

# **Uptake of Gaseous Carbon-14 in the Biosphere**

## **Development of an Assessment Model**



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Development of an Assessment Model

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## Preface

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## Abstract

Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste. In particular, the radiological consequences of potential releases of carbon-14 bearing gaseous species may be important.

The gas most likely to reach the biosphere is carbon-14 bearing methane ( $^{14}\text{CH}_4$ ) (since carbon-14 bearing carbon dioxide ( $^{14}\text{CO}_2$ ), which is also predicted to form, is expected to react with cementitious backfill in the GDF).

Despite much recent work, focused on climate change, on the behaviour of both  $\text{CH}_4$  and  $\text{CO}_2$  in soils, there remains considerable uncertainty over (a) the interaction of  $^{14}\text{C}$  with soil microorganisms and organic matter, and (b) the potential for incorporation of  $^{14}\text{C}$  by plants, which will result in  $^{14}\text{C}$  exposures to grazing animals and human consumers of plant and animal products.

Therefore, Radioactive Waste Management Limited commissioned a project:

- To obtain experimental data on the behaviour of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  in the soil zone, and the subsequent uptake of  $^{14}\text{C}$  by plants;
- To interpret the results of the experiments using appropriate techniques and models; and
- To develop an assessment model that can be used to calculate the concentration of  $^{14}\text{C}$  in plant material that arises from a below-ground flux of  $^{14}\text{C}$ -bearing gas.

This report presents a model to calculate the concentrations of  $^{14}\text{C}$  in plant material that could arise from a below-ground flux of  $^{14}\text{C}$ -bearing gas, and then assesses the consequences of those concentrations. It also explains how and why the new model differs from previous models. The key differences are improved representations of gaseous transport through the soil and the plant canopy. The result of these improvements is that this report recommends a  $^{14}\text{C}$  flux to dose conversion factor (i.e.  $0.0344 \text{ Sv yr}^{-1}$  per  $\text{Bq m}^{-2}\text{s}^{-1}$ ) which is almost twenty times less than the factor (i.e.  $0.6280 \text{ Sv yr}^{-1}$  per  $\text{Bq m}^{-2}\text{s}^{-1}$ ) used in the 2007 update to the Generic post-closure Performance Assessment.

## Executive Summary

Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste. In particular, the radiological consequences of potential releases of carbon-14 bearing gaseous species may be important. Therefore, Radioactive Waste Management Limited (RWM) has been carrying out a range of research and assessment tasks on carbon-14 to improve its understanding of the release of the gases, the transport of the gases through the geosphere, and the consequences for the calculated annual risk.

The gas most likely to escape from the near field of the GDF and reach the biosphere is carbon-14 bearing methane ( $^{14}\text{CH}_4$ ) (since carbon-14 bearing carbon dioxide ( $^{14}\text{CO}_2$ ), which is also predicted to form, is expected to react with cementitious backfill in the GDF).

Despite much recent work, driven by climate change, on the behaviour of both  $\text{CH}_4$  and  $\text{CO}_2$  in soils, there remains considerable uncertainty over (a) the interactions of  $^{14}\text{C}$  with soil microorganisms and organic matter, and (b) the potential for incorporation of  $^{14}\text{C}$  by plants, which will result in  $^{14}\text{C}$  exposures to grazing animals and human consumers of plant and animal products.

In view of these uncertainties, RWM commissioned a project:

- To obtain experimental data on the behaviour of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  in the soil zone and the subsequent uptake of  $^{14}\text{C}$  by plants;
- To interpret the results of the experiments using appropriate techniques and models; and
- To develop an assessment model that can be used to calculate the concentration of  $^{14}\text{C}$  in plant material that arises from a below-ground flux of  $^{14}\text{C}$ -bearing gas.

## Learning from the Experimental Programme

The key findings of the experimental programme, which have been incorporated into a new  $^{14}\text{C}$  gas assessment model, are summarised in Text Box ES-1 below.

### Box ES-1 Findings from the Experiments

The conclusions from the interpretation of the experimental data are as follows:

- Transport of gases through partially-saturated soils is a diffusive process, which can be described by a generalisation of Fick's law.
  - In the generalisation of Fick's law, the molecular diffusion coefficient is multiplied by a parameter called the tortuosity, to account for the presence of the soil particles. A generic value for the tortuosity is of the order of a few percent.
- Methane is oxidised in near-surface soils by methanotrophic microbes.
  - Methane oxidation can be modelled as a first-order reaction, with a rate constant likely to be in the range  $10^{-5} \text{ s}^{-1}$  to  $10^{-4} \text{ s}^{-1}$ .
- The processes of diffusion and methane oxidation are coupled. A diffusion-reaction equation will describe a quasi-steady-state flux of  $^{14}\text{CH}_4$  being oxidised to  $^{14}\text{CO}_2$  in the soil.
  - This equation has a characteristic length scale over which the  $^{14}\text{CH}_4$  will be oxidised.
  - The characteristic length scale is likely to be no more than a few tens of centimetres. Provided that the water table is at a depth which is more than a few times this length scale, then conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  will be essentially complete, regardless of the particular values of the diffusion coefficient and the oxidation rate constant.

Any plant uptake of  $^{13}\text{C}$  (as a surrogate for  $^{14}\text{C}$ ) was below the detection limit of the experiments<sup>†</sup>, and was not observed.

## Overview of the New $^{14}\text{C}$ Gas Assessment Model

The new  $^{14}\text{C}$  gas assessment model differs from previous models, which were all multi-compartment models, in that the concentrations and fluxes of  $^{14}\text{C}$  in the system are calculated from representations of the key processes (e.g. molecular diffusion through the soil; methane oxidation by microbes; turbulent transport through the plant canopy; dispersion in the overlying atmosphere; dissolution in the soil water; and uptake of contaminated water through a plant's roots).

The experimental programme found that  $^{14}\text{CH}_4$  will be oxidised to  $^{14}\text{CO}_2$  in near-surface soils by methanotrophic microbes. The  $^{14}\text{CH}_4$  will be oxidised over a characteristic length scale. Although this characteristic length scale will be specific to the site and ecosystem under consideration, it seems generally to be of the order of tens of centimetres in agricultural or arable environments, as confirmed by our experiments. In the region where  $^{14}\text{CH}_4$  originating from a GDF will be released to the biosphere, the water table could be at a depth which is more than a few times this length scale, and in that case conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  will be essentially complete. There is then the potential for the uptake of  $^{14}\text{CO}_2$  by plants.

Two major processes contribute to the uptake of  $^{14}\text{CO}_2$  by plants: photosynthesis, and transpiration.

In the case of photosynthesis, the specific activity in the biomass of a plant is equated to the specific activity of the canopy atmosphere, which can be calculated by:

- Multiplying the  $^{14}\text{CO}_2$  flux from the soil by a quantity called the aerodynamic resistance (this product gives an estimate of the  $^{14}\text{CO}_2$  concentration in the canopy atmosphere); and
- Dividing the result by the  $^{12}\text{CO}_2$  concentration in the canopy atmosphere.

The aerodynamic resistance is the key parameter in this calculation, and has values of several tens  $\text{s m}^{-1}$  for many crops.

In the case of transpiration, an additional source of  $^{14}\text{C}$  in the biomass of a plant can be computed essentially by multiplying the concentration of  $^{14}\text{CO}_2$  in the soil gas with:

- The Henry's law constant (this product gives the concentration of  $^{14}\text{CO}_2$  in the soil water); and
- The transpiration ratio (i.e. the amount of water taken up by a plant per unit dry mass of the plant).

The transpiration ratio is the key parameter in this calculation. It has values in the range from 450 to 950  $\text{kg H}_2\text{O}$  transpired per  $\text{kg}$  dry mass produced for C3 plants<sup>‡</sup> in the temperate zone. A correction factor accounts for the possibility that uptake of  $^{14}\text{C}$  through the plant's roots may be an active process, and the consideration that some of the  $^{14}\text{C}$  will be lost as a result of maintenance respiration.

<sup>†</sup> We note that the maximum flux of methane from a geological disposal facility through the overlying soils is estimated to be of the order of  $0.1 \text{ mol m}^{-2} \text{ yr}^{-1}$ , and the maximum flux of  $^{14}\text{CH}_4$  will be much less than this. It would have been challenging to replicate such a small flux in the experimental programme, and therefore the experiments had to use a larger flux. A concern with using a larger flux was to avoid stimulating the population of methanotrophic microbes, which would have invalidated the measurements of the rate of methane oxidation. Therefore, a small pulse of methane was injected at depth in the soil, but this meant that the quantity of methane was so small that the experiments were unable to detect the subsequent uptake of  $^{13}\text{C}$  by the plants.

<sup>‡</sup> C3 plants first fix atmospheric  $\text{CO}_2$  into a compound containing three carbon atoms, which then enters the Calvin cycle of photosynthesis. Examples include most plants in the temperate zone.



The total uptake of  $^{14}\text{C}$  by plants is obtained by summing the contributions due to photosynthesis and transpiration. This neglects potential interference between the two pathways (i.e. photosynthesis and transpiration) for the uptake of  $^{14}\text{C}$ . Our analysis shows that photosynthesis and transpiration will contribute similarly to the uptake of  $^{14}\text{C}$ , and for this case simply adding the two contributions is cautious by a factor of at most two.

The dose from ingestion of the  $^{14}\text{C}$ -contaminated plants is computed by assuming that animals will derive most of their food from the contaminated area, but humans will fulfil only a fraction of their dietary requirements (because major contributors to carbon in the diet, such as cereals and sugars, will be sourced mostly from elsewhere). As in previous  $^{14}\text{C}$  gas assessments, this fraction is cautiously taken as 0.3, and then a standard calculation can be used to relate the specific activity of  $^{14}\text{C}$  in humans to the effective dose rate.

## Comparison with Previous Gas Assessments

Table ES-1 lists the results obtained for the effective dose rate ( $\text{Sv yr}^{-1}$ ) to a representative member of a Potentially Exposed Group per unit flux of  $^{14}\text{C}$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ) at the bottom of the vadose zone, and compares the results with the values used in earlier key assessments for RWM. Also shown are the associated limiting release rates that would comply with the regulatory risk guidance level.

**Table ES-1 Flux to Dose Conversion Factors Used By RWM (and Formerly By Nirex and Then NDA RWMD)**

Assessment	Flux to Dose Conversion ( $\text{Sv yr}^{-1}$ ) per ( $\text{Bq m}^{-2}\text{s}^{-1}$ )	Limiting Release Rate ( $\text{TBq yr}^{-1}$ )	
		Area = $10^4 \text{ m}^2$	Area = $10^6 \text{ m}^2$
Nirex 97 and GPA (03)	$2.21 \cdot 10^{-5} A^{1/2 \dagger}$	$2.4 \cdot 10^{-3}$	$2.4 \cdot 10^{-2}$
GPA (03) Update	0.6280	$8.4 \cdot 10^{-6}$	$8.4 \cdot 10^{-4}$
$^{14}\text{C}$ -IPT Phase 1 Model <i>photosynthesis only</i>	0.0034		
$^{14}\text{C}$ -IPT Phase 1 Model <i>plus transpiration</i>	0.0086	$6.1 \cdot 10^{-4}$	$6.1 \cdot 10^{-2}$
New Model <i>photosynthesis only</i>	<b>0.0107</b>		
New Model <i>plus transpiration</i>	<b>0.0225</b>	<b><math>2.34 \cdot 10^{-4}</math></b>	<b><math>2.34 \cdot 10^{-2}</math></b>

<sup>†</sup> In Nirex 97 and GPA (03), the flux to dose conversion factor depended on the release area,  $A$ .

It is clear that the flux to dose conversion factors have changed significantly over the years. The reasons for these changes can be explained as follows.

First, comparing the similar Nirex 97 and Generic post-closure Performance Assessments (referred to as GPA (03)) with the 2007 update to GPA (03) (referred to as GPA (03) Update), the flux to dose conversion factor is much larger in the latter assessment. That is because the earlier assessments used the RIMERS model, which assumed that the soil solution, soil atmosphere, below-canopy atmosphere and above-canopy atmosphere would be mixed rapidly, and therefore would all have the same specific activity. In contrast, later assessments model the transport of  $^{14}\text{C}$  through the soil and plant canopy, and thus compute the specific activity as a function of location.

Subsequent changes to the flux to dose conversion factor correspond essentially to enhancements in the way that the transport of  $^{14}\text{C}$  through the soil or plant canopy is modelled.

Secondly, the GPA (03) Update assessment is by far the most cautious. The explanation is that the model, which was enhanced RIMERS, assumed that transport of  $^{14}\text{CO}_2$  through the lower plant canopy was a molecular diffusion process rather than a turbulent process. The consequence was that estimates of  $^{14}\text{CO}_2$  residence times in the lower plant canopy were much too long. A change

to modelling transport through the plant canopy as a turbulent process was introduced when LLW Repository Ltd. (LLWR), partly in response to an issue raised by the Environment Agency, improved its methodology for assessing effective doses from  $^{14}\text{C}$ -bearing gases going from the LLWR (2011) assessment to the LLWR (2013) assessment. Subsequent assessments, including both the  $^{14}\text{C}$ -IPT<sup>†</sup> Phase 1 model and the new  $^{14}\text{C}$  gas assessment model, use a similar approach.

Thirdly, comparing the “photosynthesis only” results for the  $^{14}\text{C}$ -IPT Phase 1 model and the new  $^{14}\text{C}$  gas assessment model, the flux to dose conversion factor is about three times larger in the latter model. That is because the new  $^{14}\text{C}$  gas assessment model makes more robustly justified assumptions about plant type and height than the  $^{14}\text{C}$ -IPT Phase 1 model, and therefore derives a slightly larger value of the aerodynamic resistance (i.e. about  $100 \text{ s m}^{-1}$  for a wind speed of  $2 \text{ m s}^{-1}$  at 2m above the ground surface, rather than a few tens  $\text{ s m}^{-1}$ ). A benefit of this approach is that it is independent of crop-specific details about the Potentially Exposed Groups and their diets.

Fourthly, comparing the “plus transpiration” results for the  $^{14}\text{C}$ -IPT Phase 1 model and the new  $^{14}\text{C}$  gas assessment model, the flux to dose conversion factor is about four times larger in the latter model. The explanation for most of this difference is that the  $^{14}\text{C}$ -IPT Phase 1 model underestimated the tortuosity of the soil, and therefore predicted  $^{14}\text{CO}_2$  diffusion coefficients that are too large and  $^{14}\text{CO}_2$  residence times in the soil that are too short (by about an order of magnitude).

Both the  $^{14}\text{C}$ -IPT Phase 1 model and the new  $^{14}\text{C}$  gas assessment model agree that transpiration could be the most significant pathway for uptake of  $^{14}\text{C}$  by plants.

## Recommended Flux to Dose Conversion Factor

Based on the considerations above, it is recommended that future  $^{14}\text{C}$  gas assessment models should assume that the effective dose rate to a representative member of a Potentially Exposed Group per unit flux of  $^{14}\text{C}$  at the bottom of the vadose zone is:

$$0.0225 \text{ (Sv yr}^{-1}\text{) per (Bq m}^{-2}\text{s}^{-1}\text{)}$$

## Advantages of the New $^{14}\text{C}$ Gas Assessment Model

This report proposes a new  $^{14}\text{C}$  gas assessment model, which is based extensively on:

- The data acquired by the experimental programme for RWM; as well as
- The conceptual understanding developed during previous assessment studies.

It is considered that the new  $^{14}\text{C}$  gas assessment model has a number of advantages. Most notably, it emphasises the key processes and parameters controlling the uptake of  $^{14}\text{C}$  by plants, and subsequently by humans. Each of the key processes is represented using a simple analytical sub-model, which is founded on widely accepted understanding. This will make it easier:

- To communicate the ideas underlying the model;
- To quantify the model parameters, and their uncertainties; and
- To audit the model.

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<sup>†</sup> This refers to the work of an Integrated Project Team (IPT), in which the partners are working together to develop an holistic approach to the issue of managing  $^{14}\text{C}$ -containing radioactive wastes in a geological disposal facility.



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# 1 Introduction

Carbon-14 ( $^{14}\text{C}$ ) is a key radionuclide in the assessment of the post-closure safety of a geological disposal facility (GDF) for radioactive waste. In particular, the radiological impact of gaseous  $^{14}\text{C}$ -bearing species is a potential issue, and has been recognised as such [1,2,3]. Therefore, Radioactive Waste Management Limited (RWM) has been carrying out a range of research and assessment tasks on  $^{14}\text{C}$  to improve its understanding of the release of the gases, the transport of these gases through the geosphere, and the consequences for the calculated annual risk.

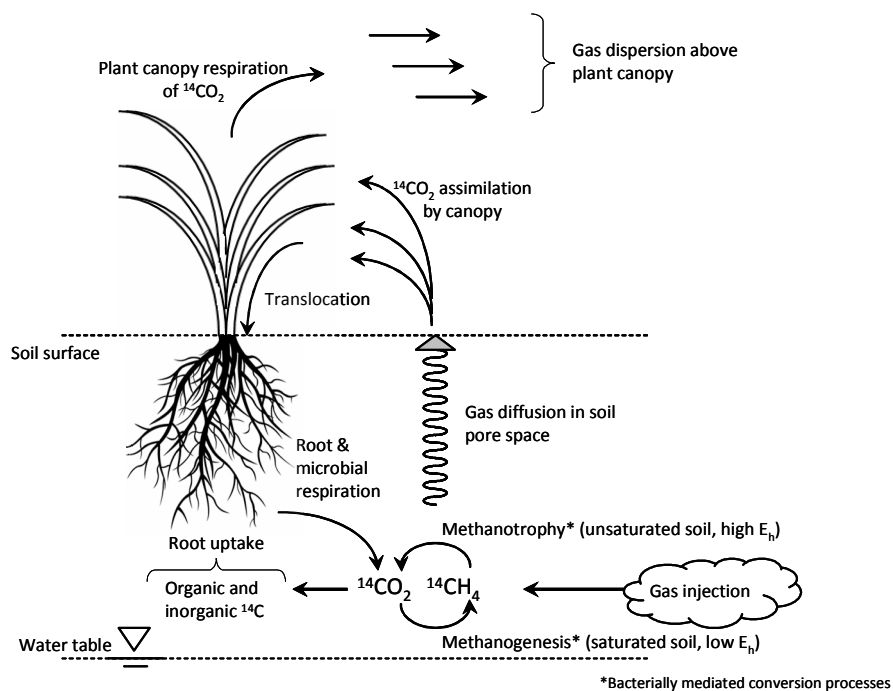
The gas most likely to escape from the near field of the GDF and reach the biosphere is  $^{14}\text{C}$ -bearing methane ( $^{14}\text{CH}_4$ ) (since  $^{14}\text{C}$ -bearing carbon dioxide ( $^{14}\text{CO}_2$ ), which is also predicted to form, is expected to react with cementitious backfill in the GDF).

Despite much recent work, driven by climate change, on the behaviour of both methane and carbon dioxide in soils, there remains considerable uncertainty over (a) the interactions of  $^{14}\text{C}$  with soil microorganisms and organic matter, and (b) the potential incorporation of  $^{14}\text{C}$  by plants, which will result in  $^{14}\text{C}$  exposures to grazing animals and human consumers of plant and animal products.

In view of these uncertainties, RWM commissioned this project:

- To obtain experimental data on the behaviour of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  in the soil zone and the subsequent uptake of  $^{14}\text{C}$  by plants;
- To interpret the results of the experiments using appropriate techniques and models; and
- To develop an assessment model that can be used to calculate the concentration of  $^{14}\text{C}$  in plant material that arises from a subsurface flux of  $^{14}\text{C}$ -bearing gas.

An experimental programme has investigated the behaviour and fate of  $^{14}\text{CH}_4$  introduced into near-surface soil under field conditions (see Figure 1.1), and the main results are reported in Atkinson *et al.* [4].



**Figure 1.1 Conceptual model of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  behaviour after injection into the soil.**

The data obtained by the experimental programme have been interpreted using numerical models [5], and thereby we have been able to demonstrate our understanding of the physical and microbial processes that will control the behaviour of  $^{14}\text{CH}_4$  in near-surface soil.

## 1.1 Objective of This Report

The objective of this report is to use this understanding to develop a numerical model to assess the effective dose rate to a representative member of a Potentially Exposed Group arising from any  $^{14}\text{CH}_4$  reaching the partially saturated near-surface soil.

## 1.2 Structure of This Report

The structure of this report is as follows:

- Section 2 provides a review of past UK studies to assess the radiological impact of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  in the biosphere, so as to provide the context for the remainder of the report.
- Section 3 introduces a new model that could be used to assess the consequences of any  $^{14}\text{CH}_4$  reaching the partially saturated near-surface soil.
- The following three sections describe key features of this  $^{14}\text{C}$  gas assessment model. In particular:
  - Section 4 presents the sub-model used to calculate the conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  in the soil.
  - Section 5 presents two sub-models used to calculate the uptake of  $^{14}\text{CO}_2$  by plants, either as a result of photosynthesis or in the transpiration flow.
  - Section 6 discusses how the specific activity of  $^{14}\text{C}$  in plants can be used to calculate the effective dose rate.
- The last section, Section 7, provides a summary of the proposed  $^{14}\text{C}$  gas assessment model, compares it with previous models, and discusses the implications of adopting it.

## 1.3 Potential Consequences of Other $^{14}\text{C}$ -bearing Gases

Although this report is concerned with the gases  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$ , a number of other  $^{14}\text{C}$ -bearing gases (e.g. carbon monoxide and hydrocarbons of low molecular mass) could be generated in a GDF [6]. Appendix 1 explains how the radiological impact of these other radioactive gases may be assessed using a similar methodology to that developed for  $^{14}\text{CH}_4$ .

## 2 History of UK $^{14}\text{C}$ Gas Assessment Models

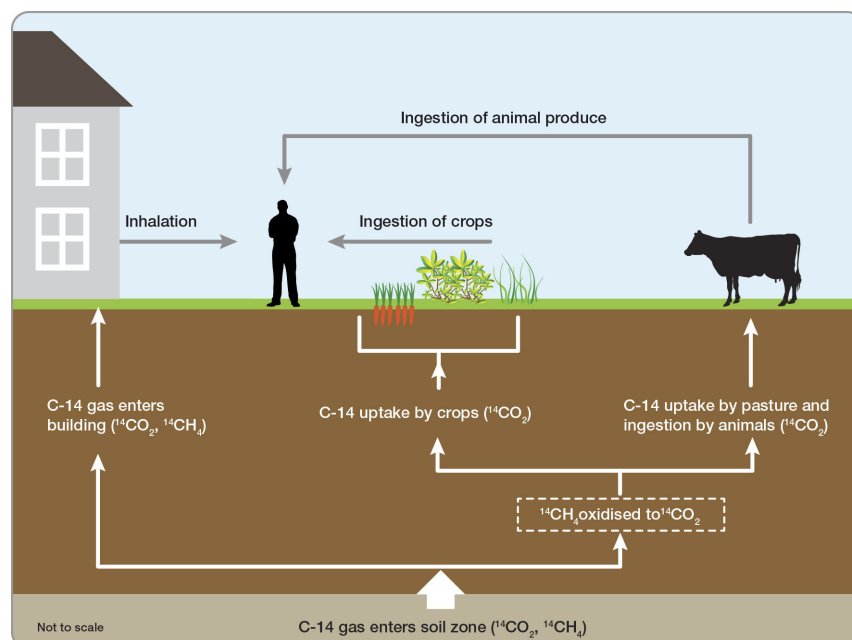
It is expected that processes such as corrosion of metals and leaching of radionuclides from irradiated graphite will occur in a GDF for intermediate-level wastes after its closure, and will generate  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$ . This section provides a brief review of past UK studies to assess the radiological impact of these radioactive gases being generated in a GDF and migrating to the biosphere. The intention of the review is to provide the context for the remainder of the report.

### 2.1 Biological Uptake Pathways

Previous assessments [7-11,2,12-15,6] of the potential consequences of  $^{14}\text{C}$ -bearing gases being released from a GDF to the biosphere post closure have considered various biological uptake pathways. Some of the more important are:

- Conversion of any  $^{14}\text{CH}_4$  in the near-surface soil to  $^{14}\text{CO}_2$ , which then is taken up (e.g. through photosynthesis) by plants and ingested;
- Release of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  directly to the atmosphere, followed by inhalation; and
- Dissolution in near-surface aquifers from which drinking water is drawn<sup>1</sup>.

When focusing on the uptake of gaseous  $^{14}\text{C}$ -bearing species, just two pathways require consideration. These are the release of  $^{14}\text{CH}_4$  and / or  $^{14}\text{CO}_2$  either into a building with exposure by inhalation, or into the near-surface soil with subsequent incorporation into plants and exposure by ingestion (e.g. see Figure 2.1).



**Figure 2.1 Schematic of the biosphere model used to assess the  $^{14}\text{C}$ -bearing gas pathway (reproduced from reference [12], with permission).**

<sup>1</sup> Abstraction of groundwater from near-surface aquifers, and its use either as drinking water or for irrigation, involves dissolved  $^{14}\text{C}$ . Therefore it is outside the scope of this work, which is concerned only with the uptake of gaseous  $^{14}\text{C}$ -bearing species.

Here, the inhalation pathway is considered in Section 2.2, and the ingestion pathway is discussed in Section 2.3. A key finding of the previous assessments is that the most significant pathway usually is ingestion of  $^{14}\text{C}$ -contaminated plants.

