



PWS
Produced Water Society

Modeling Water Soluble Organics

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Upstream **Engineering** Centre



Understanding water soluble organic components within upstream production systems to develop robust design and operating guidance.

James Carnell (BP) & John Walsh (Cetco Oilfield Services)
TEKNA 2014, Stavanger

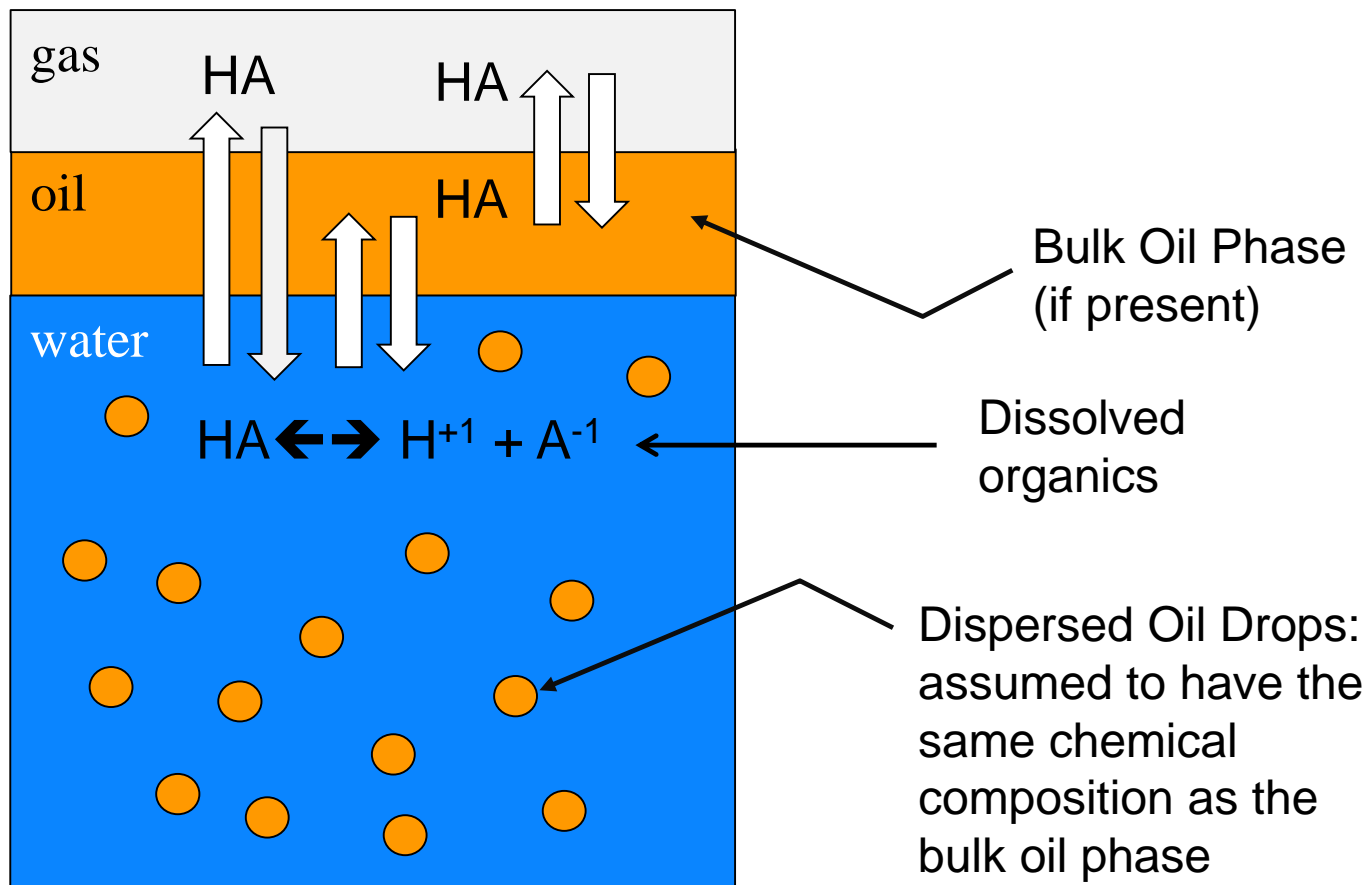
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Objectives of this Study:

- 1) Develop a model that captures the chemical characteristics of “water soluble organics”
- 2) Apply the model throughout the process facilities and to the sampling, and analysis stages (acidification, solvent extraction, evaporation) in order to confirm the ultimate fate of various WSO
- 3) Apply the model to the different classes of WSO and to the different strategies for removing them (Hi-Flow, MyCelx, acidification/oil extraction, gas stripping)

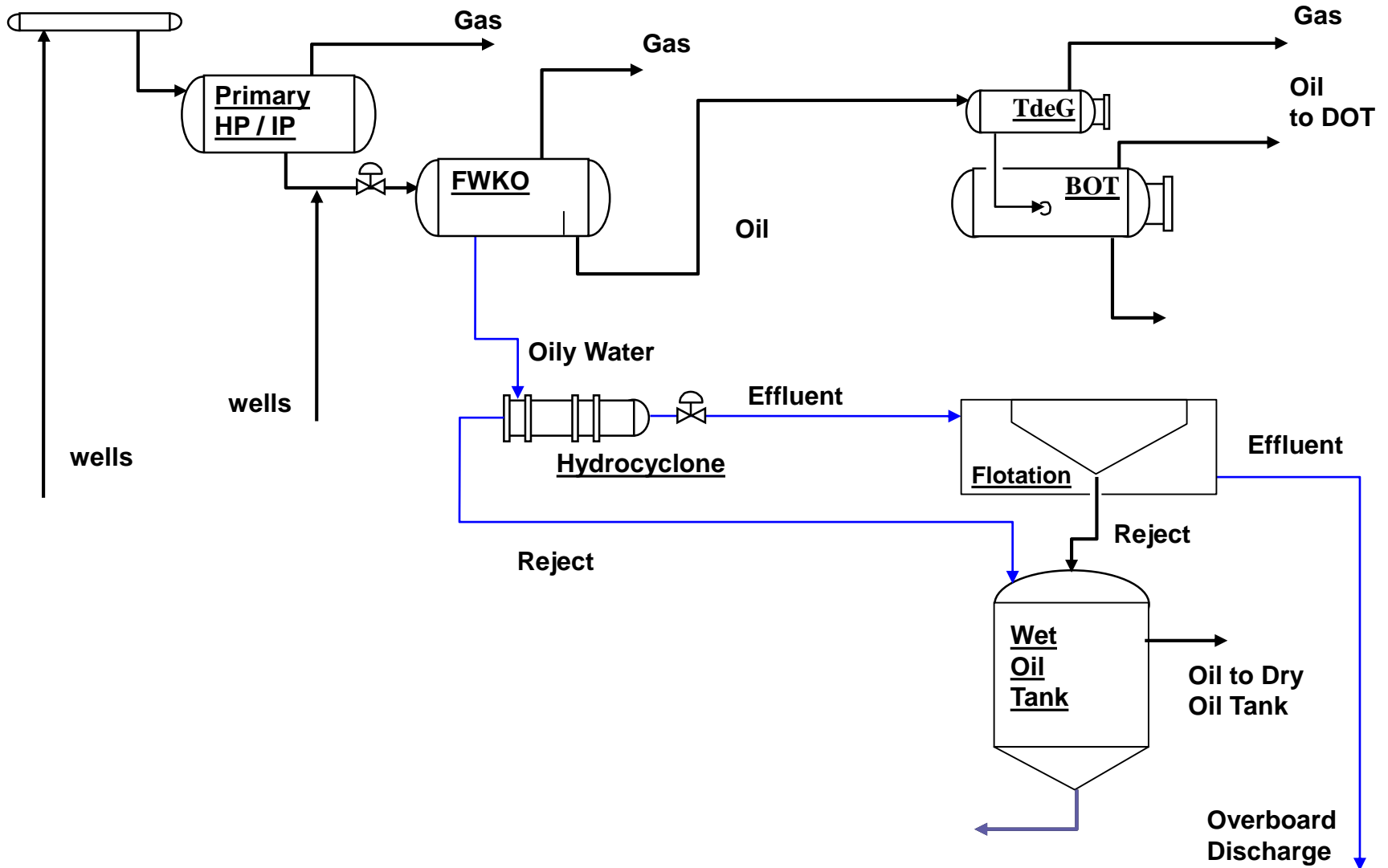
Physical Picture of Chemical & Phase Equilibria – Additional Details

General Case of an Acid (HA):

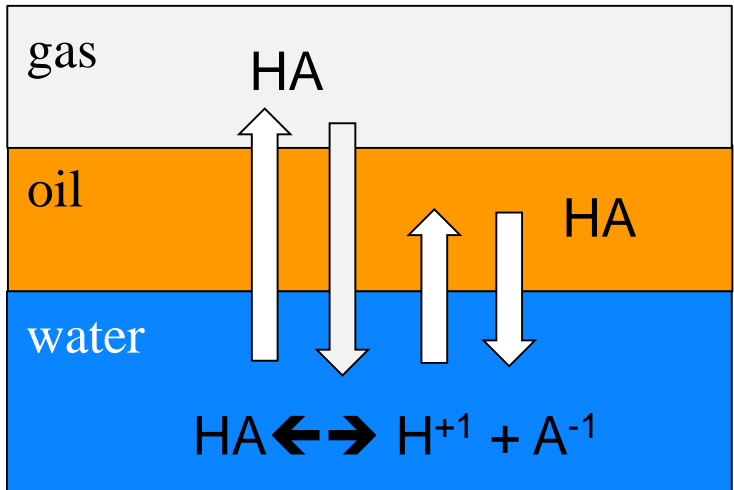
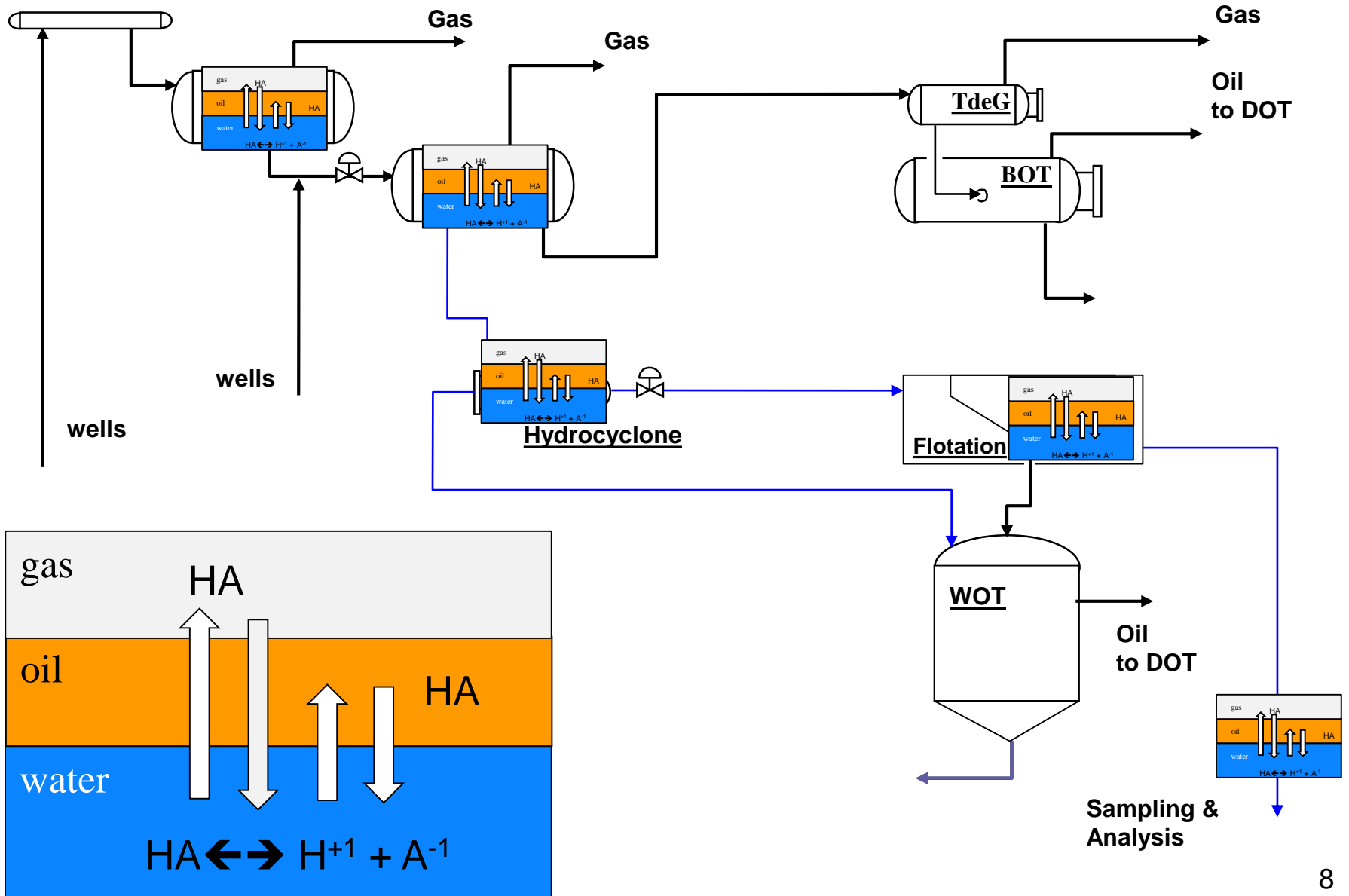


In this version of the model, kinetic effects are not included, i.e. phase equilibrium is assumed for all phases (gas, bulk oil, dispersed oil, and water).

