Chapter 13
Copper

Koen Oorts

Abstract Background copper (Cu) concentrations in soil depend on geology and typically vary between 2 and 50 mg Cu kg^{-1}. The widespread use of Cu has resulted in significant anthropogenic inputs to topsoils through atmospheric deposition and agricultural practices (fertilisers, pesticides, sewage sludge etc.). Copper mainly occurs in its divalent state (Cu^{2+}) and has high affinity for binding to organic matter. Sorption processes control the solubility of Cu under most environmental conditions, but Cu precipitates can form in alkaline soils. The solid-liquid partitioning of Cu in soil is largely controlled by the soil pH and organic matter content, with higher solubility at low pH and low organic matter content. Except for acidic soils, most (>90%) of the dissolved Cu in soil is complexed with dissolved organic matter. Copper is an important essential element for all living organisms and deficiency in plants and ruminants occur in soils with low available Cu. Copper concentrations in plant shoots typically range between 4 and 15 mg Cu kg^{-1} dry matter (DM) and are well regulated over a wide soil Cu concentration range. Elevated soil Cu concentrations cause toxic effects in all terrestrial organisms (plants, invertebrates and micro-organisms). The toxicity of Cu largely depends on soil properties, which control the bioavailability of Cu in soil through their effect on precipitation, sorption and complexation processes. Predicted no effect concentrations (PNECs), protecting 95% of all species or microbial processes, vary between approximately 10 and 200 mg Cu kg^{-1} soil and increase with increasing cation exchange capacity, clay and organic matter content.

Keywords Copper • Adsorption • Bioavailability • Ageing • Deficiency • Toxicity • Critical concentrations

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13.1 Introduction

Copper, with atomic number 29, is the first element of group Ib of the periodic table of elements. It ranks 26th in abundance in the lithosphere. The average abundance of Cu in the earth's crust is 60 mg Cu kg^{-1} [42] and concentrations in soil typically vary between 2 and 50 mg kg^{-1}. Copper was known to some of the oldest civilizations, and has a history of use that is at least 10,000 years old. The name 'copper' refers to the island of Cyprus, where Cu was principally mined in the Roman era. The first signs of Cu smelting, i.e. the refining of Cu from simple Cu compounds such as malachite or azurite, date back to 5000 before Christ (BC). Copper smelting appears to have been developed independently in several parts of the world: in the Balkans by 5500 BC, in China before 2800 BC, in the Andes around 2000 BC, in Central America around 600 BC, and in West Africa around 900 BC. Alloying of Cu with zinc or tin to make brass or bronze was practiced soon after the discovery of Cu itself. The use of bronze became so widespread in Europe approximately from 2500 BC to 600 BC that it has been named the Bronze Age.

Although Cu has been in use at least 10,000 years, more than 95% of all Cu ever mined and smelted has been extracted since 1900. Measured by weight, Cu is the third most important metal used by man. The total global demand for Cu in 2007 was approximately 24 Mt [27]. About 35% of all Cu used by industry originates from recycled Cu. The world production of Cu reached more than 15 Mt $year^{-1}$ in 2008. Copper is mainly used in electrical applications (65%), and construction (25%). Other uses are transport (7%) and coins, sculptures, musical instruments and cookware [27]. Various estimates of existing Cu reserves available for mining vary from 25 years to 60 years. In 2005, Chile was the top mine producer of Cu with at least one-third world share followed by the USA, Indonesia and Peru. The long history and widespread use of Cu has resulted in significant anthropogenic emissions, which have caused increased environmental Cu concentrations [36]. Local Cu concentrations can be far above natural background values because of agricultural practices (e.g., sludge application, Cu fungicides) and industrial activities (e.g., mining).

Copper is an essential trace element that is vital to the health of all living organisms (humans, plants, animals, and micro-organisms). It is found in a variety of enzymes and proteins, including the cytochrome C oxidase and certain superoxide dismutases. Soils with low bioavailable Cu can result in losses in crop yield and deficiency symptoms in livestock, especially in intensive farming systems.The recommended daily intake of Cu for humans is 1–2 mg Cu day^{-1} [96]. It has been assumed that most diets satisfy this requirement because of the ubiquitous presence of Cu in most foodstuffs and therefore Cu deficiency in humans is rare.

Elevated soil Cu concentrations can cause toxic effects on soil organisms (plants, invertebrates, micro-organisms) and can affect soil ecosystem functioning. Copper toxicity to terrestrial organisms strongly depends on its bioavailability in soil and the sensitivity of the organisms. Secondary poisoning of Cu though the food chain to vertebrates and humans is considered of low risk due to the strong regulation of internal concentrations of this essential element in plants and soil-dwelling invertebrates.

13.2 Geochemical Occurrence of Copper

The average natural abundance of Cu in the earth's crust is 60 mg kg^{-1} (Table 13.1). The Cu abundance in rock material is highly variable. Basaltic igneous rocks have a larger average Cu concentration (90 mg Cu kg^{-1}) than granitic rocks (15 mg Cu kg^{-1}). Sedimentary rocks, formed by weathering of igneous rocks, mainly reflect the Cu concentrations of the igneous rocks. Clays and shales have typical Cu concentrations ranging between 20 and 200 mg Cu kg^{-1}, whereas sand- or limestone generally contain between 1 and 20 mg Cu kg^{-1} g (see also Sect. 2.3.1).

Copper is one of the few metals to occur naturally as an un-compounded mineral (i.e., native copper). Minerals such as sulphides (chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covelite (CuS), chalcocite (Cu_2S)), carbonates (azurite ($Cu_3(CO_3)_2(OH)_2$) and malachite ($Cu_2CO_3(OH)_2$)) and the oxide cuprite (Cu_2O) are other sources of Cu. Most Cu ore is mined or extracted as Cu sulphides from large open pit mines in porphyry Cu deposits that contain 0.4–1.0% Cu. Large Cu ore deposits are found in the U.S., Chile, Zambia, Zaire, Peru, and Canada.

Typical background Cu concentrations in soils vary between 2 and 50 mg Cu kg^{-1} dry weight, but natural Cu concentrations above 100 mg Cu kg^{-1}can also be found in some soils (Table 13.1). The Cu content in soil shows a positive correlation with Fe content, reflecting the relative concentration in intermediate to mafic igneous rocks compared to felsic rocks (granite). The amount of Cu measured in a soil

Table 13.1 Copper background concentrations in parent materials and soils

	Cu (mg kg^{-1})			Reference
	Range	Average	Median	
Earths crust		60		[42]
Igneous rocks				[56]
Basic igneous rocks (e.g. basalt, gabbro)	30–160			
Acid igneous rocks (e.g. granite, rhyolite)	4–30			
Sedimentary rocks				[56]
Shales and clays	18–120			
Black shales	20–200			
Soils				
USA, agricultural soils	<0.6–495	29.6	18.5	[35]
China			23	[14]
Europe, natural topsoil (XRF)	0.8–256	17.3	13.0	[77]
Europe, natural topsoil (AR)	1.0–239	16.4	12.0	[77]
Europe, natural subsoil (XRF)	0.9–125	17.2	13.9	[77]
Europe, natural subsoil (AR)	<1.0–118	16.5	13.0	[77]

strongly depends on the extraction procedure. Soil Cu concentrations reported in this chapter are expressed as mg Cu kg^{-1} dry soil and are generally "near-total" concentrations based on *aqua regia* or comparable concentrated acid destructions, followed by Cu analysis by inductively coupled plasma spectrometry (ICP) or atomic absorption spectrometry (AAS). Total concentrations determined by HF extraction or X-ray fluorescence (XRF) additionally include a Cu fraction built into the crystal structure of the soil minerals. Differences in soil Cu concentrations between aqua regia destructions and real total concentrations are however generally limited ($<10\%$, Table 13.1) and most data from national or international monitoring programs report Cu-concentrations obtained after destruction with *aqua regia* (See also Sect. 4.5.2).

