

Characterization and Modeling of Produced Water Contacted with Gulf of Mexico Crude Oil

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**Ground Water Protection Council
Produced Water Conference
Colorado Springs - Oct. 16, 2002**

Specific Concerns for Off-Shore Production

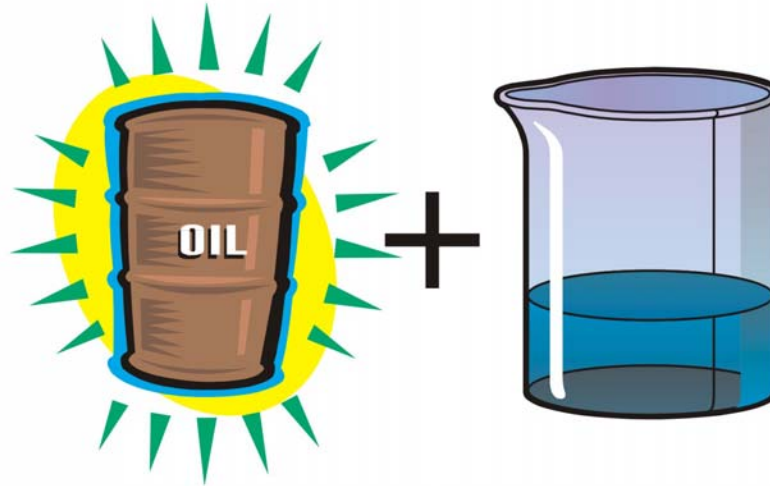
- **New wells – WSO not well known**
- **Relatively high content of polar molecules**
- **Difficulty of off-shore testing and remediation**
- **Strict limits imposed by NPDES for discharge into the ocean**
- **Want to be able to predict WSO concentrations**

Objectives

- **Differentiate water soluble organics by chemical classification and size**
- **Measure effect of physical conditions on solubility**
- **Evaluate different methods of analysis for water soluble organics**
- **Determine lumped parameter properties for chemical thermodynamic model**

