THEORETICAL AND NUMERICAL MODELING OF THE BIODEGRADATION OF OIL MICRODROPLETS MOVING IN A WATER COLUMN

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ABSTRACT

Natural seeps and accidental releases of crude oil in the sea result in swarms of droplets that are carried away by underwater sea currents. The fate of the oil droplets is determined by natural attenuation processes, mainly dissolution into the seawater and biodegradation by oil-eating microbes. We have recently developed a compound particle model for the microbial degradation of solitary oil droplets moving through a water column. The compound particle is of the core-shell type and consists of an oily core successively surrounded by an ultrathin skin of oleophilic microbes and another biofilm layer of finite thickness. In the general case of nonlinear microbial kinetics, the governing set of advection-diffusion-reaction equations is solved numerically for oxygen and solubilized oil components, whereas analytical solutions have also been established for certain limiting cases. Here, preliminary results are presented for the effects of oxygen-limitation (hypoxia) on the droplet shrinking and biofilm growth rates.

INTRODUCTION

After a natural or accidental release of crude oil in the sea, part of the oil ends up in the form of droplets moving through the seawater column. The droplets may be created either at the sea surface during the breakup of an oil slick (i.e., floating oil layer) by sea waves[1], or at the seafloor during the extrusion of crude oil from a natural crack or a broken wellhead[2]. The latter case occurred, for instance, after the blowout of the Deepwater Horizon rig in the Gulf of Mexico where the addition of the chemical dispersant Corexit in the leaking crude oil resulted in swarms of droplets travelling underwater along with sea currents[3]. At present, there are no practical means for the collection or *in situ* treatment of dispersed oil droplets in vast bodies of marine waters and, thus, their removal relies mainly on dissolution and biodegradation. Large amounts of oil droplets in the seawater column disturb the established ecosystem dynamics and pose an imminent risk of toxic effects from various crude oil components to many marine species (invertebrates, fishes, mammals, etc.)[4]. It is therefore imperative to understand and quantify the physical and biological mechanisms that rule the fate of dispersed oil droplets in marine waters and, upon that knowledge, build technologies that will enable the mitigation of pertinent adverse effects.
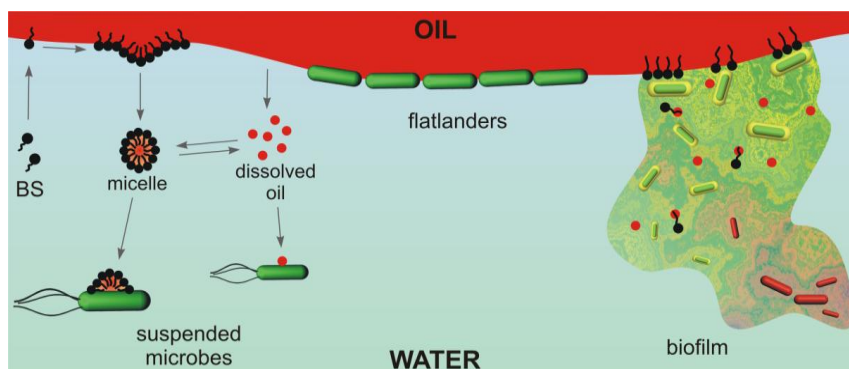

Figure 1. *Microbial strategies for accessing and assimilating oily substrates (reprinted from [5]). Hydrophilic microbes release biosurfactants (BS) and uptake emulsified oil droplets. Oleophilic microbes (flatlanders) uptake oil components directly from the oily phase. Biofilm forming microbes build complex three-dimensional communities over the oil-water interface.*

With regard to the biodegradation of oily substrates, three major microbial strategies have been identified[5] (Figure 1). In a first strategy, microbes *firmly adhere* to the oil-water interface and sip oil compounds directly from the oily phase. This approach has been observed in pure cultures of super-hydrophobic Gram-positive microbes, like *Mycobacterium* and *Rhodococcus* species. In a second strategy, microbes grow *suspended* in the bulk aqueous phase and uptake dissolved, micellar or emulsified oil components. This strategy has been observed, for example, in pure cultures of Gram-negative microbes, mainly of *Pseudomonas* species, that have hydrophilic cell surface and produce biosurfactants of low molecular weight (e.g., rhamnolipids). In a third strategy, individual or clustered microbes adhere to the oil surface and active*ly form biofilms* by secreting excessive amounts of biopolymers with high molecular weight. The biopolymers, mainly polysaccharides and proteins, do not dissolve into the bulk aqueous phase, but instead accumulate in the extracellular space and spontaneously assemble to form a three-dimensional matrix enmeshing the cells. The biofilm growth mode over oily substrates has been reported for several pure cultures and mixed microbial consortia.

