Modeling of Water Soluble Organic Content in Produced Water

NGOTP Upstream Environmental Technology Review

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Produced Water – Offshore

- **Strict regulatory limits**
- **Contamination regulated by National Pollution Discharge Elimination System permits**
  - **oil and grease discharge to 42 mg/L daily maximum**
  - **29 mg/L monthly average**
  - **no visible sheen**
  - **annual toxicity**
  - **no priority pollutants**
- **Concern is how to *measure* and *remove* trace amounts of oil and grease before discharge back into the environment**

http://www.epa.gov/region6/6en/w/offshore/

Organics

- **Water Soluble**
  - Phenols
  - Carboxylic acids (C_2-C_9)
  - Aromatic compounds (BTEX)
  - Short chain paraffins
  - Ketones, aldehydes
  - Nitrogen and sulfur containing compounds (amines..)
  - Chlorinated compounds

- **Water Insoluble**
  - Long chain paraffins
  - Asphaltenes
  - Resins
  - Polycyclic aromatic hydrocarbons (PAH)
  - Napthalenes, thiophenes (NPD)

Technologies for Produced Water Remediation

Treatment and Disposal

- Physical Methods
  - Carbon adsorption
  - Filtration
  - Dispersed oil removed by density differences
- Chemical Methods
  - Air stripping
  - UV light
  - Chemical oxidation
  - Acid springing
- Biological treatment
- Subsurface re-injection

Issues

- Pretreatment required
- Fouling, scaling
- Off-gas, radioactive waste, toxic residues
- Downtime
- Residence time
- Cost
- Buffering by oil can affect removal efficiency
- Depends on types of WSO and especially for new wells, properties and amounts of WSO not well known.
- Polar WSO (extractable organics) concentrations can be as high as 1000 ppm
- Technologies untested

A Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping by Jonathan Wills, M.A., Ph.D., M.Inst.Pet., for Ekologicheskaya Vahkta Sakhalina (Sakhalin Environment Watch); 25th May 2000

Program Goals PERF 98-04

Optimize Treatment Methods

Prediction of Solubilities of Semi-volatile Organics

Model

Empirical – Thermodynamic - Statistical

Analysis

Characterization – Sensitivity Analysis – Lumped Parameters

Technical Approach

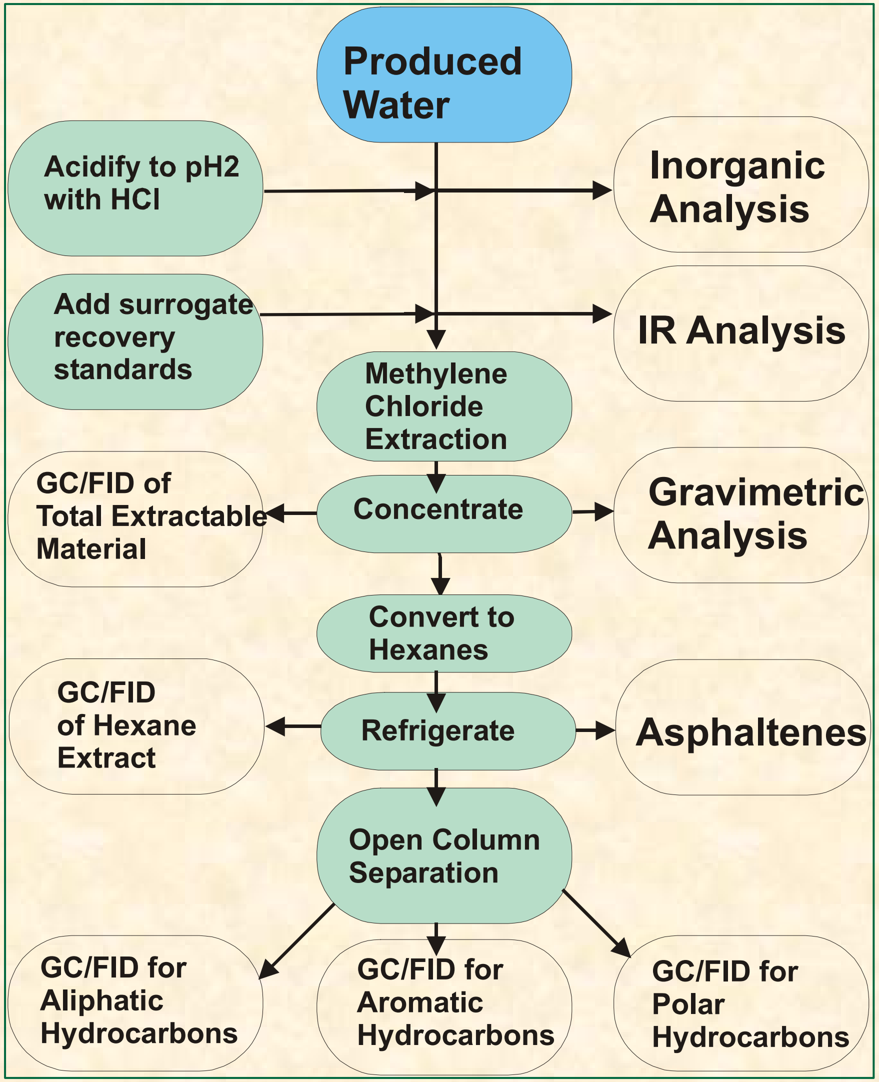
- **Stage 1**
  - Empirical analysis of 98-04 PERF data on water-soluble organic content in simulated produced water.
- **Stage 2**
  - Develop model to calculate amounts of organic compounds present in produced water from offshore oil fields.
- **Stage 3**
  - Revise model to allow predictions based on field or production parameters, as well as experimentally measured variables.

