UNIVERSITE DE LIMOGES

Ecole Doctorale Gay Lussac – Sciences pour l’Environnement
Faculté des Sciences et Techniques
Groupement de Recherche Eau Sol Environnement

Thèse
pour obtenir le grade de
DOCTEUR DE L’UNIVERSITÉ DE LIMOGES
Discipline: Eau, Sol, Environnement

Présentée et soutenue par
Loïc DELLA PUPPA

le 27/06/2014

Stabilisation of Cu, Cd, Pb and Zn using a novel manganese oxide in contaminated soil

---

Thèse dirigée par François BORDAS et Michael KOMÁREK

JURY :

Rapporteurs	
Mme. Mélanie Davranche	Maître de Conférences HDR, Université de Rennes
M. Michel Mench	Directeur de Recherche, INRA, Université de Bordeaux
Examinateurs	
Mme. Isabelle Lamy	Directrice de Recherche, INRA, Versailles
M. Michel Baudu	Professeur, Université de Limoges
M. Jean-Claude Bollinger	Professeur Émérite, Université de Limoges
M. François Bordas	Maître de Conférences, Université de Limoges
M. Michael Komárek	Assistant Professeur, Université des Sciences de la Vie Prague

UNIVERSITY OF LIMOGES

Gay Lussac Doctoral School – Sciences for the Environment
Faculty of Sciences and Techniques
Research Group on Water, Soil and the Environment

Thesis submission
for the degree of
UNIVERSITY OF LIMOGES DOCTORATE
Field of Study: Water, Soil and the Environment

Presented and defended by:
Loïc DELLA PUPPA

Date 27/06/2014

Stabilisation of Cu, Cd, Pb and Zn using a novel manganese oxide in contaminated soil

---

Thesis supervised by François BORDAS and Michael KOMÁREK

JURY MEMBERS:

Reporters

Ms Mélanie Davranche	Lecturer, University of Rennes
Mr Michel Mench	Director of Research, INRA, University of Bordeaux

Examiners

Ms Isabelle Lamy	Director of Research, INRA, Versailles
Mr Michel Baudu	Professor, University of Limoges
Mr Jean-Claude Bollinger	Emeritus Professor, University of Limoges
Mr François Bordas	Lecturer, University of Limoges
Mr Michael Komárek	Assistant Professor, Czech University of Life Sciences Prague

Acknowledgements

So many people deserve to be thanked for their efforts and assistance. This study was conducted within the Limoges-based GRESE Research Unit dedicated to Water, Soil and the Environment, in joint supervision with the Department of Environmental Geosciences in Prague, and moreover received financial support from the Limousin Regional Council. My gratitude is extended to Professor Michel Baudu, GRESE Director, for accepting me into his laboratory group and for his show of confidence. I would also like to thank the Gay-Lussac Doctoral School and Professor Hubert Bril in particular.

I wish to acknowledge my advisors, Dr. François Bordas, and Dr. Michael Komárek, for their guidance, trust and support. I would also like to acknowledge the contributions of Emeritus Professor Jean Claude Bollinger, who oversaw my Master’s training as this course of study got underway, and Dr. Vojtěch Ettler, for his valuable insight and collaboration.

Special thanks also go out to Dr. Mélanie Davranche, lecturer at the Water and Interface Geochemistry Unit in Rennes Mr Michel Mench, Director of Research at INRA in Bordeaux, for agreeing to serve as reporters on my jury committee. I am also indebted to Ms. Isabelle Lamy, Director of research at INRA in Versailles, for accepting to examine my work.

A round of thanks is also in order for all GRESE staff, with whom I developed fruitful working relationships, especially Dr. Emmanuel Joussein for his advice and knowledge on solids characterisation and Mr Patrice Fondanèche for his extensive help on the analytical part and various input. Dr. Rémy Buzier participated greatly in the DGT measurements, and staff members at the Department of Environmental Geosciences in Prague offered considerable assistance during my time spend in the Czech Republic, with a special mention for Dr. Eva Čadková and Dr. Hana Šillerová.

Last but definitely not least, I express deep appreciation to my partner Angélina Lassance for providing me with great support throughout this step of my life.

Table of contents

Introduction

The contamination of soils by metallic elements is both an environmental (Briat and Lebrun 1998; Lim and Schoenung 2010; Beyer *et al.* 2013) and human health concern (Jomova and Valko 2011; Turkez *et al.* 2012; Fu *et al.* 2013). Due to certain organic and inorganic pollutants, soil quality can deteriorate, leading to lowering the soil biological and biochemical quality (Miguens *et al.* 2007; Wang *et al.* 2009). This decrease in soil quality in turn increases the risk of dispersion into the environment, causing a potential hazard to the humans health and the ecosystem (Bogomolov *et al.* 1996).

This contamination may of different origins, e.g., agricultural (Komárek *et al.* 2008; Neugschwandtner *et al.* 2008; Bolan *et al.* 2014) and industrial activities (Loska *et al.* 2004; Lim and Schoenung 2010). Mining sites constitute an environmental hazard since waste contaminated with metallic elements can spread into the environment. Metallic elements, such as Cu, Cd, Pb and Zn are commonly found at contaminated sites (Hogstad 1996; Tembo *et al.* 2006; Mirlean *et al.* 2007; Giannis *et al.* 2009). In these cases, soils can assimilate a pool of metallic elements, which then act as a potential source of contamination. Various European policies have indirectly contributed to soils protection through prevention measures (e.g. the control of metallic element content in animal food and in sludge from sewage treatment plants yields a decrease in the diffusive contamination in soils). In 2006, the Commission submitted to the other European institutions (European Parliament, the European Economic and Social Committee, and the Committee of the Regions) a Soil Thematic Strategy (COM(2006) 231) along with a proposed Soil Framework Directive (COM(2006) 232) in order to avoid soil quality degradation (through erosion, salinization contamination, loss of organic matter, etc.). However, the other European institutions could not reach agreement due to the opposition of certain Member States. Another discussion during 2010 was unable to resolve this situation either. Given the European Council’s failure to reach an agreement, it is now up to the European Member States to amend legislation on soil protection. Even though a clearly defined European policy is still not in place, several countries have started to take an array of initiatives. Only nine European Member States have adopted specific legislation on soil protection, yet it often specifically targets threats (e.g. desertification in Greece, Italy, Portugal and Spain; contamination in the Netherlands, Germany and Belgium). The Czech Republic and France have opted for a risk assessment strategy instead of contamination control and prevention. In the Czech Republic, Act No. 167/2008 Coll. establishes this strategy, which is a transposition of Directive 2004/35/CE issued by the European Parliament and Council on 21st April 2004. In France, this strategy is based on the legislation applicable to classified installations: Article L. 512-17 in Article 27 (30 July 2003), and Decree 77-1133 in Article 34-1 (21st September 1977), which states that at the end of a site's operating life cycle, all wastes must be removed, explosion and fire risks must be eliminated, and the area must be left in the same condition as prior to operations.

When not controlling for the fate of metallic elements, they can spread into the environment and raise concerns over environmental quality and human health (Briat and Lebrun 1998; Senesi *et al.* 1999; Peralta-Videa *et al.* 2009; Bowman *et al.* 2011). For this reason, it is necessary to propose efficient and more economical stabilisation methods as an alternative to expensive options such as excavation, which can only be viable for small areas. The use of amendments such as lime, organic matter, clay, iron and manganese oxides has already proven the possibility of significantly decreasing the mobility and bioavailability of metallic elements (Mench *et al.* 1994; Sneddon *et al.* 2006; Mench *et al.* 2010). The remediation techniques available that use amendments can be summarised as follows:

- chemical stabilisation: use of stabilising amendments such as lime, organic matter, clay, iron and manganese oxide;
- phytostabilisation: use of plants and associated micro-organisms;
- aided phytostabilisation: use of chemical stabilisation associated with phytostabilisation.

The choice of amendment is influenced by: its sorption capacity, its potential to immobilise metallic elements without immobilising essential nutrients for micro-organisms, plants, etc.; its behaviour in soil, its non-toxicity for micro-organisms; and its preparation costs. The ideal amendment would include all of these characteristics.

Despite their high immobilisation potential, Mn oxides used for chemical stabilisation have been studied to a significantly lesser extent than Fe oxides (Kumpiene *et al.* 2008; Komárek *et al.* 2013). Being ubiquitous soil components, Mn (oxy)hydroxides may represent a major sink source for metal immobilisation (Post and Veblen 1990; Komárek *et al.* 2013). They typically occur as coatings and fine-grained aggregates and moreover can efficiently control the fate and mobility of metals (O'Reilly and Hochella 2003; Kanungo *et al.* 2004) even at low concentrations in soils. Except for As and Cr (Foster *et al.* 2003; Kumpiene *et al.* 2008), the use of synthetic Mn oxides has not been extensively studied for the purpose of metal stabilisation in contaminated soils though these oxides display strong sorption capacities (Komárek *et al.* 2013) and successfully reduce metallic element mobility in contaminated soils (Mench *et al.* 1994, Mench *et al.* 1997; Sappin-Didier *et al.* 1997; Hettiarachchi *et al.* 2000; Hettiarachchi and Pierzynski 2002).

The purpose of this study is to characterise a new amorphous manganese oxide (AMO) and study its potential as a chemical stabilising agent for the four selected metallic elements: Cu, Pb, Cd, and Zn. This oxide is an intermediate during the synthesis of birnessite according to the sol-gel procedure introduced by Ching *et al.* (1997). This oxide has also been chosen due to its low cost of preparation and potential sorption capacities. For starters, AMO needs to be characterised by its:

- physical properties: structure (amorphous or crystallised), specific surface area (SSA), grain size;
- chemical properties: cation exchange capacity (CEC), pH, pH at zero point charge (pH_{ZPC}), effective sorption capacities for the studied metallic elements.

Following its characterisation and evaluation as a potential sorbent for the studied metallic elements, AMO will need to be tested with soil in order to assess its potential as a chemical stabilising agent. To perform this step, a soil originating from a historically contaminated area will be used. This soil will then be mixed with AMO at various ratios to evaluate the ratio effect on the metallic element retention. Next, the soil will be spiked with metallic cations (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) in order to study the effects of AMO on this fresh contamination. Pot experiments will make it possible to study metallic elements leachability under static condition. Sequential extractions associated with $CaCl_2$ and DGT measurements will allow for a better understanding of the AMO impact on metallic elements in this soil. Dynamic column experiments including water flow, offer a better simulation of conditions found in the environment.

Although Mn is an essential element for most organisms, a high level of Mn may exhibit toxic effects. For human, an excess of Mn can cause respiratory and neurologic problems (e.g. Parkinson disease) (Michalke *et al.* 2007; Bowman *et al.* 2011; Neal and Guilarte 2013; Michalke and Fernsebner 2014). In the environment, excessive Mn in the soil induces several toxic effects on plants (symptoms are quite similar to a deficiency in Mn) (Beyer *et al.* 2013), including a decrease in chlorophyll production causing chlorosis (a disease detected by the discoloration of leaves) and leaf necrosis (Sarkar *et al.* 2004; Boojar and Goodarzi 2008). Due to its toxicity for human body and ecosystem, the Mn released by AMO will be measured in each experiment.

Chapter I:

Stabilisation mechanisms of metallic cations

I. Stabilisation mechanisms of metallic cations

Three mechanisms primarily control metallic cation mobility: specific adsorption, non-specific adsorption and precipitation. These mechanisms are dependent on several parameters such as pH, redox conditions and soil composition. The speciation of metallic cations in soil is defined by interactions with the solid phase, according to both soil constituents and the type of the metallic cations (see Fig. 1, p. 19).

I.1. Mechanisms

I.1.1. Specific adsorption

Specific adsorption (or chemisorption) can be described as a complexation reaction between surface groups (e.g. hydroxyl groups, organic functional groups) and ions (e.g. metallic cations) in a surrounding solution, forming stable inner-sphere complexes (Fig. 1). These complexes are generated without any intervening water between the metal and the surface (Sposito 1989).

In the case of (oxy)hydroxides, surface groups at the surfaces and edges are represented by hydroxyl groups, which are negatively charged at high pH values and positively charged at low pH values (Bradl 2004). The ions are directly sorbed at the surface by inner-sphere complexes, thereby changing the surface properties of the solid. This modification of surface properties can be assessed by measuring the pH_{ZPC} (pH at zero point charge) of the solid both before and after adsorption (in the case of specific adsorption). pH_{ZPC} corresponds to the pH value at which the protonic surface charge of the solid is equal to zero. The sorption of metallic cations (M^{2+}) on an uncharged oxide surface can be represented as:

Equation 1 Adsorption of M^{2+} onto a solid

$$(\equiv \mathrm{SOH})_n + M^{2+} \leftrightarrow (\equiv \mathrm{SO})_n M^{(2-n)+} + nH^+$$

Specific adsorption is strongly affected by the surface complex formation constant (K^S_n) as well as by pH (Wang and Giammar 2013), with:

Equation 2: Surface complex formation constant K^S_n

$$K_n^S = \frac{\left(\left\{\equiv (SO)_n M^{(2-n)+}\right\} \times [H^+]^n\right)}{\lfloor M^{2+} \rfloor \times \{\equiv SOH\}^n}$$

where { }indicates the concentration of surface species. The value of the complex formation constant depends on the nature of the ion and surface groups. Among the physicochemical parameters, inner-sphere complex stability is mainly influenced by pH value, which accounts for surface group protonation and the competition between adsorbed elements and protons (for cations) or hydroxide ions (for anions). For cations, the stability of surface complexes increases with pH due to both phenomena simultaneously: the competition with protons decreases and the surface charge increases (Sigg *et al.* 2000). At a high pH value however, metallic elements can form anionic complexes with OH^-, thus changing their adsorption behaviour.

After adsorption and as a result of bulk modifications, desorption may occur (i.e. decrease in pH value, increase in concentrations of competing ions). Since thermodynamic equilibrium theory assumes complete reversibility of the chemical reaction, desorption should be identical to adsorption. However, due to the possibility of slow kinetic desorption, differences between adsorption and desorption do arise (a phenomenon called pseudo-hysteresis) (Limousin *et al.* 2007).

An improvement in the chemical model consists of taking the electrostatic interaction into account (Gouy-Chapman's Theory) and superimposing it onto the chemical interactions (Stern's Theory). In considering long-range columbic interactions (electrostatic interactions), this set-up introduces additional unknowns into the equilibrium calculations, namely: surface potential Ψ_0, and the change in surface species charge Δz (Stumm 1992). As a consequence, parameter P is included in the model:

Equation 3: Dimensionless potential P

$$P = e^{-\left(\frac{F \times \Psi_0 \times \Delta z}{R \times T}\right)}$$

with: F = the Faraday constant (9.65 10^4 $C.mol^{-1}$)

Ψ_0 = surface potential (in $J.C^{-1}$)

Δz = change in the surface species charge

R = gas constant (8.314 $J.mol^{-1}.K^{-1}$)

T = temperature (in K)

In the case of a cation, the thermodynamic formation constant ($K^{s'}_n$) is corrected by this exponential parameter as follows:

Equation 4: Correction of the formation constant K^S_n by the potential P

$$\log K_n^{S\prime} = \log K_n^S + \log P$$

I.1.2. Non-specific adsorption

Non-specific adsorption (or physisorption) is a purely electrostatic phenomenon. Due to the surface charge, ions are linked with the surface by purely electrostatic bonds. The adsorption occurs through an outer-sphere complex (Fig. 1) due to the adsorption of ions with their hydration sphere. Cation exchanges can be assimilated into a non-specific adsorption and occur during physicochemical modification of the medium (pH modification, addition of a new competitor). Because of the lack of a covalent bond between ions and surface, non-specific adsorption does not modify surface properties, nor therefore the pH_{ZPC} value. Compared with specific adsorption, non-specific adsorption is weak and easily reversible by means of system modification, including the presence of competitors.

I.1.3. Precipitation, surface precipitation and coprecipitation

In addition to sorption phenomena, metallic elements can be stabilised by precipitation and coprecipitation (Martínez and McBride 1998; Kumpiene *et al.* 2008), in limiting their toxicity and (bio)availability. Precipitation occurs when the solubility product exceeds solubility of the solid (which occurs mainly for carbonates, sulphides, phosphates and hydroxides). When a cation (or anion) is adsorbed, its concentration at the surface increases and can cause surface precipitation (Stumm and Morgan 1996). These phenomena are reversible and may arise on the solid surface, even in the soil solution, resulting in either a greater surface area or the formation of a new solid.

During precipitation, some elements may be trapped in the newly-formed solid; such a phenomenon is called coprecipitation. Three processes are responsible for coprecipitation, although the distinction among them is not always clear. The first process is inclusion, i.e. the uptake from solution of a similar ion in both size and charge to form the solid. If the coprecipitation is achieved from a homogeneous solution (which yields slow crystal formation), then inclusion contributes to the coprecipitation process. This method is used to selectively remove specific elements from the solution (e.g., actinium is selectively removed from solution containing iron and aluminium through the oxalate precipitation by a controlled hydrolysis of dimethyl oxalate). The second process is due to adsorption during surface precipitation; newly-formed crystals exhibit a high degree of non-specific adsorption. Ions at the surface are incompletely coordinated and hence free to attract other oppositely charged ions from the solution. The last process is occlusion, whereby subsequent crystal layers trap impurities using mechanical means (Stumm and Morgan 1996; Multi-Agency Radiological Laboratory 2004).

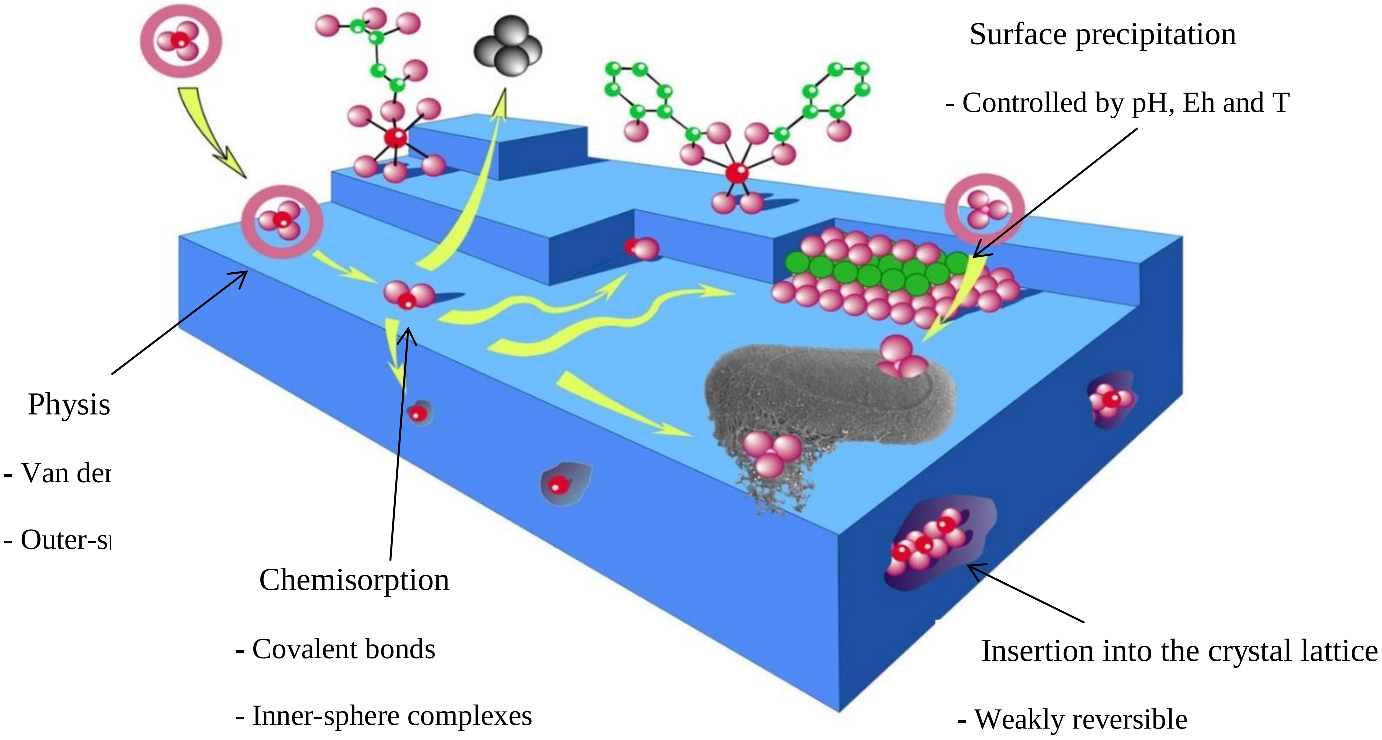

Figure 1: Interactions of metallic elements at the solid-liquid interface (Manceau *et al.* 2002).

I.2. Parameters influencing metallic cation mobility at the solid-liquid interface

I.2.1. pH

The pH value of the soil solution is the main parameter influencing metallic element behaviour. A pH variation results in the modification of metallic element speciation and, as a consequence, the modification of their adsorption (Bradl 2004). Figure 2 shows the behaviour of metallic cation (Pb^{2+} and Cd^{2+}) adsorption on three different soils *vs.* pH value. The adsorption of metallic cations increases with pH due to two simultaneous mechanisms:

- greater electrostatic interaction due to the deprotonation of the surface sites;
- less competition between protons and cations for adsorption sites.

Conversely, low pH values limit the adsorption of metallic cations on solid surfaces (Abollino *et al.* 2003; Bhattacharyya and Gupta 2008).

The pH value does not merely affect adsorption but also precipitation phenomena. A high pH value increases precipitation by favouring the formation of hydroxide solids $Me(OH)_{2(s)}$. At low pH values, the formation of these hydroxides is unfavourable, making the metallic cations more labile. This phenomenon is enhanced by the fact that at low pH values, sorption is diminished due to the competition between M^{2+} and H^+.

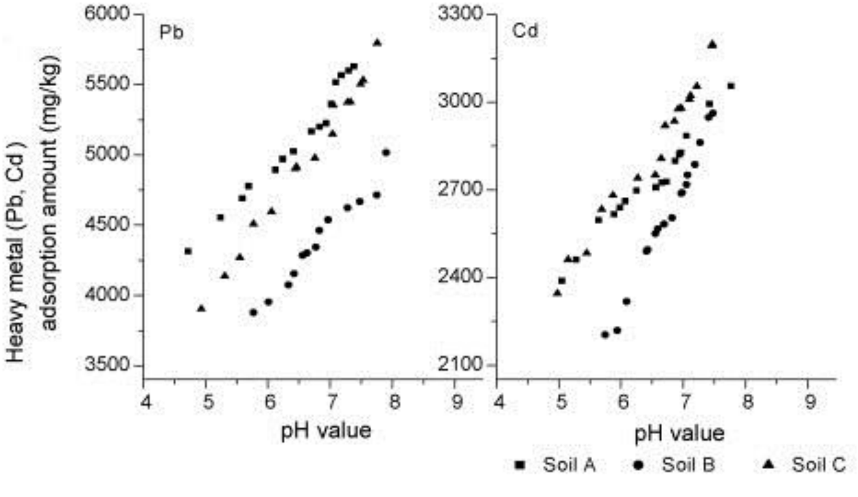

Figure 2: Adsorption of Pb and Cd on three soils *vs.* pH (adapted from Dong *et al.* 2009).

I.2.2. Redox conditions

The mobility of metallic elements is also constrained by redox processes (Du Laing *et al.* 2009), which can change due to weather events like floods or drought. Redox potential is derived by transporting electrons from the electron donor to the electron acceptor, with oxidation prevailing at a high redox potential, whereas reduction prevails at a lower potential (Frohne *et al.* 2011).

Metallic elements can be released to the soil solution due to dissolution of the carrier phases: Fe and Mn (oxy)hydroxides. These are reduced to Fe^{2+} and Mn^{2+}, which occur as soluble metals in the liquid phase (Alewell *et al.* 2008). This reduction, through dissolving metallic element carrier phases (principally Fe and Mn (oxy)hydroxides), can increase metal mobility by transforming metal elements into a more mobile form. A change in redox conditions directly affects metallic element speciation (Kelderman and Osman 2007), which may result in greater mobility (Cappuyns and Swennen 2005; Du Laing *et al.* 2009).

Redox processes can also influence pH (Du Laing *et al.* 2009; Frohne *et al.* 2011). Oxidation decreases pH by producing protons, while reduction increases pH by consuming protons (Yu *et al.* 2007). The dissolution of Fe oxides influences pH by consuming protons:

Equation 5: Reductive dissolution of $Fe(OH)_3$

$$Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$$

Consequently, a change in redox conditions can influence pH, with oxidizing conditions capable of decreasing pH and this enhancing the metallic element mobility (Kumpiene *et al.* 2009; Miller *et al.* 2010; Pareuil *et al.* 2011). A change in redox conditions might also induce the precipitation or dissolution of solids as oxide or metal sulphide. Under reductive conditions, metal sulphide precipitation and Fe, Mn-oxide dissolution can occur (Du Laing *et al.* 2009). Sulphides are provided by sulphate reduction, and when the medium becomes saturated, sulphide precipitation occurs. Sulphide solid precipitation immobilises metallic elements, whereas the dissolution of Fe, Mn-oxide increases their mobility (Grybos *et al.* 2007).

I.2.3. Soil characteristics

Soil characteristics play a major role in metallic element immobilisation and depend to a large extent on soil constituents.

The cation exchange capacity (CEC) is the amount of cations that the soil is able to exchange at a given pH value, it also represents the cation fraction available for exchange with a soil solution. It is operationally defined and depend greatly on the solution used (usually 0.1 M $BaCl_2$, 0.016 M $Co(NH_3)_6Cl_3$, 1 M NH_4OAc at pH 7). A high value would indicate good soil sorption properties (Vega *et al.* 2006; Cerqueira *et al.* 2011). Another important parameter is the soil pH. As noticed in Section I.2.1 p. 20, sorption of cations is favoured at an alkaline pH (Dong *et al.* 2009). pH influences metallic element speciation (Mouni *et al.* 2009), moreover, alkaline soil pH values promote both (oxy)hydroxide precipitation (Bradl 2004) and carbonate formation. The ionic strength of the soil solution influences metallic element sorption, with high values decreasing cation sorption (Mouni *et al.* 2009) and increasing cation mobility (Acosta *et al.* 2011). The sorption property of a soil is dependent on all these parameters.

Soil constituents (e.g. Mn and Fe oxides, organic matter, clay) play a major role in metallic element immobilisation (Vega *et al.* 2006; Covelo *et al.* 2007; Cerqueira *et al.* 2011; Sarkar *et al.* 2014). Moreover, other elements such as earthworms and plants can affect metal mobility and availability by altering soil microbial activity, pH and DOC (Almeida *et al.* 2008; Sizmur and Hodson 2009; Lee *et al.* 2014).

I.3. Interactions between soil constituents and metallic cations

I.3.1. Manganese, iron and aluminium (oxy)hydroxides

Secondary soil (oxy)hydroxides are ubiquitous soil components. They display a high specific surface area and high surface site density, along with significant redox properties (Feng *et al.* 2006; Allard *et al.* 2009; Sheng *et al.* 2009; Ross *et al.* 2013), such as the oxidation of Cr(III) into Cr(VI) (which is more toxic and labile). These components also play a major role in organic and metallic element immobilisation (McBride 1994; Tan *et al.* 2005). Sarkar *et al.* (2014) show that removing Fe and Mn oxides results in lower boron adsorption. Typically occurring generally as discrete mineral particles and coating in soils (Hudson-Edwards *et al.* 1996), (oxy)hydroxides immobilise metallic cations primarily through forming inner-sphere complexes (Peacock and Sherman 2004) yet can also appear as non-specific adsorption, surface precipitation and coprecipitation (Kumpiene *et al.* 2008). The vacant site is an important feature capable of varying across birnessite specimens. Moreover, this amount quantity of site is, not accessed during the specific surface area measurement by N_2 (BET), which can serve to underestimate the specific surface area of oxide containing a significant proportion of internal vacant site (Villalobos *et al.* 2014).

Metallic element sorption by (oxy)hydroxides may be enhanced by the presence of organic and inorganic ligands, such as dissolved organic matter and phosphate. Adsorption is improved through the formation of ternary complexes between cations and ligands, and/or between (oxy)hydroxides and ligands (Violante *et al.* 2003; Zhu *et al.* 2011).

Table 1: Examples of (oxy)hydroxides relevant to the chemical stabilisation of contaminated soils plus key properties (adapted from Komárek et al., 2013).

Oxide	Formula	Specific surface area ($m^2.g^{-1}$)	pH_{ZPC}	Surface site density (site number.nm^{-2})
Iron oxides				
Ferrihydrite	$Fe_5HO_8 \cdot 4H_2O$ (simplified as $Fe(OH)_3$)	100 – 700	7.8 – 8.8	1.6 – 9.9[b]
Goethite	α-FeOOH	8 – 200	7.5 – 9.4	6.0[b]
Lepidocrocite	Υ-FeOOH	15 – 260	6.7 – 7.5	1.5[b]
Hematite	α-Fe_2O_3	2 – 115	7.5 – 9.5	7.5[b]
Manganese oxides				
Birnessite	$(Na,Ca,K)_xMn_2O_4 \cdot 1.5H_2O$ (simplified as δ-MnO_2)	35.4[a]	1.8 – 2.2	18[c]
Manganite	Υ-MnOOH	8.9	5.4	-
Pyrolusite	β-MnO_2	0.15	7.2	-
Aluminium oxides				
Gibbsite	Υ-$Al(OH)_3$	120	9.8	8.5[d]
Boehmite	Υ-AlOOH	224	8.6	1.71[e]
Diaspore	α-AlOOH	11	2.0 – 7.5	-

[a] Higher specific surface area values were obtained with the EGME method (ethylene glycol monoethyl ether): birnessite 375.8 $m^2.g^{-1}$ (O'Reilly and Hochella, 2003).

[b] Peacock and Sherman (2004)

[c] Allard *et al.* (2009)

[d] Weerasooriya *et al.* (2002)

[e] Laiti and Öhman (1996)

The sorption properties of a solid depend on a combination of solid properties, including specific surface area, pH_{ZPC}, surface site density and the affinity between metallic cations and the solid phase. When comparing the specific surface areas (Table 1), Fe oxides (more specifically ferrihydrite) exhibit higher values and manganese oxides lower values. However, when comparing the surface site densities of all these oxides, it appears that birnessite has the highest value. The pH_{ZPC} value of birnessite and diaspore (in viewing the lower values) indicates an ease of adsorption, as the pH value of common soil generally lies above 2 (Panagos *et al.* 2012). Figure 3 shows the impact of oxide characteristics on Pb sorption.

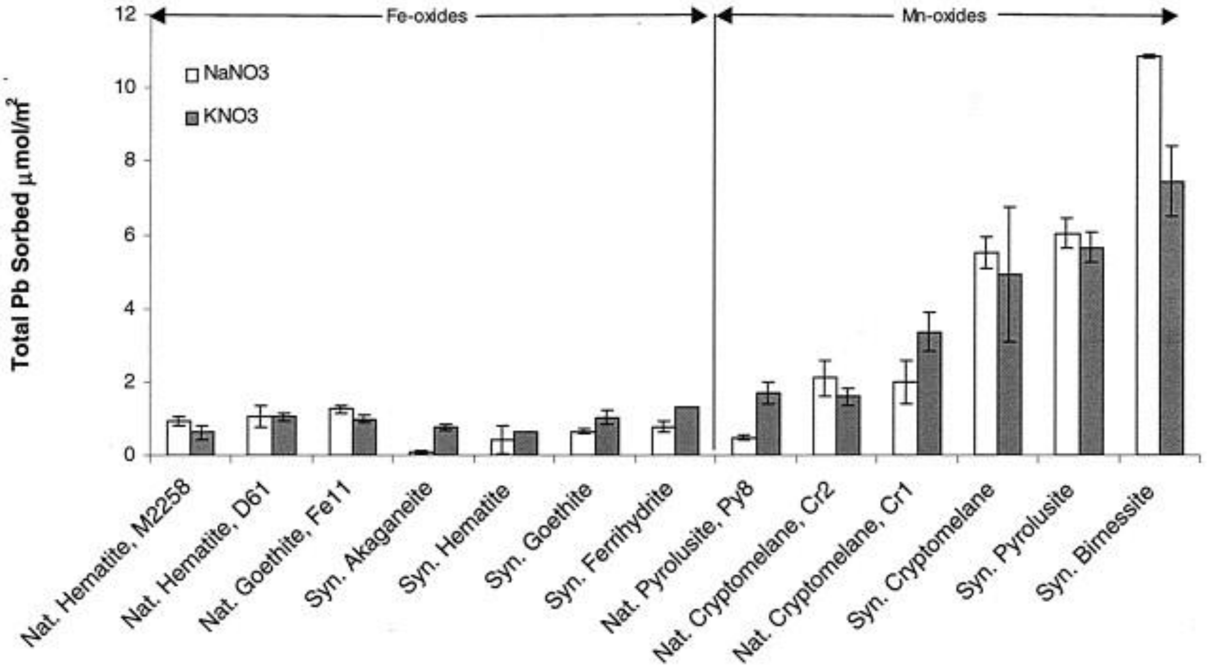

Figure 3: Pb sorption in µmol.m^{-2} of synthetic (Syn.) and natural (Nat.) oxides (normalised to the specific surface area of the solid) at pH 5.5, in a 0.01 mol.L^{-1} $NaNO_3$ or KNO_3 background electrolyte (O'Reilly and Hochella 2003).

As observed in Table 1; birnessite exhibits a very low pH_{ZPC} (1.8 - 2.2), which partially explains its high sorption capacities. The difference in Pb sorption between both electrolytes appears to stem from the electrolyte impact on the surface charge (Yousef *et al.* 1971). These data underscore the importance of certain parameters in describing the metal sorption capacity of oxides.

I.3.2. Organic matter

Organic matter is mainly provided by the decomposition of the living matter (animal or vegetal). Humification allows metabolisation of the organic matter into humic substances. Organic matter has acid/base, redox and complexing properties toward metallic cations (Park *et al.* 2011). Complexing properties originate from the ionization of functional groups as a function of the pH value. Mainly two functional groups are involved: carboxylate (COO^-) and phenolate (C_6H_5-O^-), but such functions as sulfonic (SO_3^-), thiol (SH), amine (NH_2) can play significant role. The complexation is made through inner-sphere complexe (specific adsorption) (Boudesocque *et al.* 2007).

Two types of organic matter can be distinguished, dissolved organic matter (DOM), and particulate organic matter (POM), which contributes considerably to metallic element mobility. The metallic cations are mainly complexed by DOM and adsorbed on POM. In soils, metallic cations are mainly immobilised by POM (Besnard *et al.* 2001). DOM allows for improved solubilisation through metallic cation complexation (Lu and Allen 2002). A portion of natural organic matter may be present in colloidal form, while a mobile fraction of organic matter with surface functional groups creates interactions with metallic cations. This fraction plays a major role in metallic element mobility within the environment: the mobility of these elements increases during colloidal transport (Pedrot *et al.* 2008).

I.3.3. Clays

Clays play a key role in controlling metallic element behaviour in the environment. These materials are mainly composed of aluminium phyllosilicate at varying levels of hydration. Most physicochemical properties of clays stem from their laminar morphology and small grain size (< 2 µm) as well as the isomorphic substitutions originating from the electric charge applied to the layers. Clays are composed of an octahedral layer "O" ($Al(OH)_6$) and a tetrahedral layer "T" (SiO_4) linked by O and OH atoms (Fig. 4). Given the layered structure, three categories can be distinguished: T-O clays as kaolinite $Al_2Si_2O_5(OH)_4$, T-O-T as illite $K_{1-1.5}Al_4(Si,Al)_8O_{20}(OH)_4$ and .T-O-T-O as sudoïte $Mg_2(Al,Fe)_3Si_3AlO_{10}(OH)_8$.

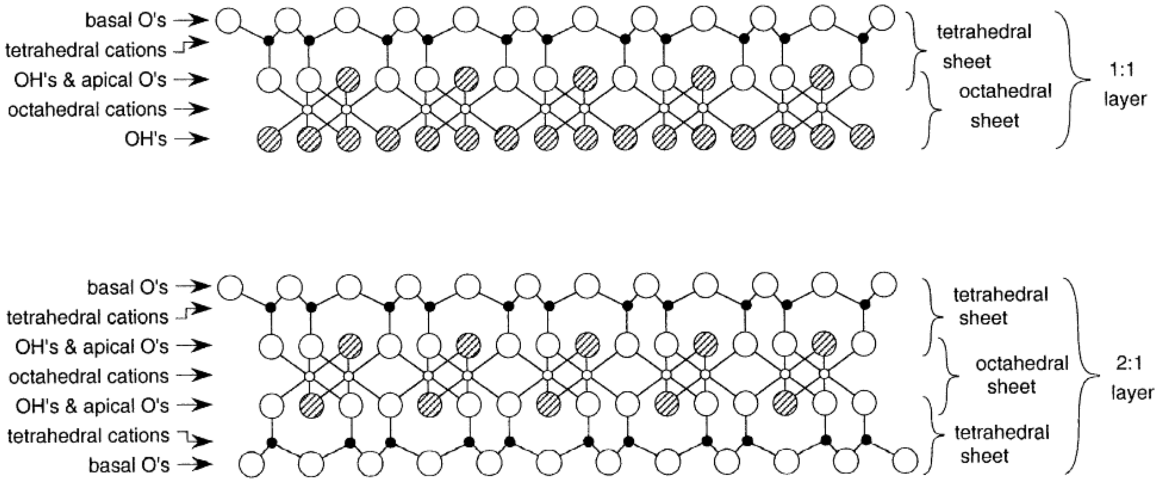

Figure 4: The aluminium phyllosilicate nomenclature (Schulze 1989).

The Surface charge can be either fixed (like for kaolinite) or variable (illite). A fixed surface charge stems from ionic substitutions within the structure, such as the substitution of Si^{4+} by Al^{3+} in the "T" layer or the substitution of Al^{3+} by Mg^{2+} or Fe^{2+} in the "O" layer resulting in a negative surface charge. If however the surface charge is due to the adsorption of ions on the surface, its variation will evolve with the pH of the medium. A negative charge, due to an alkaline pH, can be compensated by the hydrated cations present between and on the layers (Li and Li 2000). Consequently, these cations can interact with heavy metals by means of adsorption, exchange reactions, and the formation of inner-sphere complexes (Celis *et al.* 2000; Jiang *et al.* 2010). Depending on the clay structure and type of metallic elements, clay minerals can adsorb at two different sites: i) on the surface and edge (like kaolinite), and ii) between layers (smectite) (Brigatti *et al.* 1995; Sajidu *et al.* 2006).

I.4. Evaluation of metal mobility and the (bio)available fraction

Bioavailability refers to the mobile fraction, which is considered to be the fraction of total contaminant in both the pore water and soil particles that is available for the receptor organism (Mench *et al.* 1994; Vig *et al.* 2003). This concept integrates chemical, physiological and toxicological aspects. According to the ISO 17402 Standard, (bio)availability is related to the target organisms on the basis of contaminant type, soil properties and receptors properties. Bioaccessibility refers to the potentially bioavailable fraction, i.e. the fraction that can be mobile under specific conditions such as digestion (Gupta *et al.* 1996). Bioaccessibility is also associated with the human body in the ISO/TS 17924 Standard, which indicates that "bioaccessibility includes all physical, chemical and microbial processes in the human body, from chewing in the mouth to precipitation in the intestines". Whereas the mobility represents the capacity to move from one compartment to another (Baize 1997), the bioavailable fraction is correlated with the available fraction in the soil (Li *et al.* 2008).

I.4.1. Single-step extraction: water, $CaCl_2$ and EDTA extraction

In order to quickly and easily evaluate the potential of metallic elements, several single step extraction procedures are usually sufficient (Komárek *et al.* 2008; Brun *et al.* 2001). Two types of extracting solutions can be used to assess the availability: a mild or cationic exchange solution (water, acetic acid, calcium chloride, etc.) and a complexing solution (EDTA, DTPA, etc.) (Leleyter and Baraud 2005; Gupta and Sinha 2007). The metal (bio)availability potential depends however on soil characteristics, metallic element species and the target organism. For example, Houba *et al.* (2000) showed that 0.01 M $CaCl_2$ can serve as an universal extractant in order to assess the (bio)availability, but Pauget *et al.* (2012) revealed that 0.05 M EDTA is more suitable in assessing Cd (bio)availability to snails.

Water extraction is used to measure the soluble fraction of metallic elements, as this fraction is more weakly bound in the soil than the acid-soluble and complexed fractions (Sappin-Didier *et al.* 1998). Water-soluble metallic elements are an easily mobilised fraction and may be considered as bioavailable. Meers *et al.* (2007) found a good correlation between Cd phytoavailability and Cd extracted with water.

Calcium chloride is a cationic exchange extractant. Its extraction seems to better fit the content in a wild plant when used with a neutral-acid soil (Brun *et al.* 1998; Komárek *et al.* 2008). This extractant has a limited effect on soil pH (Pueyo *et al.* 2004). The use of a 0.01 M $CaCl_2$ solution has yielded a good fit with the phytoavailability of Cd, Cu, Pb and Zn in soil and a good indication of the phytoavailability of these metallic elements especially in acidic soils (Meers *et al.* 2007).

The complexing behaviour of metallic elements by root exudates can be simulated to a certain extent using EDTA as an extractant solution. EDTA is known to be a strong complexing agent and can overestimate the (bio)available fraction by both dissolution of the Fe- and Mn- oxides (Komárek *et al.* 2007) and extraction of the carbonate and organically bound fraction (Sahuquillo *et al.* 2003; Feng *et al.* 2005). Oxide dissolution tends to be lower at low pH levels (Nowack and Sigg 1996). Since use of an EDTA solution overestimates the available fraction of metallic elements, it may prove useful in predicting long-term risks (Labanowski *et al.* 2008). Use of a 0.01 M EDTA solution for extraction can provide good indicators of Cu bioavailability for a given soil type (Chaignon *et al.* 2003); however, the efficiency of EDTA extraction depends on several elements: crystallinity of the Fe (oxy)hydroxides, and presence of competitors (e.g. Ca, Fe) (Chrastný *et al.* 2008). Moreover, use of a 0.01M EDTA solution to predict the (bio)availability potential of metallic elements has been standardised (NF X 31-120). EDTA use has extended to the remediation of contaminated soils by ex-situ soil washing even though this use is not without its share of disadvantages (namely the decrease in white clover yield on remediated soil compared to natural soil, Zupanc *et al.* 2014).

