⁴	100 B
		4.34x10 ⁻⁴	4.18x10 ⁻⁴	50 B

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONTINUED)

Compound	Literature Data	Experimental		Sorbent
		Henry's Law Constants atm m ³ /mol	Concentration g/m ³	
Biphenyl				
	MW=154.21 *	3.0 x10 ⁻⁴		
	P ^S =7.45x10 ⁻⁵ atm	2.95x10 ⁻⁴	2.96x10 ⁻⁴	12.0 HA
	C ^S =7.1g/m ³	3.23x10 ⁻⁴	2.75x10 ⁻⁴	12.14 HA
	=0.0460mol/m ³	3.12x10 ⁻⁴	2.82x10 ⁻⁴	12.0 HA
	H =4.08x10 ⁻⁴ atm m ³ /mol (28)			
o-Dichlorobenzene				
	MW=147.01	1.90x10 ⁻³		
	P ^S =0.00193 atm	1.89x10 ⁻³	1.88x10 ⁻³	1.36 HA
	C ³ =145g/m ³	1.98x10 ⁻³	2.01x10 ⁻³	9.52 HA
	=0.986mol/m ³			
	H =1.95x10 ⁻³ atm m ³ /mol			
p-Dichlorobenzene				
	MW=147.01 *	2.40x10 ⁻³		
	P ^S =8.9x10 ⁻⁴ atm	2.34x10 ⁻³	2.44x10 ⁻³	20.6 HA
	C ^S =83.1g/m ³	2.48x10 ⁻³	2.44.10 ⁻³	13.6 HA
	=0.565 mol/m ³			

* extrapolated values

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONTINUED)

Compound	Literature Data	Experimental		Sorbent Concentration g/m ³
		Henry's Law Constants atm m ³ /mol		
		Water	Water + Sorbent	
1,2,3-Trichlorobenzene	MW=181.5 *	1.25 x10 ⁻³		
	P ^S =5.23x10 ⁻⁴ atm	1.245x10 ⁻³	1.195.10 ⁻³	41.3 IIA
	C ^S =31.5g/m ³	1.26 x10 ⁻³	1.12 x10 ⁻³	63.03 IIA
	= 0.170 mol/m ³			
1,2,3,5-Tetrachlorobenzene	MW=215.9	1.57x10 ⁻³		
	P ^S =1.836x10 ⁻⁴ * atm	1.59x10 ⁻³	1.49x10 ⁻³	11.6 IIA
	C ^S =3.57 g/m ³	1.57x10 ⁻³	1.55x10 ⁻³	31.8 IIA
	=0.0165 mol/m ³			
Bromobenzene	MW=157.02	2.48x10 ⁻³		
	P ^S =5.45x10 ⁻³ atm	2.51x10 ⁻³	2.53x10 ⁻³	10.71 IIA
	C ^S =410 g/m ³	2.44x10 ⁻³	2.37x10 ⁻³	13.6 IIA
	=2.61 mol/m ³			
	H = 2.06x10 ⁻³ atm m ³ /mol			

* extrapolated values

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONTINUED)

Compound	Literature Data	Experimental		Sorbent Concentration g/m ³
		Henry's Law Constants atm m ³ /mol		
		Water	Water + Sorbent	
2-Pentanone	MW=86.14		8.80x10 ⁻⁵	
	P ^S =1.58x10 ⁻² atm		8.71x10 ⁻⁵	
	C ^S =43070 g/m ³			
	=500 mol/m ³			
	H = 3.16x10 ⁻⁵ atm m ³ /mol			
2-Heptanone	MW=114.18		1.74x10 ⁻⁴	
	P ^S =3.42x10 ⁻³ atm		1.81x10 ⁻⁴	
	C ^S =4340 g/m ³		1.75x10 ⁻⁴	
	=38.0 mol/m ³			
	H = 9.0x10 ⁻⁵ atm m ³ /mol			
Acetophenone	MW=120.16		1.02x10 ⁻⁵	
	P ^S =1.32x10 ⁻³ atm		1.11x10 ⁻⁵	
	C ^S =5500 g/m ³		1.07x10 ⁻⁵	
	=45.8 mol/m ³			
	H = 2.87x10 ⁻⁵ atm m ³ /mol			

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONTINUED)

Compound	Literature Data	Experimental		Sorbent
		Henry's Law Constants		
		Water	Water + Sorbent	Concentration g/m ³
Fluorene	MW=166.2 *	1.0 x10 ⁻⁴		
	P ^S =1.64x10 ⁻⁵ atm	9.47x10 ⁻⁵	9.53x10 ⁻⁵	22.8 HA
	C ^S =1.90 g/m ³	9.52x10 ⁻⁵	9.48x10 ⁻⁵	10.5 HA
	=0.0114 mol/m ³	9.68x10 ⁻⁵	9.58x10 ⁻⁵	25 HA
		9.45x10 ⁻⁵	8.8 x10 ⁻⁵	24.6 HA
Phenanthrene	MW=178.23 *	3.6 x10 ⁻⁵		
	P ^S =4.53x10 ⁻⁵ atm	3.55x10 ⁻⁵	6.42x10 ⁻⁵	17.0 HA
	C ^S =1.29 g/m ³	3.71x10 ⁻⁵	5.38x10 ⁻⁵	15.4 HA
	=0.00724 mol/m ³	3.52x10 ⁻⁵	6.88x10 ⁻⁵	34.3 HA
	H =3.93x10 ⁻⁵ atm m ³ /mol (28)	3.55x10 ⁻⁵	8.29x10 ⁻⁵	46.86 HA
Anthracene	MW=178.23 *	7.20x10 ⁻⁴		
	P ^S =5.04x10 ⁻⁵ atm	7.50x10 ⁻⁴	2.46x10 ⁻⁴	14.0 HA
	C ^S =0.075 g/m ³	8.8 x10 ⁻⁴	4.89x10 ⁻⁴	14.0 HA
	=4.2x10 ⁻⁴ mol/m ³	6.67x10 ⁻³		
	H = 6.67x10 ⁻³ atm m ³ /mol (28)			

* extrapolated values

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONTINUED)

Compound	Literature Data	Experimental		Sorbent Concentration g/m^3
		Henry's Law Constants $\text{atm m}^3/\text{mol}$	Water + Sorbent	
Pyrene	MW=202.3 $C^S=0.135 \text{ g/m}^3$ $=0.00067 \text{ mol/m}^3$	1.10×10^{-5}	pts scattered	
1-Methylnaphthalene	MW=142.2	2.6×10^{-4}		
	$P^S = 7.8 \times 10^{-5} \text{ atm}$	2.22×10^{-4}	2.01×10^{-4}	9.43 HA
	$C^S = 28.5 \text{ g/m}^3$	2.27×10^{-4}	2.19×10^{-4}	20.3 HA
	$=0.20 \text{ mol/m}^3$ $H = 3.54 \times 10^{-4} \text{ atm m}^3/\text{mol}$	2.45×10^{-4}		18.7 HA
1,5-Dimethylnaphthalene	MW=156.23	3.5×10^{-4}		
	$C^S = 3.38 \text{ g/m}^3$	3.73×10^{-4}	3.38×10^{-4}	28.7 HA
	$=2.16 \times 10^{-2} \text{ mol/m}^3$	3.81×10^{-4}	3.62×10^{-4}	14.0 HA
		3.62×10^{-4}	3.54×10^{-4}	25 HA
1-Chloronaphthalene	MW=162.6	3.55×10^{-4}		
	$C^S = 22.4 \text{ g/m}^3$	3.67×10^{-4}	3.76×10^{-4}	15.7 HA
	$=0.138 \text{ mol/m}^3$	3.54×10^{-4}	3.65×10^{-4}	25.7 HA

TABLE 14. RESULTS OF HENRY'S LAW CONSTANT DETERMINATIONS USING THE STRIPPING APPARATUS WITH DISTILLED WATER AND IN THE PRESENCE OF FULVIC ACID (FA), HUMIC ACID (HA) AND BENTONITE (B) SORBENTS AT 25°C (REFERENCE 32) (CONCLUDED)

Compound	Literature Data	Experimental		Sorbent Concentration g/m ³
		Henry's Law Constants atm m ³ /mol	Water + Sorbent	
2-Methyl-1-propanol	MW=74.12	2.67×10^{-5}		
	$P^S = 1.32 \times 10^{-2}$ atm	2.58×10^{-5}		
	$C^S = 94875$ g/m ³	2.81×10^{-5}		
	= 1280 mol/m ³			
1-Heptanol	$H = 1.3 \times 10^{-5}$ atm m ³ /mol			
	MW=116.2	5.3×10^{-5}		
	$P^S = 1.32 \times 10^{-3}$ atm	5.82×10^{-5}		
	$C^S = 1975$ g/m ³ = 17 mol/m ³			
Acenaphthene	$H = 7.6 \times 10^{-5}$ atm m ³ /mol			
	MW=154.2	1.55×10^{-4}		
	$P^S = 3.97 \times 10^{-5}$ atm	1.60×10^{-4}		10.71 HA
	$C^S = 3.88$ g/m ³ = 0.0252 mol/m ³	1.58×10^{-4}		21.3 HA
	$H = 1.46 \times 10^{-4}$ atm m ³ /mol (28)	1.50×10^{-4}		15.0 HA
		1.67×10^{-4}		25.3 HA

* extrapolated values

atmosphere above the surface. This is the basic equation on which the measurement of evaporation rates of hydrocarbon spills in the planned experiments is based.

Several studies of wind and temperature effects on the volatilization rates have been conducted (References 13-16,18,22). Again, these studies have focused mainly on the changes in the liquid phase resistance with wind speed and water temperature. An additional process affecting evaporation rates of hydrocarbon spills is the heat transfer from the spill to the atmosphere (Reference 14). If the molar flux F_N (mols/m² hr) is:

$$F_N = k_m (P - P_\infty) / RT_p \quad (8)$$

where k_m is the mass transfer coefficient, P is the hydrocarbon vapor pressure at the surface and P_∞ is that in the atmosphere, R is the gas constant and T_p is the pool temperature, then for k_m known, the evaporation rate can be calculated if T_p is also known. An expression has been derived for dT_p/dt as a function of wind speed, solar radiation, surface albedo, long wavelength emissivity and the molecular properties of the vapor. The relation found for the mass transfer rate as a function of pool size, X , and wind speed U was (Reference 14):

$$k_m = 0.0292 U^{0.73} X^{-.11} S_c^{-0.67} \quad (9)$$

where S_c is the Schmidt number.

Another relationship was proposed for k_m variation with wind speed (Reference 16):

$$k_m = a X^b e^{cU} \quad (10)$$

where a , b , and c are constants, and X and U are as defined above. Experimental and correlated values of the gas phase mass transfer coefficient with wind speed are shown in Figure 1 (Reference 32).

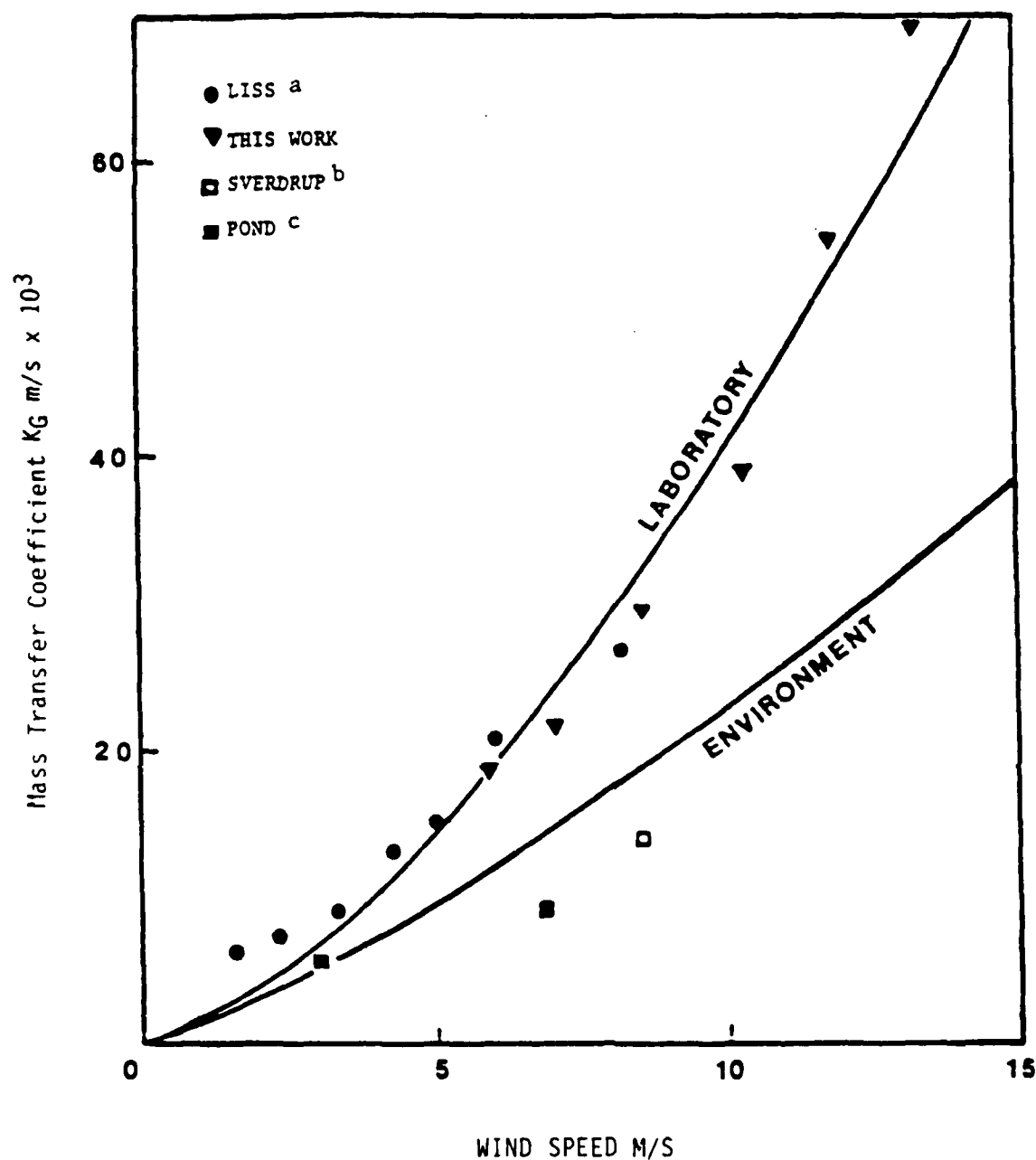


Figure 1. Experimental and Correlated Values of K_G for Schmidt Number 0.60 (REFERENCE 32).

^aLiss, P.S. *Deep Sea Res.*, 20 221 (1973)

^bSverdrup, P.S. *J. Marine Res.*, 1, 3 (1937).

^cPond, S.; Phelps, G.T.; Paquin, J.E.; McBean, G.; Stewart, N.W. *J. Atmos Sci.*, 28, 901 (1971)

Variations in the thickness of the gaseous boundary layer depends on wind speed and temperature differences. Values for z_g have been given as a function of friction wind velocity (Reference 22) and are shown in Table 15.

Studies of actual fuel oil spills have indicated the importance of evaporation in determining the fate of the hydrocarbons, particularly those with vapor pressures between that of n-octane and n-octadecane (Reference 15). Evaporation has been described as the only important fate process for the C_6 to C_9 compounds other than indan (Reference 34). Cumulative percent evaporation of gasoline at varying temperatures is shown over time in Figures 2-7 (Reference 35). A conservative value of the half life for aromatics from diesel fuel exhaust was determined to be approximately 11 days at 20°C in quiescent water (Reference 36).

