Modeling Water Soluble Organics

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Upstream **Engineering** Centre

bp

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

Objectives of this Study:

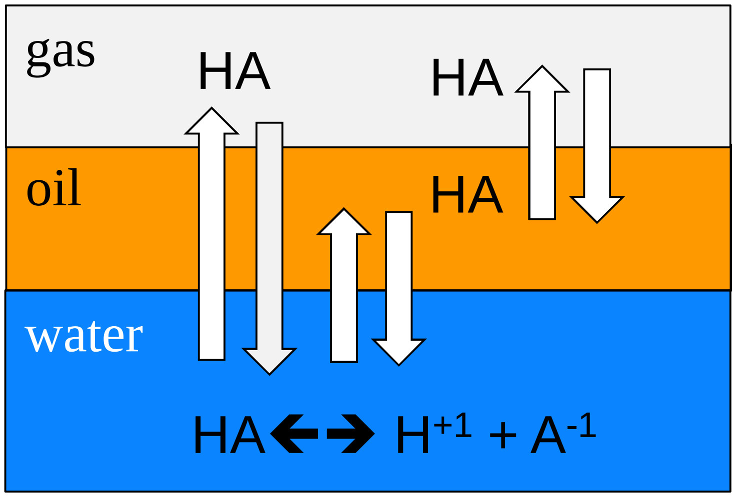
1) Develop a model that captures the chemical characteristics of “water soluble organics”

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)

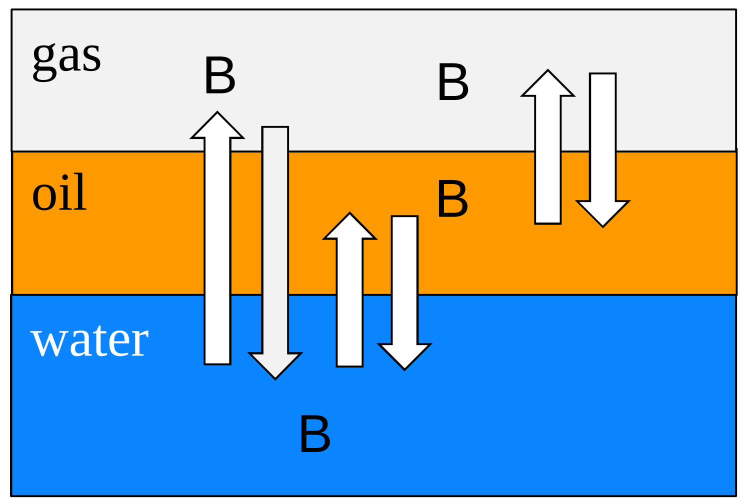
Physical Picture of Partitioning and Chemical Equilibria of “Water Soluble Organics”

General Case of an Acid (HA):



Chemical and Phase Equilibria

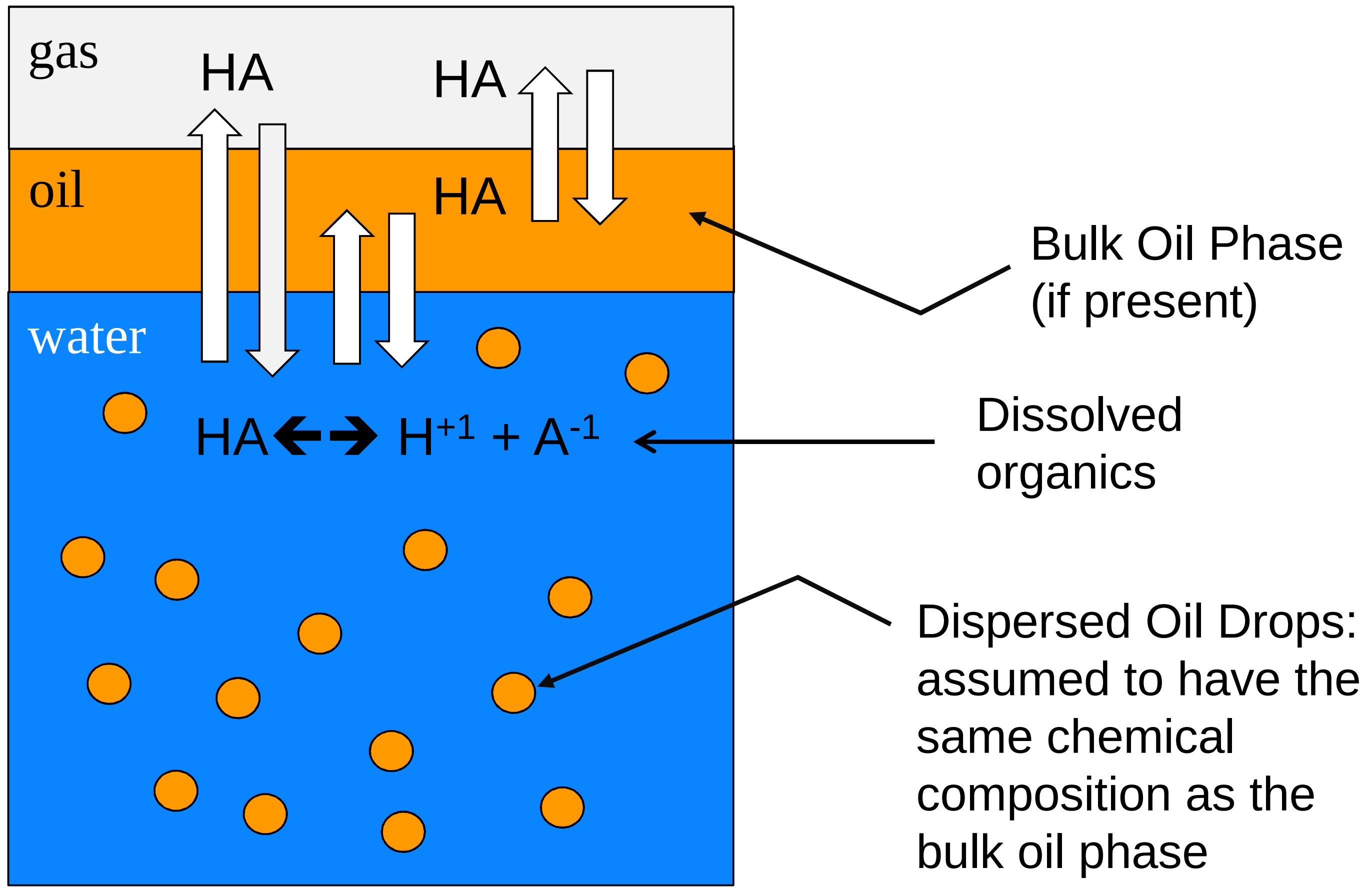
Specific Case of a non-ionic component such as an alcohol or an aromatic:



No chemical Equilibria

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).

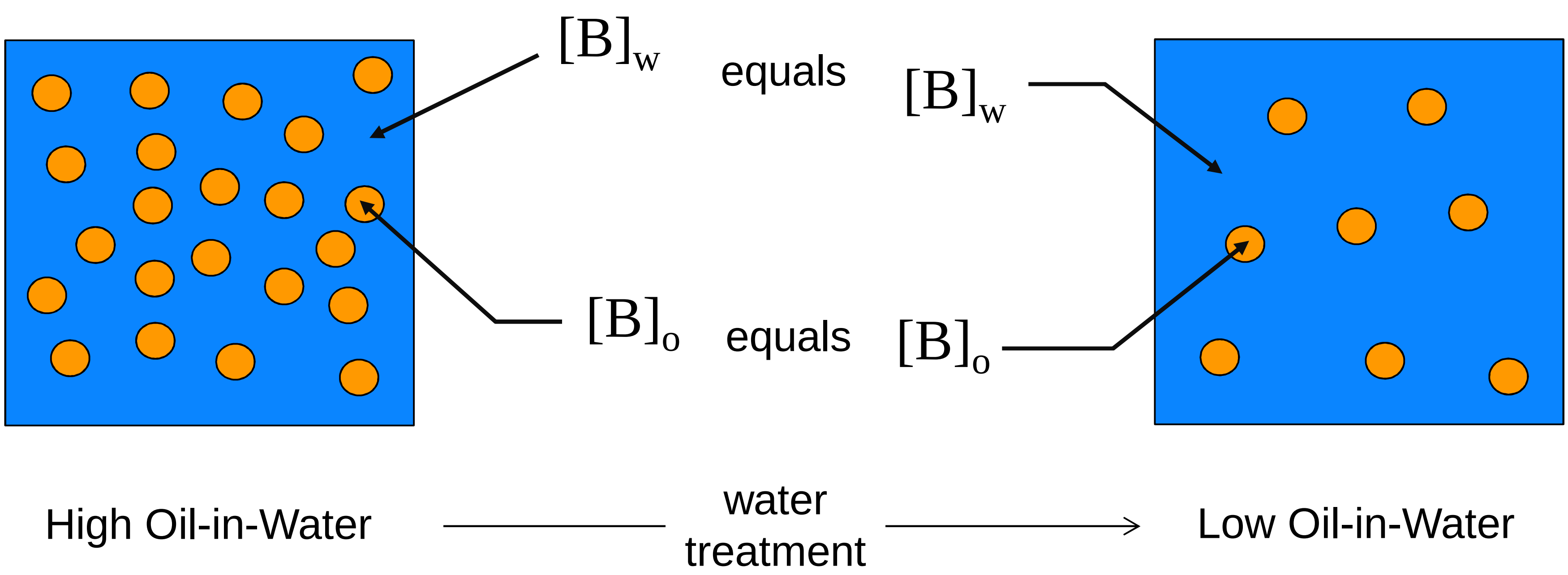
Physical Picture of Non-Ionic WSO:

B is a WSO compound. It is partially soluble in both water and in oil.

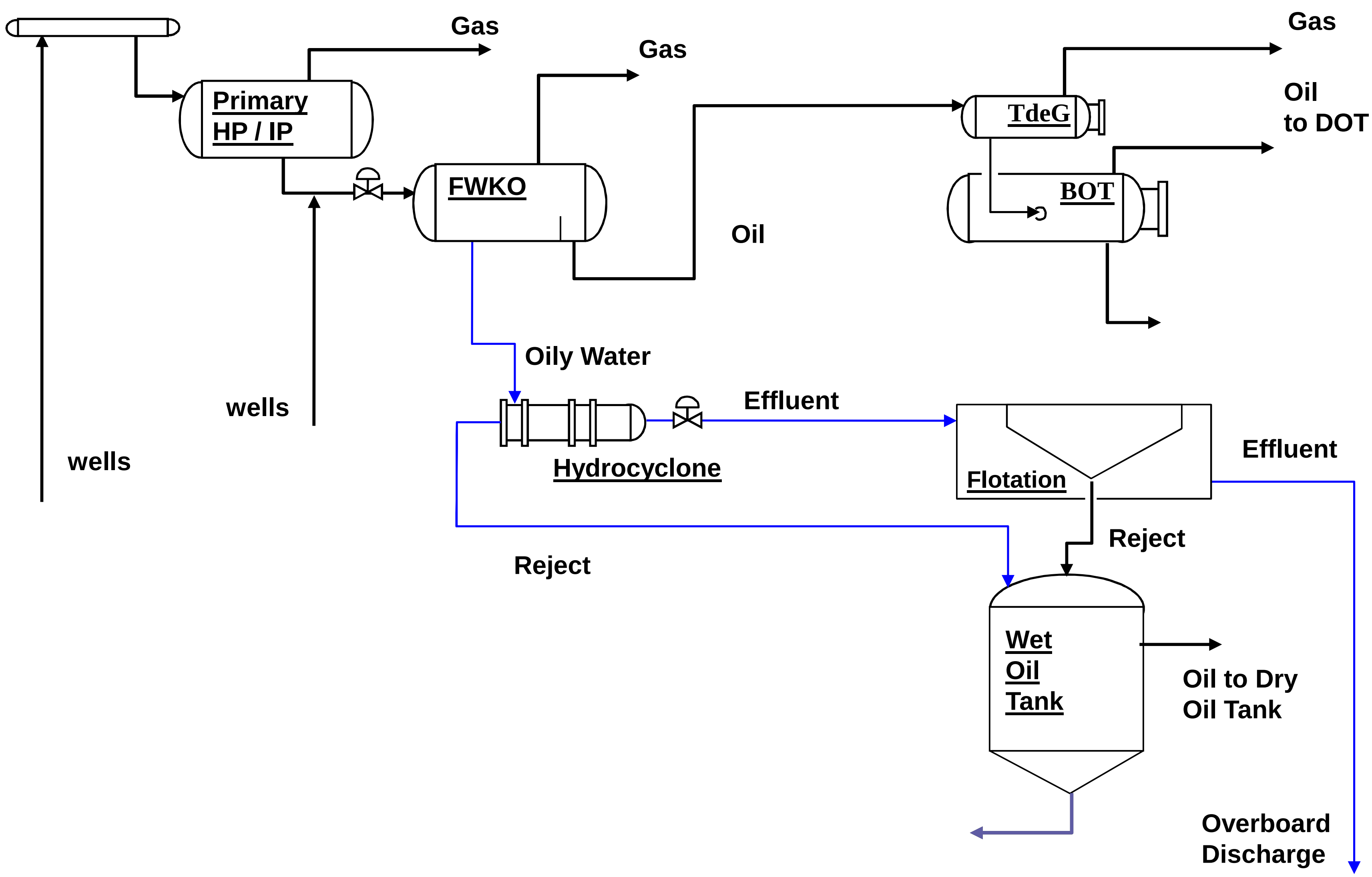
Consider some hypothetical water treatment process that can remove dispersed oil-in-water such that the concentration of B in water $[B]_w$ and B in oil $[B]_o$ do not change.

How will the WSO change?

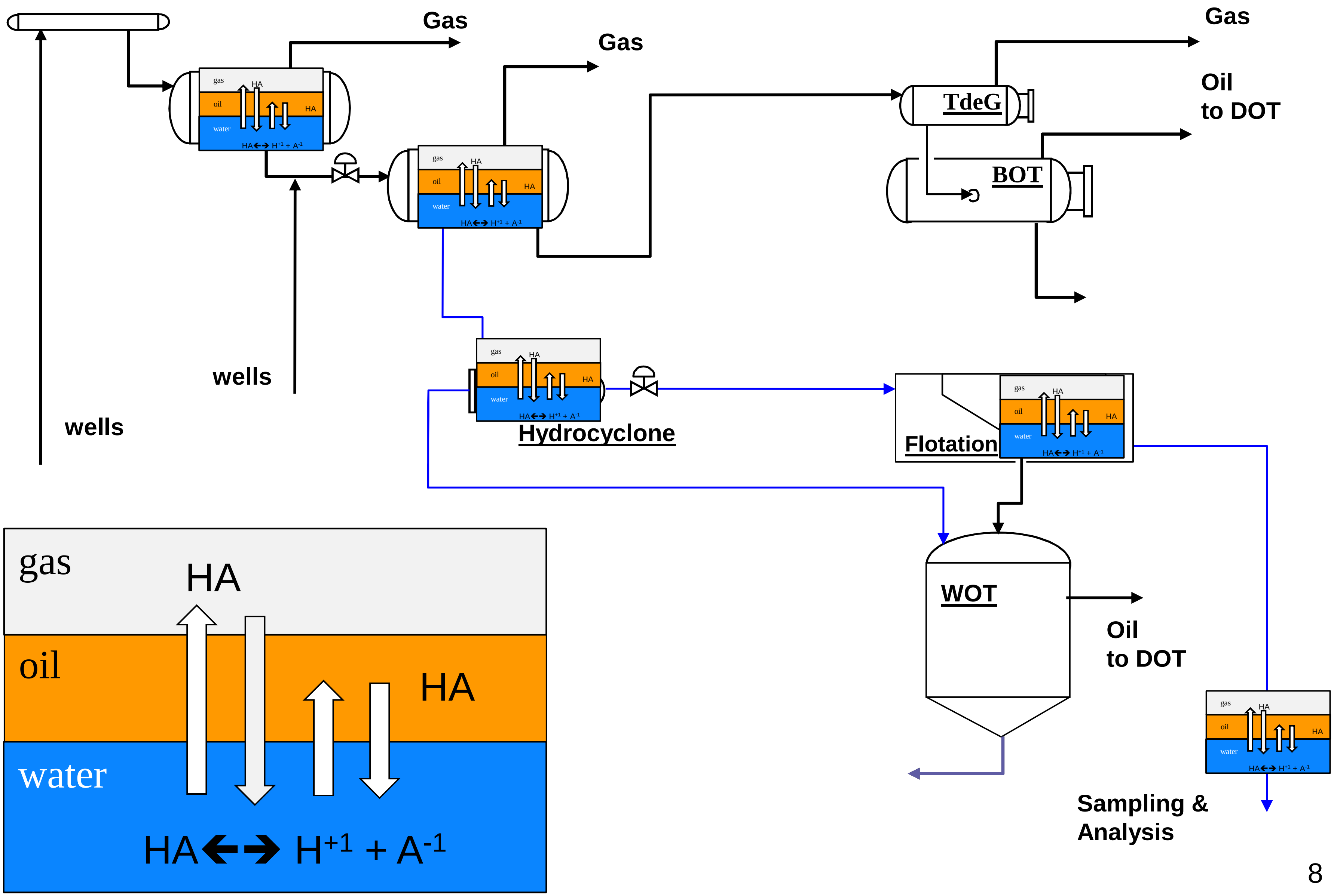
Yes, perhaps significantly.



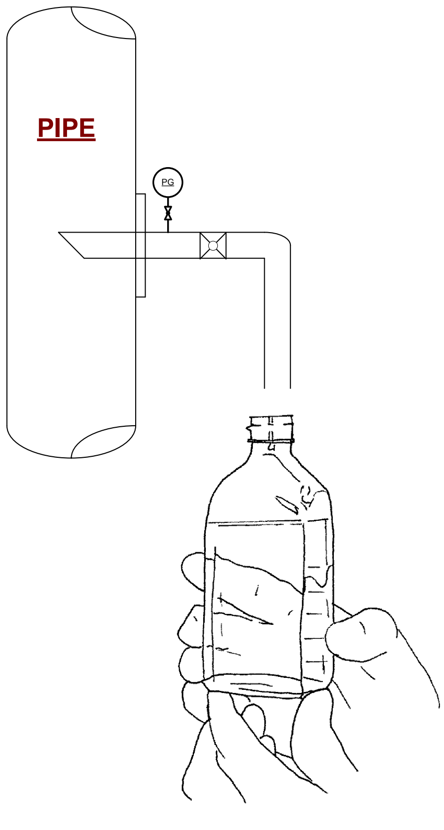
Typical Facilities Process Flow Diagram



Facilities Process Flow Diagram / Model Application



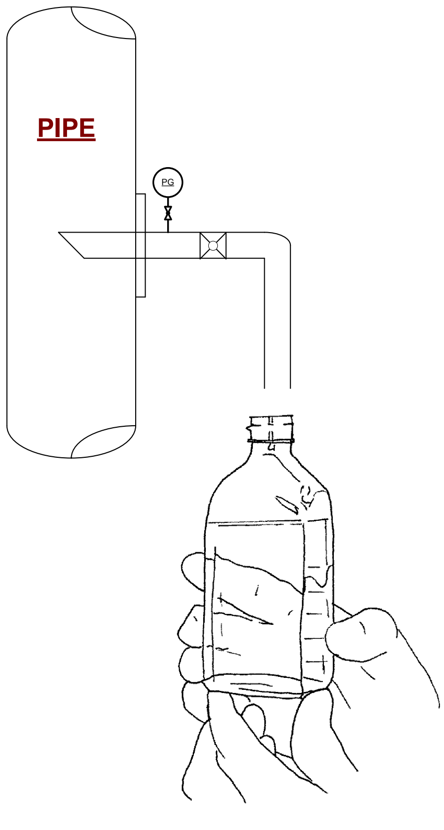
Sampling & Analysis – Model Application:

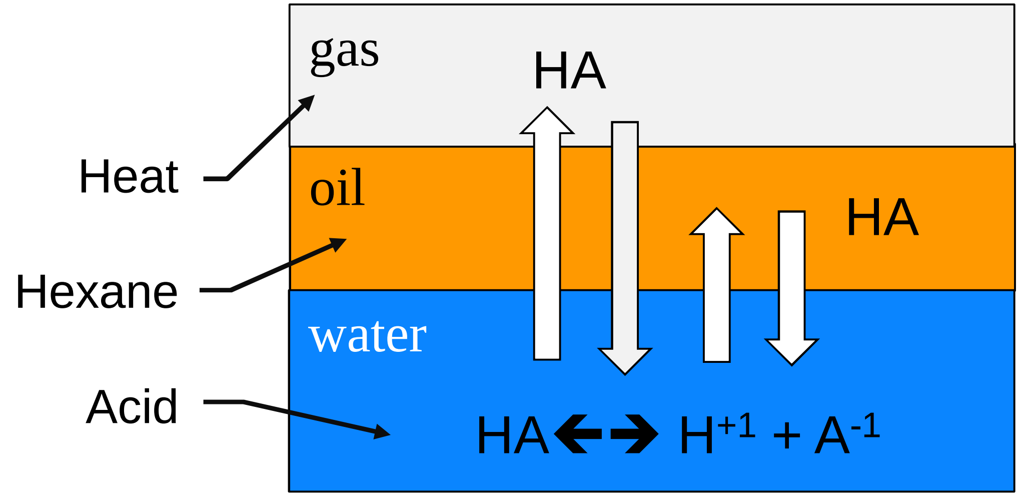


Sample + Acid + Hexane ➔ Measure

heat

Sampling & Analysis – Model Application:





Sample + Acid + Hexane ➔ Measure

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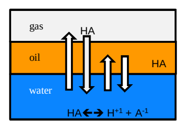
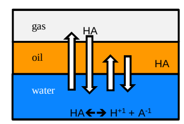
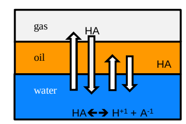




The Model (in words):

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.

