Solubility and sorption of petroleum hydrocarbons in water and cosolvent systems

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Abstract

The solubility and sorption of oil by uncontaminated clay loam and silt loam soils were studied from water and cosolvent/water solutions using batch techniques. The data obtained from the dissolution and sorption experiments were used to evaluate the applicability of the cosolvent theory to oil as a complex mixture. Aqueous solubility and soil-water distribution coefficients ($K_{d,w}$, L/kg) were estimated by extrapolating from cosolvent data, with a log-linear cosolvency model, to the volume fraction of cosolvent (f_c) 0, and were compared with direct aqueous measurements. The extrapolated water solubility was 3.16 mg/L, in good agreement with the directly measured value of 3.83 mg/L. Extrapolated values of $K_{d,w}$ for the two soils were close to each other but consistently higher than the values from direct aqueous measurements, because of the presence of dissolved organic carbon (DOC). The partition coefficient (K_{DOC}) between the DOC and the freely dissolved phase and the OC-normalized sorption coefficient (K_{OC}) were determined. The average values of $\log K_{DOC}$ and $\log K_{OC}$ were estimated as 4.34 and 3.32, respectively, giving insight into the possibility of oil becoming mobilized and/or of the soil being remedied. This study revealed that the cosolvency model can be applied to a broader range of hydrophobic organic chemicals (HOCs) than has been previously thought. The results aided in a reliable determination of water solubility and sorption coefficients and provide information about the fate of oil in solvent-contaminated environment.

Key words: cosolvent; solubility; sorption; dissolved organic carbon; oil

Introduction

Anthropogenic sources and natural seepage contribute millions of gallons of oil to the environment. Oil pollution from several large-scale oil fields in the northeast of China remains one of the major environmental problems in these areas. The amount and composition of spilled oil water-soluble components determine the subsequent aquatic toxic risk and response (Stanford *et al.*, 2007). Although the volume loss of spilled oil by dissolution can be negligible from a practical perspective, it can be significant from an ecotoxicological standpoint.

Sorption, directly influenced by the soil organic carbon present, is a central process in the bioavailability, behavior, and fate of hydrophobic organic chemicals (HOCs) in aquatic ecosystems. Soil organic carbon is present as particulate organic carbon (POC) and dissolved organic carbon (DOC). The POC fraction can be regarded as a potential pool for DOC containing nanoparticles and colloids (Kalbitz *et al.*, 2000). The DOC in the subsurface may behave as potentially mobile carriers of HOCs in soil and aquifer systems (Schumacher *et al.*, 2005). To understand and quantify the importance of POC and DOC, many researchers have studied the sorption of a wide

variety of HOCs (Caron *et al.*, 1985; Frankki *et al.*, 2006; Karickhoff *et al.*, 1979; Servos and Muir, 1989; Traina *et al.*, 1996) using various methods (Allen-King *et al.*, 1995; Garbarini and Lion, 1985; Harkey *et al.*, 1994; Hegeman *et al.*, 1995; Poerschmann *et al.*, 1997; Shimizu and Liljestrand, 1991). However, the knowledge about sorption of oil by POC and DOC is scarce (Shen and Jaffé, 2000) owing to the unique properties of oil, including its high hydrophobicity, low aqueous solubility, and an affinity for glass surfaces. Log-linear cosolvency model proposed by Rao *et al.* in 1985 has been successfully and extensively used to determine the solubility and sorption of this class of contaminants (Bouchard, 2002; Iraqi and Iraqi, 2000). However, it was limited to pure chemicals. Therefore, cosolvent and log-linear cosolvency model were employed to evaluate the applicability of the cosolvent theory to oil as a complex mixture, and to estimate its aqueous solubility, soil-water distribution coefficients ($K_{d,w}$), and further the partition coefficients between the DOC and the freely dissolved phases (K_{DOC}) by comparing the extrapolated and directly measured $K_{d,w}$. To the best of our knowledge, this is the first time a log-linear relationship between the solubility/sorption coefficients and the volume fraction of cosolvent has been considered for a mixture.

The pore water in porous sediment materials near

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hazardous waste disposal sites and accidental spill sites often contain significant concentrations of water-miscible solvents that can affect aqueous solubility, and thus the sorption of contaminants. The net result of this cosolvent effect is often an increase in contaminant flux through the unsaturated zone to groundwater (Bouchard, 1998). The present study also provides a quantitative understanding of oil movement in an environment containing water-soluble solvents.

