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^{13}C and ^{14}C evidence of pollution of a soil by fossil fuel and reconstruction of the composition of the pollutant

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Abstract- *n*-Alkanes from soils in which C₃ plants have been cultivated were analysed for their distributions and individual $\delta^{13}\text{C}$ ratios. For long-chain *n*-alkanes from unpolluted soils, both the strong odd-carbon number predominance, with a carbon preference index (CPI) of 9.2, and the light isotope composition, $\sim -35\text{‰}$, are typical of modern C₃-plant waxes. In contrast, long-chain *n*-alkanes from another soil sample show a weak odd-carbon number predominance, with a CPI of 1.2, indicating a large anthropogenic contribution from ancient and thermally mature organic matter. This derivation from ancient organic matter is strongly supported by 1) the $\delta^{13}\text{C}$ ratios of those alkanes, $\sim -30\text{‰}$, which does not match reported values for C₃ plant *n*-alkanes and which falls within the range of values reported for fossil-fuel *n*-alkanes, and 2) the ^{14}C analysis of the alkane fraction which gives an age of 8770 yrs BP. Moreover, assuming that each soil *n*-alkane is a mixture of C₃-plant *n*-alkane and fossil-fuel *n*-alkane, the isotopic composition provide a means of reconstructing the composition of the fossil fuel pollution. This method, using both isotopic and quantitative analyses of individual substances, represents a powerful means to resolve multiple sources in environmental and geochemical investigations.

Key words - carbon-13, carbon-14, soil, *n*-alkane, plant, wax, pollution, petroleum.

INTRODUCTION

n-Alkanes are occur widely wherever organic matter has been decomposed, such as waters, soils, sediments and coals. Although numerous studies have been undertaken to follow the fate of these substances in such complex media, many questions remain to be answered about their origin and their pathways of degradation. For instance, soil *n*-alkanes might derive from biological *n*-alkanes which are synthesized by a large variety of living organisms, such as bacteria, plants and insects (Schnitzer *et al.*, 1986, Dinel *et al.*, 1990, Amblès *et al.*, 1991, 1994, and refs. therein). Moreover, a large number of living organisms, especially microbes, have not yet been analysed for *n*-alkanes and *n*-alkanes can also derive from the reduction of other aliphatic precursors such as *n*-fatty acids or *n*-alcohols. Finally, and this is rarely mentioned in the literature, *n*-alkanes of anthropogenic origin, e. g. from oil spills, may be introduced in natural systems, and can thus constitute another source. Given these possibilities, means for the recognition and reconstruction of the multiple sources of individual substances from degraded organic matter are of considerable interest.

In recent studies at the molecular level, we have shown that $^{13}\text{C}/^{12}\text{C}$ ratios can provide information on the origins and fates of soil *n*-alkanes (Lichtfouse *et al.*, 1994a, Lichtfouse, 1995). Furthermore, we have presented an isotopic model allowing the multiple sources of *n*-alkanes from the Green River sediments to be partially delineated (Collister *et al.*, 1994a). Recent investigations have also shown that sources of *n*-alkanes from polluted sediments may be resolved by molecular ^{13}C analyses (Usaki *et al.*, 1993, Ishiwatari *et al.*, 1994). In the present work, $^{13}\text{C}/^{12}\text{C}$ ratios, ^{14}C age and relative concentrations are used to assess the origins of *n*-alkanes in a polluted soil.

EXPERIMENTAL

Soil samples, cultivated with *Triticum aestivum* (wheat) for the past 23 years at one crop per year, were cored in May 1993 at Boigneville, Essone, France, at various random geographical locations within the same experimental field, through the 0-30 cm ploughed horizon. Each 0-30 cm core was homogenised prior extraction. This field was previously cropped only with plants following the C_3 photosynthetic pathway. It is a Hapludalf developed on loess (Balesdent *et al.*, 1990). The polluted soil represents a point-source pollution. Wheat leaves were sampled at the same time, water-washed and freeze-dried at -20°C .