A study of an oil spill on ice showed that the properties of the ice can have a profound effect on the fate of the oil (Reference 37). The spreading rate of the oil on the ice was lower than that on water, and as the oil's temperature decreases to that of the ice, its viscosity increases. In this study, all of the gasoline had evaporated several days after the spill. However, the diesel oil, which one would have expected to have evaporated rapidly, had only lost 2-4 percent of its lightest fraction 10 days after the spill.

For fuel jettisoned from aircraft in flight, when ambient temperatures are low, the composition of JP-4 shown to reach the ground resembles that of the heavier Jet-A fuel because the more volatile components have been stripped (Reference 38). Some volatilization data for jet fuels, and jet fuel components are shown in Tables 16-19 (References 1,21,32).

C. DISSOLUTION OF JET FUELS IN WATER

Solubility studies have generally been conducted on the major components of jet fuels (Reference 5), but not the mixtures themselves. Identification of soluble components of JP-4, JP-5 and JP-8 have been made (References 1,39). A range of solubilities for various oils is shown in Figure 8 (Reference 3). Solubility data for many of the hydrocarbons which comprise jet fuel can be found in Reference 5.

TABLE 15. NORMALIZED LITERATURE VALUES OF Z_g RELATED
TO FRICTION WIND VELOCITY (REFERENCE 22)

$u^*,$ m.s ⁻¹	$z_g,$ m	$u^*,$ m.s ⁻¹	$z_g,$ m	$u^*,$ m.s ⁻¹	$z_g,$ m	$u^*,$ m.s ⁻¹	$z_g,$ m
0.050	9.5×10^{-3}	0.127	3.0×10^{-3}	0.295	1.1×10^{-3}	0.600	1.0×10^{-3}
0.050	9.8×10^{-3}	0.174	2.6×10^{-3}	0.389	9.3×10^{-4}	0.800	7.7×10^{-4}
0.050	1.0×10^{-2}	0.200	2.6×10^{-3}	0.400	1.4×10^{-3}	0.800	8.0×10^{-4}
0.092	4.2×10^{-3}	0.200	2.7×10^{-3}	0.400	1.4×10^{-3}	0.800	8.5×10^{-4}
0.100	4.8×10^{-3}	0.200	2.9×10^{-3}	0.400	1.5×10^{-3}		
0.100	5.0×10^{-3}	0.216	1.8×10^{-3}	0.600	9.5×10^{-4}		
0.100	5.3×10^{-3}	0.215	1.6×10^{-3}	0.600	9.8×10^{-4}		

CONCLUSIONS AND RECOMMENDATIONS

Fuel Components	JP-4			JP-8		
	$k_v^0 = 2.81 \text{ hr}^{-1}$	$k_v^0 = 5.82 \text{ hr}^{-1}$	$k_v^0 = 15.1 \text{ hr}^{-1}$	$k_v^0 = 2.71 \text{ hr}^{-1}$	$k_v^0 = 4.33 \text{ hr}^{-1}$	$k_v^0 = 17.0 \text{ hr}^{-1}$
	Average k_v^0/k_v			Average k_v^0/k_v		
Benzene	0.52	0.32	0.30	--	--	--
Cyclohexane	0.65	0.50	0.55	--	--	--
Toluene	0.64	0.50	0.80	0.37	0.74	0.56 ± 0.26
Ethylbenzene	0.64	0.51	0.56	--	--	--
m-Xylene and p-xylene	0.61	0.48	0.86	0.28	0.76	0.62 ± 0.30
o-Xylene	0.58	0.46	0.73	0.29	0.75	0.52 ± 0.23
1-Methyl-3-ethylbenzene	0.60	0.49	0.54	0.35	0.68	0.52 ± 0.23
1,2,4-Trimethylbenzene	0.57	0.45	0.74	0.26	0.62	0.45 ± 0.18
m-Decane	0.56	0.43	0.46	0.26	0.59	0.44 ± 0.17
1,2,3,4-Tetramethylbenzene	0.54	0.42	0.46	0.24	0.47	0.38 ± 0.13
Naphthalene	0.30	0.24	0.51	0.22	0.28	0.23 ± 0.04
2-Methylnaphthalene	0.32	0.26	0.58	0.22	0.32	0.26 ± 0.05
1-Methylnaphthalene	0.27	0.21	0.25	0.21	0.25	0.22 ± 0.03

TABLE 17. TYPICAL EXPERIMENTAL DATA OBTAINED DURING
VOLATILIZATION RATE MEASUREMENTS (REFERENCE 21)

Chemical	Number of Runs	Depth (L) (cm)	k_v^a (hr ⁻¹)	k_l^a (cm hr ⁻¹)	k_g^a (cm hr ⁻¹)	k_v^b (hr ⁻¹)
Naphthalene	35	8.5	0.060	0.94	3,480	0.058
		8.0	0.45	8.99	6,550	0.55
		8.7	1.8	53.8	2,730	1.4
		7.5	2.7	94.5	3,180	2.1
		7.2	4.0	78.5	7,050	3.2
Anthracene	6	16.0	0.16	80.2	3,710	0.18
		11.0	0.25	13.8	10,800	0.26
		11.0	0.40	121.0	4,170	0.31
		11.0	0.73	50.8	10,400	0.53
2,4-DNT	8	7.5	0.0028	8.79	3,250	0.0028
		8.3	0.0037	44.8	4,060	0.0031
		8.3	0.0045	15.1	6,370	0.0049
		7.5	0.0052	21.2	4,820	0.0042
1,3-DNB	9	8.3	0.0010	6.6	3,210	0.0014
		8.0	0.0026	10.1	8,500	0.0034
		15.5	0.0031	26.5	12,300	0.0025
		7.5	0.0031	6.6	6,130	0.0026

^aMeasured values, at room temperature.

^bCalculated by substituting measured values of k_l^a and k_g^a

TABLE 18. MASS TRANSFER COEFFICIENTS FROM THE WIND WAVE TANK (REFERENCE 32)

Compound	Air Speeds m/s x 10 ⁶					
	13.2	11.67	10.31	8.57	7.09	5.96
Benzene	94.4	73.3	62.5	51.1	36.9	31.6
Toluene	93.6	79.4	68.9	51.6	46.9	26.6
1,2 dichloro- propane	93.9		63.9		35.8	28.9
chlorobenzene	89.7	78.0		55.0	41.9	
1,2 dibromo- methane	77.2		54.7	45.3		23.6
carbontetra- chloride		79.4	63.3	51.1	39.1	
2 pentanone	33.1	29.7		21.1		13.3
2 heptanone	42.7	31.6		23.0		16.9
1 pentanol	8.11			5.75		3.80
2 methylpropanol	7.30		5.75		3.81	
n butanol	4.69			3.58		2.02
Water evaporation	71100	55200	39200	29700	22200	19400

TABLE 19. RESULTS FROM THE RELATIVE VOLATILITY
APPARATUS AT 25°C (REFERENCE 32)

Compound	Mean Solute Mass Balance Percent	Experimental Relative Volatility
methanol	- 0.8	9.62
ethanol	+ 1.6	7.66
n-propanol	- 1.0	10.7
n-butanol	+ 7.3	16.3
2 butanol	- 2.3	17.5
isobutanol	+ 3.3	22.7
n-pentanol	+ 3.9	22.0
2 butanone	- 1.4	62.9
2 pentanone	+17.2	51.8
2 heptanone	+18.6	35.8
3 heptanone	+26.0	28.8
acetophenone	+20.0	31.8
2 butanol (15°C)	+ 9.0	14.0
2 butanol (35°C)	+ 4.7	24.5
2 butanone (15°C)	-11.4	51.5
2 butanone (35°C)	-14.8	54.1

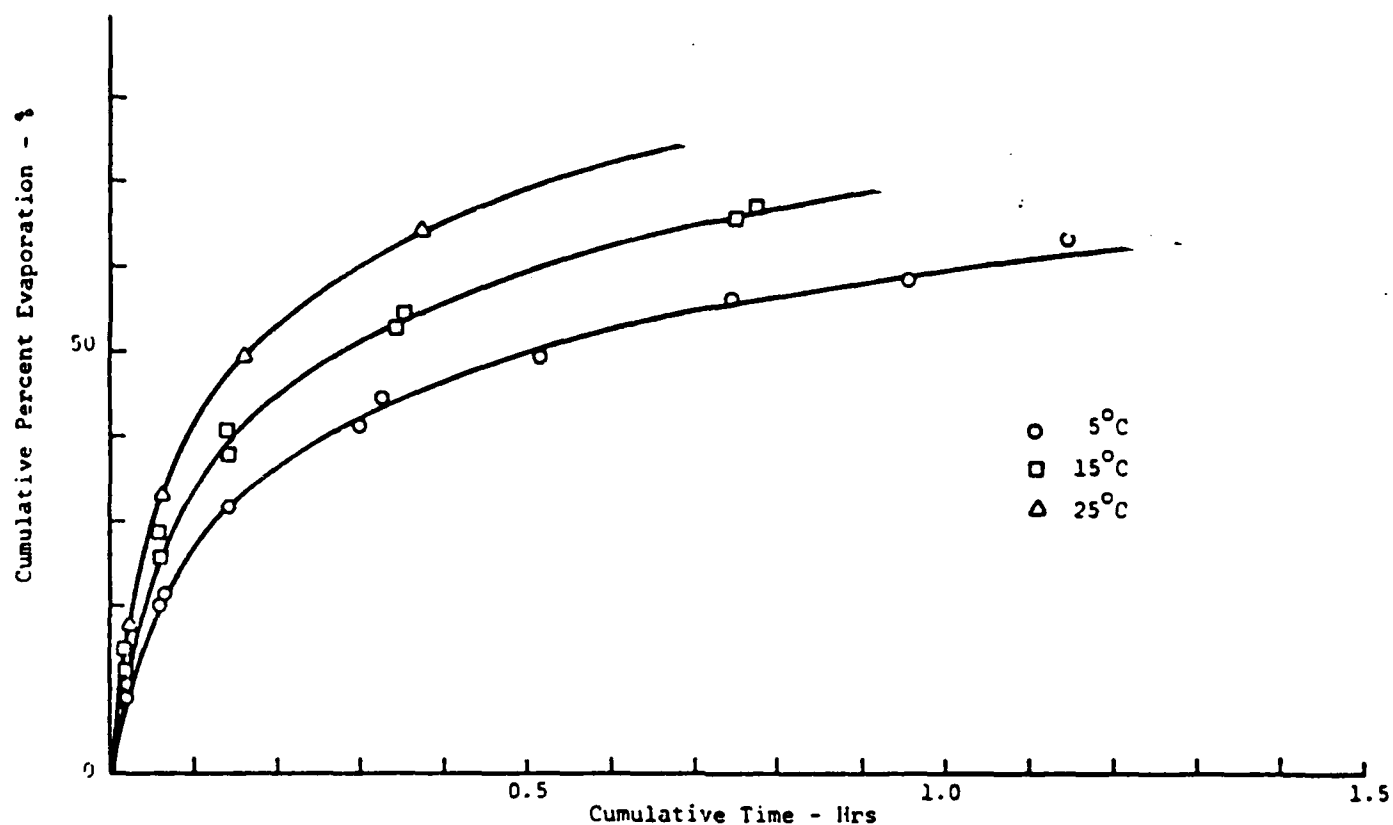


Figure 2. Cumulative Percent Evaporation - Gasoline
(REFERENCE 35).

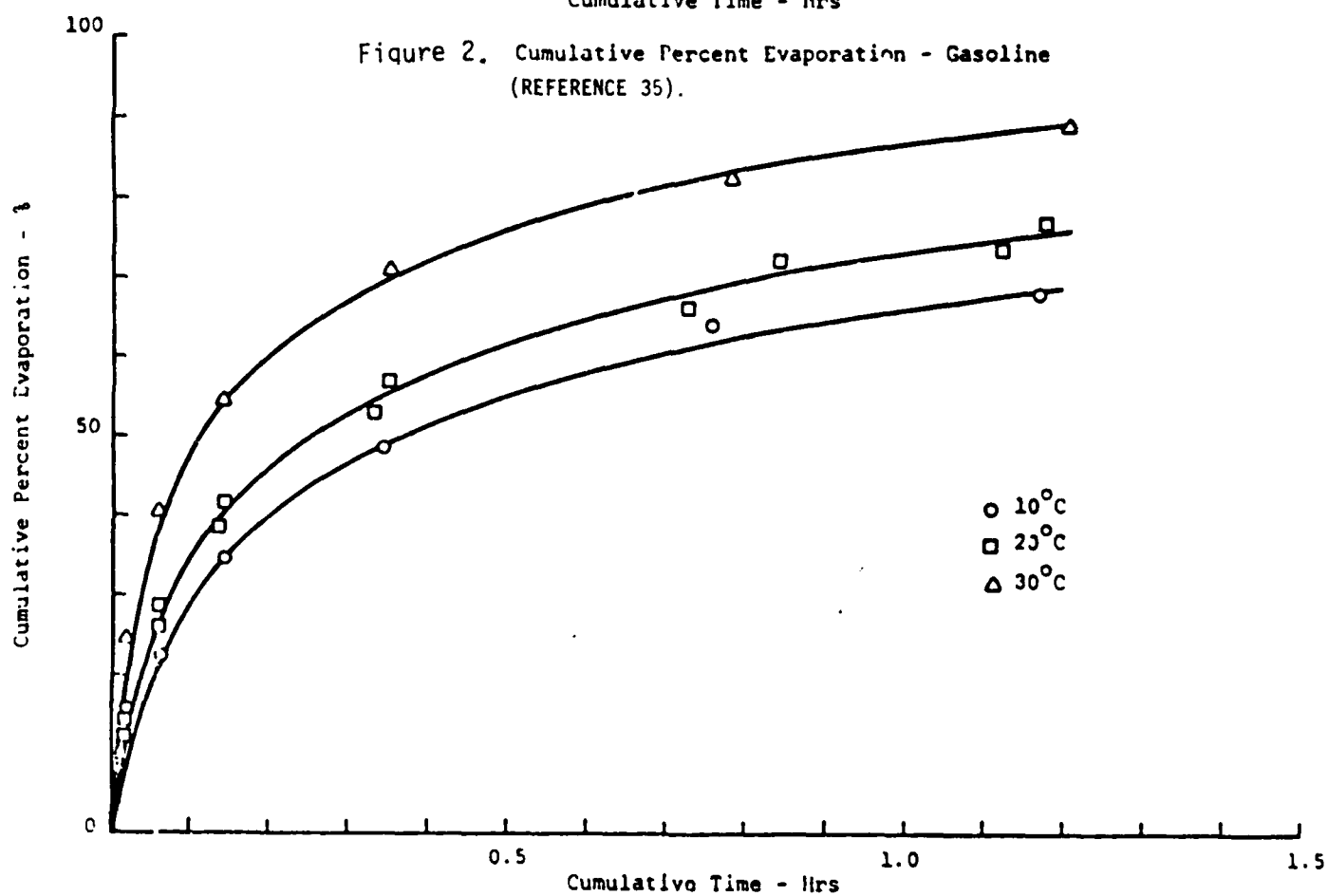


Figure 3. - Cumulative Percent Evaporation - Gasoline
(REFERENCE 35).