## 2.2 Inhalation of $^{14}\text{C}$ -Bearing Gases

For the inhalation pathway, the atmospheric concentration of  $^{14}\text{C}$  inside a building can be estimated from:

$$C = \xi \frac{F}{\lambda_v h} \quad (2.1)$$

where:

- $C$  is the concentration ( $\text{Bq m}^{-3}$ ).
- $\xi$  is a factor to allow for the possibility that the building captures either more or less gas than is implied by the footprint area (-). In reference calculations it has the value 1.
- $F$  is the flux of gaseous  $^{14}\text{C}$  at the ground surface ( $\text{Bq m}^{-2}\text{y}^{-1}$ ).
- $\lambda_v$  is the ventilation rate of the building ( $\text{y}^{-1}$ ). Empirical values of air exchange rates for buildings are given by the Chartered Institute of Building Service Engineers [16]. Reference values are in the range  $0.25 \text{ h}^{-1}$  to  $5 \text{ h}^{-1}$ , although most of the values are in the range  $0.25 \text{ h}^{-1}$  to  $2 \text{ h}^{-1}$ . In reference calculations it has the value  $1 \text{ h}^{-1}$  ( $8766 \text{ y}^{-1}$ ).
- $h$  is the height of the lowest floor of the building (m). In reference calculations it has the value 2.5m.

Having determined the concentration of gaseous  $^{14}\text{C}$  in the indoor air, the effective dose rate is calculated from:

$$H = H_{\text{inh}} B C \quad (2.2)$$

where:

- $H$  is the effective dose rate ( $\text{Sv y}^{-1}$ ).
- $H_{\text{inh}}$  is the committed effective dose per unit intake by inhalation ( $\text{Sv Bq}^{-1}$ ).
- $B$  is the breathing rate ( $\text{m}^3\text{y}^{-1}$ ). A suitable average value for an adult is  $6.5 \cdot 10^3 \text{ m}^3\text{y}^{-1}$  [8], and it is conservative to assume 100% indoor occupancy.

For  $^{14}\text{CO}_2$ , the committed effective dose per unit intake by inhalation is  $6.2 \cdot 10^{-12} \text{ Sv Bq}^{-1}$  for adults [17].

For  $^{14}\text{CH}_4$ , the committed effective dose per unit intake by inhalation is  $1.5 \cdot 10^{-13} \text{ Sv Bq}^{-1}$  [18]. As explained most recently in Shaw and Thorne [19], RWM based its original assessments on the work of Phipps *et al.* [20], which could be interpreted to give a value for  $H_{\text{inh}}$  of  $1.2 \cdot 10^{-13} \text{ Sv Bq}^{-1}$  for adults. However, the ICRP [21] recommended a larger value of  $2.9 \cdot 10^{-12} \text{ Sv Bq}^{-1}$  for adults. Subsequently, Carlisle *et al.* [22] demonstrated that the ICRP model overestimates the uptake of radioactive methane in most tissues. Based on their data, Carlisle *et al.* [22] developed a dosimetric model for  $^{14}\text{CH}_4$ . This model implies a value for  $H_{\text{inh}}$  of about  $1.5 \cdot 10^{-13} \text{ Sv Bq}^{-1}$ , and therefore this value has been retained in later assessments.

The annual risk (i.e.  $r H$ , where  $r = 0.06 \text{ Sv}^{-1}$ ) calculated using the above equations generally is below the regulatory risk guidance level.

This methodology to assess the inhalation pathway is still deemed to be appropriate, and therefore is not being considered for update.



## 2.3 Ingestion of $^{14}\text{C}$ -Contaminated Plants

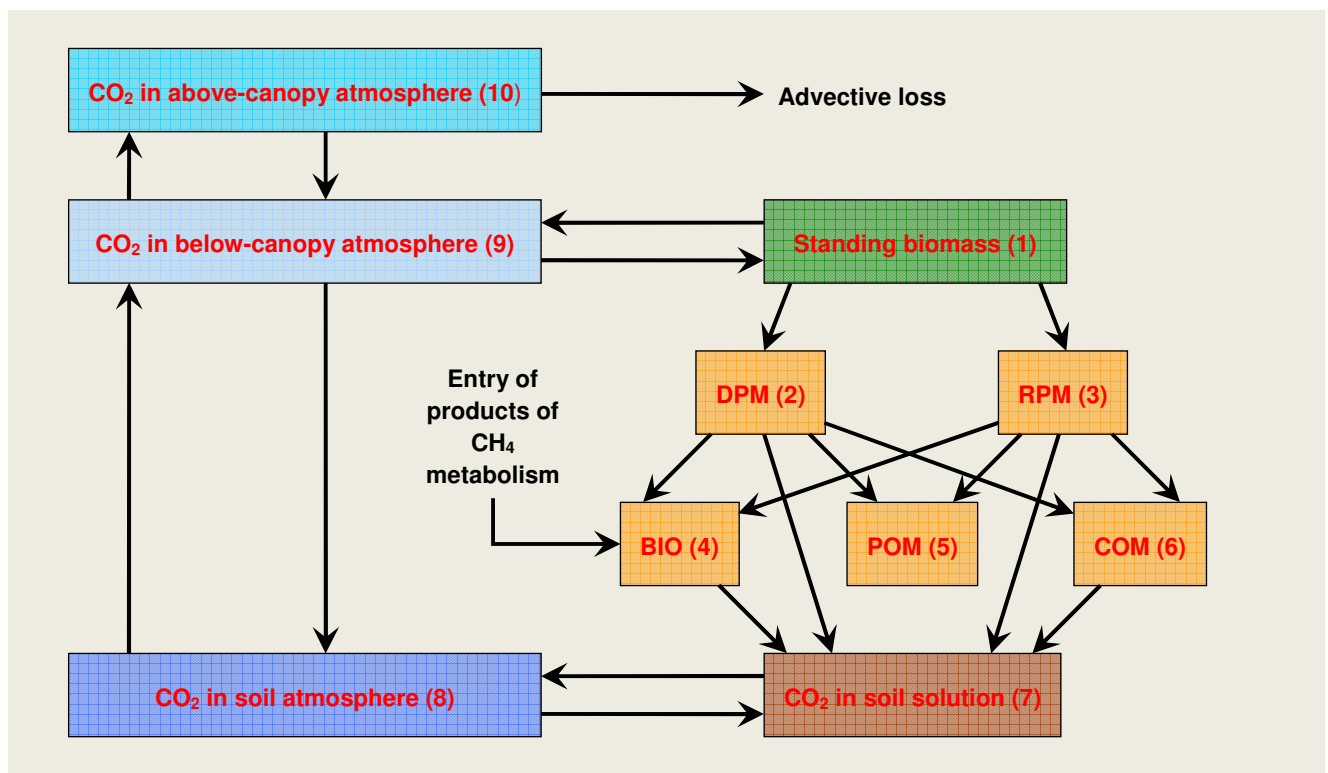
In contrast to the inhalation pathway, the methodology to assess the ingestion pathway has changed substantially over the last twenty years. This subsection presents a brief history of the changes, so that the  $^{14}\text{C}$  gas assessment model which is being proposed in this report can be properly appreciated.

### 2.3.1 RIMERS

The original  $^{14}\text{C}$  gas assessment model was developed during the early 1990's.

Based on a review of the literature, it was assumed that  $^{14}\text{CH}_4$  would be almost completely metabolised in the soil, with the  $^{14}\text{C}$  becoming incorporated into soil biomass and then available for plant uptake, either from soil solution or from air above the soil.

The computer program RIMERS [18] was developed to simulate the fate of  $^{14}\text{C}$  entering biomass by this route. It was a multi-compartment model comprising ten compartments (standing biomass; decomposable plant material – DPM; resistant plant material – RPM; soil biomass – BIO; physically stabilised organic matter – POM; chemically stabilised organic matter – COM; carbon dioxide in soil solution; carbon dioxide in the soil atmosphere; carbon dioxide in the below-canopy atmosphere and carbon dioxide in the above-canopy atmosphere; see Figure 2.2). It was based closely on the Jenkinson-Rayner model of organic matter turnover in soils [23].



**Figure 2.2 Schematic of the RIMERS system model for  $^{14}\text{CH}_4$  released to soil (redrawn from reference [18]).**

The products of  $^{14}\text{CH}_4$  metabolism entered the model by becoming incorporated into soil biomass. The subsequent  $^{14}\text{C}$  flows through the model can be summarised as follows.

Standing biomass is assumed to enter the soil as either decomposable plant material (DPM) or resistant plant material (RPM). Each of these generates, though at different rates, soil biomass (BIO), physically stabilised organic matter (POM), and chemically stabilised organic

matter (COM), as well as carbon dioxide in soil solution. Additional carbon dioxide in soil solution is generated from the degradation of BIO, POM and COM.

Carbon dioxide in soil solution exchanges with carbon dioxide in the internal soil atmosphere, and also is available for root uptake by plants. In turn, the soil atmosphere exchanges with the below-canopy and above-canopy atmospheres. The below-canopy atmosphere, where photosynthesis is taken to occur, is the primary source of carbon dioxide uptake in plants. Loss of carbon dioxide from plants, as a consequence of respiration, also is taken to occur to the below-canopy atmosphere.

In summary, RIMERS is a multi-compartment model, which assumes:

- Complete conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  in the soil; and
- Constant rate coefficients governing transfers between many of the compartments:
  - The soil solution, soil atmosphere, below-canopy atmosphere and above-canopy atmosphere were taken to be in equilibrium.
  - Otherwise, values of the rate coefficients either were taken from the original Jenkinson-Rayner model [23], or were derived by simple physical or chemical arguments.

Although this model had a particular focus on modelling the partitioning of  $^{14}\text{C}$  between different pools of organic matter in the soil, it included a representation of most of the key processes controlling the transport of  $^{14}\text{C}$  through the soil and subsequent uptake by plants and humans.

### 2.3.2 Enhanced RIMERS

Because of the rapidity of the exchanges between soil solution, soil atmosphere, below-canopy atmosphere and above-canopy atmosphere, these compartments were treated as being in equilibrium in the original implementation of RIMERS. Although this was a reasonable approximation, a further assumption was made that the specific activities of the carbon in each of these four compartments were equal [24]. This is untenable, as  $^{14}\text{CO}_2$  released from the soil will become mixed with atmospheric carbon dioxide in the below-canopy and above-canopy atmospheres, resulting in a vertical gradient of the specific activity of the carbon.

Having recognised this, an enhanced version of the RIMERS model was produced [24], and using it a set of sensitivity studies was performed [25]. The enhanced version of the model replaced the assumption of equilibrium between soil solution, soil atmosphere, below-canopy atmosphere and above-canopy atmosphere by a full kinetic formulation, as applied already to transfers between the other compartments in the model. In this formulation, the specific activities of the carbon in the four compartments are no longer equal.

The enhanced RIMERS model was used extensively in model inter-comparison studies undertaken within the BIOPROTA framework [26,27]. Following from these studies, it was recognised that a weakness of the enhanced version of the RIMERS model is that gas-exchange rates between the soil atmosphere, below-canopy atmosphere and above-canopy atmosphere have to be estimated by the user, rather than computed from a process-based model.

### 2.3.3 LLWR 2011 Model

Subsequently, a model was developed for LLW Repository Ltd. (LLWR) that overcame this deficiency. The original implementation, which we shall refer to as the LLWR 2011 model [14,28], was used in the 2011 Environmental Safety Case (ESC) [12].

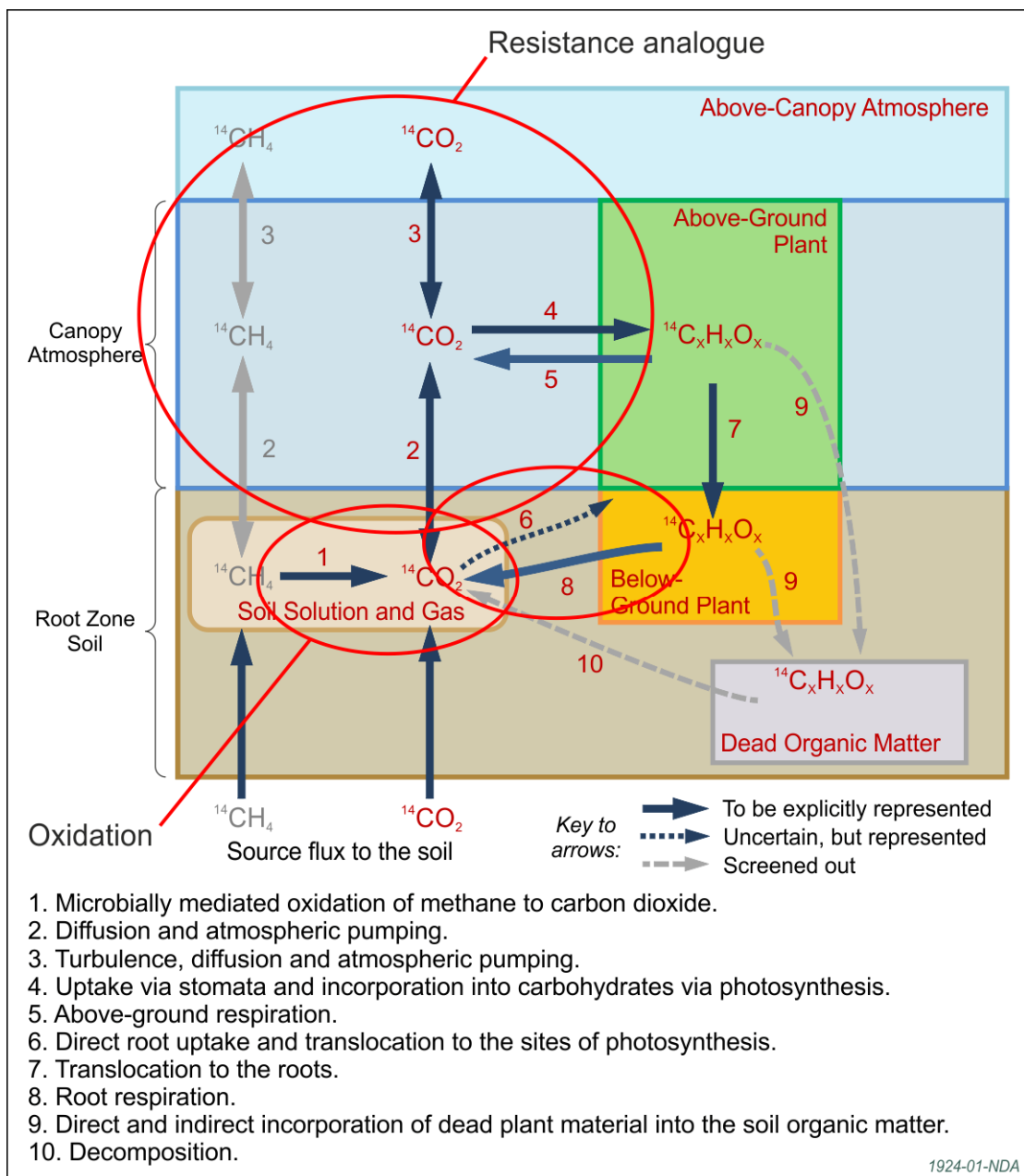
A feature of the LLWR 2011 model, in common with RIMERS and enhanced RIMERS, is that it modelled gaseous transport through the lower-canopy atmosphere as a molecular diffusion process rather than as a turbulent process. As a result, the LLWR 2011 model predicted that  $^{14}\text{CO}_2$  would move much more slowly through the plant canopy than standard models from

micrometeorology [29,30] would have done. This meant that the doses and risks reported in the 2011 ESC were unnecessarily high. The pessimism was recognised [31], and the LLWR 2011 model was modified [32] for use in an update to the Environmental Safety Case [15].

The approach adopted in this later implementation of the LLWR model is described below.

### 2.3.4 LLWR 2013 Model

The conceptual model of  $^{14}\text{CH}_4$  (and  $^{14}\text{CO}_2$ ) behaviour following its release into the vadose zone is shown in Figure 2.3. The figure summarises the various processes that have to be accounted for when quantifying the fate of  $^{14}\text{C}$  as  $^{14}\text{CH}_4$  emerges into the gas phase above the water table of a partially saturated soil.



**Figure 2.3 Schematic of the LLWR 2013 model for  $^{14}\text{CH}_4$  (and  $^{14}\text{CO}_2$ ) released to the soil (reproduced from reference [6], with permission).**

Some of the key processes are:

- Transport of  $^{14}\text{CH}_4$  through the soil.
- Oxidation of a proportion of the  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$ , mediated by methanotrophic microbes.
- Uptake of  $^{14}\text{CO}_2$  by the plant, due to either:
  - Fixation of gaseous  $^{14}\text{CO}_2$  within the plant canopy by photosynthesis; or
  - Flow of  $^{14}\text{CO}_2$  dissolved in the groundwater to the roots, replacing water the plant had lost during transpiration.
- Entry of  $^{14}\text{C}$ -contaminated plant matter into the human food chain, either:
  - Directly, for example through human consumption of crops grown on a small-holding; or
  - Indirectly, for example through human consumption of meat or milk obtained from animals that have grazed on, or otherwise have been fed on,  $^{14}\text{C}$ -contaminated plant matter.

Details of how these processes were implemented in the LLWR 2013 model are given below<sup>2</sup>.

#### 2.3.4.1 Model Implementation

The release rate of  $^{14}\text{CH}_4$  to soil is specified by the user. A release rate of  $^{14}\text{CO}_2$  can also be specified, which is added to the fraction of the  $^{14}\text{CH}_4$  release rate that is converted to  $^{14}\text{CO}_2$ . The release rates are expressed in units of  $\text{Bq m}^{-2}\text{yr}^{-1}$ .

In the assessment calculations undertaken for LLWR, the degree of conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  was cautiously taken as 1.0.

The lower boundary conditions of the model comprise  $^{14}\text{CO}_2$  and  $^{12}\text{CO}_2$  fluxes to the soil zone. The latter arises from degradation of organic matter in the soil and root respiration, and is well constrained by field observations in different agricultural conditions.

The upper boundary is a layer of air, some metres thick, overlying the plant canopy. It has been demonstrated that uptake of  $^{14}\text{CO}_2$  by plants does not significantly reduce the flux of  $^{14}\text{CO}_2$  through the plant canopy. Thus, the total area-integrated flux of  $^{14}\text{CO}_2$  from the soil is used to calculate the  $^{14}\text{CO}_2$  concentration in the above-canopy atmosphere. The concentration is calculated by diluting the area-integrated flux into the flow of air over the canopy (i.e. a “box” model is applied). The concentration of  $^{12}\text{CO}_2$  in the above-canopy atmosphere is specified by the user. Typically, a “present-day” value of 385 ppmv is used. The  $^{14}\text{CO}_2$  and  $^{12}\text{CO}_2$  concentrations constitute the upper boundary conditions of the model.

With both the lower and upper boundary conditions well defined, a resistance analogue model is used to calculate both  $^{14}\text{CO}_2$  and  $^{12}\text{CO}_2$  concentrations in the soil atmosphere and two layers of the canopy atmosphere (the canopy is subdivided into two layers, so that the stem region can be distinguished from the leaf region, where this would be appropriate to a particular crop type). This resistance analogue approach is based on observations of moisture, heat and momentum transport through plant canopies, and of carbon dioxide concentrations in soils. From the results, the specific activity of  $^{14}\text{C}$  in carbon dioxide can be calculated for the soil atmosphere and the two layers of the canopy atmosphere. In the calculations, the time evolution (i.e. growth) of the plant canopy is represented for different types of crop plants, but for pasture the plant canopy is time-independent. Different types of crop plants and different types of pasture can be simulated.

The specific activity in the biomass of plants being produced at any time is computed as a weighted combination of the specific activities in the carbon dioxide in the soil atmosphere and the two layers of the canopy atmosphere. The fraction of plant carbon derived from the soil atmosphere via

<sup>2</sup> This description of the LLWR 2013 model is based closely on the text in reference [6].

dissolution in the groundwater and root uptake is a user-defined quantity. Based on empirical observations, it would generally be legitimate to adopt a value of 0.0. However, values of up to 0.02 cannot be excluded, and values of up to 0.05 have been reported in the literature (see Section 5.2.1). A reasonably cautious value of 0.02 was adopted in the assessment calculations undertaken for LLWR. The partitioning of carbon dioxide uptake between the two layers of the canopy is determined by the relative amounts of photosynthetic activity in each of these layers. This is determined by the vertical distribution of foliage in the canopy and the associated degree of light attenuation. Thus, this partitioning is time-dependent for crop plants, but it is well constrained by available growth curves, which also determine rates of biomass production.

The specific activity of pasture is determined in a time-independent equilibrium calculation. In contrast, the specific activity of crop plants at harvest is determined from time-integrals of the activity taken up by above-ground and below-ground parts of the plant throughout the growing season. The rate of incorporation of activity at any time is calculated from the above-ground or below-ground biomass production rate (obtained from the growth curve) multiplied by the weighted specific activity computed as described above.

As pasture is included in the model, the specific activity of animal tissues is computed as the specific activity of pasture multiplied by the fraction of the animal's dietary carbon that is obtained from the contaminated area. In assessment calculations, that fraction is cautiously taken as 1.0. All animal tissues, including milk, are taken to exhibit the same specific activity. This is appropriate to conditions of chronic exposure.

Similarly, for humans, the specific activity of tissues is computed as the average specific activity of the dietary intake (including both plant and animal products, and taking into account the fraction of dietary carbon that is contaminated).

In the assessment calculations undertaken for LLWR, which were for an existing site, it was reasonable to make rather detailed assumptions about the Potentially Exposed Groups (PEGs). A set of four variant PEGs was identified:

- PEG variant A: a smallholder with 4 to 12 hectares of land, who keeps several head of cattle and uses them to provide meat and milk products.
- PEG variant B: a smallholder with 1 to 3 hectares of land, who keeps a single cow for milk production.
- PEG variant C: a smallholder with 0.5 to 1 hectare of land, who keeps two goats for milk production.
- PEG variant D: a kitchen gardener, who grows his own vegetables and fruit on 0.05 hectare.

For each PEG an assessment calculation was performed.

Once the specific activity of human tissues is calculated, the absorbed dose rate can be calculated without significant uncertainty, since it depends on only the fractional carbon content of human tissues and the energy emitted per transformation by  $^{14}\text{C}$ . As  $^{14}\text{C}$  emits only low linear energy transfer radiation and is relatively uniformly distributed throughout all human organs and tissues, the absorbed dose rate is numerically identical to the effective dose rate.

#### **2.3.4.2 Sensitivity Study**

An important result from a sensitivity study with this model [32] was the finding that the specific activity of the plant at harvest (or during the growing season for pasture) is rather insensitive to most of the model input parameters. The results are most sensitive to the fraction of plant carbon arising from the root zone. The wind speed, which influences the degree of turbulence, is also an important model input parameter.

### 2.3.5 <sup>14</sup>C-IPT Phase 1 Model

RWM has established an Integrated Project Team (IPT), in which the various partners are working together, to develop an holistic approach to the issue of managing <sup>14</sup>C-containing radioactive wastes in a geological disposal facility. The <sup>14</sup>C-IPT project has been broken down into two phases: Phase 1 [6], which lasted for six months and is now complete, and Phase 2, which is expected to last for around two years and is ongoing.

The LLWR 2013 model, albeit with a broader brush treatment of diet, was applied also during Phase 1 of the <sup>14</sup>C-IPT project [6] to assess the consequences of <sup>14</sup>C being released to the biosphere. (A new <sup>14</sup>C gas assessment model is proposed later in this report, and it is expected that this model will feed into the work during Phase 2 of the <sup>14</sup>C-IPT project.)

In the assessment calculations undertaken for RWM, which does not have a specific site, it was assumed that humans would not obtain all of their dietary requirements from the contaminated area, because major contributors to carbon in the diet, such as cereals, could not be produced locally (to any great extent). The fraction of carbon in a person's diet that could be obtained from locally-sourced foodstuffs (i.e. from the contaminated area) was cautiously taken as 0.3.

### 2.3.6 Comparison of UK <sup>14</sup>C Gas Assessment Models

Table 3.1 (at the end of Section 3) summarises the features of the above models, and compares their features with a new <sup>14</sup>C gas assessment model that could be used to assess the consequences of any <sup>14</sup>CH<sub>4</sub> reaching the partially saturated near-surface soil.



## 3 New <sup>14</sup>C Gas Assessment Model

This report proposes a new <sup>14</sup>C gas assessment model. It is based extensively on:

- The conceptual understanding developed during previous assessment studies; and
- The data acquired by an experimental programme for RWM [4], which investigated the behaviour and fate of <sup>14</sup>CH<sub>4</sub> introduced into near-surface soil under field conditions.

### 3.1 Learning from the Experimental Programme

The key findings of the experimental programme, which have been incorporated into the new <sup>14</sup>C gas assessment model, are listed in Box 1.

