

**ISSUES IN ECOLOGICAL RISK ASSESSMENTS OF INORGANIC METALS AND
METALLOIDS**

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ABSTRACT

Ecological risk assessment (ERA) is a process that evaluates the potential for adverse ecological effects occurring as a result of exposure to contaminants or other stressors. ERA begins with hazard identification/problem formulation, progresses to effects and exposure assessment, and finishes with risk characterization (an estimate of the incidence and severity of any adverse effects likely to occur). Risk management initially sets the boundaries of the ERA and then uses its results for decision-making. Key information required for an ERA includes: the emissions, pathways and rates of movement of contaminants in the environment; and, information on the relationship between contaminant concentrations and the incidence and (or) severity of adverse effects. Because of specific properties and characteristics of metals in general and of certain metals in particular, a generalized ERA process applicable to organic substances is inappropriate for metals. First, metals are naturally occurring and can arise, sometimes in very high concentrations, from non-anthropogenic sources; organisms can and do adapt to a wide range of metal concentrations. Second, certain metals (e.g., copper, zinc) are essential for biotic health, which means there is an effect threshold for both deficiency and excess, and that standard body burden indices such as bioaccumulation factors (BCFs) can be misleading. Third, metals can occur in the environment in a variety of forms that are more or less available to biota but adverse biological effects can only occur if metals are or may become bioavailable. Fourth, whereas the bioavailability and hence the possibility of toxicity of persistent organic substances are mainly dependent on their intrinsic properties (i.e., lipophilicity), those of metals are generally controlled by external environmental conditions. Examples include pH and ligands, which affect the metal speciation and coexisting cations (e.g., H^+ , Ca^{2+}) which compete with the metal ions. ERAs involving metals must include the above four major considerations; other considerations vary depending on whether the ERA is for a site, a region, or is global in scope.

Key Words: metals, metalloids, ecological risk assessment, toxicity, speciation

INTRODUCTION

Metals and metalloids are natural components of the biosphere, which are not produced *per se* by human beings, but whose form and distribution (in different environmental compartments) can be affected by human activities. Like all substances, they are a contaminant if present in excess compared to background levels and/or in a form that would not normally occur in a particular environmental compartment. Again like all substances, they are pollutants if, as contaminants, they result in adverse biological effects.

However, because they are natural, they have certain unique properties that distinguish them from human-produced contaminants as well as from organic substances in general. These differences are recognized by the scientific community, but are not yet fully accepted by the regulatory community. Ecological risk assessments (ERA) are becoming increasingly important in both assessing the results of historic pollution (retrospective ERA) and in predicting future effects of such pollution as well as of future possible contamination or remediation (predictive ERA). However, not all risk assessors appreciate the need to treat metals and metalloids differently than other substances within the generalized ERA framework. Moreover, there is presently not a good recognition of what this entails not only in the context of a site-specific ERA, but also in the context of regional or even global ERA.

The purpose of this paper is to summarize key issues related to ERA of metals and metalloids as they apply to retrospective and prospective ERA, and at three possible geographic scales (site-specific, regional, global). Specific references are provided for readers desiring more detail. The relative significance to these issues of selected ongoing research initiatives is also discussed.

GENERAL PROCESS FOR ERA

ERA has its roots as a tool for environmental decision making and has been evolving rapidly since the 1980s. It is a process that evaluates the potential for adverse ecological effects occurring as a result of exposure to contaminants or other stressors. There are two advantages to ERA. The first is that it comprises a framework for gathering data and evaluating their

sufficiency for decision-making. The second is that it recognizes, considers, and reports uncertainties in estimating adverse effects of stressors (because of the diverse and complex nature of ecosystems, uncertainty can never be fully eliminated).

Distinguishing “risk” and “hazard” is the key to understanding the process and product of ERA. Hazard is the inherent capacity or *possibility* of a stressor causing adverse effects. Theoretically, any substances can be hazardous: *sola dosis facit venenum* (there is nothing that is not a poison beyond a certain threshold dose; Paracelsus, 1493-1541). In contrast, risk is the likelihood or *probability* of such adverse effects occurring to a receptor. Adverse effects occur only when a receptor is exposed (e.g., via inhalation, ingestion, or contact) to a stressor at a sufficiently high or low concentration and after a sufficiently long duration. Thus, the risk of the stressor is determined not only by its presence in the environment, but also by its concentration and the duration of exposure.

Risk management initially sets the boundaries of the ERA and then uses its results for decision-making (Figure 1). A typical ERA process consists of three steps in the U.S.: problem formulation, analysis (exposure and effects characterization), and risk characterization (U.S. EPA, 1998), and four steps in Canada and in the European Union (EU): hazard identification, dose-response assessment, exposure assessment, and risk characterization (CCME, 1996; Chapman, 1996). Key information required for an ERA includes: the emissions, pathways and rates of movement of contaminants in the environment; and, information on the relationship between contaminant concentrations and the incidence and (or) severity of adverse effects.

The first step (i.e., Problem Formulation / Hazard Identification) involves articulating the ERA purpose, defining the problem, identifying stressors that could cause adverse effects, and determining a plan for the subsequent analysis and risk characterization. Environmental quality guidelines (EQGs) are often used in this step to identify stressors that could cause an adverse effect (i.e., stressors or contaminants of concern). ERA then moves on to the next step (i.e., Exposure and Effects Characterization) to collect and assess data to determine how exposure to stressors is likely to occur (i.e., exposure characterization) and under this exposure what are the potential and type of adverse effects that may occur (i.e., effects characterization). Different

types of information, various assumptions and their uncertainties, and different types of models or data interpretation may be required in this step. The exposure and effects profiles are then integrated in the final Risk Characterization step to estimate the incidence and severity of adverse effects likely to occur. To reduce the uncertainty, risk characterization generally builds the final risk estimates upon different lines of evidence, using a weight-of-evidence approach. Lines of evidence may include evidence from: (1) laboratory studies; (2) field observations; (3) model predictions; and (4) professional judgment.

The final ERA product is an estimate of the probability of ecological effects that may occur or are occurring. In addition, the uncertainty (or degree of confidence) in the risk estimates is indicated, lines of evidence supporting the risk estimates are cited, and the significance of observed/predicted adverse ecological effects is discussed. Stakeholders can then use the report for decision-making.