13.3 Origin of Copper in Soils

Because of historical and current anthropogenic inputs from diffuse sources, the direct measurement of real natural background concentrations for Cu (i.e. the natural Cu concentration in the environment that reflects the situation before any human activity disturbed the natural equilibrium) is not feasible in most parts of the world [23, 73]. For most soils, the Cu concentration measured is the sum of the natural Cu background concentration and diffuse anthropogenic inputs in the past or present and therefore the term ambient background is used. These anthropogenic inputs differ with land-use and the vicinity of point sources (e.g., smelters).

Average ambient background Cu concentrations in European soils away from point sources vary from 11.4 mg Cu kg^{-1} for forest soils (low anthropogenic pressure) to 15.4 and 17.0 mg Cu kg^{-1} for agricultural and grassland soils, respectively [26]. These differences in soil Cu concentrations between land uses can be attributed to both differences in soil properties and differences in Cu inputs. In the past, loamy and clayey soils were preferred over sandy soils for agricultural purposes due to their mineral composition. Consequently, many (forest) soils that were not brought into cultivation have a rather sandy texture, connected with lower Cu levels than clayey or loamy soils (see Sect. 13.3.1). Secondly, the Cu input and output also depends on the soil use. The increased Cu concentration in agricultural soils compared to forest soils may be caused by increased Cu input through the use of fertilisers and sewage sludge as well as the use of biocides and pesticides (see Sect. 13.3.3). A part of the Cu present will be removed from the soil through uptake by crops and harvest. This is less of the case for grassland soils where there is an input related to cattle manure but only a limited output (grazing), which may explain the higher Cu concentration compared to the other soil uses.

13.3.1 Soil Parent Material

The most important natural source of Cu is the geological parent material. The spatial distribution of Cu in soil is mainly related to regional and local geology.

Table 13.2 Copper concentrations in soils from different texture classes

	Cu (mg kg^{-1})	
Texture class	England and Wales (median) [99]	USA (geometric mean) [35]
Sandy	7.4	6.0
Coarse loamy	15	10.3–10.8
Coarse silty	19	18.1
Fine silty	19	28.7
Fine loamy	19	18.6–22.7
Clayey	23	33.6–37.6
Peaty	15	75.8–97.9

Table 13.3 Geometric mean total Cu concentrations in various soil orders in USA and China

	Cu (mg kg^{-1})	
Soil order	USA [35]	China [14]
Ultisol	6.2	17.8
Alfisol	10.9	15.1
Spodosol	48.3	No data
Mollisol	19.1	10.0
Vertisol	48.5	19.6
Aridisol	25.0	21.7
Inceptisol	28.4	21.8
Entisol	21.1	22.2
Histosol	183.2	No data
Oxisol	No data	10.9

The background Cu concentration in soil is correlated with texture and organic matter content. Soils containing high amounts of clay minerals and organic matter generally have higher natural Cu background concentrations (Table 13.2). Geometric mean Cu concentrations in mineral U.S. surface soils vary between 6.0 and 37.6 mg Cu kg^{-1}, while organic horizons have mean Cu concentrations up to 97.9 mg Cu kg^{-1} [35]. The effect of soil parent material and texture also reflects in different Cu concentrations across major soil types (Table 13.3). Soil types characterised by high clay content (e.g. Vertisols) or high organic matter contents (e.g. Histosols and Spodosols) have generally the highest Cu concentrations.

13.3.2 Atmospheric Deposition

Except for agricultural land, atmospheric deposition is responsible for the main input of Cu in soil. Country-specific Cu deposition rates vary from 5 to 100 g Cu ha^{-1} year^{-1} for European countries, with a European average of 34 g Cu ha^{-1} year^{-1} [57]. Copper generally exists within the atmosphere as a component of particulate matter. Copper emissions to air and subsequent atmospheric deposition on land are the results of both natural and anthropogenic processes. Copper can be released into the environment from natural sources through a variety of processes including

Table 13.4 Global natural and anthropogenic emissions (reference year 1983) of Cu to the atmosphere (10^3 t Cu year^{-1})

	Median	Range
Natural sources [59]		
Wind-blown dust	8	0.9–15
Volcanoes	9.4	0.9–18
Sea salt	3.6	0.23–6.9
Wild forest fires	3.8	0.1–7.5
Continental vegetation	0.32	0.01–0.62
Marine vegetation	0.39	0.02–0.75
Pollen & Spores	2.6	0.1–5
Total natural sources	**27.7**	**2.3–54**
Anthropogenic sources [61]		
Coal combustion	5.2	2.3–8.1
Oil combustion	2.0	0.5–3.4
Non-ferrous metal production		
Primary production	23.7	15.1–32.4
Secondary production	0.11	0.06–0.17
Pig iron and steel production	1.49	0.14–2.84
Municipal waste incineration	1.47	0.98–1.96
Sewage sludge incineration	0.11	0.03–0.18
Wood combustion	0.9	0.6–1.2
P-fertilisers	0.41	0.14–0.69
Total anthropogenic sources	**35.4**	**19.9–50.9**

volcanic eruption, forest and bush fires and wind-blown suspension of dust and sea salt spray. An evaluation of the global atmospheric natural emissions of metals, including Cu, identified volcanoes and wind-blown soil particles as the major natural sources of Cu emissions [59] (Table 13.4). Estimated anthropogenic Cu emissions to the atmosphere for 1983 are within the same order as the total natural emissions (Table 13.4). The major anthropogenic emissions of Cu to the atmosphere are from non-ferrous metal production and fuel combustion (industrial and domestic heating, power production). During the last decades, Cu emissions due to metal production significantly decreased, resulting in smaller global Cu emission to the atmosphere [26, 60] (See also Sect. 2.3.2.1.1).

13.3.3 Agricultural Materials and Sewage Sludge

Agricultural materials are responsible for the majority of Cu inputs in agricultural soils. Both the Cu content and application rate vary largely across different agricultural materials. The main sources of Cu input to agricultural soils are manure, sewage sludge, mineral fertilisers, and pesticides (Table 13.5). Copper occurs in manure through the animals' feed, like roughage, concentrate and especially Cu-containing additives [26]. Copper is especially added to growing pig diets, explaining the large contribution of pig manure to overall Cu input from manure. Across the inorganic fertilisers, phosphate fertilisers generally show the highest Cu concentrations and

Table 13.5 Copper inputs to agricultural soils in England and Wales in 2000 (data from [57])

Source	Quantity applied 10^3 t DM year^{-1})	Cu concentration (mg Cu kg^{-1})	Cu addition rate (g ha^{-1} year^{-1})	Total annual Cu input in 2000 (t)
Atmospheric deposition	NA	NA	57	631
Livestock manures	13.48	16–470[a]	168–1679	643
Cattle	10.19	16–45	168–321	215
Pigs	1.64	168–470	1488–1679	360
Poultry	1.65	32–90	175–422	70
Sewage sludge	0.44	565[a]	3210	271
Inorganic fertilisers	4.91	2–94	0.4–12	53
Agrochemicals	ND	ND	ND	8
Irrigation water	ND	ND	16	2
Composts	0.06	25	ND	<1

NA not applicable

ND no data

[a] based on application rate equivalent to 250 kg N ha^{-1} year^{-1}

they are another important source of Cu in soils. Copper is an essential element for plants and in cases of deficiency, Cu may also be applied directly to crops and soils, e.g., with a foliar spray.

