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Understanding water soluble organics in upstream production systems

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Abstract

A mathematical model has been developed which allows correlation and prediction of chemical and phase equilibrium of dissolved organic components in produced water. The model is applied primarily to prediction of results from the EPA-1664 method of analysis. The model provides a clear understanding of the contributions of dissolved organics, dispersed oil, and the effect of pH on the so-called Water Soluble Organics. This can be applied to understand the consequences of reducing temperature and pressure that typically occurs in the production train, and the increase in pH which typically accompanies release of CO₂ into the gas phase. The model does not predict the formation or resolution of oil-in-water emulsions or dispersions. Those variables, important in the application of the model, are assumed to be measured or calculated and available for input into the present model. The model is also applied to sampling and analysis, which is an important part of processing produced water containing dissolved organics.

The main objective of the model is to help select better processes to remove dissolved organics, and to explain the role of sampling and analysis meeting discharge regulations. It is demonstrated that deep removal of dispersed organics can result in lowering of both total oil and grease and water soluble organics.

Introduction:

In the oil and gas industry, process simulation models are used to design new facilities for oil/water/gas separation, and to troubleshoot existing facilities. When applied competently, a process simulation model provides an optimized facility design for a given production flow rate, production profile, fluid composition, and given output specifications (gas dew point, pressure and hydrate formation temperature; oil BS&W, and vapor pressure). Process simulation provides the engineering link between fluid composition and facilities design.

Efforts to improve the removal of dispersed hydrocarbons and dissolved organics from produced water have a long history. In some cases, particularly where regulations are difficult to meet, chemical analysis and characterization of produced water have been carried out. Such analyses are helpful in identifying the chemical species responsible for high oil-in-water concentrations. In turn, this information is sometimes helpful in determining the optimal strategy for dealing with dissolved organics, such as deep removal of dispersed oil, addition of mineral acid, liquid/liquid extraction, optimizing flotation to achieve gas stripping, and the use of consumptive media. There are several established and new technologies for treatment of dissolved organics [1 - 10], many of which have specific applicability for certain compound types and concentrations.

Mathematical modeling is typically not applied. If process simulation for facilities design is any guide, modeling may be able to provide quantitative guidance toward selection of the optimum strategy for removal of water soluble organics and prevention of unwanted overboard discharges. Granted such practical models do not yet exist for dissolved organics in produced water. But it seems a worthwhile endeavor to develop such models and test their practical utility.

Another important reason for developing a model for dissolved organics is to improve the precision with which dissolved organics are analyzed and understood. Mathematical modeling requires precision. When applied to analytical measurements, sampling and analysis, and process systems, mathematical modeling imposes a welcome rigor in defining the quantities of interest.

The main objective of the model, and the application initially developed here, is the elucidation of process and measurement variables that influence the final discharge concentration of water soluble organics. The specific objectives of this work are to:

- develop a greater understanding of the relation between WSO and dissolved and dispersed components;
- develop a better understanding of what chemical components are measured and reported in the various monitoring and reporting analytical protocols;
- understand how process design choices influence WSO behaviour;
- develop a greater understanding of WSO behaviour through typical production systems;
- understand current extent of related work within the industry and anecdotal observations;
- consider the chemical and phase distribution of water soluble organics from a process engineering perspective;
- develop tools and techniques that guide process design toward optimal solutions for specific assets.

In this paper, the background and framework for the model are set forth. Illustrative calculations are presented. The model presented in this paper is developed with the eventual idea of integration with a standard process simulation package.

This paper is organized as follows. First, the quantities of interest are defined (see next section). Second, a short review is given of the range of chemicals that typically make up dissolved organics in produced water, their origin, and the typical concentration ranges. Then the model is introduced. Finally, various applications of the model are presented.

Dissolved Organics, Dispersed Oil, TOG, TPH, WSO:

The name “water soluble organics” conjures the idea of organic compounds dissolved in produced water. However, given the industry use of the term WSO, and the association of the term with the EPA-1664 test method [11, 12], there is little reason why reported values of WSO should be equivalent to dissolved organics. In some cases, the WSO content of a produced water sample is roughly equal to the content of dissolved organics. In other cases, WSO is not an accurate measurement of dissolved organics. The reasons for this discrepancy are discussed below.

To understand what WSO are and how they differ from dissolved organics, an accurate definition is required of all of the related quantities of interest, i.e. dissolved organics, dispersed oil, Total Oil & Grease, and Total Petroleum Hydrocarbons. It is not possible to define one of these quantities without defining all of the others as well. Each of these quantities are related to each other and are defined as much by what they are, as by what they are not. Excellent discussions of these concepts are available in the literature [13 - 18].

Dissolved versus Dispersed Organics: The concept of a dissolved organic molecule is well conceived. A dissolved organic molecule is simply an organic molecule that is surrounded by water. Likewise, the concept of dispersed oil is intuitive. Dispersed oil forms a distinct second phase, typically in the shape of drops that is distributed in the water phase. Due to buoyancy, the dispersed drops may cream (rise to the top) and form a free oil phase.

But not all of the organic material in the water is quite so simple. Many acids form dimers in water. These dimers too would be regarded as dissolved. Other polar molecules form small aggregates composed of say a few molecules to dozens of molecules. These might also be considered to be dissolved. Continuing the trend toward larger assemblies, produced water contains a wide range of concentrations and types of natural surfactant molecules. These can form micelles with polar groups at the oil/water interface and hydrocarbon molecules in the interior. At some point, the distinction between dissolved and dispersed organics becomes unclear.

While there is no universally accepted definition, in colloid and surface chemistry, organic molecules in water and assemblies of organic molecules having a diameter of less than 5 nanometers are generally considered to be dissolved [19]. Drops and particles having a diameter of greater than 50 microns are considered to be dispersed. These definitions leave a middle range of size that is not defined as either dissolved or dispersed. Assemblies of molecules having a diameter in between (5 nanometers to 50 micron) are considered to be colloidal. Colloidal material tends to be influenced by Brownian forces, and separation of these colloidal materials is dominated by surface chemistry, not simply settling or creaming. This is a rigorous definition, which may be helpful in some situations, but not here in the present application.

Faksness [13, 15] et al. use a practical approach to differentiate between dissolved and dispersed organics in produced water. They use 2 L jars to allow the dispersed organics to cream for a period of 48 hours. The organics that remain in the water are referred to as the Water Accommodated Fraction (WAF). Presumably they avoid using the term dissolved organics in recognition of the above mentioned ambiguity. In reality, they treat the Water Accommodated Fraction as dissolved organics. Using Stokes Law, and guessing at the physical properties of their system, it is likely that they remove all drops with a diameter larger than 2 to 3 micron.

Furthermore, as discussed below, produced water contains an enormous number and type of chemical compounds that have

surfactant-like character. This includes the medium and long chain acids, resins and asphaltene classes of constituents. It is likely that in the produced water associated with moderate or high acid crude oils, that most of the dispersed material has these natural surfactant-like constituents residing at the organic/water interface. This detail is important in establishing the stability of the dispersed phase and whether or not it forms a free oil phase or remains dispersed. It is also important in establishing whether surfactant-like molecules reside in the dissolved phase or at the organic/water interface. Thus, at some future point in time, this detail might be incorporated in the model. This level of detail can be ignored by the use of “effective” partitioning coefficients. This is justified by the complexity of the model without considering additional detail.

Other methods to differentiate between dissolved and dispersed organics include the use of centrifugation or filtration. In either method, the result is a removal of dispersed organics with diameter in the range of 0.5 micron to 2 micron [20]. Any organics larger are generally considered to be dispersed. Those smaller are generally referred to as dissolved.

Total Oil & Grease (TOG) and Water Soluble Organics (WSO): In this paper, as well as in most of the US-based oil and gas industry, TOG and WSO are defined in terms of the EPA 1664 analytical method [11, 12]. That method is summarized here for reference.

Summary of EPA 1664 Method:

A 1-L sample of oily water is acidified to pH less than 2.

The sample is then serially extracted three times with n-hexane in a separatory funnel. The total quantity of hexane used in the extraction is 3 L.

The extract is dried over sodium sulfate.

HEM: Hexane Extractable Material: the hexane extraction solvent is distilled from the extract at 85 C. The remaining material is referred to as HEM. The HEM is desiccated and weighed.

SGT-HEM: Silica Gel Treated HEM: the HEM generated in the above step is redissolved in n-hexane. An amount of silica gel proportionate to the amount of HEM is added. The intention of the silica gel is to remove polar components. After contact, the solution is filtered to remove the silica gel, the solvent is distilled from the extract at 85 C, and the SGT-HEM is desiccated and weighed.

SGA-HEM: Silica Gel Adsorbed HEM: the weight of material adsorbed by the silica gel. It is calculated as the difference: HEM – SGT-HEM.

In this paper, TOG is equivalent to the n-hexane extractable material (HEM) of the EPA 1664 method. Likewise, water soluble organics (WSO) is equivalent to the fraction of the HEM that is adsorbed onto silica (SGA-HEM). The TPH components are those HEM components that do not adsorb on the silica gel. Those components are said to be “treated” by the silica gel. To summarize:

TOG = HEM (mg/L n-hexane extractable material)

TPH = SGT-HEM (mg/L silica gel treated, n-hexane extractable material)

WSO = SGA-HEM = TOG – SGT-HEM = (mg/L silica gel adsorbed, n-hexane extractable material)

The n-hexane extraction step is followed by evaporation of the n-hexane at 85 C. This results in vaporization of not only the n-hexane but also volatile components such as benzene and the protonated form of formic and acetic acid. Since the sample is acidified to pH < 2, almost all of the formic, acetic and in fact all organic acids will be protonated.

