

Chapter 15

The Role of **Organic Matter** in the Mobility of Metals in Contaminated Catchments

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15.1 Introduction

The concept of “role” is dependent on a theory of systems (the role is what a structural component of a system does in order to support the functioning of the integrated system). Although assumed by default in most of the current scientific literature, the theory of nested hierarchies of systems is unrealistic for the description of environmental systems (Iordache et al. 2011), because there are no true emergent properties associated with each hierarchical level (emergent properties are a conceptual must for the identification of hierarchical levels). A realistic approach is by a pseudo-hierarchy of systems, which claims that simple biological or abiotic environmental objects (and their associated new processes) are perceivable and measurable only at certain scales. There is a continuum of relevant scales of analyses in a complex environmental object (Iordache et al. 2011a, b). This continuum of relevant scales is discretized for methodological reasons in hierarchical levels, i.e., it is modeled by a limited number of hierarchically organized systems, which has not reality, but has epistemic value.

In Chap. 19 of this book, it was shown that the overall pattern of metal mobility at larger scale (e.g., catchments) apparently resulting from smaller scale processes (e.g., local sites) cannot be reduced to the small-scale mechanisms because of the intervention of larger scale processes, that are different from the small-scale

The contribution of the first two authors to this chapter is equal.

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24 processes, a difference that is observed for both abiotic processes and biological
25 processes. Thus, the patterns at large scale, while dependent on smaller scale
26 mechanisms, are *decoupled* in explanatory terms. For example, the quantity of
27 metals leached from a soil column depends not only on small-scale processes
28 occurring at soil aggregate level, but also on the hydrological conductivity partially
29 controlled by the preferential flow, which can be perceived and estimated only at
30 the scale of the whole soil column. As a result, for the particular and simpler case of
31 abiotic processes, hierarchically structured models should be not a way of reducing
32 the large level processes to smaller level processes, but only a convenient representation
33 of the relationships between the objects involved in processes overlapped in
34 space and *observable* by investigation at different space–time scales.

35 In this context, in this review article we aim to emphasize the role of a small-
36 scale simple environmental object, the presence of organic matter (OM) in the
37 processes supporting the mobility of metals in a large-scale complex environmental
38 object, i.e., a catchment. The studies and works that are reviewed in this paper
39 demonstrate that this topic has both fundamental and applied importance.

40 From a fundamental perspective, any local environmental entity delineated in
41 space and time in a catchment can be a source of metals. Whether is a primary or a
42 secondary source, or a system of both types of sources depends on the scale of the
43 analyses (scope and resolution). Metals mobilized from environmental entities at a
44 certain scale are buffered (retained temporarily) in parts of a system identifiable at a
45 larger scale. Metals retained can be then remobilized by changing of environmental
46 conditions. A key biogeochemical parameter is the space–time **scale** of retention.
47 The organic matter is involved both in the retention and in the remobilization of
48 metals at scales from soil aggregate to river system. Nevertheless, the molecular
49 identity of the organic carbon as mobility facilitator very seldom remains the same
50 over long distances, because of its degradability and its interactions with biotic and
51 abiotic compartments. Another point is that the role of OM on metals mobility is
52 controlled by feedbacks resulted from the ecotoxicological effects of metals on OM
53 production. We will explore in this chapter the existing data concerning the role of
54 OM on the mobility of metals, as well as the effects propagated in larger scale
55 systems. Also, this chapter focuses on how many hierarchical levels and at which
56 scales a catchment can be discretized in this kind of research and what kind of
57 proofs (phenomenological correlations, manipulative experiments, models) can be
58 considered relevant at each level/scale?

59 The applied aspect of this chapter is associated with the management of
60 contaminated sites, considering that managers do not work with hierarchical
61 theories, but with operational concepts. The contamination is managed at “site”
62 scale, and a “contaminated site” is an area perceived as contaminated and in need
63 for management. “Perceiving” contamination at societal level is associated with the
64 management of private and public natural resources and services disturbed by the
65 contamination. Nevertheless, the production of these resources and services occurs
66 at different scales. While for soil management a “site” is only the local area of
67 primary contamination, for water management, a “site” may extend to the surface
68 of land supporting the development of an aquifer. It may even extend to a whole

catchment, spotted by contaminated hot spots, whose water quality has to be preserved. Such a site is considered rather a “region.” In order to explain and predict the effect of myco-phyto-remediation of upland contaminated sites on downstream water quality (i.e., to integrate soil management with water management), one needs information about the effects of the interaction between microorganisms and plants on the mobility of metals from contaminated sites. What is the effect of organic matter on the mobility of metals in all kinds of contaminated sites, whatever the scale? Answering this question is a matter of biogeochemistry across scales. We will explore to what extent the existing literature supports such an approach.

The red line of the chapter is the following: first, we present general aspects about OM and details about its structure, needed as a background for the other chapters, second the role of OM at specific scale (in mobilizing, immobilizing, or influencing other processes involved in the mobility of metals) is reviewed, and third we screen the literature for the effects of these roles on the fluxes of metals occurring in larger scale entities (soil column, site, catchments of different complexities).

15.2 The Structure of the Organic Matter



Organic matter is a structural component of the ecological systems derived from living biomass, representing a control variable both in models of the effect of metals on biological systems (nutritional, toxicological, and ecotoxicological models) and in models of metal transport by abiotic fluxes. The simplest system structure of interest for understanding the effect of OM on the mobility of metals should include at least three components: mineral particles, organic matter, and microorganisms. The causal effects of OM at contaminated site level is inseparable from understanding the role of minerals (Jianu et al. 2011) and of microorganisms (review in Tabak et al. 2005). The scale in space of such a system is of the order of 10^{-6} m^2 . A system with increased complexity would also include plants and its scale in space starts from 10^{-1} m^2 .

Natural OM refers to detrital OM, excluding living organisms and manmade compounds (Warren and Haack 2001). The literature concerning the interaction of organic pollutants with metals is so scarce, that practically the natural organic matter will be discussed primarily in this chapter. In some cases, like landfills, OM from anthropogenic sources will also be referred.

OM is present in all phases in soil: solid, liquid, and gaseous. In this chapter, two aspects are of interest: the types of OM in each physical phase classified as a function of the interactions with metals, and the life time of each type of OM. Knowledge about the turnover is crucial because, for instance, a strong chemical immobilization of metals may not be relevant at larger scale if the life time of the organic complex is short because of other processes (like degradation by microorganisms). On the contrary, weak interaction may become relevant if the OM involved is refractory to physical or microbiological interactions.

110 OM includes many other elements apart from carbon, but in this chapter we will
111 review strictly the role of OM based only on measurements of carbon content.
112 There are two terminological situations in the literature: either the effect of OM is
113 reported as such (the effect is explicitly mentioned in the cited text as due to OM),
114 or it is reported under the term “organic carbon” or OC (in the cited text). Although
115 there is a difference in absolute concentrations between OM and the OC
116 corresponding to it, in this chapter the usual terminological difference between
117 OM (real entity) and organic carbon (analytical result of the measurement of carbon
118 content in OM) will not be used. We keep the original terminology of the citing
119 authors, but refer by both terms, OM and OC, to the same real entity. We do this
120 conventionally because no publication discriminating between the effects of the
121 carbon, nitrogen, or phosphorus included in OM on the mobility of metals, or
122 proving that there are such separate influences of the constituent elements of OM
123 was found. Consequently, the reader should take into consideration that all effects
124 of “organic carbon” reviewed below may be due in principle, at least to some
125 extent, also to other not-measured elements co-occurring with carbon in OM.

