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Incorporation of metal bioavailability into regulatory frameworks—metal exposure in water and sediment

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Abstract
Background, aim, and scope The cause for this position paper is the impression that risk assessors consider primarily the concentration of free metal ions dissolved in solution controlling metal bioavailability in aquatic systems. Aiming at a more realistic risk assessment of metals, bioavailability has to be discussed under the scope of main uptake routes of metals to organisms.
Materials and methods On the basis of a review on the literature relating to bioavailability approaches, this work discusses the incorporation of metal bioavailability into the risk assessment of metals in the context of metal exposure.
Results The biotic ligand model (BLM) and the concept of sulfide bound metals described by the ratio of simultaneously extracted metals and acid volatile sulfide concept (AVS) have been developed to consider the bioavailability of metals. Both approaches assume that the free ion concentration is the most relevant exposure pathway. However, apart from geochemical conditions, which control free metal concentration, bioavailability is additionally a result of contaminant/particle interaction and of organisms' activity. Asking for the relevant exposure pathways for inorganic metals to organisms, the compartments' water and sediment have been evaluated and also the importance of contaminated food.
Discussion We present a conceptual model of the main processes and sources for uptake of trace metals at a biological membrane. On the basis of this model, we have to consider free metal ions, metal complexes, and particle-bound metals. The BLM approach has been proposed for use in European Union risk assessments. However, the BLM provides a means to predict ecotoxicological effect of metals in the environment, but at present assumes that total significant uptake is from the dissolved phase. It is apparent that dietary accumulation of metals is at least as important as metal uptake from the aqueous phase and in many cases dominates metal accumulation.
Conclusions We found evidence in literature that uptake occurs via the dissolved phase, metal complexes, dietary, and particle-bound metals. In this regard, the AVS model, which considers only sedimentary metals in anoxic sediments, was more effective in predicting metal concentrations in pore waters than sediment toxicity in general.
Recommendations and perspectives Models will be improved by incorporating chronic metal effects rather than the binding to ligands. The most important for a risk assessment is a broad understanding of the relative importance of different uptake routes and the differential toxicity of metals accumulated by organisms with diverse feeding behavior.

Keywords Bioavailability · Biodynamics · BLM · Food · Metals · Sediment · Water

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1 Background, aim, and scope

During the past two decades, numerous studies have shown that sediment–water interactions in natural aquatic systems play an integral role in controlling transport and exposure processes of metals. At the same time, a mechanistic understanding of metal toxicity has evolved, and the significance of bioavailability has been widely accepted (Calace et al. 2006). As this field of biological research expanded, advanced models linking knowledge of physiological mechanisms to the many factors that alter metal toxicity in nature have been developed. At present, proposals have been made to incorporate this mechanistic understanding of exposure and toxicity into regulatory frameworks. Thus, the bioavailability concept provides justification for taking modifying factors into account when regulating discharges of metals and opens the possibility for more cost-effective regulations (Meyer 2002).

Aiming at a more realistic risk assessment of metals, bioavailability is taken into account in a tiered approach, which is described in the Metals Environmental Risk Assessment Guidance (MERAG 2007). This approach has been implemented in the guidance document assisting REACH registrants to perform risk assessments of metals but also plays a role in other legislations such as the Water Framework Directive (Förstner 2009). For example, chronic biotic ligand models (BLMs) have been accepted for use by the European Chemicals Bureau as part of the Existing Substances legislation (Europäische Gemeinschaft, EG 2006). Environmental quality criteria are the primary benchmarks against which environmental pollution is measured. Even though aquatic systems are dynamic and there is continuous interaction between solid phases (sediment, suspended matter) with aqueous phases (freshwater, groundwater, porewater), regulatory target values have had often considered the water matrix only. The BLM model for sediments assumes that the exposures from food and sediment ingestion pathways do not contribute to toxicity (Di Toro et al. 2005). However, the bioavailability of metals in sediments is more complex and has been critical reviewed by Simpson and Batley (2007).

