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SOLUBILTY BEHAVIOUR OF PETROLEUM OILS IN WATER

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ABSTRACT

The effect of water-to-oil volume ratio on the apparent solubility of oil in water is examined for six different petroleum oils. It is shown that the water-to-oil ratio used during the preparation of water soluble fractions (WSF) has a significant influence on the concentration and composition of the WSF produced. The general dissolution behaviour that emerges is that at low water-to-oil ratios, the more soluble compounds present in the oil are the dominant WSF components and the total WSF concentration is relatively high. As the water-to-oil ratio increases, the concentration of these compounds and the total WSF concentration decreases, and the less soluble compounds in the oil constitute a larger portion of the WSF.

RÉSUMÉ

L'effet du rapport eau/hydrocarbures (en volume) sur la solubilité apparente du pétrole dans l'eau a été examiné pour six pétroles différents. Il a été constaté que le rapport eau/hydrocarbures utilisé dans la préparation des fractions hydrosolubles influe considérablement sur la concentration et la composition de ces fractions. En général, aux faibles rapports eau/hydrocarbures, les composés plus solubles du pétrole dominent dans les fractions produites et la concentration totale de ces fractions est relativement élevée. Quand le rapport augmente, la concentration de ces composés et la concentration totale des fractions hydrosolubles diminuent, et les composés moins solubles du pétrole sont plus abondants dans les fractions hydrosolubles.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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INTRODUCTION

Dissolution is one of the fundamental mass transfer processes that occurs when oil is spilled on water. Although the fraction of oil that dissolves into water is relatively small when compared to the total mass of oil, it is this fraction that intimately contacts aquatic organisms and thus is an important determinant of oil toxicity.

Oil is a complex mixture of compounds and each compound will partition differently between the aqueous and oil phases. Components with relatively high aqueous solubilities will tend to transfer to the water phase while the insoluble components will stay in the oil. Thus, the composition of the aqueous mixture is usually very different from the original oil. The term "water soluble fraction" (WSF) is commonly used to describe the aqueous solution which is formed when oil and water are brought into contact. By definition, a WSF is a single phase solution comprised of individually dissolved molecules and is free of any dispersed oil-in-water emulsions or colloidal emulsions. WSF's are commonly prepared in the laboratory as the exposure media for aquatic toxicity testing. WSF's are the preferred medium for these tests because dissolved chemicals have the most intimate contact with marine biota and in comparison to oil-in-water dispersions, WSF's can be prepared with good reproducibility and are more stable. The composition and concentration of the WSF depends upon several factors such as the composition of the oil, the properties of the water, temperature and the method of preparation.

A recent significant finding is that the composition and concentration of WSF's can be extremely sensitive to the water-to-oil volume ratio used during WSF preparation (Smith and Harper, 1981; Lockhart et al., 1984; Maijanen et al., 1984). The focus of this study was to examine how the WSF composition and concentration of various petroleum oils depend upon the water-to-oil ratio.

LITERATURE REVIEW

Comprehensive lists of solubility data for pure hydrocarbon compounds have been compiled by a number of researchers Whitehouse (1984, 1985), Brookman, Flanagan and Kebe (1985), Price (1976), and McAuliffe (1966). A thorough review of the factors affecting the solubility of single compounds is presented by Brookman, Flanagan and Kebe (1985). Billington et al. (1988) examine the kinetics of dissolution and current laboratory techniques employed for determining solubility.

It has been established that aromatic hydrocarbon compounds are far more soluble than alkanes of the same carbon number (molecular weight). Cycloalkanes tend to be slightly more soluble than normal alkanes. As the carbon number increases within a homologous series of compounds, there is a marked decrease in solubility. Dissolved electrolytes are known to "salt out" hydrocarbon solutes, therefore, solubility values in sea-water are lower than in distilled water.

Studies on the solubility behaviour of simple, solid hydrocarbon mixtures showed that the equilibrium concentration of each solute component was generally equal to the concentration of the pure compound's solubility (Eganhouse and Calder, 1976; Banerjee, 1984). Liquid hydrocarbon mixtures however, have very different thermodynamic behaviour than solid hydrocarbon mixtures.

The solubility behaviour of simple, liquid hydrocarbon mixtures have been studied by a number of researchers (Burris, 1985; Burris and MacIntyre, 1985, 1986a, 1986b; Leinonen, 1972; Leinonen and Mackay, 1973; Leinonen, Mackay and Phillips, 1971; Mackay and Shiu, 1975). At equilibrium the aqueous concentration of any component of the mixture (C_W) is related to its pure compound solubility (C^*_W), the mole fraction of the component in the hydrocarbon mixture (x_H), and its activity coefficient in the hydrocarbon phase (γ_H):

$$C_W = x_H C^*_W \gamma_H$$

Ideal solubility behaviour occurs when $\gamma_{i(h)}$ is unity. Component interactions within the organic phase result in deviations from ideality. Mixtures of structurally similar compounds such as mixtures containing only aromatics or only alkanes, exhibit near ideal solution behaviour. Mixtures containing compounds that are different in structure such as mixtures containing both aromatics and alkanes together, deviate from ideality. The deviation can be either positive or negative, and for binary mixtures, it can be as great as a factor of 2.5 (Burris, 1985).

Different aspects of the dissolution behaviour of complex multi-component hydrocarbon mixtures, such as crude and refined petroleum oils, have been studied by various researchers (Bobra, Mackay and Shiu, 1979; Boehm and Quinn, 1973; Burris and MacIntyre, 1986; Coleman et al., 1984; Hamam et al., 1987; Lu and Polak, 1976; Mackay, Bobra and Shiu, 1980; Mackay and Shiu, 1976; Mackay et al., 1985; Maijanen et al., 1984; McAuliffe, 1987; Milhailova, 1986; Murray, Lockhart and Webster, 1984; Payne et al., 1987; Price, 1976; Shiu et al., 1988; Smith and Harper, 1981; Winters and Parker, 1977). It has been shown that the composition and concentration of the WSF depends upon several factors including the composition of the oil, the properties of the water, temperature and the method of preparation. The preparation and use of petroleum WSF's for bioassay purposes has been discussed by Andersen et al., (1987), Benville et al. (1981), Lockhart et al. (1984), Maher (1982); Ostgard and Jensen (1983); Vandermeulen, Foda and Stuttard (1985). A recent finding of importance is that the composition and concentration of WSF's are a function of the water-to-oil volume ratio used during preparation (Lockhart et al., 1984; Maijanen et al., 1984; Smith and Harper, 1981).

EXPERIMENTAL SECTION

Materials

The following six oils were used in this study:

Prudhoe Bay Crude Oil - API/EPA standard reference oil;
South Louisiana Crude Oil - API/EPA standard reference oil;
Fuel Oil No.2 (high aromatic) - API/EPA standard reference oil;
Fuel Oil No.6, Bunker C (high viscosity) - API/EPA standard reference oil;
Western Sweet Blend Crude Oil - EPS standard oil for dispersant testing;
Regular Unleaded Gasoline - purchased in Halifax, Nova Scotia.

