The Role of Soil Organic Matter in Trace Element Bioavailability and Toxicity

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Abstract

Soil organic matter (SOM) is a highly important pedospheric variable for agricultural practice and ecological functions. A decline in SOM content during the last two centuries has affected agricultural areas in many countries. Among multifunctional roles of SOM, one of the most crucial is that, due to its huge reactive interfaces, SOM strongly competes with other soil matrix constitutes/ligands in trace element (TE) adsorption/chemosorption. Thus, declining SOM content may cause soil degradation, particularly from the standpoint of disturbing soil's capacity to retain potentially toxic TEs and therefore increase a risk of their migration in the environment. Using geochemical modelling with realistic natural conditions, we highlighted the importance and complexity of SOM in the rhizosphere interactions with some of the widespread and potentially toxic TEs. It was shown that biogeochemistry of Cd, Zn and Cu may vary distinctly in relatively similar environmental conditions (e.g. narrow pH range, same SOM content and temperature), thus influencing their mobility and bioavailability, i.e. toxicity in the soil–plant–animal continuum.

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1 Introduction

During the past two centuries of intensive agricultural management (e.g. conventional tillage, intensive cultivation, reduction in animal manure but increased application of inorganic fertilisers) and other human activities (e.g. urbanisation, deforestation), negative influences on soil organic matter (SOM) content (i.e. declining), accompanied with land overloading by different contaminants. Many traditionally agricultural areas in developing as well as developed countries are seriously depleted in SOM content (i.e. chemically degraded). According to recent estimates, mostly as a consequence of reduced SOM, around 20% of agricultural land over the world can be considered chemically degraded, whereas around 90% of European soils are in the category from low to medium SOM content (i.e. 0–6% w/w organic carbon; Ondrasek 2008 and references therein). Chemically degraded land areas with declining SOM content in conjunction with areas contaminated by inorganic pollutants (e.g. trace elements; TEs) are identified among the most important hazards to (1) natural ecosystems, (2) food/feed production, (3) human health and (4) economy of European countries (e.g. European Commission 2006; Ondrasek et al. submitted). According to the same sources, total costs to European economy caused by soil contamination/SOM depletion are estimated in the range of US$8–32 billion annually, and do not include the damage to the soil ecological functions as these are almost impossible to quantify.

Over millennia of agricultural practice, SOM was recognised as a highly desirable soil property given its positive influence on many pedological (fertility, water/air capacity, topsoil worming, biological functioning) and crop (yield high/quality, earlier fructification) characteristics. Increasing the SOM content is a relatively slow process that takes several decades, while its substantial portion may be mineralised in only several years of cultivation. Among SOM multi-functionalities, one of the most crucial is that it has huge electro-potentially reactive interfaces, which enables SOM to strongly compete with other soil matrix constitutes (clays, hydroxides) in TEs adsorption/chemosorption. Depending on its origin (plant/animal) and characteristics (e.g. complex humics or simple root-exuded organics), SOM simultaneously represents an important source and active surface (buffer) of relatively bioavailable fractions of TEs. Declining of the SOM pool may further exacerbate soil degradation and disturb soil's buffering capacity to retain potentially toxic TEs, thus elevating a risk of exposing natural resources and food crops to their stronger influence.

Among a wide range of TE metal(loid)s, some (under specific conditions) such as Cu and Cd have a strong potential for organo-complexation, whereas Zn exhibits strong interaction with inorganic ligands (e.g. chlorides; Ondrasek et al. submitted). A wide range of metallic ligands (humics, organic acids, chlorides, carbonates, sulphates) exist in cultivated soil surface horizons, and influence presumably phytoavailable (to a certain extent) TE fractions such as free cationic metal forms. However, in which direction and to what extent chelation of particular TE will be pronounced, depends on many variables, with the two master ones being SOM (Rengel 2007) and pH (Adriano et al. 2004). In the next section, we discuss SOM (origin, dynamics in terrestrial ecosystems, characterisation) and the importance of its fractions in TEs (Cu, Zn, Cd) biogeochemistry in the rhizosphere.

2 The Origin of Soil Organic Matter

The origin of soil organic matter (SOM) varies considerably depending of the particular ecosystem. For instance, in the natural forest or grassland systems, SOM is mostly in situ produced from biomass sources (Fig. 22.1). The largest contribution to maintenance and/or rising (accumulation) of SOM comes from above-ground plant biomass production such as leaf and woody litter in addition to belowground root necromass and exuded organic substances (Kalbitz et al. 2000). For instance, leaf contribution in overall litterfall biomass production in forest/woodland
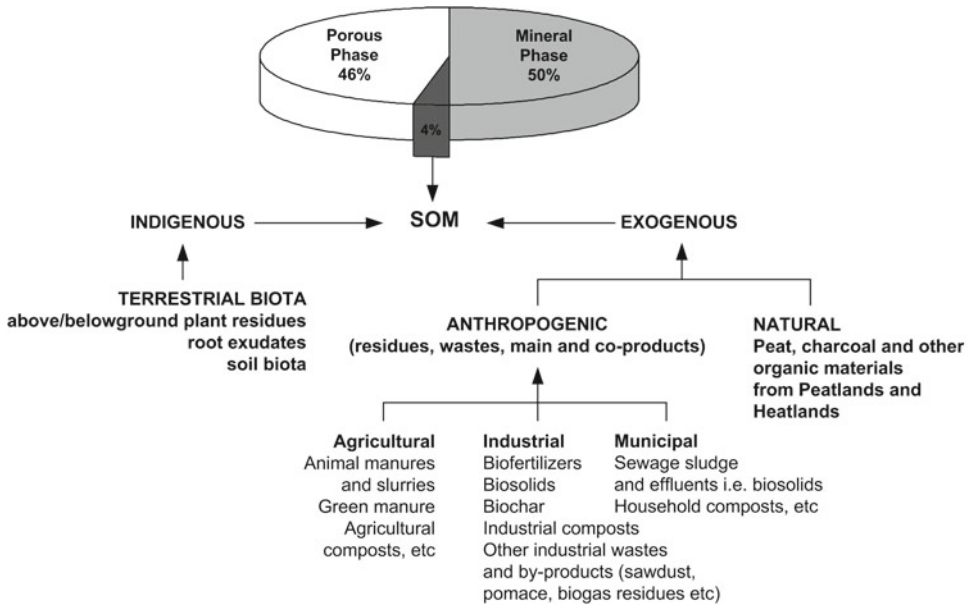
Fig. 22.1 Possible sources of SOM for commonly cultivated mineral soil (adapted from Ondrasek 2008 and references therein)

ecosystems is 70–75%, in wooded grasslands 50–60% and in sclerophyllous Mediterranean forests 54% (Matthews 1997).

Contrary, in today's modern and intensive agro-ecosystems, with possible several crop rotations over the short period, such as associated rain-fed cereal and irrigated horticultural production, the main part of above-ground biomass and litterfall (e.g. yield, straw) is exported from the system Ondrasek et al. (in press). To prevent depletion and retain its multifunctional role, SOM must be replenished, i.e. introduced into the arable topsoil layer through (1) specific land use and management practices and/or (2) other natural and/or anthropogenic exogenous resources (Fig. 22.1).

Anthropogenic exogenous sources of SOM are different sorts of organic wastes and/or co-products from urban (e.g. biosolids from sewage sludge) and peri-urban or rural activities such as agriculture (e.g. animal manures/slurries) and industry (e.g. biosolids from industrial wastewaters) (Fig. 22.1). In the last several decades there have been increasing environmental regulations that have resulted in more animal wastes treatment options, and thus affecting characteristics of residues that are subsequently applied to land. According to recent estimations (Van-Camp et al.

2004) around 1.65 billion tonnes of exogenous SOM are produced in the European Union (EU) each year, from which 61% represent animal wastes, 25% crop residues, 7% industrial wastes and 7% urban and municipal wastes (e.g. sewage sludge, biowastes and green wastes). The predominant application of exogenous SOM on arable land areas in EU is (on a weight basis) in the form of animal manure and slurries (97%), whereas almost a negligible portion comes from industrial wastes (2%) and sewage sludge (1%) application.

