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Elucidating differences in metal absorption efficiencies between terrestrial soft-bodied and aquatic species

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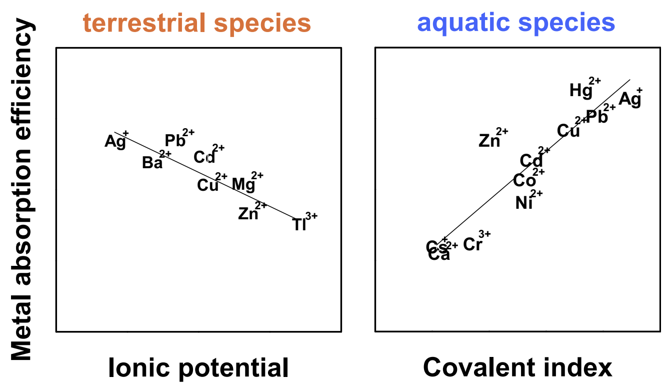
HIGHLIGHTS

- Mechanisms controlling metal accumulation in aquatic and terrestrial species are different.
- Transport through membrane determines accumulation in aquatic organisms.
- Supply to the membrane influences accumulation in terrestrial soft-bodied organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

It is unknown whether metal absorption efficiencies in terrestrial soft-bodied species can be predicted with the same metal properties as for aquatic species. Here, we developed models for metal absorption efficiency from the dissolved phase for terrestrial worms and several aquatic species, based on 23 metal physicochemical properties. For the worms, the absorption efficiency was successfully related to 7 properties, and is best predicted with the ionic potential. Different properties (8 in total) were found to be statistically significant in regressions predicting metal absorption in aquatic species, with the covalent index being the best predictor. It is hypothesized that metal absorption by soft-bodied species in soil systems is influenced by the rate of metal supply to the membrane, while in aquatic systems accumulation is solely determined by metal affinity to membrane bound transport proteins. Our results imply that developing predictive terrestrial bioaccumulation and toxicity models for metals must consider metal interactions with soil solids. This may include desorption of a cation bound to soil solids through ion exchange, or metal release from soil surfaces involving breaking of metal–oxygen bonds.

1. Introduction

The development of mechanistic bioaccumulation models for metals has, to date, focused primarily on aquatic species

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(Otero-Muras et al., 2010; Veltman et al., 2010, 2008). In these models, kinetic parameters (e.g. absorption and elimination rate constants) are predicted based on key chemical properties and organisms characteristics. For example, Veltman et al. (2008) related the metal absorption efficiency in aquatic species (including various fish, crustacea and molluscs) to a metal specific-property, the metal's covalent index. The covalent index (being a product of electronegativity of a metal ion in the crystal phase and its ionic radius) reflects the degree of covalent interactions in the metal–ligand complex relative to ionic interactions (Nieboer and Richardson, 1980). In a biotic context, it determines the strength of interactions between metal ions and sulfur donors in membrane-bound proteins, which act as channels, carriers, and/or pumps for transport of metal ions through the membrane. Metals with low covalent index (such as Cs^{+} or Cr^{3+}) are generally absorbed at lower rates by aquatic species as compared to metals with medium (such as Cd^{2+} or Co^{2+}) or high (such as Ag^{+} or Pb^{2+}) covalent index (Veltman et al., 2008; Veltman et al., 2010).

Soft-bodied terrestrial organisms, such as worms, are known to accumulate metals predominantly via pore water mediated dermal uptake (Saxe et al., 2001; Vijver et al., 2003). Analogous to metal uptake via the gills in aquatic organisms, this uptake via the skin is thought to be mediated by membrane-bound transport proteins (Li et al., 2010). This suggests that absorption rates in terrestrial worms can be related to the same metal physicochemical properties as in aquatic organisms. Indeed, for the terrestrial worm *Eisenia fetida,* Zhou et al. (2011) found a positive relationship between the covalent index and the biotic ligand stability constant across six divalent cations. Their finding indicates that a generic modeling approach of metal bioaccumulation kinetics for terrestrial and aquatic species may be possible. Such an approach would facilitate risk assessment by allowing the application of absorption rate constants derived from aquatic species to terrestrial organisms. However, biotic ligand stability constants for *E. fetida* were based on measurements in either aqueous solutions or soils spiked with soluble metal ion salts. Virtually nothing is known about which metal properties control metal bioaccumulation in earthworms exposed to aged soil contaminations from anthropogenic sources.