Characterization of Produced Water

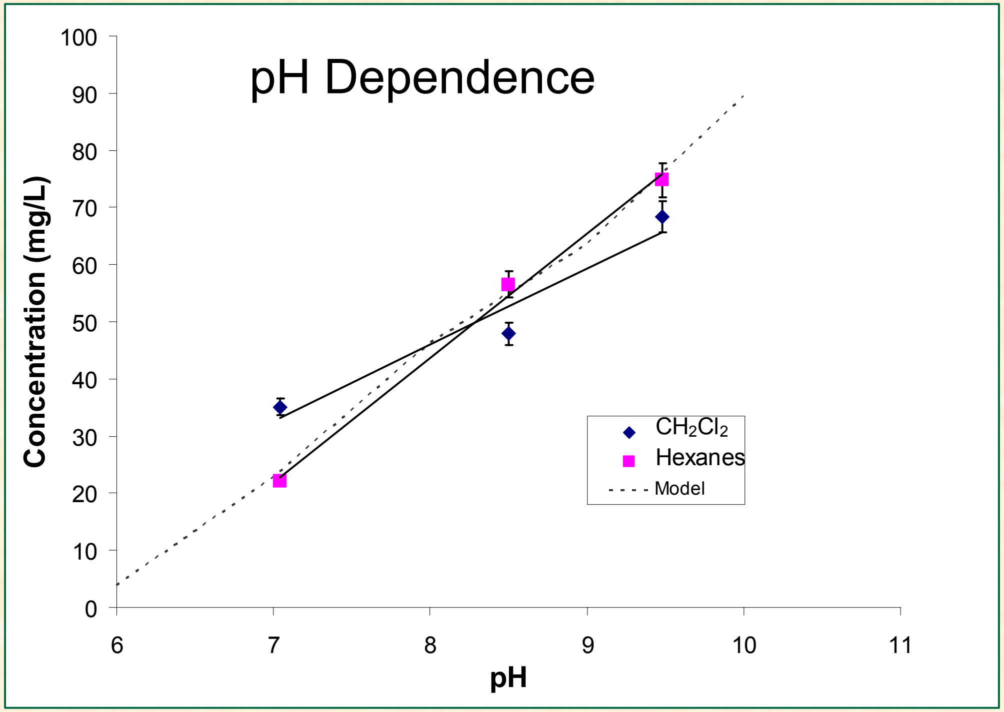
(Debbie Bostick, Catherine Mattus, Huimin Luo)

