Study of the trace metal ion influence on the turnover of soil organic matter in cultivated contaminated soils

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Measure of $\delta^{13}C$ and total metal concentrations in size fractions of contaminated soils suggests an influence of metals on the soil organic matter dynamic.

Abstract

The role of metals in the behaviour of soil organic matter (SOM) is not well documented. Therefore, we investigated the influence of metals (Pb, Zn, Cu and Cd) on the dynamic of SOM in contaminated soils where maize (C_4 plant) replaced C_3 cultures. Three pseudogley brown leached soil profiles under maize with a decreasing gradient in metals concentrations were sampled. On size fractions, stable carbon isotopic ratio ($\delta^{13}C$), metals, organic carbon and nitrogen concentrations were measured in function of depth. The determined sequence for the amount of C_4 organic matter in the bulk fractions: M_3 (0.9) > M_2 (0.4) > M_1 (0.3) is in agreement with a significant influence of metals on the SOM turnover. New C_4 SOM, mainly present in the labile coarser fractions and less contaminated by metals than the stabilised C_3 SOM of the clay fraction, is more easily degraded by microorganisms.

Keywords: Soil organic matter dynamic; Trace metal; Size fractionation; Stable isotopic carbon ratio

1. Introduction

With respect to the important environmental functions of soil organic matter (SOM): potential source or sink for greenhouse gases, contribution to soil aggregation, influence on soil fertility and bioactivity (Tiessen et al., 1994; Vanlauwe et al., 1999), the impact on its dynamics of some parameters like soil characteristics (Krull and Skjemstad, 2003), climate (Hevia et al., 2003) and agricultural practices (Pinheiro et al., 2004; Beare et al., 1994) are studied in detail.

Due to various anthropogenic activities, potentially toxic metals are accumulated in soils, with a risk of biota and groundwater contamination. Among the various reactive soil constituents, SOM has a large sorption capacity towards metal ions (Benedetti et al., 1996; Sauve et al., 2000; Yin et al., 2002) and therefore metals often accumulate in the organic topsoils. Metals influence the soil biota in its diversity, abundance and activity (Mhatre and Pankhurst, 1997; Barajas-Aceves et al., 1999). But nevertheless, their impact on the SOM turnover is not well documented.

SOM is composed of various organic constituents chemically heterogeneous (materials in various stages of decomposition for instance) with a large range of reactivity and turnover time in soil (Rethemeyer et al., 2004). In the literature, the affinity of metal ions towards humic substances is well described, but the reactivity with plant debris or bio-polymers is less documented (Spark et al., 1997). Moreover, the reactive components of the soil are in interaction (Franzluebbers and

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Arshad, 1997; Dumat et al., 1997). When plant litter compounds enter the soil, soil-inherent stabilisation mechanisms such as inclusion into aggregates or protection due to the interaction with soil minerals are operative (Sollins et al., 1996; Kaiser and Guggenberger, 2000). The interaction of SOM with the mineral surfaces may be responsible for the occurrence of a stable carbon pool in the fine clay fraction (Baldock and Skjemstad, 2000). Therefore the studies concerning the affinity of one extracted soil component for metals are open to criticism. Conversely, methods of soil particle-size fractionation can be used to assess the distribution of trace elements in soils (Ducaroir and Lamy, 1995). These size fractions can inform on the soil biogeochemistry and the evolution with time of soil components. Changes in the natural abundance of ^{13}C in SOM over time can be used to identify sources of the organic C in soil (Schwartz et al., 1996) and to determine the turnover rate of SOM (Balesdent and Mariotti, 1996).

Three pseudogley brown leached soils under maize (the primary C_4 plants cultivated in temperate countries), with a decreasing gradient in total metal concentrations were collected near a smelter plant. On samples collected at various depths, size fractions were obtained and the following measurements were done: metal ions, organic carbon and nitrogen concentrations and δ^{13}C. The aim of the present work was to determine the effect of metals on the dynamics of SOM by comparing the patterns of the δ^{13}C signals for similar soils where maize replaced the previous C_3 vegetation and differing by their metal concentration levels.

2. Materials and methods

2.1. Soils characteristics and management

The 100 year old smelter (Metaleurop) site is located near Evin-Malmaison (North of France). Dust emissions with high contents of Pb, Zn, Cd and Cu have contaminated the nearby agricultural field over tens of km². Dust particles were characterised by Sobanska et al. (1999) and consist mainly of sulphide and oxide metal ions. The soils classified as pseudogley brown leached soils (Morin et al., 1999) develop over quaternary clays (0.6−1.5 m) covering the Ostrincourt sand. Three soils were collected: M_1, continuous maize (Zea mays L.) since 10 years and 1 km away from the smelter; M_2, continuous maize since 14 years and 3 km away from the smelter and M_3, continuous maize since 13 years and 10 km away from the smelter. The field sampling has been oriented to collect representative soil samples weighing 2−40 kg in closed bags. After mixing, all the samples were air dried and sieved at 2 mm.

For these three NPK fertilised soils, conventional tillage (ploughing to 30 cm, followed by superficial tillage and sowing) was performed and liming was done every few years. In preliminary experiments we checked that soil characteristics were homogeneous in the first 30 cm. Tillage favours the SOM mineralisation, because it breaks soil aggregates, increases aeration and thereby exposes SOM, which was previously protected within the aggregate structure (Pinheiro et al., 2004; Beare et al., 1994; Chenu, 1995). Arrouays et al. (1995) observed an increase of the ratio between labile and recalcitrant SOM when a soil under forest was cultivated.

