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Controls on ^{13}C and ^{14}C variability in soil CO_2

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ABSTRACT

^{14}C dating of groundwater depends on the isotopic composition of both the solid carbonate and the soil CO_2 and requires the use of ^{14}C age correction models. To better assess the variability of the ^{14}C activity of soil CO_2 ($A^{14}C_{soil\text{-}CO2}$) and the $\delta^{13}C$ of soil CO_2 ($\delta^{13}C_{soil\text{-}CO2}$), which are two parameters used in ^{14}C age correction models, we studied the different processes involving carbon isotopes in the soil. The approach used experimental data from two sites in France (Fontainebleau sands and Astian sands) and a steady-state transport model. In most cases, the ^{14}C activity ($A^{14}C$) of atmospheric CO_2 is directly used in the ^{14}C age correction models as the $A^{14}C_{soil\text{-}CO2}$. However, we demonstrate that since 1950, the evolution of the $A^{14}C_{soil\text{-}CO2}$ reflects the competition between the fluxes of root-derived CO_2 and organic matter-derived CO_2. Therefore, the $A^{14}C_{soil\text{-}CO2}$ must be used to date groundwater that is younger than 60 years old. Moreover, the $\delta^{13}C$ of soil CO_2 ($\delta^{13}C_{soil\text{-}CO2}$) showed large seasonal variations that must be taken into account in selecting the $\delta^{13}C_{soil\text{-}CO2}$ for ^{14}C age correction models.

1. Introduction

Carbon-14 (^{14}C) is a tracer that is commonly used to date groundwater. The carbon isotopic composition (^{13}C, ^{14}C) of the soil CO_2 is a key parameter in most of the correction models described in the literature for the ^{14}C age of groundwater. This information is used to determine the so-called initial ^{14}C activity ($A^{14}C$), *i.e.*, the $A^{14}C$ of the total dissolved inorganic carbon (TDIC) acquired during groundwater recharge and before radioactive decay (Eichinger, 1983; Evans et al., 1979; Fontes and Garnier, 1979; Ingerson and Pearson, 1964; Mook, 1976; Salem et al., 1980; Tamers, 1967). The isotopic signature of the TDIC is acquired mainly during water infiltration through the unsaturated zone by dissolution of both soil CO_2 and matrix carbonates (Gillon et al., 2009). Moreover, interactions between dissolved inorganic carbon and carbonate rocks in the unsaturated zone affect the isotopic signature of the TDIC (Barbecot et al., 2000; Fontes, 1992). All these processes impact the initial $A^{14}C$ of groundwater and therefore must be considered for age calculations using theoretical models.

In most ^{14}C age correction models, the initial values for the ^{13}C content ($\delta^{13}C$) and $A^{14}C$ that are acquired during groundwater recharge are either generated from the analyses of samples collected at the site under investigation or are estimated based on the vegetation cover (Fontes, 1992; Fontes and Garnier, 1979; Kroitoru et al., 1989). However, the ^{14}C activity of atmospheric CO_2 has varied significantly over time and has led to significant changes in the ^{14}C activity of soil CO_2 ($A^{14}C_{soil\text{-}CO2}$), especially during and after the nuclear weapon tests of the 1950s and 1960s (Hua and Barbetti, 2004; Kromer, 2009; Trumbore, 2009). Subsequently, a "modern" (over the past 50 years) soil CO_2 sample is normally not representative of the recharge conditions that prevailed before 1950. The bias in selecting the initial $\delta^{13}C$ and $A^{14}C$ in the TDIC may be reduced if sound knowledge of the carbon sources in the soil, including the $A^{14}C$ distribution through time in each source, exists.

Soil CO_2 is mainly produced by (i) degradation of organic matter and (ii) root respiration (Kuzyakov, 2006). The degradation of soil organic matter is caused by heterotrophic microbial activity, *i.e.*, oxidation of organic matter from leaves and plant debris (Kuzyakov, 2006; Fig. 1). The second process is caused by (i) autotrophic living root respiration and (ii) heterotrophic rhizospheric respiration, *i.e.*, root residue mineralisation.

