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EDTA in Soil Science: A Review of its Application in Soil Trace Metal Studies

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ABSTRACT

A comprehensive review is presented on the use of EDTA (ethylenediaminetetraacetic acid) in various fields of environmental geochemistry. The existing literature has been synthesized, analysed and discussed in terms of merits and disadvantages of the use of EDTA in remediation, fractionation and bioavailability prediction focusing on various key issues surrounding different environmental methodologies. Up-to-date information by different workers in various environmental scenarios explaining possible discrepancies are also being outlined.

Keywords: ethylenediaminetetraacetic acid, fractionation, remediation, soil, trace metal

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INTRODUCTION

Many agricultural and industrial activities such as sewage sludge, wastewaters, fertilizers, and smoke from factories lead to trace metal contamination in soils. This environmental problem and its effects on the health of living organisms, including human beings, is a matter of great concern to many researchers. Investigations about metal behaviour, especially on solid-phase distribution, could be useful for the improvement of bioavailability studies of trace metals and soil-cleaning procedures. Several chemical reagents, particularly chelating agents, are used in soil science for soil trace metal analysis purposes. Among this variety of chelating agents, EDTA (ethylenediaminetetraacetic acid) is a powerful complexing reagent which has received considerable attention in agronomy for:

(i) Estimating the potential metal mobile pool (Sterckeman *et al*. 1996; Alvarez *et al.* 2006; Manouchehri *et al.* 2006; Labanowski *et al*. 2008) and the metal bioavailability (Ure 1996; Bermond *et al*. 2005; Menzies *et al*. 2007);

(ii) Soil remediation processes (Brown and Elliott 1992; Davis and Singh 1995; Tejowulan and Hendershot 1998; Zeng *et al*. 2004);

(iii) Trace metal fractionation studies (Sposito *et al.* 1982; Quevauviller *et al*. 1996);

(iv) The supply of micronutrient cations for plants (Norvell and Linsay 1969).

The application of chemical reagents, including EDTA and other chelating agents, in each of the above-mentioned environmental purposes has already been thoroughly reviewed in some recent papers (Menzies *et al*. 2007; Xie *et al*. 2007; Lestan *et al*. 2008; Rao *et al*. 2008) but the literature about the use of EDTA in different soil trace metals environmental fields reflecting the role of some key elements like as environmental chemistry, experimental conditions and complexity of soil and related material matrices, is very sparse. Moreover, the lack of uniformity in different

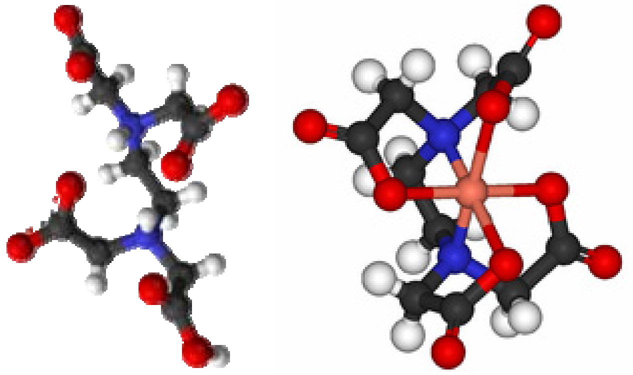

Fig. 1 Chemical structure of EDTA (left) and M-EDTA (right) (coordination with a metal ion II). Gray spheres represent carbon atoms, white hydrogen, red oxygen, and blue nitrogen (Cotrait 1972).

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Invited Review

Table 1 Complexation constants of EDTA and some metallic cations, K_{MY} corresponds to the reaction M + EDTA (Y) = MEDTA (MY).

	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Al^{3+}	Ca^{2+}	Fe^{3+}	Mg^{2+}	Mn^{2+}	Ni^{2+}
pK_{MY}	16.5	18.8	18.0	16.5	16.1	10.7	25.1	8.7	14.0	18.6

procedures does not allow the results to be compared worldwide nor the procedures to be validated. What is missing, thereby, is a comprehensive review which covers the use of EDTA in a variety of environmental procedures putting ahead the impact of different experimental and environmental conditions.

This is why the present review aims to cover several aspects of use of EDTA involved in various fields of environmental geochemistry like as soil remediation processes, heavy metal fractionation methodologies and bioavailability predictions.

APPLICATION AND CHEMISTRY

EDTA was patented in Germany in 1935 by F. Munz (Oviedo and Rodriguez 2003). It is a substituted diamine (**Fig. 1**) commercially presented as its sodium salts. This powerful chelate is mainly employed in aqueous medium for industrial and household uses such as detergents, water treatment, paper industry, metal cleaning, agrochemicals, cosmetics and pharmaceuticals (Oviedo and Rodriguez 2003) and is thereby released to the environment through the wastewaters.

EDTA is a polyacid with pK_a 2.0, 2.7, 6.2, 10.3 (Ringbom 1967). Its complexation constants are reported in **Table 1** for some metallic cations. This molecule is usually applied in soil science for its aptitude to extract metallic cations from different soil matrices. The extremely important complexing ability of EDTA enables it to act as an efficient competitor *vis-à-vis* the surface sites of the soil solid phase (S^{2-}) and to extract the metallic cations from this latter, as follows by simplified reaction (1):

$$S\text{-}M_{\text{solid}} + Y^{4-}_{\text{solution}} \rightarrow S^{2-}_{\text{solid}} + MY^{2-}_{\text{solution}} \quad (1)$$

Its complexing properties permit also to extract the precipitated or co-precipitated cations (AM) in soil solid phase (carbonates, oxides,…) according to reactions (2) and (3):

$$A\text{-}M_{\text{solid}} + Y^{4-} \rightarrow A^{2-}_{\text{solution}} + MY^{2-}_{\text{solution}} \quad (2)$$

$$M\,(OH)_{2\ \text{solid}} + Y^{4-} \rightarrow M\text{-}Y^{2-}_{\text{solution}} + 2\,OH^{-}_{\text{solution}} \quad (3)$$

In environmental systems, EDTA acts as a strong organic acid and is present as a metal complex. The metal remobilization is thus generally governed by metal-metal-EDTA exchange reactions (Nowack *et al.* 2001) as follows:

$$M_1EDTA_{\text{dissolved}} + M_{2\text{adsorbed}} \rightarrow M_2EDTA_{\text{dissolved}} + M_{1\text{adsorbed}} \quad (4)$$

In a critical review proposed by Nowack (2002), the chemistry of an aminopolycarboxylic acid like EDTA in natural environmental systems is considered to be governed

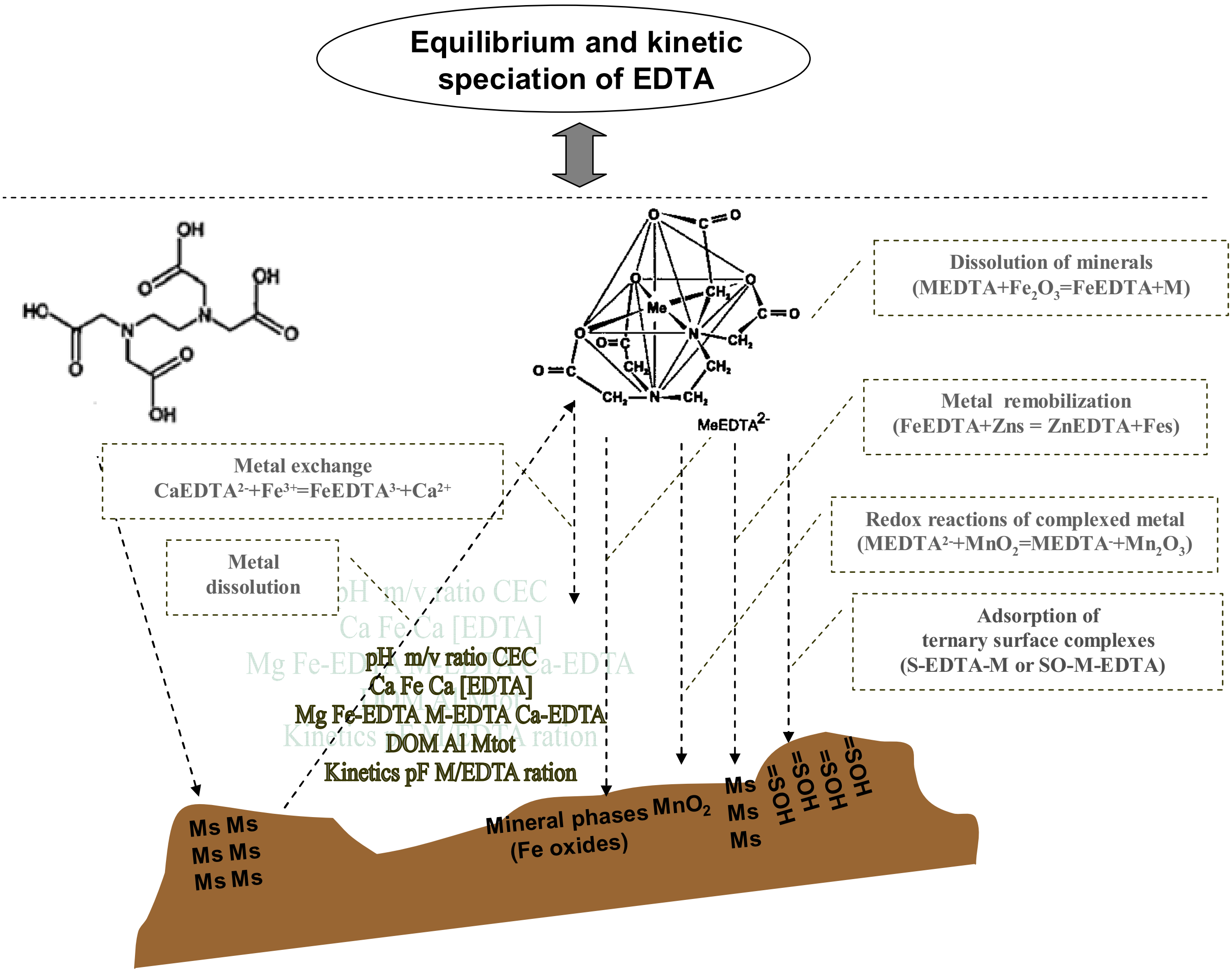

Fig. 2 Soil chemistry of EDTA (M=metal, S=soil).