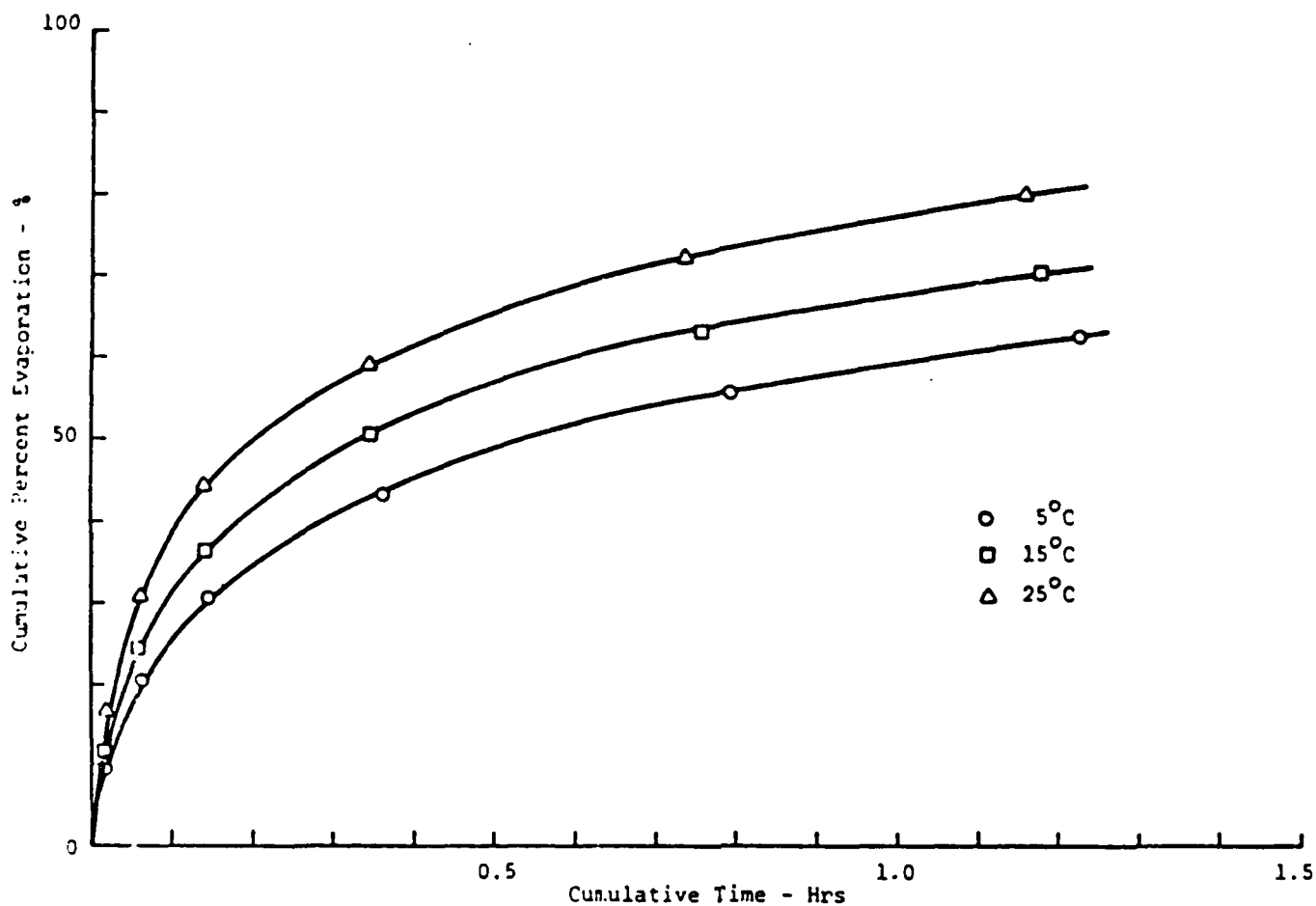


Figure 4. - Cumulative Percent Evaporation - Gasoline plus Oil
(REFERENCE 35).

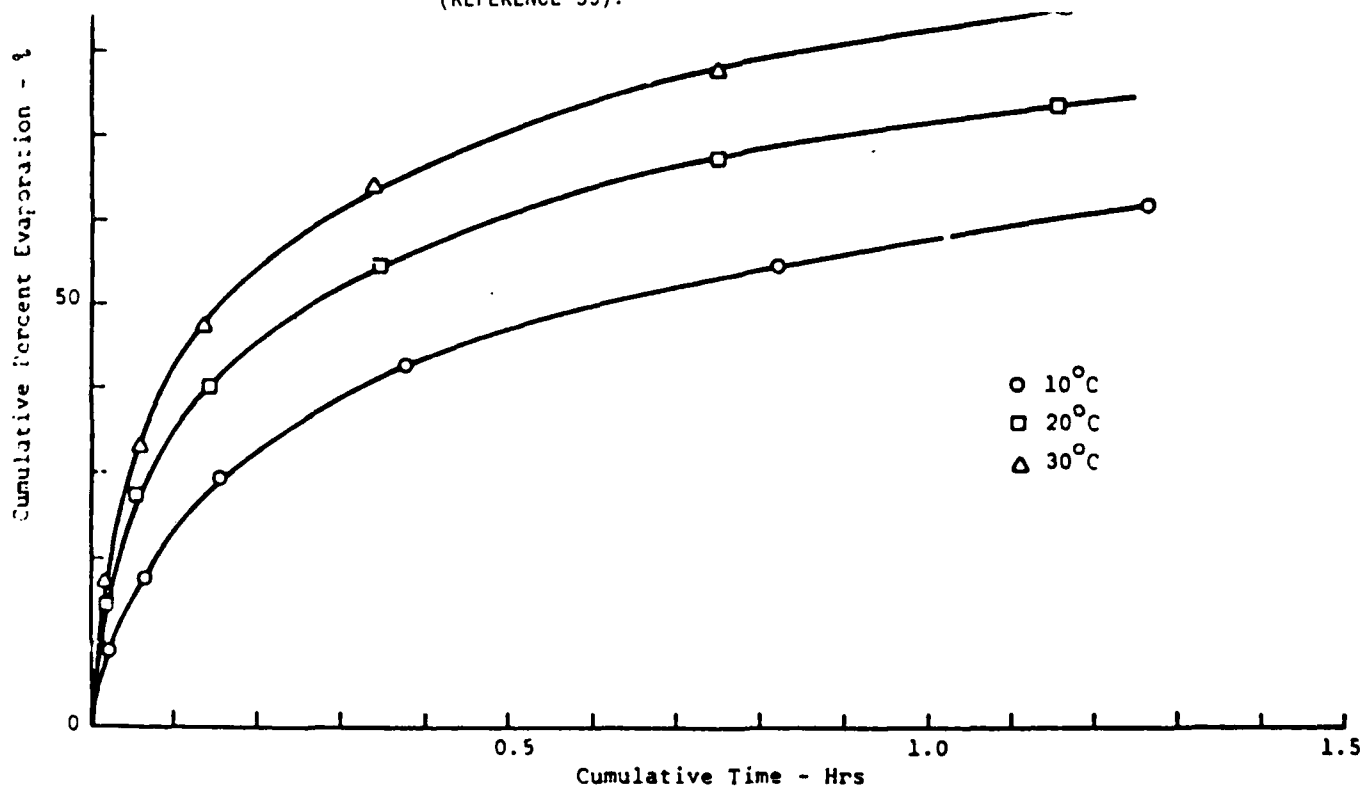


Figure 5. - Cumulative Percent Evaporation - Gasoline plus Oil
(REFERENCE 35).

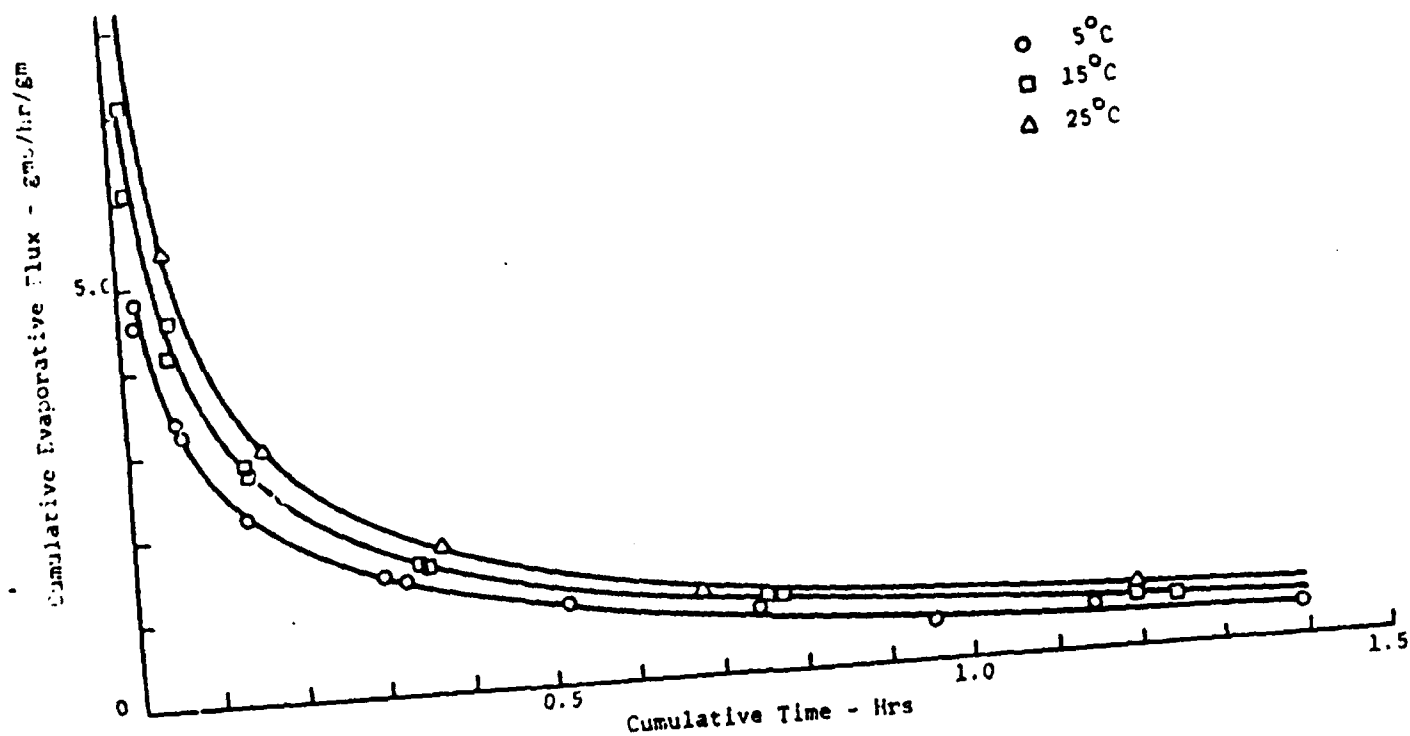


Figure 6. Cumulative Evaporative Flux - Gasoline (REFERENCE 35).

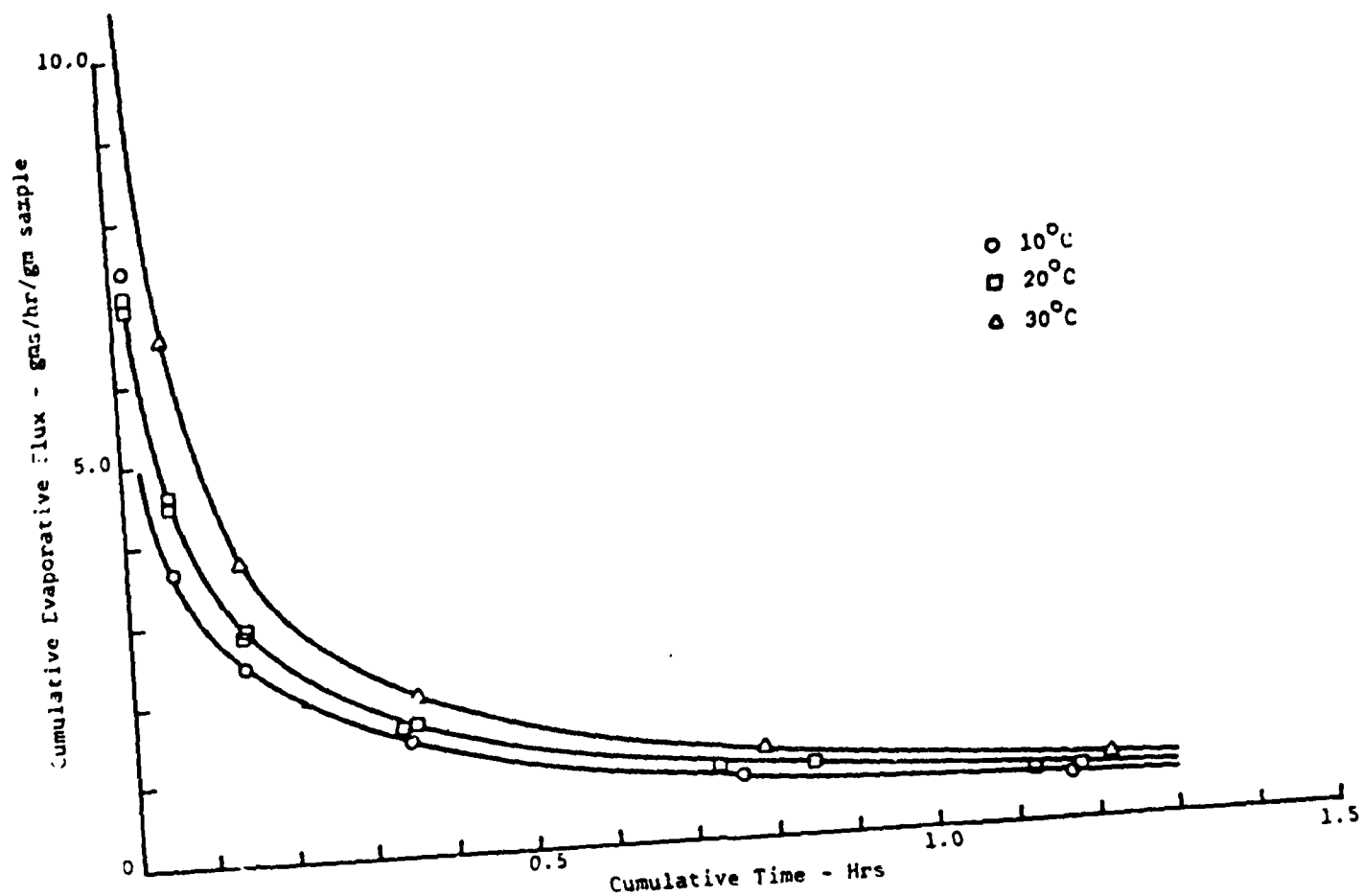


Figure 7. Cumulative Evaporative Flux - Gasoline (REFERENCE 35).