Detailed fractionation procedures are described elsewhere (Lichtfouse *et al.*, 1994b). Careful precautions were taken to prevent contamination during the sampling and treatment of samples (solvent distillation, etc.). Briefly, alkane fractions were isolated from CHCl_3 -MeOH extracts (3/1, v/v) of dried samples by several steps of silica gel chromatography. *n*-Alkane relative concentrations were measured by area integration of peaks from alkane fractions analysed by gas chromatography using a flame ionization detector. Carbon preference indexes (CPI) are based on relative concentrations and are calculated as follows: $\text{CPI} = (\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}) / (\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32})$. Isotopic analyses of individual *n*-alkanes were carried out under continuous helium flow using an HP 5890 gas chromatograph interfaced, via a CuO furnace (850°C) and a cryogenic trap (-100°C), to a VG Optima mass spectrometer (overall deviation 0.3‰). Isotope compositions are expressed in per mil. relative to the Pee Dee Belemnite standard: $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}/{}^{13}\text{C}/{}^{12}\text{C}_{\text{std}}) - 1] \times 10^3$.

For radiocarbon analysis, about 200 μg of the alkane fraction from the polluted soil, dissolved in CH_2Cl_2 , were first transferred to quartz combustion tubes. Then the solvent was removed by nitrogen blow-down and evacuation of the tube. CuO was added, and the tubes sealed under vacuum, and the alkane fraction was converted to CO_2 by combustion at 900°C for 5 hr. Afterwards the CO_2 was reduced to graphite and pressed into targets for ^{14}C analysis by accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratory. Radiocarbon data are reported according the convention of Stuiver and Polach (1977). The values were corrected for carbon blanks, based on AMS measurements of similar amounts of ^{14}C -free coal. These data were also corrected using a $\delta^{13}\text{C}$ value of -30.1‰ which was calculated with relative concentrations and individual $\delta^{13}\text{C}$ values of *n*-alkanes. This method for ^{14}C analysis is analogous to that described in detail by Eglinton *et al.* (1995).

RESULTS AND DISCUSSION

Alkane distributions

$\delta^{13}\text{C}$ values and relative concentrations of *n*-alkanes from wheat leaves and two representative soils are reported in Table 1. The distribution of *n*-alkanes in most soil samples, termed "unpolluted soils", is similar to that of wheat waxes (CPI = 48.55), exhibiting a strong predominance of odd carbon number *n*-alkanes (CPI = 9.21, Figure 1). Since those soils have been cultivated with wheat for 23 years, soil *n*-alkanes are therefore mainly derived from wheat waxes and from earlier C_3 crops. Notably, the latter contribution can be as high as 50% of each *n*-alkane, as estimated from $\delta^{13}\text{C}$ values of *n*-alkanes in a portion of the field that was planted with *Zea mays* (maize, a C_4 plant) to provide an isotopically labelled plant-wax input (Lichtfouse, 1995). The direct input of plant waxes into soils has also been demonstrated recently (Lichtfouse *et al.*, 1994a). In contrast, one of the soil samples, termed "polluted soil", displays an *n*-alkane distribution characterized by a weak odd-carbon predominance, with a CPI of 1.17. Such a distribution is more typical of thermally mature organic matter, which is usually found in ancient sediments, coals, petroleum and kerogen pyrolysates (e.g. Tissot and Welte, 1984, Behar *et al.*, 1984, Hofman and Leythaeuser, 1995). An input from a fossil fuel source can therefore be considered.