The water used was distilled in glass, filtered and degassed prior to use. The water conforms to ASTM D1193 Type II reagent grade water specifications. The vessels used to prepare the WSF's were 60 mL amber glass Hypo-vials (Pierce catalogue number: 12970) which were crimp sealed with teflon/silicone septa (Pierce catalogue number: 12720). Prior to use, all glassware was soaked in dichromate-sulfric acid for 6 hours, then well rinsed with distilled water, and dried in a 300°C oven for at least 12 hours. All syringes used were Hamilton Series 1000 Gastight Syringes. A New Brunswick Scientific Company Model G-27 Psychrotherm was used for equilibration. All chemicals used as standards and for calibration were from Aldrich Chemical Company and were 99+% pure.

Preparation of Water Soluble Fractions

WSF's were prepared at 25°C using water-to-oil volume ratios from 5:1 to 10,000:1. Oil was slowly injected through a 10 cm long, 20 gauge or smaller needle into an inverted, sealed Hypo-vial which was completely filled with water. Water displaced by the injected oil flowed out through a second (0.64 cm long, 26 gauge) needle. After injection, the needles were withdrawn and the vial was inspected for the presence of air bubbles. If bubbles were detected, the vial was not used. Vials were continuously maintained in the inverted position after the oil was injected. Vials were placed on a gyratory shaker table within a psychrotherm and mixed at 30 RPM. This speed does not supply sufficient mixing energy to cause a major deformation of the oil/water interphase. The oil/water system was allowed to equilibrate for at least 20 days. A minimum of two samples were prepared at each of the water-to-oil ratios.

This method of preparing WSF's resulted in solutions of excellent reproducibility (standard deviations of $< 3\%$) and avoided two common difficulties encountered during WSF preparation: (i) loss of compounds by volatilization and (ii) formation of oil-in-water emulsions.

Analyses of Water Soluble Fractions

Water samples were withdrawn from the vials using a syringe equipped with a 3.8 cm long, 18 gauge needle and a Mininert valve. An 8.9 cm long, 17 gauge needle was also fully inserted into the vial in order that when water was withdrawn, air could enter through this needle without disturbing the oil/water interface. The syringe was rinsed out with 2 portions of the sample and then completely filled by slowly withdrawing the plunger in order to avoid creating a vacuum headspace within the syringe barrel. Samples were then immmediately analysed.

Aqueous samples were analysed by a purge-and-trap/GC technique, using a Tekmar Model 4000 Dynamic Headspace Concentrator coupled to a cyrofocusing Tekmar Model 1000 Capillary Interphase and a temperature programmed Hewlett-Packard Model 5890 Gas Chromatograph equipped with a flame-ionization-detector and a SPB-1 fused silica capillary column (0.53 mm ID X 30 m long). Calibration and compound identification were performed using aqueous solutions saturated with pure, single hydrocarbons.

The purge vessel was thoroughly cleaned and baked between samples . Water blanks were analyzed between each sample run. Calibration standards were run daily. A minimum of 3 analyses were performed for each WSF ratio.

Purge conditions:

Purge:	40 mL/min for 11 minutes
Dry Purge:	40 mL/min for 3 minutes
Trap:	Tenax
Desorb:	180°C for 4 minutes
Bake:	225°C for 10-20 minutes

Chromatographic conditions:

Carrier gas:	helium
Column:	Supelco Fused Silica Capillary SPB-1 bonded phase 30m X 0.53 mm ID 1.5 μm film thickness
Temperature programming:	40°C for 10 minutes 5°C/min to 200°C 200°C for 10 minutes
Detector temperature:	350°C

RESULTS AND DISCUSSION

Figures 1 to 6 show the change in WSF concentration as a function of water-to-oil ratio for the six test oils. Each figure shows the total WSF concentration and the concentrations of major WSF components. Numerical tables are provided in the appendix.

Figures 1, 2 and 3 show the concentration curves for WSF's produced by the crude oils, Western Sweet Blend, South Louisiana and Prudhoe Bay. The general dependence of the WSF's on the water-to-oil ratio are very similar for the three crudes with only minor differences in the relative abundance of some compounds. As the figures illustrate, the concentration of the WSF decreases as the water-to-oil ratio increases and, more importantly, the composition of the WSF changes as the ratio changes. At low water-to-oil ratios, the WSF's are mainly comprised of benzene, toluene, ethylbenzene and xylenes. At a water-to-oil ratio of 5, these components account for about 80% of the total WSF. As the water-to-oil ratio increases, these compounds become less important and account for a smaller proportion of the dissolved compounds. At a water-to-oil ratio of 10,000, these compounds account for only 15 to 30% of the total WSF. There is thus a change in the dominant characteristic hydrocarbons found in the solubilized fraction. At low water-to-oil ratios (<100), benzene is the predominant hydrocarbon species in the WSF but at higher ratios (100 to 1000) toluene becomes the predominant component. As the ratio is increased further (e.g. up to 10,000), no single compound accounts for a significant portion of the total but instead the WSF is composed of many compounds, each accounting for only a small fraction of the WSF's composition. The concentration of less soluble compounds, such as highly alkylated benzenes and naphthalenes, is far less dependent upon the water-to-oil ratio than the more soluble compounds. Their concentration remained relatively constant over the range of water-to-oil ratios tested while the concentration of the more soluble compounds showed a dramatic decrease as the ratio increased.

Figure 1: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Western Sweet Mixed Blend Crude Oil

