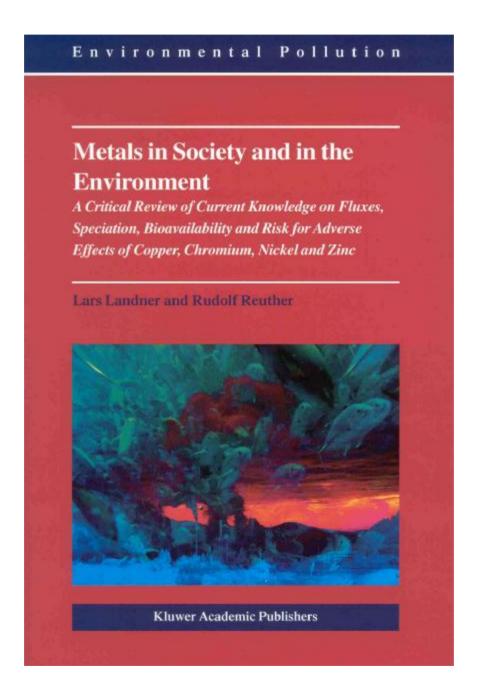
## Metals in Society and in the Environment

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#### **Summary**



Can be ordered from the Publisher by <u>www.springeronline.com</u> ISBN 1-4020-2740-0 A paper back version (ISBN 1-4020-2741-9) can be ordered from **MITF** (**Metal Information Task Force**). Price: 22 Euro per book + VAT and shipping.

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The previous metal monographes on **copper** (in English and Swedish), **zinc** (in English and Swedish) and **chromium**, **nickel** and **molybdenum** (only in Swedish) can be ordered from MITF.

### **Executive Summary and Conclusions**

#### 0.1 Introduction

Today, authorities responsible for regulating environmental quality in Europe, both at the Union and at the State level, are frequently referring to results from 'new research' in their efforts to regulate or restrict uses of metals and metal-containing materials. This has resulted in an increasing demand for critical, scientifically sound evaluations and compilations – in a transparent and holistic format – of relevant information about metal stocks and fluxes in society and the properties, behaviour and effects of trace metals in the environment.

One of the longest standing international programmes for assessing the effects of chemicals, including metals, on man and the environment, the "Environmental Health Criteria (EHC) Programme", was initiated in 1973. This effort is nowadays an integral part of the "International Programme on Chemical Safety" (IPCS), a cooperative programme of the three United Nations Agencies UNEP, ILO and WHO. While the first EHC monograph (on mercury), published in 1976, focused entirely on human health aspects, later EHCs for metals – at least since 1989 – also treated environmental aspects. For example, the EHCs for nickel (EHC # 108, publ. in 1991), for copper (EHC # 200, publ. in 1998) and for zinc (EHC # 221, publ. in 2001) included comprehensive sections on generic environmental exposure and environmental effects of the metals involved.

The environmental risk assessment of trace metals requires a cautious approach because of the natural occurrence of metals, the great variations in metal speciation, affecting the metal's bioavailability and toxicity and – for some metals such as chromium, copper, nickel and zinc – their essentiality for many organisms. These aspects were emphasized by the IPCS, e.g. in the EHCs for copper and zinc, as summarized by the following conclusions:

- The total concentration of an essential element such as copper or zinc, alone, is not a good predictor of its bioavailability or toxicity.
- The toxicity of copper or zinc will depend on environmental conditions and habitat types, thus any risk assessment of the potential effects of these metals on organisms must take into account local environmental conditions.
- Because copper and zinc are essential elements, procedures to prevent toxic levels in the environment should not incorporate safety factors that result in recommended concentrations being below natural levels or causing deficiency symptoms.

Moreover, under the "Existing Substances Regulation" (793/93) of the European Union, a thorough assessment of the human health and environmental risks associated with production and use of **zinc** and **five zinc compounds** is being conducted by Dutch environmental authorities. In parallel with this "mandatory" environmental risk assessment (RA) for zinc, as an industry initiative, a voluntary RA of **copper** and **several copper compounds** is underway in cooperation with Italian authorities and the European Commission. These current trace metal environmental RA activities have called for updates of previous compilations of data on exposure and effects of metals in the environment. The new RAs have also directly encouraged important new research programmes, some of which are sponsored by the international metals industry.