Some of mentioned organic wastes (precursors of organic soil amendments) before application must be stabilised, i.e. degraded and decomposed to a certain degree through composting or similar processes, to final product such as biosolids. Data about biosolids production and management practices across Europe and the USA (e.g. Epstein 2003; Ondrasek 2008 and references therein) show that in EU countries, from the total biosolids production (cca 7.4 million dry tones per year) 42% is disposed of in landfills, 36% is used in agriculture and 11% is incinerated, whereas in the USA, from total production (cca 4.1 million dry tones per year) 60% of biosolids is beneficially used (e.g. land application), 17% is disposed and 22% is incinerated.
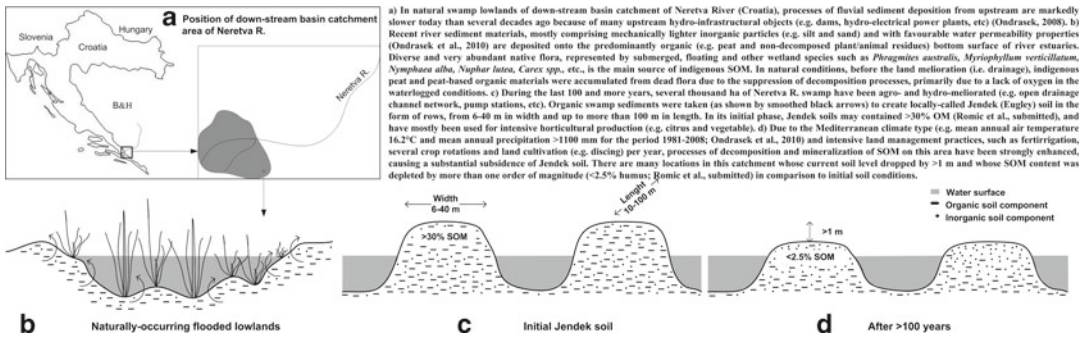
Fig. 22.2 Illustration of creation of *Jendek* soil and its decomposition over time in Neretva R. swamp, Croatia according to data from references cited in the text

A great potential of natural exogenous resources of SOM in food (agriculture) and wood (forestry) production over the millennia have been exploited from highly rich organic Histosols of peatlands and heathlands. Both systems were used as indigenous (after drainage/drying) or exogenous (as soil amendments) SOM sources for different purposes in crop production (nutrients source) and animal (bedding material, feed supplements) food, as well for wood (forestation) production. Heathlands are unique ecosystems found over the world in temperate upland regions, characterised by low-growing vegetation and organically enriched soils, which develop because environmental factors such as waterlogging and acidity constrain biomass decomposition (Holden et al. 2007). Peatlands are distributed just on around 3% of the global land surface (Strak 2008), but comprise 20–30% of the global, and ~50% of the UK's soil carbon stock (Yallop and Clutterbuck 2009). At the European scale, the current area of peatlands is estimated at 340,000 km² (Byrne et al. 2004), of which almost 50% has already been artificially drained for forestry (90,000 km²), agriculture (65,000 km²) and peat extraction (2,300 km²).

One of the oldest examples of exogenous SOM application (peat, charcoal, animal residues, etc.) to naturally occurring nutrient poorly Oxisol was found in more than 10,000-year-old man-made Terra Preta Anthrosols of Amazonia (Woods et al. 2006). Similar examples of improvement of naturally low-fertile Arenosols with different organic amendments (peat, manures, forest litter) can be recognised in European Plaggic and Terric

Anthrosols that were up to several thousand years old (e.g. Blume and Leinweber 2004). Unusual, if not unique, process of creating organic man-made soils (*Jendek*) was started in swamps of Neretva River valley (Croatia) more than 100 years ago (Fig. 22.2). Over decades that initially organic soil (>30% OM) was totally changed (up to 1-m depth) in most physical, chemical and biological properties, and became mineral soil (<2% OM) due to intensive land management practices and favourable natural conditions (i.e. Mediterranean climate) for decomposition and mineralization of indigenous OM (Fig. 22.2).

Land use and management practices may also be a powerful tool for SOM conservation and/or even improvement, when an application of exogenous organic materials is restricted or non-achievable (e.g. small livestock production) Ondrasek et al. in press). Many case studies on long-term changes of SOM in natural and agricultural systems worldwide confirmed that native (vs. arable) systems have greater SOM, i.e. carbon (C) storage, and that conversion from native to arable cropping significantly influence soil C (Soussana et al. 2004). Conversion from grassland and forest to cropland usually results in a decrease in SOM content, and the opposite conversion increases SOM content (Ondrasek 2008 and references therein). Higher SOM content in grassland and forest vs. cropland may be due to many factors: greater return of plant residues, return of dung during grazing, absence of soil disturbance and therefore restricted aeration causing decreased mineralisation.

Increased concerns for healthy food production and environment protection, i.e. increased emphasis on sustaining the productive capacity of natural resources, have raised interest in the maintenance and increasing of SOM for various land uses and management practices. For example, conservation tillage systems in which ≥30% of the crop residues remains on the soil surface after planting (IPCC 2000), mainly with the aim to restrict soil erosion, result in reduced soil compaction, disturbance and energy consumption, i.e. they conserve plant-available water and SOM. Land management practices from (1) reduced (minimum) tillage, where ploughing replaces surface tillage and/or strip tillage, to (2) complete absence (zero) tillage are increasingly used worldwide on >70 millions ha (e.g. Cerri et al. 2004). There are also other agricultural practices (crop selection, green manure, (fert)irrigation, etc.) which may improve/conserve SOM in arable topsoils.

## 3 Classification, Composition and Structure of SOM

The SOM content is one of the most varying pedosphere properties, ranging from <0.2% in salt-affected sandy soils of arid and semi-arid climate zone (Khoshgoftarmanesh et al. 2006) up to >99% in highly organic Histosoils from uplands in humid and boreal climates of northern hemisphere (Ondrasek 2008). In cultivated topsoils, SOM represents a fairly small fraction (1–4%), but it is one of the most complex, dynamic and multifunctional soil components. Although its importance was recognised from different scientific perspectives, a consensual definition of SOM is still missing, mostly because in disparities such as the following (Ondrasek 2008 and references therein): (1) inclusion/exclusion of living biomass, litter, fragmentation and humification layers and (2) threshold degree of decomposition. Disregarding this, SOM can be defined as soil biota and non-living biomass, i.e. a wide range of organic residues and effluents (Fig. 22.3).

Non-living SOM can be present in soil as fresh matter (litterfall) that is biologically and chemi-cally altered i.e. decomposed and/or polymerised (re-synthesised) and stabilised to certain extent by soil micro-organisms (Fig. 22.3). A typical fresh plant biomass is composed of (hemi)cellulose (~65%) and lignin (~20%), however, its quantity/quality vary among natural ecosystems, influencing the rate of decomposition and the balance between mineralisation/immobilisation.

As a portion of the solid SOM, there is a pool of potentially dissolved OM (DOM), which is during last few decades typically quantified as dissolved organic carbon (DOC) i.e. dissolved OM fraction able to pass through a filter 0.4–0.7 μm (Peichl et al. 2007; Ondrasek 2008). The concentration of DOC in the bulk soil and/or rhizosphere solution may differ considerably (Fig. 22.3) and is controlled by the following: (1) total SOM content (Ondrasek et al. 2009a), pH and ionic strength (Kalbitz et al. 2000), soil watering status (Yallop and Clutterbuck 2009), crop species/genotype (Rengel 2002), rhizosphere salinity (Ondrasek et al. submitted) or trace elements (TEs) contamination (e.g. Chiang et al. 2011). Usual DOC concentrations in mineral soil solutions may be up to one order of magnitude lower (e.g. <4 mg/L from mineral soil; Peichl et al. 2007) than in drainage solution from organic (peat) soils (20–110 mg/L; Kalbitz et al. 2000; Glatzel et al. 2003; Ondrasek et al. submitted). (Fig. 22.3).