TYPES OF ERA

ERA can be divided into two types related to predictive ability, and three types related to geographic areas. Overall, ERAs can be either retrospective or prospective. In other words, they can evaluate risks after the fact (e.g., contaminated sites) or before stressors enter the environment (e.g., new product releases). Although Fairbrother et al. (1997) argue that retrospective ERA is more properly “diagnostic ecology”, they do agree that such assessments bear similarities to the ERA framework. Thus the term “retrospective ERA” is retained for the purposes of this discussion and relative to various efforts to assess historic contamination (e.g., Peeters, Gardeniers & Koelmans, 2000).

Geographically, ERAs can be site-specific (e.g., related to a specific point source discharge or contaminated site), region-specific (e.g., related to a particular watershed, encompassing multiple sources), or global. Regional ERAs are a relatively new area for research and development (e.g., Landis and Wieggers, 1997).

Accuracy is higher and uncertainty lower for site-specific compared to regional ERAs, and even more so compared to global ERAs. For example, site-specific ERAs will comprise far more knowledge of the following than larger-scale ERAs: species composition; habitat; physico-chemical factors; interactions among different environmental compartments (e.g., water, sediment, air); frequency, magnitude, and duration of stressors. In addition, ERAs can involve substance-related stressors such as metals and metalloids, or can involve biotic (e.g., species introductions) or abiotic (e.g., habitat loss) stressors (e.g., Landis and Wieggers, 1997). The basic ERA paradigm for substance-related stressors is shown in Figure 2. ERAs can be done at various levels of complexity, primarily either at screening or detailed levels; simpler screening level ERAs are based on numerical hazard quotients (HQ) (Hill et al., 2000).

ERA ISSUES SPECIFIC TO METALS AND METALLOIDS

Although the above-mentioned general process for ERA applies to all stressors, approaches to acquiring and interpreting ERA information can differ greatly for different stressors. From a historical point of view, most ERA approaches have been developed for synthetic organic chemicals, in particular for those that are highly persistent in the environment such as DDT and PCBs (Lee and Allen, 1998). Given the vast difference in the environmental behavior of metals/metalloids and organic chemicals (Table 1), ERAs of metals and metalloids need be treated differently from those of organic chemicals in general (Chapman, 1996; Lee and Allen, 1998).

Source: Natural Occurrence

All metals and metalloids are naturally occurring in the environment, as they are natural components of the Earth's crust. Table 2 lists the most recent estimation of crustal concentrations of a few metals and metalloids that are of major environmental concern. Metals and metalloids present in the Earth's crust can be released into the surficial environment by many natural processes. Physical and chemical weathering, for example, break down rocks and release metals and metalloids into soils derived from such weathering, and into surface waters. Volcanic activities can also directly release crustal metals and metalloids into the atmosphere, surface waters, and soils. As a result, metals are present naturally throughout the atmospheric, aquatic

and terrestrial environments. Background concentrations of metals and metalloids in the environment are hence above zero and can vary greatly in different environmental media (e.g., soils, sediments, water) and under different geological and environmental conditions. For instance, Table 2 also shows typical concentrations of some metals and metalloids in marine and fresh waters and freshwater sediments and soils of the US. These values are not necessarily background concentrations (which are extremely difficult to determine due to global contamination), but they can be regarded as baseline concentrations because all the samples were taken from locations without known anthropogenic pollution or mineral deposits (Shacklette and Boerngen, 1984; Gough, Severson & Boerngen, 1988; Rice, 1999). A striking observation from Table 2 is that baseline concentrations of metals and metalloids in soils and sediments in different regions can vary from one to over five orders of magnitude.

Local concentrations of metals and metalloids in the environment can be influenced by human activities. However, unlike synthetic organic chemicals that are introduced into the environment by human activities, human activities do not introduce additional amounts of metals and metalloids into the environment. The global bulk concentration of any metal or metalloid in all media is constant with time. Instead, human activities influence environmental concentrations of metals and metalloids through enhancing the release of metals and metalloids from the crust and altering their distribution among different environmental media. In other words, humans dig out and distribute but do not invent metals and metalloids.

The implications of natural occurrence of metals and metalloids in the environment for ERA have not been well appreciated. Specifically, environmental concern related to metals and metalloids should not be triggered by their presence in the environment, as for some synthetic organic chemicals, but rather by any change in the level of their natural presence. Both their ambient and background (if determinable) or baseline concentrations need to be determined. The focus should not only be on the absolute value of the ambient concentration, but also on the difference between the ambient and background concentrations. In addition, since the background concentration of a metal or metalloid varies greatly in different areas, background or baseline concentrations should be measured, where possible, site specifically. A global, national or regional mean of background concentrations is often useless in an ERA.

Fate: Transformation

Once they enter the environment, both metals/metalloids and organic chemicals undergo a variety of chemical and biological processes. However, there is a fundamental difference in their fates in the environment. While organic chemicals are more or less degradable (i.e., can be broken down to simple compounds such as CO₂), metals and metalloids generally do not degrade (with the exceptions of organometallic compounds which resemble organic chemicals, and of radioactive elements). Instead, metals and metalloids can be transformed into different chemical forms or species. For example, cadmium can be present in water as dissolved cadmium ion (Cd²⁺), as dissolved complexes with humic substances and other ligands, as surface complexes coated on iron and manganese oxides, and as insoluble sulfide solids. The speciation of metals and metalloids, i.e., the relative make-up of different forms of a metal/metalloid in an environmental medium, is determined by the nature of the metal/metalloid and by many site-specific environmental parameters, such as pH, redox potential (Eh), and the constituents of the environmental medium. For more information on speciation, see:

[http://www.speciation21.plymouth.ac.uk/;](http://www.speciation21.plymouth.ac.uk/)

http://www.iupac.org/reports/provisional/abstract99/traceelements_290200.html.

The above websites contain proposed speciation definitions as follows. Speciation of an element is defined as the distribution of an element amongst defined chemical species in a system. Chemical species comprise the specific form of an element defined as to nuclear composition, electronic or oxidation state, and/or complex or molecular structure. Speciation analysis comprises the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample.

Due to the general degradability of organic substances in the environment, persistence is often used as a criterion in the first step of ERA (i.e., hazard identification). For instance, Environment Canada classifies an organic substance as persistent if any one of its half-lives in the following four environmental media exceed the following criteria (Environment Canada, 1995): air, ≥ 2 days; surface water, ≥ 6 months; soil, ≥ 6 months; and sediment, ≥ 1 year. Such a hazard identification criterion is inappropriate for metals and metalloids for which the term

“persistence” is meaningless (Chapman, 1996; OECD, 1998; IWG, in press). For example, metals are not persistent in the water column of natural water bodies (Di Toro and Paquin, 2000).

