Probability distributions of radiocarbon in open compartmental systems

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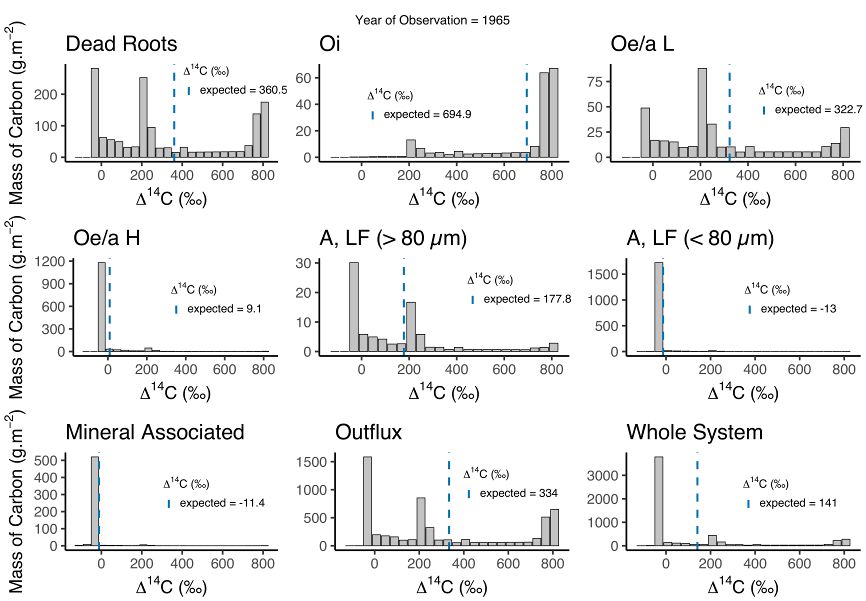
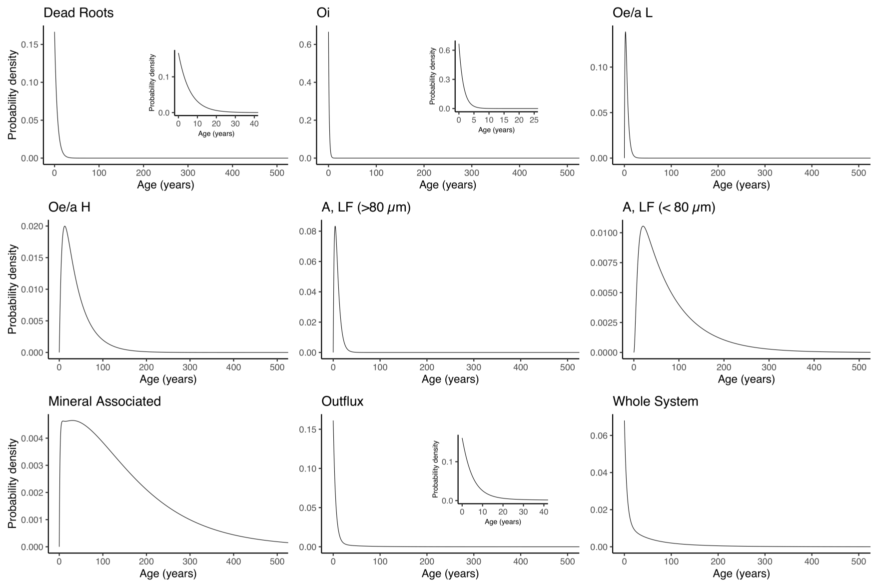
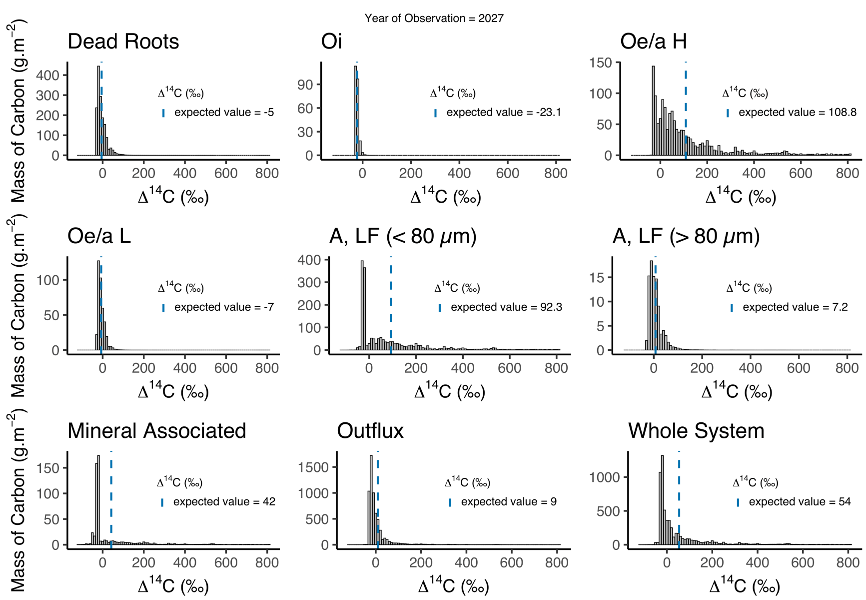
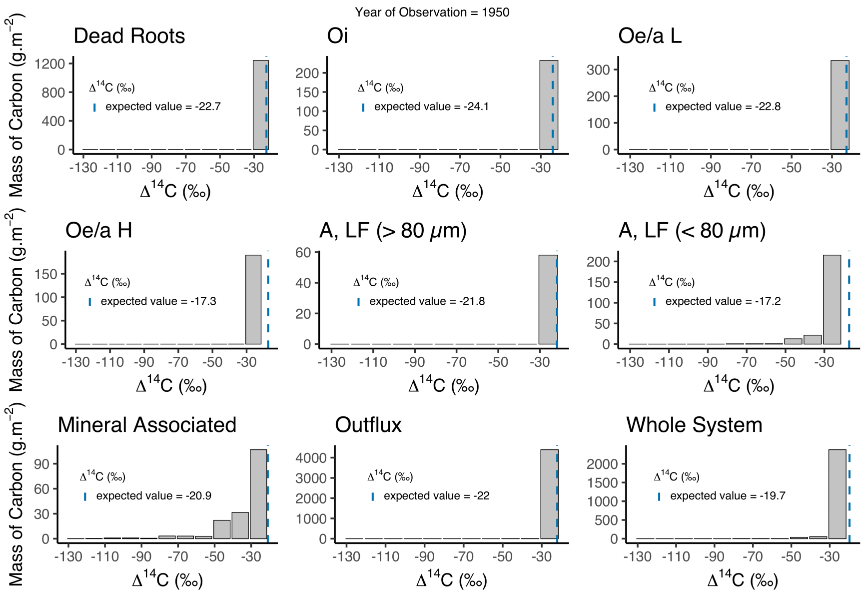
Abstract

Radiocarbon (^{14}C) is commonly used as a tracer of the carbon cycle to determine how fast carbon moves between different reservoirs such as plants, soils, rivers or oceans. However such studies mostly emphasize the mean value (as Δ^{14}C) of an unknown probability distribution. We introduce a novel algorithm to compute Δ^{14}C distributions from knowledge of the age distribution of carbon in compartmental systems at equilibrium. Our results demonstrate that the shape of the distributions might differ according to the speed of cycling of ecosystem compartments and their connectivity within the system, and are mostly non-normal. The distributions are also sensitive to the variations of Δ^{14}C in the atmosphere over time, as influenced by the counteracting anthropogenic effects of fossil-fuel emissions (^{14}C-free) and nuclear weapons testing (bomb ^{14}C). Lastly, we discuss insights that such distributions can offer for sampling and design of experiments aiming to capture the precise variability of Δ^{14}C values in ecosystems.