The solid/dissolved SOM fractions may contain labile low-molecular-weight (LMW; <10%) and more stable high-molecular-weight (HMW; >90%) substances (Fig. 22.3). LMW materials refer to carbohydrates, small proteins/peptides, organic acids (OAs), amino acids, fats, siderophores, phenolics, vitamins, hormones, etc. (e.g. Neumann and Romheld 2000; Rengel 2002). Besides preferentially originating from decomposed biomass, LMW compounds are also released as root exudates and/or microbial metabolites (Rengel and Marschner 2005). Recently, Chiang et al. (2011) have observed a significant increment in concentration of volatile (acetic, propionic and butyric acids) and non-volatile (lactic, maleic, succinic and malic) LMW-OAs in the millet rhizosphere contaminated by Cd. Another example is secretion of LMW siderophores by
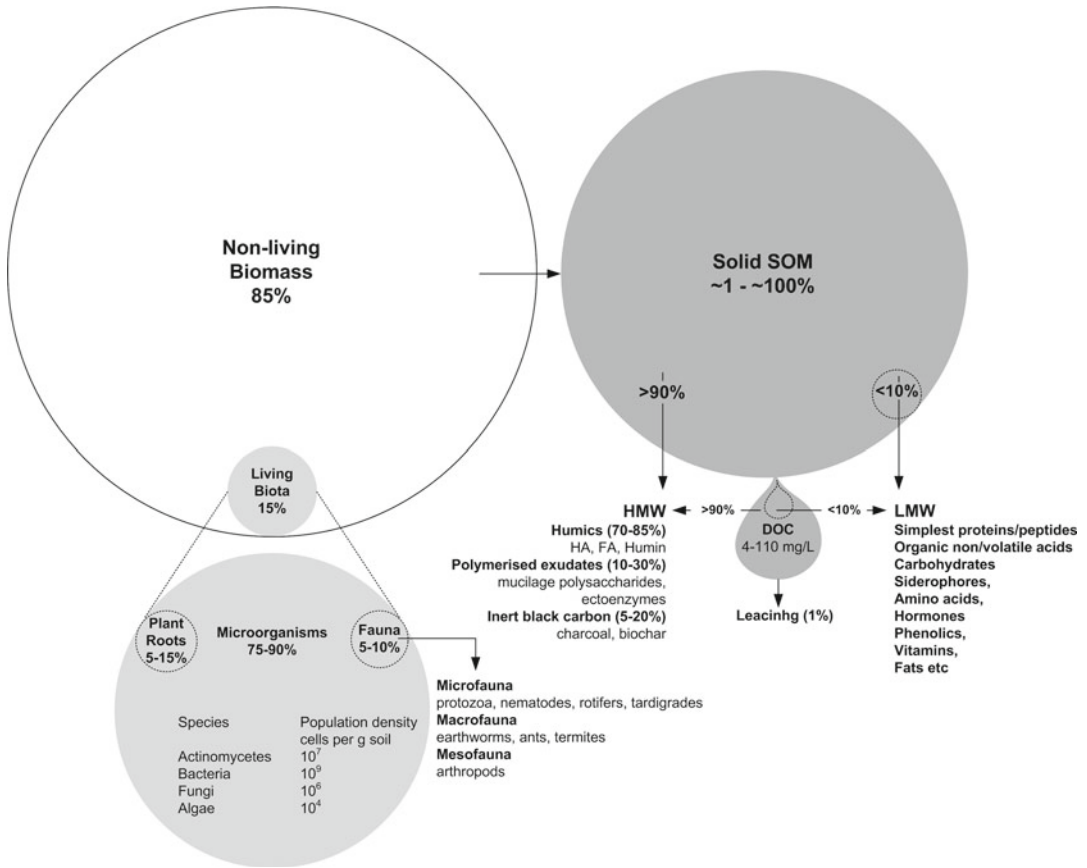
Fig. 22.3 A conceptual classification and composition of SOM according to adapted data from references cited in the text (% inside the circles are expressed on a dry weight basis)

soil microbes and phytosiderophores by plant roots that can chelate some TEs (Fe, Zn) and increase their bioavailability (Rengel 2002; Rengel and Marschner 2005).

Bulk of DOC-LMW compounds from the soil solution are rapidly decomposed/mineralised by microorganisms and are typically maintained at low concentrations (<50 μM; Van Hees et al. 2005) representing a labile (easily degradable) organic pool. Notwithstanding that the labile LMW pool has one of the shortest residence times (1–10 h), its presence in the soil (rhizosphere) solution appears to be: (1) stable, being replenished continuously by rhizosphere exudation and from fresh litterfall (Van Hees et al. 2005), and (2) much lower in comparison to a stable HMW pool. In agricultural/forest lands, Sachse et al. (2005) found that DOC-HMW compounds

(humics + polysaccharides) dominated in all samples (55–77%), whereas DOC-LMW (e.g. acids) portion was only several %s; however, not all organic fractions were accounted for (Fig. 22.3); thus, contribution of DOC-LMW/-HMW pools could be higher. For example, after a 90-day incubation, Kalbitz et al. (2003) found for fresh and less humified organic material (straw, forest floor litter) that DOC was mineralised 61–93% and the labile fraction comprised 60–90% of DOC, whereas for humified peats and Oa forest layers the mineralised and labile pools represented only 4–9% and 3–6% of DOC, respectively. Therefore, for humified sources the predominant portion (>90%) of OM in dissolved phase appears to be stable DOC-HMW substances, which is similar to a solid SOM fraction (Fig. 22.3).

A negligible portion of DOC or ~1% may be lost from pedosphere by leaching (Peichl et al. 2007), whereas the rest of SOM is stored in a complex and poorly characterised HMW pool comprising the following: (1) humics that represent the majority or 70–85% of HMW pool, (2) highly polymerised exudates from plant root (e.g. mucilage polysaccharides and secretory proteins or ectoenzymes; Neumann and Romheld 2000) or soil microbes (e.g. glomalin or Fe-containing glycoprotein from arbuscular mycorrhizal fungi) representing 10–30% of HMW and (3) an inert organic pool, i.e. black carbon (C), which is the most recalcitrant SOM fraction, contributing 5–20% of HMW (Ondrasek 2008 and references therein) (Fig. 22.3).

Even though humus is still not fully defined, there are many hypothetical chemical structures (Schnitzer 1978) from which is possible to get insight about humus complexity, heterogeneity and continuous transformation (e.g. over H-bonds or Van der Waals forces). It is known that humics are chemically highly polymerised organics containing both aromatic and aliphatic monomers. Therefore, the crucial role in humics characterisation is played by their particular constitutes i.e. functional groups; carboxyl, hydroxyl, aldehyde, ketone, ester, amino, nitro, thiol, etc. Oxygen (O) containing groups (e.g. -COOH, -OH) are much more abundant than nitrogen (N) and sulphur (S) groups (e.g. $-NH_2$, $-SH$) (Essington 2004), but all may act as acid/base and serve as proton (H^+) donor/acceptor (i.e. TEs acceptors) under certain pHs depending on their acidity constants (pKa). Given that in the most abundant carboxyl groups of humus, the pKa values range between 4 and 6, the average pKa of humics is 4–4.5 (Tan 2003). Certain humus fractions may be extracted from soil after suspending in NaOH and filtering (e.g. XAD-8 resin column). The compounds absorbed onto the resin include humic (HA) and fulvic (FA) acids that are further fractionated by acidification. In pH < 2, precipitated fraction represents HAs, a major component of natural humus materials (Schnitzer 1978), whereas FAs remain in the solution after acidification and are soluble at all pHs. According to Shintzer's (1978) "model" HA and FA data, i.e. average values compiled from different geographical (from Artic to tropical climatic zone) and pedological (acid, neutral soils) conditions, it may be concluded that the portion of C and N is higher and that of H and O lower in HAs compared to FAs.

In the soil HMW pool there are many other organics with complex and even more recalcitrant chemical structure than those elaborated for humics. One of them is organic charred material (biochar, charcoal), i.e. black C, which is during last few decades under intensive observation, principally for its influences on properties, processes and functioning of natural ecosystems (Hockaday et al. 2006). The contribution of black C as a percentage of SOM-C may be substantial (~20–50%) in specific soil type such as terric Anthrosol (e.g. Hockaday et al. 2006 and references therein). Similarly to humics, some of biochar active radicals act as proton donors/acceptors, resulting in coexisting areas whose properties can range from acidic to basic and from hydrophilic to hydrophobic. Due to high enrichment with polyaromatic rings, biochar is persistent even up to nano-scale fraction. Ultrafine biochar dust fraction, formed by condensed aromatic fullerene-like structures, is presumed to be the most recalcitrant OM in the nature, whose residence times is 10 to 1,000-fold longer than most of SOM (Lehmann et al. 2009 and references therein). Through natural weathering or oxidative depolymerization, soil charcoal slowly degrades to relatively less recalcitrant forms of humic substances (Hockaday et al. 2006).

4   Dynamics of SOM in Soil–Microbial–Plant Continuum

A bulk of SOM predominantly comprises different % of C (40–60), O (35–40) and H (4–6) (e.g. $C_{19}H_{17}O_{10}$ or calculated empirical formula of Suwanne River-FA), which are ultimately mineralised mostly to gaseous C (CO_2) and H_2O (Ondrasek 2008 and references therein). In spite of the fact that in general, dominant part of arable land areas in the topsoil horizons (usually the most SOM-enriched) contain only several %s of SOM, i.e. C, at the global scale, soil has a crucial

function in overall C budget, either by sequestering (over photosynthetic assimilation) or by emitting C (over plant/soil respiration).

Van Hees et al. (2005) distinguished three respiration processes in the soil–microbial–plant continuum: (1) autotrophic or release of photosynthetically assimilated organics through plant shoot/root and associated symbiotic mycorrhizal fungi, (2) heterotrophic or release of C from free-living decomposers biota (e.g. microbes, micro/meso fauna) during SOM degradation and (3) rhizosphere or coupled autotrophic/heterotrophic respiration in the root zone. Via respiration processes, SOM flows among different pools to be finally released into the atmosphere. There are several critical factors that may significantly influence SOM transformation/degradation, such as nutrients (NO_3^-, NH_4^+), CO_2 and H_2O. Some of them are (1) elemental composition of SOM (Kalbitz et al. 2000) and (2) environmental conditions such as pH, oxidation state, temperature and population of below-ground biota (e.g. Rengel and Marschner 2005).