In this paper, a compound particle model is presented for the biodegradation of solitary oil microdroplets moving through a water column under hypoxic conditions. The compound particle is of the core-shell type and consists of an oily core that is successively surrounded by a bioreactive skin of negligible thickness and another bioreactive shell of finite thickness (Figure 2). The bioreactive skin represents a thin layer of oleophilic microbes (*flatlanders*) that uptake oil directly from the oily phase, whereas the bioreactive shell represents a distinct biofilm phase. The mathematical analysis is simplified by introducing a set of rational hypotheses, the most important of which are: a) the compound particle is moving as a non-deforming rigid sphere, b) the flow of the aqueous phase is dominated by viscous stresses, and c) the transport of dissolved oxygen and oil components within the biofilm layer is dominated by diffusion. Upon this set of hypotheses, the analysis of the local mass balances provides the rates of droplet shrinking and biofilm growth as functions of key transport and kinetic system parameters.
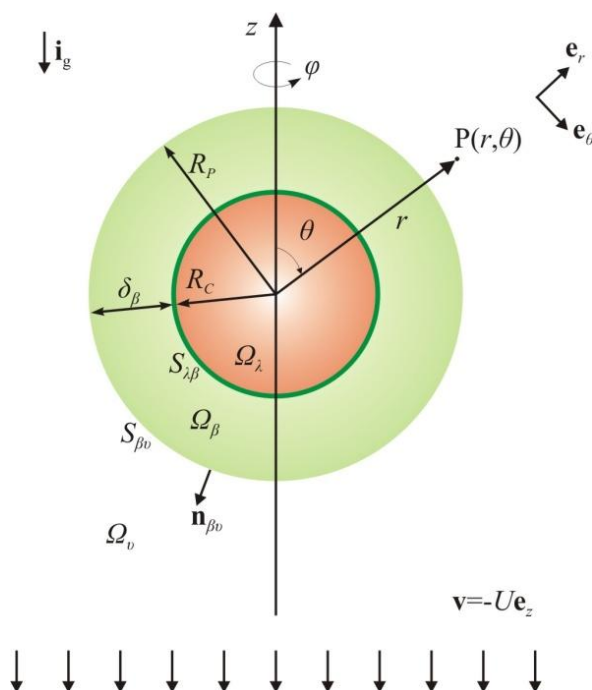

Figure 2. *Geometry and coordinate system for the compound particle model (reprinted from [6]). The oil droplet (Ω_λ) is covered by a biofilm layer (Ω_β) and, altogether, surrounded by an aqueous (Ω_υ) phase. The thick green line at the oil-biofilm interface ($S_{\lambda\beta}$) represents a thin layer of oleophilic microbes (flatlanders).*

MODEL FORMULATION

With reference to Figure 2, the transport of dissolved oxygen and oil components in each one of the three phases is described by the following *master equation* (advection-diffusion-bioreaction):

$$\lambda_{A\alpha}\frac{\partial c_{Aa}}{\partial \tau} + \text{Pe}_{A\alpha}\mathbf{v}_{\alpha}\cdot\nabla c_{Aa} = \nabla^2 c_{Aa} - \text{Da}_{A\alpha}K_{A\alpha}f_{\alpha}\left(c_{Sa},c_{Oa}\right). \tag{1}$$