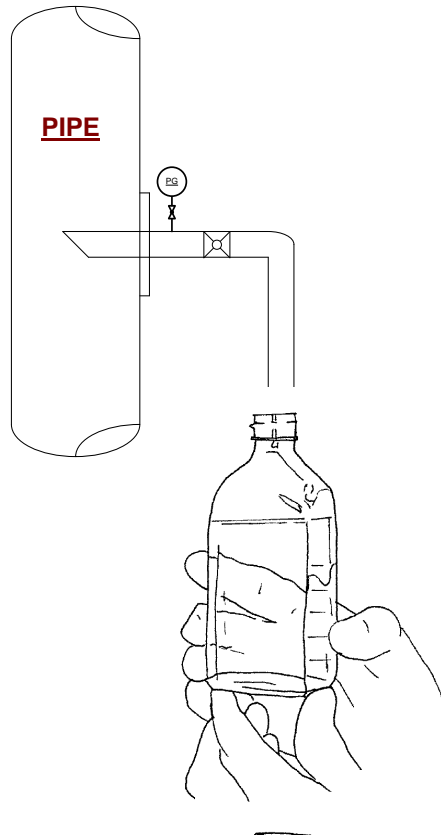
Typical Facilities Process Flow Diagram



Facilities Process Flow Diagram / Model Application



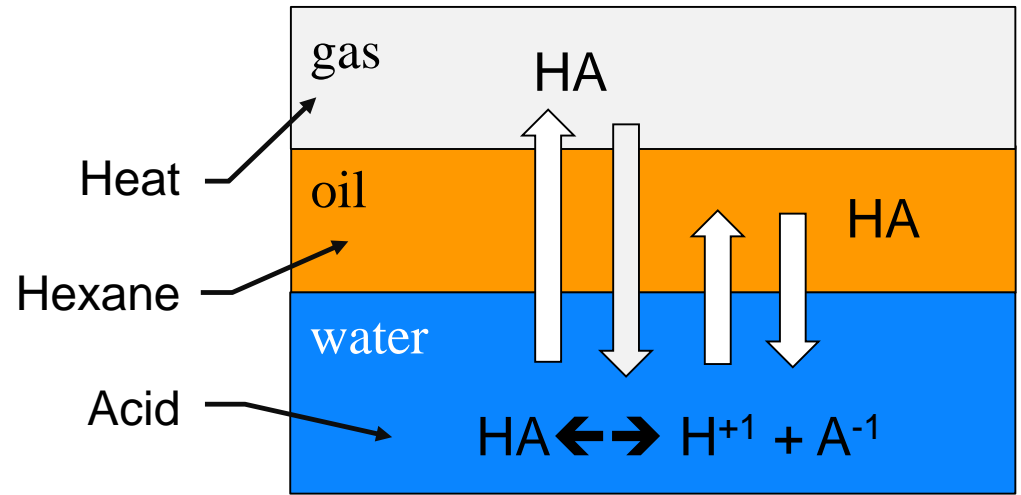
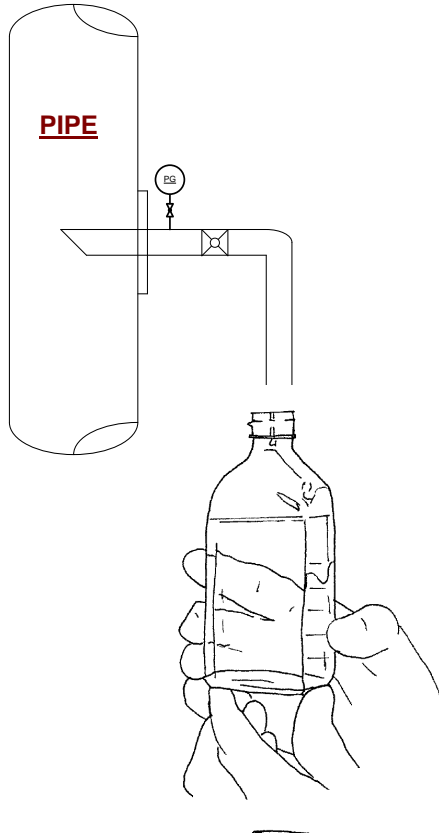
Sampling & Analysis – Model Application:



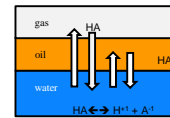
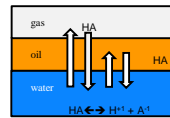
Sample + Acid + Hexane → Measure
heat



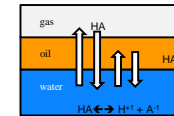
Sampling & Analysis – Model Application:



Sample + Acid + Hexane → Measure



heat



The Model (in words):

Chemical Equilibria: each acid-base reaction is governed by a chemical equilibrium constant which is a function of temperature.

Phase Partitioning: the concentration of each component in each phase is governed by partitioning coefficients which are calculated from chemical potentials for each component in each phase.

Material Balance: the total number of moles of any particular WSO component is the sum of the moles of that component in each phase.

The number of moles of each component in each phase is the product of the phase volume times the concentration of each component.

Model Applications:

The model is applied to these classes of WSO:

- 1) Acids
- 2) Partially soluble compounds
(compounds that partition into both oil and water)
- 3) Volatile compounds

These classes of WSO have distinctly different properties.

They were chosen to both illustrate the properties of the model as well as to demonstrate the unique properties of the WSO components themselves.

Four Important Quantities:

Dispersed oil – usually means oil in produced water in the form of small droplets, which may range from sub-microns to hundreds of microns. Dispersed oil will contain both aliphatic and aromatic hydrocarbons.

Dissolved oil – usually means oil in produced water in a soluble form. Aliphatic hydrocarbons in general have very low solubility in water. It is the aromatic hydrocarbons, together with things like organic acid that form the bulk of dissolved oil.

TOG = Total Oil & Grease
= Hexane Extractable Material (HEM)
= extractable by, and less volatile than hexane
= essentially all hydrocarbons and organics


WSO = TOG – SGT-HEM (TOG – Non-Polar Material)
= TOG minus the Silica Gel Treated HEM
= dissolved + polar dispersed

What is measured?

TOG = total oil & grease (all hydrocarbons / all organics)

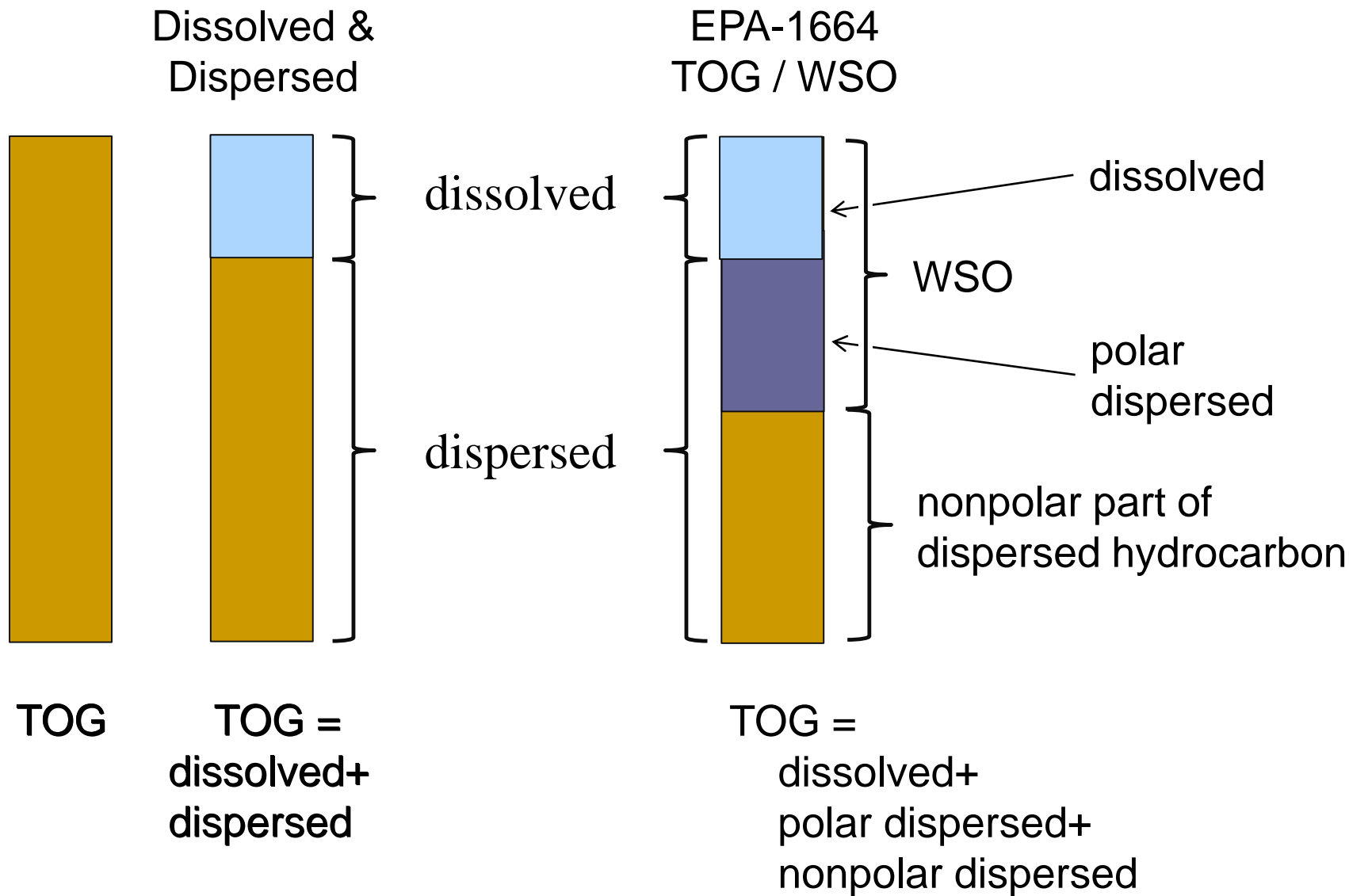
WSO = polar organics dissolved in water +
polar part of the dispersed oil

TOG = organics dissolved in water
+ polar fraction of dispersed oil
+ nonpolar fraction of dispersed oil