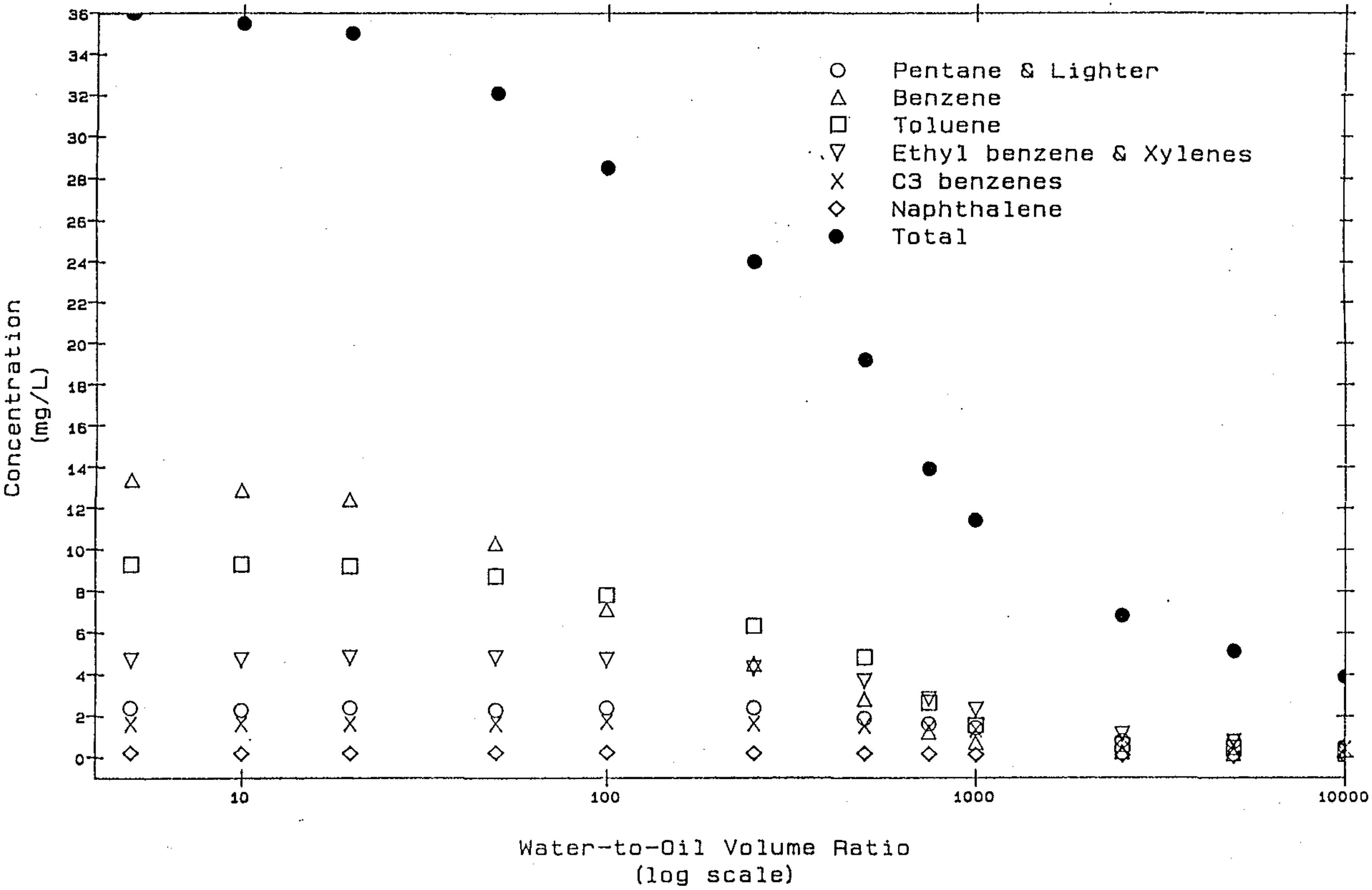


Figure 2: Concentration of Water-Soluble Components versus Water-to-Oil Ratio South Louisiana Crude Oil

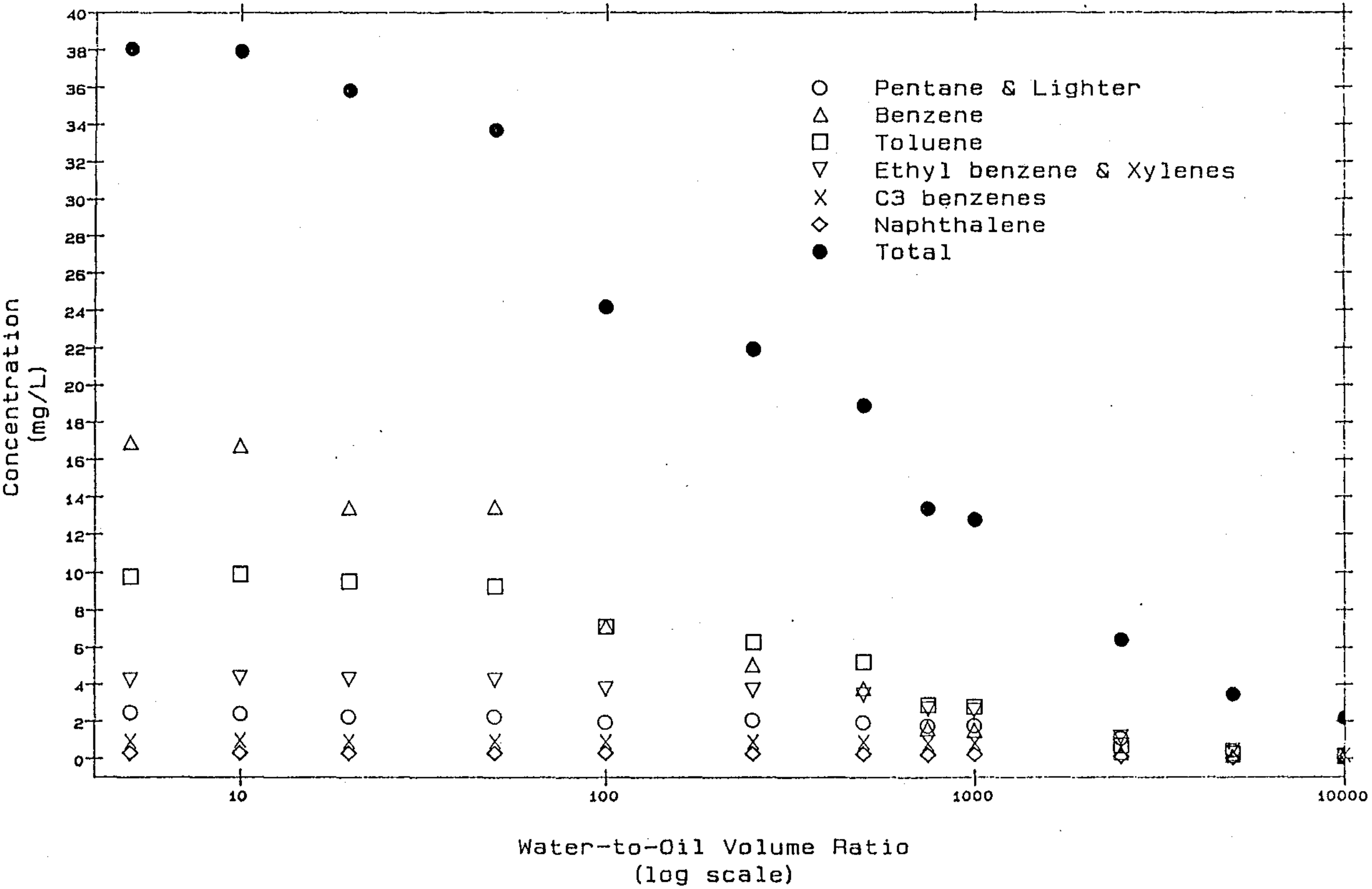


Figure 3: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Prudhoe Bay Crude Oil

