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## Temporal pools of individual organic substances in soil

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### Abstract

Two pools of plant-derived  $C_{31}$  *n*-alkane occurring respectively as free and humin-bound forms in the same soil have been distinguished by  $^{13}C/^{12}C$  analyses. The results show that the humin-bound molecule is on the average 7 years older than the free molecule. These findings indicate that apolar organic substances can be trapped temporarily into the soil matrix by weak forces.

*Dans un même sol, la teneur en carbone 13 de l'alcane en  $C_{31}$  'libre' est différente de celle de l'alcane en  $C_{31}$  'lié' à l'humine. Les résultats montrent l'alcane lié à l'humine est en moyenne 7 ans plus vieux que l'alcane libre. Ainsi, des substances organiques apolaires peuvent être séquestrées temporairement au sein de la matrice du sol par des forces faibles*

### INTRODUCTION

Historically, the organic matter occurring in geological media has been classified into two main fractions based on solvent extraction procedures : an extractable fraction including the so-called 'free' molecules, and a non-extractable fraction which contain a poorly known, partly polycondensed organic network such as humin and kerogen [1-4]. Nonetheless, small molecules could also be trapped by weak interactions into internal voids of the macromolecular network, as suggested by studies on humic substances and sedimentary organic matter [5-9]. For instance, chemical and physical treatments of fulvic and humic acids have a notable influence on extractable amounts of alkanes and fatty acids [7]. Furthermore, it was found that concentrations of lipids are usually higher in humic-bound fractions than in 'free' soil extracts [8]. Such findings suggest that during the decay of living organic matter plant-derived lipids could be split up into various pools of different turnover. If that is the case, then bound molecules should be older than free molecules. This hypothesis is confirmed in this report using  $^{13}C$  labelling of soil organic matter with maize.

## EXPERIMENTAL

Detailed experimental procedures are described elsewhere [10-14]. Soils, previously planted with wheat, were cultivated with maize during 23 years at the Boigneville experimental field (France). Free and bound *n*-alkanes were isolated from a 23 year soil sample as outlined on Figure 1.

Free *n*-alkanes : soil samples were 2 mm-sieved, dried, finely ground, then extracted with CHCl<sub>3</sub>-MeOH (3/1 v/v). The *n*-alkane-enriched fraction was isolated from the organic extract by KOH-silica-gel chromatography followed by two thin layer chromatography (TLC) steps.

Bound *n*-alkanes : a sample from the soil cropped 23 years with maize was extracted with CHCl<sub>3</sub>-MeOH 3/1 v/v to remove free lipids, then with NaOH to remove fulvic and humic acids. The remaining matter was treated with HCl and HF to yield humin. A first pool of bound alkanes was isolated from humin by extraction then chromatography as described above. A second pool of bound alkanes was isolated from the CHCl<sub>3</sub>-MeOH extracted humin by pyrolysis at 600°C followed by chromatographic fractionation of the pyrolysate. Noteworthy, gas chromatographic analyse of the alkane fraction from the pyrolysate shows two classes of *n*-alkanes : short-chain homologues along with *n*-alkenes, which are pyrolytic cleavage products, and long-chain, odd-predominant *n*-alkanes which are plant-derived waxes trapped into the humin matrix [14].

Isotopic compositions of the free C<sub>31</sub> *n*-alkane at increasing time of maize cultivation have been reported elsewhere [10]. Isotopic analyses of bound *n*-alkanes (3 to 4 replicates, deviation ≤ 0.3‰) were carried out under a continuous helium flow using a Hewlett Packard gas chromatograph coupled via a CuO furnace to a Finigan Mat 252 isotope ratio mass spectrometer. Isotope values were measured by comparison with CO<sub>2</sub>, 5α-androstane and *n*-tetracontane standards. Isotopic compositions are expressed in per mil as δ<sup>13</sup>C values relative to the Pee Dee Belemnite standard :  $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}} - {}^{13}\text{C}/{}^{12}\text{C}_{\text{std}})/({}^{13}\text{C}/{}^{12}\text{C}_{\text{std}})] \times 10^3$

## RESULTS AND DISCUSSION

### Free *n*-alkanes

‘Free’ refers to organic molecules found in the soil organic extract (Figure 1). Soil *n*-alkanes can be <sup>13</sup>C-labelled at natural abundance by cultivation of *Zea mays*, a plant containing <sup>13</sup>C-enriched C<sub>31</sub> *n*-alkane (δ -20.6‰), on soils containing <sup>13</sup>C-depleted C<sub>31</sub> *n*-alkane (δ -35.7‰) [10]. As a result, the ‘free’ soil C<sub>31</sub> *n*-alkane is enriched of +7.6‰ after 23 years of maize cultivation at a field experiment in France (Figure 2). This labelling allows to calculate the amount of maize-derived carbon within the soil C<sub>31</sub> *n*-alkane, and to predict long-term turnovers using first-order kinetics [10].

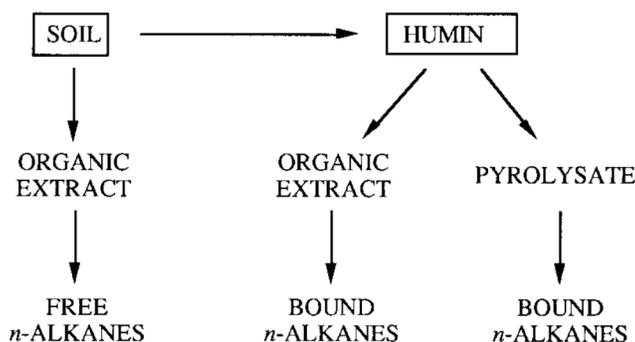


Figure 1. Isolation of free and bound *n*-alkanes from soil.