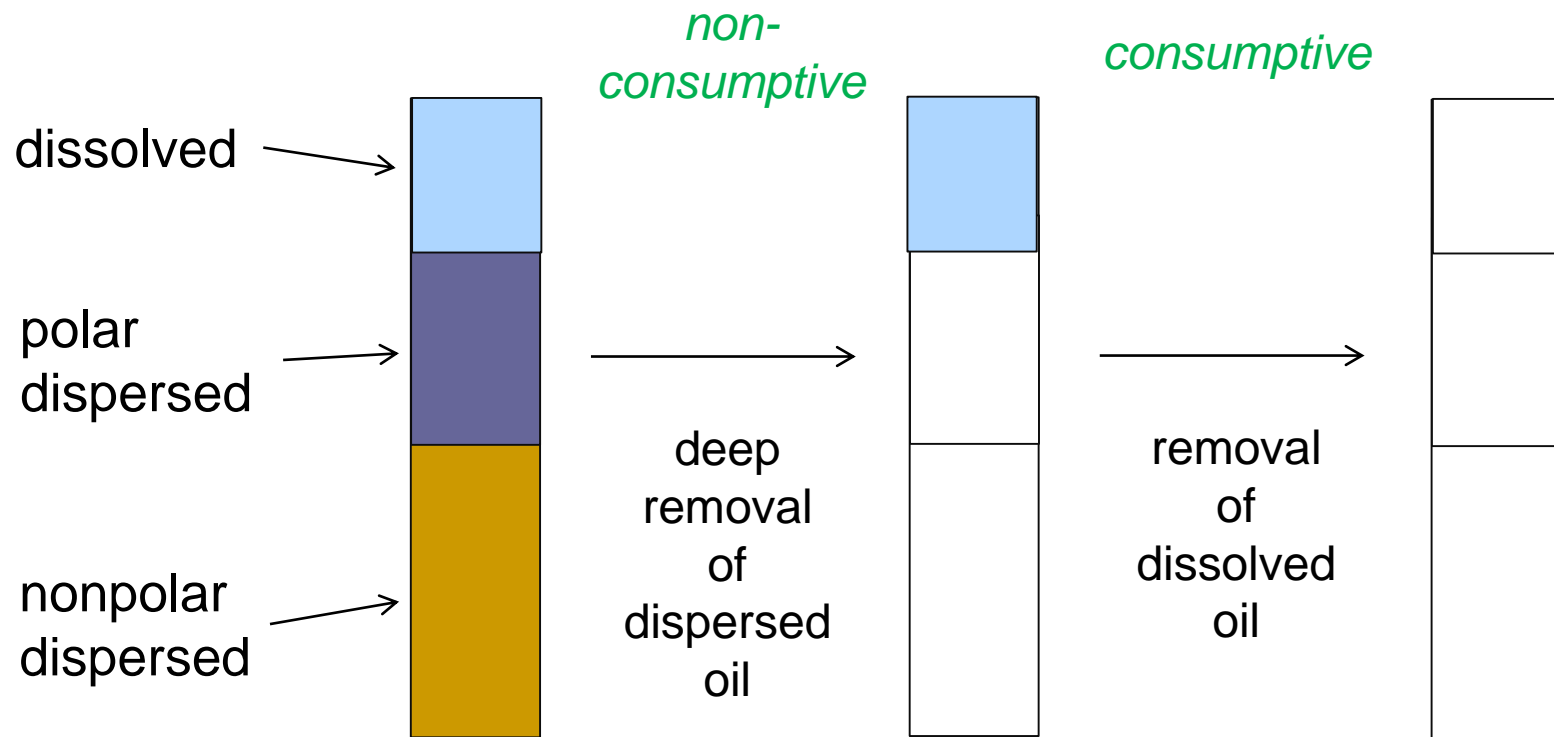


The diagram shows the acronym **WSO** in blue text on the right. Two blue arrows originate from the left side of the **WSO** text and point to the first two lines of the TOG definition: "organics dissolved in water" and "+ polar fraction of dispersed oil".

What is measured?

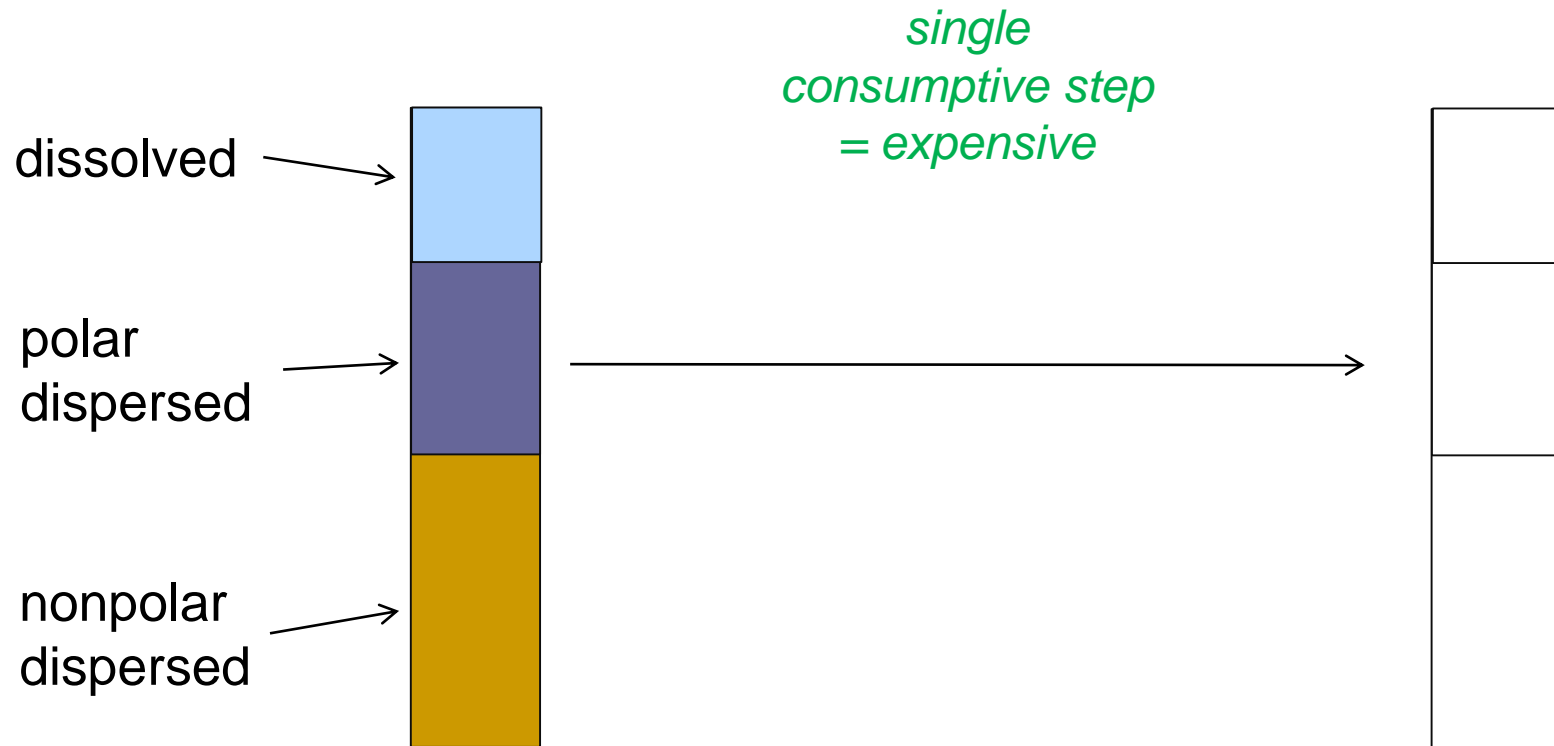


Why is this Important?



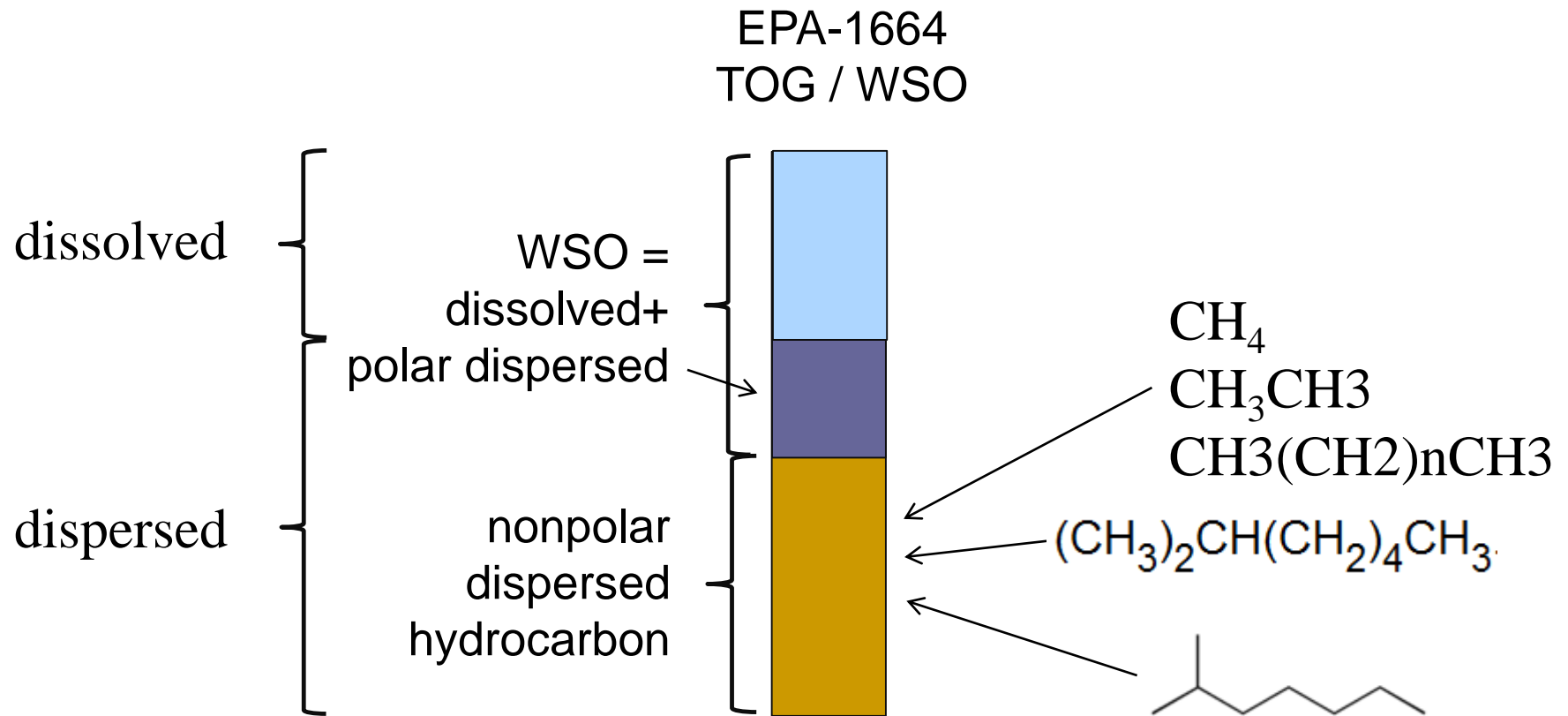
- If the client wants to remove TOG, then removal of dispersed oil is an effective approach.
- If the customer wants to remove WSO, then removal of dispersed oil by non-consumable media, is also effective. This may be followed by consumable media for deep removal of WSO. *This minimizes consumption of media.*

Why is this Important?



