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Journal of Trace Elements in Medicine and Biology 19 (2005) 125–140

Journal of  
Trace Elements  
in Medicine and Biology

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## REVIEW

# Trace elements in agroecosystems and impacts on the environment

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Received 6 February 2005; accepted 21 February 2005

## Abstract

Trace elements mean elements present at low concentrations ( $\text{mg kg}^{-1}$  or less) in agroecosystems. Some trace elements, including copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), molybdenum (Mo), and boron (B) are essential to plant growth and are called micronutrients. Except for B, these elements are also heavy metals, and are toxic to plants at high concentrations. Some trace elements, such as cobalt (Co) and selenium (Se), are not essential to plant growth but are required by animals and human beings. Other trace elements such as cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), mercury (Hg), and arsenic (As) have toxic effects on living organisms and are often considered as contaminants. Trace elements in an agroecosystem are either inherited from soil parent materials or inputs through human activities. Soil contamination with heavy metals and toxic elements due to parent materials or point sources often occurs in a limited area and is easy to identify. Repeated use of metal-enriched chemicals, fertilizers, and organic amendments such as sewage sludge as well as wastewater may cause contamination at a large scale. A good example is the increased concentration of Cu and Zn in soils under long-term production of citrus and other fruit crops.

Many chemical processes are involved in the transformation of trace elements in soils, but precipitation–dissolution, adsorption–desorption, and complexation are the most important processes controlling bioavailability and mobility of trace elements in soils. Both deficiency and toxicity of trace elements occur in agroecosystems. Application of trace elements in fertilizers is effective in correcting micronutrient deficiencies for crop production, whereas remediation of soils contaminated with metals is still costly and difficult although phytoremediation appears promising as a cost-effective approach. Soil microorganisms are the first living organisms subjected to the impacts of metal contamination. Being responsive and sensitive, changes in microbial biomass, activity, and community structure as a result of increased metal concentration in soil may be used as indicators of soil contamination or soil environmental quality. Future research needs to focus on the balance of trace elements in an agroecosystem, elaboration of soil chemical and biochemical parameters that can be used to diagnose soil contamination with or deficiency in trace elements, and quantification of trace metal transport from an agroecosystem to the environment.

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## Introduction

Trace elements are defined as elements that are present at low concentrations ( $\text{mg kg}^{-1}$  or less) in most soils, plants, and living organisms [1]. Trace elements that have been extensively studied in the last decade include copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), and selenium (Se). Cu, Zn, Fe, Mn, Mo, and B are essential to the normal growth of plants, Cu, Zn, Fe, Mn, Mo, Co and Se are essential to the growth and health of animals and human beings, and Cu, Zn, Pb and Cd are the most environmentally concerning elements that have been often reported to cause contamination of soil, water, and food chains [2]. Some plants can tolerate and accumulate much higher concentrations of trace elements such as Cu, As, and Cd than regular plants [3–5]. These plants are called super-accumulators and have been used for phytoremediation of contaminated soil or water systems [6].

Trace elements enter an agroecosystem through both natural and anthropogenic processes. Soil inherits trace elements from its parent materials. Some soils have been found to have a high background of some trace elements, which are toxic to plants and wild life, due to extremely high concentrations of these elements in the parent materials. A good example is the Se toxicity problem in the Kesterson reservoir in the West-central San Joaquin Valley where soils were derived from high

Se parent materials [7]. Anthropogenic processes include inputs of trace elements through use of fertilizers, organic manures, and industrial and municipal wastes, irrigation, and wet and/or dry deposits. These processes contribute variable amounts of trace elements to the agroecosystem.

Only a small portion of trace elements in soil is bioavailable. The mobility and availability of trace elements are controlled by many chemical and biochemical processes such as precipitation–dissolution, adsorption–desorption, complexation–dissociation, and oxidation–reduction. Not all the processes are equally important for each element, but all these processes are affected by soil pH and biological processes. Therefore, it is crucial to understand some major reactions in soils that control the release of a specific trace element in the soil and the environment in order to overcome problems related to deficiency and contamination of these elements.

Accumulation of trace elements, especially heavy metals, in the soil has potential to restrict the soil's function, cause toxicity to plants, and contaminate the food chain. In recent years, it has also been found that heavy metals from point and non-point sources impair water systems, causing lesions and/or deformation in fish [8].

In this article, sources, functions, chemical and biochemical processes in soil, and impacts of some important trace elements on agroecosystems and the environment are reviewed.

## Trace elements in agroecosystems

The normal abundance of an element in earth material is commonly referred to by the geochemist as background, and for any particular element this value, or range of values is likely to vary according to the nature of the materials [9]. Trace elements in soil are derived from parent materials and anthropogenic inputs. In remote or mountain areas where impacts of human activity are relatively small, trace elements in soil are mainly inherited from parent materials, whereas in urban areas or agricultural land with a long history of crop production, the concentrations of trace elements in soil can be higher than those found in the parent materials. For instance, Cu concentrations in some citrus grove soils in Florida have been found to be as high as several hundreds  $\text{mg kg}^{-1}$ , or 10–20 times greater than the background level, due to repeated use of Cu-containing fungicides/pesticides/herbicides for sustaining citrus production [10].

## Geochemistry of trace elements

Trace elements are highly dispersed in a wide variety of minerals [9]. Cu, Zn, Cd, and Pb are often associated with sulfur, as sulfites. Under superficial environmental conditions, sulfites are quickly oxidized and Cu, Zn, Cd, and Pb are released and separated from sulfur at an early stage of mineral weathering. During soil development, Cu, Zn and Cd tend to concentrate in Mn oxides, whereas Pb is more likely enriched in the oxides and hydroxides of Fe. Under reducing conditions, Fe and Mn oxides are slowly dissolved, as  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  and  $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$ , and sulfites of these elements are formed if there is sufficient sulfur available.