Bioavailability

Metals and metalloids also differ greatly from organic chemicals in the way in which they interact with organisms. A large group of non-ionic organic chemicals is believed to be taken up by organisms via diffusion across the lipid bilayer of biological membranes. The bioavailability of an organic substance is thus largely controlled by its lipophilicity or hydrophobicity, which is often measured by its partitioning coefficient between octanol and water (K_{ow}). Generally, a higher K_{ow} implies a higher affinity for the lipid bilayer and hence a higher potential to be taken up by organisms, with the exception of substances with very high K_{ow} s which may not be readily bioaccumulated.

Except for organometallic compounds (e.g., methylmercury) and a few lipophilic metal complexes [e.g., $HgCl_2^0$ (Mason, Reinfelder & Morel, 1996); Cd-xanthate complexes (Block and Glynn, 1992); Cu-oxine complexes (Croot et al., 1999); Cu-, Cd-, Pb-diethyldithiocarbamate complexes (Phinney and Bruland, 1994)], metals and metalloids and their inorganic compounds generally behave differently. Metals and metalloids in their elemental form (i.e., non-ionic) are less or not bioavailable (exceptions include elemental mercury which because of its low vapor pressure can be readily inhaled and can be toxic). In contrast, dissolved metal and metalloid ions are more bioavailable. Since dissolved metal ions are highly hydrophilic they cannot readily pass through the bilipid layer. Instead, uptake of metals and metalloids is thought to occur by facilitated diffusion through proteinaceous ionophores (Simkiss and Taylor, 1995). For example, cadmium has been shown to be taken up via calcium transporters in aquatic invertebrates (Craig, Hare & Tessier, 1999), fish (Wicklund and Runn, 1988) and mammals (Hinkle, Kinsella & Osterhoudt, 1987). Silver uptake by fish may occur via sodium and chloride transporters (Wood et al., 1996). However, not all the forms of a metal/metalloid can pass through these transporters and be taken up by organisms; the fraction that can be taken up by organisms is, as a simplification, called the bioavailable fraction. In fact, various metal forms or species in solution may react with the metal transporters present in the external plasma membrane, to form a simple surface metal complex (M-X-membrane) or, in some cases, a ternary surface metal complex

(L_nM-X -membrane). Normally, the metal is stripped of its ligands before/during the (slow, rate-limiting) transport across the membrane, so that the metal entering the cell "loses its identity". In other words, it is no longer associated with the ligands to which it was bound in solution or to which it was bound at the cell surface. In many cases this "bioavailable" fraction is correlated to the activity or concentration of free metal ions (Campbell, 1995). Bioaccumulation and toxicity are also controlled by other ions such as hydrogen and calcium that can compete with the metal for the specific uptake sites (Hare and Tessier, 1996; Playle, 1998; Alsop and Wood, 1999).

Biological Effects

Positive Effects: Essentiality

Whereas the biological effects of synthetic organic chemicals are generally negative (Figure 3A), uptake of metals and metalloids can be harmless (i.e., no effects), toxic or even beneficial (Figure 3B and C). For instance, many metals and metalloids are essential for the normal growth, development and reproduction of organisms. These include not only abundant elements ("essential macronutrients") such as calcium, magnesium, potassium, and sodium, but also trace elements ("essential micronutrients") such as chromium, cobalt, copper, iron, manganese, molybdenum, nickel, selenium, vanadium, and zinc (Table 3). Elements such as copper, iron, manganese, and molybdenum can exist in more than one oxidation state in cells (e.g., Fe(II) versus Fe(III)) and can catalyze essential life processes that involve electron transfer (e.g., photosynthesis, respiration, and nitrogen fixation). Elements such as nickel and zinc do not readily undergo oxidation state changes but can catalyze essential life processes that involve hydrolytic transformation (e.g., hydration and dehydration of carbon dioxide) (Stumm and Morgan, 1996; Butler, 1998). The metalloid selenium acts as a strong antioxidant in animals. Recent studies have also found that cadmium, which was usually considered a nonessential element, can be essential under certain circumstances. For instance, in zinc-depleted coastal and marine waters, cadmium can play a direct role in the enzyme carbonic anhydrase in diatoms (Price and Morel, 1990; Lee, Roberts & Morel, 1995; Lane and Morel, 2000).

The essentiality of these metals and metalloids results in a bell-shaped dose-response curve, with deficiency symptoms occurring at low concentrations and toxic effects occurring at high concentrations (Figure 3B). Between the two extremes there is generally an optimal

concentration range within which an organism experiences optimal growth, development and reproduction. When the environmental concentration of an essential element is within the optimal concentration range, organisms can regulate their internal concentrations of the element through binding and detoxification by metallothioneins in animals and bacteria (Roesijadi, 1992 or phytochelatins in algae, plants, and some fungi (Grill, Winnacker & Zenk, 1985; Ahner and Morel, 1995). This is fundamentally different from synthetic organic chemicals for which there is generally no deficiency and no optimal effects (Figure 3A).

No Effects: Tolerance and Adaptation

Non-essential metals and metalloids such as lead and antimony generally do not have explicit positive effects to organisms because they do not have direct nutritional or biochemical functions. Nevertheless, adverse effects may not be observed at low metal levels due to detoxification and adaptation (Figure 3C). Since metals and metalloids have been in existence on the Earth since the formation of the planet, organisms emerging and evolving on the Earth have more or less adapted to background levels of metals and metalloids in their habitats. In addition to functioning in the regulation of essential metals, metallothioneins (in animals and bacteria) and phytochelatins (in algae, plants, and some fungi) are also involved in the detoxification of nonessential metals because of their high affinity for these metals (Roesijadi, 1992; Ahner and Morel, 1995). When organisms are exposed to elevated levels of metals, these low-molecular-weight proteins and peptides are induced to bind and detoxify excess metals. Organisms can also detoxify metals by isolating the metals and metalloids within their tissues as granules, as insoluble metal precipitates, or by excretion. For instance, some crustaceans (i.e., organisms such as crabs and shrimp) can accumulate metals in their chitinous exterior, which is periodically shed as they grow larger and molt.