Copper-based fungicides (such as the Bordeaux mixture, $CuSO_4$ + $Ca(OH)_2$, $Cu(OH)_2$, Cu_2O, etc.) have been intensively used since the end of the 19th century to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola*. Besides vineyards, Cu-based fungicides have also been extensively used in hop fields, coffee, apple and avocado orchards [24] and during the cultivation of several vegetables (e.g., tomatoes, potatoes). Copper-based fungicides are even indispensible for organic vine and fruit cultivation. Typical application rates vary from 2 to 4 kg Cu ha^{-1} year^{-1} and their long-term application and subsequent wash-off from the treated plants have resulted in elevated Cu concentrations in some vineyard soils [38, 55, 91].

Sewage sludge is often used as a soil conditioner because of its nutrient and organic matter content. However, it may be also an important source of metals and other contaminants. The quality of sewage sludge is largely determined by the composition of the wastewater (industrial or domestic) and the removal efficiency in the wastewater treatment plant. The removal of Cu from raw sewage in sewage treatment plants is usually very effective, with removal rates varying between 80 and >95% [26]. Total Cu concentrations in sewage sludge of various European countries vary between 190 and 641 mg Cu kg^{-1} dry matter [26].

13.3.4 Traffic and Other Sources

Traffic is responsible for some important local Cu inputs in soil. This is both due to rail transport (corrosion of overhead wires) and road transport (brake and tyre wear) [26].

Road transport can result in elevated Cu concentrations in the immediate vicinity of roads [20, 29, 49]. These elevated Cu concentrations can be up to >100 mg Cu kg^{-1}, but Cu concentrations decrease rapidly with both distance and depth and fall back to ambient background levels within 30–50 m distance from the roads. Copper is also used in wood preservation products (e.g. $CuSO_4$, chromated copper arsenate CCA), resulting in additional local elevated soil Cu concentrations [31, 52]. Run-off from external building applications (e.g., Cu roofs) is another, minor, potential local source of Cu inputs into soil.

13.4 Chemical Behaviour of Copper in Soils

13.4.1 General Soil Chemical Reactions of Copper

Copper is a transition metal and thus has more than one oxidation state. The principal forms are cuprous (Cu^{1+}) and cupric (Cu^{2+}). The trivalent form (Cu^{3+}) occurs, but is relatively unimportant in physical and biological systems. Cuprous Cu is unstable in aqueous media and soluble Cu^{1+} compounds form Cu^{2+} ions or compounds and/or Cu(s) as a precipitate. However, monovalent Cu cations are only susceptible to such transformation when they are not chemically bound in insoluble compounds or stabilised in complexed forms.

When Cu^{2+} is introduced into the soil, the cupric ion typically binds to inorganic and organic ligands. In the soil pore water Cu^{2+} binds to dissolved organic matter (e.g. humic or fulvic acids). The Cu^{2+} ion forms stable complexes with $–NH_2$, –SH, and, to a lesser extent, –OH groups in these organic acids. Cupric ions will also bind with varying affinities to inorganic and organic components in soils. The general order of Cu adsorption maxima for soil constituents is: Mn oxides $>$ organic matter $>$ Fe oxides $>$ clay minerals. However, in general, soil organic matter dominates specific Cu adsorption in soil and is mainly responsible for retaining adsorbed Cu [51]. The binding affinity of Cu^{2+} with inorganic and organic matter is dependent on pH, the oxidation-reduction potential in the local environment, and the presence of competing ions. Most of the dissolved Cu in soils is complexed with dissolved organic matter [1]. The proportion of free Cu^{2+} in solution generally decreases with increasing soil pH (Fig. 13.1). Between 73% and 99.96% of the total dissolved Cu in pore water of 11 European soils (pH 3.4–6.8) spiked with $CuCl_2$ up to 3,700 mg Cu kg^{-1} was complexed [70]. In a study of Cu speciation in soil extracts (0.01 M $CaCl_2$) from 66 field soils with varying levels of contamination, Sauvé et al. observed that for most soils more than 98% of the soluble Cu was bound to organic ligands [78]. Both the quantity and quality (aromaticity) of dissolved organic matter control the mobility of Cu in soil [1].

Under most soil conditions, precipitation of Cu will be limited and sorption processes will control Cu concentrations in soil solution [13]. However, in the absence of ligands other than OH^- and depending on the Cu concentration, the solubility of Cu above pH 7–8 can be very low, due to the precipitation of

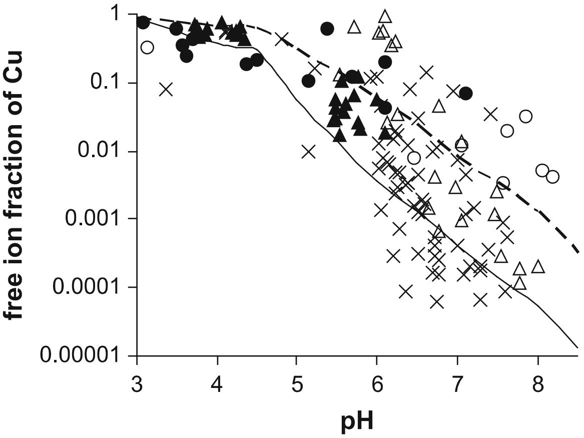

Fig. 13.1 Free-ion fractions of metals in soil solution or in a 10 mM $Ca(NO_3)_2$ extract measured with Donnan dialysis or ion selective electrode. The lines show the free-ion fractions predicted with WHAM6 for a generic composition of solution (50 mg L^{-1} dissolved organic matter, 2 mM $Ca(NO_3)_2$), for either 'low' (5×10^{-7} M Cu, *solid line*) or 'high' (5×10^{-6} M Cu, *dotted line*) Cu concentration (From Degryse et al. [19])

amorphous $Cu(OH)_2$ or tenorite (CuO). Moreover, in the presence of abundant carbonate, relatively insoluble Cu^{2+} carbonate minerals, such as malachite ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$) can precipitate. Copper is highly insoluble in reduced environments, where it precipitates as metal or as very stable sulphides. Sulphide formation indeed appeared dominant in determining the mobility of Cu in flooded soils [21, 94].

13.4.2 Solid-Liquid Partitioning

The solid-liquid partitioning of metals is a critical parameter for assessing their mobility and availability in soils. Transport of metals to deeper soil horizons and leaching to groundwater is related to the dissolved metal concentrations and the amount of metal on the solid phase buffering the metal in solution. The free metal ion is often considered to be the major determinant of bioavailability and its concentration largely depends on the total metal pool in soil, the solid-liquid partitioning and the speciation in solution. The partitioning of metals in soil is usually quantified by a distribution coefficient (K_d), i.e., the ratio of metal concentration on the solid phase (mg kg^{-1}) and in the solution phase (mg L^{-1}). There is plenty of information in the literature on the solid-liquid partitioning of Cu in soils. A sound comparison of K_d data from literature is however often complicated by methodological differences among studies. The methods used to characterise the solid and liquid phases both determine the metal pools (total, labile, free ion concentration, etc.) analysed and affect the solid-liquid distribution by their effect on the composition of the liquid phase (pH, ionic strength, concentration dissolved organic matter), which can influence competition for sorption sites and potential for complexation [19, 79]. K_d values further depend on total metal concentrations as sorption sites become saturated and K_d progressively decreases with increasing total metal loading.