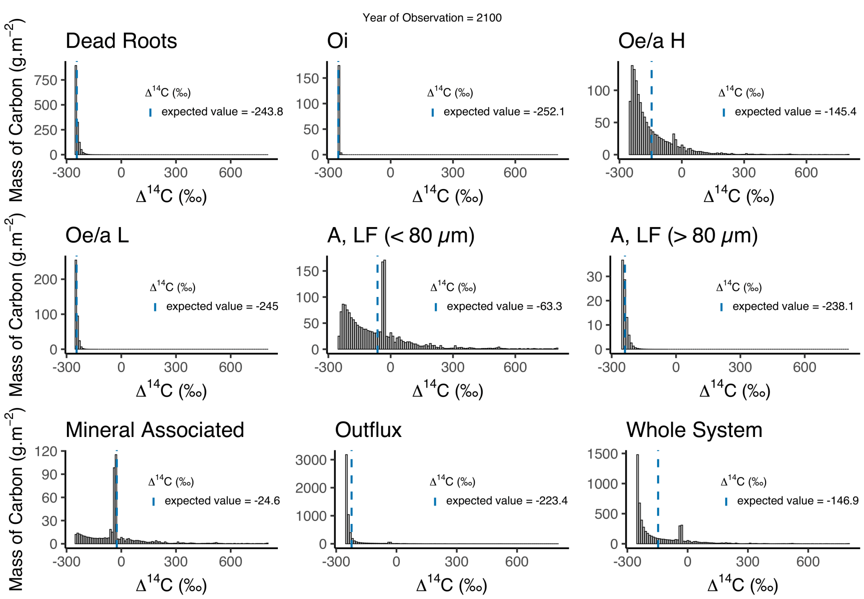



Dead Roots
Oi
Oe/a L
Oe/a H
A, LF (>80 μm)
A, LF (< 80 μm)
Mineral Associated
Outflux
Whole System
Probability density
Age (years)


Year of Observation = 2027
Dead Roots
Oi
Oe/a H
Oe/a L
A, LF (< 80 μm)
A, LF (> 80 μm)
Mineral Associated
Outflux
Whole System
Mass of Carbon (g.m⁻²)
Δ14C (‰)
expected value = -5
expected value = -23.1
expected value = 108.8
expected value = -7
expected value = 92.3
expected value = 7.2
expected value = 42
expected value = 9
expected value = 54



Year of Observation = 1950
Dead Roots
expected value = -22.7
Oi
expected value = -24.1
Oe/a L
expected value = -22.8
Oe/a H
expected value = -17.3
A, LF (> 80 μm)
expected value = -21.8
A, LF (< 80 μm)
expected value = -17.2
Mineral Associated
expected value = -20.9
Outflux
expected value = -22
Whole System
expected value = -19.7
Mass of Carbon (g.m^{-2})
Δ^{14}C (‰)



Year of Observation = 2100
Dead Roots
expected value = -243.8
Oi
expected value = -252.1
Oe/a H
expected value = -145.4
Oe/a L
expected value = -245
A, LF (< 80 μm)
expected value = -63.3
A, LF (> 80 μm)
expected value = -238.1
Mineral Associated
expected value = -24.6
Outflux
expected value = -223.4
Whole System
expected value = -146.9
Mass of Carbon (g.m^{-2})
Δ^{14}C (‰)

r babil l i di ri bu i r adi car b i e c ar e al e

[1,2] [1] [2] A [1,3]

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- Predicted radiocarbon distributions in open compartments vary according to the year of observation and model structure
- Expected $\Delta^{14}C$ values of ecosystem respiration are in accord with empirical $\Delta^{14}C$ data
- Probability distributions of radiocarbon in open compartments provide insights into ecosystem dynamics

Corresponding author: Ingrid Chanca, [illegible]

A

Radiocabon (^{14}C) is commonly used as a tacer of the cabon cycle to determine how fast cabon moves between different eservoirs such as plants, soils, rivers or oceans. However, such studies mostly emphasize the mean value (as Δ ^{14}C) of an unknown probability distribution. We introduce a novel algorithm to compute Δ ^{14}C distributions from knowledge of the age distribution of cabon in compartmental systems at equilibrium. Our results demonstrate that the shape of the distributions might differ according to the speed of cycling of ecosystem compartments and their connectivity within the system, and are mostly non-normal. The distributions are also sensitive to the variations of Δ ^{14}C in the atmosphere over time, as influenced by the contacting anthropogenic effects of fossil-fuel emissions (^{14}C-free) and nuclear weapons testing (bomb ^{14}C). Lastly we discuss insights that such distributions can offer for sampling and design of experiments aiming to capture the precise variability of Δ ^{14}C values in ecosystems.

Radiocabon is a radioactive isotope of cabon prominent in environmental sciences for tacing the dynamics of ecosystems, especially as recent changes in atmospheric radiocarbon allow tacking excess ^{14}C created by weapons testing in the atmosphere on time scales shorter than can be determined using radioactive decay. For climate change mitigation, a crucial uncertainty is the time cabon captured through photosynthesis spends in ecosystems before being released. For this purpose, radiocabon can be a valuable asa biological tacer, however, it is necessary to accurately link the real age of cabon and its radiocabon age, as they usually differ. Forests and soils systems are open systems, connecting components with intrinsically different cycling timescales, so that the mean age is representing an age distribution that is not normally distributed. Here we developed an algorithm to compute the ^{14}C content form models consisting of multiple interconnected carbon pools. Our approach, offers more accurate estimations of the mean ^{14}C content of the system and computations of the distribution of ^{14}C within the system at different points in time. From the results we can have more insights into the dynamics of the cabon cycle and how to better design experiments to improve model-observations comparisons.

1

Radiocabon (^{14}C) is a valuable tool for studying dynamical processes in living systems. In particular, radiocabon produced by nuclear bomb tests in the 1960s has been used in many contexts as a tacer for the dynamics of cabon in different compartments of the global cabon cycle, including the atmosphere, the terrestrial biosphere, and the oceans (Goudriaan, 1992; Jain et al., 1997; Randerson et al., 2002; Naegler et al., 2006; Levin et al., 2010). As a biological tacer, radiocabon can be used to infer rates of cabon cycling in specific compartments and to infer transfers among interconnected compartments. Therefore, radiocabon is used as a diagnostic metric to assess the performance of models of the cabon cycle (Graven et al., 2017), and new datasets are now emerging to incorporate radiocabon in model benchmarking (Lawrence et al., 2020).

Cabon cycling in biological systems can be represented using a particular class of mathematical models called compartmental systems (Sierra et al., 2018). As cabon enters a system such as the terrestrial biosphere, it is stored and transferred among a network of interconnected compartments such as foliage, wood, roots, soils, and other organisms. Compartmental systems represent the dynamics of cabon as it travels along the network of compartments (Rasmussen et al., 2016; Sierra et al., 2018), and provides information about the time cabon spends in particular compartments and the entire system (Rasmussen et al., 2016; Sierra et al., 2017). Although there seems to be a direct relation between the time cabon spends in a compartmental system and its radiocabon dynamics, few studies relate both concepts.

An open compartmental system contains inflows and outflows different from zero (Jacquez & Simon, 1993). Timescales in open compartmental systems are usually characterized by the concepts of *age* and *transit time* (Bolin & Rodhe, 1973; Rasmussen et al., 2016; Sierra et al., 2017). In open systems such as the biosphere, the incorporation and release of carbon occurs continuously, but it is possible to define the concept of *age* as the time elapsed since carbon enters the compartmental system until a generic time. The *transit time* can be defined as the time the carbon needs to travel through the entire system, i.e., the time elapsed between carbon entry until its exit.

In order to estimate these time metrics from ^{14}C measurements, a model linking both carbon and radiocarbon dynamics is required. Thompson and Randerson (1999) have used impulse response functions from compartmental models to obtain ages, transit times, and time-dependent radiocarbon dynamics. However, this approach is computationally expensive and can introduce numerical errors if simulations are not long enough to cover the dynamics of slow cycling pools.