## Earth crust abundance of trace elements

The earth crust is made up of 95% igneous rocks and 5% sedimentary rocks; of the latter about 80% are

shales, 15% sandstones and 5% limestone [9]. However, sediments are more frequent at the surface as they tend to overlie the igneous rocks from which they were derived. The abundance of some trace metals is shown in Table 1. Basaltic igneous rocks generally contain higher concentrations of metals, such as Cu, Zn, Cr, Co, and Ni. Cu, Zn, Co, and Mn occur mainly in the easily weathered constituents of igneous rocks such as augite, hornblende and olivine [11–13]. Of the sedimentary rock, sandstones are composed of minerals that are resistant to weathering, and usually have small amounts of trace elements. Shales, which are derived from fine sediments of inorganic and organic origin, contain larger amounts of trace elements including Cu, Zn, Mn, Pb, and Cd. Some black shales may contain  $\text{Cd} > 200 \text{ mg kg}^{-1}$ . Soils developed from these parent materials tend to reflect their chemical composition, though pedogenetic processes may modify this relationship. Soils derived from the weathering of coarse-grained materials such as sands and sandstones and from acid igneous rocks such as rhyolites and granites, tend to contain smaller amounts of nutritionally essential metals, including Cu, Zn, and Co than those derived from fine-grained sedimentary rocks such as clays and shales, and from basic igneous rocks.

## Important minerals containing trace elements

In most soils, trace metals are present in form of carbonates, oxides, sulfides, or salts. The dominant minerals of each trace metal may vary among different soils. Cu containing minerals in soil include malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ), azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ), cuprite ( $\text{Cu}_2\text{O}$ ), tenorite ( $\text{CuO}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), chalcopyrite ( $\text{CuFeS}$ ), bornite ( $\text{Cu}_3\text{FeS}_4$ ), digenite ( $\text{Cu}_9\text{S}_5$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), and tetrjedrote ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ). None of these minerals alone controls the Cu concentration in soil solution. Fe minerals in soil are siderite ( $\text{FeCO}_3$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\text{FeOOH}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), pyrite ( $\text{FeS}_2$ ), pyrrhotite

**Table 1.** Concentration range of some metals and metalloids in igneous and sedimentary rocks ( $\text{mg kg}^{-1}$ )

Elements	Basaltic igneous	Granitic igneous	Shales and clays	Limestone	Sandstone
As	0.2–10	0.2–13.8	1–17	0.1–8.1	0.6
Cd	0.006–0.6	0.003–0.18	0–11	0.05	0.05
Cr	40–600	2–90	30–590	10	35
Co	24–90	1–15	5–25	0.1	0.3
Cu	30–160	4–30	18–120	4	2
Hg	0.002–0.5	0.005–0.4	0.005–0.51	0.01–0.22	0.001–0.3
Pb	2–18	6–30	16–50	9	<1–31
Mo	0.9–7	1–6	2.5	0.4	0.2
Ni	45–410	2–20	20–250	20	2
Se	0.05–0.11	0.05–0.06		0.08	0.05
Zn	48–240	5–140	18–180	20	2–41

References: [9,11].



**Table 3.** Metal-containing pesticides used for various fruit crops and annual loading rates of metals

Common name of pesticides	Annual application (kg ha <sup>-1</sup> year <sup>-1</sup> )	Years when recommended	Fruit crops sprayed
Calcium arsenate	2.0–2.5 As	1910–1953	Apple, sour cherry
Copper acetoarsenate	1.8–1.7 As/0.2–0.4 Cu	1895–1920	Apple, sour cherry, peach, grape
Copper sulfate-calcium hydroxide	1.3–1.6 Cu	1892–1975	Apple, sour cherry, peach, grape
Fixed copper (mixtures of CuSO <sub>4</sub> and CuCl <sub>2</sub> )	1.0–3.0 Cu	1940–1975	Apple, sour cherry
Lead arsenate	4.0–8.7 Pb/1.0–2.7 As	1910–1975	Apple, sour cherry, sweet cherry, peach, grape
Zinc sulfate	5.5–7.5 Zn	1939–1955	Peach
Ferbam	0.3–0.8 Fe	1948–1975	Apple, sour cherry, sweet cherry, peach, grape
Maneb, Macozeb	0.4–0.5 Mn	1964–1975	Apple, grape
Phynyl mercuric acetate	0.07–0.10 Hg	1954–1973	Apple
Zineb	0.6–0.7 Zn	1957–1975	Apple

Reference: [25].

**Table 4.** Copper fungicides registered for controlling citrus diseases in the USA

Trade name/Common name of fungicides	Cu %	US EPA Reg. No.	Diseases controlled			
			Melanose	Greasy spot	Alternaria	Scab
Kocide 101/copper hydroxide	50	1812–300	+	+	+	+
Kocide 2000/copper hydroxide	35	1812–358	+	+	+	+
Champ dry prill/copper hydroxide	37.5	55146–57	+	+	+	+
Cuprofix disperses/basic copper sulfate	20	4581–396	+	+	+	ND
Copper-count-N/copper ammonium complex	8.0		+	ND	+	ND

Reference: [24].

metal-containing chemicals. For instance, citrus groves more than 30 years old were found to contain 200–300 mg kg<sup>-1</sup> Mehlich III extractable Cu, which is 10–15 times greater than the concentrations in non-citrus production soils [10]. In China, high Cu concentrations were also reported in soils with a >15-year grape-growing history [23]. In the USA, fungicides with high Cu concentrations are still used for preventing citrus diseases, including melonose, greasy spot, alternaria, and scab (Table 4) [24].

### Irrigation

The input of metals through irrigation varies markedly from location to location. Non-contaminated fresh and salt water contains extremely low concentrations of heavy metals, usually at or below µg L<sup>-1</sup> levels for Cu, Zn, Pb, Ni, and Cr (Table 5). Domestic and industrial wastewaters, however, often contain heavy metals in significantly higher concentrations than natural waters. Repeated use of wastewaters that have not been treated to filter heavy metals may well contribute to the accumulation of these metals in the soil.

### Dry and wet deposits

Dry and wet deposits contribute variable amounts of metals to the soil, depending on the nature and distance of point sources. Emissions from large industrial sources, including iron and steel industry, primary and secondary base metal smelters, base metal refineries, and base metal foundries often have great impact on metal accumulation in the soil [25]. Concentrations of Cu and Ni in the soil were reported to exponentially increase with a decrease in distance from the source (Fig. 1). There is also considerable emission of metals from municipal sources such as electric generating stations and incinerators [25]. Emission from automobiles that use Pb-enriched gasoline has caused a significant increase in the Pb concentration in the soils along old highways. More work is needed to quantify these sources.