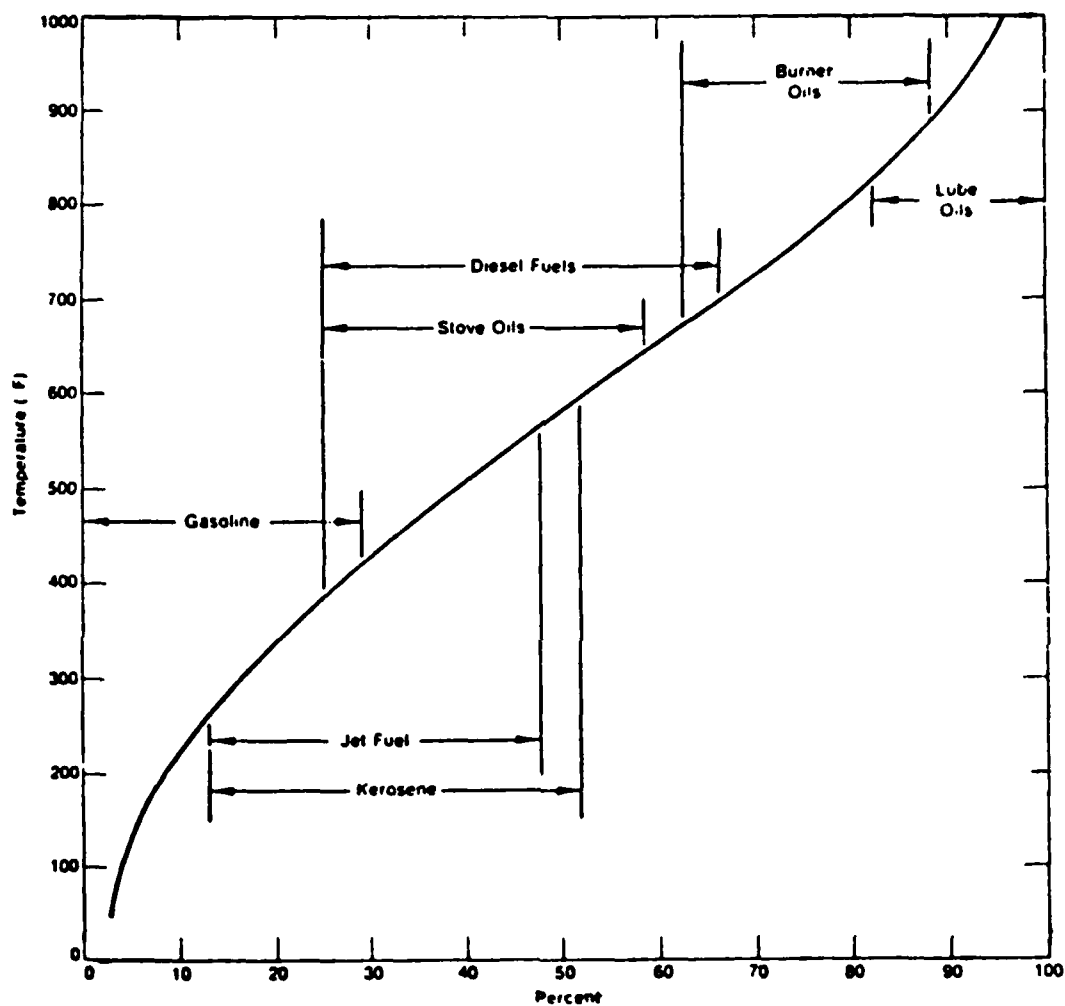


Figure 8. Percent Solubility of Different Petroleum Products (REFERENCE 3).

A number of solubility studies have been conducted on Number 2 fuel oil. Unfiltered seawater has been found to dissolve up to 1560 $\mu\text{g/l}$ of Number 2 fuel oil (Reference 40). The amount of hydrocarbons from diesel fuel and lubricating oil which are found dissolved after mixing are shown in Figure 9 (Reference 10). In general, the solubilities of the n-alkanes are proportional to their vapor pressures, and solubilities for compounds containing more than 16 carbons are negligible. The aromatic hydrocarbons and other polar hydrocarbons are much more soluble in sea water (Reference 40). Some researchers have found concentrations of the C_{12} - C_{24} n-paraffins in the water soluble fraction of Number 2 fuel oil at higher levels than their expected solubilities. These compounds may be present in dispersed or emulsified form and not in true solution (Reference 41). The dissolution of the oil displayed unusual behavior in that the amount of oil in the aqueous phase increased as oil was added up to 1000 ppm, where it reached a maximum and decreased again. This decrease was probably caused by coagulation of the dispersed oil. Soluble components of Number 2 fuel oil are shown in Table 20 (Reference 41).

Another laboratory study found no measureable concentration of Number 2 oil in a water column with a surface concentration of oil, but with minimized surface disturbance and no mixing (Reference 42). When the oil and water were mixed initially, the correlation between introduced and measurable oil in the water column was poor (Table 21). A linear relation was found for volume introduced and water column concentration for continuous mixing (Table 22). The water-soluble fractions of four oils similar to Number 2 oil have been compared (Reference 43). In addition to naphthalenes and benzenes, other compounds identified in the water fraction were phenols, anilines and indoles, specifically, methyl, dimethyl and trimethyl derivatives were found in high concentrations. Concentrations of selected compounds of the average fuel (equal volumes of all four) in the water-soluble fraction are shown in Table 23 (Reference 43).

Some studies of JP-4 and JP-5 solubility have been undertaken in combination with bioassay tests of hydrocarbon toxicity in aquatic systems. A chromatogram of a JP-4 water soluble extract is shown in Figure 10 (Reference 39). It was found that benzene, toluene and xylene (isomers) could account for 90 percent of the water-soluble hydrocarbons in the JP-4 fuel. A

TABLE 20. SPECIFIC HYDROCARBON CONTENT (ppm) OF WATER-SOLUBLE FRACTION FROM 10 PERCENT OIL-IN-WATER SOLUTION OF 4 TEST OILS (REFERENCE 41)

Compound	South Louisiana crude oil	Kuwait crude oil	No. 2 fuel oil	Bunker C residual oil
Alkanes				
Ethane	0.54	0.23	} ^a 0.39	} ^a 0.05
Propane	3.01	3.30		
Butane	2.36	3.66		
Isobutane	1.69	0.90		
Pentane	0.49	1.31		
Isopentane	0.70	0.98	} 0.02	} 0.005
Cyclopentane + 2-methylpentane	0.38	0.59		
Methylcyclopentane	0.23	0.19	0.019	0.004
Hexane	0.09	0.29	0.014	0.004
Methylcyclohexane	0.22	0.08	0.03	0.002
Heptane	0.06	0.09	0.02	0.004
C ₁₆ n-paraffin	0.012	0.0006	0.008	0.0012
C ₁₇ n-paraffin	0.009	0.0008	0.006	0.0019
Total C ₁₂ -C ₂₄ n-paraffins	0.089	0.004	0.047	0.012
Aromatics				
Benzene	6.75	3.36	0.55	0.04
Toluene	4.13	3.62	1.04	0.08
Ethylbenzene + m-, p-xylenes	1.56	1.58	0.95	0.09
o-xylene	0.40	0.67	0.32	0.03
Trimethylbenzenes	0.76	0.73	0.97	0.11
Naphthalene	0.12	0.02	0.84	0.21
1-Methylnaphthalene	0.06	0.02	0.34	0.19
2-Methylnaphthalene	0.05	0.008	0.48	0.20
Dimethylnaphthalenes	0.06	0.02	0.24	0.20
Trimethylnaphthalenes	0.008	0.003	0.03	0.10
Biphenyl	0.001	0.001	0.011	0.001
Methylbiphenyls	0.001	0.001	0.014	0.001
Dimethylbiphenyls	0.001	0.001	0.003	0.001
Fluorene	0.001	0.001	0.009	0.005
Methylfluorenes	0.001	0.001	0.009	0.004
Dimethylfluorenes	0.001	0.001	0.002	0.002
Dibenzothiophene	0.001	0.001	0.004	0.001
Phenanthrene	0.001	0.001	0.010	0.009
Methylphenanthrenes	0.002	0.001	0.007	0.011
Dimethylphenanthrenes	0.001	0.001	0.003	0.003
Total saturates	9.86	11.62	0.54	0.081
Total aromatics	13.90	10.03	5.74	1.28
Total dissolved hydrocarbons measured	23.76	21.65	5.28	1.36

^aUnresolved gas-chromatography peaks, probably include some olefins

TABLE 21. TOTAL FUEL OIL CONCENTRATIONS (mg/l) MEASURED BY INFRARED SPECTROPHOTOMETRY IN BIOASSAY WITH CONTINUOUS DISPERSION (REFERENCE 42)

Volume of Fuel Oil (ml)	Hours from Introduction	Mean Concentration	n	Standard Deviation
5	1	3.02	6	1.50
5	4	1.53	4	0.71
5	6	0.94	2	0.07
5	24	0.25	4	0.29
12.5	1	12.21	6	5.68
12.5	4	5.90	4	1.65
12.5	6	3.51	2	0.51
12.5	24	0.42	3	0.13
25	1	17.63	6	15.48
25	4	11.42	4	7.80
25	6	4.35	2	0.72
25	24	4.00	3	4.45
50	0.5	51.13	4	41.29
50	1.0	65.03	4	31.05
50	1.5	53.46	4	31.08
50	2.0	51.31	3	11.07
50	2.5	40.81	2	2.35
50	3.0	34.25	4	10.20
50	3.5	35.71	4	11.61
50	4.0	33.88	4	6.72
50	4.5	25.65	4	14.19
50	5.0	29.51	4	15.54
50	5.5	35.12	2	11.64
50	6.0	26.84	4	9.75
50	6.5	20.80	2	5.56
50	7.0	21.71	3	11.08
50	7.5	21.72	2	14.60
50	8.0	19.34	2	4.23
50	8.5	21.11	2	19.71
50	9.0	25.91	2	2.50
50	9.5	15.30	2	5.45
50	10.0	13.50	4	6.02
50	10.5	11.14	2	8.20
50	24.0	2.96	6	3.26
100	1	83.19	6	58.17
100	4	38.47	4	28.15
100	6	9.53	2	0.72
100	24	8.29	3	2.33

TABLE 22. CONCENTRATIONS (mg/l) MEASURED BY GAS CHROMATOGRAPHY FOR SOLUBLE COMPOUNDS IN BIOASSAYS RECEIVING CONTINUOUS DISPERSION (REFERENCE 42)

Compounds	Hours from Introduction	Introduced Volume (ml)			
		50 ml		100 ml	
		Rep. 5	Rep. 6	Rep. 5	Rep. 6
Benzene*					
Toluene	1	*	0.017	*	*
Ethyl benzene*					
m, p-xylene	1	*	0.023	0.015	0.019
	2	0.015	0.019	*	*
O-xylene	1	*	0.029	0.015	0.018
	2	0.019	*	*	*
1,2,3 Trimethyl benzene*					
Tot. Sol. Aromatics	1	*	0.069	0.030	0.037
	2	0.034	0.019	*	*

* Traces detected which were below the lower validated limit for the method. (0.3 mg/l for benzene; 0.01 mg/l for others)

TABLE 23. CONCENTRATION (%) OF SELECTED COMPOUNDS IN WATER-SOLUBLE SOLUBLE FRACTIONS PREPARED BY SUCCESSIVE EQUILIBRATION (REFERENCE 42)

Compound	1st equilibration (0 - 24 h)	2nd equilibration (24 - 48 h)	4th equilibration (72 - 96 h)
1,2,4 trimethylbenzene	100 ^a	98	99
Naphthalene	100	94	92
2 methyl naphthalene	100	98	102
1 methyl naphthalene	100	99	98
Dimethyl naphthalene	100	104	104
Indole + methyl indole	100	106	67
o-toluidine	100	50	11
m-toluidine	100	52	10
2,4 + 2,5 dimethylphenols,			
m + p cresol	100	57	14
3,5 dimethylphenol +			
C-3 phenol	100	49	13

^aConcentration expressed as percentage of the concentration present in 1st equilibration (0 to 24 h).

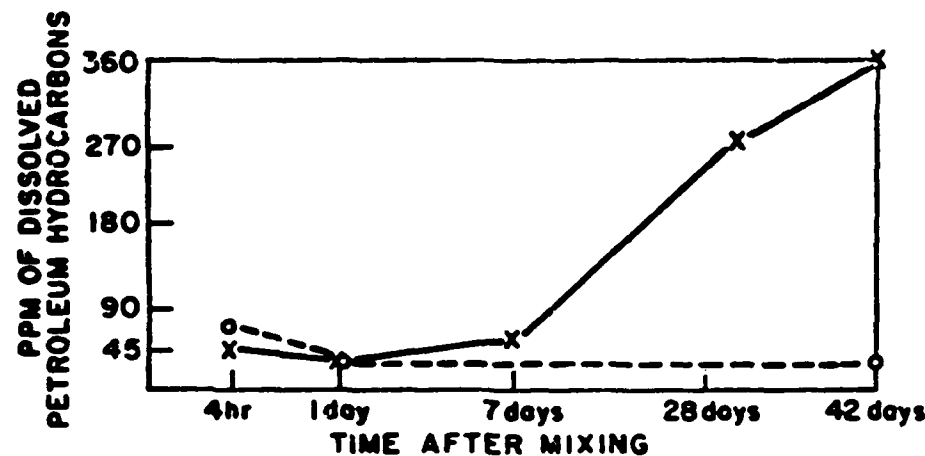


Figure 9. Solubility of Diesel Fuel and Lubricating Oil in Distilled Water (REFERENCE 10).

X = diesel fuel; O = lubricating oil

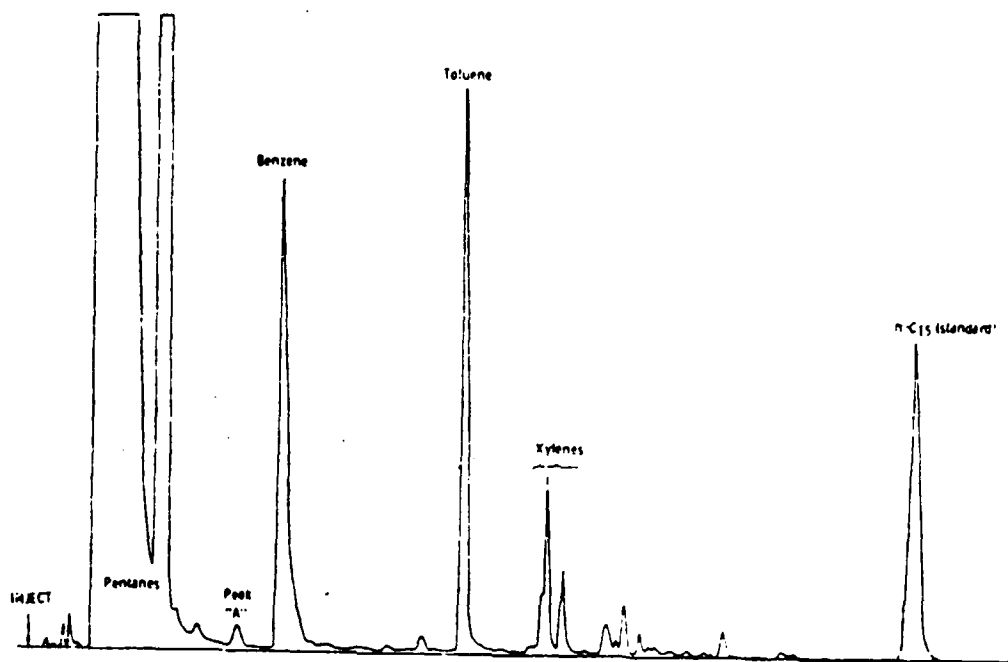


Figure 10. Chromatogram of JP-4 Water-Soluble Extract (REFERENCE 39).

comparison of petroleum-and shale-derived JP-4 chromatograms and water-solubles are shown in Figure 11 and the effect of fuel/H₂O ratio and contact times on composition is shown in Table 24 (Reference 39). Another study has shown that after the initial breakdown and equilibration of the fuel with the water, an acceleration of the rate of dissolution of the organics takes place due to chemical modifications of the water-insoluble fraction, either by oxidation or by bacterial action (Reference 10). The stable concentration period for dissolution ranged from 2 days for gasoline to 24 days for JP-5 fuel (Figure 12) (Reference 10). Major water soluble components of JP-4 and JP-5 at various water fuel ratios are shown in Tables 25 and 26 (Reference 1). Solubilities and fuel-water partition coefficients for JP-4, JP-5 and JP-8 are shown in Figures 13 and Table 27 (Reference 1). Concentrations of water solubles from a seawater extract of kerosene is shown in Figure 14 (Reference 44).