Environmental quality standards (EQS) for sediments are now gaining attention due to the increased awareness that the goal of a good environmental status can only be achieved if sediment quality is evaluated and integrated in the assessment of environmental quality (Crane 2003). When developing EQS with the intent of protecting the aquatic community, the processes that lead to an interaction of metals with different biological species need to be clearly established in each matrix if these models are to be used for regulatory purposes.

2 Uptake routes for metal bioaccumulation

Finding a link between external and internal exposure is one of the challenges in environmental toxicology and offers a great potential for risk assessment (Escher and Hermens 2004). The authors differentiate between external and internal bioavailability. Aquatic organisms are able to accumulate metals from their environment via different routes over gut epithelia as well as via diffusion over the body surface. Following absorption, metals are transported to internal organs for utilization, storage, toxic effects, and possibly release. Although external bioavailability could influence internal distribution as described by Selck and Forbes (2004), the processes of the internal distribution are not under the scope of this paper.

Currently, the relationship among exposure, bioaccumulation, and toxic effects (i.e., critical body burden or organ concentrations) needs to be clearly considered if models are to be used for regulatory purposes. At first, we summarize the processes at the interface of exposure medium and the biological surface of organisms in theory. The described exposure pathways of metals to organisms are considered in a second step; there, we review the experimental evidence of metal bioavailability for the compartment water and sediment.

The metal-specific exposure factors presented here will contribute to experimental approaches to assess metal bioavailability in estimates of Predicted Environmental Concentration and Predicted No Effects Concentration (PNEC), which should improve the basis of risk assessments. The portion of the total amount of metals in the exposure medium that correlates with the observed bioaccumulation is often defined as the bioavailable fraction. Consequently, exposure concentrations, metal species, and uptake routes are important parameters for the risk assessor. A consensus exists in the literature that trace metals are mainly transported into biological cells in ionic form due to the fact that ionic channels are involved. In addition, specific transport mechanisms cross the membrane barrier like binding with membrane carrier proteins or transport through hydrophilic membrane channels. Therefore, the speciation of dissolved metals has a strong influence on the prediction of metal effects. As a consequence, “nominal”, “free”, “internal”, and “target” concentrations are differentiated when establishing dose–response relationships (Escher and Hermens 2004). On the other hand, small lipophilic metal complexes can cross a biological membrane by diffusion. Details on these exposure routes of dissolved metals are given elsewhere in excellent reviews (e.g., Batley et al. 2004; Worms et al. 2006).

Beyond those two uptake pathways, however, the importance of exposure to particle-bound metals is much less clear. Colloids are described as important not only in scavenging trace metals but also in the interactions between metals and the biota in aquatic environments (Wang and Guo 2000a, b). Labile bound metals can be desorbed from particles and supply free metal ions to the dissolved metal pool (Fig. 1). One study has shown that the labile metal fraction correlated better than the free ion concentrations with toxicity in organisms (Martin and Goldblatt 2007). It needs to be considered whether metals labily bound to particles contributed by direct transfer to surface ligands or by desorption to the free ions concentration. The latter would be enhanced by digestive fluids increasing, e.g., the transfer from food and non-food particles to biotic ligands in the gut of organisms.

It has become clear that not only do geochemical processes control metal bioavailability but that reactions with different binding sites of the biological surface also play an important role (Worms et al. 2006). If biological surfaces (e.g., microorganisms) have direct contact with contaminated particles, metals can be transferred between solid phases (Liss and Ahlf 1997). Recently, the uptake mechanism of cadmium and zinc in gram-positive bacteria was examined (Keung et al. 2008). Metal ions were complexed with the active sites on the bacterial surface, and after binding, the metal ions were then biologically transported into the bacteria.

From the biological point of view, the most important metal uptake pathway is the mass transport through plasma membrane. According to Fig. 1, three exposure scenarios have to be considered: free metal ions, metal complexes, and particle-bound metals. Toxicity results when the rate of metal uptake from all sources exceeds the combined rates of detoxification and excretion of the metal concerned.