- By eliminating deep removal of dispersed oil, huge amounts of media will be consumed.
- So how well does deep removal of dispersed oil work?
- **How much of WSO is dissolved versus dispersed?**

What is measured – aliphatic (polar hydrocarbon):



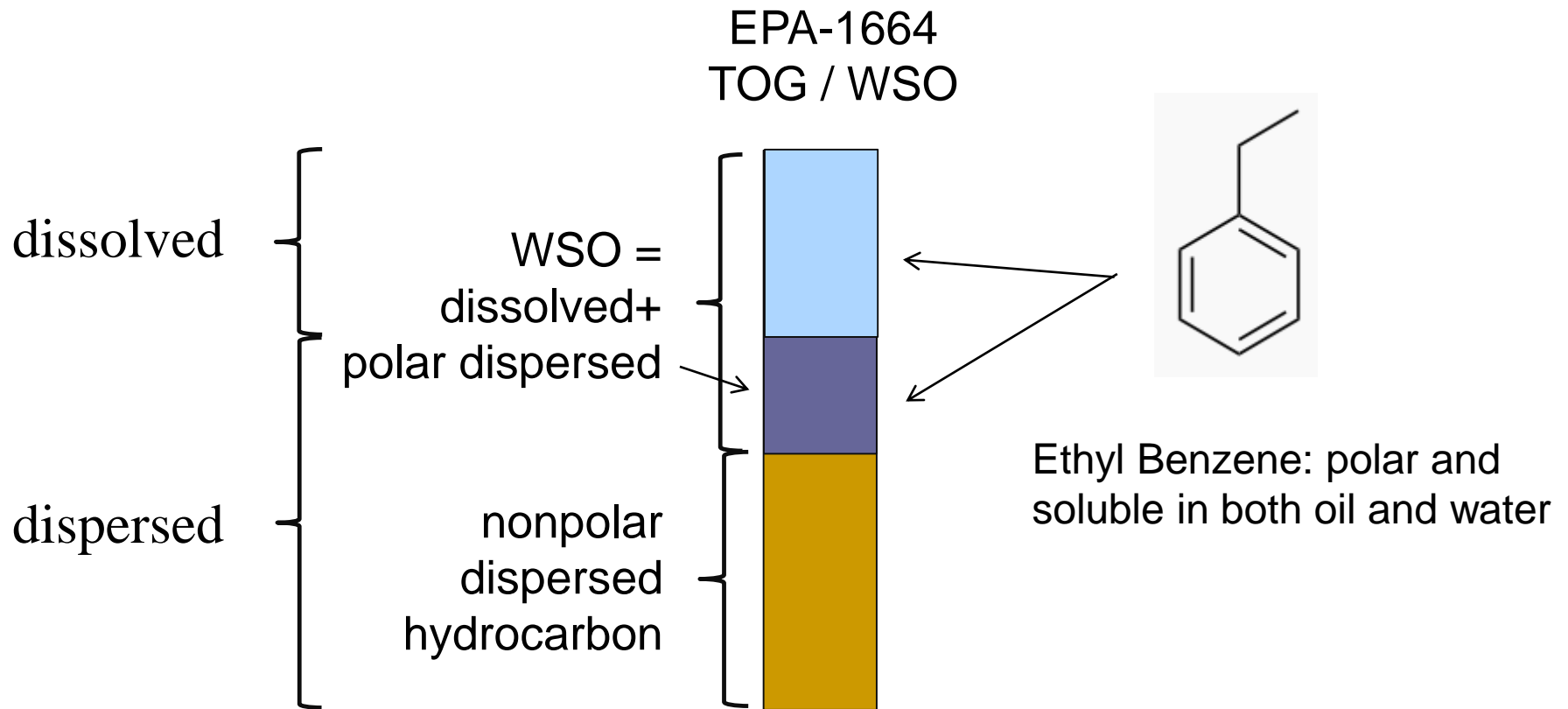
These are nonpolar hydrocarbons

They do not contribute to WSO

They have very low solubility in water

The only way to remove them is to remove the dispersed oil

What is measured – polar hydrocarbon:

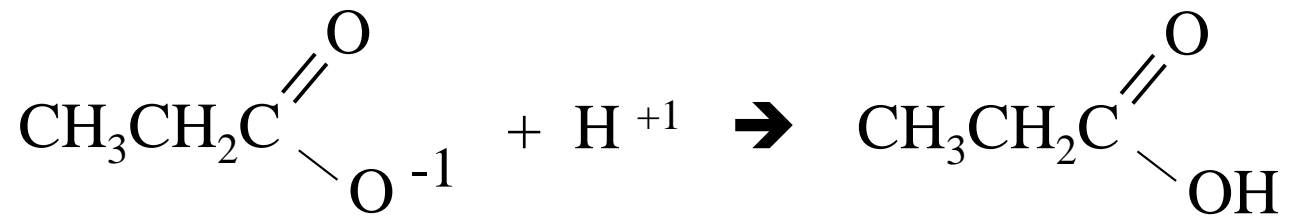


Remove dispersed oil =

Remove the aromatic hydrocarbon that is dissolved in the oil

But not the aromatic dissolved in the water

What is measured – acid:

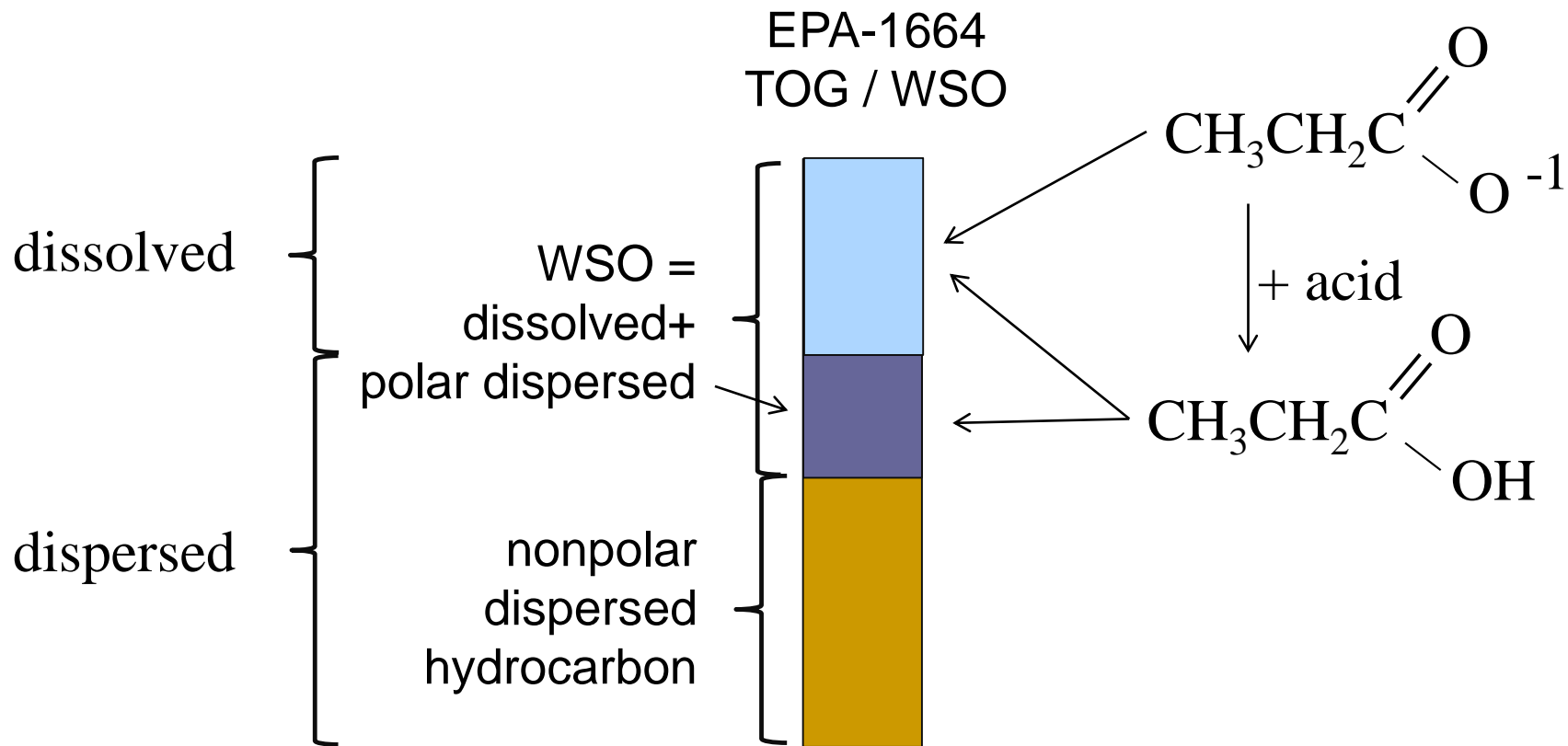


water soluble –
not soluble in oil

+ acid →

soluble in water
& soluble in oil

What is measured – acid:



Remove dispersed oil =

Remove the acid that is dissolved in the oil

But not the acid dissolved in water

First Application – Organic Acid:

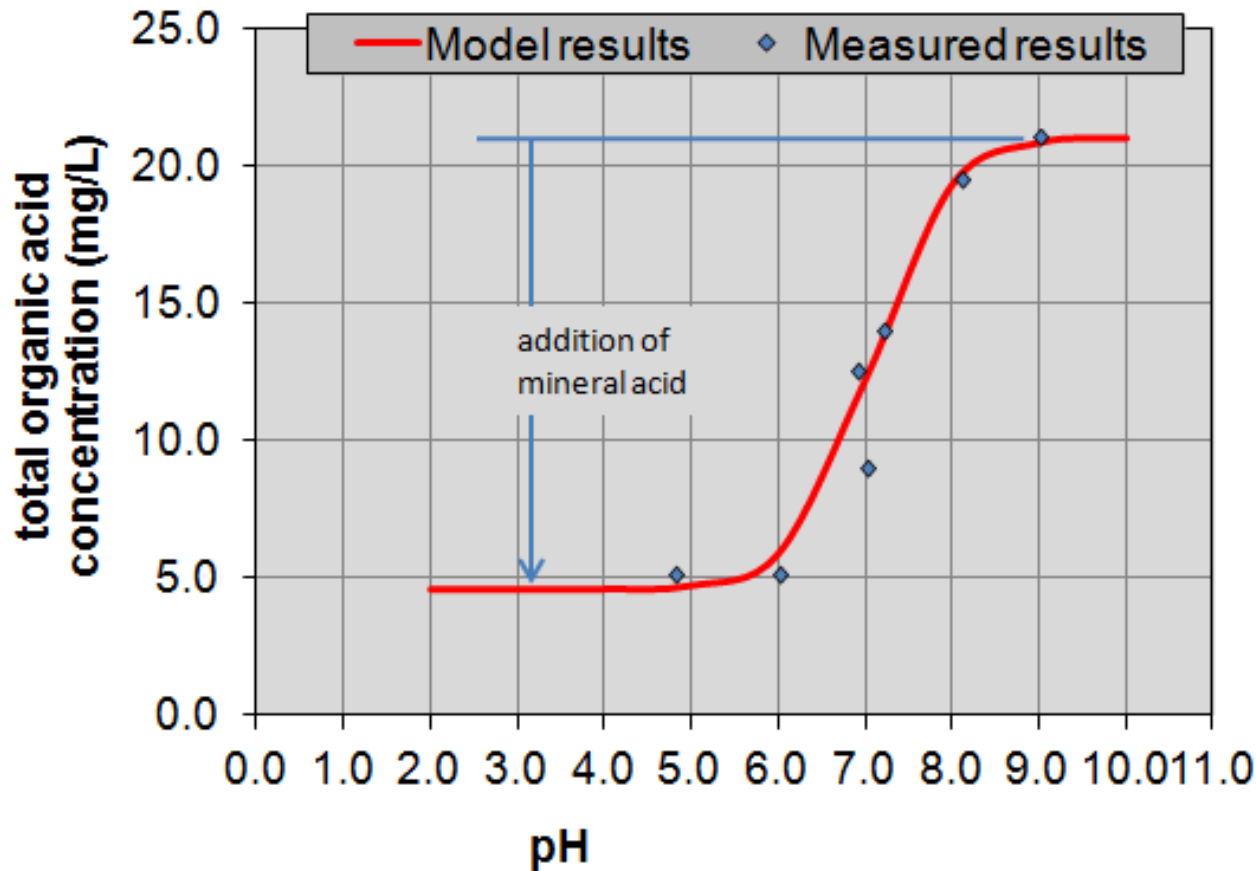
First Application:

An organic acid.

At low pH the acid is protonated (HA) and partitions between the oil and water phases.

At high pH the acid is unprotonated (A^{-1}) and has zero solubility in the oil phase.

Tuning the Model using Experimental Data:



Field data example of concepts discussed in previous slide:

At low pH, most of the acid becomes protonated and some of the protonated acid partitions into the oil phase.

$C_{10} - C_{20}$ acids

y-axis: protonated and unprotonated acid

y-axis: $[HA]_w + [A^{-1}]_w$

The parameters in the model (pK_a and k_{ow}) were adjusted in order to match the experimental data.

