



Fate and transport of petroleum hydrocarbons in engineered biopiles in polar regions



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HIGHLIGHTS

- We account for temperature-dependency of partitioning and degradation of hydrocarbons.
- We derived the energy of activation (E_a) for the degradation of various hydrocarbon fractions.
- We examine the changes of hydrocarbons fractions within five field scale biopiles in Antarctica.
- As E_a increases the percentage of TPH remaining increases, reflecting slower biodegradation.
- Despite low temperature, the predicted dominant loss process is biodegradation.

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ABSTRACT

A dynamic multi-media model that includes temperature-dependency for partitioning and degradation was developed to predict the behaviour of petroleum hydrocarbons during biopiling at low temperature. The activation energy (E_a) for degradation was derived by fitting the Arrhenius equation to hydrocarbon concentrations from temperature-controlled soil mesocosms contaminated with crude oil and diesel. The model was then applied to field-scale biopiles containing soil contaminated with diesel and kerosene at Casey Station, Antarctica. Temporal changes of total petroleum hydrocarbons (TPH) concentrations were very well described and predictions for individual hydrocarbon fractions were generally acceptable (disparity between measured and predicted concentrations was less than a factor two for most fractions). Biodegradation was predicted to be the dominant loss mechanism for all but the lightest aliphatic fractions, for which volatilisation was most important. Summertime losses were significant, resulting in TPH concentrations which were about 25% of initial concentrations just 1 year after the start of treatment. This contrasts with the slow rates often reported for hydrocarbons *in situ* and suggests that relatively simple remediation techniques can be effective even in Antarctica.

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1. Introduction

Petroleum hydrocarbon contamination has been identified as a significant environmental problem in the polar and sub-polar regions, particularly in areas with permanent settlements or bases (Gore et al., 1999; Snape et al., 2006; Tin et al., 2009). Hydrocarbon pollutants in cold soils can remain for long periods because biodegradation is often limited by temperature (Bradley and Chapelle, 1995; Boethling et al., 2009). Hydrocarbons can also ultimately migrate into adjacent marine systems where they can pose risks to sensitive ecosystems (Poland et al., 2003; Snape et al., 2006). It

is important, therefore, to investigate the potential effectiveness of different remediation techniques which can be challenged by the harsh environmental conditions and by the substantial logistical difficulties of working in remote locations (Mumford et al., 2013).

Of the various treatment methods available for the remediation of hydrocarbon-contaminated soil, “biopiling” is being increasingly considered. In this technique, contaminated soil is excavated and piled up above ground, sometimes with added nutrients and sometimes with enhanced aeration. Leaching losses of hydrocarbons with appreciable aqueous solubility and low vapour pressure are usually controlled by placing the pile on an impermeable surface and then capturing and treating any leachate produced (Coulon et al., 2012). Biopiles are technically straightforward and relatively cheap to construct and have been shown to be effective in temper-

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ate zone studies (Coulon et al., 2010a). Even in cold regions the activity of microbial degraders has been recognised as being seasonally significant (Coulon et al., 2005; Sanscartier et al., 2009) and may, therefore, have potential for hydrocarbon remediation provided factors such as aeration, temperature and nutrient supply are not limiting. That said, practical implementation of biopiling at field scale remains relatively untested in cold regions.

In any environmental technology it is useful to understand the interactions between environmental and process variables in order to optimise operational management. Multimedia fate and transport models allow such interactions to be explored and can be used to predict the environmental concentrations and associated deleterious effects of pollutants (Whelan, 2013).

In this paper, the behaviour of petroleum hydrocarbons in polar and sub-polar biopiled soils was investigated using the dynamic fugacity-based model developed by Coulon et al. (2010b) which was modified to allow for the temperature-dependence of partition coefficients and degradation rate constants. Despite widespread acknowledgement of the influence of temperature on hydrocarbon biodegradation (Atlas and Bartha, 1992; Margesin and Schinner, 1999; Gibb et al., 2001; Ferguson et al., 2003a; Coulon et al., 2005) and environmental phase partitioning (Mackay and Arnott, 2011) temperature-dependence is sometimes ignored. Although previous work has been conducted to model the behaviour of hydrocarbon fractions in cold environments, this has largely been empirical, rather than mechanistic.

2. Methods

The temperature dependency of degradation was parameterised using experimental data obtained from laboratory-scale biopiles of sub-Antarctic soils contaminated with diesel fuel and crude oil near the Port aux Français station on Kerguelen Island (Coulon et al., 2005). The parameterised model was then applied to field-scale biopiles at Casey Station, Antarctica, in order to evaluate model performance and to help with the interpretation of observed data on hydrocarbon behaviour in these systems.