Because of detoxification, organisms may show some degree of resistance or tolerance to the toxicity of metals and metalloids. If the resistance to a metal or metalloid is heritable, exposure to the metal/metalloid will likely act as a selective agent, resulting in an increased resistance of the population in subsequent generations, in other words, resulting in adaptation to metals and metalloids. Such adaptation can occur rapidly and simply without appreciable cost to the

organism (Chapman et al., 1998a). Adaptation to elevated metal concentrations has been well documented (Klerks and Weis, 1987; Chapman et al., 1998a).

Adaptation of organisms to metals and metalloids is however often ignored in ERA. For instance, one of the important information sources for ERA is laboratory toxicity tests where, prior to the testing, test organisms are often not acclimated or cultured in metal-containing media relevant to their natural habitats. Organisms' ability to adapt to metals and metalloids also has a significant implication for the non-ferrous metals industry. Specifically, some countries (e.g., Denmark) have been proposing a complete ban of the production and usage of non-ferrous metals. This would encourage the invention and application of synthetic chemicals as human society will unavoidably seek replacements, which may result in much worse environmental scenarios. Comparing Figure 3A, B, and C, there is reason to believe that the moderate application of metals and metalloids, which occur naturally in the environment and to which organisms can and do adapt, is more environment-friendly than the introduction of new synthetic chemicals with unknown environmental behaviors and effects.

Adverse Effects: Toxicity and Deficiency

At elevated concentrations when the influx of metals and metalloids exceeds the regulation (for essential elements) or detoxification capacity (for nonessential elements), toxic effects may occur. For instance, in fish, toxicity is manifest as inoregulatory dysfunction (Wood, 1992). However, as shown in Figure 3 (B, C), adverse effects occur not only at elevated concentrations, for essential elements they also occur at very low concentrations due to deficiency. For example, while selenium has received increasing attention because of its toxicity to wildlife (Chapman, 1999), people in northeastern China have been suffering from Keshan and Kaschin-Beck diseases for generations due to selenium deficiency.

The unique bell-shaped dose-response curve for essential metals and metalloids dictates that ERA, while it assesses the risk of adverse effects of toxicity at high exposure concentrations, should also take into account the risk of adverse effects of deficiency at low exposure concentrations. Implications of essentiality to ERA including risk management are outlined in Table 4 (further discussion is provided in Chapman, 1998, 2000).

Specific Issues of ERA of Metals and Metalloids

The vast differences between metals/metalloids and organic chemicals in terms of their sources, fates and biological effects imply that ERA of metals and metalloids needs to follow different approaches than those for organics in general. Approaches developed for organic chemicals may have limited or no application to metals and metalloids (Table 5).

For example, the first step of ERA in Canada and the European Union is hazard identification (Chapman, 1996), which involves the determination of the adverse effects which a substance has an inherent capacity to cause. In response to the requirements of CEPA (1999), Environment Canada is developing a system for classifying all substances on the Domestic Substances List based on the hazards they present to the environment, primarily to the aquatic environment. The criteria for classifying organic chemicals are based on their persistence, bioaccumulation and inherent toxicity. However, the same criteria cannot be used for metals and metalloids (IWG, in press), because the persistence and bioaccumulation criteria do not apply (Chapman et al., 1996a,b) and their discriminatory power is low (IWG, in press). As mentioned earlier, the term “persistence” is meaningless when applied to metals and metalloids. Because organisms can regulate their internal concentrations of essential elements and adverse effects can occur at both low (deficiency) and high concentrations (toxicity), standard body burden indices for bioaccumulation such as BCFs (bioconcentration factors) and BAFs (bioaccumulation factors) can be misleading. Therefore, the persistence and bioaccumulation criteria are not useful at any stage in an ERA of metals and metalloids. Instead, what is useful in an ERA is information on transformations between bioavailable and non-bioavailable forms (including complexation). In light of the fact that dissolved metal/metalloid species are more bioavailable than insoluble species, Environment Canada is proposing to determine the hazard of metals and metalloids (and other inorganic compounds) in use in commerce primarily as a function of their water solubility and toxicity, specifically by assessing solubility in water (≥ 1 mg/L), then the stability of the dissolved form, and finally the toxicity of either the parent compound or its dissociated components (acute LC50 or EC50 ≤ 1 mg/L) (IWG, in press).

It should be highlighted again that hazard identification is only the first step of an ERA; it identifies substances or stressors based solely on their intrinsic properties, and questions of exposure are not considered. In the subsequent steps an ERA assesses the potential exposure to and adverse effects of the stressors. As metals and metalloids are naturally present throughout the environment, it is obvious that all organisms are exposed to metals and metalloids. Since background concentrations and environmental fate of metals and metalloids vary in different regions, regional or global risk assessment of metals should be based on “metalloregions”, specifically a portion of the Earth’s surface having common geological and biological characteristics (LaPoint and Persoone, 1999a,b). This concept combines both the ecological regional or watershed approach (physical, chemical and biological boundaries/stressors) with recognition of geological differences in natural metal concentrations in the environment.

The exposure assessment of an ERA must distinguish bioavailable metals from non-bioavailable metals. For instance, water chemistry alters metal speciation and therefore bioavailability and toxicity (Chapman et al., 1998a; Mason, Laporte & Andres, 2000). The majority of metals present in the environment are not bioavailable due to binding to dissolved ligands or to particle surfaces (e.g., dissolved organic matter in sediment pore waters – Cusak and Milhelcic [1999]). The Biotic Ligand Model (BLM; DiToro et al., 1999; <www.epa.gov/science1/epecblm.pdf>), which was adapted from the free ion activity model (FIAM; Morel, 1983; Campbell, 1995; Hare and Tessier, 1996; Hudson, 1998; van Leeuwen, 1999) and the gill surface interaction model (Pagenkopf, 1983), may provide a general model for bioavailability/toxicity determinations. It is also being suggested for the derivation of site-specific acute toxicity water quality values. However, it only addresses dissolved metals, not metals accumulated from the diet.

Work summarized by Pyle, Wood & McDonald (2000) has shown that metals taken up through the diet “can confound toxicity predictions of a BLM owing to high, but nontoxic, gill metal burden resulting from dietary metal exposure.” This work has also shown that: metals taken up via the digestive tract may be less toxic; pre-exposure to dietary metals can reduce subsequent waterborne metals uptake; dietary uptake of essential metals may not be as tightly regulated as is the case for uptake from water; diet may also provide protection against metals toxicity.