#### Box 1 Findings from the Experiments

The conclusions from a mathematical interpretation of our experimental data are as follows:

- Transport of gases through partially-saturated soils is a diffusive process, which can be described by a generalisation of Fick's law.
  - In the generalisation of Fick's law, the molecular diffusion coefficient is multiplied by a parameter called the tortuosity, to account for the presence of the soil particles.
  - A number of models have been proposed for the dependence of tortuosity on soil properties (e.g. see the review in reference [33]). Our experimental data [5] are consistent with the latest proposal, the Structure-dependent Water-induced Linear Reduction (SWLR) model [33].
  - In the SWLR model, tortuosity depends on both porosity and gas saturation of the soil.
    - A porosity of about 0.4, with a range from 0.35 to 0.45, is appropriate for a generic (i.e. site-independent) agricultural soil.
    - Although the gas saturation will vary with local conditions (e.g. topography) and the amount of rainfall, we suggest that it might be about 0.5 under average conditions, might rise to about 0.75 in exceptionally dry weather, and might fall to 0.25, or less, in very wet weather.
    - For a porosity of 0.4 and a gas saturation of 0.5, the tortuosity is about 0.03.
- Methane is oxidised by methanotrophic microbes in near-surface soils.
  - Methane oxidation can be modelled as a first-order reaction (although we acknowledge that some other experimental data indicate Michaelis-Menten kinetics, this is cautious).
  - The rate constant is likely to be in the range  $10^{-5} \text{ s}^{-1}$  to  $10^{-4} \text{ s}^{-1}$ .
- The processes of diffusion and methane oxidation are coupled. A diffusion-reaction equation will describe a quasi-steady-state flux of <sup>14</sup>CH<sub>4</sub> being oxidised to <sup>14</sup>CO<sub>2</sub> in the soil.
  - This equation has a characteristic length scale over which the <sup>14</sup>CH<sub>4</sub> will be oxidised.
  - The characteristic length scale is likely to be no more than a few tens of centimetres. Provided that the water table is at a depth which is more than a few times this length scale, then conversion of <sup>14</sup>CH<sub>4</sub> to <sup>14</sup>CO<sub>2</sub> will be essentially complete, regardless of the particular values of the diffusion coefficient and the oxidation rate constant.
- On the other hand, plant uptake of <sup>13</sup>C (as a surrogate for <sup>14</sup>C) was below the detection limit of the experiments, and was not observed.

### 3.2 Overview of the New $^{14}\text{C}$ Gas Assessment Model

The new model differs from previous models, which were all multi-compartment models, in that the concentrations and fluxes of  $^{14}\text{C}$  in the system are calculated from simple representations of the key processes (e.g. molecular diffusion through the soil; methane oxidation by microbes; turbulent transport through the plant canopy; dispersion in the overlying atmosphere; dissolution in the soil water and uptake of  $^{14}\text{CO}_2$ -contaminated water through a plant's roots; and uptake of  $^{14}\text{CO}_2$  through a plant's leaves due to photosynthesis).

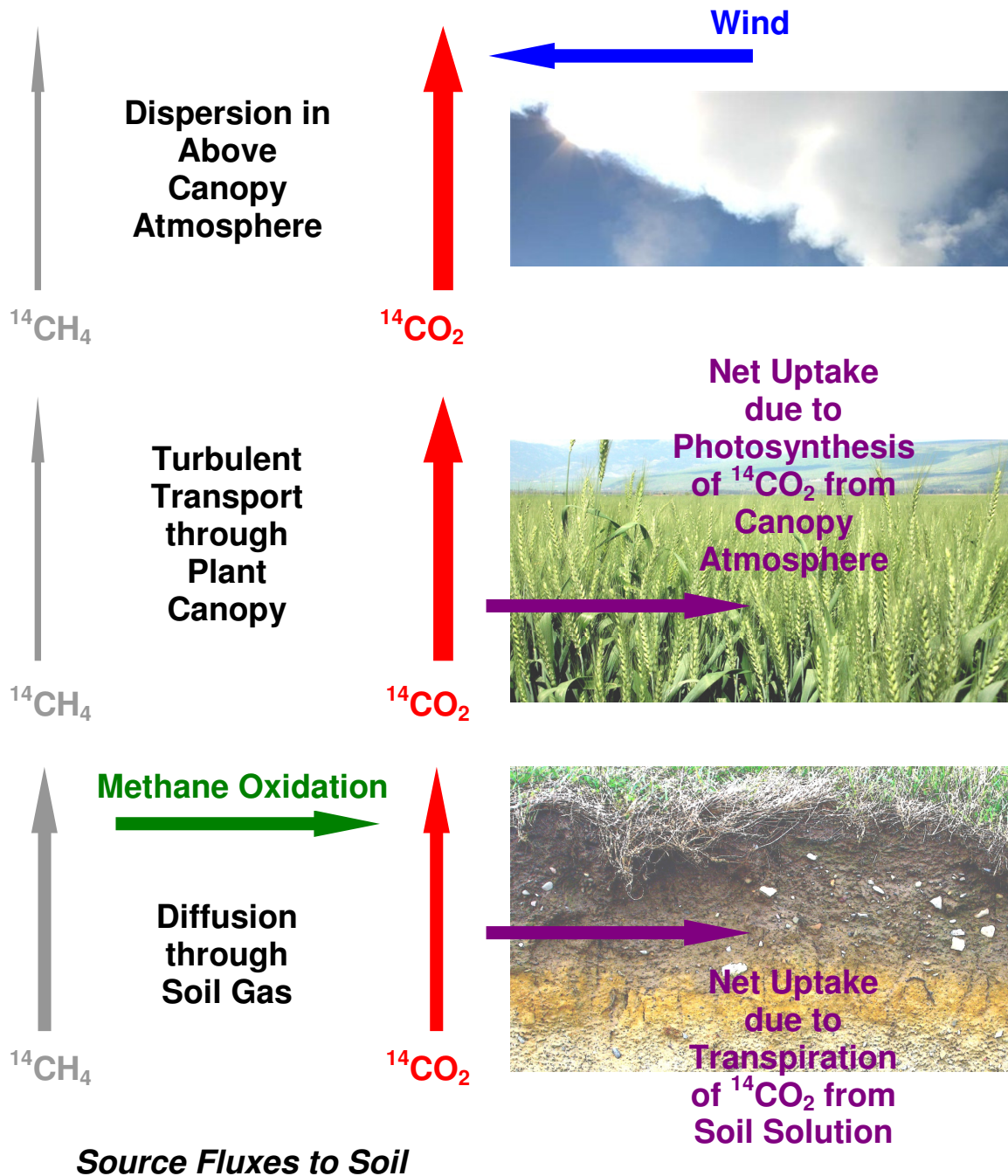


Figure 3.1 Schematic of the new  $^{14}\text{C}$  gas assessment model for  $^{14}\text{CH}_4$  (and  $^{14}\text{CO}_2$ ) released to the soil.

Other noteworthy developments from the LLWR 2013 and  $^{14}\text{C}$ -IPT Phase 1 models are listed in Box 2.

**Box 2 Differences between the New Model and the LLWR 2013 /  $^{14}\text{C}$ -IPT Phase 1 Model**

The new model:

- Accounts for the concentrations and fluxes of  $^{14}\text{CH}_4$  as well as  $^{14}\text{CO}_2$ , but does not need to simulate the transport of stable carbon dioxide (i.e.  $^{12}\text{CO}_2$ ) through the system.
- Solves a diffusion-reaction equation for gaseous transport through the soil coupled to oxidation of  $^{14}\text{CH}_4$ . The previous  $^{14}\text{C}$  gas assessment models re-interpreted the diffusion coefficient as a soil resistance, and also assumed complete conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$ .
- Calculates the concentrations of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  in the layer of air overlying the plants using an atmospheric dispersion model, whereas the recent  $^{14}\text{C}$  gas assessment models applied a “box” model. Although both approaches have challenges (*see Section 3.2.1 below*), the use of an atmospheric dispersion model avoids the problem of choosing a mixing height.
- Has a simpler representation of plants. In particular, the canopy atmosphere is modelled by a single layer (previously it was subdivided into two layers), and there is no account of either plant type or growth. The justification for this assumption, which is supported by simulations with the recent models, is that the aerodynamic resistance is only weakly sensitive to details of the plant morphology.
- Adopts a simpler, but widely used, model of the aerodynamic resistance controlling transport through the plant canopy. The recent models were based on a sophisticated “two-layer” model for transport through the plant canopy, whereas the new model is based on a so-called “big-leaf” approach. It is considered that the latter approach is appropriate for a  $^{14}\text{C}$  gas assessment model, because it requires fewer parameters and is sufficiently accurate.
- Calculates uptake of  $^{14}\text{C}$  due to photosynthesis by: (i) dividing the concentration of  $^{14}\text{CO}_2$  in the canopy atmosphere by a typical value for the local concentration of stable carbon dioxide, appropriate to daylight hours when photosynthesis will be occurring; and (ii) assuming the specific activity of the plant is equal to the specific activity of its canopy atmosphere.
- Calculates uptake of  $^{14}\text{C}$  due to transpiration by: (i) using the concentration of  $^{14}\text{CO}_2$  in the soil gas and Henry’s law to calculate the concentration of  $^{14}\text{CO}_2$  in the soil water; and (ii) multiplying the concentration of  $^{14}\text{CO}_2$  in the soil water by the transpiration ratio (i.e. the ratio of the mass of water transpired by a plant during its growing season to the mass of dry matter produced). A correction factor is applied to account for some of this  $^{14}\text{C}$  being lost through maintenance respiration.

It should be pointed out that the focus of  $^{14}\text{C}$  gas assessment models has changed from simulating the release of  $^{14}\text{C}$  incorporated into soil organic matter (as in RIMERS; see Section 2.3.1) to calculating the uptake of  $^{14}\text{C}$  by plants. The justification for the change is as follows. The  $^{14}\text{C}$  that is incorporated into plant matter could be returned to the soil, where it would become part of the soil organic matter (SOM). As a consequence, the specific activity of the SOM will tend gradually to that of the plant matter. The SOM will be decomposed by microbes, and so it will be an additional source of  $^{14}\text{C}$  within the soil. However, a cautious calculation can be used to show that this additional source of  $^{14}\text{C}$  is relatively insignificant (*see Section 5.4.2*), and therefore a  $^{14}\text{C}$  gas assessment model need not account for the release of  $^{14}\text{C}$  incorporated into the SOM.

Details of how the key processes are represented in the new model are given in outline below.

## 3.2.1 Model Implementation

### 3.2.1.1 Boundary Conditions

As in the LLWR 2013 model, the release rate of  $^{14}\text{CH}_4$  to the vadose zone is a user-specified input parameter. A release rate of  $^{14}\text{CO}_2$  can also be specified. The release rates are expressed in units of  $\text{Bq m}^{-2}\text{yr}^{-1}$ . The lower boundary conditions of the model comprise these  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  fluxes.

Again, as in the LLWR 2013 model, the upper boundary is a layer of air, some metres thick, overlying the plant canopy. The  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  concentrations in the above-canopy atmosphere can be calculated in terms of the (unknown)  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  fluxes from the soil<sup>3</sup>. In contrast to the LLWR 2013 model, the calculation is based on a widely-accepted Gaussian plume dispersion model<sup>4</sup>, the Industrial Source Complex model [35].

Once the upper boundary conditions of the model are established, a resistance analogue model is used to calculate both  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  concentrations in the canopy atmosphere, again in terms of the (unknown)  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  fluxes from the soil. These relationships between fluxes from the soil and concentrations in the canopy atmosphere constitute the upper boundary conditions of the sub-model for processes within the soil.

### 3.2.1.2 Conversion of $^{14}\text{CH}_4$ to $^{14}\text{CO}_2$ in the Soil

The key processes that occur within the soil are gaseous diffusion of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$ , and oxidation of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  by microbes. These processes can be described by a coupled set of diffusion-reaction equations [5]. With both the lower and upper boundary conditions well defined, the diffusion-reaction equations can be solved to predict quantities of interest, such as:

- The profile of  $^{14}\text{CO}_2$  concentration within the soil;
- The  $^{14}\text{CO}_2$  flux from the soil to the atmosphere; and hence
  - The  $^{14}\text{CO}_2$  concentration in both the canopy and above-canopy atmospheres.

<sup>3</sup> This calculation is cautious, because it neglects the fraction of the  $^{14}\text{CO}_2$  flux from the soil that will be taken up by the plants, and therefore overestimates the  $^{14}\text{CO}_2$  concentration in the above-canopy atmosphere. The fraction can be estimated as follows.

A typical maximum net photosynthesis rate for C3 plants is about  $25 \mu\text{mol m}^{-2}\text{s}^{-1}$  [34]. Multiplying by the leaf area index (e.g.  $4 \text{ m}^2\text{m}^{-2}$ ) and dividing by the plant height (e.g. 1m) gives a photosynthesis rate per unit volume of canopy atmosphere ( $100 \mu\text{mol m}^{-3}\text{s}^{-1}$ ). Dividing by the concentration of carbon dioxide in the atmosphere ( $16,400 \mu\text{mol m}^{-3}$ ) gives a rate constant of about  $0.006 \text{ s}^{-1}$  for uptake of carbon dioxide from the canopy atmosphere. The transit time for gas through the canopy (which can be estimated from the aerodynamic resistance, see Appendix 2, multiplied by the plant height) is likely to be of the order of 100s. On account of:

$$1 - \exp(-0.006 \times 100) \approx 0.45,$$

less than half of the  $^{14}\text{CO}_2$  flux will be taken up by the plant. Therefore it is cautious, but not unduly so, to ignore this sink of  $^{14}\text{CO}_2$ .

<sup>4</sup> There are issues involved with estimating atmospheric concentrations above the  $^{14}\text{CO}_2$  release area. In particular:

- Gaussian plume dispersion models should be applied to “on-site conditions” only with care, because the experimental data needed to calibrate the dispersion coefficients for short-range (i.e. < 100m) dispersion calculations are lacking.
- Simple mixing (or “box”) models can be applied sometimes. These models assume that the emission is uniformly mixed within a box-shaped volume and is diluted by the wind. An advantage of these models is their simplicity. A disadvantage is the uncertainty arising from assumptions about uniform mixing, mixing height, and wind speed and direction.

The new model uses an atmospheric dispersion calculation so as to avoid the LLWR 2013 model assumption of a 10m mixing height.

This sub-model is based on understanding gained from a programme of experiments for RWM, and the mathematical interpretation of the experimental data. It is a more sophisticated treatment than in previous  $^{14}\text{C}$  gas assessment models, which simply assumed complete conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  within the soil.

### 3.2.1.3 Uptake of $^{14}\text{CO}_2$ by Plants – Uncoupling Photosynthesis and Transpiration

The total uptake of  $^{14}\text{C}$  by plants is obtained by summing the contributions due to photosynthesis and transpiration. Although this neglects potential interference between the two pathways (i.e. photosynthesis and transpiration) for the uptake of  $^{14}\text{C}$ , it is cautious.

To explain the point, transpiration will move some  $^{14}\text{C}$  from the soil water through a plant to its leaves. This process will increase the internal  $^{14}\text{CO}_2$  concentration of the leaves. As a result, the rate at which  $^{14}\text{CO}_2$  diffuses from the surrounding canopy atmosphere through the stomata into the leaves will decrease, and the uptake of  $^{14}\text{C}$  due to photosynthesis may be suppressed.

Our analysis shows that photosynthesis and transpiration will contribute similarly to the uptake of  $^{14}\text{C}$ , and for this case simply adding the two contributions is cautious by a factor of at most two.

### 3.2.1.4 Uptake of $^{14}\text{CO}_2$ by Plants – Photosynthesis

The specific activity of  $^{14}\text{C}$  in carbon dioxide in the canopy atmosphere is needed to compute one contribution (i.e. uptake of  $^{14}\text{C}$  due to photosynthesis; the other contribution is uptake of  $^{14}\text{C}$  due to transpiration, and this contribution is discussed next) to the specific activity of  $^{14}\text{C}$  in the biomass of plants. Since the  $^{14}\text{CO}_2$  concentration is known, to determine this specific activity requires only a value for the  $^{12}\text{CO}_2$  concentration in the canopy atmosphere.

During the periods when photosynthesis is occurring, the  $^{12}\text{CO}_2$  concentration in the canopy will be a little less than the  $^{12}\text{CO}_2$  concentration in the overlying atmosphere, currently about 395 ppmv. The new  $^{14}\text{C}$  gas assessment model assumes that the  $^{12}\text{CO}_2$  concentration in the canopy atmosphere is 350 ppmv, or  $1.75 \cdot 10^{-4} \text{ kg[C] m}^{-3}$ . This value is appropriate for C3 plants<sup>5</sup>, with only a small uncertainty (i.e. an error that is no more than a few tens of percent), and is used to calculate the specific activity of  $^{14}\text{C}$  in carbon dioxide in the canopy atmosphere.

When considering photosynthesis as the pathway for uptake of  $^{14}\text{C}$  by plants, the specific activity in the biomass of a plant is equated to the specific activity of its canopy atmosphere. This is acceptable, because discrimination by plants against isotopes of carbon is a small effect<sup>6</sup>.

<sup>5</sup> C3 plants first fix atmospheric  $\text{CO}_2$  into a compound containing three carbon atoms, which then enters the Calvin cycle of photosynthesis. Examples include most plants in the temperate zone.

Experiments by Wong et al. [36] show that the ratio of the  $\text{CO}_2$  concentration inside a leaf to the  $\text{CO}_2$  concentration in the atmosphere is about 0.7 for a C3 plant (provided that the plant is not under stress). Therefore when photosynthesis is occurring, the concentration of  $\text{CO}_2$  in the canopy atmosphere is most likely to be in the range 280 ppmv to 395 ppmv, and probably closer to the latter value.

The strength of the photosynthetic sink varies diurnally, and depends on both meteorological conditions and plant type. The  $^{14}\text{C}$  gas assessment model would be much more complicated if it had to account for the fluctuations in the  $^{12}\text{CO}_2$  concentration within the canopy atmosphere. Therefore, instead of simulating the fluctuations, the new model assumes a constant  $^{12}\text{CO}_2$  concentration of 350 ppmv, but recognises that this could be in error by up to ~20%.

<sup>6</sup> The literature notes that isotope fractionations involving  $^{14}\text{C}$  are about twice as large as those involving  $^{13}\text{C}$  [37], but:

- Accounting for slower diffusion of heavier isotopes of carbon from the canopy atmosphere into the leaf would be responsible for only a small difference (less than 1%) in the  $^{14}\text{C}:^{12}\text{C}$  ratio [38].
- Photosynthesis favours  $^{12}\text{C}$  over  $^{13}\text{C}$  by about 3% in C3 plants [38], and so again the degree of discrimination against heavy  $\text{CO}_2$  would be small.
- Limited data for C3 plants suggest that the difference in the isotope ratio between the various organs of the plant would be small (less than 1%) [37].

Therefore this assumption is approximately correct, with an error of perhaps 5%.



This sub-model, apart from that it uses a different formulation of the aerodynamic resistance, is similar to the LLWR 2013 and  $^{14}\text{C}$ -IPT Phase 1 models.

### 3.2.1.5 Uptake of $^{14}\text{CO}_2$ by Plants – Transpiration

The other pathway for plants to take up  $^{14}\text{C}$  is transpiration. The calculated  $^{14}\text{CO}_2$  concentration within the soil gas can be multiplied by the Henry's law constant for carbon dioxide to determine the  $^{14}\text{CO}_2$  concentration in the soil water. A plant will take up some of this contaminated water through its roots. The transpiration ratio, which is the ratio of the mass of water transpired by a plant during its growing season to the mass of dry matter (usually exclusive of roots) produced, is a relevant quantity. In particular, multiplying the  $^{14}\text{CO}_2$  concentration in the soil water by the transpiration ratio gives the increment in the specific activity of  $^{14}\text{C}$  in the biomass of the plant due to transpiration<sup>7</sup>. A correction factor can be applied to account for some (i.e. about half) of the  $^{14}\text{C}$  being lost, for example through maintenance respiration.

Although both the LLWR 2013 and  $^{14}\text{C}$ -IPT Phase 1 models account for the uptake of  $^{14}\text{C}$  by plants due to transpiration, this sub-model provides a more direct route, based on the use of the transpiration ratio, to calculate the uptake of  $^{14}\text{C}$ .

### 3.2.1.6 Dose from Ingestion of $^{14}\text{C}$ -Contaminated Plants

The specific activity of animal tissues can be computed as the specific activity of pasture multiplied by the fraction of the animal's dietary carbon that is obtained from the contaminated area. In assessment calculations, that fraction is cautiously taken as 1.0.

For humans, the approach follows the  $^{14}\text{C}$ -IPT Phase 1 model. The specific activity of tissues can be computed as the average specific activity of the dietary intake (including both plant and animal products, and taking into account the fraction of dietary carbon that is contaminated). It is assumed that humans will not obtain all of their dietary requirements from the contaminated area, because major contributors to carbon in the diet, such as cereals, will not be produced locally (to any great extent). The fraction of carbon in a person's diet that could be obtained from locally-sourced foodstuffs (i.e. from the contaminated area) is cautiously taken as 0.3.

Once the specific activity of human tissues is calculated, the effective dose rate can be calculated without significant uncertainty, since it depends on only the fractional carbon content of human tissues and the energy emitted by  $^{14}\text{C}$  when it decays.

## 3.2.2 Advantages

It is considered that this new  $^{14}\text{C}$  gas assessment model has a number of advantages. Most notably, it emphasises the key processes and parameters controlling the uptake of  $^{14}\text{C}$  by plants, and subsequently by humans. This will make it easier:

- To communicate the ideas underlying the model;
- To quantify the model parameters, and their uncertainties; and
- To audit the model.

To stress one of these points, multi-compartment models, as used in the previous  $^{14}\text{C}$  assessments, require input parameters that do not have a clear physical interpretation. One

<sup>7</sup> It should be pointed out that, unlike the photosynthesis calculation, this is not a specific activity analysis. The argument is simply that:

- For every 1 kg of dry matter produced, a plant transpires  $T_R$  kg of soil water.
- $T_R$  kg of soil water will include a quantity of dissolved  $^{14}\text{C}$ .
- Of this quantity, about half will be incorporated into the 1 kg of dry matter produced, and the remainder will be respired.



example of such an input parameter is the “velocity” for transfer between adjoining compartments, which is expressed in terms of a harmonic weighting of diffusion coefficients in the two compartments. In a <sup>14</sup>C gas assessment model that represents the various processes explicitly, in contrast, all of the input parameters will be physical.

### 3.2.3 Treatment of Uncertainty

The uncertainties in the new <sup>14</sup>C gas assessment model can be considered in two categories: uncertainties in the soil sub-model; and uncertainties in the canopy and above-canopy sub-models. These are considered in turn.

The soil sub-model is concerned with gaseous diffusion through a partially saturated soil, and oxidation of <sup>14</sup>CH<sub>4</sub> to <sup>14</sup>CO<sub>2</sub> by microbes in the soil. The diffusive process has been studied extensively. Fick’s law is a good description of the process, and various models have been proposed for the dependence of the diffusion coefficient on soil properties (e.g. see the review in reference [33]). A generic estimate for the diffusion coefficient of methane in the soil gas is about  $3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  (see Section 4.2.1), with an uncertainty that is about half an order of magnitude. The oxidation process is considered to obey first-order reaction kinetics, at least for low concentrations of methane, with a rate constant in agricultural soils in the range  $10^{-5} \text{ s}^{-1}$  to  $10^{-4} \text{ s}^{-1}$  [5] (generally oxidation is observed to be faster in other ecosystems, e.g. forest soils). Although the diffusion coefficient,  $D_{CH_4}$ , and the oxidation rate constant,  $k$ , have significant uncertainties, these are not important. The key point is that the length scale:

$$\sqrt{\frac{D_{CH_4}}{k}} \quad (3.1)$$

is no more than a few tens of centimetres. Provided that the water table is at a depth which is more than a few times this length scale, then conversion of <sup>14</sup>CH<sub>4</sub> to <sup>14</sup>CO<sub>2</sub> will be essentially complete (see Section 4.1.4), regardless of the particular values of the diffusion coefficient and the oxidation rate constant. In well-drained agricultural soils, which are the soil types of most interest, the water table typically is at a depth of more than 1m [39], and for this case a large proportion of the <sup>14</sup>CH<sub>4</sub> will be converted to <sup>14</sup>CO<sub>2</sub>.

The main uncertainties concern the concentrations of <sup>14</sup>CO<sub>2</sub> in the canopy atmosphere. These uncertainties arise from necessary simplifications in the description of the canopy and the atmospheric dispersion model used to describe processes above the canopy. We assume small plants, with stable atmospheric conditions and low wind speeds. This is appropriate at the current stage of the programme, but constitutes a cautious set of assumptions.

To date there has been little focus on how uncertainty should be treated in the assessment model. Although uncertainties in diet normally are neglected, consideration could be given to other uncertainties in the soil, canopy and above-canopy models.

## 3.3 Summary

In recent years, a number of <sup>14</sup>C gas assessment models have been developed (see Section 2). A chronology of the models and a list of the key differences between them are shown in Table 3.1.

The changes reflect how our understanding of the important processes has evolved. In some cases, the representation of a process has become simpler (e.g. the soil processes); in other cases, the representation has become more complex (e.g. the canopy and above-canopy processes). For example, it has been recognised that transport of <sup>14</sup>CO<sub>2</sub> through the plant canopy is a key process controlling the uptake of <sup>14</sup>C. A specific activity approach is used to calculate the uptake of <sup>14</sup>C by the plant, and the effects of turbulence in controlling the flux of <sup>14</sup>C from the canopy to the overlying atmosphere are incorporated into the models.

Both LLWR and RWM have developed  $^{14}\text{C}$  gas assessment models (it is expected that  $^{14}\text{C}$ -bearing gases will be generated in both disposal facilities). The latest models have benefited from the ongoing work on this “ $^{14}\text{C}$  in the Biosphere” project, and now have very similar features. Perhaps the greatest remaining difference is in the choice of a Potentially Exposed Group (PEG) and its diet. This is reasonable, because the PEGs for the existing LLWR facility can be fairly well defined, whereas the PEG for a “generic” GDF can be only poorly characterised.

The following sections provide more details of the new  $^{14}\text{C}$  gas assessment model as follows:

- Section 4 presents the sub-model used to calculate gaseous transport, and the oxidation of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  by microbes within the soil.
- Section 5 presents two sub-models used to calculate the uptake of  $^{14}\text{CO}_2$  by plants, either as a result of photosynthesis or in the transpiration flow.
- Section 6 discusses how the specific activity of  $^{14}\text{C}$  in plants can be used to calculate the effective dose rate to humans.

