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Sorption and distribution of Zn in a sludge-amended soil: influence of the soil clay mineralogy

Dominique Proust

D.Proust

LIENSs UMR 7266 CNRS-Université de La Rochelle, 2 rue Olympe de Gouges, 17000 La Rochelle, France

e-mail: dominique.proust@univ-lr.fr

Phone: +33 5 46507626

Abstract

Purpose Conventional pedological survey generally assesses soil metal pollution by comparing total metal concentrations in soil to geochemical baselines in parent rock. This global approach overlooks the sorption capacities of the clay minerals which form at micrometric scale in weathering microsystems and are essential for the behaviour of metals in soil. Therefore, our aim was to investigate the impact of these weathering microsystems and their clay mineralogy upon Zn sorption and distribution throughout a sludge-contaminated soil.

Materials and methods Two soil profiles with the same diorite parent-rock were sampled: (i) an amended soil profile (AS) that received for ten years wet sewage sludges heavily loaded with Zn and (ii) a control soil profile (CS) free of sludge spreading. Soil samples were

carefully collected as undisturbed blocks using plastic core samplers to prevent sample metal contamination. Each sample was further divided into two subsamples: the first was devoted to bulk chemical analyses, mineral grains separation and X-ray diffraction (XRD) analyses, whereas the second part was used for thin sections preparation and electron probe microanalyses (EPMA).

Results and discussion Zn in the control soil is inherited from the weathering parent-rock and its concentration is always lower than in the amended soil where Zn is supplied at the surface by sludge. Each rock-forming mineral weathers into specific clay minerals: amphibole into saponite and montmorillonite and plagioclase into montmorillonite and kaolinite. Each clay mineral, with its specific sorption capacity, controls the Zn distribution within the soil: the smectites produced by the amphiboles have high sorption capacity and favor Zn retention in the upper horizons of the soil; the kaolinites produced by the plagioclases have lower sorption capacity, do not retain Zn in the surface horizons, and allow it to migrate to deeper horizons where it is sorbed onto the montmorillonites.

Conclusions The clay minerals appear to be important soil components controlling the mobility of Zn in the contaminated soils. The micrometric mineralogical approach proves to be relevant to describe the importance of the clay mineral species in the Zn fixation at the solid/solution interface. When applied to a wider range of heavy metals and clay minerals, it could be a useful improvement in the surface complexation modeling used to explain metal cation sorption in soils.

Keywords: Heavy metal, Zinc, Soil, Weathering, Clay minerals

1 Introduction

The heavy metals contaminants in the soils originate from two sources: (i) the weathering of the parent-rock which produces the natural geochemical background (Klassen 1998; Baize and Sterckeman 2001; Sterckeman et al. 2006) and (ii) the anthropogenic contamination by repeated sludge spreading (Walter and Cuevas 1999; Mbila et al. 2001) and/or atmospheric deposition (Steinnes et al. 1997; Hernandez et al. 2003). The ability of soils to adsorb and retain the heavy metal ions is mainly provided by the sorption process at the soil solid/solution interface. Since clay minerals are the essential reactive solid components in soils, their sorptive capacities for the heavy metals are of particular relevance for sludge-spreading on soils and have received considerable attention in the last decades (Kraepiel et al. 1999; Srivastava et al. 2005; Zhu et al. 2011).

Basically, heavy metals adsorption onto the clay minerals occurs at particular sites with permanent- and variable-charges (Farrah et al. 1980; Wahba and Zaghloul 2007). The permanent-charge sites are located at the interlayer basal surfaces of the clay minerals and result from the isomorphic substitutions of Al^{3+} for Si^{4+} in the silica tetrahedral sheet and $\text{Fe}^{2+}/\text{Mg}^{2+}$ for Al^{3+} in the alumina octahedral sheet. These interlayer negative charges are neutralized by pH-independent adsorption of cations as outer-sphere complexes (cation exchange reactions). The variable-charge sites are located at the crystal edge surfaces and originate in the protonation or deprotonation of surface hydroxyl (SOH) groups. These sites promote pH-dependent adsorption attributed to surface complexation reactions with silanol and aluminol groups to form inner-sphere complexes.

The origin of the clay minerals in the soils lies in the weathering reactions which affect the parent-rock and operate in two simultaneous processes: the dissolution of the primary rock-forming minerals with the release of cations and heavy metals, and the crystallization of newly-formed clay minerals and hydrous oxides which are specific to the primary mineral being weathered. Mineralogical studies have shown that the chemical weathering reactions

and their associated metals release were active in specific soil microsystems with their own solid and solution chemical properties (Wilson 2004; Caillaud et al. 2006; Proust et al. 2006). Such microsystems are typically composite aggregates of weathering rock-forming minerals, newly-formed clay minerals, oxihydroxides, and organic matter moistened with soil solutions.