The isotopic composition of the CO_2 produced in the soil by the "living plant–microbial activity" complex is tightly linked to the isotopic composition of the living vegetation. Due to carbon isotopic fractionation during photosynthesis, C3-plants are depleted in ^{13}C by $20 \pm 1‰$ compared to atmospheric CO_2. Moreover, isotopic fractionation also occurs during carbon transfer from the leaves to other parts of the plant (Bowling et al., 2008; Clark and Fritz, 1997). However, $A^{14}C$ values are referenced to an international standard known as the modern radiocarbon standard (*e.g.*, NIST Oxalic Acid I or NIST Oxalic Acid II), which was calibrated to wood grown in 1890 (absolute radiocarbon standard),

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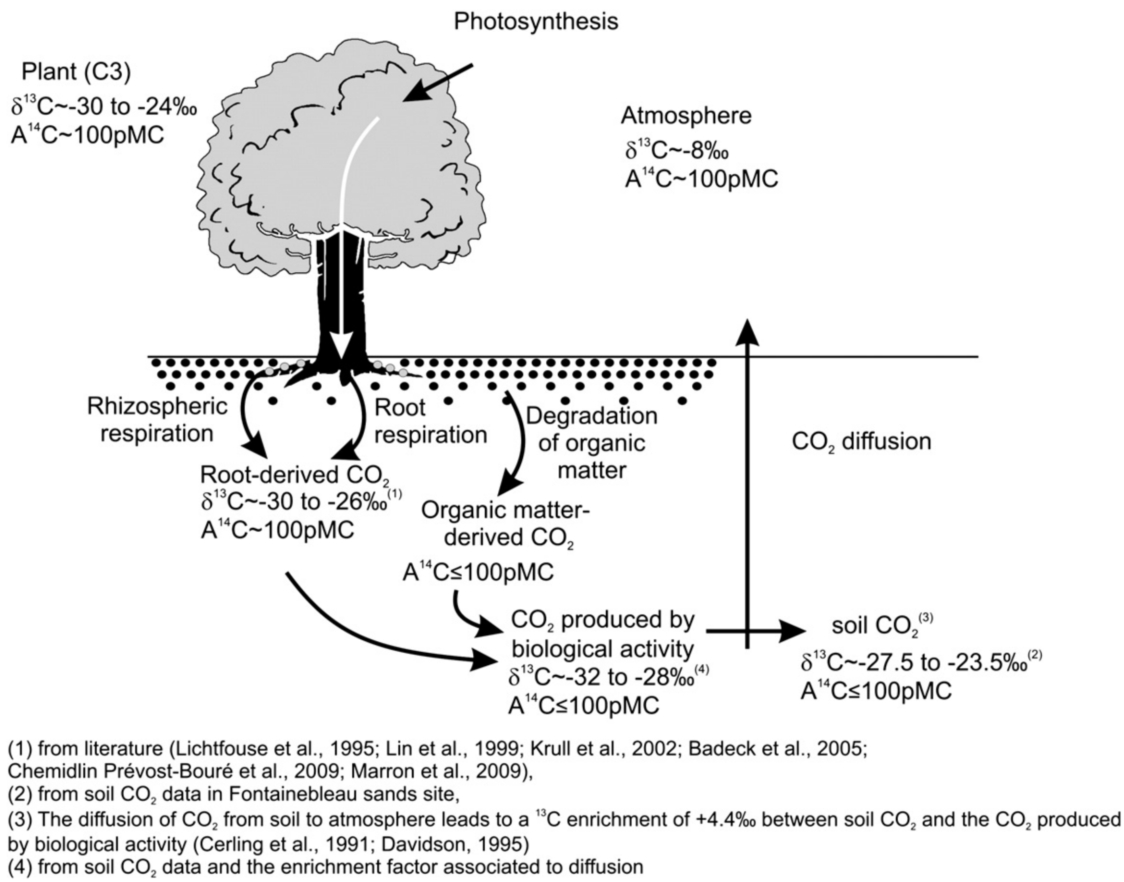