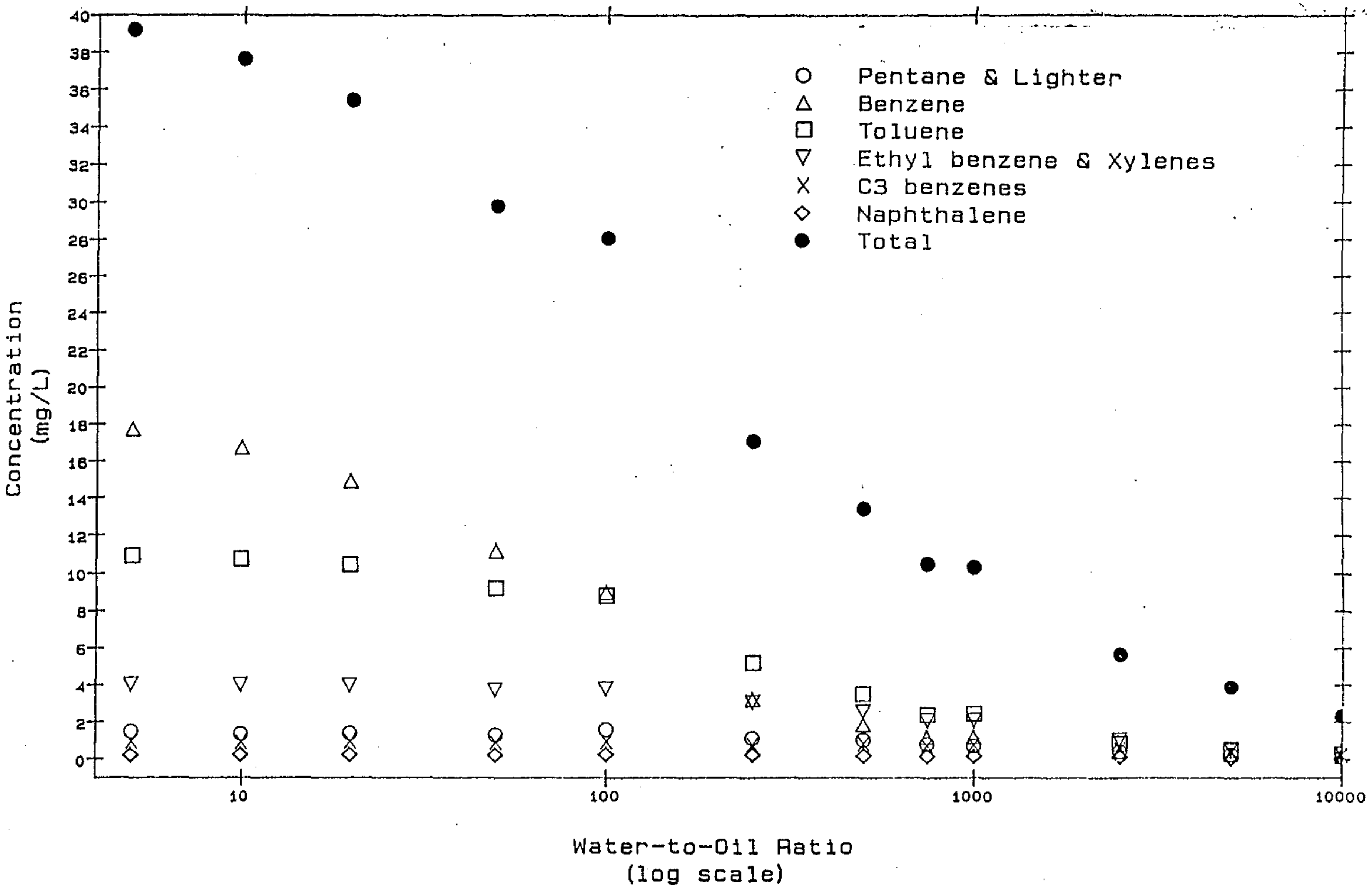


Figure 4 shows the composition and concentration of WSF's prepared from gasoline. The general form of the curves are similar to those of the crude oils except the concentrations of the volatile aromatics are significantly higher and the less volatile materials (above naphthalene) are absent.

Figure 5 shows the dissolution behaviour of Bunker C Fuel Oil. The WSF's of Bunker C lack the presence of volatile aromatics which were predominant in the WSF's of the crude oils and gasoline. These WSF's contain a larger number of compounds and a large proportion of less-soluble, non-volatile compounds.

The solubility behaviour of Fuel Oil No.2 presented in Figure 6 shows that the total concentration changes dramatically as the water-to-oil ratio is increased, especially at ratios less than 100. This dependence is primarily due to the large concentration of pentane and lighter compounds present in the WSF at these low water-to-oil ratios. The WSF's of the fuel oil contain significantly more compounds than those of the crude oils or those of gasoline, and they have a relatively high proportion of non-volatile compounds.

Total WSF concentration as a function of water-to-oil ratio for the six oils tested are presented in Figure 7.

The results show that the water-to-oil volume ratio used during oil and water equilibration can significantly influence the concentration and composition of the WSF produced. The general dissolution behaviour is that at low water-to-oil ratios, the more soluble compounds present in the oil are the predominant WSF components and the total WSF concentration is relatively high. As the water-to-oil ratio increases, the concentration of these compounds and the total WSF concentration decreases, and the less soluble compounds make up a larger portion of the WSF. Maijanen et al. (1984) described this behaviour as a "depletion effect"; the oil becomes depleted of water soluble material as the water-to-oil ratio is increased thus causing the apparent "solubility" to fall.

Figure 4: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Regular Unleaded Gasoline