Thus, the clay fraction of a saprolite or a soil is a mixture of multiple clay minerals, among which kaolinite and montmorillonite are the dominant species with specific sorptive capacities (Wilson 1999, 2004). Kaolinite is the least reactive clay mineral with a very low permanent negative charge inducing low cation exchange capacity (C.E.C.) of 16 to 34 cmol kg⁻¹ (Ferris and Jepson 1975; Ma and Eggleton 1999). Therefore, most sorption activity of kaolinite occurs at the crystal edges where amphoteric variable-charge sites are highly pH-dependent: for example, Cd(II) adsorption increases from 1.60 to 6.10 mg g⁻¹ when pH increases from 2 to 9 (Gupta and Bhattacharyya 2006). On the opposite, montmorillonite is the most reactive clay with substantial isomorphic substitutions creating high permanent negative charges and high C.E.C. of 90 to 127 cmol kg⁻¹ (Ayari et al. 2005; Srodon and McCarty 2008). In addition to cation exchange, Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol and aluminol groups creating highly reactive sites with potential pH-dependent uptake of metals ions onto montmorillonite: for example, Cd(II) adsorption increases from 19.10 to 23.20 mg g⁻¹ when pH increases from 2 to 9 (Gupta and Bhattacharyya 2006).

Montmorillonite appears in the early stages of weathering at the bottom of soils and saprolites under conditions of poor drainage, in base-rich material with high pH and high silica activity. On the contrary, kaolinite crystallizes in the uppermost horizons of soils and saprolites under acid conditions with moderate silica activity and small amount of base cations. Kaolinite can also form from a smectite precursor through intermediate mixed-layered kaolinite/smectite clay minerals (Proust et al. 2006; Vingiani et al. 2004).

In such a pedological context, the chemical reactions of weathering will thus control the solubility, the mobility and, as a consequence, the concentration of heavy metals in soils. Even though heavy metals bulk concentrations could be indicators of global soil contamination, they result from the partial heavy metals concentrations in each of the weathering microsystems. In that meaning, the detailed analysis of contaminated soils with heavy metals requires to know the bulk metals content in the soil but also their partial contents in the soil microsystems in which they are retained. The present study was undertaken to estimate the impact of long-term sludge application upon Zn distribution and migration in soil. In the bulk soil study, Zn concentrations are compared in amended and control soils to characterize the extent to which spreaded metal may have moved throughout the soil profile. In the micrometric study, Zn concentrations are measured in the weathering microsystems to detect possible zones of metal accumulation within the soil and the weathered parent-rock.

2 Material and methods

2.1 Soil characteristics

The soil samples were collected from a site located 25 km south of Limoges (Haute-Vienne, France) where sewage sludges were deposited. Two soil profiles developed on the same diorite parent-rock were sampled: (i) a soil profile free of sludge-spreading that was considered as the control soil (CS) and (ii) a soil profile that received wet sewage sludges loaded heavily with Zn (498 mg kg⁻¹ mean concentration) for ten years and was taken as the amended soil (AS). The two soil profiles display the same A, Bw, C horizons sequence which is typical of deep inceptisols (100-150 cm depth to C horizon). The coherent unweathered

parent-rock, i.e., the R horizon is a diorite which appears to the naked eye as a “salt and pepper” coarse-grained rock made up of major amphiboles, plagioclases, and minor quartz. The two soils have very similar physicochemical properties (Table 1) with slightly acidic to almost neutral pH in all horizons (6.1-6.8). The pH values increase with depth, suggesting some leaching of base cations or probably the effect of organic matter with 1.82 to 1.95 % organic carbon content in the A horizons, decreasing to 0.85-0.63 % in the Bw horizon and disappearing in the C horizon. The cation exchange capacities of the two soils are similar with medium values ranging between 26.8 and 31.9 cmol kg⁻¹, whereas the clay contents, typical of the clay loam texture observed in the inceptisols, increase slightly in the Bw horizon (cambic horizon).

Insert Table 1

Each soil was carefully sampled using plastic cylindrical corers to prevent the soil metal contamination. The cylinder, 10 cm long with a diameter of 10 cm, had cutting edges. It was smoothly and continuously pushed into the soil to collect undisturbed blocks which retained the original soil structure. Each core was divided into two subsamples. The first was disaggregated by gentle shaking in water, sieved to 2mm, air dried and reserved for the mineral grains separation, the bulk chemical and the X-ray diffraction (XRD) analyses; the second subsample was preserved undisturbed for thin sections preparation, electron probe microanalyses (EPMA) and scanning electron microscope (SEM) study.

2.2 Mineral grains separation

The first subsample was disaggregated in water, air dried and sieved at 2mm prior to physical and chemical analyses. Organic matter was destroyed using 33% hydrogen peroxide. Two

hundred grams of this subsample were gently shaken in water, sieved into the sandy fractions 50-100 μm , 100-150 μm , 150-250 μm and 250-500 μm , and dried at 50° C for 24 h. The observation of each sieved-part under optical microscopy (OM) indicated that most euhedral monomineralic grains with preserved faces were found in the 250-500 μm granulometric fraction. The smaller sized fractions were essentially made up of broken minerals fragments. About 500 monomineralic grains, 250 to 500 μm in size, of amphiboles and plagioclases (the two most important minerals in the parent-rock and soils) were then needle-sorted under the stereomicroscope for the study of their weathering products. Separation efficiency was checked by XRD.

