

Conducting Ecological Risk Assessments of Inorganic Metals and Metalloids: Current Status

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ABSTRACT

Ecological risk assessment (ERA) of inorganic metals and metalloids (metals) must be specific to these substances and cannot be generic because most metals are naturally occurring, some are essential, speciation affects bioavailability, and bioavailability is determined by both external environmental conditions and organism physiological/biological characteristics. Key information required for ERA of metals includes: emissions, pathways, and movements in the environment (Do metals accumulate in biota above background concentrations?); the relationship between internal dose and/or external concentration (Are these metals bioreactive?); and the incidence and severity of any effects (Are bioreactive metals likely to result in adverse or, in the case of essential metals, beneficial effects?) — ground-truthed in contaminated areas by field observations. Specific requirements for metals ERA are delineated for each ERA component (Hazard Identification, Exposure Analysis, Effects Analysis, Risk Characterization), updating Chapman and Wang (2000). In addition, key specific information required for ERA is delineated by major information category (conceptual diagrams, bioavailability, predicted environmental concentration [PEC], predicted no effect concentration [PNEC], tolerance, application [uncertainty] factors, risk characterization) relative to three different tiered, iterative levels of ERA: Problem Formulation, Screening Level ERA (SLERA), and Detailed Level ERA (DLERA). Although data gaps remain, a great deal of progress has been made in the last three years, forming the basis for substantial improvements to ERA for metals.

Key Words: metals, metalloids, ecological risk assessment, bioavailability, speciation.

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INTRODUCTION

There is increasing awareness among both scientists and regulators that generic ecological risk assessment (ERA) procedures need to be modified for metals and metalloids (collectively referred to as metals), but there is no consensus as to how this should be done. Although there have been major advances in metals research in the last 3 years since Chapman and Wang (2000), much of this research has not been integrated into ERA usage.

For example, terrestrial risk reduction for metals has focused on removal of contaminated materials largely because of the historical poor understanding of fate processes in soils, generally ignoring major recent advances in understanding the bioavailability and transformation of metals in terrestrial systems. Similarly, key recent advances regarding the fate and effects of metals in aquatic environments have not been fully evaluated for use in ERA. It is still too often assumed that metals bioavailability in the environment is similar to that determined in laboratory toxicity tests using soluble metal salts. In fact, bioavailability in the environment is generally lower, sometimes much lower, not only because environmental exposures do not involve solely soluble metal salts, but also due to factors such as complexation; competition with environmental ligands; sorption onto soils and sediments; precipitation in anoxic environments in the presence of sulphides (with the exception of Al, Fe(III) and Mn(IV), which are subject to precipitation reactions in oxic environments), and coprecipitation.

The purpose of this paper is to update Chapman and Wang (2000), summarizing new key findings that have accrued since that publication and providing specific advice regarding the conduct of ERA for metals. The advice provided herein is based both on research conducted by the Metals in the Environment Research Network (MITE-RN), and on research conducted outside the network. A key objective of the MITE-RN is to contribute to the improvement of ERA procedures as they apply to metals (www.mite-rn.org). To this end, the network is conducting detailed research into metals in the Canadian environment, with key findings to date summarized in this issue of *Human and Ecological Risk Assessment* (Dias and Edwards 2003; MacDonald *et al.* 2003; Johnson *et al.* 2003; Carignan *et al.* 2003; Hare *et al.* 2003; Niyogi and Wood 2003; Campbell *et al.* 2003; Norwood *et al.* 2003; Chan *et al.* 2003). These findings form a key component of our updated advice for the conduct of ERA for metals.

RECENT KEY ADVANCES

Metals Deposition/Background Metals Concentrations

Estimates of atmospheric metal deposition are necessary to evaluate metal loadings into terrestrial and aquatic ecosystems. Current ERAs obtain atmospheric deposition estimates by using wet and dry deposition data and complement these empirical data by using dispersion models (Environment Canada and Health Canada 2001). However, mechanical precipitation collectors are often relatively few, and are typically installed relatively close to industrial facilities. There is much uncertainty regarding the radius of local enrichment resulting from anthropogenic metal releases, which has been reported to vary from several tens of kilometers up to over

100 km, depending on site, media, and metal of interest (Zoltai 1988; Dumontet 1990; Henderson *et al.* 2002). Complementary approaches to better estimate atmospheric deposition such as historical records in mosses, lake sediments and/or ombrotrophic peat bogs, and soils are necessary, as is atmospheric source apportionment.

Mosses have been widely used for monitoring of atmospheric deposition of metals in Scandinavian countries (Berg and Steinnes 1997a,b) and in Canada (Goodarzi *et al.* 2003). In Canada, epiphytic lichens are also used as monitors of atmospheric metal deposition (Carignan and Gariépy 1995). Mosses are useful biomonitors of atmospheric metal deposition because they lack a root system and obtain most of their supply of nutrients from wet and dry deposition. As the carpet of living moss tissue is built up during a period of 3 to 5 years, the content of metals reflects an average exposure during that period.

Metals deposited into terrestrial environments accumulate in soils and may enter biological cycles and/or be leached into aquatic environments. The final repository for metals entering aquatic environments is typically the sediment via processes including sedimentation, adsorption to particulate matter, precipitation and/or co-precipitation. Metal accumulation in lake sediment results mainly from the deposition of metals adsorbed onto suspended particulate matter (Santschi 1984; Sigg 1998) and, to a lesser extent, from diffusion of dissolved metal species from the overlying water column to the sediment, where a change in redox potential, induced by microbial respiration (Ehrlich 1996) and bioirrigation of tunnels dug by invertebrates (Fischer 1982; Matisoff 1995), lead to precipitation and/or co-precipitation reactions (Ehrlich 1990).

Atmospheric metals inputs from anthropogenic activities date back to early mining efforts several thousand years ago (Brännvall *et al.* 1999) and can predominate in many locations (Simonetti *et al.* 2000; Elbaz-Poulichet *et al.* 2001). Some anthropogenic metals inputs are associated with specific activities. For instance, atmospheric Pb deposition due to leaded gasoline, which ended in developed countries in the late 1970s, continued Zn deposition due to runoff from population centers related to vehicular use, and other metals in runoff from point sources have left their "signatures" in aquatic sediments (Callendar and Rice 2000; Rice *et al.* 2002).

As noted by Chapman and Wang (2000), background concentrations of metals vary greatly between sites and areas. Atmospheric metals show pronounced enrichments in recently deposited soft sediments and can provide information on transport processes (short- to long-range) and sources (anthropogenic and natural). However, physical (*e.g.*, variable sedimentation rates, compaction, diffusion), chemical (*e.g.*, redox processes) and biological factors (*e.g.*, bioturbation, bioirrigation) can confound the record provided by examining metal concentration profiles in sediments. For example, geochemical analyses are affected by grain size, in particular mineralogical partitioning among grain size fractions (Klassen 1999).

Carignan *et al.* (2003) provide methodology to distinguish anthropogenic metals deposition into lakes from diagenetic processes within the sediments related to natural physical, chemical, and biological processes. They recommend the following independent approaches, which can be combined into a weight of evidence evaluation. The simplest approach would be to compare exposed and reference lake

metal profiles in sediments. More detailed approaches involve: using geochemical and diagenetic modeling to evaluate the importance of metal diffusion as an internal mobilization process; and/or using stable metal isotopes to fingerprint possible metals sources and evaluate their relative importance. Using a combination of comparative, geochemical and isotopic ratio approaches, Carignan *et al.* (2003) carefully interpreted dated sediment profiles of metals from several Canadian Shield lakes. They found that in the absence of biological mixing activities post-depositional chemical changes in lakes resulting in metal remobilization were negligible for Pb and Hg, intermediate for Cu, and high for As, Zn, and Cd.

The accumulation rates of metals in lake sediments are not generally equivalent to absolute deposition rates (Norton *et al.* 1997). Atmospheric deposition rates in lakes are likely to be overestimated because of sediment focusing (Blais and Kalff 1995) and additional catchment inputs. Metal immobility is higher in ombrotrophic peat bogs than in lake sediments (Appleby *et al.* 1997; Norton *et al.* 1997; Benoit *et al.* 1998) due to the high affinity of metals for organic matter, which comprises some 90% of the solid material contained in the bogs. Brännvall *et al.* (1997) observed that Pb concentration profiles in ombrotrophic peat bogs followed the pattern in lake sediments, but the concentrations in the bogs were lower. This was expected as ombrotrophic peat bogs only receive metals from the atmosphere, for instance, Pb profiles are strongly related to use of leaded gasoline (Shotyk *et al.* 1997). This unique feature has led some scientists to use ombrotrophic peat bogs as historical records of metal deposition (Zoltai 1988; Dumontet *et al.* 1990; Shotyk *et al.* 1997; Kettles and Dixon 2000; Novák *et al.* 2003). For example, using ombrotrophic peat bogs in southern Sweden, Bindler (2003) estimated that recent Hg deposition rates are at least one order of magnitude higher than background deposition rates.

Differentiating anthropogenic from natural sources of metals has been and will remain one of the most challenging areas in ERA of metals. Accurate estimates of anthropogenic metal emissions could provide information on background concentrations of metals in the absence of anthropogenic emissions. Dias and Edwards (2003) summarize the present state-of-the-art related to differentiating natural and anthropogenic sources of atmospheric metals to the environment. Source apportionment can be optimized through appropriate sampling, analysis and experimental design. Although there presently is no ideal method of source apportionment, combinations of different methods in a weight of evidence determination provide useful information. The most promising single technique at present for source apportionment is isotope ratio measurement, due to technological development in the field of inductively coupled plasma – mass spectrometry (ICP-MS). As illustrated by Carignan *et al.* (2003), a classical example is Pb, which exhibits significant variations in the proportions of its stable isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) in different Pb deposits. As a result, stable Pb isotope ratios have been widely used to fingerprint possible sources of Pb and to evaluate their relative significance (Brännvall *et al.* 1997; Farmer *et al.* 1997; Rosman *et al.* 1998; Sangster *et al.* 2000; Carignan *et al.* 2003; Novák *et al.* 2003). With the recent development of multiple-collector ICP-MS (MC-ICP-MS), which can achieve unprecedented high precision in isotopic measurements (Halliday *et al.* 2000), the list of metals that can be fingerprinted to differentiate their sources is expected to grow dramatically. For example, small

natural isotopic variations have been reported in Cu (Marechal *et al.* 1997; Gale *et al.* 1999), Zn (Marechal *et al.* 1997) and Hg (Evans *et al.* 2001; 2002).

Metal loadings to soils from atmospheric sources are controlled by: distance from the source; metal concentrations; and geology of the substrate (McMartin *et al.* 2002). These authors used variations in the ratios of humus and metal content in surface and deeper soil horizons to distinguish anthropogenic from natural sources of metals enrichment in soils.

Mg-bearing phyllosilicates are strongly indicated as predominant controls on trace metals in soils, at least in glaciated terrains (Huisman *et al.* 1997; Hardy *et al.* 1999; Klassen 2001). These studies indicate that it is useful to express metal concentrations (Me) in terms of the host mineral concentration (Mg), with single ratio values (Me/Mg) characteristic of large geological terrains. The ratios effectively eliminate grain size effects in characterizing metal distribution. They also provide a basis to discriminate natural versus anthropogenic metals in soils and assist in interpreting weathering rates and element reactivity.

Speciation/Bioavailability

Metal speciation is controlled by external environmental conditions (*e.g.*, pH, Eh, cations, organic matter and other metal-complexing ligands — Richards *et al.* 2001; De Schamphelaere and Janssen 2002). However, bioavailability is also controlled by intrinsic properties of organisms and by strongly complexing ligands (Smierjan *et al.* 2003). Typically, metals are less bioavailable in the natural environment than in laboratory settings, which generally do not consider metal-complexing ligands in the environment (Janssen *et al.* 2003; NRC 2003). Adverse effects of metals to organisms only occur when related to the biologically available forms of metals (MacRae *et al.* 1999; Meyer 2002).

Bhavsar *et al.* (2003) developed a coupled metal TRANsport and SPECiation model, TRANSPEC, which estimates metal speciation. They found that the remobilization of Zn in a contaminated lake was driven by insoluble ZnS under anoxic conditions (summer and winter), and by diffusion and resuspension under oxic conditions (fall).

Campbell *et al.* (2003) demonstrated large differences between total and free metal concentrations in metal contaminated lakes, especially for Cu. This finding is in agreement with a recent study in Lake Michigan (Bazzi *et al.* 2002), which showed that total dissolved Cu exists predominantly (more than 98%) as stable, largely nonbioavailable organic complexes, with < 2% as labile bioavailable Cu. Similarly, Kogut and Voelker (2003) found that up to about half of the total Cu in coastal waters is kinetically inert.

Peijnenburg *et al.* (2003) describe the findings of a Dutch workshop on bioavailability at which recommendations were made for dissolved organic carbon (DOC) corrections to metal concentrations in surface waters, recognizing that a significant fraction of metals such as Cu in water is bound to DOC and not biologically available. Similar conclusions were reached by Heijerick *et al.* (in prep).

In sulfidic waters (such as anoxic hypolimnion and sediment interstitial waters), the speciation of many metals is dominated by metal-sulfide and -polysulfide complexes (Wang *et al.* 1998; Wang and Tessier 1999). Cantwell and Burgess (2001)

emphasize the importance of colloidal organic carbon as a metal chelator in sediment interstitial waters; binding efficiencies are controlled by interstitial water chemistry. Metals bioavailability in streams contaminated by metal mining is reduced by adsorption of dissolved metal species on colloids and/or particles (Gundersen *et al.* 2001). However, colloid-bound metals in marine waters can be bioavailable to filter feeders such as mussels and clams, with the level of bioavailability dependent on the quality and sizes of the colloids (Pan and Wang 2002). Metals can also be sorbed to Al, Fe, and Mn oxides in slow sorption processes that are not generally considered in models of contaminant mobility and bioavailability (Trivedi and Axe 2001). There is a general low mobility of metals from sulfidic coastal sediments, which is not enhanced by bioturbation (Sundelin and Eriksson 2001), nor by ameliorated oxygen conditions in relatively anoxic areas such as parts of the Baltic Sea (Wiklund and Sundeline 2002).

Release of metals from estuarine sediments is determined primarily by sediment physico-chemical composition and secondarily by the level of resuspension energy; release is most likely from sediments with elevated metals concentrations and low levels of sulfides and organic carbon (Cantwell *et al.* 2002). While salting out of metals by complexation with organic ligands in outer reaches of some estuaries and dynamic cycling (bed load transport in-shore with subsequent resuspension) may favor the retention and recycling of metals in those estuaries (Turner *et al.* 2002), it may also result in movement seaward during high river flows (Achterberg *et al.* 2002). However, Garnier and Guieu (2003) showed that Cd released into estuarine (brackish) water tends to bind to particles and is not easily mobilized; mobilization is controlled by dilution of the particulate phase and by kinetic competitive complexation between particulate and dissolved ligands.