I.4.2. Multi-step extraction

Metallic elements splitting in the soil can be determined using sequential extractions (Rauret *et al.* 2000), which help assess the extent to which metallic elements are being immobilised in the soil (depending on the reactant introduced) and how easily they may be released into the soil solution (Kaasalainen and Yli-Halla 2003). Sequential extraction also allows for the fractionation of metallic elements in operationally and successively defined fractions. The technique normally divides into four fractions (Table 2Table 2). The first one corresponds to the fraction exchangeable and weakly bound by electrostatics, readily released by ion exchange processes and released during carbonate dissolution. The second fraction measures the metallic elements bound to the reducible fraction by the dissolution of Fe and Mn oxides. The third fraction roughly corresponds to the metallic elements associated with the organic fraction, though dissolving organic matter with oxidant reactants. After these successive extractions, the remaining fraction is mineralised with concentrated acids in order to determine the fraction bound to unaffected soil elements (e.g. residual silica).

Even though the results obtained from these extractions are often subject to criticism (Sahuquillo *et al.* 2003), they still provide an evaluation and comparison of the element distribution in soil fractions, in addition to indicating the portion mobilised under well-defined chemical conditions. One of the most heavily criticised points stems from the reagents, which are chosen to target specific and well-defined soil phases, yet this specificity cannot be guaranteed. Moreover, Tokalioğlu *et al.* (2003) concluded that the quantity of metallic elements extracted at each step of the sequential extraction procedure depended on both the reagent and sequence in which they were applied. Similarly, several studies (Lacal *et al.* 2003; Peltier *et al.* 2005; Burton *et al.* 2006; Vaněk *et al.* 2010) discovered that hydroxylamine hydrochloride can dissolve sulphide minerals, which suggests that sulphide-bound metals might be mistakenly interpreted as bound to the reducible fraction. Moreover, hydroxylamine hydrochloride shows a lack of efficiency in dissolving all the iron and manganese (oxy)hydroxide (Gómez Ariza *et al.* 2000). Another demonstration of sequential extraction drawbacks lies in the interpretation of the procedure employed. The use of a specific amendment shows an increase in the metal associated with the reducible fraction when applying one given procedure while it decrease with another procedure (Penilla *et al.* 2005; Dœlsch *et al.* 2006).

Several reasons explain why sequential extraction cannot be used to quantitatively determine the trace metals associated with specific mineral phases in environmental solids (Bacon and Davidson 2008), namely:

- redistribution of analytes among phases during extraction;
- non-selectivity of reagents for targeted phases;
- incomplete extraction;
- precipitation of new mineral phases during extraction.

Despite these limitations, sequential extraction procedures remain a widely used tool for providing information regarding the potential mobility of metallic element in soils. Such procedures do not determine speciation but rather an operationally-defined solid fractionation

(Bermond 2002). In order to harmonise the sequential extraction protocol, the SMTP (Standards, Measurement and Testing Program) developed a defined protocol, which was subsequently accelerated by Pérez-Cid *et al.* (1998), in replacing the conventional shaking system with an ultrasound system (Table 2).

Table 2: Sequential extraction accelerated by ultrasound (Pérez-Cid *et al.* 1998).

F1: acid soluble, "exchangeable and weakly bound fraction"	20 mL Acetic acid 0.11 M	7 min, 20 W
F2: "bound to reducible fraction"	20 mL hydroxylamine hydrochloride 0.1 M at pH 2 (with 69% HNO_3)	7 min, 20 W
F3: "bound to the oxidisable fraction"	10 mL hydrogen peroxide 30% then 25 mL Ammonium acetate 1 M at pH 2 (with 69% HNO_3)	2 min, 20 W then 6 min, 20 W
F4: residual fraction	9 mL 69% nitric acid + 3 mL 37% hydrochloric acid	

I.4.3. DGT

The Diffusion Gradients in Thin-film (DGT) technique measures the mean flux of labile species to the device during deployment (Zhang *et al.* 1995; Zhang 2003). This method is useful for measuring the (bio)available metal fraction and quantifying the labile pool (Nowack *et al.* 2004; Leermakers *et al.* 2005; Roulier *et al.* 2008; Ruello *et al.* 2008; Bade *et al.* 2012). A difference however could appear between DGT results and the concentration in soil solution, due to the presence of the colloidal fraction (Ruello *et al.* 2008).

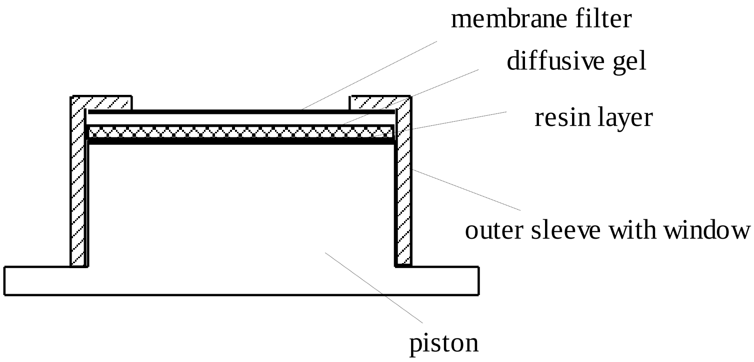

Figure 5: The DGT system.

The DGT technique is based on Fick’s first law of diffusion and is composed of an ion-exchange resin layer separated from the bulk solution by an ion-permeable hydrogel membrane (Fig. 5). Six types of gel membranes can be used depending on the target element:

- diffusive gel (open pore),
- restricted gel (restricted pore for measuring labile inorganic only),
- Chelex gel (for metals),
- Fe-oxide gel (for phosphorus),
- AMP gel (for Cs),
- AgI gel (for sulphides).

Metal ions diffuse through the gel and are bound to the resin. In the case where the resin capacity has not been exceeded, the concentration of metal sorbed on the resin is held at zero throughout the deployment (Fig. 6), creating a step concentration gradient in the gel layer. The metal ion concentration in the soil close to the DGT is decreased and can induce a supply of metal ions from the solid phase to the solution in soil layers close to the DGT.

Should this concentration gradient remain constant over the deployment time, then the ion concentration in the bulk solution may be calculated using:

Equation 6: Metallic element concentration in the bulk solution according to the DGT method

$$C = M \times \frac{\Delta g}{(D \times t \times A)}$$

with: C = ion concentration in the bulk solution (µg.dm^{-3})

M = metal mass accumulated in the resin layer (µg)

Δg = thickness of the diffusive gel and filter membrane (dm)

D = diffusion coefficient of a given metal ion at a given temperature (dm^2.s^{-1})

t = deployment time (s)

A = area of the gel membrane exposed to the bulk solution (dm^2)

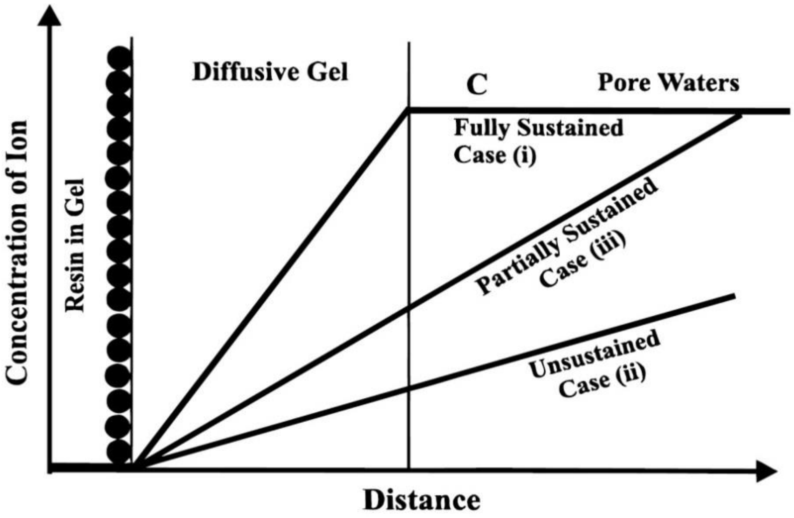

Figure 6: Schematic diagram of the concentration gradient in a DGT placed in contact with pore waters where the concentration is i) fully sustained, iii) partially sustained or ii) unsustained by resupply from the solid phase in soil (from Zhang *et al.* 1998).

When ions are diffusing through the gel, they may be resupplied from the soil phase to the soil solution according to three cases (Fig. 6):

(i) partially sustained: the ions are partially resupplied from the soil, but insufficient to compensate for the depletion;

(ii) unsustained: the ions removed from the soil solution are not resupplied from the soil. The supply of ions to the DGT is merely by diffusion from the soil solution, which gradually becomes depleted near the DGT;

(iii) fully sustained: ions removed from the soil solution by the DGT are rapidly resupplied from the soil solid phase, and the concentration in the soil solution is buffered at a constant value.

When comparing these various techniques, it appears that differences may arise, especially due to the fact that as a metal desorbs from the solid phase, its speciation changes. The DGT measurement includes all these species except colloidal forms and kinetically-inert complexes (Ruello *et al.* 2008). The DGT approach appears to be useful in avoiding underestimating or erroneously asserting contamination of a possibly contaminated soil (Ruello *et al.* 2008). When comparing the results of $CaCl_2$, EDTA extraction and DGT measurements, it appears that EDTA is the most powerful extracting solution. This finding is due to the fact that EDTA can dissolve oxides, thereby releasing the associated metallic elements into solution, in addition to extracting metallic elements from carbonates and the organically bound fraction (Komárek *et al.* 2007; Sahuquillo *et al.* 2003; Feng *et al.* 2005).

Moreover, when comparing DGT measurements (in sediments) with results obtained from sequential extractions (depending on the selected extraction protocol), it appears that metals determined using DGT can indeed be predicted. The fractions used for this prediction step are correlated with the studied metallic element. For Cd, in sediments, the amount extracted in F1, F2 and F3 seems to provide a good indicator of the value possibly obtained by DGT measurements (F1: "exchangeable fraction", F2: "fraction bound to carbonates" and F3: "fraction bound to Fe/Mn oxides") (Roulier *et al.* 2010), while for Pb, only F1 + F2 is correlated with the concentration derived by DGT (Roulier *et al.* 2010). In soils, Liang *et al.* (2014) show that Pb measured using the DGT technique is linked to F1, the exchangeable fraction.

II. Stabilisation of metallic elements in soils

II.1. Manganese oxide synthesis and properties

II.1.1. Manganese oxide synthesis

The manganese oxide structure depend to a greater extent on the synthesis protocol (Cheney *et al.* 2008). These protocols can be classified according to three processes (Feng *et al.* 1998):

- **Dry processes**: solid state reaction and melting salt flux processes

Solid-state reaction process: manganese compounds are used as manganese source and alkali metals as the templates;

Melting salt flux process: use of a melting agent during the synthesis (Boullayt *et al.* 1997).

- **Wet processes**: redox precipitation, hydrothermal and hydrothermal soft chemical processes

Redox precipitation process: use of Mn^{II} salts and/or reduction of MnO_4^- salts in solutions;

Hydrothermal process: use of high temperature and pressure, or a pressure corresponding to the saturated vapour pressure of the solution at the specified temperature (Suchanek and Riman 2006);

Hydrothermal soft chemical process: preparation of the framework precursor and, subsequent transformation of the template-inserted precursor by means of hydrothermal treatment.

- **Wet-dry processes**: sol-gel processes

Sol-gel process: use of an organic compound for reducing of Mn compound (Ching *et al.* 1997).

The Table 3 summarises some of the manganese oxide syntheses.

Table 3: Syntheses of various samples of manganese oxide.

Reactant	Heating step	Structure	Reference
$KMnO_4$ + oleic acid	60°C for 24 h, then 250°C for 5 h	Weakly crystallised	Chen *et al.* 2011
$KMnO_4$ + glucose	110°C for 12 h then 400°C for 2 h	Birnessite-type	Ching *et al.* 2004
Ethanol + H_2SO_4 + $KMnO_4$	60 or 180°C for 12 h	Amorphous or amorphous and nanocrystallised	Liu *et al.* 2012
$KMnO_4$ + Na-lactate	Ambient temperature	Birnessite-type	Händel *et al.* 2013
$KMnO_4$ + HCl	Ambient temperature	Birnessite-type	McKenzie 1971
$KMnO_4$ + HCl	400°C for 60 h	Cryptomelane	McKenzie 1971
$KMnO_4$ + $MnSO_4$ + acetic acid	80°C for 5 min	Birnessite	McKenzie 1971
$Mn(NO_3)_2$ + $NaMnO_4$ + NaOH	Ambient temperature	Amorphous	Axe *et al.* 2000
$Mn(NO_3)_2$ + $KMnO_4$ + KOH	Ambient temperature	Birnessite-type	Eren *et al.* 2011
H_2O_2 + KOH + $Mn(NO_3)_2$	Ambient temperature	Birnessite-type	Feng *et al.* 1997
Cs_2CO_3 + $MnCO_3$	800°C for 1 h, then twice 800°C for 20 h	Crystallised	Kang *et al.* 2007

As seen in Table 3, most syntheses require a heating step or strong acids/bases as reactants. Moreover, the resulting product is strongly dependent on the reagent as well as the protocol. A method called sol-gel offers a milder approach to synthesising manganese oxide, since the Mn oxide stemming from the reaction requires a heating step to access an enhanced crystallised oxide.

II.1.2. Sol-gel procedure

Mineral polymerisation, better known as the sol-gel procedure, is a soft oxide synthesis method using a wet path at ambient temperature. In the case of AMO, a $KMnO_4$ solution reacts with a glucose solution in order to form a solid that then occupies the entire space. This solid is not a precipitate but rather a gel encompassing the solvent (in this case, water). After a delay (in this case, 30 min), demixing happens, in which the gel increases its density by expelling the solvent: this step is called **syneresis**. The resulting solid is washed, dried (in this case, at ambient temperature) and grounded to yield a **xerogel**. If the solid is dried using hypercritical procedure, then the resulting solid is called an **aerogel**. Drying followed by the hypercritical procedure allows forming a gel with attractive properties, such as insulating and dielectric properties (Corriu and Trong Anh 2008).

Even if the process appears to be straightforward, three steps should be distinguished (Fig. 7):

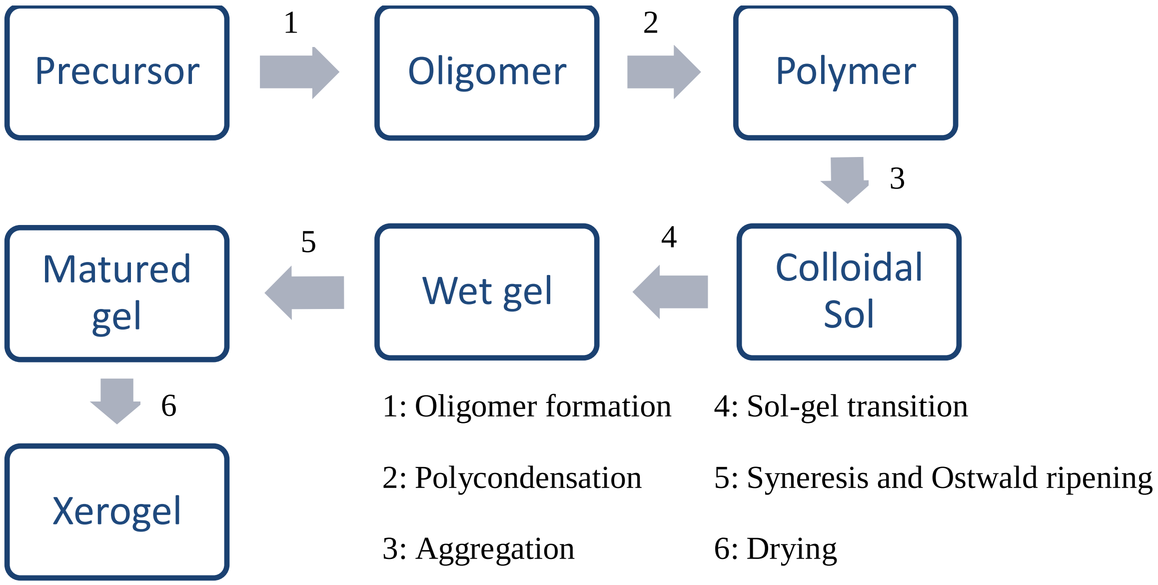

Figure 7: Presentation of the chemical transformations occurring during sol-gel procedure.

The first step comprises the first three phases (1, 2, and 3) (Figure 7). The first linear and cyclic oligomers of nanometric size are directly related to the nature of the precursor. These oligomers will become entangled by polycondensation giving rise to reticulated polymers, whose aggregation then forms micro-scale colloids. The colloidal solution turns out to be a crucial step in the synthesis since it corresponds to a viscous solution that allows the material to form. The second step consists of the solution solidifying into a gel. Called the sol-gel transition (step 4, Fig. 7), this step corresponds to a chemical reaction (condensation) taking place at the colloid surface. The speed of gelation is due to the fact that just a few chemical bonds between colloids are needed to obtain a large-mesh network capable of holding all the solvent and occupying all the space (Corriu and Trong Anh 2008).

Step 5 corresponds to the solid phase formation. The bonds between colloids expand, resulting in an acceleration of densification. The initial phase, called syneresis corresponds to solvent expulsion; it results in the formation of an amorphous solid displaying a stabilised granular distribution and porosity, both of which depend on the specific experimental conditions. The Ostwald ripening ageing step is very important because it controls the macroscopic characteristics of the solid. The last step (6) corresponds to the formation of xerogel by drying the solid after washing (in this case, the xerogel was dried at ambient temperature) (Corriu and Trong Anh 2008). The texture of the xerogel is heavily influenced by drying conditions.

II.1.3. Manganese oxide properties

Characteristics such as CEC, SSA and pH_{ZPC} greatly control the sorption properties of manganese oxides. Table 4 summarises the properties of some of the manganese oxides used in the literature to conduct remediation studies.

Table 4: Manganese oxide properties used for adsorption or remediation studies.

Mn oxide	pH_{ZPC}	CEC ($meq.100g^{-1}$)	Site density ($\mu mol.m^{-2}$)	SSA ($m^2.g^{-1}$)
Birnessite	2.7[c]	247[c]	22[l]	31 – 100[a]
AMO	7.9[c]	34[c]	-	15[c]
Cryptomelane	2.0[f]	-	-	32[d], 58[f], 90[h]
HMO	1.5[l] - 2.4[e]	-	2 – 27[l]	359[e] – 746[k]
K, H, Mg-MO	-	-	-	38, 99, 157[g]
Mn oxide[i]	-	-	-	-
MnO[j]	-	-	-	-
Verdanite	1.5[l]	-	367[l]	74[l]

[a]: Wang *et al.* (2012)

[b]: Allard *et al.* (2009)

[c]: Della Puppa *et al.* (2013)

[d]: Fan *et al.* (2008)

[e]: Fan *et al.* (2005)

[f]: McKenzie (1980)

[g]: Kang *et al.* (2011)

[h]: Hettiarachchi *et al.* (2000)

[i]: Chen *et al.* (2000)

[j]: Vandecasteele *et al.* (2010)

[k]: Pourret and Davranche (2013)

[l]: Tonkin *et al.* (2004)

-: no data

Despite the fact that key manganese oxide properties like CEC and pH_{ZPC} offer clues to a better understanding and estimation of sorption properties, they often remain undetermined as observed in Table 4. Furthermore, SSA parameters seem to be dependent on the study authors and, consequently, on the synthesis protocol or measurement protocol. Moreover, because authors use different values for a characteristic on a given manganese oxide sample, this situation does not facilitate comparison (as in the case of Cryptomelane).

Manganese oxides used in remediation studies typically have low pH_{ZPC} and high specific surface areas, as opposed to the oxide used in this study, the AMO, which exhibits a high pH_{ZPC} and low SSA.

II.2. Soil remediation

II.2.1. Summary of the various remediation approaches

Many techniques already exist for soil remediation, in relying on various mechanisms:

- **Physical approach**:

  - disposal of the pollution: soil excavation, grain sorting, water washing (Kalinovich *et al.* 2008);

  - trapping of the pollution: *in situ* encapsulation and elimination, solidification and stabilisation (Mench *et al.* 1997; Sappin-Didier *et al.* 1997; Komárek *et al.* 2013).

- **Chemical approach**:

  - chemical extraction, chemical oxidation and reduction (Mench *et al.* 1997; Crimi and Siegrist 2004b; Ruttens *et al.* 2010).

- **Biological approach**: phytostabilisation, aided phytostabilisation (Vangronsveld *et al.* 1995; Komárek *et al.* 2007; Kumpiene *et al.* 2011; Burgos *et al.* 2013).

Each remediation approach features a set of advantages and disadvantages. The price of the remediation is strongly dependent on both the selected technique and surface requiring treatment. Table 5 summarises the estimated price, advantages and disadvantages of a number of remediation techniques.

Table 5: Cost of several remediation techniques (Colombano *et al.* 2010).

Remediation technology	Estimated price	Advantages	Disadvantages
Excavation	5-7 €.m^{-3}	- Easy and quick - Reliable	- Just a preliminary operation - Available on the surface (5-6m) - Release of an explosive atmosphere (gas trapped) - Increase in the metallic element mobility (modification of the redox properties) - Migration of the pollution as dust
Soil washing	20-120 €.t^{-1} depending on the solution	- Limited soil disturbance - Easily applicable on permeable soil	- Transfer of pollutants into the groundwater - Volume of water requiring treatment - Possible alteration of soil properties - Use of solution possibly toxic for the environment
Physicochemical stabilisation	25-120 €.t^{-1} depending on the stabilising agent	- Reduction in the availability - Decrease in the mobilised fraction - Simple and inexpensive (depending on the stabilising agent)	- Unable to destroy pollutants - Monitoring is mandatory - Dependent on soil characteristics - Long-term efficacy must be proven, monitored

Phytostabilisation	18-40 €.m^{-2}	- Limited disturbance to the soil - Possibility of treating a large area - Limiting transfers of pollutant	- Significant time commitment, limited efficiency - The plant must be adapted to the pollution and soil - Strongly depending on weather, soil fertility

As shown in Table 5, the cost depends on both the technique and material (solution, chemical stabiliser, etc.). It appears that the best remediation techniques will depend on the following conditions: type of soil, nature of the pollutant, and pollutant concentration. While some techniques present significant advantages, their implementation must be proceeded with care.

Stabilising amendments are easy to use and more economical (depending on the selected amendment), in addition to providing an effective means for remediating contaminated soils.

II.2.2. The use of in-situ amendments

Several chemical stabilisation methods have been proposed to remediate soils contaminated with metals or metalloids. These methods are based on the application of various amendments (Bolan *et al.* 2014), e.g. organic compounds (Janoš *et al.* 2010), zerovalent iron (ZVI), manganese oxides, compost, phosphates, clay minerals, lime, possibly associated with phytoremediation (Mench *et al.* 2010), and phytostabilisation (Kumpiene *et al.* 2011). Table 6 indicates the effects of some amendments on the metallic elements present in contaminated soils.

Alkaline materials, such as limes, decrease metallic element mobility by increasing the soil pH, which in turn induces an increase in pH-dependent charge, resulting in greater metallic cation sorption on soil particles such as clays, organic matter and Fe and Al oxides (Lee *et al.* 2009; Gray *et al.* 2006). Moreover, the increase in soil pH value leads to the precipitation of metallic elements with carbonates, thus reducing their mobility (Mench *et al.* 1997; Lee *et al.* 2004). The application of limestone to decrease the bioavailability of Cu and Cd has been successfully demonstrated (Li *et al.* 2008).

Clay materials have proven to be effective in remediating metallic elements (Gupta and Gardner 2005; Zhang *et al.* 2011). The application of montmorillonite significantly reduces the acid-extractable fraction and increases the residual fraction for Cu, resulting in a reduction of the toxic effect of Cu on earthworms (Zhang *et al.* 2011). Copper immobilisation is both irreversible and reversible, mainly due to the ion exchange process.

Several studies have shown the effectiveness of Fe and Mn oxides in stabilising metals (Mench *et al.* 1994; Sappin-Didier *et al.* 1997; Chen *et al.* 2000). Chemical stabilisation using secondary (oxy)hydroxides constitutes another important stabilisation practice. The application of ZVI has been successfully studied for metal immobilisation. The stabilisation process is based on the fact that the initial corrosion product includes amorphous ferrous (oxy)hydroxide which is an efficient sorbent for many metals/metalloids. Their subsequent oxidation can lead to the formation of magnetite, lepidocrocite and goethite (Roh *et al.* 2000). As the outcome of corrosion, the ZVI surface is coated by a layer of iron oxides and (oxy)hydroxides. The application of ZVI can thus significantly reduce total metal concentrations in a soil solution due to the sorption of ionic and organo-metallic chemical species on the newly formed and poorly crystallised Fe (oxy)hydroxides (Bes and Mench 2008). In the case of Zn^{2+}, the metal undergoes several surface complexation and/or adsorption reactions with functional groups at the zerovalent iron surface and is able to form unidentate or bidentate surface complexes according to the model described by Stumm and Morgan (1996).

Table 6: Effect of various amendments on the mobility and bio(availability) of a number of metallic elements in contaminated soils.

Amendment				Soil			Effect	Authors
	pH$_{H2O}$	CEC	[Amendments]	pH	CEC (cmol.kg^{-1})	TOC (g.kg^{-1})		
Zeolite	8.2	170	5-20 g.kg^{-1}	8.2	10.43	21.7	↓ Pb available in soil and plants	Li *et al.* 2009
							↓ Pb extracted in water, exchangeable, bound to carbonate, Fe-Mn oxide	
							↑ Pb bound to organic matter	
Montmorillonite	8.5	8.4	1-8%	3.99	9.2	-	↑ pH	Zhang *et al.* 2011
							Cu bound to Fe-Mn oxide and in residue	
							↓ Cu exchangeable and bound to organic matter	
Phosphate rock	-	-	0.2 g.kg^{-1}	5.66	-	-	↓ Cu, Cd, Pb and Zn extracted with water	Mignardi *et al.* 2012
				5.0	12.4	24	→ Pb extracted by HCl and EDTA	Chen *et al.* 2000
							↓ Cd extracted by HCl, Ca(NO$_3$)$_2$ and EDTA	
Fe oxide	-	-	1%	5.0	12.4	24	↓ Cd extracted by HCl, Ca(NO$_3$)$_2$ and Pb extracted by EDTA, Ca(NO$_3$)$_2$	

Calcium carbonate	-	-	Until soil pH 7	5.0	12.4	24	↓	Cd and Pb extracted by HCl, $Ca(NO_3)_2$, EDTA Uptake in wheat shoot (Cd, Pb)	
ZVI grit	-	-	1 + 1%	7.96	16.1	40.4	↓	Cu and Zn in bean primary leaves Cu and Zn in soil solution	Bes and Mench 2008
Mn oxide	-	-	1%	7.4	3.9	0.028	↓	Cd extracted by water, $Ca(NO_3)_2$ Cd in Ryegrass and tobacco shoots	Mench *et al.* 1994
							→	Cd extracted by EDTA	
	-	-	1%	4.2	9	0.029	↓	Pb exchangeable and bound to organic matter Pb in Ryegrass shoots	
							↑	Pb bound to Fe-Mn oxide	
	-	-	1%		5.6	2.8	↓	Cd extracted by water, $Ca(NO_3)_2$	Sappin-Didier *et al.* 1997
							→	Cd extracted by EDTA	
							↑	Cd in Ryegrass shoots	
	-	-	1%	5.0	12.4	24	↓	Cd and Pb extracted by HCl, $Ca(NO_3)_2$, EDTA	Chen *et al.* 2000

	↓ Uptake in wheat shoot (Cd, Pb)

↓: represents a decrease;

↑: represents an increase;

→: indicates no change.

Except for As and Cr (Foster *et al.* 2003; Kumpiene *et al.* 2008), the use of synthetic Mn oxides has not been extensively studied for metal stabilisation in contaminated soils, even though they offer strong sorption capacities (Komárek *et al.* 2013) and successfully reduce metallic element mobility in contaminated soils (Mench *et al.* 1994; Mench *et al.* 1997; Sappin-Didier *et al.* 1997; Hettiarachchi *et al.* 2000; Hettiarachchi and Pierzynski 2002). Another potential remediation possibility consists of using *in-situ* permanganate oxidation. Manganese oxides are produced during the *in situ* chemical oxidation of organic contaminant with permanganate (Siegrist *et al.* 2002). According to this technique, the MnO_2 created seems to be amorphous when produced in an aquifer (Loomer *et al.* 2010). Crimi and Siegrist (2004b) studied the behaviour of Cd with a MnO_2 particle formed during the *in-situ* oxidation of permanganate. The sorption of Cd onto the newly created particle depends on: the particle concentration, soil pH, the presence of Ca in the reaction matrix, and the rates of particle generation and agglomeration. Calcium seems to play a role by affecting the rate of particle generation (Crimi and Siegrist 2004ab).

Chapter II:

Stabilisation of metallic elements in soil using AMO

III. Characterisation of the new manganese oxide

In order to study this amorphous manganese oxide (AMO), its properties will first be examined. The following article presents the characteristics and sorption properties of AMO; these data allow for a better understanding of this oxide and can provide an initial response to the beginnings question: can we use AMO as a stabiliser for the metallic elements in contaminated soils?

III.1. Article 1: Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide

Abstract: Due to its simple and inexpensive synthesis, a new amorphous hydrous manganese oxide (AMO) has been studied as a possible chemical stabilizing agent for soils contaminated with metals. Preliminary experiments evaluating the stability of AMO in pure water have reported only minor dissolution (5.70% and 0.24% depending on the w/v ratio). Sorption kinetics has shown fast metal adsorption, especially for Pb. The sorption capacities of AMO for Cu, Cd, Pb, and Zn have been described and compared with synthetic birnessite for pH 4 and 5.5. Both oxides show similar sorption capacities at pH 4 despite the fact that birnessite characteristics (pH of zero point charge, specific surface area and cation exchange capacity) are more favourable for metal sorption. Moreover, the pH adsorption-edges show that the AMO is more pH-dependent than birnessite.

Keywords: Manganese oxide, Sorption, Divalent metal cations, Birnessite

Highlights: ►A new amorphous hydrous manganese oxide (AMO) has been studied ►Easy and cheap to synthesize ►Sorption capacities of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} equal to that of birnessite ►A possible chemical stabilizing agent for soils contaminated with metals.

Journal of Colloid and Interface Science 399 (2013) 99-106

Adsorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} onto a synthetic Mn oxide

Loïc Della Puppa[a,b] , Michael Komárek[a,*] , François Bordas[b], Jean-Claude Bollinger[b] , Emmanuel Joussein[b]

[a] *Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, Prague 6 - Suchdol, 165 21, Czech Republic*

[b] *Groupement de Recherche Eau Sol Environnement, Université de Limoges, Faculté des Sciences, 123 Avenue Albert Thomas, 87060 Limoges, France*

Introduction

The behaviour and mobility of metals/metalloids in soils are significantly influenced by their sorption onto soil organic matter, clay minerals and secondary Fe and Mn (oxy)hydroxides (hereafter referred to as oxides). The main immobilization processes include adsorption and surface precipitation, and the parameters affecting these processes are mainly soil pH, soil composition and speciation of metals/metalloids (Bradl 2004).

Based on these assumptions, several methods for soil remediation (when contaminated with metals) have been studied, by the use of various amendments, e.g. zerovalent Fe, compost, phosphate, lime, clay minerals and a combined chemical method with phytoremediation (Mench *et al.* 2010). These methods are all based on the reduction of metal/metalloid mobility through adsorption, complexation and (co)precipitation processes (Kumpiene *et al.* 2008). Chemical stabilization using oxides represents another important stabilization practice. The application of zerovalent iron as a precursor of Fe oxides has been successfully studied for metal immobilization (Stumm and Morgan 1996; Roh *et al.* 2000; Bes and Mench 2008). Despite their high immobilization potential, Mn oxides have been examined to a much lesser extent for chemical stabilization than Fe oxides (Kumpiene *et al.* 2008; Komárek *et al.* 2013).

Being ubiquitous soil components, Mn oxides could offer a major sink source for metal immobilization (Acosta *et al.* 2011; Crimi and Siegrist 2004a; Komárek *et al.* 2013); they typically occur as coatings and fine-grained aggregates and moreover can efficiently control the evolution and mobility of metals even at low concentrations in soils (O'Reilly and Hochella 2003; Kanungo *et al.* 2004; Su *et al.* 2010). Except for As and Cr (Mench *et al.* 1994; Almeida *et al.* 2008; Foster *et al.* 2003; Kumpiene *et al.* 2008), the use of synthetic Mn oxides has not been extensively assessed with regard to metal stabilization in contaminated soils despite such favourable and strong sorption characteristics (Komárek *et al.* 2013). Manganese oxides could therefore become a valuable alternative in chemical stabilization (Mench *et al.* 1994; Hettiarachchi *et al.* 2000). The aim of the present study is to evaluate the sorption properties of a new synthetic amorphous hydrous manganese oxide (AMO) prepared according to a protocol modified from that developed by Ching *et al.* (1997), which is commonly applied for the preparation of birnessite.

Materials and methods

The solutions of metal elements introduced into sorption experiments were prepared using hydrated $CuNO_3$, $CdNO_3$, $ZnNO_3$ and $PbNO_3$ salts. A 0.01 M $NaNO_3$ solution served as the background electrolyte to set the ionic strength of the experimental solution. Deionized water from the Sci-aqua water system (with a conductivity of less than 0.14 $\mu S.cm^{-1}$) was part of all solution preparations. All chemicals used were of analytical grade.

Synthesis of the manganese oxides:

The amorphous manganese oxide (AMO) was prepared according to a modified sol-gel procedure (Ching *et al.* 1997) (advised for the preparation of birnessite), consisting of adding 0.5 L of a 1.4 M glucose solution to 0.5 L of a 0.4 M $KMnO_4$ solution. After gel formation, the solution was filtered and washed with 2 L of pure water in order to remove the excess of reactants. The gel was subsequently dried at room temperature. The protocol modification omitted the heating step (at 400°C) after gel drying. Pure birnessite was prepared according to the McKenzie (1971) protocol, which consists of adding drop wise 1 L of a 1 M HCl solution to 1.25 L of a 0.5 M boiling $KMnO_4$ solution. The solution was then left to cool at room temperature, filtered and washed with pure water.

Characterization of the manganese oxides:

X-ray diffraction (XRD) patterns were obtained using a Brucker-AXS D 5005 powder diffractometer featuring CuKα radiation ($\lambda K\alpha$ = 0.154186 nm) and a graphite back monochromator. These patterns were derived under the following conditions: a dwell time of 2 s, and a 0.04° (2θ) step. FTIR spectra were generated from a ThermoFischer Scientific 380 infrared spectrometer (Nicolet) by implementing the attenuated total reflection (ATR) method. IR spectra were collected between 500 and 4,000 cm^{-1}, with a resolution of 4 cm^{-1}. The commercially available software OMNIC (Nicolet Instruments) was run for the data acquisition and spectral analysis. Oxide morphology was investigated using scanning electron microscopy (SEM, Philips XL 30, 20 kV, SERMIEL - Université de Limoges, France) coupled with an EDS apparatus; over 50 SEM-EDS analyses were performed for each sample studied. The BET surface was determined at 105°C with the Quantachrome Instruments Nova® e-Series equipment.

The pH of the synthesized oxides was measured using either a 1/2.5 w/v ratio with deionized water or a 1 M KCl (ISO 10390) in conjunction with a Crimson micro pH 2000 pH-meter equipped with a combined electrode (reference Ag/AgCl) calibrated with two buffers (pH 4.01 and 7.00 at 25°C). The acidity constant and pH_{ZPC} (Zero Point Charge) were determined by acid-base titration according toDavranche *et al.* (2003). The zeta potential was calculated using Alphaphot-2 NIKON with the software ZetaPhoremeter II and a w/v ratio of 1/500. The cation exchange capacity (CEC) was measured by employing the cobalt hexammine trichloride method (NF EN ISO 23470). These samples were mixed for 3 hours with a 0.016 M cobalt hexammine trichloride solution at a w/v ratio of 1/5 and filtered on 0.2-µm cellulose nitrate filter (VWR).The excess $Co(NH_3)_6^{3+}$ was analysed with a UV-visible spectrophotometer (Shimadzu UV-160) at 470 nm.

The average oxidation state of Mn was determined by applying the method described in Murray and Balistrieri (1984), 100 mg of solid was suspended in 50 mL of water; then, 10 mL of NaI solution (90 g in 150 mL) were added followed by 3 mL of 2 M H_2SO_4. The solution was stirred until achieving complete dissolution of the solid and titrated with a 0.18 M $Na_2S_2O_4$ solution. Each characterization was performed in triplicate.

AMO stability in pure water:

The stability of this AMO was evaluated in a preliminary experiment that consisted of monitoring both the pH and amounts of Mn and K released into the solution during stirring in pure water at two different w/v ratios (1/500 and 1/10). Oxygen consumption was measured for 11 days in the Oxytop® (WTW) system in order to observe the influence of AMO on microorganism respiration at a 1/500 w/v ratio and 22°C.

Kinetics of metal sorption onto AMO and birnessite:

Kinetic batch experiments were performed at two different pH values (4.0 and 5.5) and at a 1/500 w/v ratio. The pH was manually set using 0.1 M HNO_3 and 0.1 M NaOH solutions. The initial metal concentration was fixed at 1 mM. After stirring (200 rpm on a KS501 orbital table, IKA Labortechnik), samples were filtered using a 0.2-µm cellulose acetate filter (VWR); moreover, the concentrations of studied metal elements (Cu, Cd, Zn, Pb) remaining in solution were analysed by means of ICP-OES (Agilent Technologies 720 Series). The difference between initial and final values provided the metal element amounts adsorbed per gram of adsorbent. Each experiment was conducted in triplicate (the values shown represent the average and standard deviation).

Two distinct kinetic models were introduced for data interpretation: i) a pseudo-first order, and ii) a pseudo-second order (Limousin *et al.* 2007). Modelling results indicated that only the pseudo-second order kinetic model actually fit the data:

Equation 7: Pseudo-second order

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

where k_2 is the pseudo-second-order rate constant ($g.mmol^{-1}.min^{-1}$), q_e ($mmol.g^{-1}$) the amount adsorbed at equilibrium, and q_t ($mmol.g^{-1}$) the amount adsorbed at time *t*. When t = 0 and q_t = 0 (initial conditions), the equation becomes:

Equation 8: Pseudo-second order at t = 0 and q_t = 0

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The adsorption rate constant k_2 can be obtained from the slope of the linear plot of $t/q_t = f(t)$.

Sorption isotherms and adsorption edges:

Sorption experiments (with Cu, Cd, Zn, Pb) were performed using 24 h as the equilibrium time (as determined from the kinetic study) at a w/v ratio of 1/500 in HD-PE bottles. For sorption isotherms, these experiments were conducted at two pH values (4.0 and 5.5). Each metal element was studied both individually and simultaneously in order to evaluate possible competition effects. The pH was manually set using 0.1 M HNO_3 and 0.1 M NaOH solutions. After stirring (200 rpm), samples were filtered (with a 0.2-µm cellulose acetate filter) and the concentrations of Cu, Cd, Zn, Pb and Mn remaining in solution were analysed. The difference between initial and final values yielded the amount of metal elements adsorbed per gram of adsorbent. Each experiment was conducted in triplicate, with the values shown representing the average and standard deviation.

According to pH and metal concentration values, the potential risks of metal precipitation were predicted by speciation modelling using the MINEQL+4.6 software (Schecher and McAvoy 2003). Sorption isotherms could therefore be constructed according to two distinct approaches: i) classical isotherms, where the total amount of metals was added at the start of the experiment; and ii) multiple addition sorption isotherms, where a solute concentration of 1 mM was initially introduced and another 1 mM (1 mL of a 50 mM solution) was subsequently added every day in order to limit precipitation risks at higher metal concentrations. Each step lasted 24 h (i.e. the equilibrium time as determined from the kinetic study). The data were fitted to the Langmuir isotherm as follows:

Equation 9: Langmuir equation

$$S = \frac{S_{max} * K * [M^{2+}]}{1 + K * [M^{2+}]}$$

where S_{max} denotes the maximum sorption capacities ($mmol.g^{-1}$), K the Langmuir constant ($L.mmol^{-1}$), and $[M^{2+}]$ the concentration of metal elements in solution ($mmol.L^{-1}$). The Langmuir sorption isotherm parameters were obtained from the Bolster and Hornberger (2007) spreadsheets using nonlinear fitting models based on the least sum of squared errors.

Adsorption edge studies were conducted with metal concentrations fixed at 1 mM, and the pH was manually set to vary from 4.0 to 7.5 in the presence of 0.1 M HNO_3 and 0.1 M NaOH solutions and maintained during all the experiment. The samples were then filtered (using 0.2-µm cellulose acetate) and the filtrate was analysed to determine the remaining metal concentration in solution. Each experiment was conducted in triplicate; the given values represent the average and standard deviation.

Results and discussion

Characterization of the solids:

SEM images of the amorphous manganese oxide (AMO) are presented in Figure 8 at two different scales. Figure 8a shows that particles are agglomerates several micrometers in size and display conchoidal fractures. The presence of a film covering the surface is characteristic of a solid originating from a sol-gel procedure (Fig. 8b) and does not reflect any defined morphology that would indicate the amorphous nature of the solid. When using chloroethylene instead of glucose, the Mn oxide exhibits a cluster of small needle-shaped crystals (Li and Schwartz 2004), thus underscoring the impact of the organic compound type. The measured particle size distribution follows a Gaussian curve (600-1,200 nm), with a maximum at 1,000 nm.

