CHARACTERIZATION AND MODELING OF PRODUCED WATER

Joanna McFarlane, Debra T. Bostick, and Huimin Luo

Biographical Sketch of Authors

The authors are employed by UT-Battelle at Oak Ridge National Laboratory (ORNL). Joanna McFarlane is a physical chemist in the Separations and Materials Research Group, who performs physical properties measurements and develops models for thermochemical behavior in organic-aqueous systems. Debra Bostick is an analytical chemist who has extensive experience at ORNL studying environmental samples, both radioactive and non-radioactive. After completing the water-characterization work, she is now working with the Chemical and Isotopic Mass Spectroscopy group. Huimin Luo is a chemical technologist, also in the Separations and Materials Research Group at ORNL.

Abstract

Large amounts of brine are often associated with oil and gas production. Because these produced waters are in contact with the oil at high pressures, they can become contaminated with water-soluble organic compounds. Design and construction of produced water treatment facilities for new deep-water off-shore rigs are complex and expensive. There may be significant savings to the industry if water treatment is optimized to target the removal of specific chemicals or classes of chemicals of environmental concern. Hence, a collaborative project between Oak Ridge National Laboratory and industrial partners was undertaken to find which organic compounds are the most soluble in brines contacted with crude oil and to what extent. Water-soluble organic content was established by measurement of equilibrium solubilities in simulated Gulf of Mexico brine at ambient and high pressures and temperatures. Organic solubility into the brines was measured gravimetrically and by using infrared spectroscopy. The organics were also separated into their aliphatic, aromatic, and polar fractions on an open column, and were analyzed using gas chromatography. These concentrations were then compared to the properties of the produced water (pH and salinity) as well as temperature, pressure, and water-to-oil volume ratio. Data from the characterization study indicate that of the variables studied in the laboratory, pH had the largest effect on organic solubility, followed by temperature. A simple model was used to explain the observed trend with pH. The goal of the project was to provide data for a predictive model for water-soluble organic content in produced water.
(http://www.ornl.gov/divisions/nuclear_science_technology/pprf/index.htm).

1. Introduction

Soluble organics in produced water and refinery effluents are treatment problems for the petroleum industry. Production facilities and refineries have to meet regulatory discharge requirements for dissolved organics. This is expected to become more difficult as environmental regulations become stricter and production from deep-water operations increases. Deep-water crude oil has a large polar constituent, which increases the amount of dissolved hydrocarbons in produced water and refinery effluents. Neither the chemistry involved in the production of soluble organics in the petroleum industry nor the toxicity of these compounds is well understood. Several industrial companies, including Shell, ChevronTexaco, Phillips, and Statoil, developed a collaborative Petroleum and Environmental Research Forum (PERF) project to characterize and evaluate water solubles, to better understand the production of these contaminants. The ultimate goal of the project is to recommend means to reduce production of water solubles through the development of improved guidelines for effluent treatment.

Quantitative characterization data were needed as the first step in understanding the dissolution of water-soluble organic (WSO) compounds in produced water. Hence, between 1999 and 2002, Oak Ridge National Laboratory (ORNL) completed a study of the characterization of crude oils and water solubles in produced water under a variety of experimental conditions[1]. Industrial partners provided ORNL with two separate samples of crude oil from Gulf of Mexico (GOM) deep-water wells. The oil samples had been stripped of their volatile components and little produced water was directly associated with the samples. Because of this, the study focused on the solubility behavior of semi-volatile organic compounds in simulated brine solutions, which were prepared to contain the principal inorganic components normally found in the Gulf of Mexico. The contact experiments between the crude oil and the brine were carried out under equilibrium conditions, to study the effects of brine pH, salinity, temperature, pressure and crude oil source on the transfer of organic compounds from the hydrocarbon to the aqueous phase. The ranges of the physical variables were

- pH from 4.5 to 9.5,
- salinity from 45,000 to 115,000 ppm,
- temperature from 25 to 75°C,
- pressure from 1 to 60 bar, and
- water cut of 20, 50 and 80%.

The analytical methods employed in this project primarily followed those established by the US Environmental Protection Agency (EPA)[2]. Since these procedures are also used to monitor the treatment of produced water discharged into the Gulf of Mexico, one of the goals of the project was to determine whether the recommended EPA procedures gave an accurate measurement of the oil and grease, as regulated by National Pollution Discharge Elimination System (NPDES) permits.

2. Experimental Procedure

Oil samples were shipped from two separate Gulf of Mexico drilling sites in 5-gal barrels. Treatment prior to arriving at the laboratory included degassing and removal of produced water. At ORNL, the crude oil was homogenized on a barrel roller, at 8 rpm for at least 2 h, prior to being sampled. Oil samples were withdrawn using submerged tubing attached to a peristaltic pump to eliminate the entrainment of air bubbles. Oil densities were measured as 0.84 and 0.87 $g \cdot mL^{-1}$ for the two samples respectively.

2.1. Characterization of Crude Oil Samples

The crude oil was sampled for water content. A separate aqueous phase could not be removed directly from any of the barrels, and an aqueous phase was not apparent in samples removed from the barrels even after centrifugation (2000 rpm for 20 min). Hence, water content was measured by Karl Fischer titration, using a Brinkman Model 625 KF-Coulometer. The anodic and cathodic compartments were filled with AQUASTAR®

Coulomat A and C (EM Science) respectively. Sample sizes were 10-50 mg oil diluted (1:25) in CH_2Cl_2. The titrator was calibrated with diluted aliquots of 1 mg·mL^{-1} Hydranal® Water Standard (Allied Signal).

The identities of individual semi-volatile organic compounds were determined in the as-received crude oil and prepared produced water samples using standard EPA Method 8270C[a,3], which mandates the use of gas chromatography-mass spectroscopy (GC-MS) to identify a target group of more than 45 semi-volatile organic compounds in environmental samples. The crude oil and produced water samples were analyzed off-site by Mountain States Analytical Inc.[b] for 120 semi-volatile compounds of interest to the petroleum industry. Details of the GC-MS analysis are shown in Table 1.

Table 1. GC–MS conditions for Semi-Volatile Organic Analysis

Instrumentation:	Hewlett Packard (HP) 6890 plus Gas Chromatograph with a 5973 MSD
GC column:	30 m X 0.25 mm (or 0.32 mm) ID 1-µm-film-thickness silicone-coated fused-silica capillary column
Software:	HP MSD ChemStation with EnviroQuant
Ion source:	Electron impact ionization at 70 eV, Temperature 230°C
Carrier gas	Helium, 30 cm/s, 16 psig
Inlet:	Pulsed splitless, 270°C
Oven program:	Initial 50°C (4 min), 50 to 350°C (10°·min^{-1}), hold until dibenz(a,e)pyrene elutes
Sample volume:	1 µL
Sample preparation	*Neat oil*: diluted 1:25 in CH_2Cl_2. *Produced water*: acidified to pH2. 3x30 ml contacts with CH_2Cl_2 in separatory funnel. Dried with Na_2SO_4. Concentrated to 1 ml.