Dietary uptake may not be the only issue confounding prediction of metal and metalloid bioavailability and toxicity. For instance, Mirimanoff and Wilkinson (2000) found that FIAM did not apply to a bacterium because it produced a complexing ligand capable of rapidly reducing Zn^{2+} concentrations in its external medium. This ligand appears to be part of resistance mechanisms that are activated by the bacterium in the presence of Zn. Although this resistance mechanism appears to be unique, other evolutionary metal resistance and detoxification mechanisms are common in bacteria in general (Jackson, West & Leppard, 1999).

Another important issue involves chronic toxicity as opposed to acute toxicity. At present the BLM is focused on acute toxicity; whether it will also be useful for chronic toxicity predictions is uncertain. Present chronic water quality guideline values are based on a variety of extrapolations from acute to chronic values, using safety factors which are uncertain at best (Chapman, Fairbrother & Brown, 1998b). Such extrapolations are based on the results of testing with the most sensitive organisms, which can result in regulatory limits below nutritional requirements for most organisms (Coughlin, 1997). Moreover, such extrapolations also assume that acute and chronic toxicity are due to the same mechanism, which is not always the case (e.g., Chapman, 1999).

The effects assessment of an ERA must consider not only acute but also chronic toxicity; the latter is a much more complex issue both in terms of mechanisms and predictability (McGeer et al., 2000a,b; Taylor et al., 2000). It must also allow for physico-chemical properties influencing metal and metalloid bioavailability (e.g., temperature – Rao and Khan, 2000), and for biotic factors, in particular acclimation and essentiality. Deficiency in addition to toxicity also needs to be taken into account for essential elements. Improved realism in laboratory tests can occur extrinsically and/or intrinsically. Extrinsic improvements involve consideration of other factors as shown in Figure 4. Intrinsic improvements involve making the tests themselves more realistic.

Intrinsic improvements are generally only possible for site-specific ERAs. Regional and global ERAs can be improved by the appropriate use of extrinsic normalizing factors (e.g., pH, water hardness, DOC). However, bioavailability remains highly site-specific. Thus site-specific ERA will be more certain than global ERA.

Risk assessments at any level (site-specific, regional, global) progress from conservative (protective) assumptions to more realistic scenarios. Thus standard ecotoxicity testing under defined conditions, though not designed or intended to be environmentally realistic, is appropriate for problem formulation (Figure 1) but not for final risk characterization. The effects assessment portion of an ERA must be more ecologically realistic whether a screening or detailed level risk assessment is involved. The former will be less certain than the latter (Hill et al., 2000). Increased ecological realism may involve laboratory testing reflecting site specific conditions (e.g., pH, water hardness, dissolved organic carbon [DOC], natural levels of metals and metalloids, microcosms), and/or *in situ* testing (e.g., mesocosms). For instance, testing can be conducted mimicking natural concentrations of dissolved organic matter (DOM – MacRae et al., 1999). Metals bound to DOM may be more or less bioavailable and toxic than unbound metals (Campbell, 1995; Kosalwat and Knight, 1987; Playle, 1998; Marr et al., 1999).

The final portion of an ERA, risk characterization, integrates the previous three steps (see Figure 1) to estimate the incidence and severity of any likely environmental effects. It also includes an uncertainty assessment of each component and of the overall ERA. The particular characteristics of metals need to be considered in both risk characterization and uncertainty assessment if the end product is to be realistic and useful. In particular, the Predicted Environmental Concentration (PEC) and Predicted No Effect Concentration (PNEC) (cf. Figure 2) should both be expressed in terms of the bioavailable fraction. For regional and global risk assessments, different values should apply to different metalloregions (LaPoint and Persoone, 1999a).

SELECTED CURRENT RESEARCH EFFORTS

ERA of metals and metalloids will continue to evolve as our understanding of metal and metalloid behavior in the environment improves and as the importance of metals and metalloids for human society is taken into account. Driven by the socioeconomic importance of metals and metalloids and balanced against environmental concerns, research efforts have been undertaken to understand and minimize the adverse effects of metals and metalloids.

For instance, in the Great Lakes continuing and future research efforts focus on (Kerfoot and Nriagu, 1999): quantifying regional as opposed to long-distance metal contributions to the ecosystem; identifying contaminant sources and transport mechanisms; and, distinguishing the role of different processes influencing availability and cycling of metals (e.g., organic complexing and dissolution processes). Various individual research efforts are examining the ability of organisms to modify their exposure to contaminants and how they adapt or respond to contaminant exposure. For example, researchers at McMaster University in Canada (C. M. Wood, pers. comm.) are attempting to: better define physiological endpoints for chronic toxicity; more fully address trophic transfer (dietary toxicity) of metals; and, better understand the normal homeostasis of nutrient metals in aquatic organisms.

Internationally, different attempts to determine both “safe” (e.g., PNEC – see Figure 2) and “critical” levels for metals and metalloids are underway. Such efforts include refining conventional approaches to hazard identification such as water effect ratios (WERs). They extend to attempting to apply the BLM to derivation of water and sediment quality values. And they include determining and separating natural from anthropogenic sources of metals and metalloids. Research efforts are also focussing on developing kinetic (Reinfelder et al., 1998; Wang, Qiu & Qian, 1999) and mechanistic (Borgmann, 1998) models that can address both dissolved phase and food routes of exposure in natural waters. The last effort reflects effectively a paradigm shift. Until relatively recently, it was believed that the main route of exposure to metals and metalloids in the aquatic environment was via the aqueous phase. However, it is now apparent that, in many cases, food is often an important (Farag et al., 1999) and sometimes the major route of exposure (Munger, Hare & Tessier, 1999). Efforts are underway to develop critical body residues (CBRs) for different organisms for both metals and organics (e.g., Jarvinen and Ankley, 1998; Fay et al., 2000)

As one of the world’s largest producers and exporters of metals, Canada launched the Metals in the Environment Research Network (MITE-RN) in July 1998. Jointly funded by government and industry, this research network focuses not only on improving understanding of the fundamental scientific aspects of the sources, fates and effects of metals in the environment, but also on how to integrate improved scientific understanding into ERA and regulatory practices. Specifically, in

addition to three domains (sources, processes and impacts), the network comprises an ERA component to closely align with the Canadian paradigm for ecological risk assessment as it applies to metals.