The Model (equations) – Chemical Equilibrium:

$$HA \Leftrightarrow H^{+1} + A^{-1}$$

$$K_d = \frac{[H^{+1}][A^{-1}]}{[HA]_w}$$

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

$[A^{-1}]$ = concentration of anion in the water phase (mol/L)

The equilibrium constant K_d depends on temperature.

Note that the concentration of protons and anions are assumed to be zero in the oil and gas phases.

Dimerization in the gas phase is not accounted for.

Also note that many of the components considered in this work do not dissociate. In that case, chemical equilibria is not included in the equations of material balance and phase equilibrium.

The Model – Phase Equilibrium:

Phase Equilibrium: → Defining the Partition Coefficients:

Gas/Oil:

$$[\mathrm{HA}]_g \varphi_1 P / \rho_g = [\mathrm{HA}]_o \gamma_1^o P_1^{sat} / \rho_o$$

Water/Oil:

$$[\mathrm{HA}]_w \gamma_1^w P_1^{sat} / \rho_w = [\mathrm{HA}]_o \gamma_1^o P_1^{sat} / \rho_o$$

Gas/Water:

$$[\mathrm{HA}]_g \varphi_1 P / \rho_g = [\mathrm{HA}]_w \gamma_1^w P_1^{sat} / \rho_w$$

Gas/Oil:

$$k_{g/o} = [\mathrm{HA}]_g / [\mathrm{HA}]_o = \gamma_1^o P_1^{sat} \rho_g / \varphi_1 P \rho_o$$

Water/Oil:

$$k_{w/o} = [\mathrm{HA}]_w / [\mathrm{HA}]_o = \gamma_1^o \rho_w / \gamma_1^w \rho_o$$

Gas/Water:

$$k_{g/w} = [\mathrm{HA}]_g / [\mathrm{HA}]_w = \gamma_1^w P_1^{sat} \rho_g / \varphi_1 P \rho_w$$

Note that the components considered in this work are at low concentration compared to the main components of the oil, gas, and water. Thus, these components do not affect the phase volumes. Therefore, flash calculations are not required.

The Model – Material Balance:

The material balance equation is written below for a particular component (HA):

$$[\mathrm{HA}]^0 F_T = [\mathrm{HA}]_w F_w + [\mathrm{A}^{-1}] F_w + [\mathrm{HA}]_o F_o + [\mathrm{HA}]_g F_g$$

$[\mathrm{HA}]^0 F_T$ = the total moles of HA in a sample

$[\mathrm{HA}]_w$ = concentration of HA in the water phase (mol/L)

$[\mathrm{A}^{-1}]$ = concentration of anion in the water phase (mol/L)

$[\mathrm{HA}]_o$ = concentration of HA in the oil phase (mol/L)

$[\mathrm{HA}]_g$ = concentration of HA in the gas phase (mol/L)

F_w = water volume (L)

F_o = oil volume (L)

F_g = gas volume (L)

Summary of Model Calculations:

For each component of interest, 5 equations are solved:

Material balance: $$[\mathrm{HA}]^0 F_T = [\mathrm{HA}]_w F_w + [\mathrm{A}^{-1}] F_w + [\mathrm{HA}]_o F_o + [\mathrm{HA}]_g F_g$$

Phase partitioning:

Gas/Oil:

$$k_{g/o} = [\mathrm{HA}]_g / [\mathrm{HA}]_o$$

Water/Oil:

$$k_{w/o} = [\mathrm{HA}]_w / [\mathrm{HA}]_o$$

Gas/Water:

$$k_{g/w} = [\mathrm{HA}]_g / [\mathrm{HA}]_w$$

Dissociation: $$\mathrm{HA} \Leftrightarrow \mathrm{H}^{+1} + \mathrm{A}^{-1}$$

$$K_d = \frac{[\mathrm{H}^{+1}][\mathrm{A}^{-1}]}{[\mathrm{HA}]_w}$$

An iterative numerical procedure is used.

Model Applications:

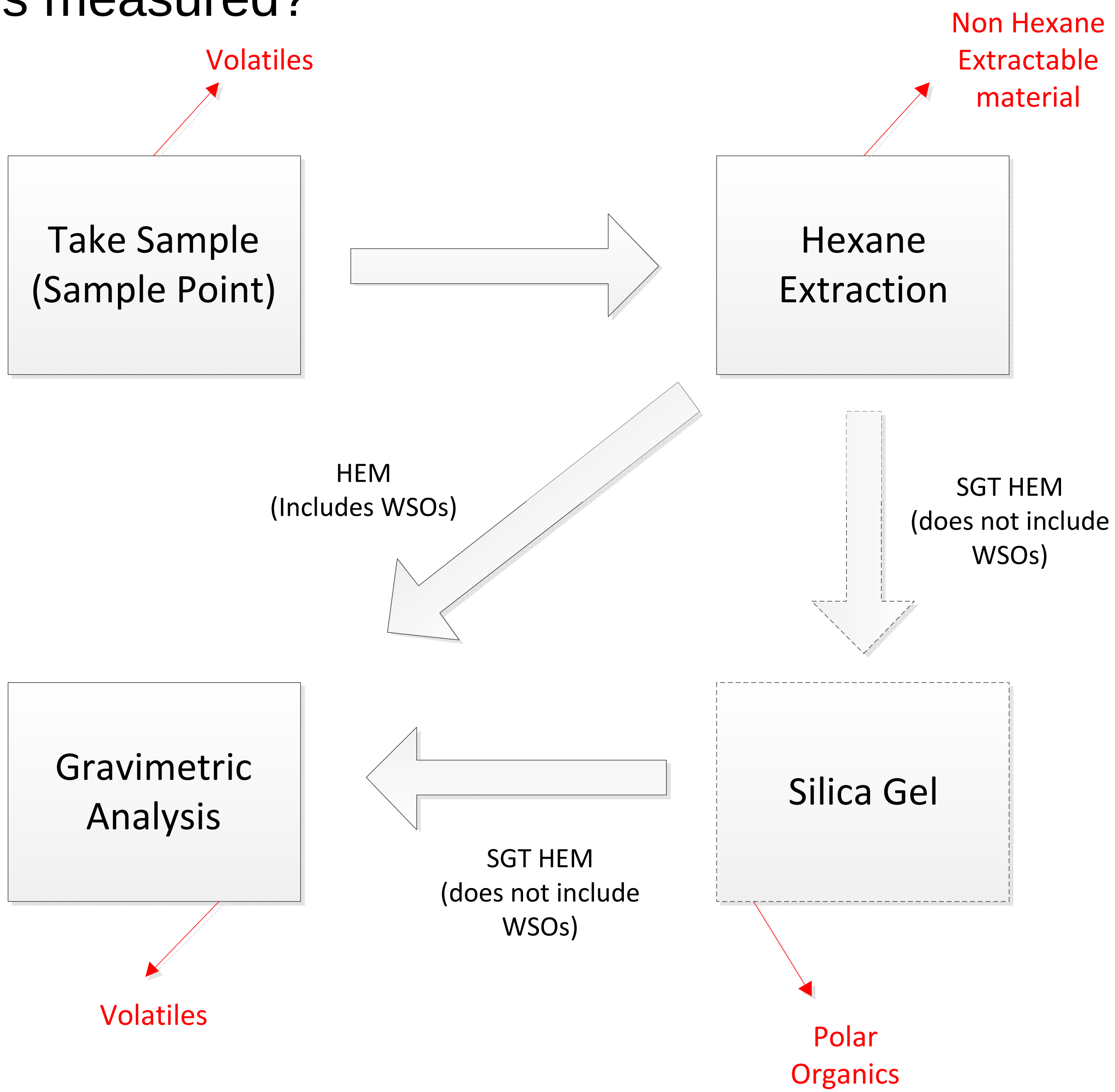
The model is applied to these classes of WSO:

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.

What is measured?



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

Ref.: Yang, Chapter 2, Measurement of Oil in Water(2011)

What is measured?

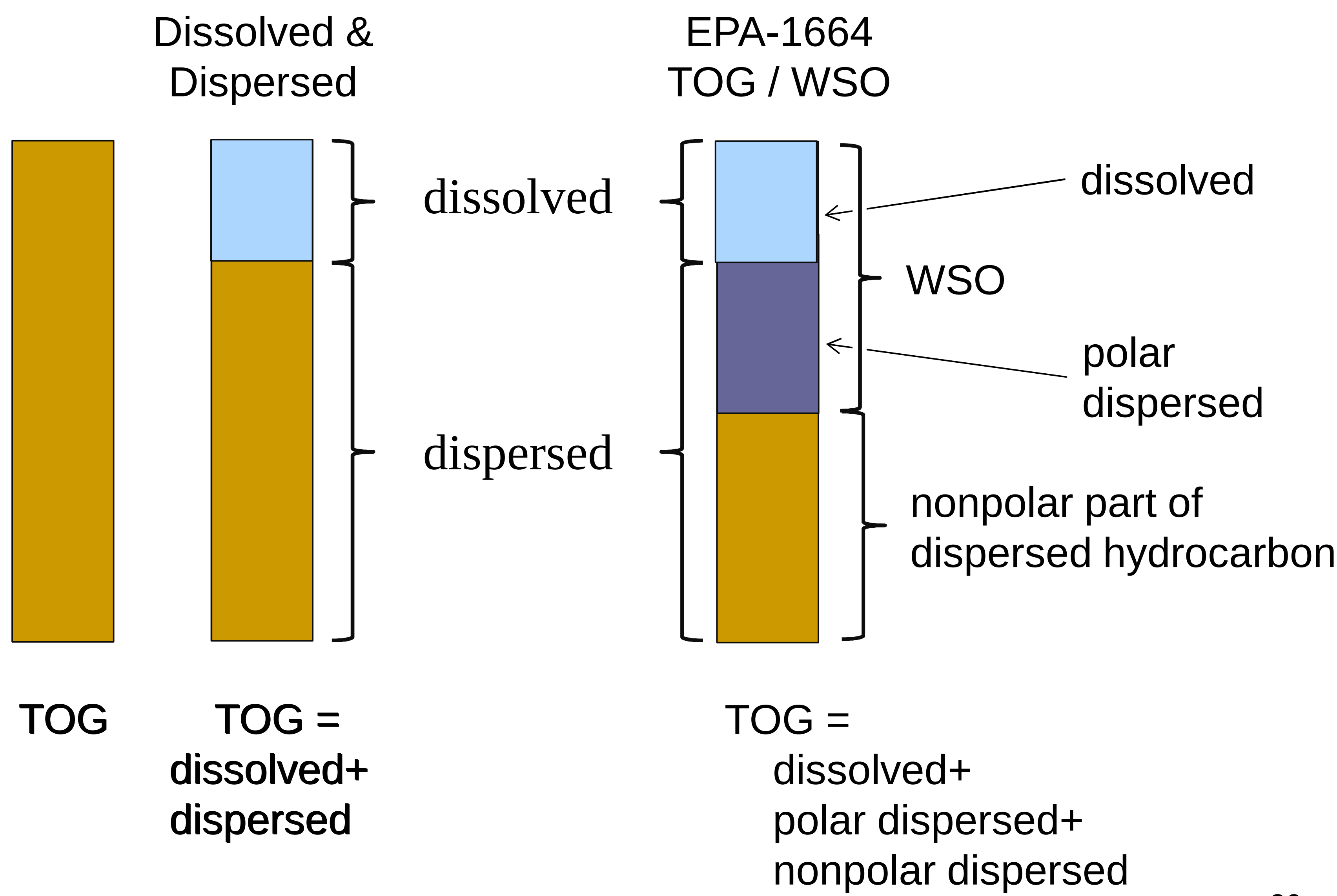
TOG = total oil & grease (all hydrocarbons / all organics)

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

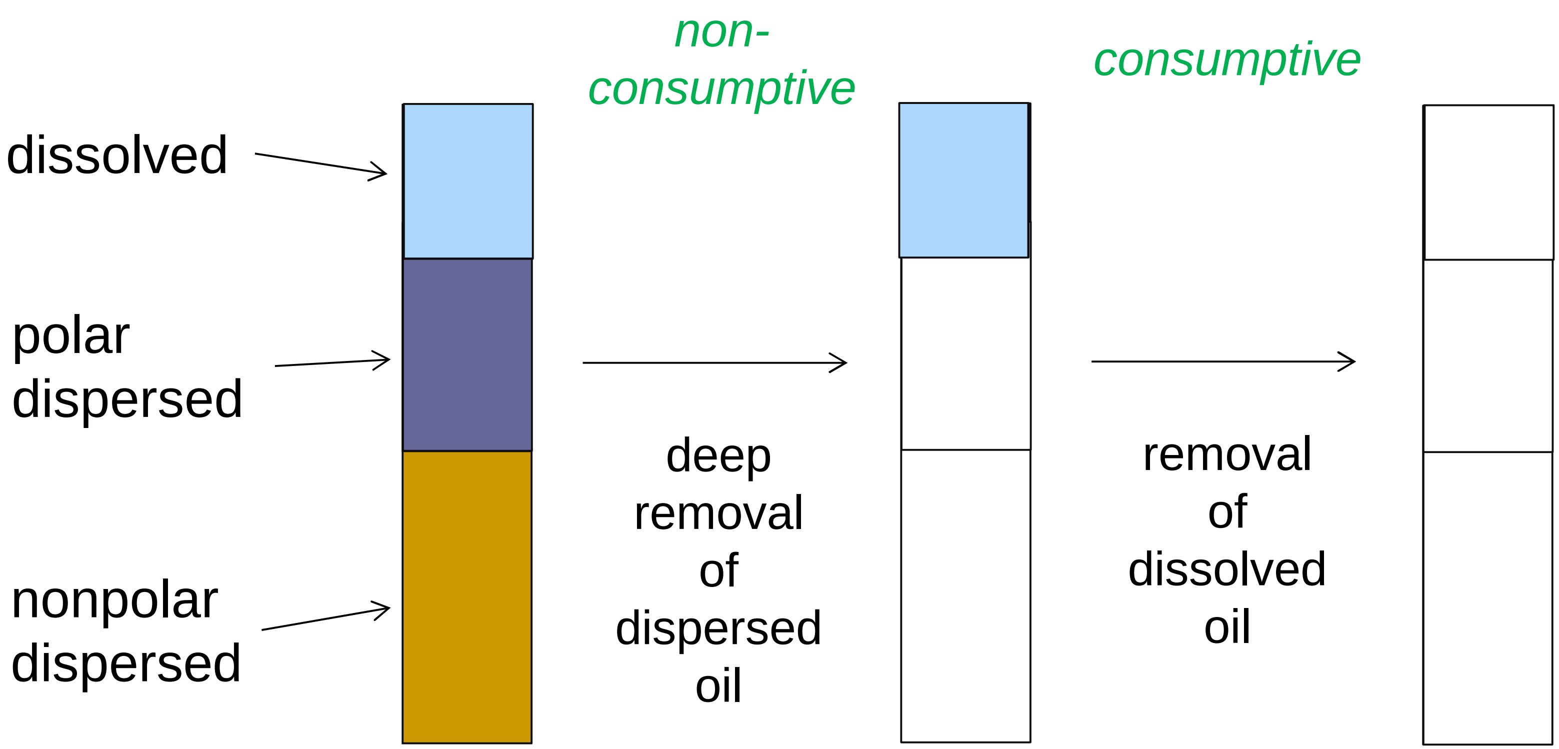
TOG = organics dissolved in water
+ polar fraction of dispersed oil
+ nonpolar fraction of dispersed oil

WSO (organics dissolved in water + polar fraction of dispersed oil)

What is measured?



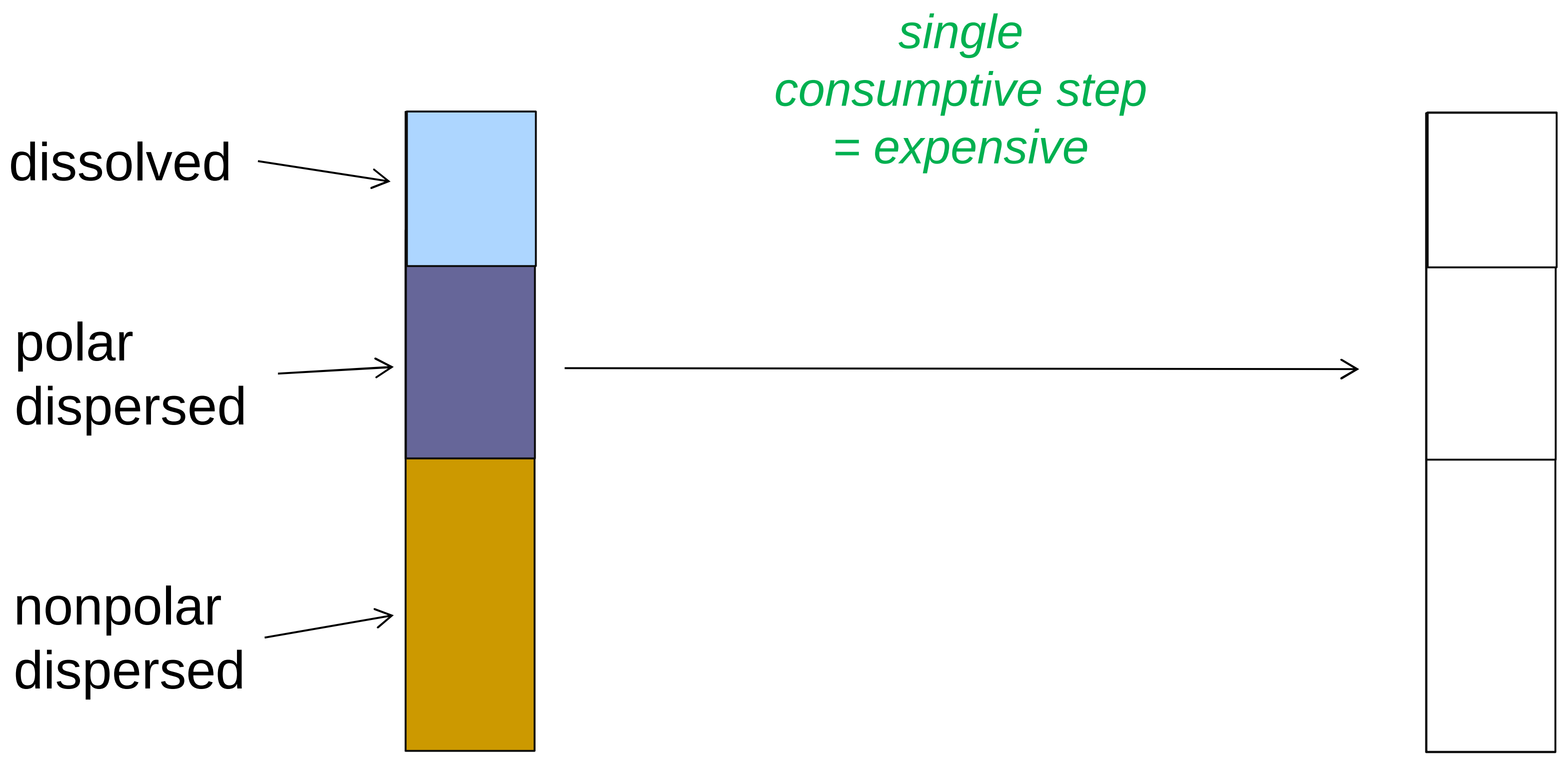
Why is this Important?



- If the client wants to remove TOG, then removal of dispersed oil is an effective approach.

