University of Huddersfield Repository

Doulgeris, Charalampos, Humphreys, Paul and Rout, Simon

An approach to modelling the impact of 14C release from reactor graphite in a geological disposal facility

Original Citation


This version is available at http://eprints.hud.ac.uk/id/eprint/24821/

The University Repository is a digital collection of the research output of the University, available on Open Access. Copyright and Moral Rights for the items on this site are retained by the individual author and/or other copyright owners. Users may access full items free of charge; copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational or not-for-profit purposes without prior permission or charge, provided:

- The authors, title and full bibliographic details is credited in any copy;
- A hyperlink and/or URL is included for the original metadata page; and
- The content is not changed in any way.

For more information, including our policy and submission procedure, please contact the Repository Team at: E.mailbox@hud.ac.uk.

http://eprints.hud.ac.uk/
An approach to modelling the impact of \(^{14}\text{C}\) release from reactor graphite in a geological disposal facility

Charalampos Doulgeris, Paul Humphreys, Simon Rout

Department of Biological Sciences, School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

Corresponding author e-mail: c.doulgeris@hud.ac.uk

ABSTRACT

Carbon-14 (C-14) is a key radionuclide in the assessment of a geological disposal facility (GDF) for radioactive waste. In the UK a significant proportion of the national C-14 inventory is associated with reactor core graphite generated by the decommissioning of the UK’s Magnox and AGR reactors.

There are a number of uncertainties associated with the fate and transport of C-14 in a post-closure disposal environment that need to be considered when calculating the radiological impacts of C-14 containing wastes. Some of these uncertainties are associated with the distribution of C-14 containing gaseous species such as \(^{14}\text{CH}_4\) and \(^{14}\text{CO}_2\) between the groundwater and gaseous release pathways. As part of the C14-BIG programme, a modelling framework has been developed to investigate these uncertainties. This framework consists of a biogeochemical near-field evolution model, incorporating a graphite carbon-14 release model, which interfaces with a geosphere/biosphere model. The model highlights the potential impact of the microbial reduction of \(^{14}\text{CO}_2\) to \(^{14}\text{CH}_4\), through the oxidation of \(\text{H}_2\), on C-14 transport. The modelling results could be used to inform the possible segregation of reactor graphite from other gas generating wastes.

Keywords: carbon-14, graphite, gas generation, geosphere, dose assessment
Introduction

Approximately 80,000 tonnes of irradiated graphite will arise from the decommissioning of Magnox and AGR reactors (NDA, 2011, 2014). This graphite contains the majority of the UK intermediate-level waste radioactive waste C-14 inventory (NDA, 2012). C-14 is a key radionuclide in the assessment of a geological disposal facility (GDF) for UK radioactive waste and the radiological consequences of gaseous C-14 transport in particular have been recognised as a potential issue (NDA, 2012).

There are uncertainties associated with the long-term release of C-14 from irradiated graphite which are related to the release mechanisms, the chemical forms, and the total releasable fraction of the C-14 inventory. In particular the partitioning of C-14 between aqueous and gaseous phases could have a significant impact on the transport of C-14 bearing species.

The release of C-14 via a gas release pathway in a fractured higher strength host rock is highly dependent on the volumes of non-radioactive gases generated within a GDF, since these gases have the ability to drive the transport of the smaller volumes of C-14 bearing gases. Microbiological and corrosion processes may generate gas within a disposal facility and the associated biogeochemical processes have been addressed in detail by several studies (Humphreys et al., 1997; Graham et al., 2003; Suckling et al., 2011). The most mobile C-14 species is likely to be CH$_4$ since this is not subject to precipitation reactions that will retard the migration of C-14 labelled CO$_2$. If C-14 labelled CH$_4$ reaches the biosphere it will be subjected to microbial oxidation to C-14 CO$_2$; once converted to CO$_2$ the C-14 is available for root and foliar uptake by plants (Hoch et al., 2014).
The mechanisms associated with the migration of radioactive gases are strongly influenced by the host rock and could be described by following a two-phase flow approach (Kuitunen, 2011; Schwartz, 2012). However, it is difficult to incorporate a complex two-phase flow modelling into assessment level models. Therefore, an alternative approach, which is more suitable for screening studies, is to describe the advection and dispersion processes in the geosphere with a simplified mass pathway (Limer et al., 2010; Towler et al., 2012).