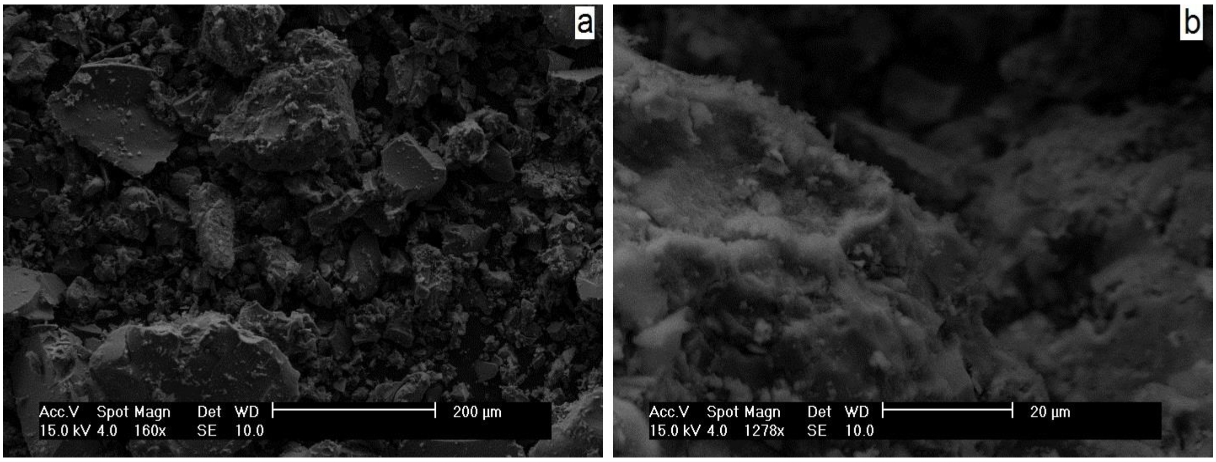

Figure 8: SEM images of the AMO.

Figure 9 shows the XRD spectra of both the AMO and birnessite. Despite a well-defined yet low-intensity peak, i.e. matching the pattern of birnessite, the XRD spectra reveal that the synthesized Mn oxide is amorphous. The prepared birnessite is a single-phase mineral, as indicated by three peaks at 3.68, 2.43 and 1.42 Å in its XRD pattern (XRD JCPDS file 23-1239), which prove to be characteristic for this mineral phase (Ching *et al.* 1997; Lu *et al.* 2009).

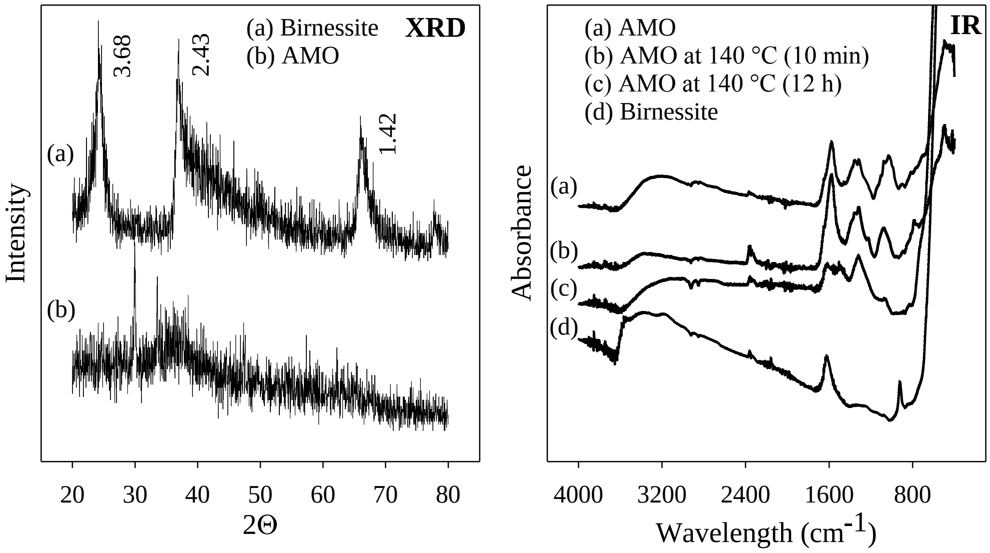

Figure 9: XRD spectra of the AMO and birnessite and IR spectra of AMO (a), AMO heated at 140 °C for 10 min (b), for 12 h (c) and birnessite (d).

The AMO IR spectra (Fig. 9) displays bands at around 1,100 cm^{-1}, 2,900 and 3,000-3,600 cm^{-1}, which might possibly correspond to glucose bands (νC-O, νC-Hn and -O-H) originating from the glucose residue present even after washing (correlated with the organic carbon content, 17.0 mg of C.g^{-1}). The band around 3,000-3,600 cm^{-1} might also correspond to the stretching vibrations of both the O-H group of water molecules and the lattice O-H groups (Eren *et al.* 2011). The band between 400 and 800 cm^{-1} can be attributed to the Mn-O lattice vibrations, while position and/or intensity changes can be associated with changes in the octahedral layered substructure (Kang *et al.* 2007; Nwachukwu and Pulford 2011; Oliveira *et al.* 2014). The band around 1,600 cm^{-1} is typically attributed to O-H bending vibrations combined with Mn atoms (Lu *et al.* 2009). When heating the AMO to 140°C, a peak appears around 600 cm^{-1}, corresponding to the birnessite structure (Feng *et al.* 1997; Nwachukwu and Pulford 2011; Oliveira *et al.* 2014). At 140°C, the band around 1,000 cm^{-1} disappears, which could be due to glucose degradation. After heating, the AMO structure changes, meaning that AMO becomes unstable as temperature increases. The IR spectra show a better fit with the birnessite spectra, indicating that AMO becomes more crystallized. The AMO can be considered as a protophase of birnessite during the sol-gel synthesis.

Chemical properties of the solids

Table 7 summarizes the main physicochemical characteristics of the AMO and birnessite.

Table 7: Characteristics of birnessite and AMO.

	pH $_{H2O}$	pH $_{KCl}$	pH $_{ZPC}$	CEC (meq.100g^{-1})	pKa$_1$	pKa$_2$	SSA (m^2.g^{-1})
Birnessite	3.3 ± 0.1	2.1 ± 0.1	2.7 ± 0.3	247 ± 29	1.1 ± 0.1	4.4 ± 0.3	76.5
AMO	8.1 ± 0.3	7.9 ± 0.1	8.3 ± 0.1	34 ± 1	6.9 ± 0.1	9.6 ± 0.1	14.8

The difference between pH$_{H2O}$ and pH$_{KCl}$ values of birnessite indicates the presence of H^+ sorbed on the surface, which is not the case for AMO. Surface acidity constants pKa$_1$ and pKa$_2$ are acidic for birnessite, while those of the AMO are basic. At pH 4.0 and 5.5 (i.e. the conditions of the sorption experiments), the birnessite surface is therefore theoretically negatively charged, as opposed to the AMO surface, which is theoretically positively charged. The pH$_{ZPC}$ value of the AMO is basic (8.3), in contrast with other Mn oxides prepared from the oxidation, for example, of trichloroethylene (pH 3.7) (Li and Schwartz 2004). This value has been confirmed by a fast method that consists of measuring the pH value of oxide suspension (1/100 w/v ratio) in a 0.01 M $NaNO_3$ solution, which lies near the pH$_{ZPC}$ value (Pan *et al.* 2004). For AMO, the measured pH under this condition equals 8.20 (3.14 for birnessite). This value is similar to that obtained by following the Davranche *et al.* (2003) protocol. The results derived with birnessite synthesized using concentrated HCl and hot $KMnO_4$ solutions are in good agreement with values found in the literature (Park *et al.* 2011); however, this value is protocol-dependent (Tan *et al.* 2008). The pH$_{ZPC}$ values found here suggest more favourable adsorption for cations onto birnessite than onto AMO, due to the negative surface charge on birnessite at pH 4 and 5.5.

The CEC value of birnessite (247 meq.100g^{-1}) is greater than that of the AMO (34 meq.100g^{-1}) and in good agreement with the value observed by Golden *et al.* (1986). Moreover, the specific surface area of birnessite is greater than that of the AMO (Table 1); however, the various BET values listed in the literature (32.6 m²/g, 34.2 m²/g, 19.3 m²/g; Arai

2011; Eren *et al.* 2011; Yin *et al.* 2011) can be explained by the fact that BET analyses are strongly temperature-dependent. Using trichloroethylene instead of glucose, Li and Schwartz (2004) found a specific surface area of 23.6 m²/g, which is closer to the AMO value (14.8).

All of the measured parameters seemed to be predicting better sorption properties for birnessite: higher CEC and BET, and a theoretically negatively charged surface due to its pH_{ZPC} value and the pH value set during the adsorption experiments. The average Mn oxidation state (AOS) in the AMO is about 2.52, which indicates that one Mn atom can be linked to 1.26 O atoms. Moreover, after 24 h of stirring in pure water at a w/v ratio of 1/500, this AOS value rises from 2.52 to 3.04, thus reflecting an increasing average Mn oxidation state. This outcome could be due to the release of weakly bound Mn from the AMO surface with an AOS greater than 3.04, originating from a residual fraction of the $KMnO_4$ reactant.

Stability of the AMO in pure water:

The w/v ratio of 1/500 reveals, to some extent, the AMO behaviour just before natural dispersion into the soil (migration, transport by pore water), whereas the 1/10 ratio simulates the behaviour before dispersion, when the solid is locally located. For both ratios, the pH is close to 7 and remains stable over time (Fig. 10).

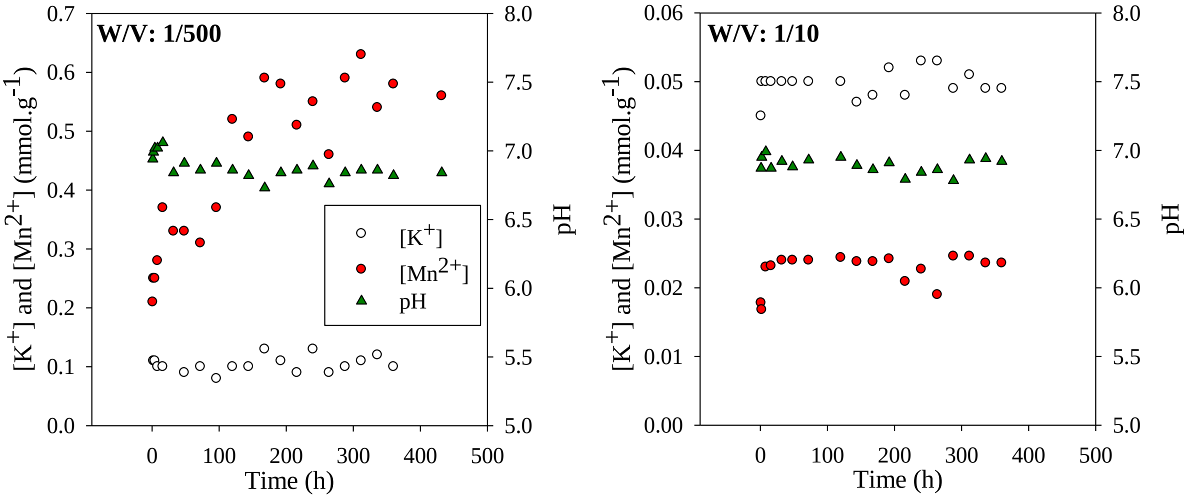

Figure 10: Stability of AMO at 1/500 and 1/10 w/v ratio in pure water.

The AMO appears to be stable for both the 1/500 and 1/10 w/v ratios after 200 h of stirring in pure water. Two dissolution steps (Fig. 10) are observable for the 1/500 w/v ratio; the first step is reached after 20 h of stirring and might correspond to the release of weakly adsorbed Mn. The second step is reached after 200 h and might correspond to dissolution of the AMO (with Mn released into the solution accounting for 5.7 % of total AMO content). For the 1/10 ratio, the AMO seems to be more stable, with less dissolution due to displacement of the dissolution balance within the solution. Another Mn dissolution step is observable (Fig. 10) near 10 h, probably due to dissolution and/or release of the weakly bound Mn (an amount representing 0.24% of the solid). Regardless of the w/v ratio, the AMO seems to be stable in water. The potassium in solution was stable throughout the experiment and might have originated from the weakly bound fraction at the oxide surface and/or, to some extent, AMO dissolution. Because Ching et al. (1997) found no potassium inside the birnessite structure synthesized by the sol-gel method means that the potassium most likely originated from both the weakly bound fraction at the oxide surface and the residue of $KMnO_4$ used during the AMO synthesis.

The effect of the presence of AMO and birnessite on microbial respiration was monitored through O_2 consumption measurements. In the presence of birnessite, low O_2 consumption was observed (Fig. 11).

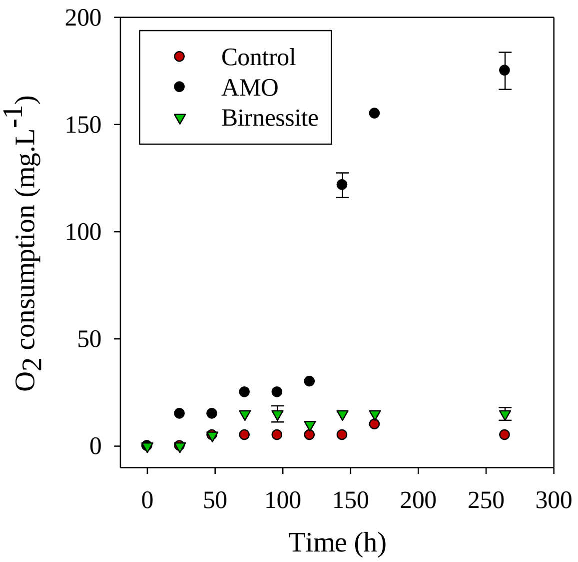

Figure 11: Consumption of O_2 in presence of AMO and birnessite in pure water using 1/500 w/v ratio.

On the other hand, the AMO increased the level of O_2 consumption, especially after 25 h, which corresponds to the activation of natural microbial flora. This result demonstrates that the AMO may exert no significant toxic effect on microbial flora. The time necessary to activate microbial flora corresponds to the start of the 2nd step observed during Mn solubilisation, a determination that could be explained by the fact that the degradation of residual glucose (used in AMO synthesis) enhances microbial activity, thus improving either AMO dissolution or the release of Mn weakly bound to the solid. The organic carbon content in AMO lies near 17.0 mg of $C.g^{-1}$, which confirms the presence of an organic glucose residue.

Sorption kinetics

The adsorption of metals on both solids occurs during the first few minutes (Fig. 12), with Pb being the most quickly adsorbed.

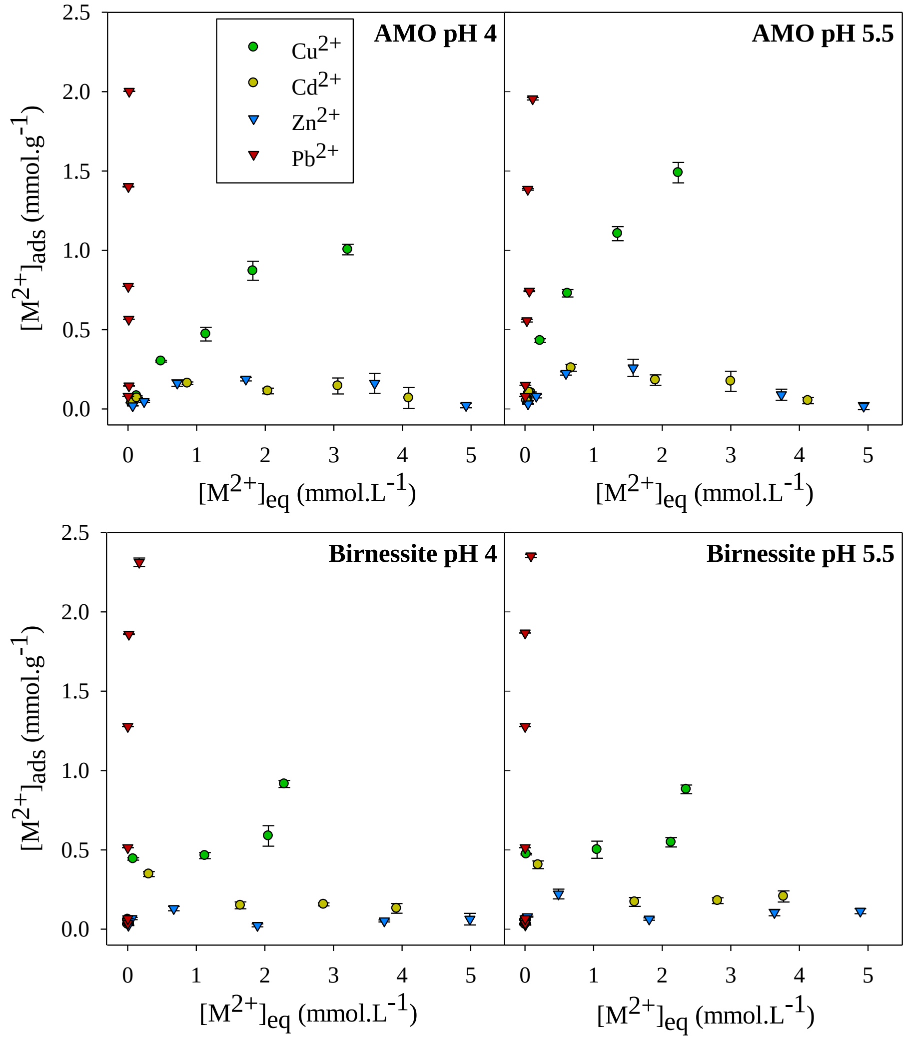

Figure 12: Kinetic sorption of Cu, Cd, Zn and Pb onto AMO at pH 4 and 5.5 and birnessite at pH 4 and 5.5 using 1/500 w/v ratio and 1 mM metallic element solutions in 0.01 M $NaNO_3$.

During subsequent experiments, a time of 24 h was set as the optimal contact time on the basis of these results and for practical reasons. In the case of birnessite, the sorption of metal elements is not modified by the pH value over the studied range, which can be explained by: the high cationic exchange capacity, high specific surface area, and low pH_{ZPC} value (2.7) of birnessite. Sorption on the AMO is more acutely affected by pH value (i.e. better at pH 5.5 than at pH 4.0) due to its lower CEC, specific surface area and pH_{ZPC} (8.3). The adsorption of metal elements increases the pH_{ZPC} values (data not shown herein), thus indicating that specific adsorption occurs on both oxides (Stumm and Morgan 1996). Manganese oxides do in fact adsorb metals primarily in the form of specific adsorption (McKenzie 1980; Sizmur and Hodson 2009).

Pseudo-first and pseudo-second order kinetic models have been applied to the experimental data, whose fit shows that the pseudo-second order is more suitable. The parameters calculated using linear regression are listed in Table 8.

Table 8: Pseudo-second order kinetic parameters of metallic elements adsorption onto AMO and birnessite at pH 4 and pH 5.5.

AMO	pH 4			pH 5.5		
	q_{max} (mmol.g^{-1})	k_2	R^2	q_{max} (mmol.g^{-1})	k_2	R^2
Cu	0.294	0.187	1.00	0.453	0.447	1.00
Cd	0.289	0.111	1.00	0.438	0.075	1.00
Zn	0.343	0.397	1.00	0.460	0.335	1.00
Pb	0.600	0.378	1.00	0.604	0.522	1.00

Birnessite	pH 4			pH 5.5		
	q_{max} (mmol.g^{-1})	k_2	R^2	q_{max} (mmol.g^{-1})	k_2	R^2
Cu	0.499	0.917	1.00	0.500	0.499	1.00
Cd	0.501	0.121	0.99	0.496	1.298	1.00
Zn	0.475	0.514	1.00	0.481	0.394	1.00
Pb	0.554	2.775	1.00	0.553	573.3	1.00

The pseudo-second order rate constant (k_2) represents the affinity of the metal element for the solid. When comparing the affinity of these metal elements for AMO and birnessite, it appears that they present a greater affinity for birnessite regardless of pH (especially in the case of Pb). This greater affinity of metal elements for birnessite can be partially explained by the pH_{ZPC} and BET values, hence resulting in a higher specific surface area and a negatively charged surface under the given experimental conditions, which favour adsorption.

Adsorption isotherms:

Standard isotherms:

As expected, Figure 13 and Table 9 show that the sorption capacities of Cu, Cd, Zn and Pb increase with pH.

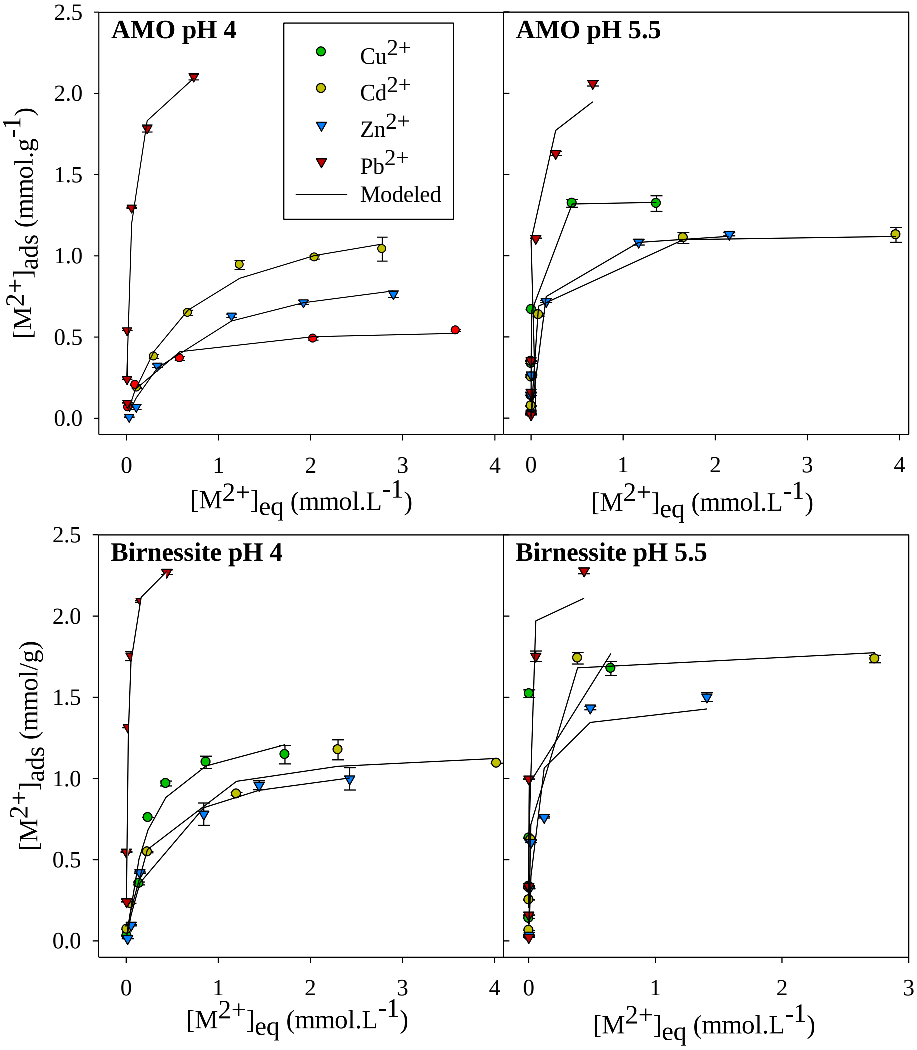

Figure 13: Sorption isotherms of Cu, Cd, Zn and Pb onto AMO at pH 4 and 5.5 and birnessite at pH 4 and 5.5 using 1/500 w/v ratio.

For the metal elements studied herein, the sorption capacity (S_{max}) of AMO at pH 4.0 respects the following order: Pb > Cu > Zn > Cd, and at pH 5.5: Pb > Cu > Cd > Zn. For birnessite, at pH 4: Pb > Cu > Zn > Cd, and at pH 5.5: Pb > Cu ≈ Cd > Zn. Similar results have been observed by other authors (Covelo *et al.* 2007; Wang *et al.* 2012). Lead is strongly adsorbed on both oxides. It has been shown that Pb is capable of occupying both the interlayer and surface edge sites (O'Reilly and Hochella 2003; Wang *et al.* 2012).

When the metal elements are considered individually, birnessite is more effective in sorbing metal elements than the AMO, as justified by the respective K values (Table 9).

Table 9: Characteristics of modelled Langmuir isotherm for birnessite and the AMO.

		Birnessite				AMO			
		Cu	Cd	Zn	Pb	Cu	Cd	Zn	Pb
pH 4	S_{max}	1.33	1.33	1.17	2.09	1.33	0.55	0.98	2.23
	K	193	19.0	10.8	21.0	1.50	4.95	1.38	20.1
	E	0.993	0.836	0.936	0.958	0.991	0.982	0.989	0.960
pH 5.5	S_{max}	1.80	1.79	1.48	2.13	1.38	1.20	1.14	2.38
	K	300	39.6	21.1	218	4.15	3.84	3.07	49.9
	E	0.815	0.972	0.892	0.929	0.960	0.980	0.987	0.960

Regarding maximum sorption capacities (S_{max}), the values are similar for the two sorbents despite the fact that birnessite has a greater CEC and specific surface area while a lower pH_{ZPC}. The accessibility of surface sites relative to both solids most certainly differs.

The results presented in Figure 14 were obtained by mixing multi-metal element solutions, containing all four elements, with the solids in order to highlight potential competition phenomena.

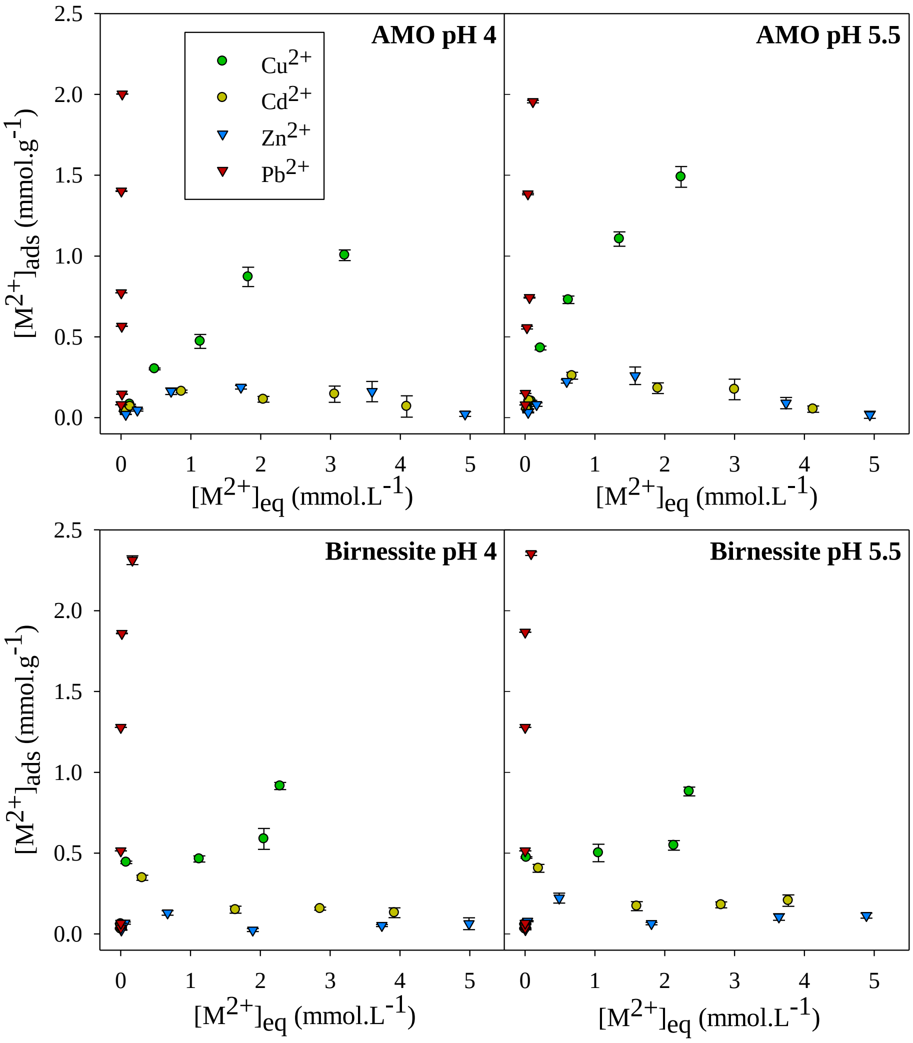

Figure 14: Simultaneous adsorption of Cu, Cd, Zn and Pb on AMO at pH 4 and 5.5 and birnessite at pH 4 and pH 5.5.

Compared to the results found for each metal examined individually (Fig. 13), the amount of adsorbed Cd and Zn decreases as the amounts of Cu and Pb increase. Lead is the most strongly sorbed and the main competitor, displaying high affinity for both oxides. These results are in good agreement with the kinetic results (Table 8), as a consequence of the competition taking place between metal elements during their sorption; as previously shown, Cd and Zn have less affinity for the oxides than Cu and Pb.

Figure 15 shows the total amount of metals sorbed onto the solid *vs.* the total amount of metal in solution at equilibrium during the competition experiments.

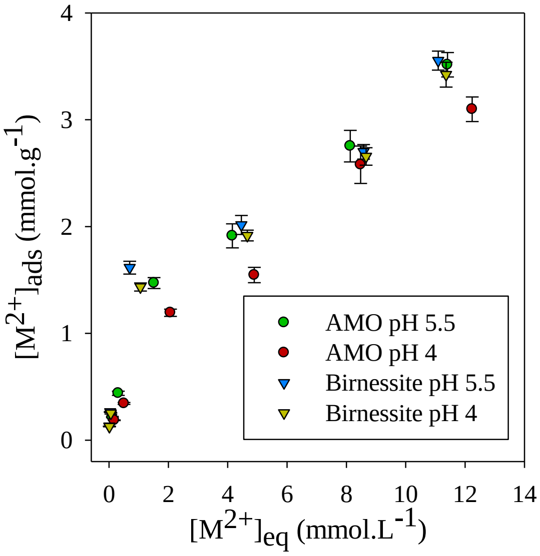

Figure 15: Total amount of Cu, Cd, Zn and Pb adsorbed onto AMO and birnessite as a function of total concentration in solution at pH 4 and 5.5.

It appears that despite the higher CEC and specific surface area of birnessite, the total sorbed amount is similar for both solids, except at pH 4.0. Therefore, the effective sorption of metal elements by AMO and birnessite is not directly correlated with their physicochemical properties (CEC, specific surface area, pH_{ZPC}). To explain these results, the surface charge of AMO was determined by zetametry (Fig. 16).

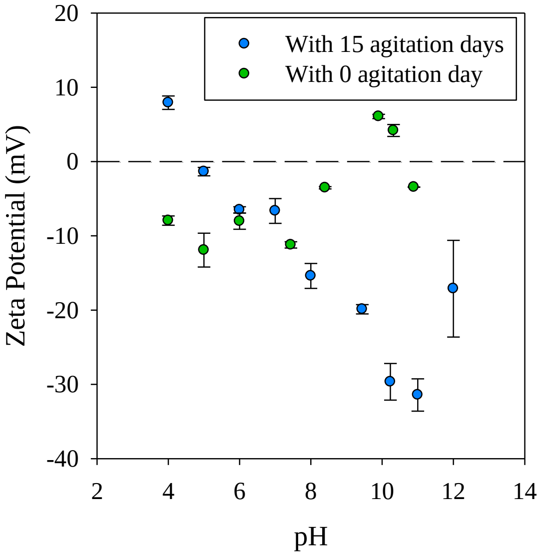

Figure 16: Zeta potential of the AMO in pure water at two different contact time (0 and 15 days) for a range of pH.

With a freshly prepared AMO suspension, a pH_{ZPC} value of 9.0 was obtained, i.e. close to the value found by titration. Under these conditions, the variation in surface charge *vs.* pH is small and not correlated with either the protonation or deprotonation of the surface. However, when the AMO is in suspension for several days before the determination step, the pH_{ZPC} value output by zetametry equals 4.8. Under such conditions, the charge increases as pH values decrease, which is in good agreement with the protonation. These results have shown that AMO surface properties change with the contact time in aqueous solutions. This instability may be explained by the release of manganese weakly bound to the solid or by hydration of the newly-formed oxide or residual MnO_4^- ions, which are unstable in solution. Under the experimental conditions of sorption isotherms (pH 4 or 5.5), the surface charge of AMO is thus near zero or even negative, which could potentially explain the sorption properties of the AMO (Fig. 16).

Moreover, as revealed for example by Tunius and Sköld (1990) with Al oxide, the entire specific surface of a solid is not necessarily available for sorption. The Mn sorbed on the oxide surface might also interfere with the specific surface area measurement, thereby clogging some of the smaller pores and reducing the available area for N_2 sorption during the BET measurement (Eren *et al.* 2011).

Multi-adding isotherms:

The speciation of metal elements in the bulk solutions was determined using the speciation program MINEQL+4.6 (Jalali and Khanlari 2008). The standard databases included with the software were applied. Each metal element has been considered separately, by taking into account the pH value, temperature, atmospheric CO_2, ionic strength, and Na and NO_3 concentrations (from the salt of metal elements as well as the background electrolyte).

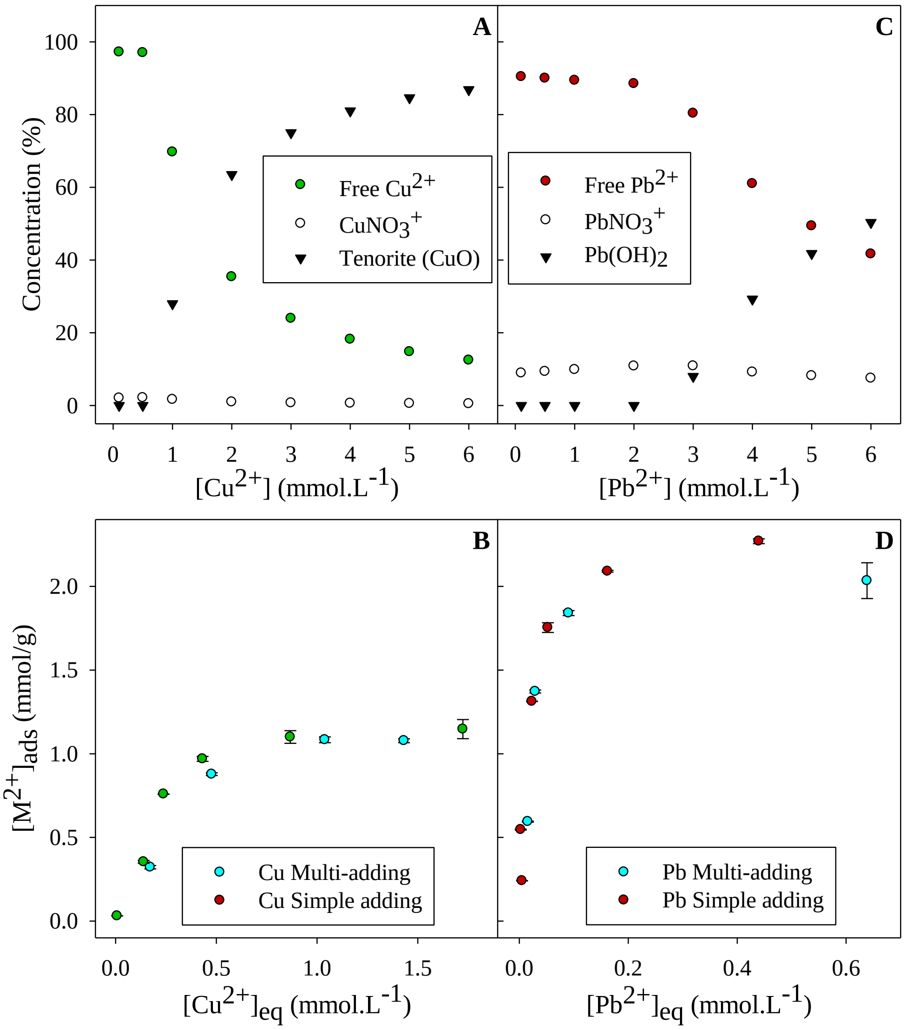

Figure 17: Cu (A) and Pb (C) speciation at pH 5.5 in $NaNO_3$ 0.01 M solution and adsorption isotherms of Cu (B) and Pb (D) at pH 5.5 onto AMO: comparison between simple and multi adding.

The figure 17A and C present the speciation of Cu and Pb at pH 5.5. Results for pH 4.0 were not shown due to the fact that free Cu^{2+} and Pb^{2+} account for over 95% of the total metal. Precipitation can occur whenever the concentration exceeds 1 mM for Cu and 3 mM for Pb. The thermodynamic calculations performed with MINEQL+4.6 indicate that Cu and Pb can precipitate at pH 5.5 (as CuO and $Pb(OH)_2$, respectively). In order to prevent any risk of precipitation, multi-adding batch experiments were conducted: 1 mM of metal elements was added on a daily basis until the desired cumulative amount was reached.

The results obtained for Pb and Cu at pH 5.5 by means of simple (classical) and multi-adding isotherms are similar (Fig. 17B and D), which confirms that Cu and Pb do not precipitate in the solution under our experimental conditions, despite speciation calculations predicting the formation of CuO and $Pb(OH)_2$. As previously shown, the AMO and birnessite adsorbed the metal elements very quickly and, consequently, limited the precipitation risk. The random nature of the first step of the precipitation phenomenon should also be mentioned and typically appears as a result of highly oversaturated solutions.

pH adsorption edges

The pH adsorption edges (Fig. 18) were determined from pH 4 to 8, since below pH 4 the AMO is altered while above pH 8 metal precipitation occurs.

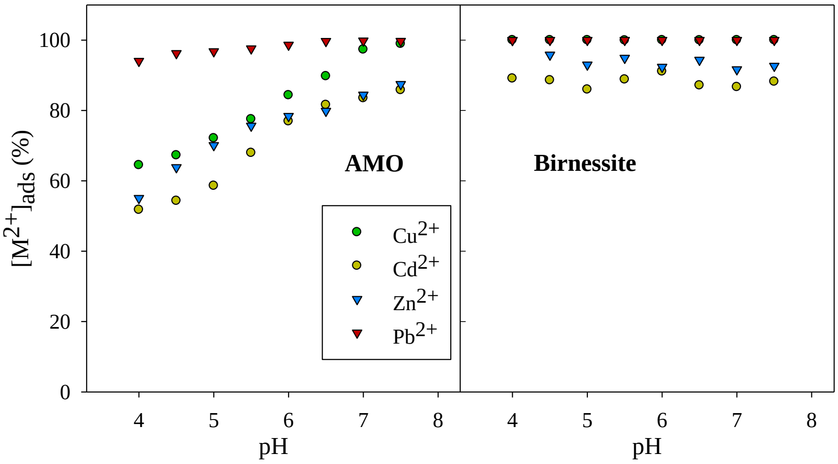

Figure 18: The pH adsorption edges of Cu, Cd, Zn, Pb onto AMO and birnessite.

For birnessite, no significant pH effect on metal adsorption has been observed. The sorption rate normally decreases at lower pH values (as both the surface charge and competition between protons and metal elements increase), though the affinity of birnessite for metals is still sufficient to maintain the high adsorption rate, with sorption starting below pH 4 due to the pH_{ZPC} value. For the AMO, the strong sorption of Pb overshadows the pH effect; only a small increase in adsorption with increasing pH values is observable. For Cu, Cd and Zn, this adsorbed amount increases significantly as pH values rise. In comparison with birnessite, the sorption properties of the AMO are considerably affected by pH values due to the lower affinity of metal elements for AMO.

Conclusion

The AMO described in this work seems to be stable in pure water despite the appearance of some dissolution shortly after its contact with water (5.70% and 0.24% of the total amount at 1/500 and 1/10 w/v ratios, respectively). Birnessite and AMO display quite similar sorption capacities for the studied divalent metal cations (Cu, Cd, Pb, Zn); however, birnessite adsorbs faster than the AMO. Even though the CEC of AMO (34 meq.100g^{-1}) seems to predict a lower sorption capacity than for birnessite (247 meq.100g^{-1}), results indicate that the AMO acts as an efficient sorbent, especially for Cu and Pb (1.38 and 2.37 mmol.g^{-1} for AMO, and 1.78 and 2.13 mmol.g^{-1} for birnessite at pH 5.5). These findings may be due to the fact that not all of the specific surface is available for sorption as well as to the evolution in surface properties of the AMO in solution *vs.* time, as determined through the zetametry experiment. Adsorption edges show that the AMO is very sensitive to pH variations, in addition to being easy and inexpensive to synthesize and capable of providing a valuable amendment for use in stabilizing metals and metalloids in soils. Nevertheless, its stability in various soil types still needs to be evaluated further.

The pH_{H2O} value for birnessite indicates that for the experimental pH values (4 and 5.5), its surface is negatively charged, unlike for AMO, which exhibits a positively charged surface. Moreover, the AMO specific surface area is less than that of birnessite. Despite the unfavourable conditions, AMO sorption capacity approximates that of birnessite, which is known to be a good sorbent and presents strong potential in a multi-element system. However, the AMO surface apparently evolves over time (as evidenced by the zeta potential measurement before and after agitation in pure water). These results show that AMO is effective in the sorption of metallic cations from a solution despite some alteration during the experiments.

III.2. Quick assessment of AMO toxicity in soil

The potential AMO toxicity was measured by monitoring the respiration of the microbial community using an OxiTop system, which consists of measuring the depression in the flask equipped with a manometric measuring head (OxiTop, WTW, Weilheim). This depression is created by the solubilisation of CO_2 by NaOH pellets, according to the following:

Equation 10: Solubilisation of CO_2 by NaOH

$$CO_{2(g)} + NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + HCO_3^{-}{}_{(aq)}$$

CO_2 is generated as a result of the microbial O_2 consumption. Initially, AMO and birnessite were mixed with soil (at 1% w/w ratio) and a sterile glucose solution (set at 10 $\mu mol.g^{-1}$, with the additional solution volume representing 90% of the soil water holding capacity; Kos and Lestan 2004). The mixture was then left at 25°C for 5 days (Fig. 19). This soil sample is the same as that used in Articles 2 and 3, extracted near a metallurgical site where copper had been refined for years. The means of three replicates are presented, along with error bars representing standard deviations.

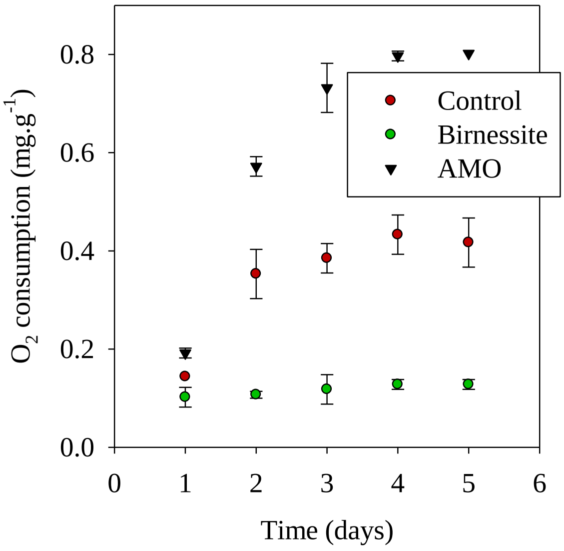

Figure 19: Microbial respiration at 25°C in soil treated with 1% w/w AMO or birnessite, expressed in µmol of consumed O_2 per g of dry soil.