In a review of over 70 studies on partitioning coefficients, Sauvé et al. [79] identified 452 K_d values for Cu in soil, ranging from 6.8 to 82850 L kg^{-1}, with a median of 2120 L kg^{-1}. All Kd values are based on aqua regia soluble soil metal content and total dissolved Cu concentrations in the actual soil solution or soil extracts. K_d values were significantly correlated with pH and organic carbon content of the soil and an empirical regression was derived to predict K_d for Cu in soil:

$$\begin{aligned}\text{Log } K_d &= 1.75 + 0.21^{*}\text{pH(soil solution)} \\ &\quad + 0.51^{*}\log(\%\ \text{Organic Carbon})\left(R^2 = 0.42,\ n = 353\right)\end{aligned}$$

Similar equations for K_d values based on aqua regia soluble total Cu concentrations and either total dissolved or free ion Cu concentration in pore-water were obtained in an excellent review on metal partitioning in soils by Degryse et al. [19]:

$$\text{Log } K_d = 0.45 + 0.34^{*}\text{pH} + 0.65^{*}\log(\%\ \text{Organic Carbon})\left(R^2 = 0.44,\ n = 128\right)$$

$$\begin{aligned}\text{Log } K_{d\,\text{free}} &= -1.88 + 1.05^{*}\text{pH} \\ &\quad + 0.65^{*}\log(\%\ \text{Organic Carbon})\left(R^2 = 0.97,\ n = 32\right)\end{aligned}$$

Compared to other metals (Cd, Ni, Pb and Zn), pH has a relatively limited effect on the solid-liquid distribution of total dissolved Cu in soils. This can be explained by the very high affinity of Cu for organic matter. If pH increases, the sorption of the free Cu^{2+} ion on solid organic matter increases, but the complexation of Cu with dissolved organic matter also increases, resulting in a small (or zero) net effect on the total solution concentration [19]. If Cu binds only on organic matter and there is no inorganic complexation in solution, the Kd of Cu is expected to reflect the solid-liquid distribution of organic matter in soils. Figure 13.2 indeed shows a good correlation between K_d values for Cu and the partitioning of organic matter between the solid and liquid phase in soils with moderate to high pH, where free-ion fractions of Cu are small [19]. Land management practices that affect soil pH and organic matter dynamics will obviously also have a directly impact on Cu mobility in soil. The application of biosolids can, e.g., increase Cu mobility through enhanced dissolved organic matter [2, 33].

13.4.3 *Ageing Processes: Effect of Time on Fate of Copper in Soils*

Initial partitioning of metals, taking place within hours after addition of soluble metals to a moist soil, are often followed by much slower reactions, termed fixation

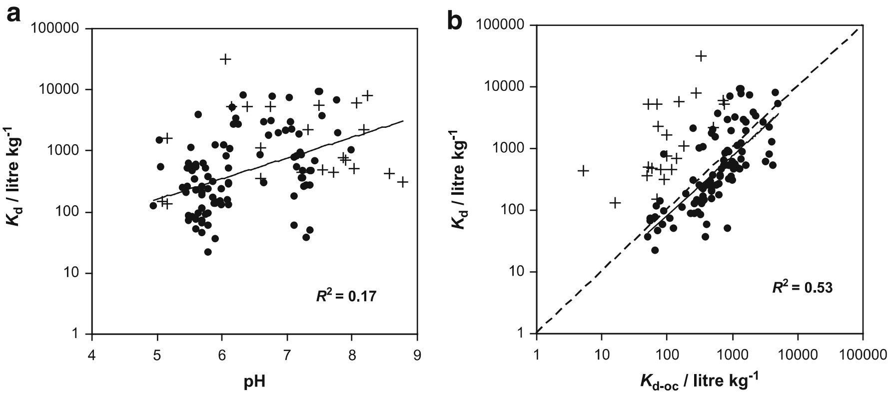

Fig. 13.2 The Kd of Cu for soils with pH > 5 (**a**) as a function of pH, or (**b**) as a function of the solid-liquid distribution of organic C, Kd-OC (*dotted line* is the 1:1 line). Solid lines are regressions relating logKd of Cu to pH or to logKd-OC (From Degryse et al. [19])

or ageing, that further decrease the bioavailability of added metal with time. Examples of such ageing reactions for Cu are diffusion of Cu into micro-pores, precipitation of insoluble Cu phases, occlusion of Cu into organic matter and inclusion of Cu in the crystal structure of soil minerals. There is substantial evidence for the decreased extractability with time after addition of soluble Cu to soils [34, 95] or soil constituents, such as peat [12], oxides [66] and clay [97]. It was also shown that the extractability of Cu fertilisers in field soils decreased over a period of 6 years after application [15]. Results from sequential fractionation schemes to partition soil Cu into various operationally-defined pools confirm that soluble Cu migrates with time from easily extracted pools to more strongly bound forms, mostly associated with organic matter and mineral oxides [30, 67].

Next to this chemical evidence for ageing reactions, there also are some biological indications for decreased availability of Cu with time. In a series of pot trials with Cu-deficient soils (<3.5 mg Cu kg^{-1}), the plant uptake of Cu was significantly reduced with increasing contact time between soil and Cu. The Cu fixation rate increased with increasing temperature, increasing pH and addition of straw [5–8]. There is however no direct evidence for reduced residual effect of Cu in non-deficient soils, which may be related to the strong regulation of plant root uptake of Cu when abundant Cu is available. At higher soil Cu concentrations, it has been shown that ageing significantly reduces Cu toxicity to plants, invertebrates and micro-organisms [64, 68, 69, 80, 81]. It must however be noticed that at these high concentration ranges, the elevated ionic strength and decreased pH in soil solution of Cu-salt spiked and unleached soil samples also may affect Cu behaviour in soil (see Sect. 13.6.1).

Ageing of Cu in soil removes Cu from available pools into a pool that is more strongly retained, from which its desorption is much slower. Consequently, two Cu pools can be defined in soil, the labile fraction and the fraction of Cu that is

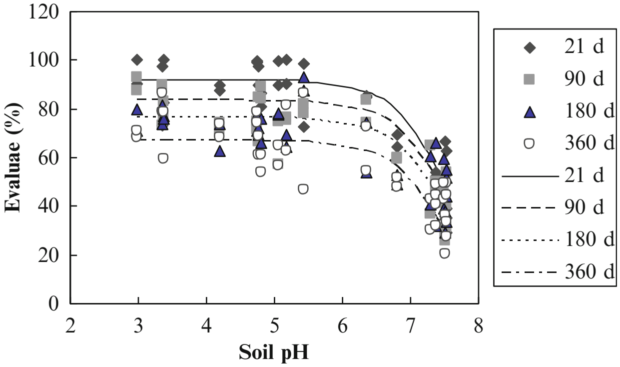

Fig. 13.3 The effect of time and pH on lability (E-values, % of total added Cu) of added Cu in soils incubated for different times. The curves are predicted by a semi-mechanistic model based on time and pH (Based on Ma et al. [47])

fixed. The labile fraction of Cu contributes to the solid-liquid distribution whereas the fixed fraction of Cu does not. Isotopic dilution is a convenient method of measuring the labile pool of Cu in soils. The radiolabile Cu in soil (or the E-value) is, by definition, that amount of Cu in soil that has the same fate as a soluble Cu salt after 24 h equilibration in the soil. The fraction labile Cu varies strongly across soils and is generally lower in uncontaminated soils (between 2% and 35%) compared to field contaminated soils (27–57%) [47, 58].

