

Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water

Katelle Quenea, Isabelle Lamy, Peter Winterton, Alain Bermond, Camille Dumat

▶ **To cite this version:**

Katelle Quenea, Isabelle Lamy, Peter Winterton, Alain Bermond, Camille Dumat. Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water. Geoderma, 2009, vol. 1 (3-4), pp. 217-223. 10.1016/j.geoderma.2008.11.037 . hal-00991544

HAL Id: hal-00991544
https://hal.science/hal-00991544

Submitted on 15 May 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive TOULOUSE Archive Ouverte (OATAO)
OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : http://oatao.univ-toulouse.fr/
Eprints ID : 3847

To link to this article : DOI:10.1016/j.geoderma.2008.11.037
URL : http://dx.doi.org/10.1016/j.geoderma.2008.11.037

To cite this version : Quenea, Katelle and Lamy, Isabelle and Winterton, Peter and Bermond, Alain and Dumat, Camille *Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water.* (2009) Geoderma, vol. 1 (n° 3-4). pp. 217-223. ISSN 0016-7061

Any correspondance concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water

K. Quenea [a,1], I. Lamy [b,2], P. Winterton [c,3], A. Bermond [d,4], C. Dumat [e,*]

[a] BioMCo, UPMC, UMR 7618, PO box 120, 4 place Jussieu, 75251 Paris cedex 05, France
[b] INRA, Unité de science du sol, 78026 Versailles, France
[c] Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 09, France
[d] AgroParisTech, 16 rue Claude Bernard 75231 Paris cedex 05, France
[e] Ecolab, UMR 5245, ENSAT Av. Agrobiopole 31326 Auzeville, France

Keywords:
Soil organic matter turnover
Stable isotopic carbon ratio
Trace metal behaviour
Size fractionation
Waste water

A B S T R A C T

Only scarce field studies concern the consequences of natural soil organic matter (SOM) and metal interactions on SOM dynamics in soils. We investigated the interactions of four metals (Pb, Zn, Cu and Cd) with the SOM associated to five different size fractions (between 2000 µm and <2 µm) of a sandy top soil contaminated by waste water. Metal, organic carbon and nitrogen concentrations were measured and chemical extractions (with $Na_4P_2O_7$ and EDTA) were also performed to assess the variations of SOM–metal interactions irrespective of the size fraction. In addition, as in that selected contaminated site, maize (C_4 plant), replaced C_3 crops 15 years ago, natural isotopic ^{13}C labelling gave new insights into SOM turnover. First, the results suggest that metals influence the SOM dynamics in that sandy soil: a C_3 "old carbon" enrichment was observed in the small or clay size fractions, while the "new" C_4 carbon associated with sandy soil particles presents a rapid turnover. Metal accumulation in the clay fraction is attributed to particulate organic matter (poorly associated) and SOM decay which overtime accumulated metals and eventually these metal–SOM associations prevent the biological decomposition of such carbon pools. Moreover, the $\delta^{13}C$ signals, C/N ratios and results from chemical extractions clearly showed differences in the origin, nature and reactivity of the SOM as a function of the size fraction with consequences on the metal behaviour. Differences were observed between metals studied: Zn seems to be mainly bound to SOM associated with clay particles, while Pb seems to prefer to interact directly with the mineral surfaces versus the SOM.

1. Introduction

Due to various anthropogenic activities, potentially toxic metals are accumulated in soils, with a risk of water and biota contamination (Alloway, 1995). The design of pertinent soil criteria for environment protection and remediation relies on an understanding of the mechanisms controlling metal behaviour (Cecchi et al., 2008; Arshad et al., 2008). Among the various reactive soil constituents, soil organic matter (SOM) has a large sorption capacity towards metals (Yin et al., 2002). The metal–SOM interaction has various and complex consequences both on the solubility, mobility and bioavailability of metals (Impellitteri et al., 2002) and on SOM turnover (Boucher et al., 2005). Generally, solid phase SOM is associated with retention, decreased mobility and reduced bioavailability of trace metals (Sauvé et al., 2000). But cationic metals that would ordinarily precipitate at the pH values of most soils are sometimes maintained in solution through complexation with soluble organics (Ferrand et al., 2006). Furthermore, metals participate and/or affect biogeochemical cycles in soils and influence the soil biota (Barajas-Aceves et al., 1999).

Reactive soil components are obviously in interaction (Dumat et al., 1997) and SOM consists of various components with a wide range of turn-over times, weight, reactivity and chemical nature: therefore the way such interactions are studied is complex (Woomer et al., 1994). The studies concerning one extracted soil component are open to criticism, conversely, methods of soil particle-size fractionation can be used to assess the distribution of metals in soils (Ducaroir and Lamy, 1995) and provide information on the SOM behaviour.

The metal distribution among the different soil components can be estimated using specific chemical reagents in order to discriminate the total metal content over various operationally defined fractions in the solid phase (Tessier et al., 1979; Dumat et al., 2001). For instance, sodium pyrophosphate ($Na_4P_2O_7$) is used to dissolve SOM:

* Corresponding author. Tel.: +33 5 62 19 39 03; fax: +33 5 62 19 39 01.
E-mail addresses: katell-quenea@enscp.fr (K. Quenea), lamy@versailles.inra1fr (I. Lamy), peter.winterton@univ-tlse3.fr (P. Winterton), bermond@inapg.inra.fr (A. Bermond), camille.dumat@ensat.fr (C. Dumat).
[1] Fax: +33 1 44 27 67 16.
[2] Fax: +33 1 30 83 32 59.
[3] Fax: +33 5 61 55 83 58.
[4] Fax: +33 1 44 08 16 46.

pyrophosphate complexes the metals which stabilize the SOM and the hydrogen bonds between OM and minerals are broken (Dumat et al., 1997). In contrast, EDTA is a powerful but unspecific complexing agent: the metals adsorbed both by SOM and oxides are extracted (Miller et al., 1986). The comparison of $Na_4P_2O_7$ and EDTA metal extractions should improve the estimation of metals specifically linked to SOM.