Theory for partitioning of the fuel between the fuel layer and the water has often followed fugacity models (References 25,26,27). The fugacities of each Component *i* in the water and the fuel phase are set equal to one another. The fugacity, *f*, is expressed in terms of the mole fraction, *X*, the activity coefficient, *γ*, and the reference fugacity *f^R*:

$$f = X \gamma f^R \quad (12)$$

For a dilute solution of one hydrocarbon in another, the partitioning of a fuel component between a bulk fuel and water is determined mostly by the activity coefficient in water *γ_{iw}* (Reference 1). Activity coefficients can be calculated (Reference 46) or determined experimentally and applied to systems with changing phase composition due to evaporation (Reference 8). For dissolved hydrocarbons, the surface renewal theory applies, in which all water parcels have approximately the same exposure time before being replaced by turbulent exchange with the bulk water.

A four-component liquid hydrocarbon phase system was studied to determine the time-dependence of the aqueous-phase composition (Figure 15) (Reference 8). Studies of transport of oil to groundwater have shown that for a disperse phase, the rate of transfer of water-soluble oil components is determined almost

TABLE 24a. EFFECT OF FUEL/H₂O RATIO ON COMPOSITION OF WATER SOLUBLES FROM JP-4 (REFERENCE 39)

	<u>Concentration, ppm "C₁₅ Units"</u>	
	<u>1:12</u>	<u>1:6</u>
Benzene	13.8	14.2
Toluene	9.1	9.5
Xylenes	4.4	4.5
Total Hydrocarbons	31.5	33.8

TABLE 24b. EFFECT OF FUEL/H₂O CONTACT TIME ON COMPOSITION OF WATER SOLUBLES (REFERENCE 39)

	<u>Concentration, ppm "C₁₅ Units"</u>		
	<u>24-h</u>	<u>48-h</u>	<u>72-h</u>
Benzene	13.5, 14.1	14.4	12.6
Toluene	8.9, 9.4	9.7	8.5
Xylenes	4.1, 4.5	4.7	4.0
Total Hydrocarbons	29.7, 31.6	32.5	29.7

TABLE 25. CONCENTRATIONS OF THE MAJOR WATER-SOLUBLE COMPONENTS
OF JP-5 (mg/l) (REFERENCE 1)

<u>Fuel Component</u>	<u>Deionized Water (20°C)</u>	<u>Artificial Seawater (20°C)</u>
Toluene	0.06	0.03
Ethylbenzene	0.03	0.01
m-Xylene and p-xylene	0.16	0.09
o-Xylene	0.09	0.06
1-Methyl-3-ethylbenzene	0.05	0.03
1,2,4-Trimethylbenzene	0.20	0.12
n-Decane	0.14	0.08
Naphthalene	0.46	0.30
2-Methylnaphthalene	0.23	0.14
1-Methylnaphthalene	0.16	0.09

TABLE 26. CONCENTRATIONS OF THE MAJOR WATER-SOLUBLE COMPONENTS
OF JP-4 AND JP-8 (mg/l) (REFERENCE 1)

Fuel Component	Fuel-to-Water Ratio							
	Deion, ^a (20°C)	Sea, ^b (20°C)	Deion, (20°C)	Sea, (20°C)	Deion, (4°C)	Sea, (4°C)	Deion, Sea, (30°C) (20°C)	Deion, Sea, (20°C) (20°C)
JP-4								
Benzene	9.82	9.06	6.99	4.86	1.41	1.50	1.32	1.33 0.94 0.07 0.02
Cyclohexane	0.65	0.54	0.48	0.32	0.46	0.39	0.19	0.25 0.31 0.14 0.22 0.07
Toluene	8.49	7.09	7.79	4.95	3.78	3.50	3.71	3.00 3.23 2.64 0.70 0.50
Ethylbenzene	0.67	0.53	0.64	0.40	0.54	0.46	0.59	0.38 0.44 0.42 0.17 0.12
m-Xylene	2.01	1.41	1.83	1.10	1.97	1.30	1.09	1.06 1.28 1.22 0.55 0.35
p-Xylene	0.41	0.46	0.49	0.33	1.97	0.37	0.36	0.31 0.35 0.34 0.10 0.11
o-Xylene	1.21	0.95	1.17	0.74	0.91	0.79	1.08	0.67 0.7 0.78 0.27 0.21
1-Methyl-3-ethylbenzene	0.28	0.21	0.26	0.16	0.29	0.23	0.36	0.18 0.23 0.24 0.17 0.12
1,2,4-Trimethylbenzene	0.67	0.49	0.63	0.38	0.68	0.53	0.87	0.44 0.57 0.60 0.40 0.28
n-Decane	0.30	0.21	0.27	0.16	0.29	0.23	0.37	0.19 0.25 0.28 0.15 0.11
Naphthalene	0.39	0.29	0.31	0.22	0.27	0.22	0.41	0.24 0.30 0.32 0.10 0.08
2-Methylnaphthalene	0.16	0.11	0.11	0.05	0.12	0.09	0.19	0.10 0.17 0.15 0.10 0.06
1-Methylnaphthalene	0.08	0.06	0.06	0.05	0.08	0.06	0.13	0.06 0.11 0.10 0.06 0.04

a) Deion, - deionized water
b) Sea, - artificial seawater.

TABLE 27. SOLUBILITY AND FUEL-WATER PARTITION COEFFICIENTS (K_{fw})
IN DEIONIZED WATER (REFERENCE 1)

Fuel Component	$-\log S^a$ (mol liter ⁻¹)	JP-4 $\log K_{fw}$	JP-5 $\log K_{fw}$	JP-8 $\log K_{fw}$
Methylcyclopentane	3.30	4.97	—	—
Benzene	1.65	3.39	—	—
Cyclohexane	3.07	4.69	—	—
2-Methylhexane	4.60	5.57	—	—
3-Methylhexane	4.58	5.56	—	—
n-Heptane	4.64	5.50	—	—
Methylcyclohexane	3.79	4.87	—	—
Toluene	2.22	3.44	—	—
n-Octane	5.42	5.98	—	—
Ethylbenzene	2.91	3.68	—	—
m-Xylene	2.90	3.57	3.83	3.89
p-Xylene	2.83	3.88	—	—
o-Xylene	2.80	3.85	4.01	4.15
1,2,4-Trimethylbenzene	3.36	3.95	4.17	4.17
i-Propylbenzene	3.34 ^b	4.25	4.26	4.38
Naphthalene	3.61	3.88	4.00	4.47
2-Methylnaphthalene	3.75 ^b	4.35	4.68	4.80
1-Methylnaphthalene	3.71 ^b	4.67	4.85	4.96

^aS = solubility of the component in water at 20°C in mol liter⁻¹.

^bLande, S.S.; Banerjee S. Chemosphere, 10 (7),
751-759 (1981)

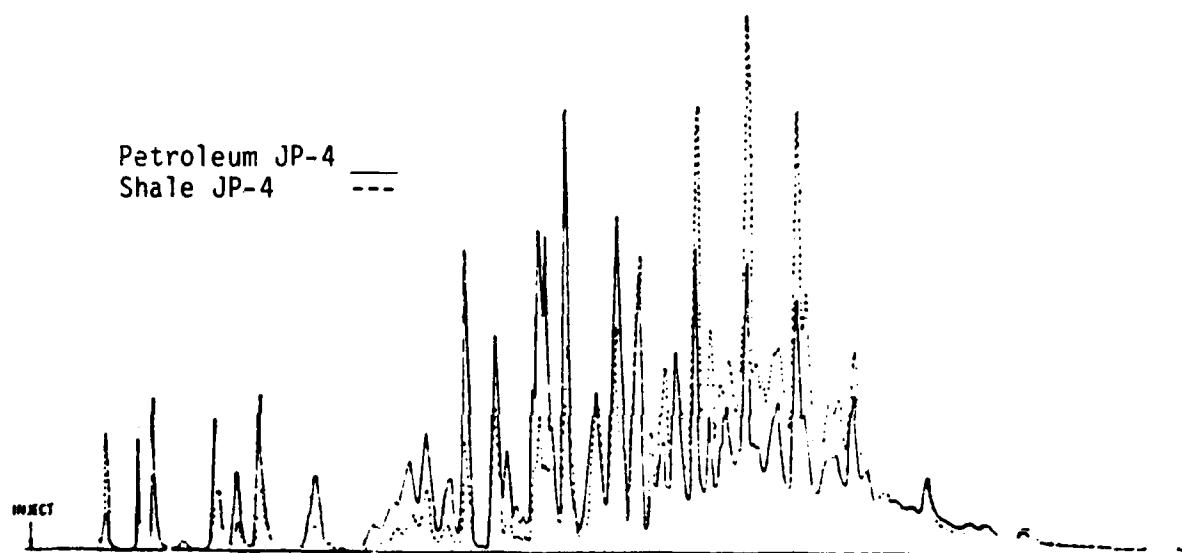


Figure 11. Comparison of Petroleum-Derived and Shale-Derived JP-4 Samples. (REFERENCE 39).

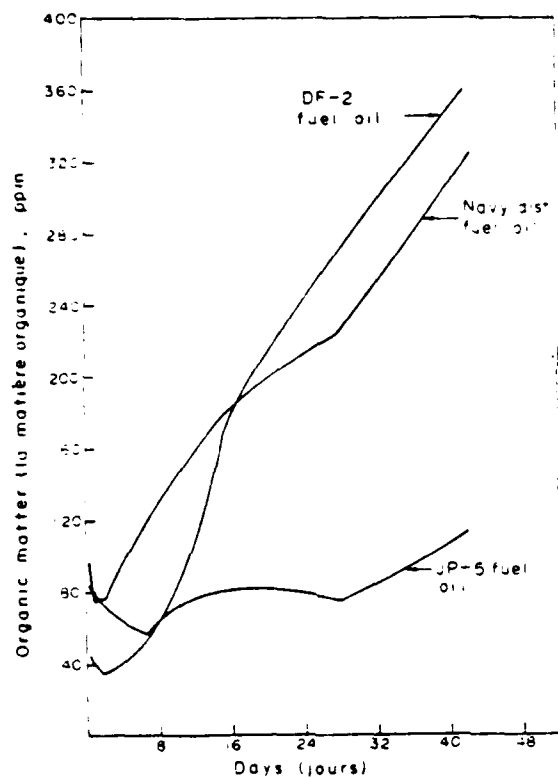


Figure 12. Dissolution of Petroleum Derived Products in Water (Reference 10).

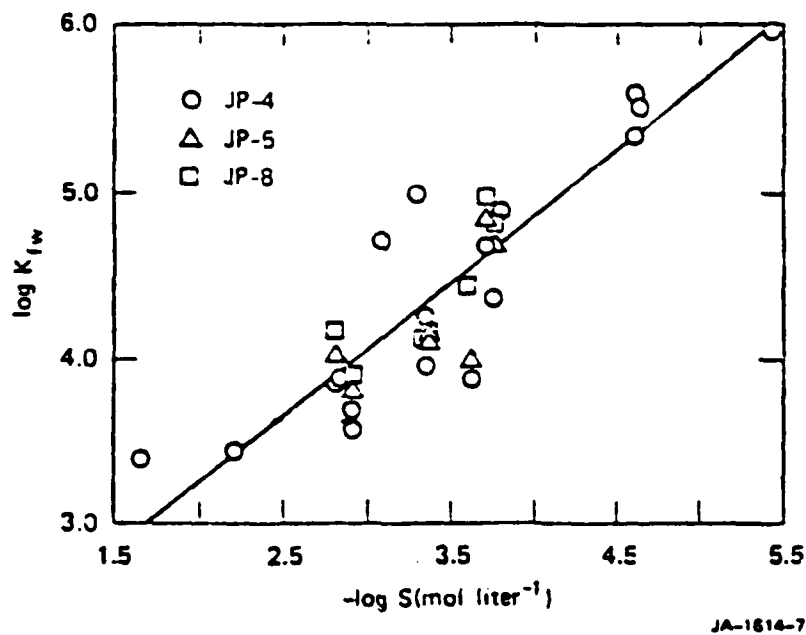


Figure 13. Aqueous Solubility of the Pure Distillate Fuel Component(s) as a Function of Fuel-Water Partition Coefficient (K_{fw}) (fuel:water = 1:1000, 20°C) (Reference 1).

COMPOUND	C ₁₇ , S.P.T.	PEAK #	CONC. (μg/L)
BENZENES			
1-METHYL-2-ETHYL BENZENE	161.3	2	6.68
1-METHYL-4-ETHYL BENZENE	161.99	2	
1:3:5-TRIMETHYL BENZENE	164.72	3	8.10
1-METHYL-2-ETHYL BENZENE	165.15	3	
1:2:4-TRIMETHYL BENZENE	169.35	4	20.15
1:2:3-TRIMETHYL BENZENE	176.08	5	18.07
		6	
1-METHYL-4-PROPYL BENZENE	183.30	7	
1-METHYL-2-PROPYL BENZENE	184.80	7	5.93
1:3-DIMETHYL-5-ETHYL BENZENE	183.58	7	
1:3-DIMETHYL-4-ETHYL BENZENE	188.20	8	
1:2-DIMETHYL-4-ETHYL BENZENE	189.40	8	
1:3-DIMETHYL-2-ETHYL BENZENE	190.01	8	18.17
1-METHYLINDANE	190.6	8	
2-METHYLINDANE	191.4	8	
1:3-DIMETHYL-2-ETHYL BENZENE	190.1	8	
1:2-DIMETHYL-3-ETHYL BENZENE	193.91	9	6.21
1:2:3:5-TETRAMETHYL BENZENE	198.00	10	16.57
1:2:4:5-TETRAMETHYL BENZENE	196.80	10	
4-METHYL INDANE	205.5	11	
1:2:3:4-TETRAMETHYL BENZENE	205.04	11	
1:3-DIMETHYL-4-PROPYL BENZENE	206.5	11	35.33
1:2-DIMETHYL-4-PROPYL BENZENE	208.5	11	
TETRAHYDRONAPHTHALENE	207.57	11	
NAPHTHALENES			
NAPHTHALENE	217.96	12	152.89
2-METHYL NAPHTHALENE	241.05	13	85.66
1-METHYL NAPHTHALENE	244.64	14	63.43
BIPHENYL	255.2	15	27.49
1:2-DIMETHYL NAPHTHALENE		16	
1:6-DIMETHYL NAPHTHALENE		16	32.95
2:6-DIMETHYL NAPHTHALENE	262	16	
TOTAL AROMATICS			610

Figure 14. Substances Isolated from Seawater Extract of Kerosene (Reference 44).

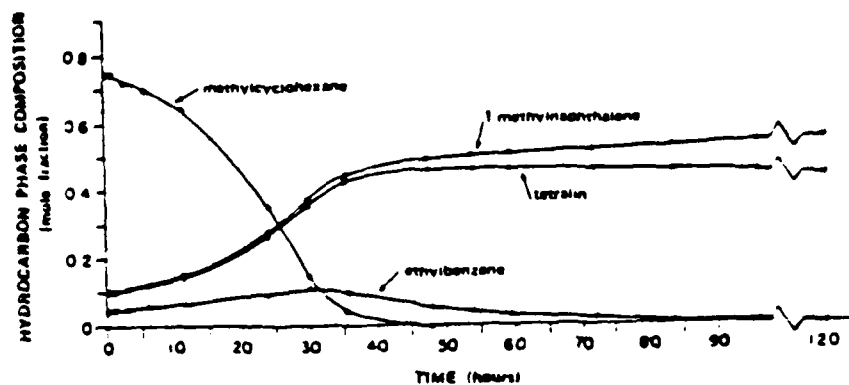


Figure 15a. Hydrocarbon Phase Composition as a Function of Time (Reference 8).