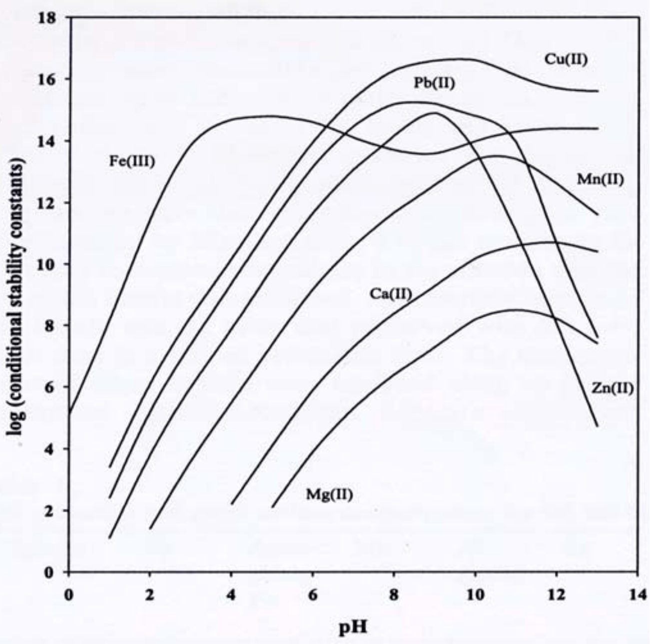

Fig. 3 Effect of pH on conditional stability constants of metal-EDTA complexes (adapted from Kim *et al*. 2003).

by exchange reactions, redox reactions and their speciation. As it is summarized in **Fig. 2**, due to the non-specific behaviour of EDTA, EDTA-soil system represents a set of interdependent reactions which govern the speciation of EDTA. This latter is affected by concentrations of all metals and ligands, the stability constants of all complexes, the equilibrium changes due to the addition of a new species and finally the kinetics. Any change that reduces or increases the concentration of one of the reactants (trace metal, major element, OH$^-$, H$^+$, or ligand concentration) affects the entire system.

Table 1 provides a comparison of stability constants of some metal-EDTA complexes. However, these stability constants are of limited value if some influencing factors such as pH, competitive behaviour of cations in the system, EDTA concentration, presence of other electrolytes and kinetics of exchanges are not considered (Ringbom 1967; Norvell and Linsay 1969; Brown and Elliot 1992; Nowack 2002; Kent *et al.* 2008).

As shown in **Fig. 3**, the stabilty of metal-EDTA complexes is affected by pH (Ringbom 1967; Kim and Ong 1993). In equal molar of cations present in solution, the affinity of metals for EDTA depends on pH of the soil. Furthermore, in equal pH conditions, the metal with the stronger affinity for EDTA will be dominant metal-EDTA coordination compound. Lindsay and Norvell (1969) have developed an equilibrium approach to study the competitive behaviour of some cations (Ca^{2+}, Fe^{3+}, Zn^{2+}, and H$^+$) in EDTA-soil system. The authors have underlined the pH-dependent character of such systems using mole-fraction diagrams. They have showed that at low pH values, ferric complex is the dominant form in comparison with zinc or manganese. Many different studies exist in the literature dealing with the interdependent behaviour of the reactions in soil-EDTA system and its major role when EDTA is used as a soil decontaminating agent from the heavy metals as well for its recycling in wastewater. The impact of different chemical conditions will be evoked within this review, particularly when EDTA is employed for remediation purposes.

USE OF EDTA IN THE REMEDIATION OF METAL-CONTAMINATED SOILS

EDTA as a chelating agent

A number of stringent regulations have been established to limit the levels of toxic metals in the environment. However, the cleanup of heavy metal contaminated sites remains highly challenging and costly. One of the permanent solutions is soil washing with solutions containing chelating agents which, contrary to acid washing processes, permit heavy metal desorption from soil solid phase by forming strong and water soluble metal ligand complexes without deterioration of soil physico-chemical properties. This technique is considered to be environmentally less disturbing (Xu and Zhao 2005) and relatively simple to execute; the polluted sample and the extractant solution are mixed *ex situ*, agitated strongly, separated and then the soil is rinsed before being made in place.

EDTA is one of the popular chelating agents that has been widely studied for removing heavy metals from soils because of its high chelating ability (Tuin and Tels 1990; Oviedo and Peters 1999; Lo and Yang 1999; Rodriguez 2003; Lee and Kao 2004; Zhang and Lo 2006). A recent paper (Lestan *et al.* 2008) reviews the use of different chemical agents in soil remediation process. According to this paper, EDTA is the most frequently cited agent in soil washing techniques literature because of its capacity to enhance the metal solubility from the soil solid phase. Many studies have compared EDTA to other chelating agents, acids and surfactants and found it better for extraction of toxic metal from soils (Brown and Elliot 1992; Allen and Chen 1993; Neal *et al.* 1997; Kim and Ong 1999; Scharmel *et al.* 2000; Sun *et al.* 2001; Tandy *et al.* 2004). Olajire *et al.* (2006) studied Pb, Hg, Cd and Zn extraction from domestic and industrial sludge using 0.05 mol.l^{-1} EDTA and found that EDTA represents the most extraction efficiency rather than other extractant used in this work such as pyridine and acetic acid. Wu *et al.* (2003) found that EDTA is a more powerful reagent to extract Pb, Zn and Cu compared with citric and oxalic acids.

Different authors have reported removal efficiencies between 40 and 100% for Pb, 55 and 100% for Zn, and 45 and 98% for Cu from various contaminated soils by EDTA (Clin and Reed 1995; Pichtel and Pichtel 1997; Ghestem and Bermond 1998; Xie and Marshall 2001; Kim *et al.* 2003; Chaiyaraksa and Sriwiriyanuphap 2004). This section aims to review, in detail, the effectiveness of EDTA to extract toxic trace metals, placing emphasis on the different factors affecting the removal efficiency in a soil-EDTA system.

Several investigations appear in the literature concerning the use of EDTA in different operational conditions (**Table 2**).

According to many different investigations on a wide variety of soil samples, uptake efficiency depends on several factors, including the source of pollution, soil pH, concentration of major cations (Ca^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+},…), metal speciation (its distribution in different soil components), the kinetics of all complexation reactions, the total content of metal in soil and finally the affinity of the target element for EDTA. In this regard, different operational procedures were proposed to obtain the optimum metal extraction efficiency in different soil matrices.

The impact of metal distribution in the soil solid phase on the removal efficiency of EDTA has been investigated by several authors using sequential chemical extraction. According to Elless and Blaylock (2000), sequential extraction of some Pb-contaminated soils showed that the EDTA extractable fraction corresponds mainly to exchangeable and carbonate fractions while oxide, organic and residual fractions were less solubilized by EDTA. Barona and Romero (1996) however, recommend the use of EDTA for Pb remediation in contaminated soils in which Pb is mainly accumulated in fractions associated with oxides and organic matter/sulphides. Lee and Kao (2004) observed higher removal efficiency of heavy metals associated with exchangeable fractions than those stronger adsorbed to Fe-Mn oxides fraction. When contaminating metals are associated with soil oxides, an extractant like oxalate (Ox) may be a superior reagent to powerful EDTA (Elliot and Shastri 2004). Despite the dramatically higher stability of Zn-EDTA complexes compared

Table 2 Some optimized leaching process using EDTA in various soils and related matrices.