In soils where the vegetation changes from C_3 to C_4 (or vice versa), the variations in the natural abundance of ^{13}C ($^{13}C/^{12}C$ ratio) in SOM over time can be used to identify organic carbon sources in the soil (Schwartz et al., 1996) or to determine the SOM turnover rate (Balesdent and Mariotti, 1996). Using that tool, Dumat et al. (2006) highlighted the influence of metals on the SOM turnover on pseudogley brown leached soils strongly contaminated by inorganic atmospheric fallout from a smelter. However, only scarce field studies concern the consequences of natural SOM–metal interactions on SOM dynamics: supplementary studies in various pedologic and pollution contexts are therefore needed.

In the present work a contaminated sandy top soil under maize that had received waste water applications was used to investigate the interactions between four metals (Pb, Cd, Zn and Cu) and SOM. The tested hypothesis throughout these experiments was a significant influence of organic matter–metal interaction both on SOM dynamics and metals fate.

2. Materials and methods

2.1. Soil sample preparation and soil properties

The studied sandy luvisols, in the north of the Paris basin, has been precisely described by Lamy et al. (2006). Moreover the site management history is widely exposed in several publications (Bourennane et al., 2006; Lamy et al., 2006; Dère et al., 2006, 2007): wastewater irrigation of garden markets occurred from 1899 to 2002 (average 40,000 $m^3\ ha^{-1}\ year^{-1}$).

In comparison with experiments performed in controlled laboratory conditions, only few study dealing with organic matter–metals interactions concern field experimentations based on concrete case. Our study offers an original experimental design from this point of view. The studied site has been considered only after metal contamination has been noticed, which means: several years after that the spreading has been forbidden, thus the waste water was not available for analysis. However Dère et al. (2006, 2007) observed that metals concentrations in the sandy topsoil have increased by tenfold compared to the pedogeochemical background and concluded to a soil metal pollution due to waste water spreading.

Field sampling was oriented to collect representative soil samples weighing 40 kg in closed bags. After mixing, all the samples were air dried and sieved to exclude particles larger than 2 mm to give the bulk soil. Thereafter trace metal, carbon and nitrogen concentrations were measured. The cation exchange capacity (CEC), determined by the ammonium acetate method at pH 7 (Metson's method, AFNOR NF X 31130) was 4.9 $Cmol(^+)\ kg^{-1}$ and the pH_{water} = 7.1.

2.2. Physical fractionation of the various soil size fractions

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 in order to minimise the potential variations of metal speciation that could occur with chemical dispersion. The solid/solution ratio was 1/5 (m/V) with the use of glass balls favouring the soil dispersion. The suspensions were then sieved through a series of grids (AFNOR French reference) with decreasing mesh size (2000, 200 and 50 µm). Then the fractions (20 µm<size<50 µm) and (2 µm<size<20 µm) were obtained by sedimentation at normal gravity (g), during times determined by Stokes' law. The <2 µm fractions were finally obtained after concentration of the suspensions by centrifuging at 39,200 g for 1 h at 15 °C on a Beckman Avanti J30I apparatus. All the particles recovered were air dried at 60 °C, weighed, ground (200 µm) and homogenised.

2.3. Measure of metal concentrations and chemical extractions

The total metal concentrations in the various soil size fractions were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Jobin Yvon JYESS 4.03 apparatus, after triple acid digestion (HF, HCl and HNO_3) of the solid samples. The digestion protocol and measurement accuracy were checked by reference to a known standard soil (GRX2). It indicated the efficiency of the digestion protocol and of the ICP-AES assay (within ±1%). All the results correspond to the mean of two replicates.

Two extractions were performed on separate sub-samples. The $Na_4P_2O_7$ extractions were performed with the procedure of Vieiriae et al. (1993). The contact time was 16 h, with 0.1 M $Na_4P_2O_7$ at pH = 10: maximum efficiency is for pH>9 (Asher and Bar-Yosef, 1982). The EDTA extraction conditions were chosen such that EDTA was in excess at equilibrium (Gesthem and Bermond, 1998). The contact time was 24 h, with 0.05 M EDTA at pH = 6.5. The various solid phase fractionations were performed at room temperature (20 °C), with a solid/solution ratio of 1/10, with two replicates per sample. In order to obtain a solution free of solid material before filtration, a strong centrifugation (50,000 g) was performed on the $Na_4P_2O_7$ extracts (20,000 g for EDTA extracts). After each extraction, the soil was rinsed with deionised water to limit precipitation of metals and to improve the extraction efficiency. The extracts and rinses were analysed after filtration (0.2 µm), for metals using ICP-AES. Analyses of soil extractions were calibrated using standard solutions made with the extracting agents.

2.4. Amounts of organic carbon and stable carbon isotopic signals ($\delta^{13}C$)

The ploughed contaminated topsoil (0–30 cm), which has been under maize (C_4 metabolism with $\delta^{13}C$ from −10 to−12‰) for 15 years, was previously used for garden markets cultures, presenting a C_3 metabolism ($\delta^{13}C$ from −27.6 to −30.5‰). That C_3–C_4 sequence allows natural labelling of organic matter in relation with the dynamics of the carbon sources (Bender, 1971; O'Leary, 1981; Collister et al., 1994). Organic carbon and nitrogen contents of the 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) (Craig, 1957), according to the following equation:

$$\delta^{13}C‰ = \frac{\left[^{13}C/^{12}C\right]_{sample} - \left[^{13}C/^{12}C\right]_{PDB}}{\left[^{13}C/^{12}C\right]_{PDB}} \times 1000.$$

All samples were sieved to 1 mm, ground to 100 µm and homogenised. Organic carbon, nitrogen and $\delta^{13}C$ were measured in duplicate, with previous elimination of carbonates by acidification. According to Balesdent and Mariotti (1996) and Boutton (1996), mean $\delta^{13}C$ (‰) reference values for carbon isotopic composition are around −27 for C_3 plants (mainly trees, rice, wheat, certain grass species), −14 for C_4 plants (mainly maize, tropical grasses and certain other grasses) and −8 for current atmospheric CO_2.