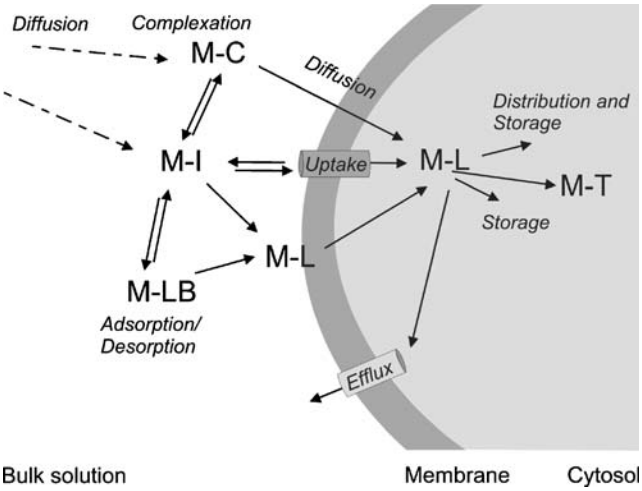

Fig. 1 Conceptual model of the main processes and sources for uptake of trace metals at a biological membrane. (*M-C* metal complex, *M-I* metal ion, *M-LB* labile particle-bound metal, *M-T* metal at target site, *M-L* metal bound to a biological ligand), redrawn and modified after Worms et al. 2006

3 Relative importance of different sources for metal bioavailability

Bioavailability is a complex result of contaminant/particle interactions and can be strongly influenced by the organisms' activity such as feeding or burrowing behavior. This renders it unlikely that a simple chemical fractionation method will be developed, which imitates the process of metal bioavailability for a range of organisms (Ahlf and Förstner 2001). Accordingly, as discussed in Meyer (2002), metal bioavailability may be more of a conceptual term than a precisely measured parameter.

After having crossed the plasma membrane, the incoming metal is bound immediately by ligands and distributed between sites of storage, efflux, or toxic action. The relationship between metal accumulation and toxicity is influenced by physiological activity and sets the stage for an accurate understanding of the effects of trace metal concentrations in aquatic organisms (Rainbow 2007). Most important for metal risk assessment is a broad understanding of the relative importance of different uptake routes and the differential toxicity of metals accumulated by these routes. Currently, the most clear cut and consistent relationships between exposure and effect have been developed for dissolved metals. The aim should be to consider the relative importance of each compartment as source of metals to aquatic organisms (Simpson and Batley 2007). The ultimate goal of exposure assessment is to estimate the target or biologically effective dose. Measuring the actual dose or toxicant concentration at the target site is usually not feasible, but simple partitioning models and more complex kinetic models offer the possibility of estimating the dose at the target site. As detailed by Batley et al. (2004), there has been a polarization of research opinions as to whether metal uptake by organisms is controlled by thermodynamic or kinetic processes. For systems where bioavailability is assumed to be determined by thermodynamic factors, measurement or calculation of the equilibrium concentrations of free metal ion is recommended. Under more dynamic conditions, labile metal concentrations will be better predictors of metal bioavailability. Again, the focus of the discussion was the assumption that site-specific geochemical conditions control the concentration of free ion metal ions and as a result biological uptake. Conversely, the bioaccumulation of metals by worms as deposit feeder was largely dominated by sediment ingestion due to the low uptake from the solute phase as well as the high metal concentrations in the sediment (Yan and Wang 2002). Thus, we have to consider the possibility that particle-bound metals are partly bioavailable and contribute to toxic effects because environmental availability refers to the ability of a metal to interact with other environmental matrices and undergo various fate and transport processes. Therefore, the main question as formulated by Fairbrother et al. (2007) is as follows: What are the relevant exposure pathways for inorganic metals to humans and ecological endpoints?

