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Eric Lichtfouse, Michel Lichtfouse, Anne Jaffrézic. ^{13}C values of grasses as a novel indicator of pollution by fossil-fuel-derived greenhouse gas CO_2 in urban areas. *Environmental Science and Technology*, 2003, 37, pp.87-89. 10.1021/es025979y . hal-00174857

HAL Id: hal-00174857

<https://hal.science/hal-00174857>

Submitted on 25 Sep 2007

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Revised version October 3, 2002

Manuscript submitted as a Current Research Paper to *Environmental Science and Technology*

$\delta^{13}\text{C}$ values of grasses as a novel indicator of pollution by fossil fuel derived, greenhouse gas CO_2 in urban areas.

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ABSTRACT

A novel fossil-fuel pollution indicator based on the $^{13}\text{C}/^{12}\text{C}$ isotopic composition of plants has been designed. This bioindicator is a promising tool for future mapping of the sequestration of fossil-fuel CO_2 into urban vegetation. Theoretically, plants growing in fossil-fuel CO_2 contaminated areas such as major cities, industrial centers, and highway borders, should assimilate a mixture of global atmospheric CO_2 of $\delta^{13}\text{C}$ value of - 8.02‰ and of fossil-fuel CO_2 of average $\delta^{13}\text{C}$ value of - 27.28‰. This isotopic difference should thus be recorded in plant carbon. Indeed, this study reveals that grasses growing near a major highway in Paris, France, have a strikingly depleted $\delta^{13}\text{C}$ values averaging at -35.08‰, versus rural grasses that show an average $\delta^{13}\text{C}$ value of - 30.59‰. A simple mixing model was used to calculate the contributions of fossil-fuel derived CO_2 to the plant tissue. Calculation based on contaminated and non-contaminated isotopic end-members shows that urban grasses assimilate up to 29.1% of fossil-fuel CO_2 derived carbon in their tissues. The ^{13}C isotopic composition of grasses thus represents a promising new tool for the study of the impact of fossil fuel CO_2 in major cities.

INTRODUCTION

Since the start of the industrial revolution after 1750 AD, there has been a steady increase of the combustion of fossil fuels and forest, leading to the emission of considerable amounts of the greenhouse gas CO₂ into the atmosphere. In particular, for the period from 1980 to 1989, CO₂ emissions from fossil-fuel burning and tropical deforestation amounted to about $7.0 \pm 1.1 \times 10^{15}$ g C per year (1). Fossil-fuel CO₂ emissions are partly responsible of the rapid rise of atmospheric CO₂ concentration from 280 ppm in 1750 AD to 370 ppm in 2000 AD (2). During approximately the same time period (1750-1990), data from ice cores and plant records indeed show that the $\delta^{13}\text{C}$ of atmospheric CO₂ has decreased from about - 6.3‰ to about - 8‰, thus confirming the input of ¹³C-depleted fossil fuel CO₂ (- 27.28‰) (3). These investigations (1-3) have therefore clearly shown the impact of fossil fuel CO₂ on the global earth scale. Nonetheless, on the more local scale, our understanding of the fate of fossil-fuel CO₂ emissions near point-sources such as highways and major cities is still poorly known. This dearth of knowledge stems partly from the lack of suitable pollution indicators, which specifically record the impact of fossil-fuel CO₂.

On the local scale, recent investigations of urban pollution in the city of Phoenix, Arizona, USA, have revealed the occurrence of an *urban CO₂ dome* with a peak CO₂ concentration at the center of the city of 650 ppm that was 75% greater than that of the surrounding rural area (370 ppm) (4). Major cities thus provide effective "natural laboratories" for global change impact studies (4). Further, since plants assimilate CO₂ by photosynthesis, and since fossil-fuel CO₂ of mean $\delta^{13}\text{C}$ of - 27.28‰ (3) is isotopically distinct from the mean atmospheric CO₂ (- 8.02‰) (3), we hypothesized that plants growing in highly polluted areas should record the impact of fossil-fuel CO₂ in their carbon tissues. Plant $\delta^{13}\text{C}$ could thus represent a new means to assess fossil-fuel CO₂ impact in major cities. Here, we report an isotopic comparison of grasses growing near a major highway in Paris, France, with grasses growing in rural, non-contaminated areas. Reviews on the use of ¹³C/¹²C ratios to study carbon sources are reported elsewhere (5-8).