126 OM molecules found in the environment sites are polyelectrolytes, heteroge-
127 neous and with no unique structure and mass (Warren and Haack 2001). They can
128 be characterized in the first instance by fractionation methods. The methodology
129 and significance of dissolved OM is a research subfield in itself. For instance, it is
130 documented that if it can pass through a filter with specific pore size (usually around
131 0.45 μm), it is referred to as dissolved organic matter (DOM) – a generic term
132 which needs to be used with caution, especially when one is concerned with its
133 ecological function (Zsolnay 2003). On the other hand, the particulate organic
134 matter (POM) is comprised of large particles of organic matter (250–2,000 μm ,
135 Bronick and Lal 2005). Using this definition, much of the colloidal material from
136 the soil that ranges from 1 nm up to 1 μm (Pédrot et al. 2008) would be considered
137 to be DOM. However, colloids have different attributes compared to the truly
138 dissolved material. Taking into account the dimension the soil particles, the OC
139 can be fractionated by filtration and ultra-filtration methods in particulate organic
140 carbon (POC), colloidal organic carbon (COC), fine colloidal organic carbon
141 (FCOC), and dissolved organic carbon (DOC) (Chow et al. 2005). Organic
142 fragments larger than 2 nm, although not categorized above, are also important
143 in the immobilization of metals directly (especially in the case of litter and
144 atmospheric deposition around smelters) or by their decomposition products.

145 DOC can be further fractionated in function of the hydrophobic and hydrophilic
146 character (Quails and Haines 1991), with direct relevance for the solubility of
147 respective fractions. Depending on the extraction procedures, other terms for
148 DOC, such as water extractable organic carbon (WEOC), or water soluble organic
149 matter (WSOM) can be used.

150 Another possibility to group organic compounds in soil is in nonhumic
151 substances (low percent and higher turnover rate) and humic substances (large
152 percent, up to 90%, and lower turnover rate). Aquatic humic and fulvic acids
153 originate in the soil, are operationally defined as refractory fractions, and occur
154 both in dissolved and particulate size classes (Warren and Haack 2001). Humic

acids account for about 5–10% of the natural organic matter in freshwaters (Warren and Haack 2001). Fulvic acids are derived from humic acids, are of smaller size, with less aromatic functional groups and account for about 40–80% of the natural OM in freshwaters (Warren and Haack 2001). We will not provide here information about the structure of the rest of OM because it has much higher turnover rate and its role in the transport or immobilization of metals is consequently lower.

The dynamic of OM in soil was reviewed by Kalbitz et al. (2000) and Bolan et al. (2004) and their general appreciation underlined the fragmentary and often inconsistent existing knowledge. The major sources of OM in soil are plants and microorganisms. Plant litter and its particulate form decomposition products (Berg and McCuagherty 2008) play a major role in metal immobilization in top soil. On the other hand, DOM turnover is dominated by microorganisms, directly and by exuded compounds, although in the rhizosphere the plants seem to play an equally important role by the root exudates. Of the total DOM in a lake, 78% originated from bacteria, compared to 50% in a forest soil (Schulze et al. 2005). Heavy metals in aqueous solution have an influence on the biodegradability of OM, either by toxicity (reduction of degradation rate), or by flocculation (increase of degradation rate by facilitating the attachment of microbial colonies on larger organic structures) (Marschner and Kalbitz 2003).

The result of the interactions between mineral particles, organic matter, and microorganisms is the formation of soil aggregates (Velde and Barré 2010), which play a key role in soil hydrology and the immobilization of metals. Bronick and Lal (2005) review in detail the role in soil structure formation of each molecular type of organic carbon (carbohydrates, polysaccharides, phenols, lignin, lipids, humic substances), and the factors influencing the OM in soil (climate, erosion, texture, porosity). POM exists as free POM light fraction (LF) or embedded with soil particles and having lower turnover rates as a result of this (Bronick and Lal 2005). Soil aggregates are grouped by size in macro-aggregates (>250 µm) and micro-aggregates (<250 µm), which differ in properties such as binding agents and carbon and nitrogen distribution. While micro-aggregates are formed from organic molecules attached to clay and polyvalent cations to form compound particles, macro-aggregates can form around POM, which can be decomposed, and microbial exudates are released. Therefore, macro-aggregates becomes more stable while C:N ratio decreases, and micro-aggregates form inside. The utilization of carbon contaminants by microorganisms leads to a demand for N and P for building cell constituents (the C:N:P ratio for microbial activity is about 100:10:1). Increases in microbial biomass are associated with increases in aggregate stability (Haynes and Beare 1997). The internally formed micro-aggregates contain a larger recalcitrant organic carbon pool. At low OC concentration, macro-aggregate stability is enhanced by carbonates, which is highly relevant for designing the amendment of contaminated and acidified soil, or of tailing substrate. Warmer climate and increased erosion result in lower OM content, increasing clay content and less pore space. This leads to more stable OM by the larger reactive surface and lower spaces for gas diffusion and water transport (Bronick and Lal 2005).

AU3

199 Turnover time of upper (down to 1 m) OC is in the range of years to decades
200 (Jardine et al. 2006), but highly variable by each category of OM. The most labile
201 OC is represented by the small molecules directly usable by organotrophic
202 microorganisms. Lower turnover rates can be associated either with free refractory
203 OM (humic and fulvic type) or with OC incorporated into soil aggregates.

204 The content of OM is different at the surface soil, the unsaturated (vadose) zone
205 and in the saturated zone; surface soils have more organic matter and, as a result,
206 contribute to a larger microbial biomass compared to the vadose or saturated zones
207 (Leug et al. 2007). The stability of OM usually increases with increasing soil depth,
208 and the stability of OM with depth is decreased by a fresh supply of OC (energy
209 source for soil heterotrophic microorganisms) from upper soil layers (Fontaine et al.
210 2007).

211 15.3 Roles of Organic Matter

212 The role of OM in metal mobility in soils was recently reviewed (Carrillo-González
213 et al. 2006), but the multiscale characteristics and consequences of this role in
214 contaminated sites are not systematically approached in the existing literature. An
215 excellent work investigating the scale-specific mechanisms of DOC mobility was
216 done by Jardine et al. (2006). In the current literature, there is no similar informa-
217 tion concerning the role of organic carbon (DOC included) in the mobility of
218 metals.

219 While the roles of microorganisms, organic carbon or minerals in the mobility of
220 metals in contaminated sites are well documented, the propagation of their effects
221 on metal mobility (in particular the consequences on the fluxes occurring at larger
222 scales) is much less clear. As already explained, understanding these up-scaled
223 effects is crucial because the scale for the management of contaminated areas is not
224 the very small scales specific to microorganisms.

225 From methodological point of view, the roles of the microorganisms and OC are
226 seldom estimated exactly at their specific scale in environmental studies. This is not
227 only because of instrumental restrictions, but also because what is often at stake is
228 not to understand organism level processes, but population and community ones in
229 heterogeneous media, more appropriate to field extrapolation. This is the reason
230 why the literature concerning the effects of OC and microorganisms in metal
231 mobility relevant for contaminated sites management results from studies at several
232 increasing scales (corresponding to pseudo-hierarchical levels usable for the
233 description of the real environmental objects), from soil aggregate up to an experi-
234 mental field plot. Nevertheless, the scales of managerial interest are still larger:
235 from site and catchment.