Organic rhizodeposition could be tightly coupled with photosynthetic activity. From net fixed C, 30–60% in annual (e.g. cereals up to 60% and vegetables up to 44%) and >70% in perennial plants (*Bouteloua gracilis*) is transferred to soil, of which 40–90% may be released into the rhizosphere in the form of organic exudates/secretions and respiration gases by roots and associated micro-organisms (Lynch and Whipps 1990). In the majority of reviewed crops (8/11) the root-translocated C was dominantly (25–76%) released as CO_2 and the rest (4–29%) was exudate-C. This is in good agreement with later findings by Liljeroth et al. (1994) who obtained similar results investigating the shoot–root translocation of net assimilated C from maize (26–34%) and wheat (40–58%). In the same study, the contribution of rhizodeposited C (exuded + respiratory) varied between 41 and 45% (maize), namely, 43–57% (wheat) and in both crops dominated C realised by respiration; in wheat 74–85% and in maize 78–86%. Recently, analysing 43 tracer studies dealing with C efflux from shoots to roots and further to rhizosphere, Nguyen (2003) have summarised that on average, shoots export ~50%

of the net fixed C to roots, half of which stay incorporated in root tissues, ~33% is respired by root + rhizomicrobs and the rest >15% is released as organic exudates.

5 Trace Elements and Their Dynamics in Soil–Plant Continuum

European Commission (2006) stated that contamination by certain trace elements (TEs) and nutrients (Cd, Cu, Pb, Zn, Hg, As, Ni, Cr, N and P), and persistent organic pollutants are recognised as one of the main threats to environmental resources and human health in EU. The same source estimates that around 3.5 million sites in EU may be considered contaminated, whereas annual costs to European economy caused by soil contamination (without the damage to soil ecological functions) are estimated to be in the range of US$3.5–25 billion.

TEs are heavy metals and metalloids that include essential nutrients as well as some of the most toxic elements for living organisms. The total content of TEs in solutions of non-contaminated surface horizons of mineral soils range from 1 to 100 mg/kg (e.g. Kabata-Pendias 2004), whereas in contaminated soils these values may be several orders of magnitude higher. Although TEs in plant tissues usually positively correlate with the content in the surrounding environment, that is not always the case because of variable bioavailability. A usual decreasing order of TEs bioavailable forms is: water soluble free metal (e.g. Cd^{2+}) > specifically complexed (e.g. $CdHCO_3^-$, $CdCl^+$) > organically complexed (e.g. FA–Cd) > Fe/Mn/Al (hydr)oxide-complexed (e.g. $\equiv FeOCd^+$) > associated with secondary clay minerals i.e. residual form (e.g. Kabata-Pendias 2004; Ondrasek et al. 2009a).

Various metals fractions in the soil solid/dissolved phase may be quantified by sequential extraction, isotopic dilution, electro-analytical methods, etc., or predicted by computational approach (see Sect. 6). Generally, bulk and rhizosphere soil/solutions considerably differ in most of physical (porosity), chemical (pH, SOM content/

composition, elements speciation) and biological parameters (microbial activity) (e.g. Hinsinger et al. 2005). For instance, in the rhizosphere (vs. bulk soil) due to rhizodeposition and microbial secretion of different inorganic/organic compounds (H^+/HCO_3^-, LMW-OAs, etc.) (Rengel and Marschner 2005) it may be expected that a relatively high proportion of TEs is in the relatively mobile free form (e.g. Zn and Mn; Rengel 2004; Rengel and Marschner 2005) and/or in their simple complexed forms (e.g. Cd-LMW-OAs, $CdCl^+$, $ZnCl^+$; Chiang et al. 2011; Ondrasek et al. submitted). Therefore, it may be concluded that solubility (mobility) and bioavailability (toxicity) of TEs, which are dominantly governed by mentioned properties, are markedly different over relatively small distances, i.e. bulk soil vs. rhizosphere. In the next sections, the focus is on the properties of the rhizosphere soil solution because it represents the interface between TE sources and root cells, i.e. soil–plant interface.

5.1 Uptake, Translocation and Deposition of TEs Within the Plant

The majority of plant species have a weak ability to selectively extract essential TEs from the rhizosphere (Marschner 1995); therefore, they take up non-essential (Si, Co) and even highly toxic ones (Hg, Pb, Cd). Some of potentially toxic metals (Cr, Ag, Sn) due to lower solubility in the most soil circumstances are practically phytounavailable. In contrast, Cd is one of the most soluble TEs with relatively high bioavailability (Adriano et al. 2004; Clemens 2006). The preferred metal forms that are taken up by roots are soluble free cations (Cd^{2+}, Zn^{2+}, Cu^{2+}), but also complexes with organic ligands (e.g. Zn, Broadley et al. 2007). Free metal forms create (bioavailable?) complexes with in/organic natural and/or synthetic ligands dissolved in the rhizosphere. However, confirmation of metallo-complex acquisition by roots is relatively scarce and based mostly on assumptions.

Increased uptake and phytoaccumulation of Cd, Zn and/or Cu in the presence of excessive inorganic ligands (e.g. Cl^-) in the soil/rhizosphere have been showed in a wide range of experimental conditions (Smolders and McLaughlin 1996; Weggler et al. 2004; Ondrasek et al. 2009a, b). Also, Chiang et al. (2011) confirmed that LMW-OAs concentration in root exudates was positively correlated with the amount of Cd accumulated in millet shoots/roots, whereas Hoffland et al. (2006) found that Zn uptake efficiency in rice correlates with exudation rates of LMW organic anions. Similar results were obtained with giant alga *Chara* whereby Al^{3+} complexation with sulphate and citrate anions increased Al uptake by up to greater than twofold (Taylor et al. 2000). Likewise to LMW, positive influence of HMW organic ligands (e.g. HAs) on phytoextraction of TEs (Cd, Cu, Zn, etc.) was confirmed in tobacco (Evangelou et al. 2004), forage (Neunhauserer et al. 2001) and recently in fodder radish (Bandiera et al. 2009) (see Sect. 6).

Undoubtedly, metal chelation and/or complexation with in/organic ligands enhance desorption from soil solids, and having mobilised TEs into a dissolved phase, improve their root uptake/ phytoaccumulation, although underlying mechanisms are unclear. Uptake of metals from the rhizosphere is mediated by a specific (Cu, Fe, Zn) and/or nonspecific (e.g. Cd) transporter proteins embedded into the plasma membrane of root cells (e.g. see review by Clemens 2006). Due to similar physical (ionic radius) and chemical (redox-activity, Lewis acidity) properties among TEs, non-essential and highly toxic ones (e.g. Cd) most probably enter roots via highly specific routes for essential nutrients (e.g. Zn), especially under stressful conditions (e.g. Ondrasek et al. 2009a).

The TEs may be adsorbed/sequestered by numerous reactive groups and constituents in the apoplast (cell wall) and finally after crossing the plasma membrane in the symplast. In most cultured species, the largest portion of taken TEs is retained in the below-ground tissues (e.g. >70% Cd, Chiang et al. 2011; 65% Mn, Pearson and Rengel 1995) and the remaining portion is translocated to aerial parts in the following decreasing order: stem>old leaves>young leaves>fruits> seed. Information on the speciation of metals

Table 22.1 Possible intake of TEs via the foodstuffs consumption [adapted from ANZFA (1997) and Ondrasek (2008a)]

Foodstuff	Cd Intake	
	µg per day	%
Potato	4.26	46.7
Wheat	1.48	16.3
Cocoa and related products	1.14	12.5
Meat of mammals	0.96	10.5
Seafood	0.55	6.0
Peanuts	0.28	3.1
Rooty vegetables	0.23	2.5
Leafy vegetables	0.17	1.9
Rice	0.05	0.5
Total	9.12	100
µg per 100 g fresh tissue weight		
Radish hypocotyls[a]	Cd 2.7(42); Zn 195(167); Cu 9.8(9.9)	
Strawberry fruit[a]	Cd 1.3(14); Zn 188(167); Cu 36(33)	
Lettuce leaf[a]	Cd 3.4(54); Zn 382(348); Cu 24(22)	
Melon pulp[a]	Cd 0.55(3.50); Zn 97.6(87); Cu 14(11.6)	
Melon leaf[a]	Cd 15(220); Zn 510(470); Cu 64(57)	

[a]Soil background TEs concentrations were (mg/kg): Cd 0.33; Zn 14.7; Cu 12.9 whereas in parenthesis are values obtained under Cd-contaminated soil conditions (mg/kg): ~10 (in trial with melon) and ~5 (in all other trials)

along the long-distance transport is deficient. Given alkaline conditions (pH ~8) and high concentration of LMW/HMW organic and inorganic (e.g. Cl^-) ligands in the phloem, polyvalent metal cations are probably more complexed there than in the xylem (Ondrasek 2008 and references therein).