The impact of C-14 release from graphite in geological disposal has been addressed in several studies. Bracke and Muller (2008) discussed possible scenarios for the release pathways and the associated processes towards a less conservative approach in the release of C-14 from a low-level waste repository. Smith et al. (2012) presented a comparison of five models used to predict uptake of C-14 to agricultural crops, within the international BIOPROTA framework. Towler et al. (2012) presented an analysis related to UK graphite in a deep repository during the EC CARBOWASTE project. The analysis presented in these studies has demonstrated that in principle, it should be possible to safely dispose of irradiated graphite wastes in isolation, in a wide range of disposal systems, including near-surface, shallow and deep geological disposal, and in a wide range of host rocks.

As part of the C14-BIG programme, a modelling framework has been developed that goes beyond that modelled by Towler et al. (2012) by integrating a range of gas generation processes with recent insights into the speciation of C-14 leaching from reactor graphite (Baston et al., 2014). This framework consists of a biogeochemical near-field evolution model, incorporating a graphite C-14 release
model, which interfaces with a geosphere/biosphere model developed in a GoldSim (GoldSim, 2010) simulation environment.

Model description

Near field Processes

C-14 release from reactor graphite

The release of C-14 from graphite is modelled using the approach recently presented by Baston et al. (2014). The conceptual model considers three fractions; a rapidly releasable fraction loosely bound to the graphite surface, a slowly releasable fraction from the graphite porosity and a retained fraction that is immobilised in the graphite structure. The released C-14 is further speciated into CO₂, CO and CH₄ before being released into the aqueous or gaseous phases. The conceptual model is illustrated in Fig. 1 and the release rate is calculated as:

\[
q = (k_{ca}F_{ca}e^{k_{ca}t} + k_{cc}F_{cc}e^{k_{cc}t} + k_{ct}F_{ct})A_0e^{-\lambda_c t}
\]  

(1)

where \( q \) is the release rate of C-14 from graphite [TBq/a], \( k_{ca} \) and \( k_{cc} \) are the rate constants for the rapid and the slow release [a⁻¹], respectively, \( F_{ca} \) and \( F_{cc} \) are the rapidly and the slowly releasable fraction respectively, \( A_0 \) is the initial activity of C-14 in the graphite [TBq], \( \lambda_c \) is the radioactive decay rate of C-14 [a⁻¹] and \( t \) is time [a].

Corrosion

<Fig. 1>
The corrosion of steel is modelled under anaerobic, saturated conditions via the following reaction scheme (Suckling et al., 2011):

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

Steel corrosion is modelled by zero-order kinetics and is given by:

$$\frac{-dQ}{dt} = \frac{\rho rA}{M}$$

where $Q$ is the mass of steel [mol], $\rho$ is the density of steel [kg/m$^3$], $M$ is effective molecular mass of steel [kg/mol], $r$ is the corrosion rate under anaerobic conditions [m/a] and $A$ is the surface area of steel [m$^2$].

**Microbial degradation**

Cellulose is the only class of organic waste considered within the model. The microbial degradation of polymeric organics such as cellulose follows a generic sequence of events (Rittmann and McCarty, 2001), where first the polymer is converted into soluble intermediates. These are then subject to microbial oxidation reactions depending on the prevailing geochemical conditions. The microbial degradation of polymeric substrates and the subsequent generation of gas is a rather complex process involving an array of microbial species. Representation of this process can be simplified by the fact that the conversion of polymeric substrates to their soluble intermediates is often the rate limiting factor in the gas generation process (Rittmann and McCarty, 2001), allowing the microbial oxidation of polymers to be coupled directly to the reduction of the relevant terminal electron acceptors. This approach has been applied in other modelling studies (McNab and Narasimham, 1994; Postima and Jacobsen, 1996; Suckling et al., 2011), since it
simplifies the model by reducing the number of kinetic parameters required. In the model reported here, organic degradation is modelled by the following reaction:

$$C_{n}H_{a}O_{b} \rightarrow \frac{4n-a+2b}{8} CO_{2} + \frac{d}{8} CH_{4} + \frac{a-4n+2b}{4} H_{2}O$$

where $d=4n+a-2b$ (for cellulose: $n=6$, $a=10$, $b=5$, $d=24$).

