



# Role of entrained droplet oil on the bioavailability of petroleum substances in aqueous exposures



A.D. Redman

ExxonMobil Biomedical Sciences, Inc., Annandale, NJ 08801, USA

## ARTICLE INFO

### Article history:

Received 6 March 2015

Revised 22 May 2015

Accepted 29 May 2015

Available online 10 June 2015

### Keywords:

Droplet oil

Dispersed oil

Oil toxicity

Oil bioavailability

## ABSTRACT

Bioavailability of petroleum substances is a complex issue that is affected by substance composition, the physicochemical properties of the individual constituents, and the exposure preparation system. The present study applies mechanistic fate and effects models to characterize the role of droplet oil on dissolved exposure and predicted effects from both neat and weathered crude oils, and refined fuel oils. The main effect from droplet oil is input of additional dissolved hydrocarbons to the exposure system following preparation of the initial stock solution. Toxicity was characterized using toxic units (TU) and shows that replenishment of bioavailable hydrocarbons by droplets in toxicity tests with low droplet content (e.g., <1 mg/L) is negligible, consistent with typical exposure conditions following open ocean oil spills. Further, the use of volumetric exposure metrics (e.g., mg/L) introduces considerable variability and the bioavailability-based metrics (e.g., TUs) provide a more consistent basis for understanding oil toxicity data.

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## 1. Introduction

Oil spill response and chemicals regulations require hazard assessment of petroleum substances to inform injury assessment, classification, and labeling activities (UN, 2009; King et al., 2001; US EPA, 2015). The common test methods include development of water accommodated fractions (WAF) using multiple substance loadings (Girling et al., 1992; OECD, 2002) as well as WAF dilutions (Anderson, 1985) under varying degrees of mixing and/or dispersant application (Mager et al., 2014; Rhoton et al., 2001; Davies et al., 1998). This approach results in complex exposures with varying degrees of droplet oil, which can potentially complicate the interpretation of toxicity results.

The present study builds on recent calls for improved characterization of exposures in ecotoxicity research (Harris et al., 2014; Redman and Parkerton, 2015) by characterizing the theoretical basis of the role of droplet oil in toxicity tests. The underlying assumption is that dissolved phase hydrocarbons are the most bioavailable form of hydrocarbons in aqueous exposures. Therefore, the main role of droplet oil is assumed to be replenishment of dissolved phase hydrocarbons (Carls et al., 2008). Typical toxicity testing involves preparing a WAF at prescribed oil-in-water loadings with stirring for a set amount of time followed by separation of the water and overlying oil phases. In dispersed systems, entrained droplet oil can be transferred from the initial WAF to the exposure system where the droplet oil will

continue to equilibrate with the aqueous phase. Earlier work has identified this process as potentially important for sparingly soluble substances (Redman et al., 2014). Additional experimental work suggests that droplets act as reservoirs of dissolved hydrocarbons (Carls et al., 2008).

The objective of this paper is to provide a theoretical basis for evaluating the role of droplet oil, and oil composition, on aquatic toxicity. The focus is on substances which would be candidates for dispersion during accidental spills such as fresh or partially weathered crude oils, and refined fuels oils. Mechanistic fate and effects models are applied to relate variable oil composition and loading, with and without droplet oil, to dissolved exposure and potential effects. Toxicity was evaluated using total toxic units (TU) as the sum of all dissolved phase constituents, as well as predicted volumetric endpoints such as median effects concentrations (e.g., EC50) in terms of simulated % WAF, concentration of total dissolved hydrocarbons, and total hydrocarbons (including both droplet and dissolved oil). General considerations and recommendations are provided to advance scientific understanding of the contribution of droplet oil to aquatic toxicity.

## 2. Materials and methods

### 2.1. Substance selection and composition

The present study evaluated substances that would be candidates for dispersion during accidental spill including a gas oil (e.g., similar to No 2 Fuel oil, Redman et al., 2012b), heavy fuel

E-mail address: [Aaron.d.redman@exxonmobil.com](mailto:Aaron.d.redman@exxonmobil.com)

oil (Redman et al., 2014), and fresh medium weight crude oil (API Gravity 23, Letinski et al., 2014). Comprehensive chemical characterization using GC×GC analytical methods was available for each of these substances and is given in the Supplemental Information. This analytical technique comprehensively characterizes the distribution of mass between structures with carbon number 6–31 across approximately 15 chemical classes including *n*- and *i*-paraffins, cycloalkanes, and 1-, 2-, 3+ ring aromatics.

To evaluate the impact of oil weathering on this study a two-film mass-transfer weathering model (Arey et al., 2007a,b) was applied to the fresh crude oil composition. The weathering model estimates environmental fate based on the solubility and vapor pressure of the individual constituents. The present study extends this prior work by including a first order biodegradation term modeled with BioHCWIN (Howard et al., 2005). See SI and Arey et al., 2007b for parameterization.

As points of comparison to the fresh crude and fuel oils, the weathering model was applied to achieve light, moderate, and heavy weathered oil compositions corresponding to an overall loss of 25%, 50% and 75% of the initial mass. The weathering model is intended to provide a reasonable estimate of composition under different degrees of weathering from volatilization and dissolution, utilizing the wealth of information in the comprehensive GC×GC data from the fresh crude oil. Due to uncertainties in relating the results of the weathering model to field conditions, the evaluation is only intended to illustrate major trends and processes that control bioavailability of dispersed petroleum substances. The modeling analysis of the neat crude oil and fuel oils are based on measured compositions, see Tables in SI.

## 2.2. Solubility model

A mass-balance spreadsheet was developed using the solubility model from McGrath et al. (2005), which is based on Raoult's Law and predicts dissolution as a function of solubility and oil phase concentration. The model uses a library of representative constituents that are mass-weighted based on the GC×GC characterization (Redman et al., 2012b) according their assigned carbon number and chemical class.