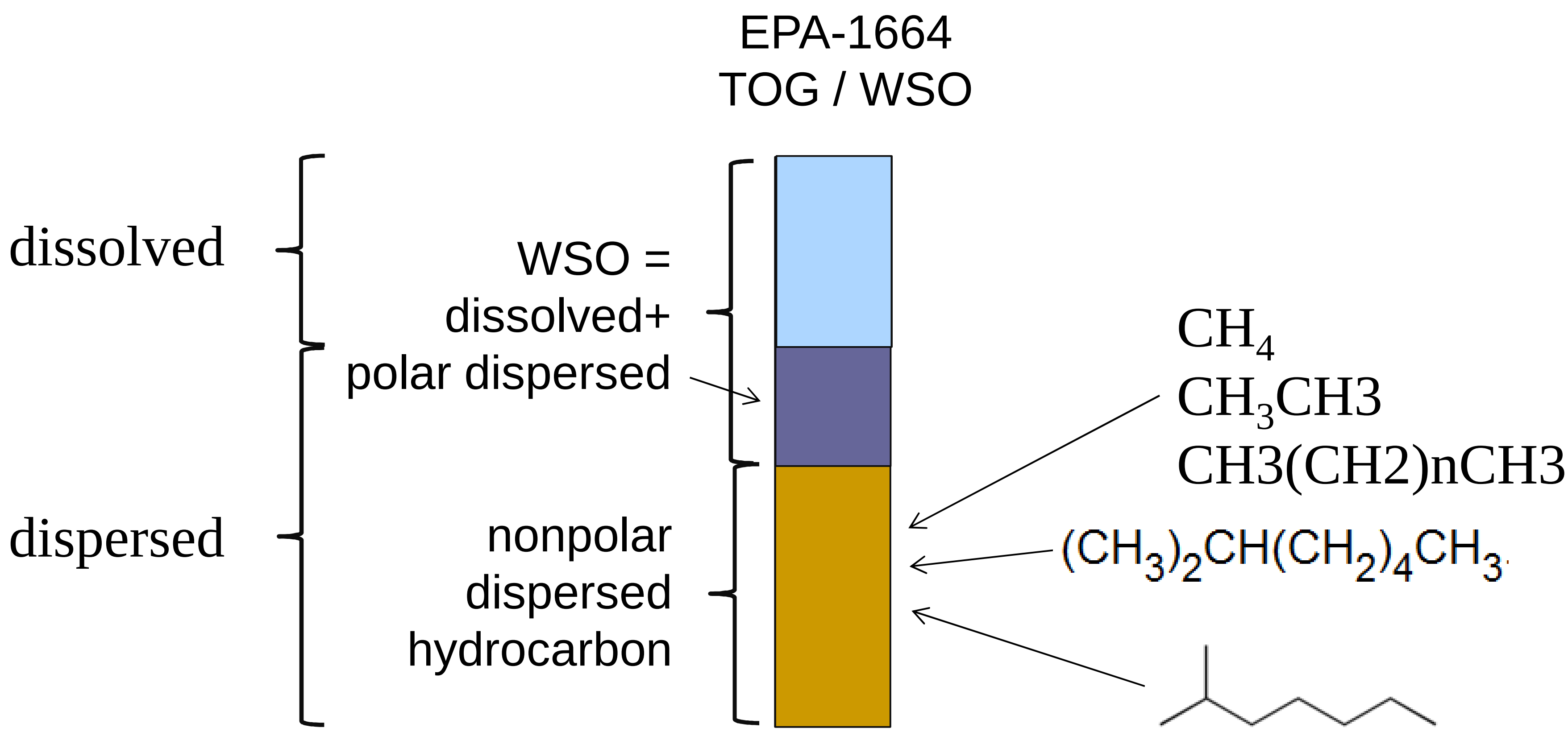
- If the customer wants to remove WSO, then removal of dispersed oil by non- consumable media, is also effective. This may be followed by consumable media for deep removal of WSO. *This minimizes consumption of media.*

Why is this Important?



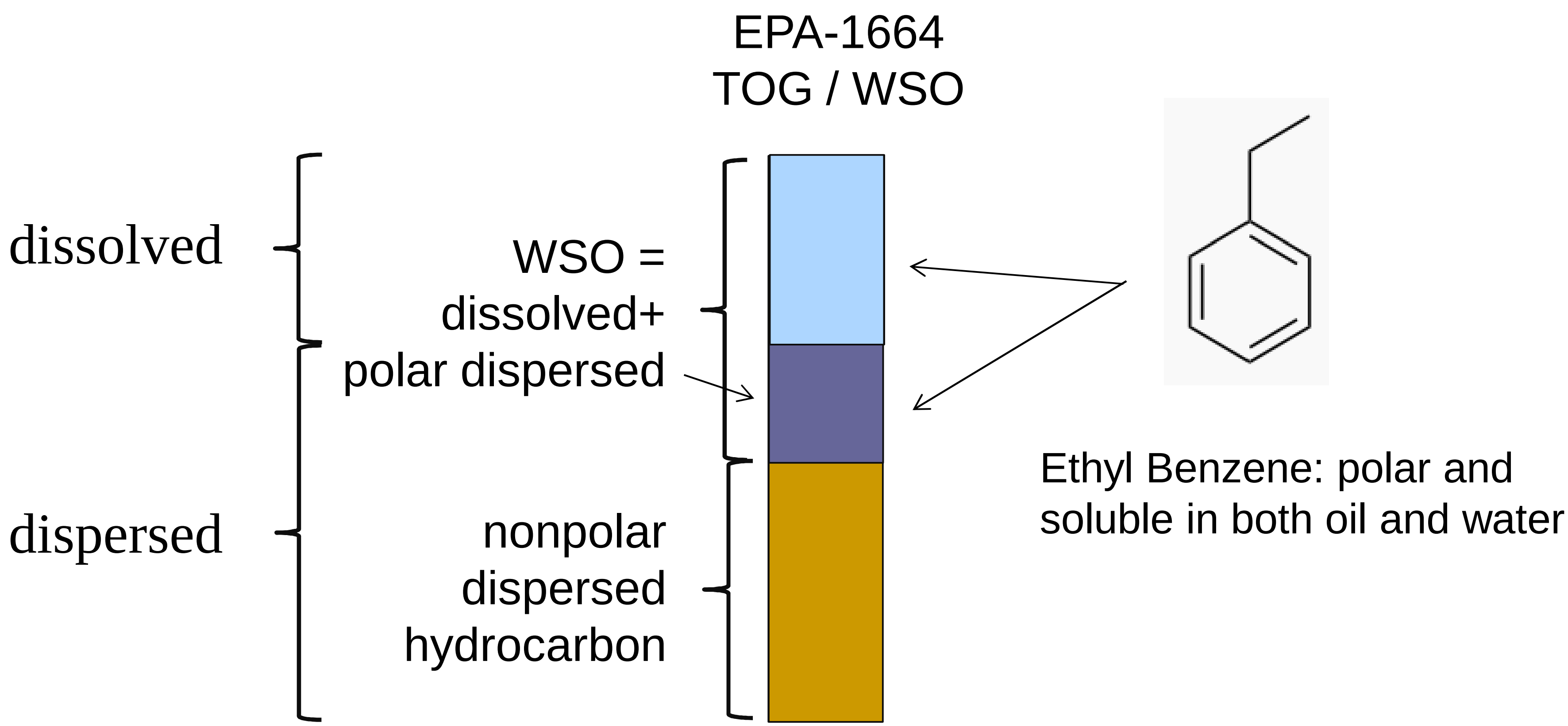
- By eliminating deep removal of dispersed oil, huge amounts of media will be consumed.
- So how well does deep removal of dispersed oil work?
- **How much of WSO is dissolved versus dispersed?**

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:

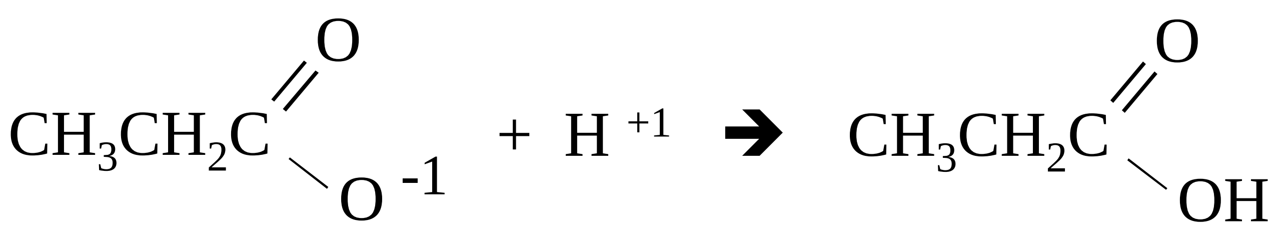


Remove dispersed oil =

Remove the aromatic hydrocarbon that is dissolved in the oil

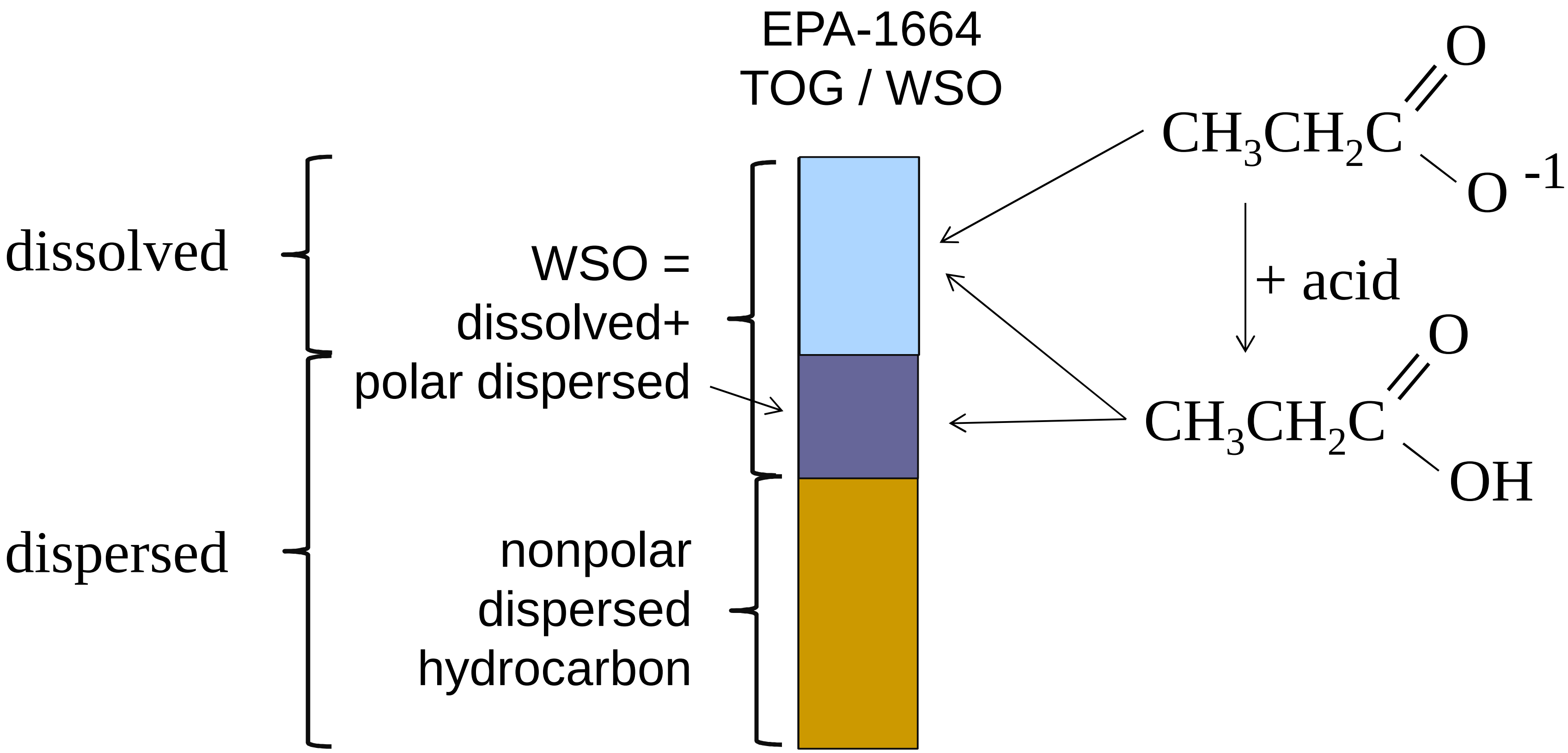
But not the aromatic dissolved in the water

What is measured – acid:



water soluble – not soluble in oil	+ acid	$\longrightarrow$	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

What is measured? – the model

$$\underbrace{}_{}\text{dispersed oil} \qquad \text{dissolved oil in water}$$

$$[\mathrm{TOG}] = \overbrace{([\mathrm{HA}]_o + [B]_o + [C]_o)F_o}^{\text{dispersed oil}} + \overbrace{([\mathrm{HA}]_w + [\mathrm{A}^{-1}] + [\mathrm{B}]_w)F_w}^{\text{dissolved oil in water}}$$

$$[\mathrm{WSO}] = ([\mathrm{HA}]_o + [B]_o)F_o + ([\mathrm{HA}]_w + [\mathrm{A}^{-1}] + [\mathrm{B}]_w)F_w$$

B	=	polar hydrocarbon which dissolves in oil and in water
C	=	non-polar hydrocarbon which does not dissolve in water
TOG	=	all hydrocarbons (in the dispersed and dissolved oil)
WSO	=	all polar hydrocarbons (in the dispersed and dissolved oil)

First Application – Organic Acid:

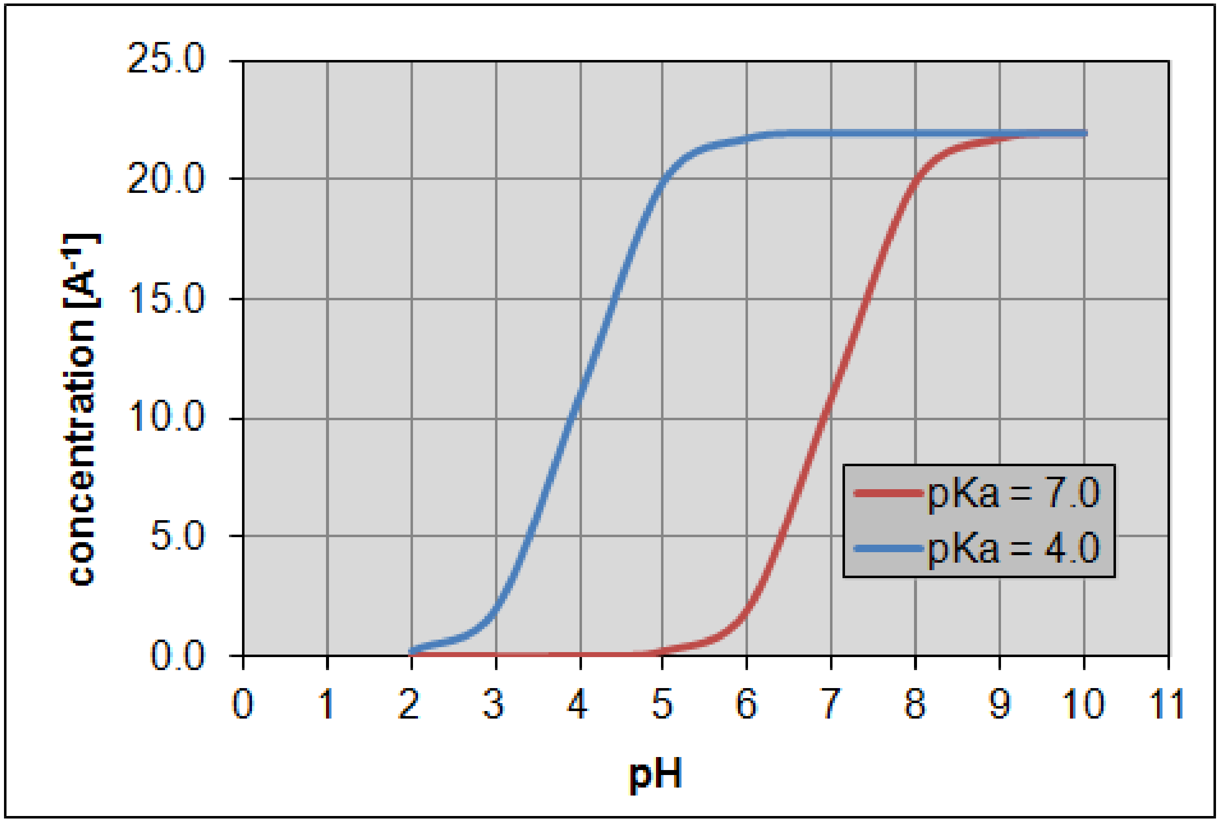
First Application:

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.

Illustrative Calculations – Chemical Equilibria in Aqueous Phase:



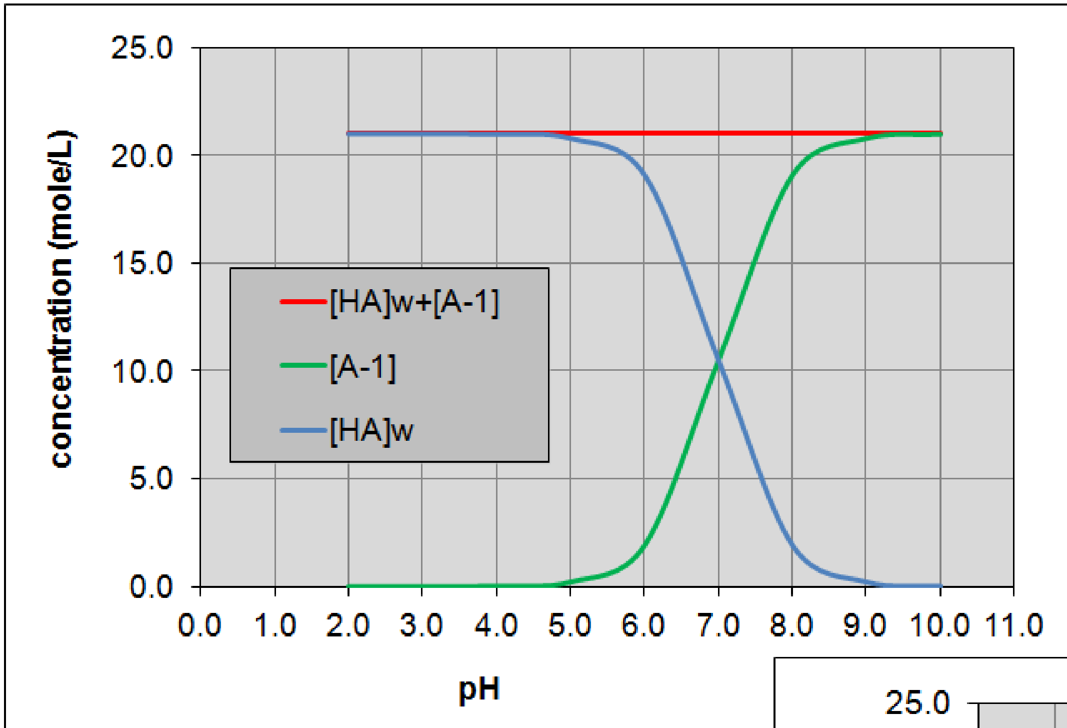
$$HA \Leftrightarrow H^{+1} + A^{-1}$$

$$K_d = \frac{[H^{+1}][A^{-1}]}{[HA]_w}$$

Anion concentration (in produced water phase) as a function of pH, for two different acids.

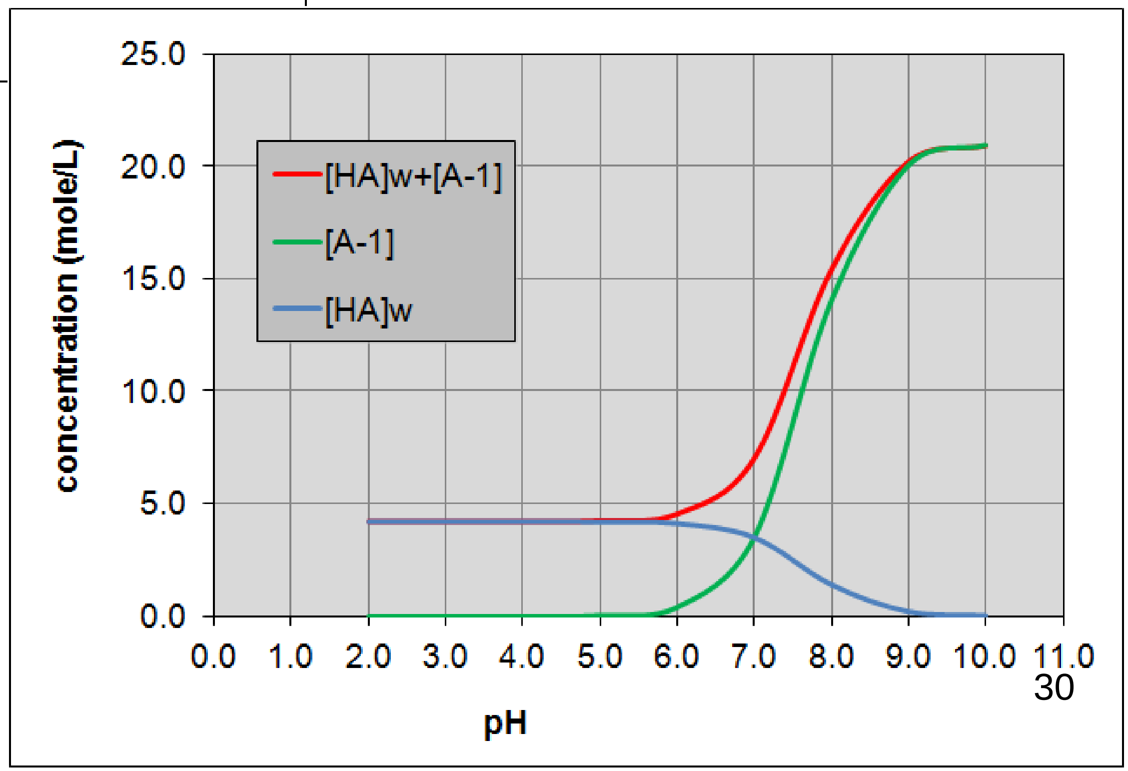
Note that pKa is the pH at which $[HA]_w = [A^{-1}]$

Illustrative Calculations – Chemical & Phase Equilibria:



Left: zero partitioning of the protonated acid (HA) into the oil or gas phase.