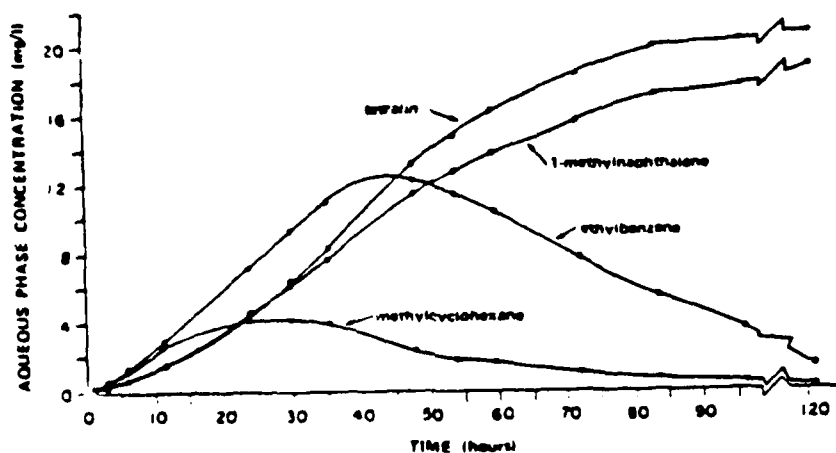


Figure 15b. Hydrocarbon Concentrations in the Aqueous Phase as a Function of Time (Reference 8).

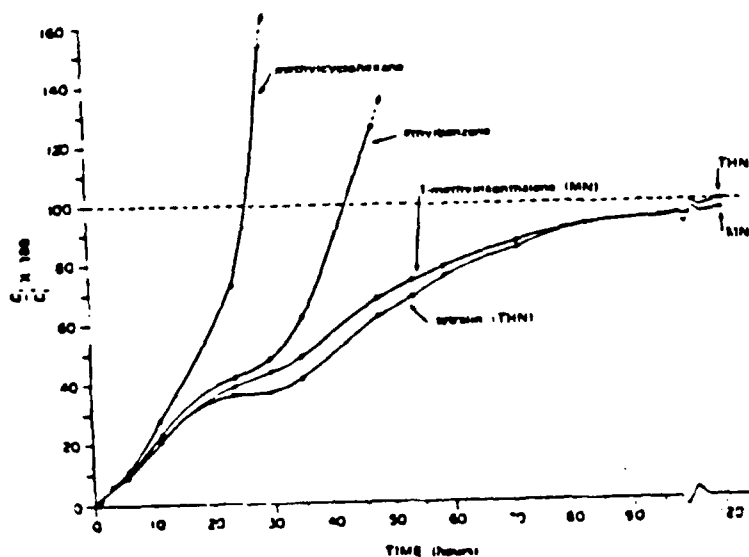


Figure 15c. Aqueous Concentrations as a Percent of Saturation Concentration with Respect to Hydrocarbon-Phase Composition as a Function of Time (Reference 8).

exclusively by the partition coefficient and oil-water ratios (Reference 47). However some researchers have suggested that organic macromolecules found in coastal and open ocean waters can solubilize certain classes of hydrocarbons found in petroleum and petroleum products (Reference 40). Octanol-water partition coefficients, K_{ow} , are an indicator of hydrophobicity and this coefficient can be related to solubility (Reference 48).

D. BIODEGRADATION IN AQUATIC COMMUNITIES

Soluble hydrocarbons may adsorb onto the surface of organic particles in water such as bacteria, algae, invertebrates and fish. Some of these organisms will degrade the compounds into simpler organic molecules, and, ultimately, into carbon dioxide and water. Hydrocarbon degradation can be measured by biochemical oxygen demand, an increase in optical density of a fat-soluble dye and direct measurement of hydrocarbon loss. The process of oil biodegradation is described as follows (Reference 49): (1) n-Alkanes, especially between C_{10} and C_{25} , are the most widely utilized; (2) Iso-alkanes are degraded slower, especially in the case of extensive branching; (3) Olefins are utilized less readily than alkanes; (4) Low-molecular weight aromatics can be metabolized when present in low, nontoxic concentrations; (5) Polycyclic aromatics are generally not metabolized; and (6) Cycloalkanes are rarely degraded by individual organisms, but may be degraded by cometabolism.

In general, the prediction of biodegradation rates for various components of a fuel mixture is complicated by many factors. Some of these factors include temperature, salinity, pH, oxygen, and nutrient concentrations (Reference 34). Also, previous site-exposure history has been shown to be important in determining the microbial capacity to degrade a contaminant. Previous exposure to hydrocarbons can lead to dramatic increases in population of biota able to degrade fuel components (Reference 34). Biodegradation rates are not necessarily proportional to total biomass. Wide variation is observed in populations taken from different environments. Fuel components released into shallow, turbid water overlying organically rich sediments could become sorbed to the sediment and resist chemical and biological weathering altogether. Generally biodegradation rates for oil are high only when temperature and nutrient supplies are optimal (Reference 50).

Quiescent fate tests of a model JP-4 fuel in various water and sediment systems were conducted (Reference 34). Of the fifteen compounds in the Model Fuel (Table 28), n-octane and tetradecane were not soluble; evaporation was the only important fate for the C₆ to C₉ compounds other than indan; naphthalene, and 2-methylnaphthalene were biodegraded in both freshwater and brackish water; indan was degraded in brackish water, with no degradation of 2,3-dimethylnaphthalene. The compounds monitored during the JP-4 tests are shown in Table 29. Little biodegradation was observed in the JP-4 tests, indicating that JP-4 must be incubated for longer periods to determine the fate of the more persistent compounds.

A spill of Number 2 Fuel oil in Buzzards Bay, MA, showed that degradation of the oil involved both bacterial utilization and partial dissolution. The ratio of N-heptadecane to pristane was suggested as a sensitive indicator of incipient oil degradation. The ratio was found to decrease more rapidly in the marshes and in lightly polluted offshore sediments than at heavily polluted stations (Reference 51). The relative increase in the more highly substituted benzenes, naphthalene and tetrahydronaphthalenes at the expense of the lower homologs suggested that dissolution was more important than bacterial utilization of the aromatic hydrocarbons.

Studies of a gasoline spill in the Ohio River showed that within 48 hours, up to 20 percent of the hexadecane and toluene, 10 percent of the pristane, and 2 percent of the naphthalene and benzanthracene had been converted to CO₂ (Reference 52). It appeared that the bacterial population in the river sediment had adapted to hydrocarbon utilization and was "ready" to respond to the input of gasoline. Other studies of gasoline biodegradation have shown the highest degradation for benzene, ethyl benzene, toluene, and xylene, while the least degraded were iso-alkanes (Reference 53). Depending on the factors listed at the introduction to this section, biodegradation may play an important role in the fate and persistence of fuel components in the aquatic environment. A literature review with 65 references to biodegradation of spilled jet fuels in water was recently published (Reference 54).

TABLE 28. WEIGHT PERCENT OF COMPOUNDS IN TEST FUEL MIXTURES
(REFERENCE 54)

<u>Compound</u>	<u>JP-4</u>	<u>Model Fuel</u>
<u>n</u> -Hexane	2.21	6.67
Benzene	0.50 ^a	0
Cyclohexane	1.24 ^a	6.67
<u>n</u> -Heptane	3.67	6.67
Methylcyclohexane	2.27	6.67
Toluene	1.33 ^a	6.67
<u>n</u> -Octane	3.80	6.67
Ethylbenzene	0.37 ^a	0
Ethylcyclohexane	--b	6.67
<u>p</u> -Xylene	0.35 ^a	6.67
Isopropylbenzene	0.30	6.67
1-methyl-3-ethylbenzene	0.49 ^a	0
1,3,5-Trimethylbenzene	0.42	6.67
1,2,4-Trimethylbenzene	1.01 ^a	0
<u>n</u> -Decane	2.16 ^a	0
Indan	--b	6.67
1,4-Dimethyl-2-ethylbenzene	0.70 ^a	0
<u>n</u> -Undecane	2.32 ^a	0
Naphthalene	0.50 ^a	6.67
<u>n</u> -Dodecane	2.00 ^a	0
2-Methylnaphthalene	0.56 ^a	6.67
<u>n</u> -Tridecane	1.52 ^a	0
2,3-Dimethylnaphthalene	--b	6.67
<u>n</u> -Tetradecane	0.73 ^a	6.67

^aMonitored during JP-4 tests

^bLess than 0.10 percent by weight.

^cModel fuel is an equal weight mixture of 15 compounds representing boiling range and hydrocarbon classes of petroleum derived JP-4

TABLE 29. HYDROCARBON RECOVERIES FROM JP-4 QUIESCENT TESTS.
CONCENTRATIONS OF INITIAL SAMPLES IN mg/l.
(REFERENCE 34)

Compound	Expected Conc.	Sasambia River 6-30-82			Range Point 7-28-82			Bayou Chico		
		AW	AS	SW	AW	AS	SW	AW	AS	SW
Benzene	38.03	13.47	17.70	20.10	18.67	21.33	22.17	27.40	19.80	23.17
Cyclohexane	94.44	69.30	64.97	70.93	66.93	67.17	74.43	91.17	64.60	55.53
Toluene	101.29	65.86	83.47	84.43	81.67	93.23	91.03	114.90	79.52	62.87
Ethylbenzene	28.18	25.70	25.07	25.00	26.20	28.23	26.50	32.83	23.20	17.57
p-Xylene	26.66	24.87	24.60	24.17	24.80	26.90	25.27	31.67	22.13	16.70
1-Methyl,3-ethylbenzene	37.32	28.47	34.53	34.23	35.90	39.07	35.87	44.43	31.47	24.01
1,2,4-Trimethylbenzene	76.92	77.30	73.50	69.13	73.77	80.57	77.97	95.70	67.17	50.21
n-Decane	164.51	160.80	155.43	153.43	158.70	173.47	160.17	197.50	141.00	107.37
1,4-Dimethyl,2-ethylbenzene	53.31	50.93	49.63	48.73	51.47	55.07	51.07	62.17	55.30	35.63
n-Dodecane	152.32	164.07	152.20	149.57	168.67	173.83	164.57	198.03	141.40	110.37
2-Methylnaphthalene	42.65	40.03	38.93	34.73	40.77	41.60	39.60	47.40	35.33	29.00
n-Tridecane	115.76	110.53	105.47	103.30	106.03	110.93	136.23	98.41	98.47	77.93
n-Tetradecane	55.60	54.63	52.90	51.43	54.23	54.37	52.97	64.70	47.60	41.13
										50.50
										62.50

E. DISPERSION AND SURFACE EFFECTS OF FUEL EVAPORATION AND DEGRADATION

Surface films have been shown to retard spreading of oil on water and reduce air-water exchange rates. Many environmental water bodies have a thin layer of organic-rich material of natural origin on the water. These films may reduce volatilization rates, altering the behavior of oil, its persistence and concentration in the water. Sorption of the oil onto the organic surface layer may also reduce initial film spreading.

The extent of retardation of volatilization depends on the coverage of the film, its thickness, chemical composition and the nature of the diffusing substance. It has been suggested that the presence of a film may reduce the overall water-to-air mass transfer coefficient altering the water and air concentrations by 25-50 percent and changing the environmental persistence by the same amount (Reference 55). A hydrodynamic effect is also present in water with thin films, in which turbulence in the interfacial region is suppressed and the liquid phase mass transfer, which is a function of friction velocity, and surface roughness, may be lower by 30-50 percent (Reference 55). The fugacity model may be extended to a three phase system (air, water, film) for calculating mass transfer of hydrocarbons and the diffusive resistance effect of films. Most studies of the effects of surface films on the fate of fuels on water have been concerned with surfactants intentionally placed on the surface to retard evaporation. Fluorochemical films of sufficient thickness have been found to reduce the rate of evaporation of JP-4 fuel by 90-98 percent (Reference 12). Surface films also tend to dampen turbulence at the airwater interface. This will have an additional effect in the reduction of volatilization rates.

F. ADSORPTION ONTO SUSPENDED SEDIMENTS IN WATER

An additional fate to consider for oil components in a fuel spill is transport into the sediments. Hydrocarbons may settle if they become attached to settling particulate material (biological debris, clays, CaCO_3 , metal oxides, etc.) (Reference 56). Water turbulence may enhance the formation of dispersed oil droplets from an oil film and, then agglomeration of the droplets with other suspended solids may be a prerequisite for sedimentation. Hydrocarbons

in the sediments are then resistant to biological oxidation, especially under anaerobic conditions (Reference 57). Depending on the level of turbulence, some of the oil in the film will be broken up into colloidal oil droplets which will coagulate or flocculate, together with other suspended solids. A model which predicts the conditions for agglomeration of dispersed oil has been proposed (Reference 56), which gives the volumetric charge density, and the mass density, q , of the colloid, in terms of the volume fractions of oppositely charged particles, e.g., negatively charged oil droplets and a positively charged hetero-colloid (Figure 16) (Reference 56).

Experiments have shown (Reference 58) that increased hydrocarbon solubility reduces uptake and retention of fuel oil into the sediments. A high concentration of organic matter in the sediment also reduces the uptake. As a hydrocarbon becomes more soluble with increasing temperature, its chances of associating with clay or other sediment particles decreases. Table 30 shows hydrocarbon association with marine sediments (Reference 58). Organic matter may mask sorption sites on the sediment, or bind the particles together, reducing surface area and therefore reducing hydrocarbon uptake. On the other hand, increase of organic matter will increase partitioning of hydrophobic solutes, such as hydrocarbon, onto the sediment surface. In a study of Number 2 fuel oil, only 15 percent of the oil was sorbed onto washed resuspended natural sediment which had previously sorbed oil. The interaction seems to consist of only weak physical adsorption. These compounds may eventually be released by dissolution or biological activity.

Ten hours after a gasoline spill in the Ohio River, sediment cores showed that the gasoline had penetrated 3 cm into the sediment. The gasoline in the sediment decreased over 43 hours to background levels found upriver (Table 31). It was concluded that evaporation, dissolution, emulsification, translocation by rapid flow of the river and biodegradation all contributed to the rapid removal of the oil from the sediment.

Fuels released in situations, such as shallow aquatic habitats such as estuaries, rivers and saltmarshes, characterized by high suspended sediment loads and bed sediment near the surface of the water, can be expected to interact readily with the sediment. In experiments with JP-4, designed to

TABLE 30a. ASSOCIATION OF HYDROCARBONS WITH
BENTONITE CLAY IN SALINE SOLUTIONS
(REFERENCE 58)

Compound	Melting point (°C)	% Uptake *
Normal alkanes:		
Eicosane	38	99% at -1° C 94% at 25° C 83% at 53° C
Hexadecane	20	56% at 25° C
Aromatic hydrocarbons:		
Anthracene	218	60% at -1° C 22% at 25° C 0% at 53° C
Phenanthrene	100	0% at 25° C

* Percentage of hydrocarbon removed from water and found associated with bentonite.