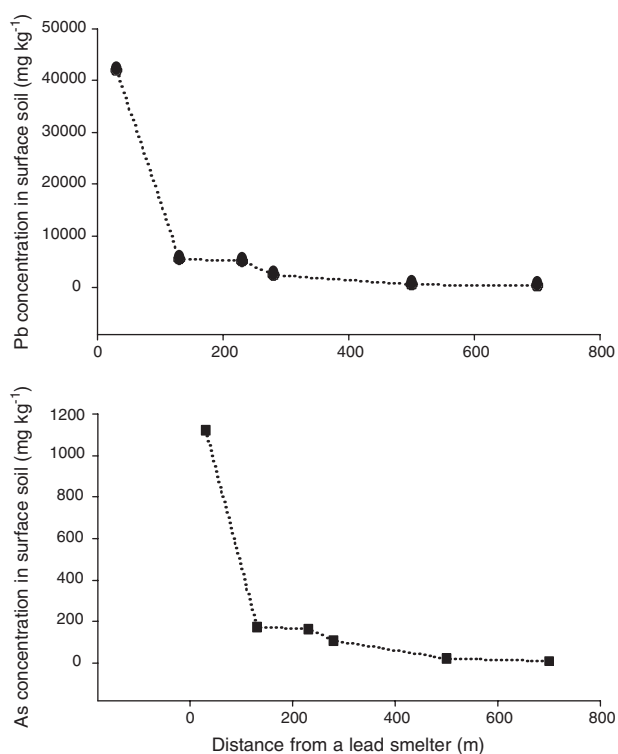
### Other point sources

Mining activities have been reported to cause heavy metal contamination to the soil in a localized area [2,25]. Metalliferous mine spoils result from disposal of metal-rich overburden and excavation wastes. The polluted soil can contain heavy metal concentrations of 100–1000

**Table 5.** Mean concentrations of some metals and metalloids in surface water and US EPA effluent limitations ( $\mu\text{g L}^{-1}$ )

Elements	Sea water	River water	US EPA wastewater effluent limitations		Major forms
			Maximum daily	Maximum monthly average	
As	3.7	0.5	84	72	$\text{HAsO}_4^{2-}$ , $\text{H}_2\text{AsO}_4^{2-}$
Cd	0.11	0.1	71	26	Particulate, $\text{CdCl}_2$
Cr	0.3	1.0	25	14	$\text{Cr}(\text{OH})_3$ , $\text{CrO}_4^{2-}$
Co	0.05	0.2	NA	NA	$\text{Co}^{2+}$
Cu	0.25	3	23	14	$\text{Cu}^{2+}$ , $\text{Cu}(\text{OH})^+$ , $\text{CuCO}_3$
Hg	0.03	0.1	2.3	1.3	$\text{HgCl}_4^{2-}$ , $\text{HgCl}_2$
Pb	0.03	3	57	32	$\text{PbCO}_3$ , particulate $\text{Pb}(\text{CO}_3)_2^{2-}$
Mo	10	0.5	NA	NA	$\text{MoO}_4^{2-}$
Ni	0.56	0.5	NA	NA	$\text{Ni}^{2+}$ , $\text{NiCO}_3$
Se	0.2	0.2	NA	NA	$\text{SeO}_3^{2-}$ , $\text{SeO}_4^{2-}$
Zn	4.9	15	82	54	$\text{Zn}^{2+}$ , $\text{Zn}(\text{OH})_2$

References: [22,23].

**Fig. 1.** Concentrations of Pb and As in surface soil as a function of distance from a lead smelter in Toronto, Canada (source: Freedman and Hutchinson, 1980).

times greater than their background [3]. Some plants that eventually adapt to the contaminated soil may develop super-accumulating traits for the metals. For instance, the ecotype of *Sedum Alfredii* Hance found in an old mining site in China has been reported to be tolerant to high concentrations of Cu, Zn, and Cd and can store large amounts of these metals in its biomass [26,27].

Disposal of metalliferous tailings causes soil contamination of heavy metals in a similar way of mine spoils.

Tailings of acid ores may produce high concentrations of metals and low pH leachates shortly after their exposure to the air. The leachate can quickly destroy soil biota and damage crops it reaches. Coal mine spoils often have this problem and cause severe pollution to the local soils [2,25].

### Outputs of trace elements from agroecosystems

Outputs of trace elements from agroecosystems include crop harvest, losses by leaching, surface runoff, and gaseous emission. Crop harvest accounts for a big proportion of the output of trace elements, although the precise amounts of metal removal vary greatly with the type of soil, crop variety, and climate conditions. For most fine texture soil, leaching of trace elements is limited because of the strong binding of these elements with soil colloids, whereas for sandy soils, especially under acidic conditions, leaching can be an important output [29]. Surface runoff losses of trace elements are often associated with transport of particulates that contain adsorbed trace elements and organic-metal complexes. Relatively few studies have been conducted to quantify surface runoff losses of trace elements. Gaseous losses are important only for Se, As, and Hg. Some volatile organic Se and As compounds are formed in plants and emitted from plant leaves. Leaf emission has been reported to be an important pathway of Se output. Hg can be converted into methyl-Hg through microbial activity and emitted from the soil.

### Biogeochemistry of trace elements in soils

The concentrations of trace elements vary greatly in soils [9]. The average concentrations of Cu, Zn, Ni, Pb, Cd and Cr in worldwide soils are 20, 10–300, 40, 10–150,

**Table 6.** Mean concentrations of some metals and metalloids in soils

Elements	Chinese soils (mg kg <sup>-1</sup> )	World soils (mg kg <sup>-1</sup> )	Metal-rich soils (mg kg <sup>-1</sup> )	Soil metal criteria (kg ha <sup>-1</sup> )
As	10.38	9.36	250–2500	15
Cd	0.097	0.06	20–800	4
Cr	< 100	20–200	—	NA
Co	5–40	10–40	100–300	NA
Cu	22	20	> 2000	NA
Hg	0.04	0.03	10–100	1
Pb	13–42	10–150	> 1%	100
Mo	0.2–6	1–5	10–100	NA
Ni	35	40	800–8000	36
Se	0.29	0.20	7	NA
Zn	< 3–790	10–300	> 1%	370
References	28	23	23	25

0.06, and 20–200 mg kg<sup>-1</sup>, respectively (Table 6). The average values of these elements in Chinese soils are comparable to these figures [28]. However, some metal-rich soils may contain trace elements at 10–1000 times greater concentrations, because of particular parent materials or contamination (Table 6).

