Measurement, Characterization, and Prediction of Organic Solubility in Produced Water

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U. S. DEPARTMENT OF ENERGY

Produced Water Generated Offshore

- **Byproduct of oil and gas production**
  - **Trillion gallons produced each year from Gulf of Mexico operations**
  - **$\$10^5$/day for operation of one well**
  - **New well can be several tens of millions of dollars**

- **Produced Water Contaminants**
  - **Organics (soluble or dispersed)**
  - **Heavy metals (e.g. Hg)**
  - **Radionuclides (e.g. Ba)**
  - **Treatment chemicals**
  - **Salt**
  - **Hydrogen sulfide**
  - **Ammonia**

Current Practices – 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)

Emerging 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**

Problems

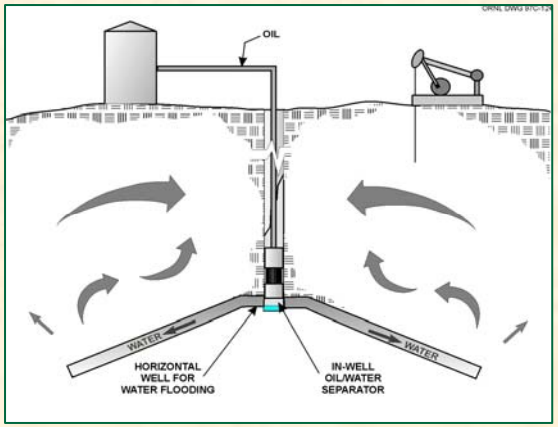
- Pretreatment required
- Fouling, scaling
- Off-gas, radioactive waste, toxic residues
- Downtime
- Residence time
- Cost
- Buffering by oil can affect removal efficiency
- Depends on types of WSO and especially for new wells, properties and amounts of WSO not well known.
- Polar WSO (extractable organics)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

Produced Water Research at ORNL

- **Measurements of contaminant concentrations using chemical analysis techniques**
- **Modeling of produced water contamination based on chemical thermodynamics**
- **Development of a predictive model based on statistical analysis**
- **Development of a sensor for organic contamination**
  - **Measure solubility of contaminants in ionic liquids**
  - **Use quartz crystal microbalance to measure organics online**

- **Testing of methods for remediation of produced water**
  - **Downhole separator (Dr. Counce, Dr. Perkins –UTK Joe Birdwell – ORNL)**
  - **Ozonolysis (Dr. Thomas Klasson – ORNL)**
  - **Bioremediation (Dr. Abhijeet Borole – ORNL)**
  - **Liquid-liquid separations (Dr. David DePaoli – ORNL)**