EXPERIMENTAL SECTION

Samples of aerial parts of grasses were collected in may 1996 in rural and urban areas in France. 16 contaminated grass samples were collected in Paris at increasing distances (1.20 - 43.25 m) from a high traffic highway with about 8 millions vehicles per day. 8 non-contaminated samples of grasses were collected in remote, well-winded, rural areas (away from fossil-fuel CO₂ sources) in meadows on top of hills, at 30-50 Kms from the cities of Rennes in Northeastern France (2 locations), Altkirch in Northwestern France (1 location), and Vienne in Southeastern France (5 locations). Noteworthy, for future investigations, non-contaminated grasses should not be sampled in non-winded areas such as dense woods because the atmosphere of those areas may contain ¹³C-depleted CO₂ from respiration and from decomposition of soil organic matter (6). No particular species of grasses were selected because our aim was to test a pollution parameter that could be easily applied anywhere in future mapping investigations. Nonetheless, all grasses collected belong to the C₃ photosynthetic pathway (6), which is common for all trees and most plants growing in temperate climates. The main species identified were *Lolium perenne*, *Hordeum murinum*, *Dactylis glomerata* and *Poa compressa*.

Each sample consisted of 5 sub-samples of about 50 g of green grass aerial parts (leaves, about 8 cm) collected over a 1 m² circle with a distilled CH₂Cl₂-prewashed scissors, then mixed and wrapped into decontaminated aluminum foil (pre-heated 4 h at 450°C). Grasses were dried at 20°C, finely ground using a CH₂Cl₂-prewashed steel-ball mortar, then analyzed for δ¹³C by isotope-ratio monitoring mass spectrometry using previously described procedures (9). δ¹³C values are expressed in per mille relative to the Pee Dee Belemnite standard: δ¹³C = [(¹³C/¹²C_{sample}/¹³C/¹²C_{std}) - 1] x 10³, where ¹³C/¹²C_{std} = 0.0112372 (7).

RESULTS AND DISCUSSION

Rural versus urban grasses

The $\delta^{13}\text{C}$ values of grasses collected in urban and rural areas are reported on Table 1 and Figure 1. The urban grasses were sampled in Paris in may 1996 near a major highway with about 8 millions vehicles per day (Figure 2). The rural grasses were collected in 8 remote, well-winded, rural areas located in Northwestern, Northeastern, and Southeastern France. $\delta^{13}\text{C}$ values of urban and rural grasses range from - 36.2 ‰ to - 29.5 ‰, which are typical values for plants using the C_3 photosynthetic pathway (6, 8). Further, urban grasses show $\delta^{13}\text{C}$ values averaging at - 35.08 ‰ that are strikingly ^{13}C -depleted of - 4.49 ‰ relative to $\delta^{13}\text{C}$ values of rural grasses averaging at - 30.59 ‰. This difference is due to the assimilation of notable amounts of fossil fuel CO_2 by urban plants as explained below.

Calculation of the fossil fuel contribution

The $\delta^{13}\text{C}$ value of C_3 plants is a function of the $\delta^{13}\text{C}$ of atmospheric CO_2 , and of fractionation effects occurring during the assimilation of CO_2 (3,7,8,10). Farquhar *et al.* (10) developed a simple expression relating the $\delta^{13}\text{C}$ value for carbon fixed by a C_3 plant to $\delta^{13}\text{C}$ of the external environment:

$$\delta_p = \delta_a - a - (b - a)p_i/p_a$$

where δ_p defines the isotopic value of the plant, δ_a denotes the isotopic value of atmospheric CO_2 used by the plant during photosynthesis, a is the change in $\delta^{13}\text{C}$ due to CO_2 diffusion (4.4‰), b is the change introduced by the action of the RuP_2 enzyme (27‰) and p_i and p_a denote the partial pressures of CO_2 in the atmosphere and in the intercellular leaf space. In this study, we assumed that the ratio of external CO_2 pressure versus internal CO_2 pressure (p_i/p_a) stays constant at increasing CO_2 concentration on the following grounds.

In a study of 17 C_3 grass and herb species grown for 5 weeks, Beerling and Woodward showed that p_i/p_a ratios derived from δ_p measurements were not modified by variations of atmospheric CO_2 concentration (11). Furthermore, an investigation of the oak *Quercus robur* grown under 350 ppm versus 700 ppm of CO_2 failed to yield a significant effect of concentration CO_2 on isotope fractionation (12). This absence of an effect of CO_2 concentration on isotope fractionation is also strengthened by a report of wheat grown under