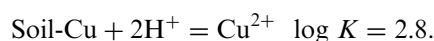
Trace elements in soils can be divided into water soluble, exchangeable, oxide-bound, carbonate-bound, organic matter-bound, and residual that is occluded in the resistant minerals and non-extractable [30]. Water soluble and exchangeable fractions are considered to be bioavailable, oxide-, carbonate-, and organic matter-bound fractions may be potentially bioavailable, but the residual fraction is mainly not available to either plants or microorganisms. The proportions of each fraction vary between soils and largely determine the availability and mobility of trace elements in the soil. Many soil factors such as pH, organic matter content, amounts and forms of oxides and carbonates, charge characteristics, as well as mineral composition influence this fractionation, the bioavailability, and transport of trace elements in the soil and within the agroecosystem [14]. Many chemical and biochemical processes are involved in the equilibria of trace elements between the solid phase and the liquid phase of the soil [11].

The major chemical processes that control mobility and availability of trace elements in the soil include precipitation–dissolution, adsorption–desorption, and chelation [11]. The relative importance of each process is dependent on soil reactions and subject to rhizospheric effects [31].

### Precipitation–dissolution

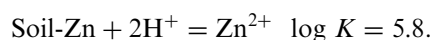
Precipitation–dissolution is an important process that controls the solubility of trace elements in calcareous soils and soils with a pH above 7.0.

According to the solubility-pH curve established under standard conditions (1 atmosphere pressure and 25 °C), soil solution Cu is controlled by the reaction:



Various Cu minerals that might be expected in soils including CuCO<sub>3</sub>, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (malachite), Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> (azurite), Cu(OH)<sub>2</sub>, and CuO (tenorite), are too soluble to persist, particularly in acidic soils [29]. The mineral CuFe<sub>2</sub>O<sub>4</sub> (cupric ferrite) has a solubility lower than the above mentioned Cu minerals, but lower than soil-Cu and therefore may control Cu solubility in soils. However, this mineral is affected by oxidation-reduction conditions and tends to dissolve under reducing conditions. The released Cu then reacts with sulfide to form much less soluble copper sulfide.

Soil solution Zn is controlled by the following reaction:



Based on solubility, ZnO, Zn hydroxides, and ZnCO<sub>3</sub> are much too soluble to persist. The mineral Zn<sub>2</sub>SiO<sub>4</sub> (willemite) that is of intermediate solubility may have some effects on Zn concentration in soil solution. ZnFe<sub>2</sub>O<sub>4</sub> (franklinite), the most stable Zn mineral and most close to soil-Zn solubility, likely controls solution Zn in soils [32].

The concentration of solution Fe in aerated soils is approximately 10<sup>-39</sup> mol L<sup>-1</sup>. Ferrihydrite (Fe<sub>2</sub>O<sub>3</sub> · 9H<sub>2</sub>O) has a solubility in the range of 37.0–39.4 [33] and, therefore, is likely the mineral that controls Fe in soil solution.

Mn concentration in soil solution is affected by both pH and redox level. In a redox environment below pe-pH (pe = -log[e]), MnCO<sub>3</sub> is the most stable Mn mineral; in a pe-pH range of 14–16.6, MnOOH limits

the solubility of Mn, and it is  $\text{MnO}_2$  (pyrolusite) that controls Mn solubility at pe-pH above 17 [32].

### Adsorption–desorption

Metals can be adsorbed onto surfaces of soil colloids through non-specific adsorption (by static electric force) and specific adsorption (formation of chemical bonds between the ion and the surface) [34]. Adsorption of Cu, Pb, and Cd in highly weathered variable charge soils (Ultisols) was found to involve both mechanisms and to have some common characteristics [35–37]. They include:

- Adsorption results in a significant decrease in soil pH due to replacement of  $\text{H}^+$  and/or  $\text{Al}^{3+}$  from soil surfaces, although the pH drop varies between soils.
- Adsorption consists of a fast stage followed by a much slower process and the isotherms of adsorption fit well with some physical-chemical models, such as the Langmuir, and Freundlich equation.
- Adsorption is pH-dependent, generally increasing with pH.
- Adsorption is affected by temperature, but in a complicated manner.
- Adsorption is not completely reversible, and a portion of the adsorbed metals cannot be desorbed even with five successive desorptions using  $\text{NH}_4\text{Ac}$ .
- Presence of competitive ions reduces adsorption of any individual metal.
- Presence of organic acids such as citric acid or oxalic acid reduces adsorption of Cu, Pb, and Cd in variable charge soils, likely because of chelating effects.
- Companion anions, especially  $\text{Cl}^-$ , influence adsorption of the metals Cu, Pb, and Cd. This influence is related to the formation and stability of Cu-anion complexes [38].

### Chelation

Chelation is a process during which trace elements form stable complexes with organic or inorganic ligands:

$\text{M}^{a+} + \text{L}^{b-} \rightarrow \text{ML}^{(a-b)}$ , with the equilibrium constant  $K = (\text{ML})/(\text{M})(\text{L})$ , in which ionic charges are omitted for simplicity. Greater  $K$  value means higher stability of the complex. Chelation enhances dissolution and bioavailability of trace elements. Under field conditions, organic matter such as humic acids, fulvic acids and organic acids produced during decomposition of organic matter or exudated from plant roots can serve as ligands to chelate trace elements in soil. Many artificial organic acids such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and *N*-(2-hydroxyethyl)ethylenetriaminetriacetic acid (HEDTA) have been used in greenhouse or field to enhance mobility and plant availability of trace elements. Some chelation reactions of organic substances with trace metals and their equilibrium constants are presented in Table 7. Chelation has been reported to be responsible for increased availability of trace elements in the plant rhizosphere, especially for those plants that can excrete organic acids in response to low availability of the metals [11,39,40].