1 Materials and methods

1.1 Chemicals

Fuel oil No.0 was obtained commercially from China Petroleum and Chemical Co. The soluble fraction was used as sorbate owing to the wide use of No.0 fuel oil. Hexane (HPLC/Spectro grade) was purchased from the TEDIA Company Inc. (OH, USA). The cosolvent used in this study was acetone (analytical reagent grade), provided by the Kemiou Agent Co., Tianjin, China. The other chemicals used included calcium chloride and sodium azide (analytical grade, Xilong Chemical Co., China).

1.2 Soils

PJ is a clay loam soil that was sampled from the uncontaminated agricultural top soil in Panjin, China. CBM is a silt loam soil with high organic matter content from the Changbai Mountain, China, with a long-established history. PJ and CBM are two typical soils in the northeast of China that represent a range in texture and organic carbon content, and are used as sorbents. The soils (0–10 cm) were passed through a 250-μm sieve, homogenized, air-dried, and stored in closed containers at room temperature. Their physicochemical properties, determined by standard techniques, are summarized in Table 1.

1.3 Log-linear cosolvency model

For HOCs, the effect of organic solvent on the solubility has been adequately described with the following log-linear relationship (Yalkowsky *et al.*, 1972):

$$\log S_{\text{mix}} = \log S_{\text{w}} + \sigma f_{\text{c}} \tag{1}$$

where, S_{mix} and S_{w} are the solubilities of the cosolvent/water mixture and cosolvent-free water, respectively; f_{c} is the volume fraction of the cosolvent; and σ is a measure of the solute-cosolvent interactions and an index of the solubilizing power of the cosolvent (Bouchard, 1998). At $f_{\text{c}} = 1$, σ is equal to the logarithm of the ratio of solubility in pure cosolvent to that in water. This method has been successfully used to estimate the aqueous solubility of organic compounds that are sparingly soluble in water

and to enhance the solubilization of pharmaceutical drugs (Yalkowsky, 1999).

Based on the inverse relationship between solubility and sorption, a similar equation to describe the effect of a cosolvent on the sorption of HOCs was derived as (Rao *et al.*, 1985):

$$\log K_{\text{d,mix}} = \log K_{\text{d,w}} - \alpha \sigma f_{\text{c}} \tag{2}$$

where, $K_{\text{d,mix}}$ and $K_{\text{d,w}}$ are the partition coefficients in a binary cosolvent/water solution and water, respectively; and α is an empirical factor representing the average deviation observed between the sorption-f_{c} relationship and solubilization, and is assumed to be constant for a given cosolvent. Eq.(2) has been successfully employed to determine the sorption coefficients of several HOCs (Bouchard, 1998, 2002; Fu and Luthy, 1986; Iraqi and Iraqi, 2000; Lee *et al.*, 1990; Nkedi-Kizza *et al.*, 1985, 1989). Eqs.(1) and (2) allow the estimation of water solubility and sorption coefficient values in water-soil systems by extrapolating from data measured in cosolvent/water solutions to $f_{\text{c}} = 0$, assuming that the log-linear behavior is exhibited.

1.4 Determination of oil solubility

The solubility was determined by "slow-stirring" experiments (Tolls *et al.*, 2002), in which a layer of neat hydrocarbons floated on the water phase or the cosolvent/water mixtures; this two-phase system was gently stirred to minimize the formation of microdroplets. The solubility of No.0 fuel oil was measured at 20 ± 1°C in water and in acetone/water solutions of 10%, 20%, 30%, 40%, and 50% volume cosolvent. The samples containing dissolved petroleum hydrocarbons (DPH) were withdrawn after 72 h, since the dissolution kinetics indicated that equilibrium was attained within 72 h. The average concentration ($n = 10$) determined the aqueous solubility. In addition, No.0 fuel-oil-saturated water was collected for further use in the sorption experiments.