Ma et al. [46, 47] assessed ageing of freshly added $CuCl_2$ in 19 soils at two total Cu concentrations, after leaching of the excess salt and 2 years of incubation outdoors. The lability of Cu added to soils rapidly decreased after addition, especially in soils with pH >6.0, followed by a slow decrease in Cu lability. The short-term (30 days) attenuation of Cu lability depended on soil pH, organic matter content, temperature and Cu addition rate [46]. The long-term changes in Cu lability were well described based on soil pH and time alone, with a semi-mechanistic model taking into account a slow diffusion process and precipitation/nucleation of Cu in alkaline soils (Fig. 13.3). There was little difference between the two Cu concentrations, suggesting that within the relevant range, total Cu concentration does not greatly affect the rate and extent of fixation [47].

Buekers et al. [10, 11] also studied the fixation of added Cu salt in 28 soils with varying pH (3.4–7.7), organic carbon (0.2–23.5%), clay content (5–81%) and Fe oxides (0.1–7.3 g kg^{-1} oxalate extractable Fe). After 850 days incubation, on average 43% of the added Cu was fixed. A significant positive effect of pH on the amount of fixed Cu was observed, but compared to Ni, Zn and Cd, fixation of Cu in soils was generally poorly related to soil properties. The relatively large fixation of Cu (approx. 50%) in two organic soils did however suggest that Cu can be fixed in organic matter [10]. In contrast to Ni, Zn and Cd, fixation on Fe oxyhydroxides does not well explain ageing of Cu and modelling fixation of Cu requires more information on fixation on organic matter [11].

13.5 Soil-Plant Relationships of Copper

Copper is an essential micronutrient for plants and is involved in several metabolic processes. It plays an important role in photosynthesis, respiration, oxidative stress responses, cell wall metabolism and hormone signalling [50]. Copper also acts as a cofactor in many enzymes such as plastocyanin, cytochrome c-oxidase and amino oxidase. Copper deficiency mainly affects young leaves and reproductive organs and typical symptoms are twisted or malformed leaves, chlorosis or even necrosis [50]. Crops known to be highly susceptible to Cu deficiency include wheat, alfalfa and lettuce. Copper deficiency is mainly related to sandy, light textured soils with low ambient background Cu concentrations or strong Cu-binding peat soils with low plant available Cu. High nitrogen levels delay the translocation of Cu from older leaves to the growing points and may enhance Cu deficiency in intensive farming systems. In Europe, it is estimated that up to 19% of the arable land is deficient in bio-available Cu [83]. Despite its essentiality, excess Cu in soil has a phytotoxic effect, resulting in plant growth retardation and leaf chlorosis. The first effect of Cu toxicity in plants is rhizotoxicity, resulting in reduction of root elongation and stunting, abnormal root branching and thickening and dark coloration of the roots [39, 50, 82]. Translocation of Cu towards shoots is efficiently restricted by the large accumulation of Cu in roots and deleterious physiological effects (e.g., altered root growth and nutrient uptake) are expected to occur before shoot Cu concentration reaches abnormal values [69].

Typical Cu concentrations in plants growing in uncontaminated soils vary between 4 and 15 mg Cu kg^{-1} dry matter [17, 56] and rarely exceed 20 mg Cu kg^{-1} dry matter [37]. The Cu concentration in plants depends on the plant species, growth stage and lime or fertiliser applications. In non-deficient soils, plant tissue Cu concentrations are rather constant over a wide range of soil Cu levels, reflecting the homeostatic control of Cu content in plants.

The onset of Cu toxicity and reduction in yield is found at shoot and leaf concentrations between 5 and 40 mg Cu kg^{-1} dry matter (Table 13.6). The small difference in Cu concentrations in shoots from healthy plants and plants affected by Cu toxicity again reflects the strong translocation barrier for excess Cu between root and shoot. Root Cu concentrations are more affected by soil Cu concentrations than shoot Cu concentrations (Fig. 13.4) and critical Cu concentrations in plant roots are in the range of 100–400 mg Cu kg^{-1} dry matter [18, 69, 82].

The efficient homeostatic mechanisms in plants, whereby Cu levels in edible crops are relatively insensitive to soil Cu, and the translocation barrier of excess Cu from roots to shoots limit Cu residues in plant shoots to levels chronically tolerated by livestock and humans [26, 76]. In contrast, Cu deficiency symptoms in livestock occur and can be caused by either low Cu concentration in herbage (<5 mg Cu kg^{-1} dry matter) or by reduced Cu absorption in ruminants due to elevated dietary Mo or S uptake [87].

Plant growth affects Cu solubility and bioavailability in soil, especially in the rhizosphere, due to their effect on pH and dissolved organic matter. Depending on the pH of the bulk soil, this may result in either increased or decreased

Table 13.6 Critical toxic Cu concentrations in plant shoots and leaves (data from [17, 48])

Plant species	Critical level (mg Cu kg^{-1} dry matter)
Ryegrass	21–40
Barley	14–25
Wheat	11–18
Maize	5–21
Lettuce	8–23
Rape	15–22
Beans	15–30
Cabbage	25
Sugar beat	17
Spinach	25–35

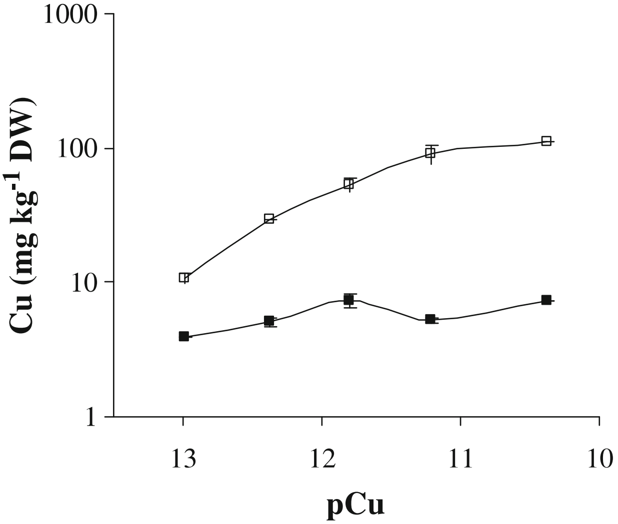

Fig. 13.4 Copper concentrations in shoots (*closes symbols*) and roots (*open symbols*) of tomato plants grown in nutrient solutions as function of the free metal activity (From Degryse et al. [18])

total dissolved Cu concentrations. The free Cu^{2+} activity in soil solution however generally decreases with plant growth due to enhanced complexation with dissolved organic carbon [4, 18, 74].