### Deficiency, contamination, and remediation

Plants require an adequate supply of trace elements or micronutrients for their normal physiological and biochemical functions. Micronutrient deficiencies and toxicities are widespread and have been documented in various soils throughout the world. Deficiencies of micronutrients occur when the plant cannot acquire sufficient amounts of micronutrients for its internal needs, whereas an excessive supply of trace elements, especially heavy metals, results in toxicity to the plant. Deficiencies of essential micronutrients induce abnormal pigmentation, size, and shape of plant tissues, reduce leaf photosynthetic rates, and lead to various detrimental conditions [41]. Specific deficiency symptoms appear on all plant parts, but discoloration of leaves is most commonly observed. Deficiency symptoms of low mobile nutrients (Fe, Zn, and Mo) appear initially and primarily on upper leaves or leaf tips, while deficiency

**Table 7.** Conditional equilibrium constants ( $\log K$ ) of complexation of some natural and synthesized organic acids with heavy metals

Metals ligands	Electrolytes	Cu	Zn	Pb	Ni	Mn	Cd
Soil fulvic acids	0.1 mol L <sup>-1</sup> KCl (pH 5.0)	4.00	3.70	4.10	4.20	3.70	4.10
Lake humic acids	0.02 mol L <sup>-1</sup> tris (pH 8.0)	9.48–9.58	5.03–5.31	ND	5.19–5.51	4.30–4.85	4.57–4.70
EDTA <sup>4-</sup>	0.01 ionic strength	19.7–22.9	10.7–17.5	19.0–22.1	19.5–23.0	14.8–18.2	17.4–20.5
DTPA <sup>5-</sup>	0.01 ionic strength	22.6–33.9	19.5–28.9	19.9–24.8	21.4–30.8	16.8–21.6	20.2–28.4
HEDTA <sup>3-</sup>	0.01 ionic strength	18.3–20.8	15.4	16.3–18.5	17.9–20.5	11.6	13.9–16.3
Citric acid	0.01 ionic strength	2.1–13.3	5.6–12.3	5.2–12.7	6.1–12.7	4.5–8.6	4.5–12.0

References: [11,39].



symptoms of mobile nutrients (B and Mn) appear primarily on lower leaves. Deficiency and toxicity symptoms may be confused with drought, diseases, insect and other damage, so that a correct diagnosis may be difficult without experience. Many plants have a narrow concentration range between deficiency and toxicity for some trace elements [14]. For instance, the Cu concentration range for normal growth of most plants is only 5–20 mg L<sup>-1</sup>, and the plant may suffer from Cu deficiency at concentrations below 5 mg L<sup>-1</sup> or from Cu toxicity at concentrations above 20 mg L<sup>-1</sup>.

Contamination of a soil with heavy metals takes place when the soil cannot sustain normal plant production or cannot produce foods that are adequate for animals or human beings in terms of health and nutrition due to an excessive supply of these elements in the soil. Soil contamination with heavy metals is often caused by industrial point sources, repeated use of metal-enriched fertilizers, biosolids, or wastewaters. Remediation of soils contaminated by heavy metals can be very costly due to strong chemical association of the metals with soil components. In recent years, phytoremediation has been suggested as a more cost-effective approach for remediating metal-contaminated soils or water systems [42]. Phytoremediation is a natural remediation of soil or water by growing plants that can efficiently take up metals from the contaminated system and then removing the metals from the system by harvesting the plant biomass [43].

### Occurrences of trace element deficiency and toxicity

Cu deficiency is often observed in plants grown in soils inherently low in Cu (coarse textured and calcareous soils) and in soils high in organic matter, where Cu is readily chelated [44]. Higher than normal Cu supplies usually inhibit root growth more than shoot growth [45]. Use of Cu containing fungicides and antihelminthic compounds (insecticides) in agriculture has resulted in Cu toxicity in some plants, but naturally occurring Cu toxicity is relatively uncommon [46].

Fe deficiency is a global problem and occurs in numerous crops [40,47]. Fe deficiency is not caused by Fe scarcity in the soil, but by various soil and plant factors that affect Fe availability by inhibiting its absorption or impairing its metabolic use [40,48]. In the majority of soils, the total concentration of soluble Fe in the rhizosphere is often far below the level required for adequate plant growth [40]. Induced Fe deficiency chlorosis is widespread and is a major concern for plants growing on calcareous or alkaline soils due to their high pH and low Fe [49]. Bicarbonate, nitrate, and environmental factors influence the occurrence of Fe deficiency chlorosis in plants, which occurs in young leaves due to inhibited chloroplast chlorophyll synthesis as a conse-

quence of a low Fe nutrition status of the plants [49]. Plant species that commonly become Fe deficient are apple, peach, citrus, grape, peanut, soybean, sorghum, and upland rice. Fe toxicity (bronzing) can be serious for production of crops in waterlogged soils. For wetland rice, Fe toxicity is the second most severe yield limiting mineral disorder after P deficiency. Audebert and Sahrawat [50] reported that application of P, K, and Zn with nitrogen to an Fe toxic lowland soil in Ivory Coast reduced Fe toxicity symptoms and increased lowland rice yields.

Mn toxicity is probably more of a problem than Mn deficiency globally. Mn deficiency occurs in plants grown in organic, alkaline, calcareous, and poorly drained, slightly acid soils and in coarse-textured sandy soils [15]. Over-liming of acid soils may induce Mn deficiency. Mn toxicity is a major factor for reduced production of crops grown in acid soils, as is aluminum toxicity. The ability of the plant to tolerate Mn toxicity is affected by the plant genotype, the concentration of silicon in the soil, the temperature, light intensity, and physiological age of the leaves [51]. Conditions leading to the buildup of high levels of Mn in soil solution are high levels of total Mn, soil pH below 5.5, high soluble Mn relative to calcium, reduction of Mn under low oxygen caused by poor drainage, soil compaction, and excess water from irrigation or rainfall [52].

