HAL
open science

Temporal pools of individual organic substances in soil

Eric Lichtfouse

To cite this version:

Eric Lichtfouse. Temporal pools of individual organic substances in soil. Analusis, 1999, 27 (5), pp.442-444. hal-02686857

HAL Id: hal-02686857

https://hal.inrae.fr/hal-02686857v1

Submitted on 1 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Temporal pools of individual organic substances in soil

É. Lichtfouse

Laboratoire Sols et Environnement, INRA/ENSAIA-INPL, BP. 172, 54505 Vandœuvre-lès-Nancy, France

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.

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

© EDP Sciences, Wiley-VCH 1999

Article available at http://analusis.edpsciences.org or http://dx.doi.org/10.1051/analusis:1999270442

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 $CHCl_3$-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 $CHCl_3$-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 $CHCl_3$-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].

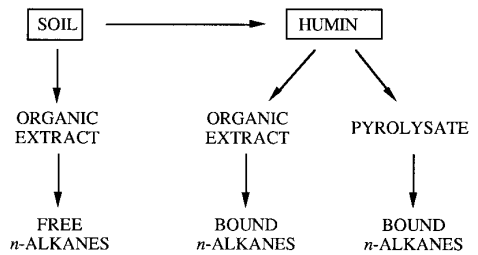

Figure 1. Isolation of free and bound *n*-alkanes from soil.

Isotopic compositions of the free C_{31} *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_2, 5α-androstane and *n*-tetracontane standards. Isotopic compositions are expressed in per mil as $\delta^{13}C$ values relative to the Pee Dee Belemnite standard: $\delta^{13}C = [(^{13}C/^{12}C\text{sample} - {}^{13}C/^{12}C\text{std})/(^{13}C/^{12}C\text{std})] \times 10^3$.

Results and discussion

Free n-alkanes

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

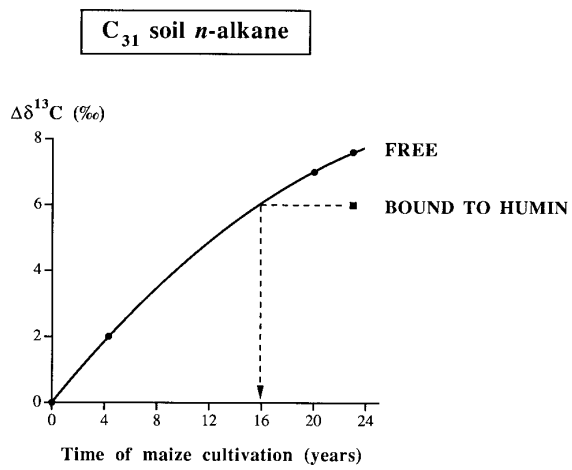

Figure 2. With increasing time of maize cultivation, the C_{31} soil *n*-alkane is enriched in ^{13}C as a result of increasing input of ^{13}C-enriched maize *n*-alkane (δ –20.6 ‰). $\Delta\delta^{13}C = \delta - (-35.7)$. After 23 years of cultivation, the C_{31} humin-bound *n*-alkane is less enriched than the C_{31} free *n*-alkane. The humin-bound *n*-alkane has thus been trapped in the humin matrix 7 years earlier, on the average.

© EDP Sciences, Wiley-VCH 1999

Table I. $\delta^{13}C$ 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

Bound n-alkanes

Here, *n*-alkanes were isolated from two bound fractions of the 23 year soil sample: a first fraction amenable by $CHCl_3$-MeOH extraction of humin, and a second fraction amenable by pyrolysis (Fig. 1). The *n*-alkane distribution of the free and the two bound fractions are similar in the C_{27}–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 I. $\delta^{13}C$ values of bound *n*-alkanes are significantly depleted in ^{13}C relatively to free *n*-alkanes. For instance, the C_{31} bound *n*-alkane is depleted by 1.6‰ relatively to the C_{31} free *n*-alkane (Fig. 2). Given that each soil *n*-alkane is a mixture of ^{13}C-enriched *n*-alkane from maize and ^{13}C-depleted *n*-alkane from previously grown wheat, this finding implies that bound *n*-alkanes have less maize carbon than their free counterparts.

The percentage M of maize carbon in each soil C_{31} *n*-alkane can be calculated using the following equation [16]:

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

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 (Fig. 2), using the following first order kinetic law established for the C_{31} *n*-alkane [10]:

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

The calculation gives a value of 16 years, meaning that if the bound C_{31} *n*-alkane of the 23-years maize cultivated soil would derive from a once free C_{31} *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.

References

1. Tissot, B. P.; Welte D. H. Petroleum Formation and Occurrence. Springer, 1984.
2. Schnitzer, M. *Soil Sci.* **1991**, *151*, 41-58.
3. Beyer, L. *Zeitsch. Pflanzenernähr Bodenk* **1996**, *159*, 527-539.
4. Hedges, J. I.; Oades, J. M. *Org. Geochem.* **1997**, *27*, 319-361.
5. Ogner, G.; Schnitzer, M. *Science* **1970**, *170*, 317-318.
6. Meyers, P. A.; Quinn, J. G. *Geochim. Cosmochim. Acta* **1973**, *37*, 1745-1759.
7. Schnitzer, M.; Neyroud, J. A. *Fuel* **1975**, *54*, 17-19.
8. Amblès, A.; Parlenti, E.; Jambu, P.; Mayoungou, P.; Jacquesy, J. C. *Geoderma* **1994**, *64*, 111-124.
9. Nanny, M. A.; Bortiatynski, J. M.; Hatcher, P. G. *Environ. Sci. Technol.* **1997**, *31*, 530-534.
10. Lichtfouse, E. Naturwissensch. **1997**, *84*, 23-24.
11. Lichtfouse, E. Naturwissensch. **1998**, *85*, 76-77. Lichtfouse, E.; Wehrung, P.; Albrecht, P. *Naturwissensch.* **1998**, *85*, 449-452.
12. Lichtfouse, E.; Chenu, C.; Baudin, F. *Org. Geochem.* **1996**, *25*, 263-265.
13. Lichtfouse, E.; Bardoux, G.; Mariotti, A.; Balesdent, J.; Ballentine, D. C.; Macko, S. A. *Geochim. Cosmochim. Acta* **1997**, *61*, 1891-1898.
14. Lichtfouse, E.; Chenu, C.; Baudin, F.; Leblond, C.; Da Silva, M.; Behar, F.; Derenne, S.; Largeau, C.; Wehrung, P.; Albrecht, P. *Org. Geochem.* **1998**, *28*, 411-415.
15. Eglinton, G.; Hamilton, R. J. *Science* **1967**, *156*, 1322-1335.
16. Lichtfouse, E. *Tetrahedron Lett.* **1995**, *36*, 529-530.
17. Jambu, P.; Fustec, E.; Jacquesy, R. *Sci. Sol* **1978**, *4*, 229-240.

© EDP Sciences, Wiley-VCH 1999