It is important to note that neither TOG, nor WSO nor TPH is equivalent to the dispersed oil content of an oily water sample. Further, WSO is not a direct or even indirect measure of dissolved organics in produced water. The term, Total Petroleum Hydrocarbon (TPH), is not entirely accurate either. Strictly speaking, a hydrocarbon compound is composed only of hydrogen and carbon. According to IUPAC there are four classifications of hydrocarbons (alkanes, unsaturated alkanes, cycloalkanes, and aromatics). As will be shown, the term TPH, as it is used in the oil and gas industry consists of much more than just hydrocarbons. It contains many polar organic molecules as well.

Dissolved/Dispersed versus WSO/TOG: There are two frameworks for analyzing organic compounds in produced water. One framework is based on the physical picture of dissolved versus dispersed organics. This is the phase partitioning framework. As discussed earlier, this framework has some complications due to difficulty in defining the dividing

line between dissolved and dispersed material, but conceptually the framework is self-evident. The other framework is the analytical framework. This framework distinguishes between organic compounds in water on the basis of the EPA 1664 analytical method which results in two main quantities, the Total Oil and Grease (TOG) and the Water Soluble Organics (WSO). There are other quantities that derive from this test such as HEM and SGTA-HEM and SGT-HEM. These are discussed in detail below. For now, the two frameworks are summarized here.

<u>Framework</u>	<u>Description</u>
Phase Partition Framework Dispersed / Dissolved	The total organic concentration of a produced water sample is the sum of the dissolved organics plus the dispersed organics.
Analytical Framework TOG / WSO	Total Oil and Grease (TOG) is the total organic content that can be extracted using hexane, and which does not vaporize when the hexane is evaporated. Water Soluble Organics (WSO) is the polar (silica adsorbing) part of the evaporated hexane extract. It includes the dissolved organics and the polar organics in the dispersed oil. The remaining part of TOG, not included in the WSO, is the nonpolar part of the dispersed organics (TPH: Total Petroleum Hydrocarbons).

The difference between these two frameworks can be described in the following figure.

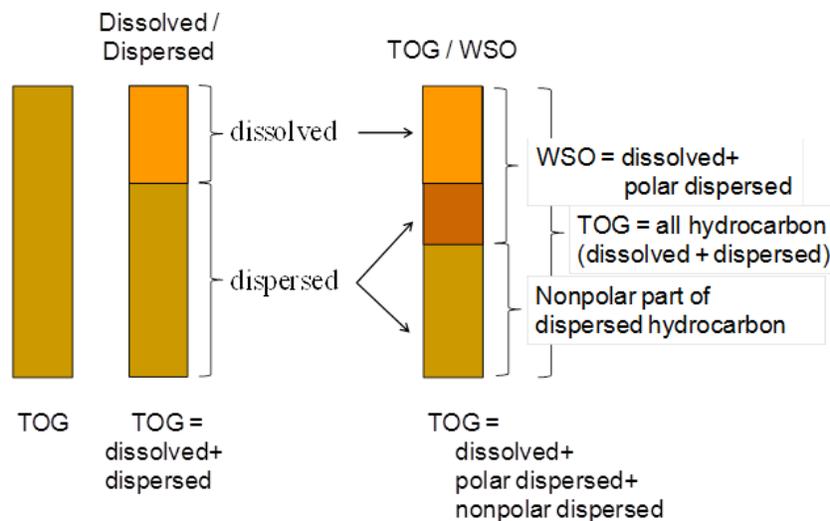


Figure 1. Schematic diagram of the two different frameworks for reporting of concentrations of organic compounds in produced water. On the far left, the total oil and grease (TOG) is shown having a certain value represented by the height of the bar graph. This TOG can be characterized as a combination of dissolved and dispersed organics, as shown by the middle bar graph. As shown on the right hand side, this same TOG value can also be characterized by WSO (Water Soluble Organics) plus TPH (Total Petroleum Hydrocarbons - the nonpolar part of the dispersed organics).

There is confusion in the literature and in the industry over the difference between the dissolve/dispersed framework and the use of the TOG/WSO framework. It is sometimes assumed that WSO refers to the concentration of the dissolved organics in water. As shown in the figure above, this is not the case. An additional component of WSO (polar dispersed component) comes from the dispersed oil. One of the objectives of present modeling project is to clarify this situation through a precise mathematical understanding of these frameworks.

Typical WSO Organic Compounds in Produced Water:

Water Soluble Organic compounds are defined as a solubility / volatility class. Individual chemical compounds can be identified, but the fundamental definition of WSO is given in the previous discussion as the fraction of the dissolved and dispersed hexane extractable material that does not flash off at 85 C and which sticks to silica gel.

This may seem like a complex and unwieldy definition. In fact it is. However, it is not entirely unique to use this kind of

definition for oil and water chemistry. In the oil and gas industry, a well-known similar case is asphaltene, which is a solubility class. Asphaltenes are those compounds that precipitate upon addition of hexane to crude oil, and which dissolve upon subsequent separation and contact with methylene chloride. In other words, the asphaltenes as a chemical aggregate group are only defined in terms of their solubility.

The table below lists the different classes of typical water soluble organics. They are defined here in terms of their abundance, solubility, and volatility.

Table 1. Six classes of compounds typically identified as water soluble organic compounds.

WSO Class	Characteristics
Phenol: C6 to C9	highly water soluble typically do not extract into hexane
Phenol: C10+	partition into dispersed oil phase extract to some extent into hexane
BTEX	high to moderate water solubility highly volatile
Acids: C1 to C4	very water soluble even at pH=2, typically do not extract entirely into hexane phase partitioning (water/hydrocarbon) strongly dependent on pH high adsorption tendency onto silica gel volatile (referred to as the volatile fatty acids)
Acids: C5+	somewhat water soluble depending on pH and carbon number extract into hexane at low pH phase partitioning (water/hydrocarbon) strongly dependent on pH high adsorption tendency onto silica gel main contributor to WSO in produced water with high WSO
PAH	low water solubility moderate solubility in hexane (but not completely soluble in hexane) most abundant components are the NPD compounds (see below)

NPD Compounds: The NPD compounds are naphthalene, phenanthrene, and dibenzothiophene. The first two of these compounds are members of the PAH class of compounds. Typically they are the most abundant of the PAH compounds. Thus, they are sometimes referred to separately.

PAH Compounds: The sixteen EPA PAH compounds are: naphthalene, phenanthrene, acenaphthylene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,b)anthracene, benzo(g,h,i)perylene. These compounds are the most carcinogenic of produced water organics. They have a high persistency in seawater and thus can be traced through the food chain to the higher order species which are harvested for human consumption. Thus, in some parts of the world, such as Norway, there is strong emphasis on eliminating these compounds from overboard discharged produced water [30, 31].

Naphthenic Acids: Use of the term “naphthenic acids” is widespread in the oil and gas industry, particularly in the downstream sector. In some instances it is synonymous with organic acids. In other cases it is used to indicate only the higher molecular weight fraction of organic acids. In general, there is not much consensus on what the term means.

One of the more widely referenced [21] early works on naphthenic acids dates back to 1955 and is likely responsible for the widespread use of the term. In those days, precise analytical methods to determine composition were not available. In fact, only two broad categories of organic acids were yet known in crude oil, and likewise then also in produced water. One category was the straight and branched paraffinic acids. Today we refer to these as volatile fatty acids. There were only two compounds identified in the other category, cyclopentanoic acid and cyclohexanoic acid. Since these were both saturated cyclic compounds they were given the name naphthenic acids. Thus the two categories that emerged to describe all organic acids in crude oil and produced water were:

- paraffinic acids – straight and branched paraffinic acids
- naphthenic acids – saturated cyclic acids and all other acids

Currently it is recognized that “all other acids” comprises an almost limitless number of different acid compounds. The concentration and variety of which in some crude oils is fascinating [22, 23]. The net result however is that the term naphthenic acid no longer has much meaning since it is too broad. In the modern literature regarding crude oil and produced water composition, it is more meaningful to discuss the specific classes of organic acid as have been done above in Table 1.

Examples of Dissolved Organics in Produced Water: Produced water varies significantly, from one reservoir to another, in the concentration and chemical species of dissolved organics. In Table 2, an example of dissolved organics from four North Sea platforms is given [24]. These components were measured directly without using an extraction solvent. The acids were measured using isotachopheresis. As shown, there is a significant concentration of acids.

Table 2. Dissolved Organics Measured in Produced Water from Four North Sea Platforms, Utkvik [24]. All values are given in mg/L.

Organic Compound Class	North Sea Platforms			
	Troll (mg/L)	Oseberg C (mg/L)	Oseberg F (mg/L)	Brage (mg/L)
Organic acids	798	717	1,135	757
Phenols	0.6	11.0	1,1.5	6.1
BTEX	2.4	5.8	8.3	9.0
NPD	1.32	1.60	1.27	0.93
PAH (not NPD)	0.11	0.08	0.15	0.07
THC	33	60	44	58

At the bottom of the table, the measured value of THC (Total Hydrocarbon Content) determined by old OSPAR (1997) protocol is given. The protocol for this measurement is: Freon extraction, quantitative IR measurement at the wave number of the aliphatic C-H stretch. Note that the sum of the concentration of the dissolved organics is much higher than the measured THC value. This is due to the fact that the Freon extraction step does not capture all, or even a large portion, of the dissolved organics. As discussed in the modeling section, solvent extraction involves phase partitioning of the dissolved organics between the produced water and the solvent. The more water soluble a component is, the less it will partition into the solvent and the lower the measured concentration in such tests as the old OSPAR protocol, and the EPA-1664 test, to name just two examples.