2.1. Model description

Briefly, the model considers an evaluative four-phase environmental system containing: (1) mineral solids; (2) organic matter, including any non-aqueous phase liquid (NAPL); (3) air and (4) water. Dimensions of the system are set to represent the biopile under consideration (Coulon et al., 2010b). The behaviour of each hydrocarbon fraction (i) is considered separately via the following mass balance equation, expressed in terms of fugacity (Mackay, 2001):

$$\frac{dM_i}{dt} = E_i - D_T \cdot f_i \quad (1)$$

where M is the mass of the fraction remaining (mol), E (mol h⁻¹) is the emission rate (i.e. the rate of hydrocarbon fraction added to the biopile, which in our case is zero), D_T is the total “D” value (mol Pa⁻¹ h⁻¹), t is time (h) and f is the fugacity (Pa) of the fraction in the biopile at a given time. The predicted total petroleum hydrocarbon (TPH) concentration is assumed to be the sum of the modelled concentrations of individual fractions. It is assumed that all phases within the biopile have equal fugacity (i.e. they are always in thermodynamic equilibrium: Paterson et al., 1994; Di Guardo et al., 1994). D -values represent loss rates due to advection out of the system and reaction within the system. The product of D and f gives a mass transfer in mol h⁻¹. D_T is calculated as the sum of the D -values for individual process rates:

$$D_T = D_A + D_V + D_L + D_R \quad (2)$$

where D_A represents loss in air by advection laterally through the system (e.g. by blowing air through the soil); D_V represents combined chemical diffusion through the air- and water-filled pore space, followed by loss via volatilisation; D_L represents leaching loss and D_R represents loss by reaction (biodegradation).

Eq. (1) differs slightly from the dynamic equation used by Coulon et al. (2010b), which was expressed in terms of the fugacity change per unit time i.e.:

$$\frac{df_i}{dt} = \frac{D_T \cdot f_i}{V_T \cdot Z_{BULK_i}} \quad (3)$$

where V_T is the total volume of the system considered. This is because fugacity capacity values (Z_{BULK}) change with temperature so fugacity increases are possible when partition coefficients change, resulting in mass balance errors when we explicitly account for the effect of temperature. Further details of the concepts and other equations used can be found in Coulon et al. (2010b). The model was coded in Microsoft Visual Basic for Applications (VBA).

2.2. Temperature dependence of partition coefficients and degradation rate

The temperature dependence of chemical partitioning between phases in the model was represented by:

$$K_{XY}(T_e) = K_{XY}(T_r) \cdot \exp\left(\frac{\Delta U_{XY}}{R} \cdot \left(\frac{1}{T_r} - \frac{1}{T_e}\right)\right) \quad (4)$$

where $K_{XY}(T_e)$ is the partition coefficient between phase X and phase Y, at the temperature (T_e , K) of the environmental compartments under consideration; $K_{XY}(T_r)$ is the partition coefficient, at the reference temperature (T_r), which is usually 298 K; ΔU_{XY} is the energy of phase transfer or solvation enthalpy (J mol⁻¹) and R is the gas constant (J mol⁻¹ K⁻¹). An attempt was made to estimate values of ΔU_{XY} from relevant literature. In the case of ΔU_{OW} (which was assumed to be equal to ΔU_{OC}) very little has been reported and a value of -20 kJ mol⁻¹ was assumed based on Foster et al. (2005). This explicitly assumes that hydrophobicity (K_{OW} and K_{OC}) decreases with increasing temperatures. A range of values for ΔU_{AW} were based on the temperature-dependence of vapour pressure derived from Foster et al. (2005) which, in turn, employed Trouton's rule (Hand, 1994) to derive the enthalpy of vaporisation from the boiling point (Table 1). Although aqueous solubility also changes with temperature, this variation tends to be compound-specific, confounding the development of a general rule for temperature correction (Foster et al., 2005). The errors introduced by the failure to adjust aqueous solubility and vapour pressure simultaneously are not systematic and are considered tolerable.

Temperature adjustments were made to degradation rate constants using the Arrhenius equation:

$$k(T_e) = k(T_r) \cdot \exp\left(\frac{E_a}{R} \cdot \left(\frac{1}{T_r} - \frac{1}{T_e}\right)\right) \quad (5)$$

where $k(T_e)$ is the rate constant at the environmental temperature, T_e (K); $k(T_r)$ is the rate constant at the reference temperature, T_r (usually 298 K) and E_a is the activation energy (J mol⁻¹). The value of $k(T_r)$ is calculated from the half-life at the reference temperature (HL_r), assuming first order kinetics:

$$k(T_r) = \frac{\ln(2)}{HL_r} \quad (6)$$

Reference half-life values in soil were estimated by Coulon et al. (2010b) using algorithms in the Estimation Program Interface (EPI) Suite™ (Syracuse Research Corp., <http://www.syrres.com/esc/est-soft.htm>) for a range of different member compounds within equivalent carbon numbers fractions

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