Right: partitioning of the protonated acid (HA) into the oil phase. Note the decrease in protonated acid at lower pH (blue and red lines).

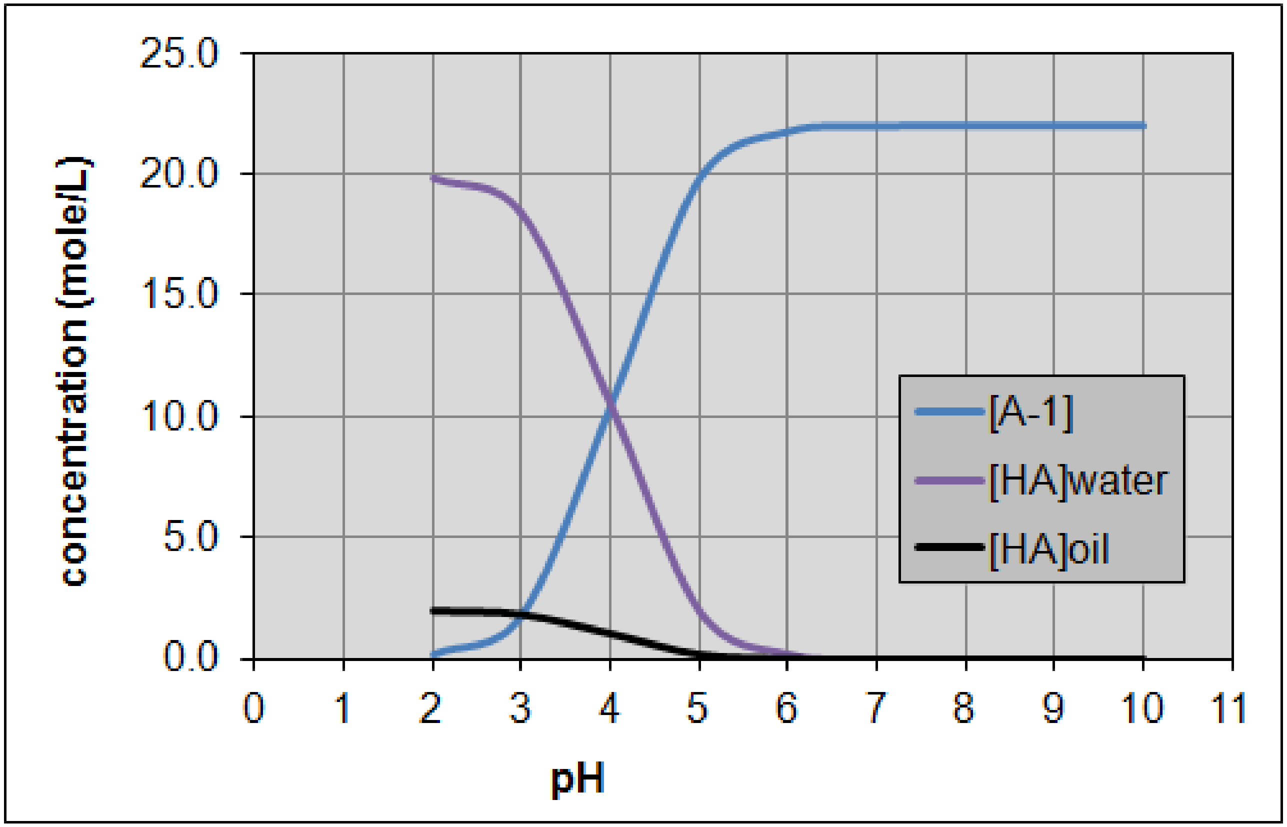


$$HA \Leftrightarrow H^{+1} + A^{-1}$$

Water/Oil:

$$k_{w/o} = [HA]_w / [HA]_o \qquad K_d = \frac{[H^{+1}][A^{-1}]}{[HA]_w}$$

Illustrative Calculations – Chemical & Phase Equilibria:



Hypothetical calculations for an acid with a pKa = 4.2 (roughly that of acetic acid), and a kow = 0.1

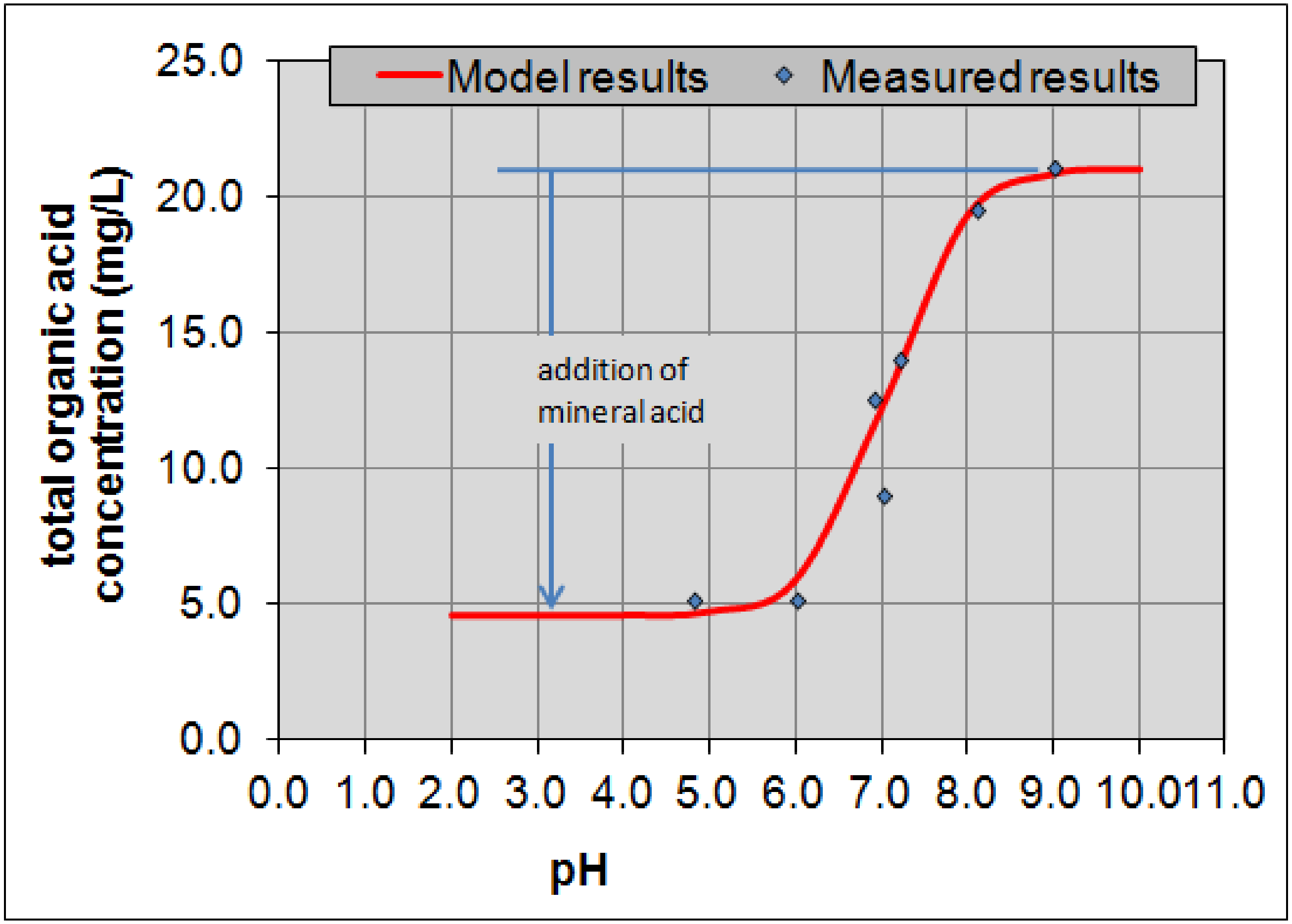
Water/Oil:

$$k_{w/o} = [\mathrm{HA}]_w / [\mathrm{HA}]_o$$

$$\mathrm{HA} \Leftrightarrow \mathrm{H}^{+1} + \mathrm{A}^{-1}$$

$$K_d = \frac{[\mathrm{H}^{+1}][\mathrm{A}^{-1}]}{[\mathrm{HA}]_w}$$

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

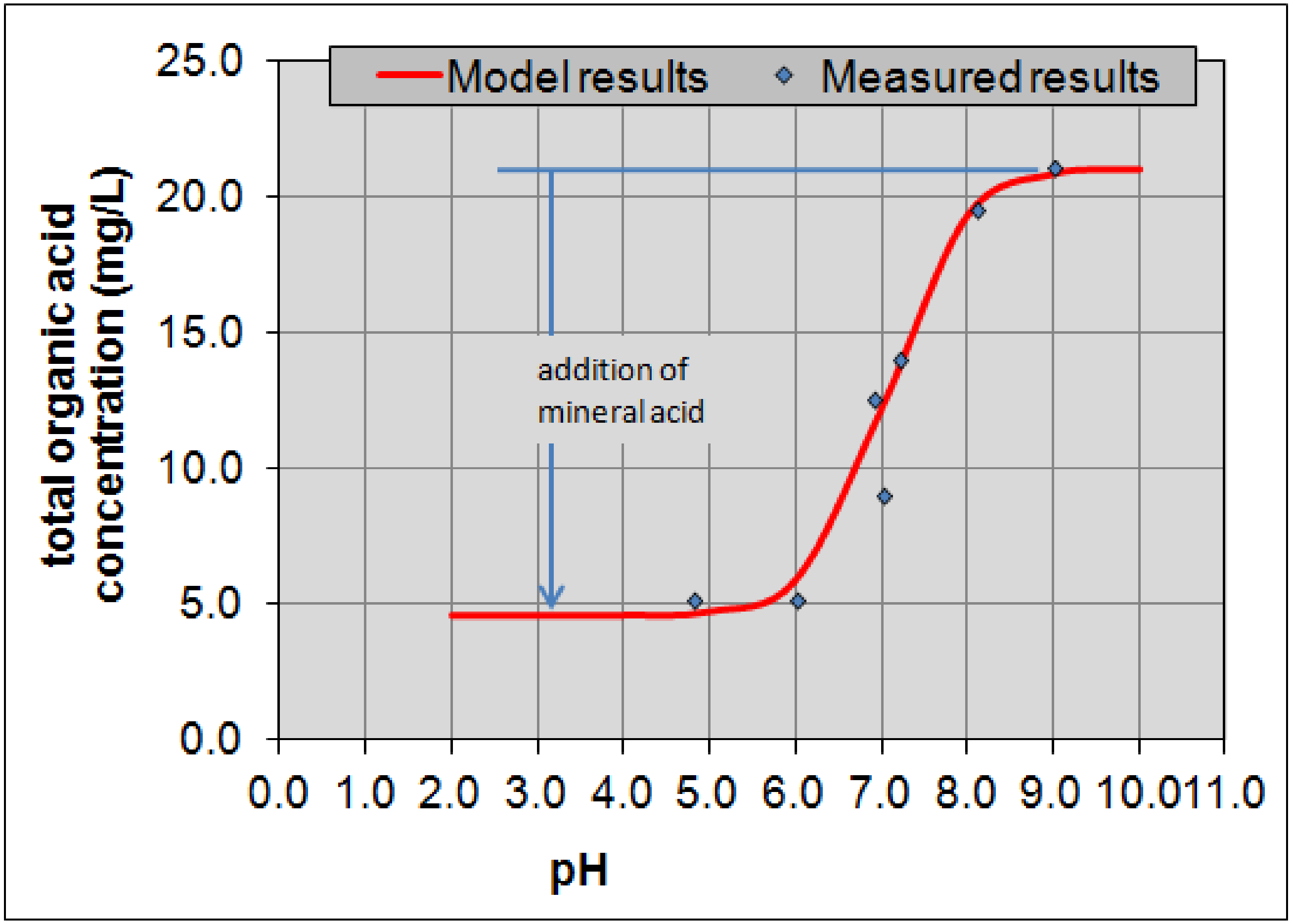
y-axis: protonated and unprotonated acid

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

The parameters in the model (pKa 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)

Tuning the Model using Experimental Data:



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$C_{10} – C_{20}$ acids

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

Water/Oil:

$$k_{w/o} = [HA]_w / [HA]_o$$

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

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Second Application – Nonionic WSO:

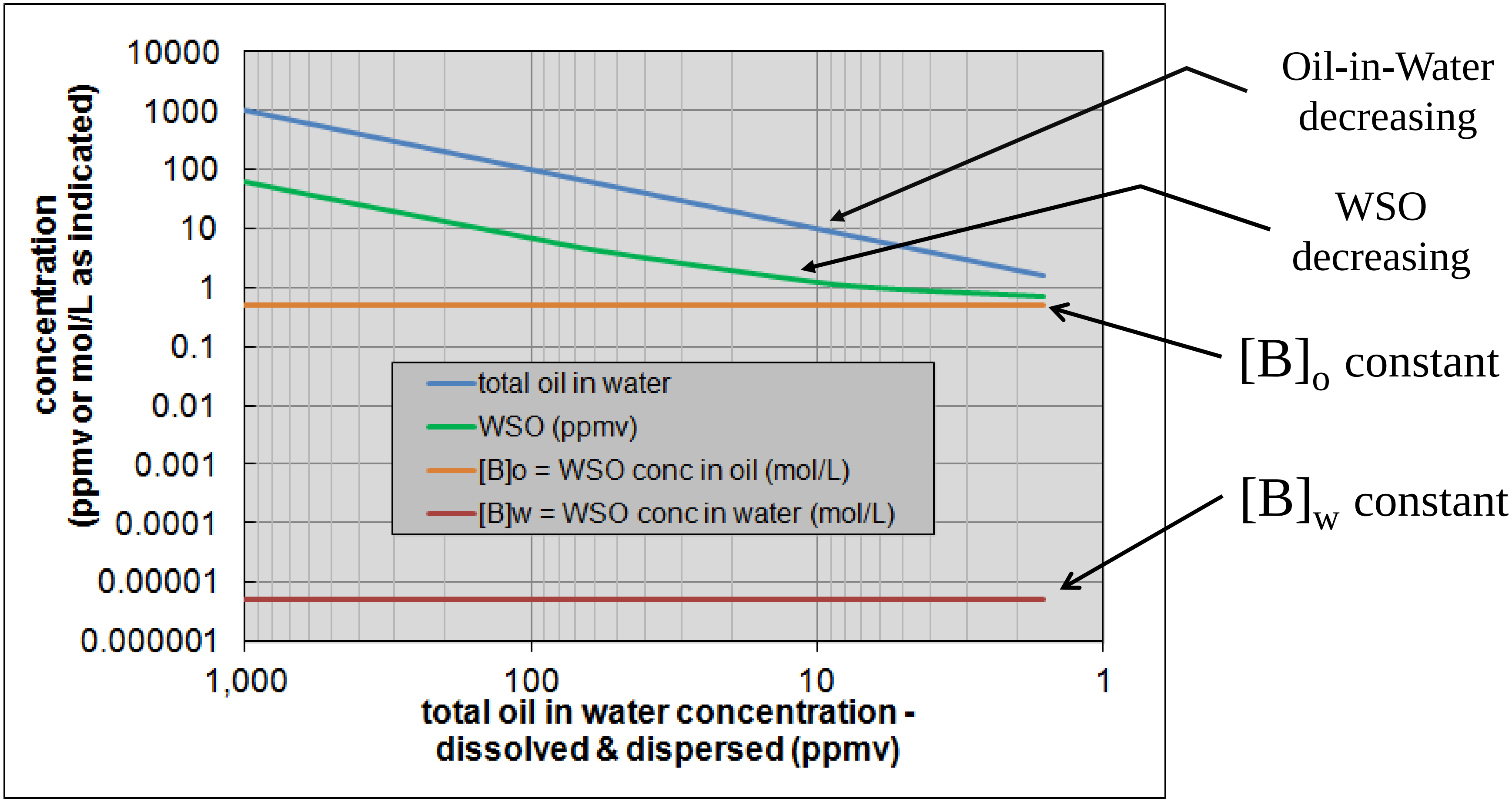
Second Application:

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.

WSO Concentration as a Function of OiW Concentration:



This slide demonstrates that the model predicts that WSO will decrease by removing oil-in-water, provided that there is a large partition coefficient:

$$k_{o/w} = [\mathrm{B}]_o / [\mathrm{B}]_w$$

Next Several Slides:

The next several slides give diagrams of concentration (TOG, WSO, dissolved, etc) as a function of the dispersed oil content.

These figures show the effect of a water treatment process that removes dispersed oil.

Overall the figures show that both TOG and WSO can be removed by such a process. But only certain WSO compounds will behave this way.

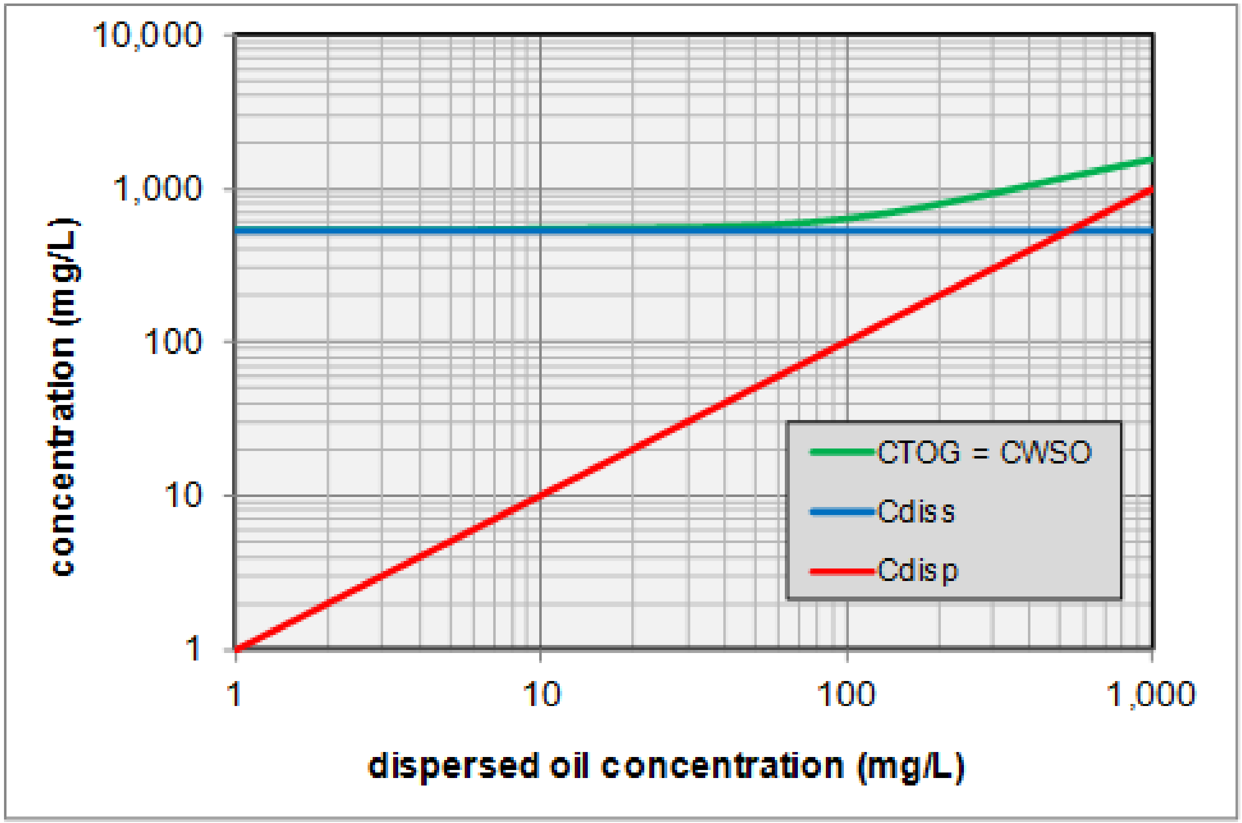
The first example is toluene in water.

toluene
(polar)

Definitions:

TOG = dissolved oil + dispersed oil

WSO = dissolved oil + polar dispersed



Oil is composed of a single polar hydrocarbon (toluene).

Dissolved oil = concentration of toluene dissolved in water (529 mg/L). As the dispersed oil concentration decreases (through water treatment), the dissolved concentration remains constant.

Polar dispersed oil = toluene dispersed as drops in the water. This is the toluene concentration in excess of the water solubility.