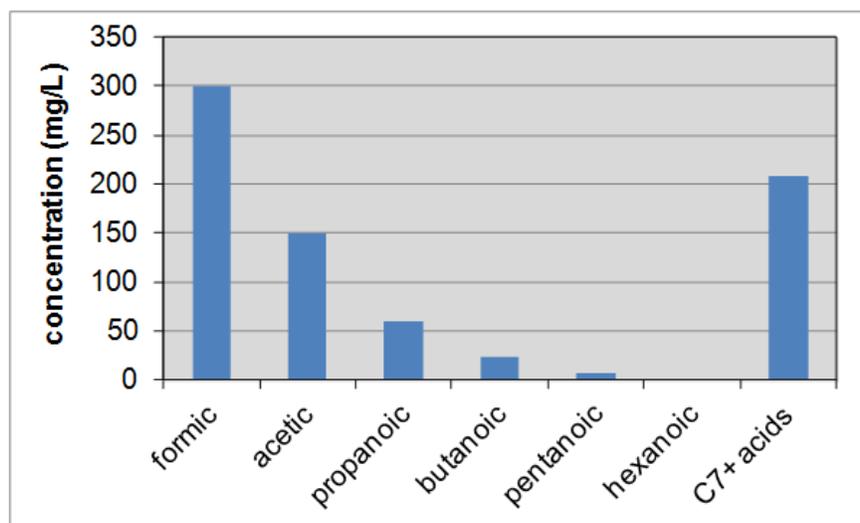


Figure 2. typical values for the concentration of specific acid compounds in produced water. Values for C1, C3-C7+ are from Utkvik. The value for acetic acid was not reported by Utkvik and was estimated independently.

For purposes of illustration, the relative concentrations of specific acids are given in Figure 2. Most of these values are reported by Utkvik [24]. However, in the Utkvik paper there is no reported value for acetic acid. An estimate for acetic acid was

made based on roughly a dozen samples from the North Sea that were gathered in relation to another separate study conducted by a major operator in relation to reservoir souring associated with the used of produced water for water flooding. These data are given here for illustration only. As will be shown, almost none of the C1 to C4 acids contribute to the WSO value reported in the EPA-1664 method.

Shown in the figure below is an illustrative trend for the concentration of organic acids extracted from produced water. These results are a composite of several data sources [4, 7, 22-25]. The intention of these data are to show the effect of solvent extraction, in this case, hexane. These data are given here for illustration only. As will be shown, almost none of the C1 to C3 acids contribute to the WSO value reported in the EPA-1664 method.

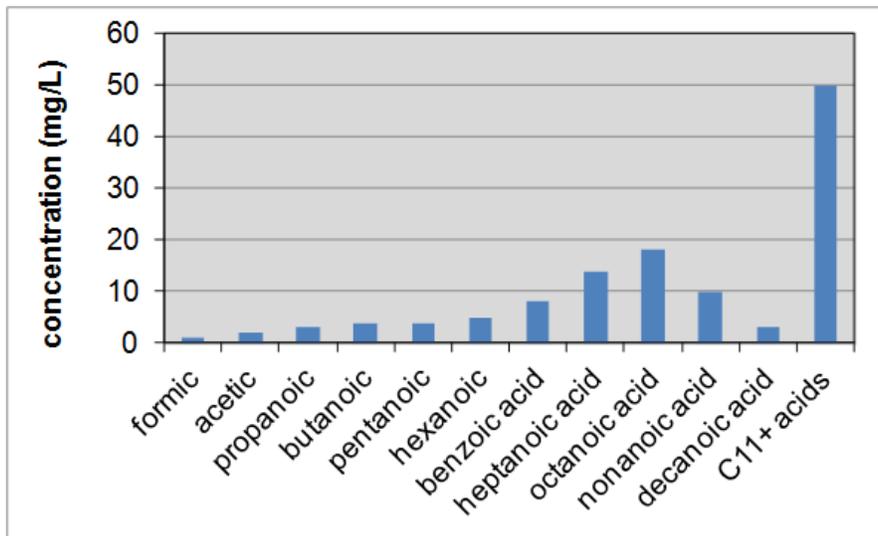


Figure 3. An illustrative trend for the concentration of specific acid compounds in a hexane extract of produced water. These data are a composite data from several sources [4, 7, 22-25].

In the above discussion, the various organic compounds involved in WSO analysis have been presented. Also presented in an earlier discussion was the difference between the phase partitioning framework (dispersed/dissolved) versus the analytical framework (TOG/WSO) for distinguishing organic compounds in water. It is worthwhile to identify which organic compound classes are typically found in which phases, and which organic compounds are typically reported in each analytical method. This is done in the figure below.

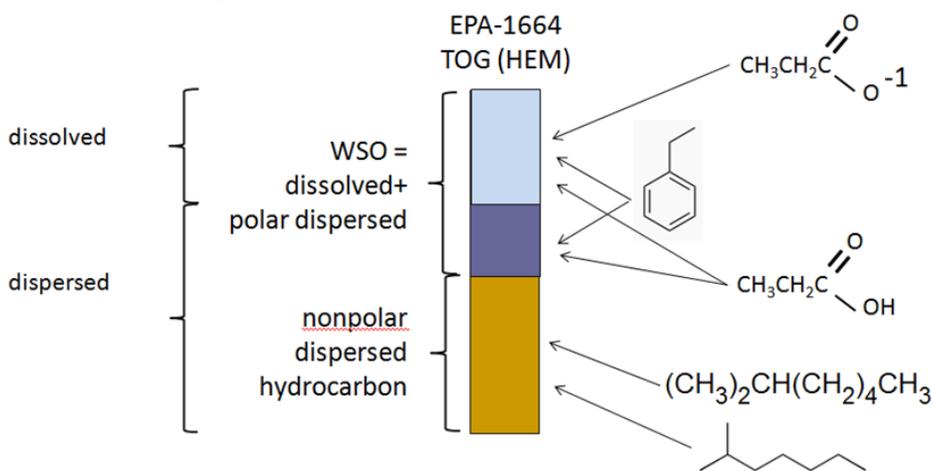


Figure 4. An illustration of the relationship between dissolved/dispersed organics and TOG/WSO, with examples of chemicals that contribute to each grouping.

The Model – General:

The model presented here builds on previous modeling work [26 - 29], but differs in certain aspects that are reviewed in the conclusions.

The model is composed of three axiomatic parts:

- Chemical Equilibria (acid dissociation)
- Phase Equilibria (partitioning across phases)
- Material Balance

These parts are described first in the form of a schematic diagram, second in the form of words, and third, in the form of equations. The schematic diagram is given first. The diagram is intended to show a particular component (HA) such as an organic acid. The acid dissociates, to some extent, in water. The protonated form of the acid dissolves in the oil and some of it vaporizes as well. The arrows are intended to show the dynamic equilibrium that is established whereby individual molecules randomly move between the various phases. The rate of movement between phases is not equal. This inequality gives rise to different equilibrium concentrations of the component in the various phases. Note that dimerization in the gas phase is not accounted for explicitly in this model. Instead, an effective concentration and partition coefficient is used.

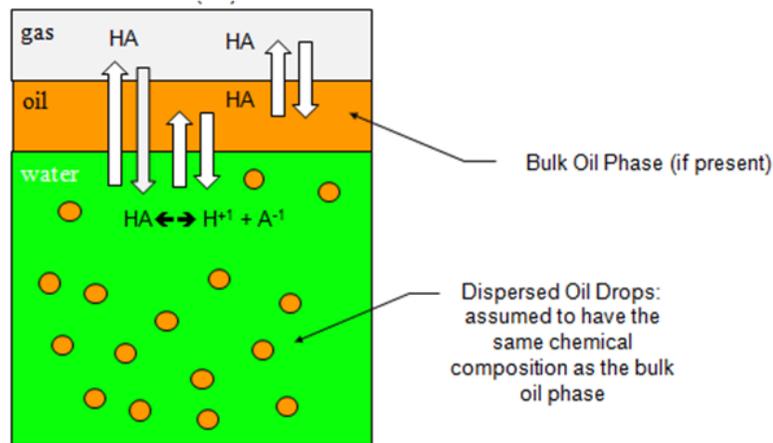


Figure 5. Schematic diagram of the model. A particular component (HA) is shown here, e.g. an organic acid.

At this point it is necessary to discuss in detail the basis of the model. The importance of the basis cannot be overstated. The model developed here, like any other model that involves a material balance, together with chemical and phase equilibria is formulated for a specific basis. The mathematical rules of carrying out a material balance require that a particular basis be selected. There are no constraints or rules governing the selection of a basis. However, once a basis is selected, it must be used consistently throughout the model. Selection of a basis is a critical part of the model because a carefully selected basis will result in a clear and unambiguous model. A poorly selected basis will result in a model that is cumbersome and difficult to understand. After considering several options, the following basis was chosen.

The basis of the model is one liter of oily water, at standard temperature and pressure. Physically we can think of a sample of oily water taken from the process, at process temperature and pressure, which is then maintained as a closed system and brought to standard conditions. The sample then contains some free oil, some gas, and roughly one liter of oily water. Some water may have flashed off into the gas phase. Several organic components may have flashed off as well. If no gas has flashed off, or if none of the water vaporized, then the volume would be identically equal to one liter. But all components originally in the sample at process conditions are still contained in the sample, albeit not necessarily in their original phase when the sample was taken from the process.