Gulf of Mexico
Crude Oil

Sample Preparation

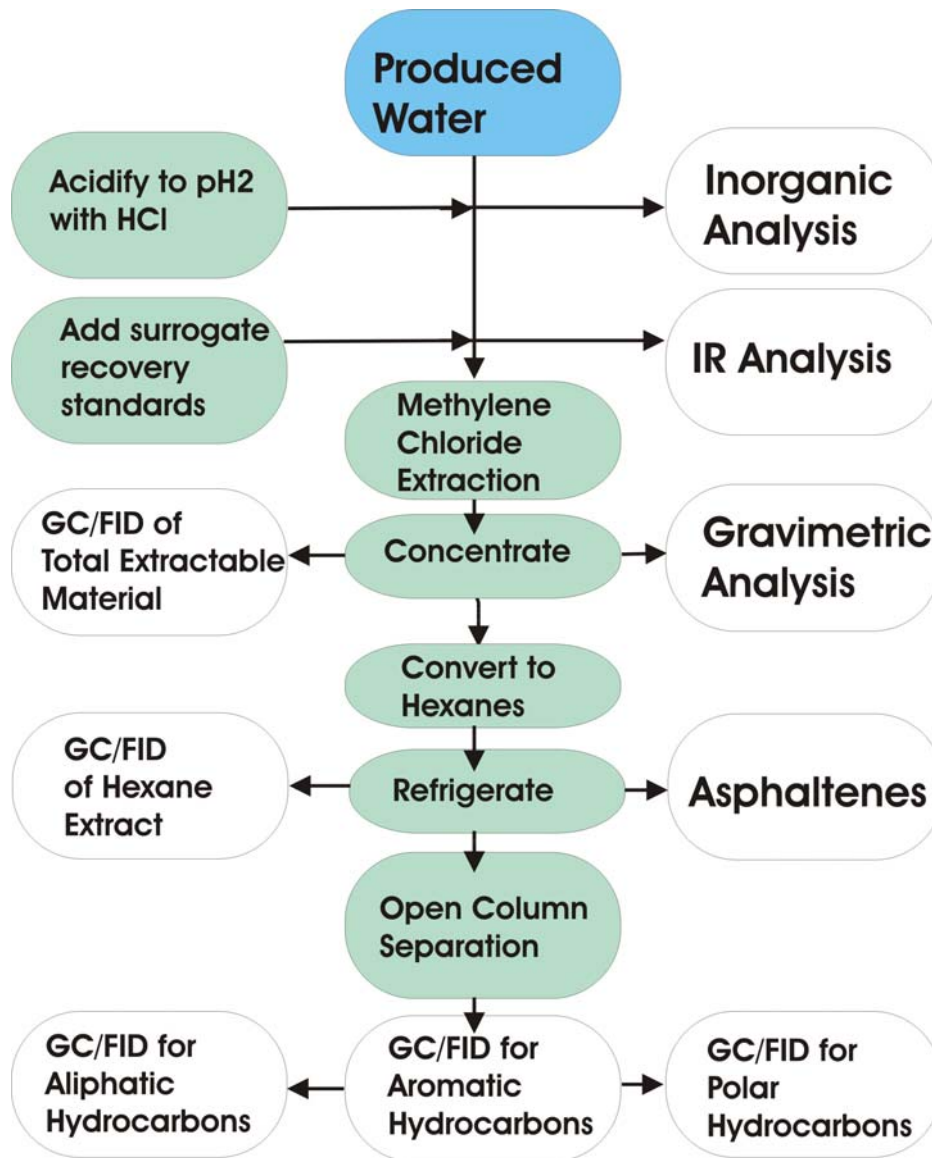


Simulated
Gulf of Mexico
Brine

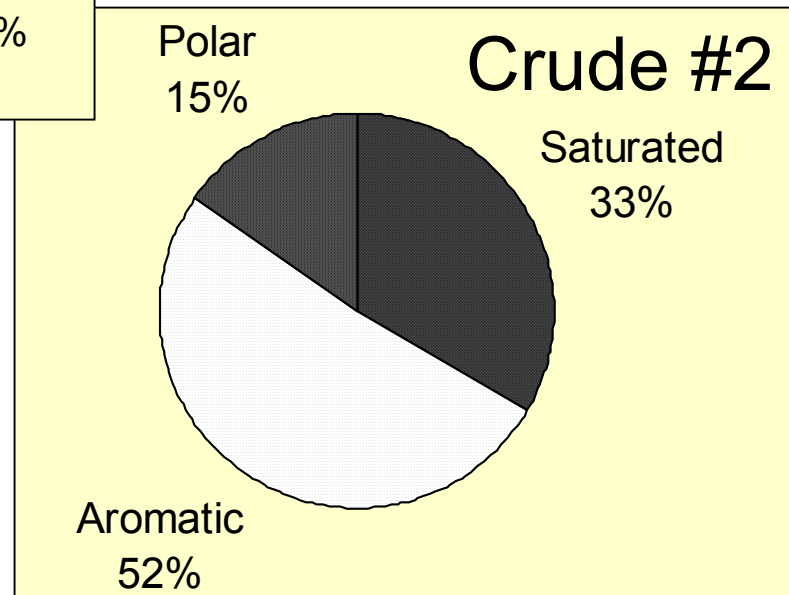
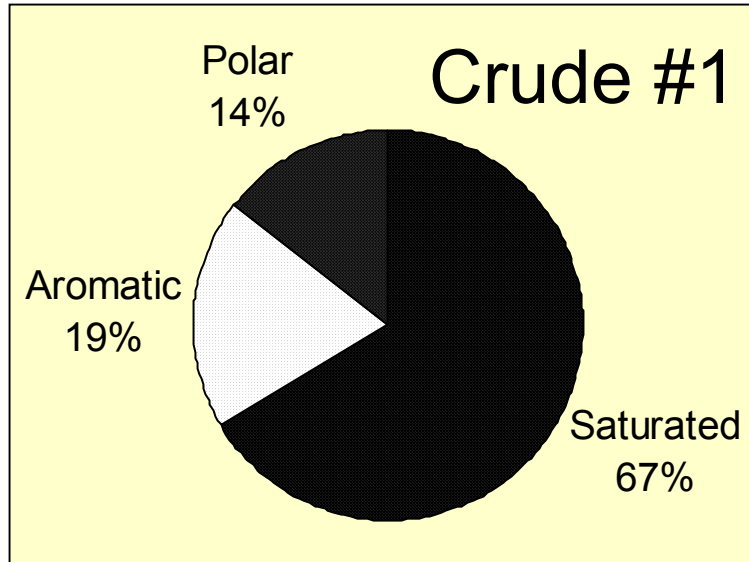
Test Conditions:
4 day contact time
pH (4.5 to 9.5)
Pressure (1 to 60 bar)
Temperature (25 to 75°C)
Salinity (45 to 115 ppt)
Water Cut (20 to 80%)