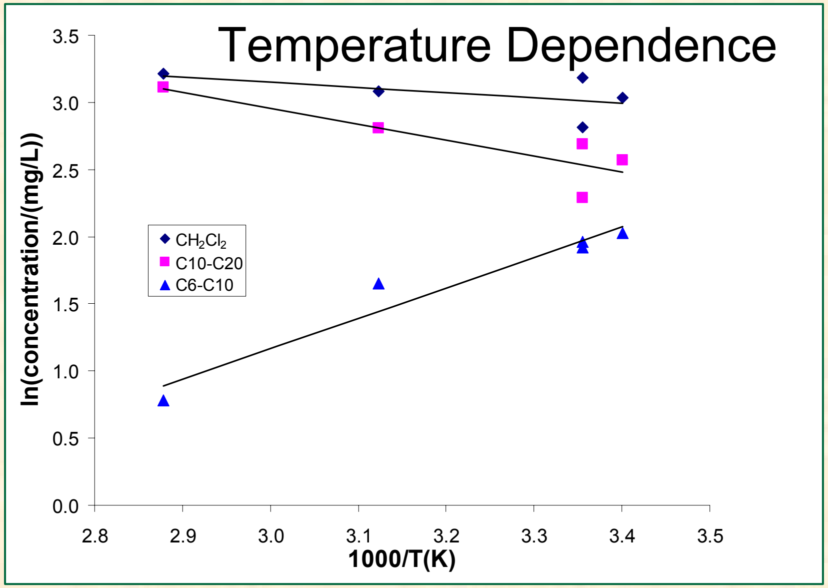
Bostick, D.T., Luo, H., Hindmarsh, B.,2002.
Characterization of soluble organics in produced water,
Oak Ridge National Laboratory Technical Memorandum, ORNL/TM-2001/78.

- Analysis of oil
- Analysis of water contacts
- Solubility as a function of
  - pH,
  - temperature
  - pressure
  - water-to-oil ratio
  - salinity
- GC, IC, ICP



Key Factors in Organic Solubility





Nominal conditions: pH=7, salinity=65,000, Fraction water = 0.8, contact time = 4 d, Temperature = 300 K, Pressure = ambient

Effect of Oil Chemistry

Components	Crude#1	Contact Produced Water
Aliphatic	67 ± 8%	1 ± 1%
Aromatic	18 ± 11%	1 ± 1%
Polar	15 ± 3%	96 ± 3%
	Crude#2	Contact Produced Water
Aliphatic	26, 40,6%	5 ± 2%
Aromatic	57, 45,7%	50 ± 20%
Polar	17, 13.7%	40 ± 20%

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Technical Approach

- Stage 1
  - Empirical analysis of 98-04 PERF data on water soluble organic content in simulated produced water.

- **Stage 2**
  - **Develop model to calculate amounts of organic compounds present in produced water from offshore oil fields.**

Modeling Choices for Prediction of Solubility of Organics in Produced Water

- **Empirical model**
  - Trend line through experimental data set, correlation coefficient
- **Thermodynamic model**
  - Assume chemical equilibrium for a defined system
  - Chose physical model for each phase – UNIFAC activity coefficients
  - Generate solution based on iterative solution of the Rachford-Rice equation for mole fraction and phase split
- **Statistical model**
  - Generate correlations/regressions based on “training data set”
  - Partial least squares approach – stepwise decomposition of matrices of independent and dependent variables
  - Apply matrices (loadings, weights) and regression coefficients to generate new response variables based on input data

Thermodynamic Modeling

System

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

Equilibria

$$u_i = Kw_i\,x_i \qquad d_i = \frac{u_i\,Ka_i\,\Gamma_i}{H} \qquad \alpha_i := \frac{Ka_i}{H + Ka_i} \qquad \Gamma_i = \frac{\gamma_H\,\gamma_{A_i}}{\gamma_{HA}}$$

Rachford-Rice Equation

$$\sum_{i=1}^{c} \frac{z_i\,(-H + Kw_i\,H + Kw_i\,Ka_i\,\Gamma_i)}{-\beta\,H + \beta\,Kw_i\,H + \beta\,Kw_i\,Ka_i\,\Gamma_i + H} = 0$$

