

## Behaviour of carbon-14 containing low molecular weight organic compounds in contaminated groundwater under aerobic conditions

Aislinn A. Boylan<sup>a,1</sup>, Douglas I. Stewart<sup>b</sup>, James T. Graham<sup>c</sup>, Ian T. Burke<sup>a,\*</sup>

<sup>a</sup> School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

<sup>b</sup> School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, UK

<sup>c</sup> National Nuclear Laboratory, Sellafield, Cumbria, CA20 1PG, UK



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### ABSTRACT

Short chain carbon-14 (<sup>14</sup>C) containing organic compounds can be formed by abiotic oxidation of carbides and impurities within nuclear fuel cladding. During fuel reprocessing and subsequent waste storage there is potential for these organic compounds to enter shallow subsurface environments due to accidental discharges. Currently there is little data on the persistence of these compounds in such environments. Four <sup>14</sup>C-labelled compounds (acetate; formate; formaldehyde and methanol) were added to aerobic microcosm experiments that contained glacial outwash sediments and groundwater simulant representative of the Sellafield nuclear reprocessing site, UK. Two concentrations of each electron donor were used, low concentration (10<sup>-5</sup> M) to replicate predicted concentrations from an accidental release and high concentration (10<sup>-2</sup> M) to study the impact of the individual electron donor on the indigenous microbial community in the sediment. In the low concentration system only ~5% of initial <sup>14</sup>C remained in solution at the end of experiments in contact with atmosphere (250–350 h). The production of <sup>14</sup>CO<sub>2</sub>(g) (measured after 48 h) suggests microbially mediated breakdown is the primary removal mechanism for these organic compounds, although methanol loss may have been partially by volatilisation. Highest retention of <sup>14</sup>C by the solid fractions was found in the acetate experiment, with 12% being associated with the inorganic fraction, suggesting modest precipitation as solid carbonate. In the high concentration systems only ~5% of initial <sup>14</sup>C remains in solution at the end of the experiments for acetate, formate and methanol. In the formaldehyde experiment only limited loss from solution was observed (76% remained in solution). The microbial populations of unaltered sediment and those in the low concentration experiments were broadly similar, with highly diverse bacterial phyla present. Under high concentrations of the organic compounds the abundance of common operational taxonomic units was reduced by 66% and the community structure was dominated by Proteobacteria (particularly Betaproteobacteria) signifying a shift in community structure in response to the electron donor available. The results of this study suggest that many bacterial phyla that are ubiquitous in near surface soils are able to utilise a range of <sup>14</sup>C-containing low molecular weight organic substances very rapidly, and thus such substances are unlikely to persist in aerobic shallow subsurface environments.

### 1. Introduction

Low molecular weight organic (LMWO) substances have long been considered a potential source of future carbon-14 (<sup>14</sup>C) release from deep subsurface environments due to the predicted accumulation of <sup>14</sup>CH<sub>4</sub> in underground repositories (Jefferies, 1990; Jackson and Yates, 2011; Limer et al., 2011, 2013; Marshall et al., 2011). Now there is concern that corrosion of activated fuel and fuel cladding may form a range of LMWO substances as a by-product (Wieland and Hummel, 2015) providing a source for its potential release to shallow subsurface

environments from storage ponds. <sup>14</sup>C is a known contaminant of the nuclear reprocessing plant at Sellafield, Cumbria, UK (Sellafield Ltd., 2016) and is of concern as a radioactive contaminant due to its long half-life (5730 ± 40a, Godwin, 1962) and its bioavailability (Bracke and Müller, 2008; Baston et al., 2012). The formation of <sup>14</sup>C occurs at each stage of the nuclear power generation process (Eabry et al., 1995) from the parent isotopes nitrogen-14 (<sup>14</sup>N), oxygen-17 (<sup>17</sup>O) and carbon-13 (<sup>13</sup>C), especially due to the presence of <sup>14</sup>N impurities in components of the fuel and fuel cladding. During fuel reprocessing the fuel and cladding (e.g. steel encapsulation, Mg-alloy) are stored in large

\* Corresponding author.

