Short Communication

Modelling biodegradation of crude oil components at low temperatures

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Article info

Article history:
Received 31 January 2020
Received in revised form 15 April 2020
Accepted 16 April 2020
Available online 22 April 2020

Handling Editor: Keith Maruya

Keywords:
biodegradation
Oil spill modelling

ABSTRACT

For oil spilled at sea, the main weathering processes are evaporation, emulsification, photo-oxidation, dispersion and biodegradation. Of these, only biodegradation may completely remove hydrocarbons from the environment in the long term, as the other processes only serve to transform and dilute the oil components. As petroleum development is moving north, the probability of Arctic oil spills increases. Hence, it is imperative to develop methods for comprehensive risk assessment of oil spills in cold and ice-covered waters. Accurate biodegradation rates are an essential part of this, as they are required to predict the long-term effects of marine oil spills. In this paper, we present experimentally determined biodegradation rates for the component groups which are used to represent oil in the OSCAR oil spill model. The experiments have been carried out at seawater temperatures of 0°C, 5°C, and 13°C.

We show that for the lighter and more soluble oil components, the changes in degradation rates between 0°C and 13°C are well captured by a constant Q10 scaling law. At lower temperatures, and for heavier and less soluble components, the rates are not well described by a constant Q10, probably indicating that oil properties become important for the biodegradation rate.

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1. Introduction

In the modelling of marine oil spills, there is a strong focus on predicting where the oil will end up in the short term, in order to direct response operations or evaluate different response strategies (Reed et al., 1995, 2000; Barker and Healy, 2001; McCay et al., 2005). Models are also used to statistically analyse the possible outcomes of an oil spill (Barker, 2011; Nordam et al., 2017), and carry out environmental risk assessments (McCay et al., 2004). Environmental risk assessments typically focus on transport of surface oil, due to risk of stranding, and exposure to birds and mammals. Yet for the ocean as a whole, transport processes do not remove oil, they only redistribute it.

If we consider processes that actually remove oil from the ocean, there are the oil spill response techniques of mechanical recovery and in-situ burning.1 Additionally, there are the natural processes of evaporation and biodegradation. In the long term, after response operations are over and there is no surface oil, the only relevant process determining the ultimate fate of the remaining oil components at sea is biodegradation.

Due to the current trend of reduced ice cover, human activity in the Arctic is on the increase. This includes, e.g., oil exploration, shipping and tourism, and leads to an increased probability of Arctic oil spills. In order to properly assess the risk of these activities, there is a pressing need for oil spill models that incorporate the effects of ice and low temperatures on the transport and fate of the oil (French-McCay et al., 2018; Nordam et al., 2019). In this paper, we present experimentally determined biodegradation rates for crude oil components at low temperatures, and assess the validity of a commonly used approach to temperature-scaling of these rates.

2. Biodegradation experiments

Biodegradation rates were established by incubating fresh Troll crude oil in seawater for periods of 28–125 days. The seawater was collected from the Trondheim fjord (63.44° N, 10.39° E), via an
intake pipe at a depth of approximately 80 m (below the thermocline). Schott flasks (2 L) were filled with seawater (no headspace) containing 2–3 mg/L of oil. The low concentration ensures that the degradation is not limited by available oxygen. The oil was pre-mixed with the Corexit 9500A chemical dispersant, in a ratio of 1:100, and dispersed as small droplets. The droplets were produced by a purpose-built oil droplet generator (Nordtug et al., 2011), and had a median droplet size in the range 10–30 μm.