For around 80 000 plants ha^{-1} cultivated on the three soils (M_1, M_2 and M_3), the maize yield is 75 000−80 000 kg ha^{-1}. Before maize, previous cultivated C_3 plants were potatoes (50 000 kg ha^{-1}), peas (1200 kg ha^{-1}) and beets (70 000 kg ha^{-1}). The type of land use is an important factor controlling organic matter storage in soils since it affects the amount and quality of litter input, the litter decomposition rates and the processes of organic matter stabilisation in soils (Shepherd et al., 2001; John et al., 2005).

One objective of the present work was to study soils contaminated by a real old industrial activity. Such long term continuous C_3 and then C_4 monoculture soils with similar characteristics (texture, land-use history, etc.) and differing only by metals concentrations are difficult to find. Therefore, it should be noted that soil M_1 is under maize monoculture only since 10 years. Moreover, for the fodder maize cultivated soil M_1, only maize roots were incorporated in the soil, whereas in M_2 and M_3, additionally the maize straw was incorporated in order to improve the soil characteristics.

2.2. Physical fractionation of the soil samples

Before particle size fractionation, an initial physical dispersion of the soil samples was performed by end-to-end shaking overnight in pure de-ionised water. The suspensions were then sieved through a series of grids (AFNOR French reference) with decreasing mesh size (2000, 1000, 500, 200 and 50 μm). Then the fractions (20 μm < size < 50 μm), (2 μm < size < 20 μm) and <2 μm were obtained by sedimentation. All the recovered particles were air dried at 60 °C, weighed, ground (200 μm) and homogenised. Particle size fractionation of soil samples resulted in the recovery of 98 ± 0.5% of the initial sample mass.

2.3. Measure of total metal concentrations

The total concentrations of Pb, Cd, Zn and Cu in the size fractions of the soil samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Jobin Yvon JYESS 4.03 apparatus, after a tri-acid (HF, HCl and HNO$_3$) digestion of the solid samples. A standard reference soil (GRX2) was used to control the digestion protocol and the measurements accuracies. All the results correspond to the mean of two replicates.

2.4. Organic carbon amounts and stable carbon isotopic signals (δ^{13}C)

All terrestrial plants discriminate against ^{13}C (in favour of ^{12}C) during photosynthesis, inducing differences between atmospheric CO_2 and the carbon isotopic composition of the plant tissues (Smith and Epstein, 1971). The degree of discrimination is dependant on the photosynthetic pathway of the plant (Ehleringer et al., 1997). It increases from C_4 plants like maize (the metabolic pathway forms initial molecules with four carbon atoms) to C_3 plants. In natural ecosystems, the fractionation of the stable carbon during decomposition of the organic matter is small relative to the original fractionation during C fixation by plants (Peterson and Fry, 1987). Therefore in soils where the vegetation changes from C_3 to C_4 (or vice versa), the changes in the natural abundance of ^{13}C in SOM over time can be used to identify sources of organic C in the soil (Schwartz et al., 1996) or to determine the turnover rate of SOM (Balesdent and Mariotti, 1996).

When C_4 plants grow on a soil that had always received C_3 plants, the δ^{13}C value of the SOM can be relevant to the proportion of the carbon from C_3 and C_4 plants to study the dynamic of the SOM (Balesdent and Mariotti, 1996). The effect of such a vegetation change on SOM isotope composition can be described as follows, with the indices 4 and 3 corresponding to the different photosynthetic pathway types. At the time of vegetation change ($t_0 = 10$, 13 and 14 years ago for M_1, M_3 and M_2, respectively), SOM have an isotopic composition δ_{3-0}, which is close to the composition of the original vegetation C_3. SOM progressively decays and is partially replaced by SOM derived from the new vegetation C_4. At a given time t, the total carbon content (C) can be expressed as: $C = C_3 + C_4$. The isotopic composition of SOM (δ) is given by the following mixing equation: $\delta(C_3 + C_4) = \delta_3 C_3 + \delta_4 C_4$ (with the approximation that the δ unit is related linearly to ^{13}C/^{12}C). Where C_3 stands for the amount of carbon derived from the C_3 old vegetation, δ_3 for the isotopic composition of that carbon, C_4 for the amount of carbon derived from the new vegetation C_4 (maize), and δ_4 for its isotopic composition. The fraction of new carbon (C_4) in the sample $(F) = C_4/C = (\delta - \delta_3)/(\delta_4 - \delta_3)$. The function $F(t)$ can be obtained from successive samples taken on the same site. The kinetics of decay of the initial organic carbon (C_3) is equivalent to $C(1 - F)$, whereas the kinetics of accumulation of the new carbon is equivalent to CF. Because the δ of the soil sample is linearly related to F, its change with time gives a direct expression of the turnover of soil carbon. δ_3 and δ_4 cannot be measured directly and must be estimated.

As there is evidence that the isotopic composition of SOM is only slightly different from that of the plant material from which it derives, most investigators using the natural ^{13}C-labelling technique assume δ_4 is equivalent to the isotopic composition of the new vegetation C_4 or its litter (δveg_{C4}), and δ_3 is equivalent to the initial δ^{13}C of the soil (at t_0) or to the isotopic composition of soil at a reference site kept under the initial vegetation (δref_{C3}). Under these assumptions: $F = (\delta - \delta ref_{C3})/(\delta veg_{C4} - \delta ref_{C3}) = C_4/C$.