To further understand this basis, it is expedient to describe the various phases. The oily water is composed of pure water, plus organic compounds and ions dissolved in the water, plus oil which is dispersed in droplets and which may be in such abundance that it forms a free oil phase. Thus, the basis of the model is composed of at least two phases (water and dispersed oil). A third phase is present depending on the amount of gas that forms.

The water phase has various components dissolved in it. These components include ions, acids, alcohols, and dissolved organics. The dispersed oil has various components dissolved in it as well. The dispersed oil does not have ions but it does have alcohols, protonated acids, and various organics. The components in the free oil and the dispersed oil phase are assumed to be in chemical and phase equilibrium with the components in the water phase. The volumetric amount of dispersed oil depends on external factors in the facilities process such as the extent of shearing, and the separation efficiency of water treating equipment. It is treated as an independent variable. Typically it is either measured, or modeled using various

produced water calculations.

There may also be a free oil phase associated with the liter of oily water. As stated already, the components in this free oil phase are assumed to be in chemical and phase equilibrium with the components in the water phase. We assume that the composition of the free oil phase is the same as that of the dispersed oil phase. The amount of free oil depends on external factors in the facilities process or analysis procedures, and is treated as an independent variable. Typically it is either measured or modeled using a process simulation package.

There may also be a gas phase associated with the liter of oily water. The components in the gas phase are also assumed to be in chemical and phase equilibrium with the components in the water phase, and with the components in the oil phase (free and dispersed). The amount of gas depends on external factors in the facilities process or analysis procedures, and is treated as an independent variable. Typically it can be modeled using a flash calculation using a process simulation package.

The model is presented below using expressions for chemical equilibria, partition coefficients, and material balance. Besides the basis of the model, the units of measure for concentration must be selected. Several different units could have been used such as grams/liter, mg/L, micro-L/L (volumetric parts per million), mg/kg (gravimetric parts per million), or moles/L. The later units were chosen. In the chemical literature, expressions and numerical values for the equilibrium constants and partition coefficients are typically written in terms of molar concentrations. Adopting molar concentrations here results in familiar expressions and allows direct use of literature values for partition coefficients and equilibrium constants. Further, using molar concentrations eliminates the need to use molecular weight and mass densities which can become cumbersome when manipulating algebraic equations.

The Model – Equations:

The equations presented below are written for a monoprotic acid (HA), where HA is the protonated form of the acid. A particular and specific chemical species was chosen for the purpose of writing the equations. However, any other compound could have been selected, including a nonionic species or even a nonpolar species. Selection of HA provides a certain degree of generality.

The electronic charge of an ion is indicated as a superscript on the right hand side of the chemical species. The dissociated anion is indicated as A^{-} . Whenever the concentration of a particular species is referred to, brackets are used, i.e. [HA]. The phase (oil, water, gas) is signified as a subscript on the right hand side of the brackets. Thus the concentration of the protonated acid in the water phase is denoted as $[HA]_w$. As discussed above, the dispersed oil and the free oil have the same composition, therefore no distinction is made between dispersed and free oil. At this point, it is worthwhile to further define the symbols:

$$[HA]_w \quad = \text{concentration of HA in the water phase (mol HA/liter water)}$$

$$[HA]_o \quad = \text{concentration of HA in the oil phase (mol HA/liter oil)}$$

$$[HA]_g \quad = \text{concentration of HA in the gas phase (mol HA/liter gas)}$$

$$F_w \quad = \text{water volume in one liter of oily water (liter water/liter of oily water)}$$

$$F_o \quad = \text{dispersed or free oil volume associated with one liter of oily water (liter dispersed oil/liter of oily water)}$$

$$F_g \quad = \text{gas volume associated with one liter of oily water (liter gas/liter of oily water)}$$

In the above definition of F_o , it is stated that F_o is the volume of dispersed or free oil per liter of oily water. If there is no free oil, then F_o is the volume of dispersed oil only. The product of the above quantities gives the molar amounts of each component in each phase. For example:

$$G_{HAw} = [HA]_w F_w \quad = \text{moles of HA in the water phase associated with one liter of oily water (mol HA/liter oily water)}$$

$$G_{HAo} = [\text{HA}]_o F_o \quad = \text{moles of HA in the oil phase associated with one liter of oily water (mol HA/liter oily water)}$$

The three parts of the model are described below both in words and in equation form. The equations given here are for a particular case of a monoprotic acid (HA). A more generalized version of the model has been written elsewhere. While the generalized version is more mathematically elegant, it lacks the physical appeal that is gained by writing the equations for a particular component.

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



$$K_{HA} = \frac{[\text{H}^{+1}][\text{A}^{-1}]}{[\text{HA}]_w} \quad \text{Eqn (2)}$$

In the above equation, the molar concentration of anion in water $[\text{A}^{-1}]$ is written without a subscript w because the anion only exists in water and thus there is no need to indicate the phase. The same is true of the proton.

It is important to note that pH is determined independently. It is not determined using the above equations. Instead pH is either given by measurement, or is determined by a modeling program such as OLI Stream Analyzer or Scale Chem. It is dependent on the CO_2 equilibria and thus it is governed by phase equilibrium flash calculations. Since flash calculations are not required in any other part of the model, they are only carried out here for the purpose of determining the pH. Once the pH is known, or estimated, it is inserted into the model and the concentrations of anion and protonated acid can be calculated.

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

Gas/Oil:

$$k_{HAgo} = [\text{HA}]_g / [\text{HA}]_o$$

Oil/Water:

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

Gas/Water:

$$k_{HAgw} = [\text{HA}]_g / [\text{HA}]_w$$

Silica Gel Adsorption Coefficient:

$$k_{HAS} = [\text{HA}]_S / [\text{HA}]_H$$

Note that the components considered in this work are at low concentration (ca 0.1 % v or less) compared to the main components of the oil, gas, and water. Thus, the components considered here do not affect the phase volumes significantly. Therefore, flash calculations are not required. It may be helpful to understand this statement by considering a counter-example. Methane, for example, has a strong influence on the fluid phase equilibria of the process system. If the concentration of methane in the reservoir fluids happened to be higher or lower than current values, the amount of gas separated, and hence the remaining amount of oil, would change accordingly as determined by a flash calculation. It is assumed that flash calculations are not required for modelling the phase equilibria of WSO.

- **Material Balance:** as discussed above, the basis for the material balance is one liter of oily water. The fundamental law of mass balance is that mass can neither be created nor destroyed. In this model, this law is expressed in terms of the number of moles of each chemical species associated with one liter of oily water. Using moles instead of mass eliminates the need to deal with molecular weights. However, it does require careful accounting whenever dissociation (or recombination) is involved. However, this is not difficult. The number of moles of any particular component associated with one liter of oily water is the sum of the number of moles of that component in each phase.

$$G_{HA} = G_{HA_g} + G_{HA_o} + G_{HA_w} = [HA]_g F_g + [HA]_o F_o + [HA]_w F_w + [A^{-1}] F_w$$

G_{HA} = the sum of moles of HA in all phases associated with one liter of oily water (mol HA/liter oily water)

The model is formulated above using expressions for chemical equilibria, partition coefficients, and material balance. In general, there are five equations that must be solved for each component. However, many of the components considered in this work do not dissociate. In those cases, chemical equilibria is not included in the equations of material balance and phase equilibrium. Some components neither dissociate nor dissolve in water. For those components, the chemical equilibrium and phase partition expressions are eliminated from the model for that component.

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 is formulated above using expressions for chemical equilibria, partition coefficients, and material balance. Altogether, there are five equations that must be solved for each component. The most convenient way of writing and solving these equations is in terms of molar concentrations. Using molar concentrations, the equations are simple and it is therefore easy to ensure that there are no errors in the calculations.

The model could have been written in terms of mass concentrations (mg/L) or other quantities. Using molar concentrations instead of mass eliminates the need to use molecular weights, and mass densities in every calculation.

While the use of molar concentrations turns out to be convenient from a calculation standpoint, it does result in quantities that are not typically measured. Typical measurements involve mass concentrations, i.e. mg/L. In order to compare the model results against results measured in field and laboratory samples, the units must be converted. The relation between molar concentrations and mass concentrations is straightforward. All of the mass concentrations are expressed as C_x . Examples are given here:

C_{TOG}	=	the mass concentration of TOG (mg TOG/liter oily water)
C_{WSO}	=	the mass concentration of WSO (mg WSO/liter oily water)
C_{TPH}	=	the mass concentration of TPH (mg TPH/liter oily water)
C_{disp}	=	the mass concentration of dispersed oil (mg dispersed oil/liter oily water)
C_{diss}	=	the mass concentration of dissolved oil (mg dissolved oil/liter oily water)

The Model – Definition of Chemical Compounds, Chemical Classes, and Aggregate Species:

Identification of individual organic compounds has been carried out and reported [22 - 24] for a limited but highly informative number of crude oils and produced water. When this has been done, an incredible variety of molecular structures have been identified. This is not surprising given that crude oil starts as living organic plant and animal matter and is then transformed by thermal and chemical processes that occur over millions of years. The composition of crude oil and produced water depends on many factors related to both the origin of the plant and animal matter, the organic deposition and maturation processes including biodegradation, migration and contact with other reservoir fluids, such as oxygen-containing meteorological water, and the procedures used to retrieve and analyze samples.

It would not be practical to model all of these individual compounds. There are far too many of them and not all of their properties are known (equilibrium constants, partition coefficients, etc). Further, many of the compounds involved are only

present in minute concentration (~ micro gram/L).

