



## Short Communication

## Modelling biodegradation of crude oil components at low temperatures

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## 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  $-2^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$ ,  $5^{\circ}\text{C}$ , and  $13^{\circ}\text{C}$ . We show that for the lighter and more soluble oil components, the changes in degradation rates between  $0^{\circ}\text{C}$  and  $13^{\circ}\text{C}$  are well captured by a constant  $Q_{10}$  scaling law. At lower temperatures, and for heavier and less soluble components, the rates are not well described by a constant  $Q_{10}$ , 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.<sup>1</sup> 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 compounds 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 ( $63.44^{\circ}\text{N}$ ,  $10.39^{\circ}\text{E}$ ), via an

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<sup>1</sup> Although burning leaves behind a fraction of residue, of which the environmental effects are not well known (Fritt-Rasmussen et al., 2015).

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  $\mu\text{m}$ .

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; Lofthus 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 against the recalcitrant oil compound 17 $\alpha$ (H),21 $\beta$ (H)-hopane (Prince et al., 1994). Biodegradation rates were determined by non-linear regression analysis as first-order rate decay curves for determination of rate coefficients. For a detailed description of the experimental protocol, see Brakstad et al. (2017).

In this paper, we present experimentally determined biodegradation rates at  $-2^\circ\text{C}$ ,  $0^\circ\text{C}$ ,  $5^\circ\text{C}$ , and  $13^\circ\text{C}$ , for the oil 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  $-2^\circ\text{C}$  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  $-2^\circ\text{C}$ , the water was probably  $-1.8^\circ\text{C}$  (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., Hundsdoerfer (2003))

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C) - \nabla \cdot (\mathbf{u}C) + R, \quad (1)$$

to track concentrations,  $C$ , of oil compounds in the marine environment. The parameters  $D$  and  $\mathbf{u}$  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

$$Q(t) = Q_0 e^{-kt}. \quad (2)$$

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 one 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  $-1.8^\circ\text{C}$  in the polar regions, and up to around  $30^\circ\text{C}$  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

$$k_T = k_0 \cdot Q_{10}^{\frac{T-T_0}{10^\circ\text{C}}}. \quad (3)$$

Here, the factor  $Q_{10}$  determines how much the rate changes with a change in temperature of  $10^\circ\text{C}$ . 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

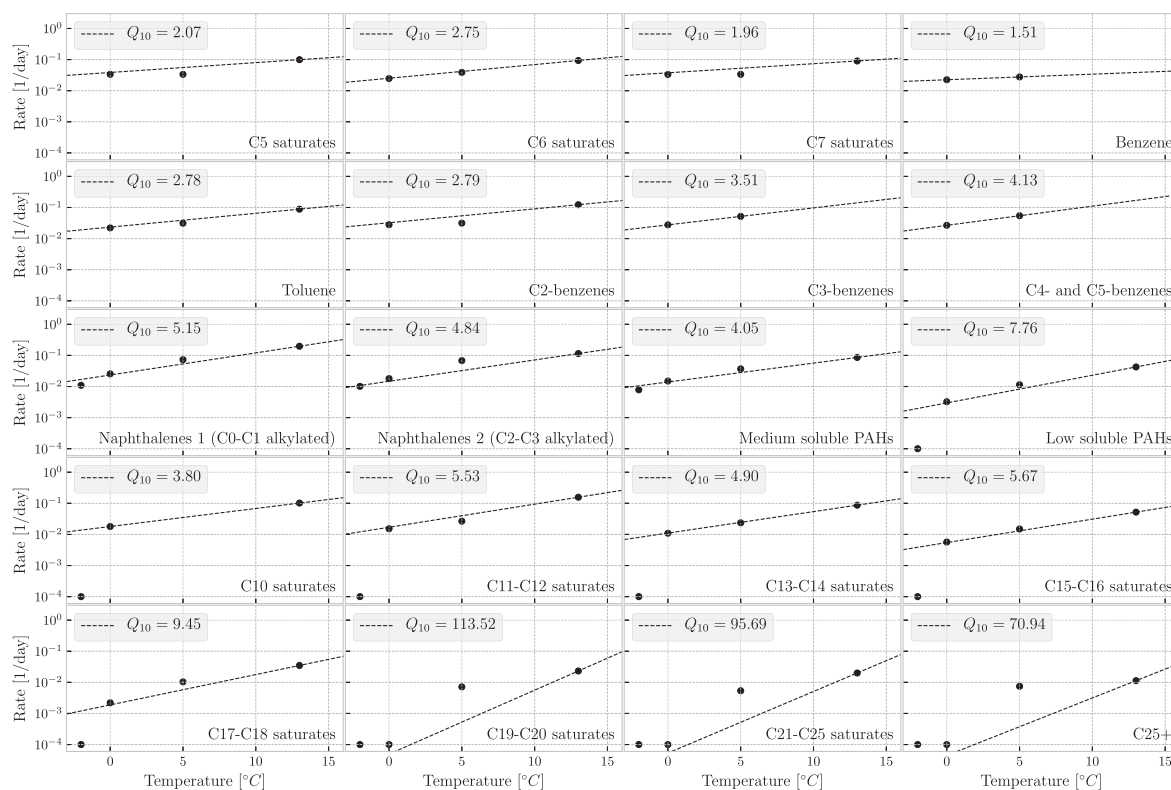
$$Q_{10} = \left( \frac{k_1}{k_2} \right)^{\frac{10^\circ\text{C}}{T_1 - T_2}}. \quad (4)$$

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  $10^{-4}\text{d}^{-1}$  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  $-36^\circ\text{C}$ .