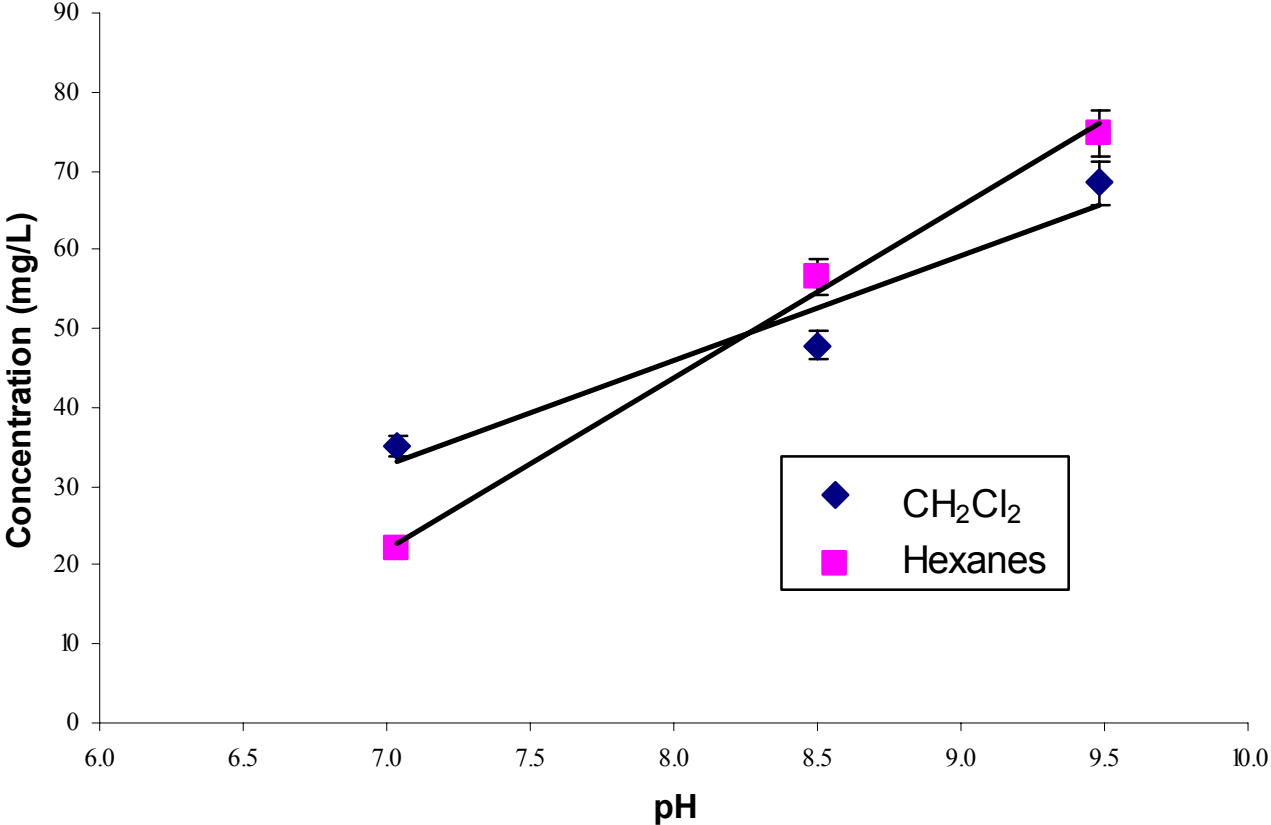
Flowsheet for Analysis of Produced Water