Key research areas for MITE-RN include natural versus anthropogenic sources, particularly related to long-range atmospheric transport. Atmospheric contamination by metals derived from human activities dates back to Roman times (Nriagu, 1989) and was particularly pronounced during medieval times (Brannvall, Bindler & Renberg, 1999). Atmospheric deposition of metals over long distances, into otherwise relatively pristine areas (Nriagu and Pacyna, 1988; Pacyna, Scholtz & Li, 1995) can have severe consequences. For instance, metals accumulating in the Arctic during winter periods are released during snowmelt when low pH waters result in a pulse of ionic metal forms (Moiseenko, 1999). Atmospheric deposition can also affect areas which are not pristine and which are subject to multiple other inputs of the same contaminants (Callender and Rice, 2000). This renders site-specific ERA exposure assessments particularly challenging. Clarifying the relative contributions from anthropogenic and natural sources is particularly important for the exposure assessment of an ERA. MITE-RN studies into sources (equivalent to the problem formulation stage of an ERA) are designed to quantify the importance of long-range transport of metals. They focus on the atmosphere (transport and transformation processes) and on the receiving environment (lake sediments; influence of diagenesis on metal stratigraphy in lake sediment cores) related to evidence for long-range transport. Lake studies include pore waters, speciation, bioturbation and bioirrigation.

As regards the exposure assessment of an ERA, MITE-RN research into “processes” involves various components. Overall, the focus is on the mobility of metals among biotic and abiotic compartments in northern forests and lakes (waters and sediments). Of key interest are the movement and transformation of metals and the forms of the metals relative to exposure. New techniques are being developed and tested for modelling, particularly for non-equilibrium systems (most previous studies have considered equilibrium systems). Key foci are on dissociation coefficients and stability constants. Laboratory and field studies are attempting to develop relationships between metal concentrations in tissues of organisms and speciation within

different tissues of organisms (i.e., their ability to detoxify metals), and exposure via water compared to exposure via food.

The effects assessment portion of MITE-RN (termed “impacts”) focuses very strongly on this latter exposure component, specifically on attempting to determine relationships between body burdens and toxicity, for both essential and non-essential metals. In the past, ERAs have attempted to relate concentrations of metals and metalloids to effects. A better way, and one of the focuses of MITE-RN involves, as for the Biotic Ligand Model (BLM), determining the dose responsible for toxicity rather than only the concentration associated with toxicity. Such studies are presently in the research mode and more appropriate for detailed rather than screening-level ERAs. For the latter, concentration data continue to be used to provide, despite their limitations, approximations of the dose. Ultimately, all levels of ERA may focus on body burdens which are not only more reliable indicators of toxicity but also allow for cause-and-effect determinations (Borgmann and Norwood, 1999). Also examined in this portion of MITE are mixtures of metals, and chronic effects; the latter studies are expected to contribute to development of a chronic BLM.

Overall, MITE-RN is intended to strengthen links between metal speciation/partitioning (exposure), tissue body concentrations, metal speciation within organisms, and individual and population level effects. Food chain linkages are also examined via effects on birds eating mercury-contaminated fish (mercury is the only metal that biomagnifies [when methylated] up food chains). A major goal is improved predictability, for both retrospective and prospective ERAs, within the context of remaining and clearly identified (and prioritized) uncertainties.

The ultimate intent of the MITE-RN project is to use the information generated by its researchers in addition to other relevant and appropriate studies, to provide a reevaluation of the overall risk of metals in the global environment (i.e., guidance in performing global ERA). This work will also result in a similar reevaluation and accompanying guidance for performing regional and site-specific ERAs.

CONCLUSIONS

Metals and metalloids are natural, indestructible components of the Earth's crust and occur naturally throughout the environment. Many must be bioaccumulated to maintain life and health. Background concentrations of metals and metalloids in different regions can vary over several orders of magnitude. Evolving across the metal/metalloid-containing environment, all living organisms on the Earth have been exposed to metals and metalloids, and metals and metalloids can be found in the tissues of all living organisms. The natural presence of metals and metalloids in the environment and in organisms' bodies by no means implies a risk to living life. In fact, it may be one among many natural climatic, geological, and biochemical processes that has led to present-day biodiversity. Natural acclimation and adaptation to metals and metalloids can and do occur and may have acted as selective agents. The presence and uptake of essential metals and metalloids is beneficial to organisms. Biological effects of metals and metalloids are related to their bioavailability, not solely concentrations. Risks of toxicity from metals and metalloids occur only at a sufficiently high bioavailability and after a sufficiently long period of exposure. For essential elements there is also a risk of deficiency when their bioavailability is very low.

Because of differences in sources, fates, and effects, ERA approaches historically developed for synthetic organic chemicals have limited or no application to metals and metalloids. Persistence and bioaccumulation criteria used for organic chemicals are not appropriate for metals and metalloids. ERA of metals and metalloids needs to consider the natural occurrence of metals and metalloids, and their essentiality to and adaptation by organisms. Above all, ERA of metals and metalloids needs to focus on their bioavailability, which is highly site-specific. Any ban of the application of naturally-occurring metals and metalloids and introduction of replacement synthetic substances is unwise unless there is sufficient evidence demonstrating that the replacements are more environment friendly, which is generally not the case.

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**Table 1. General differences in environmental behaviors
of metals/metalloids and organic chemicals**

	Organic Chemicals	Metals and Metalloids	
		Essential	Nonessential
Sources	Many are introduced by humans	Naturally-occurring; release can be enhanced by humans	
Fate	More or less degradable	Transformable but not degradable	
Bioavailability	Related to the lipophilicity of the substance	Related to only a fraction of the substance (e.g., dissolved form, free ions)	
Effects			
Positive effects	No	Yes	No
No effects	Maybe	No	Yes
Adverse effects	Toxicity	Deficiency and toxicity	Toxicity

Table 2. Average concentrations of selected metals and metalloids in the continental crust and their baseline concentrations in waters, sediments and soils