3.1 Water

The application of the bioavailability concepts to the water compartment consists of the translation of the conventional estimated effect thresholds (i.e., PNEC value, water-quality criteria) toward the free metal ion activity in certain surface waters. The most common approach to calculating the bioavailable concentration of a metal is to use a speciation model (e.g., SCAMP/WHAM). The development of the BLM was an improvement because it combines the geochemical complexities and biological ligands that affect metal exposure. The model considers the influences of speciation (e.g., free metal ion, DOC complexation) and cationic competition (e.g., K^+, Na^+, $Ca2^+$, and Mg^{2+}) on metal toxicity to organisms such as *Daphnia* or fish (Di Toro et al. 2001; Santore et al. 2001; Deleebeeck et al. 2007). From a chemical point of view, the biological surface (e.g., gill) is seen as a ligand competing with other organic molecules in the water phase. This kind of equilibrium partitioning method is a tool, which is increasingly used for regulatory purposes (US EPA 2003; Reiley 2007; MERAG 2007). Although the model has been validated in a couple of studies, some inherent limitations have been documented also.

Hassler et al. (2004) have summarized limitations of the models in well-controlled laboratory systems with the goal of extrapolating the results to complex environmental systems. For example, BLM assumes stable systems at steady state, and consequently, regulated metal uptake (e.g., of Zn) is not under the scope of this model. Previously, studies demonstrated that metal ions have been directly linked to toxicity in fish and invertebrates, while a metal complexed by dissolved organic matter does not induce toxicity to the same degree due to the reduced availability (Ma et al. 1999; Erickson et al. 1996). These forms, or species, were of key importance in understanding bioavailability, and the model modifications were driven by the intention to fit these metal species to their toxic effects. De Schamphelaere and Janssen (2004a) reported that acute Cu toxicity to *Daphnia magna* in Swedish lakes water was much higher than predicted from BLM. This discrepancy was ascribed to unusually high levels of Fe and Al, in combination with low pH of 5.5. In general, those site-specific conditions are not within the range of the model, and it has to be adjusted for temporal or spatial variability. In most cases, uptake of metals that bound to DOC is reduced; it is not reversed entirely and can contribute to the total metal burden of an organism and subsequent toxic effects (McGeer et al. 2002). In addition, the main uptake route of metals could be the complexed form from the water phase (Martin and Goldblatt 2007). Thus, this means that due to the conceptual model (see Fig. 1), the mass transport of lipophilic metal complexes through the membrane is the most important uptake pathway for microorganisms (Keung et al. 2008).

In accordance with the increasing perception of the importance of metal complexes for additional uptake, we need a better insight into the relative bioavailability of the different forms of metal as well as their specific behavior in nature. Improvements in the detection techniques for determining low free metal ion and labile bound metal concentrations provide tools for a validation of the concept. Studies have shown that some weak organic complexes and inorganic copper contribute to the bioavailable copper (Ferreira et al. 2008). The steady-state biouptake of metals from complex media was outlined for the case of two different uptake routes already by Van Leeuwen and Pinheiro (2001). The study comprises the limiting situations of inert and labile complexes and distinguishes between bioinactive and bioactive (lipophilic) complexes.

Focusing primarily on the demand of a generic model to cover the main exposure routes of metals in aquatic systems, any free ion model alone is not adequate to describe metal uptake and toxicity. Deviations from such models already have been documented, e.g., in adult bivalves, accumulating metals not only from water but also from algae, bacteria, colloidal matter, and dissolved organic matter (Roditi et al. 2000; Guo et al. 2002; Lorenzo et al. 2005; Sanchez-Marin et al. 2007). But, it remains to be discussed if exposure from additional uptake is a significant contribution to that from the water phase alone.