TABLE 30b. HYDROCARBON ASSOCIATION WITH MARINE SEDIMENTS IN SALINE SOLUTIONS AT 25°C (REFERENCE 58)

Sediment	% Sediment organic carbon ^a	Hydrocarbon	Association µg hydro-carbon/g dry sediment	% Uptake
Station B, total	0.37	Hexadecane	6.1	0.4
< 44 µm	0.78	Eicosane	176.0	8.9
< 44 µm, H ₂ O ₂	0.21	Eicosane	330.0	17
Station D, total	1.26 ^b	Hexadecane	11.8	0.8
< 44 µm	1.46	Eicosane	182.0	9.1
< 44 µm, H ₂ O ₂	0.39	Eicosane	435.0	22
Station E ₂ , total	0.98	Hexadecane	3.1	0.2
< 44 µm	1.10	Eicosane	187.0	9.3
< 44 µm, H ₂ O ₂	0.30	Eicosane	415.0	21

TABLE 30c. ASSOCIATION OF FUEL OIL WITH DIFFERENT MINERALS IN SALINE SOLUTIONS AT 25°C (REFERENCE 58)

	Resolved components *		Unresolved components †		Total	
	Weight (µg)	% Up-take	Weight (µg)	% Up-take	Weight µg	% Up-take
Initial oil	222.9	—	358.2	—	581.1	—
Clntonite	116.0	52	183.4	51	299.4	51
Kaolinite	65.4	29	96.1	27	161.5	28
Illite	32.7	15	39.1	11	71.8	12
Montmorillonite	8.8	3.9	9.5	2.7	18.3	3.1
Station B, < 44 µm	17.0	7.6	17.7	4.9	34.7	6.0
Station B, < 44 µm (H ₂ O ₂ -treated)	51.5	23	57.4	16	108.9	19
Station B, < 44 µm (washed three times)	16.4	7.4	12.9	3.6	29.3	5.0

* Summation of resolved and partially resolved oil components.

† Unresolved complex mixture of oil components. The < 44 µm fraction is about 50% illite. ^c

^aMeyers, P.A. Thesis, Univ. Rhode Island (1972)

^bFarrington, J.W. Thesis, Univ. Rhode Island (1971)

^cMcMaster, R.L.; Garrison, L.E.; Reference 54-11, Armament Branch, Office of Naval Research, (1954)

TABLE 31. CONCENTRATION OF HYDROCARBONS IN SEDIMENT
 (μg HYDROCARBON/g SEDIMENT-ppm)
 (REFERENCE 52)

Location	Hours After Spill	PPM Hydrocarbons in Sediment
Spill site	10	113.36
0.2 km downriver	10	3.76
Spill site	58	0.67
0.2 km downriver	58	0.69
Spill site	178	0.17
0.2 km downriver	178	0.69
1.0 km upriver	178	0.56
Spill site	346	1.10
0.2 km downriver	346	0.70
1.0 km upriver	346	0.55

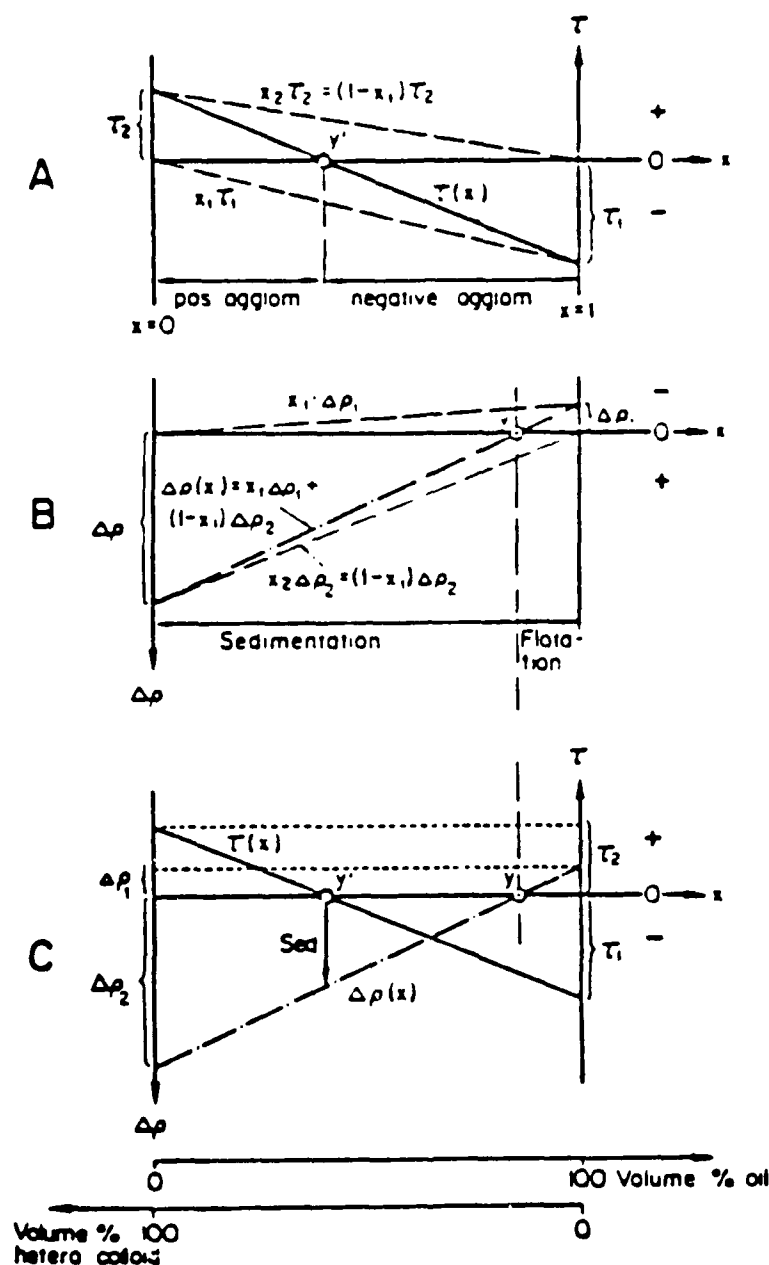


Figure 16. Simple Model for Predicting Conditions for Agglomeration of Dispersed Oil with Heterocolloid and for Evaluating whether Aggregates will Settle or Rise. (Reference 13).

- (A) A plot of the charge densities of the participating colloids versus volume-% composition indicates the compositional conditions for efficient coagulation.
- (B) A plot of the mass densities vs composition can evaluate whether the aggregates formed will settle or rise.
- (C) The superimposition of the charge density and mass density models.

simulate calm condition in the presence of sediment, the fuel volatilized rapidly and did not partition into the sediment (Reference 59). However laboratory experiments with sediment and agitation demonstrated that the interactions with the sediment held the substituted benzenes in contact with the microflora long enough for biodegradation to become important (Tables 32 and 33).

G. PHOTOOXIDATION ON WATER

Hydrocarbons in jet fuel can be photooxidized by exposure to direct sunlight on the surface of the water. A study of the formation of toxic products from photooxidation of a Number 2 fuel oil demonstrated that with UV irradiation, toxicity due to reactive peroxides reached a maximum within 24 hours (Figure 17) (Reference 60). Carbonyl compounds and phenols increased at an approximately linear rate over 7 days.

Another study was conducted on the effects of exposure to sunlight on JP-4 fuel in deionized, fresh and salt waters (Reference 1). The concentrations of naphthalene and substituted naphthalenes decreased due to direct photolysis (Figure 18 and Table 34). The half-life for photolysis of naphthalene in the summer is about 9 days. Photolysis of benzene is not expected to be significant because the absorption coefficient value above the solar cutoff wavelength is very small. The loss of benzene and alkylated benzenes is postulated to be due to the formation of triplet state oxy radicals which then oxidize the alkylated benzene by removal of the benzylic hydrogen. The authors suggest that the loss of alkylated benzenes in the environment may be at least two orders of magnitude slower than in the experiment. Photolysis is therefore not expected to be an important environmental fate for any of the water-soluble fuel components except naphthalene and the substituted naphthalenes.

H. EXPERIMENTAL METHODOLOGY FOR DETERMINING VOLATILIZATION AND DISSOLUTION RATES OF JET FUELS ON WATER

Four methods of assessing evaporation rates of hydrocarbon spills have been compared (Reference 33). These methods are: (1) tray evaporation in a wind tunnel, (2) thin film tray evaporation in a wind tunnel, (3) gas-stripping,

TABLE 32. FATE OF SELECTED JP-4 COMPONENTS IN SEDIMENT AND WATER FROM ESCAMBIA (REFERENCE 59)

<u>Compound</u>	<u>Site of Biodegradation</u>
Benzene	Volatilized
Cyclohexane	
Toluene	
Ethylbenzene	Sediment
<u>p</u> -Xylene	
1-Methyl,3-ethylbenzene	
1,2,4-Trimethylbenzene	
<u>n</u> -Decane	Water and Sediment
1,4-Dimethyl,2-ethylbenzene	
<u>n</u> -Undecane	Water
Naphthalene	
<u>n</u> -Dodecane	
2-Methylnaphthalene	Volatilized
<u>n</u> -Tridecane	
<u>n</u> -Tetradecane	

TABLE 33. FATE OF SELECTED JP-4 COMPONENTS IN
SEDIMENT AND WATER FROM RANGE POINT
SALTMARSH (REFERENCE 59)

<u>Compound</u>	<u>Site of Biodegradation</u>
Benzene	
Cyclohexane	Volatilized
Toluene	
Ethylbenzene	Water
<u>p</u> -Xylene	Volatilized
1-Methyl,3-ethylbenzene	
1,2,4-Trimethylbenzene	
<u>n</u> -Decane	Water
1,4-Dimethyl,2-ethylbenzene	
<u>n</u> -Undecane	
Naphthalene	Volatilized
<u>n</u> -Dodecane	
2-Methylnaphthalene	Water
<u>n</u> -Tridecane	
<u>n</u> -Tetradecane	Water and Sediment

TABLE 34. PHOTOLYSIS OF THE MAJOR WATER-SOLUBLE FUEL COMPONENTS OF JP-4 IN WATER (REFERENCE 1)

Fuel Component	Fuel Component Concentration (mg liter ⁻¹)											
	Deionized Water			Artificial Seawater			Pond Water					
	Control*	7 Days	14 Days	21 Days	Control	7 Days	14 Days	21 Days	Control	7 Days	14 Days	21 Days
Benzene	1.15	0.68	0.82	0.98	0.76	0.88	0.67	0.65	1.24	1.16	1.20	1.32
Cyclohexane	0.23	0.15	0.17	0.26	0.10	0.11	0.09	0.08	0.31	0.28	0.34	0.34
Toluene	2.52	1.75	1.95	2.01	2.22	2.61	2.07	1.95	2.86	2.74	2.80	2.85
Ethylbenzene	0.40	0.25	0.27	0.25	0.36	0.42	0.33	0.30	0.40	0.40	0.41	0.40
n-Xylene and p-xylene	1.43	0.87	0.85	0.63	1.30	1.64	1.15	0.99	1.46	1.38	1.34	1.20
o-Xylene	0.74	0.45	0.48	0.37	0.70	0.79	0.83	0.58	0.75	0.68	0.68	0.65
1-Methyl-3-ethylbenzene and 1-Methyl-4-ethylbenzene	0.29	0.16	0.14	0.08	0.27	0.32	0.22	0.18	0.28	0.27	0.27	0.22
1,2,4-Trimethylbenzene	0.51	0.23	0.11	0.01	0.49	0.31	0.05	--	0.52	0.37	0.27	0.10
n-Decane	0.29	0.13	0.09	0.03	0.23	0.23	0.15	0.10	0.24	0.19	0.18	0.14
Naphthalene	0.25	0.14	0.18	0.15	0.26	0.06	<0.01	--	0.29	0.16	0.09	0.01
2-Methylnaphthalene	0.10	0.04	0.05	0.02	0.10	<0.01	<0.01	--	0.11	0.03	0.02	--
1-Methylnaphthalene	0.07	0.03	0.04	0.01	0.07	<0.01	<0.01	--	0.08	0.03	0.02	--

*Average of 7, 14 and 21 day dark control samples.

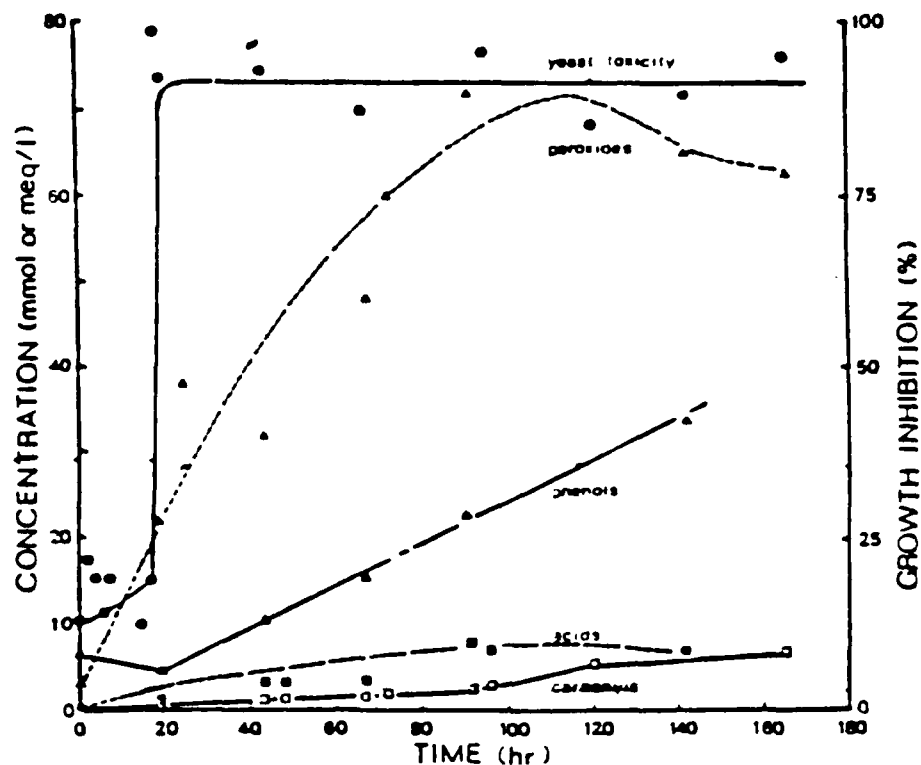


Figure 17. Photooxidation of Number 2 Fuel Oil (Reference 69)

Closed circles: Yeast growth inhibition. Closed triangles: peroxide concentration. Closed squares: acidity. Open triangles: phenol concentration. Open squares: total carbonyl compound concentration.

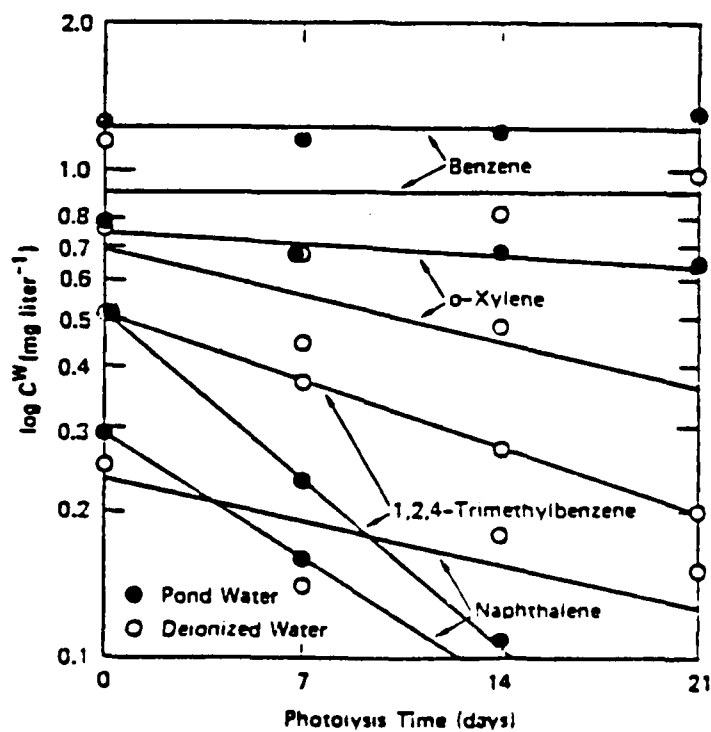


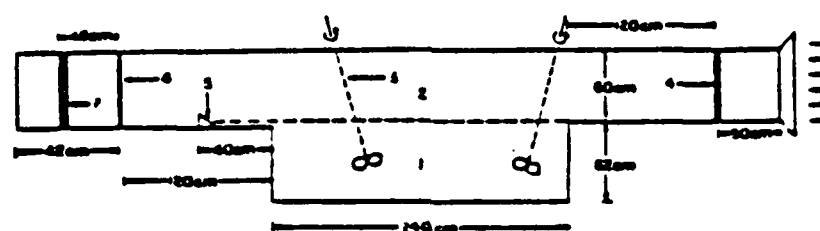
Figure 18. Photolysis of Selected Aromatic Water-Soluble Fuel Components of JP-4 (Reference 1).

air bubbled through the oil, and (4) distillation. Wind speeds in the tunnel varied from 4 to 12 m/s. Samples were analyzed using gas chromatography. The gas-stripping and tray-evaporation techniques were ideal for measuring the evaporation rates of oil. The tray evaporation curve lagged slightly behind the gas stripping curve, perhaps due to a liquid-phase resistance or to turbulence at the air-water interface. The distillation method is useful only for the prediction of the evaporation curve.