15.3.1 Role in the Immobilization of Metals



236

The overall effect of OM attachment on mineral–metal interactions depends on the nature of mineral surfaces (Kahle et al. 2004) of OM and of their environmental dependent interaction (Warren and Haack 2001). Reciprocal stabilization of Fe oxides and OM occurs in soil, eventually in ternary association with minerals (Wagai and Mayer 2007). The tertiary structure of humic and fulvic acids depends on pH and ionic strength and implicitly so does their ability to scavenge metals in free form or in interaction with mineral surfaces. There is competition for binding sites, that is dominant elements such as Al and Fe blocking the binding of other metals. Although metals sorbed by OM are more strongly bound than those to oxyhydroxides of Fe, the decomposition of labile OM leads to release of metals (Warren and Haack 2001). This may be one reason for the fact that metal transport from certain types of sites (e.g., landfills) is rather in colloidal form than in organic ligands form (details in part N.4.2.4).

Although for analytical reasons the role in immobilization is separately assessed experimentally for minerals or OC, or microorganisms, in nature it occurs on complex surfaces generated by minerals, OM and microorganisms. For microorganisms, the surface reactivity to metals is much more complex than that of OM or mineral surfaces because the complexity of the functional groups differ between major taxons, species, and individuals compared to structured consortia and biofilms. As a general rule, at low pH the adsorption of metal ions to mineral surfaces is increased by the OM, and at high pH is decreased (Warren and Haack 2006). Details by mineral type and metals can be found in this source. Mineral surface hydroxyl functional groups are effective in the sorption of metals between pHs 6 and 8, while organic surfaces can be effective sorbents at much lower pH because of the pKs of some functional groups, especially carboxylic groups (Warren and Haack 2001).

The reactivity of OC controls the mobility of metals either directly or indirectly, by interaction with mineral surfaces or bacteria. In the pH ranges of natural systems, the OM and bacterial surfaces are negatively charged (Warren and Haack 2001). Due to the polyelectrolyte and complex chemical character, the OM attaches to mineral surfaces, changing their affinity for metals (by ligand exchange, cation bridging, proton exchange, water bridging, hydrogen bonding, and van der Waals interactions). In particular, net hydrophobic expulsion is involved in the accumulation of humic and fulvic acids at mineral surfaces (Warren and Haack 2001) leading to a strong retention of OC in soil (Jardine et al. 2006), with consequences on the immobilization of metals. Controls over sorption and desorption of DOC in soils, with indirect relevance for the mobility of metals, are summarized by Neff and Asner (2001).

Another mechanism of immobilization is by diffusion to small pores. DOC, and presumably associated metals being solubilized in the near-surface soil during storm events, is transported to deeper profile depths, where it may diffuse into smaller pores where microbial degradation processes are limited (Jardine 2006).

279 This is dependent on the pore water velocity (it takes place mostly when the
 280 residence time of the solution is long), and on the absence of strong preferential
 281 flow. Colloidal transport of metals could be facilitated not only because of the
 282 larger life time of this form, but also because colloids cannot enter the smallest
 283 pores and thus keep the pathways with larger water velocity. Smucker et al. (2007)
 284 discuss in detail the micro-pores development in soil macro-aggregates with direct
 285 relevance for the transport of soluble carbon.

286 Relevant information can be extracted also from the experimental literature
 287 about phytoremediation. For instance, after a study at pot level, Banks et al.
 288 (1994) conclude that the revegetation of mining wastes may increase the leaching
 289 of Zn, and this effect is attenuated by the presence of (inoculation of) microbes. The
 290 mechanism supporting this phenomenon (in terms of OC speciation in the substrate)
 291 was not investigated. The situation seems to be highly metal and plant specific, with
 292 interplay between the effects of soil OM and the new DOC exudates by plants. In
 293 another study, the organic acids exudated by *Lupinus albus* chelated and solubilized
 294 Al, Ca, Mn, and Zn, while Cu and Pb remained bound to soil OM (Dessureault-
 295 Rompre et al. 2008).

296 OM is an important (even dominant) sorbent for metals in the surface horizons of
 297 the soils, but this depends on the type of OM (reactive surface and functional
 298 groups) and on the competition with Al and Fe compounds (Gustafsson et al. 2003).
 299 Deep soil OM has a very long residence time, and implicitly a large potential in
 300 metal retention (Rumpel and Kogel-Knabner 2010). The stabilization of OM can
 301 involve interaction with polymeric metal species (Mikutta et al. 2006). For a recent
 302 review of stabilizing mechanisms and properties of carbonic, see Rumpel and
 303 Kogel-Knabner (2010).

304 **15.3.2 Role in the Mobilization of Metals**



305 Molecular account of the interactions between organic matter and metals in the
 306 context of aqueous chemistry was given by Dudal and Gérard (2004). Trace
 307 element transport and transport pathways in soil, factors influencing mobility and
 308 transport models have been reviewed by Carrillo-González et al. (2006). Zhou and
 309 Wong (2003) reviewed the effects of DOM on the behavior of heavy metals in soil.

310 More recently, Degryse et al. (2009) reviewed in detail the problem of metal
 311 mobility estimation in soils by the distribution coefficient between solid and liquid
 312 phases (K_d). Mechanistic and regression models for predicting K_d are discussed and
 313 the influence of OM is considered in both types of models. For instance, the
 314 mechanistic model WHAM assumes an affinity of metals to DOM in the following
 315 order: $\text{Co} < \text{Ni} < \text{Cd} \approx \text{Zn} < < \text{Pb} \approx \text{Cu}$. All reported regression models have a
 316 linear relationship between K_d and the logarithm of OC (or OM) percent in soil. It is
 317 interesting to note that the K_d of elements with large affinity for OM, like Cu, can be
 318 reduced to the ratio between the concentrations of TOC and DOC in soil. K_d is of
 319 direct use for estimating the metal leaching and the bioavailability of metals to

plants. These applications are discussed in detail by the mentioned authors. From a methodological perspective, water or weak salt extracts are not recommended to estimate total dissolved metal concentrations of Cu and Pb in soil because of dilution of DOC and colloids (Degryse et al. 2009).

Zhao Lu et al. (2007) found that the decomposition of OM was the main driver of coupled DOC and metal mobility in the studied soil columns. Cu mobilization depended on DOC, whereas Zn mobilization depended mainly on Ca and to a smaller extent on DOC. The quality of DOC is also an important factor. For instance, the DOC resulted from drying and rewetting cycles has a low affinity for metals (Amery et al. 2007). The decomposition of DOM after drying and rewetting in soil may be related to the toxicity of metal (Merckx et al. 2001), probably as a result of its use by microorganisms leading to a reduction in soil redox potential and farther changes in redox sensitive metal concentrations (Cornu et al. 2007).

Pédrot et al. (2008) investigated the relative importance of OM and Fe–Mn oxyhydroxides as elemental carriers along soil columns using synthetic percolating solutions. Truly dissolved species with fastest leaching properties were the alkaline, alkaline-earth metals, Mn, Si, B, and V. Cu, Zn, Co, and Ni were partly mobilized by colloids (humic substances with weight lower than 5 kDa and fulvic acids). Fully depending on colloids in transport were Al, Cr, U, Mo, Pb, rare earth elements, Fe, Ti and Th. Moreover, it was shown that the fraction ranging between 5 and 30 kDa was the major carrier by an interaction between Fe-oxyhydroxides and complex stabilizing humic acids. The authors also cited literature demonstrating that the export of Co, Ni, Cu, Zn, and V was associated with organic carrier phases. Several other sources are cited to demonstrate the export of rare earth elements, Pb, U, Ti, and Th by iron-rich organic phases. OM was also found to increase the mobility of ¹³⁷Cs by binding as DOM complexes (Nakamaru et al. 2007).