In marine sediments, localized remobilization of metals from sediments may be due to: reductive dissolution of Fe and Mn oxyhydroxides; decomposition of organic material; release from mineral phases; release from metal sulfides translocated into oxidizing regions (Zhang *et al.* 2002). Anthropogenic activities such as dredging can facilitate such localized remobilization (Fichet *et al.* 1998), by resuspension of anoxic sediments. However, scavenging by newly released Fe and Mn oxyhydroxides occurs relatively rapidly (Saulnier and Mucci 2000). The potential for metals release from sediments by bioturbation and bioirrigation may be buffered by stable FeS and MnS phases in sediments (Simpson *et al.* 1998). Given the above constraints on sediment metals bioavailability, it is not surprising that marine macrobenthic colonization of Cd-spiked sediments (up to 10 mg/kg dw) resulted in a stable benthic community not significantly different than controls after 14 months; although initial colonization was altered, there were no long-term impacts due to the rapid decline in bioavailable Cd in the sediment (Lu and Wu 2003).

However, the significance of interactions between sediment-bound metals and sediment-ingesting organisms remains to be determined (Chen *et al.* 2000a). Chen and Mayer (1999) note that digestively enhanced solubilization can occur more rapidly than sedimentary diagenetic processes. They argue "the biochemical cycles of metals could be altered should the dissolved sedimentary metals be excreted by the organisms". This may also be the case in soils as earthworms ingest soils (Naftel *et al.* 2002). Currie *et al.* (1997) found that emerging insects could export "small but potentially significant" amounts of Cd from lakes rendering this metal more avail-

able to aquatic organisms as well as providing a pathway to the terrestrial ecosystem. These possibilities remain to be resolved.

Lock *et al.* (2000), Lock and Janssen (2000; 2001a-d; 2002) and Davies *et al.* (2003) showed that the OECD earthworm toxicity test is not environmentally relevant because it not only maximizes metal bioavailability but also considers all metal in soils to be bioavailable, which is demonstrably not the case. Davies *et al.* (2003) also found that “extractions of the type used to assess metal bioavailability to plants are not relevant to soil fauna.” In metal-deficient soils, metals will tend to become bioavailable due to diffusion along a concentration gradient; similarly, soil acidification and oxidation of insoluble metal sulfides will tend to release metals.

Lock *et al.* (2000) and Lock and Janssen (2001a-c, 2002) demonstrated the importance of soil characteristics (*e.g.*, cation exchange capacity [CEC], pH) for predicting Zn toxicity to potworms, earthworms and springtails, and developed simple predictive models. Nolan *et al.* (2003) found low bioavailability of most metals in agricultural soils.

Hg has similarities and differences in both speciation and bioavailability compared to other metals. Hg methylation and biomagnification are strongly affected by Hg speciation (Chan *et al.* 2003), which is also affected by dissolved organic carbon (Kerndorff and Schnitzer 1980; Jackson 1989), pH (Miskimmin *et al.* 1992), and reduced sulfur species such as sulfides and polysulfides (Benoit *et al.* 1999; Jay *et al.* 2000). It is generally accepted that Hg methylation is mediated by sulfate-reducing bacteria (Gilmour *et al.* 1992), which are found in reduced environments such as anoxic sediments (Gilmour *et al.* 1999). In a field study, Goulet *et al.* (in prep) showed that the maximum concentration of MeHg in a sediment pore water profile occurred at a minimum concentration of the $\text{HgS}_{(\text{aq})}$ species, which contradicts the hypothesis that bacterial Hg methylation is modulated by diffusion of the neutral $\text{HgS}_{(\text{aq})}$ across bacterial membranes (Benoit *et al.* 1999, 2001). In fact, $\text{Hg}(\text{S}_x)_2^{2-}$ and HgS_xOH^- dominate the speciation of Hg(II) in sulfidic waters where Hg methylation occurs (Jay *et al.* 2002; Goulet *et al.* in prep). This contradictory result may be due to the fact that presently available data on thermodynamic constants for sulfide- and polysulfide-Hg complexes are used to calculate Hg speciation. Goulet *et al.* (in prep.) suggest that the ensemble of thermodynamic constants proposed by Benoit *et al.* (1999) and Jay *et al.* (2000) cannot be considered as an internally consistent database, a required condition to perform meaningful speciation calculations. In addition to sulfide, selenides are also an important control on Hg speciation, methylation and biological uptake; formation of $\text{HgSe}(\text{s})$ can naturally immobilize both Hg and Se in sediments (Mercone *et al.* 1999).

Biotic Ligand Model

The development of the Free Ion Activity Model (FIAM; Morel and Hering 1993; Campbell 1995) and extensive studies on the effects of metals on fish gills have resulted in the Biotic Ligand Model (BLM — Di Toro *et al.* 2001; Santore *et al.* 2001). The BLM is based on toxicity occurring when the metal concentration bound to a biotic “site of action” exceeds a critical concentration. It provides a mechanistic basis for predicting the acute toxicity of water-borne metals to aquatic biota (Di Toro *et al.* 2001; Santore *et al.* 2001; Gorsuch *et al.* 2002). Chronic BLMs have been devel-

oped for daphnids (De Schampelaere and Janssen 2003) and are being developed for fish, and a predictive model for chronic toxicity has been developed (Heijerick *et al.* 2002a-c; De Schampelaere *et al.* 2003).

The BLM predicts that metals uptake by fish and invertebrates (*i.e.*, metals bioavailability) from water is directly proportional to the concentration of free metal ions (by “free metal ions” we mean the hydrated metal ions or aquo complexes: $M(H_2O)_x^{n+}$; there are no bare M^{n+} in aqueous solutions) with the potential for metal-cell binding, and that uptake can be reduced proportional to increasing concentrations of competing cations (*e.g.*, Ca^{2+} , H^+) binding to cells. A key assumption is that the amount of biological effect is constant at a specified accumulation of metal on the target tissue (*i.e.*, the biotic ligand) of an organism, regardless of water quality. Another key assumption is that cell characteristics are not altered during metal-cell binding, though recent research has challenged this assumption for microalgae (Franklin *et al.* 2002). The model was developed under controlled laboratory conditions with a limited number of test species and with a very limited amount of field validation data (De Schampelaere *et al.* 2002a, 2003); research is ongoing to determine the applicability of the model, for both sensitive and more tolerant species in both laboratory and natural environments.

A number of studies have shown that this model provides reasonable predictions for water exposures in most cases for acute toxicity and can, with adjustments, provide predictions of chronic toxicity to various biota from water exposures while allowing consideration of the effects of DOC on metals bioavailability (Heijerick *et al.* 2002a-c; Gorsuch *et al.* 2002; Bianchini *et al.* 2002a; Niyogi and Wood 2003). Predictions are not met under conditions including: very high hardness (Heijerick *et al.* 2002a); the presence of assimilable ligands or the presence of the metal-sensitive site on the outer surface of the target organism (Campbell *et al.* 2002); proportions of major ions constant but different organic ligands present (Borgmann and Ralph 1983); waters containing thiols or thiosulphate (Fortin and Campbell 2001; Bury *et al.* 2002); nonequilibrium conditions (Bell *et al.* 2002); metals bound to colloids, which may in some cases reduce and in other cases (*e.g.*, uptake and assimilation by filter feeding biota) increase bioavailability (Wang and Guo 2000); enhanced bioavailability and toxicity in the presence of citrate (Errécalde and Campbell 2000 — citrate-mediated exceptions also occur in soils [Berkelaar and Hale 2003]); augmented uptake of a metal due to natural variations in the concentrations of other metals in the water column (Smiejan *et al.* 2003). Although these exceptions should be a major consideration when applying the BLM, they are not expected to prevent the BLM forming the basis for revisions to regulatory water quality criteria/guidelines for at least some metals. However, the reality of dietary exposures (see below) and the fact that pharmacokinetics differ between water and dietary exposures, will require adjustments to the BLM approach (Niyogi and Wood 2003).

As indicated above, research into the development of a chronic BLM is ongoing, as is the extension of the acute BLM to species other than fathead minnows and daphnids. Such research needs to consider the reality that the properties of the biotic ligand-metal interaction and toxicological sensitivity appear to be dynamic rather than fixed (Niyogi and Wood 2003). In other words, the previous chronic history of organisms affects both the accuracy of the acute BLM and any future

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chronic BLM. Acute BLM results cannot presently be extrapolated to chronic effects for two reasons: there is no technically defensible method for such an extrapolation; and such an extrapolation would rely on the assumption that acute and chronic effects share the same toxicity mechanism, which has not been demonstrated. Although binding to the same biotic ligand seems to explain both acute and chronic toxicity of Cu to *Daphnia magna*, the magnitude and relative importance of the binding constants differ between acute and chronic models; a similar situation prevails for acute and chronic zinc toxicity (Heijerick *et al.* 2002c).

Whether the BLM is applicable to metal mining effluents has been questioned (Vigneault *et al.* 2002). Specifically, it has been noted that: sulfate is the major inorganic ligand in mining effluents and is present at concentrations above the BLM validated range; thiosulfate and polythionate are potential additional ligands; complexation is likely underestimated; elevated concentrations of Ca and Mg may also be a problem.

Dietary metals may confound BLM predictions due to the fact that dietary metals do not accumulate primarily at the gills/respiratory surfaces. However, experimental evidence regarding the role of dietary metals in toxicity is limited and sometimes contradictory. Hook and Fisher (2001a,b) found that diet-borne Zn and Cd were the main contributors to chronic toxicity in invertebrates. In contrast, De Schampelaere *et al.* (2002b) found that algae-associated Cd did not contribute to toxicity for *D. magna*. Most investigations to date on the importance of diet-borne metal uptake and accumulation have not focused on effects. For example, Weston *et al.* (2000) concluded that the principal route of metals bioaccumulation for deposit-feeding organisms is ingestion of contaminated sediment, desorption of metals in the gut, and absorption across the gut wall. However, although the gill is not a primary target for dietary metal accumulation, dietary metals such as Cu (Handy 1992; Miller *et al.* 1993; Kamunde *et al.* 2001, 2002b) and Cd (Szebedinszky *et al.* 2001) can sometimes accumulate in fish gills. Concentrations of Cu accumulated from dietary sources may exceed those associated with toxicity during waterborne exposures (MacRae *et al.* 1999), possibly because metal accumulated via diet (from blood) is protein bound by the time it reaches the gill and therefore is not toxic. Such accumulation of dietary metals in the gill can also complicate determination of lethal accumulation values for BLM purposes.

Adjustments to the BLM will also be required relative to dietary metals uptake including Na and Ca content in food. When these elements are elevated in fish diet, binding of metals such as Cu and Cd is reduced (Niyogi and Wood 2003). Adjustments will also be required for different species (Meyer *et al.* 2002a), and may be required for organisms inhabiting natural, metal-contaminated environments (Taylor *et al.* 2003) as well as areas impacted by mining effluents, as noted above. The use of resident species in the BLM would constitute a major advancement in metals ERA.

Mixtures

ERAs are typically based on individual contaminants, and metals are no exception, even though mixtures of metals (and other contaminants) typically occur in the environment. Gills are one of the most common target tissues for metals in fish,

and acute toxicity is often caused by an ionoregulatory disturbance. Metals with deleterious effects on ionoregulation can be divided into Na^+/Cl^- disruptors (Cu(I/II), Ag(I), Hg(I/II), Al(III)) and Ca^{2+} disruptors (Co(II), Zn(II), Cd(II)), based on their preferential targets. Thus, additive or synergistic effects would primarily be predicted between Cu(I) and Ag(I), and between Zn(II) and Cd(II). Additive or synergistic effects are also likely between ionoregulatory toxicants and metals such as Ni and Al whose mode of toxic action includes respiratory impairment.

Norwood *et al.* (2003) review existing literature regarding the frequency of occurrence of less than additive (antagonistic), more than additive (synergistic), and additive responses in toxicity tests with metal mixtures. They found that all three possibilities occurred with about equal frequency, and interaction responses were dependent on both the actual mixture combinations (metals and ratios) and the exposed biota. Interactions between metals and organic contaminants likely also encompass all three possibilities. Although no research has been done into such specific metal-organic interaction responses, synergistic responses have been shown between metals and PAH in terrestrial (Babu *et al.* 2001) and aquatic environments (Gust and Fleeger 2002), and additive responses have been shown between methyl mercury and chlorpyrifos (Steevens and Benson 1999).

Although the BLM approach may ultimately be refined to deal not only with acute toxicity but also with chronic toxicity and with metal mixtures, presently the most reasonable conservative modeling approach available for mixtures is probably the toxic unit (TU) approach (concentration of each metal in a mixture divided by individual toxicity endpoint concentration to provide dimensionless TU values that are then summed). However, the TU approach has been shown to overpredict adverse effects and thus is "a conservative estimator of risk that may have little ecological relevance" (Dyer *et al.* 2000). These authors recommend a combination of literature, laboratory, and toxicity data, including considerations of habitat to best deal with mixtures.

Norwood *et al.* (2003) recommend including bioaccumulation measurements for those metals and organisms where bioaccumulation has been shown to correlate with toxic effects, together with measures of contamination, toxicity, and the status of resident exposed biota. Coeurdassier *et al.*'s (2002) finding of a linear relationship between Cd tissue concentrations and growth inhibition of terrestrial snails supports this approach, which has been used successfully by Borgmann *et al.* (2001) to identify Ni as the cause of toxicity in sediments contaminated with a mixture of metals. However, Dyer *et al.* (2000) caution that such an approach needs to conform to sampling strategies that specifically investigate pulse events, not solely continuous exposures.

Uptake Routes

Throughout most of the last century, it was assumed that the primary route of metal uptake in aquatic environments was from the water via the gills or other respiratory surfaces for animals and the roots for aquatic plants. However, uptake of metals in aquatic environments tends to be more complex than originally thought.

Uptake routes of metals to aquatic macrophytes differ for littoral emergent macrophytes and submerged macrophytes. The major uptake route for the former

is sediment pore water, whereas the latter can take up metals directly from the water column by absorption through stem and leaves or from the sediment pore water through root uptake (Barko *et al.* 1991; Jackson 1998).

As discussed by Chapman and Wang (2000), metals taken up via the digestive tract of animals may be less toxic than metals taken up from the water column, though digestive inhibition may occur due to metals in the guts of organisms such as marine echinoderms (Chen *et al.* 2002). An adequate diet, which for organisms with high digestive intensities and low gut pH includes metals such that dietary uptake of metals occurs, may protect against metals toxicity (Kamunde and Wood 2003; Kamunde *et al.* 2002a,b), whereas a poor diet without any metals can increase metals toxicity (Heugens *et al.* 2001). However, this is not always the case — waterfowl have died as a result of ingesting sediments contaminated with lead, but that did not contain lead pellets (Sileo *et al.* 2001). And organisms with an exoskeleton such as calanoid copepods may accumulate metals from the dissolved phase in that exoskeleton where they are relatively inert, whereas dietary uptake by these copepods can affect processes such as vitellogenesis (Hook and Fisher 2001a; Fisher and Hook 2002). In contrast, chironomids accumulate metals during their larval stages in metal-handling granules in their guts, and these metals are almost completely shed during larval metamorphosis (Groenendijk *et al.* 1999).