2.3 Bulk chemical and XRD analyses

Five grams of the < 2mm first subsample, freed of its organic matter, were obtained by quartering with a riffle splitter and crushed into agate mortar down to less than 50 μm size. 300 mg of the total powder were fused with LiBO_2 at 1050°C and dissolved in 1 N HNO_3 for bulk chemical analyses. The major and trace elements were analyzed using ICP-AES and ICP-MS at the Service d'Analyse des Roches et des Minéraux (SARM), CRPG-CNRS (Vendoeuvre-les-Nancy, France). The major and trace elements concentrations were expressed in wt% and mg kg^{-1} , respectively.

The bulk clay fraction (less than 2 μm fraction) was extracted from 10 g of < 2 mm first subsample dispersed in 350 ml deionized water, sonicated for 2 min at 300 W/20 kHz, then shaken mechanically for 3 h. The stable suspension was then centrifugated at 20°C and 1000 rpm for 2 mn 30 s with a Jouan JR4.22 centrifuge in order to separate the < 2 μm fraction. The effectiveness of this clay separation was then checked using a laser diffraction granulometer IP Malvern Mastersizer. The bulk clay fractions, together with the clay minerals

extracted from the weathered monomineralic grains by sonification, were analyzed by XRD on Ca-saturated oriented preparations, air dried and glycolated. The diffractometer was a PHILIPS PW 1730 (40 kV, 40 mA) with a Fe-filtered CoK α radiation and a stepping motor driven with a DACO-MP recorder and the Diffrac-AT software (Socabim, Munich, Germany).

2.4 Microanalysis of the weathering microsystems

For each dominant primary rock forming mineral, i.e. amphibole and plagioclase, ten grains were selected from the 250-500 μm needle-sorted fraction and affixed to glass plates with double-sided adhesive tape. The two glass plates were then carbon-coated for SEM study.

The second undisturbed subsample was used for thin sections preparation following the procedure of Camiti and McGuire (1999). The samples were first hardened with ARALDITE 2020 epoxy resin and 20% acetone thinner, using a BROT impregnation unit at 100 mbars vacuum. Samples were cut after polymerization, and thin sections were obtained through polishing with silicon carbide (17 μm and 9 μm particle sizes) and diamond powders (6 μm , 3 μm , 1 μm , and 0.25 μm particle sizes).

The specific weathering microsystems of amphiboles and plagioclases were first located on the thin sections, marked with black circle under an optical microscope, and “in situ” analyzed for major and trace elements using a CAMECA SX50 electron microprobe with wavelength-dispersive spectrometers (WDS) at the Centre de Microanalyse CAMPARIS, Université Pierre et Marie Curie, Paris. The microprobe was calibrated using synthetic and natural oxides and each element analysis was corrected for atomic number (Z), absorption (A), and fluorescence (F) with a ZAF matrix correction. The heavy metal content in each recognized weathering microsystem was obtained with a specific trace element program for

the electron microprobe (Fialin et al. 1999); this program allows heavy metal quantification in $1\text{ }\mu\text{m}^3$ volume with a low 6 mg kg^{-1} concentration limit using $K\alpha$ line for Zn detection in a silicate matrix. Analytical conditions were 30 kV accelerating voltage, beam current of 100 nA and 500 nA for small and large minerals, respectively, and 1,000 s counting time per trace element. Major elements were also analyzed but at a lower voltage of 15 kV, a beam current of 4 nA, and a counting time of 10 s per major element. The electron probe microanalyses (EPMA) of major and trace element concentrations are expressed in wt% and mg kg^{-1} , respectively.

2.5 Geochemical mass balances

The geochemical mass balances were obtained from the calculation of enrichment factors (EF) using the method of Hernandez et al. (2003) and Sterckeman et al. (2006) with the equation:

$$EF = (X/R)_{\text{altered}} / (X/R)_{\text{reference}} \quad 1$$

where the content of element X is normalized to the content of the reference element R. A value of 1 for EF indicates no element enrichment or depletion. EF values < 1 indicate element depletion and are referred to as depletion factors in the text. The aluminium, with its narrow range of variation in soils (17.53% to 20.08% in Table 2) was chosen as the reference element. The CS8 sample with the lowest loss on ignition suffered very low weathering and was selected as the reference rock for major elements and Zn bulk analyses.

Insert Table 2

3 Results

3.1 Parent-rock mineralogy

The parent-rock mineralogy was studied from the CS8 sample of the R horizon, at 485 cm depth. This sample is the unweathered coherent diorite with high apparent density (2.92 g cm^{-3}) and the lowest loss on ignition (3.77% in Table 2). The modal composition obtained from 3,000 points counting on thin section gives a mineralogical composition with major amphiboles (38%), plagioclases (32%), orthoclase (12%) and minor quartz (8%), albite (7%), and titanomagnetite (3%). The EPMA of the major elements in the rock-forming minerals show that the amphiboles are calcic hornblende whereas plagioclases are andesine with 48% anorthite content. The EPMA of the Zn contents (Table 3) show that the amphiboles are the major Zn-bearing minerals with high Zn concentrations of 180 mg kg^{-1} versus lower Zn contents in the plagioclases (17 mg kg^{-1}), orthoclase (20 mg kg^{-1}), and albite (14 mg kg^{-1}).