The calculation scheme is presented in Fig. 1 to illustrate how the initial oil composition is used to predict the composition of dissolved constituents in the initial WAF preparation (upper panel, Step 1). This is representative of a discrete oil-in-water loading such as might be used in a loading-based evaluation, or as a stock solution used for dilution series. The total mass of a given constituent as introduced in its initial oil loading and the initial concentration in the oil phase was used as the input,  $m_i$ . Dissolved concentrations are computed using the mole fraction ( $x_i$ ) and sub-cooled solubility ( $S_{L,i}$ ).

$$C_{W,i} = x_i S_{L,i} \quad (1)$$

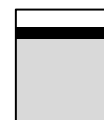
Calculations that involved droplet oil involved a second step. First, mass of dissolved constituents were computed in Step 1, as well as the composition of the oil following equilibration with the water phase. The total mass input for Step 2 (lower panel) was computed as the sum of the dissolved phase constituent plus the contribution from the droplet phase. The droplet concentration was chosen to represent a range of low to moderate levels based on prior experience (Redman et al., 2012a, 2014). The solubility calculation was repeated with this new total mass input for each combination of dilution, loading, and droplet concentration to predict the dissolved phase composition in the presence of droplet oil.

These calculations assume steady state conditions and that the presence of dispersant (e.g., to promote droplet formation), and droplet size distribution, does not impact the solubility. This is consistent with earlier model verification work indicating typical

### Step 1. Solubility in initial WAF

$$x_i = \frac{m_{i,\text{system}}}{(V_{\text{oil}} P_{\text{oil}} + V_{\text{Air}} S_{L,i} H_i + V_W S_{L,i})}$$

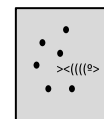
Oil phase    Headspace    Aqueous



### Step 2. Solubility in test system including droplets

$$x_i = \frac{m_{i,\text{system}}}{(V_{\text{oil}} P_{\text{oil}} + V_{\text{Air}} S_{L,i} H_i + V_W S_{L,i})}$$

Oil phase    Headspace    Aqueous



**Fig. 1.** Schematic of mass balance calculation with and without droplets. Upper panel describes solubility calculation in initial WAF where total mass of constituent  $i$  is determined by mass of oil added to the WAF chamber. The second panel describes the solubility calculation that includes the concentration of droplet oil in the exposure system:  $m_{i,\text{system}} = m_{i,\text{dissolved\_step1}} + m_{i,\text{droplet}}$ ;  $m_i$  = mass of constituent  $i$  in system. Step 1:  $m_i = C_{\text{oil},i} (\mu\text{g/g}) * \text{Loading (g/L system)} * \text{system Volume (L, } V_{\text{air}} + V_{\text{w}})$ . Step 2:  $m_i = C_{d,i} (\mu\text{g/L}) V_{\text{w}} + C_{\text{oil},i} (\mu\text{g/g}) * \text{Droplet (g/L)} * V_{\text{w}}$ .  $C_{d,i}$  = dissolved concentration from Step 1;  $C_{\text{oil},i}$  = oil composition post-equilibration,  $p_{\text{oil},i} * \text{MW (g/mol)} / \rho_{\text{oil}}$ ;  $\rho_{\text{oil}}$  = density of oil substance (g/L);  $x_i$  = mole fraction of constituent  $i$ ;  $V_{\text{oil}}$  = volume of undissolved oil phase, sole fitting parameter;  $p_{\text{oil}}$  = molar density of oil (moles constituent  $i$ /L oil);  $V_{\text{air}}$  = headspace volume (L air), assumed 25% for all calculations;  $S_{L,i}$  = sub-cooled liquid solubility (moles constituent  $i$ /L water) \* MW (g/mol);  $H_i$  = unitless Henry's Law constant for constituent  $i$ ;  $V_{\text{w}}$  = water volume (L water).

WAF preparations are near equilibrium with the oil substances (Redman et al., 2012a,b, 2014; Di Toro et al., 2007; McGrath et al., 2005). Role of kinetics of dissolution under shorter exposures was not evaluated, and since rate-limited dissolution would result in less dissolved material the results presented here are considered conservative relative to potential transient exposures. The model represents a closed-system WAF preparation with 25% headspace and as such is generally applicable to open test systems. The predicted results are generally not strongly affected by variations in headspace, or open test systems, due to the typically low content of volatiles in the test substances investigated in the present study (Redman and Parkerton, 2015).

## 2.3. Scenarios

The solubility calculations with droplets represents a WAF preparation that results in varying degrees of droplet oil, which are then transferred to the exposure chambers where the droplets continue to equilibrate with the aqueous phase. For these calculations the oil in water loading was set at 1000 mg/L for the fresh and refined oils. However, for the simulated weathered oils the maximum loadings were set at 750, 500, and 250 mg/L to reflect the loss of mass through weathering (e.g., simulated 25%, 50%, 75% total mass loss) and provides direct comparison back to the neat oil scenarios.

The dilution-droplet scenarios included a no droplet condition (e.g., solely dilution of WAF stock dissolved components), and 0.1, 1 and 10 mg/L of entrained oil in the stock solution. These are referred to as the Dilution (or None), Low, Medium, and High droplet conditions, respectively. These values represent the concentrations of entrained oil present in the WAF stock solution (100% treatment), which are then diluted linearly. For example, a 10% dilution of the WAF stock representing the High scenario would have a 10-fold lower concentration of the initial dissolved phase concentration and a droplet concentration of 1 mg/L which would be the new oil loading input to the dissolution calculation.

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