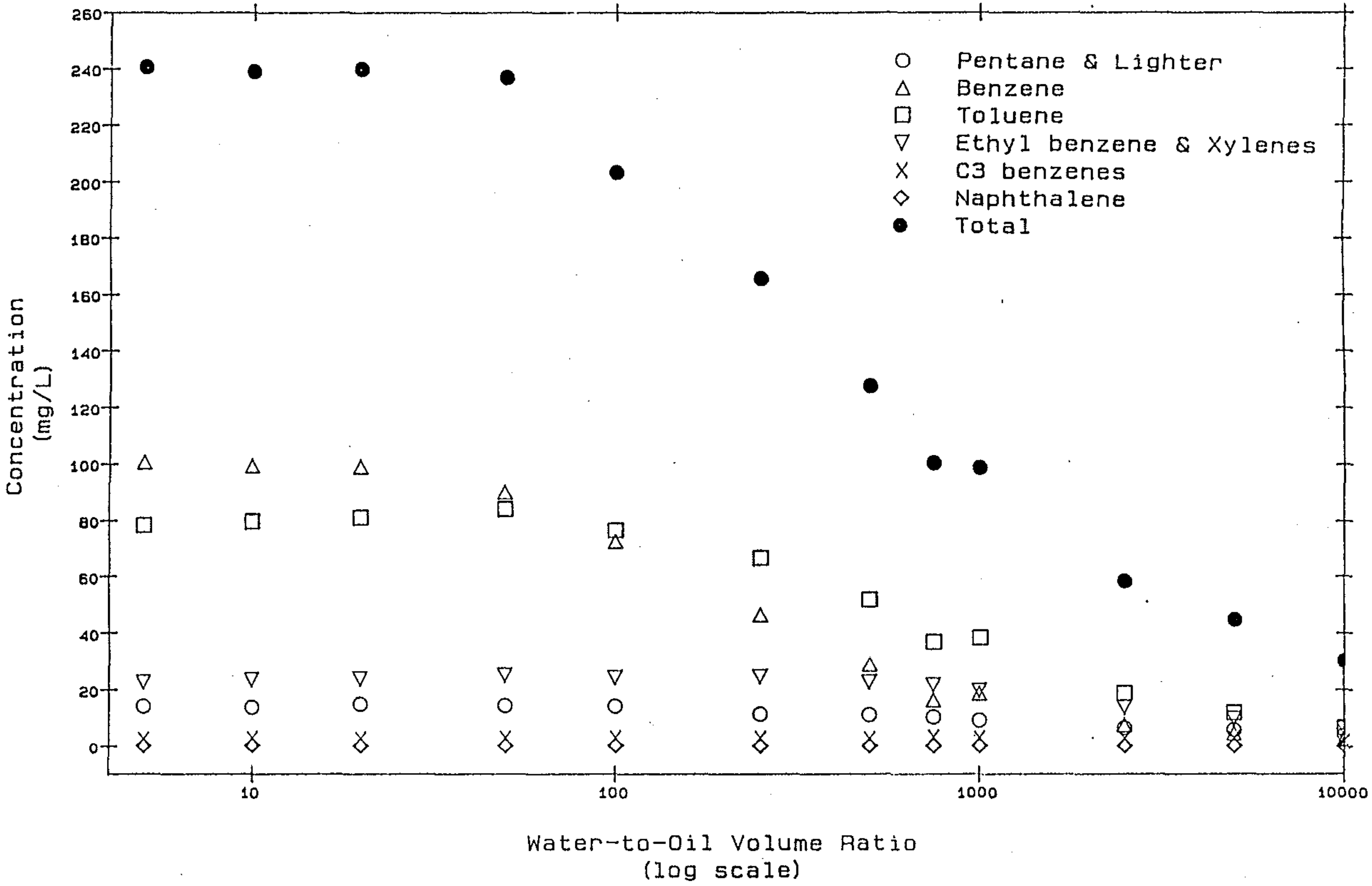


Figure 5: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Fuel Oil No. 6, Bunker C Residual (High Viscosity)

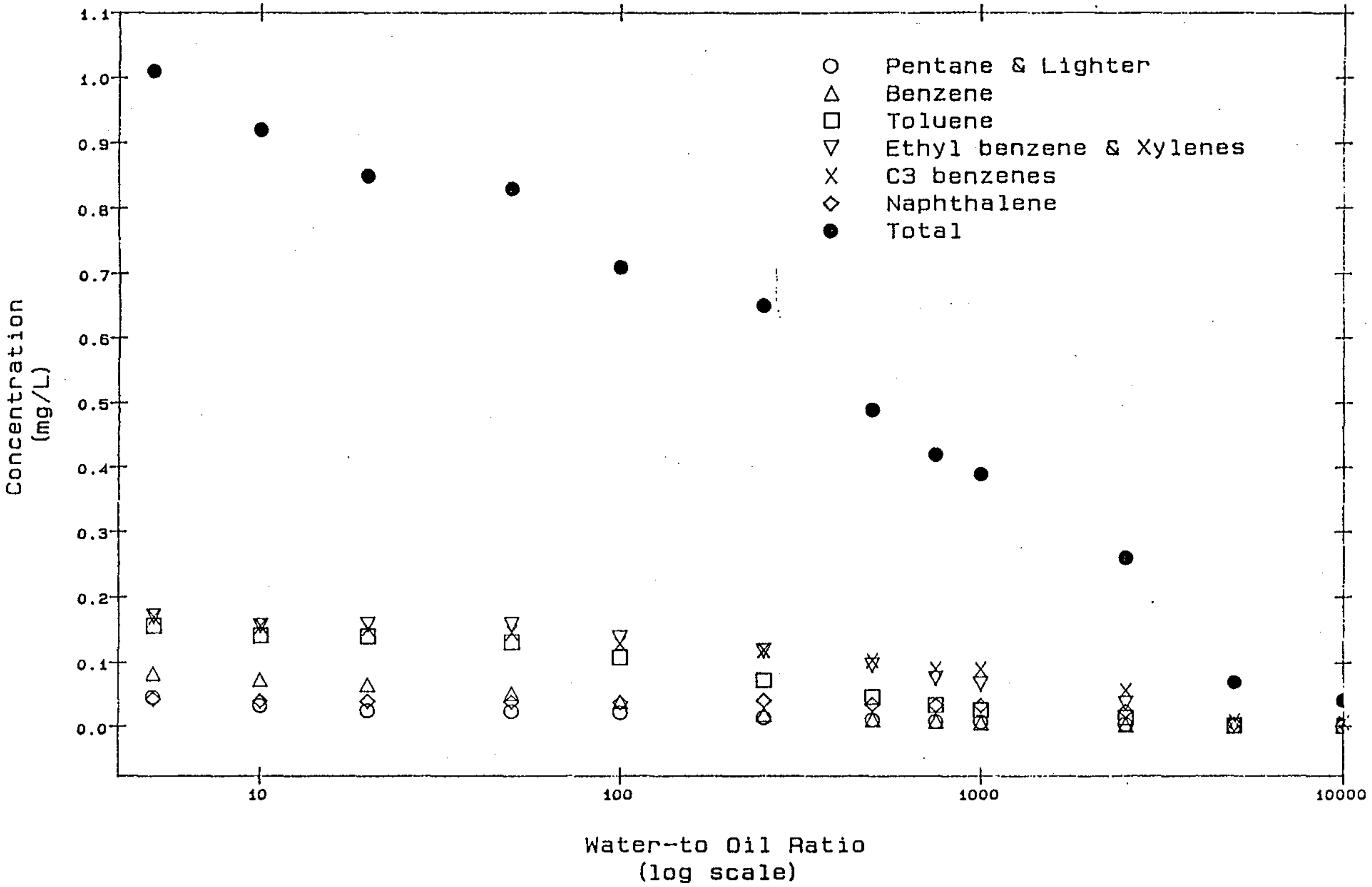


Figure 6: Concentration of Water-Soluble Components versus Water-to-Oil Ratio
Fuel Oil No.2 (High Aromatic)