Goal of Program

Prediction of Solubilities of Semi-volatile Organics

Model

Empirical – Thermodynamic - Statistical

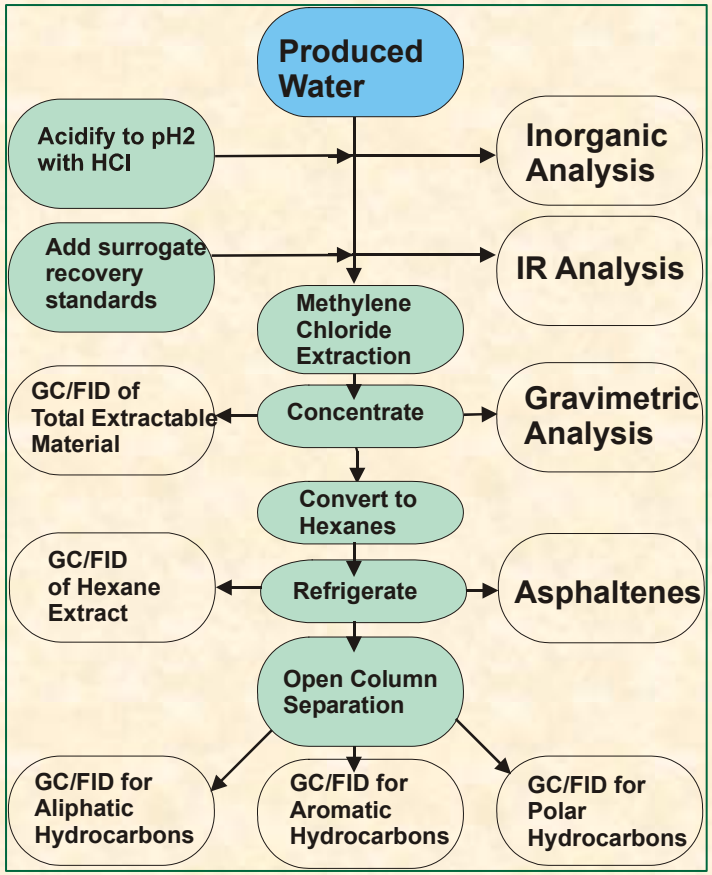
Analysis

Characterization – Sensitivity Analysis – Lumped Parameters

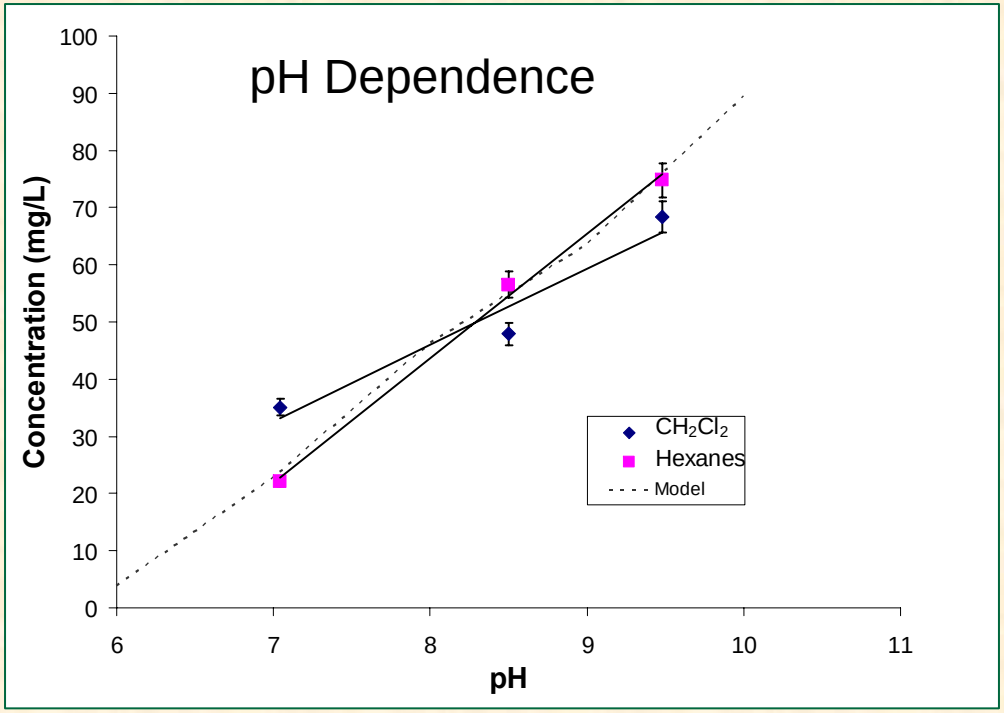
Characterization of Produced Water

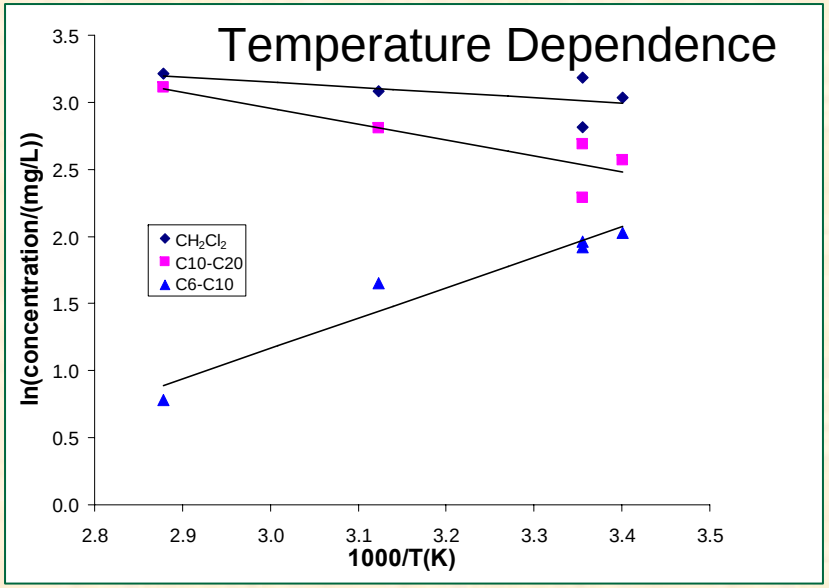
(Debbie Bostick, Catherine Mattus, Huimin Luo)

