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## <sup>14</sup>C of grasses as an indicator of fossil fuel CO<sub>2</sub> pollution

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**Abstract** 10.1007/s00410-002-0431-0

Measuring the amount of fossil fuel carbon stored in the vegetation is now crucial to understand the mechanisms ruling climate changes. In this respect, highly polluted areas such as major towns represent "natural" laboratories because fossil fuel CO<sub>2</sub> (<sup>14</sup>C-free) is isotopically distinct from mean atmospheric CO<sub>2</sub> (<sup>14</sup>C-labeled). Here, a <sup>14</sup>C study of urban grasses near a major highway in Paris, France, shows that plants store up to 13% of fossil fuel carbon. <sup>14</sup>C composition of urban grasses is thus a novel parameter to assess the fossil fuel CO<sub>2</sub> pollution.

**Keywords** CO<sub>2</sub>, <sup>14</sup>C, fossil fuel pollution, grass, climate change

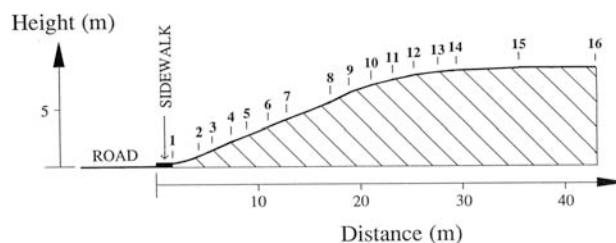
### Introduction

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 CO<sub>2</sub> into the atmosphere. Specifically, for the period from 1980 to 1989, CO<sub>2</sub> emissions from fossil fuel burning and tropical deforestation amounted to  $\sim 7.0 \pm 1.1 \cdot 10^{15}$  g C per year (Siegenthaler and Sarmiento, 1993). On the global scale, fossil-fuel CO<sub>2</sub> emissions are partly responsible of the rapid increase of atmospheric CO<sub>2</sub> concentration from  $\sim 280$  ppmv in 1750 AD to  $\sim 370$  ppmv in 2000 AD. On the local scale, investigations of urban pollution in the city of Phoenix, Arizona, USA, have revealed the occurrence of an *urban CO<sub>2</sub> dome* with a peak concentration at the center of the city of 650 ppmv that was 75% greater than that of the surrounding rural area (370 ppmv) (Idso et al., 2001, 2002).

Major cities thus provide effective "natural laboratories" to study the impact of high CO<sub>2</sub> concentrations. Nevertheless,

our understanding of the storage of fossil fuel carbon into the urban vegetation is limited due to the lack of approaches allowing specific tracing of fossil fuel carbon. Since fossil fuel carbon is <sup>13</sup>C-depleted, we have recently shown that the <sup>13</sup>C composition of grasses growing near a major urban highway is highly depleted due to the assimilation of fossil fuel CO<sub>2</sub> from vehicles (Lichtfouse et al, 2003).

Furthermore, since <sup>14</sup>C half-life is 5,739 years, fossil fuel carbon is nearly <sup>14</sup>C-free because it has lost most of its <sup>14</sup>C content during the millions of years of burial in sediments. Urban plants assimilating some fossil fuel CO<sub>2</sub> should thus be depleted in <sup>14</sup>C. This <sup>14</sup>C depletion could in turn be used to calculate the amount of fossil fuel carbon stored in the vegetation. Here, we studied the <sup>14</sup>C content of urban grasses located near a major, highly polluted highway in Paris, France (Figure 1), versus rural grasses located in remote, non-polluted areas. The results show that urban grasses are significantly <sup>14</sup>C-depleted. <sup>14</sup>C of grasses thus appears as a promising novel parameter to study the storage of fossil carbon into the vegetation.



**Figure 1.** 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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## Experimental

The  $^{14}\text{C}$  content of grasses is reported in Table 1. Sixteen urban grass samples were collected in Paris, France in May 1996 at increasing distance and height from a highly contaminated highway (Figure 1). Eight rural grass samples were collected in remote, well-winded, rural areas in Northwestern France (N°17-18), Northeastern France (N°19), and Southeastern France (N°20-24). 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. The main species identified were *Lolium perenne*, *Hordeum murinum*, *Dactylis glomerata* and *Poa compressa*. Plant leaves were dried (20°C), finely ground with a steel ball mortar then analyzed for  $^{14}\text{C}$ . Drastic precautions were taken to avoid contaminations. Fraction Modern follows the conventions of Stuiver and Pollach (1977).  $\Delta^{14}\text{C}$  values have been corrected using plant  $\delta^{13}\text{C}$  values reported by Lichtfouse et al (2003). %Fossil Fuel C =  $100 \times (1.1201 - fM_{\text{urbangrass}})/1.1201$ .