3.2 Sediment

There is an overall agreement that the bioavailability of metals in sediments is directly influenced by the environmental geochemistry (Lu et al. 2005). The equilibrium partitioning approach (EqP) assumes that chemical activity in the sediment, as indexed by chemical concentration in the interstitial water, is proportional to the chemical's bioavailability to sediment-dwelling organisms. In anoxic sediments, a key partitioning phase controlling cationic metal activity and toxicity in the sediment–interstitial water system is sulfide (Ankley et al. 1996). The magnitude of reactive sulfide is quantified by measuring the amount of sulfide released into the gas phase when sediment is extracted with 1 N HCl and is known as acid volatile sulfide (AVS). The determination of metal concentrations from the same extraction procedure is referred to as simultaneously extracted metal (SEM). The underlying assumption is that the potential bioavailability of a metal could be predicted by comparing the relative molar concentrations of the SEM and AVS. If sufficient sulfide exists to bind all SEM, metal toxicity is not expected. The SEM–AVS concept has been shown to be predictive for the lack of toxicity for metals having a high affinity for AVS, e.g., Cd, Cu, Pb, Ag, and Zn. Use of this SEM–AVS ratio as exposure estimates that are correlated with toxicity of metals in sediment has been explored closely for many metals (Berry et al. 1999; Burton et al. 2005). In contrast to these studies, uncertainty is increasing whether the AVS approach is a predictive tool of sediment toxicity in general because complementary uptake routes to the pore water route have to be considered for benthic organisms. Lee et al. (2000) pronounce that the AVS-based approach may be appropriate for protecting some benthic organisms from acute toxicity associated with exposure to very high pore water metal concentrations in extremely contaminated sediments. We agree that the SEM–AVS approach cannot completely explain metal bioavailability and additionally that severe limitations have to be considered.

At first, a practical problem for a reliable sampling strategy has to be solved because AVS concentrations are generally lower in the surface sediments, while SEM concentrations slightly decrease with depth (Liu et al. 2007). When monitoring environmental impacts by using AVS, both AVS and SEM concentrations in different sediment layers should be taken into account as well as a strong spatial dependence due to differences in sediment composition, total sulfur pools, and redox potential (Eh), which would have resulted in crucial differences in trace-metal availability within the area studied. The spatial pattern of SEM–AVS could deviate from total or normalized trace-metal patterns, and it is complicated to collect representative samples. The samples should be representative for where the benthic fauna live at ease. Even if the measurement would be performed correctly, AVS is not the sole partitioning phase for predicting sediment toxicity. Results were recorded in contaminated sediments differing in redox potential, AVS, dissolved sulfides, and organic contents, suggesting that other metal ligands are important for metal bioavailability and toxicity in anoxic and suboxic environments besides AVS (Sundelin and Eriksson 2001). In many sediments, oxic (oxyhydroxides) and anoxic (sulfide) phases coexist (Simpson and Batley 2007). The evidence showing relationships between the occurrence of these phases and the toxicity of metals to benthic organisms is not always clear cut. In addition, if we focus the analysis on the biological active layer of the sediment, the uncertainty of the AVS approach is growing regarding the relevance of the method for benthic species with different burrowing behavior. More concentration on the significance of other sediment characteristics like organic carbon in sediment and pore water, oxihydroxides, salinity, and sediment processing such as bioturbation is needed.

Burrowing into sediment provides a means of avoiding predators, and pumping oxygen-rich water through a burrow allows an animal to live at the interface of oxic and anoxic compartments. The relative importance of the water column and sediment compartments as metal sources for a given species is likely to be influenced by the form of its burrow and the composition of the burrow wall as well as by the rate at which the animal irrigates its burrow. Results presented by Hare et al. (2001) strengthen the argument that the protection of benthic communities from metal pollution should consider metals in both the water column and sediment compartments. In this regard, the AVS model, which considers only sedimentary metals, was more effective in predicting metal concentrations in pore waters than those in most animal taxa. Metal concentrations in pore waters were lowered in oxic sediments possibly because of their association with Fe-oxy-hydroxides or sediment organic matter (Lu et al. 2005).