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



Results of Contact Experiments





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%

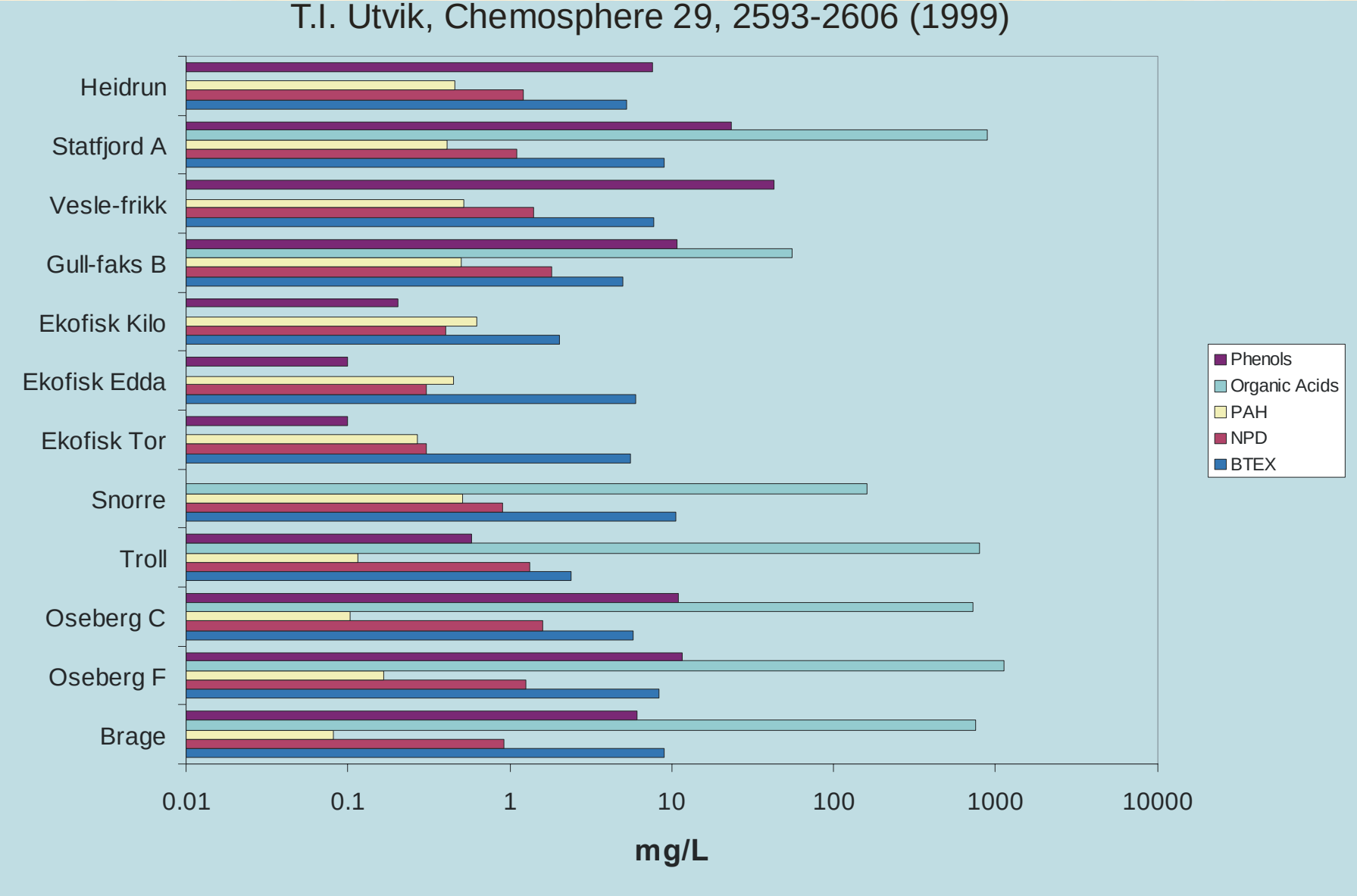
Comparison with International Studies

ORNL Analysis

- **Sampling**
  - Simulated water, actual but degassed oil
  - Effect of lab controlled physical variables
- **Results**
  - Broad classification of size and character
  - Priority pollutants low in sample
  - Acids important
  - Aromatic less important as volatile fraction not sampled
  - PAH low