In modeling WSO, it is convenient to analyze and refer specifically to some of the more abundant lower molecular weight organic compounds, while grouping together aggregates or classes of the higher molecular weight and less abundant compounds. This is a common strategy in process simulation of hydrocarbons where pseudocomponents are used for the higher molecular weight compound classes. In process simulation, the pseudocomponents are assigned various average properties, and are assigned a weighted value of composition. The manner in which the properties are assigned have a dramatic effect on the model predictions and in particular the phase distribution. The choice of which compounds to model individually, and which compounds to group together depends on the particular sample, the composition and abundance of lower molecular weight species.

In the development and application of the model, no set grouping of compounds is made. In some cases, a wide variety of individual compounds are modeled. In other cases, it is sufficient to consider a very small set of chemical aggregates. This does not lead to confusion provided that the variables are well defined.

The model was presented above in terms of a single generic acid compound, HA. The molar concentration of HA was written as [HA], with the dissociation species of proton [H^{+1}] and anion [A^{-1}]. As a simplification, proton and hydronium equilibria are implied. As discussed above, the model can be written for individual chemical compounds, chemical classes, and/or aggregate species. Each of these quantities are assigned a distinct symbol. This helps to make them readily identifiable. The following symbols are examples of the individual compounds and groups of compounds used in the model:

Examples of Individual Chemical Compounds:

FA	=	formic acid
AA	=	acetic acid
PA	=	propionic acid
BA	=	benzoic acid
HA	=	a generic acid species
BB	=	benzene
TB	=	toluene
EB	=	ethyl benzene

Examples of Chemical Classes:

XB	=	xylenes (ortho-, meta-, para-xylene)
VFA	=	short chain volatile fatty acids
BTEX	=	benzene, toluene, ethyl-benzene, xylenes
NPD	=	1-3 substituted compounds of naphthalene, phenanthrene, dibenzothiophene
PAH	=	polycyclic aromatic hydrocarbons (except the NPD compounds)

Examples of Aggregate Quantities Based on Hexane Extraction:

HEDS	=	n-hexane extractable material, dissolved in the water, at specified pH
NEDS	=	material that is not extractable, and that is dissolved in the water, at specified pH
HEDP	=	n-hexane extractable material, dispersed in the water, at specified pH
NEDP	=	material that is not extractable, and that is dispersed in the water, at specified pH

Examples of Aggregate Quantities:

R	=	nonpolar hydrocarbons in the oil phase that do not partition into the water phase
S	=	partially soluble organics that partition into the oil and water phases
C	=	partially soluble organics that partition into the oil and water phases and that contribute to WSO
D	=	nonpolar hydrocarbons that contribute to TOG but not to WSO

Aggregate Quantities Defined by the EPA-1664 Test Method:

TOG	=	n-hexane extractable material (HEM, according to the EPA-1664 test)
WSO	=	SGA-HEM (silica gel adsorbed n-hexane extractable material)
TPH	=	TOG – WSO = SGT-HEM (silica treated HEM)

It should be obvious, but perhaps worthwhile to state explicitly, that whenever chemical classes or aggregates are used together with individual chemical compounds, care is taken to insure that there is no overlap. For example, if [BTEX] is used together in a model that also has [BB] (benzene), then [BTEX] will not include the concentration of benzene ([BB]). A similar situation will exist with the PAH compounds. If NPD (naphthalene, phenanthrene, dibenzothiophene) compounds are

included individually, the PAH (polycyclic aromatic hydrocarbon) parameters and concentration will not include the NPD compounds. This will be stated explicitly.

The Model – Aggregate Quantities:

As demonstrated below, and as discussed previously, the model is formulated on the basis of individual chemical compounds, chemical classes, and aggregate quantities. In other words, the model is specifically structured and formulated to allow application to the simplest of chemical systems involving just a few chemical species, or to the most complex chemical systems, typically involving field samples with literally thousands of chemical species. This feature is referred to as extensivity. Extensivity is the unique feature that makes this model a new and important contribution to the understanding of water soluble organics.

For any model to have this property it must have certain mathematical features that provide internal self-consistency. Without going into details, the definition and use of aggregate chemical quantities is what allows extensivity in the present model.

Modeling of individual chemical components provides welcome rigor to check the accuracy of the model. When individual chemical components are spiked into produced water, the distribution of those components can be measured and checked against model predictions. Insight can be gained on the chemical identity, and the chemical and phase behavior of individual chemicals. However, practical application of such calculations becomes tedious at best, and wildly impractical in reality, for actual field samples.

When chemical classes are modeled (see above for definition of chemical classes), some detail of the identity of the chemicals responsible for TOG and WSO is retained. When aggregates are used, almost all of the chemical detail gets washed out. However, mathematical relationships between dissolved organics, dispersed oil, TOG and WSO are derived that allow correlation and extrapolation of field data. This is the practical utility of the model. This more than makes up for the lack of chemical detail in the use of aggregates. Once a high level analysis has been carried out, on the level of aggregates, chemical analysis can be applied together with modeling on the level of classes of compounds, and a specific and targeted program for treatment can be developed.

It may be difficult to understand the significance of this feature at this point. Application of the model, as discussed below, should hopefully clarify why this is so important. The two applications (individual chemicals versus chemical aggregates or classes) are given below in the next section. The present section provides a bridge between these two different applications of the model. Some of the aggregate quantities defined above are particularly important. The TOG, WSO and dispersed oil and dissolved oil are discussed here.

TOM: Total Organic Material. This is perhaps the most intuitive and easy to understand of the aggregate quantities. Hence it is the first aggregate quantity to be discussed. The TOM is just the sum of all of the organic material in the oily water (dissolved and dispersed), regardless of whether it can be extracted or not. Obviously, as such, it is difficult to measure. Nevertheless, it provides a starting point for the other quantities that can be more easily measured. The molar concentration of TOM can be expressed as:

$$G_{TOM} = [\text{TOM}] = ([\text{HA}]_o + [\text{R}]_o + [\text{S}]_o)F_o + ([\text{HA}]_w + [\text{A}^{-1}] + [\text{S}]_w)F_w$$

(mol/L oily water)

In words, the above equation is expressed as follows. The moles of total organic material associated with one liter of oily water equals the sum of molar concentrations of components in the oil phase ([HA] for example with subscript o, in units of mol/liter of oil) times the dispersed oil concentration (Fo, in units of liter of oil/liter of oily water), plus the sum of molar concentrations of components in the water phase (subscript w, mol/liter of water) times the water concentration (Fw, liter of water/liter of oily water). The above equation does not signify a particular temperature, pressure, or pH. This information must be provided.

Note that the above equation is written in terms of aggregate quantities (HA, B, C). [HA]_o is the moles of all of the protonated acid species that are dissolved in the oil phase per liter of oil. Protonated acids are partially soluble in both the oil and the water phases. This partitioning is given by the partition coefficient, k_{HAow} . The protonated acid also dissociates in the water phase to form the acid anion (A⁻¹). The chemical equilibrium is governed by an equilibrium constant, K_{HA} , as discussed above.

S represents all of the organic components that are partially dissolved in water and in oil. This partitioning is given by the partition coefficient, k_{Bow} .

R represents all of the organic components in the oil that are not appreciably soluble in the water phase. R is found only in the dispersed oil phase.

Dispersed oil: The definition of dispersed oil and dissolved organics was discussed above, from the standpoint of chemical analysis. Here, it is defined as that fraction of TOM associated with the dispersed phase:

$$G_{dp} = ([\text{HA}]_o + [\text{R}]_o + [\text{S}]_o)F_o$$

Where G_{dp} is the moles of dispersed oil components per liter of oily water. The molar concentrations inside the parenthesis are all of the components that contribute to free or dispersed oil. In this equation, G_{dp} has the units of mols of dispersed phase components per liter of oily water. The quantity, $[\text{HA}]_o$ is the molar concentration (mol HA/liter oil) of protonated organic acid dissolved in the dispersed phase oil. The quantity F_o is the volume of dispersed oil in the oily water (liter oil/liter oily water). This equation could alternatively be written in terms of the molar density of these components ρ_{mdp} (mol dispersed phase components/liter of dispersed phase components). The following equation results from this substitution:

$$G_{dp} = \rho_{mdp}F_o$$

The typical measured quantity is the mass concentration of dispersed oil. This quantity is given by:

$$C_{dp} = \rho_{gdp}F_o$$

Where C_{dp} is mg dispersed oil/liter oily water. The mass density ρ_{gdp} has the units of mg dispersed phase components per liter of dispersed phase components.

In words, the above equation is expressed as follows. The mass concentration of dispersed oil equals the product of the volumetric concentration of dispersed oil (F_o – liter oil/liter oily water) times the mass density of dispersed oil (ρ_{gFO} – milligrams dispersed oil/liter oily water).

Dispersed oil is composed of some chemical compounds that are partially soluble in both the oil and water phase (B), plus some chemical compounds that are not soluble in the water phase (C).

Dissolved Oil: The dissolved oil is defined as that fraction of total organic material that is dissolved in the water phase:

$$G_{ds} = ([\text{HA}]_w + [\text{A}^{-1}] + [\text{S}]_w)F_w$$

Where G_{ds} is the mols of dissolved organic components per liter of oily water. The details of this equation can be inferred from the details of the analogous equation for dispersed organics.

TOG: The molar concentration of Total Oil & Grease (mol TOG/liter of oily water), as defined by the EPA-1664 method, is the sum of all hexane extractable material, that does not flash off at 85 C. It is expressed mathematically as:

$$G_{TOG} = [\text{TOG}] = G_{TOM} \text{ (pH = 2; 3L hexane; evaporated 85C)}$$

(mol/L oily water)

The pH at which this equation applies is pH = 2. In words, the above equation is expressed as follows. The molar concentration of TOG (mol TOG/liter oily water) equals the total organic material that is extracted with 3 L of hexane, and which does not flash off at 85 C from an acidized sample.