Organic C and N contents of soil samples were determined by dry combustion in a Carlo Erba NA 1500 CHN elemental analyser. Stable carbon isotope ratios of SOM and plants were measured on a Fisons SIRA 10 Isotope Ratio Mass Spectrometer. ^{13}C natural abundance was expressed in δ units, by reference to the international standard PDB (marine carbonate: belemnite from the PEE Dee formation), according to the following equation:

$$\delta^{13}C\text{\textperthousand} = \frac{[^{13}C/^{12}C]_{sample} - [^{13}C/^{12}C]_{PDB}}{[^{13}C/^{12}C]_{PDB}} \times 1000$$

All samples were sieved to 1 mm, ground to 100 μm and homogenised in order to minimise the effects of sample heterogeneity. Organic carbon, nitrogen and δ^{13}C of the soil samples were measured in duplicate, with previous elimination of carbonates, by acidification. The ^{13}C natural labelling technique requires information on ^{13}C abundance of all plant materials entering the soil. Plants samples associated with the soils were collected, crushed, homogenised and analysed to obtain reference values for the stable (^{13}C/^{12}C) carbon isotopic analysis.

3. Results and discussion

3.1. General characteristics of the soil samples

Trace metals and organic carbon concentrations of the bulk samples (<2 mm) for each soil profile are reported in Table 1. All the results are given as the mean of the two replicates for each sample. The relative standard deviation of all the measured values never exceeded 7%. The organic carbon is mainly located in the topsoils (plough horizons), where most of the metals occur. The values for Pb, Zn, Cd and Cu concentrations are sometimes higher than the legal French limit NFU '44-041 (100, 300, 2 and 100 ppm for Pb, Zn, Cd and Cu, respectively). The depth versus concentration profiles depend on the metal. For Pb and Cu, below 25 cm, the metal concentrations are close to the geological background concentrations of the area estimated (Sterckeman et al., 2000). At the opposite,

for the more mobile metal ions (Zn and Cd), the enhanced concentrations are found down to 50 cm.

As reported in Table 2, the pH$_{water}$ (between 6.4 for M_3 and 7.5 for M_1) and the CEC (between 13.9 C mol$^+$ kg^{-1} for M_1 and 14.7 for M_3) are quite similar for M_1, M_2 and M_3, whereas the concentrations of the metals are significantly different and follow the sequence: $M_1 > M_2 > M_3$. Between 1.5% (for M_1) and 2.7 (for M_2), accordingly with John et al., 2005, the organic matter amount in the plough horizons is lower for the soil M_1 where the straws are exported.

The size repartition as a function of depth for the three soils is reported in Table 3 (only the 0−30 cm depth was the studied for the soil M_3). Soil texture is quite similar for M_1, M_2 and M_3: clay (<2 μm) and silt particles (2 μm < fine silt <20 μm and 20 μm < coarse silt < 50 μm) dominate and that texture is relatively constant with the depth. But the soil M_2 is significantly less clayed (9.1%) than the two others soils M_1 (25.2%) and M_3 (28.2%). According to Oades (1995), a high amount of clay decreases the biodegradation of SOM and therefore increases the stock of carbon. Muller and Hoper (2004) concluded that the capacity of soil to protect organic matter against microbial decomposition depends on its clay content. Soil clay content is an abiotic factor defining the size of protected pools of organic matter in models of SOM turnover (Parton, 1996). Therefore, the protection of SOM could be lower for M_2 in comparison with M_1 and M_3, and induces a higher turnover of the SOM in that soil.

3.2. The δ^{13}C constraints

Fig. 1 gives the δ^{13}C of the topsoils (0−30 cm) M_1, M_2 and M_3 as a function of the size fraction. For the cultivated soils under maize M_1 (10 years), M_2 (14 years) and M_3 (13 years), the δ^{13}C of the top bulk samples are respectively: −22.8‰; −22.3‰ and −15.3‰. These data were compared with the δ^{13}C signals measured for plants sampled in the field and reference δ^{13}C values (Balesdent and Mariotti, 1996; Boutton, 1996) of C_3 and C_4 plant tissues and actual CO_2 reported in Table 4. First, the measure of δ^{13}C informs on the origin of the organic matter: a variable part of the organic matter of these soils comes from the incorporation of maize residues, and old C_3 organic matter is still remains.

In agreement with previous studies, a decrease of the δ^{13}C with size fraction is observed in relation to an increase of old SOM from C_3 origin. For 13 years of maize cultivation on an uncontaminated soil, Balesdent and Mariotti (1996) calculated turnover times of 4 ± 1.5 years and 13 ± 2 years, respectively, for the 2000−200 μm and the 200−50 μm fractions. In contrast, all fractions smaller than 10 μm exhibited an annual

Table 1
Trace metals concentrations (mg kg^{-1}) and organic carbon (g kg^{-1}) of the bulk samples (fraction <2 mm) for each soil (M_1, M_2 and M_3)

Depth (cm)	[Pb] (mg kg^{-1})	[Zn] (mg kg^{-1})	[Cu] (mg kg^{-1})	[Cd] (mg kg^{-1})	C (g kg^{-1})
Soil M_1					
0−30	503	852	34	16.8	15
30−35	216	280	18	9.8	9
35−40	118	175	13	6	5
55−65	71	41	4,6	2,1	2.4
170−180	33	39	4.15	1.8	1.15
Soil M_2					
0−30	187	172.5	17.9	12.05	27
30−40	145	133	13.1	9.3	19
40−50	62.3	39	9.8	5.1	11
50−65	38.3	29	7.9	3.3	8.5
Soil M_3					
0−30	54.5	64.2	13.2	3.5	25

Table 2
Cation exchange capacity (CEC) and pH$_{water}$ of the topsoil bulk fractions

	M_1	M_2	M_3
CEC[a] (C mol$^+$ kg^{-1})	13.9	14.1	14.7
pH$_{water}$	7.5	6.8	6.4

[a] The cation exchange capacity was determined by the ammonium acetate method at pH 7 (Metson, 1956).