Explicit formulas for age and transit time distributions in compartmental systems have been recently developed (Metzler & Sierra, 2017). These formulas do not introduce numerical errors and can describe entire age distributions of carbon for specific pools and for the entire compartmental system. These age distributions suggest that radiocarbon in compartmental systems may consist of a mix of different values, i.e., compartments could be described in terms of radiocarbon distributions that relate the relative proportion of carbon with a particular radiocarbon value. However, until now radiocarbon is reported and modeled as a single quantity rather than the mean of an underlying distribution.

Knowledge of the distribution of ^{14}C over and on the ^{12}C distribution (C mass) in a compartmental system might give important insights on the model structure that better fits existing data. For example, by comparing the signature of radiocarbon in the pools and their outfluxes, we get insights on the size of the pool model that describes the ecosystem. Conversely, empirical knowledge of the radiocarbon distribution of a particular system, can play a significant role in determining the most appropriate model to describe a system.

Model-data comparisons using radiocarbon are made more complex by the fact that atmospheric ^{14}C is continuously changing. This is particularly important after the 1960s when the nuclear bomb tests liberated large amounts of thermal neutrons to the atmosphere, contributing to the formation of radiocarbon (bomb ^{14}C). In addition, large quantities of fossil-fuel derived carbon (^{14}C-free) have been emitted to the atmosphere, diluting the atmospheric radiocarbon signal and producing a fast decline of radiocarbon values in recent years (Graven et al., 2017). Therefore, we would expect a different radiocarbon distribution for every year in a compartmental system.

Obtaining a simple and accurate method to estimate radiocarbon distributions as a function of the year of observation is, therefore, of great interest for experimental and modeling studies.

The main objective of this manuscript is to introduce a method to obtain distributions of radiocarbon in compartmental systems at steady-state. In particular, we ask the following research questions: (i) How do distributions of radiocarbon change over time as a consequence of changes in atmospheric radiocarbon? (ii) How do empirical data compare to these conceptual radiocarbon distributions? (iii) What insights can these distributions provide for experimental and sampling design for improving model-data comparisons by capturing the entire variability of $\Delta^{14}C$ values?

The manuscript is organized as follows: First, we provide the necessary theoretical background to obtain age and transit time distributions from compartmental systems. Second, we describe an algorithm that computes radiocarbon distributions for particular years using an age or a transit time distribution and an atmospheric radiocarbon curve. Third, we present an application of our algorithm to a soil compartmental system addressing the research questions above. Finally, we discuss our results in the context of other applications and potential new insights from our approach.

A

1

Compartmental systems describe the temporal dynamics of material transfers through a network of compartments until its final release from the system. A set of compartments is translated mathematically as a set of linear or non-linear ordinary differential equations (ODE), whose solutions are the amount of material in each compartment at a certain time.

We will consider here linear autonomous compartmental systems, characterized by the mass of carbon at time in compartments as the vector $\boldsymbol{x}(\ )$. The mass of carbon in the compartments changes over time according to the following expression

$$\frac{\boldsymbol{x}(\ )}{\ } = \dot{\boldsymbol{x}}(\ ) = \boldsymbol{u} + \mathbf{A}\boldsymbol{x}(\ ) \qquad \boldsymbol{x}(\ = 0) = \boldsymbol{x} \tag{1}$$

where the vector $\boldsymbol{u}$ represents the inputs of carbon into the system, and the $\times$ compartmental matrix $\mathbf{A}$ contains in its diagonal entries the cycling rates of the compartments, while the off-diagonal entries consist of the transfer rates among them. In particular, the compartmental matrix in most ecosystem carbon models has an internal structure reflecting transfers between the components (coefficients , representing the proportion of C transferred from compartment to compartment i) and cycling rates k reflecting assumptions of first order kinetics of loss (a rate $C\ k$) from any given compartment

$$\mathbf{A} = \begin{array}{cccc} -\ 1 & 1\,2\,\ 2 & \cdots & \\ 2\,1\,\ 1 & -\ 2 & \cdots & 2 \\ \vdots & \vdots & \ddots & \vdots \\ 1\ 1 & 2\ 2 & \cdots & - \end{array} \tag{2}$$

This matrix contains information on the dynamics, structure, and size of a compartmental model. The rate of exit of carbon from the system can also be obtained from this matrix by summing all column elements, i.e., the outputs from a pool that are not transferred to other pools are assumed to leave the compartmental system.

The information of the amount of carbon entering the system to be partitioned among the compartments is contained in the input vector

$$\boldsymbol{u} = \begin{array}{c} 1 \\ 2 \\ \vdots \end{array} \tag{3}$$

Linear autonomous systems of the form of equation (1) have an equilibrium point or steady-state solution $\boldsymbol{x}^*$ given by

$$\boldsymbol{x}^* = -\mathbf{A}^{-1}\boldsymbol{u} \tag{4}$$

where the mass of the compartments do not change over time, and inputs are equal to outputs for all compartments.

A

We define age in a compartmental system as the time elapsed between the time of carbon entry until some generic time (Sierra et al., 2017). For a time-independent system in steady-state, a probability distribution of ages of carbon in the compartments can be obtained using stochastic methods. According to Metzler and Sierra (2017), the vector of age densities for the compartments can be obtained as

$$\boldsymbol{f_a}(\ ) = (\ ^{*})^{-1} \cdot \ ^{\boldsymbol{A}} \cdot \boldsymbol{u} \tag{5}$$

where $\ ^{*} = \mathrm{diag}(\ ^{*}_{1}\ \ ^{*}_{2}\ \ ^{*})$ is the diagonal matrix with the steady-state vector of carbon stocks as components, and $\ ^{\boldsymbol{A}}$ is the matrix exponential.

For the whole system, the age distribution is given by

$$(\ ) = -\mathbf{1}^{\mathsf{T}} \cdot \mathbf{A} \cdot \ ^{\boldsymbol{A}} \cdot \frac{\boldsymbol{x}}{\|\boldsymbol{x}\ \|} \tag{6}$$

where the symbol $\|\cdot\|$ represents the sum of the mass in a vector.

We define transit time as the time elapsed since carbon enters the compartmental system until it leaves the boundaries of the system (Sierra et al., 2017). The transit time is equivalent, therefore, to the age of the outflux. Metzler and Sierra (2017) also provide an explicit formula to obtain the transit time density distribution for a time-independent system at steady-state as

$$(\ ) = -\mathbf{1}^{\mathsf{T}} \cdot \mathbf{A} \cdot \ ^{\boldsymbol{A}} \cdot \frac{\boldsymbol{u}}{\|\boldsymbol{u}\|} \tag{7}$$

These distributions are densities, so they integrate to 1

$$\int_0^\infty (\ )\ = \int_0^\infty (\ )\ = 1 \tag{8}$$

1

We developed an algorithm to convert age and transit time distributions into Δ ^{14}C distributions for any given year of observation.

The algorithm works in three main steps: 1) homogenization, 2) discretization, and 3) aggregation (Figure 1). We describe these three steps in detail in the sections below using mathematical notation for the system age distribution, but computations are similar for the transit time distribution, and the age distribution of individual compartments.

[illegible]

The main inputs for the algorithm are an age distribution ( ), and an atmospheric radiocarbon curve ( ) that provides the Δ ^{14}C value of atmospheric CO_2 for a calendar year . To homogenize the time scales of both ( ) and ( ), we define the year of observation $_0$, as the year of interest to produce the radiocarbon distribution.

Since we are interested in determining the radiocarbon values of material observed in the system at time $_0$, we will look in the radiocarbon curve $-$ years in the past to obtain the radiocarbon values in the system with an age . Therefore, atmospheric radiocarbon can be expressed as a function of age, i. e., $(_0 -) = ( )$ (Figure 1). Now both the system age distribution $( )$ and the atmospheric radiocarbon curve $( )$ are functions of the continuous variable that represents age.