**Table 3.1 Comparison of UK <sup>14</sup>C Gas Assessment Models**

	<b>RIMERS [18]</b>	<b>Enhanced RIMERS [24]</b>	<b>LLWR 2013 model [14]</b>	<b><sup>14</sup>C-IPT Ph 1 model [6]</b>	<b>New model</b>
<b>Chronology</b>	Originated for Nirex c. 1994; used in Nirex 97 & in Drigg PCSC 2002	Developed on Nirex programme c. 2005; used in GPA(03) Update	Predecessor used in LLWR 2011 ESC; model updated in 2013	Report published in 2012; model developed in parallel with LLWR update	Developed for RWM in 2013, as part of the “ <sup>14</sup> C in the Biosphere” project
<b>Model Type</b>	Compartment	Compartment	Compartment	Compartment	Simple process representation
<b>Soil Model</b>	5 components	As RIMERS	Single component	Single component	Single component
<b>Oxidation of <sup>14</sup>CH<sub>4</sub> to <sup>14</sup>CO<sub>2</sub></b>	Complete conversion	Complete conversion	Complete conversion	Complete conversion	Can calculate degree of conversion
<b>Uptake by Roots</b>	Kinetic representation	Kinetic representation	Used 5% & 10% (chosen to be cautious)	Used 0% as reference case & 2% as variant	Passive uptake in groundwater (~1%)
<b>Canopy Model</b>	Simple representation – concentrations in equilibrium in soil solution, soil atmosphere, below-canopy atmosphere & above-canopy atmosphere	Diffusive transfer between soil solution, soil atmosphere, below-canopy atmosphere & above-canopy atmosphere	Turbulent transfer between two layers of canopy	As LLWR 2013 model	Turbulent transfer (resistance analogue model) in single layer of canopy
<b>Above Canopy Model</b>			“Box” model to calculate <sup>14</sup> C concentration above plant		ISC3 atmospheric dispersion model to calculate <sup>14</sup> C concentration above plant
<b>Uptake by Photosynthesis</b>	Kinetic representation	Kinetic representation	Specific activity of plant equals specific activity of canopy atmosphere	As LLWR 2013 model	As LLWR 2013 model
<b>Variation in Plant Type</b>	Represented as standing biomass – single value of specific activity	As RIMERS	Several types of arable crop and two types of pasture	As LLWR 2013 model	Slightly cautious model of aerodynamic resistance
<b>Diet</b>	Outside RIMERS	As RIMERS	Four variant PEGs that are specific to LLWR	Broader brush treatment – 30% carbon sourced from contaminated area	As <sup>14</sup> C-IPT Ph 1 model

## 4 Conversion of $^{14}\text{CH}_4$ to $^{14}\text{CO}_2$ in the Soil

The new  $^{14}\text{C}$  gas assessment model calculates the concentrations and fluxes of  $^{14}\text{C}$  in the system from simple representations of the key processes (e.g. molecular diffusion through the soil; methane oxidation by microbes). This section is concerned with the processes that occur within the soil.

### 4.1 Conceptual Model

The key processes that occur within the soil are gaseous diffusion of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  (see Section 4.1.1), and oxidation of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  by microbes (see Section 4.1.2). Our representation of these processes is based on understanding gained from a programme of experiments for RWM [4], and the mathematical interpretation of the experimental data [5]. It is a more sophisticated treatment than in previous  $^{14}\text{C}$  gas assessment models, which simply assumed complete conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  within the soil.

#### 4.1.1 Diffusion

Molecular diffusion of gases is a significant process in the  $^{14}\text{C}$  gas assessment model. It is assumed that the diffusive mass flux of component  $\kappa$  (either methane or carbon dioxide) in the gas phase is given by:

$$\begin{aligned} \mathbf{f}_{\kappa} &= -D_{\kappa} \nabla C_{\kappa} \\ &= -(\tau d_{\kappa}) \nabla C_{\kappa} \end{aligned} \quad (4.1)$$

where:

- $\mathbf{f}_{\kappa}$  is the diffusive flux of component  $\kappa$  in the gas phase ( $\text{kg m}^{-2}\text{s}^{-1}$ );
- $D_{\kappa}$  is the diffusion coefficient for component  $\kappa$  in the gas phase within the soil ( $\text{m}^2\text{s}^{-1}$ );
- $C_{\kappa}$  is the concentration of component  $\kappa$  present in the gas phase ( $\text{kg m}^{-3}$  of gas);
- $\tau$  is the tortuosity (–), which depends on both the porous medium and the phase saturation; and
- $d_{\kappa}$  is the molecular diffusion coefficient for component  $\kappa$  in air ( $\text{m}^2\text{s}^{-1}$ ).

A number of models have been proposed for the dependence of the diffusion coefficient on soil properties (e.g. see the review in reference [33]). Often the Millington and Quirk model [40] is used. In the new  $^{14}\text{C}$  gas assessment model, however, we assume the Structure-dependent Water-induced Linear Reduction (SWLR) model, which was derived more recently [33]. The SWLR model postulates that:

$$\tau = (S_g \phi)^{1+C_m \phi} S_g \quad (4.2)$$

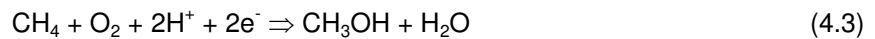
where:

- $S_g$  is the saturation of the gas phase, i.e. the fraction of the porosity occupied by gas (–);
- $\phi$  is the porosity (–); and
- $C_m$  is a model parameter called the “media complexity factor” (–).

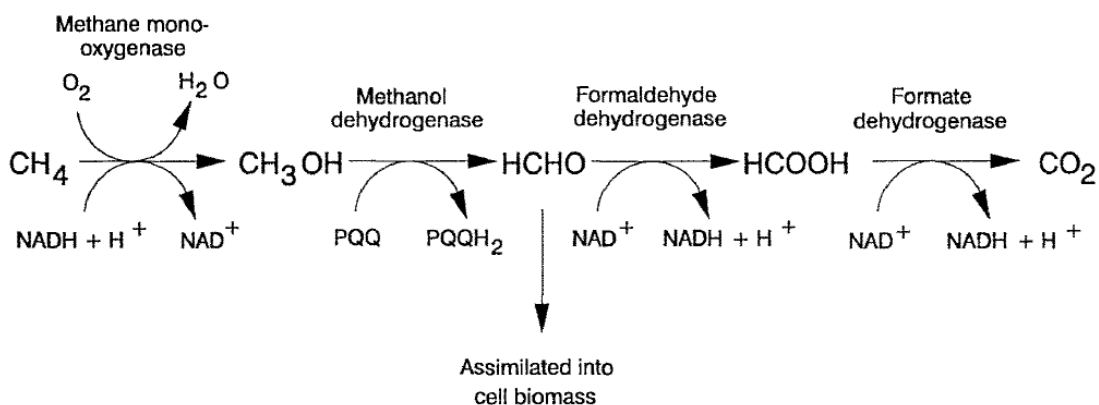
Analysis of gas diffusion through 280 intact soils led to the recommendation that  $C_m$  should be 2.1 for such systems. Furthermore, setting  $C_m = 0.3$  (which is assumed to correspond to a worst case of preferential pathways for gaseous diffusion) provides a realistic upper-bound gas diffusivity.

## 4.1.2 Methane Oxidation

Methane oxidation by microbes is another significant process in the  $^{14}\text{C}$  gas assessment model. Methanotrophic microbes metabolise methane as their source of carbon and energy. The first step (see Figure 4.1) is the introduction of one atom of  $\text{O}_2$  into  $\text{CH}_4$ . This step is catalysed by the methane mono-oxygenase (MMO) enzyme, which requires three substrates:  $\text{CH}_4$ ,  $\text{O}_2$  and a reductant for the excess O atom from  $\text{O}_2$ . That is:



Then the product, methanol ( $\text{CH}_3\text{OH}$ ), is oxidised sequentially to formaldehyde ( $\text{HCHO}$ ), methanoic acid ( $\text{HCOOH}$ ) and  $\text{CO}_2$ .



**Figure 4.1 Pathway for the oxidation of methane and assimilation of formaldehyde<sup>8</sup>.**

An analysis of the data acquired by an experimental programme for RWM [4], which investigated the behaviour and fate of  $^{14}\text{CH}_4$  introduced into near-surface soil under field conditions, suggests that methane will be oxidised in near-surface soils according to a first-order reaction:

$$\frac{dC_{\text{CH}_4}}{dt} = -k C_{\text{CH}_4} \quad (4.4)$$

Once  $^{14}\text{CH}_4$  has entered the biochemical pathway for its oxidation (according to Equation (4.4)), subsequent reaction steps will lead to either the release of  $^{14}\text{CO}_2$  (possibly after a time lag) or the assimilation of  $^{14}\text{C}$  into cell biomass. If the latter, the biomass will decompose (on a timescale of months), contributing to the flux of  $^{14}\text{CO}_2$  from the soil. Eventually the system will reach a quasi-steady-state, when the sum of the fluxes of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  is approximately a conserved quantity through the soil.

## 4.1.3 Coupled Model

The processes of diffusion and oxidation of  $^{14}\text{CH}_4$  within the soil are coupled. The diffusion-reaction equation that describes the quasi-steady-state flux of  $^{14}\text{CH}_4$  being oxidised to  $^{14}\text{CO}_2$  within the soil is:

<sup>8</sup> The figure shows some  $^{14}\text{C}$  will be assimilated into cell biomass. Although this process is potentially important when explaining experimental data [5], a  $^{14}\text{C}$  gas assessment model need not account for it. That is because the biomass will decompose, contributing to the flux of  $^{14}\text{CO}_2$  from the soil. Eventually the system will reach a quasi-steady-state, when the sum of the fluxes of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  is approximately a conserved quantity through the soil.

$$\frac{\partial}{\partial z} \left( D_{CH_4} \frac{\partial C_{CH_4}}{\partial z} \right) - S_g \phi k C_{CH_4} = 0 \quad (4.5)$$

This equation is supplemented by another equation, involving both  $^{14}CH_4$  and  $^{14}CO_2$ , which expresses conservation of  $^{14}C$ :

$$\frac{\partial}{\partial z} \left( D_{CH_4} \frac{\partial C_{CH_4}}{\partial z} + D_{CO_2} \frac{\partial C_{CO_2}}{\partial z} \right) = 0 \quad (4.6)$$

The lower boundary conditions for these two differential equations comprise user-specified fluxes (i.e.  $f_{CH_4}$  and  $f_{CO_2}$ ) of  $^{14}CH_4$  and  $^{14}CO_2$  to the vadose zone:

$$-D_{CH_4} \frac{\partial C_{CH_4}}{\partial z} \Big|_{z=-w} = f_{CH_4} \quad (4.7a)$$

$$-D_{CO_2} \frac{\partial C_{CO_2}}{\partial z} \Big|_{z=-w} = f_{CO_2} \quad (4.7b)$$

where the water table is taken to be at an elevation  $z = -w$ .

The upper boundary conditions are relationships between fluxes from the soil and concentrations in the canopy atmosphere. These relationships are:

$$-D_{CH_4} \frac{\partial C_{CH_4}}{\partial z} \Big|_{z=0} = \frac{C_{CH_4} \Big|_{z=0}}{R_T} \quad (4.8a)$$

$$-D_{CO_2} \frac{\partial C_{CO_2}}{\partial z} \Big|_{z=0} = \frac{C_{CO_2} \Big|_{z=0}}{R_T} \quad (4.8b)$$

where  $R_T$  is a total resistance (see Section 5.1.1.3;  $s \text{ m}^{-1}$ ).

The total resistance derives from a resistance analogue approach to modelling transport through plant canopies. Resistance analogue models are applied widely to the problem of describing how some property of a plant responds to a measured flux from the canopy [29,30]. Here, the approach is used to compute gaseous concentrations in the canopy atmosphere in terms of fluxes from the soil. Numerical values of the total resistance are discussed later in Section 5.1.1.3.

#### 4.1.4 Solution

The system of differential equations can be solved to predict quantities of interest, such as:

- The  $^{14}CO_2$  flux from the soil to the atmosphere; and
- The profile of  $^{14}CO_2$  concentration within the soil.

Using the computational tool *Mathematica* [41], we find that the  $^{14}CO_2$  flux from the soil to the atmosphere is:



$$-D_{CO_2} \frac{\partial C_{CO_2}}{\partial z} \Big|_{z=0} = \mathbf{f}_{CH_4} \left( 1 - \frac{1}{\cosh[w/L] + Lk R_T \sinh[w/L]} \right) + \mathbf{f}_{CO_2} \quad (4.9)$$

where:

$$L = \sqrt{\frac{D_{CH_4}}{S_g \phi k}} \quad (4.10)$$

is a characteristic length scale of the system. As discussed below, typically the water table is at a depth  $w$  several times larger than the characteristic length scale  $L$ , and for this case the  $^{14}CO_2$  flux from the soil to the atmosphere has the expected limiting behaviour:

$$-D_{CO_2} \frac{\partial C_{CO_2}}{\partial z} \Big|_{z=0} \approx \mathbf{f}_{CH_4} + \mathbf{f}_{CO_2} \quad (4.11)$$

This flux will be used to calculate the concentration of  $^{14}CO_2$  in the canopy atmosphere.

The profile of  $^{14}CO_2$  concentration (as well as the profile of  $^{14}CH_4$  concentration) satisfies a maximum principle; that means the  $^{14}CO_2$  concentration attains its maximum value either at the ground surface or at the water table. We find that the  $^{14}CO_2$  concentration at the ground surface is:

$$C_{CO_2} \Big|_{z=0} = \mathbf{f}_{CH_4} \left( R_T - \frac{R_T}{\cosh[w/L] + Lk R_T \sinh[w/L]} \right) + \mathbf{f}_{CO_2} (R_T) \quad (4.12)$$

and at the water table is:

$$C_{CO_2} \Big|_{z=-w} = \mathbf{f}_{CH_4} \left( R_T + \frac{w-L}{D_{CO_2}} - \frac{R_T - \frac{D_{CH_4} R_T}{D_{CO_2}} - \frac{L - D_{CH_4} R_T}{D_{CO_2}} \exp[-w/L]}{\cosh[w/L] + Lk R_T \sinh[w/L]} \right) + \mathbf{f}_{CO_2} \left( R_T + \frac{w}{D_{CO_2}} \right) \quad (4.13)$$

For the limiting case when the depth of the water table  $w$  is much larger than the characteristic length scale  $L$ , these concentrations are respectively:

$$C_{CO_2} \Big|_{z=0} \approx (\mathbf{f}_{CH_4} + \mathbf{f}_{CO_2}) R_T \quad (4.14)$$

and:

$$\begin{aligned}
 C_{CO_2} \Big|_{z=-w} &\approx \mathbf{f}_{CH_4} \left( R_T + \frac{w-L}{D_{CO_2}} \right) + \mathbf{f}_{CO_2} \left( R_T + \frac{w}{D_{CO_2}} \right) \\
 &= C_{CO_2} \Big|_{z=0} + \mathbf{f}_{CH_4} \left( \frac{w-L}{D_{CO_2}} \right) + \mathbf{f}_{CO_2} \left( \frac{w}{D_{CO_2}} \right) \\
 &< C_{CO_2} \Big|_{z=0} + \mathbf{f}_{CH_4} \left( \frac{w}{D_{CO_2}} \right) + \mathbf{f}_{CO_2} \left( \frac{w}{D_{CO_2}} \right) \\
 &\approx (\mathbf{f}_{CH_4} + \mathbf{f}_{CO_2}) \frac{w}{D_{CO_2}}
 \end{aligned} \tag{4.15}$$

Note that the final approximation in Equation (4.15) is justified because, as will be discussed later, the total resistance  $R_T$  is much smaller than the ratio  $w/D_{CO_2}$ .

The physical interpretation of the last two equations is clear:

- Equation (4.14) says that the  $^{14}CO_2$  concentration at the ground surface is equal to the net  $^{14}CO_2$  flux from the soil (see Equation (4.11)) multiplied by the total resistance (cf. Equation (4.8b)).
- Equation (4.15) corresponds to Fick's law, and says that the difference in  $^{14}CO_2$  concentration across the vadose zone is equal to the  $^{14}CO_2$  flux through the soil multiplied by a soil thickness and divided by the diffusion coefficient. The thickness is smaller (by the characteristic length scale  $L$ ) for a flux of  $^{14}CH_4$  than for a flux of  $^{14}CO_2$ , because it takes some distance for the  $^{14}CH_4$  to be oxidised to  $^{14}CO_2$ .

The maximum  $^{14}CO_2$  concentration in the soil gas is given by Equation (4.15) (or by its generalisation, Equation (4.13)). This concentration will be used to compute the concentration of  $^{14}CO_2$  in the soil water, which then will be used to determine the uptake of  $^{14}C$  by plants due to transpiration.

It may be worth mentioning that the LLWR 2013  $^{14}C$  gas assessment model assumed:

- Complete conversion of  $^{14}CH_4$  to  $^{14}CO_2$ ;
- A net  $^{14}CO_2$  flux through the soil that is equal to the sum of user-specified fluxes of  $^{14}CH_4$  and  $^{14}CO_2$  at the bottom of the model (cf. Equation (4.11)); and
- A relationship between  $^{14}CO_2$  concentration in the soil and  $^{14}CO_2$  flux through the soil. In particular, the ratio of concentration to flux was interpreted as a soil resistance, which was computed from  $w/D_{CO_2}$  (cf. Equation (4.15)).

The results obtained in this section, which are more general, do support these assumptions, provided that the water table is at a depth  $w$  much larger than the characteristic length scale  $L$ .

## 4.2 Data

The model described above requires numerical values for the following parameters:

- The porosity of the soil,  $\phi$ .
- The saturation of the gas phase,  $S_g$ .
  - The porosity and gas saturation together determine the tortuosity of the soil,  $\tau$  (see Equation (4.2)).

- The molecular diffusion coefficients for carbon dioxide and methane in air,  $d_{\kappa}$ .
- The depth of the water table,  $w$ .
- The rate constant for methane oxidation,  $k$ .
- The total resistance,  $R_T$ .

Porosity, gas saturation and molecular diffusion coefficients are considered in Section 4.2.1. Methane oxidation is discussed in Section 4.2.2.

An explanation of the total resistance is postponed until Section 5.1.1.

## 4.2.1 Diffusion

A database of over 5,600 soil samples from the U.S. Soil Conservation Service was analysed by Carsel and Parrish [42], who categorised the soils by their texture and then derived the set of porosity values listed in Table 4.1.

**Table 4.1 Soil Porosity**

Soil Texture	Porosity
Sand	0.43
Loamy Sand	0.41
Sandy Loam	0.41
Loam	0.43
Silt	0.46
Silt Loam	0.45
Sandy Clay Loam	0.39
Clay Loam	0.41
Silty Clay Loam	0.43
Sandy Clay	0.38
Silty Clay	0.36
Clay	0.38

This set of porosity values suggests that a porosity,  $\phi$ , of about 0.4, with a range from 0.35 to 0.45, is appropriate for a generic (i.e. site-independent) agricultural soil.

It is more difficult to quantify the gas saturation of the soil, which will depend on both local conditions (e.g. topography) and the amount of rainfall. However, based on data acquired during an experimental programme for RWM [4,43], which investigated the behaviour and fate of  $^{14}\text{CH}_4$  introduced into near-surface soil under field conditions, we suggest that the gas saturation,  $S_g$ , in a generic (i.e. site-independent) agricultural soil:

- Might be about 0.5 under average conditions;
- Might rise to about 0.75 in exceptionally dry weather; and
- Might fall to 0.25, or less, in very wet weather.

The significance of this range of values is that higher gas saturation means faster diffusion (see Equation (4.2)).

Values are needed as well for the relevant molecular diffusion coefficients; these are listed in Table 4.2.

**Table 4.2 Binary Diffusion Coefficients for Carbon Dioxide and Methane at 1 Atmosphere and 20 °C [44]**

System	Molecular Diffusion Coefficient (m <sup>2</sup> s <sup>-1</sup> )
Large excess of Air with Carbon Dioxide	1.60 10 <sup>-5</sup>
Large excess of Air with Methane	1.06 10 <sup>-5</sup>

Note that the molecular diffusion coefficient of <sup>14</sup>CH<sub>4</sub> (or <sup>14</sup>CO<sub>2</sub>) is slightly smaller than that of lighter <sup>12</sup>CH<sub>4</sub> (or <sup>12</sup>CO<sub>2</sub>). Theoretical considerations show that this difference is small (i.e. of the order of a few percent), and therefore is unimportant unless isotopic effects are being modelled explicitly.

Putting all of these values together:

- The diffusion coefficient for carbon dioxide in the gas phase within the soil is estimated to be:

$$D_{CO_2} = (S_g \phi)^{(1+C_m \phi)} S_g d_{CO_2} = 4.1 \cdot 10^{-7} \text{ m}^2\text{s}^{-1}, \text{ with a cautious upper bound of } 3.5 \cdot 10^{-6} \text{ m}^2\text{s}^{-1}$$

- The diffusion coefficient for methane in the gas phase within the soil is estimated to be:

$$D_{CH_4} = (S_g \phi)^{(1+C_m \phi)} S_g d_{CH_4} = 2.7 \cdot 10^{-7} \text{ m}^2\text{s}^{-1}, \text{ with a cautious upper bound of } 2.3 \cdot 10^{-6} \text{ m}^2\text{s}^{-1}$$

Another parameter that will depend on both local conditions (e.g. topography) and the amount of rainfall is the depth of the water table,  $w$ . However, it is reasonable to assume that in an agricultural soil the water table will be at least 1m below the surface.

## 4.2.2 Methane Oxidation

An analysis [5] of data acquired by an experimental programme for RWM [4], which investigated the behaviour and fate of <sup>14</sup>CH<sub>4</sub> introduced into near-surface soil under field conditions, suggests that methane will be oxidised in near-surface soils according to a first-order reaction with a rate constant,  $k$ , that is likely to be in the range 10<sup>-5</sup> s<sup>-1</sup> to 10<sup>-4</sup> s<sup>-1</sup>.

## 4.3 Example Calculation

The model quantity of most interest is the characteristic length scale of the system,  $L$ . Even making the most cautious assumptions, we compute:

$$L = \sqrt{\frac{D_{CH_4}}{S_g \phi k}} < 1\text{m} \quad (4.16)$$

The scientific literature confirms this result, having observed that the characteristic length scale ranges from a few centimetres under optimal conditions, to fifty centimetres or more in wet or diffusion-limited soils [45,46,47,48], with agricultural soils being towards the upper end of the range [46,47].

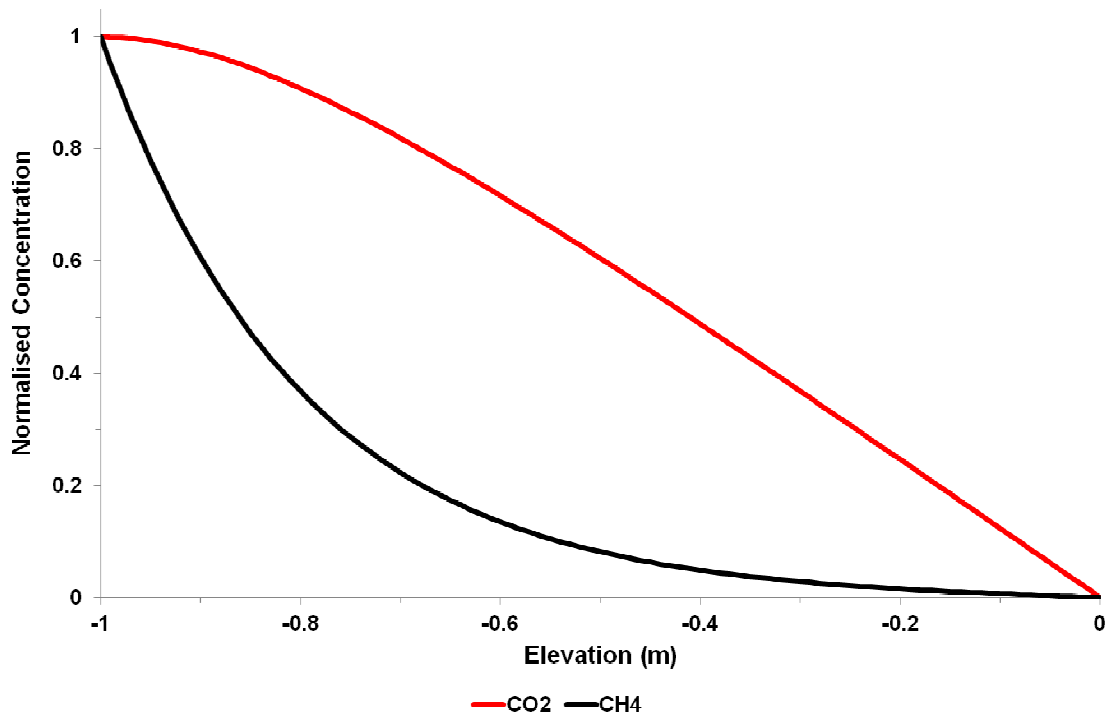
Therefore the water table is likely to be at a depth  $w$  several times larger than the characteristic length scale  $L$ . For this case, the  $^{14}\text{CO}_2$  flux from the soil to the atmosphere,  $\mathbf{F}$ , is simply the sum of the fluxes of  $^{14}\text{CH}_4$  and  $^{14}\text{CO}_2$  at the bottom of the vadose zone (see Equation 4.11):

$$\mathbf{F} = -D_{CO_2} \left. \frac{\partial C_{CO_2}}{\partial z} \right|_{z=0} \approx \mathbf{f}_{CH_4} + \mathbf{f}_{CO_2} \quad (4.17)$$

and the maximum  $^{14}\text{CO}_2$  concentration in the soil gas is (see Equation (4.15)):

$$C_{CO_2} \Big|_{z=-w} \approx \mathbf{F} \frac{w}{D_{CO_2}} \quad (4.18)$$

Actually, for typical values of the model parameters, the  $^{14}\text{CO}_2$  concentration varies approximately linearly with elevation in the soil (see Figure 4.2).