In considering the microbial O_2 consumption in the soil (Fig. 19), like in water (Fig. 11), the presence of AMO doubles the O_2 consumption after 4 days compared to the control sample, whereas the presence of birnessite inhibits soil respiration. Because this increase cannot be due to glucose residue (a glucose solution was added to both the Mn oxide and the control sample), AMO appears not to be toxic and increases soil biomass development. Since AMO and birnessite seem to differently affects soil biomass and given that they are both good sorbent, AMO is able to immobilise metals, which yields an increase in microbial activity. Zhou *et al.* (2008) showed that adding an amendment into a contaminated soil can result in increased microbial activity (depending on the amendment) due to metal immobilisation.

III.3. AMO stability

III.3.1. In water

During AMO characterisation, it appears that depending on the operating protocol, the CEC and Mn average oxidation state (AOS) values have changed. The Table 10 summarises the CEC values with respect to the various operating protocols. CEC was measured according to the cobalt hexammine trichoride method (NF EN ISO 23470). Mn AOS was measured according to the Murray and Balistrieri (1984) protocol, which consists of transforming Mn^{III} and Mn^{IV} into Mn^{II} by means of reducing and measuring Mn^{II} by colorimetric assays. For Mn AOS, AMO was agitated in pure water and then filtered using a cellulose filter.

Table 10: CEC values and Mn AOS of AMO with respect to operating protocol.

Operating protocol	CEC (meq.100g^{-1})
No pH value control (value reached: 7.1)	34 ± 1
pH value set at 5.5	45 ± 2
No pH value control, in a closed atmosphere with N_2 bubbling	15 ± 1
	Mn AOS
Before agitation in pure water, under non-sterile conditions	2.52 ± 0.04
After agitation in pure water, under non-sterile conditions	3.04 ± 0.06
After agitation in a Pb solution, under non-sterile conditions	2.98 ± 0.04
After agitation in pure-water, under sterile conditions	2.94 ± 0.08

Depending on the operating protocol, the CEC value changes. The pH of the solution significantly affects the CEC value;. theoretically however, at pH 5.5 and due to increased competition between H^+ and $Co(NH_3)_6^{3+}$, the CEC value should be lower than at pH 7.1, but such was not the case. This surprising finding could be explained by the release of Mn from the AMO surface by H^+, with H^+ perhaps being more competitive than $Co(NH_3)_6^{3+}$. In a closed atmosphere with N_2 bubbling, the CEC value decreases compared to the other conditions, potentially caused by the anoxic condition, which is capable of leading to an alteration/dissolution of AMO (Renault *et al.* 2009).

In considering Mn AOS, differences appear before and after agitation, whereas no differences appear for both after agitation. This difference may be derived from the release of Mn by AMO in pure water during agitation, as the Mn released is not reduced. No change appears between the agitation in pure water and in the Pb solution when working under sterile conditions. The experiments under sterile conditions were conducted in order to know if the Mn AOS had been modified by bacteria, as some may oxidise or reduce Mn (Gounot 1994).

III.3.2. In soils

The stability of AMO in three different soils was studied by Ettler *et al.* (2014), their findings are presented in the Appendix. Soil samples (200 g) were placed into plastics pots and equipped with rhizon to sample pore water. The AMO (0.5 g) was placed into double-layered polyamide bags (mesh size: 1 µm) and then inserted horizontally into each soil sample, in a procedure that allows retrieving AMO after incubation in soils. Each pot was maintained at 80% of the water holding capacity with pure water. The values of Eh, pH, conductivity, DOC as major cations, anions and trace elements in pore water were all monitored over 90 days. At the end of the experiment, AMO bags were retrieved and analysed for: mass loss, X-ray diffraction, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

The results obtained by Ettler *et al.* (2014) indicate that the incubation experiments were conducted under oxidising conditions (from 363 to 522 mV). AMO only slightly affected the pH of pore water for each soil sample (the increase represented less than 0.5 pH unity compared to the blanks). The AMO partially dissolved (representing 10% - 18% of the total AMO amount), resulting in a release of Mn into pore water. Della Puppa *et al.* (2013) revealed the presence of Mn provided by AMO in water, mainly due to the partial dissolution of AMO and the release of Mn weakly bound to the AMO surface. Moreover, Ettler *et al.* (2014) showed that the Mn concentration in pore water is linked to the pore water pH value, with the highest concentration being observed in the most acidic soil (pH: 4.2) and the lowest in the near-neutral soil (pH: 7.3). Increased DOC in pore water compared to the blank was also observed, mainly at the beginning of the experiment, meaning that AMO may be responsible for the dissolution of soil organic matter. However, a portion of the DOC can be derived from AMO glucose residue (AMO carbon content: 17.0 $mg.g^{-1}$).

The monitoring of AMO mass loss over time has initially resulted in a decrease in bag weight due to the partial AMO dissolution (which is significantly correlated with the pore water pH value), followed by an increase in bag weight. This increase may be tied to the massive formation of newly-formed phases inside the AMO bags (as confirmed by XRD data and SEM analyses). Moreover, EDS analyses show that AMO particles incubated in the near-neutral soil are covered by a carbonate layer. An increase in AMO particle size was also observed.

This study clearly suggests that AMO properties evolve over time, possibly resulting in sorption property changes. Furthermore, the changes in other soil properties (e.g. pH, DOC) might lead to sorption property changes, especially changes in metallic element mobility due to the alteration and solubilisation of organic matter. The next step consists of testing the AMO immobilisation potential for both historical and fresh contaminations. The soil samples introduced in the following experiments display parameters closely resembling those of the most acidic soil used by Ettler *et al.* (2014). They are forest soils presenting the same pH value and manganese content with a low organic and inorganic carbon content.

IV. Stabilisation of metallic cations using AMO in a contaminated soil

Following the AMO sorption characterisation, the next logical step calls for its use in soils for testing as an amendment for metallic elements stabilisation. The mobility and availability of the studied metallic elements will be measured under 2 distinct conditions:

- under dynamic conditions through column experiments,
- under static conditions through batch experiments.

These conditions will provide a better understanding of AMO properties under more realistic conditions. Column experiments allow studying AMO and metallic element behaviour during constant lixiviation, whereas batch experiments study the ageing effect on AMO and metallic element behaviour. In both these experiments, the soil sample was historically contaminated (mainly in Cu); and after a "stabilisation" period, it was manually polluted with a mixed metallic cation solution (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}). These steps will serve to examine AMO behaviour on a former contamination now well immobilised in the soil and then on a fresh contamination.

IV.1. Article 2: Dynamic leaching of Cu, Cd, Pb and Zn from a contaminated soil amended with an amorphous manganese oxide

Abstract: Due to its simple and inexpensive synthesis, a new amorphous manganese oxide (AMO) has been studied during column experiments as a potential chemical stabilizing agent for soils contaminated by metals. Four ratios (0, 0.01, 0.1 and 1% w/w) were evaluated as amendments for an industrially polluted soil, and contaminant leaching with pure water and a 0.025 M EDTA solution was examined. The introduction of 1% AMO to the studied soil resulted in an increase in leachate pH and in the SOM dissolution whereas for 0.1%, a decrease in the SOM dissolution was observed. The AMO decreases the amount of metals providing from the historical pollution leached by pure water for 0.1 and 1% AMO ratios. Then, the soil is percolated by a mixed metallic cations solution (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}). The

AMO immobilizes the metals provided by the percolation solution mainly for 0.1% ratio. However, Mn released in the leachates reached high values for 1% (867 mg.kg^{-1}). Only AMO added at 0.1% successfully limits Cu availability during EDTA leaching. Despite the fact that AMO is a good sorbent for the retention of metals in dynamic condition, its behaviour and sorption potential in batch system needs to be examined.

Keywords: Manganese oxide, Metal element stabilization, column experiments, EDTA leaching

Submitted to Journal of Soils and Sediments

Dynamic leaching of Cu, Cd, Pb and Zn from a contaminated soil amended with an amorphous manganese oxide

Loïc Della Puppa[a,b], François Bordas[a*], Michael Komárek[b], Vojtěch Ettler[c]

[a] *Groupement de Recherche Eau Sol Environnement, Université de Limoges, Faculté des Sciences, 123 Avenue Albert Thomas, 87060 Limoges, France*

[b] *Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, Prague 6 - Suchdol, 165 21, Czech Republic*

[c] *Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic*

Introduction

Pollution by metallic elements in soils constitutes a threat to both the environment and human health. Such pollution originates from various industrial (Loska *et al.* 2004) and agricultural activities (Komárek *et al.* 2008; Wei and Yang 2010; Robson *et al.* 2014). Numerous studies focused on the use of a chemical stabilization in order to immobilize the metallic elements and avoid spreading this contamination into the environment (Mench *et al.* 1994; Mench *et al.* 1997; Sneddon *et al.* 2006; Komárek *et al.* 2013). The present study focused on Cu, Cd, Pb and Zn, these elements being the most common metal pollutants found in the environment (Hogstad 1996; Kumpiene *et al.* 2008).

Several compounds have already been studied specifically for the remediation of soils contaminated by metallic elements, such as zerovalent Fe (Kumpiene *et al.* 2006; Bes and Mench 2008), compost (Bolan and Duraisamy 2003; Karami *et al.* 2011), phosphates (Maenpaa *et al.* 2002; Saxena and D'Souza 2006; Tica *et al.* 2011; Mignardi *et al.* 2012), clay minerals (Srivastava *et al.* 2005; Zhang *et al.* 2011), etc. Despite their considerable stabilizing potential (Wang *et al.* 2012), manganese oxides have been studied for these purposes to a much lesser extent than Fe oxides. With the exception of As and Cr (Foster *et al.* 2003; Kumpiene *et al.* 2008), the use of synthetic Mn oxides has not been examined in great depth for metal stabilization in contaminated soils even though they offer high sorption capacities (Komárek *et al.* 2013) and successfully reduce metallic elements mobility in contaminated soils (Mench *et al.* 1994; Mench *et al.* 1997; Sappin-Didier *et al.* 1997; Hettiarachchi *et al.* 2000; Tilak *et al.* 2013). An amorphous manganese oxide (AMO), synthesized according to the modified protocol by Ching *et al.* (1997) has been characterized by Della Puppa *et al.* (2013) and indicating promising characteristics in terms of metallic elements immobilization along with high pH_{H2O} and strong sorption capacities.

Encouraged by the promising characteristics and low production costs of this material, the aim of the present study is to investigate the AMO effects on a contaminated soil sample. So far, only a few studies have focused on amendments impact on metallic elements in soils under dynamic conditions (Goel *et al.* 2005; Sneddon *et al.* 2006; Lee *et al.* 2013). The entire study was conducted using column experiments which allow studying AMO impacts during dynamic conditions, i.e. closer to real-world environmental conditions. The first part of this paper will assess the effect of AMO on the initial soil pollution using three AMO / soil ratios (0.01, 0.1 and 1% w/w) in comparison with the initial soil sample. The second part will focus on introducing a solution with metallic cations (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) into the column in order to investigate the effect of AMO on a new pollution source. In the last part, to estimate the metal release under conditions simulating rhizosphere, a chelating solution (EDTA) will be used to determine the availability of the studied metallic elements under dynamic conditions.

Materials and methods

All chemicals used in this study were of analytical grade. The metallic elements solution selected to simulate new pollution were prepared using $Cu(NO_3)_2 \cdot 2.5H_2O$, $Pb(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ from Sigma-Aldrich. Nitrate salts were used to draw comparisons with the calculated AMO sorption capacities (Della Puppa *et al.* 2013). Deionized water from a Milli-Q system (with a conductivity of less than 0.06 $\mu S.cm^{-1}$) was used for all solution preparations. The pH values were measured by a Crison micro pH 2000 pH-meter fitted with a combined electrode (Ag/AgCl reference) and calibrated with two buffers (pH 4.01 and 7.00 at 25°C). Conductimetric values were recorded on a LF 538 WTW conductivity meter. Total organic carbon was measured using a Tekmar Dohrman Phoenix 8000 TOC analyser. Depending on the level of Cu, Cd, Pb, Zn, Fe and Mn concentrations, the leachates were analysed by a flame atomic absorption spectrometer (Varian SpectrAA 220), a graphite furnace atomic absorption spectrometer (Varian SpectrAA 880Z) or a microwave plasma atomic emission spectrometer (Agilent MP 4100). Validation of the analytical methodology was made using standard addition method on random samples.

AMO synthesis process

Amorphous manganese oxide (AMO) was prepared according to a modified sol-gel procedure developed by Ching *et al.* (1997) and used for preparing birnessite (Della Puppa *et al.* 2013), which consists of gradually adding 0.5 L of 1.4 M glucose solution to 0.5 L of 0.4 M potassium permanganate solution. Once gel has formed, the suspended matter was left to settle for 30 minutes, during which time the gel could completely form. The solution was then filtered and the gel was washed with 2 L of pure water to remove excess reactants before being dried at room temperature. The modification with respect to the original protocol consisted of omitting the heating step in order to form the birnessite (at 400°C) after the gel has dried. The AMO sample was ultimately characterized by Della Puppa *et al.* (2013) (Table 11). The AMO is cheap to produce due to the reactants (easy access and cheap) and to the omission of the heating step.

Soil sampling characterization

The studied soil sample was collected near a metallurgical site where copper had been refined for decades. Prior to sampling, a surface soil layer (0-5 cm) containing the main part of the litter and the majority of debris was removed. The 5-10 cm soil layer was then manually sampled at various points over a 100 m² area contaminated primarily by atmospheric fallout. This thickness was selected as a result of the soil contamination rate. The soil samples were subsequently homogenized in one sample, air-dried and sieved (< 2 mm) according to the ISO Standard.

Soil pH was determined in pure water and 1 M KCl at a 1/2.5 w/v ratio (ISO 10390). The pH of zero point charge (pH_{ZPC}) was derived according to the method by Davranche *et al.* (2003). The cation exchange capacity (CEC) was measured using a cobalthexammine trichloride solution (NF EN ISO 23470): the samples were mixed for 3 hrs in a 0.016 M cobalthexammine trichloride solution at a 1/5 w/v ratio and filtered through a cellulose nitrate filter. The excess $Co(NH_3)_6^{3+}$ was analysed in a UV-visible spectrophotometer (Shimadzu UV-160) at 470 nm. A blank was introduced in order to evaluate the interference of organic matter in the measurement.

The BCR sequential extraction procedure was accelerated using ultrasound (Pérez-Cid *et al.* 1998) in order to determine the chemical fractionation of the studied metallic elements (Cu, Pb, Cd, Zn) in soils. The BCR procedure allows dividing metallic elements into distinct defined fractions: (i) exchangeable and weakly adsorbed (0.11 M CH_3COOH), (ii) bound to reducible fraction (0.5 M $NH_2OH{\cdot}HCl$), bound to oxidisable fraction (8.8 M H_2O_2 / 1 M CH_3COONH_4) and (iv) residue (69% HNO_3 / 37% HCl). Soil metal content was measured after a microwave-assisted inverse aqua-regia digestion (1400 W for 30 min; Anton Paar, Microwave 3000) and analyses. Each experiment was conducted in triplicate; the values shown represent the average and standard deviation.

Column experiments

For the laboratory column experiments, a portion of the soil sample was homogenously mixed with AMO at four different w/w ratios (AMO weight / soil weight): 0, 0.01, 0.1 and 1%. The mixture was placed in a glass column (internal diameter = 2.6 cm; height = 6 cm; Bio-Rad equipment). The column was closed with a flow adapter to prevent water from furrowing. The columns contained a porous polymer bed support at the bottom to retain fine particles. Each experiment was performed in duplicate.

The columns were filled with the same amount of soil (28.3 ± 0.3 g), yielding a bulk density of 0.96 ± 0.04 $g.cm^{-3}$. The columns were then leached upwards from the base using a continuous leaching solution flow of 16.4 ± 0.1 $mL.h^{-1}$ (corresponding to a pore velocity of 12 ± 1 $cm.h^{-1}$). The flow was applied by a peristaltic pump. Results have been presented with respect to V/Vp, where V denotes the volume of the cumulative leachate and Vp the pore volume of the column (Vp = 8.4 ± 0.3 mL).

Pore volume was calculated as:

Equation 11: Pore volume calculation

$$V_{pore} = V_{column} - V_{soil} = (\pi \times r^2 \times d) - \left(\frac{m}{\rho}\right)$$

with: r: column radius (cm) d: column length (cm)

m: soil weight (g) ρ: soil density ($g.cm^{-3}$)

Stabilization, contamination and leaching method

The column experiment was performed in three successive steps:

- leaching with de-ionized water until reaching an equilibrium phase: assess the impact of AMO on the metal contaminants of the studied soil sample;
- contamination using a mixed metallic cation solution (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, 1mM each) during 50 Vp: assess the impact of AMO on a new pollution source followed by ultra-pure water elution;
- EDTA (set at 2.5 mM) lixiviation to determine mobility of the studied metallic elements: assess the impact of AMO on the metallic elements potential availability under conditions simulating rhizosphere.

The concentration of the contamination solution was chosen in line with soil sorption properties. Injecting a 1 mM solution of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} during 50 Vp theoretically saturates the soil sorption properties which allow a better visibility of the AMO impact on soil sorption properties. The state of columns was monitored through conductivity, pH and DOC measurements of the leachate. The pH value of each solution was set at the water pH of the soil (4.3). Leachate was collected in HD-PE tubes, filtered using a 0.2 µm cellulose acetate filter (VWR) and then acidified using 69% HNO_3 prior to analysis. Depending on the level of Cu, Cd, Pb, Zn, Fe and Mn concentrations, the leachates were analysed by a flame atomic absorption spectrometer (Varian SpectrAA 220), a graphite furnace atomic absorption spectrometer (Varian SpectrAA 880Z) or a microwave plasma atomic emission spectrometer (Agilent MP 4100).

Statistical treatment

Statistical treatments of the data were performed using the software SigmaPlot 12.5 (StatSoft Inc., USA). The data were evaluated using the analysis of variance (ANOVA) with a significant *P-value* < 0.05 using the Tukey test.

Results and discussion

Characterization of the soil sample and AMO

The physicochemical properties of the studied soil and AMO are listed in Table 11.

Table 11: Key physico-chemical properties of the soil and the amorphous manganese oxide (AMO) (from Della Puppa *et al.* 2013) and soil total metal content (mg.kg^{-1}).

Physico-chemical properties		Soil total metal contents (mg.kg^{-1})	
Polluted soil studied		Al	40682 ± 681
$\mathrm{pH}_{\mathrm{H_2O}}$	4.34 ± 0.01	Fe	24021 ± 355
$\mathrm{pH}_{\mathrm{KCl}}$	3.62 ± 0.01	Mn	424 ± 21
$\mathrm{pH}_{\mathrm{ZPC}}$	8.3 ± 0.1	Cu	356 ± 10
TOC (mg.g^{-1})	6.0 ± 0.3	Cd	5.2 ± 0.1
TIC (mg.g^{-1})	< d.l.	Pb	99 ± 2
CEC (meq.100g^{-1})	14.2 ± 0.4	Zn	115 ± 33
AMO			
$\mathrm{pH}_{\mathrm{H_2O}}$	8.1 ± 0.3		
$\mathrm{pH}_{\mathrm{KCl}}$	7.9 ± 0.1		
$\mathrm{pH}_{\mathrm{ZPC}}$	8.3 ± 0.1		
SSA (m^2.g^{-1})	14.8		
CEC (meq.100g^{-1})	34 ± 1		
pK_{a1}	6.9 ± 0.1		
pK_{a2}	9.6 ± 0.1		

The soil characteristics reveal that the soil is acidic (low H_2O- and KCl-pH values: 4.34 and 3.62 respectively), has a low organic (6.0 mg.g^{-1}) and inorganic carbon content (< d.l.), and exhibits a low cation exchange capacity (CEC value: 14.2 meq.100g^{-1}). The soil sample displays a high concentration of Cu relative to Pb, Zn and Cd, which is in accordance with past industrial activity (Table 11). The fractionation of soil metallic elements (Fig. 20) indicates that most of the Cu (40%) and Pb (30%) are bound to the oxidisable fraction (F3), whereas Cd mainly lies in the exchangeable and acid extractable (F1) and the reducible fraction (F2). Copper and Pb are known to display a high affinity for SOM (Agbenin and Olojo 2004) while Cd has high affinity for the easily exchangeable fractions (Tang *et al.* 2006). Manganese mainly stems from fraction 2 (i.e. reducible fraction) due to the dissolution of (naturally present) Mn and Fe oxides and from the residue (F4). Zinc does not appear in since its value was below the detection limit (3.4 µg.L^{-1}).

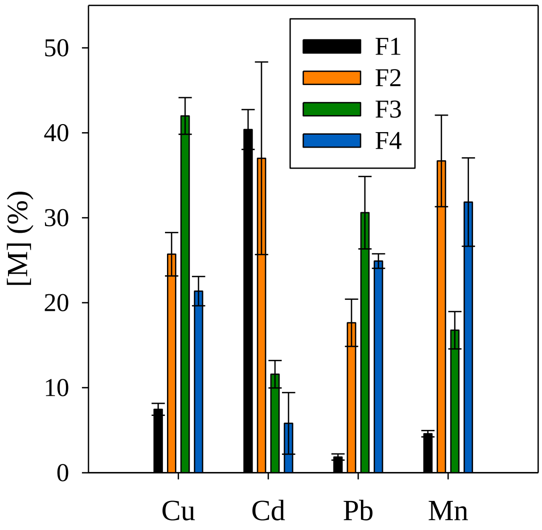

Figure 20: Fractionation of Cu, Cd, Pb and Mn in the soil.

Concerning AMO, despite its low specific surface area (SSA: 14.8 m².g^{-1}) and CEC (34 meq.100g^{-1}; for comparison, birnessite: 247 meq.100g^{-1}), it still shows strong sorption capacities (Cu: 0.453, Cd: 0.438, Pb: 0.604, Zn: 0.460 mmol.g^{-1} at pH = 5.5). Moreover, in a multi-element system, the sorption of Pb and Cu increases at the expense of Cd and Zn. The AMO exhibits higher pH_{H2O} and pH_{KCl} values (respectively 8.1 and 7.9) than the corresponding soil values (Table 11) (Della Puppa *et al.* 2013).

Column experiments

Impact of AMO on the mobility of the metals

Figure 21 shows the results of pH and conductivity monitoring, whereas Figures 22 and 23 show DOC concentration and the leaching of the metallic elements, respectively, during the soil leaching by pure water as a function of pore volume.

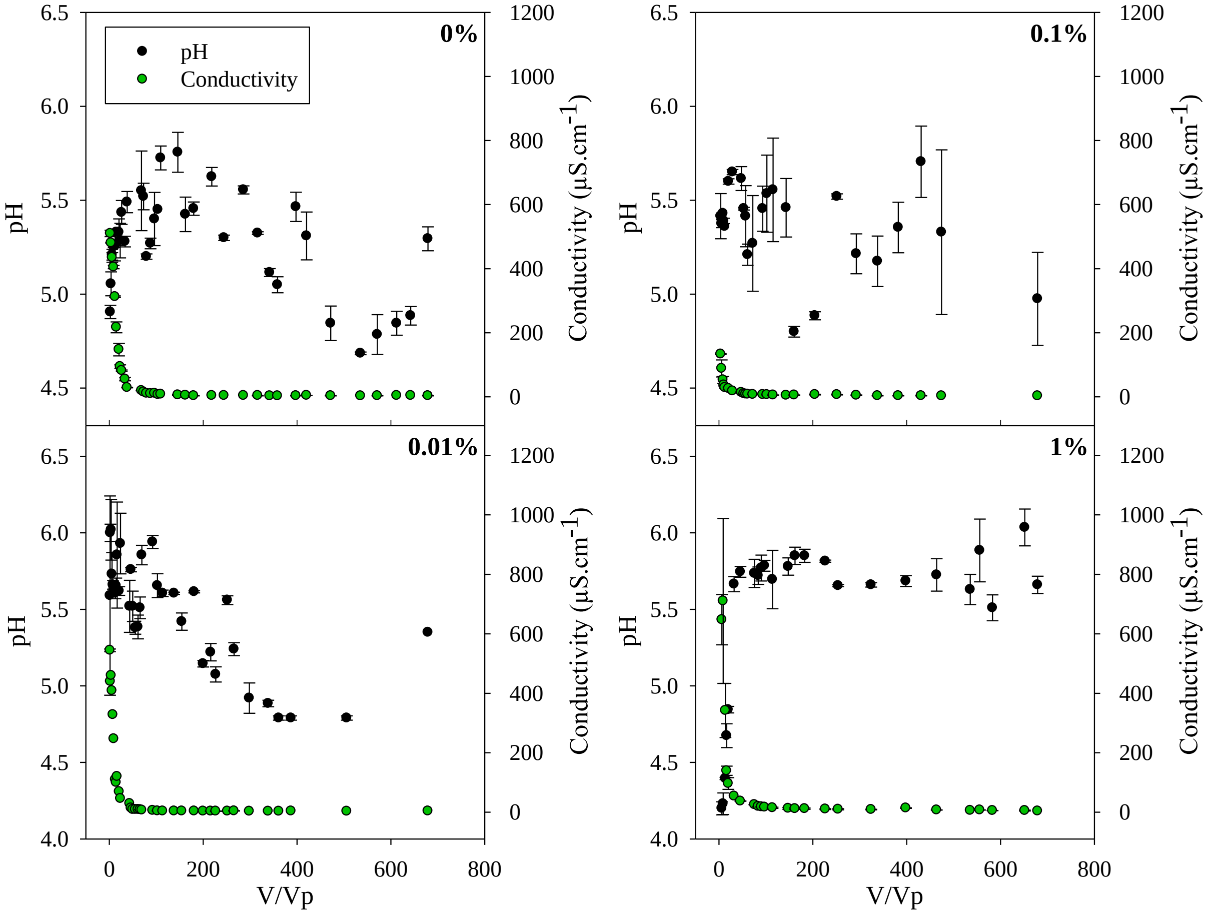

Figure 21: Variation of pH and conductivity during the column experiments with soil amended with various amount of amorphous manganese oxide (AMO) (AMO ratio, w/w): 0% , 0.01%, 0.1% and 1% during the leaching of soil with pure water.

Conductivity decreases for all w/w ratios. Some elements are easily leached (in soluble form, Lo *et al.* 2011) due to disrupting of the soil during the sample preparation step (drying and sieving). However, during the experiment, columns tend towards an equilibrium state, thus indicating that elements not leached during this step are being more strongly sorbed (Jean-Soro *et al.* 2012). The pH for the 0, 0.01 and 0.1% w/w ratios (Fig. 21) reach values less than 5, which is closer to the pH_{H2O} value of the soil (4.34). For the 1% ratio, pH reaches 5.6 and stays stable, i.e. higher than the soil pH_{H2O} value, meaning that at this w/w ratio the AMO directly impacts the lixiviate pH (AMO pH_{H2O} equals 8.1). For an AMO ratio under 1%, the pH of the leachate under dynamic conditions is not significantly affected.

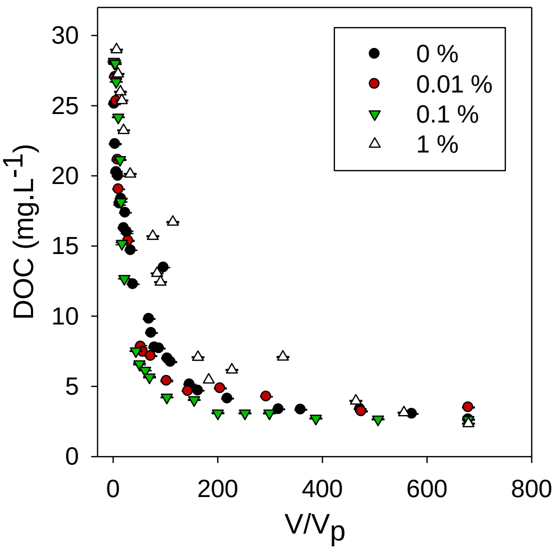

Figure 22: Dissolved organic carbon (DOC) concentration in leachates as a function of pore volumes during the leaching of soil with pure water amended at various amorphous manganese oxide (AMO) ratios.

Concerning DOC, in calculating the area under the curve, the AMO exerts a distinct impact on the SOM dissolution, which in turn yields carbon concentrations: 1.0 $mg.g^{-1}$ for 0%; 1.0 $mg.g^{-1}$ for 0.01%; 0.80 $mg.g^{-1}$ for 0.1% and 1.45 $mg.g^{-1}$ for 1% which represents respectively 17%, 17%, 13% and 24% of the soil TOC. These results suggest that less organic matter is leached when using a ratio of 0.1% compared to 1%. Moreover, an increase of the organic matter dissolution was also observed by Ettler *et al.* (2014) in soil amended by AMO at 0.25% w/w. This outcome may be due to the increase of soil pH, which promotes organic matter dissolution (Komárek *et al.* 2013), as well as the possible oxidation of organic matter by the Mn oxide (Chorover and Amistadi 2001). It also indicates that the organic matter content is higher after the column stabilisation at a ratio of 0.1% and lower at 1%. Moreover, in all cases the DOC reached the equilibrium state at the same V/Vp (160).

In Figure 23, Cd, Pb and Zn are not shown since they were below the quantification limits in leachates (14, 250 and 150 µg/L, respectively).

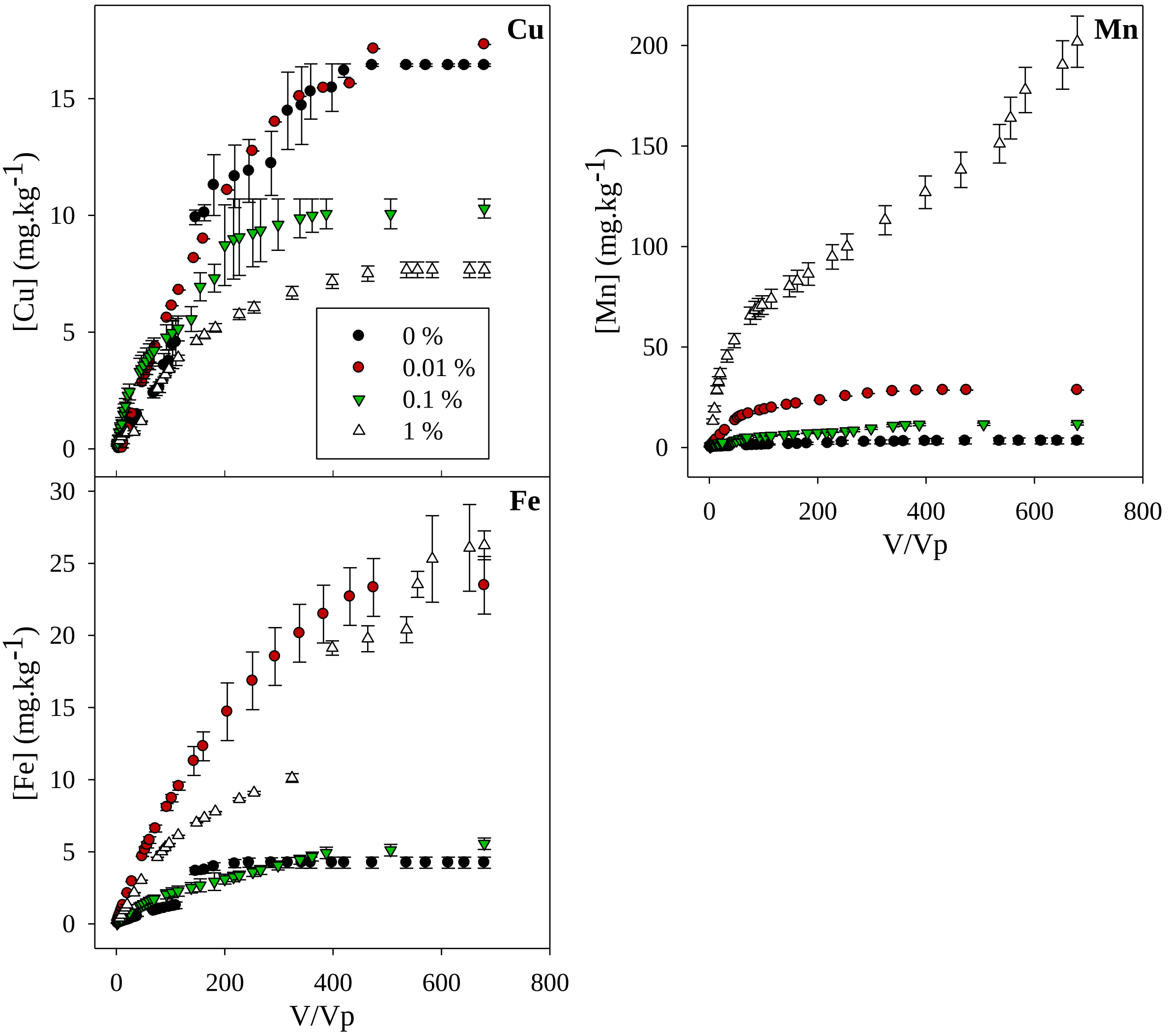

Figure 23: Cumulative concentration of Cu, Fe and Mn (mg of M^{2+} per kg of soil) in the leachate during the leaching of soil with pure water.

In the case of Cu (Fig. 23), the AMO ratio directly influences its behaviour (the AMO ratio 0.01% does not appear to affect Cu leaching in the columns). The decrease in Cu content in the leachate is directly correlated with the AMO w/w ratio. At the higher AMO level (1%), Cu in the leachate decreases from 16.0 to 7.6 $mg.kg^{-1}$. When considering Mn, it appears that the increase in AMO ratio leads to an increase of Mn in the leachate (except at 0.1% ratio, Figure 23). Figure 23 indicates that for the 1% AMO ratio, Mn does not reach the equilibrium state; possibly due to the AMO dissolution, which is more prevalent at higher ratios. Ettler *et al.* (2014) showed that in an acidic soil (pH_{H2O}: 4.2), AMO at 0.25% w/w resulted into dissolution reaching 10 to 18% of total AMO weight. Considering Fe, Figure 23 indicates a significant increase at w/w ratios 0.01 and 1%, which may be caused by the greater impact of a higher AMO ratio on the soil. Jeon *et al.* (2003) show that the amount of Fe sorbed onto hematite during a binary system (Fe + Me, where Me is a metal) greatly depend on the metal, meaning in our case that the Mn released by the AMO might compete with the sorbed Fe on soil components, resulting in a released of Fe. Moreover, the increase in Fe at 1% is related to the increase of DOC in the leachate, which can be explain by the affinity of Fe for the SOM (Wilson *et al.* 2013).

Impact of AMO on additional metallic elements

Once the columns reached the equilibrium state, a mixed metallic cation solution (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} as 1 mM nitrates) was injected into the column. The solution pH was set at the soil pH_{H2O} (4.3). Figure 24 shows the decrease in pH regardless of the AMO ratio.

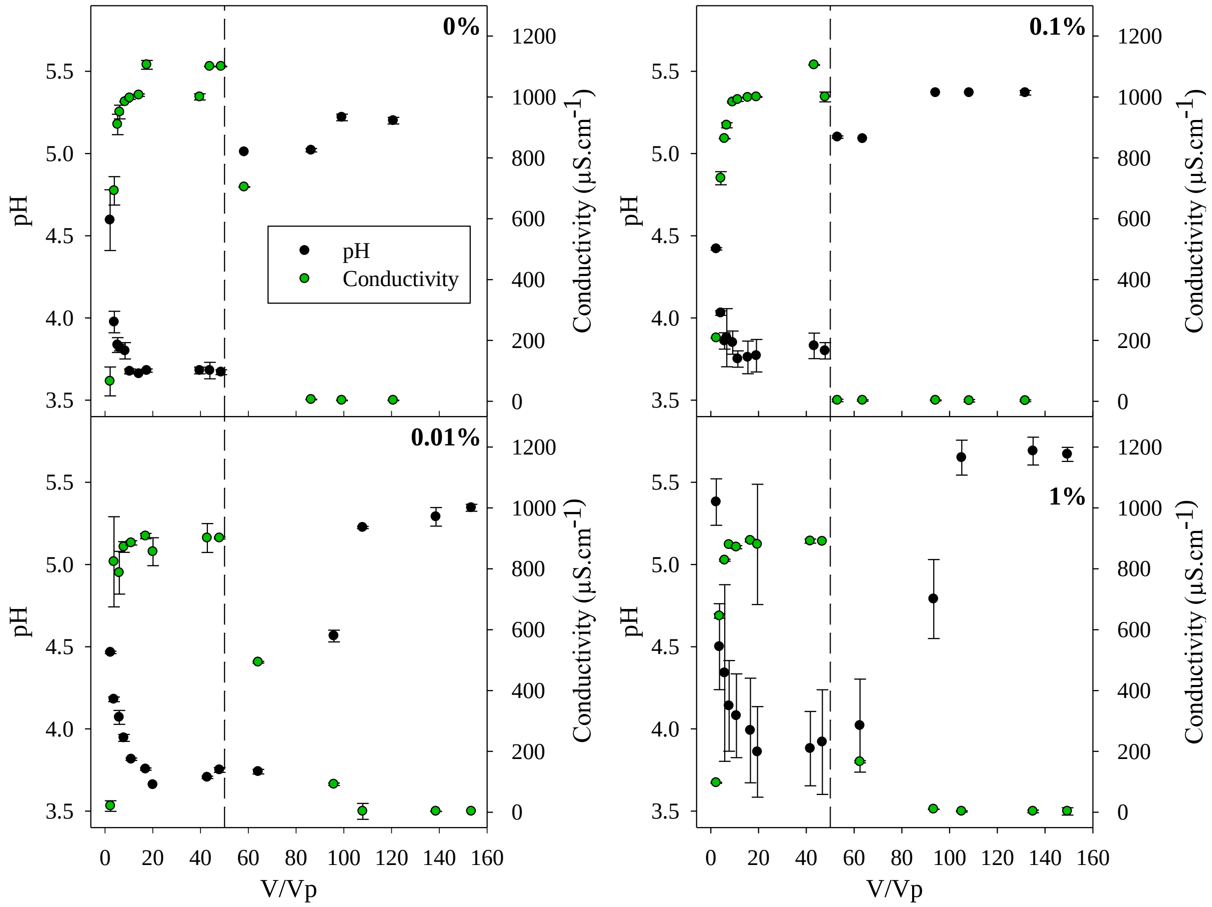

Figure 24: Variations of pH and conductivity during the injection of a Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} 1 mM mixed solution during 50 Vp into the soil amended at various amorphous manganese oxide (AMO) ratios (w/w): 0%, 0.01%, 0.1% and 1%. The line at 50 Vp represents the end of the metallic solution injection.

This finding may be explained by surface reactions, given that specific adsorption of the metallic cations results in a release of protons. Consequently, pH reaches a value close to pH_{KCl} (3.6). For conductivity, Figure 24 reveals a sudden increase then stabilisation (around 20 V/Vp) due to both the ion exchange during adsorption and the unsuccessful retention of metallic elements. When replacing the metallic cations solution by pure water (at V/Vp of 50), the pH increase and conductivity decrease both occur quickly. The AMO ratio influences pH value of the equilibrium state, with an increase at higher ratio values. In the presence of AMO, pH and conductivity seem to reach the equilibrium state more slowly (Figure 24), perhaps due to the partial retention of a fraction of metallic elements. The DOC remains constant (3.0 ± 0.5 $mg.L^{-1}$) at each ratio value (data not shown), which can be explained by the fact that stabilisation had already been reached during the first part of the experiment.

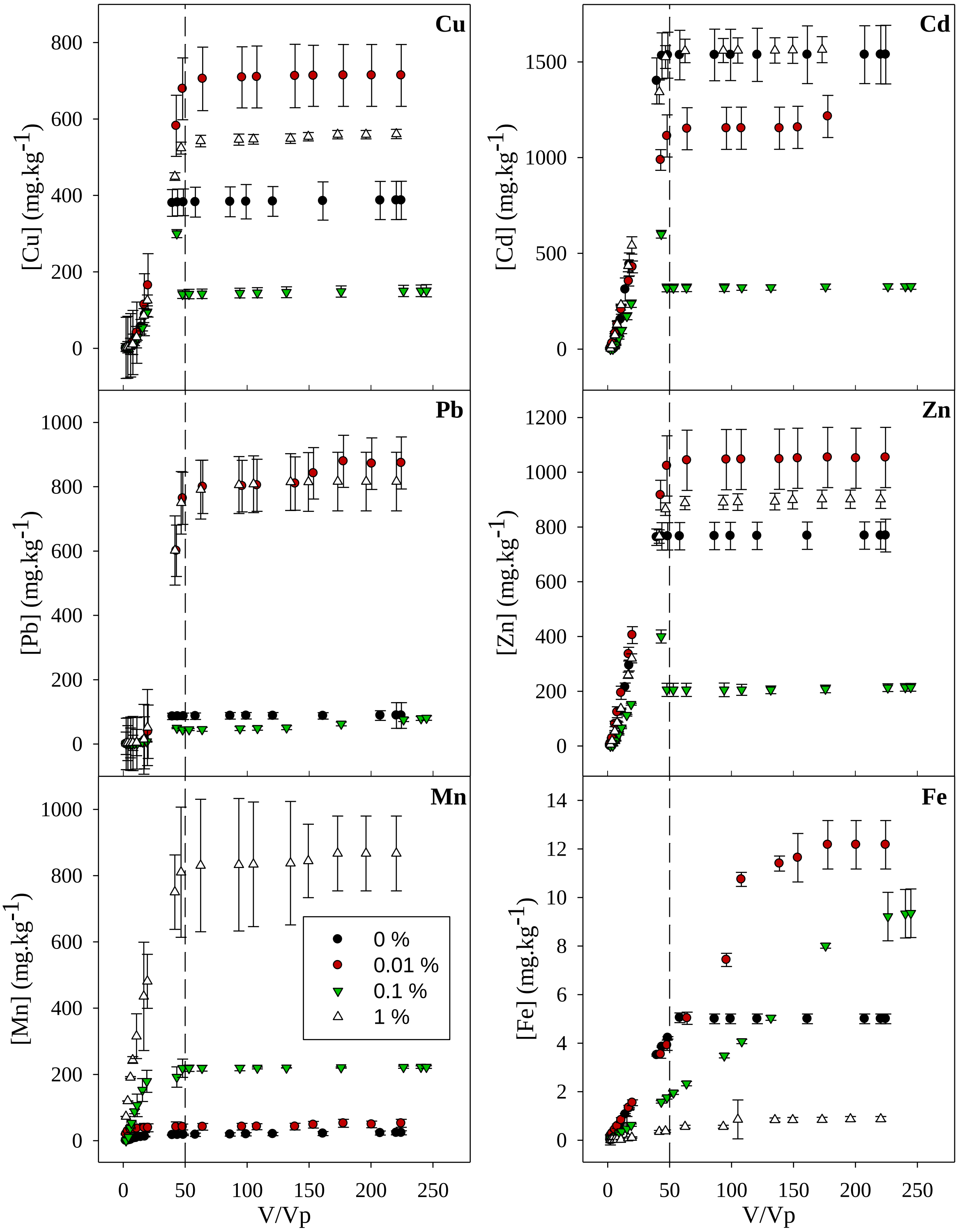

Figure 25: Cumulative concentration of Cu, Pb, Mn, Cd, Zn, and Fe (mg of M^{2+} per kg of soil) in the leachate during the injection of a Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} 1 mM mixed solution during 50 Vp in soil amended at various amorphous manganese oxide (AMO) ratios (w/w): 0%, 0.01%, 0.1% and 1%).