Several atmospheric radiocarbon datasets can be found in the literature (Reimer et al., 2013, 2020; Hogg et al., 2013, 2020; Hua et al., 2013; Levin et al., 1980; Levin & Kromer, 1997; Levin et al., 2010; Graven et al., 2017). Also forecasts of radiocarbon content in the atmosphere can be found in the recent literature (Graven, 2015; Sierra, 2018). However, these atmospheric radiocarbon datasets do not necessarily have the same resolution in time. Some of them provide predictions or data at an annual or form monthly time step, while in other datasets, some ranges are spaced by decades. To homogenize the resolution of the Δ^{14}C and to transform these radiocarbon datasets into a continuous function of , we use a cubic spline interpolation to obtain Δ^{14}C values for any value of . After this step, $( )$ can be computed for any value of $\in [0, \infty)$, and $( )$ until the latest available date in the chosen radiocarbon atmospheric dataset.

t

Although we have now the age distribution and the radiocarbon data as continuous functions of age, we need to discretize these functions in intervals of size . The reason for this discretization is that the probability density function of age $( )$ is a measure of the relative likelihood of an infinitesimal amount of mass having an age. But ultimately, we are interested in the probability that a small mass has certain radiocarbon distribution. Therefore, we need to discretize the probability density function to a probability mass function along a discrete variable $\in [0, _{max}]$. The new discrete probability function of ages can be defined as

$$(\leq \leq +) = \int^{+} ( ) \tag{9}$$

From this probability function, we can compute the proportion of total mass in the system with an age as

$$( ) = \|\boldsymbol{x}^*\| \, ( ) \tag{10}$$

where

$$\begin{aligned} \sum_0^{max} ( ) &\approx 1 \\ \sum_0^{max} ( ) &\approx \|\boldsymbol{x}^*\| \end{aligned} \tag{11}$$

Equation (11) implies that there is an approximation error by discretizing the continuous density function to a finite set of discrete intervals. This approximation error can be minimized by decreasing the size of the intervals and extending $_{max}$ as far as possible.

Once we discretize $( )$ to $( )$ and obtain discrete proportions of mass with certain age $( )$, we proceed to discretize the atmospheric radiocarbon curve with respect to the same discrete interval of ages $\in [0, _{max}]$. This is simply done by computing $(=)$, which makes the assumption that within each interval $[, +]$, the atmospheric radiocarbon value is equal to $( )$.

tA

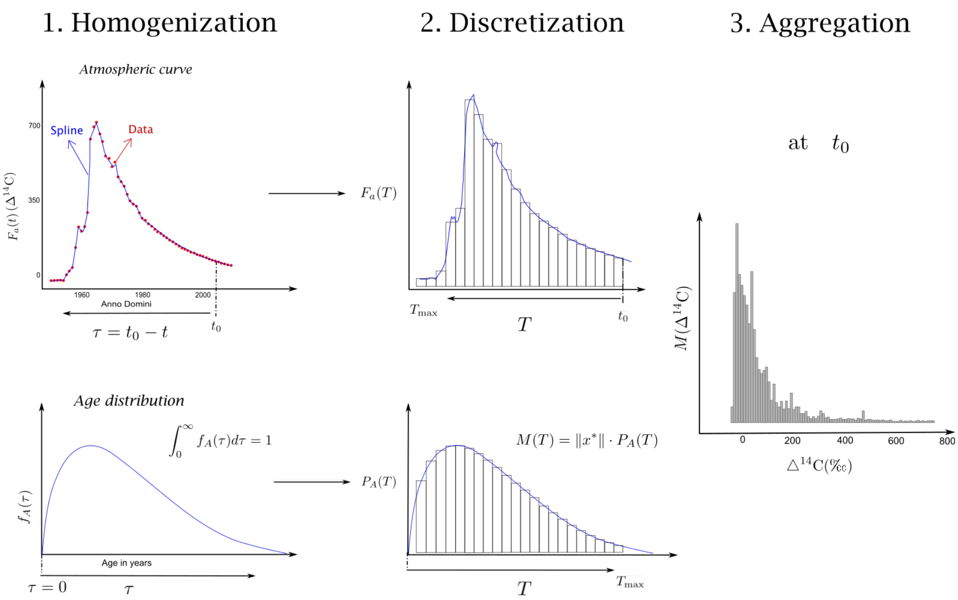
Nowwe are eadyto combine he distibution of masin he sym atdisete age intevlswih he atmospheric adiocabon cu. To do o, wefistfind foreach vlue of $\in [0 \ _{ax}]$ he corepsonding vluesof mas ( ) and adiocabon ( ). Then, we sm all he masswih similar Δ ^{14}C vlues The esltcan be organized ashe amontof masin disete intevlsof Δ ^{14}C; i. e. $(\Delta^{14}\mathrm{C}) = (\ (\ ))$.

Theestepscan also be visalized hough he gaphsin Figue 1.

We implemented hese hee stepsin he R pogamming langage, and se he package SoilR (Siea, Mller, etal., 2012) to obtain he age distibution of he pools, he whole sym, and he outpt flx (eqivlent to he ansittime) basedon eqtions(5), (6), and (7). The vesionsused here we Revsion 4.0.3 and SoilR vesion 1.1 (Siea etal., 2014).

Since atmospheric ^{14}C concentation for he past55,000 yeasis pincipally known fom he adiocabon cus, we colud easilyconvetage into atmospheric Δ ^{14}C. Bymatching he Δ ^{14}C-based-on-age vlueswih he peviosly estimated densities, we built bapplots gaining insight into he adiocabon distibutionsfor he model stdied in his wok. In he algorihm wedefined forfunctions *PoolRDC*, *SystemRDC*, *TTRDC*, and *C14hist*. The fist hee functionstake he densitiesoutpts, i. e., he cabon contentsdiscetized byage, fom built in SoilR functions, sch as *transitTime* and *systemAge*. The densitiesare hen set to build binshough he *C14hist* function. The logical statementsused to consttthe binsare basedon he atmospheric Δ ^{14}C data and according to useedefined binsize . This stat allowsone to plothistogam-like gaphs, whee he height of he basepesent he amontof maswih coresponding Δ ^{14}C vlues. Thisoral gorihm initialize fom a compatmental matix an inptvectorand a adiocabon calibation cuv, and etsan objectcontaining massof C and heirmatching decaycorected Δ ^{14}C vlues, estimated foranygiven obsevtion yeaar. The match isdone byassming he yearof obsevtion as eqivlent to he age of he pool or he sym eqal zeo ($_0 - = = 0$). Thismeansthat pastyeas, orolderpool orsym ages, are eqivlent to he Δ ^{14}C signal of he atmosphee of hose yeascorected byhe adioactive decayof ^{14}C (aveage lifetime of 8,267 yeas, i. e., half-life of 5,730 yeas).

Besidesthe adiocabon distibutionsforpools, whole sym and outptflx, one can also compte he expected vlue of Δ ^{14}C fom hese distibutionsin anygiven obsevtion year This isdone bycompting he mean of Δ ^{14}C weighted byhe amontof cabon in Δ^{14}C binsof size . The standad deviation of he distibution isobtained ashe sqae oot of he difeence between he sqae of he expected vlue and he expected vlue of he sqaesof Δ ^{14}C vlues