The metal absorption rate depends on the organism-independent metal supply rate to the membrane and the organism-dependent metal absorption rate across the membrane. Both the supply rate in the soil and the absorption rate across the membrane can be metal-dependent. In aquatic systems, the supply flux is generally sufficient to maintain the absorption flux (see Supplementary material A.1 for principles of metal supply and absorption in aquatic and terrestrial systems). Thus, metal bioaccumulation kinetics in aquatic systems is determined by the transport rate through membrane-bound proteins. In soils, diffusive or advective–dispersive transport of a metal to the organism and desorption rates from the solid phase may determine the metal absorption efficiency, next to membrane transport kinetics. For a typical soil, effective diffusivity of a metal can be up to two orders of magnitude lower as compared to the diffusivity in water, depending on soil tortuosity and hydration (Adriano, 2001). If metal absorption across the membrane is rapid as compared to diffusional supply, depletion of its concentration in the immediate vicinity of the organisms may induce its resupply from the soil solids, such as clay or organic carbon (Zhang et al., 2004). Metal desorption depends mainly on the size of the exchangeable metal pool and the response time of the (de)sorption process. This response time can be two–three orders of magnitude longer in anthropogenically-contaminated soils, compared with soils spiked with soluble salts (Zhang et al., 2004). This can influence metal absorption rates in terrestrial systems. Indeed, metal supply can limit metal uptake by plants in soils (Degryse et al., 2009). For earthworms, Vijver et al. (2005) showed that the total metal content in an earthworm was higher than the initial metal content in soil pore water, implying that desorption from the exchangeable solid phase metal pool, occurred. Thus, the absorption efficiency in soft-bodied terrestrial organisms may be controlled by those metal properties which determine metal interactions with soil solids. This has, however, not been investigated up to now.

The aim of our study was to develop and compare models for metal absorption efficiency for terrestrial soft-bodied and aquatic species, based on metal ion properties. Data was collected from literature, and linear regression models were developed to identify the physicochemical properties of selected metals that best predict metal absorption efficiency. Epigeic (*Dendrobaena veneta*, *Eisenia andrei*, and *E. fetida*), and epi-endogeic (*Lumbricus rubellus*) earthworms exposed in soils contaminated with metals from anthropogenic sources were included. For comparison with aquatic species, a study of Veltman et al. (2008) is corroborated by including more metals and more species, and by investigating whether the absorption efficiency for various fish, crustacea, and mollusks, can be related to metal physicochemical properties other than the covalent index. In total, 23 metal physicochemical properties were considered.

2. Methods

2.1. Metal absorption efficiency

To allow comparison across species, measured absorption rate constants were corrected for species wet weight by calculating metal-dependent, but organism-independent absorption efficiencies, $p_{X,w,in}$ (Veltman et al., 2008; Veltman et al., 2010). This was done by dividing the metal absorption rate constant based on the concentration of total dissolved metal ($k_{X,w,in}$) by the water influx rate ($k_{w,in}$), Eq. (1) (Wang, 2001).

$$p_{X,w,in} = \frac{k_{X,w,in}}{k_{w,in}} \quad (1)$$

where $p_{X,w,in}$ (fraction) is the metal absorption efficiency; $k_{X,w,in}$ ($L_{water}\ kg^{-1}_{wet\ weight}\ d^{-1}$) is the metal absorption rate constant based on the concentration of total dissolved metal; and $k_{w,in}$ ($L_{water}\ kg^{-1}_{wet\ weight}\ d^{-1}$) is the water influx rate, for aquatic species referred to as the pumping rate.

The influx rates were calculated using Eq. (2) (Hendriks and Heikens, 2001).

$$k_{w,in} = \gamma_0 \cdot w^{-\kappa} \quad (2)$$

where γ_0 ($kg^{\kappa}_{wet\ weight}\ d^{-1}$) is the water absorption coefficient, assumed to equal 200 for both aquatic species and soft-bodied terrestrial species (Hendriks and Heikens, 2001); w ($kg_{wet\ weight}$) is species wet weight; and κ is the rate exponent, equal to 0.25 (Hendriks and Heikens, 2001).

2.2. Data collection and treatment

2.2.1. Absorption

For terrestrial soft-bodied species, data on absorption rate constants based on the total dissolved metal concentration ($k_{X,w,in}$, in $L_{water}\ kg^{-1}_{wet\ weight}\ d^{-1}$) were included in our study when the following criteria were met: (i) organisms were exposed in controlled experimental systems using soils contaminated with metals from anthropogenic sources (including smelters, metal refineries, mine spoils, and unspecified sources); (ii) absorption rate constants were based on measured concentrations of dissolved metals; and (iii) added food was not contaminated. For model development, we excluded studies with terrestrial soft-bodied species exposed in aquatic systems, inert porous matrices, and soils spiked with soluble