2.2. Crude Oil-Water Contacts

A simulated brine based on actual Gulf-of-Mexico concentrations (private communication: D. Bourg, Phillips Co., May 9, 2000) was prepared by dissolving salts weighed using Mettler balances (AE-260 and PC4400) in distilled-deionized water, according to the recipe given in Table 2. Acid (HCl) or base (NaOH) was added for pH adjustment. Salinity, or chloride ion concentration, was measured with an Orion Model 94-17B chloride-selective electrode coupled with an Orion Model 90-02 Double-Junction reference electrode to an Orion 520A pH/ISE meter. The response was calibrated with NaCl standards (100 to 3000 ppm Cl^-). An ionic-strength adjuster solution of 5 M $NaNO_3$ was added to both the standards and the brines prior to analysis.

Carbonate (CO_3^{2-})/bicarbonate (HCO_3^-) and pH were recorded using a Metrohm DMS 716 Titrino automatic tritrator, calibrated with three NIST-traceable buffer solutions (pH4, pH7 and pH10). The OH^-, CO_3^{2-}, and HCO_3^- were determined by titrating 20 mL of produced water with a standard 0.01 *N* HCl solution to endpoints at pH 8.3 and pH 3.7.

Table 2. Target Amounts of Salts Dissolved in Preparation of 4 L of Simulated Brine

Salt – Mass(g)	Salt – Mass(g)	Salt – Mass(g)	Salt – Mass(g)
NaCl – 350	$MgCl_2·6H_2O$ – 30	$SrCl_2·6H_2O$ – 1.6	$NaHCO_3$ – 1.2
$CaCl_2·2H_2O$ – 48	$BaCl_2·2H_2O$ – 0.7	$Na_3PO_4·12H_2O$ – 0.02	$FeSO_4·7H_2O$ – 0[c]

[a] Also USEPA method 525.5.
[b] 1645 West 2200 South, Alt Lake City, Utah, 84119.
[c] Although ferrous ion was originally included in the recipe, it was found to precipitate at pH~7; necessitating a removal by filtration.

Simulated produced water samples were prepared under ambient pressure conditions using a 5-L-volume Water Accumulated Fraction vessel, fabricated according to dimensions given in ASTM D6081[4]. The brine was added to the vessel (up to 3 L) followed by the crude oil (up to 4 L), with care taken to minimize turbulence. The baseline water-to-oil volume ratio was 80% (1200 mL oil – 300 mL water), although 20 and 50% ratios were also used. The contact time was approximately 4 d, long enough to establish equilibrium, during which time the mixture was stirred slowly to minimize fragmentation of the oil layer. Water was collected after contact through a stopcock at the base of the vessel to prevent contamination with oil, and stored at 4°C for analysis. Because of the buffering capacity of the crude oil, tests at elevated pH sometimes required additions of small amounts of concentrated NaOH aqueous solution during the first couple of days of the contact.

A pressure vessel with two armored sight glasses on opposing walls was used for tests at elevated pressures. The mild-steel vessel had an internal volume of 300 mL, and could be operated up to 70 bar and 50°C. The vessel was equipped with an 83-bar-pressure relief valve (PresSure Product Co. Inc.), and was instrumented for pressure and temperature (Type-T thermocouple) measurements. The vessel was filled with 200 mL of brine and 46 to 73 mL oil. The vessel was clamped onto a Ro-Tap Model B Seive Shaker (C.M. Tyler Co.) and was rotated horizontally at 60 rpm during the contact. Pressure tests were performed at 50°C; the temperature was maintained with heating tape and insulation wrapped around the exterior of the vessel. A valve in the headspace allowed pressurization with helium (to 14, 35, and 60 bar), and venting of the chamber into a Hoke® sample chamber after the contact was complete. The aqueous phase was sampled through a valve on the bottom of the vessel after venting of the gas phase. Contact times were approximately 4 d.

After contact, the produced water was analyzed for pH, carbonate/bicarbonate content, salinity (chloride ion concentration), and low-molecular weight organic acids. Organic acids were determined by injecting produced water directly into a Dionex LC20 ion chromatograph fitted with a Dionex IonPac ICE-AS6 separation column. Elution was carried out using 0.4 *m*M heptafluorobutyric acid. The instrument was calibrated with solutions of formic, acetic, propionic, malonic and oxalic acids (10-50 ppm), and had a sensitivity of 1 ppm.

The key analyses of the produced water were the measurements of aliphatic, aromatic and polar content in the gas (C_6–C_{10}), diesel (C_{10}–C_{20}), and oil (C_{20}–C_{28}) carbon ranges. To analyze for total petroleum hydrocarbon components (TPH)[d], one liter of the produced water was acidified with HCl to pH 2. The hydrocarbons were extracted with 3x30 mL CH_2Cl_2. The volume was reduced to 2 mL in Kuderna-Danish glassware (55 to 65°C), followed by a solvent exchange into hexanes (under a light flow of N_2 at 35°C to minimize analyte losses through evaporation). The hexane extract was refrigerated overnight before further analysis for separation of asphaltenes. Open-column liquid chromatography was used to separate the aliphatic, aromatic, and polar water-soluble organic components contained in the extract using a procedure developed by Mills et al. (1999)[5]. The solvent exchange to hexanes was required so that the liquid chromatographic separation would begin with a non-polar matrix, and subsequent washes would become progressively more polar. Mills' procedure was modified to remove the polar constituents from the column with a final methanol wash. Gas chromatographic-flame ionization detection (GC-FID), USEPA SW-846 Method 8015B[6], was used to analyze the separated aliphatic, aromatic and polar fractions for carbon chain length. In addition, 100 µL of each fraction was dried on a tared glass-fiber filter for a gravimetric analysis[7]. The results from gravimetric analyses and liquid chromatography GC-FID were compared to infrared spectroscopic analyses of oil-and-grease components extracted from the produced water using C_2Cl_4 (US EPA Method 418.1[8]).