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## Results and discussion

### $^{14}\text{C}$ -depletion of urban grasses

Grasses growing in urban and rural areas in France were analyzed for  $^{14}\text{C}$  composition (Table 1). Urban grasses were sampled in Paris at increasing distance from a major highway with about 8 millions vehicles per day (Figure 1). As there are about 8 millions vehicles passing daily through this highway, it is highly polluted. Rural grasses were collected in 8 remote, well-winded, rural areas located in Northwestern, Northeastern, and Southeastern France. Noteworthy, most values of fraction modern (fM) are higher than 1 (Table 1). This bias is due to the input of  $^{14}\text{C}$  into all earth biomass, due nuclear bomb testing after 1950. Nonetheless, the results show that urban grasses are highly depleted in  $^{14}\text{C}$ , with a fraction modern ranging from 0.986 to 1.0785 and averaging at 1.0038. Whereas rural grasses give fraction Modern values ranging from 1.0985 to 1.1414 and averaging at 1.1201.

The  $^{14}\text{C}$ -depletion of urban grasses can be explained by two phenomena: 1) the assimilation of fossil-fuel  $\text{CO}_2$  by photosynthesis and 2) the deposition on plant leaves of fossil fuel particles from airborne dust. Since fossil fuels are almost N-free, a significant contribution of aerosol deposition should have increased the C/N ratios of urban versus rural plants. For instance, Accardi-Dey and Gschwend (2002) have reported a C/N ratio of 60 for diesel particulate matter. However, the mean C/N ratios of urban grasses have an average value of  $10.2 \pm 1.2$  (n = 16), ranging from 8.8 to 13.9, which is not significantly higher than that of rural grasses averaging at  $10.5 \pm 2.1$  (n = 8), and ranging from 7.5 to 14.7. Moreover, according to  $^{14}\text{C}$  data a decrease of C/N ratios with road distance should have been observed for urban grasses, because grasses growing near the road are the most  $^{14}\text{C}$  depleted samples (Table 1). However, C/N ratios do not correlate with road distance. To conclude, although the deposition of fossil fuel particulate on urban grasses is certainly occurring, its contribution to the  $^{14}\text{C}$  content of the plant biomass is minor.

Therefore, the  $^{14}\text{C}$ -depletion of urban grasses can be explained by the photosynthetic assimilation of fossil fuel  $\text{CO}_2$ .

### Fossil C content of grasses

The percentage of fossil fuel-derived carbon assimilated by urban grasses can be calculated according to the following equation:

$$\text{Fossil fuel C (\%)} = 100 \times (1.1201 - fM_{\text{urban}})/1.1201$$

where 1.1201 is the mean fraction modern of rural grasses, and  $fM_{\text{urban}}$  denotes the fraction modern of urban grass. Calculated values of fossil fuel C assimilated by urban grasses are ranging from 3.99 % to 12.56 %, and averaging at 7.35 % (Table 1). Urban plants are thus able to store a notable fraction of fossil fuel  $\text{CO}_2$  emissions. Moreover, since the grass species sampled are mostly annual species, after plant death the plant carbon will be partly stored over time into the soil. For instance, studies of ryegrass decomposition by Jenkinson (1965) have shown that about one fifth of the plant C is remaining in the soil after 4 years. Once the plant carbon is stabilized into the soil, longer period of storage can be expected. Indeed, long-term experiments of corn cropping have revealed that about 50% of initial soil carbon is still remaining after 23 years of cultivation (Lichtfouse, 1997). Whatever the fate of plant carbon in soils, our findings show that urban highway grasses are able to store up to 12.56% of fossil carbon. In the next section we discuss the fossil fuel C content of urban grasses versus distance from the highway.

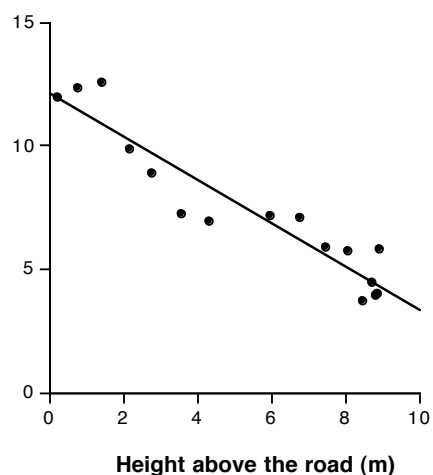
### Effect of distance from the highway

We studied the fossil carbon content of urban grasses located at increasing horizontal distance and height from the urban highway in Paris. The results reported in Table 1 and Figure 2 show that the fossil carbon content of grasses decrease with distance from as well as height above the road. Specifically, the fossil fuel C content of grasses decrease from about 12% for grasses located at 1.2 m distance and 0.20 m height to about 4% for grasses located at 43 m distance and 8.8 m height. This finding is rather surprising because one should have expected a rapid mixing of fossil fuel  $\text{CO}_2$  in the mean atmosphere, given the strong local winds of the intense vehicle traffic. On the contrary, this gradient means that pollution by fossil fuel  $\text{CO}_2$  is highly stratified as shown by linear correlation of fossil fuel derived C content of grasses versus height above the road (Figure 2).