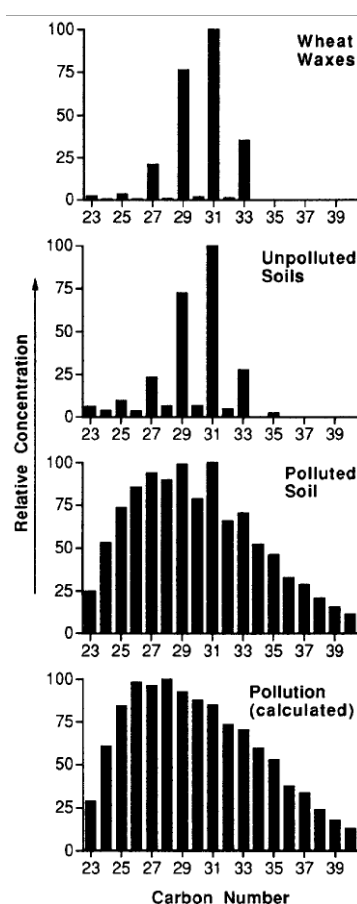


Figure 1. Distributions of *n*-alkanes from the wheat leaf waxes, from the unpolluted and polluted soils, and from the pollution source. The latter has been calculated by isotopic means (see text).

Table 1.

$\delta^{13}\text{C}$ values (‰) and relative concentrations (%) of *n*-alkanes from wheat leaf wax and from polluted and unpolluted soils.

Carbon Number	Wheat Waxes		Unpolluted Soils		Polluted Soil		x	Pollution (Calculated)	
	(‰)	(%)	$\delta_{\text{U}}(\text{‰})$	(%)	$\delta_{\text{P}}(\text{‰})$	A _P (%)		A _F (%) [†]	A _F (%) [‡]
23		2.40		6.09		24.83		24.83	28.54
24		0.66		3.95		52.82		52.82	60.71
25		3.64		9.77	-29.5	73.51		73.51	84.49
26		0.47		3.82	-29.5	85.47		85.47	98.23
27	-35.9	21.28	-34.2	23.25	-30.0	93.98	0.89	83.64	96.13
28		0.83	-35.5	6.37	-29.7	89.70	0.97	87.01	100.00
29	-36.5	76.24	-35.7	72.35	-30.7	99.16	0.81	80.32	92.31
30		1.68	-35.7	6.58	-29.7	78.62	0.97	76.26	87.65
31	-36.7	100	-35.7	100	-31.1	100	0.74	74.00	85.05
32		1.23	-35.6	4.59	-29.7	65.75	0.97	63.78	73.30
33	-36.7	35.29	-35.7	27.8	-30.3	70.46	0.87	61.30	70.45
34						51.8		51.80	59.53
35				2.62		45.95		45.95	52.81
36						32.62		32.62	37.49
37						29.01		29.01	33.34
38						20.78		20.78	23.88
39						15.65		15.65	17.99
40						11.31		11.31	13.00

[†]Values for C₂₇-C₃₃ were calculated by isotopic means (see text). Values for other *n*-alkanes are those recorded for the polluted soil because their carbon is derived only from the pollution. [‡]Values normalized to 100%.

It is also notable that the polluted soil shows a slight predominance of odd-carbon-number *n*-alkanes in the C₂₇-C₃₃ range, particularly for the C₃₁ *n*-alkane. Since *n*-alkanes from wheat waxes and from the unpolluted soils exhibit a strong odd-carbon predominance maximizing at C₃₁, the *n*-alkanes from the polluted soil sample are likely to represent both a small contribution from C₃-plant waxes and a large contribution from fossil fuel hydrocarbons. These hypotheses are confirmed by ¹³C and ¹⁴C investigations, as explained below.

Isotopic compositions of alkanes

The $\delta^{13}\text{C}$ values of *n*-alkanes from the unpolluted soils, averaging $-35.4 \pm 0.5\text{‰}$, are very close to those of wheat waxes, which average $-36.5 \pm 0.3\text{‰}$ (Figure 2) and fall within the range of isotopic compositions reported for C₃ plant waxes (Collister *et al.*, 1994b). Remarkably, even- and odd-carbon-number *n*-alkanes from the unpolluted soils have δ values that are equal within experimental error ($\sim -35.6\text{‰}$). Therefore, the even- and odd-carbon-number *n*-alkanes probably have the same biological origin, e. g. they are derived from C₃-plant lipids. On these isotopic grounds, and also because the distribution of *n*-alkanes in the unpolluted soils almost matches that in the wheat waxes, it can be deduced that these soil *n*-alkanes are derived from a single contemporary source, namely C₃ plant waxes.