2.5. Statistical data treatment

Data obtained were subjected to analysis of variance (ANOVA) with one factor, using the software Statistica, Edition'98 (StatSoft Inc., Tulsa,

Table 1
Metal concentrations (mg kg^{-1}), organic C (%), N (%) and C/N of the various size fractions of the contaminated sandy top soil

Soil size fraction	Concentration (mg kg^{-1})				%		
	Pb	Zn	Cu	Cd	C	N	C/N
2000–200 µm	43.2±5	258±19	32±11	0.06±0.02	1.26±0.075	0.04±0.005	31.5
200–50 µm	94.2±7	429±16	93.6±15	0.46±0.05	1.24±0.05	0.07±0.005	17.71
50–20 µm	340±22	1893±98	296.7±21	4±0.2	3.4±0.1	0.21±0.015	16.33
20–2 µm	749±54	4112±165	429±33	13.15±0.3	5.5±0.3	0.42±0.03	13.12
<2 µm	1560±19	7688±73	1267±94	22.5±2	7.2±0.3	0.67±0.05	10.75

OK, USA). For each bioassay, mean values with different letters represent a significant difference ($p<0.05$) as measured by the LSD Fisher test. Letters are reported on the figures.

3. Results

3.1. Amounts of trace metals, carbon and nitrogen in the various size fractions

For the bulk topsoil sample: (i) trace metal concentrations (mg kg^{-1}) were [Pb]=142, [Zn]=1233, [Cu]=68 and [Cd]=1.8; (ii) organic carbon (%) and nitrogen (%) concentrations are respectively 1.75 and 0.15, with a C/N value of 11.7. These results are given as the means of the two replicates and the relative standard deviation never exceeded 7%. Compared with the natural pedogeochemical background values ([Pb]=5.9 mg kg^{-1}, [Zn]=13.4 mg kg^{-1}, [Cu]=3.9 mg kg^{-1} and [Cd]=0.1 mg kg^{-1}), our results indicate a significant contamination of the top soil (Lamy et al., 2006).

Particle size fractionation of soil samples resulted in the recovery of 98±0.5% of the initial sample mass. The size distribution observed was: 42.3% (2000 µm>fraction>200 µm), 40.4% (200 µm>fraction>50 µm), 5.4% (50 µm>fraction>20 µm), 4.5% (20 µm>fraction>2 µm) and 7.4% fraction<2 µm i.e. the sand fractions (fine and coarse) accounted for 80% of the total weight.

The results of total metal and organic carbon concentrations in the different soil particle size classes are given in Table 1. Whatever the metal considered, the concentration strongly increased as the size decreased according to Harter and Naidu (1995): 30–40 times for Zn, Pb and Cu and 375 times for Cd. The clay fraction is also that with the highest levels of organic carbon and nitrogen. The concentrations measured increased from 1.3% C and 0.04% N in the 2000–200 µm fraction to 7.2% C and 0.7% N in the clay fraction. The proportion of the different soil particle size classes was multiplied by the concentration of the metals in each class to give the actual quantity of each metal in each size class (Fig. 1). The determination of these different metal pools demonstrated the relevance of focussing both on the clay fraction and on the sum of the different coarse fractions in order to study the SOM–metal interaction.

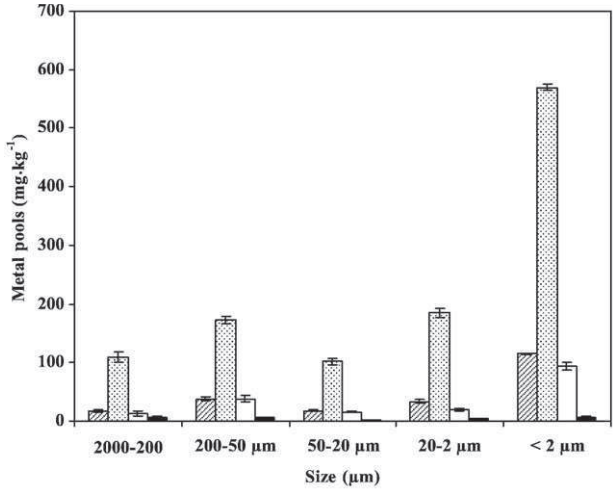


Fig. 1. Metal pools (Pb: ▨, Zn: ▩, Cu: □ and Cd: ■) in the different size fractions of the topsoil.

3.2. Chemical extractions

The results of the chemical extractions performed on the sandy top soil size fractions for Zn (A), Cu (B), Pb (C) and Cd (D) are reported both in Fig. 2: quantities of metals extracted (mg of the metal per kg of soil fraction) by EDTA or $Na_4P_2O_7$ and in Fig. 3: ratios of the quantities of metals extracted by EDTA or $Na_4P_2O_7$ divided by the total metal content of that size fraction. The data of Fig. 2 indicate that the quantities extracted per unit weight of the fraction increased with decreasing particle size. However, for the ratios (Fig. 3), the reverse trend was generally observed, in particular with $Na_4P_2O_7$ extraction: a large proportion of metals extractable from the coarse fraction and in the 20–2 µm fraction.

In the clay fraction, more Zn and Cu were extracted with $Na_4P_2O_7$ than with EDTA (Fig. 2). Moreover, higher proportions of Zn and Cu were extracted by $Na_4P_2O_7$ than Cd and Pb (Fig. 3) suggesting two different patterns depending on the metal.