The concentrations of Cu, Cd, Pb, Zn and Mn were measured in the leachates (Figure 25). As a result of the use of the manganese oxide, Mn must be taken into account in the leachates. For each element, the AMO ratio exerts an influence on behaviour. The retention capacities of each system are ranked in these orders:

- Cu: 0.01% < 1% < 0% < 0.1%
- Pb: 0.01% = 1% < 0% = 0.1%
- Cd: 0% = 1% < 0.01% < 0.1%
- Zn: 0.01% < 1% < 0% < 0.1%
- Mn: 1% < 0.1% < 0.01% < 0%

It would appear that for Cu, Pb and Zn, the orders are the same; moreover, for each element, the 0.1% ratio seems to be better at holding the metallic elements. In the case of Cu, Cd and Zn, the 0.1% AMO in soil greatly increases the soil retention capacity (Fig. 25). The fact that concentration of these elements do not increase when replacing the metallic elements solution by pure water (at 50 V/Vp) indicates that the elements are sufficiently immobilized to be not released by pure water alone. For Mn, the order represents a logical sequence: the higher the ratio, the greater the quantity of Mn that can be leached out. The Mn release can be generated mainly from the desorption of weakly bound Mn at the AMO surface (Della Puppa *et al.* 2013; Ettler *et al.* 2014). At a ratio of 1%, however, the quantity of Mn released can cause an environmental threat (867 $mg.kg^{-1}$). When comparing the retention capacity order and organic content in each column, some similarities appear. A 0.1% AMO w/w ratio results in lowering TOC solubilisation in the column and represents the most efficient ratio for immobilizing metallic elements, thus indicating that use of the 0.1% ratio leads to lower solubilisation of the organic matter, which in turns increases metallic elements retention in the soil through the formation of a metal-organic matter complex (Quenea *et al.* 2009). On the other hand, the 1% ratio increased organic matter solubilisation, resulting in a higher loss of metallic element initially immobilized by the organic matter.

The presence of the AMO in soil columns yields an increase in soil pH (dependent on the AMO ratio) (Fig. 24) along with improved immobilization of the studied metal elements (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) (Fig. 25). Moreover, the AMO ratio seems to have an optimum value close to 0.1%, as more metallic elements are retained at this value. Another ratio could present some level of threat for the immobilization of a fresh pollution source. In addition, the use of a high AMO ratio triggers a greater release of Mn and results in an increase of soluble TOC which serves as a potential environmental threat.

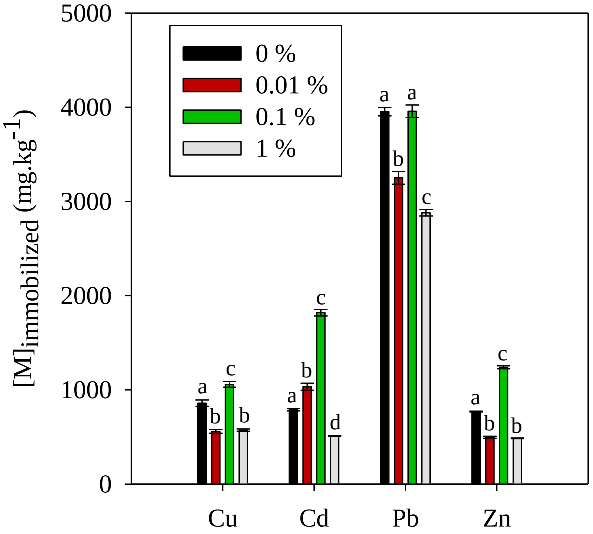

Figure 26: Amount of metallic elements immobilised in the soil column amended at various amorphous manganese oxide (AMO) ratios (w/w). Separately for each element, data with the same letter represent statistically identical values ($P < 0.05$).

Figure 26 shows the calculated amounts of metallic elements immobilised in the columns. The results obtained for Cu, Cd and Zn all reveal the same trend: the 0.1% ratio is the most effective condition to immobilise metallic elements originating from a fresh pollution source. For Cd and Zn, these results can be associated with the fact that in the presence of mobile metallic elements, a small fraction is logically immobilised by the natural soil. However, this indicates that AMO positively alters the Cu retention in the soil. Figure 26 demonstrates that Pb is naturally well retained by the soil. The AMO does not seem to affect the soil retention capacity at 0.1% ratio and lowers it at w/w ratios of 0.01 and 1%. Mamindy-Pajany *et al.* (2013) found for a sediment that immobilisation efficiency is not only dependent with the ratio introduced: the use of 5% hematite has a better stabilization effect than a ratio of 15% for Mo and Zn, while a 15% ratio proves to be more effective for the immobilization of Cu and Cd.

Even though Cu and Pb are mainly immobilised by the same fraction in the initial soil sample (oxidisable fraction), they are not affected in the same way by the presence of AMO. For Cu, AMO increases its retention at a w/w ratio of 0.1%, yet this is less effective than the initial soil at a 0.01 or 1% ratio. Moreover, Della Puppa *et al.* (2013) showed that AMO adsorption capacity for Pb is higher than for the other elements. Even if Pb is preferentially adsorbed by AMO in the setting of multi-element adsorption test (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}), this trend appears to be non-applicable in soils. Mench *et al.* (1997) found that a Mn oxide successfully reduced the mobility and availability of Pb due to the affinity of Pb for the oxide as well as to the reactive sites located on its surface layer. Moreover, Chen *et al.* (2000) successfully reduced the EDTA extractability in contaminated soils and the uptake in wheat shoots of Cd and Pb. Furthermore, the use of 1% manganese oxide decreased the exchangeable pool to unavailable Cd and Pb in contaminated soils. However, Sappin-Didier *et al.* (1997) showed no changes in EDTA extractability of Cd in contaminated soils, when using a hydrous manganese oxide.

EDTA leaching

Given that complexation is one of the most important phenomenon affecting metal mobility, EDTA was introduced as a leaching solution to simulate effect of organic ligand (Bryce *et al.* 1994). Following the contamination step and upon reaching the equilibrium state with pure water, a 2.5 mM EDTA solution was injected into the column. Measurement results are presented in Figure 27 to Figure 29. During leaching, pH values increase (Fig. 27).

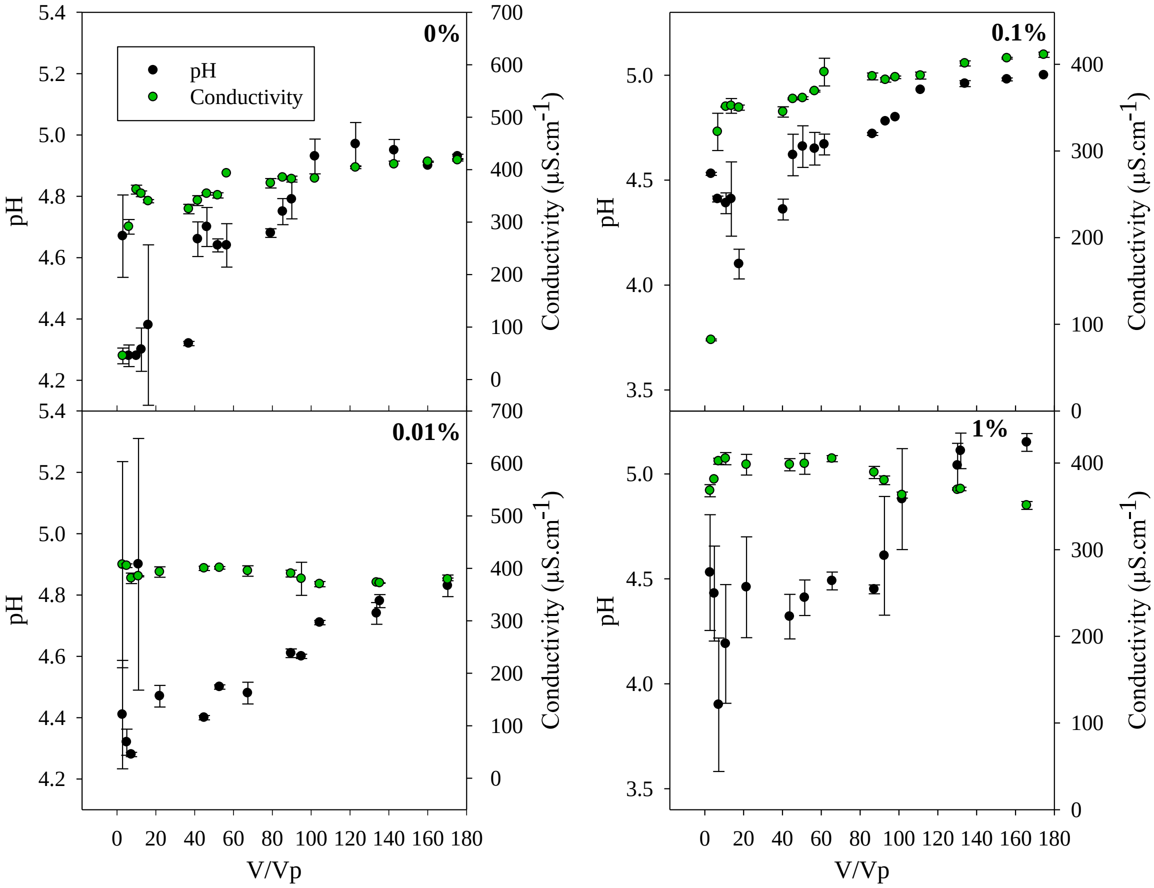

Figure 27: Variations of pH and conductivity during ethylenediaminetetraacetatic acid (EDTA) (2.5 mM) lixiviation in the soil column amended at various amorphous manganese oxide (AMO) ratios (w/w): 0%, 0.01%, 0.1% and 1%.

The pH reaches its maximum value at a 1% AMO ratio (5.15 ± 0.04). The pattern is the same in all cases: pH values first decrease (until a V/Vp of 20 in each case) and then increase. This decrease may be due to the nature of the EDTA solution and cannot be accounted for by possible differences between EDTA and soil pH (the EDTA solution pH was set equal to the soil pH_{H2O}: 4.30). According to Nowack and Sigg (1997), the formation of Me-EDTA complexes can react with Fe(III) oxides, resulting in the consumption of H^+ which in turn may explain the pH increase. This reaction can be summarised as follows:

Equation 12: Formation of Fe-EDTA complexes

$$\equiv FeOH + MeEDTA^{2-} + H^+ \rightarrow \equiv Fe\text{-}EDTAMe^- + H_2O$$

with Me denoting a divalent metal.

Moreover, Udovic and Lestan (2012) found that EDTA leaching treatment results in a pH increase to neutral values. In Figure 27, the conductivity logically increases when using the EDTA solution due to: the extraction of certain soil elements as metallic cations; the dissolution of mineral phases such as Fe, Mn or Al oxides; and the Na provided by the EDTA solution.

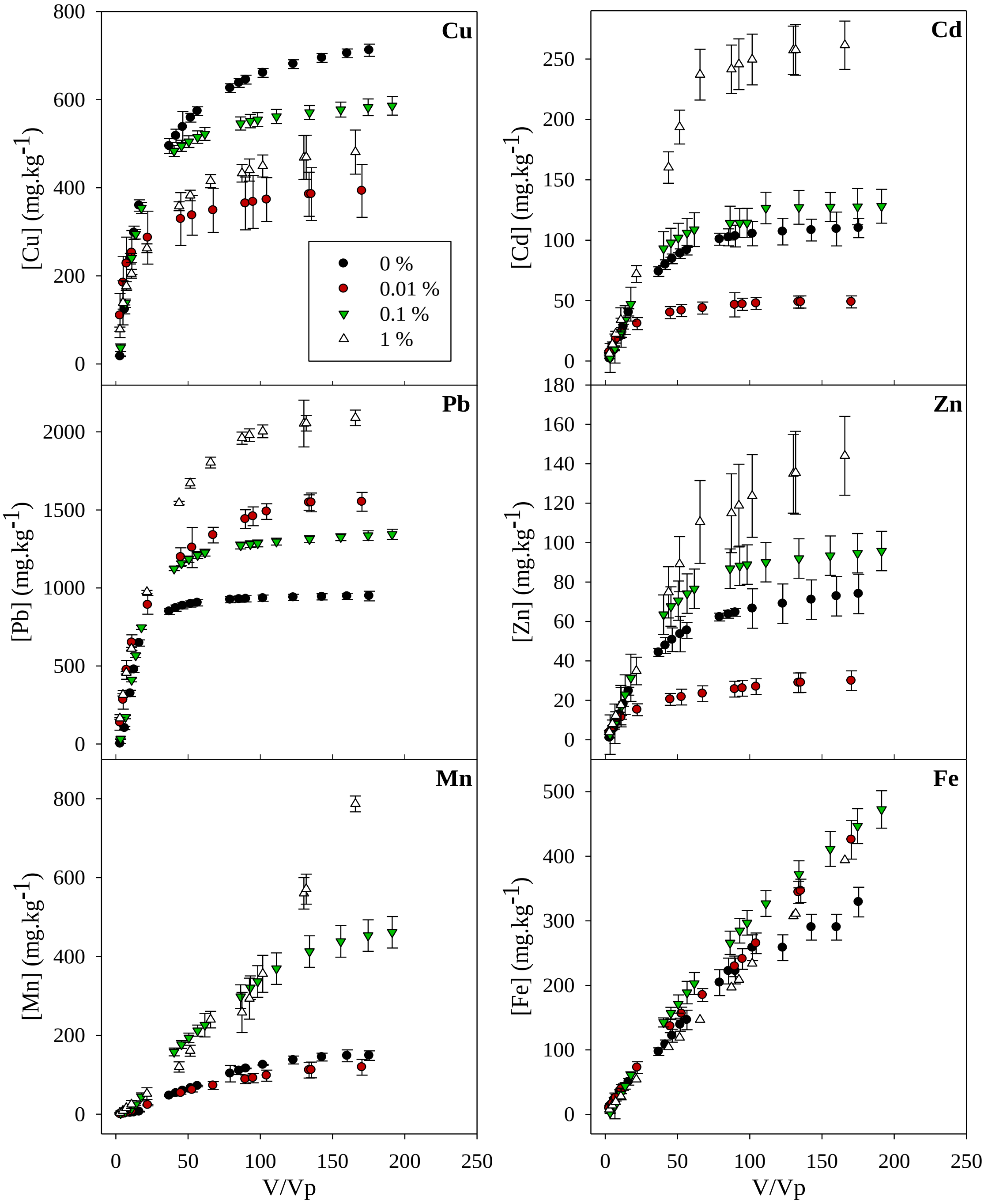

Figure 28: Cumulative concentrations of Cu , Cd , Pb, Zn, Mn and Fe in the leachate during the ethylenediaminetetraacetatic acid (EDTA) (2.5 mM) lixiviation in the soil column amended at various AMO ratios (w/w): 0%, 0.01%, 0.1% and 1%.

When comparing the cumulative metallic amount extracted by EDTA in the leachates (Fig. 28), it appears that the presence of AMO clearly exerts an impact on metal retention.

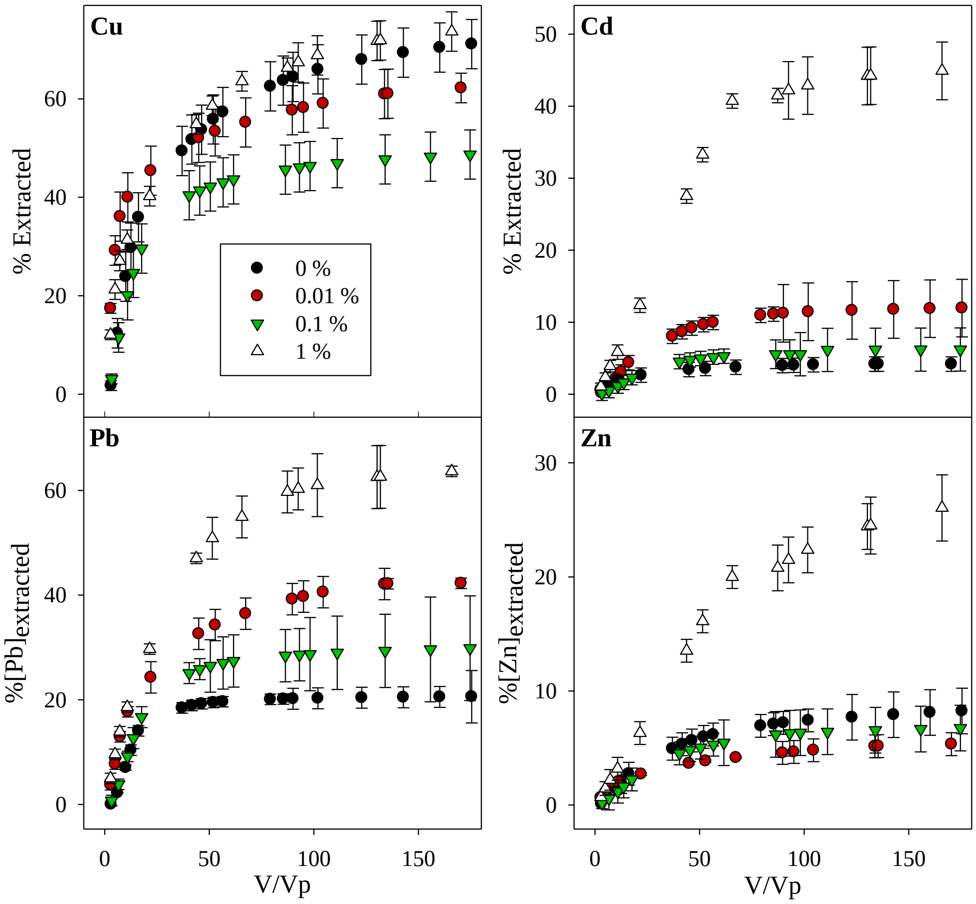

Figure 29: Evolution of the percentage of metallic cations extracted by ethylenediaminetetraacetatic acid (EDTA) (2.5 mM) for Cu , Cd, Pb, Zn in the soil column amended at various AMO ratios (w/w): 0%, 0.01%, 0.1% and 1%.

Figure 29 shows the evolution of the ratio, i.e., the cumulative extracted amount/amount retained in the column during injection of the metallic element solution.

Depending on the specific element, the improved immobilisation order is expressed as follows (Fig. 29):

- Cu: 0.01% = 1% = 0% < 0.1%
- Cd: 1% < 0% < 0.01% < 0.1%
- Pb: 1% < 0.01% < 0.1% < 0%
- Zn: 0.01% < 1% < 0% < 0.1%

- Mn: 1% < 0.1% < 0.01% = 0%

For Cu, AMO not only increases its retention, but decreases its availability as well (Figs. 26 and 29). In the cases of Cd and Zn, a 0.1% ratio results in a better retention capacity compared to the control sample. However, since the percentage extracted by EDTA is similar to the control, the corresponding availability is not reduced. Similar results were observed by Mench *et al.* (1994): the amount of Cd extracted by EDTA in a soil treated with a hydrous manganese oxide. The complexing nature of EDTA may provide a suitable explanation;. Cd and Zn are mainly immobilised through sorption or the pH effect, which is complexed into a soluble form by EDTA (Sappin-Didier *et al.* 1997). In the case of Pb, AMO does not allow for either higher or better retention. It appears that the 0.1% AMO ratio is optimal for immobilising these metallic elements. This result is in agreement with the optimal ratio found during the second step (contamination). For Mn, the order follows a logical sequence like in the contamination step: the higher the ratio, the greater the quantity of Mn capable of being complexed by EDTA. Moreover, when comparing the amount of metallic elements extracted for each AMO ratio (Fig. 29), the order follows the formation constant of EDTA-Me complex: Cu > Pb > Cd ≈ Zn. Fe does not reach an equilibrium state (Fig. 28) due to the lower kinetic dissolution of Fe oxides (Nowack and Sigg 1997; Tsang *et al.* 2007; Komárek *et al.* 2009; Noubactep 2009).

Conclusion

The AMO reduces the mobility of metals at ratios greater than 0.01% (w/w) and Cu and Cd availability at 0.1%. Moreover, AMO increases the amount of organic matter in the soil at 0.1% and decreases it at 1%. The amount of Mn in the leachate increases when increasing the AMO ratio, reaching 200 mg.kg^{-1} at 1%. On a new and acute pollution, AMO at 0.1% increases the Cu, Cd and Zn retention capacity of the soil, especially when compared to the unamended soil. At 1%, metallic elements are less readily retained than in the studied contaminated soil, which may stem from the reduction in organic matter, given the dependence of organic matter on the AMO ratio. Moreover, AMO directly alters the leachates pH, leading thus to an improved immobilization of future pollution through adsorption reactions and the precipitation of (oxy)hydroxides.

The AMO at 0.1% seems to be an effective stabilising agent for Cu, Cd and Zn in the case of the “historically” polluted soil as well as during a new pollution incident. However, the release of Mn during the experiment must be considered.

In this article, all experiments have been conducted under dynamic conditions using column systems. Results obtained indicate that a minimal ratio of 0.1 % is necessary to influence the fate of metals. Increasing the AMO ratio however results in an increase of the quantity of Mn released into the soil, which can potentially lead to toxicity for soil biomass (Bade *et al.* 2012; Sarkar *et al.* 2004; Boojar and Goodarzi 2008); also, a ratio above 0.1% results in a decrease of immobilisation potential for the soil mixed with AMO. Indeed 0.1% represents, in this experiment, the best ratio for metallic element immobilisation and improves the metal immobilisation (Fig. 26) along with a decrease in metal availability, mainly for Cu and Cd, Zn and Pb being immobilised as much as at 0%.

Furthermore, AMO more strongly influences a new and acute pollution than a former pollution, thus highlighting the strong influence of ageing on metal behaviour. Sondergaard *et al.* (2014) clearly demonstrated this ageing effect on Cu mobility, as the easily exchangeable fraction decreased over time while the reducible and oxidisable fraction increased. Nonetheless, the availability did not decrease over time, which indicates that mobility changes do not always imply changes in availability. Concerning the organic matter dissolution pointed out by Ettler *et al.* (2014), results show that the AMO ratio clearly affects the amount of organic matter leached. It would appear however that increasing this ratio does not yield an increase in organic matter solubilisation. The use of 0.1% has indeed decreased solubilisation compared to the control and other ratios, thus indicating that solubilisation of organic matter is not strictly due to the pH increase. Decreasing organic matter solubilisation results in an increase in soil organic matter content, which might explain why 0.1% is the most efficient ratio for metal immobilisation (Roth *et al.* 2012).

As in column experiments, the next article will present the AMO impact on both historical and freshly added contamination in soil. Moreover, the ageing effect on metal and AMO will be emphasised, in order to examine changes in their behaviour over time within the scope of batch experiments.

IV.2. Article 3: Ageing of an amorphous manganese oxide in soil and its impact on the mobility and availability of Cu, Cd and Pb

Abstract: Due to its simple and inexpensive synthesis, a new amorphous manganese oxide (AMO) has been studied using batch experiments as a potential chemical stabilising agent for soils contaminated by metals. Four ratios (0, 0.01, 0.1 and 1% w/w) were evaluated for an industrially polluted soil, where a fresh contamination (Cu, Cd, Pb, Zn) was added during the experiments, Zn is not shown however. Changes in mobility and availability over time of metals were evaluated through $CaCl_2$ and pore water extraction, sequential extraction and Diffusive Gradient in Thin film technique (DGT). The AMO did not alter significantly the historical pollution, in sharp contrast with the freshly added metals. Moreover, a ratio below 0.1% was found ineffective to reduce metal mobility and availability. Although the AMO showed partial dissolution, the Mn consequently released becomes unavailable over time, possibly due to the formation of a new solid phase on its surface. Because modifications of the AMO properties over time resulted in a better stabilisation of metal elements, ageing effect appears therefore to improve AMO stabilizing properties.

Keywords: Manganese oxide, Metal elements stabilisation, Extraction, Mobility, Availability

Highlights: ► Amorphous manganese oxide (AMO) decreases metals mobility and availability over time ► AMO impacts more significantly the fresh pollution than the historical pollution ► Ageing results in an increase of the metals stabilisation ► Mn released by partial dissolution of AMO is quickly immobilized.

Submitted to Journal of Environmental Management

Ageing of an amorphous manganese oxide (AMO) in soil and its impact on the mobility and availability of Cu, Cd and Pb

Loïc Della Puppa[a,b], François Bordas[a*], Michael Komárek[b], Rémy Buzier[a], Vojtěch Ettler[c]

[a] *Groupement de Recherche Eau Sol Environnement, Université de Limoges, Faculté des Sciences, 123 Avenue Albert Thomas, 87060 Limoges, France*

[b] *Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, Prague 6 - Suchdol, 165 21, Czech Republic*

[c] *Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic*

Introduction

The chemical stabilisation of metal(loid)s in soils provides an efficient non-destructive remediation strategy. The immobilisation of contaminants takes place through physicochemical processes like adsorption, complexation and (co)precipitation (Kumpiene *et al.* 2008). Numerous studies on these chemical amendments (e.g. phosphate, iron oxide, clay) can be found in the literature (O'Reilly and Hochella 2003; Hartley *et al.* 2004; Gray *et al.* 2006; Ruttens *et al.* 2010; Komárek et al. 2013; Houben *et al.* 2012). Among these, Mn oxides are ubiquitous in the environment and promising for the immobilisation of metals due to their high specific surface area, low pH_{ZPC} and strong sorption properties (Feng *et al.* 2007). They display high sorption capacities (McKenzie 1980; Covelo *et al.* 2007; Della Puppa *et al.* 2013; Komárek *et al.* 2013) and have been shown to successfully reduce metal elements mobility in contaminated soils (Mench *et al.* 1997; Sappin-Didier *et al.* 1997; Hettiarachchi and Pierzynski 2002). The Mn oxides however have been studied to a far lesser extent than Fe oxides (Kumpiene *et al.* 2008).

Metal elements availability is typically assessed using common soil testing procedures. Sequential extractions allow for a functional fractionation of metals in soil. The results however are operationally defined and strongly dependent on the reactants used (Tokalioğlu *et al.* 2003). When a specific characteristic of the soil is studied, a single extraction can be performed. The extracting solution must be chosen carefully and in accordance with soil characteristics; moreover, these operationally defined results must be interpreted with respect to the extracting solution used. A $CaCl_2$ solution is suitable and widely used for measuring availability in acid-neutral soils, in drawing a correlation with metal elements content in wild-growing plants (Brun *et al.* 1998; Komárek *et al.* 2008; Pueyo *et al.* 2004). The Diffusion Gradient in Thin-film technique (DGT) are considered to be relevant in studying metal element availability through the assessment of the labile fraction (free and easily exchangeable) of metal elements (Zhang *et al.* 1998; Nowack *et al.* 2004; Leermakers *et al.* 2005).

Most studies present their results without taking into account the ageing effect on metal and amendment behaviour following chemical stabilisation (Sappin-Didier *et al.* 1998; Kumpiene *et al.* 2006; Bes and Mench 2008; Lee *et al.* 2009). However, changes appearing in metal behaviour are not invariably linear (Farrell and Jones 2010; Jelusic *et al.* 2013), specifically in a soil system where soil biomass evolves over time (Jelusic *et al.* 2013). Moreover, ageing can result in speciation, fractionation and availability changes (Ford *et al.*

1997; Lim *et al.* 2002). Indeed, ageing plays an important role in the sorption of metals on oxides, due to intraparticle sorption. This phenomenon represents as much as 90% of the sorption sites of manganese oxide and requires from a few months to several years to reach the equilibrium state (Trivedi and Axe 2000). Moreover, Ettler *et al.* (2014) showed that the stability of an amorphous manganese oxide (AMO) in soils is dependent on soil pH and that AMO can release a significant amount of Mn. Secondary weathering products such as rhodochrosite were found to precipitate on the AMO surface, thereby altering AMO properties and metal sorption properties.

In this study, the AMO (Della Puppa *et al.* 2013) for metal stabilisation has been tested in a set of soil samples historically and freshly contaminated Cu, Cd and Pb in using different wt.% AMO (0; 0.01; 0.1 and 1%). The mobility and availability were evaluated over time through sequential and single extraction and DGT. The study of the ageing effect requires performing all experiment in batch system, thereby allowing the stabilisation of the system. The metals and AMO behavioural evolution are finally used to discuss the ageing effect on chemical stabilisation of metal by AMO.

Materials and methods

All chemicals used were of analytical grade. The metal element solutions that served to prepare the new pollution featured $Cu(NO_3)_2\cdot2.5H_2O$, $Cd(NO_3)_2\cdot4H_2O$, $Pb(NO_3)_2\cdot3H_2O$ and $Zn(NO_3)_2\cdot6H_2O$ salts. Nitrate salts were introduced to compare the calculated AMO sorption capacities (Della Puppa et al., 2013). Ultra-pure water from a Milli-Q system (conductivity less than 0.06 $\mu S.cm^{-1}$) was used for solutions preparation. pH values were measured by a Crison micro pH 2000 pH-meter equipped with a combined electrode (reference Ag/AgCl) calibrated with two buffers (pH 4.01 and 7.00 at 25°C). Total organic carbon (TOC) was measured using a Tekmar Dohrman Phoenix 8000 TOC analyser.

Synthesis of the AMO

The amorphous manganese oxide (AMO) was prepared according to the sol-gel procedure used for preparation of birnessite modified from Ching et al. (1997). This procedure consists of slowly adding 0.5 L of 1.4 M glucose solution to 0.5 L of 0.4 M potassium permanganate solution. Once the gel had formed, the solution was filtered and washed with 2 L of ultra-pure water to remove excess reactants. The gel was subsequently dried at room temperature. The modification of the protocol consisted of omitting the heating step (at 400°C) after drying of the gel. The AMO characterisation can be found in Della Puppa *et al.* (2013).

Soil sampling, preparation and characterisation

The studied soil was collected near a metallurgical site where copper had been refined for decades. Prior to sampling, a surface soil layer (0-5 cm) containing the main part of the litter was discarded. The 5-10 cm layer of soil was then sampled manually over a 100 m² area. This thickness was selected as a result of the soil contamination rate. The soil sample was then air-dried and sieved (<2 mm) according to the ISO 11464.

Soil pH was determined using pure water and 1 M KCl solutions at 1/2.5 w/v ratio (ISO 10390). The pH of zero point charge (pH_{ZPC}) was evaluated by an acid-base titration, according to Davranche *et al.* (2003). The cation exchange capacity (CEC) was measured with a cobalthexamine trichloride solution (NF EN ISO 23470). The samples were mixed for 3 h with a 0.016 M cobalthexammine trichloride solution using a 1/5 w/v ratio and filtered through a cellulose nitrate filter. The excess $Co(NH_3)_6^{3+}$ was then analysed with a UV-visible spectrophotometer (Shimadzu UV-160) at 470 nm. A soil blank was produced in order to quantify the interferences by organic matter during measurements.

Soil metal content was measured after inverse aqua regia digestion assisted by a microwave system (Anton Paar, Microwave 3000) and analysed using either a flame atomic absorption spectrophotometer (Varian 880Z) or a furnace atomic spectrophotometer (Varian), depending on the solution concentration. The accelerated BCR sequential extraction procedure (Pérez-Cid *et al.* 1998) was applied to determine the chemical fractionation of the studied metals in soils. The BCR allows dividing metal elements into various fractions defined by the reactants: F1, exchangeable and weakly adsorbed (0.11 M CH_3COOH); F2, bound to reducible fraction (0.5 M $NH_2OH·HCl$); F3, bound to oxidisable fraction (8.8 M H_2O_2 / 1 M CH_3COONH_4), and F4, residual fraction (69% HNO_3 / 37% HCl).

Each experiment was conducted in triplicate, and the values shown represent the average along with the standard deviation.

Experimental soil pot

For the laboratory pot experiments, the soil samples were homogeneously mixed with three different w/v AMO ratios and one unamended control (0, 0.01, 0.1 and 1%) and then placed in plastic pots (height: 9 cm; width: 7 cm) at ambient temperature (25°C ± 3). This set-up allowed monitoring the ageing effect on metal element mobility and availability during the experiment. The mixture was maintained at 80% of the soil water holding capacity (WHC) using ultra-pure water. Pots were performed with 200 g of soil and divided into three distinct series:

(i) One sample set was prepared for monitoring metal behaviour in the soil pore water through the rhizon experiment: pots were pitted to insert an inert and waterproofed hollow fibre soil moisture sampler (Rhizon moisture samplers, Wageningen, The Netherlands). To sample pore water, rhizons equipped with needles were connected to vacuettes. After 60 days, fresh pollution was added to each soil sample and the pore solutions were sampled for 176 days (amounting to a total 236-day duration of the experiment).

(ii) Two series intended for evaluating the impact of AMO on metal behaviour using both extractions (sequential and $CaCl_2$ extraction) and DGT measurements: one for the contaminated soil (maximum ageing time 280 days), and another for the contaminated soil into which fresh pollution was added (maximum ageing time 185 days).

The metal element solution simulating a potential fresh pollution represents 90% of the soil CEC. The key result presented in the study is the following percentage calculation:

Equation 13: Calculation of the percentage of metal extracted

$$M = \frac{M_{extracted}}{M_{initial}} \times 100$$

where: M: calculated percentage of the metal;

$M_{extracted}$: amount of metal extracted and,

$M_{initial}$: amount of metal present in the soil at the beginning of the experiment.

At the beginning of the experiment, soil contamination originated from past industrial activities, with $M_{initial}$ representing the amount of metal in the soil sample (mg.kg^{-1}). In the case where fresh contamination was added to the soil sample, $M_{initial}$ represents the amount of metal initially present in the soil plus the metal added through fresh contamination (mg.kg^{-1}). Each experiment was conducted in triplicate, and the values shown represent the average and the standard deviation.

Mobility and availability of metal elements

The mobility and availability of metal elements were measured using sequential extractions, a single extraction with 0.01 M $CaCl_2$ solution, and Diffusion Gradient in Thin-film (DGT) measurements. Extractions were performed with a 0.01 M $CaCl_2$ solution using a w/v ratio of 1/100, which allows for good correlation between extracted Cu and the Cu content in wild-growing plants in acid-neutral soil (Quevauviller 1998). Regarding DGT, all gels were prepared according to Zhang *et al.* (1998). DGT were deployed in triplicate for 24 h in a wet soil sample (with soils maintained at 80% of WHC) at room temperature (25°C ± 3). The DGT units were then retrieved from the soil and rinsed with ultra-pure water. The binding gel was retrieved and completely immersed into 10 mL of 1 M HNO_3 for at least 24 h to elute metal elements. The DGT measurements after adding the fresh contamination were not available due to saturation of the DGT system. These measurements provide an indication of the labile metal pool (Zhang *et al.* 1998; Nowack *et al.* 2004).

Statistical treatment

Statistical treatments of the data were performed using the software SigmaPlot 12.5 (StatSoft Inc., USA). The data were evaluated using the analysis of variance (ANOVA) with a significant *P-value* < 0.05 using the Tukey test.

Results and discussion

Characterisation of the soil and AMO

The basic physicochemical properties of the studied soil are listed in Table 12.

Table 12: Key physicochemical properties of the soil and AMO (Della Puppa *et al.* 2013), total metal content (mg.kg^{-1}) and sorption capacity of the AMO at pH 5.5.

Physicochemical properties		Total metal content (mg.kg^{-1})	
Polluted soil studied		Al	40682 ± 681
pH_{H2O}	4.34 ± 0.01	Fe	24021 ± 355
pH_{KCl}	3.62 ± 0.01	Mn	424 ± 21
pH_{ZPC}	8.3 ± 0.1	Cu	356 ± 10
TOC (mg.g^{-1})	6.0 ± 0.3	Cd	5.2 ± 0.1
TIC (mg.g^{-1})	< d.l.	Pb	99 ± 2
CEC (meq.100g^{-1})	14.2 ± 0.4		
AMO		Sorption capacity of the AMO (mg.g^{-1})	
pH_{H2O}	8.1 ± 0.3	Cu	28.77
pH_{KCl}	7.9 ± 0.1	Pb	125.15
pH_{ZPC}	8.3 ± 0.1	Cd	49.23
SSA (m².g^{-1})	14.8		
CEC (meq.100g^{-1})	34 ± 1		

According to pH values, the soil is acidic with poor organic matter content and a low cation exchange capacity (Table 12). The soil exhibits a high concentration of Cu (356 mg.kg^{-1}), consistent with past industrial activities close to the sampled area. The fractionation of Cu, Cd, Pb and Mn is shown in Table 13.

Table 13: Fractionation of Cu, Cd, Pb and Mn in the soil sample (%).

	Cu	Cd	Pb	Mn
Fraction 1 (weakly adsorbed and easily exchangeable)	8 ± 1	40 ± 2	5 ± 1	5 ± 1
Fraction 2 (reducible)	26 ± 3	37 ± 11	19 ± 3	37 ± 6
Fraction 3 (oxidisable)	42 ± 2	12 ± 2	32 ± 4	17 ± 2
Fraction 4 (residue)	21 ± 2	6 ± 3	27 ± 1	32 ± 6

A larger proportion of Cu and Pb is bound to both the reducible fraction (26% and 19% respectively) and the oxidisable fraction (42% and 32% respectively), which results into the relatively low mobility of these elements. Considering Cd, the major proportion is in the exchangeable form (40%) and bound to the reducible fraction (37%), meaning that Cd is more labile than Cu and Pb as expected (Pueyo *et al.* 2004). Manganese is mainly found in the reducible fraction and in the residue (37%) because this element is mainly present as Mn oxides in the soil. Except for Cd, a portion of the metals is recovered in the residual fraction (21% for Cu, 27% for Pb and 32% for Mn).

The AMO has a high pH value and low cation exchange capacity (Table 12). In considering sorption capacities at pH 5.5 (Table 12), AMO presents good characteristics compared to birnessite (Della Puppa *et al.* 2013).. In a multi-species system, the sorption of Cu and Pb increase while Cd sorption decreases due to greater affinity between Cu and Pb for the AMO (Della Puppa *et al.* 2013), indicating that Cu and Pb are preferentially sorbed in these conditions. Its pH_{ZPC} value (8.3) promotes the sorption of metallic cations in the studied soil (pH_{H2O}: 4.3) due to its negatively charged surface at this pH value.

Metal concentration in pore water as a function of AMO ratio

The metal concentrations in pore water were monitored during pot experiments conducted with the historically polluted soil relative to the added AMO ratio (Fig. 30).

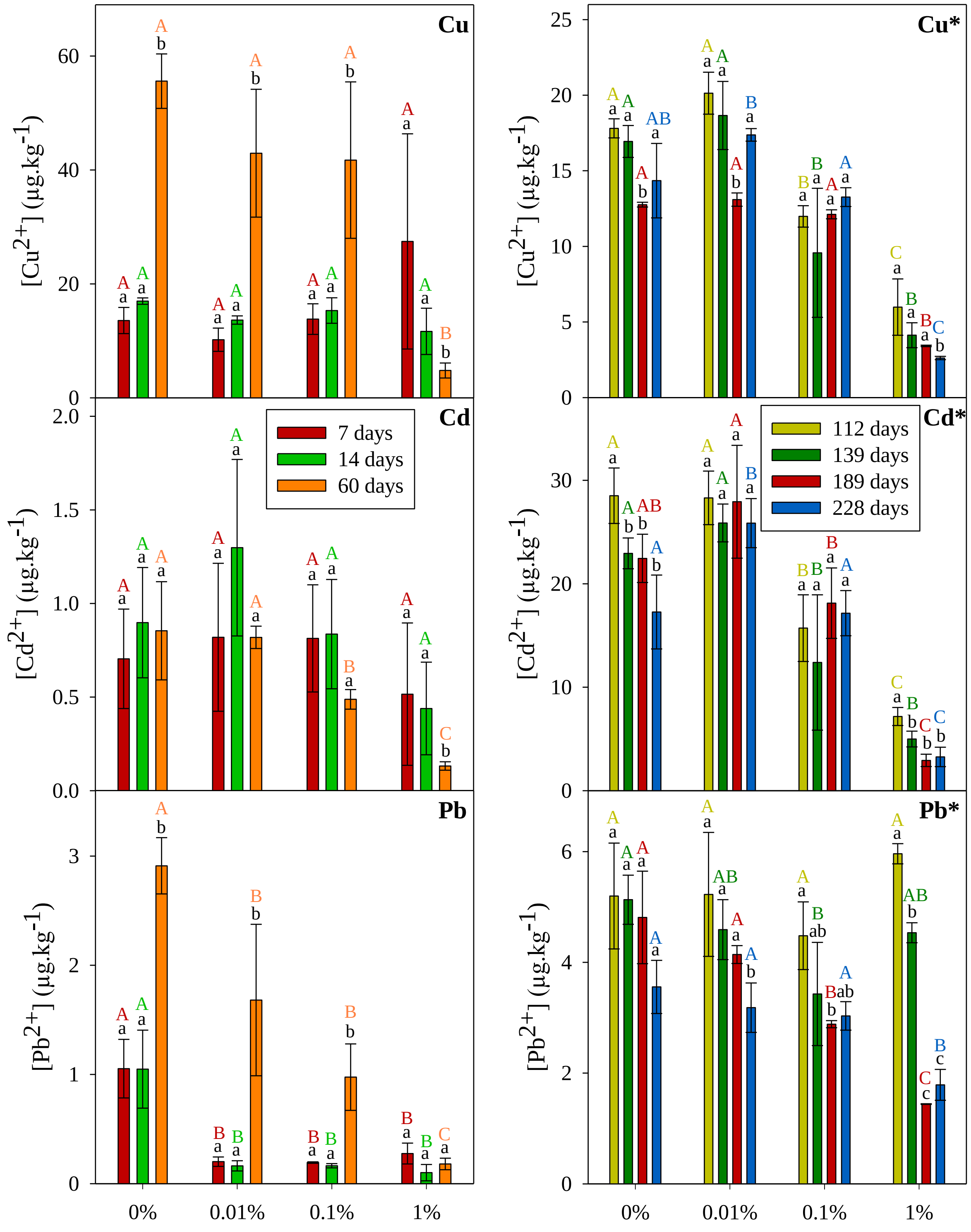

Figure 30: Pore water measurements of Cu, Cd and Pb *vs.* the w/w AMO ratio both before adding a mixed solution of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} (Cu, Cd, Pb) and after (Cu*, Cd*, Pb*). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each ratio whereas capital letters represent the statistical result for each contact time.