Mo deficiency is widespread in legumes, maize, and cauliflower grown in acid mineral soils containing high amounts of Fe oxides and hydroxides. Cu/Mo ratios <2 will normally reduce Mo deficiency in plants [53]. Occurrence of Mo toxicity is rare, but high levels of Mo in forages may induce Cu deficiency in animals. Mo concentrations >5–10 mg kg<sup>-1</sup> dry weight in forage tissue have induced toxicity in ruminants (“molybdenosis” or “teart”) [54]. Such disorders of Mo occur in forage grown in poorly drained and highly organic soils.

Zn deficiency in plants is widespread throughout the world [55,56]. Increased pH due to liming reduces plant available Zn. High clay and P supply and low soil temperatures are also known to promote Zn deficiency [40]. Lowland rice grown in limed or calcareous soils often exhibits Zn deficiency [56]. Chaney [57] indicated that after ‘natural’ phytotoxicity from aluminum or Mn in strongly acid soils, Zn phytotoxicity is the next most extensive micronutrient phytotoxicity compared to Cu, Ni, Co, Cd, or other trace element toxicities. With decreasing soil pH, Zn solubility and uptake and potential for Zn phytotoxicity increases. At comparable soil pH and total Zn concentrations, Zn phytotoxicity is more severe in plants grown in light-textured than in heavy-textured soils. This is mainly because of differences in specific Zn adsorption capacities of the soil. Continued applications of Zn to alkaline sandy soils low in organic matter and clay tend to develop Zn toxicity in plants even though occurrence of Zn toxicity is relatively

**Table 8.** Pb, Zn, and Cd concentrations in soils and radishes as affected by aerial contamination

Metals	Distance from road (m)	Soil concentrations (mg kg <sup>-1</sup> )	Concentrations in radishes (mg kg <sup>-1</sup> dry matter)			
			Protected site		Unprotected site	
			Roots	Tops	Roots	Tops
Pb	200	30	19	13	21	26
	7	299	33	25	38	41
Cd	200	0.1	0.9	1.6	1.0	3.1
	7	0.6	1.7	2.9	1.8	5.0
Zn	200	10	48	70	81	141
	7	60	82	152	121	248

Reference: [62].

rare under field conditions [58]. Liming was effective in overcoming Zn toxicity in peanuts [59].

Even though no clear evidence exists for Ni deficiency in plants, Ni toxicity is of concern for plants grown in soils receiving sewage sludge and industrial byproducts. Ni as well as Co toxicity may also be found in plants grown in soils formed from serpentinite or other ultrabasic rocks [60]. Co deficiency may occur in plants grown in highly leached sandy soils derived from acid igneous rocks and in calcareous or peaty soils [14] as well as in coarse-textured, acid-leaching alkaline or calcareous soils and humic rich soils [60].

### Heavy metal contamination

Heavy metal contamination of soils has markedly increased in the past few decades. Many factors such as metal-enriched parent materials, mining or industrial activities, non-point sources of metals, especially automotive emission, and use of metal-enriched materials, including chemical fertilizers, farm manures, sewage sludges, and wastewater irrigation, can contribute to this contamination [2,25].

In general, naturally occurring trace metal pollution is localized. Soils derived from some ultra-basic igneous rocks, especially serpentine, have been reported to contain extremely high concentrations (up to 1000–10,000 mg kg<sup>-1</sup>) of Ni and Cr and very few plants can survive in these soils [2,9,25]. Soils developed from some fine-texture shales may contain high concentrations of Mo causing molybdenosis in cattle grazing on this land.

Mining and refining of metal ores can result in severe soil contamination with heavy metals in the impacted areas. Jiang et al. measured total Cu concentrations > 5000 mg kg<sup>-1</sup> in an old mine soil and > 500 mg kg<sup>-1</sup> in a soil used for disposing tail wastes from the nearby refinery [61]. Only a few Cu tolerant plants are able to grow in this high Cu soil. Aerial emission of Pb, Cd, and

Zn from car exhausts is another common source of pollution for soils along highways. Lagerwerff [62] measured Pb, Cd, and Zn concentrations in soils and radish in two locations: 7 and 200 m from a highway, and found remarkable differences between the two locations (Table 8).

In agricultural production systems, soil contamination of heavy metals is mainly related to input and accumulation of these elements through repeated use of metal-enriched chemicals such as fungicides, farm manures, chemical fertilizers, and biosolids [2]. Fungicides and pesticides containing Cu, Zn, and As have been widely used to protect citrus, apples, peaches, strawberries, and other fruit crops. In Florida, soils from old citrus groves (> 40 years) can contain Mehlich III extractable Cu as high as > 200 mg kg<sup>-1</sup>, as compared to 10–20 mg kg<sup>-1</sup> in the soils of newly planted citrus groves [10]. Similar trends were reported for Zn and As.

P fertilizers are among the other sources of heavy metal input into agricultural systems. On average, phosphate rock contains 11, 25, 188, 32, 10, and 239 mg kg<sup>-1</sup> of As, Cd, Cr, Cu, Pb and Zn, respectively [16]. Phosphate rock from Morocco and other North African countries may contain much higher levels of these elements. The tolerable limits of soil for Cd and Cr are 2 and 100 mg kg<sup>-1</sup>, respectively, which are lower than the concentrations found in phosphate rocks. Repeated use of P fertilizers such as triple superphosphate may result in accumulation of these elements and increase the contamination potential, especially of Cd, in the soil.

Due to increased use of As, Cu, and Zn as additives to the animal diet, with > 80% of the added metals being excreted by the animals, manures from some commercial pig or poultry farms may contain considerable amounts of heavy metals. In England, application of high Cu/Zn manure was reported to raise corn grain Cu and Zn concentrations from 2.79 to 3.17, and 20.7 to 25 mg kg<sup>-1</sup>, respectively, whereas use of low Cu/Zn

manures was found to reduce grain Cu and Zn concentrations [2], due to complexation of Cu and Zn by organic substances. Biosolids and/or municipal composts made of biosolids and yard wastes often contain higher concentrations of Cu, Zn, Cd, Cr, and Ni than those found in soils [63]. Heavy application of biosolids and/or composts have been reported to increase these elements in the soils. In Florida, only class A biosolids that contain relatively low concentrations of heavy metals and other toxic elements are permitted for agricultural use. The guidelines of metal concentrations in biosolids for agricultural use from US EPA and other government agencies are presented in Table 2.