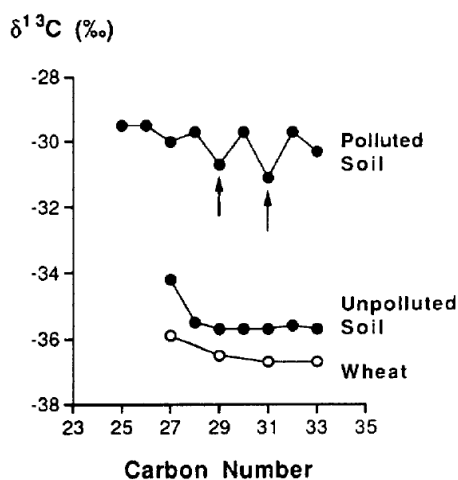


Figure 2. $\delta^{13}\text{C}$ values of *n*-alkanes from soils and wheat waxes. The ¹³C-depletion of odd-carbon number *n*-alkanes from the polluted soil (arrows) indicates a partial contribution of *n*-alkanes from C₃ plants, e.g. wheat.

The $\delta^{13}\text{C}$ values of *n*-alkanes from the polluted soil, which average -30.1‰ , are markedly ¹³C-enriched, thus indicating a contribution from a source enriched in ¹³C. The δ values do not match those reported for C₃ plant waxes, but fall within the range reported for sedimentary organic matter and petroleum (Kennicutt and Brooks, 1990, Lichtfouse and Collister, 1992, Clayton and Bjorøy, 1994, Freeman *et al.*, 1994, Hartgers *et al.*, 1994, Spooner *et al.*, 1994, Collister *et al.*, 1994a, Lichtfouse *et al.*, 1994b,c). Another remarkable feature of the isotopic compositions of *n*-alkanes from the polluted soil is the relative ¹³C-depletion of odd-carbon-numbered homologues, this depletion being most pronounced for the C₃₁ *n*-alkane (see arrows on Figure 2). Moreover, the ¹³C-depletion is associated with the odd/even predominance intensity of *n*-alkanes, e.g. the C₃₁ *n*-alkane is the lightest and shows the highest odd/even

predominance (Figure 1, 2). Therefore, those soil *n*-alkanes must represent a mixture of two sources, a small contribution of C₃-plant *n*-alkanes with a high CPI maximizing at C₃₁, and a large contribution from fossil fuel *n*-alkanes with a low CPI.

The alkane fraction from the polluted soil was also analysed for ¹⁴C. AMS dating indicated a radiocarbon age of 8770 ± 70 yrs before present (BP) corresponding to a fraction Modern (fM) of ~ 0.34. If we assume that this fraction is a mixture of modern C and fossil-fuel C (no ¹⁴C), then the fraction Modern indicates that there is only 34% of modern C, and 66% of fossil-fuel C. This additional evidence therefore demonstrates unambiguously the occurrence of ancient carbon in *n*-alkanes from the "polluted" soil.

Utilizing the stable carbon isotopic and concentration data (Table 1), it is possible to calculate a weighted average: $100 \cdot \frac{\sum(1-x) \cdot A_p}{\sum A_p}$, which estimates the overall proportion of modern *n*-alkanes in the alkane fraction of the polluted soil. This calculation suggests that only 12% of the *n*-alkanes are of modern origin. This is significantly lower than that estimated based on the radiocarbon data (34%). There are two possible reasons for this discrepancy.

First, although GC analysis of the alkane fraction was dominated by *n*-alkanes, the presence non-GC-amenable components in soil lipids was detected (Lichtfouse, unpublished results). The occurrence of non-GC-amenable components is also supported by the detection of alkanes in the range from C₁₇ to C₁₀₁ in soil humic substances using field desorption mass spectrometry (Schnitzer and Schulten, 1989, Dinel *et al.*, 1990). Non-GC-amenable components would contribute to the ¹⁴C signal (i.e. total carbon in the sample) and, if of biological origin, would give rise to a higher fM. A second explanation relates to the ¹⁴C data. The fraction modern is calculated based on 1950 a.d. as "modern" (i.e. fM = 1). This is used because it pre-dates the injection of ¹⁴C from atomic weapons testing. Carbon fixed by plants during photosynthesis *later* than this date will incorporate some bomb-derived ¹⁴C, giving rise to "greater-than-modern" values. Calculations of fM based on such ¹⁴C measurements of such samples will thus over-estimate the % modern carbon in the sample. Whatever the case, both independent approaches point clearly to a major contribution of fossil fuel hydrocarbons to the soil alkane fraction.