In the soil contaminated by past industrial activities (Fig. 30), at a 0% w/w AMO ratio, it appears that the Cu and Pb amounts increased in the pore water over time (from 13.6 to 55.3 µg.kg^{-1} and from 1.1 to 2.9 µg.kg^{-1}, respectively, for Cu and Pb between 7 and 60 days), whereas no change was observable for Cd. After 60 days, fresh pollution (mixed solution of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) was added to each soil sample, and the pore solutions were sampled for 168 days. Without AMO, the metal in pore water increased significantly over time for Cu and Pb (Fig. 30). When the AMO was added to the soil, the amounts of Cu, Cd and Pb originating from past industrial activities measured in the pore water after 60 days significantly decreased compared to 0%. In the case of Cu and Cd, the effect was only apparent after 60 days, while for Pb the decrease began 7 days after the addition. After adding the fresh contamination, the presence of AMO at 1% strongly decrease the metal in pore water, this decrease being improved over time.

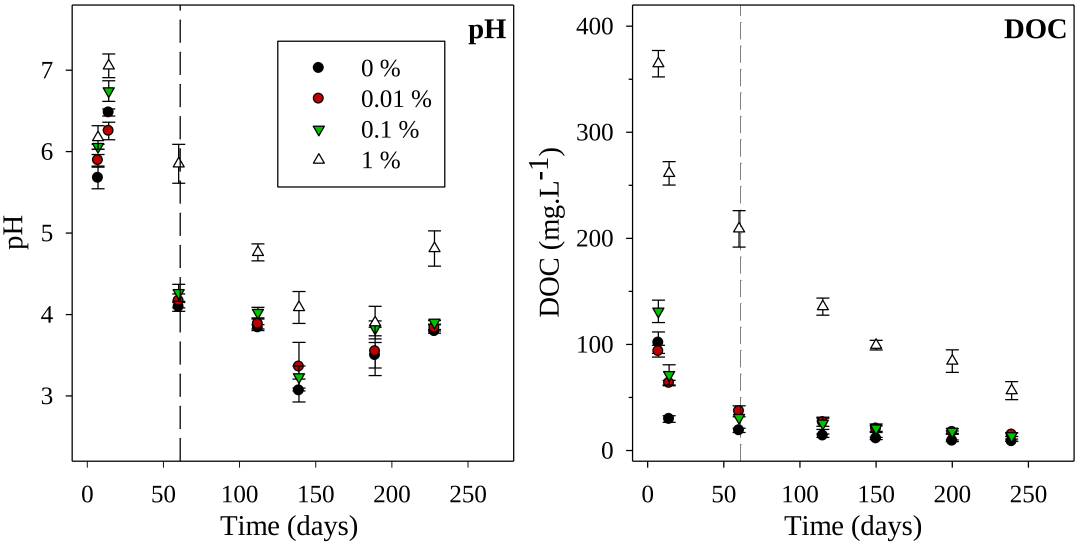

Figure 31: Evolution of pH value and DOC during pore water measurements *vs.* the w/w AMO ratio. The line indicates the day when the pollution was added (mixed solution of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}).

Concerning pH and DOC, Figure 31 shows that the presence of AMO at 1% significantly increases these parameter values. The higher DOC values reached for a 1% rate may be due to the higher pH value (which improves organic matter dissolution) as well as to glucose synthesis residue of the AMO in the pore water. Over time, pH and DOC decrease as a result of the leaching effect. When fresh contamination is added, no effect can be observed for DOC but pH values decrease below the soil pH$_{H2O}$. This outcome may stem from the adsorption of metal into the soil or AMO, which releases protons into the solution (competition between H^+ and metals on the solid surface).

The measurement of metal amount in pore water of the contaminated soil reveals that AMO reduces metal mobility at ratios above 0.1% (Fig. 30). This improved decrease is observable at 1% for all three metals studied with both the historical and fresh soil pollution. AMO promotes the retention of metal elements due to its sorption properties and through the pH increase of the system (Fig. 31). In the two cases, i.e. historical or fresh metal pollution, the effect of AMO increases over time which highlights the strong impact of ageing on both AMO and metals. This behaviour is generally attributed to micropore diffusion or cavity entrapment (Wardle and Parkinson 1990). In our case however, the precipitation of a new solid phase (rhodochrosite $MnCO_3$, Ettler *et al.* 2014) may explain this behaviour by the retention of metal elements through occlusion in solid phases, in co-precipitating or increasing the sorption capacity of the solid mixture.

Metal availability in the soil

Figures 32 and 33 present the evolution of Cu, Cd and Pb availability through 0.01 M $CaCl_2$ extractions and DGT measurements.

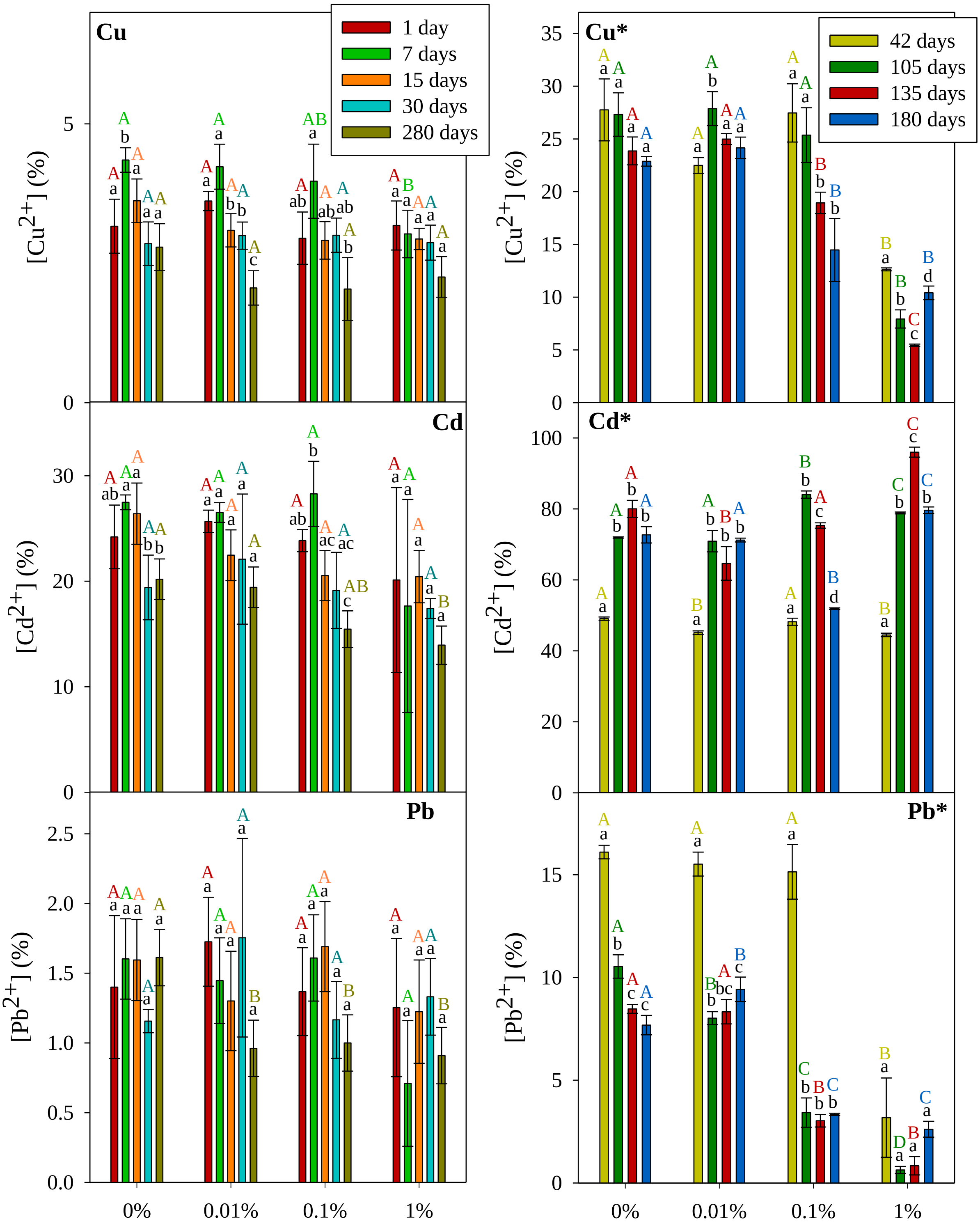

Figure 32: Amount extracted by 0.01 M $CaCl_2$ of Cu, Cd and Pb *vs.* the w/w AMO ratio for both the historical pollution (Cu, Cd, Pb) and after adding fresh contamination (Cu*, Cd*, Pb*). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each ratio whereas capital letters represent the statistical result for each contact time.

Results from the 0.01 M $CaCl_2$ extractions (Fig. 32) show that metals originating from former industrial activities exhibit no major changes over time at 0% AMO. In the presence of AMO, the amount of Cd and Pb extracted are lower compared to 0%, not for Cu, however. After adding the fresh pollution, major changes over time become apparent as the increase of Cd or the decrease of Pb over time. Results obtained for Cd and Pb at 0.01% are similar to those at 0%. At 1%, the AMO impact is clearly visible after 42 days for Cu and Pb, in displaying the lowest extracted amount compared to all other ratios (16.1, 15.5, 15.1 and 3.2% extracted Pb respectively for 0, 0.01, 0.1 and 1% added AMO). The DGT measurements (Fig. 33) show that at a 0% w/w AMO ratio, an increase in the metals contributed by past industrial activities occurs between 1 and 7 days, followed by stabilisation. AMO impact becomes visible at a 1% w/w ratio in the contaminated soil, thus resulting in a decrease of the Cu and Pb amounts extracted, though no impact is visible for Cd. The DGT measurements were not performed on soil freshly contaminated due to the saturation of the DGT gel, which rendered results meaningless.

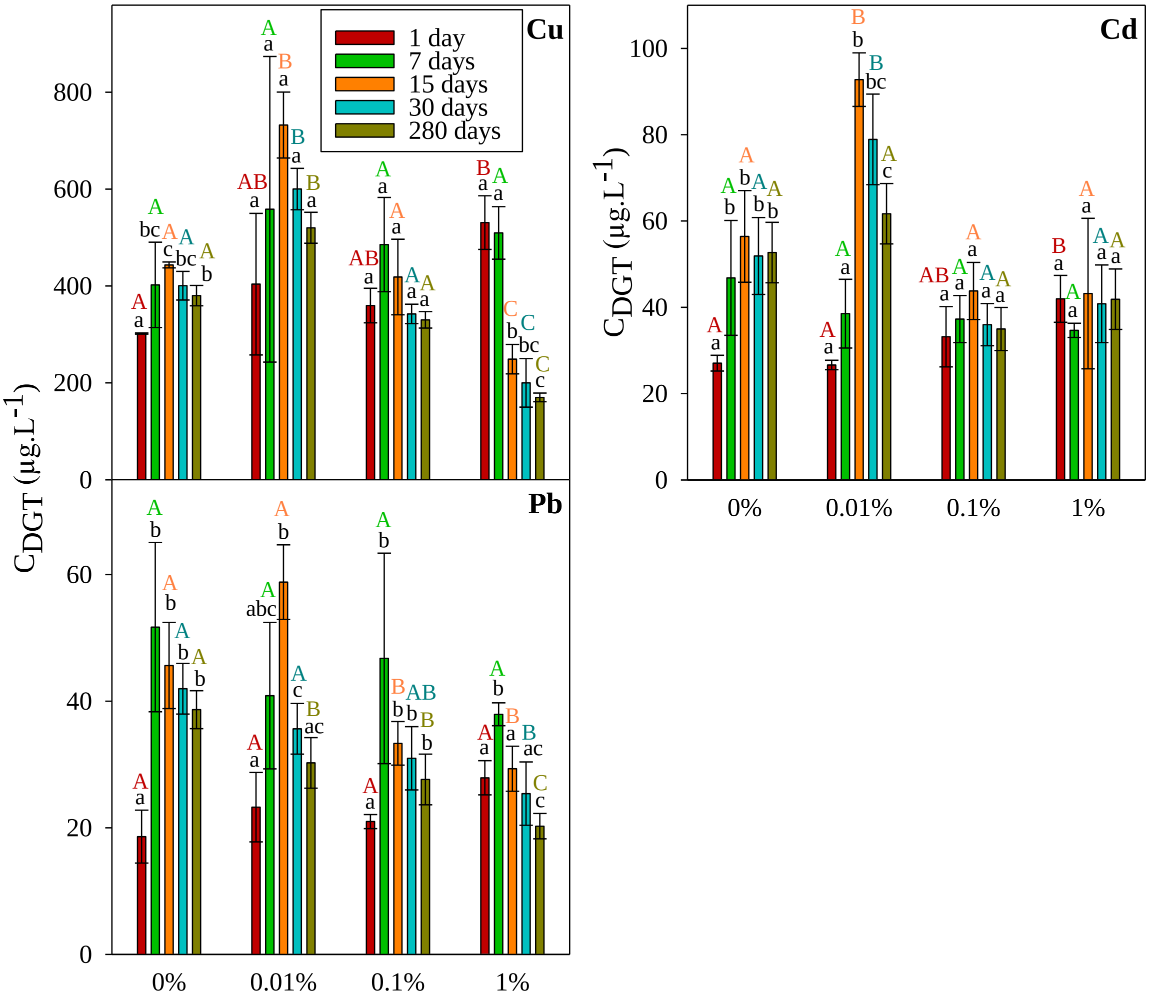

Figure 33: DGT measurements of Cu, Cd, and Pb in soil over time *vs.* the w/w AMO ratio. Data with the same letter represent statistically identical values ($P < 0.05$); non-capital letters representing the statistical result for each ratio whereas capital letters represent the statistical result for each contact time.

In the case of historical contamination, AMO has a limited impact on metal availability, which corroborates the results found by Lim *et al.* (2002) and Tang *et al.* (2006), metals provided by former pollution are typically less labile. In our case, metal elements are mainly immobilised by soil oxides and organic matter except for Cd, which is mainly exchangeable (Table 13). On the freshly added contamination however; this decrease is clearly visible for Cu and Pb with half the availability at a 1% w/w AMO ratio after 180 days. Hettiarachchi *et al.* (2000) also found that Mn oxide (cryptomelane) was effective in decreasing the bioavailable Pb, thus confirming the stabilisation potential of Mn oxides. For both these metals, the AMO effect increases over time, perhaps as the consequence of a rate-limiting retention process (Lim *et al.* 2002), such as the intraparticle surface diffusion, which can apply to 40-90% of the sorption sites (Axe and Trivedi 2002). No effect was observed for Cd, possibly due to its high mobility or possible sorption competition with Cu and Pb on the the AMO, with Pb being favoured (Della Puppa *et al.* 2013). Houben *et al.* (2012) showed that Pb and Cd do not respond in a similar way to the amendments, thereby highlighting the difficulty in finding an effective amendment for all the metal elements. The use of $CaCl_2$ as extracting solution can generate a competition between Ca^{2+} and Cu, Cd, Pb and, moreover, generate the formation of chloride complexes (Makino *et al.* 2006; Dermont *et al.* 2008); which can explain the difference between DGT measurements and $CaCl_2$ extractions.

Evolution of metal fractionation in soil

Figure 34 presents the evolution of Cu, Cd and Pb fractionation for the historical soil pollution over time at both 0% and 1% AMO. The other ratios (0.01 and 0.1%) exhibit the same effect obtained at 1% with less intensity (Figs. 35).

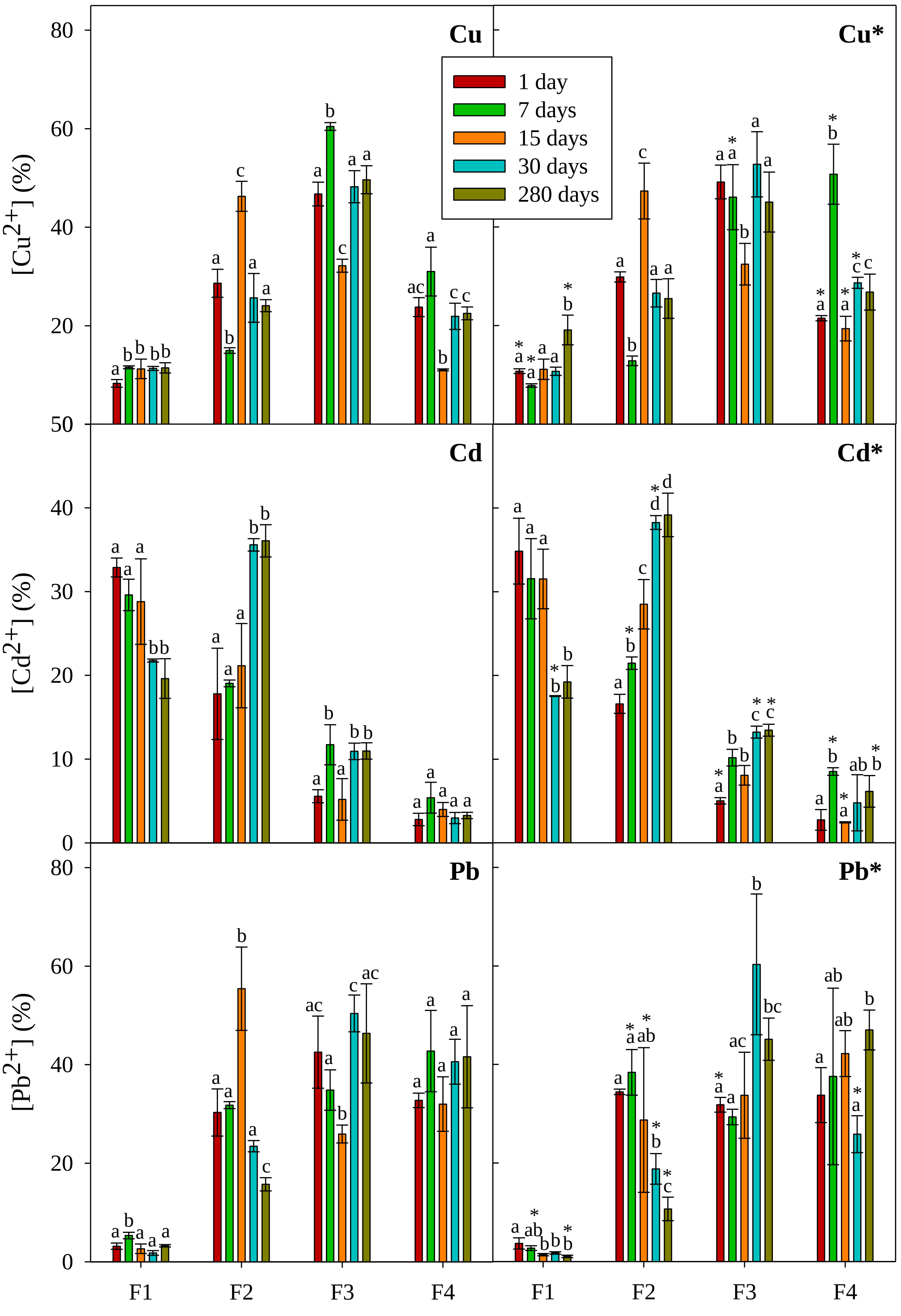

Figure 34: Fractionation of Cu, Cd and Pb for the historical pollution at various contact times *vs.* the w/w AMO ratio: 0% (Cu, Cd, Pb) and 1% (Cu*, Cd*, Pb*). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each fraction whereas * indicates a statistical difference between 0% and 1%.

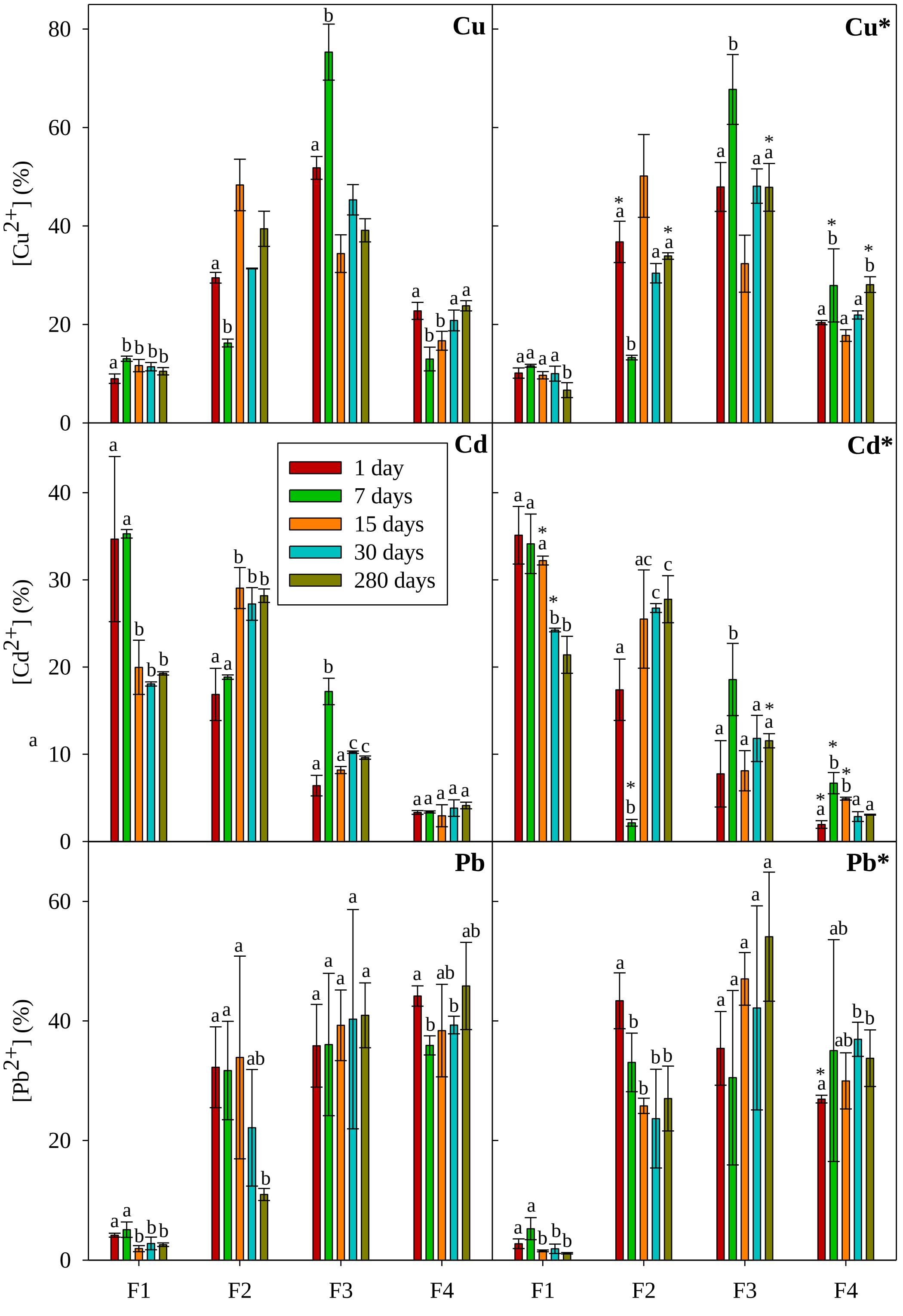

Figure 35: Fractionation of Cu , Cd and Pb for the historical pollution at various contact times *vs.* the w/w AMO ratio: 0.01% (Cu, Cd, Pb) and 0.1% (Cu*, Cd*, Pb*). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each fraction whereas * indicates a statistical difference between 0.01% and 0.1%.

At 0% w/w AMO, for Cu and Pb, no major changes appear over time (Fig. 34). For Cd, a decrease *vs.* time in the easily exchangeable fraction is visible with an increase in the Cd bound to the reducible and oxidisable fractions. Adding AMO therefore exerts only a small impact on metals fractionation in the soil, fractionation of metals being very similar to that obtained at 0%. The former contamination originating from past industrial activities is already well stabilised in the soil, which would explain why only slight changes in each metal element fractionation are visible (Lim *et al.* 2002; Tang *et al.* 2006). The minor changes occurring over time that appear in the control are mainly due to the drying and sieving treatment of the soil sample (Bordas and Bourg 1998).

After studying the fractionation from former contamination (Figure 36-37), the soil was polluted with a mixed solution of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} (Zn not shown).

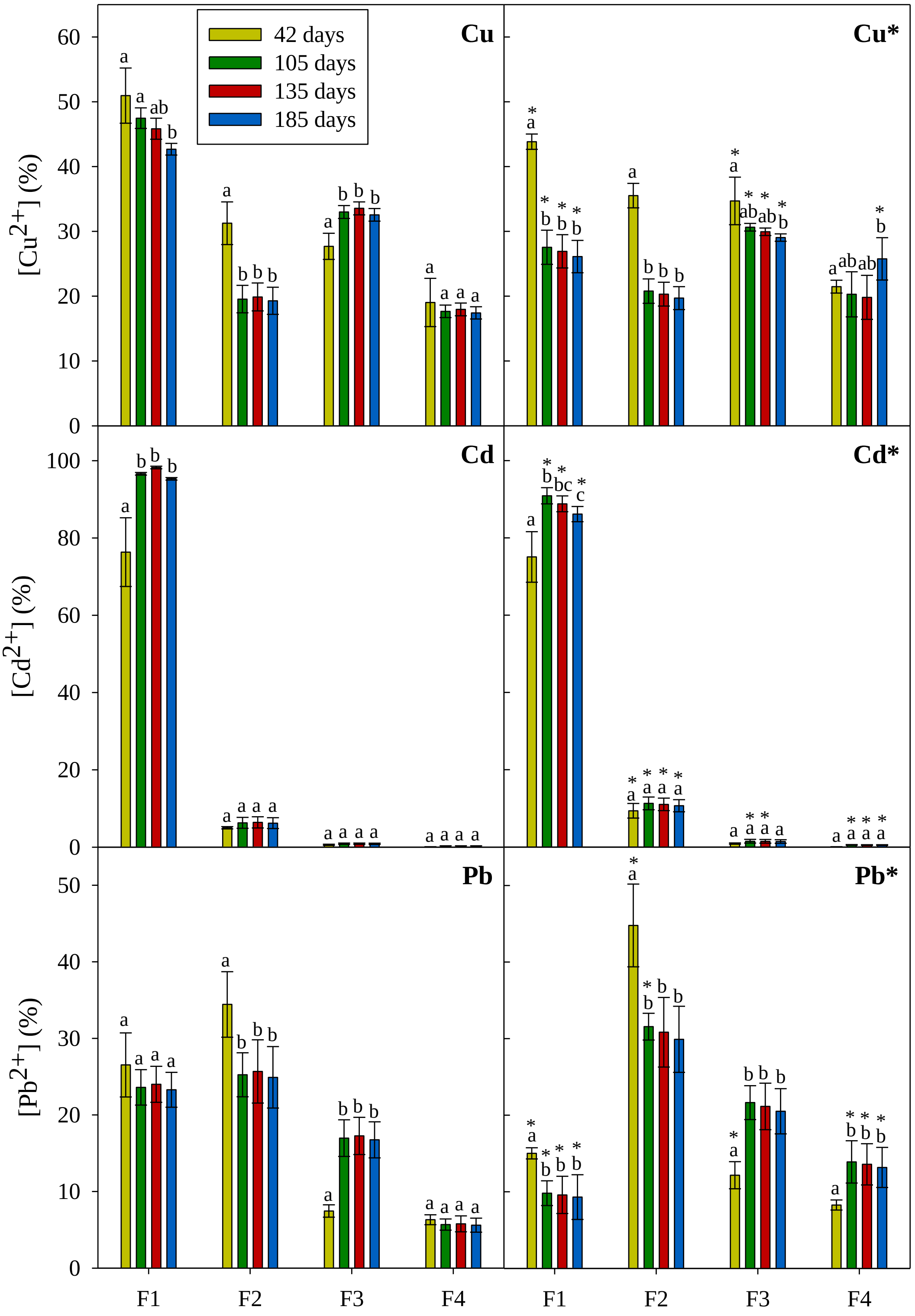

Figure 36: Fractionation of Cu , Cd and Pb at various contact times after adding the fresh contamination *vs.* the w/w AMO ratio: 0% (Cu, Cd, Pb) and 1% (Cu*, Cd*, Pb*). Data with the same letter represent statistically identical values ($P < 0.05$); non-capital letters representing the statistical result for each fraction whereas * indicates a statistical difference between 0% and 1%.

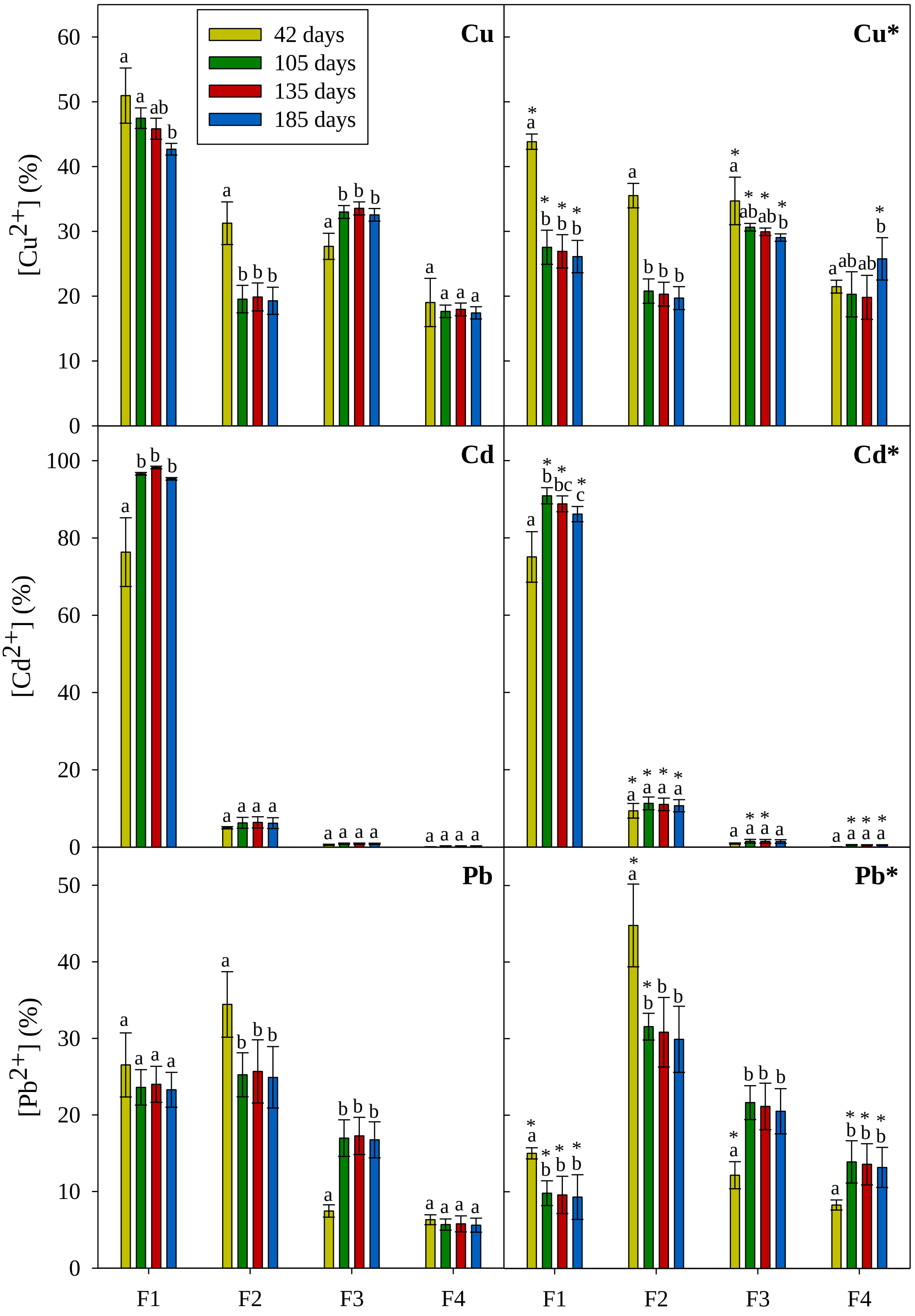

Figure 37: Fractionation of Cu, Cd and Pb) at various contact times after adding the fresh contamination *vs.* the w/w AMO ratio: 0.01% (Cu, Cd, Pb) and 0.1% (Cu*, Cd*, Pb*).). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each fraction whereas * indicates a statistical difference between 0.01% and 0.1%.

The fractionation generated by sequential extractions is exhibited in Figure 36 for 0% and 1% and in Figure 37 for 0.01% and 0.1% w/w AMO ratios.. Regarding Cu at 0% w/w AMO, Figure 36 shows that 42 days after the contamination, 51% of the Cu is present in the easily exchangeable fraction, 31% is bound to the reducible fraction, 28% is bound to the oxidisable fraction, and 19% is present in the residue. Over time, a decrease in the easily exchangeable fraction and Cu bound to the reducible fraction is visible, while Cu bound to the oxidisable fraction increases. The residue tends not to change over time. As for Cu; at 0%, most of the Cd added (Fig. 36) lies in the easily exchangeable fraction. Except for an increase between days 42 and 105, this value remains constant over time. For Pb, at 0% (Fig. 36), most of the metal is easily exchangeable and bound to the reducible fraction. An increase in the Pb bound to the oxidisable fraction appears between 42 and 105 days. For Cu at 1% (Fig. 36), AMO effects result in a major decrease of the easily exchangeable and bound to reducible fractions, and a more modest decrease of the bound to oxidisable fraction. Moreover, Cu in the easily exchangeable fraction reached a minimum at the 1% ratio (in comparing 43, 40, 35 and 26% respectively for the 0, 0.01, 0.1 and 1% ratios). Concerning Cd (Fig. 36), the amount extracted in the easily exchangeable fraction at 1% is lower after 185 days compared to 0% (95% and 86% respectively at 0% and 1%). Moreover, Fig. 36 exhibits a decrease in the Pb easily exchangeable and bound to the reducible fraction and an increase in both the oxidisable fraction and residue.

Adding AMO at 1% results in successfully reduce Cu mobility by decreasing the exchangeable fraction and increasing the residue. Cd is known as a labile element and does not immobilise as efficiently as Cu and Pb, which might indicate that Cd is less sensitive to the AMO addition than Cu and Pb. Lee *et al.* (2011) demonstrated that using zerovalent iron results in an increase of Cd bound to the reducible fraction, along with a decrease of Pb in the exchangeable and reducible fractions and an increase of Pb bound to the oxidisable fraction. The behaviour of Cd and Pb are quite similar in terms of results obtained with AMO, whereas Mench *et al.* (1994) found that after adding a hydrous Mn oxide to a soil, the amount of Pb bound to the reducible and oxidisable fractions increased and decreased, respectively. In our case, for both the historical and fresh contaminations, the amount of Pb in the oxidisable fraction increased (Figs. 34 and 36), which could be explained by the affinity of Pb for organic matter (Mench *et al.* 1994). The amount of Cu, Cd and Pb in the residue increased compared to 0%, which might indicate a modification of AMO properties during the experiments. Moreover, the time required for the stabilisation of the fresh pollution may be not reached, as some sorption processes need more time, e.g. intraparticle diffusion (Axe and Trivedi 2002). The evolution of fractionation over time is possibly due to a lack of time, as evidenced by decreases in the Cu and Pb easily exchangeable pool over time. Since the fresh contamination represents 90% of the soil CEC and exceeds AMO sorption capacity, its addition can lead to sorption competition between metals, with Cu and Pb appearing to be more competitive than Cd, which is consistent with results from Della Puppa *et al.* (2013). Furthermore, the sequential extractions may not be sensitive enough to more accurately identify AMO and ageing impacts on metals fractionation.

AMO behaviour in soil

Figure 38 depicts the evolution of Mn fractionation in soil at 0% and 1% w/w AMO. The other ratios are given in figure 39.

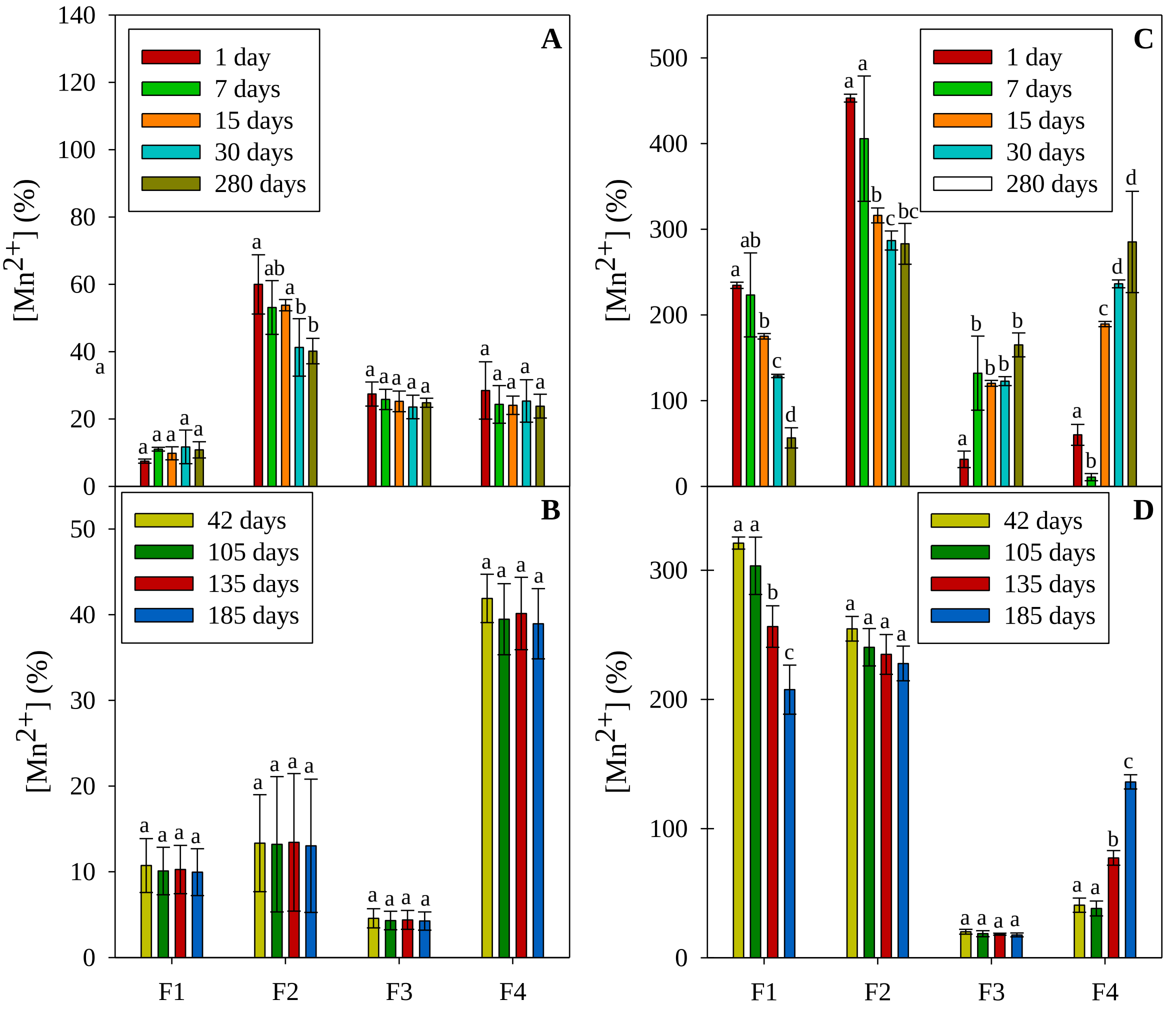

Figure 38: Fractionation of Mn at various contact times both before (A, C) and after adding the fresh contamination (B, D) *vs.* the w/w AMO ratio: 0% (A, B) and 1% (C, D). Data with the same letter represent statistically identical values (P < 0.05); non-capital letters representing the statistical result for each fraction.