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[d] The terminology used in this paper follows that of USEPA regulatory nomenclature. The stated carbon ranges (C_6–C_{10}, C_{10}–C_{20}, C_{20}–C_{28}) refer to sample components eluting from a gas chromatograph between n-alkane standards in these carbon size ranges. The terminology does not define the identity of the sample component, merely that it has a volatility within the given saturated alkane range. TPH is also regulatory nomenclature, referring to all components extracted using either USEPA SW-846 Method 8015B (GC analysis) or USEPA SW-846 Method 1664 (gravimetric analysis).

A synopsis of the overall procedure is given as a flowsheet in Figure 1, and details of the GC-FID analysis are presented in Table 3.

Table 3. GC/FID Conditions for Total Petroleum Hydrocarbon Analysis

Instrumentation:	HP 5890 Series II Gas Chromatograph with an FID
GC column:	30 m X 0.53 mm ID fused silica capillary column bonded with 5% methyl silicone (HP-5), 0.88–µm film thickness
Software:	HP ChemStation version 3365 Series II, manual baseline subtraction
Gas flow rates (carrier, makeup, FID)	Helium 4 $mL \cdot min^{-1}$, Helium, 26 $mL \cdot min^{-1}$, Hydrogen 30 $mL \cdot min^{-1}$, Air 375 $mL \cdot min^{-1}$
Temperatures	Injector - 200°C, FID - 340°C
Oven program	Initial 45°C (hold 3 min), 45°C to 275°C at 12°C/min, Final 275°C (hold 12 min)
Sample volume	0.5–3 µL
Surrogate recovery standards (40 µg each)	(*added before extraction with CH_2Cl_2*) *n*-hexanoic acid, *n*-dodecane-*d*26, naphthalene-*d*8, *n*-phenol-*d*6 or tribromophenol
Calibration	6 point (linear from 0.2 to 1.4 $mg \cdot L^{-1}$), Calibration standards from dilutions of certified 2000 $\mu g \cdot mL^{-1}$ n-alkane C_6-C_{28} standard (Absolute Standards, cat. 90814, lot 030700)

3. Characterization Results

Because of space limitations, detailed results cannot be presented in this paper, but have been reported by Bostick and coworkers (2002). Hence, this section will present results with calculated uncertainties, rather than raw data. The focus will be on those findings that highlight an aspect of the work that merits further consideration for continued produced water characterization, model development, or advancements in produced water clean-up methodology.

3.1. Crude oil

One of the objectives of these experiments was to compare various methods of analysis of crude oil and produced water. The results of the analysis of crude oil by Mountain States Analytical and at ORNL are shown in Table 4. The samples analyzed by Mountain States Analytical were from one crude oil grab sample split 2 ways. The ORNL data shown in the table were taken from crude oil samples from two separate wells, the first sampled 5 times over a period of months, and the second sampled twice. The GC analysis done at ORNL also included a separate determination of the total extractable material in the CH_2Cl_2 fraction and in the hexanes fraction. An average was not calculated where there were only two replicates of the same test.

The relative amounts of the various carbon chain lengths were approximately equal, as measured in the off-site analysis. The ORNL results indicated that the crudes contained proportionately more of the lighter hydrocarbons than C_{20}-C_{28}. This finding may be indicative of biases introduced by the open column separation and GC analysis, as will be discussed later. Sampling method may have also played a role, but that is less likely because the same phenomenon was observed for both types of crude oil.

The principal semi-volatile compounds of environmental concern in the deep-well oil were acetophenone and methylnapthalene, but these comprised only 0.1% of the total mass. This procedure was not replicated in house.

The table also shows the relative amounts of aliphatic, aromatic, and polar compounds by GC-FID for both crude oils, an average of 3 extractions for crude#1 and an average of 2 for crude#2. Visually, the aromatic fraction was lightly yellow on the open column, and the polar fraction was a reddish-brown. Both crude oil samples had a significant polar component, although less than the aliphatic and aromatic hydrocarbon fractions.

Table 4. Comparison of Analytical Methods Used in the Characterization of Deep-Well Crude

Analytical Method	Mountain States		ORNL			
	US EPA SW-846 8015B Carbon analysis in total extractable material ($g \cdot kg^{-1}$) of crude oil#1		Open liquid column followed by GC analysis ($g \cdot kg^{-1}$) of total extractable material			
			Crude oil#1		Crude oil#2	
C_6-C_{10}	179, 179 (36.5%)		107 ± 24 (53%)		46, 61 (64%)	
C_{10}-C_{20}	122, 124 (25.1%)		83 ± 20 (41%)		4, 47 (31%)	
C_{20}-C_{28}	192, 186 (38.5%)		12 ± 7 (6%)		7, 1 (5%)	
Total ΣC_6-C_{28}	493, 489		202 ± 51		57, 109	
	US EPA SW-846 8270C Analysis for specific compounds ($g \cdot kg^{-1}$)		Total Extractable Material ($g \cdot kg^{-1}$)			
			CH_2Cl_2	Hexanes	CH_2Cl_2	Hexanes
Acetophenone	0.60	0.58	201 ± 40	126 ± 35	83 ± 26	64 ± 1
Methylnapthalene	0.40	0.43				
			Aliphatic	67± 8%	Aliphatic	26, 40.6%
			Aromatic	18±11%	Aromatic	57, 45.7%
			Polar	15± 3%	Polar	17, 13.7%

3.2. Produced water

The total petroleum hydrocarbon contents of produced water samples, measured by gas chromatography and infrared spectroscopy are given in Table 5. Unless otherwise noted in the table, contacts took place under reference conditions: 4 d contact time, salinity of 65,000 $mg \cdot L^{-1}$, pH 7, water cut of 80%, 25°C, and at ambient pressure. Typical levels of total extractable material were about 4 to 83 $mg \cdot L^{-1}$. The open liquid chromatography/GC-FID analysis indicated that water-soluble organic compounds found in the simulated produced water samples were distributed differently for the two types of crude oil. Water solubles from crude#1 were primarily polar (96±3%), with small aliphatic (1±1%) and aromatic (1±1%) components. Water solubles from crude#2 were more evenly distributed between aromatic (50±20%) and polar (40±20%) compounds, and again had a smaller aliphatic (5±2%) component. The WSO from both crude samples were mainly distributed between the low and midrange carbon ranges. Some of the polar fraction are organic acids, as formic, acetic, and propionic acids were found in the produced water by ion chromatography, occurring at concentrations of up to 50 $mg \cdot L^{-1}$. Higher molecular-weight acids were not observed by ion chromatography. Individual components determined by GC-MS were 1-methylnapthalene (10 $\mu g \cdot L^{-1}$), 2-methylnapthalene (9 $\mu g\ L^{-1}$), naphthalene (14 $\mu g \cdot L^{-1}$) and phenol (30 $\mu g \cdot L^{-1}$), which together comprised only a small amount of the total water-soluble component.