Although TEs concentration in edible crop tissues may be many times lower than in non-edible ones (Table 22.1), consumption of food/feed crops grown in soils containing high concentration of TEs represents one of the main routes of metals for humans/animals. Metal intake via food, drink and/or medicaments (e.g. Al intake in tea and medications; Rengel 2004) for the majority of human population is unavoidable, even though the amount of intake would depend on the selection of foodstuff (Table 22.1). According to ANZFA (1997), for the Australian and N. Zealand population, consumption of plant foodstuffs represent a dominant route (84%) for Cd intake, with more 47% of the total Cd taken in originating from potato (Table 22.1).

Many TEs have a long biological half-life (Cd > 10 and Pb ≈ 20 years) and their accumulation in human body gradually increases with time, causing a number of health problems/diseases that are the main reasons for mandatory

reductions of annual emissions of certain TEs in many countries (e.g. Lado et al. 2008).

6 SOM and TEs Interaction: Influence on Bioavailability and Toxicity of TEs

During the last decades, Cd, Zn and Cu have been intensively studied from environmental, agricultural, medical, economical and/or social science perspectives. Only a few TEs, including Cu and Zn, are phyto-essential in small amounts, whereas at excessive concentrations they can become toxic. In contrast, Cd is one of the most biotoxic (cancerogenic, teratogenic, etc.) metals (Ondrasek 2008 and references therein).

As reviewed in previous sections, one of the most important roles of SOM is that its huge reactive, mostly negatively charged interfaces strongly compete with inorganic ligands in complexing TEs and therefore affect availability and phyto-extraction of metals. In the next part, using a geochemical modelling approach, we discuss the influence of different forms of dissolved OM substances on Cu, Zn and Cd interactions, bioavailability and toxicity for relatively realistic rhizosphere conditions.

Table 22.2 Chemical composition of "genera-lised" rhizosphere solution

Mineral components		LMW organic components	
NO_3 (mM)	1.8	Citrate (μM)[a]	70
PO_4 (mM)	0.5	Malate (μM)[b]	1,472
SO_4 (mM)	1.7	Formate (μM)[c]	563
NH_4 (mM)	0.1	Oxalate (μM)[c]	100
K (mM)	2.2	Lactate (μM)[d]	48(82[f])
Ca (mM)	4.8	Succinate (μM)[d]	−(124[f])
Mg (mM)	3.9	Acetate (μM)[d]	851(4,018[f])
Na (mM)	1.9	Propionate (μM)[d]	173(1,932[f])
Cl (mM)	1.6	Butyrate (μM)[d]	271(2,052[f])
CO_3 (mM)	4.7	HMW organic components	
Mn (μM)	0.55(5.5[e])	DOC (mg/L)	10
Zn (μM)	0.75(7.5[e])	FA1-(6) (mg/L)	0.082
Cu (μM)	0.42(4.2[e])	FA2-(6) (mg/L)	0.026
Cd (μM)	0.05(0.5[e])	pH conditions	3.5–9.0

[a]Grierson (1992)

[b]Bolan et al. (1994)

[c]Baziramakenga et al. (1995)

[d]Chiang et al. (2011)

[e]Concentrations for contaminated rhizosphere conditions (increased by one order of magnitude vs. non-contaminated)

[f]Concentrations from contaminated rhizosphere solution with 300 mg Cd/kg soil

6.1   A Model Overview

Geochemical modelling may be a powerful tool for studying various types of anthropogenic/natural pollutants, their presence/mobility in natural systems, and for environmental risk assessment purposes. Among the four main groups of geochemical models (speciation-solubility, reaction path, inverse mass balance and coupled mass transport), the first one based on a thermodynamic equilibrium conceptual approach is suitable for explaining OM–TEs interactions and assess bioavailability and toxicity of metals (e.g. Zhu and Anderson 2002).

A chemical composition of "generalised" rhizosphere solution was compiled from different soils databases, and can be considered appropriate for mineral soils (Table 22.2). Modelling on a Visual MINTEQ interface (Gustafsson 2006) was performed for two levels of TEs (non-contaminated and contaminated system) and in a pH range 3.5–9.0 (covering the most naturally occurring conditions in different soil ecosystems; e.g. Tipping 2005). However, in extreme (acid/alkaline) conditions (e.g. pH <3.5 and >10.5) it is almost impossible to characterise in full the proton affinity distribution because of a lack of reliable data (Kinniburgh et al. 1999). Input data for mineral components in non-contaminated conditions were obtained from the database of saturated soil paste extracts of arable alluvial, mostly mineral soils (Ondrasek et al. unpublished), whereas total concentration of TEs in contaminated conditions were increased (vs. non-contaminated) by one order of magnitude in accordance to Kabata-Pendias (2004).

Due to continuous CO_2 release in the rhizosphere as a consequence of the root/microbial respiration, its presence is usually markedly higher than in the atmosphere (Ondrasek 2008); hence, in all models partial CO_2 pressure was increased 15-fold compared to atmospheric. TEs speciation was calculated using a thermodynamic database from the Visual MINTEQ ver. 3.0, and all component activities were calculated with the Davies equation at 22°C (suitable for moderate soil climate conditions). An oxidising state was assumed in all models (i.e. $pH + pe = 15$). Mineral dissolution/precipitation, describing possible TEs immobilisation as a consequence of oversaturation

under certain chemical circumstances, was assessed by calculated mineral saturation indices (SI) without allowing solids to precipitate during the modelling. In a case of SI = 0, the certain mineral is at thermodynamic equilibrium in solution with its dissolved products (ions). When SI > 0, solution is oversaturated (i.e. mineral is precipitated), and if SI < 0 solution is undersaturated (i.e. mineral is dissolved) (Zhu and Anderson 2002). The LMW organic pool is strongly dependent on non/contaminated conditions (e.g. Chiang et al. 2011), i.e. may differ by more than an order of magnitude depending on metal contamination (Table 22.2), and may have very short residence time (Sect. 3). Those are the main reasons that the LMW pool was varied, whereas the HMW pool, which is mostly stable over the short/mid term period (Sect. 3), remained constant (Table 22.2).

Organo-complexation/chemosorption between TEs and HMW organics was assessed by using the Non Ideal Competitive Adsorption (NICA)-Donnan isotherm model (Kinniburgh et al. 1999) as one of the most advanced models for competitive metal ion binding to humic substances (Weng et al. 2001). The input variables required by this sub-model were presumed (e.g. DOC 10 mg/L for mineral soil solutions) or retained as default settings. For instance, whereas all of the DOC may not be reactive with respect to proton and metal binding, the ratio of active dissolved organic matter (DOM) to DOC was by default set to 1.4., which is close to the average conversion factor of 1.36 suggested by Bryan et al. (2002) and has been found to work well for modelling soil systems (Apul et al. 2010). Also, it was assumed that all active DOM is comprised from FAs, what is in a good agreement for a majority of natural soil environments and tested pHs in which FAs are soluble compared to mostly insoluble HAs (Sect. 3). However, in the case that there was not enough total FAs to make up the total active DOM, the model adjusted this parameter so that HAs may contribute to the DOM.

6.2   Cadmium

According to modelling results, the uncomplexed free Cd^{2+} pool was the predominant (50–74%) in

acid (pH ≤ 5.0) conditions, but its activity linearly decreased with pH increasing, it was almost fully depleted (<1%) at pH 9.0 (Fig. 22.4). In the very narrow range of slight acidity (pH 6.0–6.5) Cd-organocomplexation was the most pronounced (44–45%), especially in the LMW pool (>35%), whereas inorganic complexation of Cd dominated (38–97%) in basic (pH ≥ 8) conditions (Fig. 22.4). In contaminated rhizosphere conditions (vs. non-contaminated), distribution in Cd^{2+} and Cd-inorganic pools stayed rather stable, whereas in other pools Cd was redistributed from the HMW to the LMW fraction. The main cause of such Cd redistribution inside organic pools is that in contaminated conditions certain LMW organic acids were increased in the rhizosphere many times (Table 22.2) as a consequence of pronounced rhizodeposition (see the next).