3.3. Use of the $\delta^{13}C$ signal to study the organic matter dynamics in relation with metals

Fig. 4 gives: (a) $\delta^{13}C$ and (b) C_4/C: ratio between carbon of C_4 origin and total organic carbon for the different size fractions (Balesdent and Mariotti, 1996; Dumat et al., 2006). The value of $\delta^{13}C$ for the topsoil was between −21.8‰ for the coarse fraction and −23.2‰ for the fine fraction. No $\delta^{13}C$ values for organic matter from waste water are available from the literature, however a $\delta^{13}C$ signature of −25.4‰ measured for anaerobically digested sludge from South West France (Parat et al., 2007) could give a general idea. In fact, the quantity of organic carbon in waste waters is generally very low compared to the carbon inputs from plants, therefore the influence of the organic matter from waste waters on the $\delta^{13}C$ signature of the SOM can be ignored considering the much greater inputs of organic matter from C_3 and C_4 plants.

4. Discussion and conclusion

4.1. SOM and metal interaction

The comparison between EDTA (a powerful but unspecific metal chelating agent) and $Na_4P_2O_7$ (which mobilises metals bound to SOM) (Fig. 2) suggests that a significant part of all the metals is bound to the SOM. That hypothesis is moreover supported by total concentrations results: carbon from the clay fraction represented more than 25% of the total soil carbon and the highest proportion of metals was also $Na_4P_2O_7$ extracted from this fraction. For lead and zinc, two metals with high total concentrations in the sandy top soil, the following empirical equations between metal concentrations (expressed in mg kg^{-1}) and organic carbon concentrations (expressed in percent) were determined: [Pb]=228.59×[C]−294.93 with a correlation coefficient (r) of 0.96 and [Zn]=1150.4×[C]−1412.6 with r=0.95.

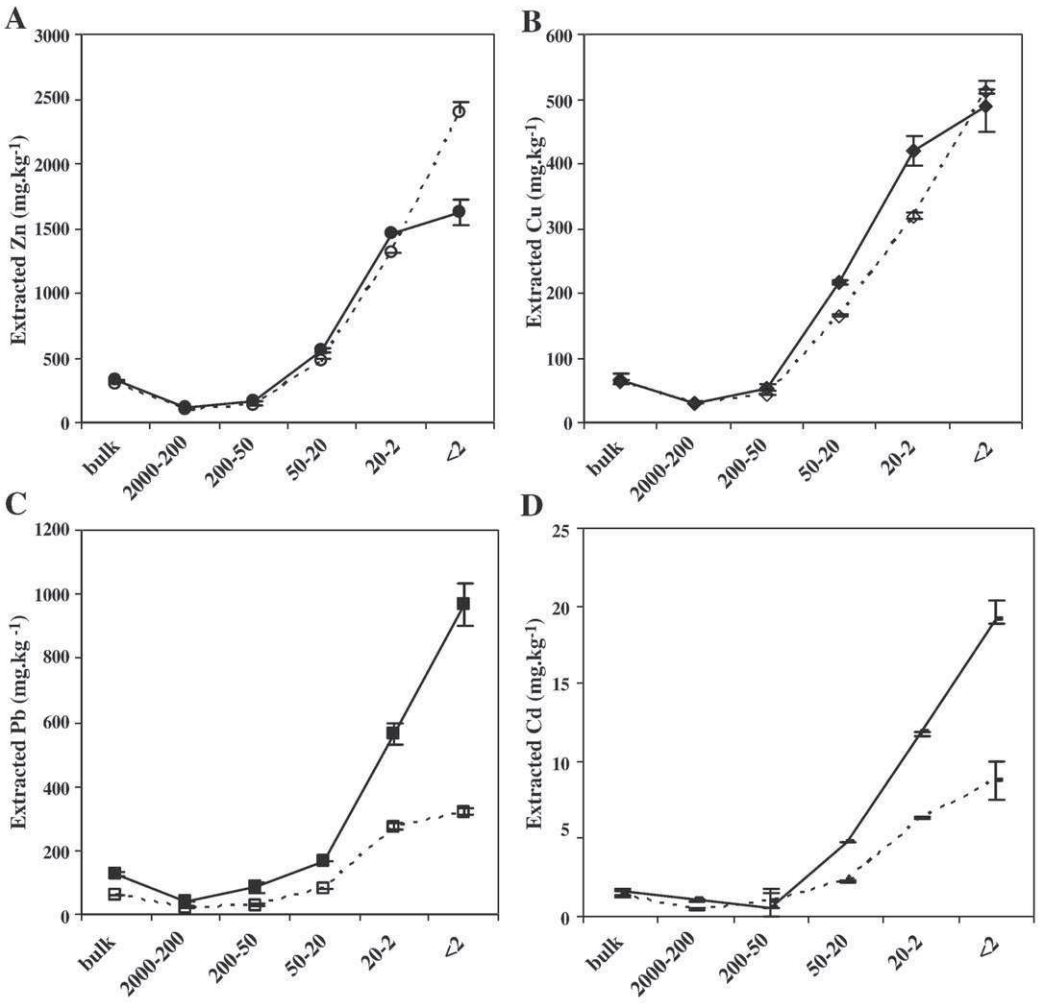


Fig. 2. Chemical extractions performed on various size fractions of the sandy topsoil. Quantities of metals extracted (mg of the metal per kg of soil fraction) by EDTA or $Na_4P_2O_7$. A) Zn-EDTA: ● and Zn-$Na_4P_2O_7$: ○; B) Cu-EDTA: ♦ and Cu-$Na_4P_2O_7$: ◊. C) Pb-EDTA: ■ and Pb-$Na_4P_2O_7$: □; D) Cd-EDTA: and Cd-$Na_4P_2O_7$: ——.