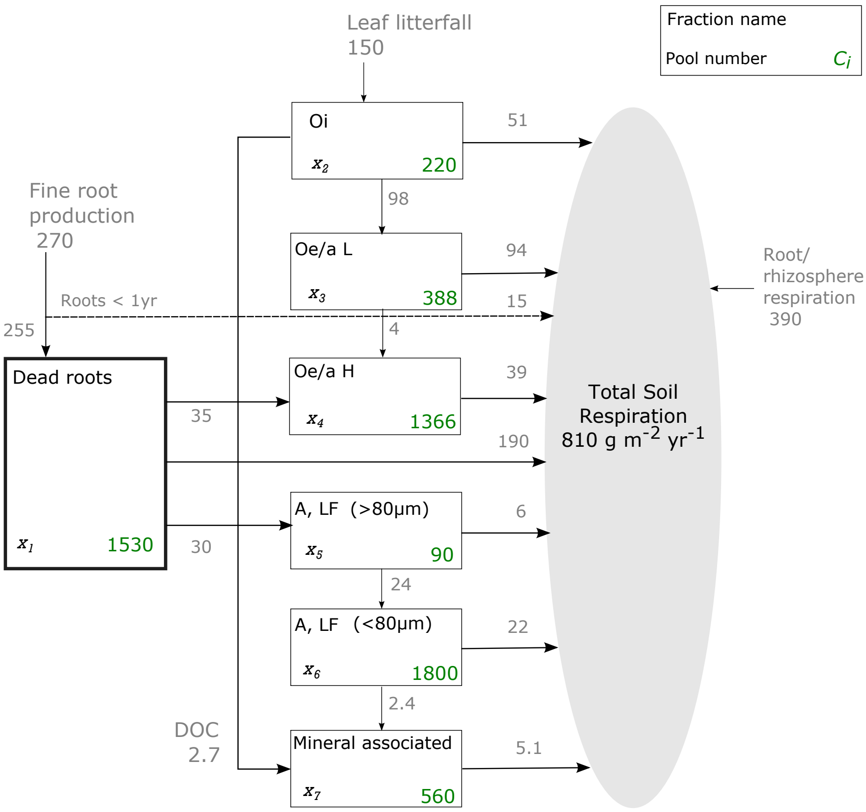
Graphical visualization of the three main steps for the computation of radiocarbon distributions in a compartmental system using an atmospheric radiocarbon curve of the carbon inputs to the systems, and the age distribution of carbon in a compartmental system. Details about each step are provided in the main text.

Oapproach can be sd to obtain adiocabon disbtionsf or linearcom patm ental model sof any ize epresnting cabon cyling pocessatdi ff erentsal esandf ordi ff erent biological sms

Wiwll focsh ee on a model hatepesnt he dyamicsof soil oganic cabon ata tem peate foes wich wcall herein he H ard ForstSoil (HFS) model. The model isbasd on measm entscondted ath e H ard Forstin Masachs USA (Gadinski etal., 2000; Siea, Tmboe, etal., 2012). Soil samplescollectedin O-horzon, coepondi ng to 0 –8 cm deph, and A-hoion (8 –15 cm deph) we factonated into sen soil factonscalled: Dead Roots Oi, Oe/a L, Oe/a H, A, IF (80 m), A, IF (80 m), and Mineal Asociated. The ywe obtained asf ollows The O-horzon wassbdivded afterhand-picking into leaf liter (*Oi* facton), ecognizable ootliter (*Oe/ a* *L* facton) andhmified, i. e., oganic materh ath asbeen tansf om edbymicobial acton, coepondi ng to he facton *Oe/ a H* Samplesfom he A-hoion we factonated bydensity into lowdensityandhigh-densitypotons The high-densitypoton coesponds to he *Minera l Assoc ia ted* facton. The lowdensitypoton is furhersbdivided bysievng into ecognizable leaf lagerhan 80 m (*A, LF(* 80 *m)* facton) andsmallerhan 80 m (*A, LF(* 80 *m)* facton). Detailsaboth e mehodsem ployd to factonate he samplescan be fondin Gadinski etal. (2000).

The com patm ental model consistof sen pools (Figue 2); one pool coespondsto dead oots $_1$, and hee poolscoepond to hee diff erentypesof oganic materin he sface layr (O) called Oi, Oe/a L, and Oe/a H, wich coespondsto pools $_2$, $_3$, and $_4$ in he model. Twadditional pools called A, IF (80 m), epresnting material fom he A hoion hatfloatsin a dense (1 g cm $^{-3}$) liqid and doesnotpasthough an 80 m siee and A, IF (80 m) (lowdensityfacton pasing he siee), epresnth e dyamics of two fractions in the soil A horizon with different granulometry $_5$ and $_6$, respectively. The seventh pool $_7$ represents the dynamics of the mineral associated fraction (Sierra, Trumbore, et al., 2012).

The HFS model was built by fitting of empirical radiocarbon data from the above described samples. Details about the use of the data to build the compartmental model are presented in Sierra, Trumbore, et al. (2012). For the same sites, there are independent data (i.e., data not used for estimating the compartmental matrix) available. The independent data used in this work consist of $\Delta^{14}C$ measurements on total soil CO_2 efflux collected in the years 1996, 1998, 2002, and 2008. The number of samples measured corresponding to the respective years was n = 12, n = 28, n = 23, and n = 10. We used these data to compare the representativity of the mean $\Delta^{14}C$ measurements to the expected $\Delta^{14}C$ values obtained through our algorithm.



Scheme of HFS model stocks ( ) and fluxes among compartments (adapted from Sierra, Trumbore, et al. (2012)).

The sy m of ODE f or h e H FS m odel can h en be epesd i n com patm enal f om as

$$
\begin{pmatrix} \dot{}_1 \\ \dot{}_2 \\ \dot{}_3 \\ \dot{}_4 \\ \dot{}_5 \\ \dot{}_6 \\ \dot{}_7 \end{pmatrix} = \begin{pmatrix} 255 \\ 159 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} -255\,1530 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -150220 & 0 & 0 & 0 & 0 & 0 \\ 0 & 98152 & -98388 & 0 & 0 & 0 & 0 \\ 35255 & 0 & 98 & -391366 & 0 & 0 & 0 \\ 30255 & 0 & 0 & 0 & -3090 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2430 & -241800 & 0 \\ 0 & 3152 & 0 & 0 & 0 & 35 & -5560 \end{pmatrix} \begin{pmatrix} {}_1 \\ {}_2 \\ {}_3 \\ {}_4 \\ {}_5 \\ {}_6 \\ {}_7 \end{pmatrix} \quad (12)
$$

As desri bed bef oe, i n oderto esm ate h e adi ocabon di stbtions and epeced vlesof Δ ^{14}C, h e al gorh m needs h e f oll owng agm ents a com patm enal m atx **A**, contai ning h e decom posi t on and tansf er ates wh i n h e pool s, an i nptvecor $\boldsymbol{u}$ contai ni ng h e i nptm as to be patt oned am ong h e com patm ents h e yar of obsvat on (equi al ent to yar of *sa mpl ing* i n an eper i m ental f am eok); h e nm ber of yars i n h e pas one ai m s to com pte h e di stbtions f or, and a stof adi ocabon vl es i n h e atm osph ee, com pri sng h e yar of obsvat on and h e nm ber of yars ch osn. An addi t onal agm ent i s , h e di sret zat on sze desri bed abow, wh i ch h as a def al tvl e of 0. 1 yars bt cold be m odi f i ed accordi ng to sr pef eences

For h e H FS m odel, **A** i s h e m atx i n eqt on (1 2), wh h e f om of eqt on (2), and $\boldsymbol{u}$ i s h e nm er c vecor i n h e sam e eqt on, wh si m i l ar f om as eqt on (3). W e esm ated h e adi ocabon di stbtions f or di f f eent yars of obsvat on, i n oder to addes di f f eent esach qt ons ai sed i n h i s ok. I n h e eslts e pesent h e di stbtions f or h e i ndi vdal pool s, otal oflx and wol e sym, f or h e yars 1 9 6 5, 2 02 7 and 2 1 00. Addi t onall y i n h e *Suppl ementa ry Ma teria l* e povde h e non-sacked adi ocabon di stbtions of i ndi vdal pool s, otal oflx and wol e sym f or h e yars 1 9 5 0, 1 9 6 5, 2 02 7, and 2 1 00. Radi ocabon di stbtions of h e *outflux* ae pesnted f or h e yars 1 9 9 6, 1 9 9 8, 2 002, and 2 008, as f or h os yars e al so h ave i ndependent Δ ^{14}C data f om soi l CO_2 efflx to com pae to or esm at ons For al l h os esm at ons h e nm ber of yars of com pat on as 1,000 yars The bi n sze ([‰]) f or pl ot ng h e h i sogam s as set as 1 0 f or m os of h e adi ocabon di stbtions exept f or h e yar 1 9 6 5, wee i t as set p to 4 0.