Reconstruction of the pollution source signature

To calculate the distribution of the fossil fuel source, we must determine the δ¹³C values of its *n*-alkanes. On first approximation, we estimate this value at -29.5‰ on the following grounds: 1) this is the heaviest value measured for the *n*-alkanes from the polluted soil and it must therefore represent the isotopic composition least influenced by light *n*-alkanes from C₃ plants (Table 1, Figure 2) ; 2) it is the δ value for the C₂₆ *n*-alkane, this compound being both the least abundant among the wheat *n*-alkanes (0.47%) and a major component of the distribution in the polluted soil (85.47%), and 3) δ¹³C values of all even-carbon-numbered *n*-alkanes from the polluted soil, from -29.7‰ to -29.5‰, are identical within the experimental error (0.3‰), suggesting that δ values of all fossil-fuel *n*-alkanes are very similar as is usually observed for mature organic matter, petroleums and kerogen pyrolysates (Clayton and Bjorøy, 1994, Wilhelms *et al.*, 1994, Bjorøy *et al.*, 1994, Eglinton, 1994, Lichtfouse *et*

al., 1994b). The latter point is also strengthened by the fact that the C₂₅ *n*-alkane, which should be only very weakly influenced by a plant contribution (see relative intensities on Figure 1), also has a $\delta^{13}\text{C}$ value of -29.5‰.

The contribution of fossil fuel to each *n*-alkane in the polluted soil can be calculated from:

$$x = (\delta_P - \delta_U) / (\delta_F - \delta_U)$$

where *x* is the carbon fraction derived from the fossil fuel source, δ_P is the $\delta^{13}\text{C}$ value of *n*-alkane from the polluted soil, δ_U is the $\delta^{13}\text{C}$ value of the same *n*-alkane in the unpolluted soil, and δ_F is the $\delta^{13}\text{C}$ value of *n*-alkane from the fossil fuel source (here -29.5‰). Values for *x* have been calculated for *n*-alkanes in the range C₂₇-C₃₃ (Table 1). It is assumed, on isotopic and quantitative grounds, that other *n*-alkanes from the polluted soil derive entirely from the fossil fuel source (Figure 1, 2). The lowest *x* value, 0.74, is observed for the C₃₁ *n*-alkane, indicating that this compound contains a significant contribution from C₃ plants (26%). Furthermore, the relative concentrations of *n*-alkanes in the fossil fuel source can be calculated from

$$A_F = x \cdot A_P$$

where *A_F* is the relative concentration of an *n*-alkane in the fossil fuel-source and *A_P* is the relative concentration in the polluted soil (Table 1). These calculations allow reconstruction of the original composition of the fossil fuel source (Figure 1). The calculated distribution of *n*-alkanes has no odd/even predominance (CPI = 1.02). This is in excellent agreement with a derivation from ancient and thermally mature organic matter (Tissot and Welte, 1984). Furthermore, the distribution maximizes at C₂₈, indicating that the fossil fuel source could be an heavy oil. Alternatively, the light end of the fossil fuel source could have been preferentially removed by water washing and biodegradation after introduction into the soil.

CONCLUSION

Two sources of soil *n*-alkanes, a modern source from plant waxes and an ancient, anthropogenic source from fossil fuel, have been resolved using relative concentrations, $\delta^{13}\text{C}$ ratios and ¹⁴C age. This method represents a promising approach in environmental and geochemical studies to decipher the possible multiple origins of organic substances at the molecular level.

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