370 ppm versus 558 ppm of CO₂ (13). Therefore, in this study it is assumed that the $\delta^{13}\text{C}$ value of grasses is solely controlled by the $\delta^{13}\text{C}$ value of atmospheric CO₂. The percentage of fossil fuel carbon assimilated by the plant can thus be calculated using the following equation:

$$P = 100.(\delta_u - \delta_r)/(\delta_f - \delta_a)$$

where δ_u refer to the $\delta^{13}\text{C}$ of urban grasses, δ_r denotes the average $\delta^{13}\text{C}$ of rural grasses (- 30.59‰), δ_f defines the $\delta^{13}\text{C}$ of fossil-fuel CO₂ (- 27.28‰) (3), and δ_a refer to the $\delta^{13}\text{C}$ of global atmospheric CO₂ (- 8.02 ‰) (3). The calculated percentage P of fossil fuel carbon in urban grasses is reported on Table 1. P values ranges from 20.8 % to 29.1 % with an average of 23.3%. These results thus confirm that a large part of urban grass carbon is derived from fossil fuels. Moreover, the $\delta^{13}\text{C}$ value of grasses represents a novel pollution parameter, which could be useful to study the impact of fossil fuel CO₂ in major cities.

Effect of distance from the road

Urban grasses were collected in Paris, France, at increasing distance from a major highway with an average daily traffic of 8 million vehicles (Figure 2). The aim of this sampling was to test a possible influence of distance from and height above the road. $\delta^{13}\text{C}$ values versus grass distance from the highway are shown on Figure 3. Linear regressions of $\delta^{13}\text{C}$ grass values versus horizontal distance and height yielded equations with poor to medium correlation coefficients r of 0.55 and 0.56, respectively. Therefore, although there is a trend toward ^{13}C -depleted values at closer distances from the road, the windy conditions generated by the heavy traffic probably dilute rapidly fossil-fuel CO₂ in the urban CO₂ dome.

LITERATURE CITED

1. Siegenthaler, U.; Sarmiento, J. L. *Nature* **1993**, 365, 119.
2. Houghton, J. T. et al. Eds. *Climate Change 2001, the Scientific Basis*. International Panel on Climate Change. Cambridge University Press.
3. Marino, B. D.; McElroy, M. B. *Nature* **1991**, 349, 127. Freyer, H. D.; Wiesberg, L. *Naturwissensch.* **1973**, 60, 517.
4. Idso, S. B.; Idso, C. D.; Balling Jr., R. C. *Atmosph. Environ.* **2001**, 35, 995. Idso, S. B.; Idso, C. D.; Balling Jr., R. C. *Atmosph. Environ.* **2002**, 36, 1655.
5. Lichtfouse, E. *Rapid Commun. Mass Spectrom.* **2000**, 14, 1337.
6. Tieszen, L. L. *J. Archaeolog. Sci.* **1991**, 18, 227.
7. Craig, H. *Geochim. Cosmochim. Acta* **1953**, 3, 53.
8. O'Leary, M. H. *Phytochem.* **1981**, 20, 553.
9. Cayet, C.; Lichtfouse, E. *Org. Geochem.* **2001**, 32, 253. Lichtfouse, E.; Dou, S.; Girardin, C.; Grably, M.; Balesdent, J.; Behar, F.; Vandenbroucke, M. *Org. Geochem.* **1995**, 23, 865.
10. Farquhar, G. D.; O'Leary, M. H.; Berry, J. A. *Aust. J. Plant Physiol.* **1982**, 9, 121.
11. Beerling, D. J., Woodward, F. I. *Functional Ecol.* **1995**, 9, 394.
12. Picon, C.; Ferhi, A.; Guehl, J.-M. *J. Exper. Bot.* **1997**, 48, 1547.
13. Leavitt, S. W., Pendall, E.; Paul, E. A.; Brooks, T.; Kimball, B. A.; Pinter Jr., P. J.; Johnson, H. B.; Matthias, A.; Wall, G. W.; LaMorte, R. L. *New Physiol.* **2001**, 150, 305.

FIGURE CAPTIONS

Table 1

$\delta^{13}\text{C}$ values of urban and rural grasses sampled in may 1996. Percentage P of fossil fuel carbon assimilated by urban grasses (see calculation in text). Urban grasses were collected in Paris, France at increasing distance and height from a highly contaminated highway (N° 1-16, see Figure 2 for precise location). "Distance" refer to horizontal distance. Rural grasses were collected in remote, well-winded, rural areas in Northwestern France (N°17-18), Northeastern France (N°19), and Southeastern France (N°20-24). The $\delta^{13}\text{C}$ analytical error is $\pm 0.03\text{‰}$ (5 standard runs). The sample deviation is lower than 0.10‰ (3 replicates).