1.5 Sorption isotherms in water and in acetone-water systems

Acetone was selected for the sorption studies because oil solubility exhibits a good log-linear cosolvency profile in acetone/water systems. Batch-equilibrium sorption isotherms were obtained in water and in acetone-water solutions of 10%, 17%, 24%, and 30% volume acetone, for each of the two soils, at 20 ± 1 °C in screw-capped glass centrifuge tubes. The background solution comprised 0.01 mol/L CaCl$_2$ in ultrapure water (Millipore-Waters, Netherlands) and 200 mg/L NaN$_3$ as a biocide. The initial concentrations of DPH ranged from 15% to 100% of the solubility. The soil (g) to solution (ml) ratios (*M/V*) were

Table 1 Physicochemical properties of the soils

Soil	Texture	pH (1:2.5 H$_2$O)	Sand (%)	Silt (%)	Clay (%)	Organic carbon[a] (OC, %)
PJ	Clay loam	7.22	0.0	80.7	19.3	0.91±0.02
CBM	Silt loam	7.06	7.8	88.8	3.4	17.70±0.05

pH at equilibrium with 0.01 mol/L CaCl$_2$ and 200 mg/L NaN$_3$ at the soil-to-solution ratio used for isotherms; [a] mean ± standard deviation ($n = 3$).

varied with the solution matrices and soil types to achieve 30%–80% removal efficiency of DPH at equilibrium, while they were constant for a given soil and acetone/water solution over the range of an isotherm. The *M/V* ratios ranged from 3:40 to 0.3:40 for water, and from 25:40 to 2.5:40 for acetone/water solutions. The isotherms consisted of 6 initial concentration points and each point was run in duplicate. The DPH of different concentrations in water or acetone/water mixture was added directly into the tubes containing the soils preweighed to no headspace; thus, the loss of the DPH's volatile components was effectively reduced. The tubes containing soil were prepared in triplicate for each soil to determine the DOC concentration in the supernatant after centrifugation.

The tubes were immediately sealed tightly using screw caps with Telfon liners, and were then tumbled at 10 r/min for 2 d in the dark at 20 ± 1°C, which was found to be sufficient to reach equilibrium in a preliminary kinetic study. After the tubes were centrifuged at 3,000 r/min for 30 min, the supernatant was withdrawn for the DPH concentration analysis. Control tubes with DPH only permitted the measurement of losses of DPH to glass-wall sorption, to volatilization, and to biodegradation. The losses were less than 3%. Hence, the DPH retained by the sorbents could be calculated by mass difference.

1.6 DPH analysis

Analysis of the DPH was performed using a 2010 gas chromatograph (GC, Shimadzu, Japan) with a flame ionization detector (FID). Samples (100 ml) were spiked with n-C_{24} (7 µg) and extracted twice with 5 ml hexane. The hexane extracts were combined, rotary-evaporated to approximately 0.5 ml, and then, column chromatography was performed according to Reddy and Quim (1999). A 2-µl sample was injected and compounds were separated into a poly (dimethylsiloxane) capillary column (Rtx-1, 30 m, 0.25 mm i.d., 0.25 µm film, Shimadzu, Japan) with N_2 as the carrier gas at a constant flow of 1.47 ml/min. The GC oven was temperature programmed from 40°C (1 min hold) to 120 at 30°C/min, and then from 120 to 280°C at 5°C/min (30 min hold). Owing to the lack of calibration solution of dissolved oil, No.0 fuel oil was used as a standard to generate the response factor. The DPH was quantified (as the unresolved complex mixture, UCM) by integrating the total area and using response factors determined from No.0 fuel-oil standards. Recoveries of No.0 fuel oil spiked into Millpore-water were (96.7 ± 8.1)%. Precision, based on the duplicate samples, as expressed by the relative standard deviation, was less than 5%. A method detection limit of 0.54 mg/L was estimated according to the procedures described by Glaser *et al.* (1981).

1.7 DOC analysis

The supernatants in the direct aqueous sorption measurements were analyzed for DOC concentrations after 2 d of equilibration. After centrifuging for 30 min at 3,000 r/min, the supernatants were acidified, and analyzed using a Shimadzu TOC-V$_{CPH}$ analyzer (Shimadzu, Japan).

1.8 Data analysis

The aqueous solubility and the soil-water distribution coefficients were determined by direct measurement and extrapolation in cosolvent/water solutions. The sorption isotherm data were fit to the linear sorption model ($C_s = K_{d,w}C_w$ or $C_s = K_{d,mix}C_{mix}$), where, C_s (µg/g) is the concentration of sorbed oil, and C_w (mg/L) and C_{mix} (mg/L) are the equilibrium concentrations in the aqueous or in the mixed cosolvent/water solution (mg/L), respectively. For each soil, the $K_{d,mix}$ values estimated at each f_c were applied in Eq.(2), and $K_{d,w}$ was determined by extrapolation to $f_c = 0$.