Table 3
Size repartitions (%) for each soil (M_1, M_2 and M_3; sizes are expressed in μm)

Depth (cm)	2000 > x > 1000	1000 > x > 500	500 > x > 200	200 > x > 50	50 > x > 20	20 > x > 2	2 μm > x
M_1							
0−30	0.7	1.2	5.4	8.0	17.1	41.0	25.2
30−35	1.0	1.1	25.7	4.2	19.4	26.3	22.1
35−40	0.7	2.1	7.0	15.2	12.7	32.9	29.3
55−65	1.8	4.4	4.2	23.8	21.2	22.8	21.7
170−180	0.5	1.9	14.9	30.2	30.3	3.4	18.6
M_2							
0−30	2.30	3.70	10.00	23.30	16.40	32.30	9.10
30−40	0.70	1.60	17.50	26.00	19.50	25.60	8.80
40−50	0.40	0.60	3.00	18.60	28.10	39.70	8.30
50−62	1.20	3.70	1.30	22.60	26.70	29.90	13.00
M_3							
0−30	0.90	2.00	4.60	14.80	30.40	19.20	28.20

rate of new organic matter input equal to $1.3 \pm 0.4\%$ of the carbon amount in the fraction. Monreal et al. (1997) reported in a long-term experiment with continuous maize cultivation that the mean turnover time of soil organic carbon was 14 years in macroaggregates, 61 years in microaggregates and 275 years in the fraction <50 μm.

The C_4/C ratios were calculated from the $\delta^{13}C$ values measured (as described in Section 2): $C_4/C = (\delta - \delta ref_{C3})/(\delta veg_{C4} - \delta ref_{C3})$ with δref_{C3} fixed to $-27\permil$ and δveg_{C4} fixed to $-14\permil$. The results are reported in Fig. 2: C_4/C as a function of the size fraction for the topsoils M_1, M_2 and M_3. From that curve we can conclude that maize replaced C_3 vegetation in various proportions on these three sites. The amount of C_4 organic matter in the bulk fractions of the soils under maize follows the sequence M_3 ($C_4/C = 0.9$) > M_2 (0.4) > M_1 (0.3). A low C_4/C ratio (in comparison with the value 1) corresponds to a situation where a high amount of old (C_3) soil organic matter is always present. The lowest value of the C_4/C ratio for the contaminated soils (M_1 and M_2) in comparison with the uncontaminated soil M_3 could be due to the influence of metals on the SOM turnover.

3.3. Organic carbon amounts for the soils as a function of depth and size fraction

Values of organic carbon of particle-size fractions as a function of depth are reported in Table 5 for M_1, M_2 and M_3 soil. The organic carbon concentration decreases quickly with the depth: SOM is mainly concentrated in the first centimetres (0−30 cm). For the soil M_1, between 0 and 180 cm depth, the clay fraction presents the highest organic carbon concentration: the ratio between clay and bulk fractions concentrations is between 1.1 and 2.5. The C/N ratio measured for M_1 decreases with depth (between 12.5 at 0−30 cm and 7.7 at 170−180 cm for the bulk fraction) and size fraction; this trend is in agreement with a change in chemical nature of SOM (Besnard et al., 2001). For the soil M_2, between 0 and 60 cm depth, the 1000−500 μm and the clay fractions have similar organic carbon concentrations, around two or three times more than in the bulk fraction. For the topsoil M_3, the clay fraction presents the highest organic carbon concentration (around 2.5 times in comparison with the bulk) and then the concentration in the 1000−200 μm fraction is around two times higher in comparison with the bulk concentration.

3.4. Trace metal amounts for the soils as a function of depth and size fraction

The total metal concentrations as a function of depth and size fractions are given in Table 6 for the soils M_1, M_2 and M_3. For the soil M_1, whatever the depth and the nature of
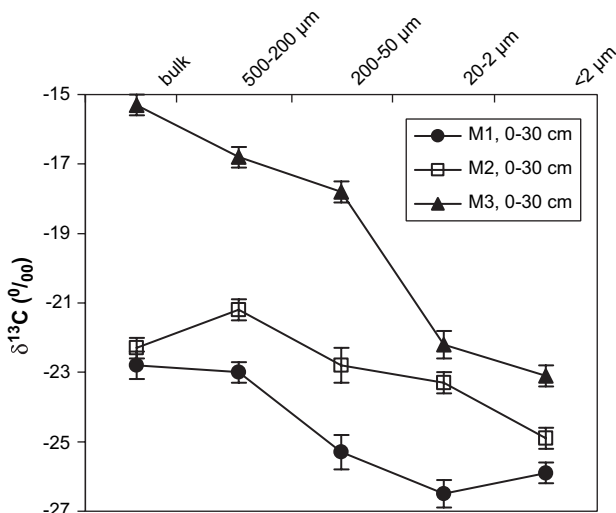

Fig. 1. $\delta^{13}C$ of topsoil samples (M_1, M_2 and M_3) as a function of size fractions.