Insert Table 3

3.2 Geochemical mass balances

The values of EF calculated using equation 1 for the major elements are plotted versus depth in Figure 1. The chemical evolution from rock to saprolite and soil appears similar in the control and amended soils. The first chemical change observed is the general increase in EF calculated for the loss on ignition (EF-L.O.I.) from the bottom to the top of the two soil profiles (Fig. 1a). EF-L.O.I. increases more than twice from the bottom (sample reference CS8) to the top of soils (EF-L.O.I. reaches 2.41 in the sample AS2 at the top of the amended soil). This trend reflects the general increase in bulk water content (loss on ignition at 1050°C ,

i.e., hydrate content in the absence of CO_2 found in carbonates and after organic matter destruction) in relation to the formation of hydrated clay minerals and oxihydroxides in saprolite and soil. EF- SiO_2 and EF- Fe_2O_3 show the same trends with values close to 1 indicative of their stability throughout the soil profiles (0.91-1.12 for EF- SiO_2 and 0.93-1.08 for EF- Fe_2O_3 in Fig. 1b). On the contrary, the EFs calculated for the alkaline earth elements, EF-MgO and EF-CaO, show a regular decrease from bottom to top (Fig. 1c). EF-MgO and EF-CaO reach, respectively, 0.69 and 0.34 in the sample AS2 at the top of the amended soil. This regular and general decrease in the two soils is indicative of the weathering processes which affect the amphiboles (EF-MgO) and the plagioclases (EF-CaO) in the saprolite and soil.

Insert Figure 1

The enrichment factors calculated for Zn (EF-Zn) are plotted versus depth in Figure 2 to show its vertical distribution throughout the control soil (CS) and the amended soil (AS). Although the sewage sludges spread on the amended soil were rich in Zn (498 mg kg^{-1} as mean concentration), its concentration in the two soils (Table 2) never exceeds the threshold value for Zn anthropogenic contamination (300 mg kg^{-1} , Baize 1997).

The bulk Zn concentrations show large variation in the two soils from 68.27 to 126.08 mg kg^{-1} which results into calculated EF-Zn ranging from 0.62 at the top of the amended soil to 1.15 at the bottom of the control soil. Thus, distributions of EFs versus depth in Figure 2 indicate pronounced Zn depletion in the surface horizons of the amended soil that may suggest migration of this metal to depth (190 cm, sample AS7), as already observed by Scokart et al. 1983. The Zn variations in the control soil are not significant.

Insert Figure 2

3.3 Soil clay mineralogy and chemistry

The clay mineralogy of the $< 2 \mu\text{m}$ granulometric fractions is similar in the control and amended soils. The XRD patterns of the Ca-oriented preparations exhibit smectite reflections at $15.10 \text{ \AA}$ shifting to $17.05 \text{ \AA}$ after ethylene-glycol solvation. This smectite is associated with the kaolinite identified by its reflections at $7.15 \text{ \AA}$ and $3.55 \text{ \AA}$ that disappear after 450°C heating. No iron oxide or hydroxide was detected on the XRD patterns of the random powders.

The EPMA of Zn in the clay fractions from the two soils are given with their mean standard errors in Table 4. The EPMA and the vertical Zn distribution profiles in the two soils (Fig. 3a) show that its concentration in the bulk clay fractions of the amended soil ranges from 144 to 203 mg kg^{-1} , and is always higher than in the control soil where it ranges from 10 to 24 mg kg^{-1} . The shape of the Zn distribution profile in the amended soil (Fig. 3a) is typically that of a downward migrating element with a regular decrease from the top to the bottom of the soil. The highest Zn concentrations are detected in the surface horizons, from 195 to 203 mg kg^{-1} at 20 cm (AS1) and 40 cm (AS2) depths, decreasing to 150 mg kg^{-1} at the bottom of the soil (190 cm (AS7) depth). For comparison, the Zn distribution profile in the control soil does not show significant variations when mean standard errors are considered. The Zn concentrations are much lower than those measured in the amended soil, and range from 10 to 24 mg kg^{-1} at 20 cm (CS1) and 40 cm (CS2) depths, and from 14 to 15 mg kg^{-1} at 180 cm (CS6) and 485 cm (CS8) depths.

Insert Table 4

Insert Figure 3

3.4 Zn behavior in amphibole weathering microsystems

3.4.1 Amphibole weathering microsystems

The early amphibole weathering microsites appear in the C horizons of the two soils. The OM study of the thin sections shows amphibole prismatic crystals, 250-500 μm size range and cross-cut by intramineral microcracks, 10-20 μm wide (Fig. 4a). The SEM study reveals that these intramineral cracks are crystallization sites for newly-formed clay minerals, produced by weathering (Fig. 4b). These clay minerals have a typical honeycomb texture in the crack plane which is commonly observed in weathered rocks and soils (Arslan et al. 2010; Karakaya et al. 2011).