Constraints

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

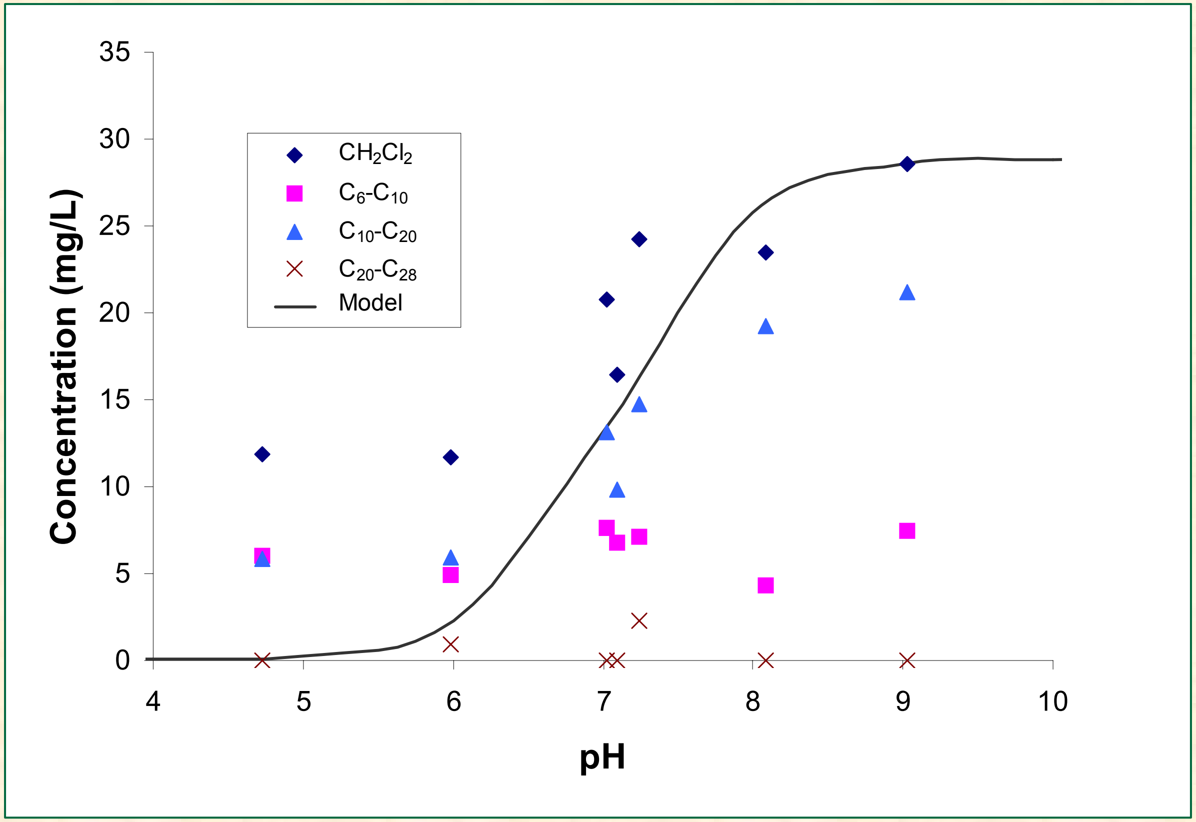
Mole fractions, Phase Split

Activity coefficient model

NRTL, UNIFAC

Distribution Coefficients

Thermodynamic Model Replicates Trend in pH Dependence



Thermodynamic Model:

2 phase liquid-liquid equilibrium

UNIFAC activity coefficients

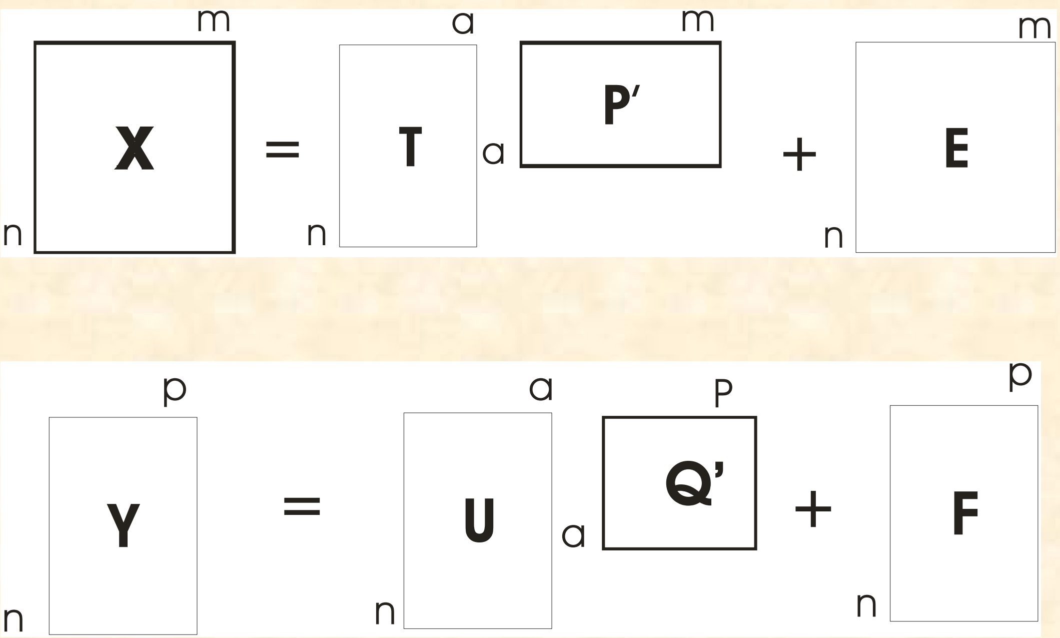
Database includes alkanes, BTEX, PAH, organic acids, phenols, ketones, benzothiophenes