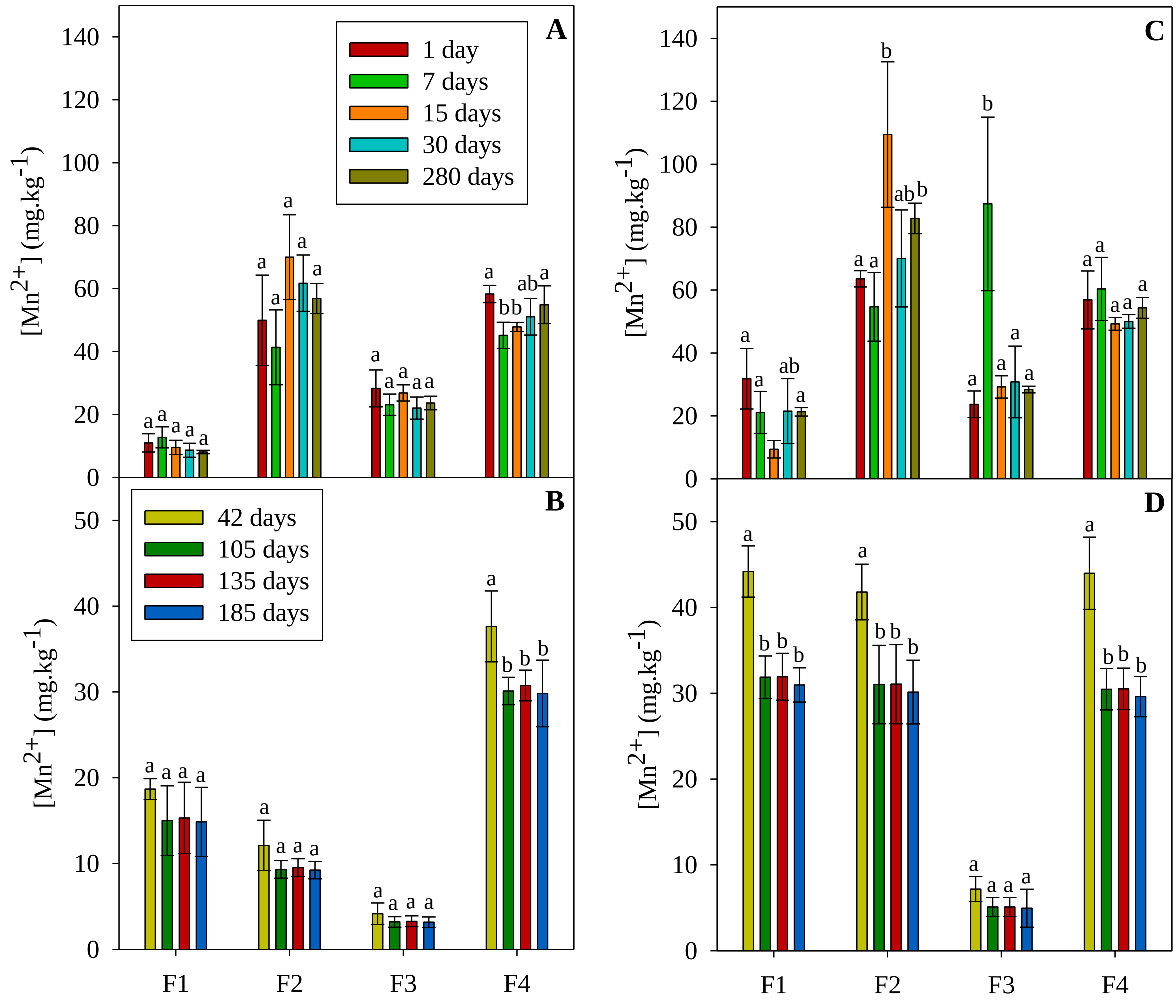

Figure 39: Fractionation of Mn at various contact times both before (A, C) and after adding the fresh contamination (B, D) *vs.* the w/w AMO ratio: 0.01% (A, B) and 0.1% (C, D). Data with the same letter represent statistically identical values (*P* < 0.05); non-capital letters representing the statistical result for each ratio.

The percentages of Mn are calculated based on the amount present in the soil without AMO. At 0%, no major changes appear over time except a decrease of the Mn in the reducible fraction. Major changes do however appear at 1%. An evolution is clearly visible over time with the decrease of Mn in the easily exchangeable and reducible fractions, while Mn in the oxidisable fraction and residue increases. After adding the new contamination, no major changes appear over time at 0%. At 1%, a decrease of Mn in the easily exchangeable fraction can be observed along with a significant increase of Mn in the residue. Figure 38 shows that AMO fractionation undergoes changes over time, with a decrease in Mn mobility and availability.

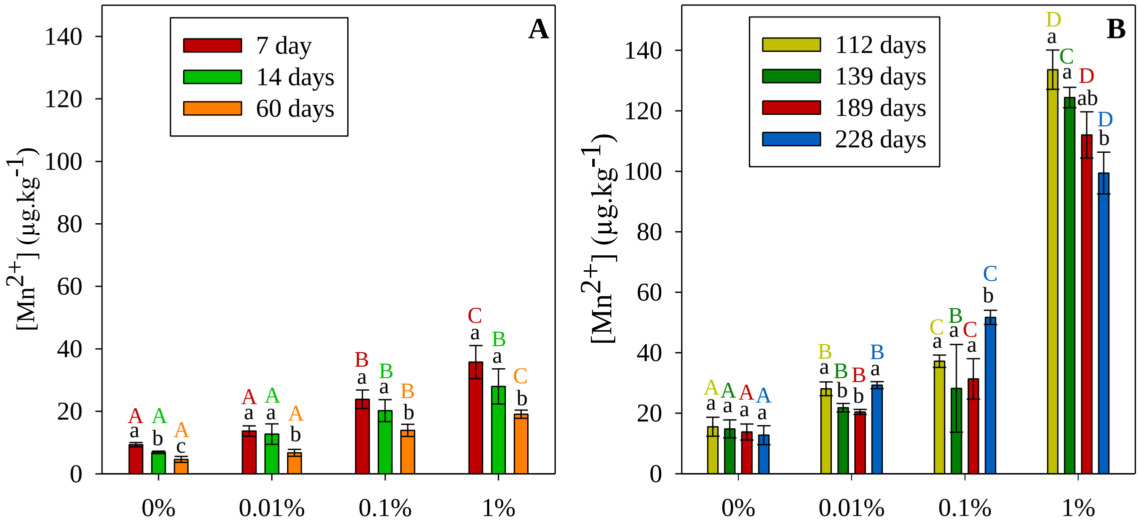

Figure 40: Pore water measurements of Mn *vs.* the w/w AMO ratio before manual contamination (A) and after (B). Data with the same letter represent statistically identical values ($P < 0.05$); non-capital letters representing the statistical result for each ratio whereas capital letters represent the statistical result for each contact time.

According to the Mn extracted during pore water measurements (Fig. 40), it can be stated that increasing AMO ratio results in an increase of Mn in the pore water (4.6, 6.7, 13.9 and 19.1 µg.kg^{-1} respectively for 0, 0.01, 0.1 and 1%). A decrease over time however is observable, the Mn released becomes stabilised over time. DGT measurements and $CaCl_2$ extractions (Fig. 41) tend to reveal the same trend, with Mn release at the beginning of the experiment, followed by a decrease in Mn availability after 180 days.

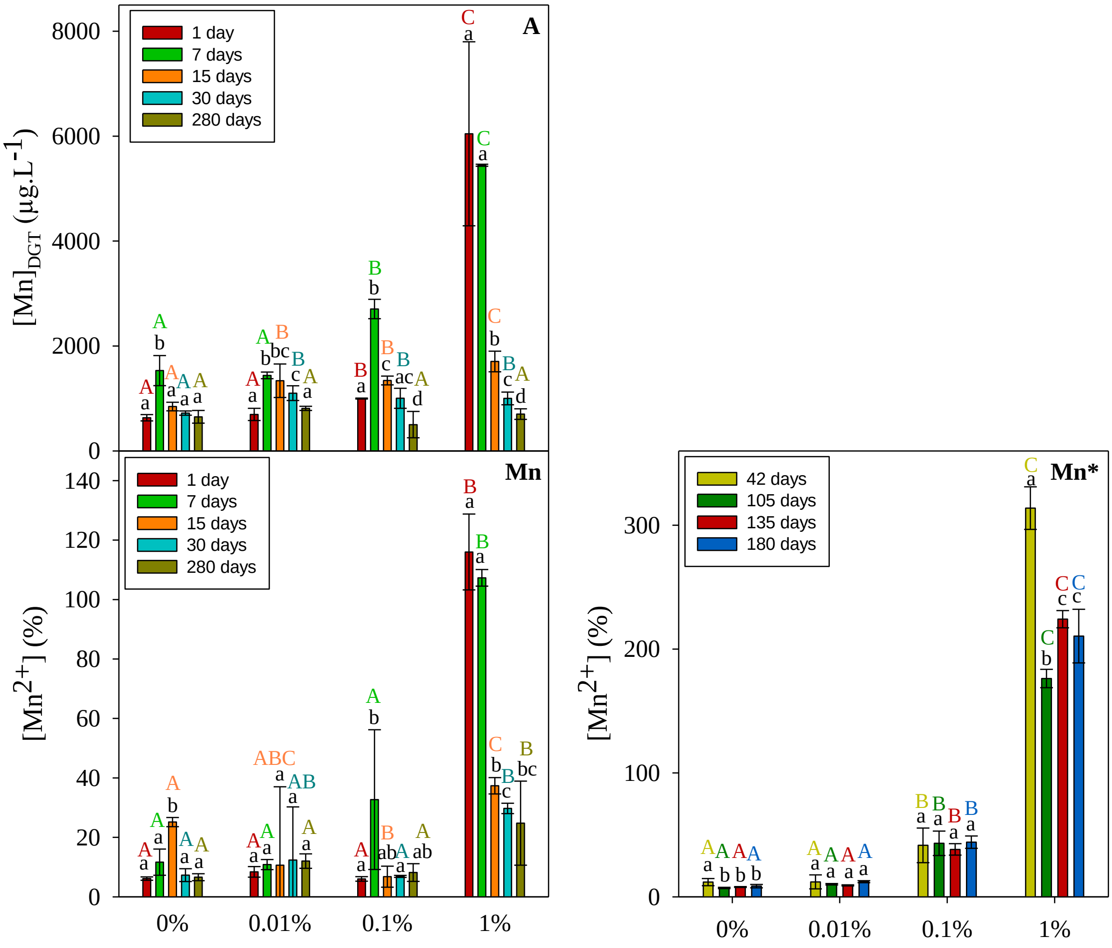

Figure 41: DGT measurements of Mn in soil (A) and the amount of Mn extracted by 0.01 M CaCl$_2$ before the manual contamination (Mn) and after (Mn*) *vs.* the w/w AMO ratio over time. Data with the same letter represent statistically identical values (P < 0.05); non-capital letters representing the statistical result for each ratio whereas capital letters represent the statistical result for each contact time.

The AMO needs a stabilisation period at the beginning of these experiments (changes in Mn fractionation, loss of Mn), which is consistent with results found by Ettler *et al.* (2014). The loss of Mn may arise from the partial solubilisation of AMO and the release of weakly-bound Mn onto the AMO surface (Della Puppa *et al.* 2013; Ettler *et al.* 2014). AMO ageing however tends to decrease the mobility and availability of Mn released. Also, the increase of Mn in the residue may be caused by the formation of rhodochrosite (MnCO$_3$) on the AMO surface (Ettler *et al.* 2014). Moreover, considering the amount of Mn released in the pore water and the pH of the pore water, rhodochrosite can precipitate under these conditions (MINEQL+4.6, Schecher and McAvoy 2003). The first step of the sequential extraction theoretically dissolves carbonates using acetic acid (Pérez-Cid *et al.* 1998), yet some carbonates can resist this dissolution, e.g. magnesite ($MgCO_3$) (Laçin *et al.* 2005), which would indicate that rhodochrosite is not being dissolved by acetic acid but rather during mineralisation (residual fraction). Furthermore, a carbonate layer has been found by Ettler *et al.* (2014) after incubating the AMO in soils.

The AMO ageing seems to increase metal immobilisation. When considering Cu and Pb, ageing decreases their mobility through the increase of the residue during fractionation. The formation of a carbonate layer on the AMO might explained the increased residue during sequential extractions and can act as a passivation layer. For Cd, AMO decreases its mobility by decreasing the easily exchangeable fraction; however, DGT measurements and $CaCl_2$ extractions have shown that AMO is unable to reduce Cd availability, most likely due to the competition between Cu, Pb and Cd (with AMO sorption capacity being exceeded after adding the fresh contamination).

Conclusion

The efficiency of AMO for stabilising metal elements (Cu, Cd, Pb) in a contaminated soil (with both historical and recent pollution) has been evaluated over time in this study by use of various methods (rhizons, DGT measurements, $CaCl_2$ extraction and sequential extractions). Experiments over time showed that ageing affects AMO through a partial dissolution and the possible formation of a new solid phase on its surface (e.g., rhodochrosite). The Mn released by AMO was quickly immobilised (within 15 days), became unavailable and could participate in the rhodochrosite formation. This study also demonstrated that AMO started to be effective in affecting metal element stabilisation at 0.1% w/w ratio. AMO does not significantly influence the historical pollution, in sharp contrast with the freshly added pollution, possibly due to the fact that metal elements are already well stabilised in the soil, thus highlighting the key role of ageing in metal element stabilisation. As for historical contamination however, the presence of AMO allows a decrease in metal availability without modifying metal fractionation in the soil.

Regarding the studied metal elements, the AMO proved to be effective in reducing their availability and mobility through decreasing the easily exchangeable fraction (mainly for Cd and Pb) and increasing the residual fraction. The stabilisation of these metal elements did not occur instantaneously but instead progressed over time due to the ageing effect, in allowing for micropore diffusion of the metal elements into the solids. Moreover, the precipitation of rhodochrosite can enhance the stabilisation potential by means of occlusion, co-precipitation and sorption onto this newly formed phase. Ageing influences both metal element behaviour and AMO properties in the soil, with AMO becoming more efficient over time.

This article has shown that ageing is an important parameter for metal immobilisation. In accordance with results found during column experiments, the AMO affects more strongly new pollution than for former pollution and becomes effective as of 0.1%. The Mn released by AMO during the experiments increases with the AMO/soil ratio, becoming quickly immobilised and unavailable. Ageing also seems to increase the AMO sorption properties.

As is the case in column experiments, organic matter solubilisation reached the highest values at a 1% AMO ratio. However, AMO increased metal immobilisation when increasing the ratio, unlike the column experiments: AMO reached its highest efficiency at 1% during batch experiments and at 0.1% in column experiments. This difference in AMO behaviour for metal immobilisation may be due to the difference in ageing time and to the fact that in column experiments, lixiviate elements are evacuated of the system unlike in batch experiments. Moreover, under dynamic conditions, the precipitation due to a saturated medium is limited because of the continuous leaching of pore water. Under static conditions however, the medium can become oversaturated (as shown by Ettler et al., 2014), resulting in the precipitation of carbonates (as rhodochrosite, $MnCO_3$). Metallic element immobilisation might increase due to the coprecipitation of these elements with newly-formed phases. Lu *et al.* (2011) showed that the coprecipitation of Pb(II) with ferric oxyhydroxides is more efficient in removing Pb from aqueous solutions than adsorption at a similar ratio and pH. Moreover, under dynamic conditions, it is not to be excluded that despite filters installed at the end of the columns, some AMO particles have been leached, thereby decreasing AMO content inside the columns.

Chapter III: Conclusion and outlook

Despite less favourable characteristics for cation sorption than with birnessite (a lower SSA and CEC), AMO sorption properties approximate those of birnessite. However, unlike birnessite and perhaps because AMO is initially a synthesis intermediate, AMO seems to be unstable at the beginning of the experiment for each system (whether pure water or soils). At the beginning of each experiment, a partial dissolution occurs. In pure water, this dissolution represents 5.70% and 0.24% respectively (depending on the ratio, for 1/500 and 1/10 w/v), whereas in soils it represents 10% to 18% of the total AMO amount (Ettler *et al.* 2014). This dissolution has been shown to be pH-dependent, more acidic soil resulting in higher dissolution rates. In addition, some modification of AMO appears in water, as the modification of zeta potential (the zeta potential decreased instead of increasing when raising pH levels after agitation in pure water), the average Mn oxidation state (agitation in pure water results in a release of Mn weakly bound on the AMO surface, which in turn causes a decrease in the Mn AOS) and CEC. This modification also appears in soil as an increase in particle size or precipitation of a new phase like rhodochrosite (Ettler *et al.* 2014). Despite the fact that AMO needs a stabilisation period at the beginning, it can still act as a potential chemical stabilising agent due to its sorption properties, in displaying sorption properties close to those of birnessite (1.38, 1.20 and 2.38 mmol.g^{-1}, respectively, for Cu, Cd and Pb at pH 5.5).

Under dynamic conditions, the 0.1% w/w AMO ratio appears to be the most efficient, in greatly increasing the soil sorption capacity (an increase of 18%, 57% and 38%, respectively for Cu, Cd and Zn compared to the control sample) and significantly decreasing the availability of metallic elements (a decrease of 22%, 48% and 17%, respectively, for Cu, Cd and Zn). However, Pb seems to remain unaffected by AMO, with the best values being obtained for the control, despite the fact that Pb seems to have a good affinity for AMO (Pb displays a better affinity for AMO than Cu and Cd, as demonstrated by kinetics and adsorption isotherm studies). Under static conditions, a 1% w/w AMO ratio is the most efficient and significantly decreases the amount of Cu, Cd and Pb in pore water for both former and newly-added contamination over time, thus resulting in a decrease of their availability (as confirmed by DGT measurements) from 21% for Cd to 55% for Cu for the former contamination. Moreover, results clearly show that AMO sorption properties increase over time, possibly due to the formation of newly-formed phase (rhodochrosite, $MnCO_3$), which immobilises metallic elements through coprecipitation processes; and slow intra-particule diffusion. This finding is in agreement with the fact that the residual fraction during sequential extraction has increased over time, hence highlighting a decrease in metal mobility. Under dynamic and static experiments, the presence of AMO generates an increase in pH value (up to a difference of 0.5 pH unity), as well as an increase in the Mn quantity in pore water. Yet under static conditions, the released Mn quickly became immobilised and unavailable. Another consequence is the increase of DOC compared to the control sample. Except at 0.1% under dynamic conditions, the presence of AMO increased DOC in the pore water, possibly due to the solubilisation of organic matter and AMO dissolution (organic carbon content of AMO: 17.0 $mg.g^{-1}$; stemming from the glucose residue of the synthesis). During the column experiments, the increase in DOC in leachates generated a decrease of soil sorption capacities; thus indicating that sorption capacity is impacted by organic matter content.

Considering the optimium ratio in static and dynamic conditions, it appears that difference arises (1% and 0.1% for static and dynamic conditions optimum ratio, respectively). This difference may originate from the experimental conditions. In static conditions, elements not adsorbed remain in the system, contrary to dynamic conditions, which allows a potential future immobilisation. In dynamic conditions, elements not immobilised in the column are leached out of the system, which does not allow their possible immobilisation. Theoritically, experiments in dynamic system approach environmental conditions compared to static conditions. However, static conditions are not useless since they offer the opportunity to study the ageing effect of the soil/AMO system. Moreover, during the study of the ageing effect on AMO and metal stabilisation, results obtained during the monitoring of metal availability with DGT measurements and 0.01 M $CaCl_2$ extractions results into contradictory findings. A lack of correlation was found by Koster *et al.* (2005), and could be due to the slow kinetics of the metal release or slow kinetics of replenishment of metal by the solid phase. Moreover, the formation of chloride-metal complexes (Makino *et al.* 2006; Dermont *et al.* 2008) can underestimates the availability of metals in the soil.

In view of the results obtained, it is recommended to use AMO in neutral soils in order to avoid high dissolution, which would result in more Mn in the pore water and a potential toxicity for soil biomass (e.g. plants). Since the Mn released is quickly immobilised, the risk of Mn poisoning nonetheless remains low. Moreover, due to the potential dissolution of soil organic matter, it is advisable to use AMO in soils containing a small amount of organic matter. Experiments reveal that 1% w/w ratio can be used for the immobilisation of metallic cations. It is highly recommended however not to use AMO in a soil presenting a high flood risk given that AMO, as an oxide, is strongly affected by reductive conditions (dissolution, alteration, etc.). A better wash could allow decreasing the quantity of Mn released by removing the weakly-bound Mn at the AMO surface.

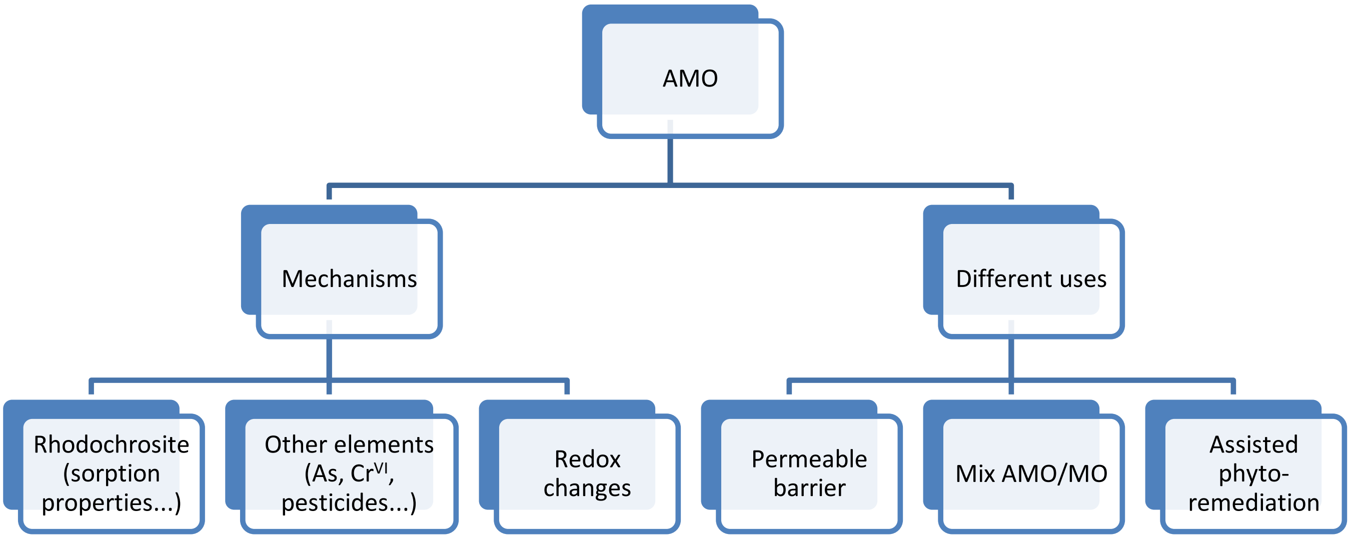

Figure 42: Future research perspectives.

Through this study, it appears that AMO is an effective amendment, capable of reducing divalent metal cation mobility and availability. Given the complexity of the environment, involving many interactions among many elements, it is quite important to fully understand interactions between AMO and the environment. This study simply represents the beginnings of a better understanding of AMO and, as such, lacks many critical data. It still needs to be completed in some important aspects. Since amendments do not generally react in the same way across several soils and since the study has taken into consideration just one soil, tests on AMO behaviour and impacts on other soils presenting different characteristics need to be performed. As Mn may become toxic and even though the Mn released by AMO seems to quickly become unavailable, it is still important to better understand the processes behind this immobilisation. Furthermore, this study has focused on divalent metallic cations, given that anions do not interact in the same way as cations, anion behaviour in the presence of AMO must also be assessed. Some soils are at times subjected to changes in redox potential, e.g. during floods, and with oxide being sensitive to those redox changes, a portion of future studies must focus on AMO behaviour during redox potential changes in the soil. Due to the oxidising properties of Mn oxides, a study of its impact on soil organic matter, soil biomass and organic pollutants (pesticides, herbicides, etc.) must also be considered. Even though AMO does not seem to be toxic for soil biomass, this aspect must be addressed thorough.

Bibliographic references

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E. (2003). "Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances." Water Research **37**: 1619-1627.

Acosta, J. A., Jansen, B., Kalbitz, K., Faz, A., Martinez-Martinez, S. (2011). "Salinity increases mobility of heavy metals in soils." Chemosphere **85**: 1318-1324.

Agbenin, J. O., Olojo, L. A. (2004). "Competitive adsorption of copper and zinc by a Bt horizon of a savanna Alfisol as affected by pH and selective removal of hydrous oxides and organic matter." Geoderma **119**: 85-95.

Alewell, C., Paul, S., Lischeid, G., Storck, F. R. (2008). "Co-regulation of redox processes in freshwater wetlands as a function of organic matter availability?" Science of the Total Environment **404**: 335-342.

Allard, S., Von Gunten, U., Sahli, E., Nicolau, R., Gallard, H. (2009). "Oxidation of iodide and iodine on birnessite (delta-MnO_2) in the pH range 4-8." Water Research **43**: 3417-3426.

Almeida, C. M., Mucha, A. P., Bordalo, A. A., Vasconcelos, M. T. (2008). "Influence of a salt marsh plant (*Halimione portulacoides*) on the concentrations and potential mobility of metals in sediments." Science of the Total Environment **403**: 188-195.

Arai, Y. (2011). "Aqueous interfacial chemistry of kaolinite for the removal of Cu(II) in the presence of birnessite: Kinetic and spectroscopic studies." Applied Clay Science **53**: 572-580.

Axe, L., Trivedi, P. (2002). "Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides." Journal of Colloid and Interface Science **247**: 259-265.

Axe, L., Tyson, T., Trivedi, P., Morrison, T. (2000). "Local Structure Analysis of Strontium Sorption to Hydrous Manganese Oxide." Journal of Colloid and Interface Science **224**: 408-416.

Bacon, J. R., Davidson, C. M. (2008). "Is there a future for sequential chemical extraction?" The Analyst **133**: 25-46.

Bade, R., Oh, S., Shin, W. S. (2012). "Diffusive gradients in thin films (DGT) for the prediction of bioavailability of heavy metals in contaminated soils to earthworm (*Eisenia foetida*) and oral bioavailable concentrations." Science of the Total Environment **416**: 127-136.

Baize, D. (1997). Teneurs totales en éléments traces métalliques dans les sols. Paris.

Bermond, A. (2002). Examen critique des protocoles d'extractions séquentielles. Les éléments traces métalliques dans les sols : Approches fonctionnelles et spatiales. e. INRA. Paris**:** 424-434.

Bes, C., Mench, M. (2008). "Remediation of copper-contaminated topsoils from a wood treatment facility using in situ stabilisation." Environmental Pollution **156**: 1128-1138.

Besnard, E., Chenu, C., Robert, M. (2001). "Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils." Environmental Pollution **112**: 329-337.

Beyer, W. N., Green, C. E., Beyer, M., Chaney, R. L. (2013). "Phytotoxicity of zinc and manganese to seedlings grown in soil contaminated by zinc smelting." Environmental Pollution **179**: 167-176.

Bhattacharyya, K. G., Gupta, S. S. (2008). "Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review." Advances in Colloid and Interface Science **140**: 114-131.

Bogomolov, D. M., Chen, S.-K., Parmelee, R. W., Subler, S., Edwards, C. A. (1996). "An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms." Applied Soil Ecology **4**: 95-105.

Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M. B., Scheckel, K. (2014). "Remediation of heavy metal(loid)s contaminated soils–to mobilize or to immobilize?" Journal of Hazardous Materials.

Bolan, N. S., Duraisamy, V. P. (2003). "Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies." Australian Journal of Soil Research **41**: 533-555.

Bolster, C. H., Hornberger, G. M. (2007). "On the use of linearized langmuir equations." Soil Science Society of America Journal **71**: 1796.

Boojar, M. M., Goodarzi, F. (2008). "Comparative evaluation of oxidative stress status and manganese availability in plants growing on manganese mine." Ecotoxicology and Environmental Safety **71**: 692-699.

Bordas, F., Bourg, A. C. M. (1998). "A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load." Water, Air, & Soil Pollution **103**: 137-149.

Boudesocque, S., Guillon, E., Aplincourt, M., Marceau, E., Stievano, L. (2007). "Sorption of Cu(II) onto vineyard soils: macroscopic and spectroscopic investigations." Journal of Colloid and Interface Science **307**: 40-49.

Boullayt, P., Hervieu, M., Raveau, B. (1997). "A new manganite with an original composite tunnel structure: $Ba_6Mn_{24}O_{48}$." Journal of Solid State Chemistry **132**: 239-248.

Bowman, A. B., Kwakye, G. F., Herrero Hernandez, E., Aschner, M. (2011). "Role of manganese in neurodegenerative diseases." Journal of Trace Elements in Medicine and Biology : Organ of the Society for Minerals and Trace Elements **25**: 191-203.

Bradl, H. B. (2004). "Adsorption of heavy metal ions on soils and soils constituents." Journal of Colloid and Interface Science **277**: 1-18.

Briat, J.-F., Lebrun, M. (1998). "Plant responses to metal toxicity." Comptes rendus de l'Académie des Sciences - Series III - Sciences de la Vie **322**: 43-54.

Brigatti, M. F., Corradini, F., Franchini, G. C. (1995). "Interaction between montmorillonite and pollutants from industrial waste-water: exchange of Zn^{2+} and Pb^{2+} from aqueous solutions." Applied Clay Science **9**: 383-395.

Brun, L. A., Maillet, J., Hinsinger, P., Pépin, M. (2001). "Evaluation of copper availability to plants in copper-contaminated vineyard soils." Environmental Pollution **111**: 293-302.

Brun, L. A., Maillet, J., Richarte, J., Herrmann, P., Remy, J. C. (1998). "Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils." Environmental Pollution **102**: 151-161.

Bryce, A. L., Kornicker, W. A., Elzerman, A. W., Clark, S. B. (1994). "Nickel adsorption to hydrous ferric oxide in the presence of EDTA: effects of component addition sequence." Environmental Science & Technology **28**: 2353-2359.

Burgos, P., Madejon, P., Madejon, E., Giron, I., Cabrera, F., Murillo, J. M. (2013). "Natural remediation of an unremediated soil twelve years after a mine accident: trace element mobility and plant composition." Journal of Environmental Management **114**: 36-45.

Burton, E. D., Phillips, I. R., Hawker, D. W. (2006). "Factors controlling the geochemical partitioning of trace metals in estuarine sediments." Soil and Sediment Contamination **15**: 253-276.

Cappuyns, V., Swennen, R. (2005). "Kinetics of element release during combined oxidation and pH_{stat} leaching of anoxic river sediments." Applied Geochemistry **20**: 1169-1179.

Celis, R., Hermosin, M. C., Cornejo, J. (2000). "Heavy metal adsorption by functionalised clays." Environmental Science & Technology **34**: 4593-4599.

Cerqueira, B., Covelo, E. F., Andrade, L., Vega, F. A. (2011). "The influence of soil properties on the individual and competitive sorption and desorption of Cu and Cd." Geoderma **162**: 20-26.

Chaignon, V., Sanchez-Neira, I., Herrmann, P., Jaillard, B., Hinsinger, P. (2003). "Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area." Environmental Pollution **123**: 229-238.

Chen, H., Chu, P. K., He, J., Hu, T., Yang, M. (2011). "Porous magnetic manganese oxide nanostructures: synthesis and their application in water treatment." Journal of Colloid and Interface Science **359**: 68-74.

Chen, Z. S., Lee, G. J., Liu, J. C. (2000). "The effects of chemical remediation treatments on the extrability and speciation of cadmium and lead in contaminated soils." Chemosphere **41**: 235-242.

Cheney, M. A., Bhowmik, P. K., Moriuchi, S., Villalobos, M., Qian, S., Joo, S. W. (2008). "The effect of stirring on the morphology of birnessite nanoparticles." Journal of Nanomaterials **2008**: 1-9.

Ching, S., Hughes, S. M., Gray, T. P., Welch, E. J. (2004). "Manganese oxide thin films prepared by nonaqueous sol–gel processing: preferential formation of birnessite." Microporous and Mesoporous Materials **76**: 41-49.

Ching, S., Petrovay, D. J., Jorgensen, M. L. (1997). "Sol-gel synthesis of layered birnessite-type manganese oxides." Inorganic Chemistry **36**: 883-890.

Chorover, J., Amistadi, M. K. (2001). "Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces." Geochimica et Cosmochimica Acta **65**: 95-109.

Chrastný, V., Komárek, M., Jrovcová, E., Štíchová, J. (2008). "A critical evaluation of the 0.05 M EDTA extraction of Pb from forest soils." International Journal of Environmental Analytical Chemistry **88**: 385-396.

Colombano, S., Saada, A., Guerin, V., Bataillard, P., Bellenfant, G., Beranger, S., Hube, D., Blanc, C., Zornig, C., Girardeau, I. (2010). Quelles techniques pour quels traitements - Analyse coûts-bénéfices. R. f. BRGM-RP-58609-FR.

Corriu, R., Trong Anh, N. (2008). Chimie moléculaire, sol-gel et nanomatériaux. Palaiseau.

Covelo, E. F., Vega, F. A., Andrade, M. L. (2007). "Competitive sorption and desorption of heavy metals by individual soil components." Journal of Hazardous Materials **140**: 308-315.

Crimi, M., Siegrist, R. L. (2004a). "Impact of reaction conditions on MnO_2 genesis during permanganate oxidation." Journal of Environmental Engineering **130**: 562-572.

Crimi, M. L., Siegrist, R. L. (2004b). "Association of cadmium with MnO_2 particles generated during permanganate oxidation." Water Research **38**: 887-894.

Davranche, M., Lacour, S., Bordas, F., Bollinger, J. C. (2003). "An easy determination of the surface chemical properties of simple and natural solids." Journal of Chemical Education **80**: 76-78.

Della Puppa, L., Komárek, M., Bordas, F., Bollinger, J.-C., Joussein, E. (2013). "Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide." Journal of Colloid and Interface Science **399**: 99-106.

Dermont, G., Bergeron, M., Mercier, G., Richer-Lafleche, M. (2008). "Soil washing for metal removal: a review of physical/chemical technologies and field applications." Journal of Hazardous Materials **152**: 1-31.

Dœlsch, E., Deroche, B., Van de Kerchove, V. (2006). "Impact of sewage sludge spreading on heavy metal speciation in tropical soils (Reunion, Indian Ocean)." Chemosphere **65**: 286-293.

Dong, D., Zhao, X., Hua, X., Liu, J., Gao, M. (2009). "Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China." Journal of Hazardous Materials **162**: 1261-1268.

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F. M. (2009). "Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review." Science of the Total Environment **407**: 3972-3985.

Eren, E., Gumus, H., Sarihan, A. (2011). "Synthesis, structural characterization and Pb(II) adsorption behavior of K- and H-birnessite samples." Desalination **279**: 75-85.

Ettler, V., Knytl, V., Komárek, M., Della Puppa, L., Bordas, F., Mihaljevič, M., Klementová, M., Šebek, O. (2014). "Stability of a novel synthetic amorphous manganese oxide in contrasting soils." Geoderma **214-215**: 2-9.

Fan, C., Lu, A., Li, Y., Wang, C. (2008). "Synthesis, characterization, and catalytic activity of cryptomelane nanomaterials produced with industrial manganese sulfate." Journal of Colloid and Interface Science **327**: 393-402.

Fan, M., Boonfueng, T., Xu, Y., Axe, L., Tyson, T. A. (2005). "Modeling Pb sorption to microporous amorphous oxides as discrete particles and coatings." Journal of Colloid and Interface Science **281**: 39-48.

Farrell, M., Jones, D. L. (2010). "Use of composts in the remediation of heavy metal contaminated soil." Journal of Hazardous Materials **175**: 575-582.

Feng, M. H., Shan, X. Q., Zhang, S., Wen, B. (2005). "A comparison of the rhizosphere-based method with DTPA, EDTA, $CaCl_2$, and $NaNO_3$ extraction methods for prediction of bioavailability of metals in soil to barley." Environmental Pollution **137**: 231-240.

Feng, Q., Kanoh, H., Ooi, K. (1998). "Manganese oxide porous crystals." Jounal of Materials Chemistry **9**: 319-333.

Feng, Q., Yanagisawa, K., Yamasaki, N. (1997). "Synthesis of birnessite-type potassium manganese oxide." Journal of Materials Science Letters **16**: 110-112.

Feng, X. H., Zhai, L. M., Tan, W. F., Liu, F., He, J. Z. (2007). "Adsorption and redox reactions of heavy metals on synthesized Mn oxide minerals." Environmental Pollution **147**: 366-373.

Feng, X. H., Zhai, L. M., Tan, W. F., Zhao, W., Liu, F., He, J. Z. (2006). "The controlling effect of pH on oxidation of Cr(III) by manganese oxide minerals." Journal of Colloid and Interface Science **298**: 258-266.

Ford, R. G., Bertsch, P. M., Farley, K. J. (1997). "Changes in transition and heavy metal partitioning during hydroux iron oxide aging." Environmental Science & Technology **31**: 2028-2033.

Foster, A. L., Brown, G. E., Parks, G. A. (2003). "X-ray absorption fine structure study of As(V) and Se(IV) sorption complexes on hydrous Mn oxides." Geochimica et Cosmochimica Acta **67**: 1937-1953.

Frohne, T., Rinklebe, J., Diaz-Bone, R. A., Du Laing, G. (2011). "Controlled variation of redox conditions in a floodplain soil: Impact on metal mobilization and biomethylation of arsenic and antimony." Geoderma **160**: 414-424.

Fu, J., Hu, X., Tao, X., Yu, H., Zhang, X. (2013). "Risk and toxicity assessments of heavy metals in sediments and fishes from the Yangtze River and Taihu Lake, China." Chemosphere **93**: 1887-1895.

Giannis, A., Nikolaou, A., Pentari, D., Gidarakos, E. (2009). "Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils." Environmental Pollution **157**: 3379-3386.

Goel, J., Kadirvelu, K., Rajagopal, C., Kumar Garg, V. (2005). "Removal of lead(II) by adsorption using treated granular activated carbon: batch and column studies." Journal of Hazardous Materials **125**: 211-220.

Golden, D. C., Dixon, J. B., Chen, C. C. (1986). "Ion exchange, thermal transformations, and oxidizing properties of birnessite." Clays and Clay Minerals **34**: 511-520.

Gómez Ariza, J. L., Giráldez, I., Sánchez-Rodas, D., Morales, E. (2000). "Metal sequential extraction procedure optimized for heavily polluted and iron rich sediments." Analytica Chimica Acta **414**: 151-164.

Gounot, A.-M. (1994). "Microbial oxidation and reduction of manganese: consequences in groundwater and applications." FEMS Microbiology Reviews **14**: 339-349.

Gray, C. W., Dunham, S. J., Dennis, P. G., Zhao, F. J., McGrath, S. P. (2006). "Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud." Environmental Pollution **142**: 530-539.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P. (2007). "Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction?" Journal of Colloid and Interface Science **314**: 490-501.

Gupta, A. K., Sinha, S. (2007). "Assessment of single extraction methods for the prediction of bioavailability of metals to *Brassica juncea* L. Czern. (var. Vaibhav) grown on tannery waste contaminated soil." Journal of Hazardous Materials **149**: 144-150.

Gupta, G., Gardner, W. (2005). "Use of clay mineral (montmorillonite) for reducing poultry litter leachate toxicity (EC50)." Journal of Hazardous Materials **118**: 81-83.

Gupta, S. K., Vollmer, M. K., Krebs, R. (1996). "The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management." Science of the Total Environment **178**: 11-20.

Händel, M., Rennert, T., Totsche, K. U. (2013). "A simple method to synthesize birnessite at ambient pressure and temperature." Geoderma **193-194**: 117-121.

Hartley, W., Edwards, R., Lepp, N. W. (2004). "Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests." Environmental Pollution **131**: 495-504.

Hettiarachchi, G. M., Pierzynski, G. M. (2002). "In situ stabilization of soil lead using phosphorus and manganese oxide: influence of plant growth." Journal of Environmental Quality **31**: 564-572.

Hettiarachchi, G. M., Pierzynski, G. M., Ransom, M. D. (2000). "In situ stabilization of soil lead using phosphorus and manganese oxide." Environmental Science & Technology **34**: 4614-4619.

Hogstad, O. (1996). "Accumulation of cadmium, copper and zinc in the liver of some passerine species wintering in Central Norway." Science of the Total Environment **183**: 187-194.

Houba, V. J. G., Gaikhorst, G. A., van Vark, W. (2000). "Soil analysis procedures using 0.01 M calcium chloride as extraction reagent." Communications in Soil Science and Plant Analysis **31**: 1299-1396.

Houben, D., Pircar, J., Sonnet, P. (2012). "Heavy metal immobilization by cost-effective amendments in a contaminated soil: Effects on metal leaching and phytoavailability." Journal of Geochemical Exploration **123**: 87-94.

Hudson-Edwards, K. A., Macklin, M. G., Curtis, C. D., Vaughan, D. J. (1996). "Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, Northeast England: Implications for metal contaminated river systems." Environmental Science & Technology **30**: 72-80.

Jalali, M., Khanlari, Z. V. (2008). "Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran." Geoderma **143**: 26-40.

Janoš, P., Vávrová, J., Herzogová, L., Pilařová, V. (2010). "Effects of inorganic and organic amendments on the mobility (leachability) of heavy metals in contaminated soil: A sequential extraction study." Geoderma **159**: 335-341.

Jean-Soro, L., Bordas, F., Bollinger, J. C. (2012). "Column leaching of chromium and nickel from a contaminated soil using EDTA and citric acid." Environmental Pollution **164**: 175-181.

Jelusic, M., Grcman, H., Vodnik, D., Suhadolc, M., Lestan, D. (2013). "Functioning of metal contaminated garden soil after remediation." Environmental Pollution **174**: 63-70.

Jeon, B.-H., Dempsey, B. A., Burgos, W. D., Royer, R. A. (2003). "Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto hematite." Water Research **37**: 4135-4142.

Jiang, M.-Q., Jin, X.-Y., Lu, X.-Q., Chen, Z.-L. (2010). "Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay." Desalination **252**: 33-39.

Jomova, K., Valko, M. (2011). "Advances in metal-induced oxidative stress and human disease." Toxicology **283**: 65-87.

Kaasalainen, M., Yli-Halla, M. (2003). "Use of sequential extraction to assess metal partitioning in soils." Environmental Pollution **126**: 225-233.

Kalinovich, I., Rutter, A., Poland, J. S., Cairns, G., Rowe, R. K. (2008). "Remediation of PCB contaminated soils in the Canadian Arctic: Excavation and surface PRB technology." Science of the Total Environment **407**: 53-66.

Kang, K. C., Ju, J. H., Kim, S. S., Baik, M. H., Rhee, S. W. (2011). "Sorption of aqueous Pb^{2+} ion on synthetic manganese oxides-intercalated with exchangeable cations." Journal of Industrial and Engineering Chemistry **17**: 565-569.

Kang, L., Zhang, M., Liu, Z. H., Ooi, K. (2007). "IR spectra of manganese oxides with either layered or tunnel structures." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **67**: 864-869.

Kanungo, S. B., Tripathy, S. S., Mishra, S. K., Sahoo, B., Rajeev (2004). "Adsorption of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} onto amorphous hydrous manganese dioxide from simple (1–1) electrolyte solutions." Journal of Colloid and Interface Science **269**: 11-21.

Karami, N., Clemente, R., Moreno-Jimenez, E., Lepp, N. W., Beesley, L. (2011). "Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass." Journal of Hazardous Materials **191**: 41-48.

Kelderman, P., Osman, A. A. (2007). "Effect of redox potential on heavy metal binding forms in polluted canal sediments in Delft (The Netherlands)." Water Research **41**: 4251-4261.

Komárek, M., Tlustoš, P., Száková, J., Chrastný, V., Balík, J. (2007). "The role of Fe- and Mn-oxides during EDTA-enhanced phytoextraction of heavy metals." Plant Soil and Environment **53**: 216-224.