Ref.: J. McFarlane, "Modeling of Water Soluble Organic Content in Produced Water," Oak Ridge National Lab (2004)

Second Application – Nonionic WSO:

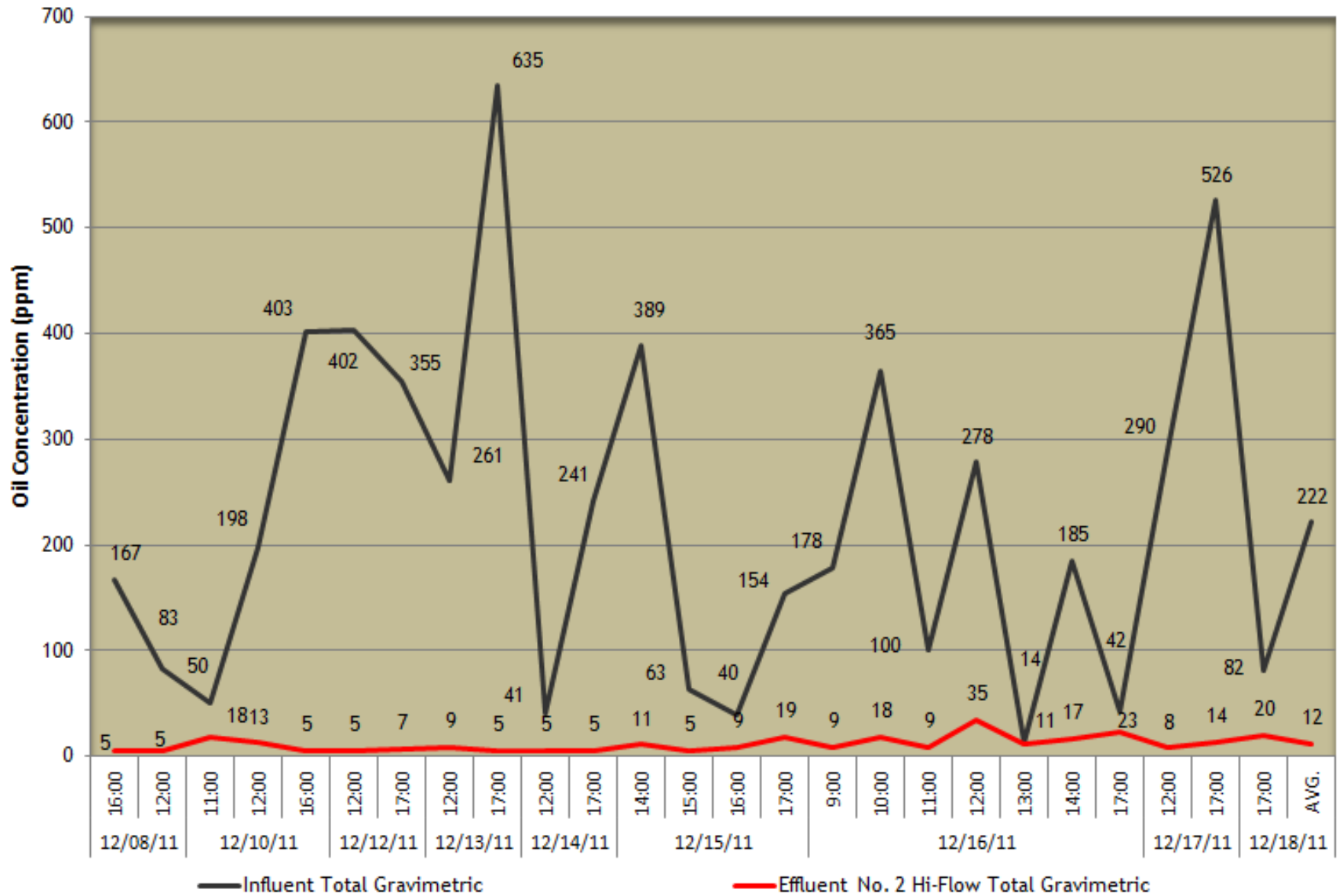
Second Application:

A polar non-ionic aggregate component (C) that partitions between the oil and the water phase (e.g. aromatics, alcohols).

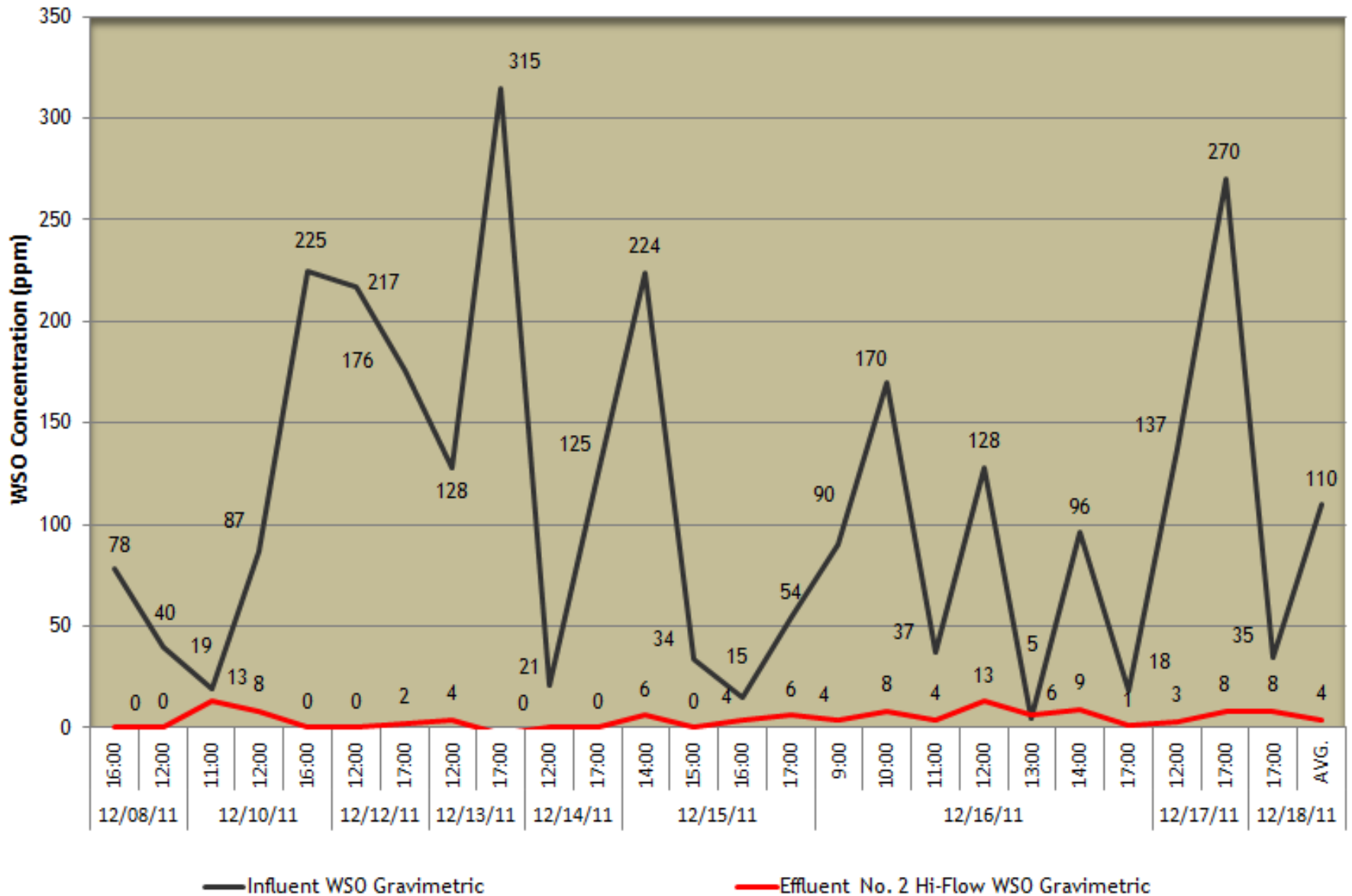
The concentration of this component is denoted as: [C].
[C]_o = mol/L in oil phase; [C]_w = mol/L in water phase.

A non-polar aggregate component is denoted as: [D].
It is not soluble in water.

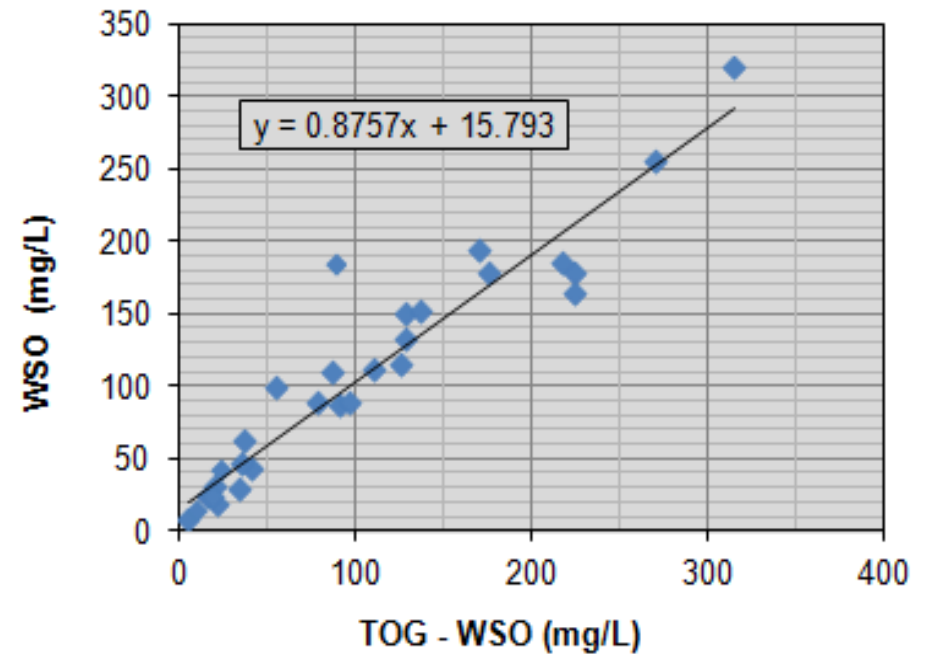
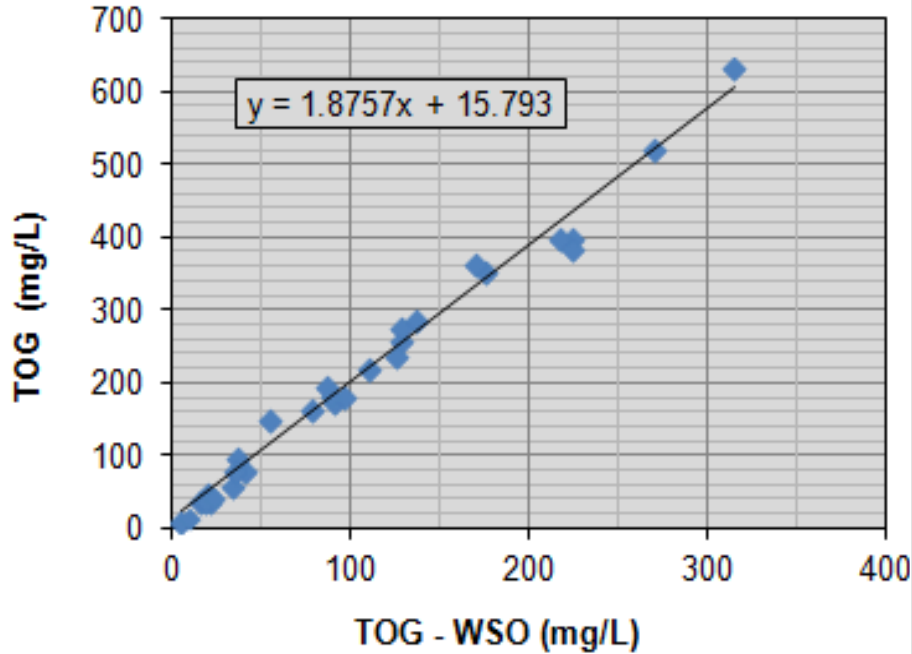
Case No.5 Total Oil Removal



No.5 Water Soluble Organics



Analysis of Field Data – Case 5



Note:

- 1) straight lines
- 2) difference in slopes = 1.0
- 3) same intercept

$$d[TOG] / dx - d[WSO] / dx = d([TOG] - [WSO]) / dx = 1$$

Two-Component Model:

$$[TOG] = ([C]_o + [D]_o)F_o + ([C]_w)F_w$$

$$[WSO] = ([C]_o)F_o + ([C]_w)F_w$$

$[C]_o$ = the concentration of the polar component in the oil phase (mol C/L oil)