[illegible]

The adi ocabon vl es sd f or yars i n h e pas, e. g., AD 1 9 6 5, ee obtai ned by m egi ng h e ecent y el eased I nCal 2 0 cal i bat on cve (Rei m er et al., 2 02 0), wi ch com bi nes adi ocabon data and Bayi an sat scal i nepol at on f or h e ange 5 5,000 –0 cal BP (BP = *b efore present* = AD 1 9 5 0), and h e ecords of atm ospher c adi ocabon data com pi l ed by Gaen et al. (2 01 7), f om 1 9 5 0 to 2 01 5. Gaen et al. (2 01 7) al so povdes adi ocabon data i n one-yar esol t on on h e ange 1 8 5 0 to 1 9 4 9. H oer, si nce i n h i s ange h e esm at ons ee pat al l y based on h e pei os Noh en H em i sph ee cal i bat on cve (I nCal 1 3, Rei m er et al. (2 01 3)), e deci ded to se Gaen et al. (2 01 7)'s data set sat ng i n AD 1 9 5 0.

For h e yars i n h e ft, sh as AD 2 02 7 and 2 1 00, e m ade se of h e f orecass sm l at ons com pted by Gaen (2 01 5), wo sm l ated Δ ^{14}C vl es i n h e atm osph ee f or f or Repesent Concenat on Pah ays of f osi l f el em i ssons RCP2. 6, RCP4. 5, RCP6 and RCP8. 5. I n h i s ok e se h e pedi ct ons based on h e h i gh em i ssons senar o (RCP8. 5), sat ng i n AD 2 01 6.

The Δ^{14}C valesin all datastsedin hi swrk are ivtn ashe deivaton fom he tandardepesenting he pe-indstal atmospheric ^{14}C concentaton. The aypublished valesare alreadycoected forfactonaton and decaywh espectto he standard. It is euivalent Δin Stiver and Polach (1977). Thsthe eqation it follows

$$\Delta^{14} = {}^{14} \quad c(10 -) - 1 \times 1\,000 [‰] \qquad (13)$$

here $F^{14}C$ ishe Facton Moden ( ), i.e., he ampleato nomalised ^{13}C byoxalic acidstandard (OXII), ishe pdated ^{14}C decayconstant (eqalsl 8267 $^{-1}$[y]), and y ishe yarof measement

4

4

Oeall, ouresltsshow hat ewn hogh he age and transittime distbtionsfor hiscompatmental systm are tatc (Figure 3), he adiocabon distbtionsae highly dynamic. Theychange damatcally ovetime ashe atmospheric CO$_2$ soue isaffected byhe bomb spike and he Sueseffect (Sues 1955), i.e., he effectof he dilton of adiocabon in he atmosphee de to he emisson of fosil fuls (^{14}C-fee). Pools hatcyle fast i.e., poolswh shap age distbtionspeaks, sch as *Lea d Roots* and *Oi*, followed most closelyhe adiocabon dynamicsin he atmosphee, hile pools hatcyle solwyshoed a wide ange of vales. Conseqently he expected Δ^{14}C valesalso vayl argely.

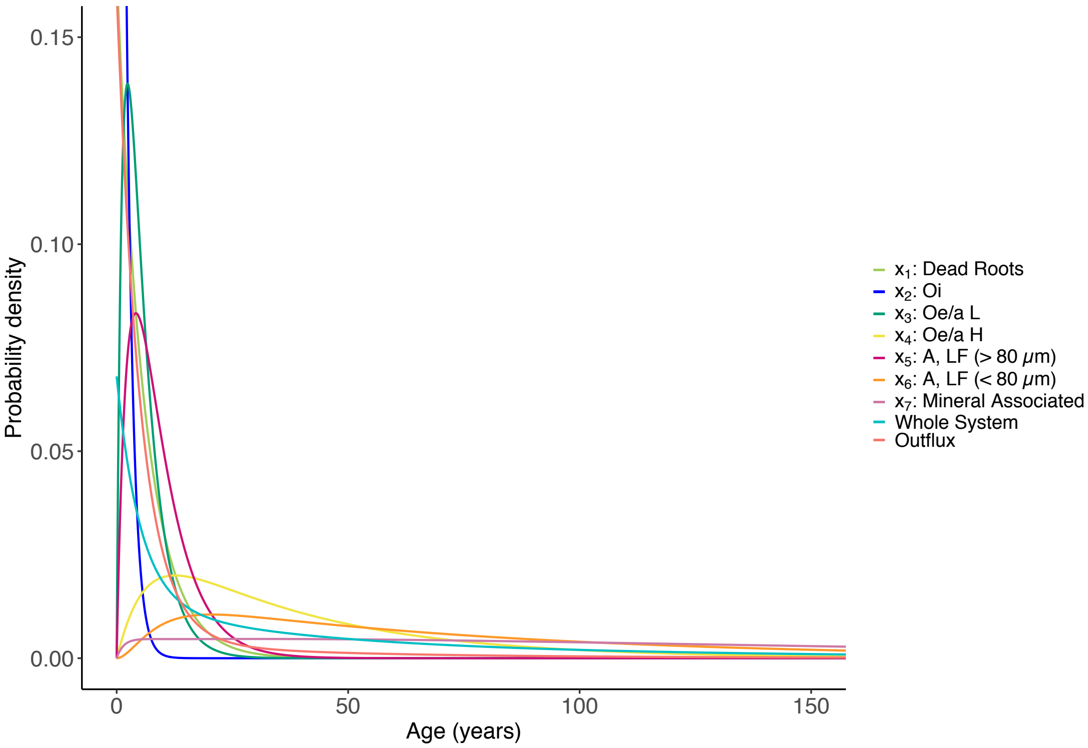
The distbtionsweobtained forhe compatmentsof he HFS model showed diffeentshapesforhe diffeentcompatments (Figures 4, 5, and 6, and Figures S2, S3, S4 and S5 in Spplementary Material). In 1965, jst afterhe peak of bomb ^{14}C in he atmosphee de to nuleaweaponstests, pools hatcyle fast had a wide Δ^{14}C ange wh high pobability de to he incopoaton of adiocabon valesthatchanged apidly ovehe period AD1950–1965. Compatments hatcyle solwy have a naowedistbton wh heimodescoesponding to negative Δ^{14}C vales, as heyepesentpe-bomb atmospheric signals hat aried les.

Forhe whole systm in AD1965 (Figure 7), he distbton of adiocabon aggegates he contbtionsof he diffeentpools, wich esltsin diffeentpeaksin he oeall distbton. The mode (i.e., he Δ^{14}C wh highestmasdensity isbelow 0 ‰ becase a lage poton of he total amountof cabon iscontbted byhe mineral asociated pool hatis pedominantystll pe-bomb cabon wh litle contbton fom cabon fixed after 1964. In addition, oherpools hatcyle fast contbte elatively small amountsof bomb ^{14}C to he oeall distbton.