13.6 Toxicity of Copper in Soils

13.6.1 Copper Toxicity to Plants, Invertebrates and Micro-Organisms

Toxicity of Cu to terrestrial organisms (plants, invertebrates and micro-organisms) is typically studied by exposing these organisms to an uncontaminated soil recently

Table 13.7 Chronic soil Cu toxicity threshold concentrations (NOEC, No Observed Effect Concentrations, or EC10, concentrations yielding 10% inhibition in response) for plants, invertebrates and microbial processes [26]

	Range (mg Cu kg^{-1} soil)	Number of data
Monocotyledon plants	18–537	32; 5 species from 3 families
Dicotyledon plants	36–698	35; 4 species from 2 families
Arthropods	31–1460	57; 5 species from 3 families
Annelida and Nematoda	8.4–728	51; 5 species from 3 families
Microbial C transformation	30–2402	49; 4 processes
Microbial N transformation	31–1270	26; 4 processes
Microbial biomass	150–500	2

amended with increasing doses of a soluble Cu salt (e.g. $CuCl_2$ or $CuSO_4$). From the resulting dose–response relationship, toxicity thresholds (NOEC, No Observed Effect Concentrations, i.e. highest dose at which no significant inhibitory effect is observed, or EC10 values, i.e. effective concentration yielding 10% inhibition in response) can be calculated for the effect of Cu on the endpoint studied (e.g., plant growth or invertebrate reproduction). In total 252 reliable NOEC or EC10 values for the effect of Cu on terrestrial organisms were identified in the framework of a European risk assessment of Cu (Table 13.7). These data cover a wide range in terrestrial organisms and are derived from tests focusing on sensitive life stages (e.g., plant root elongation, invertebrate reproduction) or from chronic exposure (e.g., growth, mortality). Data were obtained in a variety of soils with a wide range in pH (3.0–7.7), organic carbon (0.3–38%), clay (5–60%) and ambient Cu background concentration (2–158 mg Cu kg^{-1}). Copper toxicity thresholds varied almost 3 orders of magnitude (3–2,400 mg Cu kg^{-1}) across endpoints and soils and overlap with the range in ambient background Cu concentrations in soil.

The ecological relevance of standardised laboratory tests immediately or shortly after freshly spiking with soluble metal salt is however limited (Fig. 13.5). Standardised toxicity tests result in a sudden disturbance of the soil, while in field conditions Cu generally accumulates slowly with time due to e.g., industrial emissions, sludge application or the use of Cu fungicides. Spiking soils with soluble Cu salts not only increases the Cu content of a soil but also increases the ionic strength of the soil solution and decreases the soil pH by replacement of protons from the exchange complex with the metal cations (Fig. 13.6). The higher ionic strength and lower soil solution pH in freshly amended (spiked) soils compared to leached or field-contaminated soils (that are naturally leached) may affect the response of the organisms both directly and indirectly by increasing metal bioavailability. Testing soils immediately after adding Cu also ignores the ageing reactions that further decrease bioavailability of added Cu beyond the duration of these tests (Sect. 13.4.3). Standard toxicity experiments in soil result therefore in a potentially higher bioavailability compared to field conditions and soil metal concentrations needed to produce toxic effects generally are lower for laboratory contaminated than for field contaminated soils. Additionally, lower toxicity to microbial processes in field-contaminated or aged soils can also be caused by microbial

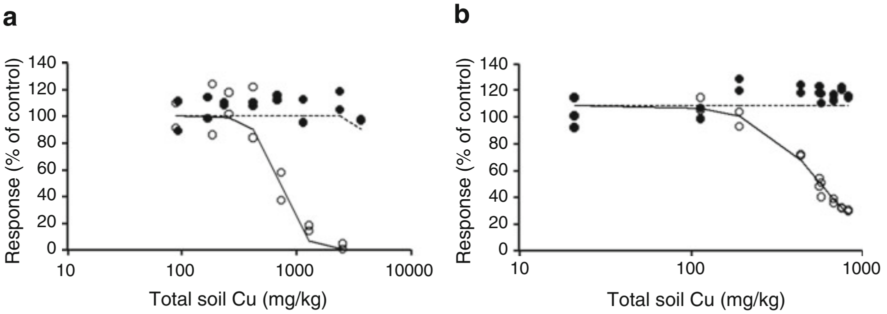

Fig. 13.5 Discrepancy of the microbial response to elevated Cu between standard toxicity tests (*open symbols, full line*) and long-term contaminated soils (*closed symbols, dashed line*). (**a**) Toxicity of Cu on nitrification measured 7 days after amending the soil with $CuCl_2$ or after spiking with $CuCl_2$ and18 months equilibration and leaching. (**b**) Effect of Cu on respiration of glucose in a field transect of a contaminated soil (70-year-old $CuSO_4$ spill) and the corresponding control soil amended with $CuCl_2$ to identical concentrations (Based on Oorts et al. [64])

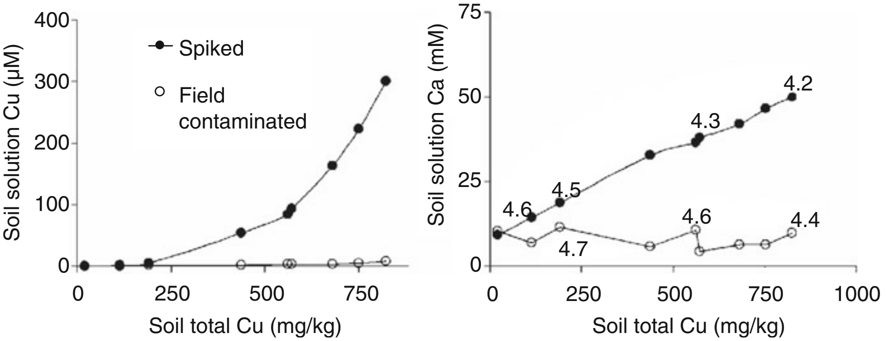

Fig. 13.6 Difference in soil solution properties of a field-contaminated soil (field gradient with a 70-year-old $CuSO_4$ spill) and the corresponding freshly spiked reference soil (amended with $CuCl_2$ to identical Cu concentrations). Soil pH (indicated in *right panel*) gradually decreases with Cu dose in spiked soils (From Smolders et al. [85], data based on Oorts et al. [64])

acclimatization or adaptation of the microbial biomass in the soil to gradually increased Cu concentrations [3, 28, 54] (see also Sect. 5.6).

Several studies have confirmed the larger Cu toxicity in soils freshly spiked with Cu salts compared to corresponding laboratory leached and aged soils or field contaminated soil [64, 68, 69, 80, 81]. The factor for the decrease in toxicity is expressed as the ratio of EC10 value after ageing to the corresponding value in freshly amended soil, both based on measured added concentrations. This factor is termed the leaching–ageing factor (L/A factor) and is the net result of effects of both leaching and ageing. Most of the L/A factors based on EC10 values were larger than 1 (i.e. decreased toxicity after leaching and ageing), with a median of 3.4 (Fig. 13.7).

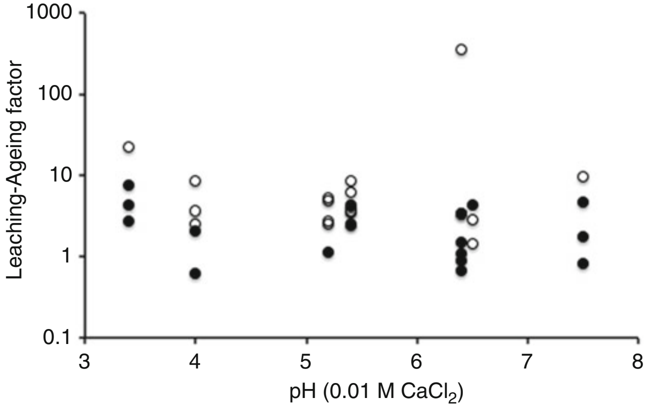

Fig. 13.7 The leaching–ageing factors that quantify the difference in Cu toxicity between aged soils (experimental or field-contaminated) and corresponding freshly amended soils. The factors are the ratios of the doses resulting in 10% inhibition (EC10 values) in aged to that in freshly amended soils. Closed symbols are bounded values; open symbols refer to unbounded values (no toxicity found in a field-contaminated or aged soil and a (*lower*) estimate for the L/A factor was selected, based on the ratio of the largest concentration in the aged soil to the ED10 of a freshly amended soil) (Based on EU [26]

The L/A factors for Cu vary largely among the species or process studied and no effect of soil pH or other soil properties was observed on the effect of leaching and ageing on Cu toxicity in soils.