Results:

Most soluble organics are polar – NOT oil and grease
Solubility most sensitive to pH, presence of polar groups (COOH, C=O, OH)

Pictorial Representation of PLS

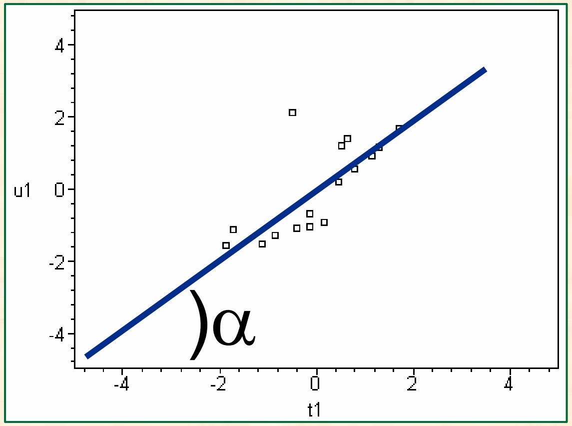
Geladi and Kowalski, Analytical Chimica Acta, 185, 1-17 (1985)



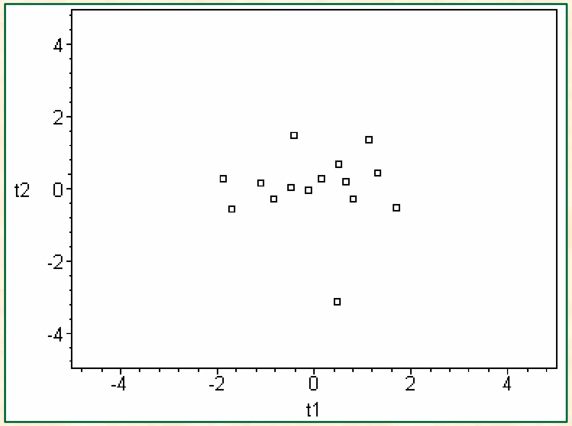
- **Model Development**
  - Scores, Loadings, Regression coefficients $b = \tan\alpha$
  - Matrix of ***weights*** (m x a) required to produce orthogonal t values
- **Prediction**
  - $t_h = X w_h$
    $Y_h = \sum b_h t_h q'_h$
    $E_h = E_{h-1} - t_h p'_h$

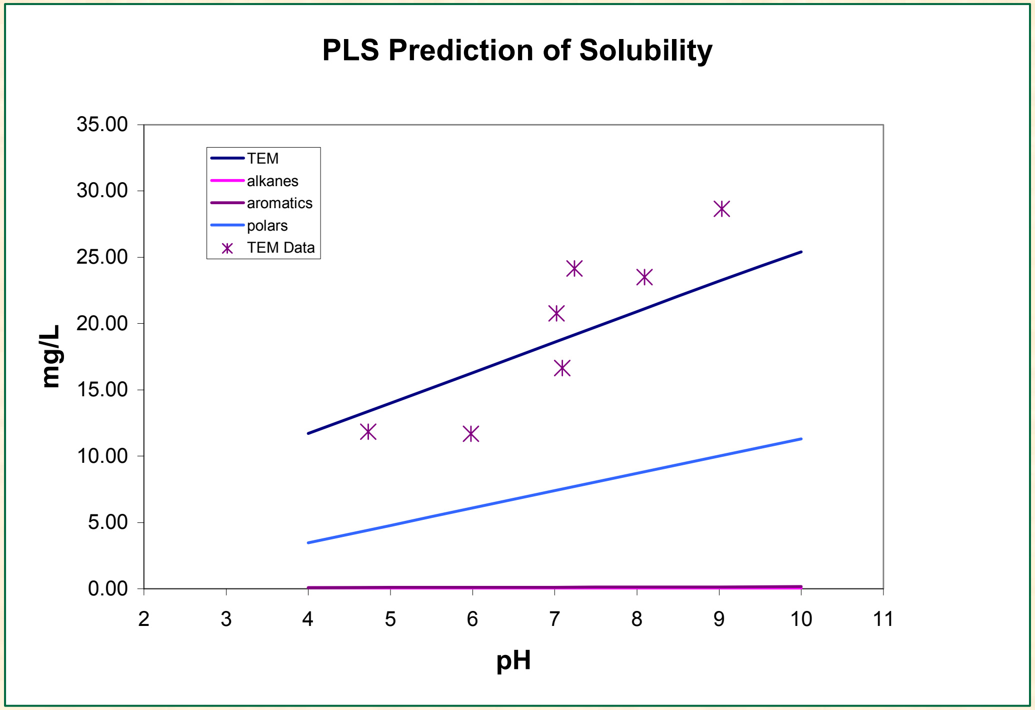
Statistical Analysis Provides Linear Model