2 Results and discussion

2.1 Solubility of oil

A good log-linear cosolvency model well described the solubility of oil in binary acetone/water solutions, although oil is a complex mixture (Fig.1). Rubino and Yalkowsky (1987) showed the value of σ to be correlated with solute properties, such as the molecular surface area, and with solvent properties such as the dielectric constant and bulk surface tension. It was in close agreement with the log-linear cosolvency relationship for oil, which can probably be explained by the fact that the difference in the cosolvency power of acetone for each component of the oil was extremely small to be observed. It also indicated that Eq.(2) was applicable to describe the sorption of oil as a complex mixture in acetone/water solutions. The water solubility of No.0 fuel oil determined by direct aqueous phase measurements was 3.83 ± 0.28 mg/L ($n = 10$). The extrapolated water solubility from acetone/water solutions was 3.16 mg/L, in good agreement with the value measured directly from water. Furthermore, water-soluble No.0 fuel oil was dominated by UCM (93.7%).

2.2 Sorption isotherms in water and acetone-water systems

To investigate the applicability of the cosolvent theory proposed by Rao *et al.* (1985) to oil sorption, No.0 fuel oil sorption isotherms by the two surface soils were
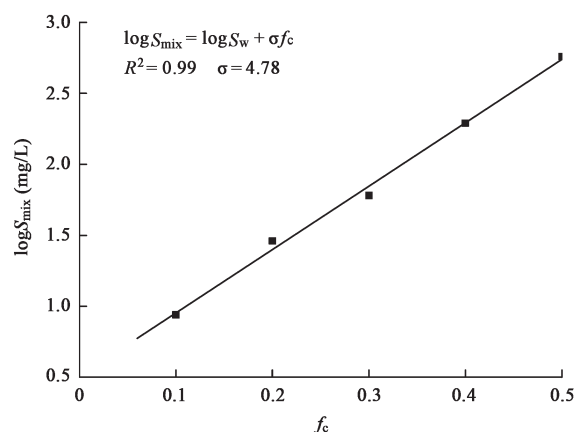

Fig. 1 Measured solubility of No.0 fuel oil in acetone/water solutions.

measured in binary solutions of acetone/water of 10%, 17%, 24%, and 30% volume acetone, respectively. The sorption isotherms of oil to PJ and CBM soils along with the linear regressions are shown in Fig.2. All sorption isotherms were well fitted by the linear sorption model as indicated by the correlation coefficients exceeding 0.95. The linear sorption coefficients estimated from the batch-equilibration studies along with the results from the application of the log-linear cosolvency sorption model are summarized in Tables 2 and 3. The aqueous sorption coefficients were well correlated with the soil OC, with average $\log K_{OC}$ values of 3.32 and 3.14 estimated by cosolvent extrapolation and direct aqueous measurement, respectively.

The values of $K_{d,mix}$ (L/kg) in acetone/water solutions, estimated from the batch-equilibration studies, were plotted as a function of f_c in Fig.3. As predicted by Eq.(2), an inverse relationship between $\log K_{d,mix}$ and f_c was observed. Regression of $\log K_{d,mix}$ on f_c yielded an R^2 greater than 0.96, indicating the high degree of linearity

of the $\log K_{d,mix}-f_c$ relationship in the cosolvent range tested (Fig.3). This reverse relationship between $\log K_{d,mix}$ and f_c suggests that solvophobic interactions dominate oil sorption from aqueous and acetone/water solutions.