It should be noted that there is no answer to the decisive question for the main uptake routes of metals to biota in sediments from the SEM–AVS concept. Furthermore, the use of organic carbon and other ligands to normalize the total metal concentrations in pore water is a physico-chemical correction and do no not represent the metal bioavailability. However, as well as sediment properties influencing metal partitioning (Kd), the speciation of the particulate phase (e.g., sulfides, organic matter, and iron hydroxides) will also influence the assimilation of ingested particles. With respect to sediment exposure pathways, the degree of assimilation of each metal from each sediment phase will depend on the organism's physiology (e.g., gut passage time, gut chemistry) as well as the properties of the sediment phase. The metal assimilation efficiency of the organism affects the exposure an organism receives from particulate contaminants that are accumulated through the digestive system (Simpson and King 2005). The theory of the AVS approach assumes that sulfides are the main limit of bioavailability universally, which may not be true, if animals oxidize sediments in their gut. The same processes occur in nature at the interface of sediment and water column, where seasonal dynamics generate a rapid exchange of toxic compounds between the top layer of the sediment and the overlaying water (Hsu et al. 2007). The evidence showing relationships between the occurrence of these phases and the toxicity of metals to benthic organisms is not always clear cut.

Sediment should be considered as a direct source for metal accumulation in benthic organisms when setting sediment quality criteria. In particular, benthic animals usually accumulated metals mainly through direct ingestion of sediment, regardless of organic or inorganic content. In one study, bivalves assimilated up to 20% body burden of Cd from metal sulfide or oxide particles (Lee et al. 2000). Recently, the consequence of particle quality for metal uptake was studied (Offermann et al. 2009). The results verified the highest assimilation efficiency from ingested food particles.

3.3 Food

The underestimation of the dietary exposure is attributed to an inherent failure of studies with spiked sediments because the pore water concentration in such experiments is often unrealistically high (Schlekat and Luoma 2000). Current studies demonstrated that diet-borne metal uptake can influence significantly total uptake, depending on the food source, animal, metal, and exposure conditions (Griscom et al. 2002; Rainbow and Wang 2001). Wang and Ke (2002) demonstrated that dietary exposure is a dominant source for Cd and Zn accumulation in the predatory gastropods. Consequently, measurements of metal concentrations in the gastropods may only indicate the bioavailable metal level in the prey organisms, instead of the bioavailable metal concentration in ambient seawater. The relative importance of different exposure pathways depends on the BCF in the prey organism, the type of prey organism, and the ingestion rate of the predator. Using a medium ingestion rate and a medium BCF in the prey organism, a model predicts that >98% of Cd and Zn in the fish studied are derived from the dietary source when copepods are the prey organisms (Xu and Wang 2002).

Although there is no general rule as for organic compounds in food chains, biomagnification of metals occurs, but more as an accidental outcome of different degrees of metal accumulation. Radiotracer techniques were used to quantify the assimilation and subsequent efflux of silver, cadmium, iron, mercury, thallium, and zinc by mesozooplankton fed ciliates, heterotrophic dinoflagellates, or heterotrophic flagellates, and the results were compared with published values measured for phytoplankton prey. The subcellular distribution of the metals within the prey cells was also determined and related to their bioavailability. The results suggest that metals contained within some protozoa are more efficiently assimilated by copepods than metals in phytoplankton. The higher bioavailability of some metals was correlated with a higher fraction of metals in the cytoplasm or liquid fraction of the protozoa (Twining and Fisher 2004). Metal compartmentalization in organisms may depend on the primary route of uptake, through the diet or across the epidermal surface, because uptake routes influence not only the total uptake but also the sequestration of metals (Selck and Forbes 2004). When assessing the effects, it is insufficient to consider whole body metal concentrations without the knowledge of tissue concentrations within the organism. After uptake of the metal (transport across the plasma membrane), the free reactive metal will reversibly bind to ligands and is transported into different compartments, where they are detoxified or not (Vijver et al. 2004).

Trophic transfer of metals from primary producers to primary consumers has been shown in a study, in which a minimal biomagnification of cadmium and copper from algae to *Ceriodaphnia dubia* was observed (Sofyan et al. 2006). However, minimal or no apparent biomagnification does not necessarily mean lack of trophic transfer because metal transfer between trophic levels can still be observed without increasing metal concentrations in the higher trophic levels. It was shown that trophic transfer of cadmium and copper was significantly different from the control. This transfer may be sufficient to produce toxicity to higher trophic levels.