North Sea + Near Shore US

- **Sampling**
  - Formation, produced water
  - Effect of production variables, additives, biological activity
- **Results**
  - Acids important, phenols
  - Broad classification as well as individual identification by GCMS
  - Dissolved hydrocarbons mainly light aromatics (BTEX)
  - PAH low


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

Offshore versus Onshore Analysis

Offshore Oil Production

- Organics from low ppm to >100 ppm
- Dominated by acetic + other organic acids
- VOC present – few ppm
- Aliphatic hydrocarbons – few ppm
- Detectable phenols, napthalenes
- PAH very low levels

Onshore Gas Production

- Organics at low ppm levels
- Dominated by acetic + other organic acids
- VOC present – few ppm
- Aliphatic hydrocarbons – few ppm
- Phenols, PAH, higher organic acids very low levels
- Sensitive to contamination of samples

Model to Predict 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

Equilibria

Rachford-Rice Equation

Constraints

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

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

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

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

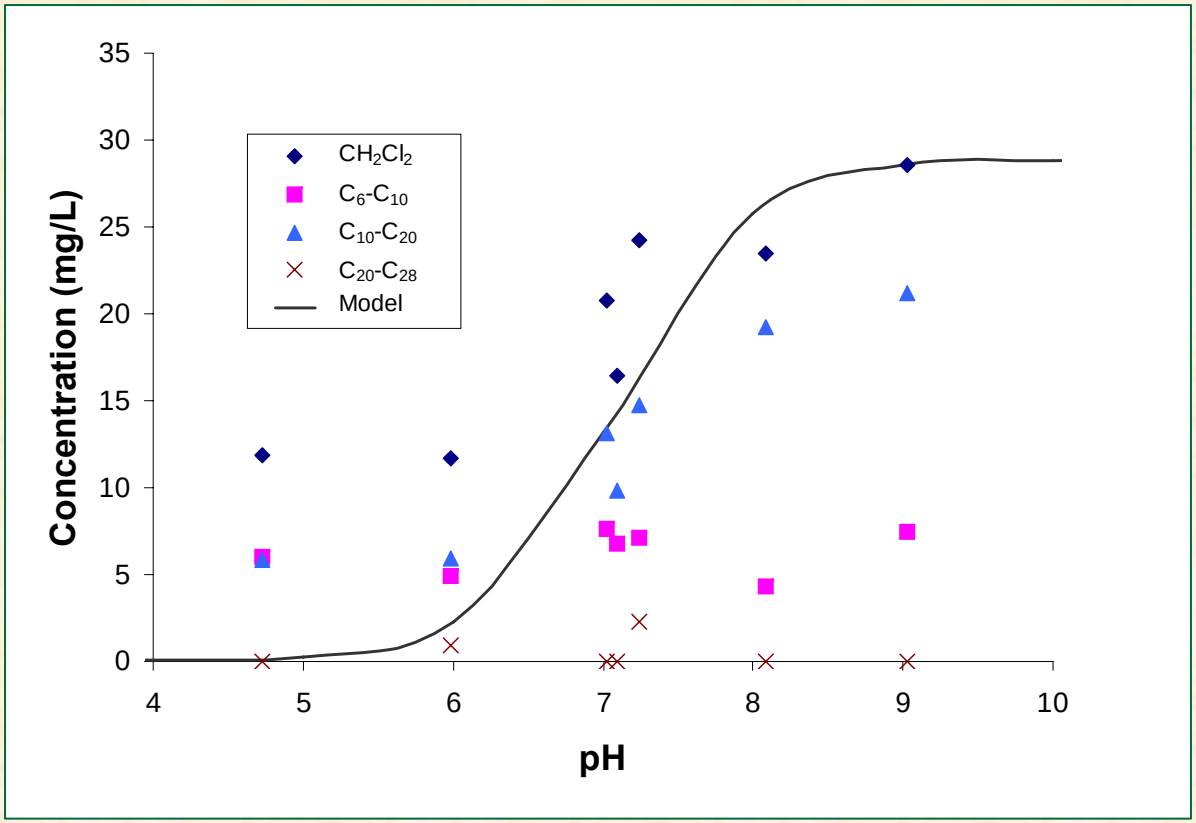
Mole fractions, Phase Split

Activity coefficient model

NRTL, UNIFAC

Distribution Coefficients

Measurement and Model of Polar Organics in Produced Water as a Function of pH



Thermodynamic Model:

2 phase liquid-liquid equilibrium

UNIFAC activity coefficients

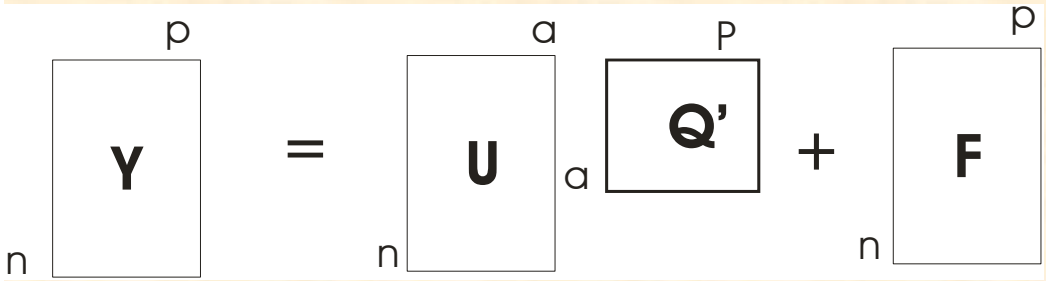
Database includes alkanes, BTEX, PAH, organic acids, phenols, ketones, benzothiophenes

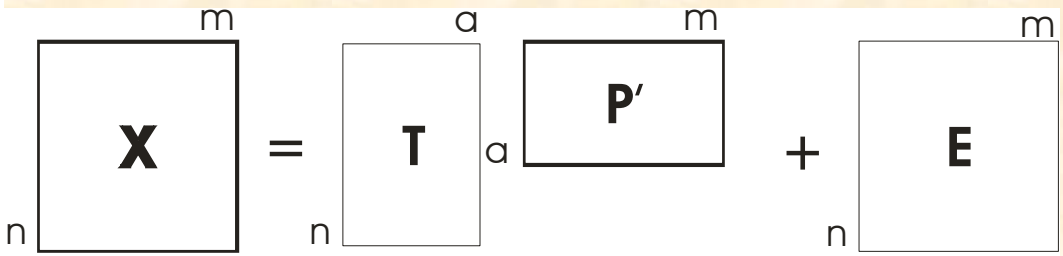
Results:

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

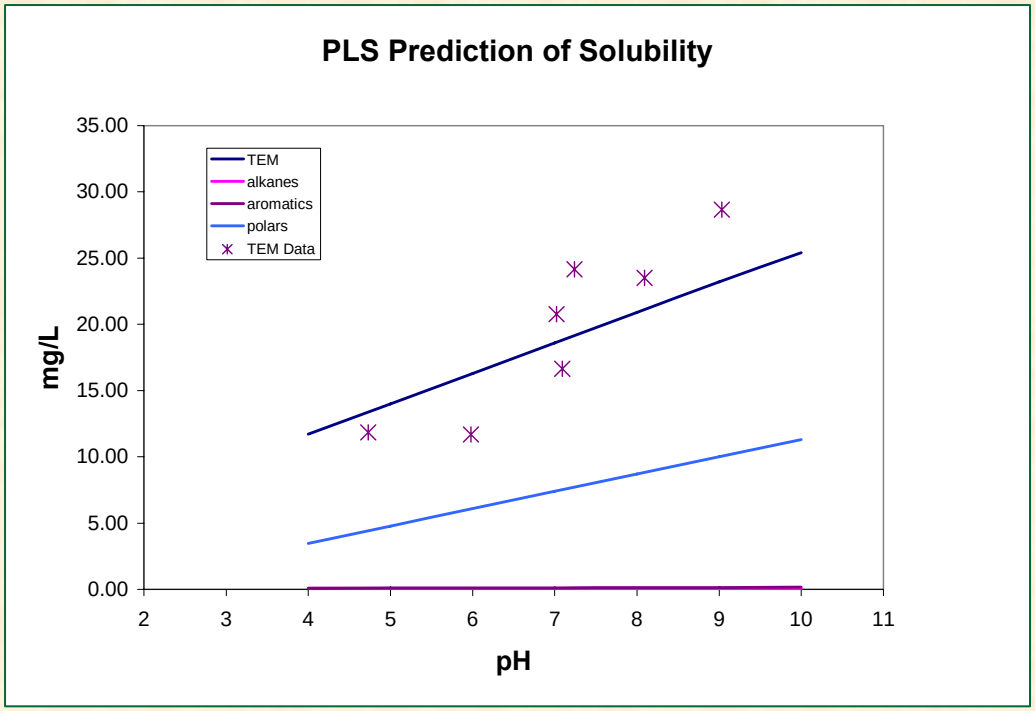
Geladi and Kowalski, Analytical Chimica Acta, 185, 1-17 (1985)