Table 4
$\delta^{13}C$ values of actual plants collected on the various soils and reference values

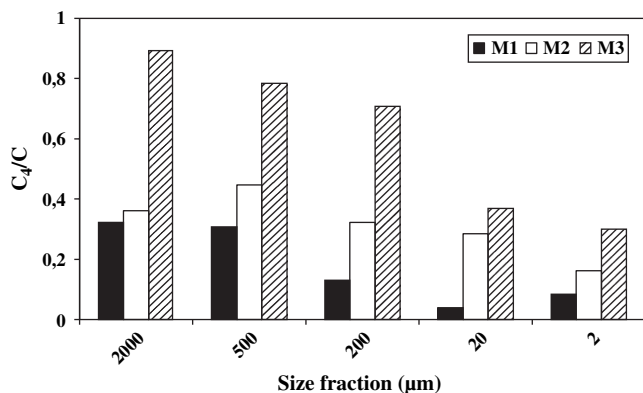| Sample	$\delta^{13}C$ (‰)
Wastes of maize	-14.8 ± 0.5
C_4 plants: maize, tropical grasses and gramineous	Mean of -14 (-17 to -10)
C_3 plants: most other plants (trees, rice, wheat, etc.) and certain grass species	Mean of -27 (-32 to -22)
Present $\delta^{13}C$ value of the atmospheric CO_2	-8

Fig. 2. C_4/C ratios of the topsoils samples (M_1, M_2 and M_3) as a function of size fractions.

the metal, the clay fraction is always the more enriched (between two and five times more in comparison with the bulk). The soil M_2 is less contaminated in comparison with M_1 and whatever the depth and the nature of the metal, the repartition among the size fractions is less heterogeneous. For lead and zinc, between 0 and 65 cm depth, the clay fraction is the more enriched and then the 1000−200 μm fraction. For Cu and Cd, the clay fraction is the only one significantly enriched in comparison with the bulk fraction. For the reference uncontaminated topsoil M_3, the clay fraction presents the highest metal concentrations. Except for cadmium, the coarse 1000−200 μm fraction of each soil presents a slight enrichment in comparison with the bulk for Pb, Zn and Cu, but always remains much less contaminated than the clay fraction.

From the results presented in Table 6 (total metal concentrations) and in Table 3 (size repartition), we calculated the stocks of the various metals as a function of the size fraction for the topsoils (0−30 cm) M_1, M_2 and M_3. These data are given in Fig. 3 for lead (a), zinc (b), copper (c) and cadmium (d). For these cultivated soils under maize, at each depth the stock of metals in the fine fraction is always higher than in the coarse fraction.

3.5. Influence of metals on the organic matter dynamics

Several mechanisms have been proposed to contribute to SOM stabilisation in soils (Sollins et al., 1996): SOM can be (1) biochemically stabilised through the formation of recalcitrant SOM compounds; (2) protected by intimate association with silt and clay particles; and (3) physically stabilised through aggregate formation. The calculated amount of C_4 organic matter in the bulk fractions of the soils under maize follows the sequence M_3 ($C_4/C = 0.9$) > M_2 (0.4) > M_1 (0.3). These differences observed between the three soils in term of SOM turnover could perhaps result from the following parameters: (i) clay amount, (ii) age of the C_4 culture and (iii) soil management (incorporation or not of the straws). Considering the individual influence of each parameter on the SOM turnover, the expected C_4/C sequence is: (i) M_2 (9% of clay) > M_1 (25%) > M_3 (28%), (ii) M_2 (14 years) > M_3 (13 years) > M_1 (10 years) and (iii) $M_3 = M_2 > M_1$. Therefore, if the clay amount was the main factor controlling the SOM of the studied soils, the C_4/C ratio of M_2 will be the highest. On the other hand, if the age of the C_4 culture or soil management were the main factors controlling the SOM of the studied soils, the C_4/C ratios of M_2 and M_3 will be quite similar and much higher than the C_4/C ratio of M_1. One hypothesis to explain the C_4/C sequence observed for the three soils is that the SOM turnover was influenced by the metal contamination (with an intensity depending on the metal concentrations).

For the three soils studied, mainly the clay fraction, and to a lesser degree the particulate (1000−200 μm) SOM fraction, are both enriched with metals and organic carbon. Chemical extractions (with $CaCl_2$, $Na_4P_2O_7$, dithionite and HNO_3) performed for a cultivated soil similar to M_1 (Ponthieu, 2003), indicated that globally, SOM and metal oxides (Fe and Mn) control the speciation of metals. For Pb, EXAFS data confirmed that trend (Morin et al., 1999). SOM displays a high reactivity for metals, lead and copper in particular (Lamy et al., 1994; Harter and Naidu, 1995). From all the results obtained for the atmospheric contaminated soils M_1, M_2 and M_3, we can hypothesis that the metal−organic matter interaction

Table 5
Organic C (%) of the samples (various depths and size fractions) for each soil