Uroz et al. (2009) presented microbial molecules acting as mineral-weathering agents (oxalate, lactate, gluconate, citrate, catechol, and pseudobactin), along with the chemical mechanisms of this process (acidolyses, chelation, and oxidation-reduction). According to this source, the organic acids liberated by microorganisms have three actions on mineral weathering: (1) they adhere to mineral surfaces and extract nutrients from mineral particles by electron transfer; (2) they break the oxygen links; and (3) they chelate ions present in solution through their carboxyl and hydroxyl groups, indirectly accelerating the dissolution rate of the mineral by creating an imbalance between cation and anion concentrations in the solution (Uroz 2009).

Chelating agents can be deliberately used for mobilizing metals in soils (Nowack 2005). Some chelating agents used in phytoremediation studies are: ethylenediaminetetraacetic acid (EDTA), *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), *trans*-1,2-diaminocyclohexane-*N,N,N*- ϕ -*N* ϕ -tetraacetic acid (CDTA), ethylenebis(oxyethylenetrinitrilo) (EGTA)-*N,N,N* ϕ -*N* ϕ -tetraacetic acid, ethylenediamine-di (*o*-hydroxyphenylacetic acid) (EDDHA), *N*-(2-hydroxyethyl) iminodiacetic acid (HEIDA), ethylenediaminesuccinate

364 (EDDS), nitrilotriacetic acid (NTA), *N,N*-di(2-hydroxybenzyl)ethyleneamide *N,N*
365 ϵ -diacetic acid (HBED), citric acid, malic acid (Alkorta et al. 2004).

366 Besides the direct effects observed in lab-scale experiments, more subtle effects
367 can be observed in field or lysimeter studies. The heterogeneity of organo-mineral
368 particles in saturated soils and in sediments leads to isolated super-saturation of
369 metals and sulfide (Stockdale et al. 2009). In a phytoremediation lysimeter experi-
370 ment, Nowack et al. (2006) found that Cu in soil solution was significantly
371 correlated with DOC, but Zn only to phosphate and pH (regression equations are
372 provided, but the statistical relation between DOC and pH is not mentioned).
373 Another interesting point is that the DOC concentration in the contaminated soil
374 was smaller than in the reference soil (probably for ecotoxicological reasons at root
375 and microbial levels), with consequences on metal mobility (Nowack et al. 2006).

376 At low metal-carbon ratios, the dominant form of Fe and Al in water extracts
377 from a sandy soil was metal-DOC complexes (Jansen et al. 2003). At high
378 metal-carbon ratios, the pH had a strong influence on Al, with insoluble (formerly
379 dissolved) OM-Al complexes at pH 4.5, but soluble Al dominating at pH < 3.5,
380 and insoluble (formerly dissolved) OM-Fe complexes at all pHs (Jansen et al.
381 2003). In another study, Jansen et al. (2005) showed that the OC in batch
382 experiments was retained mostly in the B horizon as controlled mainly by precipi-
383 tation in organic-metal complexes and adsorption to Al and Fe phases. Al was
384 mobilized within soil, mainly by acid dissolution, and transported in particulate and
385 organic form, only a small part of it in dissolved (more toxic) form (Driscoll et al.
386 1994). High total organic matter content in peaty soils led to larger concentration in
387 pore water (Van Gestel 2008), but total metal availability for soil organisms could
388 not be predicted well based only on the metal concentration in pore water.

389 The role of colloids in the mobility of metals is underlined in recent reviews
390 (Kretzschman and Schäfer 2005). Working with undisturbed soil monolith,
391 Karathanasis and Johnson (2006) showed that eluted metal loads varied with
392 metal (Mo > Cd > Cr), colloid state (increase with OM content), and soil type
393 (increase with soil porosity). In batch experiments, Klitzke and Lang 2007
394 demonstrated that drying of soil increased the hydrophobicity of the solid phase
395 in soil, but not that of the dispersed colloids. The drying-induced colloid mobiliza-
396 tion of metals was not dependent on the properties of the colloids, but on the
397 disintegration of aggregates or increase of share forces (Klitzke and Lang 2007). In
398 another study, Klitzke et al. (2008) showed that liming of contaminated soil, by the
399 increase in soil pH, resulted in an increase in the mobilization of Pb in colloidal
400 form (soil mineral stabilized by organic coatings, and Fe-organic complexes). This
401 was not the case, in similar experiments, for As and Sb (Klitzke and Lang 2009). In
402 the case of As and Sb, the Ca existing in the system strongly diminished the
403 solubility of their complexes with organic carbon.

404 In a lysimeter experiment with translocated soil, Luster et al. (2008) found a
405 decrease in the DOC that occurred in the second year of the experiment compared
406 with the first year (probably as a result of the depletion of the pools resulted from
407 initial aggregates destruction), but this was not associated with an important change
408 in the concentrations of Zn and Cu in the percolating water. A correlation between

Cu and DOC concentrations in water was found only below calcareous soils, and was missing below acidic soils (Luster et al. 2008).

15.3.3 Influence on Other Processes

The influence on the activity of microorganisms will be detailed in Jianu et al. (2011). As an example, the weathering by certain bacteria was stronger when xylose (wood) or glucose is available, whereas the weathering activity of other bacteria is increased in the presence of lactose or mannitol (herbaceous vegetation, algae and fungi) (Uroz 2009). The use of OC as energy source in acid mine drainage is discussed in part 3.2.1.

A different type of example is provided by Strobel et al. (2005). DOC increased the extractability of Cu by direct interaction, but increased the release of Cd by buffering the solution at more acidic pH.

15.4 Effects of Organic Matter on Processes Occurring at Larger Scales

15.4.1 Effects on Fluxes of Metals Transferred to Plants

The picture of metal mobilization by plants under the influence of organic carbon is complicated by the species specific preferences and mechanisms characterizing the uptake of each metal. It is beyond the purpose of this chapter to go into the physiological and molecular biology details of these processes.

One simple direction of research in this area was to look for the effect of added organic ligands on metal uptake by plants. Seuntjens et al. (2004) propose a model for metal uptake and leaching in the root zone in the presence of organic ligands. The simulations suggested that the stimulation or inhibition of uptake by the addition or exudation of ligands depended on other parameters (especially on pH).

The effect of OC on the transfer of metals to plants was studied also in the context of organic material (e.g., sewage sludge) application in agrosystems, mining dumps, or tailing dams. Iordache et al. (2004) provided a review of the agricultural type of studies performed in Romania. Neagoe et al. (2005, 2009) assess the influence of various organic amendments on the phytoremediation success of a mining dump. In this case, the main effect of organic matter is on plant development by changing the humidity status and the microbial communities, the effect on metal mobility being masked by such important ecological and physiological effects.

442 **15.4.2** *Effects on Fluxes of Metals Transferred*
443 *to Lower Soil Layers*



444 This research area developed intensively, either by experiments with soil columns
445 and lysimeters, or by field observations. In a column study, Forsberg et al. (2008)
446 investigate the effect of sewage sludge amendment on tailing material. They found
447 an initial large leaching of Al, Cu, Zn, Ni, and Pb correlated with large DOC
448 concentrations, but following this the amounts of Al, Cu, Mn, and Ni were related to
449 sulfide oxidation in each column as reflected by substrate's pH. The total amounts
450 of metals leached were not statistically different between the variants with and
451 without sewage sludge.

452 According to Citeau et al. (2003), 75% of the Pb collected by zero-tension
453 lysimeters was in colloidal form, and Cd and Zn were mainly present as free ion
454 or labile complexes. Yin et al. (2010) also found that Pb vertical transport was
455 colloid facilitated. In a sandy soil with low OC, 87% of the leached Pb was in the
456 coarse colloidal fraction (0.45–8 μm), but in sandy soil with high organic carbon
457 66% of the Pb was in the nano-sized colloid fraction ($<0.1 \mu\text{m}$) (Yin et al. 2010). Zn
458 in lysimeter water from contaminated soils was not correlated with TOC;
459 biocolloids contained Zn and Pb and mineral colloids (smectites) contained only
460 Zn (Denaix et al. 2001).