Figure 1

$\delta^{13}\text{C}$ values of grasses collected in urban and rural areas in France. The high ^{13}C -depletion of urban grasses is due to the assimilation of ^{13}C -depleted fossil fuel CO_2 by plants growing near vehicle exhaust emissions.

Figure 2

Urban grass samples were collected in Paris, France, at increasing distance from a major highway. Numbers refer to sampling locations. Distances and heights from the road are reported in Table 1.

Figure 3

$\delta^{13}\text{C}$ values of urban grass samples collected in Paris, France, at increasing distance from a major highway. Note the trend toward ^{13}C -depleted values near the road. This trend can be explained by the assimilation by plants of ^{13}C -depleted CO_2 from vehicles. Distance refers to horizontal distance. Linear regression gives $\delta^{13}\text{C} = (0.026 \times \text{distance}) - 35.55$ (r 0.55).

Table 1

$\delta^{13}\text{C}$ values of urban and rural grasses sampled in may 1996. Percentage P of fossil fuel carbon assimilated by urban grasses (see calculation in text). Urban grasses were collected in Paris, France at increasing distance and height from a highly contaminated highway (N° 1-16, see Figure 2 for precise location). "Distance" refer to horizontal distance. Rural grasses were collected in remote, well-winded, rural areas in Northwerstern France (N°17-18), Northeastern France (N°19), and Southeastern France (N°20-24). The $\delta^{13}\text{C}$ analytical error is $\pm 0.03\text{‰}$ (5 standard runs). The sample deviation is lower than 0.10‰ (3 replicates).

N°	height (m)	distance (m)	$\delta^{13}\text{C}$ (‰)	P (%)
Urban grasses				
1	0.20	1.20	-36.2 ± 0.1	29.1
2	0.74	3.68	-35.0 ± 0.1	22.9
3	1.38	5.06	-34.6 ± 0.1	20.8
4	2.15	6.94	-35.8 ± 0.1	27.1
5	2.73	8.42	-35.2 ± 0.1	23.9
6	3.57	10.57	-35.3 ± 0.1	24.5
7	4.29	12.32	-36.2 ± 0.1	29.1
8	5.97	16.81	-34.7 ± 0.1	21.3
9	6.73	18.70	-34.8 ± 0.1	21.9
10	7.45	20.90	-35.3 ± 0.1	24.5
11	8.03	23.11	-35.1 ± 0.1	23.4
12	8.46	25.19	-34.2 ± 0.1	18.7
13	8.72	27.52	-34.6 ± 0.1	20.8
14	8.81	29.42	-34.7 ± 0.1	21.3
15	8.90	35.59	-34.9 ± 0.1	22.4
16	8.84	43.25	-34.6 ± 0.1	20.8
Average			-35.08 ± 0.56	23.3
Rural grasses				
17			-31.1 ± 0.1	
18			-30.7 ± 0.1	
19			-30.6 ± 0.1	
20			-29.9 ± 0.1	
21			-30.6 ± 0.1	
22			-29.5 ± 0.1	
23			-31.5 ± 0.1	
24			-30.8 ± 0.1	
Average			-30.59 ± 0.59	

Figure 1

$\delta^{13}\text{C}$ values of grasses collected in urban and rural areas in France. The high ^{13}C -depletion of urban grasses is due to the assimilation of ^{13}C -depleted fossil fuel CO_2 by plants growing near vehicle exhaust emissions.

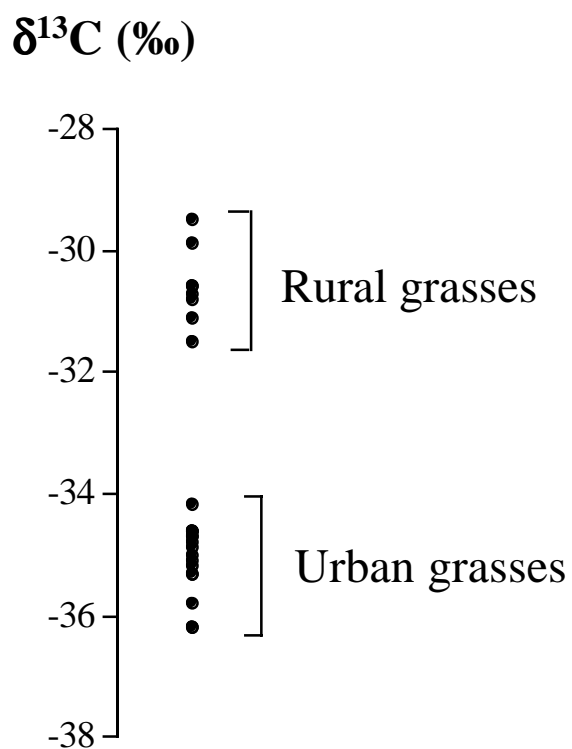


Figure 2

Urban grass samples were collected in Paris, France, at increasing distance from a major highway. Numbers refer to sampling locations. Distances and heights from the road are reported in Table 1.