Depth (cm)	1000−500 μm	500−200 μm	200−50 μm	50−20 μm	20−2 μm	<2 μm
(a) Soil profile M₁						
0−30		1.22 ± 0.065	1.26 ± 0.05		0.48 ± 0.055	1.75 ± 0.1
30−35		0.55 ± 0.032	0.18 ± 0.04		0.24 ± 0.05	1.36 ± 0.07
35−40		0.69 ± 0.04	0.21 ± 0.03		0.11 ± 0.02	0.93 ± 0.1
55−65		0.26 ± 0.01	0.15 ± 0.02		0.09 ± 0.005	0.5 ± 0.004
170−180		0.19 ± 0.012	0.11 ± 0.05		0.08 ± 0.005	0.27 ± 0.1
(b) Soil profile M₂						
0−30	7 ± 0.42	3.85 ± 0.1	2.7±0.1	1.5±0.1	1.2 ± 0.02	8.3 ± 0.3
30−40	5.1 ± 0.3	2.7 ± 0.1	1.9 ± 0.12	1.8 ± 0.11	1 ± 0.02	4.5 ± 0.16
40−50	2.9 ± 0.17	1.6 ± 0.03	1 ± 0.02	1 ± 0.02	0.85 ± 0.01	3.2 ± 0.13
50−65	1.3 ± 0.06	2 ± 0.06	1.1 ± 0.04	1 ± 0.05	0.7 ± 0.03	1.6 ± 0.06
(c) Topsoil M₃						
	4.5 ± 0.4	4.7±0.42	3.1±0.27	1.1±0.09	2.35±0.24	6.1±0.53

Table 6
Metals concentrations (mg kg^{-1}) for the samples of each soil at various depths and size fractions

Depth (cm)	1000−500 μm	500−200 μm	200−50 μm	50−20 μm	20−2 μm	<2 μm
(a) Soil M₁						
[Pb] (mg kg⁻¹)						
0−30	514.5 ± 15.4	450 ± 13.5	139.3 ± 4.1	115.5 ± 6.8	298.5 ± 11.8	1327.3 ± 39.5
30−35	83 ± 2.5	67.7 ± 2	32 ± 1	29 ± 1.65	83 ± 3.3	742 ± 2.5
35−40	77 ± 2.5	62.1 ± 1.8	24.3 ± 0.7	18.7 ± 1	67 ± 2.6	280 ± 8.4
55−65	68 ± 2.1	62.3 ± 1.9	24 ± 0.7	17 ± 1	45 ± 1.65	140 ± 7.3
170−180	24 ± 0.7	25.5 ± 0.65	21.3 ± 0.6	16.5 ± 0.95	25 ± 1	112 ± 3.4
[Zn] (mg kg⁻¹)						
0−30	394 ± 11.8	321 ± 9.5	203 ± 6.1	112.5 ± 6.7	274 ± 10.8	3286 ± 98.7
30−35	72 ± 2.15	49.1 ± 1.5	50.4 ± 1.45	32 ± 1.8	102.3 ± 4.1	1081 ± 45.6
35−40	47 ± 4	37.2 ± 1.1	22 ± 0.65	17 ± 1.05	98 ± 3.75	603 ± 33
55−65	38 ± 1.1	39.7 ± 1.2	20.3 ± 0.65	19 ± 1.1	58 ± 2.3	154 ± 11.2
170−180	26 ± 0.75	20.8 ± 0.65	16.2 ± 0.55	13 ± 0.75	16 ± 0.66	174 ± 5.7
[Cu] (mg kg⁻¹)						
0−30	17.5 ± 0.55	14.05 ± 0.4	4.3 ± 0.42	10 ± 0.55	28.2 ± 1.2	93.7 ± 3
30−35	11 ± 0.3	8.7 ± 0.25	10.7 ± 0.3	7 ± 0.4	15.3 ± 0.65	51 ± 1.7
35−40	10 ± 0.3	8.6 ± 0.25	3.7 ± 0.1	2.3 ± 0.15	17 ± 0.7	55 ± 1.9
55−65	7 ± 0.2	7.3 ± 0.2	3.2 ± 0.1	2.5 ± 0.15	7 ± 0.25	22 ± 0.05
170−180	3.5 ± 0.1	2.4 ± 0.07	1.7 ± 0.05	0.8 ± 0.05	2 ± 0.08	21 ± 0.7
[Cd] (mg kg⁻¹)						
0−30	11.7 ± 0.35	10 ± 0.3	5.8 ± 0.17	4.5 ± 0.15	14.4 ± 0.55	53.5 ± 1.6
30−35	8.3 ± 0.25	6 ± 0.18	4.1 ± 0.12	3 ± 0.18	8.1 ± 0.35	30 ± 0.9
35−40	6.4 ± 0.18	5.8 ± 0.17	3.6 ± 0.1	1.5 ± 0.09	5 ± 0.2	13 ± 0.4
55−65	5.1 ± 0.15	5.3 ± 0.15	1.9 ± 0.05	1 ± 0.06	3.8 ± 0.15	8 ± 0.3
170−180	0.8 ± 0.02	0.5 ± 0.015	0.4 ± 0.012	0.2 ± 0.012	2 ± 0.08	7 ± 0.3
(b) Soil M₂						
[Pb] (mg kg⁻¹)						
0−30	273 ± 13.7	224.5 ± 18	207.5 ± 10.4	155 ± 5.4	163 ± 7.5	318 ± 15.9
30−40	165 ± 8.5	178 ± 14.2	142 ± 7	131 ± 4.7	142 ± 6.4	187 ± 9.5
40−50	86 ± 4.3	84 ± 6.7	75 ± 3.8	62 ± 2.25	65 ± 3.1	86 ± 4.5
50−65	89 ± 4.5	81 ± 6.5	49 ± 2.3	33 ± 1.2	25 ± 1.2	91 ± 4.7
[Zn] (mg kg⁻¹)						
0−30	235.5 ± 11,9	200 ± 16	184 ± 9	161 ± 5.8	162.5 ± 7.6	258 ± 12.8
30−40	153 ± 7.7	169 ± 13.7	125.5 ± 6.3	122 ± 4.7	127 ± 5.9	164 ± 8.5
40−50	38.5 ± 1.9	42 ± 3.3	36.1 ± 1.75	27 ± 0.9	28 ± 1.3	67 ± 3.7
50−65	34 ± 1.7	34 ± 2.5	22.4 ± 1.3	23 ± 0.65	32 ± 1.45	51 ± 2.8
[Cu] (mg kg⁻¹)						
0−30	23.8 ± 1.2	17.15 ± 1.35	17.4 ± 0.9	14.95 ± 0.55	14.25 ± 0.65	55 ± 2.65
30−40	15.3 ± 0.8	11.4 ± 0.9	10.4 ± 0.55	9.7 ± 0.35	8.5 ± 0.4	44 ± 2.5
40−50	9.5 ± 0.45	9.2 ± 0.7	6.2 ± 0.4	8 ± 0.3	9 ± 0.4	39 ± 1.65
50−65	6.9 ± 0.3	7.4 ± 0.5	4.3 ± 0.2	3.5 ± 0.12	2.8 ± 0.1	41 ± 2.1
[Cd] (mg kg⁻¹)						
0−30	16.25 ± 0.8	12.95 ± 1	10.05 ± 0.5	11.9 ± 0.4	9.7 ± 0.4	30.4 ± 1.5
30−40	12.5 ± 0.65	8.8 ± 0.7	7.7 ± 0.4	6.3 ± 0.22	6.8 ± 0.305	33 ± 1.65
40−50	7.3 ± 0.365	5.9 ± 0.45	3.8 ± 0.2	4.8 ± 0.165	5.1 ± 0.225	17 ± 0.85
50−65	6.7 ± 0.335	7.1 ± 0.565	6.2 ± 0.35	2.7 ± 0.095	1.9 ± 0.08	13.2 ± 0.66
(c) Topsoil M₃						
[Pb] (ppm)	57 ± 3.8	66 ± 3.3	49 ± 1.5	41 ± 0.8	39 ± 1.5	84 ± 2.4
[Zn] (ppm)	91 ± 6.2	86 ± 4.2	48 ± 1.4	40 ± 0.75	35 ± 1.35	121 ± 3.5
[Cu] (ppm)	16 ± 1.1	14 ± 0.7	11 ± 0.35	7.5 ± 0.15	8.2 ± 0.3	21 ± 0.65
[Cd] (ppm)	3.6 ± 0.25	2.4 ± 0.12	2.5 ± 0.065	2.7 ± 0.4	2.1 ± 0.08	5.3 ± 0.2