3.3. Dependence of organic solubility on physical conditions

The water-soluble organic content of produced water was quantified as a function of several experimental parameters. The Gulf-of-Mexico simulant was contacted with as-received crude oil to study the effects of water cut, produced-water pH and salinity, pressure, temperature, and crude oil source on the type of water-soluble organic content in produced water.

Of the six tested parameters, the factor that most controlled the total WSO in produced water was that of aqueous phase pH. Data presented in Figure 2 are from the gravimetric analyses of contacts with crude#2. Results presented in Figure 7 are from the GC-FID analysis of contacts with crude#1 at different brine pH. Thermodynamic calculations of the brine-hydrocarbon equilibrium, discussed later, are also presented on the graph.

Table 5. Total Petroleum Hydrocarbon Content of Simulated Produced Water

	LC/GC-FID ($mg \cdot L^{-1}$)[e]	IR ($mg \cdot L^{-1}$)[f]	Gravimetric ($mg \cdot L^{-1}$)[g]	Notes
Reference conditions	25, 17, 21	10, 11	18, 23, 17	Crude oil sample#1
Temperature Studies	22	18	35	47.2°C
	25	23	46	74.5°C
Water Cut	30		19	20%
	24		14	50%
	12		27	66.7%
	24		14	50%, pH 8.7
Salinity	12	50	19	40 $g \cdot L^{-1}$ Cl^-
	14	12	16	144 $g \cdot L^{-1}$ Cl^-
Pressure	4		32	1 bar
	48		83	14 bar
	6		39	35 bar
	4		29	60 bar
pH crude oil#1	12		29	4.73
	12	9	16	5.98
	29		29	9.03
	24		14	9.50
Reference conditions	6		35	Crude oil sample #2 pH 7.04
pH crude oil#2	11		48	8.50
	4		68	9.50

The effects of water cut, pressure, temperature, and salinity are given in Figures 3 through 6. These results were all taken from tests with crude#1, and unless specifically referenced as the dependent variable on the graph, the physical conditions for the contact tests were carried out under reference conditions (Section 3.2). Figure 3 summarizes the trends in gravimetric data for changing water cut or water-to-(oil+water) volume ratio. There was no apparent change in overall water-soluble organic content in CH_2Cl_2 and hexane fractions as the water cut increased. Figure 4 shows the effect of applied helium pressure on the relative concentrations of C_6-C_{10}, C_{10}-C_{20} and C_{20}-C_{28}. Although the data is scattered, higher pressures appeared to enhance the water-soluble organic content by increasing the relative quantity of dissolved material in the C_6–C_{10} range. A large change was not expected; however, because the organics that were investigated have low vapor pressures. Temperature data are plotted in the form of a Van't Hoff plot, or the logarithm of concentration as a function of reciprocal temperature, to illustrate the apparent heat of solution (Figure 5). Temperature primarily altered the relative ratio of soluble organic carbon ranges within the overall envelope, without significantly elevating the total water-soluble organic content in the brines. The decrease in C_6-C_{10} solubility with temperature may be attributed to losses through volatility. Salinity appeared to have no effect on the chemical character or the carbon size of water-soluble organics in produced water. For example, results derived from the ion chromatographic analyses of organic acids are presented in Figure 6. Finally, the concentrations of water-soluble organics derived from crude#1 and crude#2 were not substantially different, as can be seen by comparing rows in Table 5 above. However, the distribution of WSO into the various classes was markedly different, the WSO being almost exclusively polar for contacts with crude#1, and being split between aromatic and polar in the case of contacts with crude#2.

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[e] Modified US EPA Method SW-846 8015B
[f] US EPA Method 418.1
[g] US EPA Method 1664

In summary, water characterization data were collected from contact experiments with crude oil taken from two separate wells in the Gulf of Mexico. Results indicated that of the brine properties tested, pH had the most influence on organic solubility in the brine. The effects of temperature and pressure were small, and scatter in the data precludes their use in the development of a quantitative model. Uncertainty in the measurements is discussed in the next section.

4. Discussion

4.1. Uncertainty in environmental data.

Uncertainties in the measured variables are presented in Table 6, along with a brief description of how they were derived. The uncertainty in some of the data, particularly those involving a number of steps in the analysis, is as high as ±60%. Because the collection of these same data sets required a substantial effort, the uncertainties were not reduced by replicate analyses. The overall result is that trends in the data are hidden by the noise for the most part, with the exception of the pH dependence. It is suggested in the future that a large number of replicate tests be performed rather than a few detailed analyses, focusing on a particular aspect of the problem. For example, measuring the total petroleum hydrocarbon fraction by gravimetric analysis is a reasonably simple experiment. Many replicate measurements of TPH under various conditions would provide lower uncertainty values in the data set. This will assist in the evaluation of a model for water-soluble organic contamination of produced water under a range of conditions.

Table 6. Results of Uncertainty Analysis in Water Characterization Experiments

Variables	Measurement Method	Uncertainty	Explanation of Estimate
Temperature	Type T thermocouple	±1°C or 0.75%	Manufacturer supplied
Pressure	US Gauge	± 25 psi	Manufacturer supplied
PH	Orion 520A meter	± 0.01	Daily phosphate buffer calibration
Salinity	Orion 520A meter	± 10%	Calibration with standard solutions
CO_3^{2-}, HCO_3^- concentration	DMS Titrino (model 716)	± 5 ppm pH<9	HCl tritrated with NaOH standard solution. Daily phosphate buffer
Water cut	Volumetric + gravimetric	± 0.01	Propagation of uncertainties
Densities	Volumetric + gravimetric	±0.03 $g \cdot mL^{-1}$	Repeated measurements
Water content	Brinkman 625F Coulometer	± 5μg up to 1000 μg ± 0.5% above 1000 μg	Hydranal standard calibration
Total petroleum hydrocarbon	Gravimetric analysis on CH_2Cl_2 extracted sample	±20% crude sample 1 ± 4% crude sample 2	Repeated measurements
Organic fractionation and GC analysis	Open liquid column HP GC	±40% oil components ±60% water-soluble organics	Repeated measurements
Organic acids	Ion chromatography	±1 ppm formic/propionic acids ±4 ppm acetic	Repeated measurements

4.2. Comparison of different analytical methodologies.

Many different methodologies have been used to characterize organic content in produced water: the analysis of individual hydrocarbons (US EPA method SW-846 8270C), the analysis of total hydrocarbon content (US EPA method SW-846 8015B), and the characterization based on chemical classes and carbon-chain length. One of the goals of this project was to compare these methods, at least with the limited number of samples described here.