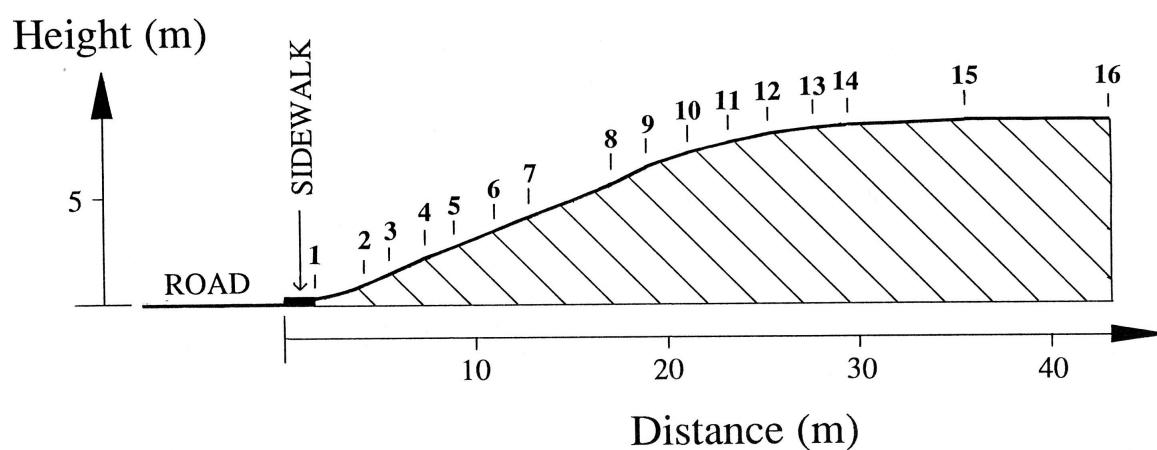
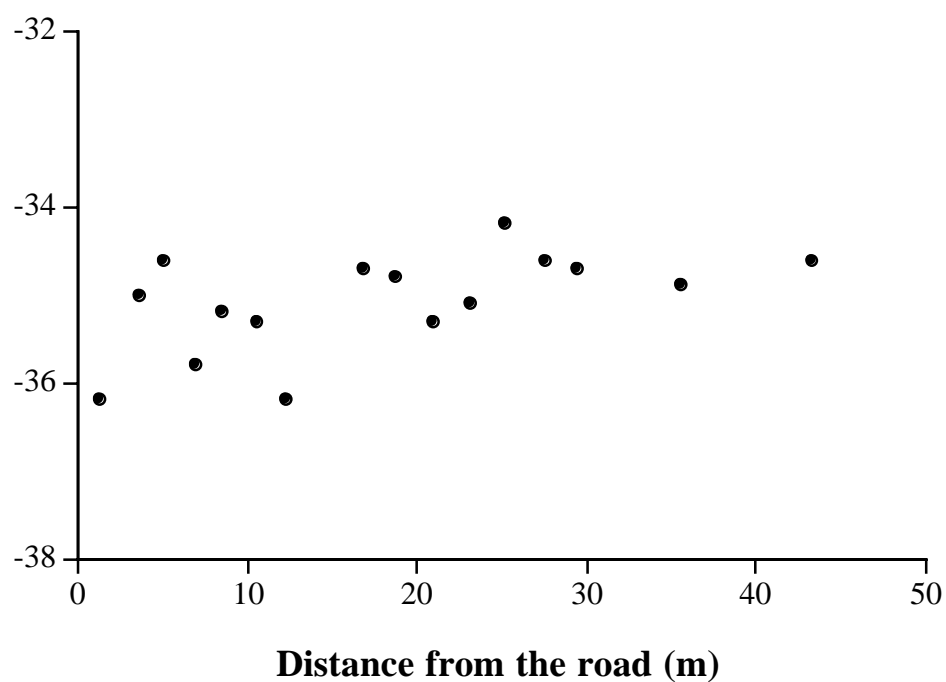


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$\delta^{13}\text{C}$ of urban grasses (‰)



Brief

A novel indicator of atmospheric pollution by fossil-fuel CO₂ based on the ¹³C/¹²C composition of plants shows that urban grasses contain up to 29% of fossil fuel carbon.