Hare *et al.* (2003) summarize evidence showing that, for freshwater invertebrates in soft sediments, the overlying water column is the primary metal source for many insect larvae that live in the sediments, whereas the sediments are the primary metal source for oligochaete worms. The reason for this difference is related to the behavior of these organisms. Many of the insect larvae interact primarily with the overlying water via aerated burrows (Wang *et al.* 2001), while worms burrow into and feed in the sediments without constructing burrows. Insect larvae that burrow into the sediments (*e.g.*, chironomids) like the oligochaetes will, similarly, get most of their metals from the sediments (Bendell-Young 1999). Hare *et al.* (2003) also note the primary importance of dietary sources of metals to some freshwater aquatic invertebrates (*e.g.*, predatory insects), and the dual importance of water and food for metals uptake by other aquatic invertebrates (*e.g.*, amphipods). Similarly, the freshwater mollusk *Dreissena polymorpha* accumulated Ag, Cd, Cr, Cu, Hg, and Se from both water and food in proportion to ambient concentrations (Roditi and Fisher 1999). These findings likely also apply to marine environments. In fact, Griscom and Fisher (2002) found that sediment-burrowing marine clams took up metals from oxic pore water, burrow water, and overlying water, with the relative importance of each uptake route differing among metals. Ingested sediment was a major source of Ag and Cu to these clams, but Co was primarily accumulated from the dissolved phase (Griscom *et al.* 2002). Couture and Kumar (2003) and Chen *et al.* (2000b) similarly found that, although both diet and water were sources of metals for zooplankton, sources “differ greatly among metals”. Campbell *et al.* (2003) reported that food was an important source of Cd and possibly other metals to juvenile (1+) yellow perch in metal-impacted lakes. Similar metal- and species-specific considerations may also apply to terrestrial environments, where the dietary route of exposure for terrestrial invertebrates may be important under environmentally relevant conditions (Lock and Janssen 2001a; Oste *et al.* 2001).

The proportions of metals that organisms may accumulate from different exposure routes (*e.g.*, ingestion versus water for aquatic organisms) are probably variable depending on the degree of contamination of those different exposure routes. Thus metal-accumulation tends to be both organism- and situation-specific.

Höss *et al.* (2001) noted that nematodes living in sediments may incur toxicity from Cd despite the metal being bound by the dissolved organic matter (DOM) in the pore water. They hypothesized that bacteria, serving as food for the nematodes, might have functioned as vectors, or the nematodes might have ingested Cd bound to organic matter directly. Nematodes are not the only organisms that feed on sediments containing bacteria and organic matter; bacteria in sediments may be a primary route of exposure for other benthic organisms such as some aquatic oligochaetes. And oligochaetes may be a primary route of exposure for higher-level organisms feeding on them or their caudal regions (which in many species are raised and waved above the sediments to obtain oxygen). Bouché *et al.* (2000) have shown that the common aquatic oligochaete worm, *Tubifex tubifex*, accumulated Cd in its caudal segments and that these tail segments could be autotomized by the worms, providing both a novel decontamination method, and a potential exposure route to higher level organisms. Similar findings have been reported for another oligochaete, *Sparganophilus pearsei*, exposed to Hg (Vidal and Horne 2003a). Autotomy in *T. tubifex* has been shown with exposure to Cu, Cd, Hg and Zn (Rathore and Khangarot 2003).

In freshwater streams the biofilm may be a source of metals to grazing animals. Courtney and Clements (2002) demonstrated significant metal accumulation and reduced growth of the grazing mayfly *Baetis tricaudatus* feeding on biofilm. Biofilm is ubiquitous in many cobble-bottom streams and forms the base of the food chain in these environments.

Intestinal metal uptake is particularly important in marine environments where anion complexation reduces the influence of the branchial (gill) pathway. In many osmoregulators, drinking opens the intestinal route of uptake for waterborne metals. Because of the digestive functions of the intestine the imbibed water becomes heavily modified in the gut, and water constituents that ameliorate gill toxicity may no longer be protective. Dietary uptake of metals from feeding, including sediment ingestion, may be direct in deposit or suspension feeders, or indirect through consumption of metal contaminated prey, or by accumulation of metals from suspended sediments or water.

Intestinal metal uptake is more complex than that of the gills because of the presence of food mixtures, secretions of mucus and digestive enzymes, and modification of osmolyte composition. The gut essentially functions as a biochemical reactor, aimed at breaking down food particles to simpler compounds, including secretion of enzymes to break down proteins, lipids, and carbohydrates, addition of surfactants, and in some organisms vast changes in pH and redox potential. In addition, bacteria present in the gut likely change metal speciation as they feed on metals chelated to organic materials in the gut contents. A cross-phyletic study of digestive fluids in benthic invertebrates indicates that the relative importance of ingestion and digestion as routes of metals uptake are likely to be taxa dependent and generalizations will apply only to taxa with similar digestive capabilities (Mayer *et al.* 2001).

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Meyer *et al.* (2002b) note that the implications of toxicity from dietary metals to aquatic biota are unclear but that different accumulation patterns and probably tissue distributions of metals will occur depending on whether metals are taken up from water or diet, probably governed by chemical form and physico-chemical partitioning. Water-borne and diet-borne metals can interact to increase or decrease metal toxicity in a manner that is not presently predictable. In most cases, toxicity does not correlate well with whole body metal concentrations, which is not surprising given that whole body measurements bear no relationship to the specific sites of action. Diet-borne metals can result in both direct (physiological) and indirect (food web) effects. Although there appear to be no effects of diet-borne metals when water quality criteria are met, there have been few such comparison studies. Meyer *et al.* (2002b) suggest three means to address diet-borne metals uptake: inferences from existing data; kinetic modeling and the establishment of tissue-specific concentration-response relationships (which would not include indirect effects such as change in nutrition, effects on prey, avoidance); or food-residue criteria (which would be empirical, approximate, and difficult to relate to water or effluent quality).

Barata *et al.* (2002a) found that Cd uptake by *D. magna* was independent of route of uptake and additive in effect. Although more Cd was accumulated from water than food, accumulation efficiency from the diet was over an order of magnitude higher (similar results have been noted for Cr and *D. magna* by Liu *et al.* (2002)). Surprisingly, uptake and toxicity were inversely related. In fish under control conditions, the uptake rate of dietary Cu is more than an order of magnitude higher than uptake of waterborne Cu (micro-g/g/h - Kamunde *et al.* 2002b). Thus it appears that toxicity of dietary metals is not necessarily linked to reduced total uptake of metals, which makes predictions of toxicity based on total dietary uptake problematic without consideration of the bioavailable fraction in the diet and in tissues.

There are differences in effects related to dietary compared with waterborne exposure (Lee *et al.* 2000a). Metal toxicity is a function of the amount of metal accumulated and retained in a bioreactive or toxic form, and not the concentration of total metals in environmental media. Rate of metal accumulation affects tissue bio-reactivity; faster uptake rates tend to increase bioreactivity (Andres *et al.* 1999; Baudrimont *et al.* 1999).

Metals responsible for toxicity may be identifiable based on internal metal concentrations, or the internal effect concentrations (IECs) of those metals. Borgmann *et al.* (2002) used lethal body concentrations of various metals that caused 25% mortality to the amphipod *Hyaella azteca* (LBC₂₅) to identify causes of sediment toxicity to the amphipods. This amphipod accumulates metals in tissues from dissolved metals in water, not from total metals in sediments, thus the exposure route is relatively simple and direct. The authors noted more difficulty in determining the LBC₂₅ values for essential metals, which are regulated by the organism, than for nonessential metals. Dixon *et al.* (2002) have developed LBC₂₅ values for ten metals for this amphipod and recommend that they be compared to actual tissue concentrations in exposed populations; exceedance of the LBC₂₅ would indicate potential for chronic toxicity. It is likely that the LBC₂₅ values determined for this amphipod are species specific, thus similar values would need to be determined for

other test/exposed organisms if this approach were to be used for other species (and possibly for other populations, depending on their level of tolerance — see below).

The demonstrable correlation between body burden and toxicity in *H. azteca* (Norwood *et al.* 2003) is likely due to the fact that in small organisms, whole body is a good surrogate for toxic sites. Thus mayfly larvae appear to be good biomonitors of metal bioavailability (Fialkowski *et al.* 2003). For larger organisms such as fish, the gill is the main site of toxic action for acute exposures and only the metal accumulated on this organ determines acute toxicity of waterborne metals. Moreover, elaborate organs for detoxification exist in fish (*e.g.*, the liver) and preferentially sequester metals from sensitive organs. Whole body residues are always useful indicators of exposure and toxicity in small organisms. Under conditions of chronic (life-time) exposure, whole-body metal burdens in larger organisms can also be useful indicators. For instance, metals concentrations in indigenous fish such as yellow perch increase in all tissues in response to metal contamination gradients (Campbell *et al.* 2003).

Trophic Transfer

Biomagnification (increasing concentrations up three or more trophic levels) is only demonstrated for organo-metallic compounds, which can move readily across lipid membranes, and is only of significant concern for methylated Hg (Chan *et al.* 2003). The risk of secondary poisoning from metals (increase in concentrations through two trophic levels) may be highest in terrestrial ecosystems, mediated not only by metals bioavailability but also by the physiology of predators feeding on prey with elevated tissue metal concentrations (Scheifler *et al.* 2002), and/or of grazers feeding on plants (Punshon *et al.* 2003).

Inorganic forms of metals tend to decline along aquatic food chains (USEPA 2002); biodilution clearly occurs for metals such as As and Pb (Chen and Folt 2000; Chen *et al.* 2000b). However, metals can still be transferred to other organisms via the food chain, though such transfer is a function of the ability of predators to both metabolize and depurate metals in prey (Mason *et al.* 2000). Blackmore and Morton (2002) found that metal accumulation by marine intertidal invertebrates was related not only to the amount ingested but also to the metal handling strategy of the prey. Robinson *et al.* (2003) suggest that metals adsorbed to prey surfaces such as carapaces may be an important mechanism of exposure to predators “dependent on mode of feeding action, and potential absorption capacity of the gut tissues.” Within planktonic food webs, herbivorous marine zooplankton may accumulate metals such as Cu primarily by trophic transfer, with dissolved uptake assuming increasing importance in contaminated waters (Chang and Reinfelder 2002); however, high physiologic turnover rates will tend to reduce ultimate body burdens (Xu *et al.* 2001). Food chain transfer of metals also occurs in freshwater foodwebs (Barata *et al.* 2002) and via other marine herbivores (Barata *et al.* 2002a).

Food chain transfer of metals in aquatic invertebrates is related not solely to the quantity of metal in prey (which can be subject to interpopulation differences — Blackmore and Wang 2003) but also its physicochemical form (Rainbow 2002). Thus, it is not surprising that Liu *et al.* (2002) found that efficiency of trophic

transfer of metals from *D. magna* to zebrafish was metal-specific and no generalizations were possible. Similarly, Wang (2002) found that bioconcentration potential in marine food webs via food (his paper focuses on “secondary poisoning”, increasing metals concentrations across two trophic levels, which he refers to as “biomagnification”) is species-specific, related to assimilation efficiencies and depuration rates. Thus, metals are unlikely to bioconcentrate in marine copepods due to their high capacity for depuration. However, bioconcentration from food of Cs, Zn, Se and methyl-Hg can occur in marine fish, and of Zn, Cd, Se, and Co in marine bivalves.

Wallace *et al.* (1998) found that the development of metals tolerance (see below) in oligochaete worms influenced the absorption of Cd by shrimp feeding on those worms; absorption (assimilation efficiency — AE) was lower in Cd-tolerant worms than in non-tolerant worms. Bioaccumulation of metals and trophic transfer are both strongly related to AEs, particularly for dietary uptake (Wang and Fisher 1999; Wang and Rainbow 2000; Fan *et al.* 2002; Wang 2002). Metals tolerance based on reduced uptake also minimizes the potential risks of trophic transfer (Gale *et al.* 2003).

Tolerance

The term “tolerance” as used here includes both acclimation (non-genetic tolerance) and adaptation (genetic tolerance). Tolerance can involve the development of new tolerance in a population in response to metal contamination, or it can involve the selection of tolerant individuals within a population. Individuals within the same species and population will show differential genetic susceptibility (Kolok *et al.* 2002); some will not survive exposure to elevated concentrations of toxic metals. The degree of tolerance to metals exposure is related to an organism’s previous history of exposure (Vidal and Horne 2003b). The more severe the concentrations of toxic metals to which naïve organisms are exposed, the more individuals will be killed initially and the longer it will take for tolerant organisms to repopulate. Thus the impact of metals on populations and communities can involve loss of sensitive individuals within a species as well as loss of sensitive species (Peeters *et al.* 2000). Tolerance of biota to metals has occurred naturally as a result of evolutionary exposures to metals (Chapman and Wang 2000), and the genes enabling metal tolerance are found in most biota. Tolerance can be directly to metals the organisms are exposed to, or can arise as a result of exposure to other metals as “co-tolerance”. For example, Díaz-Raviña *et al.* (1994) observed co-tolerance between zinc and lead in soil bacteria.

Metallothionein (MT) induction is one way by which organisms of various types acclimate to elevated metals concentrations. Such acclimation is common in fish (Klerks and Lentz 1998). Acclimation via synthesis of MT provides microalgae with tolerance to Cd (Pérez-Rama *et al.* 2001), provides similar protection to benthic oligochaete worms (Deeds and Klerks 1999), and may also provide protection to the predatory insect genus *Chaoborus* (Croteau *et al.* 2002a). Induction of MT in the gut offers a means of retaining dietary metal in gut tissues with subsequent excretion through sloughing of intestinal epithelial cells, thus limiting absorption and potential toxicity to internal organs (Clearwater *et al.* 2002). The tolerance of marine biota

living around and depending on hydrothermal vents, which release large quantities of metals into the surrounding environment, is based partly on MT induction as well as on sequestration of bioavailable metals into nonbioavailable forms (Cosson 1997; Rapoport *et al.* 2002).

Other mechanisms of tolerance additional to MT induction include increased excretion (Grosell *et al.* 2001) and reduced uptake (Kamunde *et al.* 2002b; Gale *et al.* 2003). Since laboratory experiments have demonstrated that chronic exposure to metals results in acclimation (Muysen and Janssen 2001a-c; 2002a), it is likely that organisms in metals-impacted environments undergo similar acclimation.

Clark *et al.* (2000) classify plants into three categories relative to metals uptake: accumulators (high tissue concentrations), excluders (no change to tissue concentrations), and indicators (proportional uptake). Excluders are able to minimize uptake of toxic metals. Indicators and accumulators take up metals but tolerance mechanisms include: sequestration, binding, selective secretion, and leaf fall to rid plants of excess metals. Their review of metals tolerance in terrestrial plants and invertebrates living in soil indicates that tolerance occurs at the individual but not at the population level. However, metal tolerance in plants can emerge within a single generation and with no detrimental effects.

Biota can and do adapt to a wide range of metal concentrations without necessarily incurring any fitness costs (Barata *et al.* 2002b); genetically based physiological mechanisms allow adaptation to occur. However, physiological acclimation to elevated metals concentrations, that is not genetically based, may decrease energy reserves and consequently also reduce such critical population-level parameters as reproduction (Muysen and Janssen 2001a-c). Levels of metal adaptation in natural populations can change relatively rapidly related to gene flow and thus can be highly dynamic (*e.g.*, reduction with gene flow from noncontaminated areas — Groenendijk *et al.* 1999, 2002). However, selection for contaminant resistance appears to become less effective as more contaminants are involved (Klerks and Moreau 2001).