From the results of the off-site analysis of crude oil and produced water, it appears as if the US EPA SW-846 8207C method has limited usefulness in assessing the amount and constituents of the water-soluble organic fraction in produced water, because so few of the 120 compounds searched for were actually found in the analysis. The use of this method is in assessing the toxicity of a particular compound in the environment, rather than a survey of the overall oil and grease load of the water.

Because the EPA 8207C method failed to identify most of organic character of the oil, an open liquid column protocol was used to separate the oil into aliphatic, aromatic, and polar constituents. Table 7 shows results of the total extractable material analyzed at ORNL for both deep-well crude oil samples. The results indicate that there is a ~10% loss in material during the solvent exchange from CH_2Cl_2 to hexanes, mainly lighter organics in the C_6-C_{10} range. The greatest loss; however, occurs during GC analysis[h]. From the data presented in section 3 and Table 4, it is apparent that the proportionately greatest loss occurred for the longest carbon chain length molecules, C_{20}-C_{28}. Higher temperatures were needed to elute these molecules through the GC, which led to a reduced response because of column bleeding and sample decomposition. In addition, losses certainly occurred in the liquid column separation and solvent concentration steps. Larger molecules, particularly if polar, may not have passed as efficiently through the liquid column as the smaller molecules, as evidenced by colored material remaining on the column even after washing with methanol. The difference between the mass of water solubles by gravimetric analysis and by GC analysis is presented as the calculated "asphaltenes" fraction in the table. An attempt was made to measure the asphaltene fraction directly in the oil by refrigerating the hexane fraction and precipitating the asphaltenes, but the results were not reliable because of their huge spread.

The utility of the chemical classification method was demonstrated by this investigation, as it showed that most of the material soluble in the aqueous phase was polar with little aliphatic and aromatic content. In addition, GC-FID was more sensitive than gravimetric analysis, the latter limited to 12 ppm by the resolution of the balance. Total petroleum hydrocarbon results from GC-FID appeared to be comparable to results from IR analysis. Because of the number of steps involved in the open column procedure; however, there appeared to be a substantial loss in analyte. There was an apparent selectivity against long-chain constituents, and the number of steps increased the uncertainty in the results, making the data less useful for model development.

Table 7. Results from Total Petroleum Hydrocarbon Analyses of Crude Oil Samples

Method/solvent	Crude#1 ($g \cdot kg^{-1}$)	Crude#2 ($g \cdot kg^{-1}$)
Gravimetric/CH_2Cl_2	615±119	566±25
Gravimetric/hexanes	533±16	532±80
GC/CH_2Cl_2	201±40	83±26
GC/hexanes	126±35	64.2±0.9
Asphaltenes/CH_2Cl_2	414±159	483±50
Asphaltenes/hexanes	407±51	468±81
Asphaltenes – measured	700±800[i]	Not detected

[h] Fractional recoveries of surrogate standards: n-hexanoic acid (0.005-0.05), n-dodecane-d26 (0.03-0.2), naphthalene-d8 (0.1-0.3 in aromatic fraction, 0.03-0.2 in polar fraction), n-phenol-d6 (0-0.3), tribromophenol (0.4-0.7).

[i] Average of 3 for crude#1. Residue not detected in 2 of the refrigerated hexane samples of crude#1, or any of the samples of crude#2.

4.3. Approach to modeling

Aqueous-hydrocarbon systems can be modeled in a variety of ways. This has been done here using a thermodynamic liquid-liquid equilibrium model[9], with the solubility predicted by NRTL activity coefficients in the aqueous and hydrocarbon phases. The model was successfully used to fit the pH-dependence data that were generated in a crude-oil/simulated brine system, presented in Figure 7. This model incorporated the acidity of the polar components[10], in this case assuming a composite pKa of 5.5. As can be seen in Figure 7, the methylene-chloride extractable material (particularly in the C_{10}–C_{20} range) became more soluble as the brine became basic, pH>7, as shown by the apparent inflection point in the data at ~pH7.

The advantage of a thermodynamic equilibrium model is that physical variables, such as temperature and salinity, can be incorporated into the expressions for the activity coefficients[11]. Volatile components and the dependence of solubility on pressure can be introduced with an additional gaseous phase, described by an equation of state. The difficulty of formulating the model is in the selection of which components will represent the system. The uncertainties in the data generated in this project preclude their use for lumped parameter properties. Although the data reported here give clues to the identity of the polar components, a direct analysis of actual produced water for phenols, thiols, nitrogen-containing compounds, and substituted carboxylic acids would be very helpful in formulating a model that correctly represents an actual crude-brine chemical system.

Other questions raised by thermodynamic modeling are how well binary and ternary parameters represent a multi-component system, especially one that is non-ideal. In addition, cross-correlations – such as between salinity and pH – were not investigated in this characterization project. Answers to such questions, as well as the investigation of correlations of solubility measurements to field parameters, should be addressed in future model development.

4.4. Impact on water-soluble mitigation methodology

The ORNL analysis of produced water, generated by contacting shipped oil samples with simulated Gulf-of-Mexico brine, probably reflects a negative bias because the oil had already been contacted with injection water at the well, thus stripping some of the water-soluble organic compounds. Analysis of actual produced water would allow an estimate of the amount of stripping.

In summary, the work at ORNL has shown that polar organic compounds are highly soluble in produced water in comparison with aliphatic oil and grease hydrocarbons. Polar organic compounds are also extracted in the EPA procedures, and so are included in the oil and grease fraction of the measured total petroleum hydrocarbon content. A large component of the polar fraction, the organic acids; however, is not efficiently extracted by CH_2Cl_2 (less than 5%), and even less is transferred to hexanes because of volatilization (less than 1%). It is possible that standard analytical methods will introduce a positive bias into the measured total petroleum hydrocarbon values, used to administer NPDES permits for oil drilling and operation, but this will depend on the chemical nature of the polar component. This complicated situation suggests that modeling of the extraction process used for sampling key organic constituents is required to bring about improved methodologies for total petroleum hydrocarbon measurements.

5. Conclusions

Simulated produced water in contact with actual Gulf-of-Mexico crude oil was characterized using a variety of analytical techniques. Open-column liquid chromatography was used to separate the water-soluble organic component into aliphatic, aromatic and polar fractions. Even though the polar component comprised less than 20% of the crude oil, after partitioning into the aqueous phase the polar component was 99% and 40% respectively for the two oil samples analyzed. It appears unlikely that the open-column fractionation method can

be used for regulatory purposes; however, because of losses during analysis leading to a large uncertainty in the concentration data.