Initiated by the Nordic metal industry, three monographs on "Metals in Society and in the Environment", covering copper, zinc and major alloying metals in stainless steel (chromium, nickel and molybdenum), were prepared by the Swedish Environmental Research Group (MFG) in the late 1990s, and were published both in Swedish and in English (Landner and Lindeström, 1996; 1997; 1998; 1999; Walterson, 1999). The aim was to make a balanced and comprehensive compilation, together with a scientific appraisal, of available data on fluxes and stores of metals in the anthroposphere, on metal flows to and between environmental compartments, and on metal behaviour, exposure and effects in humans and in natural ecosystems. However, the current intense research on metal speciation and the upcoming new methodologies for prediction of metal bioavailability in water, sediments and soils, as a result of important scientific advances, made it urgent to bring this information up-to-date.

For this reason, the Swedish "Metal Information Task Force" took an initiative, in the middle of 2002, to engage MFG to prepare an updated monograph on metals. In this follow-up work, special emphasis was given to new scientific advances made in the field of metal speciation in environmental media and to the interpretation of its consequences for the mobility, bioavailability and toxicity of trace metals in water, sediments and soils. Among the highlights that we will present and discuss in this monograph are two metal speciation-based concepts or tools recently developed to improve our understanding of environmental effects of metals, the "Acid Volatile Sulphides" (AVS) concept to predict metal bioavailability in sediments and the "Biotic Ligand Model" (BLM) to calculate the availability and toxicity of metals to aquatic biota. The metals included in this updating effort are, primarily, copper, nickel and zinc, and to some extent also chromium.

# 0.2 Metal Fluxes from Society to the Environment and between Environmental Media

The use of 'materials (or substance) flow analyses' to establish metal mass balances in defined geographical areas has turned out to be an efficient approach to improving our understanding of resource availability and long-term environmental change. The construction of well-quantified metal cycles for a country – or a continent – may be helpful for designing sound policies for production, consumption and recycling of metals and can be used as a basis for decisions supporting an environmentally sustainable economic and social development.

A good example of such an exercise, where a team of researchers from Germany, Switzerland and the USA worked out a comprehensive copper cycle for an area covering the European Union and Poland, is presented and examined. The justification for this broad definition of the system boundaries is that both mining, primary and secondary production sites as well as a multitude of consumption sites are present within the boundaries. This exercise was made to incorporate all life stages and dissipative flows of copper in Europe, i.e. both recycling rates, various waste fluxes and dissipative flow rates have been estimated with greater accuracy than earlier. Consequently, the effort has been successful in providing a clearer picture of current copper fluxes and future needs to improve sustainability with regard to copper production and use on a continent-wide basis. Other recent attempts to develop practical tools for selecting the best options for nation-wide metals management, e.g. a research programme for dynamic mathematical modelling of metal flows in the Netherlands, turned out to be less successful.

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In the effort to design sound management systems for metals on a continental scale, it may also be of great value to broaden our understanding of nature's tolerance to long-term metal exposure. Hence, we have included a brief summary of a recent book by L. Lindeström, containing detailed descriptions of the variable environmental impacts caused by the mining and smelting activities that went on for one thousand years at the Falun Copper Mine.

On the other hand, studies of metal fluxes to and from systems covering a limited geographical area, e.g. a single city, may be used to focus on specific aspects, such as:

- the impacts of urban metal flows on society's metal recycling systems and on the local environment:
- the role and relative significance of diffuse sources of metal dispersion to the natural environment; and
- the transformation and speciation of metals during transport from sources in the anthroposphere to the final metal sinks.

A comprehensive analysis of the stores and fluxes of seven metals, including chromium, copper, nickel and zinc, within and out from the City of Stockholm was carried out, in 1995, as part of a broad Swedish research programme ("Metals in the Urban and Forest Environment"). This effort has generated invaluable information, that will be presented and critically discussed in Chapter 3 of this monograph.