Assessing acclimation/adaptation to varying metal concentrations is particularly important in ERA due to the need to account for both natural (background) and anthropogenic metal exposures. Muysen and Janssen (2001a-c; 2002a,b) demonstrated that the susceptibility of algae and daphnids to Zn changes by up to a factor of 5 when these organisms are acclimated from very low to very high background Zn concentrations. Similar tolerance changes occur in terrestrial potworms exposed to Cd (Lock and Janssen 2001e).

Sloman *et al.* (2003) have shown socially induced changes in metals uptake in rainbow trout (*Oncorhynchus mykiss*). Subordinate fish take up more Cu and Ag during waterborne exposures than dominant fish. These differences appear to be due to differences in sodium uptake rates between dominant and subordinate fish. This study and other work by Sloman *et al.* (2002) indicate that metals tolerance can change at the individual level, relatively rapidly. Though it could be argued that in evolutionary terms, dominant fish are more likely to survive metals exposure, removal of subordinate fish usually results in other fish becoming subordinate so the hierarchy readjusts itself (Sloman, personal communication).

Adaptation to contamination can take several forms in patchy environments. For instance, Salminen and Haimi (2001) found that enchytraeid worms in metal-contaminated soils prospered because they: avoided heavily contaminated soils,

increased their energy allocations to reproduction, and thus maximized their dispersal patterns. In fact, worms from the metals-contaminated soils reached a larger population size than worms from an uncontaminated site. The authors noted that laboratory toxicity tests would have indicated high mortality at the observed average soil metal concentrations, when in fact this did not occur in the natural environment. Similarly, Ginocchio *et al.* (2002) found that vegetative growth of plants can provide a metal avoidance mechanism in soils where contamination is heterogeneous. The same considerations, though not explicitly demonstrated, could apply to contaminated sediments. However, Spurgeon and Hopkin (1999) found that zinc tolerance was unlikely to be a major factor influencing the distribution of an earthworm species in contaminated soils. Thus Millward *et al.* (2001) are probably correct that feeding strategy, habitat preferences, and metal availability are “key to understanding the effects of metal enrichment on benthic meifauna” and on other fauna exposed to elevated concentrations of metals in the environment. Hence it is not surprising that Blanck *et al.* (2003) found differences in Zn tolerance between Dutch, Swedish, and Spanish periphyton (15 European river stretches were assessed), which they ascribed to factors including inherent differences between the communities, and differences in water chemistry and/or contaminant loadings. Key water chemistry parameters controlling tolerance were phosphate, which controls Zn bioavailability in nutrient-rich environments, and pH, bicarbonate, Ca and DOC in waters with low concentrations of metals.

Population- and Ecosystem-Level Effects

Typically, risk characterization in ERA is based on a combination of individual level effects measurements (toxicity, bioaccumulation tests), and population-level effects surveys (of resident communities). Integration often involves a weight of evidence approach (see below), but may also involve life history analysis to integrate toxic effects on population growth (Calow *et al.* 1997). It has been suggested that relatively short toxicity tests can provide the information necessary for life-history analysis (Barata and Baird 2000). However, partly because such analyses do not consider functional redundancy (species having similar roles in ecosystem processes; Mermillod-Blondin 2001), Forbes *et al.* (2001) found that species extrapolation models were often “very overprotective”. However, such models also do not consider indirect effects.

Indirect effects of concentrations of metals on populations can be positive (density dependent) or negative (density dependent or independent). Moe *et al.* (2002) describe positive effects of Cd exposure on blowfly populations due to density-dependent compensatory reactions. Specifically, although the Cd exposures were toxic to some individuals, at the population level these exposures resulted in increased larva-to-adult survival, as well as increased mean pupal mass and biomass production due to reduced larval competition as a result of lower adult reproduction and lower survival of young larvae. Similar findings were reported for Trichoptera exposed to the pesticide fenvalerate (Liess 2002). Slightly different findings were reported by Nascarella *et al.* (2002), also exposing blowflies to Cd. These authors reported a hormetic-like biphasic response for one life-stage followed by toxicity at a later life-stage. In food-limited chironomid populations, Cd exposure more than

doubled population growth rate due to reduced larval competition (Postma *et al.* 1994). Thus, as noted by Moe *et al.* (2002): “the various types of interactions that may arise between density-dependent and density-independent effects may make it more difficult to predict the outcome of a single abiotic factor on a population without a good understanding of the density-dependent processes in the population.” Further, the presence of excess food can reduce metals toxicity due to metals uptake by a greater biomass. For example, the toxic effects of mercury on growth of a rotifer species were reduced when large numbers of algae, on which the rotifers feed, were present (Sarma *et al.* 2001). Conversely, food deprivation can increase metal toxicity, and water-borne metals can affect fish predator avoidance strategies (Scott *et al.* 2003).

Campbell *et al.* (2003) summarize extensive field research into the relationships (both direct and indirect effects) between physiological and population status of fish (yellow perch) in metal-impacted lakes. Metals accumulation was accompanied by only partial detoxification by metallothionein; thus, toxicity was detected at multiple levels of biological organization (cells to organs/tissues to individuals to populations). Direct effects included alteration of the morphological characteristics of gills, interrenal tissue, thyroid, and gonads, resulting in both endocrine and physiological impairment. Indirect, food-web-mediated effects of metals occurred in the most metals-contaminated lakes: stunted growth and a higher degree of dependence on smaller-sized prey (*e.g.*, zooplankton) than the fish would normally feed on as they matured. These indirect effects were ascribed to a bioenergetic bottleneck (growth efficiency reduced with the smaller-sized prey), arising because of metals toxicity to the invertebrate species that are most vital to the growth and diet development of yellow perch. Although yellow perch are more tolerant to metals toxicity than the invertebrates they feed on, loss of prey species results in a “stunted perch” phenomenon. Other lines of evidence indicative of effects of metals on yellow perch from other areas include metabolic capabilities and morphometric indicators (Rajotte and Couture 2002; Audet and Couture 2003; Couture and Rajotte 2003; Couture and Kuman 2003).

Three different examples of indirect effects (both positive and negative) of toxic contaminants are shown in Figure 1. Clearly, functional redundancy did not ameliorate the “stunted perch” phenomenon described by Campbell *et al.* (2003). However, we are far from describing and understanding population- and ecosystem-level effects. The nature of bottom-up and top-down impacts on natural populations differs (Gliwicz 2002). Growth and reproduction rates are controlled from the bottom up, however biomass, individual body size and population density are controlled from the top down “and are fixed at a specific level regardless of the rate at which they are produced”.

Terrestrial Environments

Metals can reach terrestrial environments via natural processes including weathering of rocks (rates uncertain — Hodson and Langan 1999); plants rooting in contaminated dredged sediment (Vandecasteele *et al.* 2002); applications of sewage sludge to soil; applications of fertilizers to soils; industrial discharges; atmospheric deposition. As in the aquatic environment, physical, chemical and biological factors

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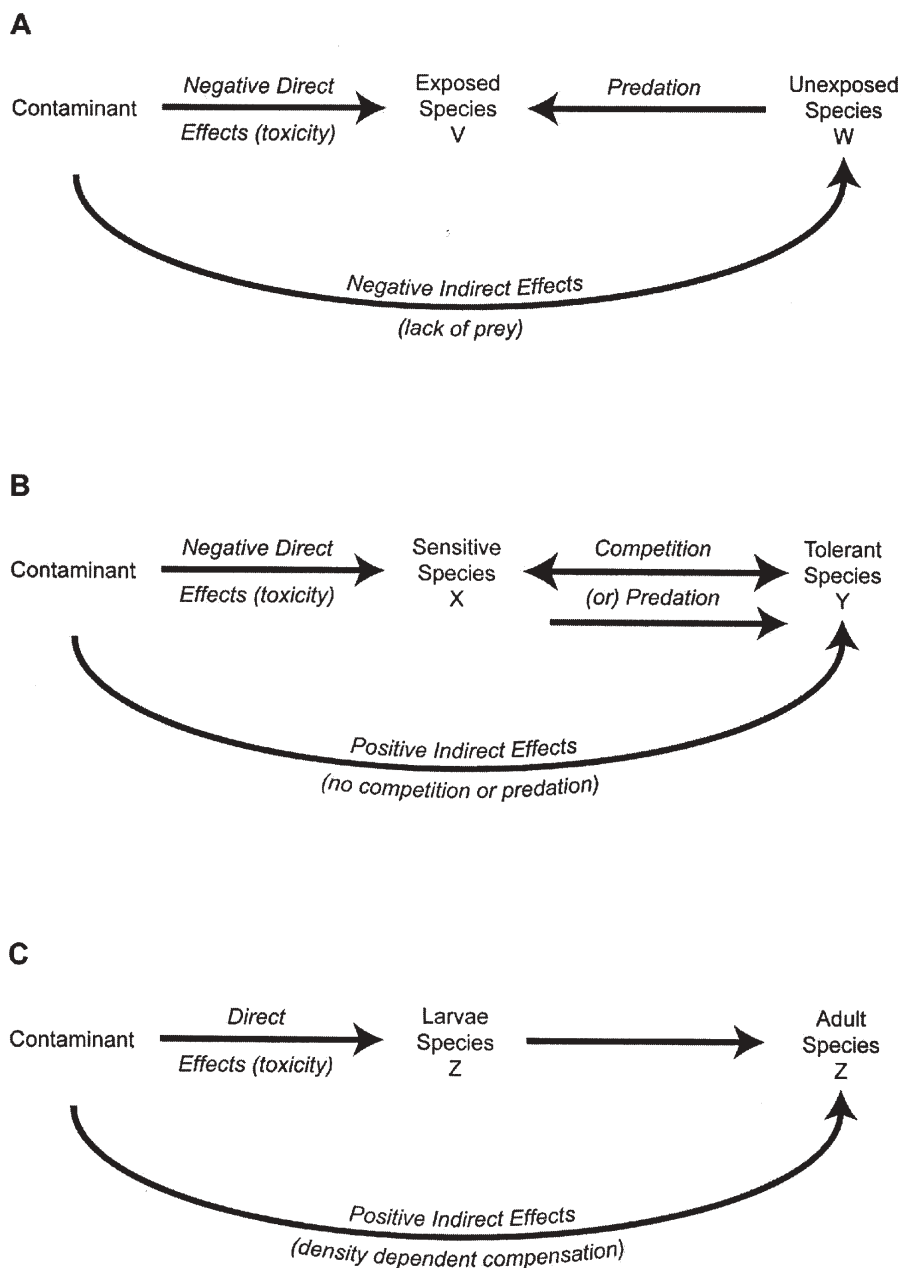


Figure 1. Examples of indirect effects of toxic contaminants. A – indirect negative effects on unexposed species W due to loss of prey species V following direct exposure to toxic contamination (*e.g.*, stunted yellow perch — Campbell *et al.* 2003). B — indirect positive effects on tolerant species Y due to toxic effects of contamination on sensitive species X, a competitor or predator. C — indirect positive effects on adult population of species Z resulting from toxic effects of contamination on larval species Z combined with density dependent compensation (*e.g.*, blowfly larvae — Moe *et al.* 2002).

affect the mobility, solubility and toxicity of metals in soil ecosystems, in particular pH and organic matter (Knight *et al.* 2000; Lock and Janssen 2001a-d; Allen 2002) as well as texture and nutrients (Allen *et al.* 2001). Under most environmentally relevant scenarios (pH 4 to 8.5), metals entering soils are typically either precipitated (by association with organic or inorganic ligands — *e.g.*, forming sparingly soluble complexes with inorganic soil constituents such as carbonates, sulfates, hydroxides, sulfides), or adsorbed. Most metals in soils are found as: stable organic complexes in humus; sorbed by Fe and Mn oxyhydroxides; adsorbed on clay-humus colloidal complexes; bound to mineral crystal lattices. Because soluble forms of metals in soil solution are only present at low concentrations, typically metal bioavailability in soils is low (Ge *et al.* 2002).

Metals partitioning to pore waters and bioavailability in soils are reduced by aging (Alexander 1995; Lock and Janssen 2002); similarly, aging reduces the availability of organic contaminants in soils (Stroo *et al.* 2000). Thus, spiking soils with metals will produce conservative data on metals bioavailability and toxicity compared to aged soils (Casteel *et al.* 2001; Lock and Janssen 2001d, 2002), and will overestimate risks from soil contamination (Alexander 2000), as is also the case for sediments (Conrad *et al.* 2002). However, additional research is needed into the factors controlling the release of metals from soils, particularly to waterbodies.

Nonbiotic release of metals in soils other than by weathering only occurs when the soils contain water, allowing the possibility of metals partitioning into pore waters where they may persist as either charged species or as soluble complexes. However, metals can also enter biota via soil ingestion. Collembola, which live in air-filled pores in the soil and in the litter layer on top of the soil, can accumulate metals both from the water phase of the soil, from the soil itself and from food (Pedersen *et al.* 2000). Snails accumulate metals from soils primarily from digestive but also from cutaneous routes of exposure (Coeurdassier *et al.* 2002) and though most uptake of metals such as Cd is from the labile pool, a small portion of their uptake can be from the nonlabile pool via digestive processes (Scheifler *et al.* 2003). Earthworms, commonly used as test organisms to determine the toxicity of metal-containing soils (Hellin *et al.* 2000), move material through soil and can also change the chemical species of some metals via their digestive processes (Naftel *et al.* 2002). Marine polychaetes perform a similar function in marine sediments; sediment processing by *Capitella capitata* is unaffected by sediments heavily contaminated with cadmium (Méndez and Baird 2002).

Metals in soils can act synergistically to increase accumulations into plants (Nan *et al.* 2002), though protective mechanisms exist. For example, phytosiderophores (iron chelators excreted by plants under conditions of iron limitation) have been shown to reduce uptake of Cd by maize (Hill *et al.* 2002). In agricultural soils, metals tend to be removed by leaching and by uptake into plants that are harvested. However, metals tend to be more persistent in forest soils where the forests are not harvested. Research by Johnson *et al.* (2003) suggests that plant-associated metal inputs in northern forest ecosystems rival or exceed atmospheric metal deposition as sources of metals to soils as a result of the mortality of plant tissues. Fine roots sequester, relative to their biomass, a large proportion of the metals in soils. Metal distributions through these forest ecosystems vary depending on plant species composition and/or soil characteristics. In complementary research, MacDonald *et*

al. (2003) found that reductions in atmospheric inputs to northern forest ecosystems have been mirrored by reductions in soil metal concentrations. They found that ecosystem properties are more important in predicting potential impacts to biota than atmospheric inputs and that soil contaminant measurements based on total metal concentrations were inadequate. Johnson *et al.* (2003) recommend that soil metals bioavailability should be estimated based on free ion concentrations; Cheng and Allen (2001) recommend additional measurement of pH and Ca concentration. MacDonald *et al.* (2003) recommend that generalized regression equations including free ion metal concentrations, soil pH and organic carbon, be integrated into mass balance calculations to evaluate metal mobility and bioavailability in forest ecosystems. Development and field validation of statistical models predicting metal toxicity to soil invertebrates as a function of soil parameters such as CEC and pH are described by Lock and Janssen (2001b,d). The technique of diffusive gradients in thin films (DGT) has been used to determine the fractions of metals in soils available for uptake by plants (Adam Peters, UK Environmental Agency, pers comm.).