As an illustrative example, the previous aggregate quantities are used (HA, S, R). The equation for TOG can be written as:

$$[\text{TOG}] = ([\text{HA}]_H + [\text{R}]_H + [\text{S}]_H)F_H + ([\text{HA}]_{wH} + [\text{S}]_{wH})F_w$$

(mol/L oily water)

The TOG can be related to the original TOM in the sample. In fact, separate equations can be written for each chemical species as well as for their sum. One interesting relation is that for the acid dissolved in water. When the sample is acidized, all of the A-1 converts to HA. Some of this HA partitions into the oil phase. When the hexane is added, even more of the HA is transferred from the water phase into the hexane. This relation is given by:

$$[\text{HA}]_H = \frac{(F_o + F_w / k_{HAHw})}{(F_H + F_w / k_{HAHw})} [\text{HA}]_o$$

In words, this equation says that the concentration of HA in hexane is roughly 1/3 the concentration of HA in the oil, in the acidified sample. The factor of 1/3 comes from the volume of hexane that is used (3L). The 1/3 relation is not exact however since the addition of the hexane pulls some of the HA out of the water phase. That is the purpose of the large volume of hexane. A mathematical relation for this can also be derived:

$$[\text{HA}]_{wH} = \frac{(k_{HAHw} F_o + F_w)}{(k_{HAHw} F_H + F_w)} [\text{HA}]_w$$

In words, this equation says that the HA remaining in the water phase after addition of the hexane is significantly less than the HA in the water phase before the addition of hexane, as expected.

Note that the above equation is written in terms of molar quantities. This simplifies the equation. The quantity [TOG] is closely related to a measured quantity, C_{TOG} .

$$C_{\text{TOG}} = [\text{TOG}] \times (\rho_{g\text{TOG}} / \rho_{m\text{TOG}}) = [\text{TOG}] \times M_{\text{TOG}} \times 1000 \text{ mg/gr}$$

Where:

$$\begin{aligned} C_{\text{TOG}} &= \text{mg TOG/liter oily water} \\ [\text{TOG}] &= \text{mol of TOG components/liter oily water} \\ \rho_{g\text{TOG}} &= \text{mass density of TOG (mg TOG/liter TOG)} \\ \rho_{m\text{TOG}} &= \text{molar density of TOG (mol TOG/liter TOG)} \\ M_{\text{TOG}} &= \text{molecular weight of oil (gr/mol)} \end{aligned}$$

WSO: The molar concentration of Water Soluble Organics (mol WSO/liter oily water), can be calculated from the above equations for TOG by application of the silica gel adsorption coefficient: $k_{HAS} = [\text{HA}]_S / [\text{HA}]_H$.

TPH: The Total Petroleum Hydrocarbons, as defined above, can be calculated as: $\text{TPH} = \text{TOG} - \text{WSO}$.

Illustrative Calculations:

In this section, illustrative calculations are given. These calculations are carried out for two systems. The first system is composed of water, a hydrocarbon compound, and an acid compound. This is an ideal system which can be modeled using well defined physical and chemical parameters. Most of the chemical and phase equilibria of much more complex field samples can be illustrated with this simple system. The second system is an actual field case. The analysis of field data helps to explain what is meant by aggregates discussed previously. Applying the model to these two extreme systems helps to show what is meant by extensivity.

Illustrative Case 1 – Hydrocarbon plus Organic Acid: One of the simplest systems that has relevance to the study of dissolved organics is that of a single hydrocarbon compound plus a single organic acid in water. This is a very simple system which demonstrates important features of actual field mixtures. The basic chemistry of organic acids in water is so fundamental that it is discussed in introductory chemistry text books. The new aspect presented here is the relation between the simple elementary chemistry and an oil/water separation process, and the results of the sampling and analysis methods such as routine IR measurements, or the EPA-1664 test.

The first calculation is that of a small concentration of organic acid in water. The concentration is small enough that the organic acid is completely dissolved. For this dilute two-component system of acid and water, there is no hydrocarbon and hence no dispersed phase. It should be mentioned that the water does have some nominal quantity of dissolved ions such as Na^{+1} and Cl^{-1} . It is assumed that the values of the chemical equilibrium constant, and the partition coefficient are determined in a solution of these ions. Mineral acid (such as HCl), or alkali (such as NaOH) is added to adjust the pH. There are three chemical species of interest, $[\text{HA}]$, $[\text{A}^{-1}]$, and $[\text{H}^{+1}]$. The chemical reaction for the addition of mineral acid is given by the following expression:

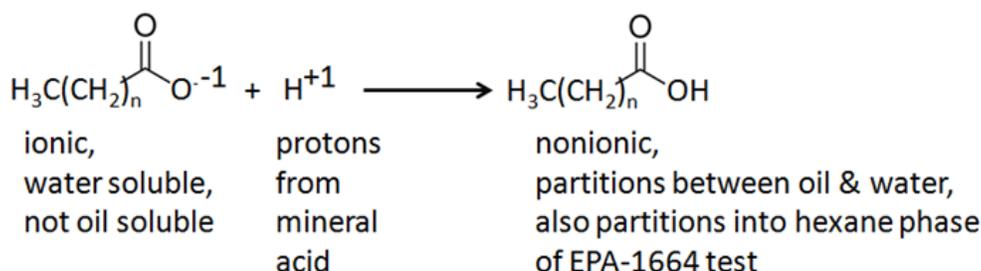


Figure 6. Schematic diagram of the model. A particular component (HA) is shown here, e.g. an organic acid.

In words, this equation says that the anion of the organic acid (on the far left), plus a proton from the mineral acid will combine to form the nonionic form of the acid (on the far right). The anion is not soluble in hexane (or oil, if it is present). The nonionic protonated form of the acid will partition into both the hexane phase and the water phase. However, at this point in the calculation, there is no hexane or oil phase present. The material balance and chemical equilibria for this reaction are given by equations (1) and (2) which are presented above.

A plot of the anion concentration as a function of pH is given in the figure below. Two curves are given in the figure. In the blue curve (to the left), the organic acid is moderately strong (low PKa value). In the red curve (to the right), the acid strength is lower (higher pKa value). Recall that the pKa value is the pH at which half of the molar concentration of the acid is in the anion form and half is in the protonated (nonionic) form.

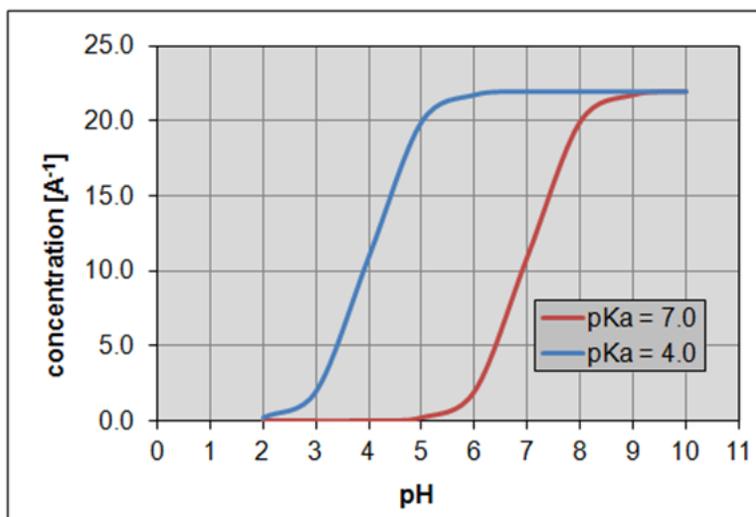


Figure 7. The concentration of acid anion as a function of the pH of the water. The pH is adjusted by addition of a mineral acid such as HCl.

The next figure shows the concentration of both species $[HA]$ and $[A^{-1}]$, dissolved in water, as a function of pH. Also plotted is their sum (red or top line), which remains constant. When no hydrocarbon solvent or oil phase is present, and when the acid does not vaporize, the total acid concentration (molar sum of HA and A^{-1}) in the water remains constant.

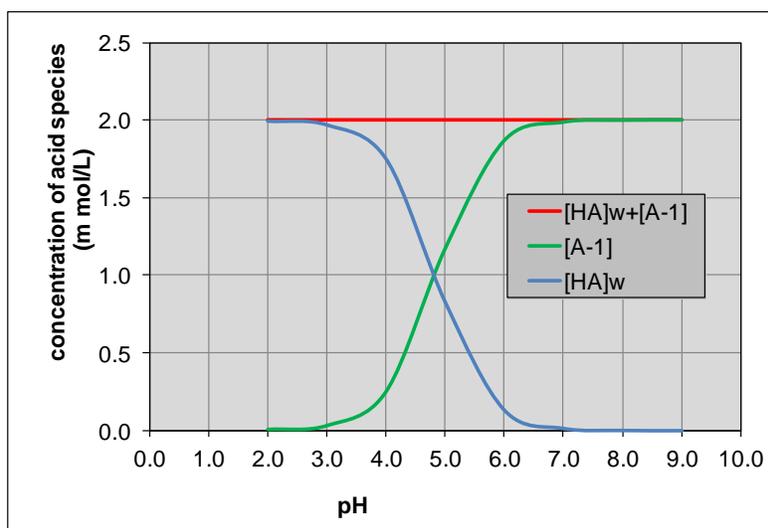


Figure 8. The concentration of acid anion as a function of the pH of the water. The pH is adjusted by addition of a mineral acid such as HCl.