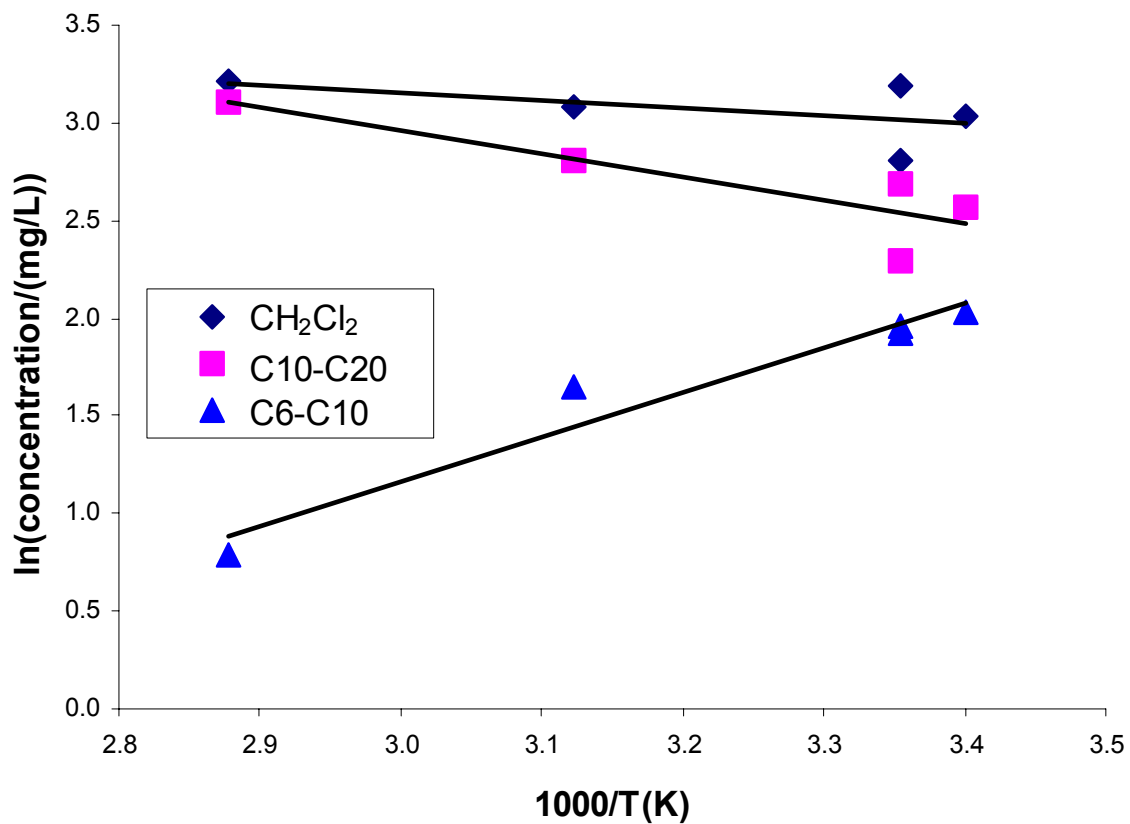
Percentages of Components in Crude Oil



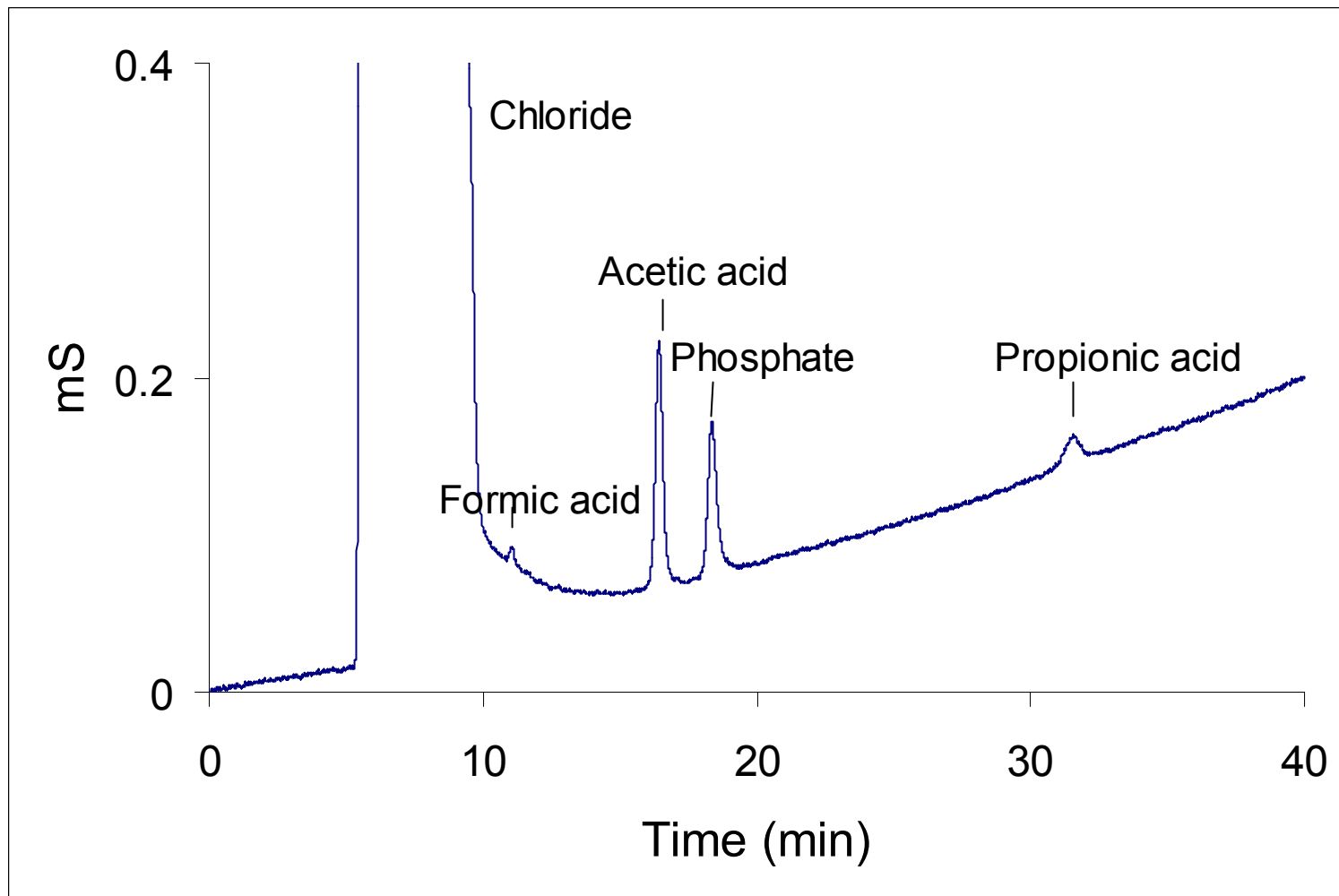
pH Dependence



Temperature Dependence



Organic Acid Analysis



Inorganic Analysis

- **ICP-AES**
 - **Crude oil:**
 - **Mainly alkaline and alkaline earths**
 - **Na, Ca, Al, Si, B in g/kg range,**
 - **Some transition metals (Ni, V, Zn in 1 to 100 mg/kg)**
 - **Produced water: Little transfer from oil to water**
 - **Cd (to 0.1 ppm) and Sb and Se (to 1 ppm)**
- **HCO_3^- , CO_3^{2-} : confirmation of pH**
- **Chloride content confirmed with ion selective electrode**

Liquid-Liquid Equilibrium Model

- **System**

$$F z_i = L x_i + W u_i + W d_i \quad \beta = \frac{W}{F}$$

- **Equilibria**

$$u_i = K w_i x_i \quad d_i = \frac{u_i K a_i \Gamma_i}{H} \quad \alpha_i := \frac{K a_i}{H + K a_i} \quad \Gamma_i = \frac{\gamma_H \gamma_{A_i}}{\gamma_{H A_i}}$$