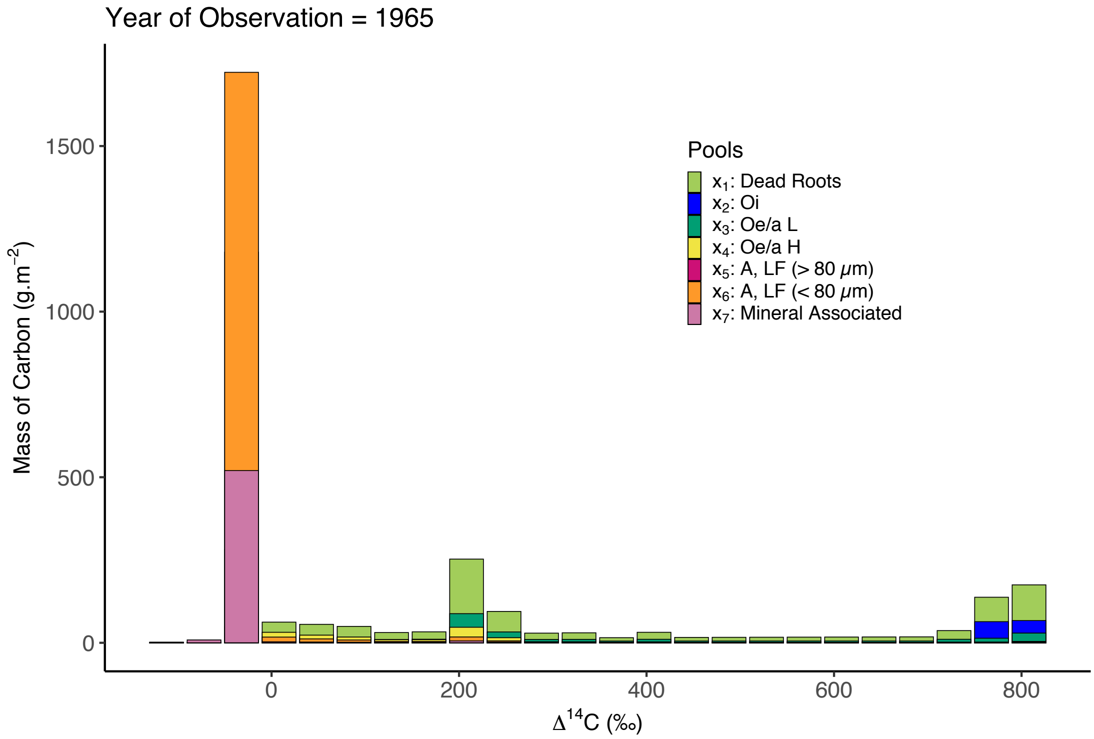
The adiocabon distbton in he otptfluxin AD1965 (Figure 7), i.e., he adiocabon distbton hatcoespondsto he transittime distbton forhis yar, hashee distinctpeaksin he distbton. This distbton isveysimilarto hatof he *Lea d Roots* pool (Figure S3), wich ishe main contbtorto he total espiaton flux. Howeer, oher poolsalso contbte to he espiaton flux wh heiradiocabon signatesandemphasize fluxesfom he fastestcyling pool (Oi) andespiaton of cabon hat waspesentin oher poolsbefoe he bomb peak.

The shapesof he distbtionschange damatcally forsbseqentyearsafterhe bomb spike (Figure 5). ForAD2027, he expected Δ^{14}C valesof fastpools dop consideablyin paralel wh atmospheric ^{14}C, compared to AD1965. Thes fastpools do notstoe mch adiocabon fom he bomb period, and heiradiocabon signatesreflectecentcabon fom he atmosphee. In contast, sowcyling poolsin AD2027 hadelatively high Δ^{14}C vales, mostlybecase heystll contain adiocabon fom he bomb period. In he otpt flux, asexpected, since he espiaton flux isdominated byhe fastecyling pools sch as *Dead Roots* and *Oi*, most of the radiocarbon is narrowly distributed around the recent atmospheric Δ^{14}C value in 2027, with almost no contributions from bomb ^{14}C.

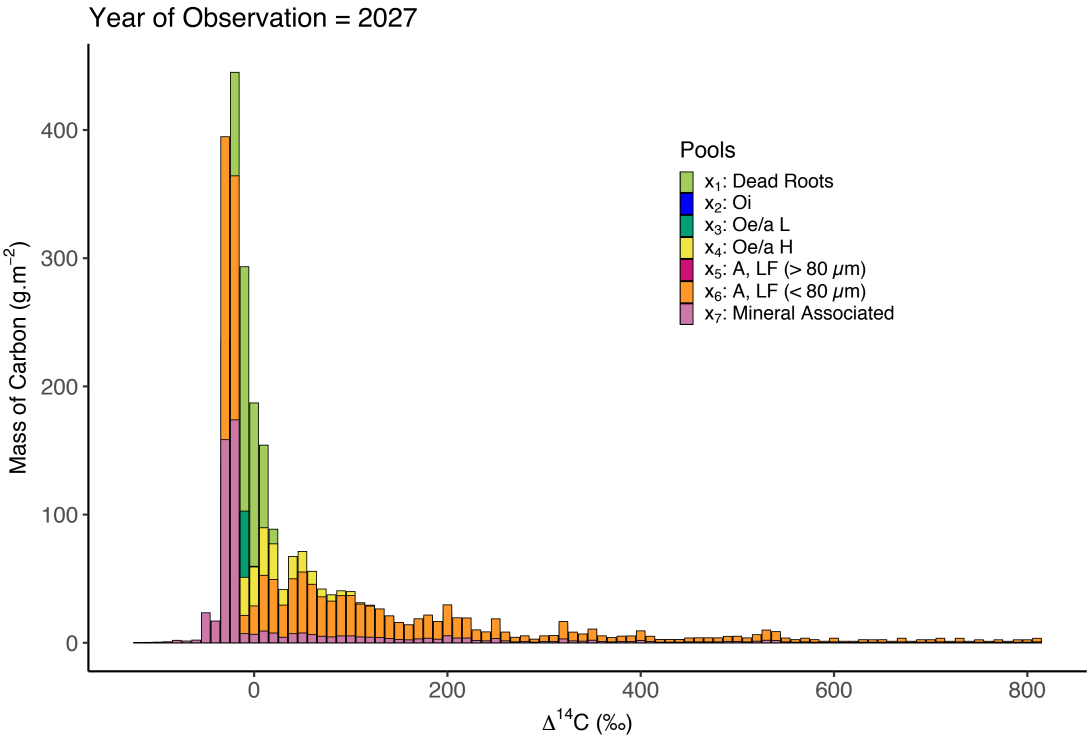
By the year 2100, the atmospheric Δ^{14}C values have dropped to -254.5 ‰ (Graven, 2015), reflecting the Suess effect. The distributions of most pools are less variable. Faster cycling pools have dropped to reflect negative Δ^{14}C in the atmosphere over the 73 years since 2027, while the slow pools (*Mineral Associated*, *A, LF (< 80 μm)* and *Oe/a H* pools) still show a wide range of Δ^{14}C values that includes C fixed during the bomb period (now ~150 years previously).



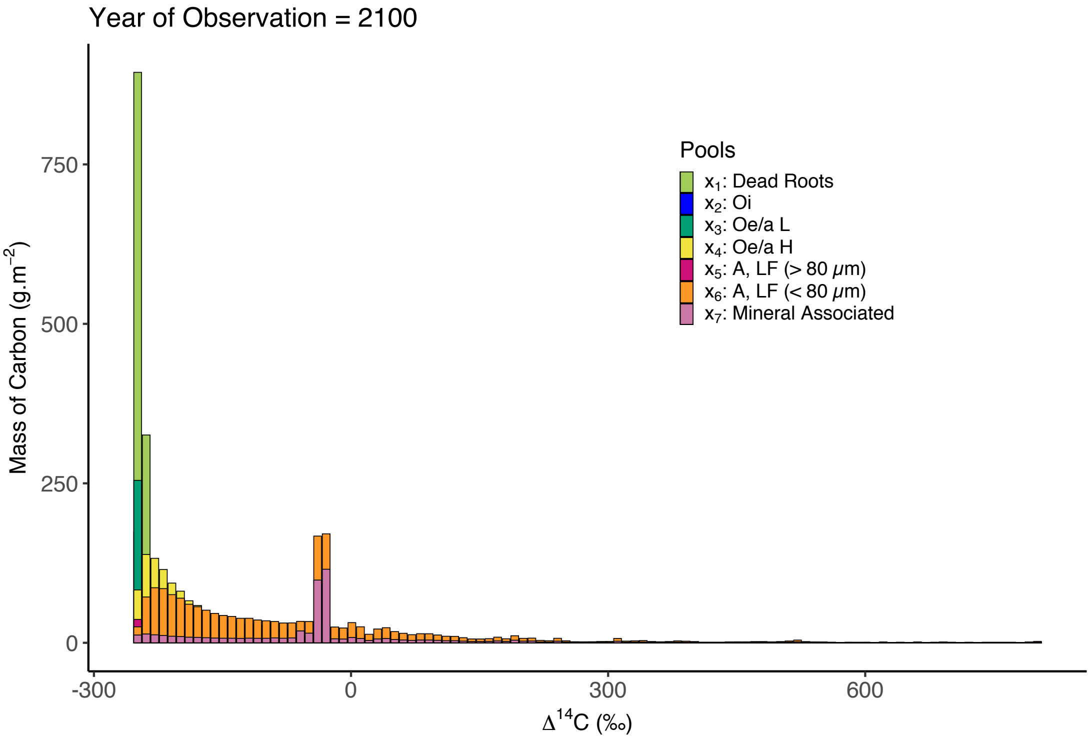
] Age distributions for the Harvard Forest Soil model computed in a span of 1,000 years with a resolution of 0.1 year. The x-axis is limited to 150 years and the y-axis is limited to 0.15 for better visualization of the data.