After filling, the flasks were mounted on carousels rotating at 0.75 rpm, to prevent the droplets from settling out, and incubated at constant temperature. The incubation period varied from 28 to 125 days, depending on temperature (Ribicic et al., 2018a, b; Brakstad et al., 2018; Lothhus et al., 2020). Several identical bottles were prepared, and bottles were sacrificed for sampling at intervals throughout the run of the experiment. At each sampling point, three bottles were sacrificed. Remaining concentrations of hydrocarbons were measured by GC-FID and GC-MS, and normalised to refer to the relevant oil must be analysed to be used in the OSCAR oil spill model (Reed et al., 2000, 2001). All component groups used in the OSCAR oil spill model (Reed et al., 2000, 2001). All the experiments have been carried out in the same way, as described above. For the experiment at −2°C the water remained liquid throughout the incubation period due to the continuous movement of the carousel. This indicates that even though the temperature in the room was −2°C, the water was probably −1.8°C (the freezing point of seawater).

3. Oil spill modelling

Numerical models for marine oil spills generally solve the advection-diffusion-reaction equation (see, e.g., Hunds dorfer (2003))

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) - \nabla \cdot (uC) + R,$$

(1)

to track concentrations, $C$, of oil compounds in the marine environment. The parameters $D$ and $u$ respectively represent mixing due to eddy diffusivity, and advection by currents. The reaction term, $R$, includes loss mechanisms such as evaporation and biodegradation. Biodegradation is usually modelled as a first-order decay (Reed et al., 2001), i.e., the mass as a function of time is given by

$$Q(t) = Q_0 e^{-kt}.$$

(2)

Here, $Q_0$ is the initial amount, and $k$ is the degradation rate.

To model weathering and biodegradation in an oil spill model, some approximations must be made. Different hydrocarbons have different solubilities, vapour pressures, biodegradation rates, etc. However, a crude oil typically consists of thousands of organic compounds, and it is not feasible to establish, e.g., biodegradation rates for each one. Therefore, the oil is represented by groups of components, which are assumed to have similar properties. These component groups are sometimes called pseudocomponents (Reed et al., 2000; McCay, 2003).

Physical properties, such as solubility and vapour pressure, are established for each component group. Similarly, biodegradation rates must be established per component group. Prior to modelling, the relevant oil must be analysed to find its composition in terms of these groups. In this paper, we present results for the component groups used in the operational oil spill model OSCAR, developed at SINTEF (see, e.g., Reed et al. (2000, 2001); Nordam et al. (2018, 2019)). The model is commonly used for, e.g., oil spill risk assessment on the Norwegian Continental Shelf. The component groups are shown in Table A1, together with experimentally determined degradation rates for those groups, at different temperatures.

The implicit assumption ones makes in such an approach, is that the properties of each component group are independent of the overall composition of the oil. For the case of evaporation, this is essentially the assumption that Raoult’s law (see, e.g., Zumdahl (2002, p. 822)) applies. For biodegradation, we assume that the first-order rate constant, $k_i$, of component group $i$, is independent of the concentration of other component groups in the oil.

The advantage to this approach is clear: Once the different properties (including biodegradation rates) have been established for each component group, one can model the behaviour of any oil, as long as the composition is known in terms of the same component groups. Given that it is far cheaper to establish the composition of a crude oil, than to run a set of biodegradation experiments, this is a huge practical advantage in numerical oil spill modelling.

Temperatures in the ocean can vary from −1.8°C in the polar regions, and up to around 30°C in equatorial regions. Hence, it is similarly a great advantage if one can establish biodegradation rates at one, or a few, reference temperatures, and use some kind of scaling law to calculate the rate at other temperatures. One approach to scaling biodegradation rates is the $Q_{10}$ approach, which is based on Arrhenius’ law (see, e.g., Zumdahl (2002, p. 720)). Using $Q_{10}$ scaling, the rate $k_T$ at temperature $T$ is determined from the experimentally established rate $k_0$ at temperature $T_0$ by the relation

$$k_T = k_0 \cdot Q_{10}^{\frac{T - T_0}{10}}.$$

(3)