The extrapolated $K_{d,w}$ values were significantly higher than those determined by direct measurement from aqueous solutions, with the difference being soil-dependent. High aqueous $K_{d,w}$ values estimated by extrapolation from acetone/water solutions may be owing to cosolvent-enhanced mass-transfer, cosolvent modification of soil sorption characteristics, or the effect of DOC from aqueous soil suspensions in reducing sorption. Dividing the ασ values of slopes 4.20 and 3.73 for PJ and CBM soils, by σ estimated from the solubility data, the cosolvent-sorbent interaction terms (α) were determined to be 0.88 and 0.78, respectively (Table 2). The small deviation of α from unity indicates that the impact of acetone on sorption appears to be dominated by acetone-induced changes in the solution phase activity of No.0 fuel oil.
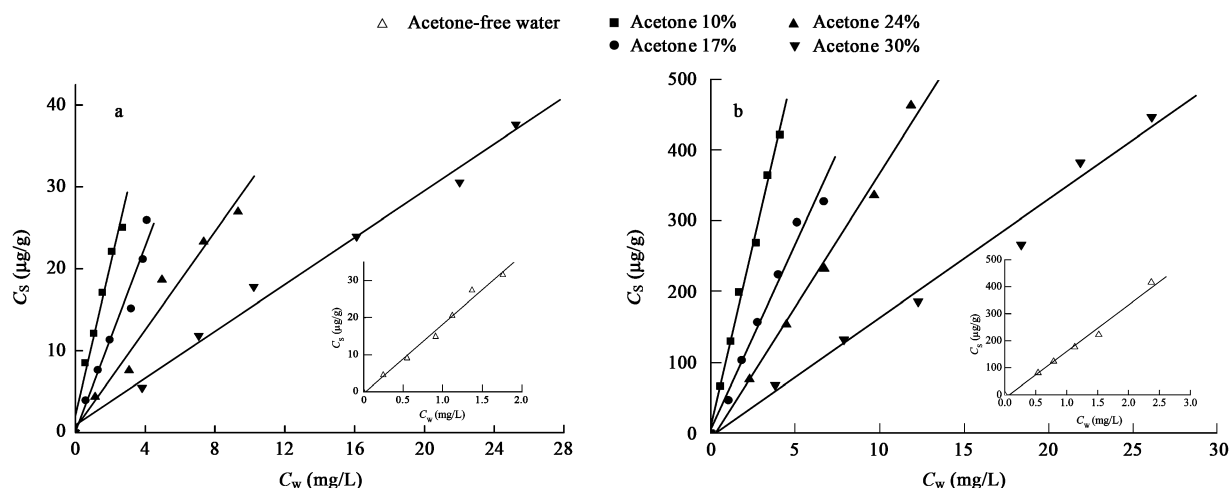

Fig. 2 Sorption isotherms of No.0 fuel oil to PJ (a) and CBM (b) soil in acetone-free water and in acetone/water solutions. The solid lines are the linear sorption model fits. C_S: solid phase concentration; C_W: equilibrated solution phase concentration.

Table 2 Linear sorption coefficients at various volume fractions of acetone

f_c	PJ soil			CBM soil		
	$K_{d,mix}$ (L/kg)	$\log K_{d,mix}$	R^2	$K_{d,mix}$ (L/kg)	$\log K_{d,mix}$	R^2
10%	10.24	1.01	0.955	102.89	2.01	0.994
17%	5.66	0.75	0.967	52.36	1.72	0.980
24%	3.00	0.48	0.969	37.81	1.58	0.995
30%	1.43	0.16	0.990	16.78	1.22	0.986
ασ		4.20			3.73	
α		0.88			0.78	

$K_{d,mix}$: linear sorption coefficients in cosolvent/water solutions, respectively; σ: cosolvency power of the solvent for the solute; α: empirical factor representing the average deviation.

Table 3 Sorption coefficients extrapolated from the log-linear cosolvency model and measured directly in aqueous solutions

Soil	OC (%)	$K_{d,mix}$ (L/kg)		$\log K_{OC}$ (L/kg)		C_{DOC} (mg/L)
		Extrapolation	Measurement	Extrapolation	Measurement	
PJ	0.91	28.18	18.70	3.49	3.31	18.01
CBM	17.70	245.47	164.36	3.14	2.97	29.01
$\log K_{OC}$ (SD)				3.32 (0.25)	3.14 (0.24)	

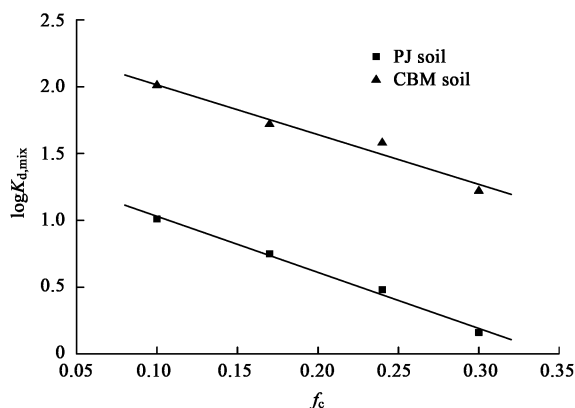SD: standard deviations; K_{OC}: OC-normalized sorption coefficient.