**Figure 4.2** Plot showing the variation of  $^{14}\text{CO}_2$  (and  $^{14}\text{CH}_4$ ) concentration in the soil gas with elevation.

## 4.4 Uncertainty

This section, Section 4, has developed simple representations of the key processes (i.e. molecular diffusion through the soil; methane oxidation by microbes) that will occur within the soil, and thereby has computed the fluxes and concentrations of  $^{14}\text{C}$  in the system.

The important parameters in the model are:

- The diffusion coefficients,  $D_{\text{CH}_4}$  and  $D_{\text{CO}_2}$ ; and
- The oxidation rate constant,  $k$ .

Although these parameters have associated uncertainty, a key point is that the characteristic length scale (see Equation (4.10)) is likely to be no more than a few tens of centimetres. Provided that the water table is at a depth which is more than a few times this length scale, then conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  will be essentially complete, regardless of the particular values of the diffusion coefficient and the oxidation rate constant.

For this case, the expressions for the fluxes and concentrations of  $^{14}\text{C}$  in the soil can be simplified as described in Section 4.3.



## 5 Uptake of $^{14}\text{C}$ by Plants

The new  $^{14}\text{C}$  gas assessment model calculates the concentrations and fluxes of  $^{14}\text{C}$  in the system from simple representations of the key processes (e.g. turbulent transport through the plant canopy; dispersion in the overlying atmosphere; dissolution in the soil water; and uptake of contaminated water through a plant's roots). This section is concerned with uptake of  $^{14}\text{C}$  by plants as a consequence of photosynthesis and transpiration.

In contrast to the previous section, which was concerned with the conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  within the soil, our experiments for RWM [4] were unable to detect any uptake of  $^{13}\text{C}$ -labelled carbon dioxide by the plants. Therefore, in this section the representation of processes is based on understanding gained from reviews of the literature (e.g. [49]).

### 5.1 Uptake due to Photosynthesis

The key processes that occur above ground are turbulent transport through the plant canopy, and dispersion in the overlying atmosphere.

#### 5.1.1 Conceptual Model

When considering photosynthesis as the pathway for uptake of  $^{14}\text{C}$  by plants, the specific activity in the biomass of a plant is equated to the specific activity of its canopy atmosphere. (This is acceptable, because discrimination by plants against isotopes of carbon is a small effect.) The specific activity of the canopy atmosphere is calculated from:

- The concentration of carbon dioxide ( $^{12}\text{CO}_2$ ) in the atmosphere; and
- The flux of  $^{14}\text{C}$  from the soil, which is multiplied by the “aerodynamic resistance” of the plants to determine the concentration of  $^{14}\text{CO}_2$  in the canopy atmosphere.

In equations, the model essentially assumes that:

$$\begin{aligned} S_p &= S_o \\ &= \frac{{}^{14}\text{C}_o}{{}^{12}\text{C}_o} \end{aligned} \quad (5.1)$$

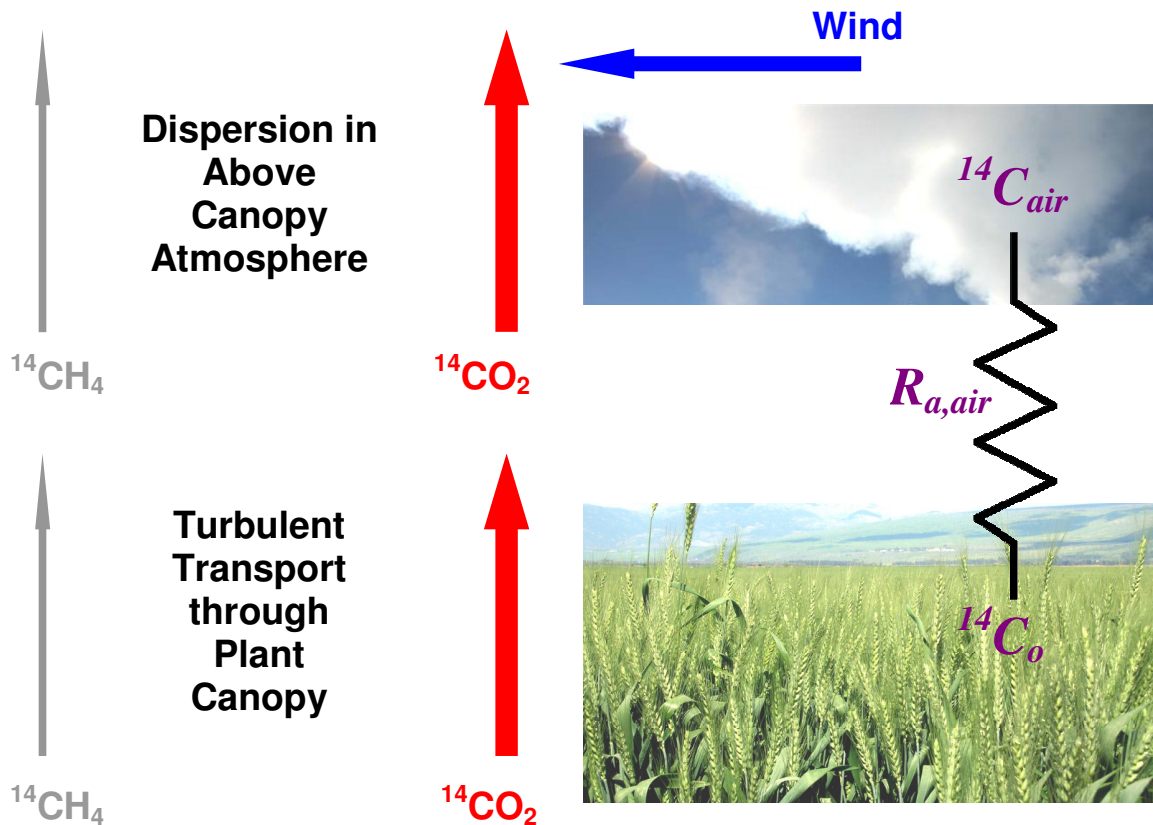
and:

$${}^{14}\text{C}_o = {}^{14}\text{C}_{air} + \mathbf{F} R_{a,air} \quad (5.2)$$

where:

- |                         |  |
|-------------------------|--|
| $S_p$                   | is the specific activity of the plant ( $\text{Bq kg}[\text{C}]^{-1}$ );   |
| $S_o$                   | is the specific activity of the canopy atmosphere ( $\text{Bq kg}[\text{C}]^{-1}$ );   |
| ${}^{14}\text{C}_o$     | is the concentration of $^{14}\text{CO}_2$ in the canopy atmosphere ( $\text{Bq m}^{-3}$ );  |
| ${}^{12}\text{C}_o$     | is the concentration of $^{12}\text{CO}_2$ in the canopy atmosphere ( $\text{kg}[\text{C}] \text{m}^{-3}$ );                             |
| ${}^{14}\text{C}_{air}$ | is the concentration of $^{14}\text{CO}_2$ in the above-canopy atmosphere at a reference height above the plants ( $\text{Bq m}^{-3}$ ); |
| $\mathbf{F}$            | is the flux of $^{14}\text{CO}_2$ from the soil ( $\text{Bq m}^{-2}\text{s}^{-1}$ ); and   |
| $R_{a,air}$             | is the aerodynamic resistance of the plant canopy ( $\text{s m}^{-1}$ ).   |

In this model, it is necessary to calculate the concentration of  $^{14}\text{CO}_2$  both in the atmosphere above the plants and in the canopy atmosphere (see Figure 5.1).



**Figure 5.1** Schematic illustrating a plume of  $^{14}\text{CO}_2$  rising up from the ground surface, and dispersing through the plant canopy and into the overlying atmosphere. The difference between the  $\text{CO}_2$  concentrations in the canopy atmosphere ( $C_o$ ) and in the above-canopy atmosphere ( $C_{air}$ ) is equal to the aerodynamic resistance ( $R_{a,air}$ ) multiplied by the  $\text{CO}_2$  flux.

#### 5.1.1.1 Atmospheric Dispersion

The concentration of  $^{14}\text{CO}_2$  in the atmosphere at a reference height above the plants can be estimated using atmospheric dispersion theory.

For a continuous release from a ground-level area source, atmospheric dispersion theory [50] can be used to estimate<sup>9</sup> the concentration of  $^{14}\text{CO}_2$  at a reference height  $z$  above the surface as:

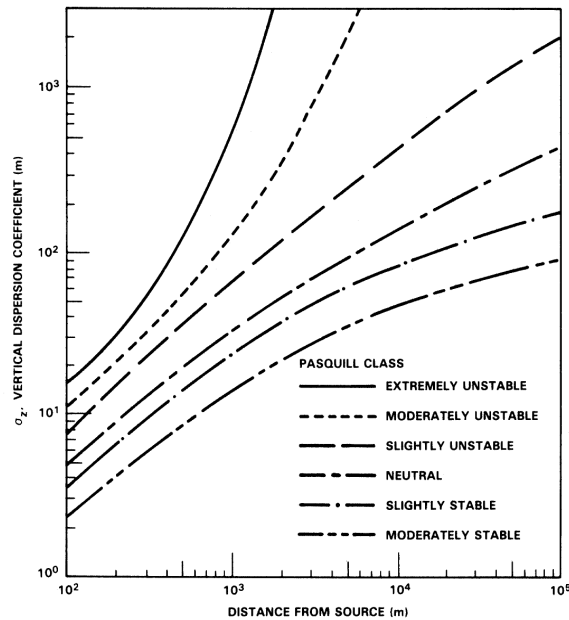
$$\begin{aligned}
 {}^{14}C_{air} &\approx \frac{\mathbf{F}}{u_a} \left( \sqrt{\frac{2}{\pi}} \int_0^x \frac{\exp(-z^2/2\sigma_z^2)}{\sigma_z} dx \right) \\
 &= \frac{\mathbf{F}}{u_a} \Psi(X)
 \end{aligned} \tag{5.3}$$

<sup>9</sup> This estimate uses the “narrow plume hypothesis” [51] to eliminate the dependence on  $y$ , the crosswind coordinate.

where:

- $^{14}C_{air}$  is the concentration of  $^{14}CO_2$  in the above-canopy atmosphere at the reference height ( $Bq\ m^{-3}$ );
- F** is the flux of  $^{14}CO_2$  from the soil ( $Bq\ m^{-2}s^{-1}$ );
- $u_a$  is the mean wind speed (i.e. the time average of the wind speed at a height that is representative of the plume) affecting the plume ( $m\ s^{-1}$ );
- $x$  is the horizontal coordinate aligned with the wind direction (m);
- $X$  is related to the length scale over which the release is occurring (m);
- $\sigma_z$  is the vertical dispersion coefficient of the plume (m; it is a function of position,  $x$ ); and
- $\Psi$  is a dimensionless proportionality constant (-; it is a weak function of the downwind extent of the release region,  $X$ ).

In this equation, the vertical dispersion coefficient describes how the plume of  $^{14}CO_2$  spreads, and is a function of both the Pasquill stability class and downwind distance (see Figure 5.2).



**Figure 5.2 Vertical dispersion coefficient.**

Pasquill categorised atmospheric turbulence into six stability classes (see Table 5.1).

**Table 5.1 Pasquill Stability Classes**

Stability Class	Definition
A	Extremely unstable
B	Moderately unstable
C	Slightly unstable
D	Neutral
E	Slightly stable
F	Moderately stable

Table 5.2 gives the meteorological conditions that define each of the stability classes.

**Table 5.2 Meteorological Conditions that Define the Pasquill Stability Classes**

Surface Wind Speed	Daytime Incoming Solar Radiation			Night-time Cloud Cover	
	m s <sup>-1</sup> (at 10m)	strong	moderate	slight	> 50%
< 2	A	A – B	B	–	–
2 – 3	A – B	B	C	E	F
3 – 5	B	B – C	C	D	E
5 – 6	C	C – D	D	D	D
> 6	C	D	D	D	D

Note: neutral class D should be assumed for overcast conditions, at any wind speed day or night.

During the day (i.e. when photosynthesis will be occurring), the most relevant stability classes in the UK are B (moderately unstable), C (slightly unstable) and D (neutral).

Many parameterizations have been developed to predict the vertical dispersion coefficient. The rural mode option of the Industrial Source Complex (ISC3) model<sup>10</sup> [35] implements a parameterization that approximately fits measured dispersion curves [52]. The equation used to compute the vertical dispersion coefficient is given by:

$$\sigma_z = a x^b \quad (5.4)$$

where the coefficients  $a$  and  $b$  (see Table 5.3) depend upon the Pasquill stability class and downwind distance,  $x$  (in km).

**Table 5.3 Coefficients for Pasquill (ISC3) Vertical Dispersion Parameterization**

Stability Class	$x$ (km)	$a$ (m)	$b$ (–)
B	< 0.2	90.673	0.93198
	0.2 – 0.4	98.483	0.98332
	> 0.4	109.300	1.09710
C	all	61.141	0.91465
D	< 0.3	34.459	0.86974
	0.3 – 1.0	32.093	0.81066
	1.0 – 3.0	32.093	0.64403
	3.0 – 10.0	33.504	0.60486
	10.0 – 30.0	36.650	0.56589
	> 30.0	44.053	0.51179

Note: if the value of  $\sigma_z$  calculated for classes B and C exceeds 5,000m, then  $\sigma_z$  is set to 5,000m.

<sup>10</sup> The U.S. Environmental Protection Agency's ISC3 model is a widely available, generally accepted atmospheric dispersion model.

This particular parameterization of the vertical dispersion coefficient can be used in Equation (5.3) to estimate the concentration of  $^{14}\text{CO}_2$  in the above-canopy atmosphere.

It still remains to decide on the value of the length scale  $X$ . In general, the concentration of  $^{14}\text{CO}_2$  in the atmosphere above a point within the irregularly-shaped release region will vary with both:

- Wind direction and speed (i.e. the wind rose); and
- The distance upwind of the point that is still within the release region.

In the absence of these details, which are partly site-specific, it seems reasonable to assume:

$$X = \sqrt{\frac{A_R}{\pi}} \quad (5.5)$$

where  $A_R$  is the area of the release region ( $\text{m}^2$ ). This corresponds to approximating the release region as a circle<sup>11</sup>, and computing the concentration above the midpoint of the circle.

Then, performing the integral in Equation (5.3) for a reference height 2m above the plant canopy, we find the values of the proportionality constant  $\Psi$  listed in Table 5.4.

**Table 5.4 Dimensionless Proportionality Constant  $\Psi$  between  $^{14}\text{CO}_2$  Concentrations at a Reference Height 2m above the Plant Canopy and the Ratio of  $^{14}\text{CO}_2$  Flux to Wind Speed**

Stability Class	$\Psi$		
	Release area $10^4 \text{ m}^2$	Release area $10^5 \text{ m}^2$	Release area $10^6 \text{ m}^2$
B	9.0	17.5	26.5
C	9.5	21.3	34.9
D	9.0	26.8	49.7

For comparison<sup>12</sup>, the LLWR 2013 model used a simple mixing (or “box”) model approach. It assumed that the upwind distance  $X$  was 500m and the mixing height was 10m, and therefore in the LLWR 2013 model the proportionality constant  $\Psi$  is 50 (release area  $2.5 \cdot 10^5 \text{ m}^2$ ). This is similar to the values derived here.

An important conclusion from Table 5.4 is that the concentration of  $^{14}\text{CO}_2$  in the above-canopy atmosphere does depend (albeit weakly) on the area of the release region.

It is cautious to assume a release area of  $10^4 \text{ m}^2$  (i.e. 1 hectare). If the area is smaller than this, then the concentrations of  $^{14}\text{C}$  in plant matter will be larger, but any food derived from the contaminated area will need to be supplemented by food from elsewhere. Thus, the effective dose rate will not depend on the area of the release region. If the area is larger, then the effective dose rate will be smaller (in inverse proportion to the area of the release region).

<sup>11</sup> Strictly, the crosswind extent of the release region should be large enough that the “narrow plume hypothesis” [51], which was used when deriving Equation (5.3), holds true. This refinement would have a negligible effect.

<sup>12</sup> Another comparison is with the data of Gifford and Hanna [53], who measured concentrations due to ground-level emissions in urban areas. The proportionality constant  $\Psi$  ranged from 5 to 220, with a mean of about 50 for gases (release area  $10^9 \text{ m}^2$ ).

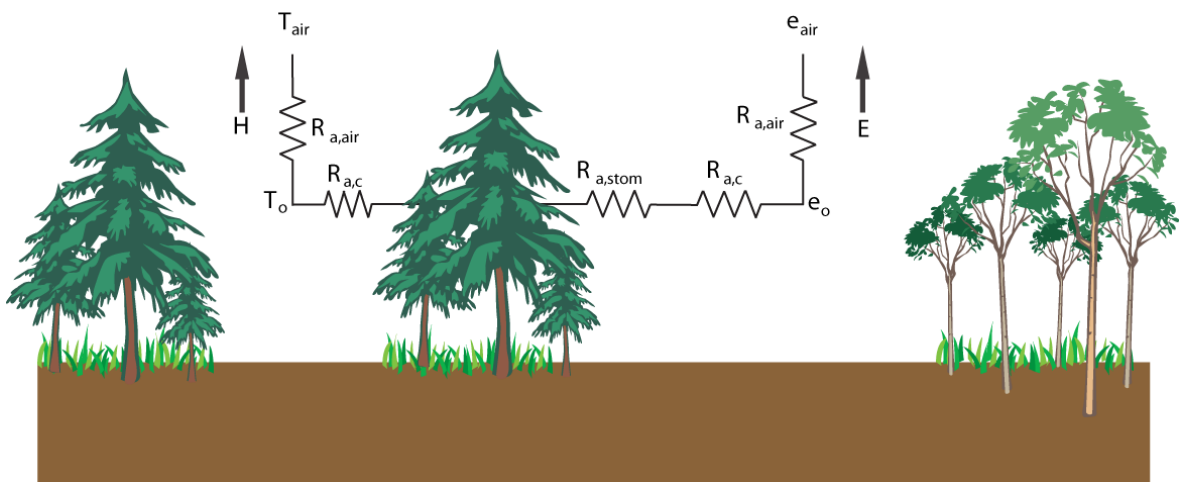
For a release area of  $10^4 \text{ m}^2$ , it is appropriate to assume that the concentration of  $^{14}\text{CO}_2$  in the above-canopy atmosphere is:

$$^{14}C_{air} \approx 10 \frac{F}{u_a} \quad (5.6)$$

This is less than for the LLWR 2013 model, mainly because the assumed size of the release region has diminished.

### 5.1.1.2 Aerodynamic Resistance

Equation (5.2) equates the difference between the concentrations of  $^{14}\text{CO}_2$  in the atmosphere above the plant and in the canopy atmosphere to the flux of  $^{14}\text{CO}_2$  multiplied by the aerodynamic resistance of the plant. The resistance analogue approach [29, 30] to modelling transport through plant canopies (see Figure 5.3) is widely used. Typically, it is applied to the problem of describing how some property of a plant responds to a measured flux above the canopy. Therefore it is appropriate for our problem, in which we want to use the flux of  $^{14}\text{CO}_2$  to the atmosphere to estimate the concentration of  $^{14}\text{CO}_2$  in the plant canopy that is available for photosynthesis and growth.



**Figure 5.3** Schematic showing an example of a resistance network, which can be used to calculate the transport of sensible heat (H) and water vapour (E) through the plant canopy.

$T_{air}$  and  $T_o$  are respectively the temperature in the atmosphere above the plant and in the canopy;  $e_{air}$  and  $e_o$  are the partial pressure of water vapour in the atmosphere above the plant and in the canopy;  $R_{a,air}$  is the aerodynamic resistance, which determines transport between the atmosphere above the plant and the canopy;  $R_{a,c}$  is the canopy resistance, which determines transport within the canopy;  $R_{a,stom}$  is the stomatal resistance, which controls transport of water vapour from the canopy into the leaf.

Appendix 2 provides a brief overview of the theory underlying the concept of the aerodynamic resistance. The main result is that the transport of water vapour, carbon dioxide and sensible heat<sup>13</sup> into the air above the plant canopy is determined by an aerodynamic resistance:

<sup>13</sup> In meteorology, sensible heat refers to heat that is transferred by conduction and convection.



$$R_{a,air} = \frac{\ln\left(\frac{z-d}{z_{0m}}\right) \ln\left(\frac{z-d}{z_{0c}}\right)}{\kappa^2 u_a} \quad (5.7)$$

where:

- $z$  is the reference height (above the plant canopy) where the wind speed and the concentration of  $^{14}\text{CO}_2$  are measured (m);
- $d$  is the height of the zero plane displacement (i.e. the height at which the wind speed tends to zero because of flow obstacles such as trees; m);
- $z_{0m}$  is the roughness length controlling transfer of momentum (m);
- $z_{0c}$  is the roughness length controlling transfer of water vapour, carbon dioxide and sensible heat (m; often in practice, this is taken to be the same as  $z_{0m}$ );
- $\kappa$  is von Karman's constant, 0.41 (-); and
- $u_a$  is the wind speed at height  $z$  ( $\text{m s}^{-1}$ ).

Strictly, this equation applies only to neutral stability conditions. Although it is possible to include a correction that accounts for unstable conditions, it is cautious to neglect this correction, because unstable conditions would mean faster transport through the canopy.

The heights of the zero plane displacement and the roughness lengths are relevant when the ground surface is covered by vegetation. Many studies have investigated these parameters, which depend upon plant height and morphology, and various empirical relations have been developed for estimating  $d$ ,  $z_{0m}$  and  $z_{0c}$ . Therefore it is possible to calculate crop-specific values for the aerodynamic resistance, and hence for the  $^{14}\text{CO}_2$  concentration in the canopy atmosphere.

If the Potentially Exposed Groups and their diets could be clearly specified, then it might be appropriate to follow a crop-specific approach, and in fact this was done in the recent LLWR 2013 assessment [15].

Here, however, we propose a simpler approach. Generally the aerodynamic resistance increases with shorter vegetation, and so it is cautious (but by a factor of two or three at most) to apply the aerodynamic resistance of a grass reference surface to all plant types, when calculating the specific activity in the biomass of the plants.

A standard work on crop evaporation-transpiration [54] states that the aerodynamic resistance of the grass reference surface, assuming that the grass has a constant height<sup>14</sup> of 0.12m, is:

$$R_{a,air} = \frac{208}{u_a} \quad (5.8)$$

where

- $u_a$  is the wind speed at a reference height that is chosen to be 2m above the ground surface ( $\text{m s}^{-1}$ ).

Substituting this aerodynamic resistance into Equation (5.2), and also using Equation (5.6), the concentration of  $^{14}\text{CO}_2$  in the canopy atmosphere is predicted to be:

<sup>14</sup> The calculation assumes that the height of the grass  $h = 0.12\text{m}$ , the zero plane displacement  $d = \frac{2}{3} h$ , the roughness length controlling transfer of momentum  $z_{0m} = 0.123 h$ , and the roughness length controlling transfer of carbon dioxide  $z_{0c} = 0.1 z_{0m}$ .

$${}^{14}C_o = F \frac{\Psi}{u_a} + F \frac{208}{u_a} \quad (5.9)$$

where the dimensionless proportionality constant  $\Psi$  is approximately 10 for a release area of  $10^4 \text{ m}^2$  (see Table 5.4).

### 5.1.1.3 Total Resistance

Equation (4.8) in Section 4.1.3 introduced the concept of a total resistance, which is the proportionality factor relating flux from the soil to concentration in the canopy atmosphere. From the analyses above:

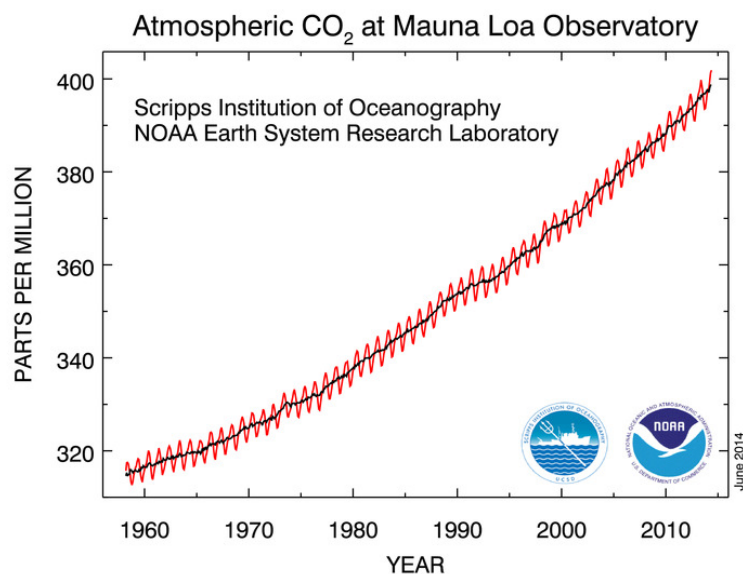
$$R_T = \frac{\Psi}{u_a} + \frac{208}{u_a} \quad (5.10)$$

### 5.1.1.4 Specific Activity of ${}^{14}\text{C}$ in Carbon Dioxide in the Canopy Atmosphere

The specific activity of  ${}^{14}\text{C}$  in carbon dioxide in the canopy atmosphere is also needed to compute the uptake of  ${}^{14}\text{C}$  by plants due to photosynthesis (see Equation (5.1)). To determine this specific activity requires a value for the  ${}^{12}\text{CO}_2$  concentration in the canopy atmosphere.