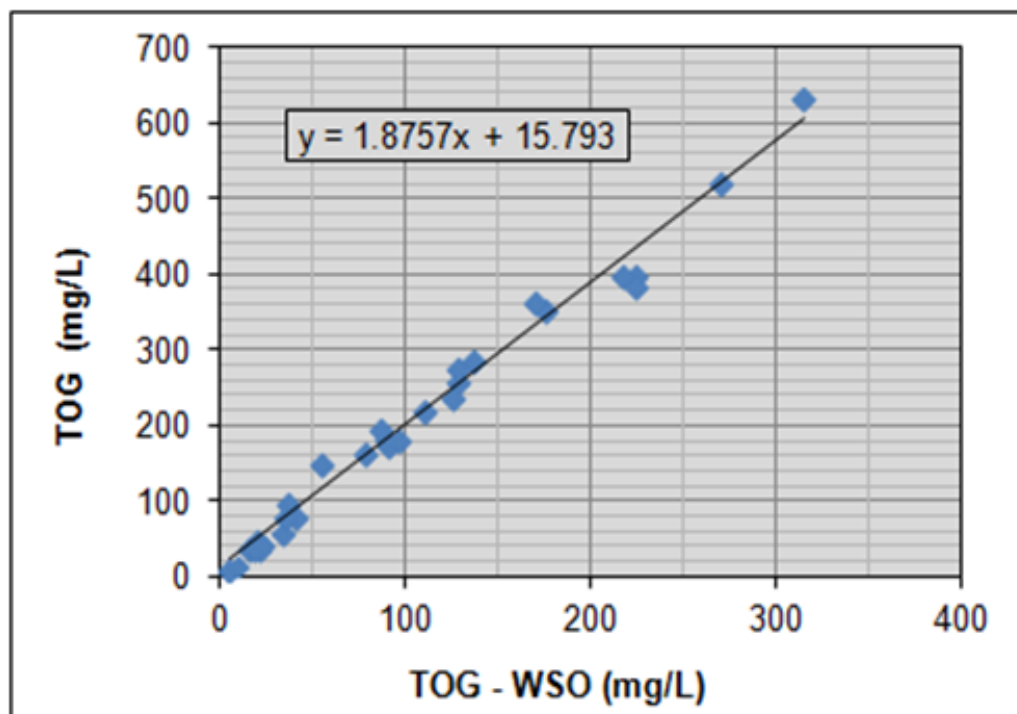
$[C]_w$ = the concentration of the polar component in the water phase (mol C/L water)

$[D]_o$ = the concentration of the nonpolar component in the oil phase (mol D/L oil)

After some math:

$$x = [TOG] - [WSO]$$

$$[TOG] = (1 + [C]_o / [D]_o)x + ([C]_w)F_w$$



slope of TOG line = $1 + [C]_o / [D]_o$

intercept of TOG line = $[C]_w$

Two-Component Model:

$$[TOG] = ([C]_o + [D]_o)F_o + ([C]_w)F_w$$

$$[WSO] = ([C]_o)F_o + ([C]_w)F_w$$

$[C]_o$ = the concentration of the polar component in the oil phase (mol C/L oil)

$[C]_w$ = the concentration of the polar component in the water phase (mol C/L water)

$[D]_o$ = the concentration of the nonpolar component in the oil phase (mol D/L oil)

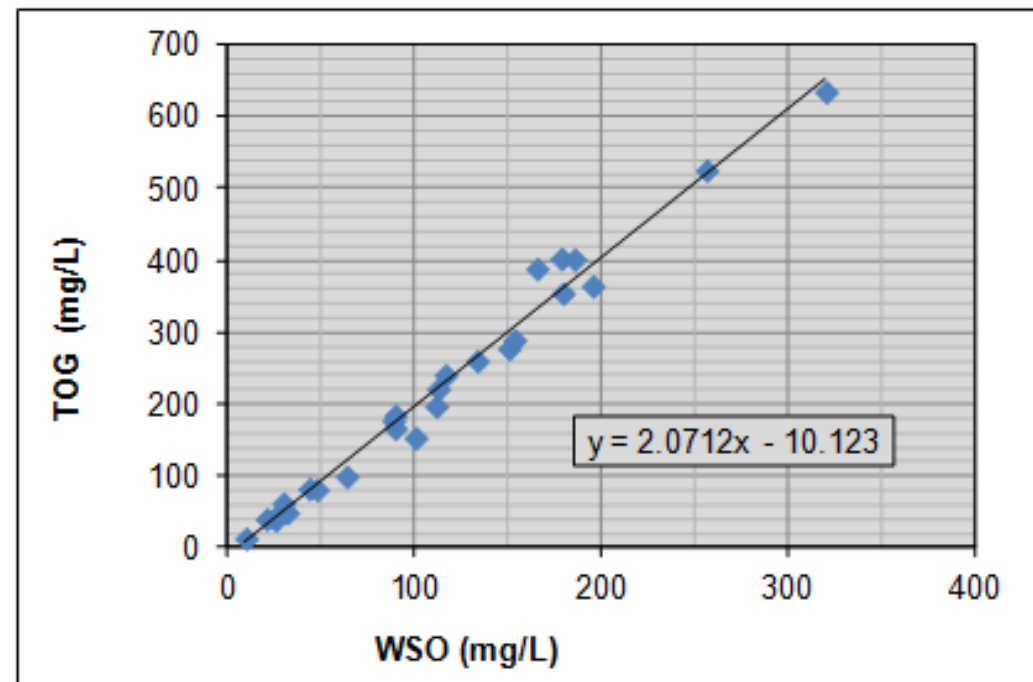
After some math:

$$x = [WSO]$$

$$\text{slope TOG line} = 1 + [D]_o / [C]_o$$

$$\text{intercept of TOG line} = - [D]_o / k_{owC}$$

$$[TOG] = (1 + ([D]_o / [C]_o))x - F_w [D]_o / k_{owC}$$



Two Component Model – Application to Field Data

Parameters in the Two-Component Model:

$[C]_o$ = the concentration of the polar component in the oil phase (mol C/L oil)

$[C]_w$ = the concentration of the polar component in the water phase (mol C/L water)

$[D]_o$ = the concentration of the nonpolar component in the oil phase (mol D/L oil)

Parameters obtained from plots of the field data.

α_1 = slope of C_{TOG} vs $C_{TOG} - C_{WSO}$ (dimensionless)

α_2 = intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$ (mg C/L water)

α_3 = intercept of C_{TOG} vs C_{WSO} (mg/L)

α_4 = ρ_{go} / M_o (mol oil / L oil)

Where:

C_{TOG} = the mass concentration of TOG (mg TOG/liter oily water)

C_{WSO} = the mass concentration of WSO (mg WSO/liter oily water)

ρ_{go} = measured gravimetric density of the oil (gr oil/L oil)

M_o = measured molecular weight of the oil (gr oil/mol oil)

Parameter Values:

$[C]_o$ = $\alpha_4 (\alpha_1 - 1) / \alpha_1$ (mol C / L oil)

$[C]_w$ = $(\alpha_1 - 1) \alpha_3 / (M_o \times 1000)$ (mol C / L water)

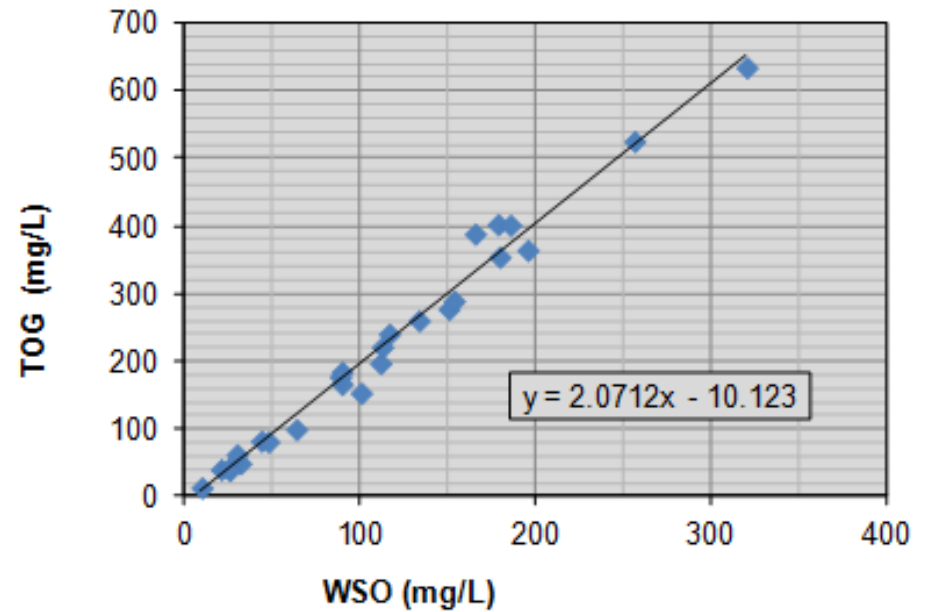
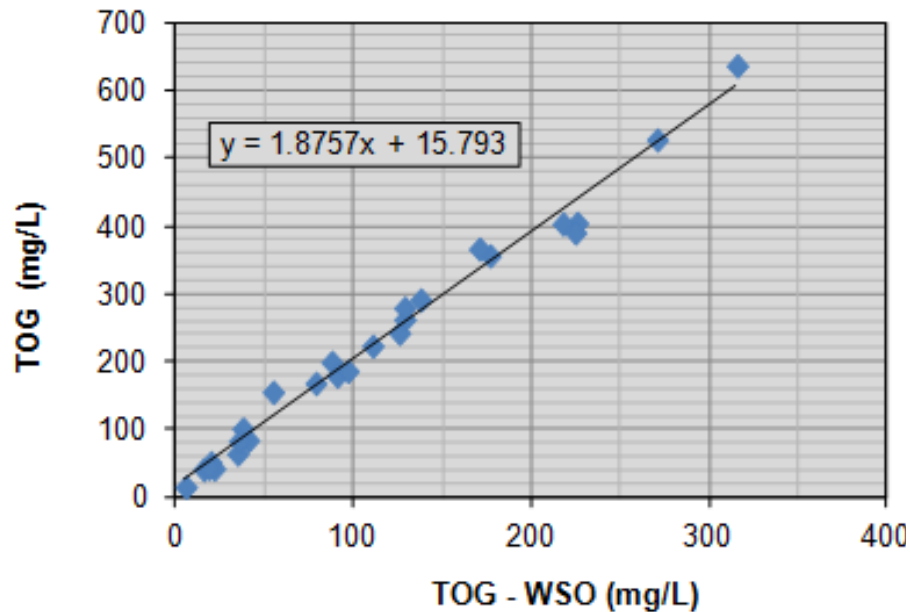
$[D]_o$ = α_4 / α_1 (mol D / L oil)

k_{owC} = $-(\alpha_4 / \alpha_1 \alpha_3) \times (M_o \times 1000)$ (mol C / L oil) / (mol C / L water)

M_C = $\alpha_2 / (1000 \times [C]_w)$ (gr C / mol C)

M_D = $(\rho_{go} - M_C \times [C]_o) / [D]_o$ (gr D / mol D)