### Phytoremediation

Phytoremediation is a new technology for the clean-up of heavy metal polluted soils and water systems. It is a cost-effective “green” technique, and can remediate a site without dramatically disturbing the landscape [6,64]. The unique capacity of hyperaccumulators to accumulate high metal concentrations in the shoots make these plants suitable for the development of phytoremediation [6]. The effectiveness and efficiency of phytoremediation are largely dependent on plant characteristics such as fast growing, large biomass, easy to harvest, and tolerance and accumulation of a range of heavy metals in shoots.

Two types of plants are currently investigated widely in laboratory and greenhouse. The first type is the naturally occurring metal hyperaccumulator, such as *Thlaspi caerulescens*, a Zn hyperaccumulator which is capable to accumulate and tolerate  $> 10,000 \text{ mg kg}^{-1}$  Zn in its aboveground biomass. However, its application in the field is limited due to its small size and slow growth [5,6,64]. The second type is the metal tolerant plant, such as *Brassica juncea* (Indian mustard), which can take up large quantities of metal contaminants from the soil due to its high biomass, and despite of its modest metal concentration in the plant [5,64]. To extract significant quantities of metals from soils by plant accumulation, the ideal plant species should have a greater biomass potential while accumulating high concentrations of metal contaminants.

The Chinese native herbs *E. splendens*, the dominant plants in old Cu mining deposits, have evolved metal tolerance over years of adaptation [26,27,65]. *E. splendens* can tolerate high levels of Cu, which has been confirmed by field surveys in old mining areas [27,65,66], and solution culture studies [67]. In the fields of the mined area, this plant accumulated  $2288 \text{ mg kg}^{-1}$  Cu in the root and  $304 \text{ mg kg}^{-1}$  Cu in the shoots. In solution culture, the growth of *E. splendens* was found to be optimal at Cu supply levels of up to  $100 \mu\text{mol L}^{-1}$ , and

at 500 and  $1000 \mu\text{mol L}^{-1}$  Cu supply levels, shoot Cu concentrations reached 1133 and  $3417 \text{ mg kg}^{-1}$  on a dry weight basis, respectively [61]. Moreover, *E. splendens* had an average shoot biomass of  $11,000 \text{ kg ha}^{-1}$  and an average root biomass of  $2420 \text{ kg ha}^{-1}$  in the field experiment [3]. The characteristics of large biomass and great tolerance and accumulation of Cu make *E. splendens* a great candidates for the phytoremediation of Cu contaminated soil.

More recently, *Sedum Alfredii* Hance has been found to be a Zn hyperaccumulating plant species native to China [5]. *S. alfredii* showed no visible symptoms of metal toxicity when exposed to  $3671 \mu\text{mol L}^{-1}$  Zn [68], the highest Zn concentration in shoots was 2% [5,26]. Recently, *S. alfredii* has been observed to have exceptionally high tolerance to Cd, both in terms of solution concentration and tissue Cd concentration [27]. Cd concentrations in leaves and stems were found to be over  $9000 \text{ mg kg}^{-1}$  when plants were grown at Cd levels of  $400 \mu\text{mol L}^{-1}$ , at which no obvious visual toxic symptoms were observed.

The phytoremediation approach seems promising, but its successful application in the field is still limited. More work is needed to develop technologies for more efficient harvest and safe disposal of the metal-containing plant biomass.

### Interactions between trace elements and microorganisms

When a soil is contaminated with heavy metals, microorganisms in the soil are the first living organisms subjected to their impacts. Therefore, microbial biomass ( $C_{\text{mic}}$ ), the living component of soil, has been used as an early indicator of heavy metal contamination [19–21,69,70]. Heavy metals decrease microbial biomass by directly killing or biochemically disabling organisms in soil. The amounts of  $C_{\text{mic}}$  in agricultural soils where sewage sludge or sewage sludge-containing composts had been applied were much smaller than in soils having received farmyard manure over the same period [19].  $C_{\text{mic}}$  decreased with increasing amounts of EDTA-extractable Ni and Cu. These effects were detectable even after 20 years of application. A combination of Zn and Cu at high concentrations had an additive adverse effect on the amounts of  $C_{\text{mic}}$  present [20]. At similar concentrations, Cu decreased  $C_{\text{mic}}$  by 50% more than did Zn. Addition of Cu to three red soils at rates of  $500 \text{ mg kg}^{-1}$  lowered  $C_{\text{mic}}$  by 10 to  $>40\%$ , depending on soil texture [71]. The toxic effect was more pronounced in sandy soil than in clayey soil, probably due to differences in adsorption and bioavailability of Cu between the two soils.

The microbial quotient (MQ) is defined as percent of  $C_{\text{mic}}$  in the total organic biomass ( $C_{\text{org}}$ ) [72] and is a

measure of heavy metal contamination [20,21,69,70]. The MQ was reported to decrease from 1.5% in soil receiving uncontaminated sewage sludge to 1% in soil receiving Zn contaminated sludge ( $457 \text{ mg kg}^{-1}$  soil) and to 0.5% in soil receiving Cu contaminated sludge ( $415 \text{ mg kg}^{-1}$  soil) [20]. This implies that the MQ is more sensitive to increased heavy metal concentrations than  $C_{\text{mic}}$  itself. The decrease in MQ could be caused by decreased microbial biomass and/or partially disabled function of its ability to mineralize organic matter. As a result of decreased MQ, the turnover rate of organic matter decreased in soil with the application of heavy metal contaminated sewage sludge. Valsecchi et al. [21] found that high input of heavy metals through long-term effluent decreased the MQ by more than one order of magnitude, i.e. from 4% in the slightly contaminated soil to 0.2% in the heavily contaminated soil. These results suggest that the MQ can provide a sensitive indicator of the adverse effects of increased heavy metal concentrations on the soil microbial biomass.