The first study, which explicitly demonstrated that Cd can be magnified along certain food chains in nature, was presented by Croteau et al. (2005). Trophic enrichment of Cd increases the vulnerability of consumers at the highest trophic levels. However, the Cd source for organisms from higher trophic levels is not easy to find within complex food webs. For some metals, analyzing ecosystem complexity will be necessary before the species most exposed and at risk can be identified. In the described Cd-contaminated environment, it was found that the biomagnification took place among species ingesting Cd-rich epiphytes. The results suggest that to accurately predict Cd biomagnification in nature, physiological biodynamics, habitat, food web structure, and trophic position have to be considered. These factors seem to provide an initial “set point” at lower trophic levels that determines the concentration from which Cd transfers within the food web. Understanding those conditions will allow a greater appreciation of whether ingested metals need to be considered when developing regulatory guidelines designed to protect aquatic animals.

4 How should regulations consider metal bioavailability?

An important step forward would be to determine the plausibility of the methods applied in existing regulatory guidelines in order to delineate the main uptake routes for metals in different compartments. The BLM approach has been proposed for use in European Union risk assessments (Europäische Gemeinschaft, EG 2006). Their data requirements are small, and only routine measurement are needed as model inputs (Allen and Janssen 2006). The mechanistic basis of the physiology behind the BLM has been well established for several metals under acute exposures (Di Toro et al. 2001). The BLM provides a means to predict ecotoxicological effect of metals in the environment, but at present assumes that all significant uptakes are from the pool of free metal ions (Fig. 2).

A tiered approach is recommended by the European Chemicals Bureau for the prediction of metal bioavailability in sediments. In this regard, an extension of the SEM/AVS procedure was presented that predicts the acute and chronic sediment metal effect concentrations (Di Toro et al. 2005). A

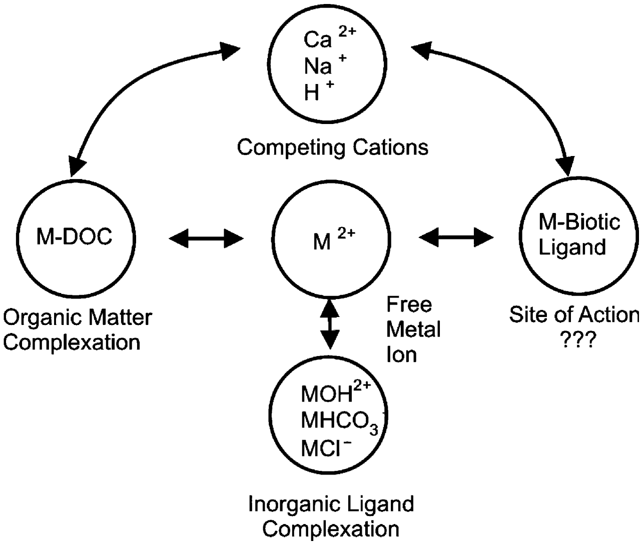

Fig. 2 Schematic diagram of the biotic ligand model (from Di Toro et al. 2001; slightly modified)

BLM and a pore water-sediment partitioning model are used to predict the sediment concentration that is in equilibrium with the biotic ligand effects concentration. The initial application simplifies the complex situation and considers only partitioning to sediment particulate organic carbon in competition with organic biotic ligands. This sediment BLM was demonstrated to have considerable potential for predicting metal toxicity associated with metal-spiked sediments, but metal-spiked sediments may erroneously overemphasize the porewater exposure route (Simpson and Batley 2007).

For regulatory purposes, a generic model will be required that explicitly consider chronic toxicity from both water and particle-ingestion exposure. The application of the BLM concept to other organisms has been accomplished by directly measuring toxicity, instead of measuring the accumulation of metal on the biotic ligand model and extrapolating the toxicological significance of this accumulation. This approach has been available since 2002 for acute toxicity (De Schamphelaere and Janssen 2002). Chronic BLMs are available and validated for some metals (Cu, Ni, and Zn), and the mechanistic basis for these chronic models have also been evaluated for certain organisms (De Schamphelaere and Janssen 2004b). Recently, a model for long-term effects was offered that can be used to improve Ni risk assessments beyond currently available approaches that depend on total dissolved Ni concentrations or estimates of Ni speciation (Deleebeeck et al. 2008). The validation exercise using the European surface waters, however, indicated that the model may not fully capture all the effects of water chemistry on Ni toxicity.