Leachability parameter	**pH (m_{soil}/v_{EDTA})**	**[EDTA] (mol.l^{-1})**	**Time of reaction (h)**	**Leaching step**	**Removal (%)**	**EDTA salt**
Silty-clay loam Cu-contaminated soil (Udovic and Lestan 2007)	7.5	2.5	18	6 steps	38.8 % Cu	Na_2-EDTA
Non-contaminated calcareous soils (Manouchehri *et al*. 2006)	6.5	2	24	1 step	16-19% Pb 15-22% Cu 24-57% Cd	Na_2-EDTA
Non-contaminated non-calcareous soils (Manouchehri *et al*. 2006)	6.5	2	24	1 step	36-42% Pb 25-48% Cu 67-79% Cd	Na_2-EDTA
Calcareous contaminated soils (Tejowulan and Hendershot 1998)	8-8.4	$2.7*10^{-3}$	24	1 step	53.2% Cd, Cu, Pb, Zn	Na_2-EDTA
Sandy contaminated soils (Barona and Romero 1996)	pH not adjusted	0.1	2	1 step	26-81% Pb	Na_2-EDTA
Non-calcareous polluted soil (Zeng *et al*. 2004)	3.24-3.69	0.02	3	7 steps	95% Cd 101% Cu 93% Pb 102% Zn	Ca-EDTA
Loam (Wasay *et al*. 1998)	3.8-9	0.02-0.08	24	1 step	97% Cd, 95% Pb	Na_2-EDTA
Sandy clay loam (Wasay *et al*. 1998)	3.9-9.7	>0.08	24	1 step	99-100% Cd 90-95% Cu 96-99% Pb 86-87% Zn	Na_2-EDTA
Artificially contaminated soil Battery recycling area Rifle range Lead smelter area (Kim *et al*. 2003)	6.5	2.10^{-4}	24	1 step	75% Pb 55% Pb 40% Pb 10% Pb	Na_2-EDTA
Heavily contaminated soils (Papassiopi *et al*. 1999)	pH not adjusted	0.25	22	2 steps	50-71% Pb 38-49% Zn 18-48% Cd 0-21% As	Na_2-EDTA
Alkaline contaminated soil (Theodoratos *et al*. 2000)	pH not adjusted	0.25 0.25	768 768	1 step 1 step	51% Pb 77% Pb	$Na_2CaEDTA$ Na_2H_2EDTA
Contaminated sandy and clayey soils (Lo and Yang 1999)	4.51-4.62	0.05-0.1	2	1 step	90% Cu and Zn 50% Pb	
Contaminated urban soil (Xie and Marshall 2001)	8 (1/1)	0.01	24	1 step	32-54% Pb, Mn, Cu, Zn	Na_2-EDTA
Radio-labelled soils (Degryse *et al*. 2004)	Soil A 4.3 Soil B 7.2	10, 100, 1000 and 10000	16	1 step	Cd 20-40% Zn 10-30%	Na_2-EDTA
Biomass (Nunez-Lopez *et al*. 2008)	6-8 (1/100)	0.3	72	1 step	Pb 99%	Na_2-EDTA
Contaminated soils due to mining activities (Xia *et al*. 2008)	Soil Y 4.8 Soil C 6.3	0.05	24	1 step (column experience)	Pb 42%, Zn 43%, Cu 41%, Cd 61% Pb 27%, Zn 45%, Cu 40%, Cd 46%	Na_2-EDTA
Clay loam loam sandy clay loam soils (Wasay *et al*. 2007)	3.7 6 6	0.02 0.02 0.08	24 1-36 24	1 step	Pb 40-90%, Zn 80%, Cu 85%, Cd 92-98%	Na_2-EDTA
Pb contaminated soils due to smelting and recycling activities (Tawinteung *et al*. 2005)	6 (1/5)	2:1 (mole to Pb)	1	1 step	Pb 85-95%	Na_2-EDTA
Contaminated forest soils (a) Unpolluted area (b) Smelting area (Chrastny *et al*. 2008)	4.1-4.7 (1/10)	0.05	1	1 step	(a) Pb 17-95% (b) Pb 70-90%	Na_2-EDTA
Soil and sludge (Chaiyaraksa and Sriwiriyanuphap 2004)	2.7-8.5 (1/2.5)	0.01 0.1	2	1 step	Cd 67-97%	Mixture of Na_2EDTA and $Na_2S_2O_5$

to Zn-Ox, Ox released more Zn than EDTA, in a polluted soil from a Pennsylvania smelter site, because 40% of total Zn was associated with the oxide fraction. Hence, it is essential to thoroughly establish metal solution chemistry and its fixation behaviour within the soil when extractive decontamination is proposed for site remediation. However, as will be discussed later, the association of metal to a given fraction seems to be dependent on the source of contamination (Ettler *et al*. 2005; Chrastny *et al*. 2008).

Besides, as seen in **Table 2**, each cation differs from the others in a significant manner, in terms of extractability by EDTA. It is generally recognized that the order of mobility of the most studied cations (Pb, Cu, Cd and Zn), disregarding of their stability constants of complex formation with EDTA (**Table 1**), may be classified as follows (Tejowulan and Hendershot 1998; Ghestem and Bermond 1998; Bermond and Varrault 2004; Manouchehri 2006; Wasay *et al*. 2007; Xia *et al*. 2009):

Cd > Zn > Cu > Pb

In fact, Cd and Pb are, respectively, considered as “relatively mobile” and “highly immobile” because of their large and small hydrated radius; with a valency of two, Pb has a higher ionic charge and is therefore more adsorbed and less extractable while Cu and Zn are intermediate in terms of hydrated radius and extractability. This extractability trend has been, as well, proved by some kinetic investigations. Wasay *et al.* (2007) studied the kinetics of metal release by EDTA from three naturally contaminated soils and defined the coefficient rate of different heavy metals extraction. They concluded that Cd leached out faster followed by Zn, Cu, Pb, Hg and Cr. Varrault and Bermond (2004) observed the same order of extractabilty rate for Cu, Pb and Cd in naturally contaminated soils.

The data gathered in **Table 2** indicates the use of EDTA for different soil pHs. However, the pH, EDTA concentration and major cation contents are interdependent factors affecting the extraction efficiency. Ghestem and Bermond (1998) concluded that EDTA extraction depends on pH, EDTA concentration and the content of major cations for two sewage sludge amended soils. The extraction efficiency was reported to be at least 60% of total content in one extraction for Cu, Zn, Cd and Pb, depending on pH and EDTA concentration. The authors consider that Pb-, Cu- and Cd-EDTA extraction is nearly pH-independent for a high concentration of EDTA (0.05 mol.l^{-1} in this work) whatever the type of soil. Fangueiro *et al.* (2002) precluded any pH changes during the extraction of Cd, Cu, Zn and Pb from sediments for high concentrations of EDTA (0.05 mol.l^{-1}) and initial pH values in the interval 5.5-7.5. Contrary, for low concentrations of EDTA, extraction efficiency becomes dependent on pH and major cation contents, especially Ca and Fe (Ghestem and Bermond 1998; Chrastny *et al.* 2008). Calcium could play a competitor role *vis-à-vis* the trace elements (M) according to the following reaction (5):

$$\text{M-EDTA}^{2-} + \text{Ca}^{2+} = \text{Ca-EDTA}^{2-} + \text{M}^{2+} \qquad (5)$$

Regarding the classical constants of complex formation, this reaction seems to be impossible (**Table 1**). However, in calcareous soils with alkaline pH, reaction (6) will be displaced to the left and causes a decrease in trace metal extraction. Hence, considering the trace metal and calcium affinities for the soil component, pH may contribute to the extraction efficiency in lack of EDTA.

$$\text{M}^{2+}_{\text{soil}} + \text{H}_2\text{Y}^{2-} = 2\text{H}^{+}_{\text{soil}} + \text{MY}^{2-} \qquad (6)$$

Some authors consider that pH of soil-EDTA extracts is altered by the natural acid-neutralizing capacity of the soil (Peter and Shem 1992; Shu and Liu 1994; Manouchehri 2006) and do not buffer the initial EDTA solution. Tejowulan and Hedershot (1998) found that for 2.10^{-3} mol.l^{-1} EDTA, the pH of EDTA solution increased significantly from 2.6 to 7.4 after being in contact with soil for 24 h. So, in some studies the pH changes are neglected in soil EDTA remediation processes (Barona and Romero 1996; Wu *et al.* 2003).

The extraction efficiency of trace elements could vary due to the competition effects of major elements such as Ca, Fe, Al, Mn, Mg, etc. However, among several studies on the reactions of EDTA-metal complexes in soils, most research effort has been devoted to studying the performance of EDTA for the extraction of trace metals from contaminated soils. Little attention has been paid to the fate of the co-extraction of major elements, including alkaline-earth cations, due to the non-selective nature of EDTA. Some studies have reported the Ca co-dissolution on the efficiency of trace metal extraction by EDTA (Chaudri *et al.* 1995; Rodriguez *et al.* 2003). Theodoratos *et al.* found an important co-dissolution of soil Ca resulting in a low degree of heavy metal complexation by EDTA. According to the experimental work of García-Delgado (1996), a high stoichiometric excess of EDTA with respect to Pb was needed to recover Pb in a carbonate-rich soil. Brown and Elliott (1992) found that for alkaline pH conditions, there is competition between Ca or Mg with Pb for EDTA.

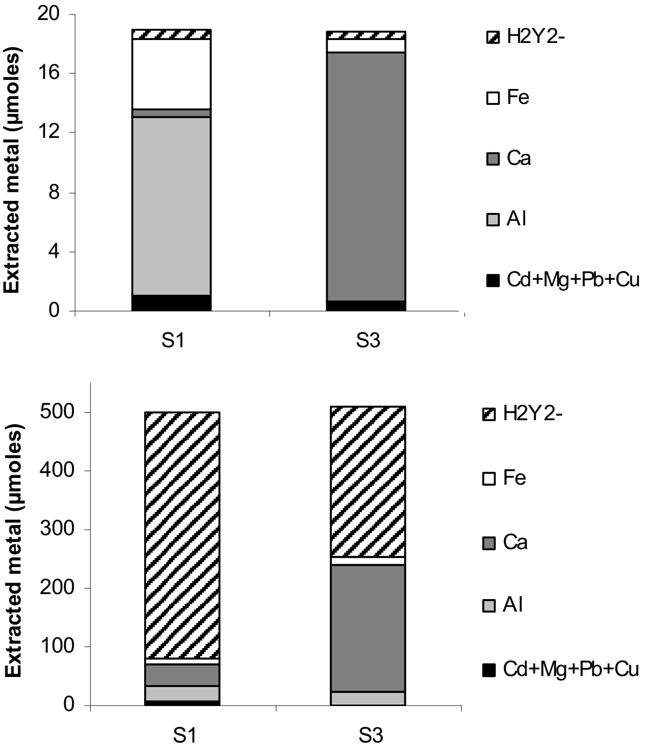

Fig. 4 Mass-balance of metal-EDTA in two soils mixed with two concentrations of EDTA for 24 hours. (**Top**) 0.002 mol.l^{-1}, (**Bottom**) 0.05 mol.l^{-1} (adapted and modified from Manouchehri *et al.* 2006).