The increasing weathering of the amphiboles in the Bw horizons results in the fragmentation of the amphibole crystals into 20-100 μm pieces (OM study, Fig. 4c). This fragmentation is produced by the opening of the intramineral microcracks, up to 50 μm wide. The SEM observation of amphibole grains shows the honeycomb morphology of smectite clay minerals which cover the saw-tooth terminations of the dissolving amphibole crystals (Fig. 4d).

The most advanced weathering stages of amphiboles is observed in the surface A horizons. The OM study indicates that amphiboles crystals are highly fragmented and almost completely replaced by a clayey weathering plasma (Fig. 4e). The SEM study provides more details on the amphibole pseudomorphism with the identification honeycomb smectites already observed in the C and bw horizons of the two soil (Fig. 4 f).

The XRD patterns of the clay minerals extracted from the amphiboles grains by sonification exhibit the same typical reflections of smectite in the C, Bw, and A horizons of the two soils. The Ca-oriented preparations show strong reflections ranging from 14.50 Å to 15.49 Å. The Ca-ethylene-glycol solvation produces a shift of the reflections to 16.87-17.14 Å with higher orders at 8.46 Å and 3.40 Å which is typical of expanded smectite layers.

The EPMA of the major elements in the amphibole weathering products characterize two chemically distinct smectite populations. The first is detected in the C horizons of soils and is made up of magnesian smectites belonging to the trioctahedral group of saponites. The second population is found in more advanced weathering stages (Bw and A horizons) as aluminous smectites belonging to the dioctahedral smectite group of montmorillonites.

Insert Figure 4

3.4.2 Zn behaviour during amphibole weathering

The EPMA of Zn in the weathering clay minerals of amphiboles are given in Table 5 and plotted versus depth in Figure 3b. The early amphibole weathering into saponites leads to the leaching of Zn from 180 mg kg⁻¹ in the unweathered amphibole (Table 3) to 76-85 mg kg⁻¹ in the R horizons (CS8 and CS7). More intense weathering stages in the C, Bw, and A horizons result in very different Zn distribution as the control soil or the amended soil is considered. When taking into account the mean standard errors, the Zn concentrations in the control soil appear almost constant in the saponites and montmorillonites throughout the profile (Fig. 3b). More complicated is the Zn behavior in the amended soil. In the first place, Zn concentrations are very similar in the C horizons of the amended and control soil profiles where amphibole weathers into saponite (72 to 82 mg kg⁻¹ in AS7, AS6, AS5 versus 72 to 81 mg kg⁻¹ in CS6

and CS5). In the second place, Zn concentrations in the Bw and A horizons of the amended soil differ strongly from that in the control soil. The concentrations in the amended soil increase in the horizons where amphibole weathers into montmorillonite, from 105 mg kg⁻¹ at 110 cm depth (AS4) to 220 mg kg⁻¹ at 20 cm depth (AS1).

Insert Table 5

3.5 Zn behaviour in plagioclase weathering microsystems

3.5.1 Plagioclase weathering microsystems

The first plagioclase weathering microsystems are found in the C horizons of the two soils. The OM study reveals etch pits in the heart of the plagioclase crystals which are filled by newly-formed clay minerals (Fig. 5a). The SEM study gives more details about these clay minerals which display a typical honeycomb habit previously observed for the smectites in the amphiboles (Fig. 5b).

The plagioclases observed under OM in the Bw horizons show more advanced weathering stage. The plagioclase crystals are fragmented into small pieces, 200 µm as largest size, with enlarged dissolution pits filled with clay minerals (Fig. 5 c). The SEM study reveals that these clay minerals have a spheroidal habit (Fig. 5d) very different from the honeycombs observed in the first plagioclase weathering stage.

The most advanced weathering stage of plagioclases is observed in the A horizons where plagioclase crystals are almost totally replaced by a light-grey clayey weathering plasma (Fig. 5e). The SEM reveals that these clay minerals have an exfoliated "booklet-type" morphology

(Fig. 5f) which is commonly observed for kaolinite crystallizations in altered rocks (Jeong 2000; Papoulis et al. 2004).

The XRD patterns of the clay minerals extracted from the plagioclase grains differ according to their location in the two soil profiles. The clay minerals in the C horizon of the two soils are similar and made up of a smectite with a 15.56 Å reflection in Ca-oriented state, shifting to 17.06 Å in Ca-ethylene-glycol-solvated state, with second order reflection at 8.48 Å. The XRD patterns of the clay minerals with spheroidal habit in the Bw horizons are more complex, but similar in the two soils. At the bottom of the Bw horizons (140-130 cm depth) they characterize a random kaolinite/smectite (K/S) mixed layer with 65% smectite component. This clay mineral is typified by its reflections at 15.03 Å, 7.36 Å, and 3.55 Å in Ca-oriented state shifting to the 17.14 Å-8.28 Å-and 3.42 after Ca-ethylene-glycol solvation. This K/S is replaced at the top of the Bw horizons (70-65 cm depth) by a second random K/S with only 5% smectite component. This K/S differs from the first one by its very low expansion at 7.36 Å (17.14 Å for the first K/S) after Ca-ethylene-glycol solvation. The XRD patterns of the clay minerals with the exfoliated "booklet-type" observed in the A horizons characterize a kaolinite clay mineral with a typical 7.17 Å-4.44 Å-3.57 Å reflection group in Ca-air-dried state, unchanged in the Ca-ethylene-glycol-solvated state.