The basal or maintenance respiration rate ( $q\text{CO}_2$ ,  $\text{mg CO}_2\text{-C kg}^{-1}$  per day) is a measure of microbial activity [69,73]. Increasing concentrations of heavy metals often increase the  $q\text{CO}_2$  and the ratios of  $q\text{CO}_2/C_{\text{mic}}$  and  $q\text{CO}_2/\text{organic carbon (C)}$ . This means that heavy metal toxicity reduces the energy utilization efficiency of the microbial metabolic processes, which then require greater amounts of C for maintenance, thus reducing the quantity of C incorporated into the microbial biomass [21].

The microbial metabolic quotient (MMQ), also called specific respiration, is defined as respiratory  $\text{CO}_2$  released per unit microbial biomass (the ratio of  $q\text{CO}_2/C_{\text{mic}}$ ,  $\% \text{ day}^{-1}$ ) [74,75]. The MMQ was found to significantly increase with increasing concentrations of heavy metals whereas the ratio  $q\text{CO}_2/C_{\text{org}}$  decreased in the soils contaminated with heavy metals [21], indicating a state of microbial stress due to heavy metal toxicity.

Microorganisms differ in their sensitivity to nutritional and environmental changes [70]. Some populations more tolerant to stress can survive whereas more sensitive populations may disappear under changed conditions. Thus, parameters of microbial community structure, which can be assessed by various physiological, biochemical or molecular techniques, have been recommended as a biological indicator of metal contamination in soils. The soil microbial community is sensitive to increased concentrations of heavy metals [70]. An increase in heavy metals concentrations by sewage sludge application decreased biomarkers of actinomycetes, arbuscular mycorrhizal fungi, and total fungi, but increased relative amount of bacteria [76]. Bacteria have been observed to be more resistant to high concentrations of heavy metals than other microbial populations [77,78].

## Transport of trace elements from agroecosystems to the environment

Increased anthropogenic inputs of heavy metals in soils have received considerable attention, since transport of the metals may result in an increased content of heavy metals in the groundwater or surface water [79–81]. High Cu and Zn concentrations were detected in the sediments of St. Lucie Estuary in South Florida [82,83]. Heavy metal inputs include those from commercial fertilizers, liming materials, and agrochemicals, sewage sludges and other wastes used as soil amendments, irrigation waters and atmospheric deposition [84]. Soils receiving repeated applications of organic manures, fungicides, and pesticides exhibited high concentrations of extractable metals [81,85–90] and subsequently resulted in increased heavy metal concentrations in runoff [81].

The mobility of metals depends not only on the total concentration in the soil but also on soil properties, metal properties and environmental factors. Heavy metals accumulate in soils in various forms: water soluble, exchangeable, carbonate associated, oxide associated, organic associated and residual forms. The metals present in these categories have different mobility [81,91,92]. Water soluble and exchangeable fractions are readily released to the environment, whereas the residual fractions are immobile under natural conditions. Dowdy and Volk [93] suggested that the movement of heavy metals in soils could occur in sandy, acid, low organic matter soil if subjected to heavy rainfall or irrigation.

Field monitoring was conducted by He et al. [94] to evaluate heavy metal loadings in surface runoff from Florida sandy soils under commercial citrus and vegetable production and their relations to extractable metal concentrations in the soils. The concentrations of dissolved metals (Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn, Mn, and Mo) in surface runoff were monitored over a two-year period at 11 sites of vegetable farms and citrus groves in St. Lucie and Martin counties, Florida, USA. A total of 1277 surface runoff samples were collected for measuring dissolved metals using an inductively coupled plasma atomic emission spectrometer. Surface soils of each field site were sampled and analyzed for extractable metals. The concentrations of the metals in the runoff ranged widely from nondetectable level to 2.80, 18.5, 14.1, 1475, 9227, 39.3, 30.4, 1401, 2118, and  $15.0 \mu\text{g L}^{-1}$  for Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn, Mn, and Mo, respectively. Spatial and temporal variations in the concentrations of the heavy metals and runoff discharge were noted among the different sites. The concentrations of Cd, Co, Cr, Ni, Pb, and Mo were generally low, and 94%, 96%, 55%, 32%, 93%, and 61% of the samples had metal concentrations below the detection limits for Cd ( $0.22 \mu\text{g L}^{-1}$ ), Co ( $0.52 \mu\text{g L}^{-1}$ ), Cr ( $0.42 \mu\text{g L}^{-1}$ ), Ni ( $0.61 \mu\text{g L}^{-1}$ ), Pb ( $1.96 \mu\text{g L}^{-1}$ ), and Mo ( $0.81 \mu\text{g L}^{-1}$ ),

respectively. However, 0.62%, 30% and 23% of the samples had Cu, Fe, and Mn concentrations higher than their drinking water standards, respectively. Annual loads of dissolved metals in the runoff varied widely among monitoring sites and were different between the years 2001 and 2002. The concentrations of the metals in the surface runoff were associated with the accumulation of heavy metals in the soils, and 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> extractable Cu, Fe, Zn, and Mn were significantly correlated with Cu, Fe, Zn, and Mn concentrations in the surface runoff [94].

Zhang et al. [95] compared five extraction methods (0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>, Mehlich I, Mehlich III, DTPA-TEA, and 1 mol L<sup>-1</sup> NH<sub>4</sub>OAc) for their extractable Cu and Zn amounts in soils in relation to concentrations of these elements in surface runoff from citrus and vegetable production systems. They found that mean dissolved Cu in field runoff water was significantly correlated with the extractable Cu obtained only by the 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>, Mehlich I, or DTPA-TEA methods. Dissolved Zn in runoff water was only significantly correlated with Zn extractable by 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. The highest correlations to dissolved Cu in runoff were obtained when soil-available Cu was extracted by 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. These results indicate that 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> extractable Cu and Zn are the best soil indexes for predicting readily released Cu and Zn in sandy soils [95]. Both runoff discharge and 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> extractable Cu and Zn levels had significant influences on Cu and Zn loads in surface runoff water [95]. Whether these results are applicable to other soils remains to be tested.

## Acknowledgements

This study was, in part, supported by an Outstanding Young Scientist Grant and a research grant (20177020) from the Natural Science Foundation of China (# 40025104) and a grant from the Science and Technology Ministry of China (# 2002CB410800).

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