Other studies have been carried out to determine volatilization rates of hydrocarbons in solution. Cohen et al. (Reference 18) have made volatilization measurements in a wind-wave tank, 240 cm long, 60 cm deep and 60 cm wide. Velocity profiles along the tank were measured, using a pitot-static tube mounted on a motor-driven vertical traversing mechanism. Air humidity, water evaporation rate, and air and water temperature measurements were also made. The unsteady-state volatilization of benzene or toluene was monitored using a Beckman (DK-2A) spectrophotometer. The wind varied up to 11.6 m/s. A diagram of the tank is shown in Figure 19.

Small-scale volatilization studies were carried out in a 30 cm deep glass tank containing 6 liters of water and the compound being studied in solution (Reference 32). Wind-induced waves were generated at the air-water interface by blowing air saturated with water vapor from a blower into the tank. A diagram of the wind-wave tank is shown in Figure 20. Syringe samples were collected and analyzed by gas chromatography. The volatilization rates of 20 organic compounds were determined. Smith et al. (Reference 21) measured volatilization rates from solutions in 1- or 2-liter beakers, or in 19 cm crystallizing dishes stirred with a magnetic stirring bar. Coutant and Penski (Reference 61) measured rates of evaporation various liquid drops using a recording microbalance having its sample pan flush with the floor of a wind tunnel (Figure 21). This is the basic wind tunnel system which will be used in the experimental task of this project.

There are three basic methods for determining water-soluble hydrocarbon concentrations. These are: (1) direct aqueous injection and analysis by GC or HPLC, (2) extraction followed by GC analysis, and (3) purge and trap. Berry and Stein (Reference 62) describe a direct aqueous injection method of



- | | |
|----------------|-------------------------------|
| 1. Water tank | 5. Wave damper |
| 2. Wind tunnel | 6. Screen to control air flow |
| 3. Stirrers | 7. Fan |
| 4. Grid | |

Figure 19. Diagram of Wind-Wave Tank
(Reference 18).

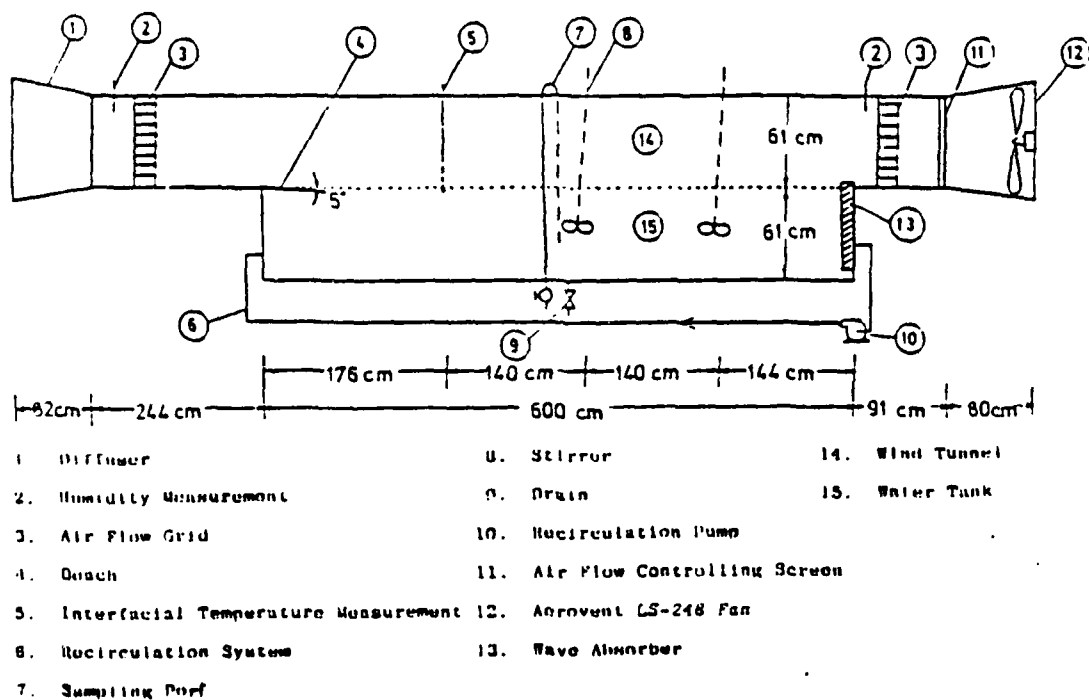


Figure 20. Diagram of Wind-Wave Tank
(Reference 32).

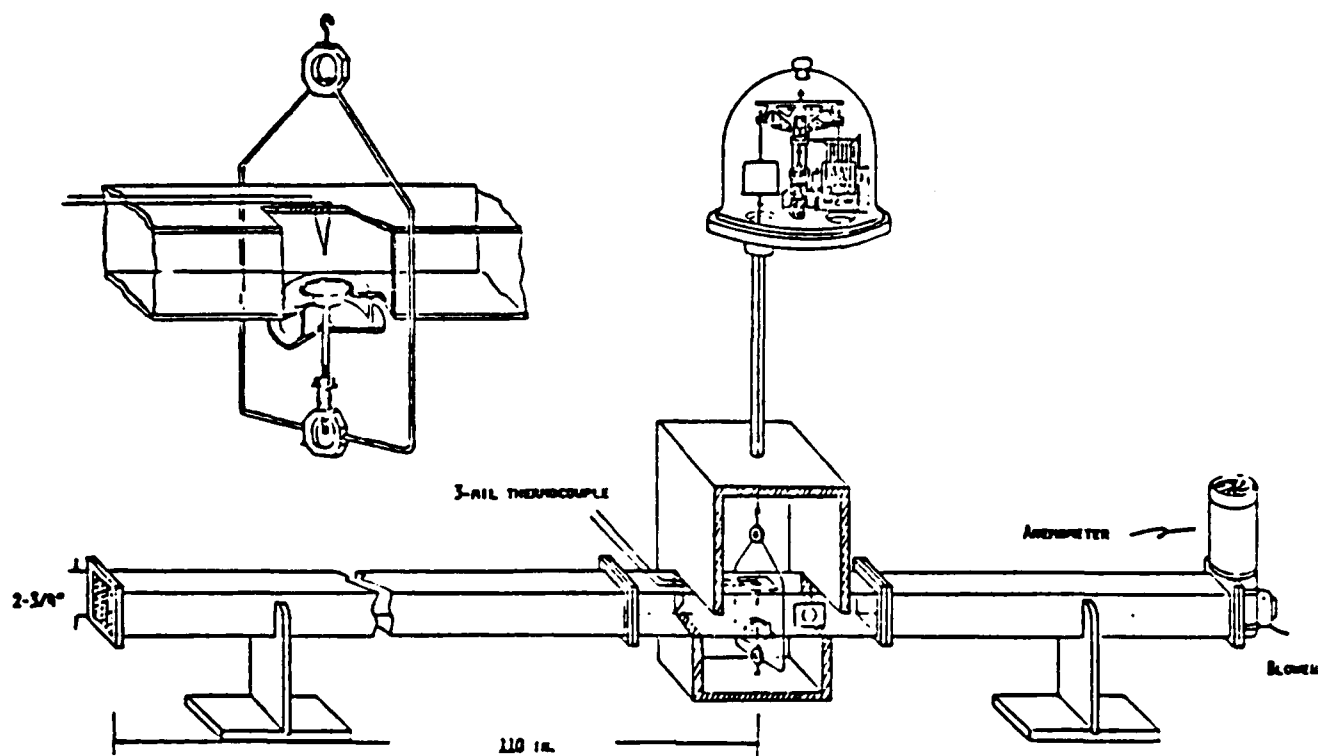


Figure 21. Wind Tunnel/Microbalance Assembly
(Reference 61).

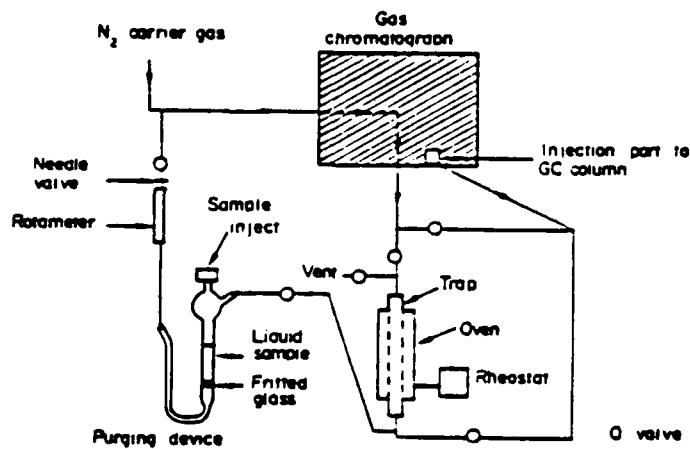


Figure 22. Purge and Trap Apparatus for
of Water-Soluble Fraction of
Jet Fuel (Reference 63).

analyzing samples of gasoline dispersed in water on packed GC columns using a flame ionization detector (FID). Hydrocarbon extraction has been done with pentane (References 39,63), carbon tetrachloride (References 10,41,64), CS₂ and hexadecane (Reference 65), petroleum ether (Reference 66), hexane followed by uv spectroscopy (Reference 67), and trichlorotrifluoroethane followed by infrared spectrophotometry (Reference 64).

Two concentration methods for analysis of water-soluble fractions of jet fuels were compared (Reference 63): pentane extraction and purge and trap. They used n-pentadecane for extraction of JP-8 and n-tetradecane for extraction of JP-4. The pentane extracts were passed through a column of anhydrous Na₂SO₄ and evaporated in a rotary evaporator. In the purge-and-trap method, 60/30-mesh Tenax GC was overlaid with 100/120 mesh Porapak Q. Initially only 5 percent of the N₂ flow was directed through the trap, and finally all of the N₂ was directed through the trap. This method gave the best differentiation of early peaks. Flow diagrams of the purge and trap techniques are shown in Figures 22. The results suggest that quantitation of water solubles in JP-4 is best achieved through the purge and trap method, while the pentane extraction is best for analysis of components of JP-8.

Four analytical procedures for determination of organic materials in aqueous solution have been compared (Reference 10). These are: (1) Beckman total organic carbon analysis, (2) Envirotech total organic carbon analysis, (3) Rocketdyne pyrolytic analysis, and (4) Carbon tetrachloride, infrared method. These four methods were compared using JP-5 as a test fuel, and gasolines and lubricating oils. The indirect method of CCl₄ extraction produced lower results than the other three. Good agreement was obtained for the other three methods (Table 35). An evaluation of 5 solubility methods was conducted (Reference 68) and the results suggest that, with the exception of the very hydrophobic chemicals, precisions of 3-7 percent relative to the measured solubilities can be expected.

TABLE 35. COMPARISON OF DIRECT AND EXTRACTIVE METHODS FOR ANALYSIS
OF WATER SOLUBLE JP-5 FRACTION (REFERENCE 10)

	Concentration of organics in aqueous phase after 24-h equilibration (ppm)
Direct	
Beckman TOC analysis	82
Envirotech TOC analysis	85
Rocketdyne pyrographic analysis	83
*Extractive	
CCL ₄ -Extraction	<10
Infra-red detection	

SECTION III

CONCLUSIONS

A review of the literature has suggested that the two major fates of jet fuel spills on water are evaporation and dissolution, although biodegradation, photooxidation and adsorption onto suspended sediments can also be important. Factors which influence the fate of the hydrocarbon components in the spill include, water and air turbulence and temperature, fuel composition, sediment load in the water, past history of biological components in the water, the presence of surface films, and ultraviolet radiation. A prediction of the environmental distribution of compounds representative of distillate fuel is shown in Table 36. While many studies have been conducted to determine mass transfer rates for dissolved fuel components, fewer studies exist which involve mass transfer of oil films due to jet fuel spills.

TABLE 36. MACKAYS LEVEL 1 ENVIRONMENTAL DISTRIBUTION OF REPRESENTATIVE DISTILLATE FUEL COMPONENTS (REFERENCE 26)

	n-Pentane	n-Decane	Benzene	Ethylbenzene	Naphthalene
Aqueous solubility (g m^{-3})	39.0	5.14 ^b	1760	141	31.4
$H(P_a \text{ m}^3 \text{ mol}^{-1})^c$	126	1200	0.61	0.86	0.049
$z^a = 1/RT \text{ (mol m}^{-3} P_a^{-1})$	4.1×10^{-4}	4.1×10^{-4}	4.1×10^{-4}	4.1×10^{-4}	4.1×10^{-4}
$z^H = 1/H \text{ (mol m}^{-3} P_a^{-1})$	7.9×10^{-3}	8.3×10^{-4}	1.6	1.2	20
K_{oc}^d	1600	2.0×10^4	51	600	1000
$K_p \text{ (soil)}^e$	32	400	1.0	12	20
$K_p \text{ (sediments)}^f$	64	800	2.0	24	40
$z^S = K_{p^a_s}/H \text{ (soil)}$	0.38	0.50	2.5	21	610
$z^S = K_{p^a_s}/H \text{ (sediment)}$	0.76	1.0	5.0	42	1200
K_b^g	200	2000	8.2	91	120
$z^b = K_{b^a_b}/H$	1.6	1.7	13	110	2400
Concentrations (mol m^{-3}) ^h					
Air	9.8×10^{-9}	9.9×10^{-9}	2.5×10^{-9}	2.9×10^{-9}	1.9×10^{-10}
Soil	9.1×10^{-6}	1.2×10^{-5}	1.5×10^{-5}	1.5×10^{-4}	2.9×10^{-4}
Water	1.9×10^{-7}	2.0×10^{-8}	9.9×10^{-6}	8.4×10^{-6}	9.4×10^{-6}
Biota	3.8×10^{-5}	4.1×10^{-5}	8.0×10^{-5}	7.7×10^{-4}	1.1×10^{-3}
Suspended Sediments	1.8×10^{-5}	8.5×10^{-4}	1.1×10^{-3}	2.9×10^{-4}	5.7×10^{-4}
Sediments	1.8×10^{-5}	8.5×10^{-4}	1.1×10^{-3}	2.9×10^{-4}	5.7×10^{-4}
Percentage of Total					
Air	98.2%	99.2%	25.3%	28.7%	1.9%
Soil	0.1	0.1	0.1	1.3	2.6
Water	1.3	0.1	74.0	63.8	70.8
Biota	0.0	0.0	0.0	0.0	0.0
Suspended Sediments	0.0	0.0	0.0	0.0	0.0
Sediments	0.4	0.5	0.6	6.2	24.6

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