Plants regulate the process of photosynthesis so that under a wide variety of circumstances the rate of diffusion of  $\text{CO}_2$  into a leaf (the supply of  $\text{CO}_2$ ) is approximately equal to the biochemical capacity of the leaf to fix  $\text{CO}_2$  (the demand for  $\text{CO}_2$ ) [55]. Experiments by Wong *et al.* [36] showed that when photosynthesis is occurring, the ratio of the leaf's internal  $\text{CO}_2$  concentration to the atmospheric  $\text{CO}_2$  concentration is about 0.7 for a C3 plant (provided that the plant is not under stress). Subsequent studies [56] have confirmed the approximate value of this ratio, even for elevated concentrations of atmospheric  $\text{CO}_2$ .

In 2013, the concentration of atmospheric  $\text{CO}_2$  was about 395 ppmv (see Figure 5.4). Therefore, inside the leaf of a C3 plant the  $\text{CO}_2$  concentration will be about 280 ppmv.



**Figure 5.4** Concentration of atmospheric  $\text{CO}_2$  measured at the Mauna Loa Observatory [57].

CO<sub>2</sub> migrates from the atmosphere into the leaf<sup>15</sup> through a network of resistances in series (i.e. the aerodynamic resistance, the laminar boundary layer around a leaf, and the stomata pores; see Figure 5.3). Except when the wind speed is low (i.e. less than a few m s<sup>-1</sup>), the resistance associated with diffusion across the laminar boundary layer and through the stomata pores is likely to be larger than the aerodynamic resistance. Therefore during periods when photosynthesis is occurring, the concentration of CO<sub>2</sub> in the canopy atmosphere will be in the range 280 ppmv to 395 ppmv, and probably closer to the latter value.

Although it is difficult to compute precisely <sup>12</sup>C<sub>o</sub>, the <sup>12</sup>CO<sub>2</sub> concentration in the canopy atmosphere, the considerations above imply that 350 ppmv, or 1.75 10<sup>-4</sup> kg[C] m<sup>-3</sup>, is an appropriate value for this quantity at present, with only a small uncertainty.

Over the past 400,000 years, the concentration of atmospheric CO<sub>2</sub> has varied from about 180 ppmv during the glaciations of the Holocene to about 280 ppmv during the interglacial periods. The CO<sub>2</sub> concentration has increased to over 390 ppmv only very recently in geological history (and it continues to increase, mainly because of human CO<sub>2</sub> emissions). If in the future the concentration of atmospheric CO<sub>2</sub> were to fall towards its long-term minimum value, then that would mean approximately halving our estimate of the <sup>12</sup>CO<sub>2</sub> concentration in the canopy atmosphere, or doubling our estimate of the uptake of <sup>14</sup>C by plants due to photosynthesis (i.e. making only modest changes to our results).

## 5.1.2 Data

The results of the previous sections can be summarised in equations as:

$$\begin{aligned} S_p &= S_o \\ &= \frac{{}^{14}C_o}{{}^{12}C_o} \end{aligned} \quad (5.11)$$

and:

$${}^{14}C_o = \mathbf{F} \frac{10}{u_a} + \mathbf{F} \frac{208}{u_a} \quad (5.12a)$$

$${}^{12}C_o = 1.75 \cdot 10^{-4} \text{ kg[C] m}^{-3} \quad (5.12b)$$

where:

- $S_p$  is the specific activity of the plant (Bq kg[C]<sup>-1</sup>);
- $S_o$  is the specific activity of the canopy atmosphere (Bq kg[C]<sup>-1</sup>);
- ${}^{14}C_o$  is the concentration of <sup>14</sup>CO<sub>2</sub> in the canopy atmosphere (Bq m<sup>-3</sup>);
- ${}^{12}C_o$  is the concentration of <sup>12</sup>CO<sub>2</sub> in the canopy atmosphere (kg[C] m<sup>-3</sup>);
- $\mathbf{F}$  is the flux of <sup>14</sup>CO<sub>2</sub> from the soil (Bq m<sup>-2</sup>s<sup>-1</sup>); and
- $u_a$  is the wind speed at 2m above the ground (m s<sup>-1</sup>).

The outstanding datum is the wind speed at 2m above the ground,  $u_a$ . Because the variation in the wind speed averaged over monthly periods is small, it is possible to estimate monthly values of wind speed. These monthly values will depend on the particular site, and should take seasonal changes into account. General values are suggested in Table 5.5.

<sup>15</sup> In addition, CO<sub>2</sub> will be respired by both the plant and microorganisms in the soil.

**Table 5.5 Classes of Mean Monthly Wind Speed Data**

Description	Monthly Wind Speed at 2m (m s <sup>-1</sup> )
Light wind	< 1
Light to moderate wind	1 – 3
Moderate to strong wind	3 – 5
Strong wind	> 5

In general, the wind speed at 2m should be limited to  $u_a > 0.5 \text{ m s}^{-1}$ , because the effects of instability and buoyancy (of warm air) become more significant at lower wind speeds. If no wind speed data are available, then a value of  $2 \text{ m s}^{-1}$  is reasonable, and most likely cautious. This is the average value measured at a large number of weather stations.

### 5.1.3 Example Calculation

Assuming a wind speed of  $2 \text{ m s}^{-1}$  at 2m above the ground<sup>16</sup>, it follows from Equations (5.11) and (5.12) that the specific activity of the plants,  $S_p$  (Bq kg[C]<sup>-1</sup>), is proportional to the flux of <sup>14</sup>CO<sub>2</sub> from the soil,  $\mathbf{F}$  (Bq m<sup>-2</sup>s<sup>-1</sup>):

$$S_p = \frac{10 + 208}{2 \times 0.000175} \mathbf{F} = 6.23 \cdot 10^5 \mathbf{F} \text{ Bq kg[C]}^{-1} \quad (5.13)$$

### 5.1.4 Uncertainty

This section, Section 5.1, has developed simple representations of the key processes (i.e. dispersion in the overlying atmosphere; turbulent transport through the plant canopy) that will occur above ground, and thereby has computed the uptake of <sup>14</sup>C by plants due to photosynthesis.

The important parameters in the model are:

- The dimensionless proportionality constant,  $\Psi$  (see Section 5.1.1.1); and
- The aerodynamic resistance,  $R_{a,air}$  (see Section 5.1.1.2).

In the case of the proportionality constant,  $\Psi$ , a generally accepted atmospheric dispersion model has been used to estimate its value as a function of Pasquill stability class and release area (see Table 5.4). Although Gaussian plume dispersion models should be applied to “on-site conditions” only with care, because the experimental data needed to calibrate the dispersion coefficients for short-range (i.e. < 100m) dispersion calculations are lacking, the estimate is appropriate. The values obtained imply that the parameter actually controlling the specific activity of the plant is the aerodynamic resistance (see Equation 5.11a).

In the case of the aerodynamic resistance,  $R_{a,air}$ , a standard formulation for a grass reference surface has been adopted. Because the aerodynamic resistance decreases with plant height, it is cautious (but by a factor of two or three at most) to apply this aerodynamic resistance to all plant types. The benefit of making this assumption is that it avoids the necessity of computing crop-specific values for the aerodynamic resistance and specific activity.

<sup>16</sup> Currently in the UK, a mean annual wind speed of about  $5 \text{ m s}^{-1}$  is often measured at 2m above the ground, and therefore assuming a value of  $2 \text{ m s}^{-1}$  may be cautious by a factor of about 2.5. Assuming a wind speed of  $2 \text{ m s}^{-1}$  accommodates uncertainty about meteorological conditions both at a specific site and in the future.

Resistance analogue models have been used to model a large number of experimental datasets. However, there have been fewer studies focused on comparing various parameterisations of the aerodynamic resistance, both with one another and with field data.

Using the experimental data of Choudhury *et al.* [58], Kalma [59] compared a number of aerodynamic resistance parameterisations, and found deviations from the measurements that were fairly insignificant (i.e. for some parameterisations, the aerodynamic resistance was as little as 50% of its experimental value).

Subsequently, Liu *et al.* [60] extended Kalma's study to include additional aerodynamic resistance parameterisations, which were applied to a more recent experimental dataset. The experimental data were sensible heat fluxes from a developing maize canopy (i.e. from bare soil, through the emergence of the crop and on to full vegetative development), which were measured at an experimental field in Beijing, China using an eddy correlation system. Most of the parameterisations showed a good correlation between predicted values and experimental values (i.e. the mean absolute percentage error was about 20%). The key parameters when estimating the aerodynamic resistance were the roughness length and the wind speed.

In another study, Demarty *et al.* [61] implemented six different aerodynamic resistance parameterisations within a two-layer model, and then applied the model to the Alpillles experimental dataset<sup>17</sup>. Although the different parameterisations differed in their partition of water and energy between the soil and vegetation, they gave very similar predictions for the aerodynamic resistance. This is an important point, because it means that for a given total flux, all of the models predict similar potential differences. In other words, the resistance analogue approach can be used to relate a total flux to the potential difference in a quantity (i.e. <sup>14</sup>CO<sub>2</sub> concentration) between the plant canopy and the overlying atmosphere.

The conclusion is that the differences between measured and computed aerodynamic resistances are small, typically no more than a factor of about two.

## 5.2 Uptake due to Transpiration

Considering next the key processes that occur below ground, these are dissolution of <sup>14</sup>CO<sub>2</sub> in the groundwater, and then uptake of contaminated water through a plant's roots.

### 5.2.1 Conceptual Model

This pathway for a plant to take up <sup>14</sup>C is due to transpiration. The calculation of the increment in the specific activity of <sup>14</sup>C in the biomass of the plant proceeds through a number of steps.

Firstly, we note that an estimate (see Section 4.3, and in particular Figure 4.2) of the <sup>14</sup>CO<sub>2</sub> concentration within the soil gas,  $C_{CO_2}$  (Bq m<sup>-3</sup>), at depth  $z$  (m) is:

$$C_{CO_2} \approx F \frac{z}{D_{CO_2}} \quad (5.14)$$

<sup>17</sup> The Alpillles experiment was focused on agricultural land and practices. In particular the experiment:

- Took place at a small agricultural site in the south-east of France, which had a large diversity of crops; and
- Lasted for about a year, so as to gather data for a complete cycle of the different crops.

Besides characterising crop production, a large part of the experimental dataset was concerned with water and energy exchanges between the soil, the vegetation and the atmosphere.

where:

- $\mathbf{F}$  is the flux of  $^{14}\text{CO}_2$  through the soil ( $\text{Bq m}^{-2}\text{s}^{-1}$ ); and
- $D_{\text{CO}_2}$  is the diffusion coefficient for carbon dioxide in the gas phase within the soil ( $\text{m}^2\text{s}^{-1}$ ).

Next, this concentration is converted into a mass fraction of  $^{14}\text{C}$  within the soil water,  $w_{\text{CO}_2}^{(\text{aq})}$  ( $\text{kg}[^{14}\text{C}] \text{kg}^{-1}$ ), as follows.

- The  $^{14}\text{CO}_2$  partial pressure within the soil gas,  $P_{\text{CO}_2}$  (Pa), is:

$$P_{\text{CO}_2} = RT \frac{1}{N_A \lambda} \mathbf{F} \frac{z}{D_{\text{CO}_2}} \quad (5.15)$$

where:

- $R$  is the gas constant,  $8.3144621(75) \text{ J K}^{-1} \text{ mol}^{-1}$ ;
  - $T$  is the soil temperature, taken to be  $288.15 \text{ K}$ ;
  - $N_A$  is the Avogadro constant,  $6.02214129(27) 10^{23} \text{ mol}^{-1}$ ; and
  - $\lambda$  is the decay constant of  $^{14}\text{C}$ ,  $3.833 10^{-12} \text{ s}^{-1}$ .
- Multiplying the  $^{14}\text{CO}_2$  partial pressure by the Henry's law constant,  $H_{\text{CO}_2} = 4.49 10^{-7} \text{ mol L}^{-1}\text{Pa}^{-1}$  [62] at  $15 \text{ }^\circ\text{C}$ <sup>18</sup>, gives the molar concentration of  $^{14}\text{C}$  within the soil water,  $c_C^{(\text{aq})}$  ( $\text{mol L}^{-1}$ ):

$$c_C^{(\text{aq})} = H_{\text{CO}_2} P_{\text{CO}_2} \quad (5.16)$$

- The molar concentration is converted into a mass fraction of  $^{14}\text{C}$  within the soil water,  $w_C^{(\text{aq})}$  ( $\text{kg}[^{14}\text{C}] \text{kg}^{-1}$ ), by multiplying by the atomic mass of  $^{14}\text{C}$ ,  $m_a = 0.014003241 \text{ kg}[\text{C}] \text{mol}^{-1}$ , and dividing by the density of water at  $15 \text{ }^\circ\text{C}$ ,  $\rho = 0.9991026 \text{ kg L}^{-1}$ .

$$w_C^{(\text{aq})} = \frac{m_a}{\rho} c_C^{(\text{aq})} \quad (5.17)$$

The plant will take up some contaminated water through its roots. The transpiration ratio, which is the ratio of the mass of water transpired by a plant during its growing season to the mass of dry matter (usually exclusive of roots) produced, is a relevant quantity. Black [63] has shown that the transpiration ratio,  $T_R$ , for C3 plants ranges from 450 to 950  $\text{kg H}_2\text{O}$  transpired per  $\text{kg}$  dry mass produced (this is much higher than for either C4 plants<sup>19</sup>, from 250 to 350  $\text{kg H}_2\text{O}$  transpired per  $\text{kg}$  dry mass produced, or CAM plants<sup>19</sup>, from 50 to 125  $\text{kg H}_2\text{O}$  transpired per  $\text{kg}$  dry mass produced).

<sup>18</sup> This is a reasonable estimate of the soil temperature during the summer in the UK. The Henry's law constant refers to the bulk solubility of carbon dioxide, i.e. all chemical species of the gas and its reaction products with water are included. Note that the Henry's law constant will increase when the soil temperature decreases towards  $0 \text{ }^\circ\text{C}$ .

<sup>19</sup> C4 carbon fixation is one of three biochemical mechanisms, along with C3 and CAM photosynthesis, used in carbon fixation. It is named for the 4-carbon molecule which is the first product of carbon fixation in the small subset of plants known as C4 plants. This is in contrast to the 3-carbon molecule which is the first product in C3 plants. CAM photosynthesis is another carbon fixation pathway that evolved in some plants as an adaptation to arid conditions.



Schlesinger [64] has noted that the carbon content of biomass is almost always between 45% and 50% (by dry mass). Therefore, dividing the transpiration ratio by the factor  $\Theta \approx 0.475$  gives the ratio between the mass of water transpired and the carbon content (by mass) of the plant.

Multiplying the latter ratio by the mass fraction of  $^{14}\text{C}$  within the soil water,  $w_C^{(\text{aq})}$  ( $\text{kg}[^{14}\text{C}] \text{kg}^{-1}$ ), gives the ratio between the mass of  $^{14}\text{C}$  transpired and the carbon content (by mass) of the plant.

It is likely that some (assumed to be a half) of the  $^{14}\text{C}$  taken up through the plant's roots will be lost, for example as a result of maintenance respiration. A correction factor,  $\Omega$ , is applied to account for this effect.

Combining all of the various factors, the increment in the specific activity of  $^{14}\text{C}$  in the biomass of the plant due to transpiration,  $\Delta S_p$  ( $\text{Bq kg}[\text{C}]^{-1}$ ), is:

$$\begin{aligned} \Delta S_p &= \frac{N_A \lambda}{m_a} \Omega \frac{T_R}{\Theta} w_C^{(\text{aq})} \\ &= \Omega \frac{T_R}{\Theta} \frac{H_{\text{CO}_2}}{\rho} R T F \frac{z}{D_{\text{CO}_2}} \end{aligned} \quad (5.18)$$

## 5.2.2 Data

In addition to well-known physical properties, the model described above requires numerical values for the following parameters:

- The diffusion coefficient for carbon dioxide in the gas phase within the soil,  $D_{\text{CO}_2}$ .
  - This is discussed in Section 4.2.1, which suggests that a realistic value is  $4.1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ .
- The average depth from which roots take up water in the soil,  $z$ .
- The transpiration ratio,  $T_R$ .
- The correction factor to account for some of the  $^{14}\text{C}$  taken up through the plant's roots being lost as a result of maintenance respiration,  $\Omega$ .

Bishop and Beetham [65] have reviewed root distributions for a range of mature crops. Based on data quoted in this study, it is cautious<sup>20</sup> to assume that a typical depth from which roots will take up water in the soil is about 0.5m.

The transpiration ratio has been fairly well characterised for crops growing in the temperate zone. Table 5.6 lists measured values of the transpiration ratio for various plant types.

<sup>20</sup> This depth is appropriate for cereal crops grown in well-drained soils, but may be too deep for other crops (e.g. green vegetables, root vegetables and tubers). The IAEA [66], for example, recommends using a standardised rooting depth of 0.1m for grass, and 0.2m for all other crops.

**Table 5.6 Average Transpiration Ratios (kg H<sub>2</sub>O Transpired per kg Dry Mass Produced) for Various Plant Types [67]**

Plant Type	Transpiration Ratio (kg H <sub>2</sub> O per kg dry mass)
<b>Herbaceous C3 Plants</b>	
Cereals	500 – 650
Legumes	700 – 800
Potatoes and root crops	400 – 650
Sunflowers (young)	280
Sunflowers (flowering)	670
<b>Woody Plants</b>	
Broadleaved trees of tropical zone	600 – 900
Broadleaved trees of temperate zone	200 – 350
Coniferous trees	200 – 300
Oil palms	~300
<b>C4 Plants</b>	
Maize / sorghum	260 – 320
<b>CAM Plants</b>	
e.g. Pineapples	50 – 100

In the calculations below, we shall use a transpiration ratio of 500 kg H<sub>2</sub>O transpired per kg dry mass produced.

Although there is uncertainty about how much of the <sup>14</sup>C taken up through the plant's roots will be lost, for example because of maintenance respiration, it is known that the ratio of respiration to gross photosynthesis in plant ecosystems is usually in the range 0.4 – 0.5. This observation motivated us to take the correction factor,  $\Omega$ , to be 0.5.

That this assumption is reasonable can be confirmed by using the same approach to compute the uptake of <sup>12</sup>C due to transpiration. Data acquired during an experimental programme for RWM [4], which investigated the behaviour and fate of <sup>14</sup>CH<sub>4</sub> introduced into near-surface soil under field conditions, show that the concentration of carbon dioxide in the soil gas will be about 30,000 ppmv. Hence, the partial pressure of carbon dioxide in the soil gas will be about 3,040 Pa. Using Equations (5.16) and (5.17), the mass fraction of dissolved <sup>12</sup>C within the soil water will be about  $1.64 \cdot 10^{-5} \text{ kg}[\text{<sup>12</sup>C}] \text{ kg}^{-1}$ , and therefore the fraction of <sup>12</sup>C that the plant will absorb through its roots is:

$$\Omega \frac{T_R}{\Theta} w_C^{(\text{aq})} = 0.5 \times \frac{500}{0.475} \times 1.64 \cdot 10^{-5} = 0.86\% \quad (5.19)$$

This result is consistent with observations in the literature (see below) on the uptake of dissolved carbon dioxide, which validate the model.

### 5.2.2.1 Review of Literature on the Uptake of $^{12}\text{C}$ due to Transpiration

$\text{CO}_2$  forms bicarbonate ( $\text{HCO}_3^-$ ) when it dissolves in water. Root uptake of  $\text{HCO}_3^-$  and its incorporation into plant C, via phosphoenolpyruvate (PEP) carboxylase, is well documented.

For example, early studies considered the effects of carbonated irrigation water on crop yields, and showed that plants were able to derive C from  $\text{CO}_2$  dissolved in water. A series of studies using a labelled-C source showed that potatoes growing in nutrient solution absorbed  $\text{CO}_2$  through their roots and transported it to the site of photosynthesis in the plant leaves [68,69]. Substantial increases in tuberization, stolon length, the number of tubers per stolon, and plant dry weight were observed in plants that had had their roots exposed to a gas stream consisting of 45%  $\text{CO}_2$  for twelve hours. Root uptake of  $\text{CO}_2$  was measured also in tomato, eggplant, rice, peas, beans, oats, corn, wheat, and citrus [70–76].

For most plants, plant productivity appears not to be affected substantially by the quantity of  $\text{CO}_2$  absorbed. Schafer [74] found that root uptake of  $\text{HCO}_3^-$  accounted for only 0.44% to 1.21% of the total carbon assimilated by wheat shoots. Others have suggested that <5% of the  $\text{CO}_2$  fixed by a plant could be absorbed by the root system, and it was unlikely that crop yields could be increased by the use of carbonated irrigation water [77,78].

More recently, Ford *et al.* [79] found that approximately 1% of total plant C originated from root uptake of  $\text{HCO}_3^-$ , and there was a higher incorporation of this inorganic C in root than shoot tissue.

These observations are consistent with an analysis of root uptake of C in rice (see Appendix 1 in reference [49]), which suggests that no more than 2% of plant C is absorbed through the roots.

### 5.2.3 Example Calculation

Once the model parameters are well specified, it is straightforward to calculate the increment in the specific activity of  $^{14}\text{C}$  in the biomass of the plants due to transpiration. The result is proportional to the flux of  $^{14}\text{CO}_2$  from the soil,  $\mathbf{F}$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ):

$$\Delta S_p = 6.91 \cdot 10^5 \mathbf{F} \text{ Bq kg[C]}^{-1} \quad (5.20)$$

Interestingly, this “increment” in the specific activity is slightly larger (by a factor of about 1.1) than the calculated contribution to the specific activity due to photosynthesis (see Equation (5.13)).

### 5.2.4 Uncertainty

This section, Section 5.2, has developed simple representations of some of the key processes (i.e. dissolution of  $^{14}\text{CO}_2$  in the groundwater; uptake of contaminated water through a plant’s roots) that will occur below ground, and thereby has computed the uptake of  $^{14}\text{C}$  by plants due to transpiration.

The most uncertain parameter in this model is:

- The correction factor to account for the possibility that uptake of  $^{14}\text{C}$  through the plant’s roots may be an active process, and the consideration that some of the  $^{14}\text{C}$  will be lost as a result of maintenance respiration,  $\Omega$ .

It seems that there are no direct measurements of this correction factor, which therefore could take any value. However, we have shown that choosing the correction factor to be 0.5 is consistent with observations in the literature on the uptake of dissolved carbon dioxide.

## 5.3 Coupling Uptake by Photosynthesis and Transpiration

The total uptake of  $^{14}\text{C}$  by plants is obtained by summing the contributions due to photosynthesis (see Equation (5.13)) and transpiration (see Equation (5.20)). The result is proportional to the flux of  $^{14}\text{CO}_2$  from the soil,  $F$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ), and is given by:

$${}^{\text{TOTAL}}S_p = 1.3 \cdot 10^6 F \text{ Bq kg[C]}^{-1} \quad (5.21)$$

Although this result neglects potential interference between the two pathways (i.e. photosynthesis and transpiration) for the uptake of  $^{14}\text{C}$ , it is cautious.

To explain the point, transpiration will move some  $^{14}\text{C}$  from the soil water through a plant to its leaves. This process will increase the internal  $^{14}\text{CO}_2$  concentration of the leaves. As a result, the rate at which  $^{14}\text{CO}_2$  diffuses from the surrounding canopy atmosphere through the stomata into the leaves will decrease, and the uptake of  $^{14}\text{C}$  due to photosynthesis may be suppressed.

Our calculations have shown that photosynthesis and transpiration will contribute similarly to the uptake of  $^{14}\text{C}$ , and for this case simply adding the two contributions is cautious by a factor of at most two. Therefore, it is reasonable to use Equation (5.21).

## 5.4 Justification for the Neglect of Some Processes

The LLWR 2013 model (see Figure 2.3) recognises some processes that have not been discussed as yet in this report. Notable examples of such processes are:

- Barometric pumping; and
- Cycling of  $^{14}\text{C}$  back to the soil.

The following subsections explain why it is reasonable for a  $^{14}\text{C}$  gas assessment model to neglect these two processes.

### 5.4.1 Barometric Pumping

In general, diffusion dominates the transport of gaseous compounds through the soil, and therefore advection (i.e. barometric pumping) need not be considered. The justification for neglecting barometric effects is based on research by Buckingham [80], Thibodeaux and Hwang [81], Nilson *et al.* [82], Massman and Farrier [83], and Auer *et al.* [84]. These studies show that transport due to barometric pumping is small compared to diffusion, except in fractured media. For example, the study by Thibodeaux and Hwang [81] found that barometric pumping enhanced emissions by 13% compared with diffusion alone. For the purposes of a  $^{14}\text{C}$  gas assessment model, this magnitude of error is acceptable, especially when it is noted that substantial model complexity would be required to account for barometric effects.

Another important observation is that fluctuations in the barometric pressure do not affect the rate of diffusion significantly [80,84]. In other words, diffusion proceeds at the same rate as when there is no displacement of soil gas because of barometric pumping. The rate of diffusion is stable because, even though barometric pumping moves gases up and down, the concentration gradients within the soil that control diffusion remain fairly constant.

Hence, a  $^{14}\text{C}$  gas assessment model, in general, need not account for the coupling to surface atmospheric boundary conditions.