However, in all cases, the BLMs have been developed for freshwater systems without considering the dietary uptake of metals. A move toward a unifying model was presented with the underlying idea to link the BLM approach with biodynamics (Croteau and Luoma 2007). Cadmium influx rates correlate with changes in the affinity of the biotic ligand, whereas those of Cu correlate with changes in both site affinity and capacity. A relationship between metal influx rate and ligand character asks whether toxicity is the result of accumulation at the biotic ligand or the rate at which metal is transported by that ligand. Merging knowledge of transport physiology and biodynamics may provide key insights to understand metal bioaccumulation and likely help to better predict metal toxicity. The problem of internal distribution is often neglected, but could be overcome by measuring directly toxic effects rather than binding to ligands.

It is evident that dietary accumulation of metals is at least as important as metal uptake from the aqueous phase and in many cases dominates metal accumulation, e.g., in bivalves from marine environments. Models could be improved or even replaced by incorporating dietborne metals. There is increasing perception of biodynamics because understanding the biological processes that modulate dietborne metal uptake is crucial to assess the toxicity of dietborne metals (Croteau et al. 2007). These models can improve predictions of metal bioaccumulation in aquatic organisms because they incorporate different exposure routes (e.g., water vs. diet) and the dynamic nature of metal bioaccumulation processes. For example, Luoma and Rainbow (2005) reviewed the DYNBAM model (a single-compartment, kinetic-based bioaccumulation model) and found it to accurately predict metal bioaccumulation for a wide range of metals, organisms, and habitats based on data derived from 15 separate studies. Importantly, DYNBAM and similar such models require experimental data measured under environmentally realistic conditions in order to derive model parameters for each metal–species combination (e.g., uptake and elimination rates, assimilation efficiency, and food ingestion rates).

The most widespread regulatory task is to protect aquatic ecological systems considering contaminated sediments. As a result from the conceptual model pore water, overlying water, particles in general, and diet-borne metals have to be considered as potential uptake routes of metals for aquatic organisms. Because the current water-quality criteria assumes that metal toxicity primarily occurs via the dissolved phase, the finding that metal complexes, dietary, and particle-bound metals were toxic may have consequences for determining the water-quality criteria of metals. A first excellent example of dietary uptake in regulations is selenium. USEPA (2004) proposed Se water-quality criteria based on dietary uptake.

The value of the methods for measuring bioavailability in sediments can be significantly improved when the species-, metal-, and particle-specific aspects of bioavailability are more accurately taken into account in the design of chemical simulation methodologies (Peijnenburg et al. 2007). Most important for a risk assessment is a broad understanding of the relative importance of different uptake routes and the differential toxicity of metals accumulated by these routes. Currently, sediment toxicity of metals for benthic organisms is mainly assessed using toxicity tests. Referring to chronic toxicity, additional information is needed to incorporate a bioavailability model into regulations. An added value that may increase the understanding of the accumulation–toxicity relationship may be provided from in situ sediment toxicity testing.

Using in situ toxicity tests direct measurements of bioavailability and toxicity of metals in living organisms could summarize all influencing factors and avoid unrealistic metal concentrations in pore water. Such toxicity tests must consider the following:

- The bioaccumulation of metals from dietary exposure in order to account for chronic effects.
- Different feeding types to test, like deposit feeding and suspension feeding organisms.
- Accessible metals using passive samplers (Camusso and Gasparella 2006).

Such risk assessment based on in situ or field studies meets the demand of the European Water Framework Directive to develop a toxicity-based bioavailability model to estimate the risk of sediment-associated metals.

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