depends in two different ways on two size fractions: fraction <2 μm and fraction >50 μm. Plants are contaminated (soil−plant transfer or direct absorption by leaves) and after their death, a selective degradation takes place depending in particular on their metal content and the soil characteristics. Even in metal contaminated soils, biological activity occurred (Aoyama and Nagumo, 1997), but an alteration of the decomposition of organic matter was reported (Berg et al., 1991; Balabane et al., 1999; Cotrufo et al., 1995; Valsecchi et al., 1995), generally explained by an inhibition of microbial activity by bio-available toxic metals (Brookes, 1995; Mhatre and Pankhurst, 1997). Therefore an accumulation of highly contaminated coarse plant debris can result (Hughes et al., 1980; Harter and Naidu, 1995). However, the particulate
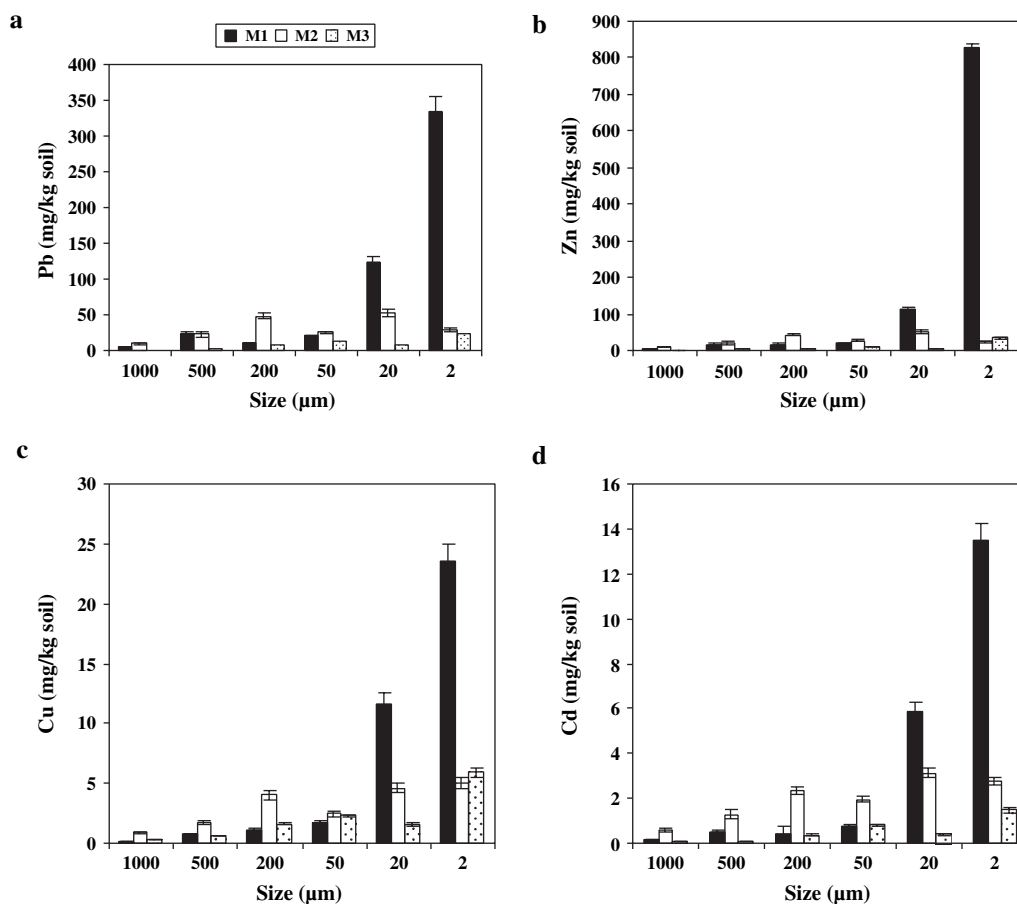
Fig. 3. Stocks of metals for the topsoil samples as a function of size fractionations: (a) lead, (b) zinc, (c) copper and (d) cadmium.