However in relation to SOM influence, two different behaviours were observed for the four studied metals. For Zn and Cd, the quantities extracted by EDTA and $Na_4P_2O_7$ were fairly similar (except for Zn in the case of clay fraction: $Na_4P_2O_7$>EDTA) suggesting that these two metals were preferentially linked to the SOM (Fig. 2). In contrast, for lead and cadmium, the quantities extracted by EDTA were significantly higher than the quantities extracted by $Na_4P_2O_7$: other soil components (like clay minerals or oxides) significantly interact with these two metals (Dumat et al., 2001; Cecchi et al., 2008).

The general trend observed was that of a decrease of metal proportions extracted by $Na_4P_2O_7$ with the decrease of the soil particle size: the metal extraction yield was greater in sand and in the 20–2 µm fractions compared with the clay fraction (Fig. 3). The efficiency of $Na_4P_2O_7$ could be influenced by the nature of the SOM and by the interactions between SOM and other soil components. Indeed, with decreasing particle size, Table 1 shows a decrease in C/N ratio, in agreement with a change in the chemical nature of the SOM (Dormaar, 1984; Besnard et al., 2001). Two different pools of metals with contrasting behaviours (in relation with the SOM characteristics) could be present in the soil: metals in the coarse fractions and metals in the clay fraction.

The coarsest fraction was mainly composed of sand and poorly degraded particulate organic matter (POM) (Cambaradella and Elliott, 1992). Minerals in the 2000–20 µm fraction were relatively inert, so the interaction between these minerals and metals should mainly be weak such as electrostatic bonding; POM (with high specific surface area) may therefore play a significant role (Besnard et al., 2001). Sequential extraction performed by Dère et al. (2007) on the bulk fraction of the same sandy topsoil ranked lability (potential to be remobilized from solid phase to soil solution) as: Zn ≫ Cu>Pb>Cd. Doelsch et al. (2006) also observed the high lability of Zn in sewage sludge. In the coarse fractions of the soil, the metals associated with POM will therefore mainly be under relatively labile forms.

During biodegradation, the level of SOM oxidation increases (Baldock et al., 1997), leading to an increase of its reactivity towards metals. Since the level of humification increases as particle size decreases, SOM from the fine fraction constitutes a highly reactive pool for binding metals. Moreover, the metals arrived in the sandy top soil simultaneously with organic matter from the waste water, the metals could therefore have already been associated with dissolved organic matter (Vaca-Paulín et al., 2006; Doelsch et al., 2006). In addition, Wong et al. (2007) concluded that dissolved organic matter interacts with the clay minerals becoming less accessible to microorganisms. Due to its higher stability against microorganism degradation, the SOM of the clay fraction could have a stabilization effect on the metals and reduce their bioavailability (Dabkowska-Naskret, 2003).

4.2. Use of the $\delta^{13}C$ signal to study organic matter dynamics in relation with metals

The measurement for the topsoil (under maize for 15 years) of $\delta^{13}C$ (‰) between −21.8 (coarse fraction) and −23.2 (clay fraction), whereas the value of −12.5‰ has been measured on a maize sample