461 Zhang and Zhang (2010) suggest that because of the competition with DOC at
462 adsorption sites, excessive phosphorous application on soil leads to leaching of Cu,
463 Cd, and Zn in organic forms. Interestingly, they found a decrease of the Pb leaching
464 by the added phosphate in the experimental conditions.

465 After studying a 2 m deep vadose zone, Dudal et al. (2005) found a fivefold
466 decrease of the soluble OM concentration, but the profile of the complexation
467 constant for Cu, Fe, and Mn was homogenous. They interpreted this result as
468 indicating that only a small part of the organic carbon was responsible for metal
469 binding. Strong rainfalls were able to transport only a small amount of metal-
470 binding organic matter, but freeze-thaw cycles release more such OM (Dudal
471 et al. 2005). The concentrations of Cu, Cr, Ni and Cd in the water transferred
472 from the organic rich forest ecosystem soil layer to lower layers were significantly
473 correlated with DOC (that of Zn was not correlated) at 20 cm depth the correlation
474 for Cd disappeared, and at 90 cm depth there was no significant correlation (Huang
475 et al. 2010).

476 In a soil amended with sewage sludge, the OC had an indirect effect on metal
477 mobility by determining a disaggregation of soil macro-aggregates responsible for
478 the accumulation of heavy metals in the coarsest fraction (Parat et al. 2007).
479 Another interesting finding in field experiments with sewage sludge was the
480 importance of space–time variations of OM distribution on the mobility of Cu,
481 Ni, and Pb, when increase of mobility of these elements especially at high pHs was
482 noticed (Ashworth and Alloway 2008).

483 The leaching of metals in bioremediation experiments was found to correlate
484 with soil contamination, pH, redox conditions, particulate and DOM, previous

washing from the soil, timing of rainfalls with respect to the plants development, 485
and ecological characteristics of the plants and microorganisms (e.g., potential of 486
mycorrhization), in a complex manner (Iordache et al. 2006). Careful microcosm 487
experiments involving the full plant cycle development and hydrological conditions 488
reflecting the natural ones were recommended in order to find indications about the 489
effects of a certain bioremediation solution on the export of metals from the 490
targeted contaminated site (Iordache et al. 2006). 491

In an interesting study, Besser and Rabeni (2009) evaluate the toxicity of 492
leachates resulting from phytoremediation experiments with tailings material on 493
aquatic invertebrates. Bioaccumulation and toxicity were greatest in treatments 494
leading to organic/metal complexes in the leachate. However, the leachate was 495
sampled just below the test plot and it is not clear what its content of organic/metal 496
complexes would have been after traversing the full length of tailing material. 497

15.4.3 Effects at Site Scale – Site Scale Immobilization of Metals 498

In metal mining areas, the OM is usually not taken into consideration as a parameter 499
controlling the metal mobility because of the strictly mineral nature of the substrate. 500
However, in restoration situations, the OM may become relevant, either directly by 501
organic amendments or indirectly by the result of plant life cycle in 502
phytoremediation projects (Mendez and Maier 2008). The use of organic covers 503
for acid mine drainage control from reactive sulfide wastes is reviewed by Peppas 504
et al. (2000). More recently, Vangronsveld et al. (2009) also discussed the applica- 505
tion of biosolids for site remediation. 506

An experiment for the stabilization tailing dam with different amendments 507
showed that when the material was covered with sewage sludge, the leachate had 508
the lowest metals concentration, redox potential and highest pH compared to 509
variant without organic matter (Alakangas and Öhlander 2006). 510

In an attempt to simulate the fate of tailings placed above alluvial soils, Flores 511
and Sola (2010) performed mixed column experiments. Al, Ba, Cd, Cu, Mn, Pb, and 512
Zn were mobilized when the tailing was leached, but they were retained in the soil. 513
Fe and Sr remained mobile through the soil after leaching from the tailing material. 514
The mechanisms involved in the immobilization were primarily related to the pH 515
increase, but sorption (including on organic matter) played also a role for Cu, Pb, 516
and Zn (Flores and Sola 2010). An alternative with strong retardation effect of 517
heavy metals is the use of compacted sewage sludge as bottom barrier to acid mine 518
drainage from tailing dams (Wang et al. 2010). 519

Another relevant situation is that of acid mine drainage treatment. Reactive 520
layers with organic carbon may be useful for such purposes. For instance, Hulshof 521
et al. (2009) compared the efficiency of different organic carbon materials. Various 522
types of organic carbon have different efficiency as substrate for the bacteria 523
involved in the treatment (Zagury et al. 2006). A review of remediation options 524
for acid mine drainage, including the use of organic matter is provided by Johnson 525



526 and Hallberg (2005). Recent work in acid mine drainage treatment using OM is, for
527 instance, that of Wu et al. (2010).

528 Up-scaling the role of OM at site scale based on knowledge at smaller scale is
529 not trivial because of its heterogeneity in space. The variability of OM in space is
530 moderate to high compared to other soil variables, having a coefficient of variation
531 of 21–41% (Keur and Iversen 2006). The autocorrelation length of soil organic
532 matter is reported to be in the range 34–250 m (Keur and Iversen 2006).

533 **15.4.4 Site Scale Mobilization of Metals**

534 Various amendments rich in organic carbon may be added on soils or on
535 contaminated sites like tailing dams (Antoniadis and Alloway 2002), either directly
536 generating pollution with metals or changing the mobility of existing metals.
537 Example of such amendments are: lime stabilized biosolid, anaerobic digested
538 biosolid, aerobically digested biosolid, sewage sludge, cattle manure, poultry
539 manure, pig manure, paper mill sludge, and secondary digested sewage sludge.

540 At field scale, Burckhard et al. (1994) found that the mobility of Pb and Cd was
541 not affected by organic acids, being probably limited along the vertical profile by
542 heterotrophic bacteria using the chelating organic carbon. Li and Zhou (2010)
543 showed in a field lysimeter study that colloids decreased the leaching depth of Cd
544 by blocking the soil matrix capillary and, in the case of preferential flow, by
545 deposition on the wall of the macropores. But the addition of OC increased the
546 penetration of Cd by 10 cm (Li and Zhou 2010).

547 Alakangas and Ohlander (2004) found that the amendment with sewage sludge
548 generated a larger export of As from a tailing material than in the variants lacking
549 OM.

550 **15.4.5 Site Scale Transfer to Plants**

551 Although OM is not a factor directly correlated to the distribution of vegetation in
552 mining areas (Guo et al. 2010; statistical correlations being observed mainly for
553 macro-nutrients such as nitrogen), it plays an important role in the primary and
554 secondary succession processes occurring in these areas (Neagoe et al. 2009).
555 A general discussion of the management of metal fluxes in contaminated zones is
556 provided by Robinson et al. (2006). The spatial relationship between metals and OC
557 heterogeneities and the distribution of plants is important for understanding and
558 predicting the phytoextraction remediation solutions (Robinson et al. 2006).

559 For the reasons mentioned in part N.4.1.1 and because certain aspects
560 concerning the plant population and community ecology would have to be
561 presented in detail, this role is not discussed in detail in this chapter.

15.4.6 Site Scale Transfer to Groundwater and Surface Water



The fate of the carbon associated with the erosion of soil OM, and implicitly of the associated metals, is not clarified, and it is an important topic of research (recent reviews, Lal 2009). The proofs for this effect are many: occasionally from experiments with amendments, and dominantly from correlations between metals and organic carbon in water (in some studies manipulated by injection experiments), and from catchment scale studies.