Regression



Correlation





Which Model is Most Useful?

Thermodynamic?

Empirical?

Statistical?

Type of data available for model development

Requirements of model

Empirical – simple, univariate data, demonstrable relationships

Phenomenological – well characterized system, understand and extrapolate

Statistical – qualitative as well as quantitative data, disparate data sets, non-equilibrium effects, examine correlations, physical information is camouflaged

What output is required?

Can we combine the various approaches?

Technical Approach

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- **Stage 3**
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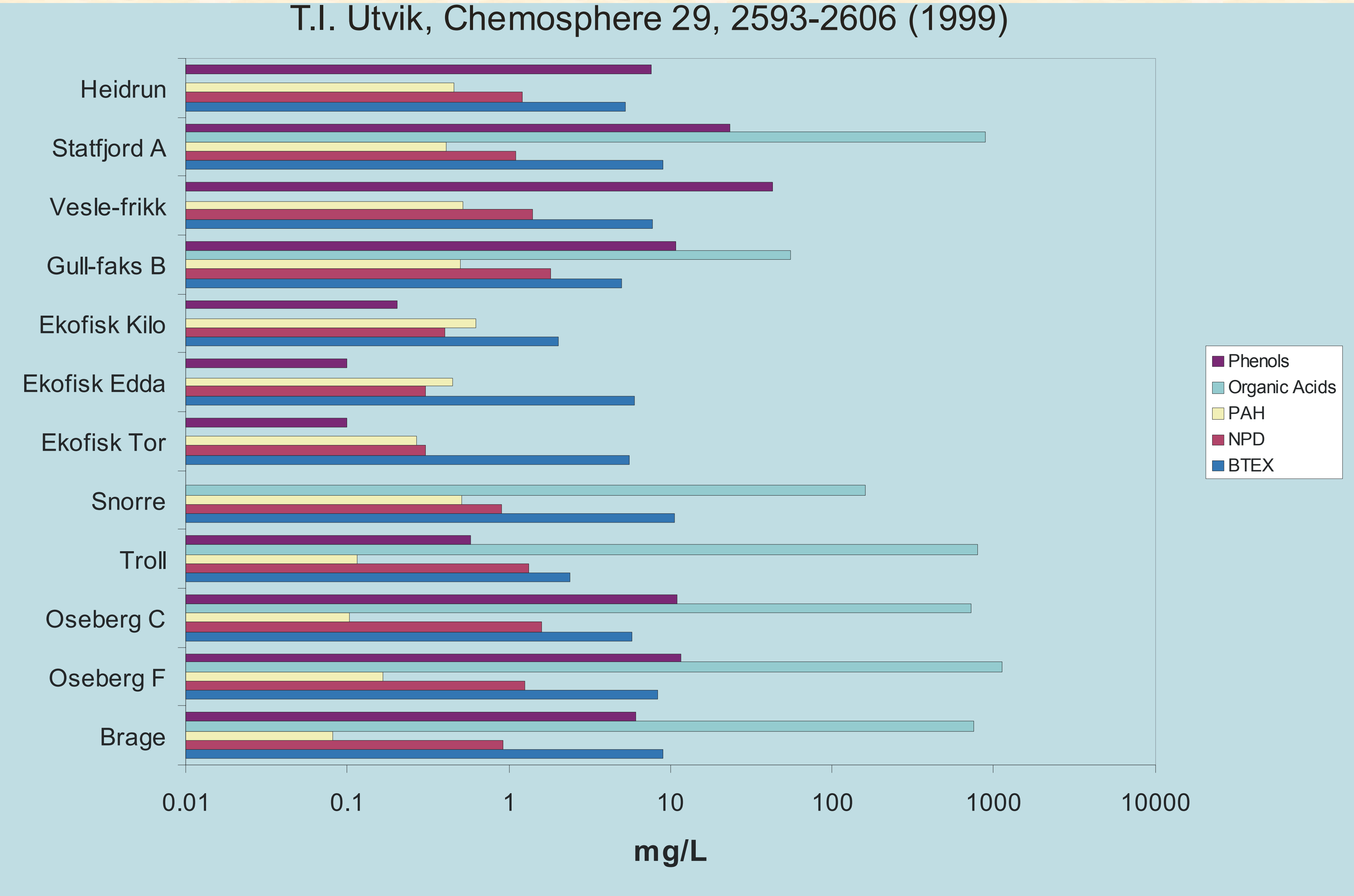
Comparison with International Studies