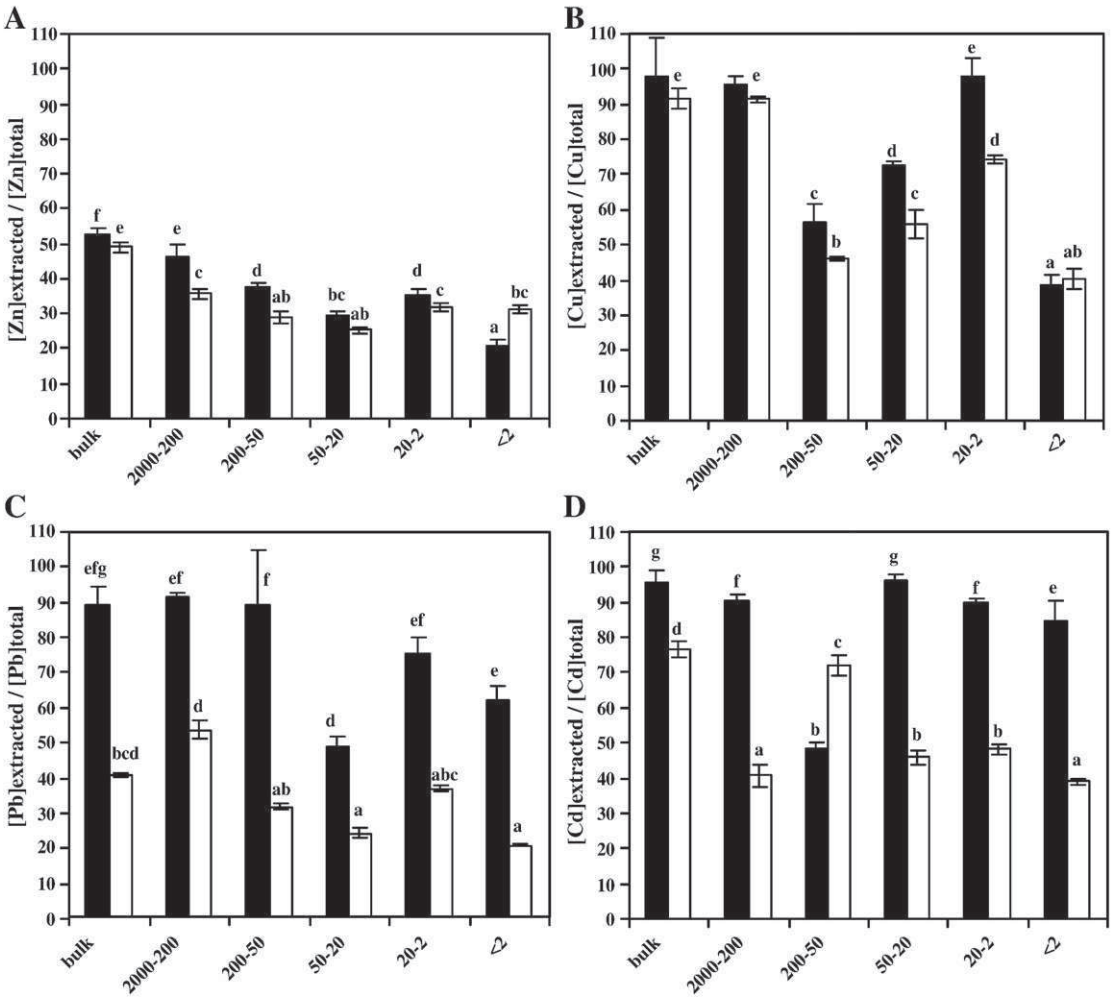


Fig. 3. Chemical extractions performed on various size fractions of the sandy topsoil. Ratios (%) of the quantities of metals extracted by EDTA (■) or $Na_4P_2O_7$ (□) divided by the total metal content of that size fraction. A) Zn, B) Cu, C) Pb and D) Cd.

composed of crushed leaves and stalks by Jolivet et al. (2003), indicates that the SOM is relatively unaffected by the maize $\delta^{13}C$. From the C_4/C ratios calculated, the amount of SOM of C_4 origin was seen to be under 40% and decreased with the soil size fraction: 0.4 for the 2000–200 µm fraction and 0.3 for the clay fraction. Balesdent and Mariotti (1996) or Balesdent et al. (1987) estimated the residence time of carbon in size fractions of different uncontaminated soils under maize for 13 years: the expected proportion of new C_4 carbon from maize in the coarse fraction (2000–200 µm) of these uncontaminated soils was 80%. Balesdent and Mariotti (1996) concluded that turnover times were 4 ± 1.5 years for the 2000–200 µm fraction and 13 ± 2 years for the 200–50 µm fraction. In contrast all fractions finer than 10 µm exhibited a slow turnover. Our results are therefore consistent with a preferential accumulation of old C_3 organic matter in the polluted soil, particularly in the clay fraction. Even in heavily metal contaminated soils, biological activity occurs (Valsecchi et al., 1995; Aoyama and Nagumo, 1997), but alterations of organic matter decomposition are reported (Berg et al., 1991; Cotrufo et al., 1995).

In comparison with more contaminated "old" C_3 plant residues in the clay fraction, the "new" C_4 maize residues left in the soil (after the harvest) were mineralised more quickly. The POM is poorly associated with the soil mineral matrix and has a relatively rapid turnover in comparison with the finest SOM in the clay fraction (Cambaradella and Elliott, 1992; Balesdent, 1996). Parat et al. (2007) suggest an accumulation of plant residues in the coarse fraction of a sludge-contaminated soil by physical protection as the sludge could enhance aggregate formation. However, the topsoil studied here had been intensively used for crops for several decades and its sandy texture limits the physical protection of SOM (Guggenberger et al., 1995). Moreover, the soil we studied received mainly waste water amendment, so the effect on aggregation was limited.

Some metals are progressively released during the decay of C_3 POM. Then, part of the metals was adsorbed by the reactive colloidal organic matter in the clay fraction (Besnard et al., 2001; Boucher et al., 2005). According to Brookes (1995) or Mhatre and Pankhurst (1997), decreased organic matter decomposition in polluted soils could result from the inhibition of microbial activity by bio-available toxic metals. However, Hattori (1996) concluded that the recalcitrance of plant residues towards microorganism degradation should also be considered. The formation, in the clay fraction, of organo-metallic complexes relatively resistant to biodegradation (Orlov et al., 1988) could therefore result. This hypothesis is consistent with the lack of accumulation of highly contaminated coarse plant residues in the top soil i.e. the microorganisms degrade the fresh organic matter (relatively free of metals and not protected by clay minerals), but tend to leave the old C_3 organic matter residues stabilized by chemical and physical phenomena.

Finally from the results obtained in the present study, it can be concluded that the presence of metals carried by waste water modified the turnover rate of the SOM in the contaminated sandy top soil. A decrease of SOM turnover due to the influence of metals was previously observed for pseudogley brown leached soils strongly contaminated by inorganic atmospheric fallout from a smelter (Dumat

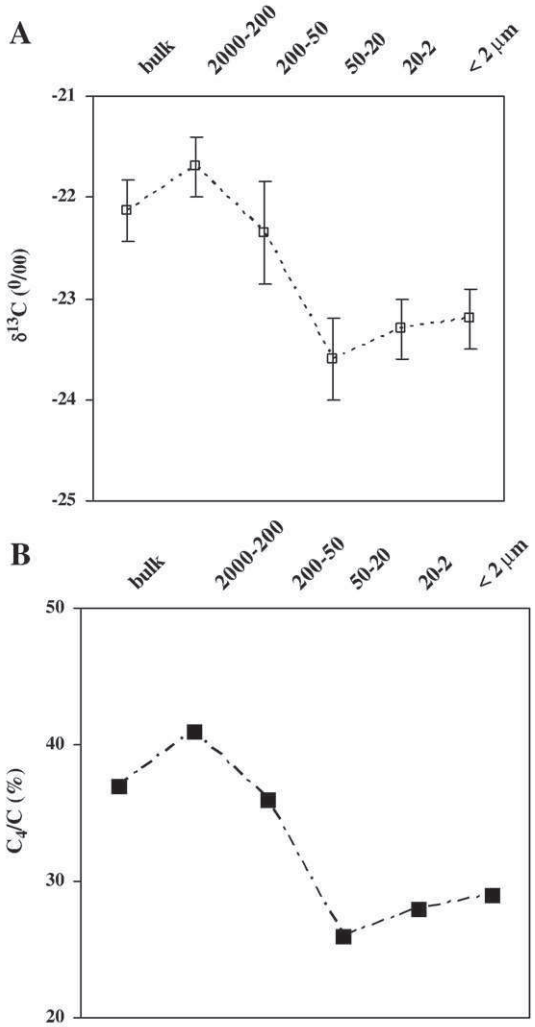


Fig. 4. (a) $\delta^{13}C$ and (b) C_4/C ratios (%) of the topsoil for the different size fractions.

et al., 2006), i.e. in a very different context. Decreased SOM turnover could therefore be considered as a general phenomenon to take into account when studying carbon sinks and organic matter turnover in polluted soils.