The degradation of cellulose is modelled by first-order reaction kinetics:

$$-\frac{dC}{dt} = kC$$

where $C$ is the mass of polymer [mol] and $k$ is the degradation rate constant under anaerobic conditions [a$^{-1}$].

Microbial metabolism of corrosion derived hydrogen follows a first-order reaction kinetics and is coupled to the reduction of carbon dioxide:

$$4H_{2} + CO_{2} \rightarrow CH_{4} + 2H_{2}O$$

The microbial consumption of hydrogen and the generation of hydrogen from corrosion have independent reaction rates. If the rate of microbial hydrogen metabolism is higher than that of corrosion and the associated hydrogen generation, then the rate of corrosion becomes the limiting process.

Microbes utilize part of the degraded organic material to produce new biomass of the composition $C_{5}H_{7}O_{2}N$. Microbes are also subject to natural turnover since cells have finite lifetimes and the model assumes that a fraction of the dead biomass is recycled to the organic material. The production rate of biomass is controlled by the degradation rate of the organic material and the decay rate of biomass, and is given by:

$$\frac{dX}{dt} = \gamma \frac{dC}{dt} - DX$$

(4)
where $X$ is the biomass [mol], $Y$ is the biomass yield coefficient, and $D$ is the biomass decay rate [$a^{-1}$].

The microbial groups required to catalyse the above processes are assumed to be present within the repository. This can be justified on the basis that microbes will enter the repository during the construction and operational phases, and in the waste and the groundwater entering the repository.

Microbial activity in the near field of a cementitious GDF will be influenced by the ambient pH conditions. In a homogenous highly alkaline environment (pH>12.5) (NDA 2010a), microbial activity is unlikely (Humphreys et al., 2010), and in this case only corrosion and cellulose hydrolysis will proceed. In a heterogeneous near field, lower pH niches (between 10 and 12.5) may occur, allowing microbial activity to take place. Microbial activity at pH values lower than pH 12.5 has been demonstrated by experimental work carried out as part of the C-14 BIG project (Rout et al. 2015) which has shown that microbially driven organic degradation and associated methane generation can occur at pH 11.0 in completely mixed systems.

Chemical Processes

The model does not simulate an evolving near-field chemistry or take into account temperature variations, rather a scenario based approach is employed to simulate qualitatively different near-field evolutions. In addition, the model does not take into account any potential disequilibria between C-14 and C-12 and the model implicitly assumes initial isotopic equilibrium in all phases. One key process considered by the model is carbonation, where dissolved CO$_2$ has the potential to be retained in the near field via carbonation reactions with cementitious materials.
within the GDF (NDA, 2010a). Carbonation is important since it has the potential
to retain C-14 in the near-field through the precipitation of C-14 bearing CO₂.

**Additional aspects of near field modelling**

In the modelling approach presented here, the generation of biogenic and C-14
bearing gases in a GDF is influenced by microbial activity, metal corrosion and the
release of C-14 from graphite. The migration of C-14 to the geosphere/biosphere
environment follows a groundwater pathway or a gas pathway and is influenced by
the magnitude of groundwater flow and the partitioning of gas between the solution
and the gaseous phase. The relevant modelling assumptions are discussed below.

The model assumes, for simplicity in run time, constant (in time and space)
values of rock permeability and hydraulic gradient and uses Darcy’s law to
estimate groundwater inflow and outflow in the near field. C-14 bearing species
dissolved in the groundwater entering the far field from the near field constitutes
the groundwater release pathway.