organic matter fraction, the coarse sized SOM fraction composed by recently accumulated organic matter, is poorly associated with the soil mineral matrix and has a relatively rapid turnover in comparison with other SOM (Cambaradella and Elliott, 1992; Balesdent, 1996). Metals of the coarse fractions are progressively released during the decay of particulate organic matter. A part of these metals is then sorbed by the colloid organic matter of the clay fraction (high CEC and specific surface) (Besnard et al., 2001). According to Wattel-Koekkoek et al. (2003) and Gregorich et al. (2003), the interaction between SOM and polyvalent cations can induce SOM stabilisation.

Comparison of the C_4/C ratios for the 500−200 µm fraction (M$_1$:0.3, M$_2$ 0.45, M$_3$ 0.78) and the clay fraction (M$_1$ 0.08, M$_2$ 0.15, M$_3$ 0.3) of the three topsoils suggest that the transformation of coarse organic matter (from C$_4$ origin) into humic substances present in the clay fraction (Baldock et al., 1992) could be reduced by metals. Moreover, the distribution of recently incorporated organic carbon is not homogeneous in soil aggregates. For instance, Puget et al. (2000), found that maize residue carbon was enriched in particular in the particulate organic matter located in macro-aggregates. In the studied soils, metals are mainly concentrated in the clay fraction enriched by the old C$_3$ SOM. In contrast, the particulate organic matter is less contaminated. We can therefore conclude that the stabilisation effect of metals is stronger for the old C$_3$

SOM in comparison to the C$_4$ young SOM (mainly present in the labile coarser fractions). Consecutively to metal contamination, if the C$_4$ SOM is more degraded by the microorganisms than the C$_3$ SOM, then the C_4/C ratio decreases.

4. Conclusions

The determined sequence for the amount of C$_4$ organic matter in the bulk fractions: M$_3$ (0.9) > M$_2$ (0.4) > M$_1$ (0.3), cannot result only from the differences observed between the three soils in terms of clay amount, age of the C$_4$ culture and soil management. On the contrary, the lowest value of the C_4/C ratio for the contaminated soils (M$_1$ and M$_2$) in comparison with the uncontaminated soil M$_3$ could be due to the influence of metals on the SOM turnover.

The organic carbon is mainly located in the topsoils (plough horizons), where most of the metals occur. For the three studied soils, the clay fraction, and to a lesser degree (except for cadmium) the particulate (1000−200 µm) SOM fraction, are both enriched with metals and organic carbon. Chemical extractions performed for a cultivated soil similar to M$_1$ (Ponthieu, 2003), indicated that SOM and metal oxides control the speciation of metals.

The δ^{13}C results demonstrated differences in the nature of the SOM as a function of the size fraction and depth. The clay fraction is strongly enriched with old C$_3$ SOM in

comparison with the coarse fractions. The comparison of the C_4/C ratios for the 500−200 μm and the clay fractions of the three topsoils suggest that the transformation of coarse organic matters (from C_4 origin) into humic substances present in the clay fraction could be reduced by metals.

The less contaminated (in comparison with the clay fraction) particulate organic matter fraction composed by recently accumulated organic residue has a relatively rapid turnover in comparison with the clay SOM (Cambaradella and Elliott, 1992; Balesdent, 1996). Metals of the coarse fractions are progressively released during the decay of particulate organic matter. A part of these metals is then sorbed by the colloid organic matter of the clay fraction, therefore the clay fraction (enriched with old C_3 SOM) is progressively more contaminated and more stabilised (Wattel-Koekkoek et al., 2003; Gregorich et al., 2003). Consecutively to metal contamination, the proportion of the young C_4 organic matter relative to old C_3 (or C_4/C ratio) decreases because the young C_4 SOM (mainly present in the labile coarser fractions) is more easily degraded by the microorganisms than the C_3 SOM.

Understanding of mechanisms involved in SOM dynamic is an important challenge in regard to the global influence of that natural compartment. The size fractionation and profile sampling permit access to various pools of SOM with different stability and reactivity for pollutants. In order to better understand the mechanisms, we could test in detail, on various pieces of the same experimental long term site: the influence of the nature of the metal on the turnover of SOM; the effect of increasing metal concentrations; and investigate various metallic sources (influence of initial metal speciation).

Acknowledgements

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