In fact, in many of these experimental works the strong impact of major cations on removal capacity of EDTA is suggested, but no further detailed investigation is available concerning the choice of EDTA concentration with respect to all extractable cations, including the major ones. Manouchehri *et al.* (2006) concluded that the mass balance of the EDTA-Metal-Soil system is governed by the extraction of major cations, especially Ca, in calcareous soils. Accordingly, the molar amounts of major metals are to be considered, when choosing the optimum concentration of a non-selective chelating reagent such as EDTA in remediation soil processes. So, the stoichiometric ratio of EDTA/metal needs to be estimated with respect to all extractable cations present in the soil in order to ensure the availability of reagent *vis-à-vis* the cation to be removed. **Fig. 4** shows an example of EDTA consumption (for lack 0.002 mol.l^{-1} and excess 0.05 mol.l^{-1} EDTA) by major and trace cations in one calcareous (S_3) and one non-calcareous (S_1) soil, revealing the EDTA availability in both cases. In the case of lack of EDTA, about 80% of EDTA is consumed by Al and Fe cations in non-calcareous soil, while in the calcareous sample the major part of the reagent (about 85%) is complexed by Ca cations. On the contrary, for excess EDTA, the chelating of all cations (major and trace) seems to be completed and at least 50% of free EDTA is available in solution.

In the same way, according to Papassiopi *et al.* (1999), the simultaneous dissolution of calcite led to consume approximately 90% of the available EDTA for Zn and Pb removal from contaminated calcareous soils. The low extracted amount of trace metal at alkaline pH and in the presence of calcium carbonate is reported in the literature by several authors (Ghestem 1997; Bermond et al. 2004; Palma and Ferrantelli 2005). These conditions favour trace metal fixation on the soil solid phase. Some studies affirm that trace metals may be adsorbed strongly onto calcite (Papassiopi *et al.* 1999; Theodoratos *et al.* 2000) resulting in less important extractability of trace elements in soils rich in carbonate. Hence, in order to use EDTA as a cost-effective remedial option for calcareous soil treatment, the design criteria and cost estimations should be based on the calcite content of the soil.

Other studies underline the role of concentration and crystallinity of Fe on metal removal by EDTA and interpretation of results in metal availability investigations. Chrastny *et al.* (2008) found that Fe concentration and its different species may play a very important role on Pb removal efficiency from low to moderately contaminated forest soils with a high concentration of amorphous Fe. According to the work of Kim *et al.* (2003) on lead extraction by EDTA, none of the lead was extracted from a highly calcareous soil, even for a high EDTA-Pb stoichiometric ratio. This lack of lead extraction has been linked to the type of lead species present, the occlusion of lead within the iron species and possible competition with other metal ions present in the soil (Ca^{2+} in this case). Hence, the knowledge about the concentration and the forms of competing cations seems to be indispensable in soil remediation procedures as well as in the estimation of the mobile metal pool.

Another important factor affecting extraction efficiency is the source of contamination (Barona *et al.* 2001). The source of contamination affects the metal association in different soil fractions, e.g. in polluted soils, Pb is generally considered to be associated with the "potentially labile" fractions or EDTA extractable fractions (Tawinteung *et al.* 2005) whereas some recent studies found that the dominant fraction of Pb is associated with the reducible (Fe- and Mn-oxides) fraction (Ettler *et al.* 2005). Low extraction efficiency is generally observed in soils with the natural origin of trace elements due to the strong binding of metal to different soil components. The maximum extraction efficiency reported by Manouchehri *et al.* (2006) in non-calcareous soils with naturally-occurring trace cations is about 45% for Pb and Cu and 75% for Cd, while these percentages exceed 50% of total content in soils with an anthropogenic source of contamination (Ghestem 1997; Tejowulan and Hendershot 1998; Barona *et al.* 2001; Kim *et al.* 2003). In a recent work by Chrastny *et al.* (2008), older Pb bound more strongly to the unpolluted matrices is markedly less EDTA-extractable than Pb in a smelting area originating from recent anthropogenic activity. Several studies prove that extraction by EDTA is not a suitable and efficient treatment for soils containing a high percentage of metal in strongly bound fractions (Elless and Blaylock 2000; Tandy *et al.* 2004). On the other hand, soils with low concentrations of heavy metals are the hardest to remediate because the metals are preferentially adsorbed by the sites of highest binding energies, which require a higher concentration of chelating compounds (Wasay *et al.* 1998). According to Tawinteung *et al.* (2005), initial Pb concentration, Pb partitioning within soil and particle size of the soil matrix are three major factors influencing the removal of Pb from industrial polluted soils.

Some authors have studied the eventual role of chemical form of EDTA salt as another factor affecting the mobilizing of metal from the soil solid phase. EDTA is generally used as a sodium salt, although some authors recommend the use of EDTA as a calcium salt in order to avoid the co-dissolution of calcium cations in calcareous matrices (Brown and Elliott 1992; Zeng *et al.* 2004). Papassiopi *et al.* (1999) found that the tetrasodium salt of EDTA (Na_4-EDTA) is less effective for metal removal compared to the disodium salt (Na_2-EDTA), though applied at higher concentrations for treatment of soils contaminated due to smelting and mining activities. According to Theodoratos *et al.* (2000), the major benefit of calcium EDTA salt ($Na_2CaEDTA$) in comparison with the disodium EDTA salt is the preservation of calcite soil. They consider that Ca-EDTA is an extractant agent which does not modify the physico-chemical properties of soil and recommend the use of Ca salt with low liquid/solid ratios and repetitive treatment stages of 24 h for contaminated calcareous soils. However, they observed that Ca-EDTA decreased the extraction efficiency of Pb and Zn. According to Zeng *et al.* (2004), no significant differences of metal desorption were observed using Ca-EDTA and Na-EDTA salts in removing trace metals from non-calcareous polluted soils. These authors found that Ca-EDTA can supply Ca to soils and attenuate the dissolution of organic matter. Nowack *et al.* (2001) found that Ca-EDTA and Na-EDTA have a similar ability to remobilize metal (Cu, Zn and Mn) from river sediments.

Another interesting field of investigation in soil cleaning procedures by EDTA is the recycling of metal-EDTA complexes. In fact, the high cost of EDTA has hampered its wide use for remediation of metal-polluted soils. Furthermore, another difficulty with using EDTA is that a large volume of wastewater containing metal-EDTA complexes is generated and must be treated before disposal (Kim *et al.* 1999). To reduce the cost of using EDTA, recycling of used EDTA and reduction of the wastewater volume are needed (Allen and Chen 1993; Hong *et al.* 1999; Barona *et al.* 2001; Zeng *et al.* 2004).

Several recycling methods have been demonstrated as a laboratory-scale like electrolysis application for the metal recovery in metal-EDTA solution (Allen and Chen 1993) or addition of a chemical agent to discharge the EDTA from metallic cations (Chang 1995). In these methods, the possibility to reuse the recovered EDTA has not been demonstrated. Kim and Ong (1999) proposed a method for recycling Pb-EDTA wastewater and for evaluating the effectiveness of recovered EDTA to further treat contaminated soils. The recycling method involves substituting the Pb in an EDTA complex with Fe(III) ions at low pH values, followed by precipitation of lead ions with either phosphate or sulfate ions. In this method, Pb-EDTA wastewater can be recycled several times without losing much of its extracting capacities. Zeng *et al.* (2004) studied the feasibility of EDTA recovery by the addition of Na_2S and $Ca(OH)_2$. They found that Na_2S was capable of separating Cd, Cu and Pb from EDTA; however, the precipitation of Zn required the addition of $Ca(OH)_2$. The metal precipitates contained high concentrations of metals and were recycled to recover and reuse EDTA. According to this work, after reusing the reclaimed EDTA seven times, EDTA losses ranged from 19.5 to 23.5%.

Udovic and Lestan (2007) evaluated the feasibility of using EDTA for Cu soil leaching and using ozone/UV for treatment of the washing solution. The impact of the proposed method on soil quality was investigated. According to this study, EDTA leaching of Cu-contaminated soil do not extensively alter the soil properties but the Cu-removal efficiency of EDTA is soil specific. The greatest advantage of this method is its near-zero emission into the environment.

In another study (Zhang *et al.* 2007), the feasibility of recovery and reuse of EDTA was extensively investigated using batch experiments for remediation of Pb- and/or marine diesel fuel-contaminated soils. According to their experimental results, 97% of Pb was removed using 0.54 $mmol.l^{-1}$ of EDTA, which has been recovered and reused for at least 4 cycles without a significant loss of its chelating capacity.

Some authors have attempted to use mixtures of EDTA with another expensive reducing agent as an alternative to the high cost of EDTA utilization. The mixture of Na_2EDTA with $Na_2S_2O_5$ was proposed by Abumaziar and Smith (1999) as an economical solution for Cd and Zn removal. This technique was evaluated for Cd removal from different soils and sludges by Chaiyaraksa and Sriwiriyanuphap (2004). High removal efficiencies (between 67 to 97% of Cd) were reported in these studies.