Acknowledgement

The authors thank the French National Environment Program (PNSE 2005) for financial support.

References

Alloway, B.J., 1995. Heavy Metals in Soils. Blackie Academic and Professional, Glasgow, Scotland.
Aoyama, M., Nagumo, T., 1997. Comparison of the effects of Cu, Pb, As on plant residue decomposition, microbial biomass and soil respiration. Soil Sci. Plant Nutr. 43, 613–622.
Arshad, M., Silvestre, J., Pinelli, E., Kallerhoff, J., Kaemmerer, M., Shahid, M., Pradere, P., Dumat, C., 2008. A field study of lead phytoextraction by various scented Pelargonium cultivars. Chemosphere 71, 2187–2192.
Asher, L.E., Bar-Yosef, B., 1982. Effects of pyrophosphate, EDTA and DTPA on zinc sorption by montmorillonite. Soil Sci. Soc. Am. J. 46, 271–275.
Baldock, J.A., Oades, J.M., Nelson, P.N., Skene, T.M., Golchin, A., Clarke, P., 1997. Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy, Aust. J. Soil Res. 35, 1061–1083.
Balesdent, J., 1996. The significance of organic separates to carbon dynamics and its modelling in some cultivated soils. Eur. J. Soil Sci. 47, 485–493.
Balesdent, J., Mariotti, A., 1996. Measurement of soil organic matter turnover using ^{13}C natural abundance. In: Boutton, T.W., Yamasaki, S. (Eds.), Mass Spectrometry of Soil. Marcel Dekker, New York, pp. 83–111.
Balesdent, J., Mariotti, A., Guillet, B., 1987. Natural ^{13}C abundance as a tracer for studies of soil organic matter dynamics. Soil Biol. Biochem. 19, 25–30.
Barajas-Aceves, M., Grace, C., Ansorena, J., Dendooven, L., Brookes, P.C., 1999. Soil microbial biomass and organic C in a gradient of zinc concentrations in soils around a mine spoil tip. Soil Biol. Biochem. 31, 867–876.
Bender, M., 1971. Variations in the $^{13}C/^{12}C$ ratios of plants in relation to the pathway of photosynthetic carbon dioxide fixation. Phytochemistry 10, 1239–1244.
Berg, B., Ekbohm, G., Soderstrom, B., Staaf, H., 1991. Reduction in the decomposition rates of Scots Pine needle litter due to heavy-metal pollution. Water Air Soil Pollut. 59, 165–177.
Besnard, E., Chenu, C., Robert, M., 2001. Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. Environ. Pollut. 112, 329–337.
Boucher, U., Lamy, I., Cambier, P., Balabane, M., 2005. Decomposition of leaves of metallophyte *Arabidopsis halleri* in soil microcosms: fate of Zn and Cd from plant residues. Environ. Pollut. 135, 323–332.
Bourennane, H., Dère, C., Lamy, I., Cornu, S., Baize, D., van Oort, F., King, D., 2006. Enhancing spatial estimates of metal pollutants in raw wastewater irrigated fields using a topsoil organic carbon map predicted from aerial photography. Sci. Total Environ. 361, 229–248.
Boutton, T.W., 1996. Stable carbon isotope ratio of soil organic matter and their use as indicators of vegetation and climate change. In: Boutton, T.W., Yamasaki, S. (Eds.), Mass Spectrometry of Soil. Marcel Dekker, New York, pp. 47–82.
Brookes, P.C., 1995. The use of microbial parameters in monitoring soil pollution by heavy metals. Biol. Fertil. Soils 19, 269–279.
Cambaradella, C.A., Elliott, E.T., 1992. Particulate soil organic matter changes across a grassland cultivation sequence. Soil Sci. Soc. Am. J. 56, 777–783.
Cecchi, M., Dumat, C., Alric, A., Felix-Faure, B., Pradère, P., Guiresse, M., 2008. Multi-metal contamination of a calcic cambisol by fallout from a lead-recycling plant. Geoderma 144, 287–298.
Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. Org. Geochem. 21 (6/7), 619–627.
Cotrufo, M.F., De Santo, A.V., Alfani, A., Bartoli, G., De Cristofaro, A., 1995. Effects of urban heavy metal pollution on organic matter decomposition in *Quercus ilex* L. woods. Environ. Pollut. 89, 81–87.
Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12, 133–149.
Dabkowska-Naskret, H., 2003. The role of organic matter in association with zinc in selected arable soils from Kujawy region, Poland. Org. Geochem. 34, 645–649.
Dère, C., Lamy, I., van Oort, F., Baize, D., Cornu, S., 2006. Trace metal inputs reconstitution and migration assessment in a sandy Luvisol after 100 years of massive irrigation with raw wastewaters. C.R. Geosci. 338, 565–573.
Dère, C., Lamy, I., Jaulin, A., Cornu, S., 2007. Long-term fate of exogenous metals in a sandy Luvisol subjected to intensive irrigation with raw wastewater. Environ. Pollut. 145, 31–40.
Doelsch, E., Deroche, B., van de Kerchove, V., 2006. Impact of sewage sludge spreading on heavy metal speciation in tropical soils (Réunion, Indian Ocean). Chemosphere 65, 286–293.
Dormaar, J.F., 1984. Monosaccharides in hydrolysates of water-stable aggregates after 67 years of cropping to spring wheat as determined by capillary gas chromatography. Can. J. Soil Sci. 64, 647–656.
Ducaroir, J., Lamy, I., 1995. Evidence of trace metal association with soil organic matter using particle size fractionation after physical dispersion treatment. Analyst 120, 741–745.
Dumat, C., Cheshire, M.V., Fraser, A., Shand, C., Staunton, S., 1997. The effect of removal of soil organic matter and iron on the adsorption of Cs. Eur. J. Soil Sci. 48, 675–684.
Dumat, C., Chiquet, A., Gooddy, D., Aubry, E., Morin, G., Juillot, F., Benedetti, M., 2001. Metal ion geochemistry in smelter impacted soils and soil solutions. Bull. Soc. Geol. Fr. 172, 539–548.
Dumat, C., Quenea, K., Bermond, A., Toinen, S., Benedetti, M.F., 2006. A study of the trace metal ion influence on the turn-over of soil organic matter in various cultivated contaminated soils. Environ. Pollut. 142, 521–529.
Ferrand, E., Dumat, C., Leclerc-Cessac, E., Benedetti, M., 2006. Phytoavailability of zirconium in relation with its initial speciation and soil characteristics. Plant Soil 287, 313–325.
Gesthem, J.P., Bermond, A., 1998. EDTA extractability of trace metals in polluted soil: a chemical–physical study. Environ. Technol. 19, 409–416.
Guggenberger, G., Zech, W., Haumaier, L., Christensen, B.T., 1995. Land-use effects on the composition of organic matter in particle-size separates of soils. II. CPMAS and solution ^{13}C NMR analysis. Eur. J. Soil Sci. 46, 147–158.
Harter, R.D., Naidu, R., 1995. Role of the metal-organic complexation in metal sorption by soils. Adv. Agron. 55, 219–263.
Hattori, H., 1996. Decomposition of organic matter with previous cadmium adsorption in soils. Soil Sci. Plant Nutr. 42, 745–752.
Impellitteri, C.A., Lu, Y., Saxe, J.K., Allen, H.E., Peijnenburg, W.J.G.M., 2002. Correlation of the partitioning of dissolved organic matter fractions with the desorption of Cd, Cu, Ni, Pb and Zn from 18 Dutch soils. Environ. Int. 28, 401–410.
Jolivet, C., Arrouays, D., Lévèque, J., Andreux, F., Chenu, C., 2003. Organic carbon dynamics in soil particle-size separates of sandy spodosols when forest is cleared for maize cropping. Eur. J. Soil Sci. 54, 257–268.
Lamy, I., van Oort, F., Dère, C., Baize, D., 2006. Use of major- and trace-element correlations to assess metal migration in sandy Luvisols irrigated with wastewater. Eur. J. Soil Sci. 57, 731–740.
Mhatre, G.N., Pankhurst, C.E., 1997. Bioindicators to detect contamination of soils with special reference to heavy metals. In: Pankhurst, C.E., Doube, B.M., Gupta, V.V.