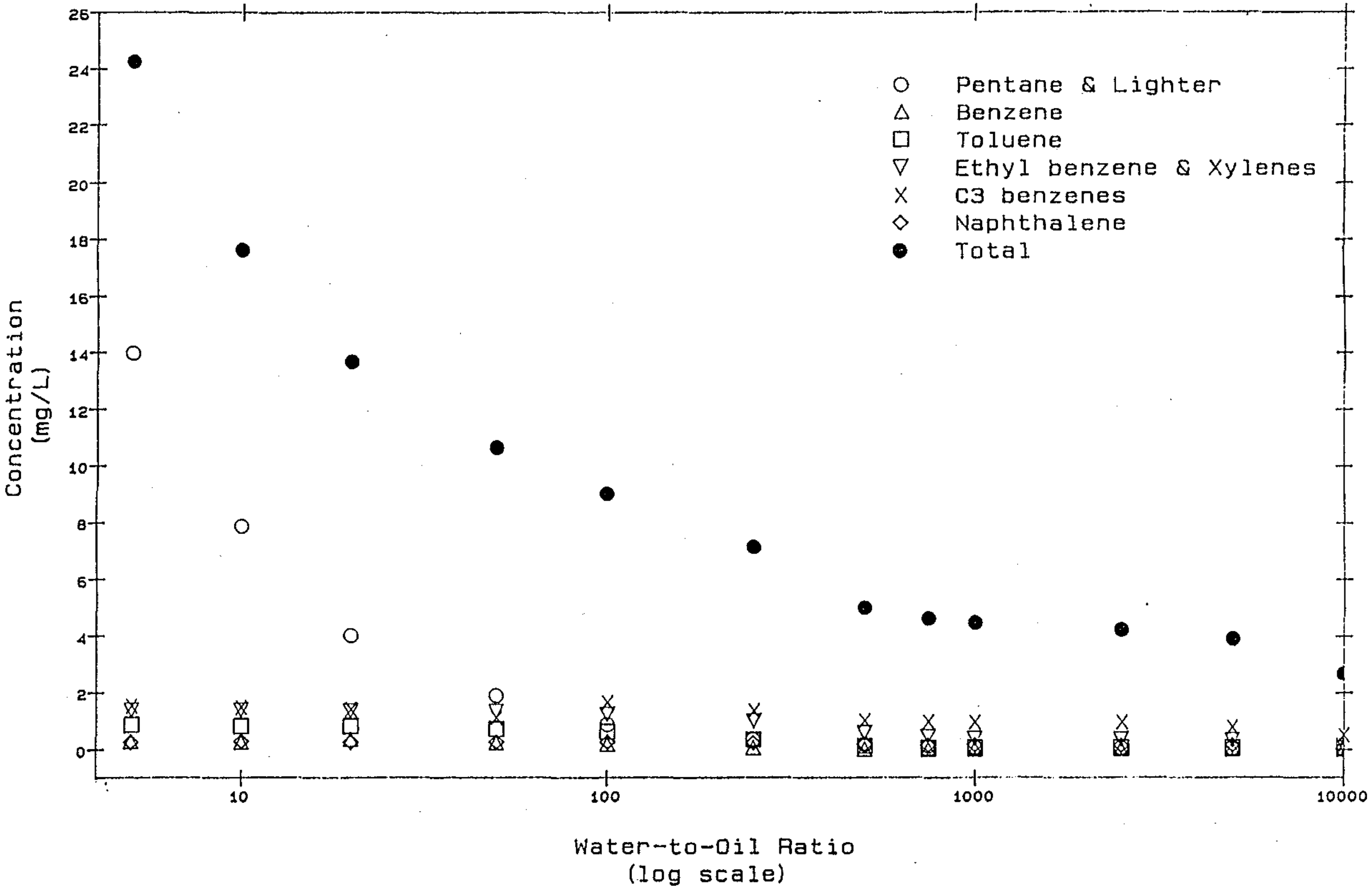
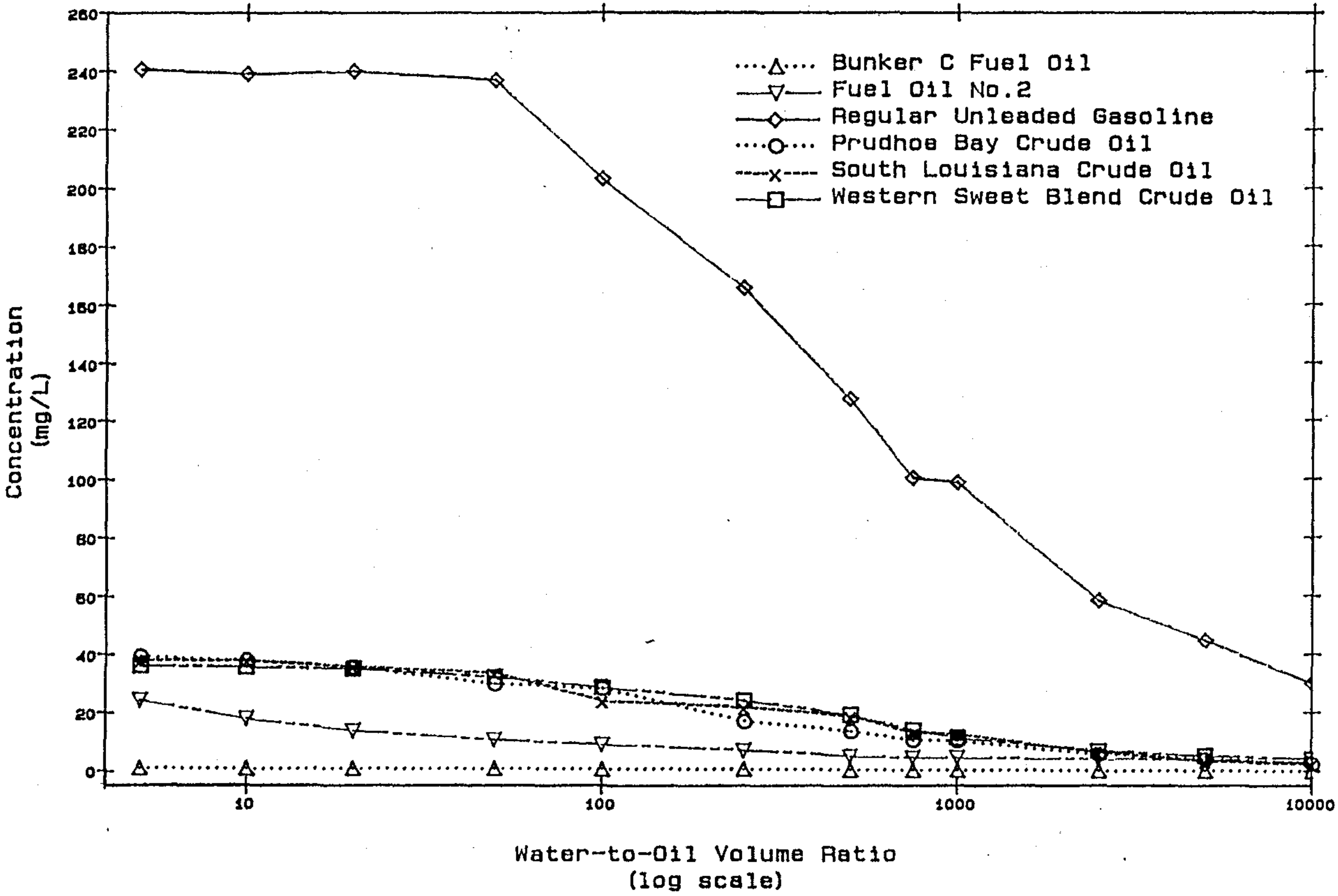


Figure 7: Concentration of Water-Soluble-Fractions versus Water-to-Oil Ratio



Calculated oil-water partition coefficients for selected hydrocarbons are presented in Table 1. The form of the equation fitted to the experimental data was that proposed by Shiu et al (1988). This theoretical equation based upon a simplified mass balance predicts that the concentration of any individual component in the water phase will be:

$$C_W = C_{W0}/(1 + (Q/K))$$

where: K is the oil-water partition coefficient
Q is the water-to-oil volume ratio
C_{W0} is the concentration of the component in the water phase at $Q = 0$.