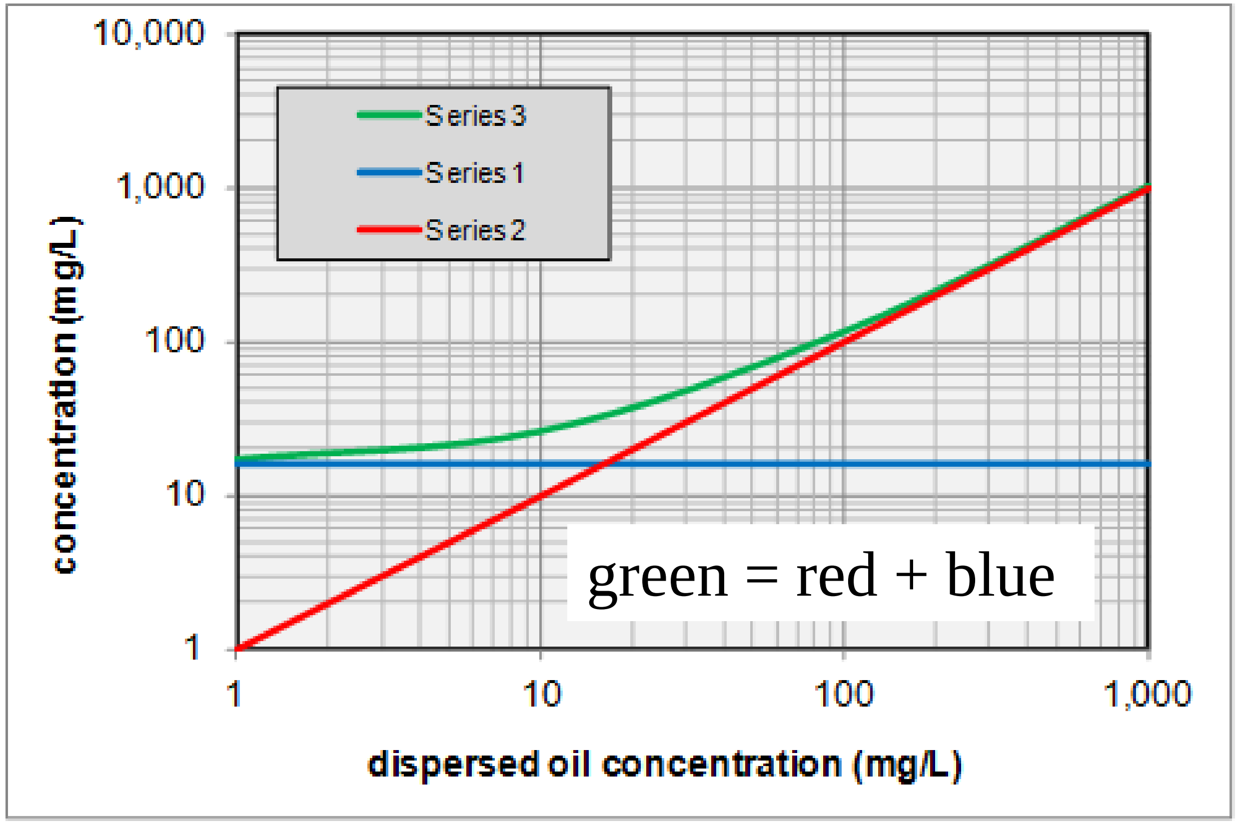
WSO = dissolved oil + polar dispersed oil = TOG

toluene + polar compound

Definitions:

TOG = dissolved oil + dispersed oil

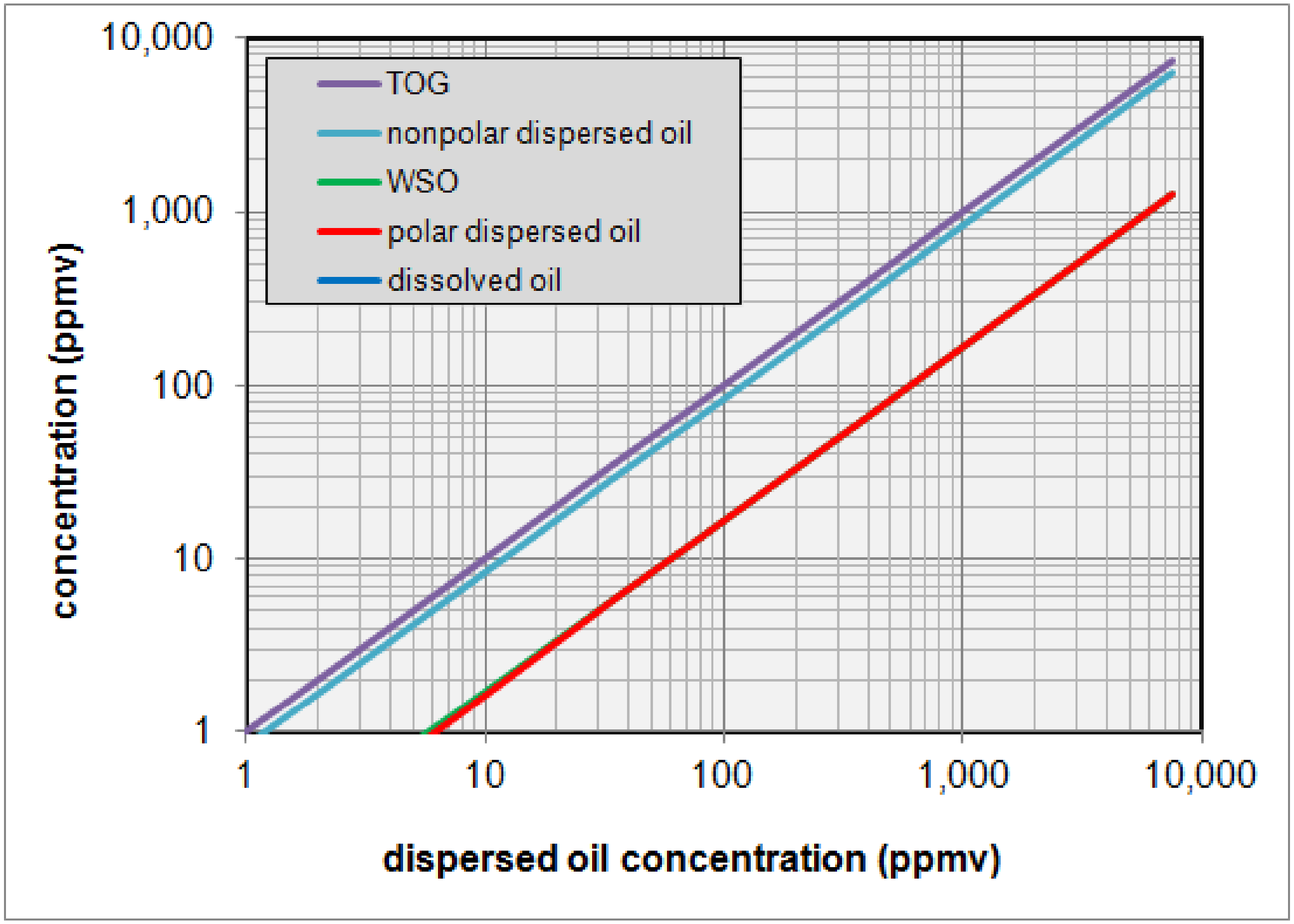
WSO = dissolved oil + polar dispersed



Oil is composed of toluene plus a polar compound.

The second compund dilutes the toluene in the oil phase. This reduces the solubility of the oil, as a whole.

polar C10 +
nonpolar C20



Definitions:

TOG = dissolved oil + dispersed oil

WSO = dissolved oil + polar dispersed

Oil is composed of a polar C10 plus a nonpolar C20. The polar C10 has limited solubility in water.

WSO ~ polar dispersed oil

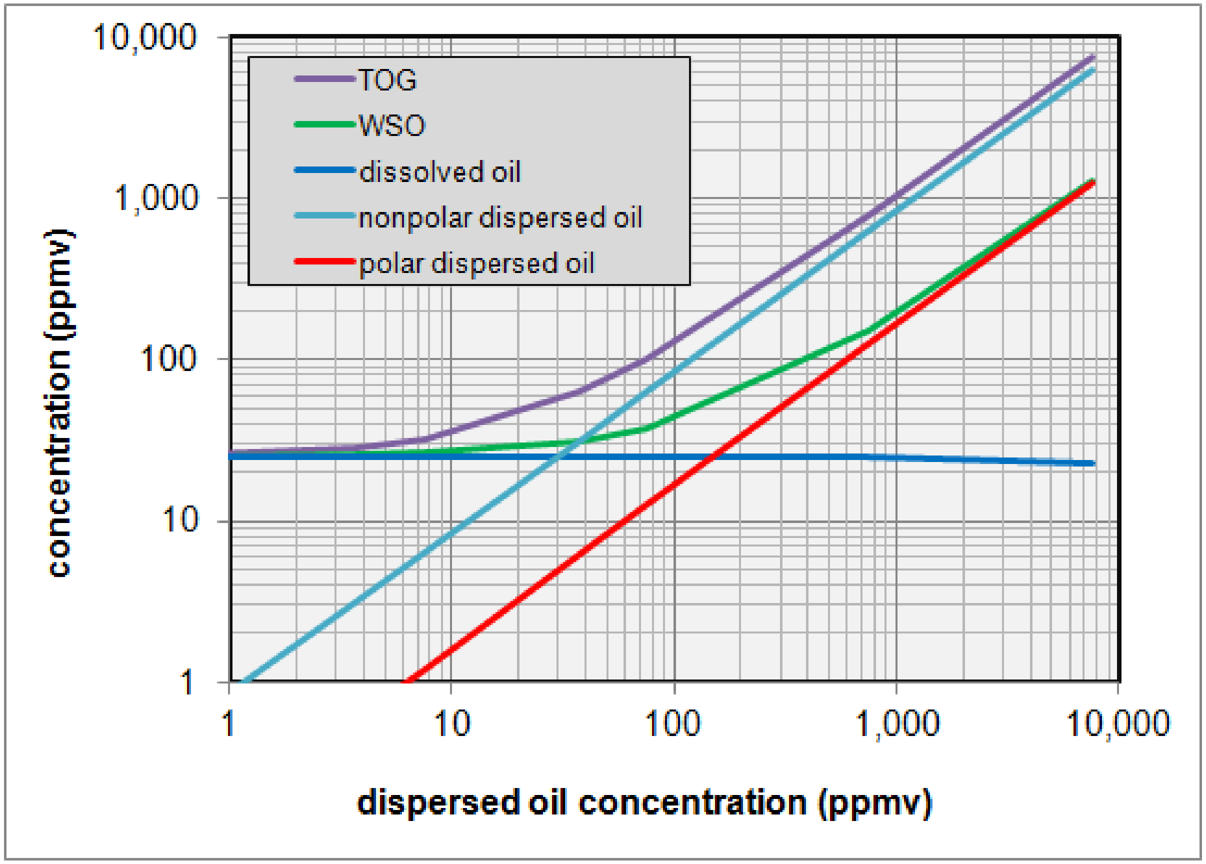
Note that TOG approaches zero as dispersed oil is removed. This is due to very low dissolved oil concentration.

toluene + nonpolar C_{20}

Definitions:

TOG = dissolved oil + dispersed oil

WSO = dissolved oil + polar dispersed



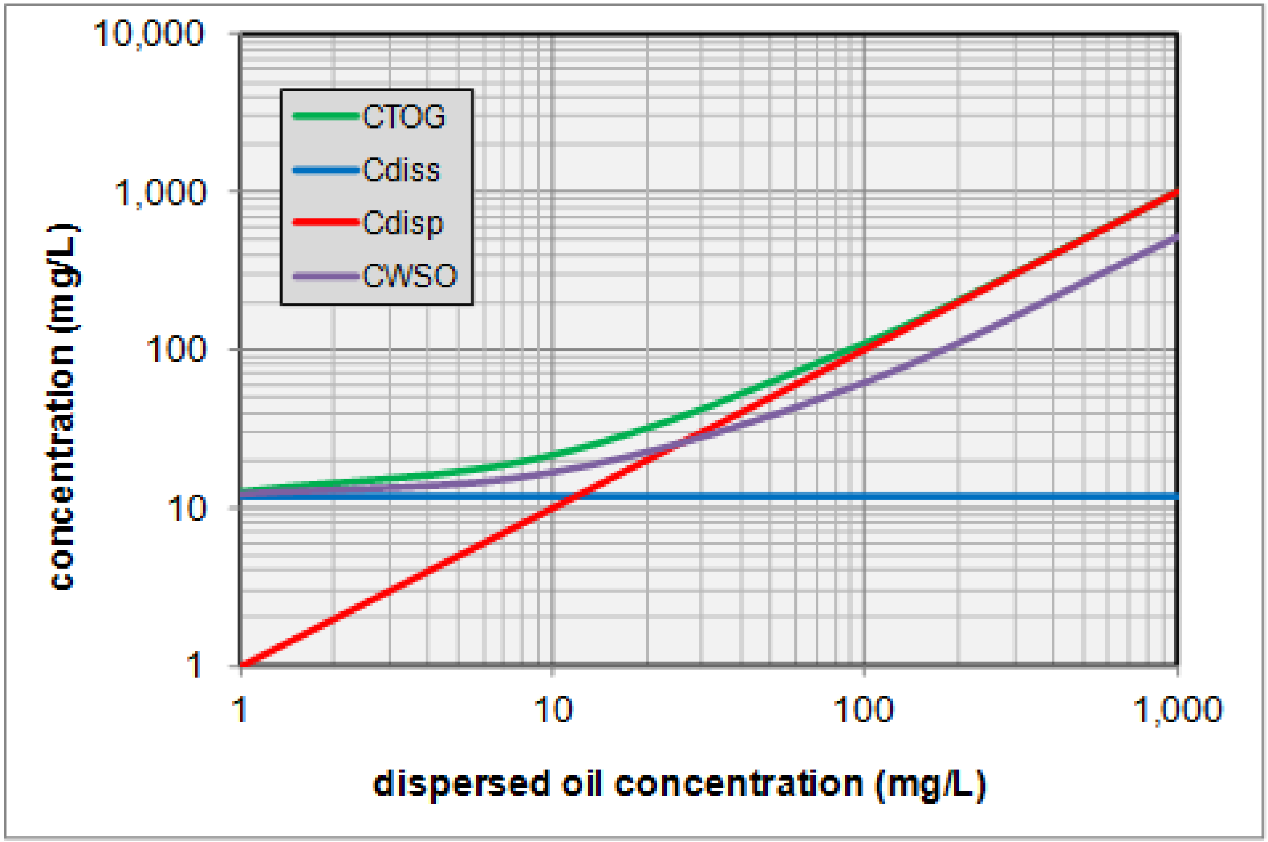
Oil is composed of a polar hydrocarbon (toluene) plus a nonpolar hydrocarbon (C20).

Dissolved oil = concentration of toluene dissolved in water (as previous slide).

Nonpolar dispersed oil = concentration of C20.
Polar dispersed oil = toluene dispersed as drops in the water (as previous slide).

WSO = dissolved oil + polar dispersed oil (as previous slide)

toluene +
polar C_{10} +
nonpolar C_{20}



Definitions:

TOG = dissolved oil + dispersed oil

WSO = dissolved oil + polar dispersed

Oil is composed of toluene plus a polar aggregate (C) and a nonpolar aggregate (D).

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

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

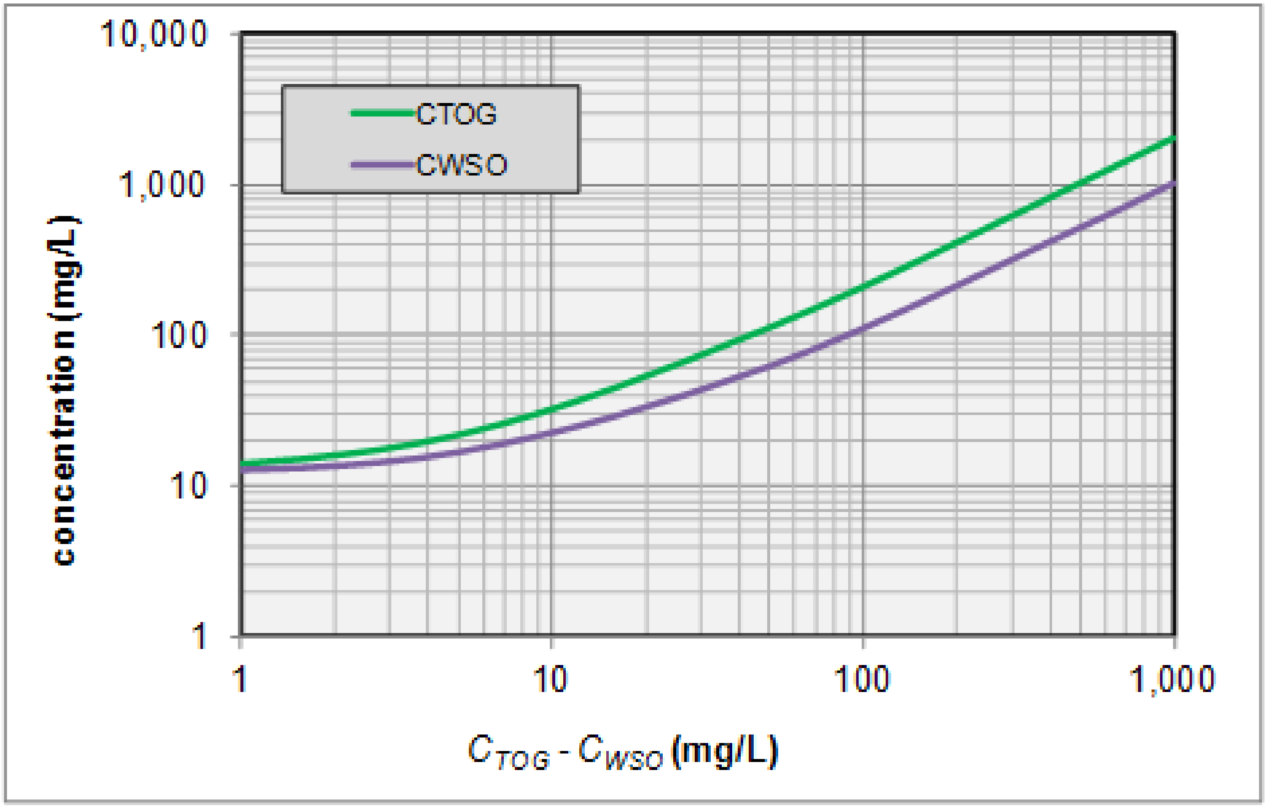
TB = toluene
C = partially soluble hydrocarbons that contribute to WSO
D = hydrocarbons that contribute to dispersed oil but not to WSO

toluene +
polar C_{10} +
nonpolar C_{20}

Definitions:

TOG = dissolved oil + dispersed oil

WSO = dissolved oil + polar dispersed



Oil is composed of toluene plus a polar aggregate (C) and a nonpolar aggregate (D).

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

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

$$[TOG] - [WSO] = [D]_o F_o$$ ← Proportional to dispersed oil, but not equal. Intercept is equal to [WSO].