The EPMA of the major elements in the plagioclase weathering products are in good agreement with the XRD results. The chemical analyses characterize two weathering sequences producing different clay minerals. The first sequence appears in the parent-rock and the C horizons of soils with the early plagioclase into aluminous smectites of the montmorillonite group. The second sequence occurs in the Bw and A horizons where montmorillonite weathers first into K/S (Bw horizons) and finally into kaolinite (A horizons).

Insert Figure 5

3.5.2 Zn behaviour during plagioclase weathering

The EPMA of Zn in the weathering clay minerals of plagioclases are given in Table 5 and plotted versus depth in Figure 3c. The early plagioclase weathering into montmorillonites leads to a general enrichment in Zn from 17 mg kg^{-1} in the unweathered plagioclase (Table 3) to $77\text{-}66 \text{ mg kg}^{-1}$ in the R horizons CS8 and CS7. The Zn distribution in the C, Bw, and A horizons show similar trends in the control and amended soils. The Zn concentrations in the control soil decrease regularly from 42 mg kg^{-1} at 180 cm depth to 27 mg kg^{-1} at the soil surface (20 cm depth). A similar evolution is observed in the amended soil, but concentrations in the deepest levels are higher: 67 mg kg^{-1} at 190 cm and 64 mg kg^{-1} at 170 cm depths (Fig. 3c). In both soils, the decrease in Zn concentrations from bottom to top follow the decrease in smectite contents observed in the clay minerals: 100% smectite in the C horizons (montmorillonites), followed by 65% and 5% smectite in the K/S from the Bw horizons and 0% smectite in the kaolinite from the A horizons.

4 Discussion and conclusions

First of all, two significant observations must be discussed at the scale of the soil profiles. The first observation is that the control and the amended soils have the same diorite parent-rock with similar physiochemical properties in their C, Bw and A horizons (Table 1). These data were not modified by the sludge spreading. Most important are the pH values which can affect the variable-charge sites in the clay minerals through protonation or deprotonation of the hydroxyl (SOH) groups. The higher the pH, the higher the adsorption of the heavy metals at the clay-water interfaces (Coles and Yong, 2002; Eloussaief and Benzina, 2010; Farrah and Pickering, 1977; Veli and Alyüz, 2007) and the lower their mobility (Kirkham, 2006). The pH values measured in the amended soil are even closer to neutrality (6.5-6.8) than in the control soil (6.1-6.5), and thus will favor adsorption of the heavy metals at the clay surfaces. The second observation is that the geochemical mass balances display the same EF distribution in

the two soil profiles (Fig. 1). This distribution of the major elements is typical of similar weathering and pedogenetic processes with increasing LOI content (crystallization of newly-formed clay minerals), alkaline earth leaching (weathering of primary rock-forming minerals) and stability of SiO_2 and Fe_2O_3 . This latter observation indicates that SiO_2 and Fe_2O_3 , initially released by the weathering of rock-forming minerals, are precipitated in the newly-formed clay minerals and do not leave the soil profiles.

These two significant observations show that the two soils were formed from the same parent-rock and have suffered similar weathering and pedogenetic processes which lead to the same horizons development and the same weathering clay mineralogy (smectites, K/S, kaolinite). These converging data validate the choice of these two soils to follow the behaviour of the Zn when applied to the amended soil by long-term sludge spreading.

The Zn concentrations in the bulk soil samples (Table 2) are always below the baseline value of 300 mg kg^{-1} , that is taken as the higher limit for non-polluted soil in the French regulation. Thus, repeated sludge spreadings on the area did not induce Zn pollution. The distribution of the EF-Zn versus depth in the amended soil (Fig. 2) shows a pronounced Zn depletion from the surfaces horizons which weakens downward and indicates Zn migration down to 190 cm depth.

These data, however, were collected at the scale of the soil sample, but a thorough study of the soil components indicate that local Zn concentrations may occur in specific soil particle-size fractions, such as $< 2\mu\text{m}$ clay fraction and weathering microsites at the scale of the rock-forming minerals. The Zn concentrations in the bulk clay fractions of the amended soil (Table 4) reveal clearly the anthropogenic contamination of the clay minerals in the surface horizons (20 to 40 cm depth) when compared to the control soil. This surface contamination is associated with the downward Zn migration down to 190 cm depth (Fig. 3a). These bulk clay fractions, however, are the collection of the clay minerals which formed during the

weathering of the rock-forming minerals. Thus, the study of Zn behaviour in the two soils will be greatly improved by considering the clay minerals in their crystallization sites, i. e., the weathering microsites.

The Zn concentration profiles obtained from the amphiboles weathering microsites (Fig. 3b) reveal a general anthropogenic contamination of the amended surface horizons with Zn. This contamination can be related to the crystallization of large amount of montmorillonite as weathering product of amphibole. This montmorillonite, with high sorption capacity of 90 to 127 cmol kg⁻¹ (Ayari et al. 2005; Srodon and McCarty 2008) may fix a part of Zn provided by the sludges in the surface horizons. This surface accumulation is followed by a regular Zn decrease in the deeper horizons of the amended soil, in relation with the decrease in amphibole weathering intensity and, accordingly, a decrease in smectite content and sorption capacity with depth.