Here, the factor $Q_{10}$ determines how much the rate changes with a change in temperature of 10°C. Commonly used values for $Q_{10}$ in oil spill modelling are in the range 2–3 (Bagi et al., 2013). In order to find a $Q_{10}$ factor from experimental data, the simplest approach is to establish biodegradation rates, $k_1$ and $k_2$, at two different temperatures, $T_1$ and $T_2$. From Eq. (3), we then obtain

$$Q_{10} = \left(\frac{k_1}{k_2}\right)^{\frac{T_2 - T_1}{10}}.$$

(4)

This assumes that $Q_{10}$ is constant with temperature. An alternative approach is to make use of an Arrhenius plot to determine the activation energy of the degradation reaction (see Bagi et al. (2013) and references therein).

4. Results and discussion

In Fig. 1, we show experimentally determined biodegradation rates at different temperatures, for different component groups. The numerical values for the rates are given in Table A1. A rate of $10^{-4}$ d$^{-1}$ means that no detectable degradation took place during the experiment, and represents an upper limit on the actual value. The experiments were carried out with a fresh Troll crude, which is a naphtenic oil with a low pour point of $−36°C$.

For those components where data are available at multiple temperatures, Fig. 1 also shows biodegradation rates scaled by Eq. (3). The scalings use a reference temperature $T_0 = 13°C$, or 5°C for those component groups where data for $13°C$ is missing. The $Q_{10}$ values were obtained separately for each component. Up to three
Q_{10} values for each component group were calculated by Eq. (4), using the change in degradation rates from 0 °C to 5 °C, from 5 °C to 13 °C, and from 0 °C to 13 °C. Then, an overall Q_{10} value was obtained as the geometric mean of these. The resulting mean Q_{10} scalings are shown as dashed lines in Fig. 1, and the value of each Q_{10} factor is listed in the legend of each subplot.

### 4.1. Validity of the Q_{10} scaling

It is clear from Fig. 1 that a Q_{10} scaling works reasonably well for the lighter components, although with a different Q_{10} parameter per component group. However, for the heavier components, it seems that a constant Q_{10} value cannot capture both the change from 0 °C to 5 °C and the change from 5 °C to 13 °C. We also note that the rates at −2 °C are not at all well described by the scaling parameters derived from the three other temperatures.

The motivation behind using the Q_{10} scaling in the first place is to model a reduction in biological activity at lower temperatures. This is based on the assumption that the biological activity required for degradation is the rate-limiting step. Hence, the biological availability may be the rate-limiting step in this case, rather than the biological activity. This would explain why we find a very poor match with the constant Q_{10} scaling for the heavy components at low temperatures.

### 5. Conclusion

Biodegradation experiments, with incubation periods of up to 125 days, are necessarily time consuming and thus expensive to carry out. As discussed in Section 3, it is therefore a great advantage to practical application of oil spill modelling if degradation rates can be established once, for each component group, and for two different temperatures, and thereafter applied to any crude oil, scaled to the appropriate temperature.

The results presented here indicate that such an approach works well for light components, at high temperatures (well above the pour point of the crude oil in question), but does not work as well for heavy oil components, at low temperatures. Given that many fresh crude oils have pour points far higher than the −36 °C of Troll crude, and that oil exploration and production is moving further northwards into colder temperatures in the Arctic, more experimental work is needed. Biodegradation experiments should be carried out at low temperatures, using crude oils with different properties, in order to establish limits of validity for the Q_{10} scaling, and develop alternative approaches that can be used at low temperatures.

**CRediT authorship contribution statement**

Tor Nordam: Conceptualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization.
Synneve Loftus: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. Odd Gunnar Brakstad: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. Data curation, Supervision.

Acknowledgements

The analysis and writing of this paper, as well as the experimental work to establish biodegradation rates at −2 °C, was carried out under the Fatever project (255385/E30), supported by the PETROMAKS2 programme of the Norwegian Research Council, and by AkerBP, ConocoPhillips, Equinor, Lundin Norway, Neptune Energy, OMV, and Vår Energi.