13.6.2 *Effect of Soil Properties on Copper Toxicity in Soils*

Toxicity thresholds for the effect of Cu on the same endpoint can vary up to two orders of magnitude among different freshly spiked soils [9, 16, 40, 41, 65, 75]. It is generally accepted that the total metal concentration in soil is a poor predictor for toxicity to the environment. However, there is as yet no generally accepted method for measurement of the bioavailable fraction of Cu or other metals in soil [53, 98]. The free metal ion concentration in soil solution is generally regarded as the most active Cu species and the determinant of bioavailability. It is however often observed that toxicity thresholds based on total soluble Cu or free metal ion activity of Cu are more variable than other indices of Cu doses in Cu spiked soils (Fig. 13.8) [9, 65, 98]. This observation that free metal ion activities do not explain variability in toxicity does not necessarily violate the concept that the free metal ion in solution is the directly available and toxic metal species. This is readily explained by the concept of the biotic ligand model (BLM), which is an extension of the free metal ion model. According to the BLM, toxicity depends on the metal bound to a target location at or in the organism (the biotic ligand), which, in turn, depends

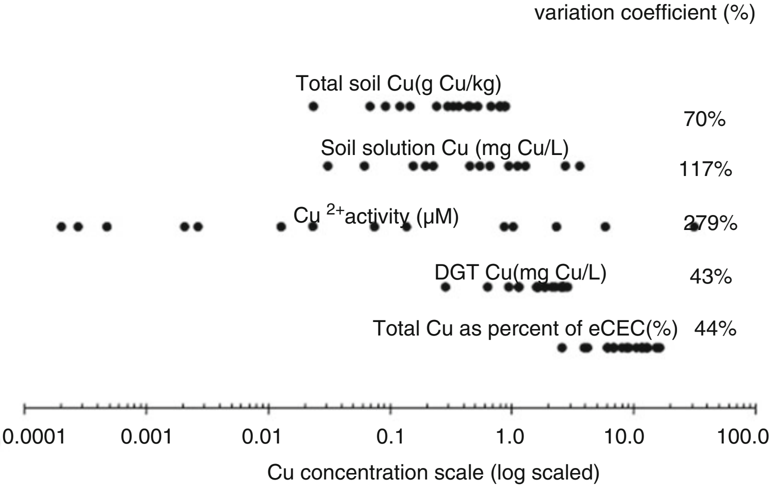

Fig. 13.8 Five different expressions of the toxic Cu concentrations at the 50% effective concentration (EC50) in 17 freshly amended soils, with shoot growth of tomato seedling as the measured endpoint. The coefficients of variation (standard deviation divided by mean of untransformed EC50 values) of the EC50 values for the 17 soils are given. DGT = diffusive gradients in thin film technique; eCEC = effective cation exchange capacity (i.e. CEC at pH of the soil) (From Smolders et al. [85], data based on Zhao et al. [98]

on the metal ion activity in solution and the concentrations of competing ions (e.g. protons, Ca^{2+}, and Mg^{2+}). A BLM has been successfully calibrated with the data from soils freshly amended with Cu salts and this revealed protective effects of protons for all endpoints and additionally of Mg for the nitrification assay [88, 89]. A meta-analysis of metal toxicity data also suggested that protons strongly mitigate the toxicity of the free metal ion on the biotic ligand [43].

Soil properties can explain a significant part of the variation in Cu toxicity thresholds for plants, invertebrates and micro-organisms based on total soil Cu concentrations and empirical regression models are derived for a wide range of European, Chinese and Australian soils (Table 13.8). Copper toxicity is generally best related to the effective CEC (‘eCEC’ i.e. CEC at pH of the soil), compared to pH, organic matter or clay content. The importance of the eCEC may refer to the role of cation exchange processes in short-term sorption of Cu in soils [92]. Although soil pH generally is acknowledged as a key factor in determining Cu solubility and speciation in soils, no consistent effects of soil pH on total soil Cu toxicity thresholds were found. This is explained by the counteracting effect of soil pH on free Cu ion toxicity at the biotic ligand (increasing toxicity of free Cu ion with increasing pH because of decreasing competition of protons) and on Cu solubility and speciation in soil (decreasing free Cu ion concentration with increasing pH due to increasing sorption) [43, 65]. The similar pH effect on metal toxicity and metal adsorption suggests that metal binding on the biotic membrane and on soil components are controlled by the same reactions.

Table 13.8 Soil properties best predicting Cu toxicity (EC50 values) in freshly-spiked soils

Endpoint	Soil properties	Reference
Eisenia fetida (earthworm) reproduction	eCEC[a]	[16]
Folsomia candida (springtail) reproduction	eCEC	[16]
Potential nitrification rate	eCEC	[65]
Substrate induced respiration	Organic carbon and clay content	[65]
Maize residue mineralisation	pH and eCEC	[65]
Barley root elongation	eCEC	[75]
Tomato shoot yield	eCEC	[75]
Substrate induced nitrification	pH	[9]
Substrate induced respiration	clay	[9]
Wheat shoot yield	CEC	[93]
Substrate induced nitrification	Total calcium concentration	[41]
Barley root elongation	pH and organic carbon	[40]

[a] eCEC = effective cation exchange capacity, i.e. CEC at pH of the soil

13.6.3 Toxicity of Copper in Soils Amended with Sewage Sludge and Manure

Application of sewage sludge and manure to agricultural land is an important source of Cu in agricultural land (Sect. 13.3.3). The bioavailability of Cu in these soil amendments is however generally lower compared to Cu salts. The ecotoxicological assessment of Cu added with sludge or manure to soils is different from Cu added as salt because the application of these products also changes a range of other soil properties apart from the total Cu content. Application of sewage sludge or manure to a soil may increase metal binding capacity of the soil as these products contain organic matter and Fe or Al oxyhydroxides, which all have Cu binding properties. Additionally, metals present in these materials have a different speciation, and typically lower availability, than metal salts [32, 33, 62]. Both mechanisms may decrease the risk of increasing total trace metal concentrations. On the other hand, long-term mineralisation of organic matter from biosolids may again decrease the Cu binding capacity of the soil and increase bioavailability of Cu.

Results on the difference of Cu bioavailability between biosolids- and $CuSO_4$-amended soils in 12 Australian field trials were inconclusive due to the strong regulation of Cu concentration in plant shoots and the confounding effect of dissolved organic matter on Cu extractions [33]. A comparison of toxicity of added Cu-salt in 22 paired sets of soils amended with sewage sludge, manure or compost and corresponding control soils from field trials in Europe, Asia and Australia, showed that the protective effect of additional metal binding capacity in biosolids-amended soil was limited (average factor 1.4 difference in EC50 for barley root elongation) [84]. A larger difference was observed in the lability (E-values) of Cu added via these biosolids compared to soluble metal salts, even after correcting for ageing. Therefore, it seems that application of biosolids indeed results in a protection of Cu availability, and that this protection is mainly related to the

Table 13.9 Copper limit concentrations in soil according to various legislations

Legislation	Limit (mg Cu kg^{-1} DM)	Comment	Reference
Europe (Regulation (EEC) 793/93)	10–200	Predicted No Effect Concentration (PNEC, 95% protection level) for plants, invertebrates and micro-organisms; depending on eCEC, pH, clay and organic matter content	[26]
US EPA	70 (plants) 80 (invertebrates) 28 (birds) 49 (mammals)	Ecological soil screening level (ECO SSL); no correction for soil properties	[90]
Australia	8–970	Added contaminant level for soils with varying pH (4–8) and organic carbon content (1–6%). Based on protection of 95% of plant species	[32]
Australia	11–2078	Added contaminant level for biosolids amended soils with varying pH (4–8) and organic carbon content (1–6%) Based on protection of 95% of plant species	[32]
Europe (EU Directive 86/278/EEC)	50–140 1000–1750	Limit values for Cu in soil Limit values for Cu in sludge for use in agriculture.	[25]

speciation and low availability of Cu originally present in the sewage sludge and manures and less to the additional Cu binding capacity of a biosolids-amended soil [84]. The marginal effect of increased binding capacity also explains the lack of significant release or mobilisation of Cu in biosolid-amended soils due to organic matter decomposition within the time frame of the field trials studied [63, 84].