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  $T_0 = 13^\circ\text{C}$ , or  $5^\circ\text{C}$  for those component groups where data for  $13^\circ\text{C}$  is missing. The  $Q_{10}$  values were obtained separately for each component. Up to three



**Fig. 1.** Experimentally determined biodegradation rates at temperatures  $-2^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$ ,  $5^{\circ}\text{C}$ , and  $13^{\circ}\text{C}$  for different component groups (shown as black dots). Also shown are the  $Q_{10}$  scalings (see Eq. (3)), with  $T_0 = 13^{\circ}\text{C}$  (or  $T_0 = 5^{\circ}\text{C}$  if data are missing for  $13^{\circ}\text{C}$ ), and  $Q_{10}$  values obtained per component group as the geometric mean of the rates calculated from the change in rate from  $0^{\circ}\text{C}$  to  $5^{\circ}\text{C}$ , from  $5^{\circ}\text{C}$  to  $13^{\circ}\text{C}$ , and from  $0^{\circ}\text{C}$  to  $13^{\circ}\text{C}$  (see Eq. (4)).

$Q_{10}$  values for each component group were calculated by Eq. (4), using the change in degradation rates from  $0^{\circ}\text{C}$  to  $5^{\circ}\text{C}$ , from  $5^{\circ}\text{C}$  to  $13^{\circ}\text{C}$ , and from  $0^{\circ}\text{C}$  to  $13^{\circ}\text{C}$ . 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  $0^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  and the change from  $5^{\circ}\text{C}$  to  $13^{\circ}\text{C}$ . We also note that the rates at  $-2^{\circ}\text{C}$  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. Since a constant  $Q_{10}$  appears to work well for the lighter components, it seems the assumption holds in these cases. However, when we consider the data for heavy components at  $-2^{\circ}\text{C}$ , and partially also at  $0^{\circ}\text{C}$ , the constant  $Q_{10}$  scaling does not work very well. This may indicate that some mechanism other than the biological activity is responsible.

Since the heavy components have the least mobile molecules, and are typically the least soluble in water, the oil droplets will become enriched in heavy components as the lighter components dissolve and biodegrade. This will increase the pour point, limiting the diffusive transport of compounds to the surface of the droplet.

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  $-36^{\circ}\text{C}$  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.

**Synnøve Lofthus:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. **Odd Gunnar Brakstad:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing, Data curation, Supervision.

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## 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); Lofthus et al. (2020).

**Table A1**

Biodegradation rates [ $\text{d}^{-1}$ ] for different oil component groups. The rates have been obtained experimentally at different temperatures. All experiments were carried out with fresh Troll crude oil, dispersed as small droplets in seawater as described in Section 2. The value 0.0001 is inserted where the degradation was below the detection limit, and represents an upper bound on the actual value. A dash (–) indicates that the component group was not measured in the experiment. All component groups used in the OSCAR model are shown for reference, even if some of the groups were not measured in this set of experiments.

Component	$-2^{\circ}\text{C}$	$0^{\circ}\text{C}$	$5^{\circ}\text{C}$	$13^{\circ}\text{C}$
C1–C4 gases (dissolved in oil)	–	–	–	–
C5 saturates	–	0.0336	0.0335	0.0992
C6 saturates	–	0.0246	0.0387	0.0934
C7 saturates	–	0.0333	0.0336	0.0902
C8 saturates	–	–	–	–
C9 saturates	–	–	–	–
Benzene	–	0.0225	0.0276	–
Toluene	–	0.0220	0.0312	0.0883
C2-benzenes	–	0.0279	0.0315	0.1228
C3-benzenes	–	0.0276	0.0518	–
C4- and C5-benzenes	–	0.0267	0.0544	–
Naphthalenes 1 (C0–C1 alkylated)	0.0109	0.0255	0.0731	0.1973
Naphthalenes 2 (C2–C3 alkylated)	0.0101	0.0180	0.0682	0.1147
Medium soluble PAHs	0.0078	0.0150	0.0368	0.0860
Low soluble PAHs	0.0001	0.0032	0.0114	0.0425
C10 saturates	0.0001	0.0180	–	0.1018
C11–C12 saturates	0.0001	0.0152	0.0267	0.1571
C13–C14 saturates	0.0001	0.0109	0.0237	0.0872
C15–C16 saturates	0.0001	0.0057	0.0150	0.0521
C17–C18 saturates	0.0001	0.0022	0.0103	0.0349
C19–C20 saturates	0.0001	0.0001	0.0072	0.0231
C21–C25 saturates	0.0001	0.0001	0.0054	0.0200
C25+	0.0001	0.0001	0.0075	0.0113
Phenols (C0–C4 alkylated)	–	–	–	–

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