ORNL Analysis

- **Sampling**
  - Simulated water, actual but degassed oil
  - Effect of lab controlled physical variables
- **Analysis**
  - Broad classification of size and character
  - GCMS offsite
- **Results**
  - Organics from less than100 ppm
  - Aliphatic hydrocarbons – few ppm (less than permitting levels)
  - Acids important (C2-C6)
  - Aromatic less important as volatile fraction not sampled
  - PAH low
  - Priority pollutants low in sample

North Sea + Near Shore US

- **Sampling**
  - Formation, produced water
  - Effect of production variables, additives, biological activity
- **Analysis**
  - Broad classification as well as individual identification by GCMS
- **Results**
  - Organics from low ppm to >100 ppm
  - Aliphatic hydrocarbons – few ppm
  - Acids important, phenols
  - Dissolved hydrocarbons mainly light aromatics (BTEX)
  - PAH low, detectable napthalene


T.I. Utvik, Chemosphere 29, 2593-2606 (1999)
Heidrun
Statfjord A
Vesle-frikk
Gull-faks B
Ekofisk Kilo
Ekofisk Edda
Ekofisk Tor
Snorre
Troll
Oseberg C
Oseberg F
Brage
0.01
0.1
1
10
100
1000
10000
mg/L
Phenols
Organic Acids
PAH
NPD
BTEX

Reasons to go beyond a thermodynamic model…

- **Thermodynamic Variables**
  - Aromatic organics (BTEX and napthalenes) will depend on conditions in reservoir
  - Soluble oil and grease have very low concentrations
  - Predict dependence based on pH, salinity, temperature, pressure and phase ratio

- **Production Variables**
  - Concentration of oxidized organics can depend on separation methods and aging
  - Heteronuclear organics can be introduced during production
  - Higher molecular hydrocarbons may be present in the disperse phase

Inputs

Thermodynamics
pH
Temperature
Pressure
Salinity
Oil Components
Water cut

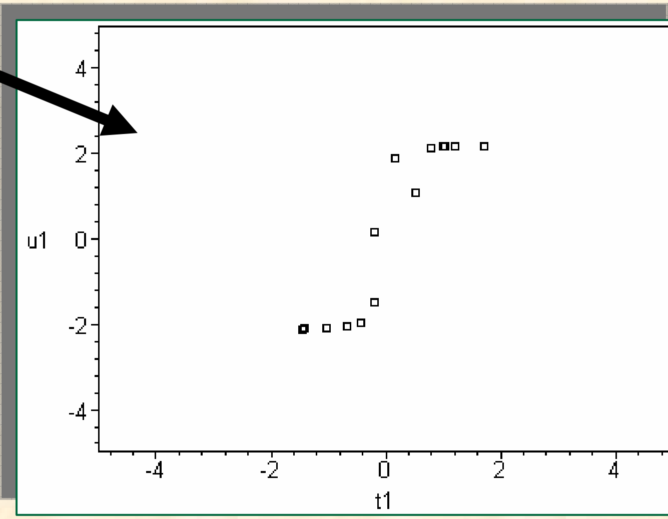
Production Variables
Age of formation
Age of well
Separation methods
Production additives
Geographic location