Element	Rank in the Crust ¹	Continental Crust ¹ (mg/kg)	Ocean Water ² (µg/L)	Laurentian Great Lakes Water ³ (µg/L)	Sediments of the conterminous US ⁴ (mg/kg)	Soils of the US ⁵ (mg/kg)
Ag	66	0.07	0.002	ND	ND	<0.7 - 5.0
Al	3	79,600	0.03	ND	ND	5,000 - 100,000
As	48	1.7	1.2	ND	2.2-21	<0.1 – 750
Cd	64	0.1	0.07	0.002-0.009	0.1-0.5	<1 – 10
Co	29	24	0.0012	0.009	ND	<2 – 70
Cr	19	126	0.21	0.06-0.39	20-100	1 - 2,000
Cu	28	25	0.15	0.70-0.89	10-53	<1 – 810
Fe	4	43,200	0.03	0.48-1.23	ND	100 - 100,000
Hg	68	0.04	0.0001	0.00016-0.00024	0.01-0.08	<0.01 - 4.6
Mn	12	716	0.02	0.126-0.187	ND	<2 - 7,000
Mo	52	1.1	10	ND	ND	<2 – 15
Ni	25	56	0.48	0.76-0.88	12-51	<3 – 700
Pb	35	14.8	0.0027	0.0046-0.026	9-35	<4 – 700
Sb	61	0.3	0.2	ND	ND	<1 - 8.8
Se	63	0.12	0.155	ND	0.2-1.0	<0.1 - 4.3
Sn	45	2.3	0.0005	ND	ND	<0.1 – 41
Zn	22	65	0.35	0.012-0.19	33-140	<5 - 2,900

1. Wedepohl (1995).

2. Median concentrations in oceanic water (Quinby-Hunt and Turekian, 1983; Nozaki, 1997).

3. Values reflect the range of average reported concentrations from studies that sampled sites in the open waters of the Laurentian Great Lakes using trace metal clean techniques (pers. comm., Michael Twiss, Ryerson University, Toronto, Ontario, Canada)

4. 4. Baseline values determined from probability plot of ambient sediment metal concentrations in the conterminous US (Rice, 1999).
5. 5. Baseline values measured from relatively unpolluted soils of the conterminous US and Alaska (Shacklette and Boerngen, 1984; Gough, Severson & Boerngen, 1988).

ND: Not determined.

Table 3. Examples of some essential trace elements and their functions (Stumm and Morgan, 1996; Butler, 1998; Lane and Morel, 2000)

Element	Biological Functions
Cd	Cofactor of carbonic anhydrase when Zn is depleted.
Co	Component of vitamin B ₁₂
Cr	Cofactor for insulin action
Cu	Cofactor of cytochrome, ascorbate oxidase, and plastocyanin
Fe	Cofactor of cytochrome, catalase, peroxidase, and chelatase
Mn	Cofactor of superoxide dismutase and O ₂ evolving enzyme
Mo	Cofactor of nitrogenase
Ni	Cofactor of urease
Se	Cofactor of glutathione peroxidase
Zn	Cofactor of DNA and RNA polymerases, carbonic anhydrase, and alkaline phosphatase

Table 4. Implications of essentiality for ERA

Step	Present Focus	Future Focus
Hazard identification	<ul style="list-style-type: none"> Few and generally high toxicity test exposures 	<ul style="list-style-type: none"> More exposures; both high and low exposure concentrations
Exposure Analysis	No changes needed	
Effects Analysis	<ul style="list-style-type: none"> Few and generally high toxicity test exposures Assumption of monotonic/linear data pattern 	<ul style="list-style-type: none"> More exposures; both high and low exposure concentrations No preconceived assumptions (or confining statistics)
Risk Characterization	<ul style="list-style-type: none"> Application of safety factors 	<ul style="list-style-type: none"> No safety factors
Risk Management	<ul style="list-style-type: none"> Removing all chemicals 	<ul style="list-style-type: none"> Determining appropriate amounts of some chemicals

Table 5. Differences between ERAs of metals/metalloids and organic chemicals

Step	Organic Chemicals	Metals and Metalloids
Hazard identification	<ul style="list-style-type: none"> ▪ Persistence ▪ Bioaccumulation ▪ Inherent toxicity 	<ul style="list-style-type: none"> ▪ Water solubility ▪ Stability of dissolved forms ▪ Inherent toxicity of the parent and dissociated compounds
Exposure Analysis	<ul style="list-style-type: none"> ▪ Environmental concentration ▪ Exposure duration 	<ul style="list-style-type: none"> ▪ Concentration added to background concentration ▪ Bioavailability ▪ Exposure duration
Effects Analysis	<ul style="list-style-type: none"> ▪ Toxicity testing 	<ul style="list-style-type: none"> ▪ Toxicity testing with organisms pre-acclimated to natural levels of metals and metalloids ▪ Deficiency testing ▪ Tolerance testing
Risk Characterization	Integrating the above steps	

Figure Legends

Figure 1. A general ERA framework

Figure 2. Basic ERA paradigm

Figure 3. Dose-response relationships for synthetic organic chemicals (A), essential metals and metalloids (B) and nonessential metals and metalloids (C).

Figure 4. Uncertainty decreases and realism improves as laboratory data are adjusted extrinsically for factors influencing hazard and risk. PNECs can be further improved if laboratory data are based on both aqueous and food exposures (Munger, Hare & Tessier, 1999).

Figure 1.