E-mail address: [I.T.Burke@leeds.ac.uk](mailto:I.T.Burke@leeds.ac.uk) (I.T. Burke).

<sup>1</sup> Present address: EPFL ENAC IIE EML, CH C2 392 (Bâtiment CH), Station 6, CH-1015 Lausanne, Switzerland.

water filled ponds, often as a short term measure prior to decanning and reprocessing (NDA, 2014; Morozov et al., 2016; Sellafield Ltd., 2016). At the free surface of such ponds oxic conditions are expected whereby  $^{14}\text{C}$  formed from carbides in the fuel cladding would be expected to oxidise to  $^{14}\text{CO}_2$  (McCullom and Seewald, 2007). At greater depth the oxygen penetration is minimal and corrosion of readily oxidised metals, such as magnesium, uranium and iron, leads to chemically reducing conditions forming within storage ponds (Equations (1)–(3)).

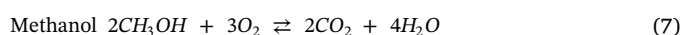
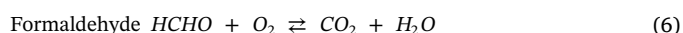
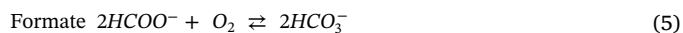
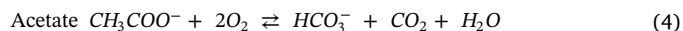


This potential redox stratification, with oxic conditions at the pond surface becoming more reducing with depth, would allow a variety of soluble  $^{14}\text{C}$ -containing organic compounds ( $^{14}\text{C}$ -DOC) to form within the storage ponds (Kaneko et al., 2002). Organic forms of  $^{14}\text{C}$  such as formaldehyde and methanol are also present within in nuclear waste due to their formation within pressurised water reactors (Matsumoto et al., 1994; Vance et al., 1995; Petit et al., 2013). In the past leaks have occurred in storage silos/ponds in Canada and the UK, (Evenden et al., 1998; Killey et al., 1998; Bird et al., 1999; Marshall et al., 2015; Sellafield Ltd., 2016), at Sellafield reprocessing site this has led to groundwater contamination from organic acids and pH variance across site (Law et al., 2010; Thorpe et al., 2012) which may affect the microbial populations within the subsurface.

A range of  $^{14}\text{C}$ -containing LMWO substances can form from oxidation of carbide in spent fuel and corrosion of the fuel cladding (Fig. 1). The most abundant will be  $\text{CO}_2$  and  $\text{CH}_4$ , whose concentrations are expected to be orders of magnitude higher than any other  $^{14}\text{C}$ -containing molecules produced (Wieland and Hummel, 2015), but  $\text{CO}_2$  and  $\text{CH}_4$  are not expected to persist in shallow subsurface environments. At circumneutral pH  $^{14}\text{CO}_2$  speciates as  $\text{H}^{14}\text{CO}_3^-$  in water, and isotopic exchange reactions with atmospheric  $^{12}\text{CO}_2$  can rapidly deplete  $^{14}\text{C}$ -dissolved inorganic carbon (DIC) concentrations in storage ponds that are open to atmosphere (see Boylan et al., 2017 for full discussion of  $^{14}\text{C}$ -DIC behaviour in surface and groundwater environments).  $^{14}\text{CH}_4$  has very low solubility at surface pressures and temperatures (Clever and Young, 1987) and is therefore expected to strongly partition to the gas phase and is assumed to be present as either pore gas or is released and diluted in atmosphere. Thus acetate, formate, formaldehyde and methanol have been identified as the main chemical forms for aqueous, organic  $^{14}\text{C}$  released to groundwater by leaks from reprocessing waste storage ponds (Kaneko et al., 2002; Wieland and Hummel, 2015). The presence of these different highly soluble  $^{14}\text{C}$ -DOC molecules in groundwater is potentially a source for aqueous  $^{14}\text{C}$  release and transport in the shallow subsurface at nuclear sites.