## 5.4.2 Cycling of $^{14}\text{C}$ Back to the Soil

The  $^{14}\text{C}$  that is incorporated into plant matter could be returned to the soil by various processes, either directly (e.g. plant material from a previous crop, that is dug into the soil) or indirectly (e.g. grazed material, after it has passed through an animal).

Any  $^{14}\text{C}$  that is returned to the soil, either directly or indirectly, will become part of the soil organic matter. Microbes will decompose this soil organic matter, at rates which depend on the nature of the organic matter, and therefore this could be an additional source of  $^{14}\text{C}$  within the soil.

A cautious calculation<sup>21</sup> can be used to show that this additional source of  $^{14}\text{C}$  is relatively insignificant.

From Equation (5.21), the total uptake of  $^{14}\text{C}$  by plants is proportional to the flux of  $^{14}\text{CO}_2$  from the soil,  $\mathbf{F}$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ), and is given by:

$$1.3 \cdot 10^6 \mathbf{F} \text{ Bq kg[C]}^{-1} \quad (5.22)$$

From consideration of the yields of pasture and a wide variety of crop types, typical values of the yield are in the range 1 – 3.5 kg dry mass produced per  $\text{m}^2$  [86]. Remembering that the carbon content of biomass is almost always between 45% and 50% (by dry mass) [64], it follows that the maximum amount of  $^{14}\text{C}$  that could be incorporated into plant matter is:

$$2.3 \cdot 10^6 \mathbf{F} \text{ Bq m}^{-2} \quad (5.23)$$

If all of this  $^{14}\text{C}$  were to be returned to the soil, and later released over a period of 150 days (i.e. approximately the duration of the growing season for a crop, or five months), this additional source would increase the flux of  $^{14}\text{CO}_2$  from the soil by:

$$0.17 \mathbf{F} \text{ Bq m}^{-2}\text{s}^{-1} \quad (5.24)$$

This result shows that, in general, cycling of  $^{14}\text{C}$  back to the soil will not cause a large increase in the flux of  $^{14}\text{CO}_2$ ,  $\mathbf{F}$ , from the soil. Hence, although it is a (small) bias, a  $^{14}\text{C}$  gas assessment model need not account for the process.

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<sup>21</sup> That this is an upper-bound calculation can be confirmed as follows.

For a yield of 3.5 kg dry mass produced per  $\text{m}^2$ , with a carbon content of 47.5% (by dry mass), the maximum amount of carbon that could be returned to the soil is  $1.66 \text{ kg[C]} \text{ m}^{-2}$ .

If all of this carbon were to be respired over a period of 150 days, then the rate of production of carbon dioxide would be  $1.28 \cdot 10^{-7} \text{ kg[C]} \text{ m}^{-2}\text{s}^{-1}$ . This is at the upper end of observations of carbon dioxide production from soils, which for conditions appropriate to a UK summer are in the range from  $10^{-8} \text{ kg[C]} \text{ m}^{-2}\text{s}^{-1}$  to  $10^{-7} \text{ kg[C]} \text{ m}^{-2}\text{s}^{-1}$  [85].

## 6 Dose from Ingestion of $^{14}\text{C}$ -Contaminated Plants

The radiological hazard from  $^{14}\text{CH}_4$  will depend on the manner of any release to the biosphere, including for example the area over which it is released and the biological uptake pathway that is followed.

In assessing the impact of  $^{14}\text{C}$ , various pathways have been considered:

- Dissolution in near-surface aquifers from which drinking water or irrigation water is drawn;
- Release of  $^{14}\text{CH}_4$  directly to the atmosphere, followed by inhalation; and
- Conversion of  $^{14}\text{CH}_4$  in the near-surface soils to  $^{14}\text{CO}_2$ , which then is taken up (e.g. through photosynthesis) by plants and ingested. Usually this “ingestion” pathway is the most significant.

This report is concerned with the uptake of gaseous  $^{14}\text{C}$ -bearing species, and so just two pathways require consideration. These are the release of  $^{14}\text{CH}_4$  and / or  $^{14}\text{CO}_2$  either into a building with exposure by inhalation, or into the near-surface soil with subsequent incorporation into plants and exposure by ingestion (e.g. see Figure 2.1). Moreover, the methodology to assess the inhalation pathway is well-established (see Section 2.2). Therefore, the objective of this section is to develop a simple model to assess doses for the ingestion pathway.

### 6.1 Conceptual Model

It is assumed that:

- Animals present on the contaminated area will achieve the same specific activity as the plants; and
- Humans will obtain only a fraction,  $\xi$ , of their dietary requirements from the contaminated area.

Reference Man comprises 16 kg of carbon in a total body mass of 70 kg [87], and therefore the concentration of  $^{14}\text{C}$  in human tissues,  $C_{human}$  ( $\text{Bq kg}^{-1}$ ), will be given by:

$$C_{human} \approx \xi \times \frac{16}{70} \times S_p \quad (6.1)$$

where  $S_p$  ( $\text{Bq kg}[\text{C}]^{-1}$ ) is the specific activity of the plants grown on the contaminated area (see Equations (5.13) and (5.20) in Section 5).

The consequent absorbed dose rate can be calculated without significant uncertainty, since it depends on only the concentration of  $^{14}\text{C}$  in human tissues and the energy emitted by  $^{14}\text{C}$  when it decays. Because  $^{14}\text{C}$  will be distributed relatively uniformly throughout all human organs and tissues and emits only low linear energy transfer radiation, the effective dose rate is numerically equal to the absorbed dose rate:

$$H_{ingestion} \approx C_{human} \times E \times s \quad (6.2)$$

where:

- $H_{ingestion}$  is the effective dose rate ( $\text{Sv yr}^{-1}$ );
- $E$  is the energy emitted by  $^{14}\text{C}$  when it decays ( $7.926 \cdot 10^{-15}$  J per transformation); and
- $s$  is the number of seconds in a year ( $3.15576 \cdot 10^7$  s  $\text{yr}^{-1}$ ).

## 6.2 Data

The model described above requires a value for the fraction of carbon in a person's diet that could be obtained from locally-sourced foodstuffs (i.e. from the contaminated area). It is assumed that humans will not obtain all of their dietary requirements from the contaminated area, because major contributors to carbon in the diet, such as cereals, will not be produced locally (to any great extent). Therefore, as in previous  $^{14}\text{C}$  gas assessments, this fraction is cautiously taken as 0.3.

### 6.2.1 Area of Smallholding

Although not explicit in the equations above, there are questions about what area of smallholding could provide this fraction of carbon in a person's diet, and how the smallholding relates to the release region.

It is cautious to assume that the total  $^{14}\text{C}$  release from the GDF is to a smallholding with an area of  $10^4$  m<sup>2</sup> (i.e. 1 hectare).

- If the area is smaller than this, then the concentrations of  $^{14}\text{C}$  in plant matter will be larger (mainly because the  $^{14}\text{C}$  flux, which is equal to the total  $^{14}\text{C}$  release from the GDF divided by the area over which it is released to the biosphere, will be larger), but any food derived from the contaminated area will need to be supplemented by food from elsewhere. Thus, the effective dose rate will be fairly insensitive to the area of the release region.
- If the area is larger, then the effective dose rate will be smaller (in inverse proportion to the area over which the  $^{14}\text{C}$  is released to the biosphere).

## 6.3 Example Calculation

Considering uptake of  $^{14}\text{C}$  by plants due to photosynthesis, and assuming a wind speed of  $2 \text{ m s}^{-1}$  at 2m above the ground, Equation (5.13) states that the specific activity of the plants,  $S_p$  ( $\text{Bq kg}[\text{C}]^{-1}$ ), will be proportional to the flux of  $^{14}\text{CO}_2$  from the soil,  $F$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ):

$$S_p = 6.23 \cdot 10^5 F \text{ Bq kg}[\text{C}]^{-1} \quad (6.3)$$

If uptake of dissolved  $^{14}\text{C}$  is to be taken into account, then Equation (5.20) states that this specific activity must be incremented by:

$$\Delta S_p = 6.91 \cdot 10^5 F \text{ Bq kg}[\text{C}]^{-1} \quad (6.4)$$

Hence, we can calculate the effective dose rate ( $\text{Sv yr}^{-1}$ ) to a representative member of a Potentially Exposed Group per unit flux of  $^{14}\text{C}$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ) at the bottom of the vadose zone. Table 6.1 lists the results.

**Table 6.1 Flux to Dose Conversion Factor**

Description	Flux to Dose Conversion ( $\text{Sv yr}^{-1}$ ) ( $\text{Bq m}^{-2}\text{s}^{-1}$ )
Photosynthesis only pathway for $^{14}\text{C}$ uptake by plants	0.0107
Transpiration also contributes to $^{14}\text{C}$ uptake by plants	0.0225



## 6.4 Uncertainty

The only new parameter introduced in this section is the fraction of carbon in a person's diet that could be obtained from locally-sourced foodstuffs. Although it is considered that this fraction could be in the range from 0.2 to 0.3, a cautious assumption of 0.3 is used.

There is additional uncertainty about what area of smallholding could provide this fraction of carbon in a person's diet, and how the smallholding relates to the release region.

## 7 Summary of the Proposed $^{14}\text{C}$ Gas Assessment Model

This report is proposing a new  $^{14}\text{C}$  gas assessment model, which is based extensively on:

- The data acquired by an experimental programme for RWM [4], which investigated the behaviour and fate of  $^{14}\text{CH}_4$  introduced into near-surface soil under field conditions; as well as
- The conceptual understanding developed during previous assessment studies.

### 7.1 Learning from the Experimental Programme

The key findings of the experimental programme, which have been incorporated into the new  $^{14}\text{C}$  gas assessment model, are listed in Box 3.

#### Box 3 Findings from the Experiments

The conclusions from the interpretation of the experimental data are as follows:

- Transport of gases through partially-saturated soils is a diffusive process, which can be described by a generalisation of Fick's law.
  - In the generalisation of Fick's law, the molecular diffusion coefficient is multiplied by a parameter called the tortuosity, to account for the presence of the soil particles. A generic value for the tortuosity is of the order of a few percent.
- Methane is oxidised in near-surface soils by methanotrophic microbes.
  - Methane oxidation can be modelled as a first-order reaction, with a rate constant likely to be in the range  $10^{-5} \text{ s}^{-1}$  to  $10^{-4} \text{ s}^{-1}$ .
- The processes of diffusion and methane oxidation are coupled. A diffusion-reaction equation will describe a quasi-steady-state flux of  $^{14}\text{CH}_4$  being oxidised to  $^{14}\text{CO}_2$  in the soil.
  - This equation has a characteristic length scale over which the  $^{14}\text{CH}_4$  will be oxidised.
  - The characteristic length scale is likely to be no more than a few tens of centimetres. Provided that the water table is at a depth which is more than a few times this length scale, then conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  will be essentially complete, regardless of the particular values of the diffusion coefficient and the oxidation rate constant.

### 7.2 Overview of the New $^{14}\text{C}$ Gas Assessment Model

The new model differs from previous models, which were all multi-compartment models, in that the concentrations and fluxes of  $^{14}\text{C}$  in the system are calculated from representations of the key processes (e.g. molecular diffusion through the soil; methane oxidation by microbes; turbulent transport through the plant canopy; dispersion in the overlying atmosphere; dissolution in the soil water; and uptake of contaminated water through a plant's roots).

Section 4 discussed the conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  within the soil. It introduced the concept of a characteristic length scale over which methane is oxidised by methanotrophic microbes. Although this characteristic length scale is specific to the site and ecosystem under consideration, it seems generally to be of the order of tens of centimetres in agricultural or arable environments, as confirmed by our experimental programme [4,5]. In the region where  $^{14}\text{CH}_4$  originating from a GDF

will be released to the biosphere, the water table could be at a depth which is more than a few times this length scale, and in that case conversion of  $^{14}\text{CH}_4$  to  $^{14}\text{CO}_2$  will be essentially complete. There is then the potential for the uptake of  $^{14}\text{CO}_2$  by plants.

Section 5 discussed the uptake of  $^{14}\text{CO}_2$  by plants. It argued that two major processes contribute to the uptake of  $^{14}\text{CO}_2$  by plants: photosynthesis, and transpiration. The processes of barometric pumping and cycling of  $^{14}\text{C}$  back to the soil were also considered, but were discounted as minor contributors.

In the case of photosynthesis, the specific activity in the biomass of a plant is equated to the specific activity of the canopy atmosphere, which can be calculated by:

- Multiplying the  $^{14}\text{CO}_2$  flux from the soil by a quantity called the aerodynamic resistance (this product gives an estimate of the  $^{14}\text{CO}_2$  concentration in the canopy atmosphere); and
- Dividing the result by the  $^{12}\text{CO}_2$  concentration in the canopy atmosphere.

The aerodynamic resistance is the key parameter in this calculation, and has values of several tens  $\text{s m}^{-1}$  for many crops.

If the Potentially Exposed Groups and their diets could be clearly specified, then it might be appropriate to follow a crop-specific approach, and in fact this was done in the recent LLWR 2013 assessment [15]. Here, however, we propose a simpler approach. Generally the aerodynamic resistance increases with shorter vegetation, and so it is cautious (but by a factor of two or three at most) to apply the aerodynamic resistance of a grass reference surface to all plant types, when calculating the specific activity in the biomass of the plants. A standard work on crop evaporation-transpiration [54] states that the aerodynamic resistance of the grass reference surface, assuming that the grass has a constant height of 0.12m, is:

$$R_{a,air} = \frac{208}{u_a} \quad (7.1)$$

where

$u_a$  is the wind speed at 2m above the ground surface (generically, about  $2 \text{ m s}^{-1}$ ).

In the case of transpiration, the additional source of  $^{14}\text{C}$  in the biomass of a plant can be computed essentially by multiplying the concentration of  $^{14}\text{CO}_2$  in the soil gas with:

- The Henry's law constant (this product gives the concentration of  $^{14}\text{CO}_2$  in the soil water); and
- The transpiration ratio (i.e. the amount of water taken up by a plant per unit mass of the plant).

The transpiration ratio is the key parameter in this calculation. It has values in the range from 450 to 950  $\text{kg H}_2\text{O}$  transpired per  $\text{kg}$  dry mass produced for C3 plants in the temperate zone. A correction factor accounts for the possibility that uptake of  $^{14}\text{C}$  through the plant's roots may be an active process, and the consideration that some of the  $^{14}\text{C}$  will be lost as a result of maintenance respiration.

Section 6 has discussed the dose from ingestion of  $^{14}\text{C}$ -contaminated plants. It assumed that animals will derive most of their food from the contaminated area, but humans will fulfil only a fraction of their dietary requirements (because major contributors to carbon in the diet, such as cereals and sugars, will be sourced mostly from elsewhere). As in previous  $^{14}\text{C}$  gas assessments, this fraction is cautiously taken as 0.3, and then a standard calculation can be used to relate the specific activity of  $^{14}\text{C}$  in humans to the effective dose rate.

## 7.3 Comparison with Previous Assessments

Table 7.1 lists the results obtained for the effective dose rate ( $\text{Sv yr}^{-1}$ ) to a representative member of a Potentially Exposed Group per unit flux of  $^{14}\text{C}$  ( $\text{Bq m}^{-2}\text{s}^{-1}$ ) at the bottom of the vadose zone, and compares the results with the values used in earlier key assessments for RWM. Also shown are the associated limiting release rates that would comply with the regulatory risk guidance level.

**Table 7.1 Flux to Dose Conversion Factors Used By RWM (and Formerly By Nirex and Then NDA RWMD)**

Assessment	Flux to Dose Conversion ( $\text{Sv yr}^{-1}$ ) per ( $\text{Bq m}^{-2}\text{s}^{-1}$ )	Limiting Release Rate ( $\text{TBq yr}^{-1}$ )	
		Area = $10^4 \text{ m}^2$	Area = $10^6 \text{ m}^2$
Nirex 97 [8] and GPA (03) [9]	$2.21 \cdot 10^{-5} A^{1/2 \dagger}$	$2.4 \cdot 10^{-3}$	$2.4 \cdot 10^{-2}$
GPA (03) Update [10]	$0.6280 \ddagger$	$8.4 \cdot 10^{-6}$	$8.4 \cdot 10^{-4}$
$^{14}\text{C}$ -IPT Phase 1 Model [6] <i>photosynthesis only</i>	0.0034		
$^{14}\text{C}$ -IPT Phase 1 Model [6] <i>plus transpiration</i>	0.0086	$6.1 \cdot 10^{-4}$	$6.1 \cdot 10^{-2}$
New Model <i>photosynthesis only</i>	<b>0.0107</b>		
New Model <i>plus transpiration</i>	<b>0.0225</b>	<b><math>2.34 \cdot 10^{-4}</math></b>	<b><math>2.34 \cdot 10^{-2}</math></b>

<sup>†</sup> In Nirex 97 and GPA (03), the flux to dose conversion factor depended on the release area,  $A$ .

<sup>‡</sup> In GPA (03) Update, the flux to dose conversion factor included a term  $F_{\text{metab}}$  to account for the possibility that a large flux of bulk methane could overwhelm the oxidative capacity of the soil, in which case the oxidation of  $^{14}\text{CH}_4$  might be incomplete. This term has been ignored here because we now recognise that the oxidative capacity of a soil will respond to the flux of bulk methane [88]; for example, observations show that most of the methane above landfills, from which the fluxes of bulk methane could be orders of magnitude larger than from a GDF, can be oxidised [89]. As a matter of fact, the reported peak values of the effective dose rate in GPA (03) Update did not depend on  $F_{\text{metab}}$ , because the flux of bulk methane was small at the time of the peak (i.e. shortly after closure of the GDF).

It is clear that the flux to dose conversion factors have changed significantly over the years. The reasons for these changes can be explained as follows.

First, comparing the similar Nirex 97 and Generic post-closure Performance Assessments (referred to as GPA (03)) with the 2007 update to GPA (03) (referred to as GPA (03) Update), the flux to dose conversion factor is much larger in the latter assessment. That is because the earlier assessments used the RIMERS model (see Section 2.3.1), which assumed that the soil solution, soil atmosphere, below-canopy atmosphere and above-canopy atmosphere would be mixed rapidly, and therefore would all have the same specific activity. In contrast, later assessments model the transport of  $^{14}\text{C}$  through the soil and plant canopy, and thus compute the specific activity as a function of location.

Subsequent changes to the flux to dose conversion factor correspond essentially to enhancements in the way that the transport of  $^{14}\text{C}$  through the soil or plant canopy is modelled.

Second, the GPA (03) Update assessment is by far the most cautious. The explanation is that the model, which was enhanced RIMERS (see Section 2.3.2), assumed that transport of  $^{14}\text{CO}_2$  through the lower plant canopy was a molecular diffusion process rather than a turbulent process. The consequence was that estimates of  $^{14}\text{CO}_2$  residence times in the lower plant canopy were much too long. In particular, the GPA (03) Update model computed the  $^{14}\text{CO}_2$  residence time as:

$$t_r = h^2/d_{CO_2} \sim 1^2/10^{-5} = 10^5 \text{ s} \quad (7.2)$$

where  $h$  is a length scale and  $d_{CO_2}$  is the molecular diffusion coefficient of carbon dioxide in air, whereas now we calculate the  $^{14}CO_2$  residence time as:

$$t_r = h R_{a,air} \sim 1 \times 10^2 = 10^2 \text{ s} \quad (7.3)$$

where  $R_{a,air}$  is the aerodynamic resistance.

The change to using the aerodynamic resistance was introduced with the update from the LLWR (2011) assessment to the LLWR (2013) assessment. All subsequent assessments, including both the  $^{14}C$ -IPT Phase 1 model and the new  $^{14}C$  gas assessment model, use the aerodynamic resistance approach.

Thirdly, comparing the “photosynthesis only” results for the  $^{14}C$ -IPT Phase 1 model and the new  $^{14}C$  gas assessment model, the flux to dose conversion factor is about three times larger in the latter model. That is because the new  $^{14}C$  gas assessment model makes more robustly justified assumptions about plant type and height than the  $^{14}C$ -IPT Phase 1 model, and therefore derives a slightly larger value of the aerodynamic resistance (i.e. about  $100 \text{ s m}^{-1}$  for a wind speed of  $2 \text{ m s}^{-1}$  at 2m above the ground surface, rather than a few tens  $\text{m s}^{-1}$ ). A benefit of this approach is that it is independent of crop-specific details about the Potentially Exposed Groups and their diets.

Fourthly, comparing the “plus transpiration” results for the  $^{14}C$ -IPT Phase 1 model and the new  $^{14}C$  gas assessment model, the flux to dose conversion factor is about four times larger in the latter model. The explanation for most of this difference is that the  $^{14}C$ -IPT Phase 1 model underestimated the tortuosity of the soil, and therefore predicted  $^{14}CO_2$  diffusion coefficients that are too large and  $^{14}CO_2$  residence times in the soil that are too short (by about an order of magnitude).

Both the  $^{14}C$ -IPT Phase 1 model and the new  $^{14}C$  gas assessment model agree that transpiration is a significant pathway for uptake of  $^{14}C$  by plants (i.e. transpiration contributes slightly more than photosynthesis to the uptake of  $^{14}C$ ).

## 7.4 Recommended Flux to Dose Conversion Factor

Based on the considerations above, it is recommended that future  $^{14}C$  gas assessment models should assume that the effective dose rate to a representative member of a Potentially Exposed Group per unit flux of  $^{14}C$  at the bottom of the vadose zone is:

$$0.0225 \text{ (Sv yr}^{-1}\text{) per (Bq m}^{-2}\text{s}^{-1}\text{)}$$

## 7.5 Advantages of the New $^{14}C$ Gas Assessment Model

It is considered that the new  $^{14}C$  gas assessment model has a number of advantages. Most notably, it emphasises the key processes and parameters controlling the uptake of  $^{14}C$  by plants, and subsequently by humans. Each of the key processes is represented using a simple analytical sub-model, which is founded on widely accepted understanding. This will make it easier:

- To communicate the ideas underlying the model;
- To quantify the model parameters, and their uncertainties; and
- To audit the model.

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# Appendices

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- Appendix 1      Assessment of Other <sup>14</sup>C-bearing Gases (by Mike Thorne)
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# Appendix 1

## Assessment of Other <sup>14</sup>C-bearing Gases (by Mike Thorne)

### Contents

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# Assessment of Other $^{14}\text{C}$ -bearing Gases

In the radiological assessment model described in the main body of this report, attention is focused on the behaviour of  $^{14}\text{C}$ -bearing methane after its entry into the soil zone. For the purposes of assessment, it is argued that it is appropriate to assume that:

- The methane is completely oxidised to carbon dioxide within the soil; subsequently
- Some of the  $^{14}\text{CO}_2$  is taken up by plants either via the roots or via the foliage; and then
- Some of the  $^{14}\text{C}$  is incorporated in plant biomass through photosynthesis.

However, other  $^{14}\text{C}$ -bearing gases could be released to the soil zone. Possibilities include organic compounds containing:

- One carbon atom, for example C1 compounds:
  - Carbon monoxide, CO
  - Formaldehyde, HCHO
- Two carbon atoms, for example C2 compounds:
  - Acetylene,  $\text{C}_2\text{H}_2$
  - Ethene,  $\text{C}_2\text{H}_4$
  - Ethane,  $\text{C}_2\text{H}_6$
- More carbon atoms

In this list, chemical compounds that contain a small number of carbon atoms are of most interest because (a) it is reasonable to suppose that only simple molecules will be formed by the chemical processes that will occur in a GDF (e.g. corrosion of metals and leaching of radionuclides from irradiated graphite), and (b) there is a general trend for the boiling points of organic compounds to increase as their molecular masses increase.

Therefore, this appendix considers acetylene, ethylene and ethane, and also carbon monoxide. The metabolism of these gases in soils and the potential for their uptake by plants are addressed, with a particular emphasis on carbon monoxide.

## Acetylene, Ethylene and Ethane

### Processes of Metabolism in the Soil Zone

In an earlier report, Thorne [1] considered:

- Whether there are microbial communities in the soil zone that can metabolise acetylene, ethylene and ethane;
- Whether the processes used by those communities to metabolise acetylene, ethylene and ethane would be suppressed by the presence of an excess of methane, or, equivalently, whether they would metabolise methane in preference to those other gaseous hydrocarbons.

Thorne [1] pointed out that the utilisation of acetylene as a microbial substrate is well known in the context of dinitrogen fixation [2]. The process of biological  $\text{N}_2$  fixation is restricted, so far as is known, to prokaryotic microbes including many genera of soil bacteria, cyanobacteria and a few actinomycetes. These microbes can fix dinitrogen as either free-living forms or in associative symbioses with higher plants. Fixation is mediated by the nitrogenase complex. Under molybdenum sufficiency, it comprises a Mo-Fe protein (dinitrogenase) and a Fe-protein (dinitrogenase reductase). Under molybdenum deficiency, molybdenum can be replaced by



vanadium and there is at least one alternative nitrogenase that can operate in conditions of both molybdenum and vanadium starvation [2].

In the late 1960s, it was discovered that nitrogenase can reduce acetylene to ethylene. From this was born the simple acetylene reduction assay for nitrogenase activity. Thus, there is extensive evidence for the assimilation of acetylene in various experimental and field contexts. In particular, it has been demonstrated that the nitrogenase complex is under strong regulation by the level of combined nitrogen (ammonium, nitrate and organic nitrogen) in the medium or the environment. Such strong regulation is required because dinitrogen fixation is extremely costly in energy [2]. High levels of oxygen also inhibit nitrogenase activity, so higher rates of dinitrogen fixation are typically associated with seasonally or chronically wet soils. Other significant factors are temperature, phosphorus supply, other inorganic nutrients (particularly trace metals) and the pH of the environment. However, methane does not seem to have been identified as a substrate for nitrogenase activity [2]. Dihydrogen can be a product of nitrogenase activity, but it is not a substrate [2].