Statistical Analysis

PLS

- Regression parameters
- Correlations between predictor and response variables
- Functionality with respect to physical and chemical variables

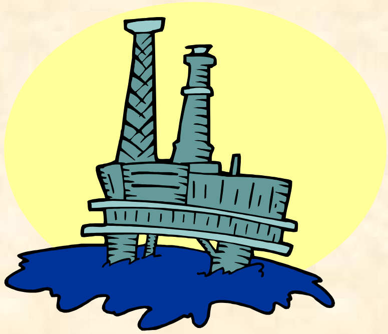
Outputs



Major Tasks for FY 2004/05

- **Final model development (September 2004)**
  - **Merge thermodynamic database with statistical analysis**
  - **Perform verification tests (range of response of models, goodness of fit)**
- **Model testing (December 2004)**
  - **Survey international data and compare model predictions to the nature and concentration of produced water contaminants**
  - **Map out boundaries for application of model**
- **Documentation (March 2005)**
  - **Model, tests and application**
  - **Final report, peer reviewed publication**
  - **Presentations**

Industry Participation



- Project planning and oversight
  - Guidance in model development.
  - Recommendations for additional characterization tests if required.
  - Facilitate liaison with other PERF projects (e.g., UMIST), contractors
- Produced water/crude data sets
  - Industrial measurements in laboratory and offshore.
  - Crude/brine samples characterized at ORNL.
- Advice on relevant field parameters for predictive model
- Testing and evaluation of model with feedback to developers

Milestones

- First year (FY2002)
  - Evaluate trends in PERF 98-04 characterization data.
  - Test empirical model to describe trends.
  - Select additional data sets for comparison with model calculations.
- Second Year (FY2003)
  - Develop thermodynamic model and compare results to PERF data.
  - Evaluate statistical methodology for model development
- Third Year (FY2004)
  - Modify model to use field parameters to calculate the solubility of organic components in produced water.
  - Document recommended model and parameters useful in model predictions.

Project Impact

- A model will be developed to predict the *amounts* and *types* of environmentally important classes of organic compounds in produced water knowing key characteristics of the oil field.

- Industrial partners can use this information to
  - reduce production of the water-soluble contaminants on existing platforms
  - develop methods of treatment that are efficient and cost effective for new oil fields

Technology Transfer

- Papers and Reports
  - J. McFarlane, “Offshore Versus Onshore Produced Water Characterization and Models”, for Proceedings of GTI's Natural Gas Technologies II Conference and Exhibition, February 8-11, 2004, Phoenix, Arizona.
  - J. McFarlane, D.T. Bostick, H. Luo, “Analysis of Water Soluble Organics from Gulf of Mexico Crude Oil”, Submitted to Organic Geochemistry.
  - J. McFarlane, “Application of Chemometrics to Modeling Produced Water Contamination”, Separations Science and Technology 40, 593-610 (2005).
  - J. McFarlane, D.T. Bostick, H. Luo. 2002. “Characterization and Modeling of Produced Water”, in Proceedings of the Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16, 2002.

- Presentations
  - J. McFarlane, “Measurement, Characterization and Prediction of Organic Solubility in Produced Water”, Gas Technology Institute Natural Gas Technologies II Conference, Phoenix, AZ, Feb. 8-11, 2004.
  - J. McFarlane, “Gulf of Mexico Produced Water. Characterization and Simulation”, 13th Separations Science and Technology Conference, Gatlinburg, TN, October 27, 2003.
  - J. McFarlane, “Gulf of Mexico Produced Water: Characterization and Simulation”, American Association of Petroleum Geologists Mid-continent Meeting, Tulsa, OK, October 14, 2003.
  - J. McFarlane, University of Tennessee Chemical Engineering Department, Knoxville, TN, September 23, 2003.
  - J. McFarlane, D.T. Bostick, H. Luo, “Characterization and Modeling of Produced Water Contacted with Gulf of Mexico Crude Oil”, Presented at the Southeast Regional Meeting of the American Chemical Society, Charleston, SC, November14, 2002.
  - J. McFarlane, D.T. Bostick, H. Luo, “Characterization and Modeling of Produced Water Contacted with Gulf of Mexico Crude Oil”, Presented at the Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16, 2002.