The various attempts to establish metal balances for defined geographical areas have helped to identify gaps in the available knowledge and to initiate new research to fill in these gaps. In many cases, it was deemed necessary to quantify a specific metal flux more accurately, e.g. by using better experimental designs or improved measuring techniques. The new and more reliable data on metal fluxes that we will review in Chapter 4 relates to:

- fluxes resulting from corrosion of roofs and other metallic materials, followed by runoff from buildings and other urban constructions;
- fluxes from the traffic sector in built-up urban areas to biota in receiving waters; and
- metal releases from plumbing systems in houses followed by fluxes to sewage treatment plants, sewage sludge and agricultural soils.

#### 0.2.1 The European Copper Cycle in the Mid-1990s

Some of the major findings from the recently published copper cycle for Europe (EU + Poland), valid for the year 1994, may be summarized as follows:

- The European smelting industry was supplied with about 600 kt of copper from ores mined within the region and 280 kt in imported concentrates.
- However, most of the copper used in Europe, 1,900 kt, is mined, smelted and refined outside of the region.
- The industrial output of non-alloyed copper products amounts at 2,650 kt, while copper in alloys is about 780 kt (75% of copper in finished products is in pure form).
- Since about 920 kt of copper enters the waste management system, the yearly growth of the copper stock in Europe is about 2,500 kt or 6 kg per capita.
- The annual growth rate of copper in landfills and tailings ponds is 1.4 kg per capita.
- The fastest growing copper waste category is waste from electrical and electronic equipment (growth rate 5-10%), which requires more efficient recycling strategies.

• Since about 2 kg of copper is generated annually in consumer waste in the region, and only about half of this amount, on average, is recycled, the study gives valuable information as to what waste categories should be given priority in improving the recycling rate, e.g. by developing appropriate technologies to separate waste streams.

#### 0.2.2 Metal Fluxes from Mining Waste - Falun Copper Mine

During the lifetime of the Falun Copper Mine, where mixed sulphidic ores were mined for more than a millennium, huge amounts of mining and smelting waste were emitted to the surrounding environment. Current estimates have arrived at total emissions in the order of 6,000 kt of sulphur dioxide and 15 kt of copper released to the atmosphere, and 500 - 1,000 kt of copper, lead, zinc and cadmium discharged to forest soils and watercourses, at the time causing dramatic impacts on the environment as well as on human health. However, a detailed assessment of the present environmental situation has revealed that the soils and terrestrial ecosystems in the vicinity of Falun have recovered to a remarkable degree during the  $20^{th}$  century after a series of emission-reducing measures had been introduced .

After the late 1980s, when treatment of the mine-water started, also the effluent-receiving river and lakes, that used to be exposed to very high metal concentrations in the water (for total copper 140-fold, and for total zinc 1,000-fold increases above regional background levels), exhibited clear signs of recovery. Only based on a clear appreciation of the speciation and the low bioavailability of harmful metals and of possible antagonistic (protective) interactions between metals such as zinc and other, more toxic metals, e.g. cadmium, lead and copper, was it possible to explain this rapid return to functioning aquatic ecosystems.

#### 0.2.3 Urban Metal Flows - the Case of Stockholm

According to the final reports from the project "Metals in the Urban and Forest Environment", the stocks and fluxes of metals in the City of Stockholm, in 1995, were as follows:

Stock/flux	Unit	Copper	Zinc	Chromium	Nickel
Total stock in city	ktonnes	123	28	5.6	2.5
Net growth rate	% per year	1.6	4.3	4.6	6.4
do.	kg per capita	2.8	1.7	0.4	0.2
Loss (as solid waste)	% per year	0.24	2.5	1.8	1.2
Loss (to environment)	% per year	0.01	0.09	0.02	0.04
do.	tonnes/year	12	24	0.8	0.6
Emissions to water	tonnes/year	2.6	9.1	0.4	1.5
Increase over background	%	15-24	41-54	29-40	14-15
Flux to aquatic sediments	tonnes/year	1.7	4.0	1.0	0
To sewage sludge	tonnes/year	9.0	12	0.9	0.8

Per capita growth of the copper stock (2.8 kg/year), thus, was about half of that in Europe. The types of goods causing the greatest releases of metals in Stockholm were found to be:

- for copper: water pipes in buildings, followed by motor vehicle brakes;
- for zinc: motor vehicle tyres, followed by various galvanized materials;
- for chromium and nickel: road pavements, followed by tyres.

