$^{13}C/^{12}C$ composition, a novel parameter to study the downward migration of paper sludge in soils†

Article

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$\delta^{13}C$ values of crop and forest soils were measured 8 years after disposal of paper sewage sludge. The carbon transfer from paper sludge downward to the first humic layer is evidenced by a ^{13}C-enrichment of up to +5.6‰ due to the input of ^{13}C-enriched sludge carbonates. $^{13}C/^{12}C$ composition is thus a novel, sensitive parameter to follow the downward transfer of paper sludge carbon.

Introduction

Large amounts of agricultural, industrial and municipal wastes are produced daily by human activities.[1–5] In 1980, France's annual waste production reached about 5.5 million dry tonnes (m.d.t.) of municipal waste, 1.8 m.d.t. of urban and industrial sewage sludge, 78 m.d.t. from the agriculture and agro-industry, and 6.75 m.d.t. from forestry.[6] Disposal of organic wastes onto agricultural and forestry lands has several potential benefits such as long-term fertilisation, improving soil water-holding capacity and improvement of aggregate stability. However, land-based waste disposal must be carefully controlled because of potential hazards associated with application of wastes, include pathogens, heavy metals and toxic organic by-products, as reviewed by Wilson *et al.*[2] So far, the long-term changes of soil properties induced by organic waste disposal such as paper sludge are not well understood, notably due to the lack of analytical approaches to follow the fate of waste matter into the soil profile. Nonetheless, several recent reports show that stable carbon isotopes can be used to study environmental issues.[7–9] More specifically, since the main biochemical components of plants are isotopically distinguished, *e.g.* cellulose being ^{13}C-enriched *versus* lignin and lipids,[10–12] we hypothesised that paper sludge might have a distinct $\delta^{13}C$ ratio which could be used to study their long-term fate in soils. Moreover, since paper sludges contain carbonates, which are ^{13}C-enriched, it could be feasible to isotopically distinguish soil carbon from sludge carbon. Here, we wish to report an isotopic investigation of crop and forest soils treated with paper sludge in 1992.

Experimental

Sites disposed of with paper sludge in 1992

Four experimental sites from the Lorraine region, France, were selected for this study. The woodland site (4950 m^2) is located in a forest planted with red oaks. The crop site (5200 m^2), located about 500 m away from the forest site, previously cultivated with wheat, was planted sporadically with some pine trees after paper sludge disposal. Two control sites with the same characteristics are located beside the woodland and crop sites. All soils are mainly sandy, with silt, some clay (4–8%), and are acidic with pH ranging from 4.3 to 5.4. In July 1992, a 5–10 cm layer of paper sludge was evenly distributed over the woodland site (186 tons) and the crop site (306 tons). Paper sludge properties were: 42 wt.% dry matter (110 °C), 36 dry-wt.% organic matter (combustion 650 °C), pH 6.8, 23% CaO, 22% organic C, 0.4% N, 0.14% P_2O_5, 0.05% K_2O, 0.4% MgO.

Soil sampling and isotope analysis

In August 2000, solid chunks of blue paper from the surface, organic litter from woodland sites, grasses from crop sites, and soils of increasing depth were sampled from $\sim$1 m^3 holes cored at the four sites, as shown on Fig. 1 for the woodland site. Samples were air-dried at 20 °C, 2 mm-sieved (soils), then finely ground using a ball mortar. Total %C and $\delta^{13}C$ values (‰) were measured by continuous flow isotopic ratio mass spectrometry as described elsewhere.[13–15] Note that %C and $\delta^{13}C$ values refer to total soil carbon, including organic and inorganic (carbonates) carbon. TOC and $\delta^{13}C_{(org)}$ values of all demineralised samples were also measured and show that the total %C and $\delta^{13}C$ have notable contribution of carbonates, as detailed at the end of this article. Demineralisation was performed by overnight treatment of the sample in 1 M HCl, followed by washing with distilled water and centrifuging the samples until neutral. The samples were air-dried and treated in the same manner as above.

Results and discussion

Paper sludge disposal

In 1992, crop and woodland sites from the Lorraine region, France were treated with 186–306 tons of paper sewage sludge in order to study the effects of waste recycling. Precautions were taken to minimise potential environmental hazards, *e.g.* input of heavy metals. From 1992 to 1997, comparison of plants grown on both the treated and control sites showed the absence of visual toxic effects. Plants developed well with roots growing through the blue sludge layer. An investigation of the blue sludge layer from 1992 to 1997 showed a decrease of calcium content, from about 23 to 10%, and of organic matter content, from about 35 to 20%. In 2000, the blue sludge layer is still clearly apparent under a fern litter layer, as shown for the woodland site on Fig. 1. Here, we analysed samples of