Fig. 3 Log-linear plot of the linear sorption coefficients $\log K_{d,mix}$ vs. the volume fraction of acetone f_c for sorption of No.0 fuel oil by PJ and CBM soils.

2.3 Effects of DOC on sorption

Nkedl-Kizza et al. (1985) proposed that high extrapolated $K_{d,w}$ is mainly owing to the reduced sorption by DOC in aqueous soil suspensions. Moreover, it was confirmed that K_d, the apparent sorption coefficient in the presence of DOC, determined with the method of batch-equilibration technique, was usually underestimated because of the presence of DOC (the particle concentration effect). The DOC fraction represents a potentially mobile pool of soil organic carbon. The partitioning to DOC suggests the likelihood for contaminants to become mobilized and/or for the soil to be remedied. Thus, the K_{DOC} value for No.0 fuel oil was determined according to the Eq.(3) (Liu and Lee, 2005):

$$K_d = K_{true}/(1 + K_{DOC} \times C_{DOC}) \tag{3}$$

where, K_{true} is the true sorption coefficient on the particulate organic matter (POM) in the absence of DOC, and C_{DOC} (mg/L) is the DOC concentration. Theoretically, it is assumed that the concentration of DOC is low relative to the percent of acetone present, and thus, the presence of cosolvent should minimize the effect of DOC on sorption. It can also be assumed that only DOC is responsible for the difference between direct and cosolvent-extrapolated sorption coefficients. The extrapolated $K_{d,w}$ value for a given soil can be considered equal to the K_{true} in Eq.(3) along with the DOC associated with that soil. The DOC concentrations of 18.01 and 29.01 mg/L were measured for supernatants obtained from PJ and CBM soils, respectively, at the M/V ratios used in the sorption isotherms. According to Eq.(3), the $\log K_{DOC}$ values were calculated to be 4.45 and 4.23 for PJ and CBM soil, respectively. Thus, the overall average $\log K_{DOC}$ was 4.34 ± 0.16. It is noted that the $\log K_{DOC}$ value was approximately 1 order of magnitude greater than the average K_{OC} value. The observed greater partitioning to DOC relative to POC reveals that the DOC phase possesses more favorable properties toward oil than POC, and that DOC has a significantly higher affinity toward oil. DOC may behave as a potentially mobile carrier of oil.

2.4 Environmental implications

The log-linear relationship between the solubility or sorption coefficients and the volumetric fraction of water-miscible solvent was successfully applied to the complex mixture of No.0 fuel oil. This suggests that the cosolvent powers of acetone for the components of oil are similar. This relationship quantitatively describes the effects of acetone, which are found in most waste streams from industrial waste, on the dissolution and sorption processes of No.0 fuel oil. The small deviation from the extrapolated average $\log K_{OC}$ (relative standard deviation, RSD = 7.53%) indicates that hydrophobic partitioning dominates the sorption of oil by soils. The estimated high average $\log K_{DOC}$ of oil demonstrates that the sorption of oil is significantly affected by the DOC and indicates a high potential for DOC-associated transport, especially, when levels are elevated. Furthermore, the extrapolation of the batch-measured adsorption characteristics of oil to field conditions should be done with caution because of the varying soil-water ratios and thus the uncertainties of DOC concentrations.

3 Conclusions

This study demonstrates that the log-linear relationship between the solubility or sorption coefficients and the volumetric fraction of water-miscible solvent is operative for oil, and thus, a reliable aqueous solubility (S_w) and $K_{d,w}$ for No.0 fuel oil from water and cosolvent/water solutions were obtained. For oil, $K_{d,mix}$ decreased log-linearly as f_c increased. This log-linear relationship is also very important in understanding the contaminant sorption and transport in the presence of water-miscible cosolvents.

Furthermore, the logarithm of the partition coefficient between the DOC and freely dissolved phases ($\log K_{DOC}$) was estimated as 4.34, indicating that DOC may behave as a potentially mobile carrier of dissolved-phase oil constituents. In addition, the sorption isotherms in aqueous and acetone/water solutions contribute to a better understanding of the effects of cosolvents on oil constituents, and indicate that sorption of oil appears to be driven by hydrophobic partitioning.

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