Fig. 1. Schematic illustration of CO_2 sources in soil and related $A^{14}C$. The example is for a C3-plant considering steady-state fluxes from before 1950, *i.e.*, an $A^{14}C$ of atmospheric CO_2 equal to 100 pMC (percentage of modern carbon).

and are all corrected for isotopic fractionation to a normalised $\delta^{13}C$ value of −25‰ (Eq. (1); Clark and Fritz, 1997; Saliège and Fontes, 1984).

$$A^{14}C_{\text{normalised}} = A^{14}C_{\text{no-normalised}} \times \frac{(1+0.001\times(-25))^{2.3}}{(1+0.001\times\delta^{13}C_{\text{no-normalised}})^{2.3}} \quad (1)$$

The normalisation to $\delta^{13}C$ of −25‰ removes the effects of mass-dependent isotopic fractionation; in other words, the $A^{14}C$ values are independent of ^{13}C fractionation. The $A^{14}C$ of CO_2 produced by root respiration is thus assumed to be equal to that of atmospheric CO_2.

The $A^{14}C$ of CO_2 produced by degradation of soil organic matter is more difficult to determine and is therefore less well documented. Indeed, soil organic matter includes a wide range of organic compounds, from fresh to refractory components, with different degradation rates (Trumbore, 1993). The oxidation of old organic fractions produces ^{14}C depleted CO_2 and consequently induces an ageing of the TDIC. The magnitude of this source of "old" CO_2 must be quantified to determine its contribution to the $A^{14}C$ of soil CO_2.

The temporal fluctuations of the $A^{14}C$ in atmospheric CO_2, as well as the competition between root respiration and degradation of different pools of organic matter, have significant impacts on the $A^{14}C_{\text{soil-CO2}}$. Because this soil CO_2 is isotopically different from atmospheric CO_2, the $A^{14}C$ of TDIC in groundwater cannot be merely considered to be similar to the $A^{14}C$ of atmospheric CO_2.

Here, we study the variations of $\delta^{13}C$ and $A^{14}C$ in soil CO_2 with regard to different biological and physical processes. This information is then used to investigate the variability of $\delta^{13}C$–$A^{14}C$ of CO_2 in soils and its impact on the radiocarbon dating of groundwater. The impacts of the water–rock carbonate interactions on the $\delta^{13}C$ and $A^{14}C$ of soil CO_2 have been detailed in a previous study (Gillon et al., 2009). Hence, we focus the present study on ^{13}C–^{14}C variations in soil CO_2 associated with biological processes in the first metre of the soil. Therefore, the water–rock carbonate interactions have only minor influences at this scale and have not intentionally been taken into account here.

The first part of this paper presents and discusses a large set of experimental data (*e.g.*, carbon isotopic compositions of soil CO_2 and organic matter) obtained from two different sites in France: the Fontainebleau sands (Paris basin, 48°43′ 13.34″N; 2°03′ 28.3″E) and the Astian sands (Mediterranean coast, 43°24′ 13.84″N; 3°11′ 50.36″E). A modelling approach is then used to interpret the experimental data sets to better assess the $A^{14}C_{\text{soil-CO2}}$ distribution through time. Finally, the temporal variations of the $A^{14}C$ in soil CO_2 are modelled by assuming an exponential distribution and several pools of organic matter with different residence times under steady-state conditions.

2. Materials and methods

2.1. Description of the investigated sites

The Fontainebleau site is located in the Paris Basin, France (Fig. 2). It is composed of fine, homogeneous and carbonate-free Oligocene sands that primarily contain silicates (up to 99% silica; Afchain et al., 1975). In the unsaturated zone, the sandy facies are overlaid by a sandy–clayey layer containing millstones (carbonate-free siliceous limestone with complete silicification; Fig. 2). The study site is within an outcrop of sand that is covered by grassland or forest (oak, beech, and chestnut trees) belonging to the C3-plant group (Deines, 1980).

The Astian site is located on the Mediterranean coast of France (Fig. 2). It is composed of fine and homogeneous sands that are composed mainly of quartz, between 0 and 30% calcite, micas, potassic