Although the BLM has yet to be applied to terrestrial environments, a soil BLM may be possible by considering wetted soils as an aqueous solution containing metals that may be taken up by plants or soil invertebrates. However, development of a terrestrial BLM will be more problematic than the aquatic BLM. Weather effects such as effects of differences in water content and bioavailability during rainy/dry seasons or during snowfalls will have to be incorporated. Activities and metal uptake by microorganisms in the vicinity of roots will influence metal binding to the roots. Any terrestrial BLM will have to consider both plants and animals. The relative biomass and metal binding capacities of these two biotic components of the terrestrial BLM will need to be determined.

Predictions of free metal ions in soils are possible based on measured pH and total metals content in terms of a "free metal activity approach" (Sauvé *et al.* 1998). However, Parker *et al.* (2001) express skepticism that accurate speciation of metals in soil solution will allow accurate predictions of bioavailability and toxicity; accurate speciation measurements in soils are both technically difficult and resource intensive (Berkelaar and Hale 2003). Predictions need to be compared to actual toxicity tests (*e.g.*, phytotoxicity), and to field observations as all pools of metals in soil do not have equal bioavailability. Initial work by Lock and Janssen (2001b) relating Zn toxicity to an earthworm, potworm, and springtail to pH and CEC of artificial and natural soils is promising in this regard.

Microorganisms

There has been relatively little work conducted on the use of microorganisms in ERA of metals, or of other contaminants (MacLeod *et al.* 2001), even though adverse effects of metals on soil microorganisms are well documented and indicate higher sensitivities than plants or soil invertebrates (Giller *et al.* 1998). This omission probably reflects the differing interests of toxicologists and microbiologists rather than any deficiencies related to using microorganisms in ERA (Chapman 1999), particularly given the pivotal role of microorganisms in the functioning of aquatic and terrestrial ecosystems. Arguably, the properties of microorganism communities

deserve to be an ERA endpoint in their own right. In fact, a variety of microbial tests have been developed (Chapman 1999; MacLeod *et al.* 2001), and bacterial biosensors exposed to pore water from soils have been used to assess Cu bioavailability (Vulkan *et al.* 2000). However, presently, bacterial microorganism tests/methodologies are more appropriate for research projects than for routine use in ERA. For instance, Ellis *et al.* (2001) noted that microbial community analyses “for field evaluation of the impact of industrial pollution may be possible provided care is taken when interpreting the data”.

Giller *et al.* (1998) worry that “moderate but insidious” metal stress resulting from long-term sewage sludge applications on land may result in subtle changes to the competitive abilities of microorganisms, including possible changes in community structure. Although they note that this may not affect community function due to functional redundancy, they express concern that overall resilience may decrease relative to other stressors. Giller *et al.* (1998) recommend mechanistic studies to determine if their concerns are well founded. Unfortunately, such studies have not been conducted to date, though there are indications that bacteria possess “diverse mechanisms of [metals] detoxification” (Jackson *et al.* 1999), including production of complexing ligands capable of rapidly reducing concentrations of ionic metals in water (Mirimanoff and Wilkinson 2000). Further, microorganism responses to metals in sewage sludge will vary according to differences between soil physico-chemical properties (Khan and Scullion 2000).

CONDUCTING ERA FOR METALS

In the following sections, the recent key advances detailed previously are related to specific ERA components. The basic requirements of an ERA for metals are: the form(s) or chemical species of the metal in the environment; environmental conditions (physical, chemical, biological) affecting those form(s); the presence of receptors of potential concern (ROPCs); plausible uptake pathways for form(s) of the metal to reach the ROPCs; and knowledge of potential adverse effects on organisms, populations and communities resulting from biological uptake of the form(s) of the metal. Three iterative tiers of ERA exist. The first, Problem Formulation, is part of any ERA but can also stand on its own. The next tier, a Screening-Level ERA (SLERA) uses conservative default values. The final tier, Detailed-Level ERA (DLERA) uses more specific data with less uncertainty and greater realism. DLERAs typically conduct detailed analyses of at least one exposure scenario and/or conduct probabilistic analyses that provide an integrated distribution of potential risk.

Problem Formulation

Conceptual diagrams

Metals uptake by aquatic biota usually occurs via food and/or from solution (*e.g.*, gill, roots, digestive tract for imbibed water); for terrestrial biota such as plants, air provides an additional exposure route. ERA conceptual diagrams (the relationship between metals and assessment endpoints) need to focus on food chains, assessing exposure routes, recognizing the reality that food chain characteristics influence

metal bioaccumulation and effects (both components and length are important). In some cases dietary exposures including ingestion of particles can be predominant, water only bioassays can be misleading (Farag *et al.* 1994, 1999; Lee *et al.* 2000a, b; Hook and Fisher 2001b, 2002; Szebedinszky *et al.* 2001; Hare *et al.* 2003). Unique potential exposure pathways such as biofilm in rivers (Clements 2002) must be considered. Conceptual diagrams must also consider behavior in cases where it influences exposure, affecting bioaccumulation (burrowing, types of burrows and irrigation are important considerations). Basically the conceptual diagrams must consider all likely metal forms and exposure routes, which may require iterative temporal diagrams showing the various reasonable possibilities. Examples of generic conceptual diagrams for aquatic and terrestrial environments are provided in Figures 2 and 3.

Hazard identification

Hazard identification of metals and other substances has typically been based on a determination of PBT (persistence, bioaccumulation, toxicity). For reasons detailed by Chapman and Wang (2000), IWG (2001), and USEPA (SAB 2002), P and B are not useful predictors of the hazard of metals. The primary focus should be on T.

With the exception of radioactive elements, metals are infinitely persistent in the environment. Persistence provides no information on bioavailability, which can and does change depending on the physico-chemical conditions in the environment; metals can interconvert to different forms, affecting both exposure and potential toxicity. Thus, Di Toro *et al.* (2001) define persistence as “a characteristic of a metal that is indicative of the constancy and duration of exposure of the available metal forms in a particular medium” — the emphasis is on the bioavailable metal form, not the total metal. Similarly, Skeaff *et al.* (2002) suggest that persistence can only reasonably be determined based on the partition half-life of the bioavailable fraction of the total dissolved metal concentration determined in the laboratory under standardized conditions. SAB (2002) recommends stability and environmental residence time as more appropriate than persistence “for characterizing the temporal dynamics of metals” and also notes that, for metals, persistence may be protective rather than detrimental.

MacKay *et al.* (2003) define persistence as the residence time attributable to irreversible degrading reactions, typically evaluated using a four-compartment multimedia environment or “unit world” consisting of air, water, sediment and soil (Klecka *et al.* 2000). These authors do not recommend considering bioavailability during the hazard identification of an ERA because doing this effectively requires consideration of not only toxicity but also exposure, which latter is more realistically considered in the Exposure Assessment of an ERA (see below).

Bioaccumulation has been used as a surrogate for chronic toxicity, and as a measure of both bioavailability and potential for biomagnification. However, as discussed previously, numerous papers have shown that bioaccumulation cannot be used as a surrogate for chronic toxicity of metals. Additionally, metals do not biomagnify in their inorganic forms; biomagnification is a feature of organometallic compounds, specifically of methylated Hg (Hendriks and Heikens 2001; Gray 2002;

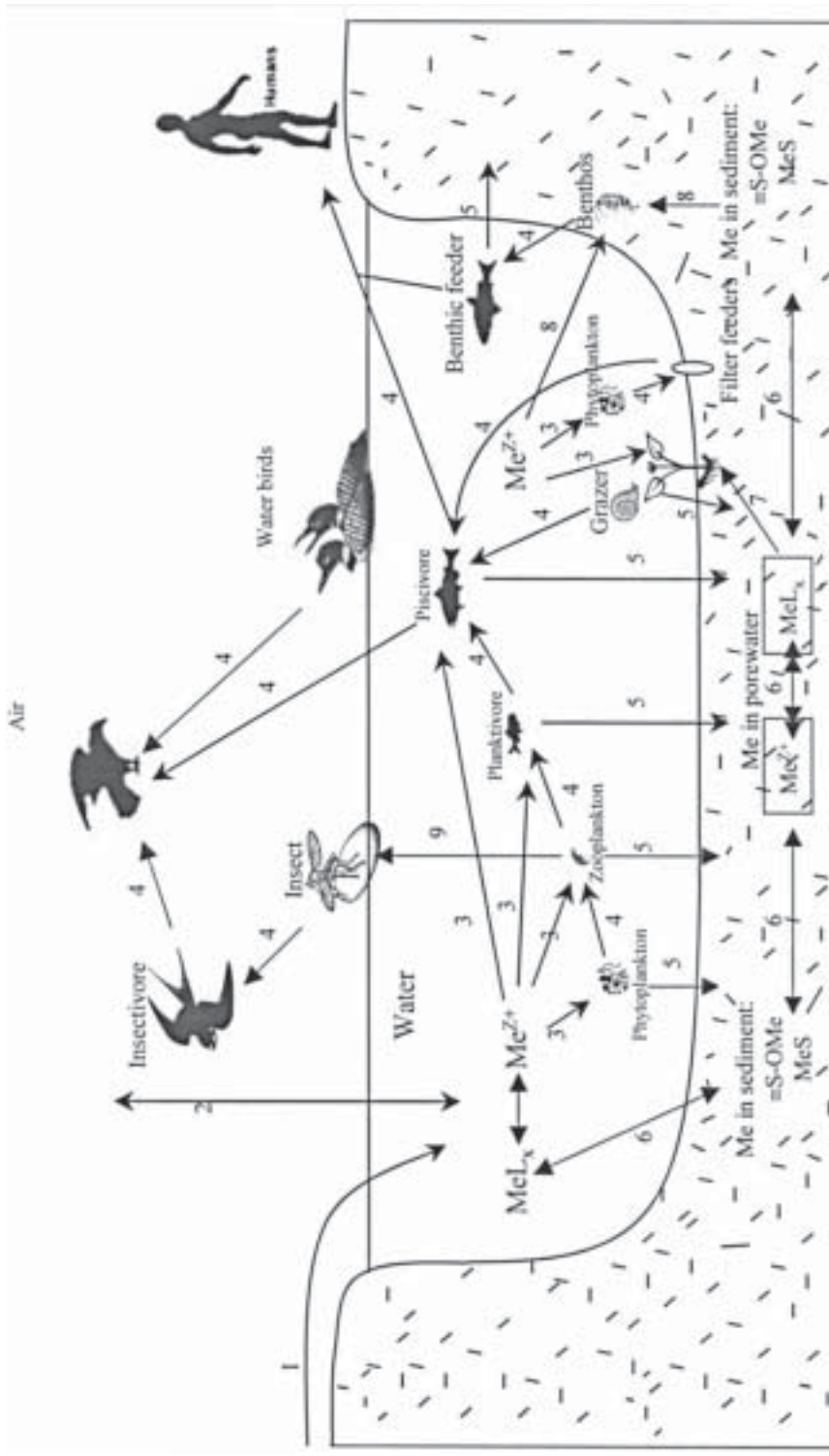


Figure 2. Conceptual model for metals in aquatic systems. (1) runoff and point sources; (2) atmospheric deposition (and volatilization for Hg); (3) uptake from dissolved phase; (4) trophic transfer; (5) deposition of detrital organic matter; (6) precipitation/dissolution and sorption/desorption; (7) uptake by rooted macrophytes; (8) benthic organisms may ingest sediment or irrigate their burrows and take up metals from water column; (9) emergence of insects. Me^{Z+} : free metal ions (metal aquo complexes); MeL_n : metal complexes with ligand L (charges are neglected for simplicity); $\equiv S-OMe$: metal precipitates; MeS : metal adsorbed on particles.

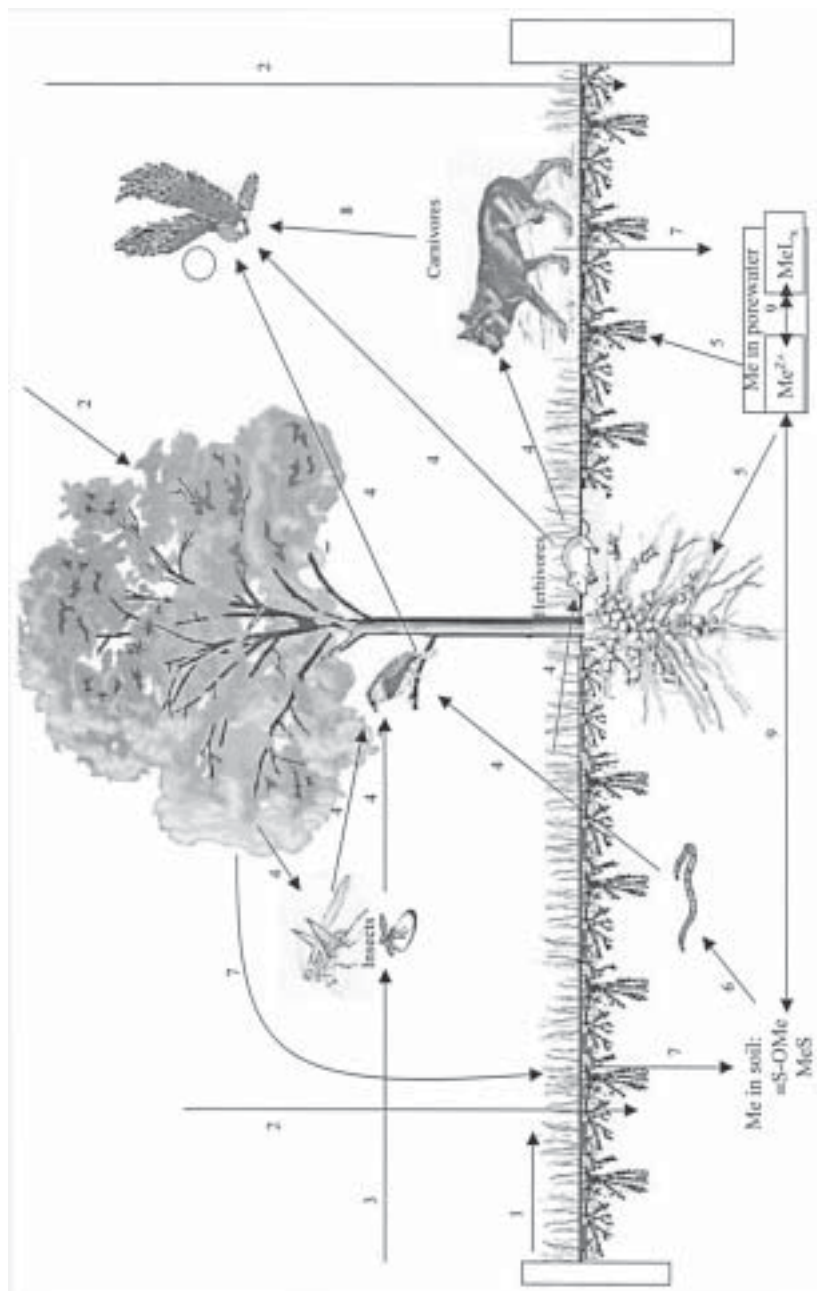


Figure 3. Conceptual model for metals in terrestrial systems. (1) surface runoff/erosion; (2) atmospheric deposition; (3) insect emergence from aquatic systems; (4) trophic transfer; (5) metal uptake from soil pore water; (6) soil ingestion; (7) organic matter decay; (8) scavenging of dead organic matter; (9) precipitation/dissolution and sorption/desorption. Me^{2+} : free metal ions (metal aquo complexes); MeL_n : metal complexes with ligand L (charges are neglected for simplicity); MeS : metal precipitates; $MeS-OMe$: metal adsorbed on particles.