Here, $c_{A\alpha}$ is the concentration of the Ath solute in the αth phase, $\mathbf{v}_{\alpha}$ is the velocity of the αth phase, τ is a dimensionless time, and $\lambda_{A\alpha}$, $\text{Pe}_{A\alpha}$, $K_{A\alpha}$ and $\text{Da}_{A\alpha}$ are dimensionless numbers that depend on physicochemical and kinetic parameters. The *growth factor* f_{α} for the metabolic activity of microbes in the αth phase is considered to follow multi-Monod kinetics:

$$f_{\alpha}\left(c_{Sa},c_{Oa}\right) = \frac{c_{S\alpha}}{K_{S\alpha}+c_{S\alpha}}\frac{c_{O\alpha}}{K_{O\alpha}+c_{O\alpha}}. \tag{2}$$

The detailed mathematical formulation for our system of three phases (oil, biofilm, water) and two solutes (hydrocarbons, oxygen) is presented in Figure 3. In the general case of non-linear growth factor, the equations are solved numerically with a finite difference scheme. For advection-dominated transport in the aqueous phase ($\text{Pe}_{A\alpha} \gg 1$), analytical solutions have also been established for the cases of carbon-limited[6] ($K_{S\alpha} \gg c_{S\alpha}$, $K_{O\alpha} \ll c_{O\alpha}$) and oxygen-limited ($K_{S\alpha} \ll c_{S\alpha}$, $K_{O\alpha} \gg c_{O\alpha}$) growth factor. The oil concentration field is used to calculate the oil mass flux, which is then used to determine the droplet dissolution rate:

$$\tilde{W}_{S,\lambda/\beta} \equiv \int_{S_{\lambda/\beta}} \tilde{\mathbf{j}}_{S\beta}\cdot\mathbf{n}_{\lambda\beta}d\tilde{S} = \left(\frac{\tilde{D}_{S\beta}}{2\tilde{R}_P}\right)Sh_{\lambda/\beta}\tilde{S}_{\lambda\beta}\tilde{c}_{S,\lambda/\beta}, \tag{3}$$

where $\tilde{\mathbf{j}}_{S\beta}$ is the Fickian mass flux of dissolved oil in the biofilm, $\tilde{D}_{S\beta}$ is the diffusivity of dissolved oil in the biofilm, $Sh_{\lambda/\beta}$ is the Sherwood number, $\tilde{S}_{\lambda\beta}$ is the oil-biofilm interfacial area, and $\tilde{c}_{S,\lambda/\beta}$ is the oil solubility in the biofilm. The Sherwood number depends on transport and kinetic parameters[6] and may be interpreted as a dimensionless droplet dissolution speed. The droplet dissolution rate can be subsequently used to calculate the evolution of the compound particle dimensions following the analysis presented in Ref [6].
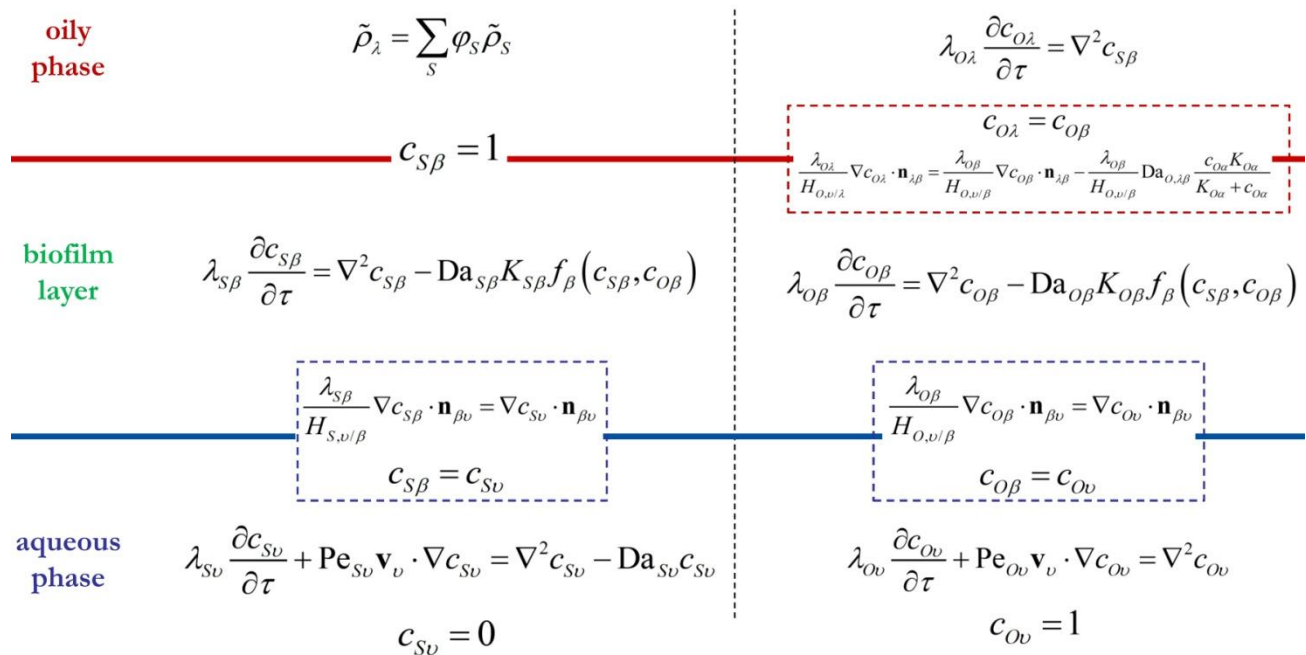