It is also important to note that due to its wide exploitation and its low biodegradability (Egli 2001; Tandy *et al.* 2004), EDTA is unfortunately very persistent in the environment. This can pose a rather high risk to metal leaching to the groundwater (Nowack 2002; Xie and Healy 2007). This is why recently some studies have focused on the use of easily biodegradable chelating agents such as SS-EDDS (S,S-ethylendiaminedisuccinic acid) which are considered a safe and environmentally benign replacement for EDTA in soil washing (Tandy *et al.* 2004; Evangelou *et al.* 2007). The use of SS-EDDS seems to give extraction efficiencies comparable to or better than the results reported in the literature (Tandy *et al.* 2004). According to Nowack *et al.* (2006), due to relatively weak Ca-EDDS stability, the presence of carbonate does not result in a high effect of Ca co-dissolution reducing the metal extraction efficiency. Besides, some authors consider that, compared to chelating agent, the use of salts of organic acids is less selective for major elements like Ca, Mg and Fe and tend to have less impact on soil media; an alternative which permits to provide remediation techniques with a limited impact on the environment (Wasay *et al.* 1998).

Finally, an interesting section in the review of Lestan *et al.* (2008), entitled "the fate of metals left after soil remediation", is devoted to the fate of partial extraction of toxic metals by remediation techniques. It is generally thought that the residual fraction of metal left in soil after remediation is chemically stable, though this stability is not permanent because of various biotic and abiotic soil factors able to transit the metal to more mobile fractions. According to Udovic *et al.* (2007), although EDTA decreased the mobility of Pb by 87.3% in soils contaminated due to smelting activities, its mobility increased in remediated soil exposed to earthworm species. So, further works are required to study the metal behaviour after remediation.

EDTA-assisted phytoremediation

During the last two decades, a large part of studies in the soil depollution field has focused on using plants to remediate metal-contaminated soil, usually called phytoremediation. For this purpose, hyperaccumulator plants with exceptional capacity of metal uptake are used for removing large amounts of trace metals. However, natural phytoremediation is considered as a technique with advantages of being *in situ*, cost-effective and environmentally sustainable (Jiang and Yang 2004) but due to the limits of plant species with high accumulating capacity and low bioavailability of some trace elements in the soil solid phase, such as lead (Jiang and Yang 2004; Lestan *et al.* 2008), the use of chemical agents has been proposed in order to improve metal uptake (Marschner 1995). Amendment of metal-contaminated soils by EDTA has been reported several times in the literature as a useful *in-situ* tool to increase metal solubility making its translocation to the shoots easier (Huang *et al.* 1997; Groman *et al.* 2001; Madrid *et al.* 2003; Lesage *et al.* 2005; Panwar *et al.* 2005; Kiasari *et al.* 2006; Chen *et al.* 2007). According to Madrid *et al.* (2008), EDTA can concentrate metals in barley roots and stabilize them at the soil surface. A recent paper (Lestan *et al.* 2008) reviews and compares, in detail, the use of different chemical agents, including EDTA, in the phytoremediation process. According to this paper, EDTA is recognized as the most efficient chelator to increase metal accumulation and to improve the solubility of low bioavailable cations such as Pb (Ellesse and Blaylock 2000). However, the poor biodegradability of EDTA (Oviedo and Rodriguez 2003), selection of plants which tolerate the metal contamination in addition to the influence of plant cultivar (Liphadzi *et al.* 2003; Turgut *et al.* 2004; Luo *et al.* 2005), and reducing the dosage of EDTA (for economically reasons) for a given uptake efficiency remain real issues in large-scale field applications. Some new research areas are thereby developing in order to overcome these restrictions. As previously mentioned, studies are shifting towards the use of more biodegradable agents such as SS-EDDS (Kos and Lestan 2004; Evangelou *et al.* 2007) which is the replacement of EDTA in laundry detergents (Schowanek *et al.* 1997), NTA (Ebina *et al.* 1986) or citric acid (Meers *et al.* 2005). Besides, other studies exist in the literature on EDTA dosage optimization and its important role in metal uptake by different plant species (Huang *et al.* 1997; Epstein *et al.* 1999; Elkhatib *et al.* 2001; Li *et al.* 2005).

Finally, the enhanced phytoextraction technique compared to soil washing technique remains a more economical approach and could be a promising subject in the future to develop methods for recovery of extracted metal.

SPECIATION OR FRACTIONATION OF SOIL TRACE METALS USING EDTA

Many soil scientists are greatly interested in the prediction of trace metal mobility and availability which are the results of their reactivity in the soil solid phase or, in other words, their localization in different soil constituents, usually called ***speciation*** or ***fractionation***. In order to evaluate the metal migration ability to soil biota (metal lability or metal mobility), the scientists focus their investigation on different physical and chemical speciation approaches. The physical methods are generally not enough sensitive, and could only be used for severely contaminated samples. Chemical methods are more sensitive and consist of using different chemical reagents for extraction of trace elements followed by their quantification usually at equilibrium. Two prominent chemical extraction schemes exist in literature to estimate the labile metal pools: Sequential extraction procedures (SEP) and Single extraction schemes. Several chemical reagents are used in both extraction procedures. EDTA is one of the chemical reagents widely used in different soil and sediment fractionation methodologies, especially in single extraction procedures (Viro 1955; Ure *et al.* 1993; Leleyter and Baraud 2005; Bermond *et al.* 2005; Young *et al.* 2006) in order to assess mobile metal pool in polluted soils. There are a number of publications in the literature in which EDTA is also reported as extractant in sequential extraction procedures allowing the fractionation of metal associated to different fractions in soil solid phase (Sposito *et al.* 1982; Stalikas *et al.* 1999; Gleyzes *et al.* 2002; Young *et al.* 2006). Finally, certain authors use this reagent in kinetic fractionation studies in an attempt to identify the kinetically metal labile pool (Tack and Verloo 1995; Bermond *et al.* 2005; Fangueiro *et al.* 2005; Wasay *et al.* 2007; Labanowski *et al.* 2008).

EDTA in sequential extraction fractionation

According to the definition proposed by Ure (1991), Sequential Chemical Extraction is an example of *Operational* speciation which refers to the use of different reagents to extract metals defining different species such as "moderately reducible", "heavily reducible" or "organically bound". In this field, there are two basic protocols: Tessier scheme (1979) and BCR Community Bureau of Reference (now Standards, Measurement and Testing Programme) protocols (Ure *et al.* 1993; Quevauviller 1994). Most recent papers have employed different variations of these two protocols for heavy metal fractionation.

Despite of their widespread use, the great variety of protocols and their development for non-traditional analytes (Bacon and Davidson 2008) such as Mercury and Arsenic, the sequential extractions have been subject to several criticisms such as lack of reagent specificity and selectivity (Ure *et al.* 1993; Rauret *et al.* 1999; Mocko and Waclawek 2004; Fernández *et al.* 2004), lack in the uniformity of the different procedures (Quevauviller *et al.* 1996, 1997), lack of quality control (Rauret 1998), operational quality of results, readsorption and redistribution of metal on the soil solid phase (Bermond and Malenfants 1990; Bermond and Eustache 1993; Yousfi and Bermond 1997; Bermond 2001; Song and Greenway 2004; Brunori *et al.* 2005) resulting in the underestimation on the metal fraction bound to a given component or overestimation at least of one of the subsequent fractions. It is to be noted that the application, limits and future role of sequential extractions are adequately covered in some excellent recent reviews (Gleyzes *et al.* 2002; Young *et al.* 2006; Bacon and Davidson 2008;

Table 3 Use of EDTA in some particular sequential schemes.