Although Cd-inorganic complexation started to increase from pH 5.5 (Fig. 22.4a), $CdCl^+$ activity from the Cd-inorganic pool continued decreasing throughout the pH range (Fig. 22.4b). The main reason is that Cd sorption with other ligands (HCO_3^-, CO_3^{2-}, HPO_4^{2-}, etc.) dominated over Cd-chlorocomplexation (data not shown). The most dominant LMW- and HMW-Cd forms were Cd-malate and FA1-Cd(6) (i.e. Cd bound to FAs via carboxylic groups) over the whole pH range (data not shown), with Cd-malate concentrations being the highest in slightly acidic pH (5.5–6.0), and those of FA1-Cd(6) in neutral to slightly basic pH (7–7.5) (Fig. 22.4b). In contaminated conditions, the curves showing activity of Cd forms retained the same shape but the activities were an order of magnitude higher than in non-contaminated model (data not shown).

Calculated saturation indices for over 200 possible mineral phases included in the Visual Minteq database were checked, and several of observed TE minerals were found to be oversaturated (i.e. SI > 0), but only in contaminated and basic conditions: at pH 8 malachite (Cu mineral), hydrozincite and smithsonite (Zn minerals) and otavite (Cd mineral) and at pH 9 all Zn and Cd minerals as at pH 8 plus zincite (Zn mineral) (data not shown).

The mobility and uptake of Cd, Zn and Cu is strongly dependent on chemical speciation/distribution and concentrations (activities) of TEs in
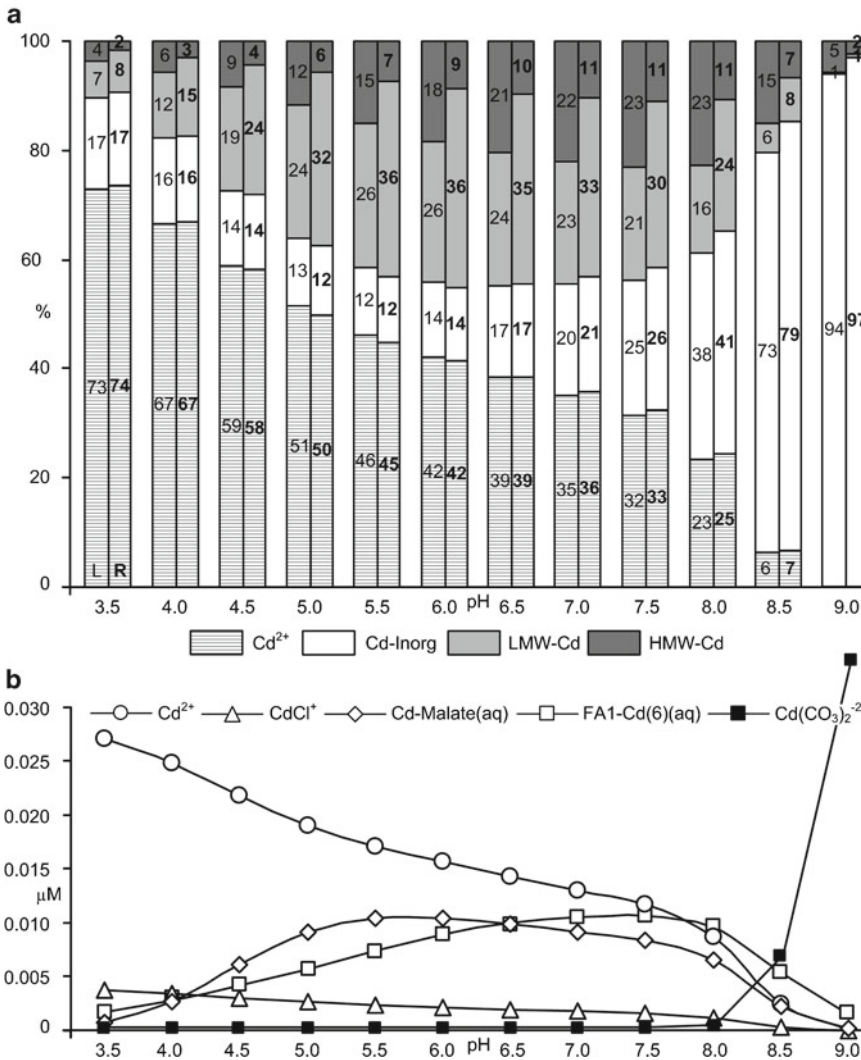
Fig. 22.4 Distribution of Cd species (**a**) among four pools [non-contaminated conditions=L (left bars); contaminated conditions=R (right bars with *bold %*)]

and activities of some of the most abundant Cd species (**b**) inside each pool (non-contaminated conditions only)

the rhizosphere solution. Although it is believed that only uncomplexed i.e. free cationic metal form may be taken up by roots, there is increasing evidence that Cd (Zn, Cu) can be mobilised in soil/nutrient solution and then taken up/phytoaccumulated complexed with inorganic ligands such as chlorides (Smolders and McLaughlin 1996; Khoshgoftar et al. 2004; Weggler et al. 2004; Khoshgoftarmanesh et al. 2006; Ondrasek et al. 2009a) or sulphates (McLaughlin et al. 1998b). Indeed, Weggler et al. (2004) observed that shoot Cd concentrations of wheat grown in a biosolid-amended soil were most closely correlated with

CdCl$^+$ activity in soil solution, whereas the correlation with the Cd^{2+} activity was weak. McLaughlin et al. (1998a) observed that Cd shoot/root concentrations in Swish chard were unaffected by additions of sulphate to nutrient solution despite Cd^{2+} activities decreasing markedly in the rhizosphere. The above studies suggested that Cd-inorganic complexes (CdSO$_4$, CdCl$^+$) could be phytoavailable and enter root plasma membrane either directly as a metal-complex and/or dissociating in the apoplast and entering cells as the free metal cation (Smolders and McLaughlin 1996).

With pH decreasing, the acid functional groups of LMW/HMW organic substances deprotonate, influencing solubility and formation of metallo-organo complexes. In many field/laboratory experiments with a range of species (including hyperaccumulators), increased mobility and improved uptake of Cd (Zn, Cu, Pb, etc.) was elicited by application of synthetic LMW chelating agents (e.g. EDTA, NTA, etc. See review by Schmidt 2003). In the models proposed here, we did not consider synthetic but only naturally occurring LMW-OAs that markedly impact TEs phytoextraction. LMW-OAs are common constituents of root/microbial exudates (see review by Jones 1998), which are present in relatively lower concentrations in non-contaminated vs. contaminated conditions (Table 22.2). Evangelou et al. (2006) observed improved Cu accumulation (up to 2.3-fold) in tobacco shoots with the addition of LMW-OAs (citric, tartaric and oxalic) to soil, similarly to Nigam et al. (2001) who recorded enhanced Cd concentrations in maize shoots (up to greater than twofold) after soil application of citric and malic acid. Rhizosphere contamination with Cd induced higher root exudation of certain LMW-OAs (propionic by 11.2-fold, butyric by 7.6-fold, acetic by 4.7-fold), with their concentrations in the rhizosphere positively correlating with the amount of Cd accumulated in millet shoots ($r^2=0.96$ $P<0.001$) and roots ($r^2=0.98$ $P<0.001$) (Chiang et al. 2011).

Studying the leaching of TEs from highly contaminated soils, Fischer et al. (1998) depleted total Cd by 75% (Cu by 54% and Zn by 56%) with the application of acidic (pH 4.4) grass silage effluent. Such metal removal efficiency was attributed to effluent's main component i.e. lactic acid, which under acid pHs acts as a proton-donor and strong metallo-complexing agent. According to the same authors, there are several crucial mechanisms that explain TE mobilisation by LMW-OAs: (1) chelation, (2) proton-initiated solubilisation, (3) surface complexation, (4) ion exchange and (5) reductive dissolution of metal binding substrates i.e. hydr/oxides.

Complexation of free metals ions (the most bioavailable and potentially the most toxic forms) with certain HMW SOM substances could be important in safe food production on metal-contaminated soils. In recent studies with horticultural crops (melon, strawberry, lettuce and radish) in slightly acidic pH (~6.0) and organically enriched (DOC > 76 mg/L) rhizosphere solution (Ondrasek 2008; Ondrasek et al. 2009a, submitted) using the same chemical modelling approach as described above, dissolved FAs dominated in Cd (Cu) sorption processes and formation of soluble metallo-organic complexes with relatively poor bioavailability (Otto et al. 2001). Similar findings were reported in maize (Shuman et al. 2002), mustard grown in organic soil contaminated by Cd (Bolan et al. 2003), sorghum grown in OM-enriched nutrient solution (Pinto et al. 2004), whereby a decrease in phytotoxicity and Cd content in the shoots caused by the addition of OM was attributed to redistribution of Cd from the water-soluble/exchangeable to the organically bound fraction. Similarly to FAs, HAs may also influence TE bioavailability given they also contain acid functional groups. However, in most natural soil conditions, HAs are insoluble compared to naturally more soluble FAs.