Δ^{14}C distributions of each of the seven pools of the HFS model through the algorithm described above. The year of observation is 1965 – just after the bomb peak in 1964 – and the distributions are computed over 1,000 years. The bin size is equal to 40 ‰. The expected value and standard deviation of this distribution is 141 ± 280.



Δ^{14}C distributions of each of the seven pools of the above-mentioned HFS model through the algorithm described above. The year of observation is 2027 and the distributions are computed over 1,000 years. The bin size is equal to 10 ‰. The expected value and standard deviation of this distribution is 54 ± 144.



Δ^{14}C distributions of each of the seven pools of the above-mentioned HFS model through the algorithm described above. The year of observation is 2100 and the distributions are computed over 1,000 years. The bin size is equal to 10 ‰. The expected value and standard deviation of this distribution is -147 ± 146.

Figure 7. $\Delta^{14}C$ distributions of *Outflux* and *Whole System* of the HFS model for the years 1965, 2027 and 2100. The bin size b for all the three years is equal to 40 h .

Figure 8. Evolution of the expected $\Delta^{14}C$ values of *Outflux* and *Whole System* for the HFS model between the years 1900 and 2100.

Table 1. ^{14}C ranges with the highest masses of radiocarbon according to our estimations; ^{14}C expected values according to weighted mean of mass distribution of radiocarbon; and observed ^{14}C mean values of soil CO_2 e ux.

	^{14}C [h]			
Year	Primary Peaks[a]	Secondary Peaks[b]	Expected value[c]	Mean value[d]
1996	(112, 122]	(-28, -18], (102, 112], (122, 212]	153 107.6	129.5 17.3
1998	(-37, -17], (93, 153]	(153, 273], (323, 333], (493, 503]	139.4103.3	117.6 26.2
2002	(82, 102]	(-28,-18], (72, 82], (102, 152]	115.9 96.3	100.8 8.4
2008	(51,61]	(41, 51], (61, 121], (-29, -19]	85 89.7	74.8 13.6

a For 1996, 2002 and 2008, masses 10^3 g m ^{2}; For 1998, masses 10^2 g m ^{2};
b For 1996, 2002 and 2008, masses 10^2 g m ^{2}; For 1998, masses 10 g m ^{2};
c Expected value of theoretical radiocarbon distribution of the Out ux (weighted mean);
d Mean value of the ^{14}C values measured on soil CO_2 e ux from the Harvard Forest.

Figure 9. Comparison between theoretical radiocarbon distribution and independent empirical data. a: Year of observation equals to AD 1996; b: Year of observation equals to AD 1998; c: Year of observation equals to AD 2002; d: Year of observation equals to AD 2008.

t m e di s btions f om com patm ental s m s, one h olud be abl e t a h atonl y one com bi nat on of tes i n h e com patm ental m at xbiul ds h e es m ated di s btions

Moreow, as poi nted otbyGadi nski etal. (2 000), l i m i ted i nf orm at on abotth e cyl i ng tes ae obtai ned by ^{14}C m eam ents of bl k SOM m ade at a s ngl e poi nt i n t m e. Th eef oe, bei ng abl e t com pt adi ocabon di s btions f or di ff eent yas of obsat on colud i m pov h e i nt ep at ons of h e t m e-evl t on of s i l adi ocabon i n em s of cabon dyam i cs

Com patm ental m odel s ae a com m on appoach t desi be h e dyam i cs of open s em s, pat cl al y en m odel i ng h e cabon cyl e i n ecos m s Th e m ah em at cal eq t ons devl oped t obtai n age and t ans t t m e di s btions ae a obs appoach al eady sd i n s eal cont s and, h eef oe, s ng h es di s btions t obtai n adi ocabon di s t btions i n h e s ame s m s i s a poef l m eh od. Th e al gor h m p esnted, besi des bei ng s m pl e, dem onsted h e potent al poeof h e m eh od. I t al s h owd h owf or a speci fi c m odel , p edi ct ons can be com paed wh expei m ental data.

Radi ocabon di s btions can be sd t geh erwh h e know ch anges i n atm osph er c $\Delta^{14}CO_2$ t eval ate h ow m odel s p edi ct h e ch angi ng di s btions of adi ocabon i n each com patm entand i t optover h at l at decades Th i s povi des a poef l m eh od t es m odel s agai ns obsat ons and t ef i ne m odel epesnt at ons of C dyam i cs i n s i l s and ecos m s

Ou esl t al s h ave h own h at h e h et ogenei y of h e ecos m s desi bed h ogh h e m i xng of m at i n h e pool s, i s el ated t h e s h apes of h e adi ocabon di s btions As opposed t age and t ans t t m e di s btions f or s m s i n s ead s ate, adi ocabon di s btions ae expect ed t vayovert m e, s ongl y dependi ng on h e y ar of obs at on as a consequ ce of h e dependence on h e atm osph er c ^{14}C i npt i n h e s m. Th s notonl y h e di s btions' s h apes wl l ch ange accordi ng t h e y ar of obs at on, bt al s h ei r expected v l es, m odes, and v r ance.

Ov al l , f as cyl i ng pool s wh l es h et ogenei y p esnt nao s h apes f or al l h e yas of obs at ons, wer eas s owr cyl i ng pool s as wl l as m oe h et ogeneos com patm ents p esnt wi der s h apes and m l t pl e peaks of Δ^{14}C f or h i gh l abel l ed yas (e. g. , 1 9 6 5 , wen h e concent at ons of ^{14}C i n h e atm osph ee we al m os t t m es h i gh er h an h e nat al l evl s).

Th e h eoet cal di s btions can be es m ated f or speci fi c t m e poi nts h ow, h at i s notal ways f eas bl e i n expei m ents Th at m eans h e es m at ons h ogh h e al gor h m h ave t be t aken caef l l y en one ai m s t com pae h em t em pi r cal dat a. I t i s al s i m potant t be awe of h e adi ocabon atm osph er c v l es sd t es m ate h e di s btions, as h e v r at on of atm osph er c Δ^{14}C can i nfl ence h e s h apes and m ean v l es of h e di s btions I n h i s s ens, h avi ng accate dat a on h e ^{14}C contents i n h e atm osph ee i s key f or h e det m i nat on of h e adi ocabon di s btions i n m l t pl e i nt connected com patm ental s m s

A

Th e ah os wolud l i ke t h ank I ngebog Levin f or h e m eani ngf l com m ents and s g ges t ons on h i s wok. Th i s wok i s al s s m l ated by h e s i ent fi c esach devl oped at h e Am azon Tal l Tow Obs at oy (ATTO), wi ch i s pat y f nded by h e Germ an Fed eal M i ni s y of Edcat on and Resach (gant nm ber 01 LK1 6 02 A) and h e Max Planck Soci ey

The atmospheric $\Delta^{14}CO_2$ datasets used in this research are available through Graven (2015), Graven et al. (2017), and Reimer et al. (2020). Data on the compartmental model presented in this research, including the independent $\Delta^{14}C$ data used for comparisons with other estimations are available through Sierra, Trumbore, et al. (2012).

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