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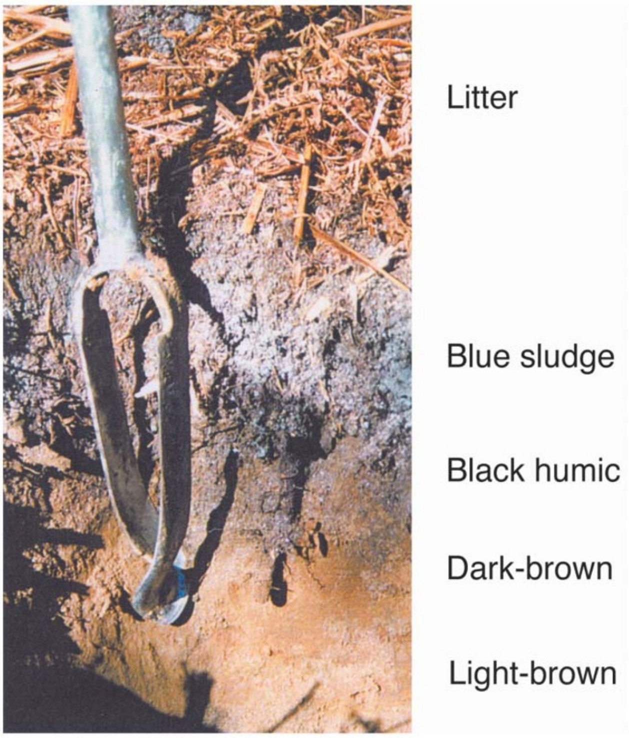

Fig. 1 Sampling of soil layers from the wood plot in August 2000. A layer of paper sludge has been disposed of to this soil in 1992.

litter, grasses, sludge layer, and soil layers of increasing depth cored in August 2000, in order to study the downward carbon transfer from the paper sludge.

Carbon content

Total carbon content and $\delta^{13}C$ values of samples from woodland and crop sites treated with paper sludge are reported on Table 1. All sites show a decrease of total C content with depth from $\sim$42% for litter and grasses, to 0.5–1% at the bottom of the core. Although the blue sludge layers yielded high carbon contents, 18.2% for the woodland site and 5.8% for the crop site respectively, carbon contents do not clearly show the transfer of paper sludge-derived carbon to other layers. Specifically, while the total C content of litter in the woodland sludge-treated site (45%) is higher than the woodland control site (40%), the reverse is observed for the crop sites: 43 *versus* 44%. Similarly, the black humic horizon underlying the sludge give higher total C values in the crop sludge-treated site, 5.2 *versus* 2.5%, but lower C values in the woodland sludge-treated site amounting to 4.3 *versus* 4.8%. Therefore, although one should expect the upward and downward transfer of some carbon from the blue sludge layer 8 years after disposal, carbon values do not show unambiguous differences. Nonetheless, the next section will show that the migration of sludge carbon can be clearly evidenced by isotope analysis.

$^{13}C/^{12}C$ isotopic composition

$\delta^{13}C$ values of samples from sites treated with paper sludge and from control sites are drawn on Fig. 2. We observe a notable ^{13}C-enrichment in the blue sludge layer for both sites, yielding $\delta^{13}C$ values of -20.97% for the woodland site and -22.81‰ for the crop site, and in the underlying black humic layer (-25.72, -21.84% respectively), relative to the average $\delta^{13}C$ values from control plots amounting to -27.6 ± 0.2‰ for the woodland site and to -27.9 ± 0.3‰ from the crop site. Moreover, the soil $\delta^{13}C$ values of sludge-treated sites increase toward the original isotopic value of the paper sludge (-16.84‰) with decreasing depth. These findings have several implications. First, the blue sludge layer is composed of a mixture of carbon derived from the $\delta^{13}C$-enriched paper sludge and from the soil, in agreement with visual observation of both blue and dark particles in the blue sludge layer. Second, the notable ^{13}C-enrichment of the underlying black humic horizons shows clearly the downward migration of sludge-derived carbon where other data such as %C contents and visual observation do not yield clear trends. Third, the fraction x of paper sludge-derived carbon can be calculated by isotope balance according to the following equation:

$$\delta_{\text{layer}} = x\delta_{\text{sludge}} + (1 - x)\delta_{\text{control}}$$

where δ_{layer} refer to the soil layer, δ_{sludge} to solid chunks of pure paper sludge (-16.84‰), and δ_{control} to average $\delta^{13}C$ values of control plots. In the woodland sites, the percentage $x100$ of sludge-derived carbon amounts to 76% in the blue sludge layer and to 21% in the underlying black humic layer, thus showing a notable downward carbon transfer. In crop plots, values amount respectively to 56 and 67% as the result of a downward carbon transfer, which could be explained by the lesser initial stratification of crop soils.