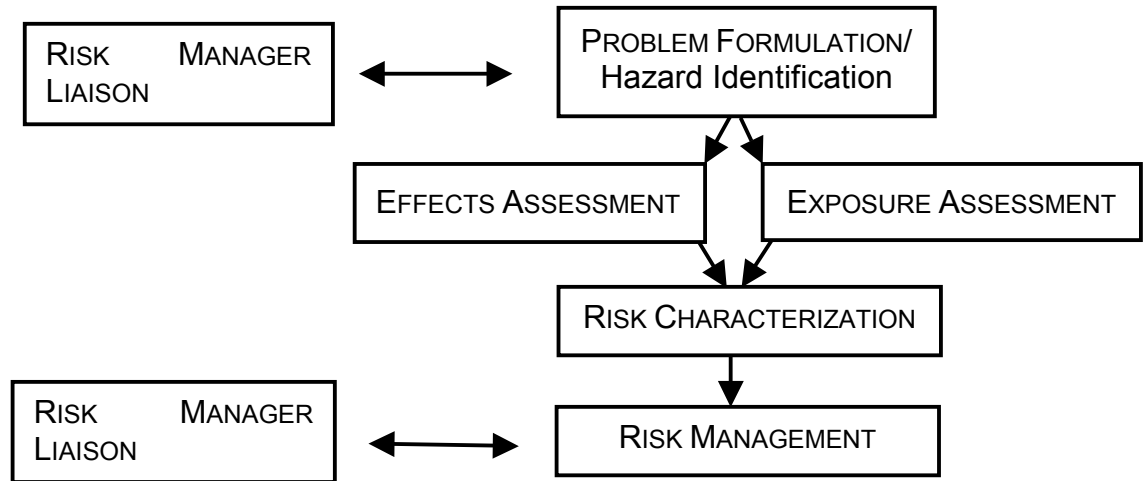


Figure 2

Basic Risk Assessment Paradigm

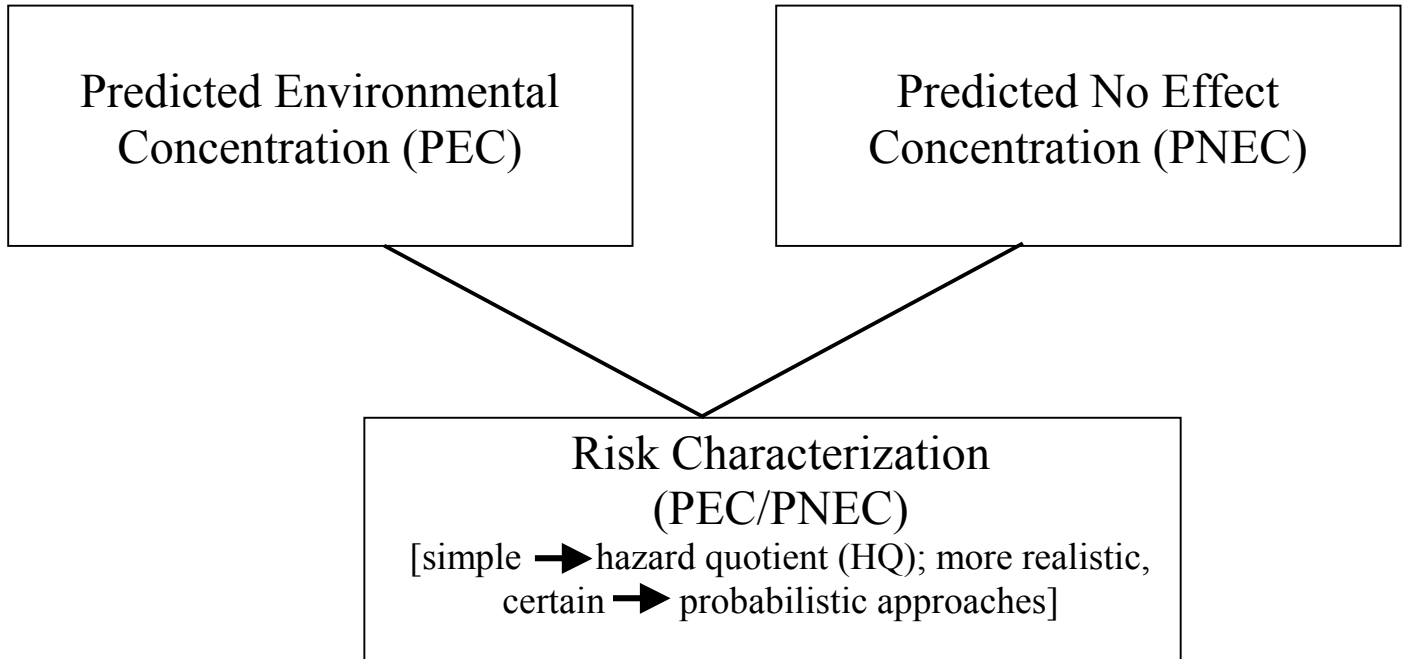


Figure 3

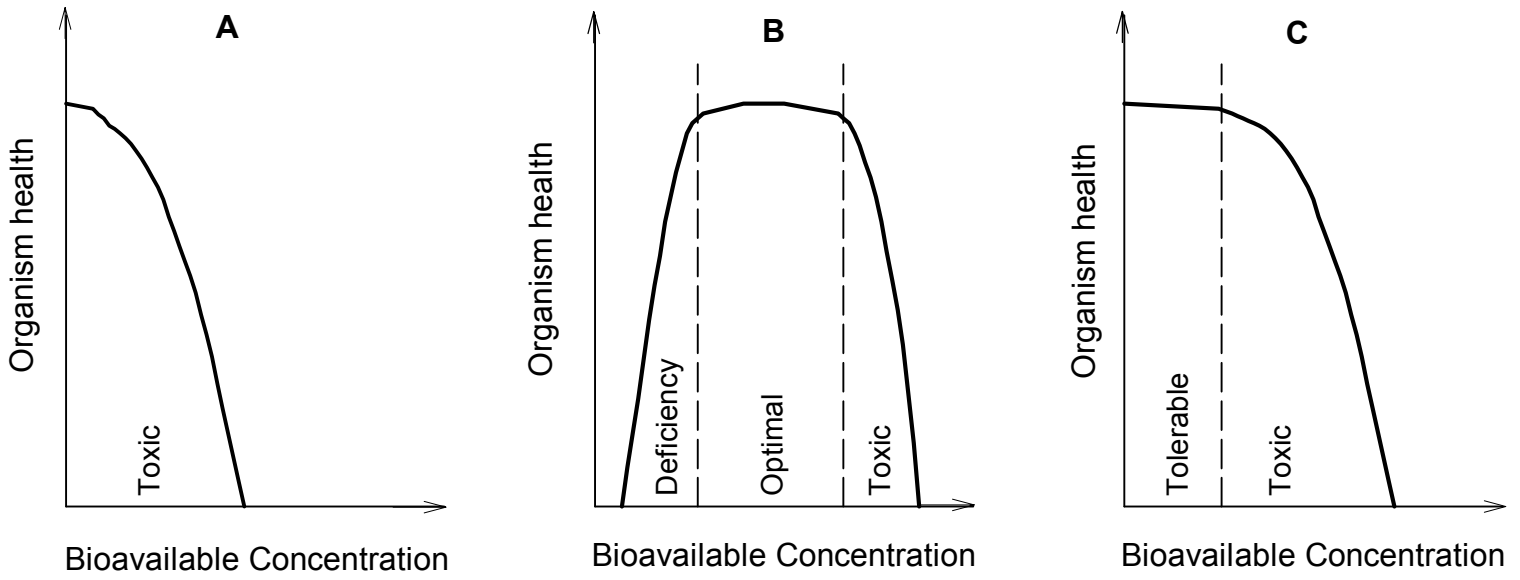


Figure 4.

Uncertainty vs. Realism