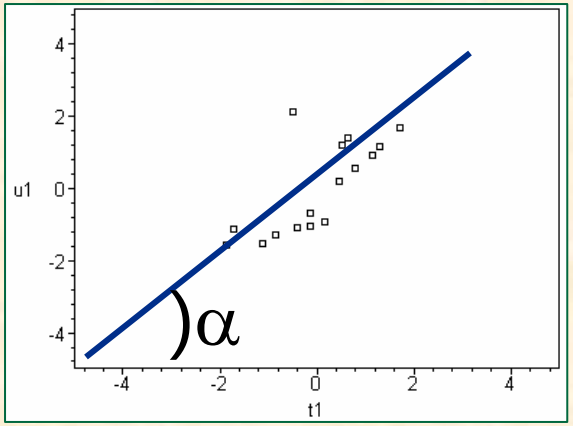


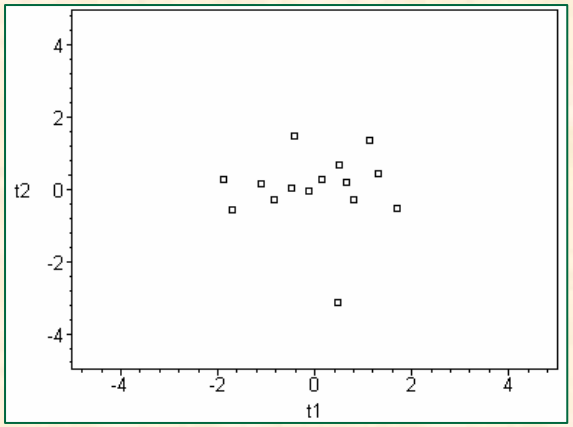


- **Model Development**
  - Scores, Loadings, Regression coefficients $b=\tan\alpha$
  - Matrix of ***weights*** (m x a) required to produce orthogonal t values
- **Prediction**
  - $t_h = X w_h$
    $Y_h = \sum b_h t_h q'_h$
    $E_h = E_{h-1} - t_h p'_h$

Results of Statistical Analysis







What 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, examine correlations, physical information is camouflaged

In this particular application, statistical approach most appealing

- **Can bring in disparate data sets**
- **Can account for non-equilibrium effects**

Produced Water Organics

- **Soluble oil and grease generally lower than permitting levels**
- **Oxidized organics more soluble than aliphatic**
  - **Carboxylic acids and alkyl phenols**
  - **Concentration can depend on separation treatment and aging**
- **Other heteronuclear organics have low solubility**
  - **Some introduced during processing**
- **Aromatic organics can be significant fraction of water soluble component (BTEX and napthalenes)**
  - **Soluble fraction will depend on conditions in resevoir**
- **Polyaromatic hydrocarbon concentrations low**
  - **Will be present in disperse phase**

Common Research Goals?

Offshore

- Statistical modeling based on world-wide data set
- Must include process variables
- Volatile organics
- Oil and grease removal
- Implementation in planning/design of well

Onshore

- Statistical modeling based on local or regional data
- Processing less important for volatiles
- Gas separations
- Salinity
- Target beneficial use of produced water or design of separators

Acknowledgements

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