C_{W0} was determined by extrapolating the concentration to a water-to-oil ratio of 0. All fitted equations gave correlation coefficient values of at least 0.985.

The oil-water partition coefficients presented in Table 1 provide a numerical indication of the sensitivity of water soluble components to the water-to-oil ratio. From the equation $C_W = C_{W0} / (1+(Q/K))$, it can be seen that when the water-to-oil ratio (Q) equals the partition coefficient (K), the concentration of that component will be half of the value of C_{W0}. Therefore, components with low partition coefficients are most sensitive to the water-to-oil ratio. The calculated values in Table 1 also show that partition coefficients are extremely dependent upon the oil matrix. How an individual compound partitions itself between the oil and water phases will depend upon its concentration in the oil and its interactions with other solutes in both the oil and water phases.

Table 1 : Oil-Water Partition Coefficients of Test Oils

Component	Western Sweet Blend crude	South Louisiana crude	Prudhoe Bay crude	Gasoline	Fuel Oil no. 6	Fuel Oil no. 2
pentane & lighter	1883	1556	1043	2420	40	11
benzene	121	106	75	228	72	80
toluene	386	382	249	934	207	161
ethylbenzene & xylenes	1105	1248	895	4758	568	524
naphthalene	2126	1975	1947	5986	1178	2319
methyl naphthalenes	-	-	-	-	3930	5160
dimethyl naphthalenes	-	-	-	-	7716	42351

One implication of the WSF dependence on the water-to-oil ratio is that bioassay and solubility results obtained by researchers using different ratios may not be directly comparable. A review of the literature showed that water-to-oil ratios used for bioassay testing varied from 6:1 to 10,000:1. Also, it was not uncommon to find terminology in the literature that referred to "saturated" WSF solutions which were produced when an "excess" of oil was contacted with water. Unfortunately, the water-to-oil ratio that is assumed to provide an excess of oil has varied with time, and in some cases, researchers failed to specify the ratio used. For most recent studies, an excess of oil implies a water-to-oil ratio of about 20:1 or less. Our findings show this asssumption may not be valid for all petroleum mixtures. The results for Fuel Oil No.2 (Figure 6) show that the WSF concentration is particularly sensitive to the water-to-oil ratio in this range. The fuel oil contains a low concentration of material with a relatively high solubility (pentane and more volatile compounds). The aqueous concentration of these compounds drops from 14 mg/L to 4 mg/L when the water-to-oil ratio is increased from 5:1 to 20:1 and as a result, the apparent "solubility" of the oil drops by the same appreciable amount.

As noted by Shiu et al. (1988) and Lockhart et al. (1984), the effect of water-to-oil ratio on WSF's must be taken into account when extrapolating bioassay results to environmental conditions. The water-to-oil ratios in most spill situations are likely to be several orders of magnitude larger than those used in most bioassays. Since the relative proportions of the individual components of the WSF vary with the water-to-oil ratio and each component exhibits a different toxicity, the use of a dilution factor is unlikely to produce compatible results. The use of high water-to-oil ratios in bioassays would be necessary to produce WSF's more similar to those found in the environment. It is suspected that this effect is a contributing factor for the anecdotal observation that oil spills do not cause the high levels of mortality to marine organisms which are expected from a consideration of currently available WSF bioassay data.

The vessel used for oil/water contacting in this study was a closed system, thus loss of compounds by evaporation was prevented. In an open system such as a marine oil spill, volatile compounds would quickly evaporate. However, there are several real spill scenarios which could be considered closed to evaporation. Examples of situations where evaporation is inhibited would include: an oil spill under ice cover; a leak from an underground petroleum storage tank contaminates ground water; and a processing unit such as a separator or slop tank through which oil and water pass. The results obtained in this study likely provide an indication of the dissolution behaviour of oils in such circumstances.

CONCLUSIONS

The water-to-oil volume ratio used during the preparation of water soluble fractions can have a significant influence upon the composition and concentration of the water soluble fraction. This influence of the water-to-oil ratio upon the dissolution of oils must be taken into account if results from laboratory tests, especially for bioassay purposes, are to be indicative of environmental behaviour. The results show that the more soluble components of oil make up a large fraction of the WSF's composition at low water-to-oil ratios. At high water-to-oil ratios, these compounds become less significant and the less soluble compounds constitute a larger portion of the WSF.

Data from this study show that the three crude oils yield WSF's that are very similar in terms of both composition and concentration with slight differences in the relative abundance of some compounds. Gasoline was the most soluble petroleum mixture studied; its WSF's were enriched with benzene, toluene, ethylbenzene and xylenes. Compared to the WSF's of the crude oils and gasoline, the WSF's of the fuel oils lacked the presence of volatile aromatics but they were comprised of a relatively large number of less volatile, less soluble compounds such as tri-methyl benzenes, propyl benzenes, naphthalene, and alkylated naphthalenes.

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APPENDIX

Table 2: Analyses of Oils (mg/L)

component	Western Sweet Blend crude	South Louisiana crude	Prudhoe Bay crude	Gasoline	Fuel Oil No. 6	Fuel Oil No. 2
pentane & lighter	24750	28730	12520	203520	2	214
benzene	2600	3360	2860	23960	6	60
toluene	6130	6640	6260	63520	32	480
ethyl benzene & xylene	13420	13270	9210	61610	97	3770
naphthalene	1090	2020	1070	32	437	5050
methyl naphthalenes			-		7290	23210
dimethyl naphthalenes					11950	26640

Table 3: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
Western Sweet Blend Crude Oil

Water -to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	2.40	2.30	2.40	2.30	2.40	2.40	1.90	1.60	1.40	0.81	0.77	0.53
benzene	13.40	12.90	12.40	10.30	7.10	4.50	2.80	1.20	0.69	0.23	0.16	0.12
toluene	9.30	9.30	9.20	8.70	7.80	6.30	4.80	2.60	1.50	0.55	0.42	0.27
ethylbenzene & xylenes	4.70	4.70	4.80	4.80	4.70	4.30	3.70	2.80	2.30	1.10	0.75	0.38
C3 benzenes	1.60	1.60	1.60	1.60	1.70	1.60	1.50	1.40	1.30	0.90	0.60	0.42
naphthalene	0.21	0.20	0.20	0.21	0.21	0.19	0.18	0.16	0.13	0.09	0.06	0.05
others	4.39	4.50	4.40	4.19	4.59	4.71	4.32	4.14	4.08	3.12	2.34	2.13
Total	36.00	35.50	35.00	32.10	28.50	24.00	19.20	13.90	11.40	6.80	5.10	3.90