Rainbow 2002; USEPA 2002; Chan *et al.* 2003). Bioaccumulation determinations such as bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) do not have a role in determining the hazard of metals in the environment, but may have a role in DLERAs where exposure and background concentrations are known (see below). However, BCFs determined under laboratory conditions may not be applicable to conditions prevailing in the field (Wang and Dei 2001).

At present, for metals in aquatic environments, the most appropriate procedure to assess whether or not specific metals are hazardous is to focus on their potential toxicity: first, determine whether they are readily soluble in water; if they are, then determine the thermodynamic and kinetic stability of the dissolved forms; and finally determine the toxicity of the parent and dissociated substances (IWG 2001). Similar procedures are recommended for metals in terrestrial environments. Toxicity data should ideally be (in order of preference): determined site- and situation-specifically; predicted using the BLM under site-specific conditions relative to appropriate species sensitivity distributions (SSDs, see below); assumed, by default, to equal the results of laboratory toxicity tests with soluble metal salts. The last approach is the least satisfactory and the most unrealistic, and should be avoided unless it is clear that only a highly conservative screening effort is being undertaken.

For hazard identification at impacted sites, spatial analyses of contaminant and effects gradients (which indicate correlations, not cause-and-effect) provide useful information (Preston 2002a), but must be based on the "selection and collection of samples that are representative of the feature(s) of the parent material being investigated in the context of the decision(s) to be made" (Crumbling *et al.* 2001). Comparisons to reference areas, background conditions (see below) and / or environmental quality guidelines (see below), can be useful but should not be regarded as definitive.

Environmental quality guidelines

Environmental quality guidelines (EQGs) have been developed for metals and other substances in attempts to determine and predict concentrations above which effects occur and below which effects do not occur. EQGs include water, sediment, and soil values, which vary by jurisdiction and by proponent. New research is refining these values and providing new information on species-specific sensitivities to individual metals (Hunt *et al.* 2002) and to combinations of metals (Franklin *et al.* 2002), indicating some situations in which toxicity is increased (Hansen *et al.* 2002), and others in which it is decreased (Norwood *et al.* 2003). However, presently EQGs do not adequately consider bioavailability (Mountouris *et al.* 2002). Thus the role of EQGs in ERA should, at present, be restricted to assisting in determining whether contaminants pose relatively low or very high potential for significant toxicity to resident organisms (Wenning and Ingersoll 2002). And EQGs should only be applied in the context of exposure routes; for instance, as noted above, some sediment-dwelling biota may be affected by contaminant concentrations in the overlying water, not in the sediment, thus rendering sediment quality guidelines (SQGs) inappropriate for these biota, unless the relationship between overlying water chemistry and metal bioavailability from sediments is understood.

Exposure Assessment

Typically, exposure of biota to metals is expressed as a concentration; given the importance of dietary sources of uptake and the reality that it is the bioactive or toxic metal within organisms that is responsible for any toxicity, exposure is best expressed as a dose. Similarly, exposure needs to be considered on a site-specific basis, considering spatial variability and patchiness (Kooistra *et al.* 2001). For soils, Allen *et al.* (2001) recommend an operational 0.01 M HCl soil extraction “as the best extraction that potentially represented bioavailable metals.” Dilute acid extractable metals have also been found to correlate to bioavailable metals in sediments (Bryan and Langston 1992; Lee *et al.* 2000a).

Transport and fate models are required for determining exposure in DLERA. Modeling of metals transfer and concentration between environmental compartments can be either deterministic or stochastic. Deterministic models, typically used in SLERA, use a single set of assumed conditions from the range of possible environmental conditions. Stochastic models, typically used in DLERA, use a probabilistic approach to consider all possible environmental conditions.

Natural Occurrence

Metals, other than those metals after uranium on the periodic table that were produced artificially in the laboratory, are naturally occurring. Exposure can result from non-anthropogenic sources, including weathering, volcanic, and hydrothermal activities (Chapman and Wang 2000); anthropogenic inputs can come from atmospheric deposition as well as from aquatic and terrestrial sources. The magnitude of metal emissions from natural compared to anthropogenic sources is a major continuing uncertainty in ERA. Atmospheric inputs should be evaluated using appropriate source apportionment methodologies in a weight of evidence assessment (Dias and Edwards 2003).

Background concentrations of metals in sediments or soils can vary greatly on a site-specific basis. For instance, naturally mineralized areas in proximity to metal mines will typically have elevated metals concentrations in environmental media (water, sediment, soil) compared to most nonmineralized areas. However, nonmineralized areas can also contain naturally elevated metals concentrations (*e.g.*, areas of black shale, Hg; ultramafic rock, Ni, Cr; volcanic rock, As). Further, modern-day reference areas are subject to atmospheric deposition and/or regional changes in land use conditions that differ from historical reference conditions.

The simplest approach to determining background concentrations is to compare exposed to reference areas and/or to evaluate dated cores from sediments where metals are immobilized upon deposition, such as ombrotrophic peat bogs. Such determinations must be made in a geological context, accommodating both mineralogy and provenance (the origins of the soil parent materials; their source terrain(s)). The use of cores requires: a relatively continuous depositional environment; core samples to sufficient depth to predate anthropogenic activities; and a sufficient number of samples for statistical significance. The use of enrichment factors (normalizing metal concentrations to an average total crustal value) is theoretically and practically flawed and should not be used in risk assessments. Natural geological factors can result in natural variation (in either time or space) in concentrations of

immobile elements (*e.g.*, Ti, Zr) that are believed to be either unreactive in elemental form, or resistant to weathering because they are locked in resistant minerals. Instead, background concentrations should be based on “raw data, collected over a large enough area to reach background levels or to allow meaningful comparisons” (Reimann and De Caritat 2000). In rivers impacted by anthropogenic activities such as mining, but lacking baseline data Helgen and Moore (1996) recommend modeling the downstream dispersion of metal anomalies based on dilution mixing of anomalous and tributary sediments. Anthropogenic activities tend to amplify naturally occurring metal anomalies. Such modeling must, of course, respect provenance and mineralogy (Bianchini *et al.* 2002b).

However, reductions in metal inputs do not necessarily equate to reduced metals uptake by organisms. Croteau *et al.* (2002b) reported increases in food web Cd following reductions in atmospheric inputs to lakes impacted by metal smelter emissions. Reductions in the smelter emissions also result in decreasing lake water acidity. This resulted in a decrease in hydrogen ion competition with Cd for biological uptake sites, which resulted in an increase in Cd concentration in aquatic organisms. The authors concluded “the risk to organisms from metals has increased in some lakes recovering from smelter emissions”.

Rapid screening of sediments to determine acid-volatile sulfide (AVS) contents (to predict the absence of toxicity to Cd, Cu, Ni, Pb, and Zn) can be useful. AVS mainly limits release of metals to pore waters, though it provides no information on solution bioavailability (because of possible dissolved binding phases); it is a reflection of redox status of the sediments and hence chemical form/bioavailability of solid phase metals. However, the utility of such screening is limited by the following caveats: the screening method produces very conservative (overprotective) values (Simpson 2001); both fine-scale vertical gradients and seasonal variations occur (Boothman *et al.* 2001); AVS is not the only metal binding phase in sediments (Correia and Costa 2000) and does not generally control bioaccumulation of metals (Lee *et al.* 2000b); exposure to oxic pore water rather than anoxic sediments occurs for some organisms (Warren *et al.* 1999); and, AVS-bound metals can be assimilated by some clams and possibly other biota as efficiently as metals bound with oxic sediments (Lee *et al.* 2000a), except possibly in highly contaminated sediments (Fan *et al.* 2002). Similar rapid screening methods for soils have yet to be developed, though rates of processes such as nitrification rate may be useful in future (Smolders *et al.* 2001). Additional screening methods for sediments involving color image analysis to predict both AVS and iron oxyhydroxide concentrations are being developed (Bull and Williamson 2001) and should in future be more useful than AVS measurements alone given that in oxic sediments non-AVS binding factors (organic carbon, Fe and Mn oxyhydroxides) control metal bioavailability (Dong *et al.* 2000; Hagopian-Schlekat *et al.* 2001).

In aquatic systems metal dynamics including sediment reworking by organisms can complicate assessments, particularly the use of sediment cores for predicting historical metal loadings. Modeling metal diffusion and/or isotope fingerprinting can also be useful in lakes where there is no significant biological reworking of the sediments. Fingerprinting is most useful if the chemical speciation of emissions is reasonably well known. The most common form of fingerprinting involves the use of Pb related to historic use of leaded gasoline.

Risk Assessments of Inorganic Metals and Metalloids

Human activities can serve to redistribute metals in different environmental media and locations, however human activities do not create, destroy or otherwise change overall concentrations of metals in the biosphere. Thus, a total metals comparison of site-specific ambient against background (or baseline) concentrations is only useful at the hazard assessment stage of an ERA. In order to truly determine exposure, the focus must be on the bioavailable form(s) of the metals, as discussed below.

Speciation/Bioavailability

Metals occur in the environment in a variety of forms or species. Metal species are differentiated by isotopes, (*e.g.*, ^{200}Hg , ^{202}Hg), oxidation states (*e.g.*, $\text{Hg}(0)$, $\text{Hg}(\text{I})$, and $\text{Hg}(\text{II})$), and complexes (*e.g.*, Hg^{2+} , HgCl^+ , methyl Hg). Whereas the isotopic ratios of a metal can be useful to fingerprint the sources of the metal, the oxidation states and complexes of the metal are often related to the bioavailability of the metal. Bioavailability of metals to organisms is strongly site-specific and is controlled by: the species of the metal the organisms are exposed to; physico-chemical factors in the environment including sorption and partitioning; organisms' abilities to reduce or eliminate metals uptake and effects to vulnerable tissues (*e.g.*, by sequestration). Bioavailability is a necessary prerequisite for toxicity.

Predictions of transition metals availability in freshwaters based solely on a hardness adjustment do not reflect present knowledge of factors affecting metal toxicity (*cf.* previous discussion regarding the BLM), and can give misleading results. Extrapolations beyond the midrange of hardness can "drastically overpredict metal toxicity" (Meyer 1999).

Similarly, simply measuring total metal concentrations and attempting to determine total concentrations added to background as a result of anthropogenic inputs (Crommentuijn *et al.* 2000) is not sufficient to determine exposure and can provide misleading results. For example, this "added risk" approach presumes in practice (although not in theory) that there is no essential metal deficiency, which may not be true depending on both the concentration and bioavailability of background essential metals (Zhang 2000). Organic and mineral surfaces can serve to bind metals and thus affect both metal bioavailability and movement within environmental compartments. Similarly, exposure duration is affected by binding processes, and organisms can bind and sequester metals within their tissues (Hook and Fisher 2002); where such binding is to an exoskeleton, the metals are relatively inert (Hook and Fisher 2001a). Further, interspecific differences occur in metal uptake rates (Wang 2001).

Current practice in the European Union is to use the K_d to determine solid/solution partitioning, however there is growing recognition that "average" values are of little utility given high variability. The United Kingdom Environment Agency (Adam Peters, personal communication) is currently evaluating the use of speciation models to provide a more reliable estimation of the environmental partitioning of metals. These models can also provide an indication of the "availability" of a metal in the environment, although this may not always be equivalent to bioavailability.

The biologically available forms of metals tend not to persist in aquatic systems (Paquin *et al.* 2003). However, modeling validated by appropriate empirical field

data are required to determine persistence of expected species in the receiving environment. The stability of metals in the final repository of sediments or soils must also be assessed, by determining the stability of those sediments or soils to disturbances or processes (either natural or anthropogenic), which could release available forms of metals. Such phenomena can be intermittent or unusual in occurrence (*e.g.*, storms, floods, dredging, excavation), or relatively common (*e.g.*, boat traffic in shallow waters).

In terrestrial systems, metals concentrations released when soils are wetted (*i.e.*, into pore waters) are generally the bioavailable forms. However, release varies with the pH of the water entering the soils (*e.g.*, rain water), and while these metals may be leached from soils, they may also cycle into vegetation via root uptake, and back to the soil via plant tissue mortality (Johnson *et al.* 2003). Thus the traditional method of measuring soil accumulation via a mass balance (output from soils = accumulation in plants [including meat and milk of herbivores, *e.g.*, cows] and leaching) needs to be adjusted for possible recycling of metals, more likely a feature of undisturbed forests than periodically harvested agricultural areas.

Soil metals bioavailability should be estimated based on free metal ion concentrations (Sauvé *et al.* 1998; Ge *et al.* 2002); such measurements need to recognize the variability inherent in different plant communities and soil characteristics. Ideally, in future such measurements can be incorporated into a BLM for terrestrial environments as discussed previously. However, it is unlikely that predictions will replace toxicity tests and field observations in DLERA; rather they will serve primarily in SLERA and as adjuncts to site-specific determinations in DLERA.

In summary, for both aquatic and terrestrial environments, the metal species of concern, the bioavailable species, must be identified along with relevant receptor characteristics and environmental conditions, and must match the metal species used in exposure and toxicity values to estimate risk. Metal speciation should be used to predict metal cycling with changing environmental conditions (Dollar *et al.* 2001). Estimates of bioavailability should rely on empirical biological data combined with appropriate investigative studies (*e.g.*, laboratory and/or field toxicity tests), rather than only relying on one or the other line of evidence.

Metal Mixtures

The toxicity of metal mixtures cannot reliably be predicted based on the toxicity of individual metals; additive, synergistic, or antagonistic interactions may result (Franklin *et al.* 2002; Norwood *et al.* 2003). The BLM does not account for the toxicity of mixtures of metals; presently additivity must be assumed (results for individual metals in a mixture are summed). Although this is generally a reasonable worst-case assumption (Mowat and Bundy 2002), it is not always the case. For instance, selenium exhibits antagonistic effects on mercury bioavailability (Nuutinen and Kukkonen 1998; Chen *et al.* 2001; Chan *et al.* 2003). Mixtures of sediment-associated Cu, Pb, Ni, and Zn have greater than additive effects (Hagopian-Schlekat *et al.* 2001).

BLM predictions for metal mixtures need to be validated by water effects ratio (WER) tests, which compare toxicity in site or other waters to laboratory waters, and thus can reveal synergistic and antagonistic as well as additive effects of metal

mixtures under site-specific and other conditions. In such a comparison for Cu in the Hammel Creek watershed (MI, USA), Linton *et al.* (2002) found that the BLM consistently underestimated acute toxicity.