The gas generated in the near field is partitioned between the solution and the
gas phase using Henry’s law. The gas phase is hosted in an assumed headspace
within the repository (Humphreys et al., 1997; Graham et al., 2003). The aqueous
phase is in equilibrium with the headspace gases and it is assumed that there is a
perfect mixing between the gases both in the headspace and the aqueous phase. The
carbonate chemistry associated with carbon dioxide solubility is not modelled
explicitly. Rather the carbonation process is modelled as a sink term for carbon
dioxide removal, an approach consistent with other gas generation models
(Rodwell 2004). A fractured higher strength host rock is assumed to host the
repository and as such is assumed not to represent a significant barrier to gas
migration (NDA, 2010c). Gas is released to the far field via the headspace based on the mean near field gas pressure, which is determined by assuming that hydrostatic conditions exist. This release of C-14 bearing gases to the far field constitutes the gaseous release pathway.

Far field modelling

The migration of C-14 from the near field follows the groundwater or the gaseous release pathway through the geosphere before entering the biosphere environment. A detailed representation of the geosphere/biosphere system is beyond the scope of the model presented here. The model presented here simplifies these processes in order to understand the impact of a number of near field assumptions around the transformation and release of C-14 with the aim of informing future methodological developments.

Fig. 2 shows the groundwater and gas pathway of C-14 from the repository to the biosphere. Along the groundwater pathway, the model considers a constant groundwater flow and advection and dispersion processes through a homogeneous and isotropic geological medium. Groundwater abstraction is modelled from a near surface aquifer system. The model allows dissolved C-14 species to be released into the gas phase as the groundwater approaches the surface since water pressure decreases along with associated solubility of C-14 bearing gases. Gaseous species released from the groundwater are assumed to travel to the biosphere through faults in the higher strength host rock following mostly a vertical elevation. The migration of the free gas phase generated in the near field and in the groundwater
pathway is controlled by a constant gas flow rate depending on rock permeability, flow area and pressure difference according to the Darcy flow equation.

The biosphere environment is simulated by using three discrete model compartments: the soil-plant, the animal uptake and the human uptake. The soil-plant compartment is based on the enhanced RIMERS model (Thorne, 2005) and is interfaced both with the gas and the groundwater pathway. Within the soil compartment, \(^{14}\)CH\(_4\) in the free gas phase is conservatively assumed to be fully metabolised by microbes to \(^{14}\)CO\(_2\). The animal and the human uptake compartments are based on the ingestion rates of particular food sources and the C-\(^{14}\) dose coefficients; these are only interfaced with the groundwater pathway. The biosphere is modelled in line with the approach described by Limer et al. (2010).

Scenarios description

The modelling framework is applied to an assumed repository at a depth of 650 m containing intermediate level radioactive wastes based on the UK inventory. Fully saturated and anaerobic conditions are assumed from the beginning of the simulation since only the post-close environment is considered here. The initial inventory data and associated model parameters are specified in Table 1.

A scenario based approach is employed to investigate the release and transport of the C-\(^{14}\) associated with reactor graphite. In Scenario A, graphite is assumed to be segregated from the other wastes and packaged in concrete. Carbonation is
assumed to dominate the behaviour of carbon dioxide and processes such as corrosion and microbial activity which may influence C-14 transport are considered to be negligible.

In Scenario B, the release of C-14 is modelled alongside the generation of hydrogen from the corrosion of steel packaging and waste components. Microbial activity is assumed to be negligible due to the ambient pH of the repository and once again the behaviour of carbon dioxide is assumed to be dominated by carbonation.

In Scenario C, a biotic environment is considered and microbial activity is modelled, alongside corrosion and the release of C-14 from graphite. In this scenario two cases are examined, in the first case, (C1), microbial activity is able to utilise carbon dioxide in the metabolism of corrosion hydrogen and the generation of methane with only excess carbon dioxide being removed by carbonation. In the second case (C2) all the carbon dioxide generated during cellulose degradation is removed by carbonation.