Proofs from experiments with amendments: In an experiment for leaching from tailings covered with different amendments, the lowest concentrations of metals, of redox potential, and highest pH and As concentrations were found in the variant amended with sewage sludge (organic rich material) (Alakangas and Öhlander 2006). Most of the literature in this area is not directly at field scale, but rather at lysimeter or plot scale. The situation is due to the difficulty to organize large-scale experimental settings linking surface soil processes with groundwater quality.

Proofs from correlations between metals and organic carbon in water: A review of colloid associated contaminants transport (Sen and Khilar 2006) underlines the importance of organic coatings and of bacteria (beside mineral and oxyhydroxide colloids) on mineral phases in the transport of metals in saturated environments. An excellent review about the occurrence of inorganic pollutants in ground waters, with source-sink aspects in function of environmental conditions (including the role of DOC for Cu and Pb at neutral conditions) was done by Helvoort et al. (2009).

In seepage water from a landfill, 77% of heavy metals were bound to particles, most of them to humic colloids (other particle types included silicates, insoluble salts, iron (hydro) oxides and carbonates – Klein and Niessner 1998). Baun and Christensen (2004) review the speciation of heavy metals in landfill leachates. They conclude that free ions are less than 30% and, typically less than 10% of the total metal concentration, a more important part being that of colloids and organic complexes. The general topics of landfill leachate plumes biogeochemistry and their long-term composition are reviewed by Christensen et al. (2001) and Kjeldsen et al. (2002). DOC and heavy metals are important categories of landfill leachate pollutants but the export of metals is low and its association with organic carbon is highly variable from site to site, not showing according to models an increasing trend within thousands of years (Kjeldsen et al. 2002). DOC in the leachate from landfills acts as a substrate for microbial redox processes, and heavy metals have low concentrations and a rapid attenuation by sorption and precipitation (Christensen et al. 2001).

Although the role of DOC is important in a landfill context, high concentrations of Pb, Cd, Zn, Cu, and Fe were carried by groundwater at contaminated sites on long distances only when groundwater was highly acidic (pH 3–3.5) (Lee and Saunders 2003). Kjoller et al. (2004) also point out the role of acidification in the mobilization of Ni, Be, Cd, and Co in a sandy aquifer. The acidification front functioned as a geochemical trap for the accumulation of these trace elements (Kjoller et al. 2004). In such cases, DOC has no significant role.

605 An ash pound had a 600–900 m zone of attenuation for Ba, Fe, Cu, Mn, S, and Zn
606 in groundwater, but Pb did not show any significant attenuation within 1,200 m
607 (Praharaj et al. 2002). It is not clear whether OC played a role in the generation of
608 this pattern. Goldberg et al. (2007) review the adsorption–desorption processes in
609 subsurface reactive transport modeling, with issues directly relevant for the role of
610 DOC in the transport of elements. An experimental proof on the role of OC in the
611 mobility of metals is provided by Muller (2000). He injected metals with and
612 without EDTA and DOC from a lignite pit in a gravel aquifer and studied the
613 mobility at a 10 m scale. The mobility of elements decreased in the following
614 order: As > Se > Ni > Hg >> Zn > Co > Cr >> Sb > Cu ≈ Cd ≈ Pb. EDTA
615 decreased the mobility of As, Sb, Cr, Hg, and Se, and increased the mobility of Pb,
616 Cd, Cu, Zn, Co, and Ni. Lignite pit DOC decreased the mobility of As, Sb, Cd, Co,
617 Ni, and Cr, and increased the mobility of Pb, Hg, Cu, Se, and Zn. One can conclude
618 that the effect of DOC on the mobility of metals in groundwater is element specific
619 and for some elements is DOC type specific. Tang and Weisbord (2009) also
620 showed experimentally that organic–mineral colloidal Pb was mobile in fractured
621 rocks, while lead carbonate particles were not mobile. By spiking a landfill-leachate
622 polluted groundwater with Cd, Ni, Zn, Cu, and Pb, Jensen et al. (1999) found that a
623 large part of the metals was associated with the organic colloidal fraction, except
624 for Zn, that associated mainly with the inorganic colloidal fraction. The majority of
625 the metals was found in colloids smaller than 0.4 μm (Jensen et al. 1999).

626 The measurement of transport capacity of DOC in complex groundwater matrices
627 is a matter of ongoing research not only for metal, but also for organic pollutants
628 (Persson et al. 2010).

629 Boy et al. (2008) tested the hypothesis that the concentrations of elements in
630 stream water depend on the depth of water flow through soil. Peak concentrations of
631 Al and Mn have been associated with lateral flow (near-surface flow in saturated C
632 and nutrient-rich topsoil). Greatest Na concentrations appeared during low
633 baseflow conditions. This was not correlated with larger concentrations of elements
634 in the soil-layer traversed by the flowing water, as all concentrations were larger in
635 the topsoil. Different processes controlled the exports, e.g., weathering and
636 oxidations of sulfides in the subsoil was responsible for the export of P, S, and
637 Na, while OC probably played a role in the export from the topsoil.

638 The buffering effect of DOC–metal complexes could be lower in mountain
639 shallow soils, leading to a larger indirect role in mountainous contaminated
640 catchments. The DOC pool in shallow mountain soil is replenished after hydrologic
641 events within days during summer and longer in the autumn because of lower
642 temperatures (Halland and Mulder 2010). The pool of potential DOC and its
643 replenishment rates depend on the season and are at maximum during the growing
644 season. Under nonleaching conditions, the pool of potential DOC for export
645 becomes constant, probably due to conversion to other forms or to consumption
646 by microorganisms (Halland and Mulder 2010).

647 Metal inputs from groundwater to surface water may be important. Spinelly et al.
648 (2002) reported that about 60% of the Co unknown sources of metals in a surface
649 water system could be allocated to seepage from groundwater, but at most 4% in the

case of Ag, Cd, Cu, Ni, and Zn. It is likely that such input may involve organic carbon–metal complexes only when the underground path is short (not the case in the cited study). Atekvana and Krishnamurthy (2004) studied the hyporheic ecotone near a landfill and found evidence for water enrichment in inorganic carbon attributable to the landfill.

15.4.7 *Effects at Catchment Scale*



Mixing of metal sources at basin scale is documented (Bird et al. 2010a, b), and part of it may be due to mechanisms influenced by OC. However, few studies have adequately investigated the migration of trace elements in the slope area hydrosystem (Miller and Miller 2007), and none, according to actual knowledge, looked for the role of OC in the export of metals from slope areas by hydrological processes. Also, the literature concerning the direct relationship between metals and organic carbon at basin scale is not very rich, but the correlation between the export of carbon and that of macro-nutrients is documented (for instance, most of the nitrogen exported from catchments with mature forests is in the organic form; Hedin et al. 1995). In this context, we attempt here to extract information from studies about the export of organic carbon and then from reported metals–organic carbon correlations.

In a pioneering study, Brooks et al. (1999) analyzed the pools of DOC available for export in catchments. Both surface water DOC concentrations and watershed DOC export were lower in areas where pyrite weathering resulted in lower soil pH, compared to neutral rocks weathering (Brooks et al. 1999). They also noticed important differences within catchments between land use types, and a correlation of the snow melt flushing of DOC and the heterotrophic activity in soils during winter. The mechanism of DOC export at catchment scale involved vertical preferential flow to the soil–bedrock interface and then lateral downslope flow, with a finite source of DOC in the organic horizon (Verseveld et al. 2008). Organic horizon leachate and transient groundwater were characterized by high DOC, deep groundwater was characterized by low DOC, and the mixing of deep groundwater and shallow transient groundwater was different at the hill-slope scale compared to the catchment scale (Verseveld et al. 2009).