(Eds.), Biological indicators of soil health. CAB International, Wallingford, pp. 349–369.
Miller, W.P., Martens, W.C., Zelazny, L.W., 1986. Effect of sequence in extraction of trace metals from soils. Soil Sci. Soc. Am. J. 50, 598–601.
O'Leary, M., 1981. Carbon isotope fractionation in plants. Phytochemistry 20 (4), 553–567.
Orlov, D.S., Min'Ko, O.I., Demin, V.V., Sal'Nikov, V.G., Izmaylova, N.B., 1988. Nature and mechanisms of formation of metal–humus complexes. Sov. Soil Sci. 21, 32–41.
Parat, C., Denaix, L., Lévêque, J., Chaussod, R., Andreux, F., 2007. The organic carbon derived from sewage sludge as a key parameter determining the fate of trace metals. Chemosphere 69–4, 636–643.
Sauvé, S., Martinez, C.E., McBride, M., Hendershot, W., 2000. Adsorption of free lead by pedogenic oxides, ferrihydrite and leaf compost. Soil Sci. Soc. Am. J. 64, 595–599.
Schwartz, D., de Foresta, H., Mariotti, A., Balesdent, J., Massimba, J.P., Girardin, C., 1996. Present dynamics of the savanna–forest boundary in the Congolese Mayombe: a pedological, botanical and isotopic (^{13}C and ^{14}C) study. Oecologia 106, 516–524.
Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.
Vaca-Paulín, R., Esteller-Alberich, M.V., Lugo-de, la Fuente, J., Zavaleta-Mancera, H.A., 2006. Effect of sewage sludge or compost on the sorption and distribution of copper and cadmium in soil. Waste Manage. 26, 71–81.
Valsecchi, G., Gigliotti, C., Farini, A., 1995. Microbial biomass, activity and organic matter accumulation in soils contaminated with heavy metals. Biol. Fertil. Soils 20, 253–259.
Vieiriae, J.M., Domingues, H., Mesquita, M.E., 1993. Sequential extraction of copper and zinc from sewage sludges. Use of organic solvents. Int. J. Environ. Anal. Chem. 51, 109–112.
Wong, J.W.C., Li, K.L., Zhou, L.X., Selvam, A., 2007. The sorption of Cd and Zn by different soils in the presence of dissolved organic matter from sludge. Geoderma 137, 310–317.
Woomer, P.L., Martin, A., Albrecht, A., Resck, D.V.S., Scharpenseel, H.W., 1994. The importance and management of soil organic matter in the tropics. In: Woomer, P.L., Swift, M.J. (Eds.), The Biological Management of Tropical Soil Fertility. John Wiley, Chichester, pp. 47–80.
Yin, Y., Impellitteri, C.A., You, S.J., Allen, H.E., 2002. The importance of organic matter distribution and exact soil: solution ratio on the desorption of heavy metals from soils. Sci. Total Environ. 287, 107–119.