The total molar concentration of acid for these calculations is 2 m mol/L (milli mol/liter). This value was chosen arbitrarily. If the acid of interest is acetic acid (molecular weight 59 mg/m mol), then the total acid concentration is 118 mg/L. If the acid of interest is hexanoic acid (molecular weight 115 mg/m mol) then the total acid concentration is 230 mg/L. The value of the equilibrium constant used for these calculations is $pK_a = 4.85$ mol/L. Note that $[HA]_w = [A^{-1}]$ at the point where $pH = pK_a$, as expected. This value is close to the typical value for C2 through C6 straight chain acids. The lowest pH chosen for these calculations is $pH = 2$. This corresponds roughly to the pH at which the EPA-1664 test is specified.

As mentioned, these initial calculations are straightforward and can be found in an introductory textbook of organic or physical chemistry. Nevertheless, they are useful background to the next set of calculations which involve a second non-aqueous phase.

In the next set of calculations, hexane is added as a component. Calculations similar to those previously given are carried out, i.e. concentrations of the acid species are calculated as a function of pH. The material balance is now given by:

$$G_{HA} = G_{HAo} + G_{HAw} = [HA]_o F_o + [HA]_w F_w + [A^{-1}] F_w$$

where G_{HA} remains constant, as pH changes, since it is the sum of material in both the oil and the water phases. This equation can be stated in words as:

$$G_{HA} = \text{the sum of moles of HA in all phases associated with one liter of oily water (mol HA/liter oily water)}$$

Calculation results are shown in the figure below. As before, all of the anion (A^{-1}) stays in the water phase. The blue line (bottom curve) gives the concentration of the protonated acid in water. The red line gives the sum of the protonated and unprotonated acid dissolved in the water phase. Unlike the previous figure, the total concentration of acid in the water is not constant. Instead, some of the protonated acid $[HA]_o$ partitions into the hexane phase. Due to this partitioning, the concentration of organic acid in the water phase decreases.

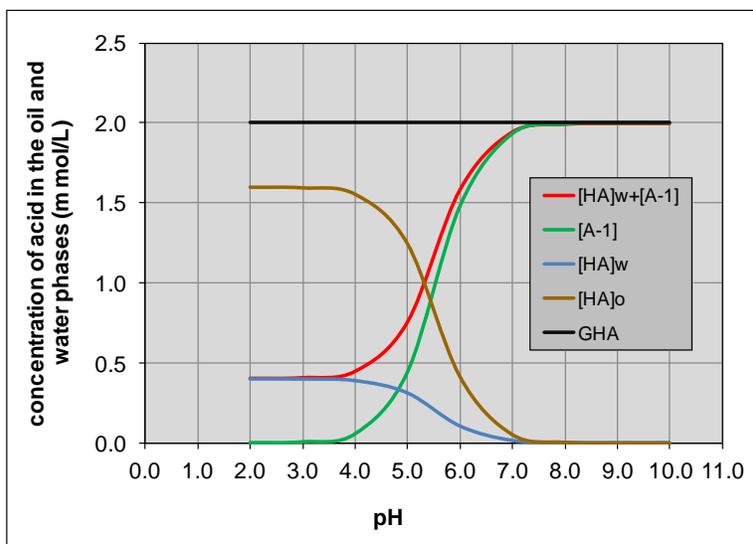


Figure 9. The concentration of all relevant species in the hydrocarbon/acid system as a function of pH. The pH is adjusted by addition of mineral acid such as HCl, or alkali such as NaOH.

The total molar concentration of acid for these calculations is again 2 m mol/L (milli mol/liter) and the $pK_a = 4.85$, as in Figure 8. For the calculation in Figure 9, an equal volume of water and hexane was used. The hexane/water partition coefficient was chosen as 4. This is typical of the C_8+ acids.

The preceding calculations, while simple, provide important insight into the behavior of organic acids in both real process systems, and in sampling and analysis procedures that are used. In a process system, the pH is governed by the presence of organic acids; the CO_2 concentration in the water (which is dominated by temperature and pressure); related produced water chemistry (e.g. alkalinity); and production chemicals (e.g. scale inhibitors, H_2S scavengers). If the contribution of the production chemicals is not significant, then the pH of the system increases as the fluid traverses through the system. This is due to the degassing of crude oil through the facilities pressure cascade, which vaporizes the CO_2 .

If the hexane used to calculate Figure 9 is assumed to be an analog for crude oil (roughly speaking), then Figure 9 gives insight into the fate of organic acids in the production system. Referring to Figure 9, if the produced water pH is 6, then roughly 75 % of the acid will be dissolved in the water (red line). The other 25 % will be dissolved in the oil phase (brown line). If the produced water in the Free Water Knockout has this pH value, then 25 % of the acid would partition into the oil phase and not the water phase.

If, on the other hand, the produced water in the Free Water Knockout has a $pH = 4.5$, then roughly 25 % of the acid will be dissolved in the water. The other 75 % of the acid will be dissolved in the oil phase. Thus, the pH of the process has a dramatic impact on the fate of the dissolved organics.

When a sample is acidized, the organic acids that are present in the produced water are completely converted to the protonated form (right hand side of the reaction, left hand side of the figures). These molecules are still polar, but less so than the ionic form, and have a much greater tendency to partition into the hexane (or other organic) extraction solvent.

If a sample is not acidized, the organic acids that are present in the produced water are mostly in the form of the anion (left hand side of the reaction, right hand side of the figures). These molecules are completely insoluble in hexane or similar organic solvent. Thus, unacidized samples have a lower test reading regardless of the method (IR, UV, EPA-1664), provided that an organic solvent is used for extraction.

In fact, a simple test of whether or not organic acids are present and contributing to the TOG and WSO reading is to carry out a measurement of both the acidized and unacidized samples. If there is a difference of more than 20 % or so, then organic acids are contributing.

Illustrative Case 2 – The Two-Component Model:

In the present Illustrative Case, field data are analyzed. Only two aggregate species are included in the model. One component is polar (adsorbs on silica gel) and partitions between the oil and water phases. The second component is nonpolar and does not partition. Both of these components are considered here to be aggregate components of many hundreds of

chemical species.

The two components are defined in this model as:

- C = partially soluble organics that contribute to both dissolved and dispersed oil as well as WSO
- D = nonsoluble hydrocarbons that contribute to dispersed oil but not to WSO

The mass balances are written in terms of TOG and WSO as:

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

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

Where:

- $[C]_o$ = concentration of the silica adsorbed hexane extractable component in the oil phase (mol C/L oil)
- $[C]_w$ = concentration of the silica adsorbed hexane extractable component in the water phase (mol C/L water)
- $[D]_o$ = concentration of the hexane extractable non-silica-adsorbed component in the oil phase (mol D/L oil)

In the above definition of chemical aggregate groups (C, D), and TOG and WSO it is implicitly understood that only the non-volatile fractions of these chemicals are considered. In other words, the chemicals identified in the model from this point on are those that do not flash off in the evaporation step of the EPA-1664 method.

It is demonstrated presently that the concentration of the polar component in water $[C]_w$ and the ratio $[C]_o/[D]_o$ can be determined from a plot of C_{TOG} versus the difference $C_{TOG} - C_{WSO}$. This is first demonstrated mathematically. To do so, we first take the difference:

$$[TOG] - [WSO] = [D]_o F_o$$

In the analysis, the quantity $[TOG] - [WSO]$ is treated as an independent variable. To do so mathematically, it is expedient to substitute the variable x , as follows:

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

Upon substitution, the following equations are obtained:

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

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

These equations suggest that a plot of $[TOG]$ versus x will have a slope of $1 + [C]_o/[D]_o$ with an intercept of $[C]_w$. In the above equations, it appears that the intercept would have a value of $[C]_w F_w$. However, as the concentration of dispersed hydrocarbon goes to zero, F_o goes to zero and thus F_w goes to one (unity). Thus, the intercept is just the value $[C]_w$.

The above mathematics also suggest that a plot of $[WSO]$ versus x will have a slope of $[C]_o/[D]_o$ with an intercept of $[C]_w$. Thus, these two plots ($[TOG]$ and $[WSO]$ versus $[TOG] - [WSO]$) will be very similar, differing only in their slope by a value of 1.

The definition of dispersed oil and dissolved organics was discussed above. In the two-component model, the following equations are obtained:

$$G_{dp} = ([C]_o + [D]_o)F_o$$

$$G_{ds} = [C]_w F_w$$

Where G_{dp} is the mols of dispersed oil per liter of oily water, and G_{ds} is the mols of dissolved organic components per liter of oily water.

The next step is to apply the two component model to actual field data. The following set of parameters are obtained from field data.

α_1	= slope of C_{TOG} vs $C_{TOG} - C_{WSO}$	(dimensionless)	= $1 + [C]_o/[D]_o$
α_2	= intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$	(mg C/L water)	= $[C]_w \times M_c \times 1000$
α_3	= intercept of C_{TOG} vs C_{WSO}	(mg/L)	= $- [D]_o \times M_o \times 1000 / k_{owC}$
α_4	= ρ_{go} / M_o	(mol oil / L oil)	= $[C]_o + [D]_o$

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)

Once the above data are obtained, the following calculations must be carried out to determine the values of the parameters in the model.

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

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

$$[D]_o = \alpha_4 / \alpha_1 \quad (\text{mol D / L oil})$$

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

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

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

Field data are plotted in Figures 10 and 11.