Results

The three scenarios considered generated different radiological dose profiles when modelled up to $10^5$ years (Fig. 3). In scenario A, the dose remains below 0.01 $\mu$Sv/a with the groundwater release pathway dominating over the gaseous release pathway. The release of C-14 via the gas pathway is low in scenario A, due to the absence of a driving force associated with the generation of bulk gases by corrosion and organic degradation. Releases to the biosphere via the groundwater pathway are low due to the combined impacts of low near-field conductivity, carbonation, dispersion and radioactive decay.
Scenarios B and C2 have broadly similar dose profiles, the increased doses over and above those seen in scenario A are due to the generation of bulk gases which in turn drive the release of C-14 bearing gases. The doses are slightly higher in scenario C2, than those in scenario B; the difference being due to the higher gas volumes generated by microbial activity in scenario C2.

In scenario C1, the dose is significantly higher than that simulated in the other scenarios. This is largely due to the microbial reduction of C-14 bearing CO\(_2\) to C-14 bearing CH\(_4\). This contrasts with the other scenarios where the majority of the C-14 bearing CO\(_2\) is retained in the near field via carbonation reactions with cement.

Fig. 4 shows the groundwater and the gas components of the effective dose for scenario C1, which are related with the groundwater pathway and the gas pathway, respectively. The gas component increases earlier and is the only component of the dose for almost 1000 years. After this time, the groundwater component also becomes an important contribution to the peak dose estimate. The double peak in the gas component is related to changes in the volumes of non radioactive gases generated in the near field and driving the release of C-14 bearing gases. The start of the second peak represents the point at which corrosion derived hydrogen begins to appear alongside microbially generated methane (Fig. 5). This occurs when the supply of CO\(_2\) derived from organic waste degradation is not sufficient to account for all the hydrogen generated by corrosion.
Discussion and conclusions

The modelling work reported here highlights a number of key processes that influence the radiological assessment of the disposal of reactor graphite and the associated C-14. The approach aligns with the opinions expressed by Bracke and Muller (2008) who argued for less conservative approaches to C-14 assessment modelling. The results are also in agreement with those of Towler et al. (2012) who took a different approach to represent a similar system. The modelling framework reported here could help inform the possible segregation of reactor graphite from other gas generating waste forms to minimise C-14 transport via the gas pathway.

The work also highlights the significance of the potential role of microbial reduction of C-14 bearing CO$_2$ to C-14 bearing CH$_4$ through the oxidation of corrosion hydrogen in increasing the mobility and possible radiological impacts of C-14. The importance of this process is being emphasised by experimental evidence for the release of C-14 from graphite as CO$_2$ (Baston et al., 2014).

Assessment and modelling studies have generally reduced the calculated impact of this process by invoking carbonation as a mechanism for the diversion of C-14 bearing CO$_2$ into an immobilised and biologically inert form (Jackson and Yates, 2011; Towler et al., 2012; Hoch et al., 2008). The modelling results reported here indicate that microbial generation of C-14 bearing CH$_4$ is only significant when microbes have access to C-14 CO$_2$ prior to carbonation. In this case, the conversion of CO$_2$ to CH$_4$ becomes controlled by the availability of H$_2$ generated by corrosion. The importance of carbonation as an attenuating process for C-14 transport should also be viewed in the context of experimental evidence of the direct utilisation of
calcite by hydrogen oxidising microbes under neutral and alkaline conditions
(Suzuki et al., 2014; Virden and Kral, 2010).

Acknowledgements

This study was supported financially by the Engineering and Physical Sciences Research Council (EPSRC) and the Nuclear Decommissioning Authority’s Radioactive Waste Management Directorate (NDA-RWMD). Since April 2014, NDA-RWMD has become a wholly-owned subsidiary of the NDA, Radioactive Waste Management Limited (RWM). Additional technical input and comments from RWM staff are gratefully acknowledged and special thanks to Steve Williams are given.

References


NDA (2010b) Generic Post-closure Safety Assessment. NDA/RWMD/030, NDA, UK.