A substantial part of the released metals is channelled through the city sewerage system (including storm-water sewers) to sewage treatment plants, where metals are partitioned between sludge and effluents to the recipient, where a certain fraction is deposited in the bottom sediments and the remainder transported further out to the Baltic Sea. Some recent attempts to determine the degree of bioavailability – in the aquatic environment – of the fraction of metals that is emitted from the street traffic have not been entirely conclusive.

#### 0.2.4 Critical Steps in Metal Fluxes from Cities to the Environment

New and accurate information on critical metal fluxes has been produced in studies, e.g. by Swedish researchers. The annual runoff of metals from copper, galvanized steel or stainless steel sheets (of different age), after atmospheric corrosion in a relatively clean urban air (in Stockholm, with sulphur dioxide,  $SO_2$ , levels of about  $3 \mu g/m^3$ ), has been measured during extended periods of exposure on roofs. While the corrosion rate shows a typical variation with time, the runoff rate remains relatively constant when atmospheric variables do not change. The runoff rate of copper from copper roofs is in the range 1.0-2.0 g Cu/m² and year, depending on the age of the roof. Runoff rates are clearly a function of the atmospheric  $SO_2$  concentration, which has fallen dramatically in most major cities over the past 20-30 years, of rainwater pH and of the annual precipitation. Thus, in Singapore with up to 8 times higher air pollution and rainfall than in Stockholm, the copper runoff rate is about 5.7 g/m² and year.

For zinc, the annual runoff rate in Stockholm was determined to be 3.1 g Zn/m², while those of chromium and nickel from stainless steel were 0.2-0.7 mg/m² and 0.1-0.8 mg/m².

The speciation and fate of the released metals (copper, zinc) were studied in the runoff water on its transport from the roofs to the natural receiving water bodies. At the edge of a roof, copper and/or zinc in runoff largely occurs in the form of free, hydrated ions, but after the metal-laden water had percolated through soil or come in contact with concrete or limestone, 96-99.8 % of the total metal content in the runoff was retained and the remaining small residue of copper and zinc in the percolate had a very low bioavailability. These results indicate that environmental dispersal of bioavailable species of copper and zinc as a result of corrosion and runoff from roofs and galvanized structures can be effectively controlled by letting the runoff water percolate over concrete surfaces or through soil.

The extensive use of water pipes and heat exchangers made of copper may cause significant releases of copper, especially in areas with corrosive drinking water (rich in carbonate and/or organic ligands, forming soluble copper complexes). The released copper usually does not constitute any risk for human water consumers, but the copper in the sewage is finally incorporated into the sewage sludge. This is one reason why some concern has been expressed regarding the safety of sewage sludge in cases where such sludge is applied on arable land. However, studies (over 18 growth seasons) of possible impacts of yearly application of copper-enriched sewage sludge to agricultural fields have come to the conclusion that an application rate in the range of 1.4-4.2 kg Cu per ha and year would not be harmful on soils used to raise cereals. The conclusion was drawn on the basis of no-observed-effects on soil fauna or soil microbes, on crop yields and copper content in crops even at the higher loading rate. Moreover, copper accumulation in the soil was marginal at the lower loading rate, with an insignificant risk of exceeding existing limit values for copper in agricultural soils to be fertilised with sludge, even in the long term. Thus, a provisional limit value for a sustainable copper loading would be  $\sim 1.4$  kg Cu per ha and year.