In the shallow subsurface LMWO molecules can be metabolised by many of the diverse range of microbes found in these environments.

Balanced equations for the use of the four most common  $^{14}\text{C}$ -DOC compounds produced from the nuclear fuel cycle during aerobic metabolism are shown below (Equations (4)–(7); Lovley and Phillips, 1988; Ferry, 1990). All of these reactions convert organic carbon into inorganic forms (Equations (4) and (5) indicate that oxidation of acetate and formate produce bicarbonate suggesting that these reactions have the potential to increase groundwater pH). Further, carboxylates and similar LMWO molecules can sorb to, or become incorporated into soil particulates, which may also contribute to their low natural aqueous concentrations (0.1–1000  $\mu\text{M}$ ) in aquifers (van Hees et al., 2002; Fischer and Kuzyakov, 2010).



This study examines the fate of  $^{14}\text{C}$  added as acetate, formate, formaldehyde and methanol in aerobic groundwater systems. The specific objectives were: 1) to investigate the behaviour of aqueous, organic  $^{14}\text{C}$  in contact with sediment and atmosphere; 2) to establish the extent of the oxidation of organic  $^{14}\text{C}$  to  $^{14}\text{CO}_2(\text{g})$ ; 3) to assess the potential for organic and inorganic  $^{14}\text{C}$  accumulation in sediment; 4) to determine which part of the indigenous microbial community found in the sediment favour the organic compounds under aerobic conditions; and 5) to assess the implications of these processes for  $^{14}\text{C}$ -DOC release and migration in shallow, oxic subsurface environments.

## 2. Materials and methods

### 2.1. Sediment

Sediment was collected from the River Calder valley near Calder Bridge, Cumbria, UK (Lat. 54°26.3'N, Long. 3°28.2'W) in August 2015. This sediment is representative of the glacial/fluviol superficial deposits that underlie the neighbouring Sellafield nuclear reprocessing site, UK (Wallace et al., 2012; Law et al., 2010). Sediment was collected in HDPE plastic containers before being transferred to sterile HDPE bags and stored at 4 °C. All experiments were started within three months to ensure that the microbial community remained representative of the unaltered sediment. Prior to use the fresh sediment was sieved to retain < 2 mm fraction. X-ray powder diffraction (Cu K-alpha radiation) using a Bruker D8 Advance XRD was used to characterise the sediment mineralogy. Sediment pH was measured at collection site using standard methodology (ASTM, 2006).

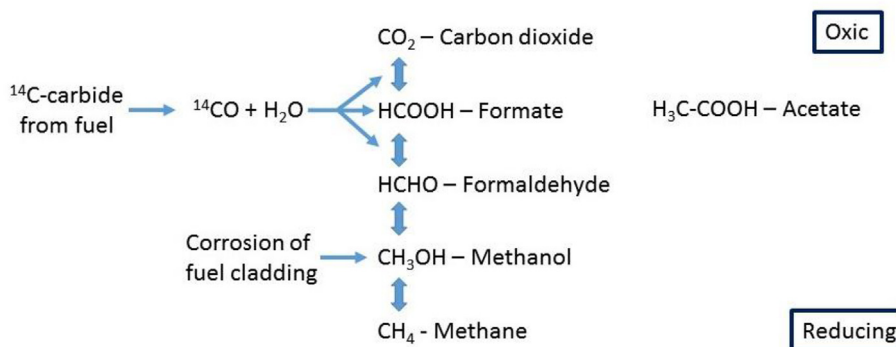


Fig. 1. The formation of organic  $^{14}\text{C}$  compounds in the nuclear fuel cycle under varying redox conditions (McCullom and Seewald, 2007; Kaneko et al., 2002; Wieland and Hummel, 2015).

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