Sludge carbonates

$\delta^{13}C_{(org)}$ analysis of demineralised samples show that the ^{13}C-enrichment of the non-demineralised samples is due to the presence of carbonates. Specifically, demineralised blue paper chunks yield $\delta^{13}C_{(org)}$ values of -25.41‰ *versus* -16.84‰ for the non-demineralised sample. The blue sludge layers give $\delta^{13}C_{(org)}$ values of -27.22‰ for the woodland site and -26.28‰ for the crop site, *versus* respectively -20.97‰ and -22.81‰ for the non-demineralised samples. Similarly, the black humic layers give $\delta^{13}C_{(org)}$ of -26.97‰ for the woodland site and -26.27‰ for the crop site, *versus* -25.72‰ and -21.84‰ respectively for the non-demineralised samples. Since the demineralised values are similar to control values (Table 1), the

Table 1 $\delta^{13}C$ values and %carbon of non-demineralised soil samples cored in August 2000 from experimental control sites and from sites treated with paper sludge in 1992. Light-blue chunks of solidified paper sludge found on the soil surface yielded a %C value of 17.36% and $\delta^{13}C$ value of -16.84‰. Sample deviation: ± 0.05% and ± 0.05‰ (3 repeats)

	Wood soils				Crop soils			
	C (%)		$\delta^{13}C$ (‰)		C (%)		$\delta^{13}C$ (‰)	
Horizon, thickness	Control site	Paper site	Control site	Paper site	Control site	Paper site	Control site	Paper site
Litter $\sim$3 cm, grasses[a]	40.24	44.94	−27.63	−27.24	44.25	43.01	−28.20	−27.58
Blue sludge[b], 10 cm		18.28		−20.97		5.82		−22.81
Black humic[c], 10 cm	4.80	4.34	−27.66	−25.72	2.50	5.20	−27.48	−21.84
Dark-brown[c], 20 cm	2.26	2.30	−27.79	−27.63	1.04	0.56	−28.16	−28.70
Light-brown[c], 20 cm	1.03	1.03	−27.35	−27.34	0.55	0.31	−27.72	−27.81

[a]Woodland sites: litter, mostly fern debris. Crop site: living grasses. [b]Horizon visibly composed of about half black soil and half 2 mm-blue chunks. [c]Horizons without visible blue chunks.

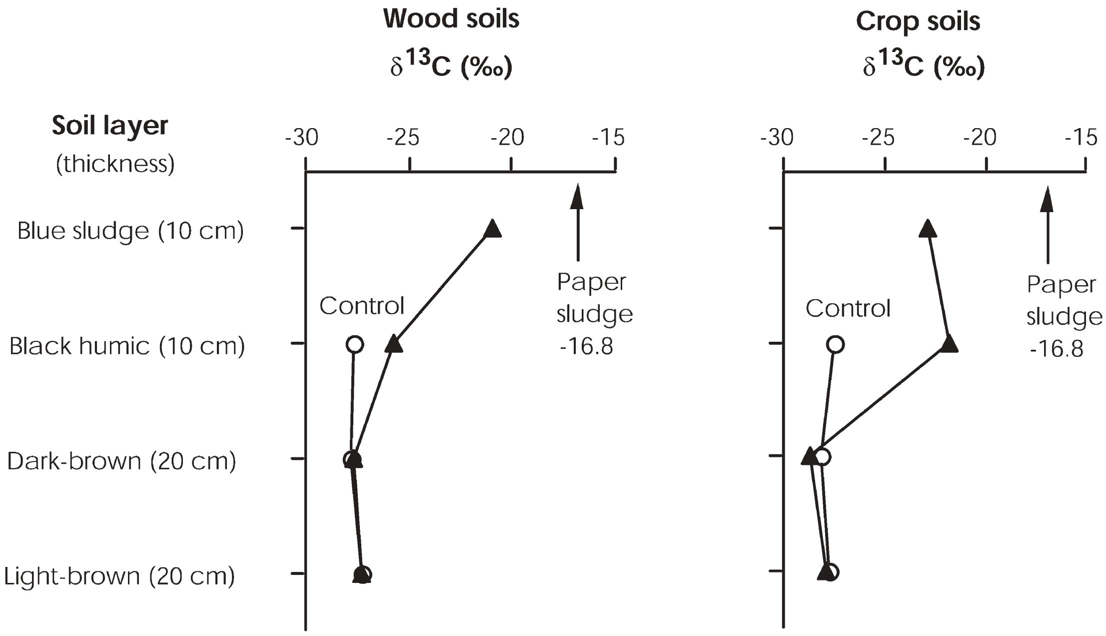

Fig. 2 $^{13}C/^{12}C$ isotopic composition measured in 2000 of woodland and crop soils treated with paper sludge in 1992, *versus* non-treated soils (control). Note the ^{13}C-enrichment of the black humic layer is due to the downward carbon transfer from the paper sludge.

observed ^{13}C-increases of non-demineralised layers can be explained by the total carbonate contribution from the sludge.

Conclusion

The downward transfer of paper sludge 8 years after its disposal to crop and woodland soils has been assessed using ^{13}C isotope analyses. The observed isotopic shifts are due to the presence of enriched carbon, derived from carbonates in the paper sludge.

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