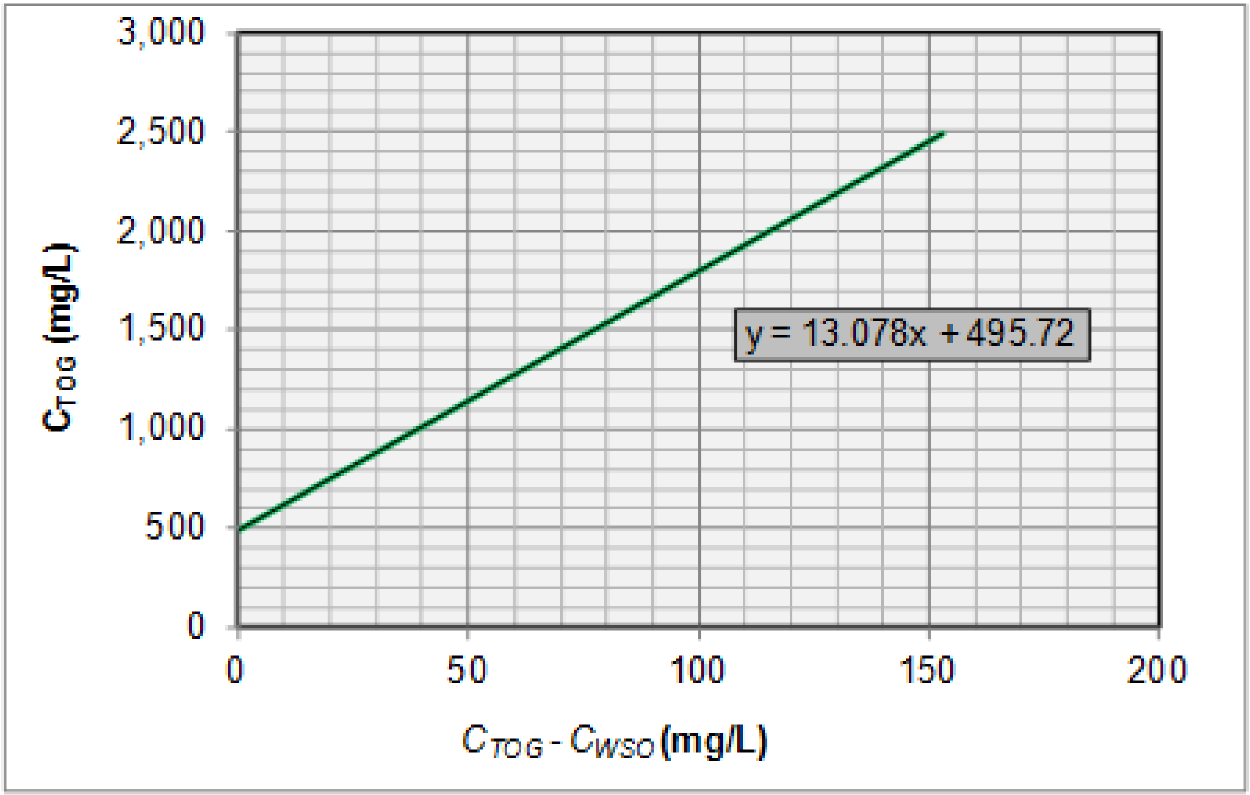
TB	=	toluene
C	=	partially soluble hydrocarbons that contribute to WSO
D	=	hydrocarbons that contribute to dispersed oil but not to WSO

Two Component Model

C_{TOG} vs
$C_{TOG} - C_{WSO}$

calculations carried out using the model

trendline used to determine slope and intercept



slope of TOG line = $1+[C]_o/[D]_o = 1 + 8.46/0.7 = 13.08$

intercept of TOG line = $[C]_w \times M_C \times 1000 =$
= (0.00518 mol C/L water) x (92.1 gr C/mol C) x 1000 mg/gr = 477.08 mg C/L water

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

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

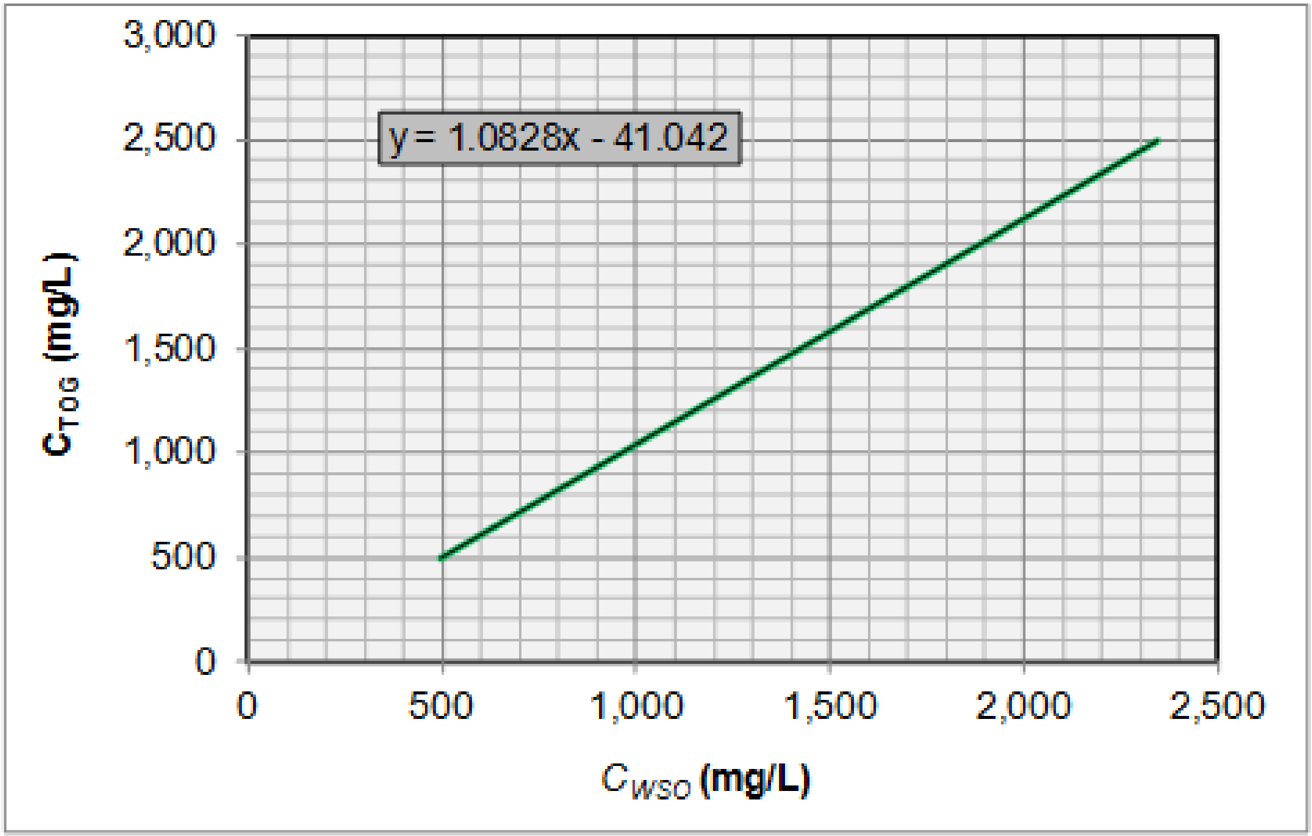
The model is used to generate the values plotted in the figure. The slope and intercept of the trend line equals the value calculated by the equation to the left.

Two Component Model

C_{TOG} vs
$C_{TOG} - C_{WSO}$

calculations carried out using the model

trendline used to determine slope and intercept



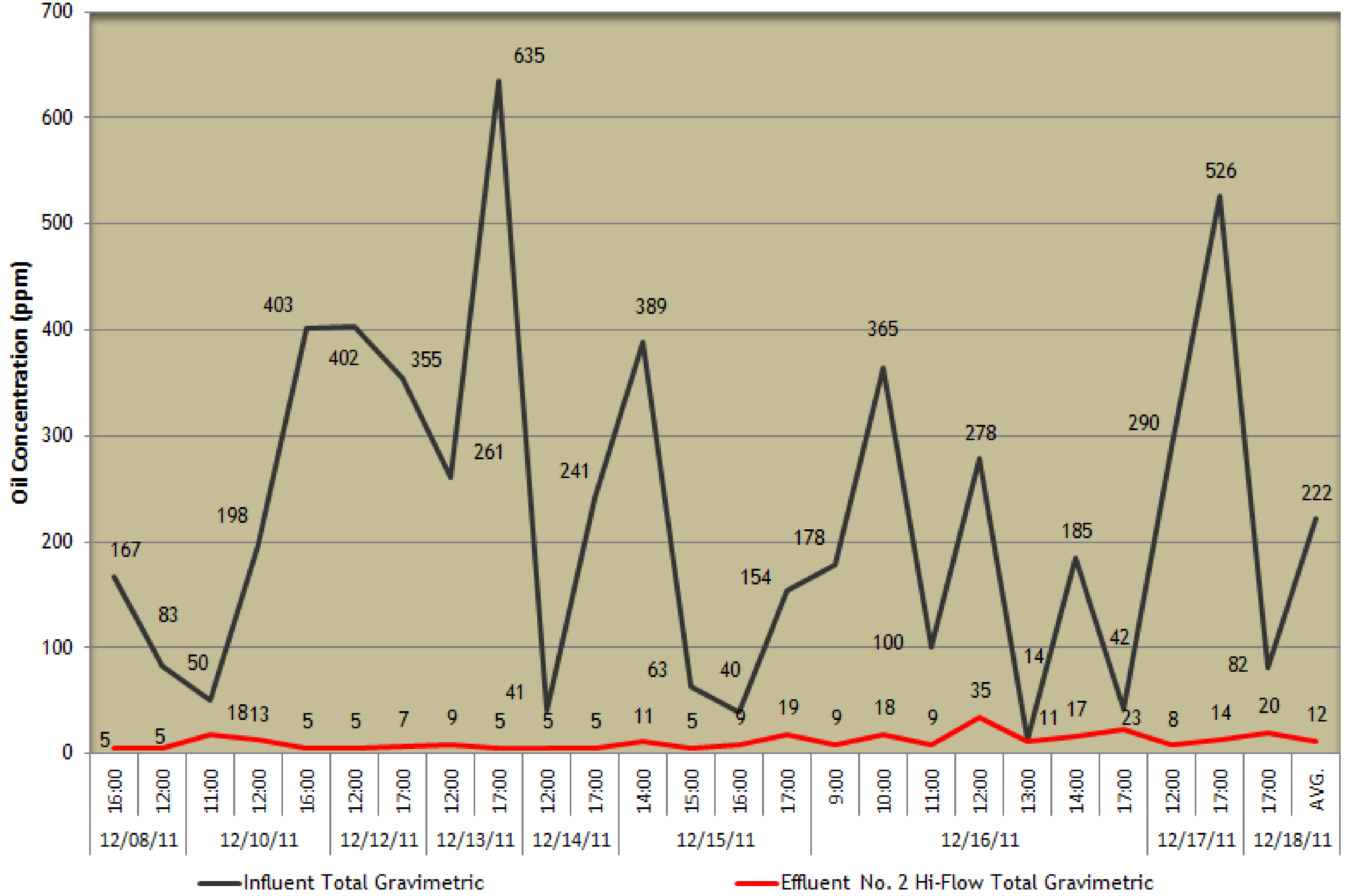
The model is used to generate the values plotted in the figure. The slope and intercept of the trendline equals the value calculated by the equation below.

slope TOG line = $1+[D]_o/[C]_o = 1 + 0.7/8.46 = 1.083$

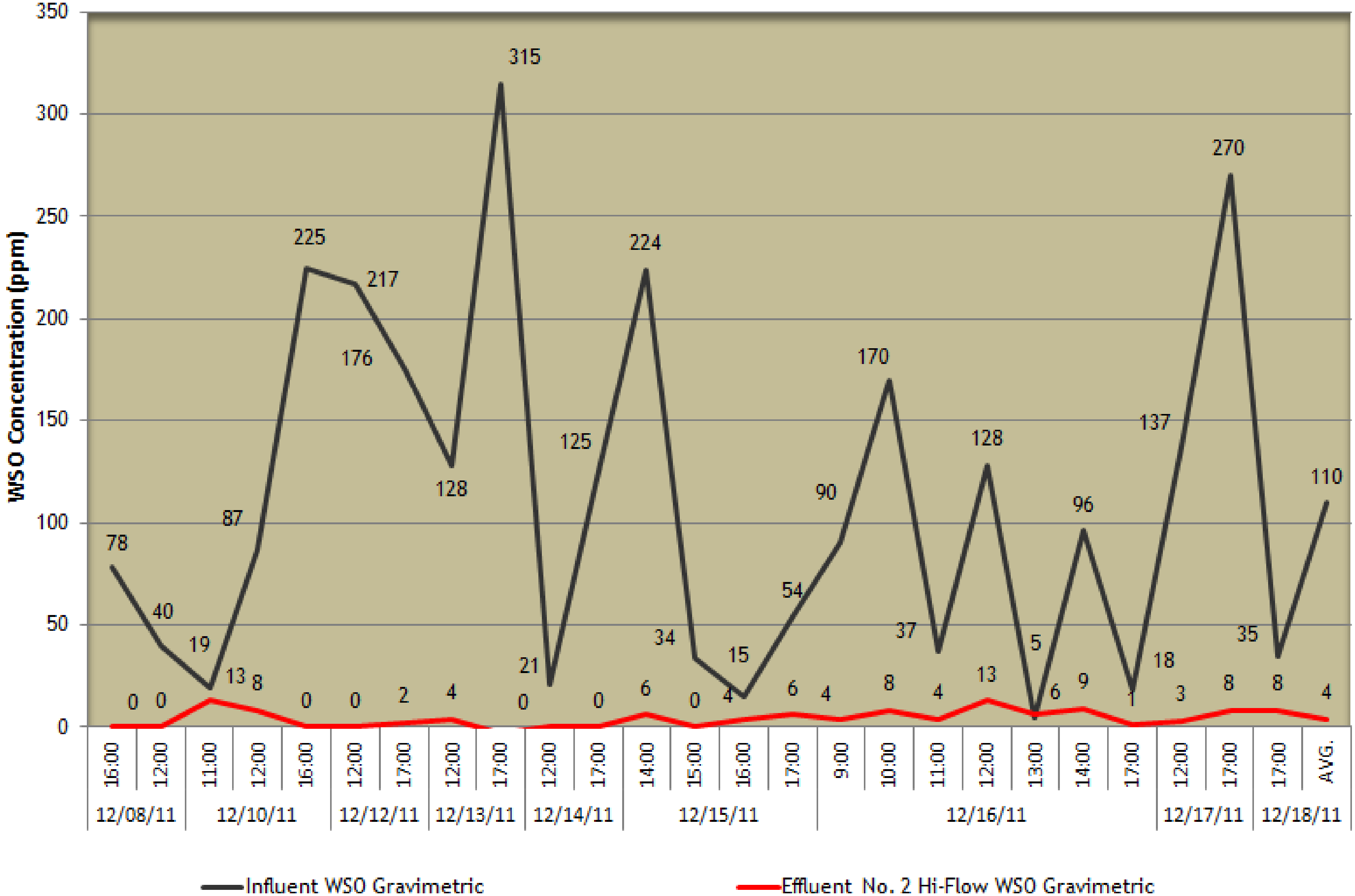
intercept of TOG line = $-[D]_o \times M_o / k_{owC} = 0.7 \times 95.7 \times 1000/1633 = -41.02$

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

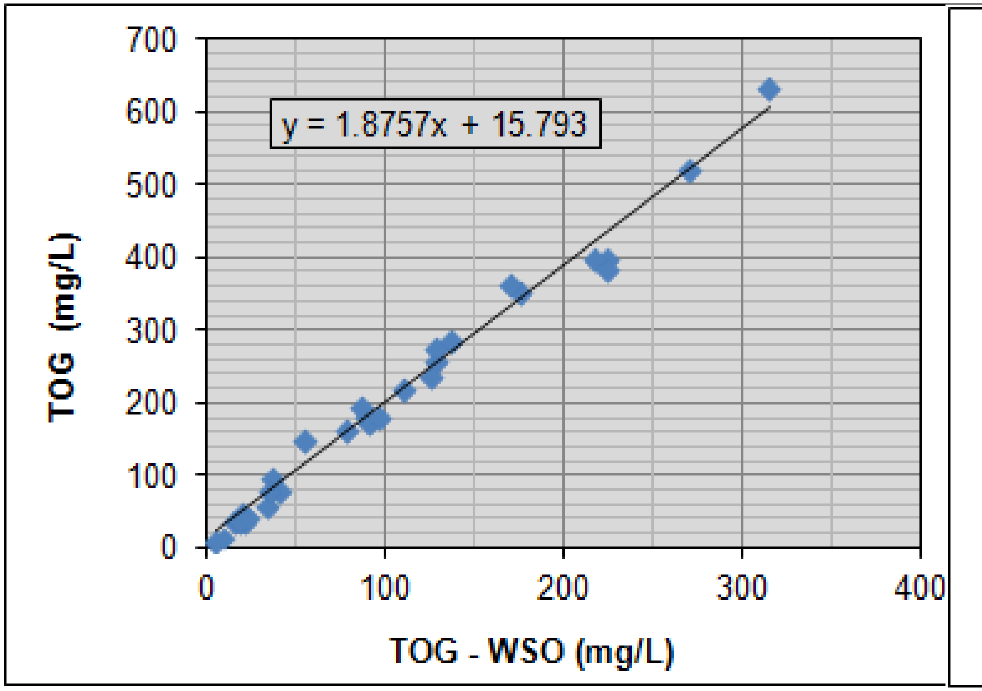
Case No.5 Total Oil Removal

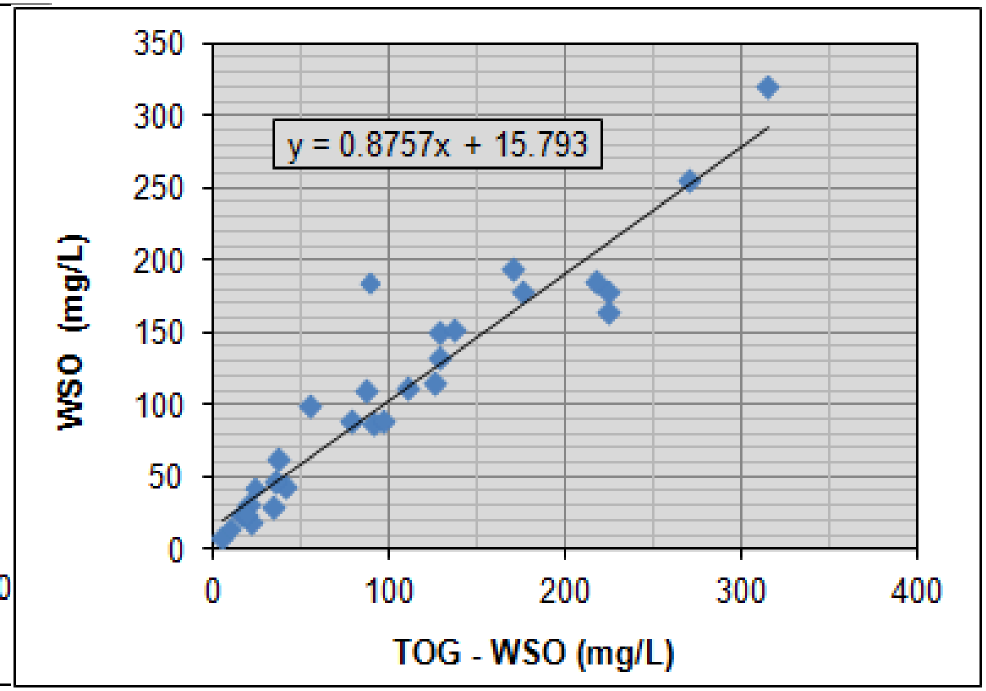


No.5 Water Soluble Organics



Analysis of Field Data – Case 5





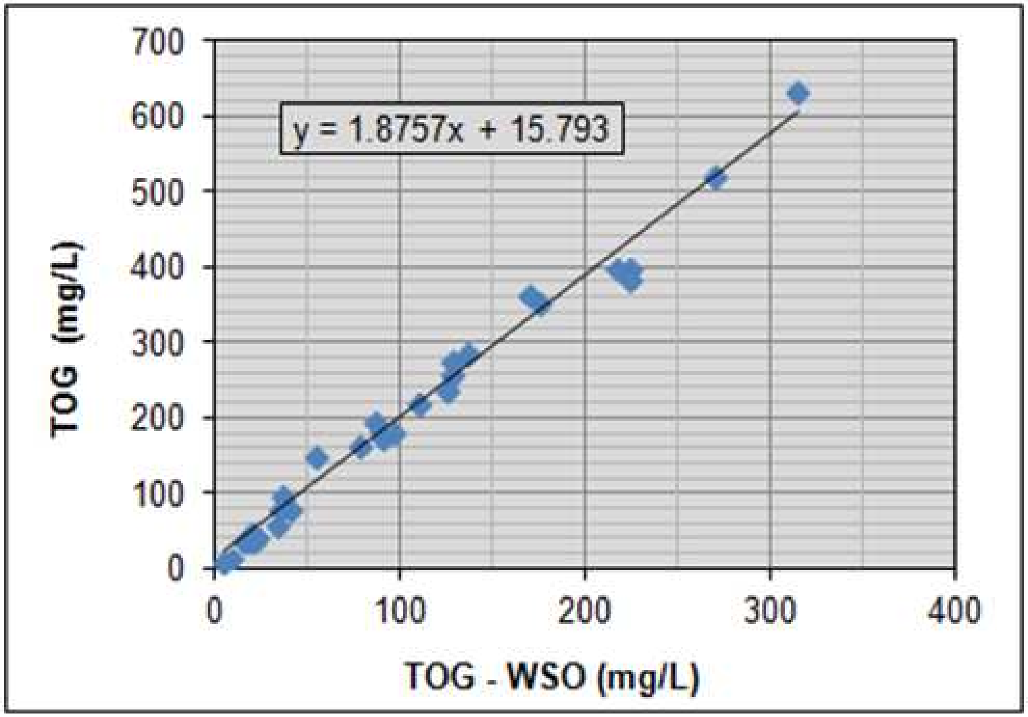
Note:

1) straight lines

2) difference in slopes = 1.0 $d[TOG]/dx - d[WSO]/dx = d([TOG]-[WSO])/dx = 1$

3) same intercept

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:

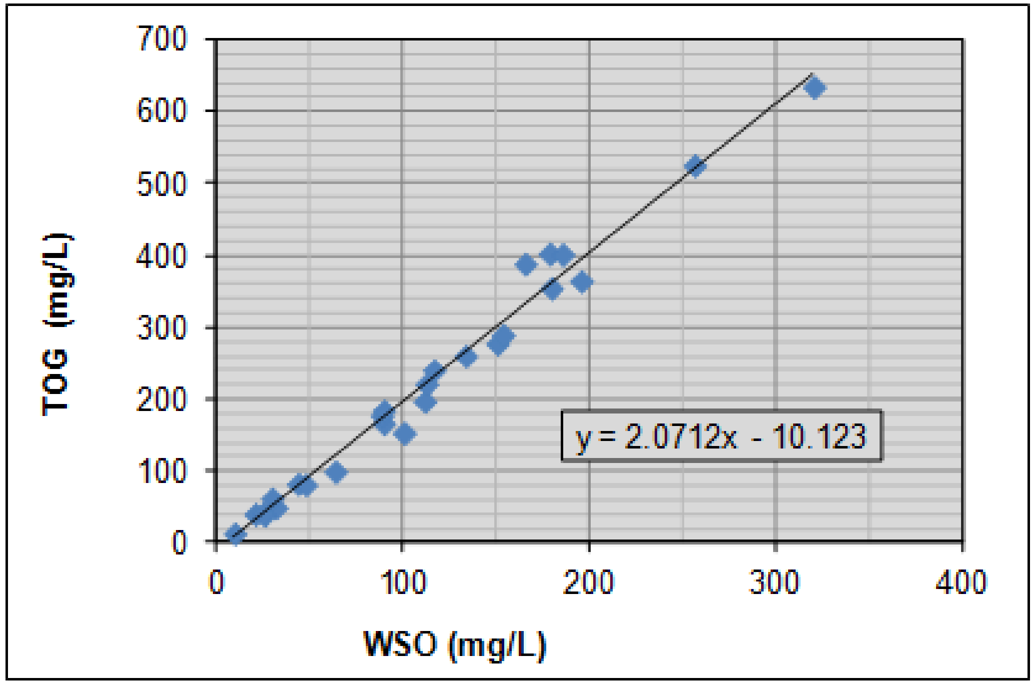
$$x = [TOG] - [WSO]$$

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

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:

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

$$x = [WSO]$$

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)

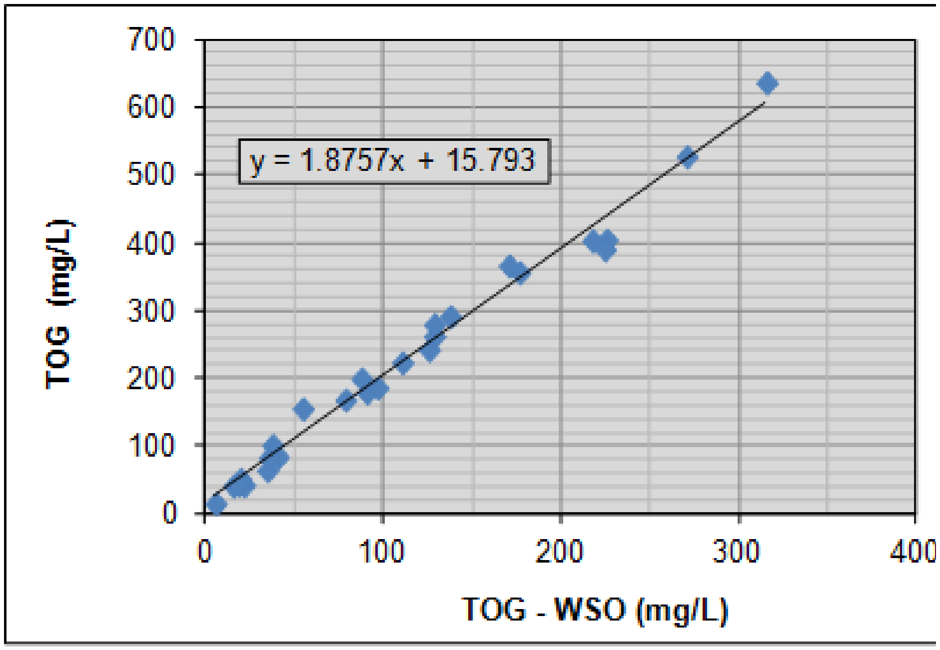
ρ_{go} = measured gravimetric density of the oil (gr oil/L oil)

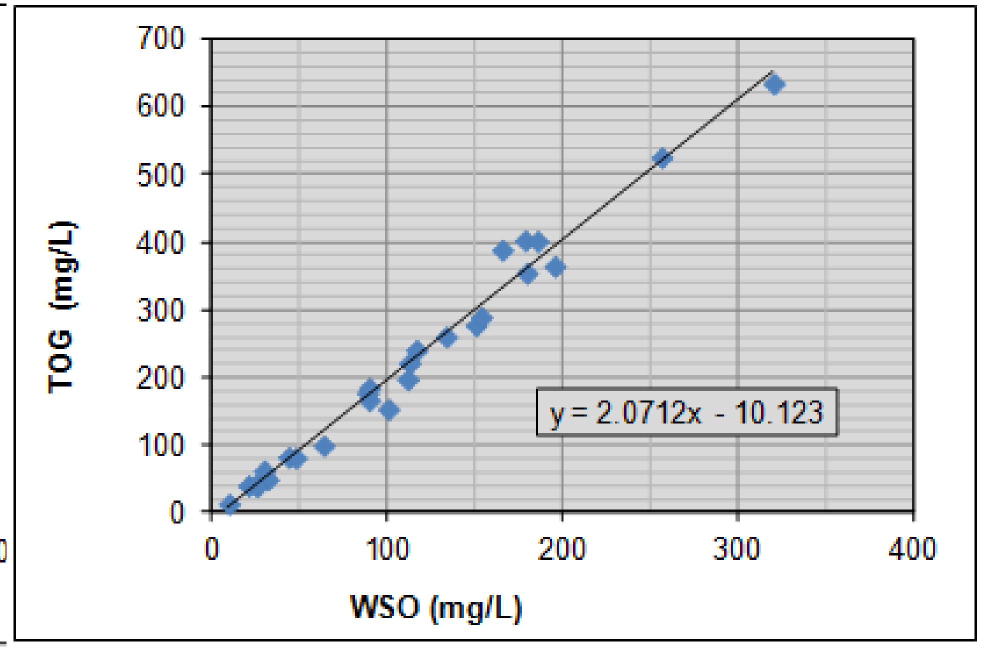
M_o = measured molecular weight of the oil (gr oil/mol oil)

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





α1	1.876
α2	15.793
α3	-10.123
ρgo	860
Mo	300
α4	2.9

[C]o	1.34
[D]o	1.53
kowC	4.529E+04
[C]w	2.955E-05

Mc	534.5
Md	94.68

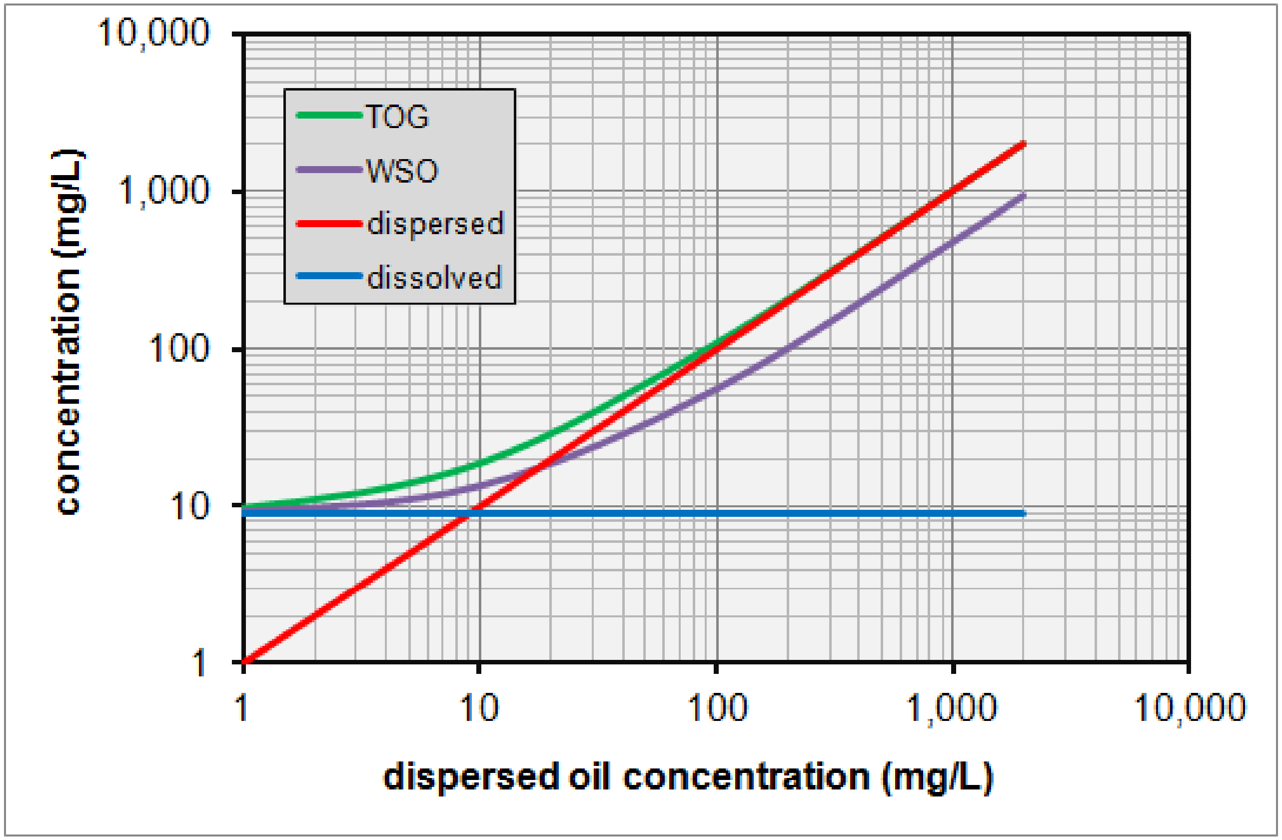
α_1 = slope of C_{TOG} vs $C_{TOG} - C_{WSO}$

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

Model Application – Case 5



Curves are calculated using the model.

Model is based on previous slide field data.

TOG = disp'd + dissolved
green = red + blue

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

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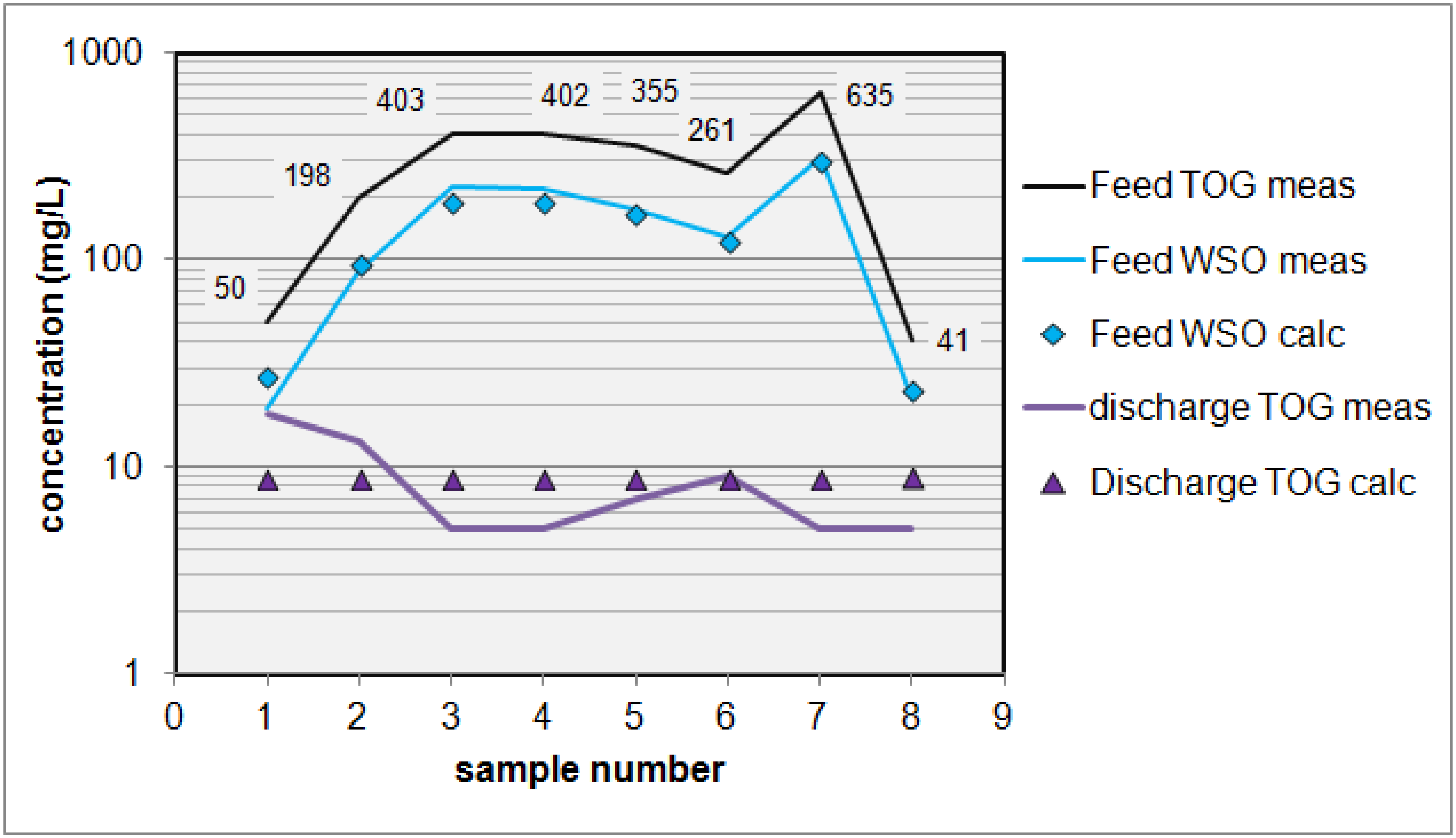
Field data confirm that after Hi-Flow removal of dispersed oil, TOG & WSO are in the range of 0 to 13 mg/L

Model Application – Case 5



Reality Check – Partition Coefficients

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

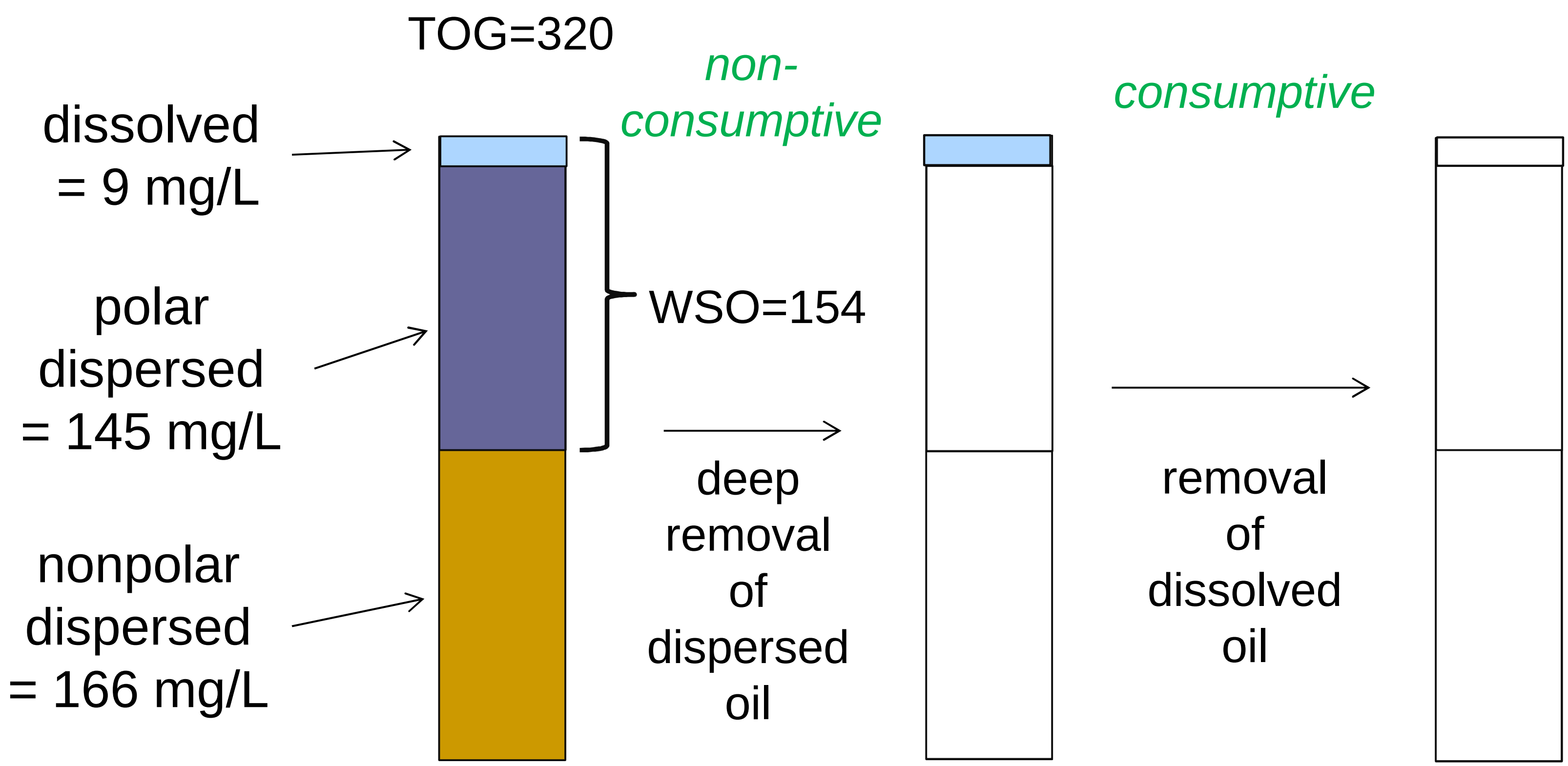
Chemical Name	CAS Number	Octanol Water Partition Coefficient log Kow (12)	Formula
C1			
o-cresol	95-48-7	1.97-2.03	$CH_3C_6H_4OH$
p-cresol	106-44-5	1.62-2.06	$CH_3C_6H_4OH$
C2			
2-ethylphenol	90-00-6	2.43-2.51	$C_2H_5C_6H_4OH$
4-ethylphenol	123-07-9	2.39-2.58	$C_2H_5C_6H_4OH$
C3			
2-propylphenol	644-35-9	3.21-3.25	$CH_3CH_2CH_2C_6H_4OH$
4-propylphenol	645-56-7	3.18-3.30	$CH_3CH_2CH_2C_6H_4OH$
C4			
4-tert-butylphenol	98-54-4	3.04-3.31	$(CH_3)_3CC_6H_4OH$
C5			
4-tert-amylphenol	80-46-6	3.72-3.96	$C_2H_5C(CH_3)_2C_6H_4OH$
C6			
2,6-diisopropylphenol	2078-54-8	3.96-4.03	$[(CH_3)_2CH]_2C_6H_3OH$
C8			
4-octylphenol	1806-26-4	4.12-4.18	$CH_3(CH_2)_7C_6H_4OH$
C9			
4-nonylphenol	84852-15-3	4.20-6.36	$C_9H_{19}C_6H_4OH$

Measured partition coefficients are consistent with model predictions.