Procedures	Fractions	Elements and samples	References
0.1 mol.l^{-1} CaCl$_2$	Exchangeable	Pb, Cu, Zn, Ni, Cd and Cr in Contaminated sewage sludges	McGrath and Cegarra 1992
0.5 mol.l^{-1} NaOH	Organically bound		
0.05 mol.l^{-1} Na$_2$-EDTA	**Bound to carbonates**		
aqua regia	Residual		
1 mol.l^{-1} KNO$_3$	Exchangeable	Cu, Zn and Cd in digested sludges	Gupta *et al.* 1990
0.5 mol.l^{-1} KF	Adsorbed		
0.1 mol.l^{-1} Na$_4$P$_2$O$_7$	Organically bound		
0.1 mol.l^{-1} EDTA	**Bound to carbonates**		
1 mol.l^{-1} HNO$_3$	Sulphides		
0.1 mol.l^{-1} EDTA	**Mobilisable**	Fe-rich industrially polluted soils	Gleyzes *et al.* 2002
0.1 mol.l^{-1} (EDTA+ ascorbic acid)	Reducible phase		
H$_2$O	Water soluble	Zn, Pb and Cd in contaminated soils	Barbafieri and Dadea 1998
1 mol.l^{-1} KNO$_3$	Linked with electrostatic forces, Exchangeable		
	Linked covalent forces		
EDTA 1%	**Complexed/adsorbed**		
0.5 mol.l^{-1} KNO$_3$	Exchangeable “mobile”	Ni, Cu, Zn, Cd and Pb in sewage sludges	Sposito *et al.* 1982
H$_2$O	Adsorbed (soluble “mobile”)		
0.5 mol.l^{-1} NaOH	Organically bound		
0.05 mol.l^{-1} Na$_2$EDTA	**Carbonates “mobilisable” or Organically complexed**	Cu, Zn, Pb and Ni in sewage sludges compost	Amir *et al.* 2005
4 mol.l^{-1} HNO$_3$	Sulphides “mobilisable”		
0.1 mol.l^{-1} CaCl$_2$	Exchangeable	Cd, Cr, Cu, Ni, Pb, and Zn in citrus soil received sewage sludges and composted municipal solid waste	Canet *et al.* 1997
0.5 mol.l^{-1} NaOH	Organically bound		
0.05 mol.l^{-1} Na$_2$-EDTA	**Carbonates**		
EDTA + Ascorbic acid	**Available** in reducible conditions	Sb in agricultural soils	Fuentes *et al.* 2004
Oxalic acid/oxalate+ascorbic acid	Extractable in reducible conditions		
HNO$_3$+HCl+HF	Residual		
1 mol.l^{-1} MgCl$_2$	Ionically bound	As in industrially contaminated wetland	Keon *et al.* 2001
1 mol.l^{-1} NaH$_2$PO$_4$	Strongly adsorbed		
1 mol.l^{-1} HCl	Carbonates, Mn-Fe-oxides		
0.2 mol.l^{-1} ammonium oxalate	Fe oxyhydroxides		
0.051 mol.l^{-1} Ti-citrate-EDTA-bicarbonate	**Crystalline Fe oxyhydroxides**		
10 mol.l^{-1} HF	Oxides and silicates		
16 mol.l^{-1} HNO$_3$+H$_2$O$_2$	Residual		
0.5 mol.l^{-1} Ca(NO$_3$)$_2$	Exchangeable	Cd, Pb and Zn in contaminated soils (mining and smelting activities)	Basta and Gradwohl 2000
1 mol.l^{-1} NaOAC	Mobilisable		
0.1 mol.l^{-1} Na$_2$-EDTA	**Bound to carbonate/organic matter**		
4 mol.l^{-1} HNO$_3$	Residual		
1 mol.l^{-1} NaOAC	Exchangeable+carbonate	Contaminated soils	Zeien and Bruemmer 1989
0.1 mol.l^{-1} NH$_2$OH	Moderately reducible		
0.2 mol.l^{-1} (NH$_4$)$_2$EDTA	**Organic/sulfidic**		
NH$_4$OX+ascorbic acid (0.2/0.1) mol.l^{-1}	Heavily reducible		Schramel *et al.* 2000
Aqua regia	Residual		
1 mol.l^{-1} NH$_4$NO$_3$	Mobile	Cu, Zn, and Pb in soils treated by biodegradable chelating agent (SS-EDDS)	Tandy *et al.* 2004
1 mol.l^{-1} NH$_4$OAC	Easily mobilisable		
0.1 mol.l^{-1} NH$_2$OH-HCL+NH$_4$OAC	Bound to Mn oxide		
0.25 mol.l^{-1} (NH$_4$)$_2$EDTA	**Bound to organic matter**		
0.2 mol.l^{-1} NH$_4$OX	Bound to amorphous Fe oxides		
(0.2/0.1) mol.l^{-1} NH$_4$OX/ascorbic acid	Bound to crystalline Fe oxides		
X-ray fluorescence analysis	Residual fraction		

Rao *et al.* 2008) and are not the scope of our review. Our principal objective is to focus on the status of EDTA in different sequential schemes.

In **Table 3** some special schemes in which EDTA is used in one of the steps of sequential extraction procedures are presented. In our knowledge, EDTA is used in particular sequential extraction schemes and does not feature in Tessier (1979) and BCR (Quevauviller 1998a, 1998b) sequential extractions which are the most adopted methods by various workers in the literature. Its application is almost considered for determination of chemically mobile fractions especially the metal fractions bound to organic matter or carbonate.

Because of its non-specific nature, EDTA extracts cations bound to several components of soil solid phase (exchangeable, surface adsorbing sites, carbonate, organic matter and amorphous Fe and Mn oxides). Indeed, it cannot give metal speciation information in terms of a specific soil component. So, in order to distinguish the different soil solid phase fractions in sequential extraction protocols, the extraction by EDTA must necessarily be preceded by a set of reagents capable to extract the metal bound to the fractions susceptible to be "attacked" by EDTA.

However, according to several authors there is no more advantage than the single use of EDTA (Koeckritz *et al.* 2001; Alvarez *et al.* 2006). Some other workers consider that the sequential extractions are not very cost-effective for bioavailability prediction purposes (Bacon *et al.* 2008). For the reasons mentioned above, several authors used the single extraction schemes which permit to estimate the metal mobile pool under the action of a single reagent particularly the chelating complexing agent. In this field, we will discuss in the following section the use of EDTA as a well-known chelating agent for estimation the metal mobility in soil solid phase or prediction of its bioavailability *vis-à-vis* the soil biota.

It is also to be noted that a major part of literature corresponding to EDTA in relation with sequential extraction procedures concerns some comparative works in which both principal schemes (Tessier and BCR) and single EDTA scheme have been subject of many comparative studies in different soil and sediment matrices. These comparative studies will be more developed in single extraction section.

EDTA in single extraction fractionation

A large range of extraction schemes have been developed by several authors using EDTA to simulate trace metal mobility, soil plant transfers (phyto-toxic and nutritional deficiency effects) and the study of physico-chemical processes. This single extraction procedure has been tested in the frame of BCR inter-laboratory studies (Quevauviller *et al*. 1996b) in order to validate the procedure and the analytical techniques used and also to improve the quality of extractable metal determinations in two soils (sewage sludge-amended and terra rossa soils) (Quevauviller *et al.* 1995). In another work (Quevauviller *et al*. 1996a), this study was completed by an inter-laboratory project on EDTA and DTPA extraction schemes applied to a calcareous soil reference material. On the basis of the results obtained in this project, EDTA was widely accepted whereas DTPA was more criticized because of its operational difficulties.

The BCR single extraction scheme recommends the use of 0.05 mol.l^{-1} EDTA as an indicator of mobile contents of metal. The use of this scheme has been particularly widespread (Ure *et al.* 1993, 1996). In the paper of Rauret (1998) which summarises the state of the art of extraction procedures used for heavy metal speciation in contaminated soils, EDTA extraction is outlined as a method proposed in some European countries such as France (0.01 mol.l^{-1} EDTA + 1 mol.l^{-1} CH_3COONH_4), Italy (0.02 mol.l^{-1} EDTA + 0.5 CH_3COONH_4) and United Kingdom (0.05 mol.l^{-1} EDTA).

Singh *et al.* (1996) used 0.05 mol.l^{-1} to assess mobile metal pools in surface soil sampled from confined dredged sediment disposal sites. Garrabrants and Kosson (2000) used a single batch extraction with 0.05 mol.l^{-1} EDTA to assess leachability of metals in municipal solid waste incinerator ash, while Stalikas *et al.* (1999) used the same procedure for soil samples contaminated by lake water. Alvarez *et al.* (2006) used 0.05 mol.l^{-1} EDTA to extract Zn and Mn from 28 high-calcareous cultivated soil samples with a wide range of physico-chemical properties. According to a study of Tipping *et al.* (2003) on the solid-solution partitioning of heavy metals in upland soils of England, the extractable contents of Cu, Zn, Pb and Cd provide the best estimation of "geochemically" active metal *i.e.* metal that enters into interactions with the soil solids controlling soil solution concentrations compared with the extractable contents by concentrated acid mixtures.

In fact, the metal mobile pool measured by EDTA is generally an "operationally" defined fraction because, as previously mentioned, EDTA extractability depends strongly on experimental conditions and soil matrix (soil physico-chemical properties, source of metal contamination and metal distribution within different mineral phases). Perez-Cid *et al.* (2002) found that, contrary to acetic acid, EDTA causes a more elevated mobility of Cu, Cr, Ni, Pb, Zn and Fe in the domestic sludges whereas little or no metals were released from the industrial sludges compared with acetic acid. In an experimental work carried out by Lintschinger *et al.* (1998) on the speciation of Sb in industrial contaminated soils, substantial amounts of Sb were found in EDTA extracts due to Sb association to immobile Fe and Al oxides and organic substances. According to Ghestem and Bermond (1998) EDTA enhances the metal extraction but EDTA-extractable fraction depends on pH, EDTA concentration, major metal concentrations and soil matrices. Similarly, Manouchehri *et al.* (2006) consider that EDTA extractable metal pool is mainly dominated by carbonate soil contents, by EDTA concentration and, depending on the nature of target element, by some physico-chemical soil properties.

Other works liken the EDTA extractable pool to different fractions extracted using different sequential extraction protocols and conclude that EDTA alone represents a reliable pool of mobilizable metals and could be used to assess the environmental risks. In a comparative work, Koeckritz *et al.* (2001) propose a simplification of sequential extraction scheme replacing a five step extraction scheme by a simple single EDTA extraction. According to this paper, a single extraction by EDTA was capable to extract the same amount of metal extracted in the first four steps of sequential scheme. The Authors consider EDTA as a heavy metal mobility predictor in the soil solid phase.

Others compare the EDTA single and sequential schemes to evaluate the capacity of each one in assessment of the metal mobility. Wilson and Pyatt (2006) employed 0.05 mol.l^{-1} EDTA to determine the availability of tungsten (W) in spoil and vegetation samples and it has been appeared to authors that W is relatively more mobile when subjected to EDTA whereas the bioavailability decreased when sequential extraction is employed; probably due to the capacity of EDTA to extract the metals associated to different pools. Alvarez *et al.* (2006) have compared the EDTA extractability of Zn and Mn with two sequential extraction procedures [modified Tessier (Elliot 1990) and BCR (Quevauviller 1997)] and observed that in terms of phytoavailability predictions the sequential extractions are not better than EDTA single extraction.

Aside from EDTA, DTPA (diethylenetriamine pentaacetate) is another powerful chelating agent widely used in single extraction procedures (Lidsay and Norwell 1978; Maiz *et al.* 1997; Obrador *et al.* 1997; Maiz *et al.* 2000). Some authors have attempted to compare the capacity of these two reagents to assess the soil trace metal mobility. According to the experimental works of McGrath (1996), EDTA was twice as effective an extractant as was DTPA for Cd, Cu, Cr, Ni, Pb and Zn in 15 agricultural soil samples. Sahuquillo *et al.* (2003) compared the effectiveness of EDTA and DTPA for a range of agricultural soils found in the literature and indicated that higher percentages are extracted with EDTA in comparison with DTPA. Accordingly, DTPA seemed to provide no more information than EDTA and for the reason of analytical performance during the measurement and eventual calcium interference in measurement of DTPA extracts, EDTA is recommended as complexing agent.