Figure 3. *Governing equations for dissolved oil (S) and oxygen (O) in the three phases of the compound particle model.*

RESULTS

Indicative results are presented in Figures 4-6. One of the most intriguing features of the studied process is the counter transport of dissolved oil and oxygen. Oil is outwardly transported, from the oily core through the biofilm and towards the aqueous phase. Oxygen is supplied in the bulk aqueous phase and moves in the opposite direction. For an oil droplet rising through a seawater column, the concentration profile of dissolved oil exhibits a very characteristic *tail*, whereas the concentration profile of oxygen displays radial stratification (Figure 4). Under certain conditions, the biofilm acts as a *diffusive barrier* in the dissolution of the oily core; meaning that a small increase in the biofilm thickness results in reduced speed of oil dissolution and this effect is accentuated under hypoxic conditions (Figure 5). The most pronounced impact of the oil/oxygen counter transport is on the pattern of microbial activity within the biofilm. Depending on the system parameters, the maximum microbial activity might be close to the oil-biofilm interface (as intuitively expected), or close to the biofilm-water interface, or anywhere in-between (Figure 6).
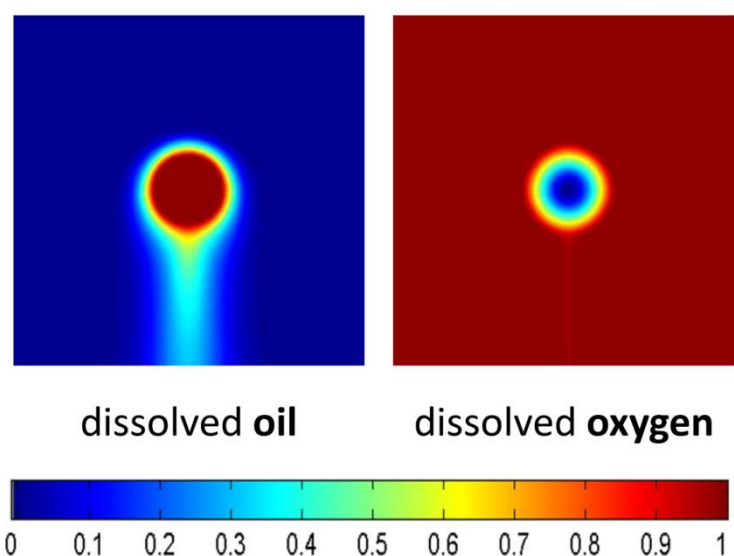