Komárek, M., Száková, J., Rohošková, M., Javorská, H., Chrastný, V., Balík, J. (2008). "Copper contamination of vineyard soils from small wine producers: A case study from the Czech Republic." Geoderma **147**: 16-22.

Komárek, M., Vaněk, A., Ettler, V. (2013). "Chemical stabilization of metals and arsenic in contaminated soils using oxides - a review." Environmental Pollution **172**: 9-22.

Komárek, M., Vaněk, A., Száková, J., Balík, J., Chrastný, V. (2009). "Interactions of EDDS with Fe- and Al-(hydr)oxides." Chemosphere **77**: 87-93.

Kos, B., Lestan, D. (2004). "Chelator induced phytoextraction and in situ soil washing of Cu." Environmental Pollution **132**: 333-339.

Koster, M., Reijnders, L., van Oost, N. R., Peijnenburg, W. J. (2005). "Comparison of the method of diffusive gels in thin films with conventional extraction techniques for evaluating zinc accumulation in plants and isopods." Environmental Pollution **133**: 103-116.

Kumpiene, J., Lagerkvist, A., Maurice, C. (2008). "Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments--a review." Waste Management **28**: 215-225.

Kumpiene, J., Mench, M., Bes, C. M., Fitts, J. F. (2011). "Assesment of aided phytostabilization of copper-contaminated soil by X-ray adsorption spectroscopy and chemical extractions." Environmental Pollution **159**: 1536-1542.

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A., Maurice, C. (2006). "Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil." Environmental Pollution **144**: 62-69.

Kumpiene, J., Ragnvaldsson, D., Lovgren, L., Tesfalidet, S., Gustavsson, B., Lattstrom, A., Leffler, P., Maurice, C. (2009). "Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil." Chemosphere **74**: 206-215.

Labanowski, J., Monna, F., Bermond, A., Cambier, P., Fernandez, C., Lamy, I., van Oort, F. (2008). "Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate." Environmental Pollution **152**: 693-701.

Lacal, J., Da Silva, M. P., Garcia, R., Sevilla, M. T., Procopio, J. R., Hernandez, L. (2003). "Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment." Environmental Pollution **124**: 291-305.

Laçin, O., Dönmez, B., Demir, F. (2005). "Dissolution kinetics of natural magnesite in acetic acid solutions." International Journal of Mineral Processing **75**: 91-99.

Laiti, E., Öhman, L.-O. (1996). "Acid/base properties and phenylphosphonic acid complexation at the boehmite/water interface." Journal of Colloid and Interface Science **183**: 441-452.

Lee, S.-J., Lee, M.-E., Chung, J. W., Park, J. H., Huh, K. Y., Jun, G.-I. (2013). "Immobilization of Lead from Pb-Contaminated Soil Amended with Peat Moss." Journal of Chemistry **2013**: 1-6.

Lee, S. H., Ji, W., Lee, W. S., Koo, N., Koh, I. H., Kim, M. S., Park, J. S. (2014). "Influence of amendments and aided phytostabilization on metal availability and mobility in Pb/Zn mine tailings." Journal of Environmental Management **139C**: 15-21.

Lee, S. H., Lee, J. S., Choi, Y. J., Kim, J. G. (2009). "In situ stabilization of cadmium-, lead-, and zinc-contaminated soil using various amendments." Chemosphere **77**: 1069-1075.

Lee, S. H., Park, H., Koo, N., Hyun, S., Hwang, A. (2011). "Evaluation of the effectiveness of various amendments on trace metals stabilization by chemical and biological methods." Journal of Hazardous Materials **188**: 44-51.

Lee, T. M., Lai, H. Y., Chen, Z. S. (2004). "Effect of chemical amendments on the concentration of cadmium and lead in long-term contaminated soils." Chemosphere **57**: 1459-1471.

Leermakers, M., Gao, Y., Gabelle, C., Lojen, S., Ouddane, B., Wartel, M., Baeyens, W. (2005). "Determination of high resolution pore water profiles of trace metals in sediments of the rupel river (Belgium) using DET (diffusive equilibrium in thin films) and DGT (diffusive gradients in thin films) techniques." Water, Air, & Soil Pollution **166**: 265-286.

Leleyter, L., Baraud, F. (2005). "Évaluation de la mobilité des métaux dans les sédiments fluviaux du bassin de la Vire (Normandie, France) par extractions simples ou séquentielles." Comptes Rendus Geoscience **337**: 571-579.

Li, H., Shi, W. Y., Shao, H. B., Shao, M. A. (2009). "The remediation of the lead-polluted garden soil by natural zeolite." Journal of Hazardous Materials **169**: 1106-1111.

Li, L. Y., Li, R. S. (2000). "The role of clay minerals and the effect of H^+ ions on removal of heavy metal (Pb^{2+}) from contaminated soils." Canadian Geotechnical Journal **37**: 267-307.

Li, P., Wang, X., Zhang, T., Zhou, D., He, Y. (2008). "Effects of several amendments on rice growth and uptake of copper and cadmium from a contaminated soil." Journal of Environmental Sciences **20**: 449-455.

Li, X. D., Schwartz, F. W. (2004). "DNAPL remediation with in situ chemical oxidation using potassium permanganate." Journal of Contaminant Hydrology **68**: 39-53.

Liang, S., Guan, D. X., Ren, J. H., Zhang, M., Luo, J., Ma, L. Q. (2014). "Effect of aging on arsenic and lead fractionation and availability in soils: Coupling sequential extractions with diffusive gradients in thin-films technique." Journal of Hazardous Materials **273C**: 272-279.

Lim, S. R., Schoenung, J. M. (2010). "Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays." Journal of Hazardous Materials **177**: 251-259.

Lim, T.-T., Tay, J.-H., Teh, C.-I. (2002). "Contamination time effect on lead and cadmium fractionation in a tropical coastal clay." Journal of Environmental Quality **31**: 806-812.

Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Barthès, V., Krimissa, M. (2007). "Sorption isotherms: A review on physical bases, modeling and measurement." Applied Geochemistry **22**: 249-275.

Liu, J.-L., Fan, L.-Z., Qu, X. (2012). "Low temperature hydrothermal synthesis of nano-sized manganese oxide for supercapacitors." Electrochimica Acta **66**: 302-305.

Lo, I. M., Tsang, D. C., Yip, T. C., Wang, F., Zhang, W. (2011). "Influence of injection conditions on EDDS-flushing of metal-contaminated soil." Journal of Hazardous Materials **192**: 667-675.

Loomer, D. B., Al, T. A., Banks, V. J., Parker, B. L., Mayer, K. U. (2010). "Manganese valence in oxides formed from in situ chemical oxidation of TCE by $KMnO_4$." Environmental Science & Technology **44**: 5934-5939.

Loska, K., Wiechuła, D., Korus, I. (2004). "Metal contamination of farming soils affected by industry." Environment International **30**: 159-165.

Lu, A., Zhang, S., Qin, X., Wu, W., Liu, H. (2009). "Aging effect on the mobility and bioavailability of copper in soil." Journal of Environmental Sciences **21**: 173-178.

Lu, P., Nuhfer, N. T., Kelly, S., Li, Q., Konishi, H., Elswick, E., Zhu, C. (2011). "Lead coprecipitation with iron oxyhydroxide nano-particles." Geochimica et Cosmochimica Acta **75**: 4547-4561.

Lu, Y., Allen, H. E. (2002). "Characterization of copper complexation with natural dissolved organic matter (DOM)-link to acidi moieties of DOM and competitionby Ca and Mg." Water Research **36**: 5083-5101.

Maenpaa, K. A., Kukkonen, J. V., Lydy, M. J. (2002). "Remediation of heavy metal-contaminated soils using phosphorus: evaluation of bioavailability using an earthworm bioassay." Archives of Environmental Contamination and Toxicology **43**: 389-398.

Makino, T., Sugahara, K., Sakurai, Y., Takano, H., Kamiya, T., Sasaki, K., Itou, T., Sekiya, N. (2006). "Remediation of cadmium contamination in paddy soils by washing with chemicals: selection of washing chemicals." Environmental Pollution **144**: 2-10.

Mamindy-Pajany, Y., Hurel, C., Geret, F., Romeo, M., Marmier, N. (2013). "Comparison of mineral-based amendments for ex-situ stabilization of trace elements (As, Cd, Cu, Mo, Ni, Zn) in marine dredged sediments: a pilot-scale experiment." Journal of Hazardous Materials **252-253**: 213-219.

Manceau, A., Marcus, M. A., Tamure, N. (2002). "Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques." Reviews in mineralogy and geochemistry **49**: 341-428.

Martínez, C. E., McBride, M. B. (1998). "Coprecipitates of Cd, Cu, Pb and Zn in iron oxides: solid phase transformation and metal solubility after aging and thermal treatment." Clays and Clay Minerals **46**: 537-545.

McBride, M. B. (1994). Environmental Chemistry of Soils. Oxford.

McKenzie, R. M. (1971). "The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese." Mineralogical Magazine **38**: 493-502.

McKenzie, R. M. (1980). "The adsorption of lead and other heavy metals on oxides of manganese and iron." Australian Journal of Soil Research **18**: 61-73.

Meers, E., Samson, R., Tack, F. M. G., Ruttens, A., Vandegehuchte, M., Vangronsveld, J., Verloo, M. G. (2007). "Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by Phaseolus vulgaris." Environmental and Experimental Botany **60**: 385-396.

Mench, M., Amans, V., Sappin-Didier, V., Fargues, S., Gomez, A., Löffler, M., Masson, P., Arrouays, D. (1997). A study of additives to reduce availability of Pb in soil to plants. Northwood, U. K.

Mench, M., Lepp, N. W., Bert, V., Schwitzguébel, J.-P., Gawronski, S. W., Schröder, P., Vangronsveld, J. (2010). "Successes and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859." Journal of Soils and Sediments **10**: 1039-1070.

Mench, M. J., Didier, V. L., Löffler, M., Gomez, A., Masson, P. (1994). "A mimicked in-situ remediation study of metal-contaminated soils with emphasis on cadmium and lead." Journal of Environmental Quality **23**: 58-63.

Michalke, B., Fernsebner, K. (2014). "New insights into manganese toxicity and speciation." Journal of Trace Elements in Medicine and Biology **27**: 106-116.

Michalke, B., Halbach, S., Nischwitz, V. (2007). "Speciation and toxicological relevance of manganese in humans." Journal of Environmental Monitoring **9**: 650-656.

Mignardi, S., Corami, A., Ferrini, V. (2012). "Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn." Chemosphere **86**: 354-360.

Miguens, T., Leiros, M. A., Gil-Sotres, F., Trasar-Cepeda, C. (2007). "Biochemical properties of vineyard soils in Galicia, Spain." Science of the Total Environment **378**: 218-222.

Miller, F. S., Kilminster, K. L., Degens, B., Firns, G. W. (2010). "Relationship between metals leached and soil type from potential acid sulphate soils under acidic and neutral conditions in Western Australia." Water, Air, & Soil Pollution **205**: 133-147.

Mirlean, N., Roisenberg, A., Chies, J. O. (2007). "Metal contamination of vineyard soils in wet subtropics (southern Brazil)." Environmental Pollution **149**: 10-17.

Mouni, L., Merabet, D., Robert, D., Bouzaza, A. (2009). "Batch studies for the investigation of the sorption of the heavy metals Pb^{2+} and Zn^{2+} onto Amizour soil (Algeria)." Geoderma **154**: 30-35.

Multi-Agency Radiological Laboratory (2004). "Multi-Agency Radiological Laboratory Analytical Protocols Manual Volume 2." http://www.epa.gov/rpdweb00/marlap/manual.html#voli.

Murray, J. W., Balistrieri, L. S. (1984). "The oxidation state of manganese in marine sediments and ferromanganese nodules." Geochimica et Cosmochimica Acta **48**: 1237-1247.

Neal, A. P., Guilarte, T. R. (2013). "Mechanisms of lead and manganese neurotoxicity." Toxicology Research **2**: 99-114.

Neugschwandtner, R. W., Tlustoš, P., Komárek, M., Száková, J. (2008). "Phytoextraction of Pb and Cd from a contaminated agricultural soil using different EDTA application regimes: Laboratory versus field scale measures of efficiency." Geoderma **144**: 446-454.

Noubactep, C. (2009). "Characterizing the effects of shaking intensity on the kinetics of metallic iron dissolution in EDTA." Journal of Hazardous Materials **170**: 1149-1155.

Nowack, B., Koehler, S., Schulin, R. (2004). "Use of diffusive gradients in thin films (DGT) in undisturbed field soils." Environmental Science & Technology **38**: 1133-1138.

Nowack, B., Sigg, L. (1996). "Adsorption of EDTA and metal-EDTA complexes onto goethite." Journal of Colloid and Interface Science **177**: 106-121.

Nowack, B., Sigg, L. (1997). "Dissolution of Fe(III) (hydr)oxides by metal-EDTA complexes." Geochimica et Cosmochimica Acta **61**: 951-963.

Nwachukwu, O. I., Pulford, I. D. (2011). "Microbial respiration as an indication of metal toxicity in contaminated organic materials and soil." Journal of Hazardous Materials **185**: 1140-1147.

O'Reilly, S. E., Hochella, M. F. (2003). "Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides." Geochimica et Cosmochimica Acta **67**: 4471-4487.

Oliveira, D. D., Souza-Santos, L. P., Silva, H. K., Macedo, S. J. (2014). "Toxicity of sediments from a mangrove forest patch in an urban area in Pernambuco (Brazil)." Ecotoxicol Environ Saf **104C**: 373-378.

Pan, G., Qin, Y., Li, X., Hu, T., Wu, Z., Xie, Y. (2004). "EXAFS studies on adsorption–desorption reversibility at manganese oxides–water interfaces." Journal of Colloid and Interface Science **271**: 28-34.

Panagos, P., Van Liedekerke, M., Jones, A., Montanarella, L. (2012). "European Soil Data Centre: Response to European policy support and public data requirements." Land Use Policy **29**: 329-338.

Pareuil, P., Hamdoun, H., Bordas, F., Joussein, E., Bollinger, J. C. (2011). "The influence of reducing conditions on the dissolution of a Mn-rich slag from pyrometallurgical recycling of alkaline batteries." Journal of Environmental Management **92**: 102-111.

Park, J. H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., Chung, J. W. (2011). "Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils." Journal of Hazardous Materials **185**: 549-574.

Pauget, B., Gimbert, F., Scheifler, R., Coeurdassier, M., de Vaufleury, A. (2012). "Soil parameters are key factors to predict metal bioavailability to snails based on chemical extractant data." Science of the Total Environment **431**: 413-425.

Peacock, C. L., Sherman, D. M. (2004). "Copper(II) sorption onto goethite, hematite and lepidocrocite: A surface complexation model based onad initio molecular geometries and EXAFS spetroscopy." Geochimica et Cosmochimica Acta **68**: 2623-2637.

Pedrot, M., Dia, A., Davranche, M., Bouhnik-Le Coz, M., Henin, O., Gruau, G. (2008). "Insights into colloid-mediated trace element release at the soil/water interface." Journal of Colloid and Interface Science **325**: 187-197.

Peltier, E., Dahl, A. L., Gaillard, J. F. (2005). "Metal speciation in anoxic sediments: when sulfides can be construed as oxides." Environmental Science & Technology **39**: 311-316.

Penilla, S., Bordas, F., Bollinger, J. C. (2005). "Sequential heavy metals extraction from polluted solids: influence of sulfate overconcentration." Journal of Colloid and Interface Science **292**: 20-28.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G., Gardea-Torresdey, J. (2009). "The biochemistry of environmental heavy metal uptake by plants: implications for the food chain." The International Journal of Biochemistry & Cell Biology **41**: 1665-1677.

Pérez-Cid, B., Lavilla, I., Bendicho, C. (1998). "Speeding up of a three-stage sequential extraction method for metal speciation using focused ultrasound." Analytica Chimica Acta **360**: 35-41.

Post, J. E., Veblen, D. R. (1990). "Manganese oxide minerals: crystal stucture determinations of synthetic sodium, magnesium, and potassium birnessite using TEM and the Rietveld method." American Mineralogist **75**: 477-489.

Pourret, O., Davranche, M. (2013). "Rare earth element sorption onto hydrous manganese oxide: a modeling study." Journal of Colloid and Interface Science **395**: 18-23.

Pueyo, M., López-Sánchez, J. F., Rauret, G. (2004). "Assessment of $CaCl_2$, $NaNO_3$ and NH_4NO_3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils." Analytica Chimica Acta **504**: 217-226.

Quenea, K., Lamy, I., Winterton, P., Bermond, A., Dumat, C. (2009). "Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water." Geoderma **149**: 217-223.

Quevauviller, P. (1998). "Operationally defined extraction procedures for soil and sediment analysis; I. Standardization." Trends in Analytical Chemistry **17**: 289-298.

Rauret, G., López-Sánchez, J.-F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A. M., Davidson, C. M., Gomez, A., Lück, D., Bacon, J., Yli-Halla, M., Muntau, H., Quevauviller, P. (2000). "Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content." Journal of Environmental Monitoring **2**: 228-233.

Renault, P., Cazevieille, P., Verdier, J., Lahlah, J., Clara, C., Favre, F. (2009). "Variations in the cation exchange capacity of a ferralsol supplied with vinasse, under changing aeration conditions." Geoderma **154**: 101-110.

Robson, T. C., Braungardt, C. B., Rieuwerts, J., Worsfold, P. (2014). "Cadmium contamination of agricultural soils and crops resulting from sphalerite weathering." Environmental Pollution **184**: 283-289.

Roh, Y., Lee, S. Y., Elless, M. P. (2000). "Characterization of corrosion products in the permeable reactive barriers." Environmental Geology **40**: 184-194.

Ross, D. S., Hales, H. C., Lanzirotti, A. (2013). "Oxidation of Added Mn(II) in Soils Observed by XANES Spectroscopy and Cr(III) Oxidation." Soil Science Society of America Journal **77**: 1996-2003.

Roth, E., Mancier, V., Fabre, B. (2012). "Adsorption of cadmium on different granulometric soil fractions: Influence of organic matter and temperature." Geoderma **189-190**: 133-143.

Roulier, J.-L., Belaud, S., Coquery, M. (2010). "Comparison of dynamic mobilization of Co, Cd and Pb in sediments using DGT and metal mobility assessed by sequential extraction." Chemosphere **79**: 839-843.

Roulier, J.-L., Tusseau-Vuillemin, M. H., Coquery, M., Geffard, O., Garric, J. (2008). "Measurement of dynamic mobilization of trace metals in sediments using DGT and comparison with bioaccumulation in Chironomus riparius: First results of an experimental study." Chemosphere **70**: 925-932.

Ruello, M. L., Sileno, M., Sani, D., Fava, G. (2008). "DGT use in contaminated site characterization. The importance of heavy metals site specific behaviour." Chemosphere **70**: 1135-1140.

Ruttens, A., Adriaensen, K., Meers, E., De Vocht, A., Geebelen, W., Carleer, R., Mench, M., Vangronsveld, J. (2010). "Long-term sustainability of metal immobilization by soil amendments: cyclonic ashes versus lime addition." Environmental Pollution **158**: 1428-1434.

Sahuquillo, A., Rigol, A., Rauret, G. (2003). "Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments." Trends in Analytical Chemistry **22**: 152-159.

Sajidu, S. M. I., Persson, I., L., M. W. R., Henry, E. M. T., Kayambazinthu, D. (2006). "Removal of Cd^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} cations and AsO_4^{3-} anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterisation of the clay." Water SA **32**: 519-526.

Sappin-Didier, V., Mench, M., Gomez, A., Masson, P. (1998). "Evaluation by single extractions of Cd immobilization following the addition of inorganic amendments in two metal-contamined soils." Comptes rendus de l'Académie des Sciences - Series III - Sciences de la Vie **320**: 413-419.

Sappin-Didier, V. L., Mench, M. J., Gomez, A. N., Lambrot, C. (1997). Use of inorganic amendments for reducing metal bioavailability to ryegrass and tobacco in contaminated soils. Northwood, U. K.

Sarkar, D., De, D. K., Das, R., Mandal, B. (2014). "Removal of organic matter and oxides of iron and manganese from soil influences boron adsorption in soil." Geoderma **214-215**: 213-216.

Sarkar, D., Pandey, S. K., Sud, K. C., Chanemougasoundharam, A. (2004). "In vitro characterization of manganese toxicity in relation to phosphorus nutrition in potato (*Solanum tuberosum* L.)." Plant Science **167**: 977-986.

Saxena, S., D'Souza, S. F. (2006). "Heavy metal pollution abatement using rock phosphate mineral." Environment International **32**: 199-202.

Schecher, W. D., McAvoy, D. C. (2003). MINEQL+: A chemical equilibrium modeling system, version 4.6 for Windows, user's manual, v2.00. Environmental Research Software: Hallowell, Maine.

Schulze, D. G. (1989). An introduction to soil mineralogy. In "Minerals in the Soil Environment", Soil Science Society of America.

Senesi, G. S., Baldassarre, G., Senesi, N., Radina, B. (1999). "Trace elements inputs into soils by anthropogenic activities and implications for human health." Chemosphere **39**: 343-377.

Sheng, G. D., Xu, C., Xu, L., Qiu, Y., Zhou, H. (2009). "Abiotic oxidation of 17beta-estradiol by soil manganese oxides." Environmental Pollution **157**: 2710-2715.

Siegrist, R. L., Urynowicz, M. A., Crimi, M. L., Lowe, K. S. (2002). "Genesis and effects of particles produced during in situ chemical oxidation using permanganate." Journal of Environmental Engineering **128**: 1068-1079.

Sigg, L., Behra, P., Stumm, W. (2000). Chimie des milieux aquatiques. Dunod Ed., Paris.

Sizmur, T., Hodson, M. E. (2009). "Do earthworms impact metal mobility and availability in soil?--a review." Environmental Pollution **157**: 1981-1989.

Sneddon, I. R., Orueetxebarria, M., Hodson, M. E., Schofield, P. F., Valsami-Jones, E. (2006). "Use of bone meal amendments to immobilise Pb, Zn and Cd in soil: A leaching column study." Environmental Pollution **144**: 816-825.

Sondergaard, J., Bach, L., Gustavson, K. (2014). "Measuring bioavailable metals using diffusive gradients in thin films (DGT) and transplanted seaweed (Fucus vesiculosus), blue mussels (Mytilus edulis) and sea snails (Littorina saxatilis) suspended from monitoring buoys near a former lead-zinc mine in West Greenland." Marine Pollution Bulletin **78**: 102-109.

Sposito, G. (1989). The chemistry of soils. Oxford University Press, New York, USA.

Srivastava, P., Singh, B., Angove, M. (2005). "Competitive adsorption behavior of heavy metals on kaolinite." Journal of Colloid and Interface Science **290**: 28-38.

Stumm, W. (1992). Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems. Wiley-Interscience, New York, USA.

Stumm, W., Morgan, J. (1996). Aquatic chemistry. Wiley-Interscience, New York, USA.

Su, Q., Pan, B., Wan, S., Zhang, W., Lv, L. (2010). "Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water." Journal of Colloid and Interface Science **349**: 607-612.

Suchanek, W. L., Riman, R. E. (2006). "Hydrothermal synthesis of advanced ceramic powders." Advances in Science and Technology **45**: 184-193.

Tan, W., Liu, F., Feng, X., Huang, Q., Li, X. (2005). "Adsorption and redox reactions of heavy metals on Fe-Mn nodules from Chinese soils." Journal of Colloid and Interface Science **284**: 600-605.

Tan, X. L., Chang, P. P., Fan, Q. H., Zhou, X., Yu, S. M., Wu, W. S., Wang, X. K. (2008). "Sorption of Pb(II) on Na-rectorite: Effects of pH, ionic strength, temperature, soil humic acid and fulvic acid." Colloids and Surfaces A: Physicochemical and Engineering Aspects **328**: 8-14.

Tang, X. Y., Zhu, Y. G., Cui, Y. S., Duan, J., Tang, L. (2006). "The effect of ageing on the bioaccessibility and fractionation of cadmium in some typical soils of China." Environment International **32**: 682-689.

Tembo, B. D., Sichilongo, K., Cernak, J. (2006). "Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia." Chemosphere **63**: 497-501.

Tica, D., Udovic, M., Lestan, D. (2011). "Immobilization of potentially toxic metals using different soil amendments." Chemosphere **85**: 577-583.

Tilak, A. S., Ojewole, S., Williford, C. W., Fox, G. A., Sobecki, T. M., Larson, S. L. (2013). "Formation of Manganese Oxide Coatings onto Sand for Adsorption of Trace Metals from Groundwater." Journal of Environment Quality **42**: 1743.

Tokalioğlu, S., Kartal, S., Birol, G. (2003). "Comparison of three sequential extraction procedures for partitioning of heavy metals in car park dusts." Journal of Environmental Monitoring **5**: 468-476.

Tonkin, J. W., Balistrieri, L. S., Murray, J. W. (2004). "Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model." Applied Geochemistry **19**: 29-53.

Trivedi, P., Axe, L. (2000). "Modeling Cd and Zn sorption to hydrous metal oxides." Environmental Science & Technology **34**: 2215-2223.

Tsang, D. C., Zhang, W., Lo, I. M. (2007). "Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils." Chemosphere **68**: 234-243.

Tunius, M., Sköld, R. (1990). "Adsorption on γ-aluminium oxide from a multicomponent aqueous solution. Effect of cosolvent, concentration, temperature, pH and substrate surface porosity." Colloids and Surfaces **46**: 297-325.

Turkez, H., Geyikoglu, F., Tatar, A., Keles, M. S., Kaplan, I. (2012). "The effects of some boron compounds against heavy metal toxicity in human blood." Experimental and Toxicologic Pathology **64**: 93-101.

Udovic, M., Lestan, D. (2012). "EDTA and HCl leaching of calcareous and acidic soils polluted with potentially toxic metals: remediation efficiency and soil impact." Chemosphere **88**: 718-724.

Vandecasteele, B., Du Laing, G., Lettens, S., Jordaens, K., Tack, F. M. (2010). "Influence of flooding and metal immobilising soil amendments on availability of metals for willows and earthworms in calcareous dredged sediment-derived soils." Environmental Pollution **158**: 2181-2188.

Vaněk, A., Grygar, T., Chrastný, V., Tejnecký, V., Drahota, P., Komárek, M. (2010). "Assessment of the BCR sequential extraction procedure for thallium fractionation using synthetic mineral mixtures." Journal of Hazardous Materials **176**: 913-918.

Vangronsveld, J., Van Assche, F., Clijsters, H. (1995). "Reclamation of a bare industrial area contaminated by non-ferrous metals: in istu metal immobilization and revegetation." Environmental Pollution **87**: 51-59.

Vega, F. A., Covelo, E. F., Andrade, M. L. (2006). "Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics." Journal of Colloid and Interface Science **298**: 582-592.

Vig, K., Megharaj, M., Sethunathan, N., Naidu, R. (2003). "Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review." Advances in Environmental Research **8**: 121-135.

Villalobos, M., Escobar-Quiroz, I. N., Salazar-Camacho, C. (2014). "The influence of particle size and structure on the sorption and oxidation behavior of birnessite: I. Adsorption of As(V) and oxidation of As(III)." Geochimica et Cosmochimica Acta **125**: 564-581.

Violante, A., Ricciardella, M., Pigna, M. (2003). "Adsorption of heavy metals on mixed Fe-Al oxides in the absence or presence of organic ligands." Water, Air, & Soil Pollution **145**: 289-306.

Wang, Q.-Y., Zhou, D.-M., Cang, L. (2009). "Microbial and enzyme properties of apple orchard soil as affected by long-term application of copper fungicide." Soil Biology and Biochemistry **41**: 1504-1509.

Wang, Y., Feng, X., Villalobos, M., Tan, W., Liu, F. (2012). "Sorption behavior of heavy metals on birnessite: Relationship with its Mn average oxidation state and implications for types of sorption sites." Chemical Geology **292-293**: 25-34.

Wang, Z., Giammar, D. E. (2013). "Mass action expressions for bidentate adsorption in surface complexation modeling: theory and practice." Environmental Science & Technology **47**: 3982-3996.

Wardle, D. A., Parkinson, D. (1990). "Response of the soil microbial biomass to glucose, and selective inhibitors, across a soil moisture gradient." Soil Biology and Biochemistry **22**: 825-834.

Weerasooriya, R., Wijesekara, H. K. D. K., Bandara, A. (2002). "Surface complexation modeling of cadmium adsorption on gibbsite." Colloids and Surfaces **207**: 13-24.

Wei, B., Yang, L. (2010). "A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China." Microchemical Journal **94**: 99-107.

Wilson, C. A., Cloy, J. M., Graham, M. C., Hamlet, L. E. (2013). "A microanalytical study of iron, aluminium and organic matter relationships in soils with contrasting hydrological regimes." Geoderma **202-203**: 71-81.

Yin, H., Liu, F., Feng, X., Liu, M., Tan, W., Qiu, G. (2011). "Co^{2+}-exchange mechanism of birnessite and its application for the removal of Pb^{2+} and As(III)." Journal of Hazardous Materials **196**: 318-326.

Yousef, A. A., Arafa, M. A., Malati, M. A. (1971). "Adsorption of sulfite, oleate and manganese (II) ions by β-manganese dioxide and its activation in flotation." Journal of Applied Chemistry and Biotechnology **21**: 200-207.

Yu, K., Böhme, F., Rinklebe, J., Neue, H.-U., DeLaune, R. D. (2007). "Major biogeochemical processes in soils — a microcosm incubation from reducing to oxidizing conditions." Soil Science Society of America Journal **71**: 1406-1417.

Zhang, G., Lin, Y., Wang, M. (2011). "Remediation of copper polluted red soils with clay materials." Journal of Environmental Sciences **23**: 461-467.

Zhang, H. (2003). DGT for measurements in waters, soils and sediments. .

Zhang, H., Davison, W., Knight, B., McGrath, S. (1998). "In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT." Environmental Science & Technology **32**: 701-710.

Zhang, H., Davison, W., Miller, S., Tych, W. (1995). "In situ high measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT." Geochimica et Cosmochimica Acta **59**: 4181-4192.

Zhou, S.-W., Xu, M.-G., Ma, Y.-B., Chen, S.-B., Wei, D.-P. (2008). "Aging mechanism of copper added to bentonite." Geoderma **147**: 86-92.

Zhu, J., Cozzolino, V., Fernandez, M., Sánchez, R. M. T., Pigna, M., Huang, Q., Violante, A. (2011). "Sorption of Cu on a Fe-deformed montmorillonite complex: Effect of pH, ionic strength, competitor heavy metal, and inorganic and organic ligands." Applied Clay Science **52**: 339-344.

Zupanc, V., Kastelec, D., Lestan, D., Grcman, H. (2014). "Soil physical characteristics after EDTA washing and amendment with inorganic and organic additives." Environmental Pollution **186C**: 56-62.

Appendix

Stabilisation de Cu, Cd, Pb et Zn par un nouvel oxyde de manganèse dans un sol contaminé

La contamination en éléments métalliques (EM) des sols est un danger pour l'homme et l'environnement. Sans moyen efficace pour stabiliser ou retirer les EM des sols, ils peuvent se disperser dans l'environnement, augmentant ainsi les risques. C'est pourquoi il est important de proposer des méthodes de remédiation efficaces et peu onéreuses. L'ajout d'un stabilisant chimique est un moyen efficace pour diminuer la mobilité et la biodisponibilité de certains EM. Le choix de l'amendement est influencé par ces propriétés adsorbantes, son potentiel à immobiliser les EM sans immobiliser les nutriments nécessaires à la biomasse du sol ou du couvert végétal, son comportement dans les sols, son innocuité pour les micro-organismes et son coût. Les oxydes de manganèse, malgré leur importantes propriétés d'adsorption, ont été et sont beaucoup moins étudiés que les oxydes de fer pour l'immobilisation des EM même si leur utilisation a permis de diminuer de façon significative la mobilité des EM dans des sols contaminés. Dans cette étude, un nouvel oxyde de manganèse a été synthétisé selon la méthode sol-gel et caractérisé comme stabilisant chimique pour diminuer la mobilité et la disponibilité dans les sols contaminés de quatre EM : Cu, Cd, Pb et Zn.

Synthèse et caractérisation de l'oxyde de manganèse

Cet oxyde de manganèse nouvellement caractérisé est un intermédiaire de synthèse de la birnessite. Il est synthétisé en faisant réagir une solution de $KMnO_4$ et une solution de glucose ($C_6H_{12}O_6$) à température ambiante. L'oxyde ainsi synthétisé est amorphe et a été dénommé AMO (Amorphous Manganese Oxide). La caractérisation de l'AMO a montré qu'il possède un pH de surface élevé (pH_{H2O}: 8.1), une faible CEC (34 $meq.100g^{-1}$) et surface spécifique (14.8 $m^2.g^{-1}$). Cependant, il présente des capacités d'adsorption importantes (respectivement pour Cu, Cd, Pb et Zn à pH 4 : 1.33, 0.55, 2.23, 0.98 $mmol.g^{-1}$), équivalente à celle de la birnessite (respectivement pour Cu, Cd, Pb et Zn à pH 4 : 1.33, 1.33, 2.09 et 1.17 $mmol.g^{-1}$). Lors des isothermes d'adsorption multi-métaux (solution composée des 4 EM étudiés), Pb et Cu sont adsorbés préférentiellement par rapport à Cd et Zn. De plus, la quantité d'EM adsorbée en système multi-métaux par l'AMO et la birnessite sont quasiment similaires aux pH étudiés (4 et 5.5). L'AMO nécessite une période de stabilisation lors de son utilisation. En effet, un relargage de manganèse a été observé lors de son utilisation dans l'eau ultra-pure. De plus, le potentiel zêta mesuré varie entre l'AMO et l'AMO stabilisé dans de l'eau ultra-pure, indiquant une évolution de l'AMO et de ses propriétés de surface ce qui entraine une période de stabilisation dans le milieu.

Stabilité de l'AMO dans les sols

La stabilité de l'AMO, étudiée dans 3 sols différents, a montré une évolution de l'AMO avec une dissolution partielle (la quantité dépendent de l'acidité du sol, plus l'acidité est importante, plus la quantité de manganèse libéré est importante et atteint 18% pour le sol le plus acide). De plus, l'AMO augmente le COD lixivié à l'eau ultra-pure, ce qui s'explique par une dissolution du carbone organique provenant de l'AMO (résidu de glucose) et/ou une altération (oxydation et/ou effet du pH) de la matière organique de l'échantillon de sol. De plus, il a été montré par microscopie électronique la précipitation de nouvelles phases solides (rhodochrosite, $MnCO_3$). De plus, les particules d'AMO se sont agglomérées au cours de l'expérience, ce qui augmente la taille des particules et entraine donc une diminution de la surface spécifique. En parallèle, un test de respiration du sol en présence d'AMO/birnessite a montré que l'AMO, contrairement à la birnessite, engendre une augmentation de la production de CO_2. Cela peut provenir d'un stress des micro-organismes ou plus vraisemblablement de l'apport de résidus de glucose pouvant facilement être dégradés et donc augmenter leur activité.

Stabilité de l'AMO dans les sols

La stabilisation des EM par l'AMO a été étudiée selon 2 méthodes distinctes : en colonne et en batch. Dans les 2 cas, le sol utilisé a été prélevé sur un site contaminé par des activités métallurgiques (raffinage du cuivre). L'AMO a été utilisé à 3 ratios différents (0.01%, 0.1% et 1% en masse) et comparé avec le contrôle.

Etude en colonne

Dans le cas de l'étude en colonne, la colonne est tout d'abord stabilisée à l'eau ultra-pure, puis est injectée une solution de cations métalliques (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) pendant 50

Vp, ce qui représente une quantité totale de métaux injectée équivalent à 100% de la CEC de l'échantillon de sol. Après avoir injecté 50 Vp de solution métallique, de l'eau ultra-pure est de nouveau injectée pour éliminer les éléments présents et non stabilisés dans la colonne. Ensuite, une solution d'EDTA 2.5 mM est injectée pour mesurer la quantité d'élément extrait, l'EDTA permettant une évaluation de la quantité d'élément métalliques biodisponibles en simulant la rhizosphère. Un ratio en AMO de 1% a augmenté le pH du lixiviat (5.6, le pH obtenu pour les autres ratios et le contrôle étant inférieur à 5). De plus, le COD lixivié augmente en présence d'AMO, excepté pour un ratio de 0.1% où le COD lixivié est inférieur au contrôle. Pour un ratio de 1%, le Cu lixivié diminue de 16.0 à 7.6 mg.kg^{-1} alors que la quantité de Mn libéré augmente avec le ratio. En effectuant un bilan de masse, il apparait qu'un ratio en AMO de 0.1% permet une meilleure rétention des EM. Cela peut venir du fait que pour un ratio de 0.1%, la dissolution de la MO du sol était la plus faible (même comparée au contrôle), ce qui peut entrainer une stabilisation des EM sous forme de complexes organométalliques. De plus, la rétention des EM a été la plus faible pour un ratio de 1%, ratio qui avait entrainé la plus forte quantité de COD dans le lixiviat. Pendant l'injection de la solution d'élément métalliques, la quantité de Mn lixivié est directement corrélée au ratio en AMO utilisé, plus le ratio est important, plus la quantité de Mn dans le lixiviat est importante. Après avoir injecté la solution d'EDTA 2.5 mM, il apparait qu'un ratio en AMO de 0.1% permet une meilleure rétention des EM. L'étude en colonne a montré que 0.1% est le ratio optimal à utiliser dans ces conditions, permettant de réduire la quantité de COD lixivié, une meilleur rétention des EM étudiés (Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) et de diminuer leur biodisponibilité.

Etude en système batch

L'AMO a également été étudié en système batch, ouvert à l'atmosphère. Cela a permis d'étudier l'évolution de l'AMO dans le temps ainsi que l'effet du temps sur la rétention des EM. Pour ce faire, 3 séries de batch ont été effectuées :

- série A dédiée à l'étude de l'échantillon de sol historiquement contaminé,
- série B dédiée à l'étude de l'échantillon de sol historiquement contaminé où une solution de cations métalliques a également été ajoutée (la quantité ajoutée représente 90% de la CEC de l'échantillon de sol),

- série C dédiée à l'étude de l'échantillon de sol historiquement contaminé puis manuellement contaminé au bout de 60 jours, par l'extraction de l'eau interstitielle.

Les 3 séries sont maintenues à 80% de la capacité de rétention d'eau du sol tout au long de l'étude. Pour les séries A et B, l'impact de l'AMO sur les EM a été suivi dans le temps par différentes extractions : $CaCl_2$, extractions séquentielles et extractions par des systèmes DGT. Dans le cas de la série A, les différentes extractions ont montré peu d'impact de l'AMO sur les quantités extraites et sur le fractionnement des EM. Cela provient du fait que la contamination est déjà stabilisée dans le sol. Pour la série B, une forte diminution de Cu et Pb extrait est visible, la diminution étant plus importante pour un ratio de 1% en AMO. De plus, la stabilisation de ces métaux augmente avec le temps. Concernant le fractionnement, un ratio de 1% diminue la mobilité de Cu en diminuant la fraction échangeable. De plus, une augmentation de la fraction résiduelle apparait pour Cu, Cd et Pb pour un ratio de 1% comparé au contrôle. Pour la série C, il a été observé une augmentation du pH comparé au contrôle en présence d'AMO (surtout pour un ratio de1%) ainsi qu'une augmentation du DOC. Dans les 2 cas (avant et après ajout d'une solution d'EM), la quantité de Cu, Cd et Pb dans la solution interstitielle diminue en augmentant le ratio en AMO. Concernant l'évolution de l'AMO, une forte augmentation de Mn relargué par l'AMO a été observée, cependant, il est rapidement stabilisé. De plus, le fractionnement du Mn montre une diminution au cours du temps du Mn présent dans la fraction échangeable et une augmentation du Mn dans le résidu. Cela est dû à la précipitation d'une nouvelle phase solide ($MnCO_3$, rhodochrosite), immobilisant le Mn relargué. L'étude en système batch a montré un ratio optimal de 1% en AMO. Elle a également montré que l'AMO est capable de stabiliser majoritairement Cu et Pb.

Conclusion

Malgré des propriétés pouvant paraitre défavorables pour la stabilisation des EM dans les sols contaminés, les différentes études en colonne et en système batch ont montré que l'AMO diminue la mobilité et la disponibilité de Cu et Pb et permet également une augmentation de la capacité de rétention des EM dans l'échantillon de sol. Cependant, le ratio optimum dans ces 2 situations est différent : 0.1% dans le cas des colonnes et 1% dans le cas des batchs. Cela provient de la différence des conditions expérimentales. Dans le cas des colonnes, le système est dynamique, les éléments non stabilisés sont évacués hors de la colonne ce qui ne permet pas leur future stabilisation, alors que dans le cas des systèmes batch, les éléments non immobilisés restent dans le milieu et peuvent être éventuellement stabilisés dans le temps. Cela est clairement visible pour Mn. Le Mn relargué pendant les colonnes est évacué, alors que dans les systèmes batchs, il précipite (ou du moins une partie) sous forme de rhodochrosite. L'utilisation d'AMO dans l'échantillon de sol étudié entraine une augmentation du pH et du COD (qui peut être due à l'augmentation du pH) : une augmentation du pH pouvant être favorable à la stabilisation des EM et une augmentation du COD défavorable (augmentation de la mobilité des EM associés à la MOS).

Stabilisation of Cu, Cd, Pb and Zn using a novel manganese oxide in contaminated soil

Abstract: A novel manganese oxide was synthesised and characterized in order to be used as chemical stabilizing agent to reduce metal elements mobility and availability in contaminated soils. This amorphous manganese oxide (AMO) is not absolutely stable in soil and water, resulting in Mn released in the beginning of each experiments, but presents high sorption properties. Its presence in soil seems to promote biomass respiration, showing its non toxicity. Both column and batch experiments show that AMO becomes effective to reduce Cu, Cd and Pb mobility from 0.1% w/w ratio. Moreover, AMO increased soil sorption capacity and increased the pH of the studied contaminated soil sample, depending on the ratio. This AMO impacted more significantly new pollution than former pollution. An increased of the metallic elements immobilisation and changes in AMO properties were observed over time, highlighting the importance of ageing effect. This is coupled with a decrease of Mn released, which became unavailable over time due to the precipitation of rhodochrosite at the AMO surface.

Keywords: Amorphous Manganese Oxide, Divalent cations stabilisation, EDTA leaching, Column experiments, Batch experiments, Ageing effect, Mobility and availability