Apart from trace elements, another application of EDTA is the determination of anionic species such as phosphorous forms in soils and sediments (Ruban *et al.* 1999; Wenzel *et al.* 2001). Golterman (1996) used EDTA to extract Ca-bound and Fe-bound phosphorus without disturbing clay-bound or organic phosphorous. In this method 0.05 mol.l^{-1} Ca-EDTA was used to determine Iron-P bioavailable and 0.1 mol.l^{-1} Na_2-EDTA was used for Ca-P non-available in order to provide some information on bioavailable fractions. Turner *et al.* (2003) have investigated the phosphorus soil composition using EDTA-NaOH soil extracts by ^{31}P nuclear magnetic resonance spectroscopy (NMR).

In spite of the widespread deployment of chemical extraction schemes, whether sequential schemes or single stage protocols, it is to be noted that the measurements are made in equilibrium and only thermodynamic information is obtained. However, because of the dynamic characteristics of soil-soil solution systems, the rate of metal availability seems to be a more correct approach to study the metal distribution in dynamic environmental systems (Nirel and Morel 1990; Yu and Klarup 1994; Whalley and Grant 1994; Bermond *et al.* 1998; Ortíz Viana *et al.* 1999; Fangueiro *et al.* 2002; Bermond *et al.* 2005). Thereby, some authors have recently paid particular attention to kinetic aspects of soil trace metal transfer in soil-plant systems, usually called "kinetic fractionation". In these kinds of studies, the relationship between metal toxicity and metal leaching kinetics is outlined *via* leaching rate constants in order to complete the knowledge of metal remobilization in environmental conditions.

EDTA in kinetic fractionation

A number of papers exist in the literature concerning the kinetic aspects of heavy metal migration from the soil solid phase to soil solution and soil biota (Yu and Klarup 1994; Zhang *et al*. 2004; Ernstberger *et al*. 2005; Wasay *et al*. 2007; Labanowski *et al*. 2008). In this section, we will focus our survey on kinetic methodologies in which EDTA is implied to evaluate the dynamic of metal distribution.

One of the kinetic speciation methods reported in literature consists of monitoring the extraction of soil or sediment trace metal *vs.* time with a given reagent, to provide two distinct pools of trace metal called "labile" (quickly extracted) and "slowly labile" (less quickly extracted); generally called "two-reaction model" or "two-component model". Eq. (7) corresponds to the evolution of the metal concentration during a given reaction time, in which Q_1 and Q_2 corresponds, respectively, to the readily extractable metal fraction, called labile, associated with the apparent rate constant k_1, and to the less readily extractable metal fraction, called slowly labile, associated with the apparent rate constant k_2.

$$Q(t) = Q_1\,(1-\exp(-k_1t)) + Q_2\,(1-\exp(-k_2t)) \qquad (7)$$

Application of Eq. (7) to the kinetic experimental data permit to calculate the kinetically labile fraction of metal and the associated kinetic parameters.

This operationally-defined method does not involve the real soil fractions such as iron oxides or carbonates but it can be applied in mobility prediction field. Hence, the chemical reagent used in this kind of methods should be able to extract the labile metal associated to different soil components because labile cations may be bound to more than one of chemical soil constituents. For this reason, EDTA has been extensively used for kinetic fractionation of heavy metals in the soil or sediment samples. The feasibility of two-reaction kinetic model using EDTA was, at first, tested and validated by Ghestem and Bermond (1998) for a series of slightly polluted soil samples. Since then, several authors used this approach for different soil and sediment matrices using EDTA. Bermond *et al*. (2005) demonstrated that the kinetic fractionation method by EDTA permits to calculate the kinetic parameters of metal extraction from the soil solid phase and these parametrs were used to bioavailability prediction pusrpose. Labanowski *et al*. (2008) used EDTA and citrate for kinetic extraction of Zn, Cu, Cd and Pb and confirmed the existence of two metal pools (labile and less-labile). According to their results, EDTA extracts greater amounts of metal from the soil solid phase compared to citrate; hence it may used as an indicator of the upper potential of metal availability or long-term risks prediction.

According to a survey of the literature on kinetic fractionation, EDTA kinetic extraction and sequential schemes seem generally to reveal concordant and complementary results and the confrontation of both methods may permit to push on some conclusions in terms of metal mobilization in natural or contaminated soils or sediments. In a work by Gismera *et al*. (2004), metal fractionation in sediment samples was compared using kinetic and sequential fractionation procedures. Accordingly, the labile metal pool estimated by EDTA kinetic fractionation was correlated with the metal amounts extracted in the first step of the sequential scheme (exchangeable and carbonate metal bound). These results confirmed that EDTA is able to extract the labile metal pool from different sediment constituents. Cornu *et al*. (2004) have similarly compared the EDTA kinetic fractionation with sequential extraction for As speciation in contaminated soils. According to their results, the different fractions defined by sequential extraction were in agreement with those defined by kinetics. Brunori *et al*. (2005) have used EDTA kinetic two component model in soil treated with compost and red mud, compared the obtained data with a sequential extraction procedure and concluded that EDTA kinetic extraction furnishes adequate information on metal bioavailability. Song and Greenway (2004) studied the relative lability of some heavy metals in compost samples using EDTA kinetic extraction and found that the metal amounts identified by this method were in good agreement with the labile fractions extracted by sequential extractions.

However, the kinetic fractionation is also an "operational" classification tool to evaluate the metal lability and mobilization rate. The rate parameters, estimated by this approach, seem to be more influenced by experimental conditions than the arbitrary response of reagent. Gismera *et al*. (2004) have compared the results obtained from a kinetic fractionation study using EDTA and acetic acid and observed no significant difference in terms of metal mobilization rate. Labanowski *et al*. (2008) found, likewise, similar results in terms of the rate of labile metal pool extraction for EDTA and citrate kinetic extractions in contaminated soil. Wasay *et al*. found the same order of rate parameters, estimated by two-component models, in the kinetic extractions of Cd, Zn, Cu, Pb and Hg by citric acid, tartaric acid and EDTA.

Finally, the EDTA kinetic fractionation method seems to be a relatively rapid and simple procedure which gives adequate information about trace metal mobility and bioavailability but the simplified assumptions made in kinetic modelling of this method (extraction reactions are considered as pseudo first-order reactions) are actually inadequate for complex matrices including non-characterised geochemical phases such as soil compost. Besides, the application of pseudo-first order two-component model implies the use of EDTA in excess *vis-à-vis* the extractable metal; usually 0.05 mol.l^{-1} in the literature; whereas, the use of 0.05 mol.l^{-1} EDTA, as a natural ligand model, does not represent the environmental reality. Low EDTA concentrations have been used to investigate the kinetics and equilibrium of trace metal reactivity in soil solid phase (Manouchehri *et al*. 2006), but the lack of the reagent seems to render the kinetic simulation complicated so further works are required to improve the kinetic modelling for different operational conditions and different soil matrices.

EDTA AS BIOAVAILABILITY PREDICTOR

Numerous studies exist in the literature which link the metal mobile pools measured using EDTA with experimental bioavailable results (metal amounts taken by plants) for different trace elements (Tuin and Tels 1990; Barona and Romero 1996; Mench *et al*. 1997; Gray *et al*. 1999b; Yaman *et al*. 2000; Nowack *et al*. 2001; Afyuni *et al*. 2002; Nolan *et al*. 2005; Krishnamurti 2008). In these methodologies, the objective is to evaluate whether or not the mobile pools extracted by EDTA diagnostic the plant-available contents.

As mentioned previously, a single extraction scheme using EDTA has been proposed by Measurement and Testing Programme (BCR) in order to assess the bioavailable metal fraction (Ure *et al* 1993; Quevauviller *et al*. 1998). We will discuss in this section the existing literature on the relationship of mobile metal pool using EDTA, by single stage extraction (equilibrium) or by kinetic extractions, with experimentally measured bioavailable concentrations. However, most comparison of bioavailability with EDTA extractable metals use measurements at equilibrium in single extraction schemes.

In **Table 4** some data from different studies on EDTA extractable diagnostics of plant uptake are gathered.

The predictive feature of single extraction procedures has been subject of a review by Ure (1996) in which the correlation of EDTA extractable contents with plant health or uptake is outlined. In an experimental task by Barona and Romero (1996), Pb amounts extracted by 0.05 mol.l^{-1} EDTA were significantly correlated with Pb contents in plants for a series of soils belonging to different regions in Spain. Yaman *et al*. (2000), observed that Pb extracted by 0.05 mol.l^{-1} EDTA from seven agricultural soils are cor-

Table 4 Correlations between EDTA extractable pools and bioavailable contents.