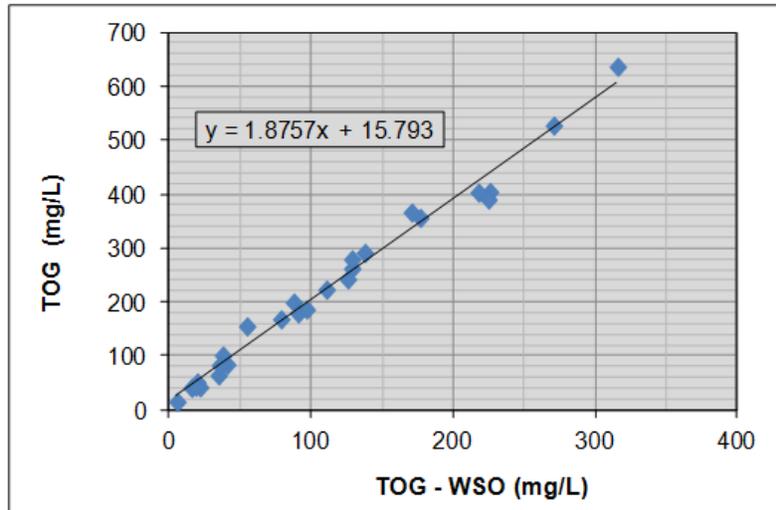


Figure 10. Measured field data for the concentration of TOG versus the concentration of TOG – WSO.

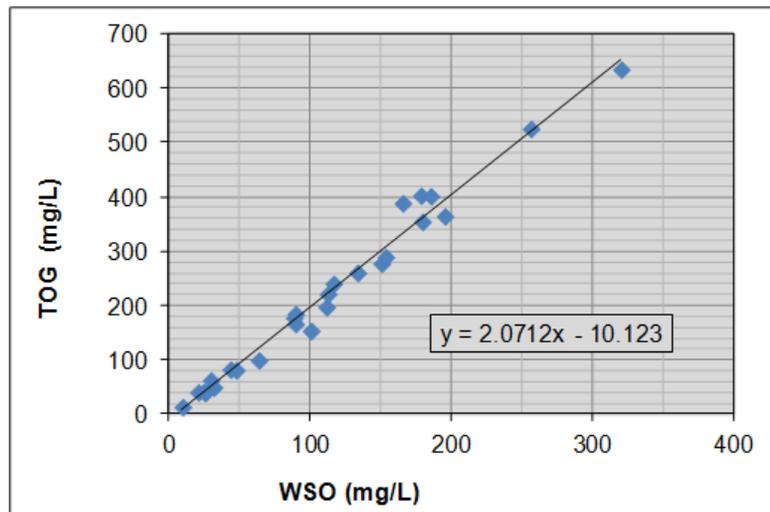


Figure 11. Measured field data for the concentration of TOG versus the concentration of TOG – WSO.

The parameters in the model are determined from the above plots and reported in the table below.

Table 3. Parameters in the two-component model determined form field data plots.

α_1	slope of C_{TOG} vs $C_{TOG} - C_{WSO}$	1.876
α_2	intercept of C_{TOG} vs $C_{TOG} - C_{WSO}$	15.793
α_3	intercept of C_{TOG} vs C_{WSO}	-10.123
ρ_{go}	independent measurement/correlation	860
M_o	independent measurement/correlation	300
α_4	$\rho_{go} / M_o = [C]_o + [D]_o$	2.9

$[C]_o$	$[C]_o = \alpha_4 (\alpha_1 - 1) / \alpha_1$	1.34
$[D]_o$	$[D]_o = \alpha_4 / \alpha_1$	1.53
k_{owC}	$k_{owC} = -(\alpha_4 / \alpha_1 \alpha_3) \times (M_o \times 1000)$	4.529E+04
$[C]_w$	$[C]_w = (\alpha_1 - 1) \alpha_3 / (M_o \times 1000)$	2.955E-05

Mc	$M_C = \alpha_2 / (1000 \times [C]_w)$	534.5
Md	$M_D = (\rho_{go} - M_C \times [C]_o) / [D]_o$	94.68

Trends calculated based on the two-component model and based on the parameters given above. Based on the two-component model, the below figure was constructed.

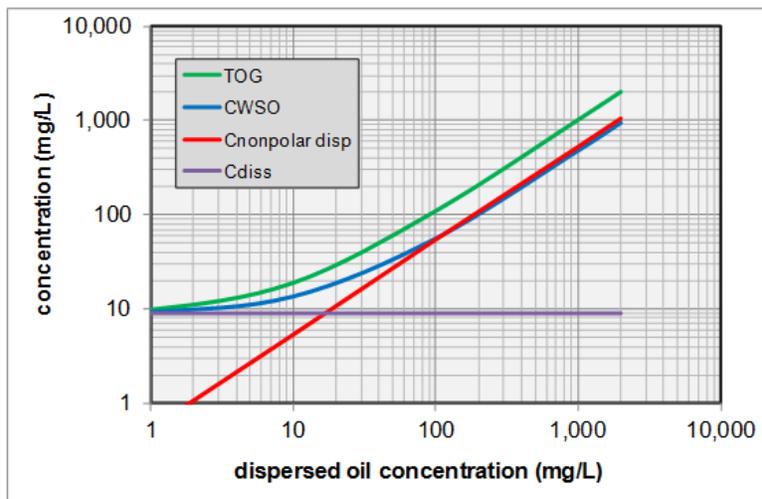


Figure 12. Calculations using the Two-Component Model using parameters based on field data.

Given the above equations, it is demonstrated that the two component model can be used to show explicitly the difference between the two frameworks for analyzing the systems. As discussed in the Introduction, there are two frameworks for understanding organics in produced water. The most readily understood framework is the phase partitioning framework, which distinguishes between dissolved organics and dispersed oil. This framework has some complications due to difficulty in defining the dividing line between dissolved and dispersed material, but conceptually the framework is self-evident. The other framework is the TOG/WSO framework. This is the regulatory framework. It is more difficult to understand but using the two-component model, the contributions from each framework is readily understood. Having a model that allows calculation of all of the quantities in both frameworks is useful because it makes explicit and precise the difference.

As shown in Figure 12, as the concentration of dispersed oil is reduced, the concentration of both TOG and WSO goes down. This is demonstrated by starting at the upper right hand side of the figure and following the lines toward the lower left hand side. The only curve that stays constant as the concentration of dispersed oil is reduced is the dissolved organics (purple horizontal line). It is logical that if dispersed and not dissolved oil is being removed, the model should predict a horizontal line, as shown.

From the above field data and modeling one of the data points was selected for further discussion. Throughout this paper, a set of bar graphs have been used to explicitly point out the difference between dissolved organics and WSO. For illustration, one data point was plotted on the bar graph as shown in the figure below. The highest value of TOG was selected (TOG = 320 mg/L). Based on the field data and the model, this TOG is broken down into WSO = 154 mg/L, of which 145 mg/L comes from the dispersed phase, and only 9 mg/L is dissolved in the water phase. This is a striking demonstration that if all of the dispersed oil is removed, most of the WSO is removed as well. Once the dispersed oil is removed, by a technology such as CETCO Hi-Flow, then only 9 mg/L is left. This final truly dissolved fraction can be removed by a number of media technologies.

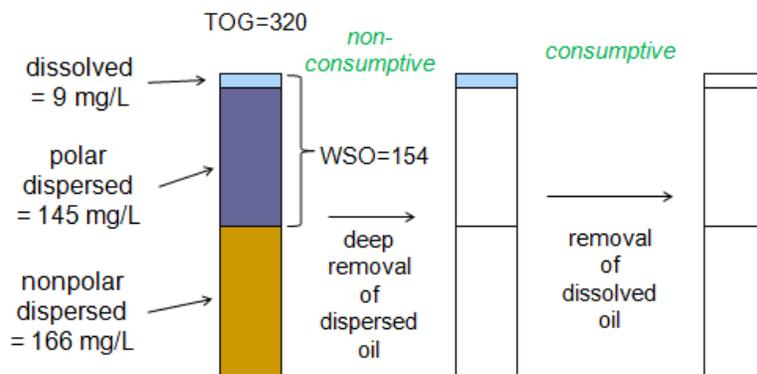


Figure 13. Calculations using the Two-Component Model using parameters based on field data.

Conclusions:

A mathematical model was developed which allows correlation and prediction of chemical and phase equilibrium of dissolved organic components in produced water. In developing the model, the relation between dissolved and dispersed components, and their relation to TOG and WSO was made explicit. The so-called WSO, as commonly identified with the silica adsorbed, hexane extractable material of the EPA-1664 test, is a combination of dissolved and dispersed components from produced water. To qualify as WSO a chemical compound must be polar enough to adsorb on silica gel but nonpolar enough to partition into hexane. Another somewhat easier way to say this is the following. WSO are composed of dissolved organics from the water phase plus the polar part of dispersed oil. In this case, “polar” refers to the tendency to adsorb onto silica gel. Various classes of compounds were discussed which have this property.

The model was applied to two systems. The first system is a simple hydrocarbon / acid system which demonstrates the importance of pH and phase partitioning in systems dominated by organic acids. The second system was that of actual field data for which it was demonstrated that most of the WSO was associated with the dispersed oil. The generality of this finding is currently being investigated.

The mathematics of the model may appear at first to be somewhat complex. This is mostly a consequence of the frequent use in this paper of illustrative calculations and manipulations, which demonstrate the chemical and phase equilibria of the chemical species involved. In practical application, linear algebra methods would be applied in a general framework such that no mathematical manipulation would be required.

A conclusion from this analysis is that for many produced water systems, WSO can be significantly reduced by deep removal of dispersed oil. Technologies that accomplish this are CETCO Hi-Flow, and some other media based systems. As dispersed oil is removed, both TOG and WSO are reduced. If all of the dispersed oil is removed, all that is left is the dissolved oil. Typically, very little of the dissolved fraction of produced water contributes to WSO (via EPA-1664).

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