Conversely, the Zn concentration profiles obtained from the plagioclases weathering microsites (Fig. 3c) show a Zn depletion of the clay minerals in the amended surface horizons and a Zn enrichment deeper in the amended soil. This particular behaviour appears to be controlled by the clay mineral weathering sequence of plagioclases. Kaolinite with low sorption capacity of 16 to 34 cmol kg⁻¹ (Ferris and Jepson 1975; Ma and Eggleton 1999) crystallizes at the top of the amended soil and does not retain Zn. Thus, Zn can migrate downwards to more smectitic assemblages (K/S) and finally to montmorillonite where it is retained at 190 cm depth.

All data presented in this article demonstrate clearly that the behavior of Zn in the soils is highly controlled by the clay minerals and their specific sorption capacities. As described in this paper, soils are complex assemblages of clay minerals which formed in weathering microsystems. Therefore, there is a need for accurate studies at the scale of these weathering microsystems to identify each clay mineral species and to estimate the sorption capacity of the

weathering microsite as regards heavy metals. This micrometric mineralogical approach could be relevant to describe the location and the behaviour of heavy metals in contaminated soils and improve the modeling of the heavy metals surface complexation in soils (Hizal and Apak 2006).

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Table 1 Physicochemical properties of the control (CS) and amended (AS) soils

Soil	pH water		Organic C, %		C.E.C. ^a		Clay, %		Zn ^b	
	CS	AS	CS	AS	CS	AS	CS	AS	CS	AS
A	6.1	6.5	1.95	1.82	31.90	26.90	27.90	29.70	116	82
Bw	6.4	6.8	0.63	0.85	30.80	27.90	28.70	31.80	126	93
C	6.5	6.8	-	-	27.50	26.80	25.20	24.20	124	90

^a Cation Exchange capacity (C.E.C.) expressed in cmol kg⁻¹^b Zn concentrations expressed in mg kg⁻¹**Table 2** Chemical analyses of major elements (wt%) and Zn (mg kg⁻¹) in control soil (CS) and amended soil (AS) samples

Sample	CS8	CS7	CS6	CS5	CS4	CS3	CS2	CS1	AS7	AS6	AS5	AS4	AS3	AS2	AS1
Depth (cm)	485	450	180	160	130	65	40	20	450	180	160	110	65	40	20
SiO ₂	48.79	49.00	47.99	47.53	47.15	49.12	47.48	46.07	51.2	50.21	51.27	52.34	50.83	51.23	50.95
TiO ₂	1.08	1.32	1.14	1.32	1.33	1.30	1.22	1.37	1.28	1.24	1.27	1.31	1.42	1.48	1.51
Al ₂ O ₃	18.78	18.25	19.10	19.37	19.22	19.84	20.08	18.98	18.76	18.47	18.41	17.93	18.67	17.53	18.74
Fe ₂ O ₃ ^a	9.58	10.04	10.03	10.08	10.29	9.41	10.13	9.75	8.87	9.53	8.99	9.47	9.26	9.65	9.13
MnO	0.17	0.21	0.18	0.19	0.21	0.20	0.17	0.16	0.14	0.15	0.15	0.12	0.11	0.12	0.11
MgO	4.47	4.55	4.20	4.06	3.89	3.88	4.09	3.52	3.25	3.44	3.19	3.29	3.36	3.36	3.08
CaO	7.52	6.97	6.97	7.05	6.69	6.19	4.15	6.26	5.7	5.83	5.24	2.11	3.55	2.41	4.26
Na ₂ O	3.54	3.29	3.36	3.13	2.94	3.25	3.88	2.82	3.19	3.08	3.19	3.5	2.96	3.18	3.25
K ₂ O	1.44	1.40	1.50	1.19	1.37	1.27	1.51	1.47	1.54	1.35	1.69	1.68	1.66	1.64	1.63
P ₂ O ₅	0.59	0.70	0.60	0.66	0.70	0.67	0.47	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LOI ^b	3.77	3.94	4.68	5.21	5.04	4.62	6.50	8.53	5.91	6.48	6.19	7.77	7.74	8.49	6.72
Total	99.73	99.67	99.75	99.80	98.85	99.73	99.62	99.50	99.84	99.78	99.59	99.52	99.56	99.09	99.38
Zn	111.18	124.46	113.06	119.32	126.08	120.42	108.24	115.56	115.36	103.04	80.64	72.15	79.64	68.27	69.29

^a Total iron expressed as Fe₂O₃^b LOI: Loss on ignition**Table 3** Mean EPMA of Zn (*n* analyses, mg kg⁻¹) in the rock-forming minerals

	Amphibole		Plagioclase		Orthoclase		Albite	
	<i>n</i> =14 ^a	SE ^b	<i>n</i> =10	SE	<i>n</i> =10	SE	<i>n</i> =10	SE
Zn	180	4	17	2	20	2	17	6