- **Rachford-Rice Equation**

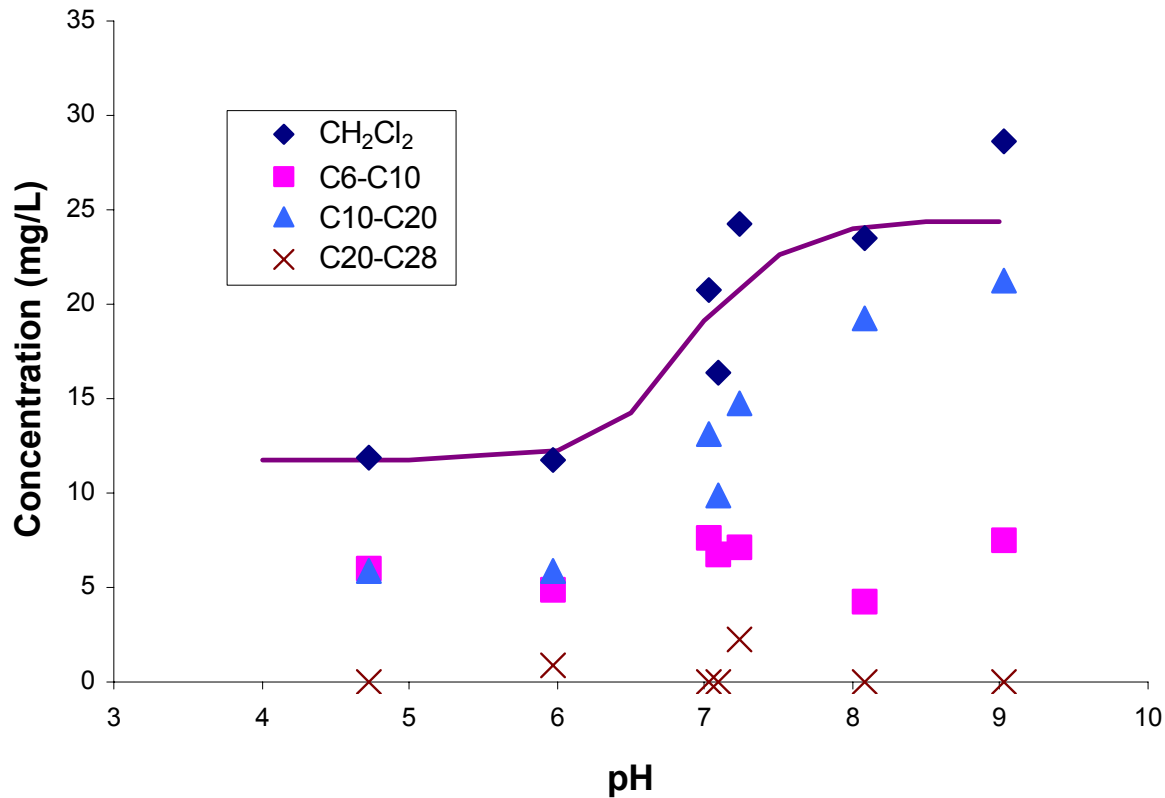
$$\sum_{i=1}^c \frac{z_i (-H + K w_i H + K w_i K a_i \Gamma_i)}{-\beta H + \beta K w_i H + \beta K w_i K a_i \Gamma_i + H} = 0$$