Model Application – Case 5



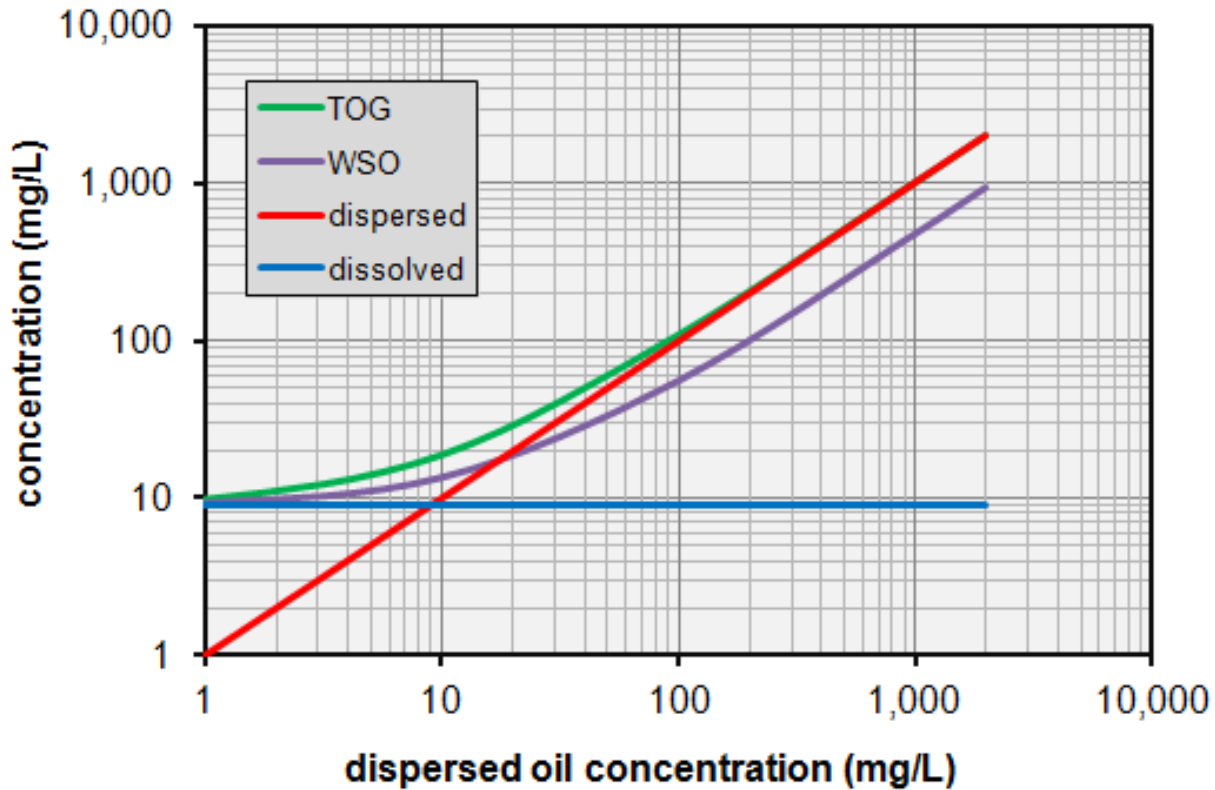
- α_1 = slope of C_{TOG} vs $C_{TOG} - C_{WSO}$
- α_2 = intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$
- α_3 = intercept of C_{TOG} vs C_{WSO}
- α_4 = ρ_{go} / M_o

α_1	1.876
α_2	15.793
α_3	-10.123
ρ_{go}	860
M_o	300
α_4	2.9

[C] _o	1.34
[D] _o	1.53
k _{ow} C	4.529E+04
[C] _w	2.955E-05

Mc	534.5
Md	94.68

Model Application – Case 5



Curves are calculated using the model.

Model is based on previous slide field data.

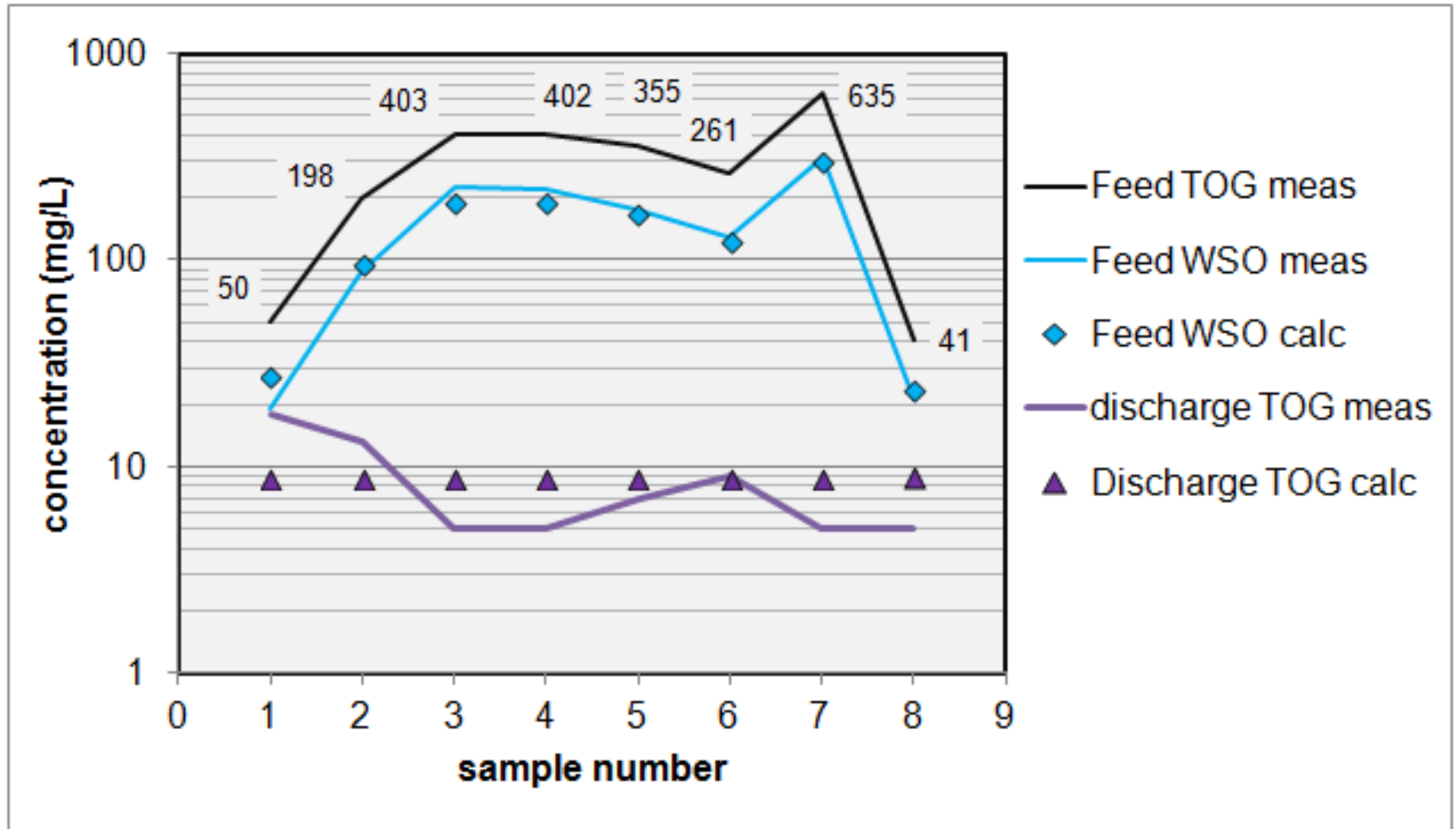
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green = red + blue

TOG and WSO are calculated as a function of the dispersed oil concentration.

It shows that removal of dispersed oil also removes most of the WSO.

Field data confirm that after Hi-Flow removal of dispersed oil, TOG & WSO are in the range of 0 to 13 mg/L

Model Application – Case 5



Reality Check – Partition Coefficients

Table 1. List of Alkyl Phenols Used To Evaluate Zero Discharge Crudesorb ® Removal Efficiency

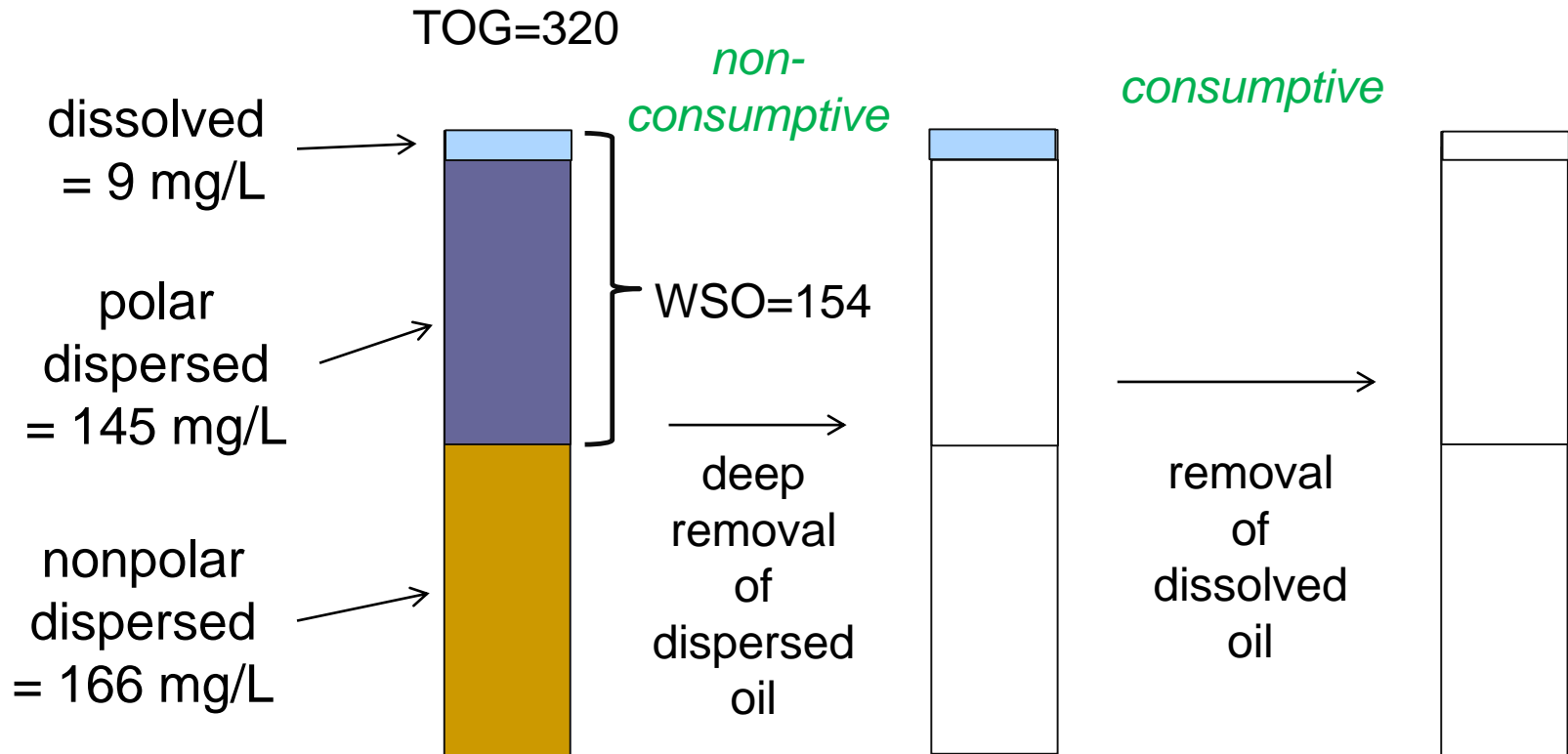
Chemical Name	CAS Number	Octanol Water Partition Coefficient log Kow (12)	Formula
C1			
o-cresol	95-48-7	1.97-2.03	CH ₃ C ₆ H ₄ OH
p-cresol	106-44-5	1.62-2.06	CH ₃ C ₆ H ₄ OH
C2			
2-ethylphenol	90-00-6	2.43-2.51	C ₂ H ₅ C ₆ H ₄ OH
4-ethylphenol	123-07-9	2.39-2.58	C ₂ H ₅ C ₆ H ₄ OH
C3			
2-propylphenol	644-35-9	3.21-3.25	CH ₃ CH ₂ CH ₂ C ₆ H ₄ OH
4-propylphenol	645-56-7	3.18-3.30	CH ₃ CH ₂ CH ₂ C ₆ H ₄ OH
C4			
4-tert-butylphenol	98-54-4	3.04-3.31	(CH ₃) ₃ CC ₆ H ₄ OH
C5			
4-tert-amylphenol	80-46-6	3.72-3.96	C ₂ H ₅ C(CH ₃) ₂ C ₆ H ₄ OH
C6			
2,6-diisopropylphenol	2078-54-8	3.96-4.03	[(CH ₃) ₂ CH] ₂ C ₆ H ₃ OH
C8			
4-octylphenol	1806-26-4	4.12-4.18	CH ₃ (CH ₂) ₇ C ₆ H ₄ OH
C9			
4-nonylphenol	84852-15-3	4.20-6.36	C ₉ H ₁₉ C ₆ H ₄ OH

Measured partition coefficients are consistent with model predictions.