However, when added to soil, FAs and HAs may cause contrasting effects on TEs, i.e. the formation of soluble metallo-organic complexes may enhance metal bioavailability and leaching, whereas interaction of metals with the solid phase of humics may lead to their immobilisation and thus decrease their potential hazardous environmental influence (Gondar and Bernal 2009). The phytoavailable forms of Cd (Zn, Cu, Pb) in soils were increased by adding HAs to two metal contaminated mineral soils (Halim et al. 2003). In contrast, application of HAs to Cd-contaminated mineral soil did not change phytoavailable soil Cd, but phytoaccumulation of Cd in tobacco increased by up to 65% accompanied by toxicity.

6.3 Zinc

Although total Zn concentration in the modelled rhizosphere solution was more than an order of magnitude higher compared to Cd (Table 22.2), modelling results show that a free Zn^{2+} pool was
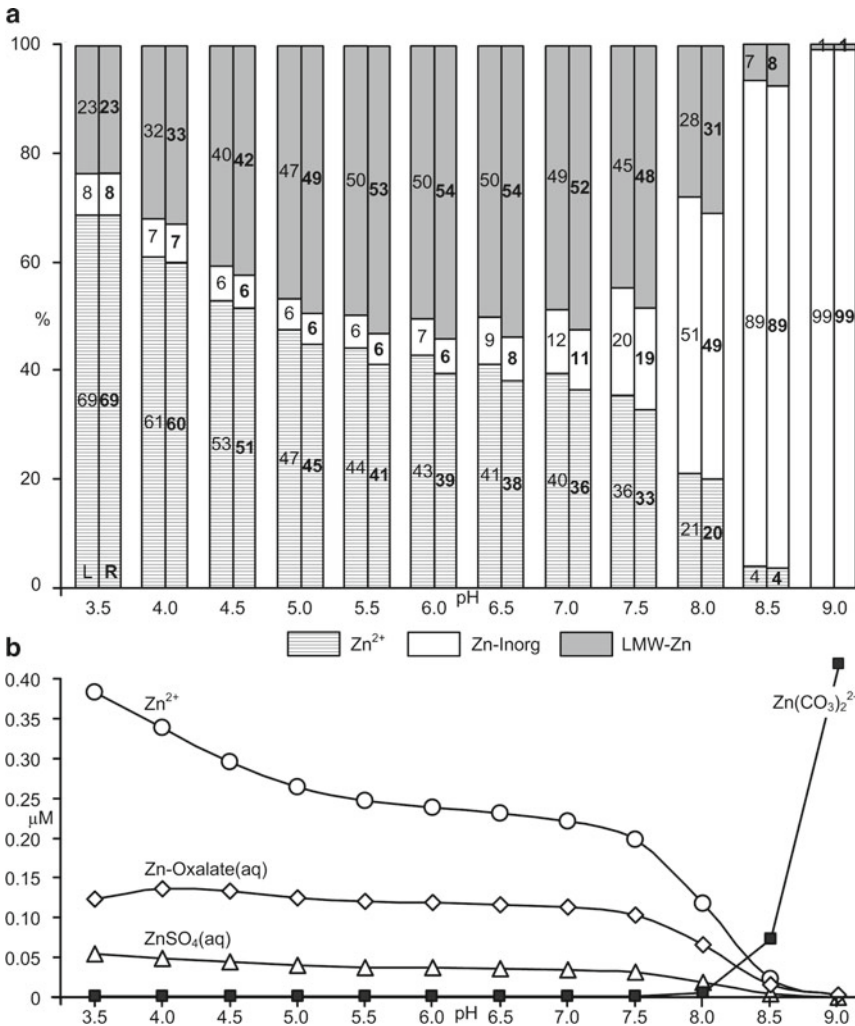
Fig. 22.5 Distribution of Zn species (**a**) among four pools [non-contaminated conditions=L (left bars); contaminated conditions=R (right bars with *bold %*)]

and activities of some of the most abundant Zn species (**b**) inside each pool (non-contaminated conditions only)

lower by several %s compared with that of Cd^{2+} under the same conditions, dominating in acidic pHs (≤4.5) similarly to Cd (Figs. 22.4 and 22.5). With pH rising, Zn^{2+} (and Cd^{2+}) activity decreased, whereas the activities of $ZnSO_4$ and Zn-oxalate stayed rather stable up to pH 7.5, and thereafter got depleted (Fig. 22.5b). Inorganic complexation of Zn, mostly with SO_4^{2-} under low pHs, and CO_3^{2-} under high pHs, dominated in basic conditions (pH≥8.0). LMW organo-complexation prevailed in slightly acidic to neutral pH (5.0–7.5) and that with HMW was negligible over the whole tested conditions (Fig. 22.5a).

However, compared to Cd, chloro-complexation with Zn barely present (<1%; data not shown).

Numerous Zn-in/organic ligand complexes (>20; data not shown) exist in the rhizosphere solution and are strongly pH dependent (Fig. 22.5). In slightly acid pHs (5.5–6.5), even in Zn-contaminated conditions (i.e. 7.5 μM Zn) Zn^{2+} typically accounts for around 40% of the soluble Zn fraction (Fig. 22.5a). Nutrient solution studies commonly suggest that free ionic metal form is the one most easily absorbed by plants, and Zn^{2+} is recognised as dominant plant-available Zn fraction, although there is a possibility it can enter

the root cells complexed with certain organic (Broadley et al. 2007) and/or inorganic ligands. Accordingly, Lorenz et al. (1997) reported that for Zn and Cd free ionic concentrations in the soil solution from ten different contaminated soils did not predict concentrations in tested radish leaves/tubers better than total Zn and Cd concentration in solution. One of the possible explanations is that Zn^{2+} is not the only form able to enter plant root. In the pH range from 3.5 to 7.5 activity of Zn^{2+} lineally decreased and thereafter sharply dropped due to inorganic complexation, mostly with CO_3 forms (e.g. $ZnCO_3(aq)$ data not shown and $Zn(CO_3)_2^{2-}$, Fig. 22.5b). These results confirm strong potential of Zn for inorganic complexation with pH increasing, especially in relatively low dissolved OM, and explain why Zn is the most common crop micronutrient deficiency under alkaline pHs (e.g. Rengel et al. 1999).

Intake of Zn and most other TEs (e.g. Cd, Cu) via consuming the food crops is their main route into the human body. Given that substantial areas of cultivated land worldwide are alkaline/saline (high pH/Na in saturated soil extract; Ondrasek et al. (in press) and also Zn-deficient soils (e.g. Broadley et al. 2007), deficiencies of Zn in human populations affect up to three billion people. One of the promising solutions for improving Zn levels in edible crop tissues is soil application of inorganic Zn salts such as $ZnSO_4$ (Rengel et al. 1999). Accordingly, Khoshgoftar et al. (2004) showed that $ZnSO_4$ application to alkaline (pH ~8), salinised (up to 180 mM NaCl) and Cd-contaminated soil solution (0.01 mg Cd/L) may be a successful strategy, not only for Zn enrichment in cereal shoots (up to 90%), but also in other ways. They observed enhanced salt tolerance and increased dry matter of wheat shoots, as well as reduced shoot Cd accumulation (down to less than 50%) with Zn salt application. Similar antagonistic relationship between Zn (or Cu) and Cd in soil solution and their shoot phytoaccumulation under salinity has been recently confirmed in wheat genotypes by Khoshgoftarmanesh et al. (2006) and in radish by Ondrasek et al. submitted), what authors mainly contribute to the Zn–Cd competition for ligands as well as soil adsorption and root uptake sites.

As confirmed by the model (Figs. 22.4 and 22.5) between Zn and Cd species distribution and particular activities curves (e.g. their free cationic and carbonate-complexed forms), exist a quite coincidence as a consequences of their explained similar (physical/chemical) properties (Sect. 5.1). Relatively high presence of their most bioavailable free forms over the most tested pHs may induce competition effects among Zn^{2+} and Cd^{2+} for ligands and binding sites in soil matrix, and thus influence their uptake and potentially toxicity. Furthermore, although the Zn-inorganic pool over the most pHs represented a relatively small (<20%) contribution in Zn speciation (Fig. 22.5a), under certain circumstances (e.g. excessive rhizosphere salinity), it may be of great importance for TEs mobility/uptake (Ondrasek et al. submitted).

6.4 Copper

An uncomplexed Cu pool was the smallest among observed TEs and almost completely depleted (down to ~1%) even at slightly basic conditions (pH 7.5). Over the most tested pHs organo-complexation of Cu dominated, with exception at pH 9.0 (Fig. 22.6a). In non-contaminated conditions at pHs ≤5.0 the LMW-Cu pool dominated, and thereafter chemosorption with humic substances (55–99%) prevailed. Compared to non-contaminated conditions, in the contaminated model the Cu^{2+} pool increased only by several %s, but Cu was markedly redistributed in all other pools (Fig. 22.6a). Under contaminated conditions, Cu complexation in the LMW pool occurred over a wider range of pHs (vs. non-contaminated conditions) and dominated at pH ≤6.5, whereas complexation with inorganic ligands (mostly with CO_3; data not shown) started to increase from the neutral pH, and dominated (63%) in the basic (9.0) pH (Fig. 22.6a).