For SLERA the toxic unit approach, though it generally overpredicts adverse effects, is appropriate, as is the mathematical algorithm proposed by Mowat and Bundy (2002). However, for DLERA, a weight of evidence approach incorporating contamination, toxicity, status of resident exposed biota and tissue concentrations is more appropriate (Borgmann *et al.* 2001; Norwood *et al.* 2003). Additionally, sequential toxicity tests to determine concentration or dose combinations that define the dose boundary for a specific acceptable risk level, can be used in DLERA to provide situation-specific experimental data (Price *et al.* 2002).

Biomarkers

The most common, and probably the best, biomarkers for metal exposure are tissue metal burdens. Other commonly used biomarkers for metals exposure include the metallothioneins (MT), low-molecular-weight proteins that naturally regulate the level of labile essential metals (Zn, Cu) in cells and reduce the damaging effects of reactive oxygen species. Synthesis of some forms of MT is strongly and relatively specifically stimulated by the presence of bioreactive and potentially toxic metals. However, incomplete metal detoxification has been noted in chronic/life-long metal exposures for yellow perch (Campbell *et al.* 2003).

Biomarkers such as MT induction can provide information on exposure to metals (Laflamme *et al.* 2000; Giguère *et al.* 2003), but there does not appear to be a predictable relationship between MT concentrations and toxicity (Deeds and Klerks 1999). Because MT is induced by stressors other than metals, and is not a specific biomarker of metals exposure, it is not surprising that the relationship between MT induction and metals exposure is not fully predictable. Confounding variables such as limnological conditions in lakes can also obscure the relationship between metal accumulation and MT induction; there is a need to ensure comparability between exposed and reference sites (Perceval *et al.* 2002). Similar restrictions apply to other biomarkers of metal exposure such as heat shock proteins (Agell *et al.* 2001) and gene expression.

Morphological deformities in chironomid mouthparts can also be considered biomarkers of exposure to metals. Increased deformities in freshwaters are typically related to sediment metal contamination (Janssens de Bisthoven *et al.* 1998). However, laboratory studies have failed to show clear dose-response relationships (Martinez *et al.* 2001). Thus chironomid deformities cannot presently be considered to indicate more than potential exposure to bioavailable metals in sediments. However, as noted by Lam and Gray (2001), a positive response by a sensitive exposure biomarker can lead to Effects Assessment.

Bioaccumulation

Bioaccumulation of metals in tissues can result from exposure via water, air, food, soil or sediment; bioaccumulation is specifically defined as net accumulation in tissue resulting from exposure to all environmental sources (Newman 1998). Predictive mechanistic bioaccumulation models for water-only exposures based on organ-

ism- and site-specific data exist (Thomann *et al.* 1997; Borgmann 1998) but are of only limited applicability. Experimental bioaccumulation measurements are only valid for concentrations and time series tests (Kahle and Zauke 2002). Bioaccumulation following uptake through food is difficult to predict since this phenomenon depends on organism-specific metal handling strategies and on the amount of metal ingested, including gut contents (Walker *et al.* 2002). However, kinetic bioaccumulation models do exist for several aquatic invertebrate species (Stephenson and Mackie 1993; Munger and Hare 1997; Roditi *et al.* 2000; Croteau *et al.* 2001; Croisetière *et al.* 2002; Yu and Wang 2002).

Presently, determination of metals bioaccumulation relies heavily on empirical data (*i.e.*, direct measurements). Bioaccumulation data for soft tissues (*e.g.*, avoiding chitinous exoskeletons and shells) are useful for both the exposure and effects assessment (see Internal Effect Concentrations below) phases of ERA, particularly a DLERA. However, as previously noted, bioaccumulation of metals is not directly linked to toxic effects in all species (Barata *et al.* 2002b), and biodilution along food chains is common, though bioconcentration can occur in some cases. Further, selective feeding (Croteau *et al.* 2001) negates the usual lumping in ERA (Brix *et al.* 2001), as does the reality of species differences in metals bioaccumulation and body burdens. And, as noted by Rainbow (2002), metal concentrations in organisms comprise both metabolically active and stored, detoxified metals. Toxicity is related to a threshold concentration of metabolically available metal and not to total accumulated metal concentration. If that threshold can be determined, then such information can be used not only for assessing the risk of single metal exposures, but also of mixtures and of pulsed exposures (Escher and Hermens 2002), which latter can be more toxic than steady state exposures (Tucker and Burton 1999).

Effects Assessment

ERAs of chemical substances basically involve determination and then comparison of the Predicted Environmental Concentration (the PEC) and the Predicted No Effect Concentration (PNEC). The PNEC is intended to be protective of both ecosystem structure and function. In its simplest form, a Hazard Quotient (HQ) is derived, such that if $PEC/PNEC > 1$, there is a potential risk. More complex assessments conduct this comparison probabilistically, using cumulative frequency curves (*i.e.*, cumulative genera affected on the Y axis; concentration of the contaminant on the X axis). Typically, these comparisons are based on concentrations of contaminants in the water column, not on the actual dose in the organism.

It may be possible to estimate PECs and PNECs using bioavailable metal concentrations predicted using the BLM (though presently this is only realistically possible for acute, not chronic toxicity). Certainly PNECs can be determined based on site-specific WER testing (*i.e.*, $PNEC_{site-specific} = WER \times PNEC_{generic/laboratory}$). Arguably, there is no need for safety (uncertainty) factors for PNECs that are additional to the safety factors presently included in their development (*e.g.*, increased bioavailability in laboratory tests compared to natural systems, emphasis on sensitive species — Toll *et al.* 2001).

Any effects assessment must consider the type of exposure, which can be of three basic types: a gradual accumulation of metals; a long period of exposure to moder-

ate metals concentrations; or drastic, sudden exposure to elevated metals concentrations. There are fundamental differences between these three types of exposure, and failure to understand these differences or account for them in ERA can lead to confusing and conflicting results between different studies. Differences also occur in the sensitivity of different life-stages of the same organism to metals (Kosalwat and Knight 1987), thus the timing of drastic, sudden exposures can be critical. Regardless of the type of exposure, combining field observations with controlled experimentation is essential for determining cause, significance and extent of any environmental effects due to metals contamination (Kiffney and Clements 1994).

Essentiality

Some metals (*e.g.*, Fe, Mn, Co, Cu, Zn, Mo, Se, Cr, Ni, V, Cd) are essential for biotic health of all or at least some organisms (*e.g.*, Cd is essential to certain marine diatoms — Lane and Morel 2000), thus there is a threshold for both deficiency and excess, resulting in a bimodal dose-response. ERA for metals need to focus on the optimal concentration range (between deficiency and excess), within which organisms will experience optimal growth, development, and reproduction (Muysen and Janssen 2001a-c; 2002a,b). For ERA purposes this could be defined at the median or upper boundary of this optimal concentration range, constituting a realistic PNEC. However, care must be taken in determining a “realistic” PNEC given that the range of metal concentrations causing deficiency and toxicity probably overlap for different species under different environmental conditions.

Toxicity tests

In general, metals are not readily soluble; toxicity tests are typically conducted with soluble salts, which will overestimate both bioavailability and toxicity under real world conditions (USEPA 2002). Similarly, the general lack of DOC in toxicity tests and lack of reaction time between added metals and any DOC present in test waters will result in conservative PNEC values (Kim *et al.* 1999). Toxicity tests conducted with organisms that are not pre-acclimated to natural metals concentrations in water and food will also result in unrealistically low toxicity endpoints (Muysen and Janssen 2001a,b), and metal concentrations in maternal food may alter responses to metals (Enserick *et al.* 1990, 1993). Further, there are problems with existing metals toxicity data including information on chemical metal forms, possible shifts in forms during testing, and adequate control of pH (Wolterbeek and Verburg 2001). The use of uncensored toxicity data from the literature will generally result in very conservative inputs to risk assessments (Batley *et al.* 1999).

Relationships between laboratory toxicity tests, which represent a snapshot in time, and actual toxicity relationships can be tenuous. For instance, seasonal differences in metals sensitivity occur, possibly related to different physiological states (Garnacho *et al.* 2000), including molting in crustaceans (McGee *et al.* 1998; Kater *et al.* 2000). Changes due to manipulations during collection and testing affect the utility of bulk and pore water toxicity tests (and of chemical analyses — Bull and Williams 2002; Chapman *et al.* 2002a; Simpson *et al.* 2002). For example, static sediment toxicity tests may give results requiring careful interpretation because metals in sediments are likely to move from the sediment to the water column (Hare

et al. 2001). Lowered oxygen concentrations (which do not occur in typical highly aerated laboratory toxicity tests) can increase uptake of Cd by clams (Tran *et al.* 2001). Environmental stress from exposure to UV-B and shortage of food increased the toxicity of Cu to an Antarctic amphipod (Liess *et al.* 2001).

Toxicity testing must be based on realistic exposure scenarios. For example, organisms that burrow into sediments while maintaining an oxic environment in their burrows are not affected by pore water toxicity. The most appropriate toxicity tests for these organisms would involve overlying waters. As noted by Hare *et al.* (2003), the PNEC needs to be based not only on the forms (species) of metals present, but also on the correct environmental medium. For example, if uptake is primarily via the water, then traditional water exposure toxicity tests apply. However, if uptake is also via the sediment and/or the diet, then PNECs need to be developed considering organisms as multicompartiment systems, in which metal distribution within organisms (and any accompanying toxicity) will vary depending on the metal uptake pathway (*i.e.*, internal vs. external). Ideally, toxicity should be expressed in terms of a dose rather than a concentration. In addition, seasonal variation in organism sensitivity to contaminants must be considered, including temperature effects which can increase uptake rates of metals (Bervoets *et al.* 1996; Gresen 2001; Croteau *et al.* 2002c).

Realistic thresholds of toxicity need to be established for both excess metals and for deficiency of essential metals, which latter can also occur as a result of interactions between metals (*e.g.*, Cu and Mo; Erdman *et al.* 1978). The results should be analyzed with no preconceived assumptions, or confining statistics (the dose response will typically be bimodal or U-shaped). Toxicity testing should be conducted with organisms preacclimated to natural levels of metals, and should include deficiency testing. We need to understand the bioavailability of metals taken up from food compared to metals taken up from the water column. Laboratory protocols need to be more realistic (*e.g.*, avoid artifactual release of metals into the overlying water during sediment toxicity testing or abnormally higher concentrations of metals in the dissolved than in the particulate phase as typically occurs in sediment spiking tests [Schlekat *et al.* 2002]). For example, Borgmann and Norwood (1999) and Borgmann *et al.* (2001) recommend conducting sediment toxicity tests in larger containers than is usual so that a relatively large water to sediment ratio is used to reduce the effect of sediment on overlying water quality, specifically metal-complexation capacity and pH. They conduct sediment toxicity tests in Imhoff settling cones with a 67:1 water to sediment ratio (v:v), and a sediment depth of 2.3 cm at the bottom of the cones.

Ideally, toxicity tests should be conducted in the field where test organisms will be exposed to a natural mixture of contaminated food (Dorward-King *et al.* 2001). In all cases, because the form of the metal governs its bioavailability and toxicity, sufficient information about water chemistry during testing should be provided to allow prediction of the metal form, specifically: temperature, pH, alkalinity, hardness/salinity, TSS, DOC, and dissolved metal concentrations. In sediment or porewater toxicity testing, the concentration of sulfide, which is a strong complexing ligand with many metals, should also be measured and reported. Where organisms are fed during testing or as part of testing, feeding regimes, including food metal contents need to be reported. In addition, the results for all measured toxicity

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endpoints should be reported, including means, estimates of variability (*e.g.*, sample size and either standard error of the mean or 95% confidence interval), and a clear indication of statistical significance for differences between means. In addition to reporting results on the basis of the mass of toxicant present, metals concentrations should also be reported in molarity units. Molarity units allow a direct comparison of potencies among toxicants on a toxicologically relevant basis (number of atoms or molecules present), and remove ambiguity as to the element, ion, or compound used in testing (Meyer *et al.* 2003).

The BLM can be used to compute toxicity values for different metal and aqueous ligand concentrations. If diet is the main exposure pathway, modification of the biotic ligand metal characteristics will be required. The BLM is appropriate when water is the main exposure pathway, but may need to be modified when acclimation has occurred (dependent on the importance of the acclimation factor). Minimum water chemistry parameters required by the BLM are those listed above for water chemistry determinations during toxicity testing. More detailed analyses would require information on the concentrations of specific major cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+) and anions (Cl^- , PO_4^{3-} , SO_4^{2-} , CO_3^{2-}) in addition to sulfide, and the organic carbon content of the suspended solids. Computed toxicity values should be verified, by confirmatory toxicity tests, ideally by conducting water effect ratio (WER) studies in which toxicity under different water quality conditions is evaluated relative to standard laboratory waters. Additionally, bioavailable metal concentrations may, in some cases, be determined by measuring free ion activity and/or complexation. This approach will allow the use of probabilistic ERA.

Internal effect concentrations (IECs)

The basis for the BLM is knowledge of the affinity of metals for target site(s). Essentially the BLM replaces exposure-based (external aqueous) effect concentrations with mechanistically based internal (including surface-active) effect concentrations (IECs). Further refinement of the BLM to incorporate chronic exposures and both aqueous and dietary routes of exposure will enable toxicity comparisons despite variable exposure conditions, and a better determination of the hazard of metals than the present reliance on arbitrary aqueous effect concentrations. IECs will also enable better assessments of metal mixtures (and other contaminants), and of pulsed exposures (Escher and Hermens 2002).

Previous attempts to determine IECs involved standard body burden indices such as BCFs, which can be misleading for metals because higher BCFs can be associated with lower tissue residues (Chapman and Wang 2000; USEPA 2002). This is particularly true for essential metals (Muysen and Janssen 2002). Many studies (Shephard 1998; Jarvinen and Ankley 1999; Borgmann and Norwood 1999; Dyer *et al.* 2000; Borgmann *et al.* 2001) clearly indicate the importance of the dose or contaminant body residue in determining potential risk, and that metal body concentrations in small exposed organisms can be related to metal-induced effects at the organism and population levels of organization. As such they can provide useful screening-level predictors (Borgmann *et al.* 2001). Specifically, where IEC data exist for specific species, total body concentrations of appropriate, small organisms, can be determined and compared to IECs for those species; any metal exceeding the IEC

indicates high potential for toxicity. Such comparisons can also be used for causal determinations of observed effects, and need to “be considered relative to added metal body burden” focusing on the bioavailable fraction (Hook and Fisher 2002). Norwood *et al.* (2002) have determined IECs for 10 metals and the relationship between bioaccumulation and chronic toxicity for the freshwater amphipod, *H. azteca*. However, IECs may not exist for all metals, fauna and situations; for instance, Lock and Janssen (2001c) found that fixed IECs did not exist for cocoon production of terrestrial oligochaetes exposed to Cd.