Thus, when acetylene enters the soil, either carried by methane or molecular hydrogen, it has the potential to be metabolised by the nitrogenase system. However, this metabolism leaves the carbon backbone of the molecule (though transforming the triple bond to a double bond) and ethylene is evolved. Conversely, ethylene and ethane will not be utilised as substrates by the nitrogenase system. This strongly suggests that when  $^{14}\text{C}$ -bearing acetylene, ethylene and ethane enter the soil system, no  $^{14}\text{C}$  will be retained through the activities of the nitrogenase system, though there may be some transformation of  $^{14}\text{C}$ -acetylene to  $^{14}\text{C}$ -ethylene on its passage through soil. The degree of such transformation will depend on the combined nitrogen status of the soil, its oxygenation and various other factors of rather less significance.

As to whether methanotrophs (obligate aerobes that use methane as a sole carbon and energy source) can use acetylene, ethylene and ethane as substrates, it should be noted that the methanotrophs are a subset of the methylotrophic bacteria, all of which oxidise compounds lacking C-C bonds, i.e. C1 compounds [3]. This characteristic seems to have arisen early in evolutionary history as the methanotrophs and methanogens share many homologous genes for C1 metabolism, despite the large evolutionary distance between the *Archea* and *Proteobacteria* [3]. This lack of ability to metabolise C-C bonds means that methanotrophic and methanogenic activities in soil would not be a factor in determining the metabolism of acetylene, ethylene and ethane.

In summary, although acetylene may be metabolised to ethylene in some soil contexts, there seems no reason to suppose that any significant fraction of  $^{14}\text{C}$  entering the soil system as acetylene, ethylene or ethane would be either retained in the soil or taken up by plants.

## Carbon Monoxide

### Processes of Metabolism in the Soil Zone

Like methane, carbon monoxide may be either produced or consumed in soil. Thus, for example, in forest soils, optimal uptake occurred at water contents of 30 to 60 percent of saturation, but extended drying led to decreased uptake and net carbon monoxide production [4]. Carbon monoxide production is thought to be largely abiological in nature. This production has been attributed in part to photochemical organic matter oxidation. However, profiles obtained under light and dark conditions for both pine forest and cultivated soils suggest that other processes may be more important [4]. Kinetic analyses [5] of field measurements of carbon monoxide production and consumption demonstrated that whereas carbon monoxide consumption was an apparently first-order reaction, carbon monoxide production was apparently a zero-order reaction. In these experiments, the consumption rates varied between  $0.13$  and  $1.03 \text{ nL cm}^{-2}\text{min}^{-1}$ , whereas production rates varied between  $0.01$  and  $0.26 \text{ nL cm}^{-2}\text{min}^{-1}$ . A typical net consumption rate from these experiments was  $0.5 \text{ nL cm}^{-2}\text{min}^{-1}$ . This corresponds to  $9 \text{ mg}[\text{CO}] \text{ m}^{-2}\text{d}^{-1}$ .

As production arises from the oxidation of organic matter in soil, it is of limited relevance in the current context. Hence attention is focused on processes of oxidation.

Carbon monoxide serves as a growth substrate for a similar diversity of bacteria to those served by H<sub>2</sub>. The best-studied bacterial groups are the aerobic CO-oxidizing (carboxydophilic) bacteria and the CO-utilizing homoacetogenic bacteria. The aerobic carboxydophilic bacteria possess a molybdopterin cofactor and dehydrogenate CO plus water to CO<sub>2</sub> plus reducing equivalents. The homoacetogenic bacteria catalyze the same reaction with a nickel-containing enzyme whose main function is the synthesis or degradation of acetyl coenzyme A (CoA). Carbon monoxide consumption has also been reported for methanogens that possess a nickel-containing CO dehydrogenase, and in phototrophic bacteria. In addition to these various bacteria that are all able to use carbon monoxide as a substrate for growth, carbon monoxide can be oxidized by monooxygenases without being used for bacterial growth [6].

Although no threshold for aerobic carbon monoxide utilization has been reported, the commonly known aerobic CO-utilizing bacteria have a much lower affinity for carbon dioxide than is observed in soils, so these bacteria cannot account for observed consumption in soils. CO-oxidizing nitrifying bacteria or oligotrophic bacteria have been suggested as possible alternative agents [6]. More generally, the CO-oxidizing microorganisms in soil seem only to use CO as a substrate to a very limited degree and assimilate only minor amounts of <sup>14</sup>CO into biomass [6,7].

Conrad [6] commented that the role that anaerobic carbon monoxide utilizers (acetogens, methanogens, etc.) may play in anoxic soils is unexplored. The turnover of carbon monoxide in paddy fields is thought to be low. Submerged paddy soil seems to be a small source of atmospheric carbon monoxide, but the plants of these wetlands emit significant amounts of the gas. Peat soils emit significant amounts of carbon monoxide when the water table is high, but act as a sink for atmospheric carbon monoxide when the water table is low. It is thought possible that the CO production at high water table is due to photodynamic effects ("photodynamic effect" is a term used in photobiology to refer to photo-induced damage requiring the simultaneous presence of light, a photo-sensitizer and molecular oxygen) acting on the *Sphagnum* plants.

## Processes of Metabolism in Plants

Carbon monoxide is reported to be metabolized by plants [6]. In addition to the studies referenced by Conrad [6], Bidwell and Fraser [8] described a study in which <sup>14</sup>CO was supplied to bean leaves in light or darkness at 200-360 ppmv in air. In light, the CO was converted mainly to sucrose and proteins. The distribution of <sup>14</sup>C among the products suggested that most of the absorbed CO was reduced and incorporated into serine and this was converted into sucrose. Some CO was oxidized to CO<sub>2</sub>, part of which may have been re-fixed in photosynthesis, but this was not the major pathway of metabolism. In darkness, CO was absorbed nearly as fast as in the light, but was almost completely converted to CO<sub>2</sub> and released. In the light, the rate of fixation was roughly proportional to the concentration of CO, but was unrelated to rates of photosynthesis. The CO-fixing capacity of vegetation was calculated to be 12-120 kg[CO] km<sup>-2</sup>d<sup>-1</sup> (12-120 mg[CO] m<sup>-2</sup>d<sup>-1</sup>), which was stated to approach the rate found in soils at much higher concentrations of CO than those used in these experiments.

## Oxidation Rates in Soils

Ingersoll [9] tested a wide range of soil types for their ability to remove carbon monoxide from the atmosphere. The observed rates ranged from 2.16 to 16.99 mg[CO] m<sup>-2</sup>h<sup>-1</sup> (52 to 408 mg[CO] m<sup>-2</sup>d<sup>-1</sup>). These rates are higher than the typical rate of 9 mg[CO] m<sup>-2</sup>d<sup>-1</sup> found by Conrad and Seiler [5]. Ingersoll [9] found that, generally, soils high in organic content and low in pH had the highest rates of carbon monoxide uptake. For comparison, Spratt and Hubbard [10] measured oxidation rates of 2.2 to 12.6 nmol[CO] g<sup>-1</sup>h<sup>-1</sup> for moistened or humidified soils. Assuming that oxidation occurs in the top 0.1m of soil, these rates correspond to 150 to 850 mg[CO] m<sup>-2</sup>d<sup>-1</sup>. Bartholomew and Alexander [7] measured a rate of 0.81 nmol[CO] oxidized per 5g of soil per hour. Again, assuming that oxidation occurs in the top 0.1m of soil, this

corresponds to a rate of about  $11 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . Bartholomew and Alexander [7] cite rates measured in other studies of 8.2, 0.54 and  $0.08 \text{ mg[CO] per m}^2$  of soil surface per hour (note that this is the area of the soil particles, not the area of the upper surface of a soil column in the field) compared with their value of  $0.019 \text{ mg[CO] per m}^2$  of soil surface per hour. These other values correspond to field values of about 46 to  $4,750 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . For Maine forest soils, King [4] reported a mean net *in situ* oxidation rate of  $6 \text{ mg[CO] m}^{-2}\text{d}^{-1}$  and compared this with a typical methane consumption rate of 1 to  $3 \text{ mg[CH}_4\text{] m}^{-2}\text{d}^{-1}$ .

Overall, it appears that carbon monoxide oxidation rates in soils can range from about  $10 \text{ mg[CO] m}^{-2}\text{d}^{-1}$  up to more than  $1,000 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . The reasons for this wide range of variation are not well understood (though major factors may be that they derive from a mix of field measurements and laboratory measurements on small soil samples, and at very different concentrations of carbon monoxide), but it is clear that net oxidation rates are higher than those for methane, which are typically in the range of 0.2 to  $3.6 \text{ mg[CH}_4\text{] m}^{-2}\text{d}^{-1}$  [11].

In respect of the kinetics of the oxidation process, Ingersoll [9] found half times for reduction in carbon monoxide concentrations in test chambers embedded in the soil surface of one to two hours. With chambers containing amounts of dried soil ranging from 0.2 kg to 2.9 kg, half times for concentration reduction ranged from less than 2 hours (2.9 kg) to about 18 hours (0.2 kg). It should be noted that the various studies by Ingersoll [9] seem to have been undertaken at 100 ppmv[CO], i.e. at much higher than ambient concentrations (see below). For comparison, Conrad and Seiler [5] found rate coefficients for oxidation of  $0.072 \text{ min}^{-1}$  (half time 9.6 minutes) under aerobic conditions and  $0.016 \text{ min}^{-1}$  (half time 43 minutes) under anaerobic conditions. When the soil was pre-incubated anaerobically, the anaerobic consumption rate increased to  $0.019 \text{ min}^{-1}$  and the aerobic rate decreased to  $0.042 \text{ min}^{-1}$ .

Spratt and Hubbard [10] examined the kinetics of carbon monoxide oxidation in one roadside soil. They found that the reaction exhibited Michaelis-Menten kinetics with a  $K_m$  value of 14.9 ppmv. This could be compared with the mean carbon monoxide concentration at this site for 1979 of 1.4 to 1.8 ppmv with highest one-hour-average values from the various monitoring stations in the vicinity of 17 to 23 ppmv. King [4] found that an O-horizon forest soil had a  $K_m$  value of  $16.9 \pm 1.7$  ppmv and a  $V_{max}$  of  $6.9 \pm 0.4 \mu\text{g[CO] g(fresh weight)}^{-1}\text{h}^{-1}$  or about  $16,500 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . For a typical air concentration of 0.1 ppmv and no threshold in the Michaelis-Menten kinetics, this would give a field oxidation rate of  $97 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . For a concentration of 1.4 to 1.8 ppmv, as observed by Spratt and Hubbard [10], the oxidation rate would be 1260 to  $1590 \text{ mg[CO] m}^{-2}\text{d}^{-1}$ . These simple calculations demonstrate that much of the observed variability in carbon monoxide oxidation rates can be explained by variations in the ambient and experimental concentrations at which they were measured.

## Implications for Assessment Modelling

From the above review, it is clear that carbon monoxide oxidation occurs in soils in both aerobic and anaerobic conditions. Oxidation rates, expressed as  $\text{mg[CO] m}^{-2}\text{d}^{-1}$ , are significantly higher than those of methane and the kinetics of oxidation are at least as rapid. As with methane, the oxidation rate appears to exhibit Michaelis-Menten kinetics without a threshold and high oxidation rates occur even at low ambient concentrations of carbon monoxide, e.g. below 1 ppmv. For comparison, mean monthly atmospheric concentrations of carbon monoxide in the atmosphere range up to 0.3 ppmv [12]. Global background concentrations of carbon monoxide range between 0.05 and 0.12 ppmv. In urban traffic environments of large European cities, the 8-hour average carbon monoxide concentrations are generally lower than 17 ppmv with short-lasting peaks below 53 ppmv [13]. Oxidation can result in the incorporation of a small fraction of the carbon from oxidised carbon monoxide into the soil biomass, but the majority of the carbon seems to be co-metabolized and converted directly to carbon dioxide. Overall, this indicates that it is appropriate to assume that  $^{14}\text{C}$ -bearing carbon monoxide entering soil from below is completely oxidized to  $^{14}\text{C}$ -bearing carbon dioxide within the soil. This is the same assumption as is made for  $^{14}\text{C}$ -bearing methane, so the same assessment methodology can be used. Even if a small amount of carbon monoxide were to escape from the soil surface, it would be available for uptake by plants

and, in daylight hours, any such uptake would be effectively incorporated into biomass via the serine-sucrose pathway.

## Recommendations

Although acetylene may be metabolised to ethylene in some soil contexts, there seems no reason to suppose that any significant fraction of  $^{14}\text{C}$  entering the soil system as acetylene, ethylene or ethane would be either retained in the soil or taken up by plants.

It is appropriate to assume that  $^{14}\text{C}$ -bearing carbon monoxide entering soil from below is completely oxidized to  $^{14}\text{C}$ -bearing carbon dioxide within the soil. This is the same assumption as is made for  $^{14}\text{C}$ -bearing methane, and so the same assessment methodology can be used.

For completeness, we record that the committed effective dose per unit intake of  $^{14}\text{CO}$  by inhalation is  $8.0 \times 10^{-13} \text{ Sv Bq}^{-1}$  for adults [14].

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# Appendix 2

## Transport through Plant Canopies

### Contents

Layers of the Atmosphere

Turbulent Transport in the Atmosphere

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Flux of Carbon Dioxide

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# Transport through Plant Canopies

One of the processes that should be included in an assessment model is the transport of gases through plant canopies. This section summarises current understanding about the transport of gases through and above plant canopies. It focuses, in particular, on the “aerodynamic resistance”, which was identified as a key variable in Section 5.1.1. Much of the following material can be found in standard works on micrometeorology, e.g. [1,2].

## Layers of the Atmosphere

The atmosphere is divided into five main layers, the lowest of which is the troposphere. The troposphere is heated mostly by transfer of energy from the Earth’s surface, and so on average the lowest part of the troposphere is warmest and temperature decreases with altitude. This promotes vertical mixing.

The part of the troposphere that is closest to the Earth, and that is affected by the Earth’s surface, is called the planetary boundary layer. During the day the planetary boundary layer usually is well-mixed, mainly through turbulent diffusion, while at night it becomes stably stratified, with weak mixing. The depth of the planetary boundary layer ranges from about 100m on clear, calm nights to more than 3,000m during the afternoon in dry regions. (In wet regions, the depth of the planetary boundary layer can reach up to about 2,000m.)

The lowest 10% of the planetary boundary layer is called the atmospheric surface layer. It also is called the constant flux layer, because of the assumption that fluxes are constant with height within this layer. Transfer in the atmospheric surface layer is due to turbulence; molecular exchange processes become important only within a few millimetres of the Earth’s surface.

The atmospheric surface layer can be divided into the roughness sublayer and the inertial sublayer.

Turbulent flow just above a crop’s canopy will be influenced by the distribution and structure of the foliage elements. This is the roughness sublayer, and it extends from the top of the canopy to about 1.5 times the canopy height [1].

The inertial sublayer is above the roughness sublayer. Fluxes are constant with height within this sublayer. Therefore micrometeorological measurements (of turbulence or of vertical profiles) can be interpreted most easily to determine fluxes within this sublayer.

## Turbulent Transport in the Atmosphere

Reynolds introduced the standard technique of decomposing a turbulent flow into the sum of a mean value and a randomly fluctuating value.

For example, if the  $z$ -component of the wind velocity is  $w$ , then:

$$w = \overline{w} + w'(t) \quad (\text{A2.1})$$

where:

$\overline{w}$  is the mean value (indicated by an overline) of the velocity component; and  
 $w'$  is the fluctuating part (indicated by a prime symbol) of the velocity component.

This “Reynolds decomposition” technique, together with some assumptions (i.e. density fluctuations are negligible, and the mean vertical flow is zero), can be used to show that within the atmospheric surface layer the  $z$ -component of the turbulent flux of a scalar quantity  $c$  is:



$$F_c = \overline{\rho_a w' c'} \quad (\text{A2.2})$$

where:

$F_c$  is the  $z$ -component of the turbulent flux;  
 $\overline{\rho_a}$  is the mean value of the air density; and  
 $c'$  is the fluctuating part of the scalar quantity.

Thus the  $z$ -component of the turbulent flux of the scalar quantity  $c$ , or “eddy flux”, is computed as a covariance between the fluctuating part of the vertical wind speed and the fluctuating part of the scalar quantity, multiplied by the mean density of the air.

### Flux-gradient Method or K-theory

Next, the concept of the “mixing length”  $l_c$  is introduced.

It is assumed that a small volume of air will conserve its properties when it moves through a characteristic length scale  $l_c$ , before mixing with the surrounding air. The fluctuation in  $c$  that the small volume experiences when it moves is  $c'$ . This fluctuation is assumed to correspond to the difference in  $c$  between the small volume, after it has moved through the mixing length, and the surrounding environment. In equations:

$$\begin{aligned} c' &= c(z) - c(z + l_c) \\ &\approx -l_c \frac{\partial c}{\partial z} \end{aligned} \quad (\text{A2.3})$$

Substituting this result into Equation (A2.2):

$$\begin{aligned} F_c &= \overline{-\rho_a w' l_c \frac{\partial c}{\partial z}} \\ &= \overline{-\rho_a K_c \frac{\partial c}{\partial z}} \end{aligned} \quad (\text{A2.4})$$

This equation is the first-order closure approximation for turbulent transfer. The quantity  $K_c = \overline{w' l_c}$  is called the turbulent transfer coefficient<sup>22</sup>, or sometimes the “eddy diffusivity”.

Equation (A2.4) has been used to develop empirical relations between fluxes of momentum, mass and heat, and their respective gradients.

### Logarithmic Wind Profile

If the quantity is the horizontal component of momentum  $u$ , then the vertical component of the turbulent flux of horizontal momentum is:

$$F_M = \overline{\rho_a u' w'} \quad (\text{A2.5})$$

<sup>22</sup>  $K_c$  has units of  $\text{m}^2\text{s}^{-1}$ , and can be determined from measurements of wind speed profiles (the aerodynamic approach) or from measurements of net radiation balance, and humidity and temperature profiles (the energy balance approach).

Provided that the turbulent flux  $F_M$  is constant with height, then it is equal to the force per unit ground area, or the shearing stress  $\tau$ :

$$\tau = \overline{\rho_a u'w'} \quad (\text{A2.6})$$

The ratio:

$$\sqrt{\frac{\tau}{\overline{\rho_a}}} = \sqrt{\overline{u'w'}} = u_* \quad (\text{A2.7})$$

is called the “friction velocity”  $u_*$ .

From Equation (A2.4), the shearing stress also can be written as:

$$\tau = -\overline{\rho_a} K_M \frac{\partial u}{\partial z} \quad (\text{A2.8})$$

where  $K_M$  is the turbulent transfer coefficient for momentum.

Observations suggest that both turbulent mixing and wind speed increase with height. The simplest assumption for the dependence of  $K_M$  on height is:

$$K_M = \kappa u_* z \quad (\text{A2.9})$$

where  $\kappa$  is a constant called the von Karman constant, which usually is assigned a value of 0.41, as determined by experiment. (The product  $\kappa z$  is analogous to the mixing length, and gives an indication of the mean size of turbulent eddies.)

Because the shearing stress is assumed to be constant with height, it follows that the gradient of wind speed is:

$$\frac{\partial u}{\partial z} = \frac{u_*}{\kappa z} \quad (\text{A2.10})$$

Finally, integration of Equation (A2.10) gives:

$$u = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_0}\right) \quad (\text{A2.11})$$

where  $z_0$  is a constant called the “roughness length”. This is the well-known logarithmic wind profile, which is valid over many types of uniform surface.

## The Effects of Vegetation

The wind profile is displaced upwards over tall vegetation.

In this situation, a “zero plane displacement”  $d$  is introduced. Raupach and Thom [3] define the zero plane displacement as the mean level where momentum is absorbed by a canopy. This leads to new definitions of the turbulent transfer coefficient for momentum:

$$K_M = \kappa u_* (z - d) \quad (\text{A2.12})$$

and of the logarithmic wind profile:

$$u = \frac{u_*}{\kappa} \ln \left( \frac{z - d}{z_0} \right) \quad (\text{A2.13})$$

## Roughness Length and Zero Displacement Plane

In practice, the parameters  $z_0$  and  $d$  are evaluated from the logarithmic wind profile by plotting the logarithm of height versus wind speed during near-neutral conditions. In this case, the intercept is:

$$\ln(z_0)$$

and the slope is related to:

$$\frac{u_*}{\kappa}$$

Textbooks, e.g. [1,2], give rules of thumb for the roughness length and zero plane displacement. Based mainly on measurements over agricultural crops,  $z_0$  is in the range 8%–12% of canopy height and  $d$  is in the range 60%–70% of canopy height (see Table A2.1).

**Table A2.1 Aerodynamic Properties of Surfaces [1]**

Surface	Roughness Length (m)	Zero Plane Displacement (m)
Water	$10^{-4} - 0.001$	n/a
Sand	0.0003	n/a
Soil	0.001 – 0.01	n/a
Grass (short)	0.001 – 0.003	<0.07
Grass (long)	0.04 – 0.1	<0.66
Crop	0.04 – 0.2	<3
Orchard	0.5 – 1	<4
Deciduous Forest	1 – 6	<20
Conifer Forest	1 – 6	<30

## The Aerodynamic Resistance

A quantitative assessment of the radiological impacts of  $^{14}\text{C}$  bearing gases has to relate the flux of  $^{14}\text{CO}_2$  above the canopy to processes within the canopy. Micrometeorologists find it helpful to use an electrical analogue to do this. The rate of exchange between a leaf and its environment, for example, can be estimated when:

- The potential of a quantity (e.g.  $^{14}\text{CO}_2$  concentration) is known both at the leaf and in the overlying air; and
- The resistances can be measured or estimated.

The electrical analogue approach depends on the observation that Equation (A2.8), which expresses momentum flux in terms of the gradient of horizontal momentum, can be rewritten in a form analogous to Ohm's law. An aerodynamic resistance  $R_{a,air}$  to momentum transfer between heights  $z_1$  and  $z_2$ , where the wind speeds are  $u_1$  and  $u_2$  respectively, is introduced:

$$\tau = \bar{\rho}_a \frac{u_2 - u_1}{R_{a,air}} \quad (\text{A2.14})$$

As a special case, the aerodynamic resistance for momentum transfer between a height  $z$ , where the wind speed is  $u$ , and the level  $d + z_0$ , where the extrapolated value of  $u$  is zero, can be evaluated as:

$$\begin{aligned} R_{a,air} &= \frac{u}{u_*^2} \\ &= \frac{\ln\left(\frac{z-d}{z_0}\right)}{\kappa u_*} \\ &= \frac{\left[\ln\left(\frac{z-d}{z_0}\right)\right]^2}{\kappa^2 u} \end{aligned} \quad (\text{A2.15})$$

Note that this particular resistance equation applies to momentum transfer in neutral conditions.

## Flux of Carbon Dioxide

Turning to the concentration of carbon dioxide  $c$ , by analogy with Equation (A2.8) a flux-gradient equation in neutral conditions can be written as:

$$F_c = -K_c \frac{\partial c}{\partial z} \quad (\text{A2.16})$$

In this equation, the turbulent transfer coefficient for carbon dioxide  $K_c$  is approximately equal to the turbulent transfer coefficient for momentum  $K_M$ :

$$K_c \approx K_M \quad (\text{A2.17})$$

This is a consequence of the "similarity hypothesis", which asserts that turbulent eddies should transport all quantities equally effectively in neutral conditions [1]. Actually, empirical evidence shows that in slightly unstable conditions  $K_c$  can exceed  $K_M$  by a few tens of percent<sup>23</sup> [1]. However, the aerodynamic resistances to transfers of water vapour, carbon dioxide and sensible heat are identical<sup>24</sup>, i.e. approximately equal to  $R_{a,air}$ .

<sup>23</sup> One explanation of this observation is that momentum transfer is affected by pressure fluctuations, whereas mass (or heat) transfer is not.

<sup>24</sup> Strictly, this statement also depends on whether the sources and sinks of the different quantities are co-located.

To emphasise, the “similarity hypothesis” is important, because it means that information obtained from, for example, studies of evaporation-transpiration in crops, can be used to make predictions about the transport of carbon dioxide between a crop canopy and the atmosphere.

In the case of the new assessment model (see Section 5.1.1, where the equation is given), we assumed that:

$${}^{14}C_o = {}^{14}C_{air} + \mathbf{F} R_{a,air} \quad (\text{A2.18})$$

where:

- ${}^{14}C_o$  is the concentration of  ${}^{14}\text{CO}_2$  in the canopy atmosphere ( $\text{Bq m}^{-3}$ );
- ${}^{14}C_{air}$  is the concentration of  ${}^{14}\text{CO}_2$  in the atmosphere at a reference height above the plants ( $\text{Bq m}^{-3}$ );
- $\mathbf{F}$  is the flux of  ${}^{14}\text{CO}_2$  from the soil ( $\text{Bq m}^{-2}\text{s}^{-1}$ ); and
- $R_{a,air}$  is the aerodynamic resistance of the plant ( $\text{s m}^{-1}$ ).

It follows from the arguments above, that it is possible to substitute the aerodynamic resistance from Equation (A2.15) (or maybe a development thereof) into this equation.

## References

- 1 J.L. Monteith and M.H. Unsworth, *Principles of Environmental Physics, 2<sup>nd</sup> Edition*, Butterworth-Heinemann, 1990.
- 2 T. Foken, *Micrometeorology*, Springer-Verlag, 2008.
- 3 M.R. Raupach and A.S. Thom, *Turbulence in and above Plant Canopies*, Annu. Rev. Fluid Mech. **13**, 97-129, 1981.