Table 4: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
South Louisiana Crude Oil

Water -to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	2.50	2.42	2.29	2.26	1.96	2.09	1.96	1.78	1.78	1.09	0.470	0.210
benzene	16.89	16.71	13.40	13.44	7.11	5.06	3.76	1.64	1.53	0.31	0.150	0.077
toluene	9.74	9.86	9.49	9.24	7.10	6.25	5.20	2.89	2.75	0.69	0.290	0.110
ethylbenzene & xylenes	4.23	4.33	4.26	4.24	3.73	3.66	3.45	2.69	2.59	1.13	0.480	0.210
C3 benzenes	0.96	0.98	0.96	0.97	0.90	0.92	0.90	0.84	0.83	0.57	0.340	0.210
naphthalene	0.32	0.32	0.32	0.32	0.31	0.28	0.28	0.24	0.23	0.13	0.065	0.041
others	3.45	3.31	5.10	3.21	3.05	3.63	3.34	3.27	3.06	2.48	1.685	1.332
Total	38.09	37.93	35.82	33.68	24.16	21.89	18.89	13.35	12.77	6.40	3.480	2.190

Table 5: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
Prudhoe Bay Crude Oil

Water -to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	1.52	1.38	1.42	1.33	1.58	1.13	1.06	0.86	0.74	0.44	0.290	0.110
benzene	17.72	16.70	14.91	11.15	8.98	3.21	1.86	1.20	1.20	0.39	0.230	0.130
toluene	10.93	10.74	10.43	9.14	8.77	5.20	3.50	2.39	2.41	0.85	0.460	0.290
ethylbenzene & xylenes	4.03	4.00	3.98	3.74	3.78	3.06	2.59	2.10	2.08	1.03	0.590	0.320
C3 benzenes	0.94	0.93	0.94	0.90	0.93	0.75	0.83	0.73	0.78	0.54	0.380	0.230
naphthalene	0.26	0.26	0.26	0.25	0.25	0.23	0.21	0.18	0.18	0.11	0.069	0.049
others	3.74	4.36	3.50	3.27	3.75	3.52	3.34	3.04	2.94	2.31	1.870	1.180
Total	39.16	37.62	35.44	29.78	28.04	17.10	13.43	10.50	10.33	5.67	3.890	2.310

Table 6: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
Regular Unleaded Gasoline

Water-to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	14.30	13.80	14.90	14.50	14.20	11.50	11.20	10.50	9.40	6.70	5.90	4.20
benzene	100.70	99.20	99.10	90.00	72.40	46.40	29.10	16.40	18.70	7.70	4.60	2.60
toluene	78.20	79.30	81.00	83.90	76.10	66.50	51.60	36.80	38.40	18.80	11.90	6.70
ethylbenzene & xylenes	22.70	23.50	24.00	25.10	24.30	24.60	22.60	21.70	19.80	13.90	9.90	6.40
C3 benzenes	2.50	2.70	2.70	2.90	2.80	3.00	2.70	3.40	2.90	2.70	2.80	2.00
naphthalene	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.12	0.12	0.09	0.06	0.17
others	22.17	20.37	18.17	20.47	13.37	13.57	10.37	11.48	9.36	8.58	9.59	8.22
Total	240.70	239.00	240.00	237.00	203.30	165.70	127.70	100.40	98.68	58.47	44.75	30.29

Table 7: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
Fuel Oil No.6, Bunker C Residual (High Viscosity)

Water-to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	0.046	0.033	0.025	0.024	0.022	0.015	0.011	0.0083	0.0080	0.0034	0.0017	0.00098
benzene	0.082	0.073	0.065	0.051	0.038	0.019	0.011	0.0076	0.0054	0.0030	N/D	N/D
toluene	0.156	0.141	0.139	0.130	0.107	0.072	0.046	0.0330	0.0250	0.0130	0.0014	0.00089
ethylbenzene & xylenes	0.171	0.156	0.158	0.158	0.137	0.118	0.096	0.0750	0.0660	0.0360	0.0040	0.00270
C3 benzene	0.170	0.156	0.152	0.146	0.129	0.119	0.104	0.0900	0.0900	0.0570	0.0098	0.00680
naphthalene	0.025	0.022	0.023	0.022	0.021	0.022	0.018	0.0160	0.0150	0.0084	0.0016	0.00100
methyl-naphthalenes	0.042	0.039	0.039	0.038	0.037	0.040	0.035	0.0330	0.0330	0.0240	0.0049	0.00460
dimethyl-naphthalenes	0.041	0.039	0.039	0.043	0.042	0.048	0.040	0.0380	0.0380	0.0300	0.0062	0.00840
others	0.277	0.261	0.210	0.218	0.177	0.197	0.131	0.1190	0.1420	0.0850	0.0394	0.01550
Total	1.010	0.920	0.850	0.830	0.710	0.650	0.490	0.4200	0.3900	0.2600	0.0690	0.04100

Table 8: Concentration (mg/L) of WSF's Components as a Function of Water-to-Oil Ratio
Fuel Oil No.2 (High Aromatic)

Water -to-oil ratio	5	10	20	50	100	250	500	750	1000	2500	5000	10000
pentane & lighter	13.98	7.88	4.03	1.90	0.89	0.350	0.200	0.130	0.090	0.053	0.031	0.019
benzene	0.30	0.27	0.37	0.25	0.18	0.055	0.019	0.018	0.018	0.014	0.013	0.006
toluene	0.85	0.82	0.80	0.72	0.61	0.340	0.110	0.074	0.053	0.058	0.073	0.030
ethylbenzene & xylenes	1.37	1.37	1.35	1.33	1.24	1.010	0.590	0.460	0.390	0.370	0.340	0.140
C3 benzenes	1.53	1.47	1.40	1.10	1.64	1.350	1.010	0.970	0.950	0.950	0.780	0.500
naphthalene	0.27	0.28	0.27	0.27	0.27	0.250	0.190	0.170	0.160	0.140	0.160	0.058
methyl-naphthalenes	0.68	0.66	0.61	0.66	0.63	0.610	0.540	0.520	0.510	0.500	0.430	0.290
dimethyl-naphthalenes	0.34	0.34	0.34	0.36	0.35	0.390	0.340	0.340	0.340	0.270	0.350	0.260
others	4.95	4.83	4.51	4.08	3.22	2.805	2.011	1.978	1.999	1.885	1.763	1.377
Total	24.27	17.62	13.68	10.67	9.03	7.160	5.010	4.660	4.510	4.240	3.940	2.680