Species sensitivity distributions

Species sensitivity distributions (SSDs) are used to determine the concentration of a substance protective of most species in the environment, with a point estimate based on the 95% protection level (= the HC₅ or hazardous concentration for 5% of species). There are shortcomings to this approach (*e.g.*, arguable representativeness of test species including possible over-representation of sensitive species, comparability of different endpoints, arbitrary choice of trigger values, exclusion of site-specific data). However, Brix *et al.* (2001) have shown that, for metals, available field data support the use of the HC₅ as protective. A minimum of 10 data points are required to generate reliable estimates for regulatory purposes, but this minimum is typically not achieved, and results can vary depending on the model applied (*e.g.*, log-normal, log-logistic, boot-strap regression) (Wheeler *et al.* 2002a). Further, use of SSDs needs to consider site-specific food web considerations (Brix *et al.* 2001), otherwise SSDs will not reflect realistic trophic structures and will provide misleading results (Forbes and Calow 2002a).

Presently, SSDs are based on water-only exposure concentrations, not internal doses. If high sensitivity results from such exposures compared to dietary exposures, then present SSD comparisons will provide conservative, probably over-protective data in cases where dietary uptake is significant. To determine whether this is in fact the case, there is a need to determine SSDs for species using primarily dietary routes of exposure, or both dietary and water routes of exposure, comparing these to SSDs based on water-only exposures within caveats noted by Forbes and Calow (2002a). However, in the interim, SSDs tailored to the assessment problem should be used in Effects Assessment, for Problem Formulation or SLERA.

Risk Characterization

General considerations

A key assumption of all ERAs to date is that structural protection implies functional protection (ERAs are based on measurements of ecosystem structure, not of ecosystem function). Because this assumption is probably overprotective (*e.g.*, functional redundancy is not considered), there presently is no reason to dismiss it. However, verifying this assumption remains an outstanding data gap in ERA.

Accurate metals risk characterizations require information on: the original metal species entering the environment and any subsequent transformations; physico-chemical conditions; presence of biotic receptors and potential pathways and uptake routes; and, potential effects on organisms. Metal ERAs need to consider both bioenergetics and the protection of key prey species because food chains change in

metal-contaminated waters. Bioavailable metals in lakes can result in simplified food webs that reduce the efficiency of energy transfer, resulting in reductions in energy allocations to such processes as growth and reproduction (Sherwood *et al.* 2002a,b). Such indirect effects of metals can be profound despite ecosystem functional redundancy (Salminen *et al.* 2002) and need to be fully addressed in ERA, including conceptual models that are not overly simplified (Preston 2002b), and appropriate extrapolations from individuals to populations (Jensen *et al.* 2001). Forbes and Calow (2002b) recommend the use of population growth rate analysis to identify the most vulnerable species for ERA and to “incorporate more detail into models with regard to individual-level variables and the ecological context in which the species exist and pollution occurs.”

Spatial and temporal scales

The levels of complexity involved in an ERA are often dictated by the spatial and temporal scales within which the ERA is conducted. Geographically, ERA can be (Chapman and Wang 2000) site-specific (*e.g.*, related to a specific point source discharge or contaminated site), regional-specific (*e.g.*, related to a particular watershed, a particular geological setting, or encompassing multiple sources), or global. ERA can also be conducted following temporal variations in exposure and effects of metals to the ecosystem of concern. These include, for example, temporal variations in sources (*e.g.*, operating cycles and life history of metal-discharging source(s)) and transformation of metals (*e.g.*, seasonal), as well as the activities of the organisms (*e.g.*, diurnal, seasonal, life cycle), and the dynamics of the ecosystem.

While distinguishing the spatial and temporal scales of an ERA is often a prerequisite to defining the problem and the complexity of the ERA, it should be noted that heterogeneity occurs at all spatial and temporal levels due to geochemical, biological, hydrological, and climatological variations in the environment. This is particularly the case for terrestrial environments, aquatic sediments, and land-water interfacial areas (*e.g.*, wetlands, marshes). For example, DeVries and Wang (2003) showed that the two-dimensional distribution of sulfide in sediment porewater from a Prairie wetland varied significantly within submillimeters. Since sulfide binds strongly with many metals of environmental concern (*e.g.*, Cu, Pb, Zn, Cd, Hg, Ag), a similar degree of heterogeneity would be expected in the speciation and bioavailability of these metals in the porewater.

Even if an ERA is concerned only with metals in a specific area and at a specific time scale, it should also account for trans-boundary exposures and effects. Given the continuous exchange of matter and energy in space and in time, there is in fact no boundary among ERA of metals (or other substances) at different spatial and temporal scales. Metals (the stressors) at one specific site, regardless of source (natural or anthropogenic), can be transported to another site by the movement of air, water, suspended sediments, and biota. Similarly, the receptors at a specific site may include species that immigrated from other sites.

Quantitative analyses

Current ERA risk characterizations are often based on a single quantitative analysis using default assumptions and simplistic bounding procedures that were

originally intended only as screening procedures (*e.g.*, HQs, PBT, extrapolation factors). Extrapolation factors are a conservative approach for dealing with uncertainty related to assessing chemical risks. They usually involve adjusting a point estimate (itself often conservative) by an arbitrary factor to estimate an acceptable concentration for a substance in the environment. The advantage of such an approach is that the probability of underestimating risk is greatly reduced, particularly as the extrapolation factor increases. The disadvantage is that the application of such factors generally bears little or no resemblance to ecological reality, and the use of generic application factors increases the probability of overestimating risk, too often leading to unrealistically conservative conclusions in risk assessments (Chapman *et al.* 1998). For example, evaluation of metals toxicity extrapolations based on species sensitivity distributions (SSDs) indicates that using more common freshwater toxicity data as surrogates for less common saltwater toxicity data will be overprotective but to different degrees depending on the metal (Wheeler *et al.* 2002b).

There are significant opportunities to improve the current methods of quantitative risk assessment through less reliance on default assumptions, greater use of available data and expert judgment, increased use of probabilistic techniques, more informative exposure characterizations, more biologically based dose metrics, and more mechanistically based dose-response models.

Probabilistic analyses (*e.g.*, Monte Carlo analysis) describe the variability of key factors by parameter distributions that serve as inputs to a probability analysis procedure, to provide an integrated distribution of potential risk levels. Problems with such analyses include developing appropriate distributions for key parameters, including potential correlations, which are typically highly complex for metals. However, they remain useful for DLERA.

Weight of evidence

Weight of evidence (WOE) determinations applicable to ERA have been developed (Burton *et al.* 2002; Chapman *et al.* 2002b) and need to be applied specifically to metals ERA. Collier (2003), in a summary of 12 papers on causality in field studies, published in the February 2003 issue of *Human and Ecological Risk Assessment*, found the following six criteria appropriate for establishing causality: strength of association; consistency of association; time order; biological gradient; experimental evidence; and biological plausibility. A criterion used by other researchers, specificity of association (*i.e.*, the effect is diagnostic of exposure), was found to be of little utility for establishing causation in field studies.

The importance of WOE in ERA is expected to increase as ERAs expand to the determination of watershed-level risks (Diamond and Serveiss 2001; Obery and Landis 2002; Serveiss 2002), considering chemical, physical and biological stressors. A key area presently for WOE related to metals ERA is the determination of added versus total risk. Specifically, if there are naturally high concentrations of metals to which are added anthropogenic metals, how are these separate potential risks evaluated (both separately and jointly — what are the aggregate and cumulative risks)? Another key area for WOE is the possibility of adaptation to long-term exposure to metal contamination, which may be a feature of some (but not all)

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species and populations (Ross *et al.* 2002). Adaptation is of particular importance in long-term, chronic exposures, but has been generally ignored in most ERA, with only the occasional exception (*e.g.*, Hattemer-Frey *et al.* 1995).

As previously noted, there are various examples of toxicity demonstrable in the laboratory but not realized in the field because of factors additional to tolerance and differences in water chemistry such as avoidance of patchily contaminated soils. WOE determinations in ERA need to consider contaminant patchiness together with associated (sink-source — Salminen and Haimi 2001) population dynamics, for both soils and sediments.

CONCLUSIONS

As Eaton and Greenlee (2002) note: “Fostering better research is a primary goal of our discipline. But building better ways to put fundamental knowledge into risk assessment and regulatory practice is also vital.” As is apparent from Table 1, the specific requirements for metals ERA have not changed from Chapman and Wang (2000). However, the means for implementing these requirements have improved dramatically. Table 2 summarizes key improvements to metals ERA discussed above.

It is clear that ERA for metals (and other contaminants/stressors) is and will continue to expand beyond the usual site-specific assessments to watershed-level and regional-level assessments (Butcher *et al.* 1998), particularly since findings of no risk in the headwaters of a watershed may not hold true downstream due to changes in water chemistry (*e.g.*, pH). New developments such as the BLM, which enable probabilistic analyses of different potential exposure conditions, are expected to assist in these larger ERA (Di Toro *et al.* 2001). However, to take maximum advantage of such new developments, both researchers and risk assessors need to bear in mind the three key questions that need to be addressed to fully assess the environmental risk of metals:

1. Do metals accumulate in biota above background levels?
2. Are these metals bioreactive?
3. If so, are they likely to result in adverse (or beneficial in the case of essential metals) effects? [Predictions of effects in contaminated areas need to be ground-truthed with field observations.]

Fully utilizing recent research advances, as summarized in this paper, together with future advances (rather than simply relying on historic techniques and knowledge), will enable risk assessors to provide the best answers to these three pivotal questions — answers that both protect the environment, and enable human development.

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Table 1. Specific Requirements for Metals ERA and Implementation. Updated from Chapman and Wang (2000).

ERA COMPONENT	SPECIFIC REQUIREMENTS ^a	IMPLEMENTATION ^b	
		Metal-Specific	Contaminated Site
Hazard Identification ^c	Water solubility Thermodynamic and kinetic stability of dissolved form Toxicity of the parent and dissociated compounds	Measure or predict	Not applicable
Exposure Analysis	Concentration added to background	Conduct specific toxicity tests and/or predict toxicity under site-specific conditions using BLM	Conduct spatial analyses of contamination and effects gradients and/or predict under site-specific conditions using BLM; use EQGs to determine low or high potential for toxicity
	Bioavailability	Determine background site-specifically by: comparison to reference or, in the absence of significant biological mixing activity: modeling metal diffusion, isotope fingerprinting. Do not rely on regional or other mean concentrations. Determine prevalent metal forms in the environment via chemical speciation measurements or modeling focused on bioavailability (<i>e.g.</i> , complexation capacity, free ion activity) and/or predict toxicity using the BLM	
	Exposure duration	Determine duration of bioavailable metal forms in the environment, including seasonal (and possibly diel) variations, and biotic modifiers of exposure (<i>e.g.</i> , behavior, adaptation)	
Effects Analysis	Toxicity testing with organisms pre-acclimated to natural levels of metals	Measure body burdens of test organisms to assist in establishing causation, consider toxic effects relative to added metal body burden; provide detailed information on water chemistry during toxicity testing (<i>i.e.</i> , minimum information required by the BLM)	
	Deficiency testing	Background, reference and guideline/criteria doses or concentrations should not result in toxicity due to essential metal deficiency, including seasonal variations	
	Tolerance testing	Consider the potential for adaptation in resident populations and any related energetic costs	
Risk Characterization	Integration of the above steps	Focus on food chains and their characteristics, and consider behavior as it may modify exposure. Base the risk characterization on bioavailable metal.	

^a Per Chapman and Wang (2000)

^b Metal Specific = consideration of individual metals during categorization or risk assessment, including both prospective and retrospective assessments; Contaminated Site = consideration of metals as part of a suite of potential contaminants, only applicable to retrospective risk assessment

^c Use of BCF/BAF values and/or Persistence is inappropriate, see text

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Table 2. Different Levels of ERA Complexity Require Different Information on Metals. The different levels are tiered and iterative. This is only a summary of some of the key points made in the text.

Information Required	Problem Formulation ¹	SLERA	DLERA
Conceptual Diagrams	Consider all possible exposure pathways, whether or not these are "traditional" pathways (e.g., biofilm in rivers)	Refine, focus on food chain components and length; consider behavior as it may influence exposure	Refine, possibly develop iterative temporal diagrams of all reasonable possibilities
Bioavailability (avoid "added risk" approach based on total metals concentrations)	Generic not site-specific - a "standard environment" or "Unit World"	Consider key site-specific considerations - normalization of "standard environment"	Incorporate key site-specific considerations -modification of "standard environment" (e.g., adjust standard soil mass balance in forests for possible metals recycling)
PEC	Compare reference and exposed media; use adequate level of raw data, not enrichment factors	Deterministic modeling – transport and fate (e.g., metal anomalies in rivers near metal mines in the absence of baseline data); screening procedures (e.g., acid-volatile contents)	<ul style="list-style-type: none"> ➤ Background atmospheric concentrations via source apportionment and weight of evidence ➤ Stochastic modeling – transport and fate (e.g., geochemical and diagenetic processes in sediments and/or fingerprint via stable metal isotopes)
PNEC (based on forms of metals present and correct environmental medium; expressed as a dose rather than a concentration (also report molarity units); adequate information on water chemistry during testing and measured endpoints)	<ul style="list-style-type: none"> ➤ Literature values and/or predicted with BLM ➤ Reasonable "worst case" values (e.g., upper 95% CL of the mean²) 	<ul style="list-style-type: none"> ➤ BLM predictions (acute toxicity) ➤ Standard laboratory test species (acute and chronic toxicity) ➤ Culture and test conditions within natural concentration range of essential elements ➤ Laboratory waters for aqueous exposures ➤ IECs as appropriate for screening 	<ul style="list-style-type: none"> ➤ Overlap between laboratory test species and resident species ➤ Culture and test conditions within natural concentration range of essential elements ➤ Natural waters or amended laboratory waters for aqueous exposures ➤ Determination of bioavailable metal concentrations ➤ Consideration of spatial and seasonal variability and behavior in soils and sediments ➤ Median or upper boundary of the optimal concentration range for essential metals
Tolerance	Not considered	Considered in terms of relationship between laboratory and field (weight of evidence comparisons)	Evaluated in terms of differences between the laboratory and field including experimental manipulations (e.g., responses of naive versus field organisms)
Application (Uncertainty) Factors	Not relevant, sufficient conservatism "built in"	Not relevant, increased realism	Not relevant, highest degree of realism

Table 2. (continued)

Risk Characterization (Based on weight of evidence determinations and appropriate criteria for establishing causality)	> Hazard Quotients	> Refine Hazard Quotients > Toxic Unit approach to mixtures > Comparative SSDs	> Probabilistic modeling – cumulative frequency curves > WER determinations for aqueous exposures > Consideration of: adaptation; type of exposure; contaminant patchiness and possible related population dynamics > Empirical biological data combined with appropriate investigative studies (laboratory or field) – contamination, toxicity, status of resident exposed biota, tissue concentrations > Determine stability of contaminated soils and sediments relative to depth required for assessment > Where appropriate, ground-truth laboratory tests and models with field observations
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¹ Problem Formulation: initial data scoping; development of assessment and measurement endpoints; development of initial conceptual model; initial entry, exposure and effects characterization

² 95% UCL: mean value = one-sided t statistic (standard deviation / square root of number of samples)

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