\[ ^{13}\text{C}/^{12}\text{C} \] composition, a novel parameter to study the downward migration of paper sludge in soils

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Abstract. \(\delta^{13}\text{C} \) 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 \(^{13}\text{C} \)-enrichment of up to +5.6‰ due to the input of \(^{13}\text{C} \)-enriched sludge carbonates. \(^{13}\text{C}/^{12}\text{C} \) composition is thus a novel, sensitive parameter to follow to 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 tons (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 \(^{13}\text{C} \)-enriched versus lignin and lipids\(^8,10-12\), we hypothesised that paper sludge might have a distinct \(\delta^{13}\text{C} \) ratio which could be used to study their long-term fate in soils. Moreover, since paper sludges contain carbonates, which are \(^{13}\text{C} \)-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.

Figure 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.
Horizon visibly composed of about half black soil and half 2 mm-blue chunks.

| HORIZON, thickness  | C (%) | δ¹³C (%) | C (%) | δ¹³C (%) |
|---------------------|-------|----------|-------|----------|
|                     | Control site | Paper site | Control site | Paper site |
| Litter ~ 3 cm, grasses¹       | 40.24 | 44.94 | -27.63 | -27.24 |
| Blue sludge², 10 cm        | 18.28 | 18.00 | -20.97 | -20.97 |
| Black humic², 10 cm       | 4.80  | 4.34  | -27.66 | -25.72 |
| Dark-brown², 20 cm        | 2.26  | 2.30  | -27.79 | -27.63 |
| Light-brown², 20 cm       | 1.03  | 1.03  | -27.35 | -27.34 |

¹Woodland sites: litter, mostly fern debris. Crop site: living grasses. ²Horizon visibly composed of about half black soil and half 2 mm-blue chunks.

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 Figure 1. Here, we analysed samples of litter, grasses, sludge layer, and soil layers of increasing depth cored in July 2000, in order to study the downward carbon transfer from the paper sludge.

Carbon content

Total carbon content and δ¹³C 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 ~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

Table 1 δ¹³C values and %carbon of non-denitrified 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 δ¹³C value of -16.84‰. Sample deviation: ± 0.05 % and ± 0.05‰ (3 repeats).
$^{13}$C/$^{12}$C isotopic composition

$\delta^{13}$C values of samples from sites treated with paper sludge and from control sites are drawn on Figure 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

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

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:

where $\delta_{\text{sludge}}$ refer to the soil layer, $\delta_{\text{sludge}}$ to solid chunks of pure paper sludge (-16.84%), and $\delta_{\text{control}}$ to average $\delta^{13}$C values of control plots. In the woodland sites, the percentage $x$ 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 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 disposal of 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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