^a Each analysis is already the mean of ten measurements^b Standard error

Table 4 Mean EPMA of Zn (*n* analyses, mg kg⁻¹) in the clay fractions of amended (AS) and control (CS) soils

	AS7		AS6		AS5		AS4		AS3		AS2		AS1	
Depth (cm)	190		170		140		110		70		40		20	
	<i>n</i> = 4 ^a SE ^b		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE	
Zn	150	12	158	12	144	11	153	10	177	9	203	13	195	12

Sample	CS8		CS7		CS6		CS5		CS4		CS3		CS2		CS1	
Depth (cm)	485		450		180		160		130		65		40		20	
	<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE		<i>n</i> = 4 SE	
Zn	15	2	14	1	14	2	17	2	18	3	19	3	24	5	10	3

^aEach analysis is already the mean of ten measurements^bStandard error**Table 5** Mean EPMA of Zn (*n* analyses, mg kg⁻¹) in clays as weathering products of amphiboles and plagioclases in control (CS) and amended (AS) soils

Table 5 Mean EPRMA of Zn (or analyses, mg kg ⁻¹) in clays as weathering products of amphiboles and plagioclases in Condon (CS) and amended (AS) soils																														
Amphiboles	Saponites								Montmorillonites				Saponites				Montmorillonites													
Sample	CS8	CS7	CS6	CS5	CS4	CS3	CS2	CS1	AS7	AS6	AS5	AS4	AS3	AS2	AS1															
Depth (cm)	485	450	180	160	130	65	40	20	190	170	140	110	70	40	20															
	<i>n</i> = 4 ^a SE ^b		<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE														
Zn	76	7	85	7	72	4	81	5	77	4	68	4	82	6	75	4	72	8	75	7	82	2	105	4	165	4	192	8	220	6

Plagioclases	Montmorillonites								K/S mixed layers				Kaolinites				Montmorillonites				K/S mixed layers				Kaolinites					
Sample	CS8	CS7	CS6	CS5	CS4	CS3	CS2	CS1	AS7	AS6	AS5	AS4	AS3	AS2	AS1															
Depth (cm)	485	450	180	160	130	65	40	20	190	170	140	110	70	40	20															
	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE	<i>n</i> = 4 SE														
Zn	77	15	66	10	42	4	39	5	37	4	35	3	31	3	27	2	67	8	64	7	39	3	36	4	32	4	25	2	30	2

^aEach analysis is already the mean of ten measurements^bStandard error

Fig. 1 Variations in the enrichment factor (EF) calculated for **a:** Loss on Ignition (L.O.I.), **b:** SiO₂ and Fe₂O₃ and **c:** Cao and MgO in the amended (AS) and control (CS) soils

Fig. 2 Variations in the enrichment factor (EF) calculated for Zn in the amended (AS) and control (CS) soils

Fig. 3 Vertical distribution profile of Zn in the amended (AS) and control (CS) soils; **a**: Zn concentrations in the < 2μm clay fraction, **b**: Zn concentrations in the amphiboles and their clay minerals weathering products, **c**: Zn concentrations in the plagioclases and their clay minerals weathering products

Fig. 4 Optical microscopy (OM) and scanning electron microscopy (SEM) of the amphibole weathering.

a: OM view of an early weathering microsite in the C horizon of the control soil, with 1: elongated amphibole crystal, 2: intramineral microcrack with clay minerals infillings.

b: SEM view of the microsite (a) with 1: amphibole crystal, 2: honeycomb texture of clay minerals in a microcrack.

c: OM view of a weathering microsite in the Bw horizon of the control soil with 1: amphibole fragments, 2: dense microcrack network with clay minerals infillings.

d: SEM view of the microsite (c) with 1: saw-tooth amphibole terminations, 2: honeycomb clay minerals cover.

e: OM view of a weathering microsite in the A horizon of the control soil with 1: increasing amphibole fragmentation with clay minerals crystallizations, 2: complete replacement of amphibole fragments by a clayey plasma.

f: SEM view of the microsite (e) with 1: amphibole fragment, 2: honeycomb-textured clay mineral.

Fig. 5. Optical microscopy (OM) and scanning electron microscopy (SEM) of the plagioclase weathering.

a: OM view of an early weathering microsite in the C horizon of the control soil, with 1: tabular plagioclase crystal, 2: clay minerals infilling dissolution pits.

b: SEM view of the microsite (a) with 1: plagioclase remnant, 2: honeycomb texture of clay minerals in a dissolution pit.

c: OM view of a weathering microsite in the Bw horizon of the control soil with 1: plagioclase fragmentation, 2: clay minerals infillings in enlarged dissolution pits.

d: SEM view of the microsite (c) with 1: plagioclase remnant, 2: spheroidal clay minerals filling a dissolution void.

e: OM view of a weathering microsite in the A horizon of the control soil with 1: increasing plagioclase fragmentation with clay minerals crystallizations, 2: complete replacement of plagioclase fragments by a clayey plasma.

f: SEM view of the microsite (e) with 1: plagioclase fragment, 2: “booklet-type”-textured clay mineral.