13.6.4 Critical Soil Copper Concentrations

Based on the toxicity data available, critical soil Cu concentrations can be derived for risk assessment purposes. These critical Cu concentrations vary between legislations as they depend e.g., on the protection goal (organisms covered), the toxicity data included, the application of normalisation models for the effect of soil properties on Cu bioavailability, the protection level and the margin of safety included to correct for remaining uncertainty (Table 13.9).

The incorporation of bioavailability models into the derivation of ecological soil standards (Predicted No Effect Concentrations, PNEC) in the European risk assessments of Cu and other metals is described by Smolders et al. [85]. In summary, this European risk assessment for Cu [26] was based on reliable chronic toxicity data (NOEC and EC10) from standard tests in soils freshly amended with Cu salts and sufficient information on the soil properties (Table 13.7). In order

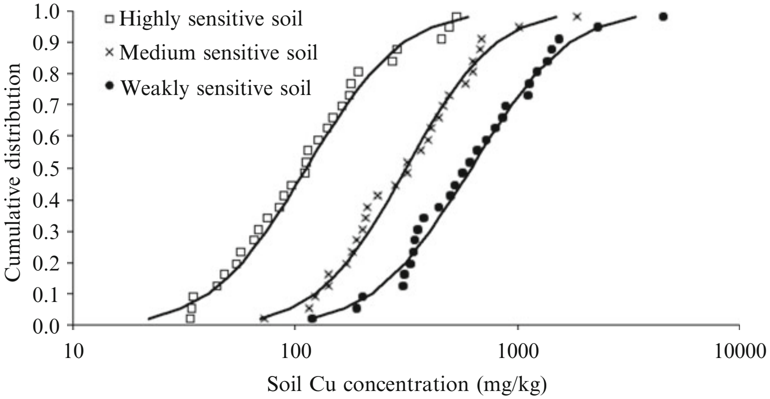

Fig. 13.9 Species sensitivity distribution (SSD) of species-mean NOEC or EC10 values for plants, soil invertebrates and micro-organisms, corrected for ageing processes and normalised for soil properties of a highly sensitive, medium sensitive and weakly sensitive soil according to the models selected for the European risk assessment of Cu [26]. Properties for these three soils are, respectively, eCEC, 4, 15, and 35 $\text{cmol}_c\ \text{kg}^{-1}$; pH, 4.5, 5.5, 7.0; % organic carbon, 1.0, 2.9, and 12% and % clay, 5, 15, and 30%. Corresponding PNEC values, based on a 95% protection level, are 30, 93 and 162 mg Cu kg^{-1} soil, respectively

to correct for differences in bioavailability and toxicity of Cu between such freshly amended soils and realistic field conditions due to leaching and ageing processes (Sect. 13.6.1), all toxicity data based on added Cu concentrations were multiplied with a generic leaching-ageing factor of 2. This L/A factor is obviously only applied on the added dose as the bioavailability of the background Cu concentration in soil is not expected to further change with time. After adding the background concentration, the total ‘aged’ NOEC and EC10 values were normalised for differences in metal availability between the tested soil and the soil to which the PNEC is calculated, using the slope of the regressions between toxicity and selected soil properties (eCEC, pH, organic carbon and clay content). Based on these normalised values, a species mean threshold was calculated for each plant, invertebrate and microbial process covered. A critical concentration protecting 95% of all species or processes was derived as the 5th percentile of the cumulative distribution of species mean thresholds (species sensitivity distribution, Fig. 13.9). This results in soil specific PNEC values for direct ecotoxicological effects of Cu to terrestrial organisms, between 10 and 200 mg Cu kg^{-1} for the relevant range of soil properties in European soils. Because plants and invertebrates are good Cu regulators and they maintain internal Cu levels over a large range in environmental Cu concentration, the direct toxicological effects on terrestrial organisms are most critical and risks for secondary poisoning to birds, mammals and humans are absent at PNECs for direct effects to terrestrial organisms [26, 76].

Clean-up standards for Cu in soils are generally higher than these ecological standards for risk assessment purposes and clean-up limits for Cu in residential and industrial land vary between 63–3,100 and 91–41,000 mg Cu kg^{-1}, respectively among individual legislations [71].

13.7 Contaminated Soils

High Cu concentrations, potentially requiring remediation, can be found in topsoils affected by e.g., mining and smelting activities (up to $>$2000 mg Cu kg^{-1}) (e.g. [22, 45, 86]), wood treatment facilities (up to $>$1000 mg Cu kg^{-1}) [52], or long-term application of high doses of Cu pesticides (200–500 mg Cu kg^{-1}) [38]. When Cu levels affect soil functions or exceed soil clean-up values, Cu contaminated land can be remediated by either excavation of contaminated soil and off-site treatment or landfilling, or the on-site stabilisation by limiting the mobility and bioavailability of Cu in soil. The first option is very invasive and hence only suitable for small highly contaminated areas. Decreasing the mobility and bioavailability in soil can be done by raising the pH by liming or by adding soil amendments, such as organic matter or oxides, to increase the Cu binding capacity of the soil [44, 86]. It seems however that the major effect of most soil amendments on Cu bioavailability can still be attributed to the associated increase of the pH [44]. Because the effect of increased pH on Cu bioavailability is reversible, a continuous land management is required in order to prevent re-acidification and corresponding increase in Cu bioavailability. Phytostabilisation has also some potential in case of large areas of relatively low contamination levels [72]. A vegetation cover will prevent spreading of the contamination by e.g. air or wind erosion. The low transfer of Cu to aboveground plant parts further limits Cu dispersion by litter fall or increased exposure to herbivores.

13.8 Concluding Remarks

Copper is probably among the best-studied heavy metals in soil. Although the long history of global use of Cu resulted in significant diffuse anthropogenic emissions of Cu to soil, natural processes (e.g., geology) drive the regional and continental distribution patterns of soil Cu concentrations. At a local scale, the main anthropogenic input comes from point sources (e.g. mining or smelting activities) and agricultural practices (use of sewage sludge, Cu-pesticides etc.). Soil organic matter and pH are the main soil factors controlling solid-liquid partitioning of Cu in soil, with higher solubility at low pH and low organic matter content. Copper is an essential element and internal Cu concentrations are well regulated in plants and soil-dwelling invertebrates. Elevated soil Cu concentrations first affect plant root growth and translocation of excess Cu to shoots is efficiently restricted over a wide concentration range. Toxicity of Cu to terrestrial organisms varies largely depending on the species sensitivity and the bioavailability of Cu in soils. Chronic soil Cu toxicity thresholds even overlap with the range in ambient background Cu concentrations. However, both background Cu concentration and Cu toxicity are partly controlled by the same soil factors (organic matter and clay content). When bioavailability of Cu in soil is taken into account and toxicity data are normalised for soil properties, there is a factor 2–10 difference between the ambient background concentrations and predicted no effect concentration of Cu in soil.

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