[Na_2-EDTA]	Element	organism	Reference
0.05 $mol.l^{-1}$	Cd, Cu, Ni, Pb, Zn	Arable crops	Ure 1996
0.05 $mol.l^{-1}$	Se, Mo	Greenhouse crops	Ure 1996
0.02 $mol.l^{-1}$ + 0.5 $mol.l^{-1}$ ammonium acetate	Cu, Fe, Mn, Zn	Wheat	Ure 1996
0.05 $mol.l^{-1}$	Cd	Wheat	Bermond *et al*. 2005
0.002 $mol.l^{-1}$	Cd, Pb	Wheat	Manouchehri 2006
0.05 $mol.l^{-1}$	Pb	Invertebrates	Weimin *et al*. 1992
0.05 $mol.l^{-1}$	Mn, Zn	Leaves of barley	Alvarez *et al*. 2006
0.05 $mol.l^{-1}$	Cu, Zn	Grass	Madrid *et al*. 2004
0.1 $mol.l^{-1}$	Zn, Pb	Wide plant	Barona and Romero 1996
0.05 $mol.l^{-1}$	Cu, Zn	Barely roots	Feng *et al*. 2005
0.05 $mol.l^{-1}$	Sb, As, Cu	Alfalfa plants	De Gregori *et al*. 2004
0.05 $mol.l^{-1}$	Zn, Pb, Ni, Cd, Cu, As, Cr	Maize grain	Jamali *et al*. 2006
0.05 $mol.l^{-1}$	Fe, Zn, Ni, Cd	Sesame	Gupta and Sinha 2006
0.05 $mol.l^{-1}$	Cd	Lettuce and cabbage	Jackson *et al*. 1991
0.05 $mol.l^{-1}$	La, Sm, Ce, Gd, Y	Wheat	Yang *et al*. 1999
0.01 $mol.l^{-1}$	Cu	Tomato shoots	Chaignon *et al*. 2003

related with Pb concentrations in strawberries and apples cultivated on these soils ($R^2 = 0.95$, $P > 0.99$). In the same way, Barona *et al*. (1997) found that Zn- and Pb-EDTA (0.1 $mol.l^{-1}$) extractable concentrations give significant correlation with plant available contents of target elements for five studied plant cash. Labile quantities of Cd, estimated by kinetic two component model, were significantly correlated with Cd wheat contents for 11 non-polluted soil samples (Bermond *et al*. 2005). Gupta and Sinha (2006) studied the heavy metal accumulation in sesame using different single extractants such as EDTA, DTPA, NH_4NO_3, $CaCl_2$ and $NaNO_3$ in soil amended with sludge. Accordingly, among this group of reagents, metal extracted by EDTA seemed to be most efficient indicator of metal bioavailability. Nyamangara and Mzezewa (1999) reported, likewise, the use of EDTA-extractable metals as an indicator of bioavailable fraction in sewage sludge contaminated area.

Given that the soil-plant transfer emphasis is strongly influenced by soil physico-chemical properties, some authors used the soil characteristics when studying the relationship between EDTA extracted metal pool and bioavailable contents. Mench *et al*. (1997) have showed that Cd in wheat shoot was well explained by CEC (Cation Exchange Capacity), pH and Cd-EDTA extracted concentrations from 16 non-polluted soil samples. Oliver *et al*. (1993) reported that Cd-EDTA fraction was poorly correlated with Cd in grain, though Cd-EDTA and soil pH together explained 78% of Cd concentration variability in grain. According to the work of Feng *et al*. (2005), EDTA is only capable to estimate Cu and Zn availability to barely roots in acidic soil samples. The authors have tested the EDTA methods for acidic, neutral and near alkaline Chinese soil samples. According to Gupta and Sinha (2006) significant positive correlations were found between Zn-, Pb-, Cu- and Cd-EDTA extracted (significantly correlated with bioavailable contents) and some soil characteristics such as pH, organic matter, CEC, organic carbon and electrical conductivity. Alvarez *et al*. (2006) proved that Mn- an Zn-EDTA extractable concentrations and some soil properties such as clay or carbonate contents predict significantly Mn and Zn phytoavailability for barely in greenhouse experiment on agricultural alkaline soils. Contrary to Cu-EDTA, Pb- and Cd-EDTA extracted amounts from 15 agricultural soils were significantly correlated with wheat available contents using 0.002 $mol.l^{-1}$ EDTA (Manouchehri 2006).

Regarding to the data gathered from literature for a wide range of soil samples with varying physico-chemical properties and various sources of contamination, EDTA extraction could be considered as an effective tool to represent the available-plant pool of different heavy metals. However, a number of studies exist in literature showing poor correlation between metal plant uptake and EDTA extractable contents (Zhang *et al*. 2001; Menzies *et al*. 2007).

In fact, to properly define the bioavailable fraction of metal, both solid phase pool and concentration in soil solution pore, must be necessary controlled. Two terms "capacity" and "intensity" are attributed (Barber 1995), respectively, to the replenishment from the soil and the concentration of metal in solution, both controlling the metal speciation. So, bioavailability investigations deal with the "speciation" of target element in both soil solid and solution phases. Thereby, EDTA single scheme, which correspond only to "capacity" factor, could not adequately assess the plant uptake and solution speciation is also important to assess the toxicity. In this way, DGT *in situ* technique (Diffusive Gradients in Thin-films) was applied by Hooda *et al*. (1999) for measurement of labile species in soils reflecting the concentration in soil solution, the rate of re-supply from the soil solid phase and the kinetic aspects of metal transport through the soil. However, a limited number of investigations are devoted to kinetic patterns of metal transport within the soil and soil solution simultaneously. In an attempt to improve the knowledge of how kinetics could affect the metal availability in soil-plant systems, the kinetic extraction of Pb, Cu and Cd was studied in soil-EDTA (Manouchehri *et al*. 2006) and EDTA extracts-Chelex100 (Manouchehri and Bermond 2006). Comparison of kinetic monitoring in these two systems seemed useful to identify the dominant kinetics in the transfer of each element. In this way, some promising kinetic patterns are envisaged to be developed and discussed in the immediate future.

Finally, numerous other factors including soil environmental conditions, chemical speciation of metal in soil and solution, kinetics of metal transfer, diffusional and convective transport to the root, influence of root exudates, the plant specific physiology and great diversity of uptake route affect bioavailability predictions. Consequently, a simple chemical treatment using EDTA could be considered as a conformational tool to reduce the complexity of natural environmental systems to give some useful information on potential mobility of trace elements.

CONCLUDING REMARKS

This literature review tackles the use of EDTA as a complexing agent for extraction of heavy metals in different soils and related materials. It covers several fields such as soil remediation procedures, functional speciation of heavy metals, their bioavailability and toxicity assessment. In fact, EDTA behaves as a multi-actor agent which contributes in different geochemical environmental purposes.

The use of EDTA as an additive in soil washing process is well-known for its major role to enhance the metal solubilization. In a large number of papers the use of EDTA is proposed as a decontamination technique in soils contaminated by heavy metals. However, this technique is conditioned by numerous factors such as co-dissolution of major cations (Fe and Ca particularly), m_{soil}/v_{EDTA} ratio, source of contamination, soil pH, soil type, cation exchange capacity, temperature, particle size, permeability, dissolved organic matter and kinetic of exchanges, which affect widely the removal efficiency. Therefore, in order to achieve optimal efficiency, the choice of optimum operational conditions must be related to all these factors and there is not an ideal reference protocol for general use.

On the other hand, in the best case scenario, where EDTA is used to remediate a soil under optimal conditions, some strategies are required to achieve optimal efficiency in recovery of EDTA. Moreover, the non-biodegradability of EDTA remains a real issue and several researches have been recently carried out on potential biodegradable alternatives like as EDDS.

The research in metal fractionation area corresponds to the use of EDTA in operational (sequential extraction) and functional (single extraction) fractionation schemes providing useful informations, not available by measuring the total element contents, on potential mobility of metal contaminants.

Due to its non-specific nature, the use of EDTA in sequential schemes is generally limited. Some particular schemes are reported in the literature using EDTA to identify the metal bound to “carbonate” or/and “organic” fractions. These schemes are reliable to provide precise information on mineral soil constituents to which trace elements are bound. However, they suffer from some draowbacks like as readsorption phenomenon, measurements at equilibrium and non-uniformity of different procedures. So, standard protocols (BCR) have been adopted to provide a general frame of reference for the interpretation of results on a broad scale (different laboratories). EDTA does not feature in these standard sequential schemes.

Contrary to sequential schemes, the use of EDTA in single schemes has been widespread. There are two aspects to the use of EDTA as a single extractant. Firstly, it is used to predict the potential labile or mobile fraction. In other cases, the EDTA-fraction is directly related to plant uptake in some environmental conditions. Among many single-step extraction procedures proposed, 0.05 mol.l^{-1} EDTA extraction is widely used to quantify the labile pool or to predict the bioavailable pool. The capacity of EDTA to predict the toxicity in plant-soil exposed depends on some factors like as kinetics of exchanges within soil solid phase and soil solution, nature of target element, source of contamination, distribution of metal within different soil constituents and environmental conditions (agricultural or industrial contexts).

Chemical extraction schemes proposed in the literature tend generally to extract some operationally defined metal fractions from the soil solid phase with no particular regard to the soil solution, kinetics of exchanges and real environmental conditions. Nevertheless, under controlled conditions, EDTA extraction could be an effective tool to estimate the metal capacity to migrate.

In the field of risk assessment analysis, EDTA is widely used as a bioavailabilty predictor. However, given that a number of important factors affect the metal transfer in soil-plant system, the study of an explicit relationship between EDTA-extractable fraction and toxicity seems to be a simplistic approach for metal uptake by plant. That being said, EDTA scheme remains a useful tool to evaluate the role of soil solid phase kinetic and equilibrium chemical speciation in bioavailability, but it does not equate with comprehensive understanding of metal ecotoxicity in environmental circumstance. In the authors’ opinion, the most appropriate scenario for the use of EDTA in prediction of bioavailable fraction corresponds to the cases where the kinetic desorption of metal from the soil solid phase is the limiting stage in the metal transfer to soil biota. However, further works are required to develop this kinetic point of view in different environmental circumstances.

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