Appendix A. Biodegradation rates

The experimentally determined biodegradation rates are given in Table A1, for the component groups used in the OSCAR oil spill model (Reed et al., 2000, 2001). For additional information on the individual component groups, see Brakstad and Faksness (2000). Note that not all component groups were measured in the experiments presented here. For complete descriptions of the experimental procedures, see Ribicic et al. (2018a, b); Brakstad et al. (2018); Loftus et al. (2020).

Table A1

<table>
<thead>
<tr>
<th>Component</th>
<th>−2 °C</th>
<th>0 °C</th>
<th>5 °C</th>
<th>13 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1–C4 gases (dissolved in oil)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C5-saturates</td>
<td>–</td>
<td>0.0336</td>
<td>0.0335</td>
<td>0.0992</td>
</tr>
<tr>
<td>C6-saturates</td>
<td>–</td>
<td>0.0246</td>
<td>0.0387</td>
<td>0.0934</td>
</tr>
<tr>
<td>C7-saturates</td>
<td>–</td>
<td>0.0333</td>
<td>0.0336</td>
<td>0.0902</td>
</tr>
<tr>
<td>C8-saturates</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C9-saturates</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Benzene</td>
<td>–</td>
<td>0.0225</td>
<td>0.0276</td>
<td>–</td>
</tr>
<tr>
<td>Toluene</td>
<td>–</td>
<td>0.0220</td>
<td>0.0312</td>
<td>0.0883</td>
</tr>
<tr>
<td>C2-benzenes</td>
<td>–</td>
<td>0.0279</td>
<td>0.0315</td>
<td>0.1228</td>
</tr>
<tr>
<td>C3-benzenes</td>
<td>–</td>
<td>0.0276</td>
<td>0.0318</td>
<td>–</td>
</tr>
<tr>
<td>C4- and C5-benzenes</td>
<td>–</td>
<td>0.0267</td>
<td>0.0544</td>
<td>–</td>
</tr>
<tr>
<td>Naphthalenes 1 (C0–C1 alkylated)</td>
<td>0.0109</td>
<td>0.0255</td>
<td>0.0731</td>
<td>0.1973</td>
</tr>
<tr>
<td>Naphthalenes 2 (C2–C3 alkylated)</td>
<td>0.0101</td>
<td>0.0180</td>
<td>0.0682</td>
<td>0.1147</td>
</tr>
<tr>
<td>Medium soluble PAHs</td>
<td>0.0078</td>
<td>0.0150</td>
<td>0.0368</td>
<td>0.0860</td>
</tr>
<tr>
<td>Low soluble PAHs</td>
<td>0.0001</td>
<td>0.0032</td>
<td>0.0114</td>
<td>0.0425</td>
</tr>
<tr>
<td>C10 saturates</td>
<td>0.0001</td>
<td>0.0180</td>
<td>–</td>
<td>0.1018</td>
</tr>
<tr>
<td>C11–C12 saturates</td>
<td>0.0001</td>
<td>0.0152</td>
<td>0.0267</td>
<td>0.1271</td>
</tr>
<tr>
<td>C13–C14 saturates</td>
<td>0.0001</td>
<td>0.0109</td>
<td>0.0237</td>
<td>0.0872</td>
</tr>
<tr>
<td>C15–C16 saturates</td>
<td>0.0001</td>
<td>0.0057</td>
<td>0.0150</td>
<td>0.0521</td>
</tr>
<tr>
<td>C17–C18 saturates</td>
<td>0.0001</td>
<td>0.0022</td>
<td>0.0103</td>
<td>0.0349</td>
</tr>
<tr>
<td>C19–C20 saturates</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0072</td>
<td>0.0231</td>
</tr>
<tr>
<td>C21–C25 saturates</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0054</td>
<td>0.0200</td>
</tr>
<tr>
<td>C25+</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0075</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

References