Moreover, a logarithm regression of fossil fuel C values of urban grasses versus distance from the road yields an exponential decrease (Table 1). Those point-source observations in local areas are in good agreement with larger-scale investigations of  $\text{CO}_2$  levels in major cities, which show the occurrence of an urban  $\text{CO}_2$  dome in Phoenix, Arizona (Idso et al. 2001, 2002). Furthermore they provide a good explanation for the specific thermal behavior of city atmosphere, the so-called "urban heat island" (Goward, 1981, Oke, 1982). In this respect, our study using an isotope tracer ( $^{14}\text{C}$ ) demonstrates unambiguously the involvement of  $\text{CO}_2$  from fossil fuels in processes leading to local climate changes

in major cities.  $^{14}\text{C}$  composition of grasses is also a promising new parameter to map the fossil fuel  $\text{CO}_2$  pollution in contaminated areas such as major towns, highways, and industrial centers.

**Fossil fuel C in grasses (%)**



**Figure 2.** Calculated fossil fuel carbon content of urban grasses, based on  $^{14}\text{C}$  composition, versus height above a major highway in Paris, France. See Figure 1 for sample locations. Note that the high fossil fuel content of grasses near the road is due to the assimilation of fossil fuel  $\text{CO}_2$  from road vehicles.

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## Conclusion

Urban grasses located in a major city are strongly  $^{14}\text{C}$ -depleted due to the assimilation of fossil fuel  $\text{CO}_2$  emitted by vehicles. The highest values show that grasses near the highway store up to 12% of fossil fuel C. In this respect, the  $^{14}\text{C}$  content of grasses represent a novel parameter to study atmospheric  $\text{CO}_2$  pollution in major cities. Furthermore, the fossil fuel content of grasses decrease with distance from and height above the road.

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**Table 1.**  $^{14}\text{C}$  composition of urban and rural grasses. Urban grasses were collected in Paris, France in May 1996 at increasing distance and height from a highly contaminated highway (Numbers 1-16, see Figure 1 for precise location). "Distance" refers to horizontal distance. Rural grasses were collected in remote, well-winded, rural areas in Northwestern France (N°17-18), Northeastern France (Number 19), and Southeastern France (Numbers 20-24). %Fossil Fuel C =  $100 \times (1.1201 - f_{\text{Murbangrass}})/1.1201$ . Linear regression yields Fossil fuel C =  $-0.874 \times (\text{height}) + 12.101$  (r 0.95). Logarithm regression of fossil fuel C versus horizontal distance from road gives Fossil fuel C =  $-6.55\text{Log}(\text{distance}) + 14.653$  (r 0.91).

Number	height (m)	distance (m)	$\Delta^{14}\text{C}$ (‰)	fraction Modern	Fossil fuel C (%)
<b>Urban grasses</b>					
1	0.20	1.20	-19.5 ± 6.4	0.9860 ± 0.0064	11.97
2	0.74	3.68	-23.9 ± 5.4	0.9816 ± 0.0054	12.36
3	1.38	5.06	-26.1 ± 5.4	0.9794 ± 0.0053	12.56
4	2.15	6.94	+4.3 ± 5.7	1.0099 ± 0.0057	9.84
5	2.73	8.42	+15.2 ± 5.1	1.0208 ± 0.0051	8.86
6	3.57	10.57	+32.9 ± 5.7	1.0387 ± 0.0057	7.27
7	4.29	12.32	+36.6 ± 7.1	1.0424 ± 0.0071	6.94
8	5.97	16.81	+34.1 ± 4.9	1.0399 ± 0.0049	7.16
9	6.73	18.70	+34.8 ± 7.1	1.0406 ± 0.0071	7.10
10	7.45	20.90	+48.1 ± 7.4	1.0540 ± 0.0074	5.90
11	8.03	23.11	+50.0 ± 6.3	1.0559 ± 0.0063	5.73
12	8.46	25.19	+72.5 ± 8.5	1.0785 ± 0.0085	3.71
13	8.72	27.52	+64.3 ± 6.0	1.0702 ± 0.0060	4.45
14	8.81	29.42	+69.7 ± 5.5	1.0757 ± 0.0055	3.96
15	8.90	35.59	+48.9 ± 6.0	1.0548 ± 0.0060	5.83
16	8.84	43.25	+69.4 ± 7.0	1.0754 ± 0.0070	3.99
<b>Average</b>				<b>1.0038 ± 0.0324</b>	<b>7.35</b>
<b>Rural grasses</b>					
17			+135.1 ± 7.0	1.1414 ± 0.0070	
18			+119.8 ± 7.3	1.1260 ± 0.0073	
19			+103.3 ± 5.2	1.1094 ± 0.0052	
20			+92.4 ± 6.1	1.0985 ± 0.0061	
21			+115.9 ± 6.2	1.1221 ± 0.0062	
22			+126.1 ± 6.4	1.1324 ± 0.0064	
23			+107.8 ± 6.1	1.1140 ± 0.0061	
24			+110.7 ± 5.6	1.1169 ± 0.0056	
<b>Average</b>				<b>1.1201 ± 0.0126</b>	