Table 1 – Log P (Heptane/Water) for $H(CH_2)_nCOOX$

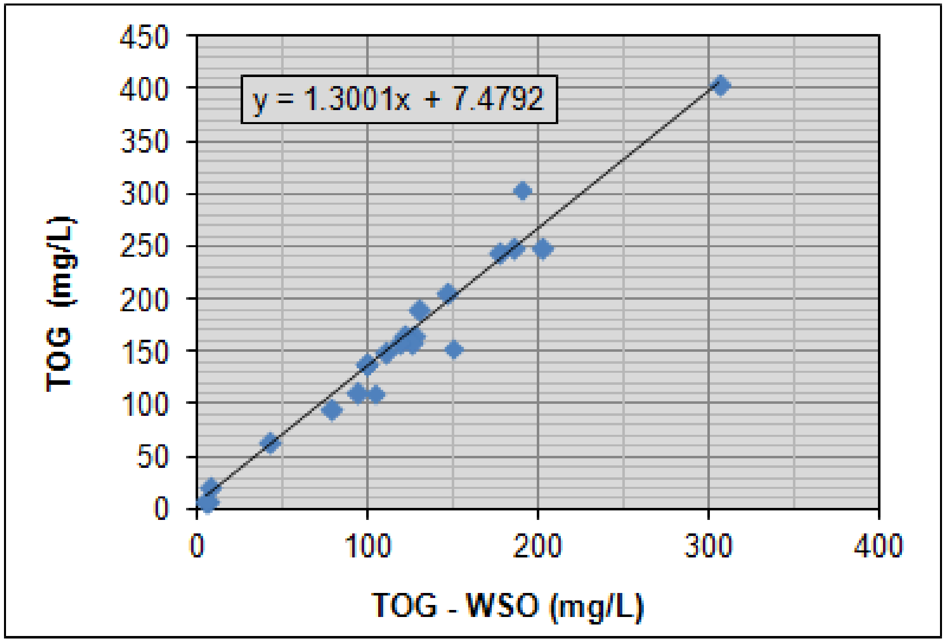
n	X=Na	X=H	X=H:HOOC$(CH_2)_n$H
0	-20.76	-3.72	-2.02
1	-20.15	-3.11	-1.41
2	-19.53	-2.49	-0.79
3	-18.92	-1.88	-0.18
4	-18.31	-1.27	0.43
5	-17.70	-0.66	1.04
6	-17.09	-0.05	1.65
7	-16.47	0.57	2.27
8	-15.86	1.18	2.88
9	-15.25	1.79	3.49
10	-14.64	2.40	4.10

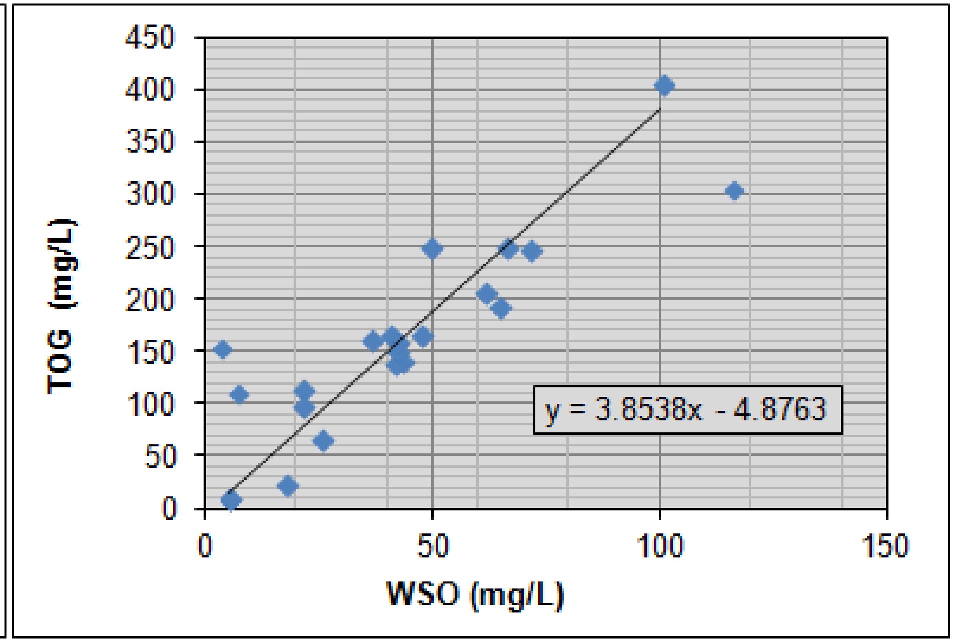
Why is this Important?



- *This minimizes consumption of media.*

Model Application – Case 4





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

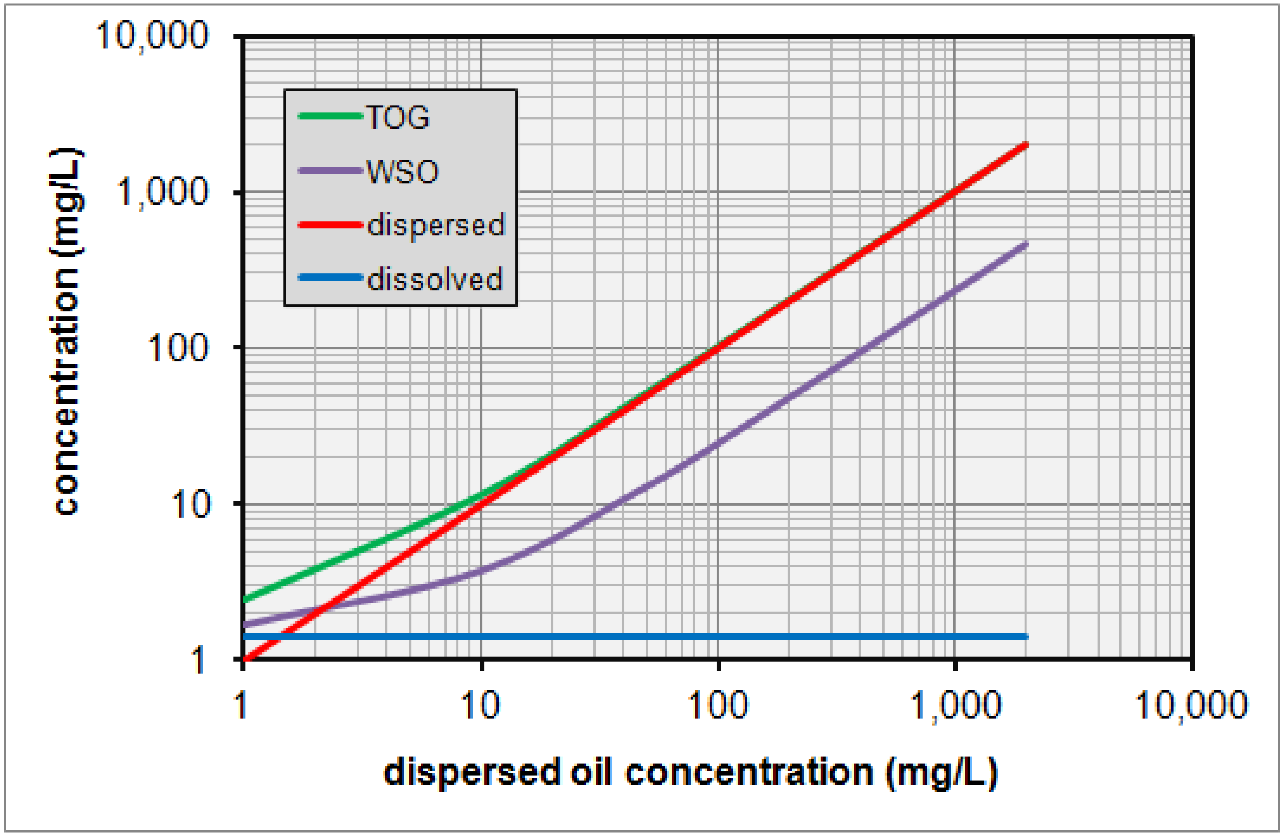
α_2 = intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$

α_3 = intercept of C_{TOG} vs C_{WSO}

α_4 = ρ_{go} / M_o

α1	1.3000
α2	7.4792
α3	-4.8763
ρgo	800
Mo	200
α4	4.0
[C]o	0.92
[D]o	3.08
kowC	1.262E+05
[C]w	7.314E-06

Model Application – Case 4



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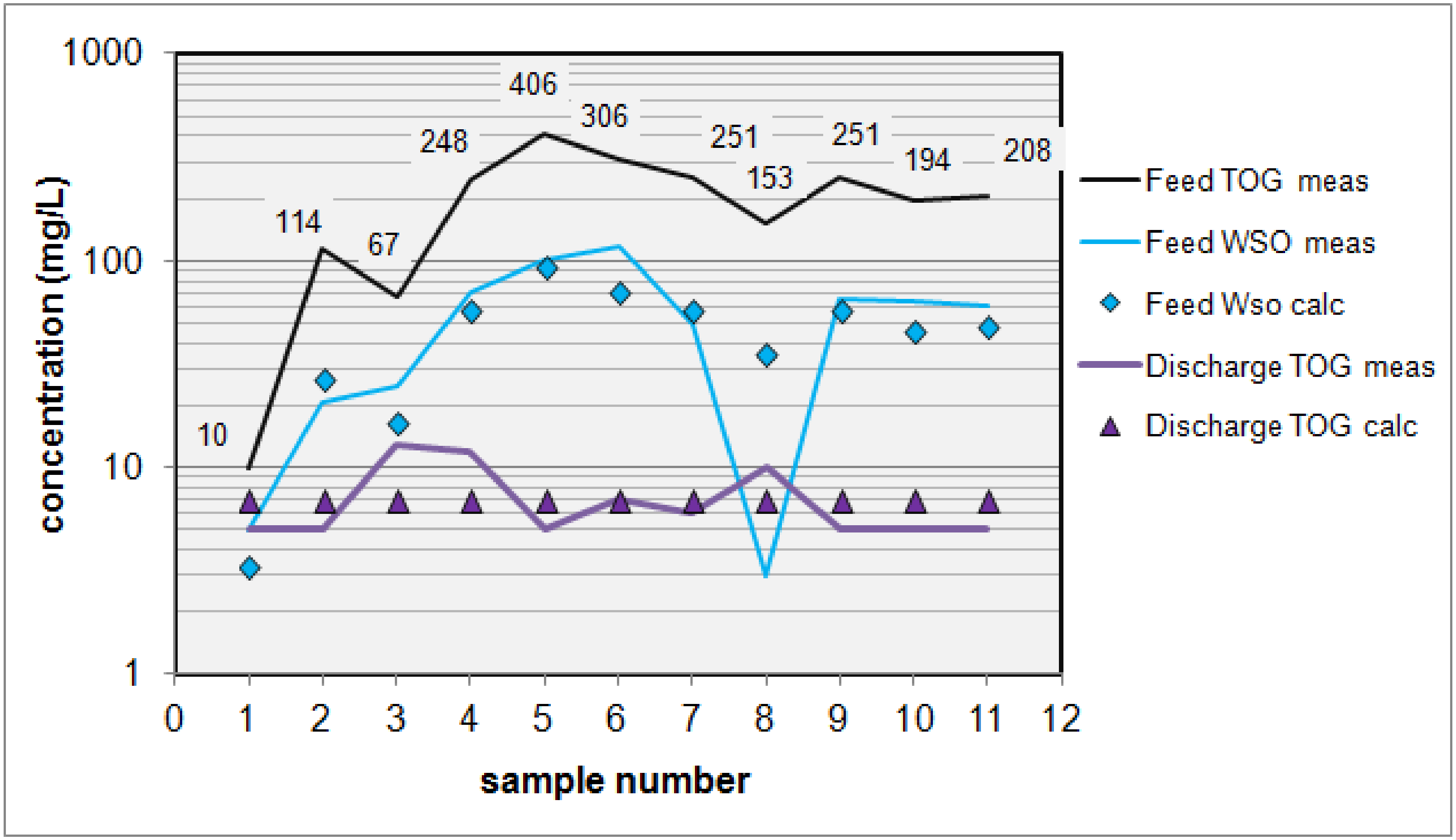
Model Application – Case 4



Third Application – Volatile Compound:

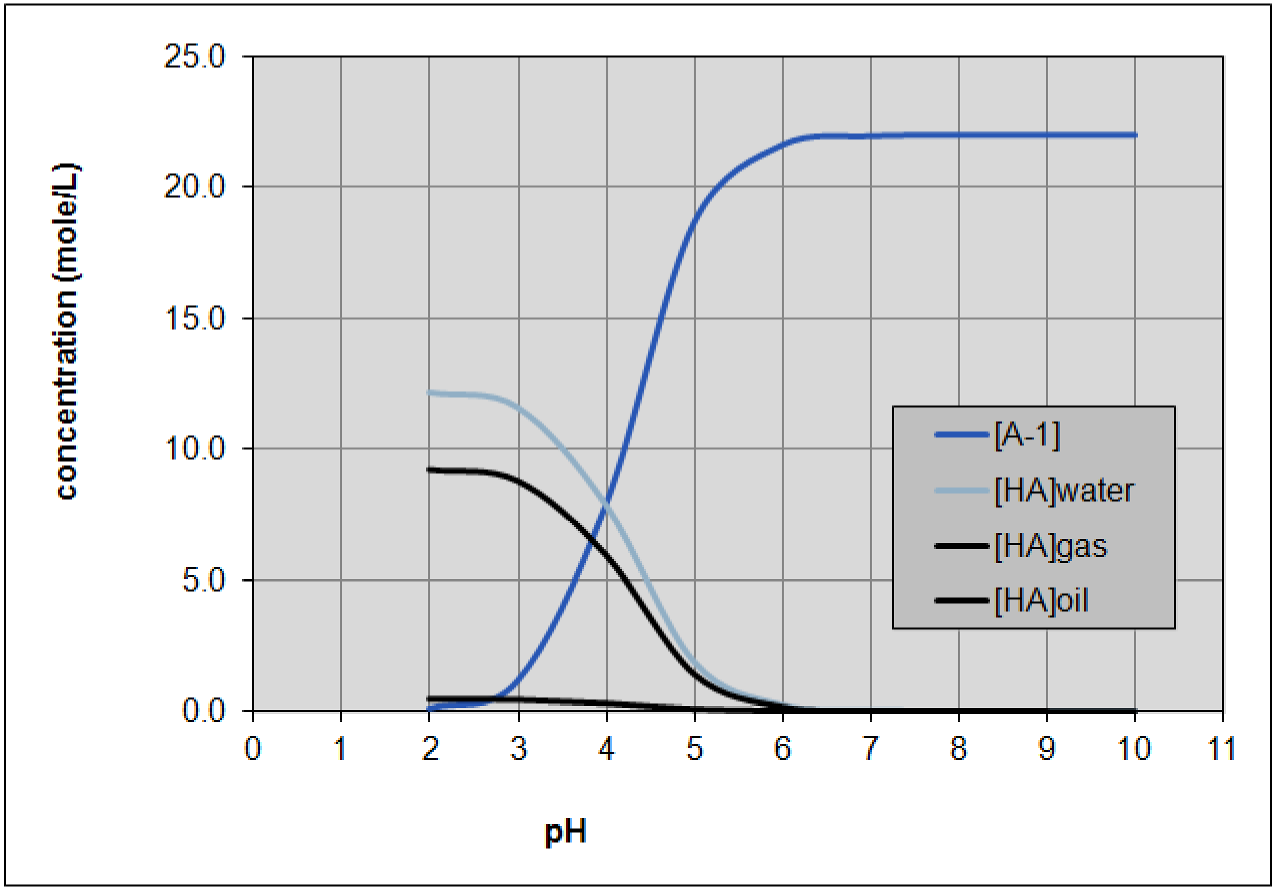
Third Application:

A non-ionic component (B or HA) that partitions into the gas phase.

This component can be stripped from the oily water by gas breakout, or by flotation.

It can also be stripped from the sample during analysis when the solvent is evaporated.

Modeling:

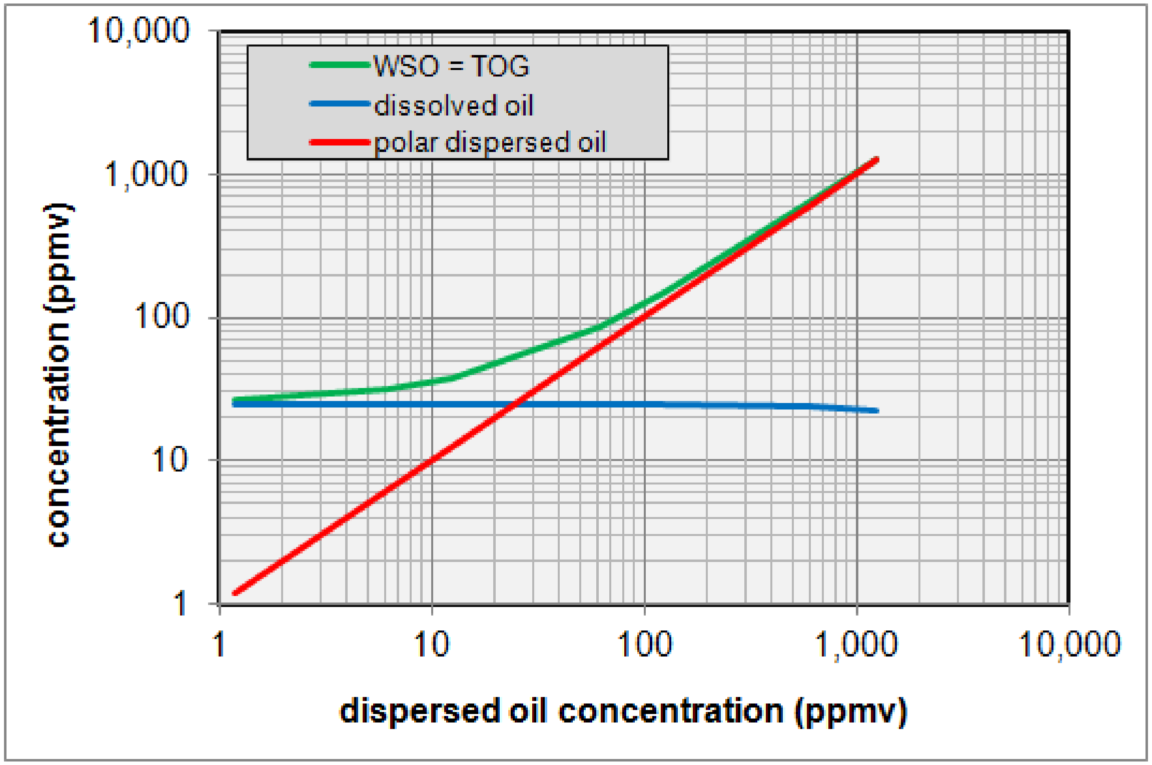


This application shows the importance of gas partitioning in reducing the WSO content of oil-in-water samples.

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.

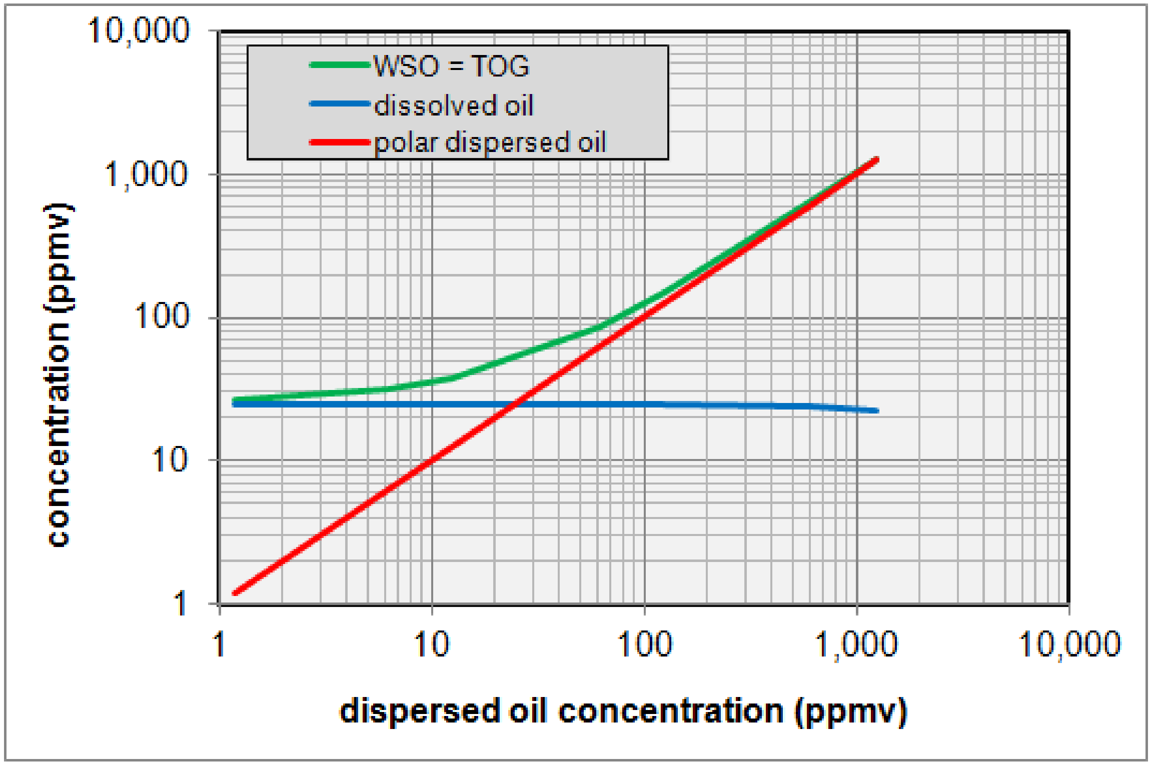


Example where the oil is composed of a single polar hydrocarbon
In this case, toluene.

Dissolved oil = concentration of toluene dissolved in water.

Polar dispersed oil = toluene dispersed as drops in the water. This is the toluene concentration in excess of the solubility limit.

WSO = dissolved oil + polar dispersed oil = TOG



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Dissolved oil = concentration of toluene dissolved in water.

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WSO = dissolved oil + polar dispersed oil = TOG

What is measured?

There are 4 important quantities:

dispersed oil = polar hydrocarbons and non-polar hydrocarbons

dissolved oil = polar hydrocarbons

TOG = all dispersed and dissolved hydrocarbons

WSO = polar dispersed and dissolved

The model mathematically relates the dissolved polar hydrocarbons to the dispersed polar hydrocarbons through the use of partition coefficients and equations for chemical equilibrium:

$$HA \Leftrightarrow H^{+1} + A^{-1}$$

$$k_{HAow} = [HA]_o / [HA]_w$$

$$K_d = \frac{[H^{+1}][A^{-1}]}{[HA]_w}$$