## 0.3 Speciation, Bioavailability and Effects of Trace Metals in the Environment

Assessments of the fate and biological effects of trace metals in the environment based solely on total concentrations of the metals in the various media (water, sediment or soil) is no longer state-of-the-art or scientifically justified. Although water, sediment and soil quality criteria for metals in most countries are still based on the total concentrations, it is now becoming more and more evident also for regulatory authorities that it is the actual metal species that determines mobility, bioavailability and toxicity of a metal, but also that metal speciation depends on the site-specific seasonal and spatial variations existing in a particular water, sediment or soil system.

The scientific community has vigorously responded to this new understanding by swiftly developing a whole array of new methods to describe and quantify the distribution and dynamics of various metal species occurring under different physico-chemical conditions in the environment. New, detailed models and descriptions of the mechanisms of formation of metal species and their transformations have been developed. A broad review of the new investigative tools and how to use them for widening our understanding of the behaviour and effects of trace metals in the environment is given in Chapters 5-7 of this monograph.

#### 0.3.1 In the Water Column – BLM as a Tool for Prediction of Toxicity

It has been repeatedly demonstrated that the toxicity, e.g. the acute median lethality, LC<sub>50</sub>, of a trace metal to a single aquatic species, varies widely between different tests. Variations in toxicity of the same metal are directly related to variations in water hardness, pH, content of suspended solids and the concentration of organic ligands that can form complexes with the metal. All these water quality characteristics modify the speciation of a metal and, thereby, its bioavailability. The most available (and toxic) species of a divalent metal in aqueous solution usually is the free ion (e.g. Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>), but also a few inorganic complexes (e.g. CuOH<sup>+</sup> and CuCO<sub>3</sub>) have the potential to contribute to the total toxicity of these metals to aquatic organisms. It has also been shown that various common cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and H<sup>+</sup>) compete with the trace metals for binding sites at the organism-water interface and, thus, tend to reduce the overall toxic response.

The recently developed "Biotic Ligand Models" (BLMs) for copper, nickel, silver and zinc interacting with fish, daphnids and algae, are able to handle all the above mentioned sources of apparent variation in toxicity and are now, after refinement, powerful tools for making accurate predictions of the toxicity of a trace metal in natural waters with widely differing chemical composition. A basic assumption of the BLM is that metal toxicity occurs as a result of metal ions reacting with binding sites at the organism-water interface, e.g. the gills, thus forming a metal-biotic ligand (metal-BL) complex. The concentration of this metal-BL complex directly reflects the magnitude of the resulting toxic effect, independent of the physico-chemical characteristics of the surrounding water. Hence, the metal toxicity can be predicted when metal speciation, the activity of each cation in solution, and the stability constant for each cation binding to the BL of the actual organism are known.

It has been demonstrated that the concentrations of trace metals in gills of fish were constant predictors of the acute toxicity of the metals to the fish, although water hardness varied up to tenfold. In contrast, total metal concentrations (e.g., for copper, nickel or zinc) in the water or the free-ion activities of these metals could not be used as accurate toxicity predictors. Also with regard to the prediction of chronic toxicity, the BLM has been successfully used. Chronic toxicities of copper and zinc to rainbow trout, *Daphnia magna* and green microalgae could be predicted within a factor of two compared to the observed values, when performing toxicity tests both in laboratory waters and in waters collected from the field. Dietary uptake of copper in daphnids did not enhance the chronic toxicity of waterborne copper, an observation that does not exclude, however, that dietary uptake of trace metals may influence the toxic response, e.g., in typically particle-ingesting organisms.

#### 0.3.2 In Aquatic Sediments – AVS as a Tool for Prediction

Bioavailability and toxicity of sediment-associated trace metals towards bottom-dwelling organisms are governed by site-specific factors like sediment properties, the redox potential, the chemistry of pore-water and overlying water, and by the physiology and feeding behaviour of the fauna. In oxidized sediment layers, iron and manganese oxy-hydroxides and particulate organic carbon mainly control the bioavailability of trace metals, while in anoxic sediments, the most important regulating factors are pH and sulphides. Undisturbed sediments rich in organic matter may have a very sharp gradient in redox potential, so that anoxic conditions appear at a depth of 2-5 mm, although the sediment surface is well oxidized.