In a unique and insightful study, Jardine et al. (2006) discussed the multiscale characteristics of organic carbon flow: “Common features across scales persist, including preferential flow, matrix diffusion, and geochemical reactions. However, new important phenomena, such as lateral subsurface flow, develop at the field scale and can significantly influence the movement of organic C through the soil profile. Storm intensity and duration also influence C dynamics and the extent of lateral flow.” All these aspects are relevant for the role of OC in metals transport at various scales, although direct studies about carbon–metal interactions at multiple scales do not yet exist. The particularities of DOC export at site and small catchment scale depend on the characteristics of the hydrological event, especially

691 on its intensity (Jardine et al. 2006). The area providing runoff changes seasonally,
692 between storms, and during a rainfall event (Miller and Miller 2007). The intensity
693 of the hydrological event controls the relative importance of vertical and subsurface
694 flows and, because the vertical flow (via groundwater) allows a better filtration of
695 organic carbon, controls the patterns of DOC export (Jardine et al. 2006), and
696 presumably of the associated metals.

697 Gauthier (2009) studied the production of DOM and its fate in the catchment at
698 scales from microcosm to catchment. During discharge events, DOM was
699 mobilized from multiple sources, wetlands having an important role in the pattern
700 generation. As wetlands function as buffer zones for element fluxes the export of
701 OC during storms may be associated with an important export of metals.

702 The situation seems to be catchment specific, but possibilities for identifying
703 general patterns exist to some extent. Luider et al. (2006) analyzed 581 low order
704 streams and observed significant differences between biogeoclimatic zones and
705 moisture subzones with respect to conductance, turbidity, pH, and DOC concentra-
706 tion. OC mean values and confidence intervals were generally larger in drier
707 biogeoclimatic zones, and these zones accounted for 25% of the variation in
708 DOC concentrations between catchments.

709 In another meta-analysis, Raymond and Saiers (2010) processed the data
710 obtained in 30 small forested watersheds without wetlands. Eighty-six percent of
711 the DOC was exported during storms and snowmelts, with the majority of the flux
712 during the rising hydrograph. The highest DOC concentrations and flux were
713 observed in warmer periods and when the preceding discharge was low. Such
714 results underline the importance of timing in field studies estimating the indirect
715 role of OC in metal mobility.

716 We illustrate now the literature explicitly approaching the influence of OC on
717 metal export in catchments. The patterns of metal associated with OC in rivers as
718 revealed by size fractionation methods (Contado et al. 2003) appear to be very
719 heterogeneous. High Hg concentrations are associated with high DOC in
720 catchments in late summer and early autumn presumably because of OM decom-
721 position (Driscoll et al. 1994). Methylmercury is associated mainly with small size
722 OC, while inorganic Hg is associated mainly with high molecular humic material.
723 Mobilization and immobilization of Pb in catchments is also associated with the
724 dynamic of the OM (Driscoll et al. 1994). The hydrogeochemistry of Mn and Fe in
725 small boreal catchments depended on season, landscape structure (estimated by
726 land cover and soil cover, with key parameter the number of wetlands), the size
727 catchment, and the gradient of the catchment (Björkvald et al. 2008). The authors
728 found that the temporal variation of Fe was likely related to varying hydrological
729 pathways and that the wetland area and DOC were important for Fe concentrations,
730 whereas silt deposits strongly influenced Mn concentrations (Björkvald et al. 2008).
731 Based on their results, they recommend a landscape approach to the study of metal
732 distribution in rivers. The Cd-binding capacity in stream water was due mainly to
733 inorganic carbon, for Pb was predominantly due to OM, and for Cu to both
734 inorganic and organic forms of Cu (Alberts et al. 1984). Park et al. (2007) analyze

the climatic control on the export of DOM from a catchment and its influence on metal transport. DOM differed in quantity and quality along the river and depended at a sampling point on the timing of hydrological events, and was positively correlated with some of the trace elements analyzed such as As, Co, and Fe.

The above paragraph referred to stream water. But riparian areas are important as well in the mobility of metals. The sediment load of runoff is reduced when it crosses vegetation strips (transversal buffer zones). For instance, Abu-Zreig et al. (2004) measured efficiency in sediment trapping of 84% in vegetative strips compared to 25% in control. The major factor controlling sediment deposition was the width of the strip (up to 10 m in the mentioned study, then with no influence in the experimental conditions). Other factor influencing the efficiency were the incoming flow and the vegetation cover. The influence of sediment quality, in particular its content in organic matter, was not studied so far, according to our knowledge. To the extent that OM changes the properties of the particles relevant for sedimentation, one can expect to have an influence on the retention of the associated metals in transversal buffer strips. Vidon et al. (2010) reviewed the role of buffer systems, underlining the co-occurrence between the retention of OC and of other pollutants, including Hg. In the floodplain, U was found to be entrapped mainly by adsorption to OM in the water permeable sediment layer (Driscoll et al. 1994), but it can be easily remobilized (either from soil or from sediment) by acidification and introduction of complexing agents. The mobility of metals from overbank deposited sediments in floodplain contaminated by mining and smelter activities is crucial for downstream water quality (Gäbler 1997, Gäbler and Schneider 2000). The risk is relevant for both surface and underground water (Hürkamp et al. 2009). In a seminal article dedicated to the effect of DOM on the export of metals and As from contaminated floodplains, Kalbitz and Wennrich (1998) found that the concentrations of Cu, Cr, Hg, and As in the soil percolates was positively correlated with DOC, but Cd and Zn mobilization depended on pH, and not on DOC (the statistical relation between DOC and pH is not mentioned in the article, but presumably the contribution of these parameters to the multiple regression were not redundant by the chosen algorithm). DOM had no significance in alluvial soils with pH less than 4.5 (Kalbitz and Wennrich 1998). Grybos et al. (2007) identified four types of trace metal behavior in wetland soil: metals bound to OM and released by DOM (rare earth elements), metals bound only to Fe-oxyhydroxides and released by reductive dissolution (Co), metals bound both to organic matter and Fe-oxyhydroxides and released by DOM and reduction on ferric iron (Pb, Ni), and metals with unclear mechanism of release because reduction changes also their redox state and/or speciation (Cu, Cr, U and Th). Schulz-Zunkel and Krueger (2009) reviewed the dynamics of trace metals in the soils of Elbe floodplain and underlined the role of OM and its mineralization in the export of metals, with direct relevance for the Water Framework Directive. Iordache (2009) extensively characterized the role of lower Danube river floodplain in the longitudinal buffering of metal fluxes, pointing out the complex role of litter in mobilizing/immobilizing metals (see also Karavanova et al. 2006). In the same system, Neagoe



779 and Iordache (2002) demonstrated that fast decomposition of detritus coupled with
780 autumn floods play a key role in the export of metals (Fe, Mn, Zn, Cu, Pb, Cd) from
781 alluvial islands in bioavailable forms, an aspect even more important taking into
782 consideration that plants acted as pumps for metals from the soil to aboveground
783 ecosystem parts (Neagoe et al. 2002). As a possible indirect proof of metals
784 transport in organic form, I. Van Damme et al. (2010) identified Zn-humic acid
785 and Zn-fulvic acid complexes in the overbank sediments of a river contaminated by
786 mining and smelter using extended X-ray absorption fine structure spectroscopy.
787 A recent review of trace metal behavior in estuarine and riverine floodplain soils is
788 provided by Laing et al. (2009). They showed that the net effect of OM on metals
789 mobility can be a decrease or an increase of the mobility depending on the situation
790 (oxic/anoxic condition, other parameters).