Of all of the variables tested in the laboratory, only one showed a significant effect on organic solubility in the brine. The trend of an increase in solubility with increasing pH was reproduced with a model of two-phase liquid-liquid thermodynamic equilibrium. Being able to fit laboratory data is the first step in demonstrating our ability to understand the solubility of contaminants in produced water. This knowledge will lead to the development of a predictive model for use in new oil fields or changing environmental conditions, and ultimately will assist the petroleum industry target produced water cleanup to best protect the environment.

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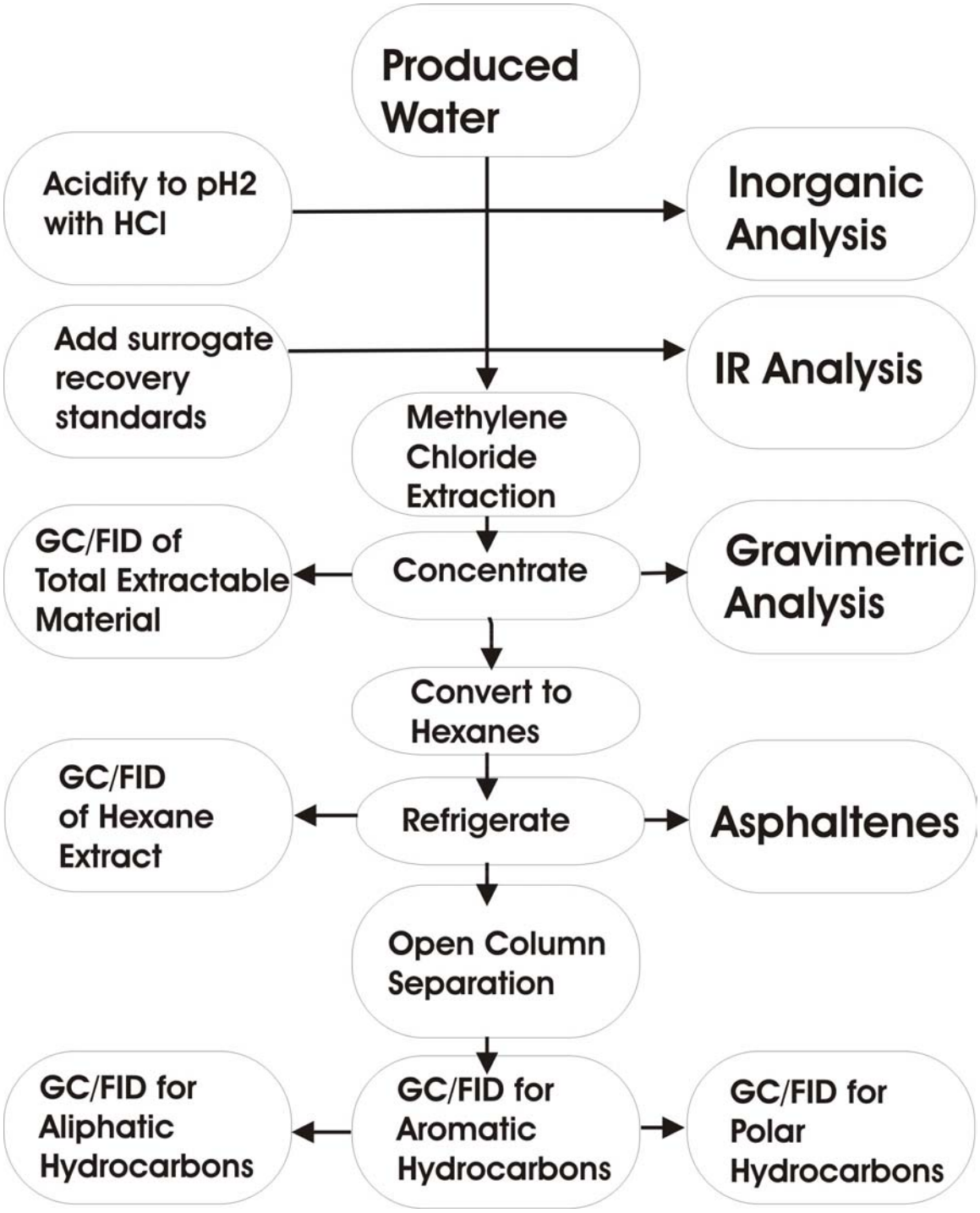

Figure 1: Flowsheet for analysis of produced water. Total petroleum hydrocarbons (TPH) include aliphatic, aromatic and polar fractions.

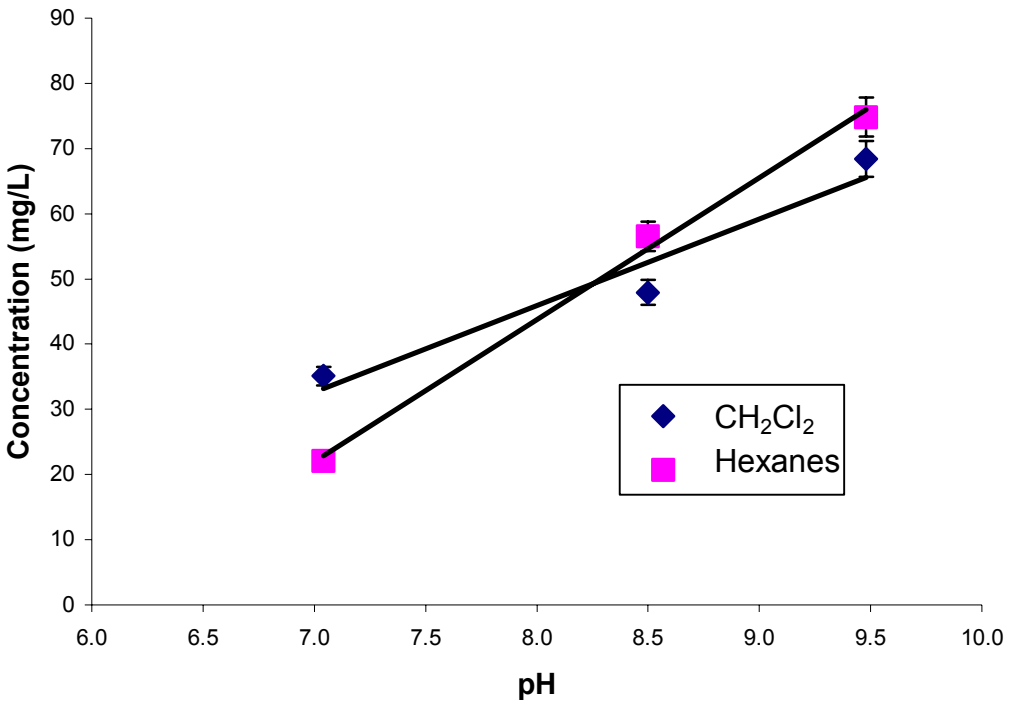

Figure 2. Dependence of concentration on pH, as determined gravimetrically for crude #2.