Figure 4. *Concentration profiles of dissolved oil and oxygen for an oil droplet rising through a water column.*
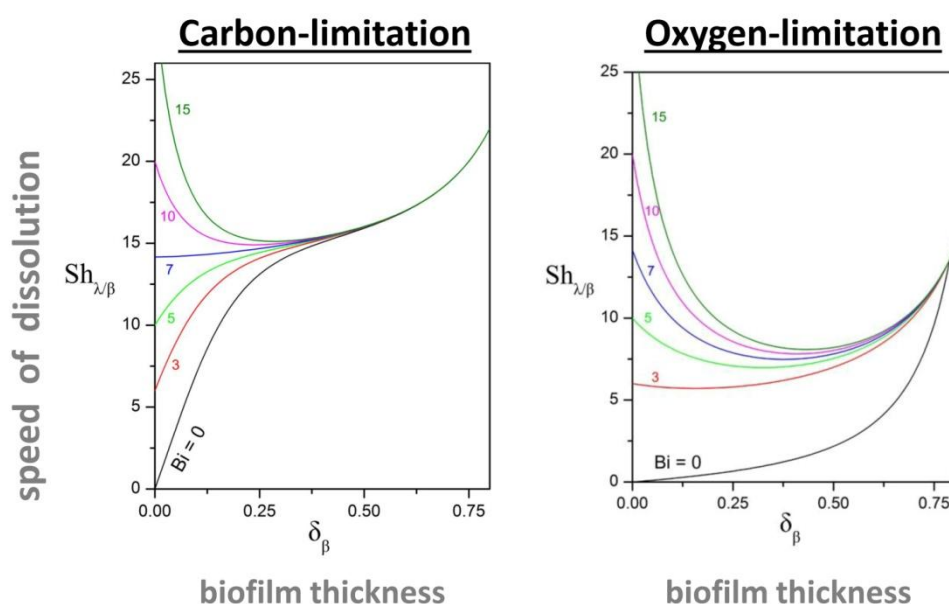

Figure 5. *Effect of biofilm thickness on the speed of dissolution for individual oil droplets.*
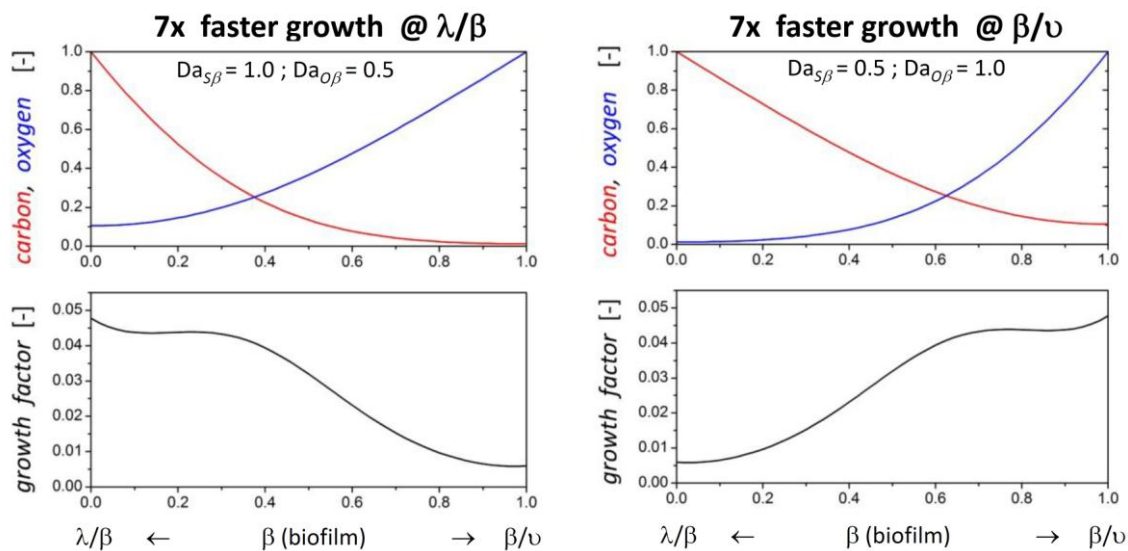
Figure 6. *Distribution of dissolved chemical species (oil, oxygen) and microbial activity (growth factor) within a biofilm for different sets of characteristic parameters.*

CONCLUSION

Current theoretical models for the fate of oil droplets in marine waters account only for the biodegradation via direct interfacial uptake and neglect any effects resulting from the formation of biofilms around the droplets or the limitation in the oil consumption rate that may be caused by low oxygen availability. The developed compound particle model is the first and simplest possible model to account for (some) biofilm and hypoxia effects on the biodegradation of oil droplets. More physical and mathematical complexity will be added in future versions of the model.

ACKNOWLEDGEMENTS

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