791 The relative roles of upland and riparian areas in the hydrological export of DOC
792 from catchments vary during a storm. The riparian runoff was larger on the rising
793 than falling limb of the hydrograph, while the hillslope runoff was larger on the
794 falling than rising limb of the hydrograph (McGlynn and McDonnell 2003). This
795 once more underlines the importance of timing in studies for tracing the sources of
796 metals exported associated with organic carbon from a catchment.

797 Mass balance and modeling of metals at catchment scale provide another line of
798 evidence for the role of OC. In a recent study on metal stocks and fluxes at
799 catchment scale, Huang et al. (2010) demonstrated positive and statistically signifi-
800 cant correlations between Cu, Cr, and Ni concentrations and DOC concentrations in
801 runoff. Shotbolt et al. (2008) estimated that the observed increase of DOC leaching
802 from soils of a studied Nordic catchment could result in an increase in Pb export.
803 The effect of OC on the retention of metals in catchments was evaluated also by
804 modeling (Tipping et al. 2006). The retention of deposited metals strongly adsorbed
805 in soils was 89–95% for Cu and 95–100% for Pb, while for metals which sorb
806 weakly this depended on soil pH and varied from 5% for Ni to 57% for Zn (Tipping
807 et al. 2006). For Ni, Cu, Zn, and Cd, the parameters describing the interaction with
808 OM allowed a good agreement between observed and simulated metals in soil and
809 surface water (Tipping et al. 2006).

810 The export from natural, noncontaminated systems also provides information
811 about the role of OC at site scale. Sevel et al. (2009) concluded, by comparing the
812 Cd budgets of two forest grown on soils with different pHs, that the forest on acid
813 soil is a net source of Cd by soil leaching, with OC probably playing a role in this
814 export (Boissier and Fontvieille 1993). However, their study was limited to the
815 0–90 cm layer. As the lower soil layers were not studied, this could lead to a
816 homogenization of the percolating fluxes by intra-ecosystem buffering effects
817 (Currie et al. 1996).

818 Finally, several words on the indirect role of OC in the atmospheric export of
819 metals, with direct relevance for human health problems (e.g., Cheyran et al. 2000).
820 The situation of organometal(loid) compounds and their mobility has been exten-
821 sively reviewed by Thayer (2010). The atmospheric export of such compounds
822 occurs especially in organic rich environment, such as landfills. The atmospheric
823 export of organic forms of Hg, As, Sb, Bi, Se, and Te is documented.

Complementary sources of information in this respect are the reviews about capabilities of certain microbial groups to be involved in the volatilization of metals and metalloids (Meyer et al. 2008).

15.5 Conclusions

The number of pseudo-hierarchical levels needed to understand the influence of OC on metal mobility in catchments vary with the complexity of the catchment and include: soil aggregates and other small-scale soil subsystems, soil layer, soil column, site, slope area, elementary catchments, higher order catchments with transversal buffer zones (riparian areas), higher order catchments with longitudinal buffer zones (floodplains).

Depending on its quality, quantity, and physical phase, the OM can induce either the mobilization or the remobilization of metals. The general concept of “organic matter” is too roughly defined to draw any conclusions on the mobility of metals from simple parameters characterizing it. It means that carbon biogeochemistry and the biogeochemistry of metals cannot be approached separately without an important loss of knowledge. From a different perspective, i.e., the metal effects on plants, Neaogoe et al. (2011) arrived to a similar conclusion for the biogeochemistry of heavy metals, nitrogen, and phosphorus.

There is no extensive explicit knowledge about the role of OM in controlling the intensity of metal fluxes from environmental entities, whatever their scale, although the very small-scale mechanisms supporting their role in mobilization and immobilization of metals is rather clear. The buffering and remobilization of metal fluxes as a result of OM turnover across scales is even less understood.

Table 15.1 synthesizes the existing knowledge about the role of organic carbon (and of microorganisms, as revealed by the above analysis) in the mobility of metals and its effects on fluxes in contaminated sites at soil layer scale. For organic carbon, whose particulate forms are much larger than the microorganisms, there is available information also about its effects on fluxes occurring at site scale, categorized by the type of contaminated sites existing in a contaminated mining area, and at catchment scale (Table 15.2).

The nutrient spiraling concept in river biogeochemistry (Ensign and Doyle 2006) introduced the idea of spiraling length as the distance needed for an atom to pass from dissolved form to particulate form, to biological form and back to dissolved form (Newbold et al. 1981). In the multiscale framework proposed above for OM role in metal mobility by hydrological fluxes, specific hypotheses in metal biogeochemistry could be formulated with respect to the transient storage on metal spiraling at multiple-scale units of analyses in contaminated areas (soil column, underground flowpath, slope area flowpath, small catchment, and large catchment). Also, ecotoxicological hypotheses can be formulated with respect to the storage units about the effects of metal stock and retention time on the overall productivity in the storage units (primary productivity and productivity of microorganisms) and



Table 15.1 Roles of microorganisms and organic matter observable at soil aggregate scale and of their effects on fluxes of metals from soil layers

Soil layer	Roles	Role by immobilization metals	Role by mobilization of metals	Role by supporting the mobilization or immobilization of metals	Effects on mobility at larger scale	
t1.1	(Aggregates in) Soil layer relevant for plants	Microorganisms	K1 Biosorption, intracellular accumulation, biomimetic formation, redox immobilization, metals sorption to biogenic minerals	K1 Chemolithotrophic leaching, chemoorganotrophic leaching, bioweathering, redox mobilization, methylation	K2 Organic matter decomposition, organic acid and siderophores exudates	K3 Transfer of metals to plants, and to lower soil layers
t1.3						
t1.4		Organic matter	K1 Immobilization in litter, immobilization in soil aggregates, chelates in fine pores	K1 Organochemical weathering, soluble chelates, organocolloids, free enzymatic degradation of immobile organic carbon	K1 Energy source for microorganisms, buffering of soil solution	
t1.6	(Aggregates and particles in) Lower soil layers	Microorganisms	K2 Same as in upper layer	K2 Same as in upper layer	K2 Same as in upper layer	K4 Transfer of metals to lower soil layer or to subsoil
t1.5		Organic matter	K2 Immobilization in soil aggregates, chelates in fine pores	K2 Same as in upper layer	K2 Same as in upper layer	
t1.7						

Legend of the extent and coherence of existing knowledge: K1 = max to K5 = min

Table 15.2 Effects of organic matter on fluxes of metals observable at scales ranging from sites and buffer zones to catchments 12.1

Type of entity/effect	Immobilization	Mobilization	Effect at larger scale	
Site with contaminated soil in the slope area	K2 Immobilization in litter, immobilization in soil aggregates	K3 Soluble chelates, organocolloids	K4 Transfer to subsoil and groundwater and then to surface water, transfer to surface water by lateral types of flows, transfer to floodplains, volatilization	12.2
Mining dump or tailing dam	K3 None, or same as above only in case of organic amendments			12.3
Contaminated soil in the floodplain, contaminated stream ecotone	K3 Immobilization in litter, immobilization in soil aggregates		K4 Transfer to surface water during floods, transfer to groundwater, volatilization	12.4 12.5
Catchments	K5 Complex influence resulted from mixture of hydrological fluxes and from the retention and turnover of dissolved and particulated organic matter		K5 Export to higher order catchments	12.6

on functional parameters of the bacterial community (e.g., by comparison of soil columns with different trace elements biogeochemical parameters). 865
866

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