A multitude of speciation methods is now available to determine typical species of trace metals in sediments, their relative distribution among various sediment fractions, or the kind and kinetics of transformations between different metal forms. Examples are wet chemical methods like sequential extractions, which successively extract metals from the sediment matrix by using increasingly powerful extractants. The outcome provides information about the strength of binding between a metal and the major sediment fractions, and hence on its potential mobility and bioavailability. Other, more sophisticated approaches include measurements of the sediment's capacity to buffer protons and electrons, thermodynamic and kinetic solubility calculations, new spectroscopic techniques (like X-ray absorption spectroscopy) and the determination of the acid-volatile sulphides (AVS).

The AVS approach has attracted a lot of interest, since it turned out to be a rapid, simple and cheap method for predicting at least the <u>absence</u> of trace metal-related toxicity of aquatic sediments. It is well known that sulphide, derived from sulphate-reducing bacteria in the porewater of anoxic sediment layers, forms relatively insoluble complexes with various trace metals, thereby rendering them non-bioavailable and non-toxic. These metal sulphides (AVS) can be liberated from sediments by treatment with 1 N HCl. In fact, sediments containing an excess of AVS over "simultaneously extracted metals" (SEM) are characterized by very low pore-water metal concentrations, as well as low metal bioavailability and toxicity. Both the U.S.EPA and the Environmental Directorate of the European Commission have now proposed the  $\Sigma$ SEM / AVS ratio, or the  $\Sigma$ SEM – AVS difference, as a reliable measure of the bioavailability of sediment-associated metals, e.g. cadmium, lead, copper, nickel and zinc.

In general, the model has been found to be a good predictor of the <u>non-toxicity</u> of trace metals in sediments after normalisation to the sediment organic matter content, but may not be fully reliable in predicting that a certain sediment <u>is</u> toxic to the benthic fauna. In other words, the

SEM/AVS approach tends to overestimate the toxicity of a sediment, i.e. a greater number of sediments are predicted to be toxic than what is really the case.

Although the SEM/AVS approach has been rather successful, so far, in predicting the bioavailability and toxicity of trace metals in sediments, recent studies have pointed to some weaknesses in the model that leave room for future improvements. Moreover, there is a need to apply more fine-scale sediment sampling techniques, such as the "diffusive gradients in thin films" (DGT) technique, which allows the documentation of metal releases from solid phases in discrete locations within a sediment core, thus providing a better understanding of the exact interactions between burrowing organisms and sediment-associated trace metals.

#### 0.3.3 In Soils - Laboratory versus Field Tests

In spite of the many differences between sediment and soil systems, their geochemical similarity has justified the development and use of similar methods for metal speciation in both media. A first approximation for the speciation of soil-associated metals may be achieved by experimentally determining solid-liquid partitioning coefficients ( $k_d$ ). Such coefficients help to differentiate between metals dissolved in the soil solution and those bound to particulate phases. But they tell us very little about the dynamic relationships existing between free, labile and non-labile metal species. Measured  $k_d$  values depend above all on the dissolved organic matter (DOM) content and on the total dissolved metal concentration in the soil solution. Thus, it is evident that every factor influencing soil DOM will also affect metal partitioning. Therefore, competitive adsorption models rather than simple solid-solution ratios (as expressed by  $k_d$ ) are increasingly used to predict concentrations of dissolved metals.

Dissolved metal concentrations in soils vary widely with seasonal changes in redox potential, which may be triggered by light and temperature variations and, hence, by the activity of micro-organisms. Effects of soil aging on trace metal fluxes usually become manifest as a stronger adsorption and reduced extractability of metals. Depletion of trace metals in the vicinity of plant roots, due to uptake, promotes metal transfer from solid phases into solution. Plants can actively mobilise essential metals such as iron, copper and zinc from solid phases under deficiency conditions. Due to these site-specific phenomena, it is increasingly important to describe the kinetic, rather than only the thermodynamic equilibria for metals in soils.