Table 1 – Log P (Heptane/Water) for H(CH₂)_nCOOX

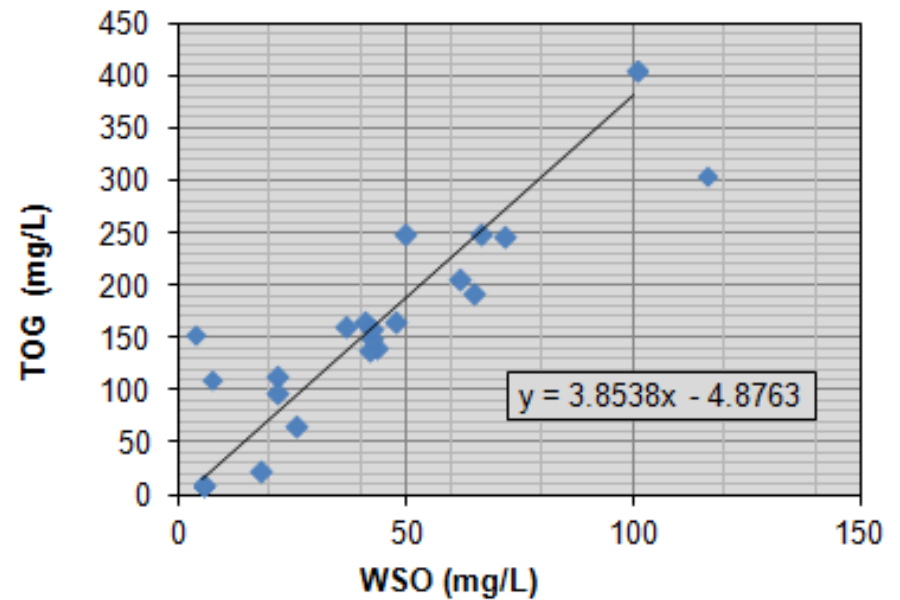
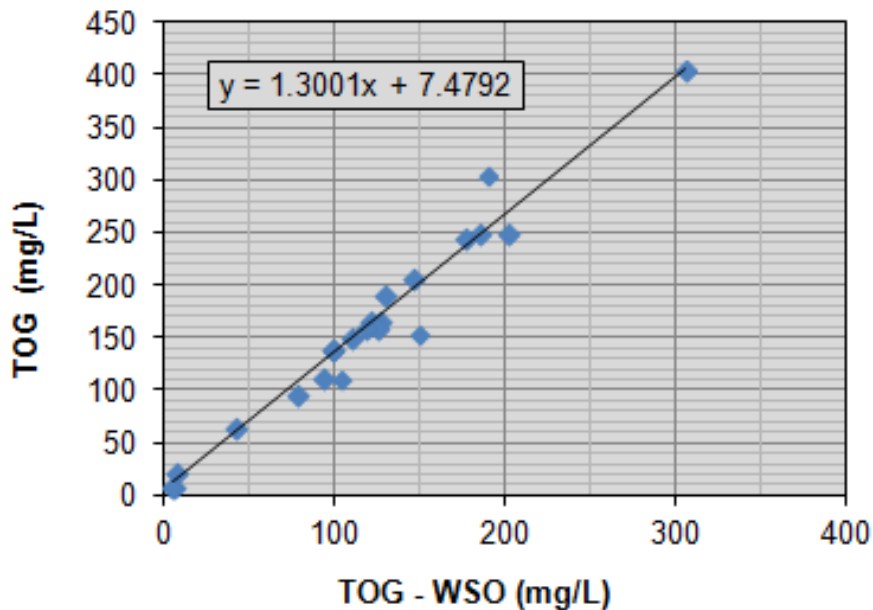
n	X=Na	X=H	X=H:HOOC(CH ₂) _n H
0	-20.76	-3.72	-2.02
1	-20.15	-3.11	-1.41
2	-19.53	-2.49	-0.79
3	-18.92	-1.88	-0.18
4	-18.31	-1.27	0.43
5	-17.70	-0.66	1.04
6	-17.09	-0.05	1.65
7	-16.47	0.57	2.27
8	-15.86	1.18	2.88
9	-15.25	1.79	3.49
10	-14.64	2.40	4.10

Why is this Important?



➤ *This minimizes consumption of media.*

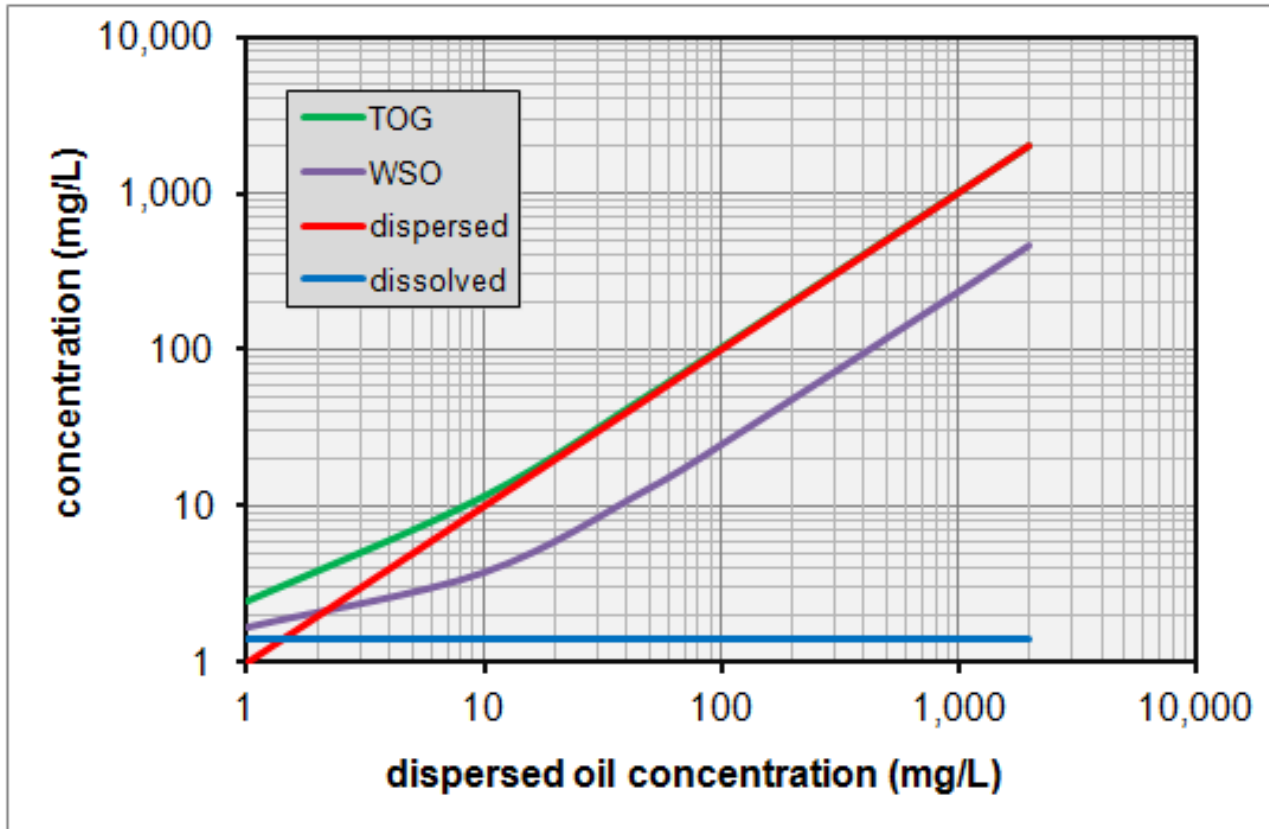
Model Application – Case 4



- α_1 = slope of C_{TOG} vs $C_{TOG} - C_{WSO}$
- α_2 = intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$
- α_3 = intercept of C_{TOG} vs C_{WSO}
- α_4 = ρ_{go} / M_o

α_1	1.3000
α_2	7.4792
α_3	-4.8763
ρ_{go}	800
M_o	200
α_4	4.0
$[C]_o$	0.92
$[D]_o$	3.08
k_{owC}	1.262E+05
$[C]_w$	7.314E-06

Model Application – Case 4



Curves are calculated using the model

Model is based on previous slide field data

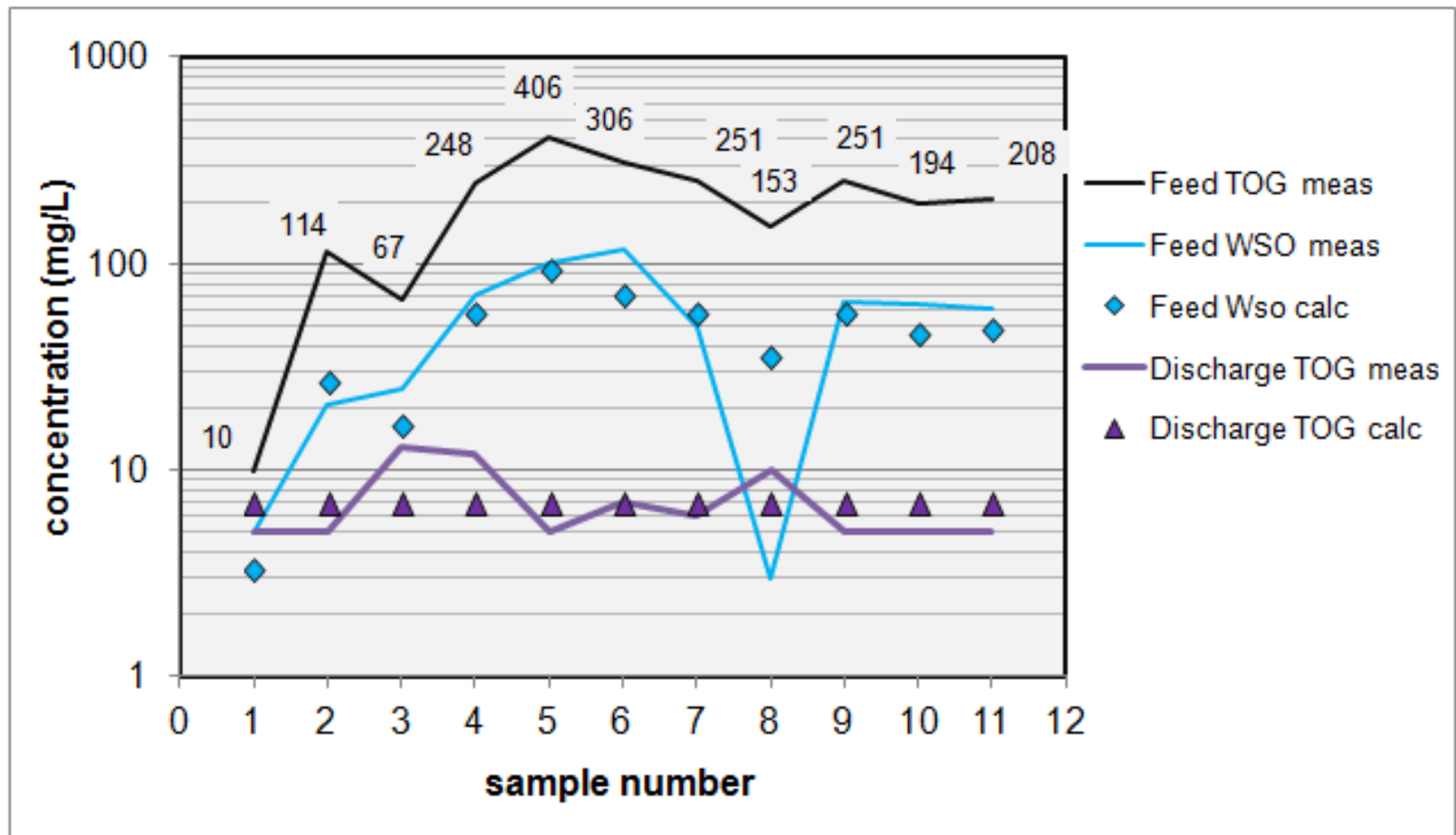
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Model Application – Case 4



Conclusions:

- 1) The modeling suggests that the following quantities can be understood:
 - a) TOG
 - b) WSO
 - c) dissolved oil
 - d) dispersed oil

With an understanding of these components, a more effective strategy for addressing WSO can be developed on a platform-by-platform basis.

- 2) The Model should be tested using synthetic mixtures of non-polars, acids, and aromatics. All four quantities should be measured and compared with the model predictions.
- 3) The model suggests that there may be significantly different types of WSO.
- 4) If correct, the model indicates that WSO in some systems / produced water chemistries can be treated by deep removal of dispersed oil, which can then be followed by consumptive removal of a small concentration of dissolved oil.