### Bound *n*-alkanes

Here, *n*-alkanes were isolated from two bound fractions of the 23 year soil sample : a first fraction amenable by  $\text{CHCl}_3$ -MeOH extraction of humin, and a second fraction amenable by pyrolysis (Figure 1). The *n*-alkane distribution of the free and the two bound fractions are similar in the  $\text{C}_{27}$ - $\text{C}_{33}$  range [11], showing the typical odd carbon-numbered predominance of plant waxes [15].

Isotope values of free and bound *n*-alkanes are reported in Table 1.  $\delta^{13}\text{C}$  values of bound *n*-alkanes are significantly depleted in  $^{13}\text{C}$  relatively to free *n*-alkanes. For instance, the  $\text{C}_{31}$  bound *n*-alkane is depleted by 1.6‰ relatively to the  $\text{C}_{31}$  free *n*-alkane (Figure 2). Given that each soil *n*-alkane is a mixture of  $^{13}\text{C}$ -enriched *n*-alkane from maize and  $^{13}\text{C}$ -depleted *n*-alkane from previously grown wheat, this finding implies that bound *n*-alkanes have less maize carbon than their free counterparts.

Table 1.  $\delta^{13}\text{C}$  values (‰) of plant-derived *n*-alkanes from a soil cultivated 23 years with maize. ‘Free’ refers to alkanes from the soil organic extract. ‘Bound’ refer to alkanes from the humin extract and from the humin pyrolysate.

| Carbon number | FREE  | BOUND         |            |
|---------------|-------|---------------|------------|
|               |       | Humin extract | Pyrolysate |
| 27            | -24.0 | -26.0         | -26.5      |
| 29            | -28.3 | -30.0         | -29.5      |
| 31            | -28.1 | -29.7         | -29.7      |
| 33            | -25.6 | -27.6         | -27.8      |

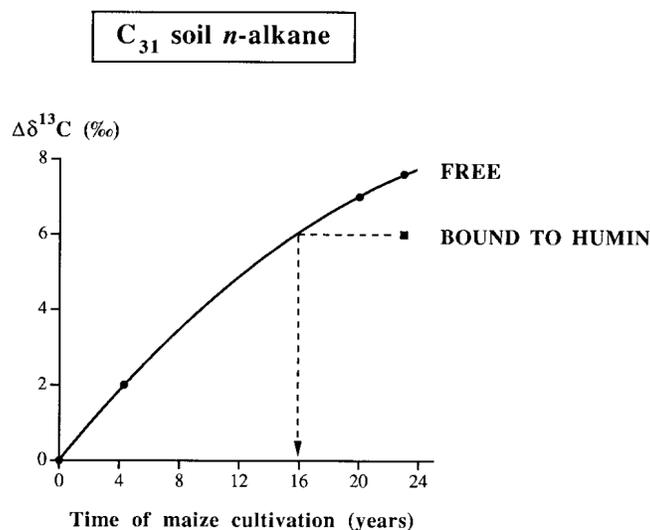


Figure 2. With increasing time of maize cultivation, the C<sub>31</sub> soil *n*-alkane is enriched in <sup>13</sup>C as a result of increasing input of <sup>13</sup>C-enriched maize *n*-alkane (δ -20.6 ‰). Δδ<sup>13</sup>C = δ - (-35.7). After 23 years of cultivation, the C<sub>31</sub> humin-bound *n*-alkane is less enriched than the C<sub>31</sub> free *n*-alkane. The humin-bound *n*-alkane has thus been trapped in the humin matrix 7 years earlier, on the average.

The percentage M of maize carbon in each soil C<sub>31</sub> *n*-alkane can be calculated using the following equation [16] :

$$M = 100 \cdot (\delta - (-35.7)) / (-20.6 - (-35.7)),$$

where δ refers to free or bound isotope values. After 23 years of maize cultivation, M amounts to 50.3% for the free molecule, and only to 39.7% for the bound molecule. Bound *n*-alkanes are therefore composed of molecules that have on the average a lower turnover and a lower age than free *n*-alkanes. This age difference can be determined by calculation of the cultivation time t at which free *n*-alkanes have had the same maize carbon content as the bound *n*-alkanes from the 23-years maize cultivated soil (Figure 2), using the following first order kinetic law established for the C<sub>31</sub> *n*-alkane [10] :

$$\text{Ln}[(100 - M)/100] = -0.031 t$$

The calculation gives a value of 16 years, meaning that if the bound C<sub>31</sub> *n*-alkane of the 23-years maize cultivated soil would derive from a once free C<sub>31</sub> *n*-alkane, then the trapping has occurred 7 years earlier on the average.

Our results show that the same organic substance can occur in different pools of various ages, namely ‘temporal pools’, within the soil matrix. Moreover, the absence of chemical alteration of plant wax *n*-alkanes during encapsulation shows that apolar molecules can be sequestered by weak interactions, e.g. Van der Waals forces. It suggests that similar processes should take place for apolar xenobiotics. Furthermore, it has been shown that the amount of soil aggregates increases with lipid content [17]. Here, the occurrence of humin-bound *n*-alkanes may play an important role in sustaining the stability of soil minerals. Further work is in progress to identify other chemical classes of weakly bound molecules.

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