In order to predict trace metal bioavailability to plants, the new "effective concentration" ( $C_E$ ) concept has attracted considerable interest, because it fulfils the requirement of including kinetic aspects into the assessment. It relies upon using the "diffusive gradients in thin films" (DGT) technique, by which a metal chelating resin is introduced into the soil to mimic metal uptake by plants. Like plants, the DGT responds to the labile metal pool, re-supplied from both the soil solution and the solid phases. Measured DGT fluxes can be quantitatively related to  $C_E$ , and thus, provide a measure of the potential hazard of metals in contaminated soils.

In general, soil quality guidelines for trace metals are still not expressed in terms of bioavailable metals. A problem is, of course, that the bioavailable fraction of a trace metal in soil is typically variable and organism-specific, i.e. it may not be the same for a higher plant, a soil invertebrate or micro-organism species. Some soil scientists have stressed that it is necessary to consider the regional, natural background concentration of the metal in question and to formulate permissible levels in terms of "critical enhancement", i.e. the number of times that a metal is allowed to increase in the soil relative to the background level. However,

metals freshly introduced into the soil matrix have a different behaviour (mobility, bioavailability and toxicity) than metals gradually introduced over a long period of time, so the question on metal aging in the soil has to be taken into account. This was demonstrated in some recent studies of copper, lead and zinc. In one major study, zinc toxicity was shown to be consistently lower in field contaminated soils than in corresponding zinc-spiked soils. The importance of soil properties for the degree of toxicity, that a specific zinc addition will cause, became evident. We may even deepen our understanding of the observed metal-related toxicity variations in soils by normalizing the toxicity data to the particular soil type, thereby deriving specific "soil sensitivity factors".

### 0.4 General Conclusions

One of the most popular subjects of investigation among environmental chemists and ecotoxicologists for at least three decades has been the behaviour and effects of trace metals in the environment. The upsurge of this research happened concomitantly with the rapid and widespread introduction and use of atomic absorption spectrometric (AAS) methods. Over several decades, a huge amount of analytical data have accumulated describing total metal concentrations, e.g. of chromium, copper, nickel or zinc in water, in sediment or in soil samples (after extracting the target metal(s) in the sample). Now, most of the data has turned out to be of rather limited or no value for the understanding of trace metal interactions with biota. So, real advances in metal eco-toxicology were rather poor during that period.

It may be stated that the science of metal eco-toxicology did not really take off the ground until eco-toxicologists understood that trace metals, including the essential elements, occur in many different forms (species) in the environment and that only a few of these species, under certain circumstances, are bioavailable, i.e. can be taken up by a target plant, animal or microorganism. Thus, it was not until people started to take a more sceptical attitude to the previously felt all-pervading blessings of the AAS and new analytical techniques were developed to consider metal speciation in environmental media that metal eco-toxicology entered its 'Golden Age'.

Today, when performing generic environmental risk assessments of trace metals (such as chromium, copper, nickel or zinc) or when evaluating the environmental impact of trace metal emissions in a defined geographical area, it is no longer acceptable to routinely start out from laboratory toxicity data and divide them by conventional safety (or application) factors to derive "predicted no-effect concentration". First, the natural background concentration of the relevant species of the assessed metal is usually fully considered. In case it is an essential element, it is state-of-the-art to consider the possibility of rectifying a situation of deficiency. An indispensable part of the assessment is to investigate (or predict) the potential distribution of bioavailable metal species under site-specific, realistic environmental conditions and to base this assessment – as far as possible – on long-term data from the field (rather than on laboratory data or short-term metal-spiking experiments), in order to take into account kinetic equilibria that may form in the real world and under realistic time scales. Since it is a highly dynamic habitat in which trace metals have to be assessed, direct measurements of the occurring metal species may only give a snapshot, and therefore, an erroneous picture of the true situation. Consequently, it may be more correct to base the assessment on a thorough knowledge of stability constants and ion activities of critical metal species, and on the use of mathematical models, such as the BLM, to calculate the potential risk of adverse effects, in view of possible, relevant combinations of site-specific environmental characteristics.