- **Constraints**

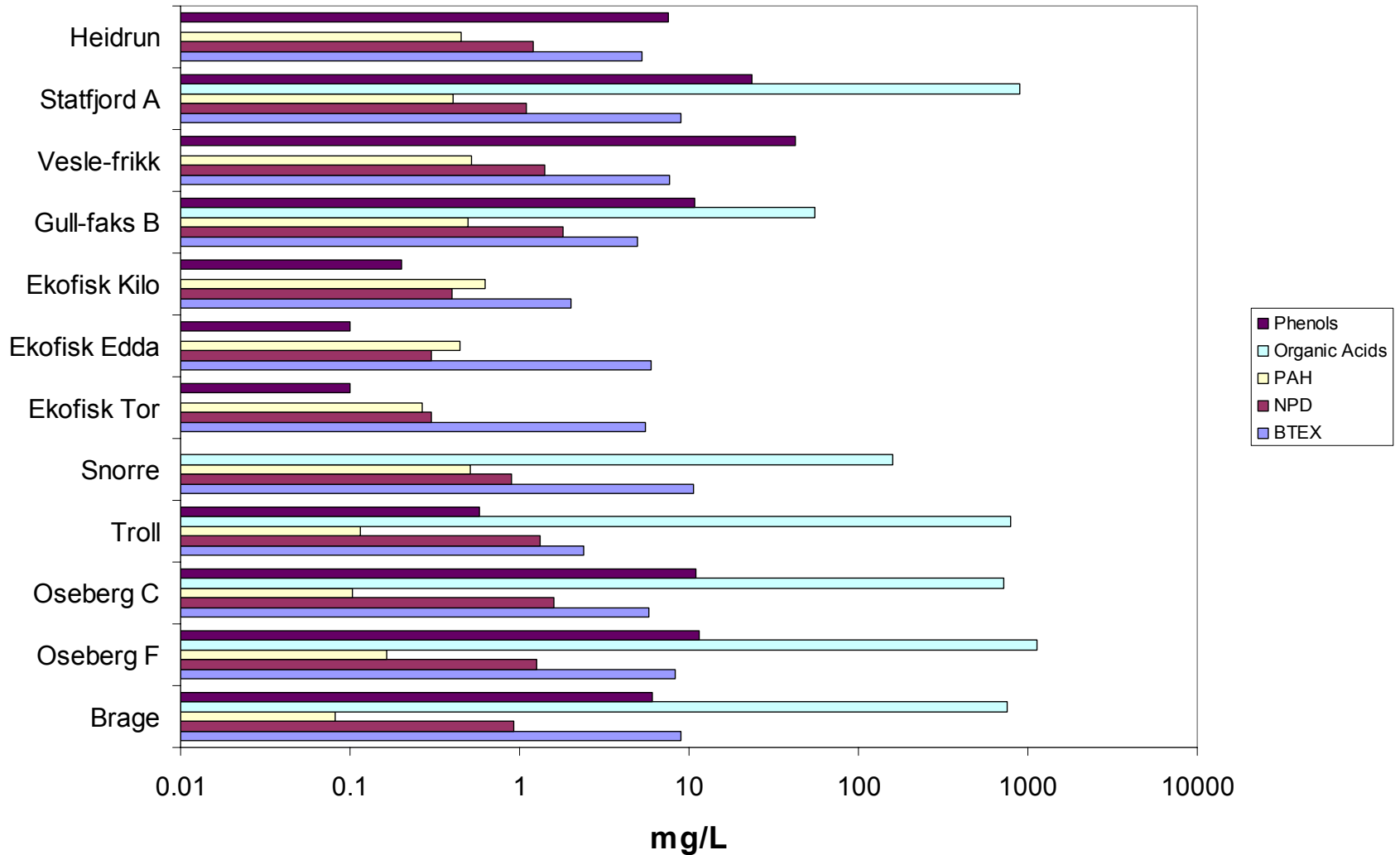
$$\sum_{i=1}^c x_i = 1, \quad \sum_{i=1}^c z_i = 1, \quad \sum_{i=1}^c (u_i + d_i) = 1$$

- **NRTL activity coefficients**

Experimental Data and LLE Model of pH Dependence



T.I. Roe Utvik Chemosphere, 29, 2593-2606, 1999



Future Direction

- **Development of thermodynamic model**
 - Description of produced water system
 - Activity coefficients from UNIFAC
 - Volatile components
- **Investigation of statistical correlations**
 - Compilation of international data
 - Dependence of solubility on field variables
 - geographic location, chemistry of oil and water

Summary

- **Most semi-volatile water soluble organic material is polar or polar+aromatic**
- **Solubility is most affected by pH**
- **Trend in data reproduced by LLE model using NRTL activity coefficients**
- **Temperature and pressure may have small effects on solubility**

Conclusions

- + After stripping, much of the WSO transferred into the brine consists of polar molecules, likely organic acids**
- None of the sampling methods were optimal: losses evident, important components missed**
- Not able to derive lumped parameter values for WSO components**
- + Demonstrated ability to fit laboratory data – first step in developing predictive model**

Acknowledgements

- **DOE FE contract number
DE-AC05-00OR22725**
- **Petroleum Energy Research Forum
partners**