### Table 1. Wastes in the assumed repository and the parameters of the modelling framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite radioactivity [TBq]</td>
<td>6000</td>
<td>Limer et al. (2010)</td>
</tr>
<tr>
<td>Cellulose mass [Mmol]</td>
<td>9.3</td>
<td>NDA (2010c)</td>
</tr>
<tr>
<td>Steel mass [Mmol]</td>
<td>1298</td>
<td>NDA (2010c)</td>
</tr>
<tr>
<td>Rapidly releasable fraction of C-14</td>
<td>$1.5 \times 10^{-4}$</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Slowly releasable fraction of C-14</td>
<td>$5 \times 10^{-2}$</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Fraction of C-14 released as CH₄</td>
<td>$10^{-2}$</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Fraction of C-14 released as CO</td>
<td>$5 \times 10^{-3}$</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Rate of rapid release of C-14 [a⁻¹]</td>
<td>50</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Rate of slow release of C-14 [a⁻¹]</td>
<td>$2.5 \times 10^{-3}$</td>
<td>Baston et al. (2014)</td>
</tr>
<tr>
<td>Steel corrosion rate [μm/a]</td>
<td>$10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Surface area of steel [km²]</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cellulose degradation rate [a⁻¹]</td>
<td>$5 \times 10^{-4}$</td>
<td>Walke et al. (2011)</td>
</tr>
<tr>
<td>Hydrogen metabolism rate [a⁻¹]</td>
<td>250</td>
<td>Walke et al. (2011)</td>
</tr>
<tr>
<td>Biomass yield coefficient [-]</td>
<td>0.23</td>
<td>Walke et al. (2011)</td>
</tr>
<tr>
<td>Biomass decay rate [a⁻¹]</td>
<td>10</td>
<td>Walke et al. (2011)</td>
</tr>
<tr>
<td>Recycling fraction of dead biomass</td>
<td>0.9</td>
<td>Walke et al. (2011)</td>
</tr>
<tr>
<td>H₂ solubility [mol/m³/atm]</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>CH₄ solubility [mol/m³/atm]</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>CO₂ solubility [mol/m³/atm]</td>
<td>34.17</td>
<td></td>
</tr>
<tr>
<td>Length of repository [m]</td>
<td>1500</td>
<td>NDA (2010b)</td>
</tr>
<tr>
<td>Width of repository [m]</td>
<td>1000</td>
<td>NDA (2010b)</td>
</tr>
<tr>
<td>Height of repository [m]</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Height of headspace [m]</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Permeability in the near field [m²]</td>
<td>$10^{-16}$</td>
<td></td>
</tr>
<tr>
<td>Permeability in the far field [m²]</td>
<td>$3.3 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>Hydraulic gradient of groundwater [-]</td>
<td>0.001</td>
<td>Limer et al. (2010)</td>
</tr>
<tr>
<td>Porosity in the near field [-]</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Porosity in the far field [-]</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Dispersivity [m]</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Diffusivity [m²/s]</td>
<td>$4.3 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>Length of the groundwater pathway [m]</td>
<td>6000</td>
<td></td>
</tr>
<tr>
<td>Release area of the gas pathway [m²]</td>
<td>$18 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>Flow area of the groundwater pathway [m²]</td>
<td>20000</td>
<td></td>
</tr>
<tr>
<td>Flow area of the gas pathway [m²]</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>
List of Figures

400  Fig. 1. Conceptual model of C-14 release from graphite (adapted from Baston et al., 2014)

402  Fig. 2. Groundwater and gas pathways in the geosphere

403  Fig. 3. Radiological effective dose for the scenarios in the near field environment

404  Fig. 4. Groundwater and gas components of the effective dose for scenario C1

405  Fig. 5. Activity of C-14 bearing gases and biogenic gas mass for scenario C1
rapidly releasable fraction of $^{14}$C

slowly releasable fraction of $^{14}$C

unreleasable fraction of $^{14}$C

$^{14}$CO$_2$

$^{14}$CO

$^{14}$CH$_4$