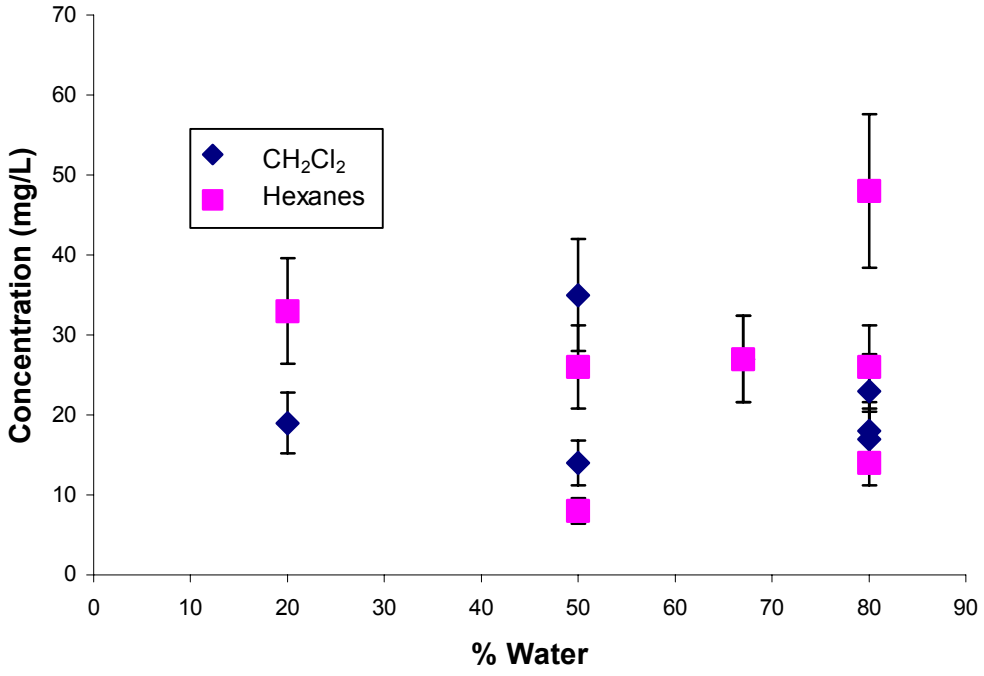

Figure 3. Dependence of concentration on water cut, as determined gravimetrically for crude #1.

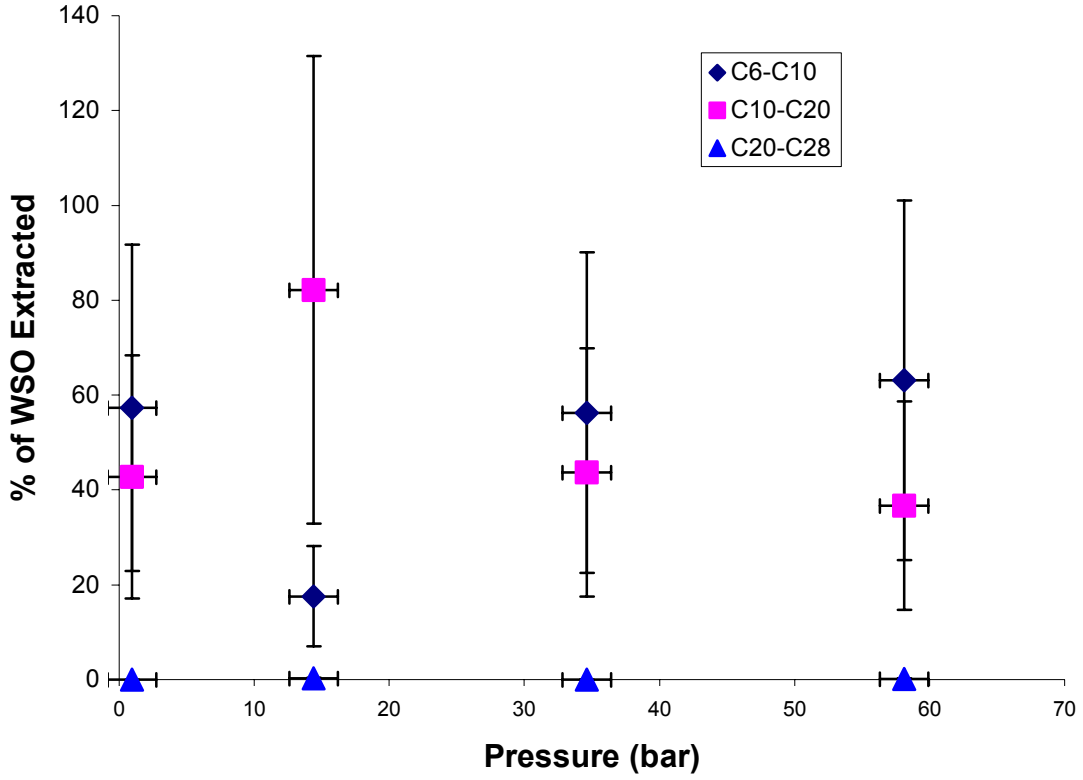

Figure 4. Relative carbon chain length concentration versus pressure, determined by GC.