As confirmed by the model, Cu possesses the highest affinity to OM among observed TEs. In the model were included organics differing in functional, mostly acidic radicals, with strong potential to complex Cu. Soluble metallo-organo complexes undergo microbial degradation and thereafter (1) a portion of metal is able to enter
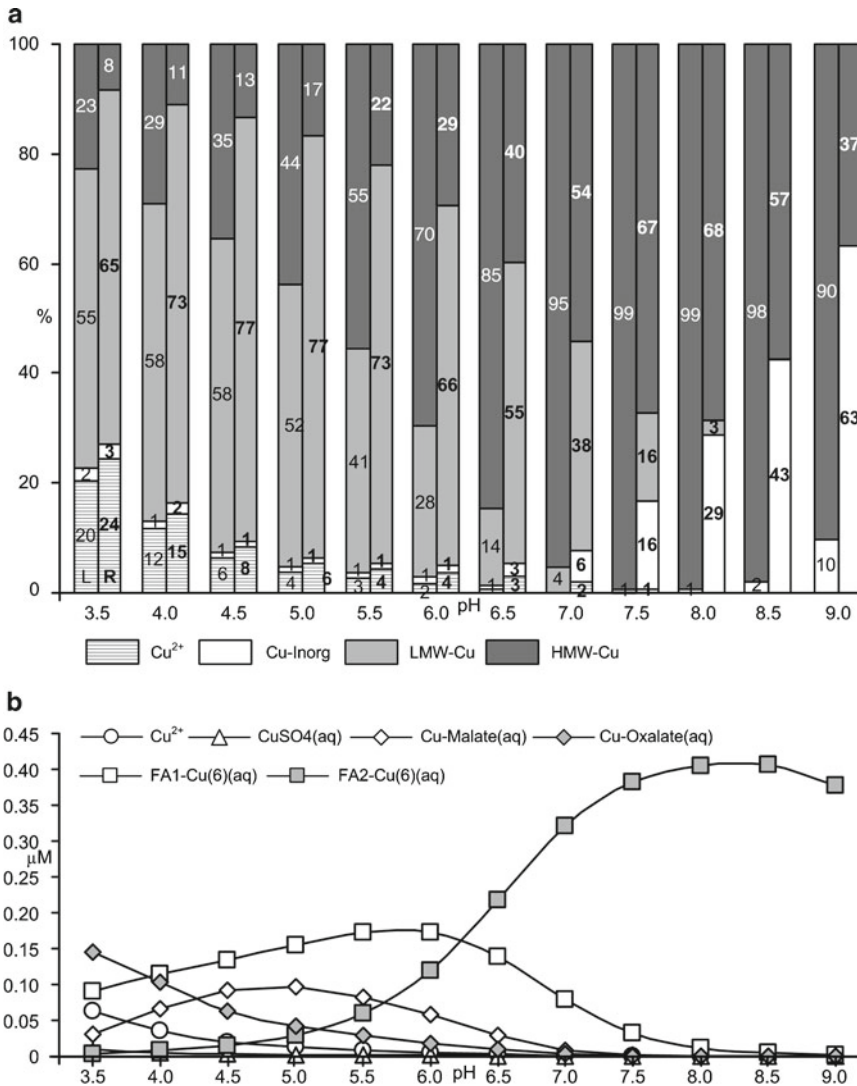
Fig. 22.6 Distribution of Cu species (**a**) among four pools [non-contaminated conditions = L (left bars); contaminated conditions = R (right bars with *bold* %)] and activities of some of the most abundant Cu species (**b**) inside each pool (non-contaminated conditions only)

plants roots as complex fragments (Evangelou et al. 2004), whereas the remaining portion may be (2) leached to deeper soil profiles/groundwater and/or (3) re-adsorbed to soil matrix (e.g. Gondar and Bernal 2009). To what extent a certain process would prevail depends on many physical (soil temperature, moisture), chemical (thermodynamic stability of particular metallo-complexes, salinity, DOC) and biological (microbial activity) conditions in the rhizosphere. Recently, Ondrasek et al. (submitted) working with salty (0–60 mM NaCl) and Cd-contaminated (4.9–39 μg/L) rhizosphere solution have confirmed a significant decrease in DOC (probably under diminished photosynthetical and microbial activity) and an increase in Cu (Zn, Cd) concentrations, either in the rhizosphere or in leaf/fruit tissues of radish. In the same study, under slightly acidic rhizosphere (pH ~6) organically complexed Cu predominated (>99%) in all tested conditions. Evangelou et al. (2006) observed improved Cu uptake and accumulation (up to

2.3-fold) in tobacco shoots with the addition of LMW-OAs to soil. Although LMW and HMW organics have significantly different properties, particular components such as acidic radicals are inherent to both of them (Sect. 3).

Investigating Cu binding to OM fractions in soil amended with olive mill residue, Gondar and Bernal (2009) found that at low metal concentrations (at pH 5.3), the amount of Cu bound by FAs and HAs was much higher than the water soluble (WS) fraction, whereas with metal concentration increasing, WS bound Cu to the same extent as FA, but the HA binding capacity was significantly lower. Such behaviour authors explained by qualitative/quantitative differences among OM fractions, i.e. lower content of carboxylic and higher content of phenolic groups in HAs (0.96 and 2.06 me/g, respectively) compared to FAs (5.32 and 1.26 me/g, respectively), and also by greater than twofold lower metal binding capacity of HAs (vs. FAs). Also, FAs are known to form more soluble and mobile metallo-complexes than HAs due to their higher acidic functional group content, smaller molecular weight and solubility over a wider range of pHs (2–12) (e.g. Smith and March 2007).

Phenolic functional groups have weaker tendency for deprotonation than carboxylic groups under acid conditions, and acidity of the hydroxyl groups in phenols (pKa 10–12) is lower than in carboxylic groups (e.g. pKa of acetic, formic and oxalic acids are 4.76, 3.77 and 1.27, respectively) (e.g. Smith and March 2007). Therefore, it appears that carboxylic groups are more important for metals binding under lower pHs, whereas in higher pHs other functional groups such as phenolic could be more involved in metallo-complexation. This hypothesis has been confirmed by the proposed model (Fig. 22.6b) where organo-complexation of Cu with carboxylate anions from LMW (e.g. oxalate and malate) and HMW [i.e. FA1-Cu(6)] dominated in acidic pHs (<6.0), whereas a continuous increase in organo-complexation with an increase in pH was due to enhanced deprotonation of LMW phenolic groups and Cu chemosorption with phenolate anions [i.e. FA2-Cu(6)].

With their huge reactive interfaces, predominantly polycarboxylic (FAs) and polyphenolic (HAs) (e.g. Gondar and Bernal 2009), HMW ensure a plenty of sorption sites for Cu and other TEs. Such sorption is mostly with a higher metal affinity than for mono/di carboxylic LMW-OAs, and therefore indirectly decreases TE bioavailability, although underlying mechanisms remain unclear.

7 Conclusions and Future Perspective

This review highlights the importance and complexity of SOM in the rhizosphere with respect to interactions with some of widespread and potentially toxic TEs in terrestrial ecosystems. It was shown that biogeochemistry of TEs (e.g. chemical activities, speciation distribution) may vary markedly between certain elements (e.g. Zn vs. Cu) and for a particular element (e.g. Cu) in very similar environmental conditions (e.g. from slightly acidic to slightly basic pHs at the same temperature and SOM content). It is of great importance that such environmental variations exist on a micro-scale and are inherent to the root zone (e.g. plant root vs. rhizosphere solution) and may therefore be relevant for TEs mobility, i.e. toxicity to plants and thus entering into a food chain.

Rhizosphere modelling presented here was based on relatively realistic natural conditions; however, many important variables, such as those from still undefined SOM fractions, were not included, but presumably may exert considerably influence on TEs interactions and bioavailability. The recent intensive scientific work and significant improvements in instrumental methodology (e.g. solid-state CP/MAS ^{13}C NMR spectroscopy, FT-ICR mass spectrometry) have ensured characterisation of various highly complex and recalcitrant SOM fractions (humics, black C) that should further help in elucidating interactions between SOM and TEs. Therefore, some of the future research perspectives, more focused on (in)organic complexation of TEs, are likely going to uncover novel mechanisms for uptake of certain TE forms that currently have not featured in the uptake studies (e.g. metal-HAs) or re-evaluate some that have been presumed to be taken up (e.g. metal-chloride complexes).

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