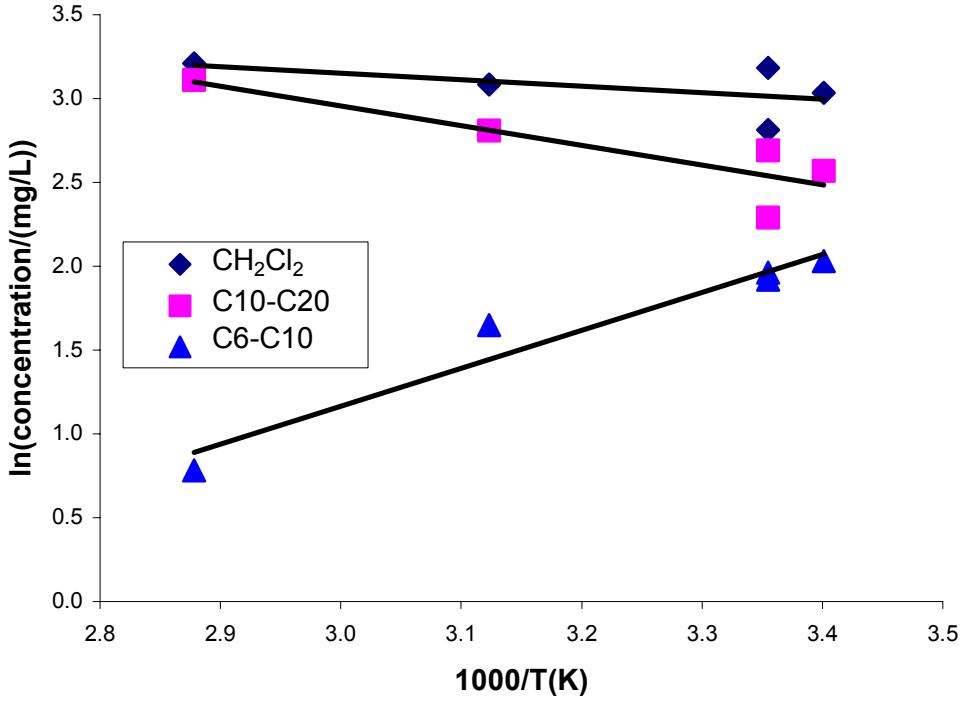

Figure 5. ln concentration versus reciprocal temperature, determined by GC on crude #1.

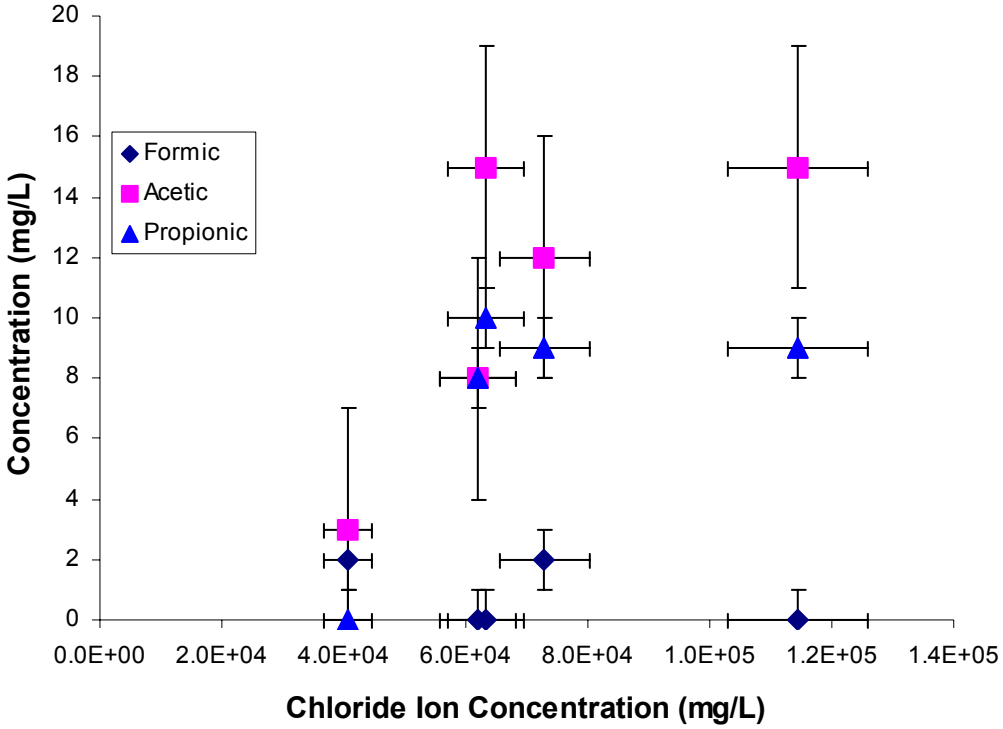

Figure 6: Variation of acid concentration with salinity, determined by ion chromatography.

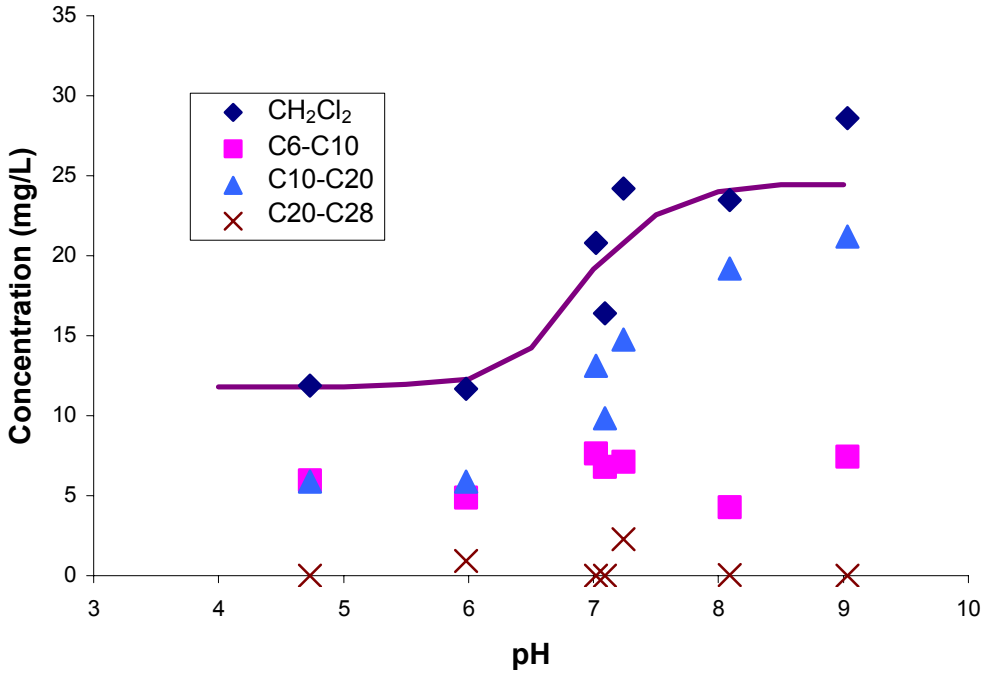

Figure 7: Plot of water-soluble organic concentration for different carbon sizes as a function of pH. Superimposed on the plot are results of liquid-liquid equilibrium calculations with pKa=5.5, salinity=65,000 $mg \cdot L^{-1}$.