Hydrobiologia 149: 43–52 (1987)
R. Thomas, R. Evans, A. Hamilton, M. Munawar, T. Reynoldson and H. Sadar (eds)
Ecological Effects of *In Situ* Sediment Contaminants
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Partitioning of trace metals in sediments: Relationships with bioavailability

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Abstract

As a result of complex physical, chemical and biological processes, a major fraction of the trace metals introduced into the aquatic environment is found associated with the bottom sediments, distributed among a variety of physico-chemical forms. As these different metal forms will generally exhibit different chemical reactivities, the measurement of the total concentration of a particular metal provides little indication of potential interactions with the abiotic or biotic components present in the environment. In principle, the partitioning of sediment-bound metals could be determined both by thermodynamic calculations (provided equilibrium conditions prevail) and by experimental techniques. The modelling of sediment-bound metals is far less advanced than is that of dissolved species, primarily because the thermodynamic data needed for handling sediment-interstitial water systems are not yet available. The partitioning of a metal among various fractions obtained by experimental techniques (e.g., sequential extraction procedures) is necessarily operationally defined. These methods have, however, provided significant insight into the physico-chemical factors influencing the bioavailability of particulate trace metals; some of these factors are discussed.

Introduction

In recent years, the fluxes of many trace metals from terrestrial and atmospheric sources to the aquatic environment have increased (Förstner & Wittmann, 1981). The resulting accumulation of certain metals in the food chain, their toxicity to aquatic organisms and their potential health hazard in drinking water supplies have led to an upsurge in interest on the part of both environmental scientists and governmental authorities.

When a trace metal is added to a natural water, it partitions among various compartments (Fig. 1): a portion will be associated with dissolved inorganic and organic ligands in solution whereas another fraction will become associated with the particulate matter following adsorption, precipitation, co-precipitation, or uptake by planktonic living organisms. As a result of complex physical, chemical and biological processes, a major fraction of the trace metals introduced into the aquatic environment eventually becomes associated with the bottom sediments. The partitioning of trace metals in these sediments will depend on many variables (nature and concentration of ligands in the ambient water; nature and concentration of solid substrates; E_H; pH; I; etc.). Variations in environmental variables (e.g., dredging of anoxic sediments or acidification of the overlying water column) may change this partitioning.

Determining the biological significance of particulate trace metal contamination in aquatic environments is a complicated problem. Many aquatic organisms are in contact with both dissolved and particulate trace metals and can in principle accumulate the trace metals either directly from the water or from the solid phases. The determination of trace metal availability from the solid phases is often difficult, even in laboratory experiments, due to the tendency of trace metals added in particulate forms to establish solute-solid equilibrium. Uptake from either source will be influenced by physico-chemical factors in the aqueous and particulate phases. In particular, bioaccumulation has been shown to depend upon such physico-chemical characteristics of the sediment as the levels of iron

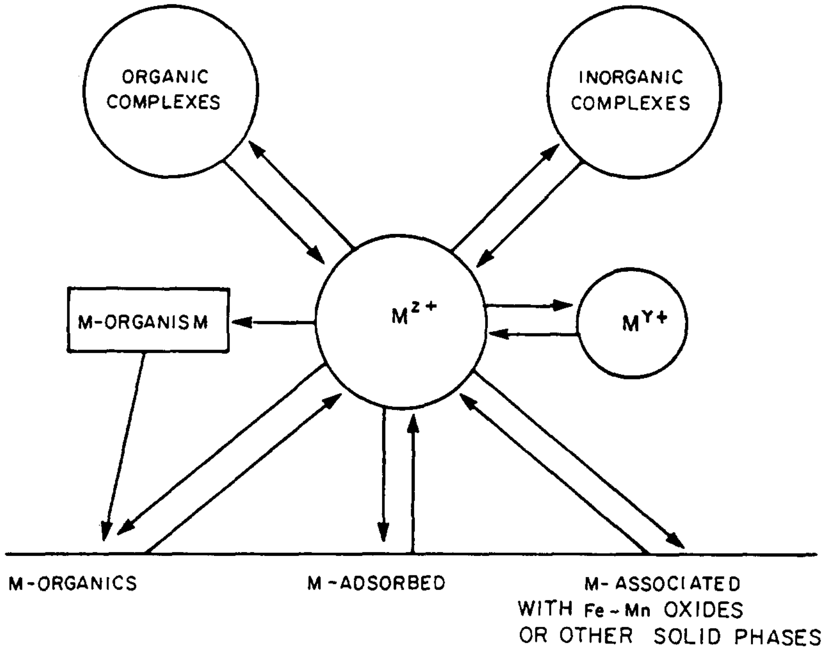

Fig. 1. Schematic representation of metal partitioning in the aquatic environment.

oxides and organic matter (Luoma & Bryan, 1978, 1982; Langston, 1980, 1982; Tessier *et al.,* 1984a) and the particular geochemical phases with which the trace metals are associated (Luoma & Jenne, 1977). With reference to this latter aspect, there is presently no satisfactory method for determining unambiguously the forms of association of particulate trace metals in natural sediments. Finally, the problem of assessing the bioavailability of sediment-bound metals is compounded by the fact that metal levels in the organisms may be influenced by physiological factors such as age and sexual condition.

The purpose of this paper is to give an overview of the difficulties inherent in determining the partitioning of particulate trace metals and to discuss the importance of partitioning in assessing their bioavailability.

Complexity of trace metal-sediment associations

Trace metals can be associated with various phases of the sediments; for example, they can be: (i) adsorbed at particle surfaces (e.g., clays, humic acids, metal oxyhydroxides); (ii) carbonate-bound (e.g., discrete carbonate minerals co-precipitated with major carbonate phases); (iii) occluded in iron and/or manganese oxyhydroxides (e.g., discrete nodules, cement between particles, coatings on particles); (iv) bound up with organic matter in either living or detrital form; (v) sulphide-bound (e.g., amorphous sulphides formed *in situ* or more crystalline forms); (vi) matrix-bound (e.g., bound in lattice positions in aluminosilicates, in resistant oxides or sulphides). The great variety of solid phases that can bind trace metals, the small amounts of some phases that have a scavenging action far out of proportion to their own concentration, the amorphous character of many of these important solid phases, and the fact that trace metals are usually only minor constituents of these phases, all converge to render difficult, if not impossible, the direct measurement of trace metals associated with a particular solid phase.

Thermodynamic calculation of particulate trace metal partitioning

In principle, the partitioning of sediment-bound metals could be determined by thermodynamic calculations, provided equilibrium conditions prevail. The modelling of the behavior of sediment-bound metals is far less advanced than is that of dissolved species because the thermodynamic data needed for handling sediment-interstitial water systems are as yet incomplete.

Thermodynamic calculations on the bulk solution of most freshwaters or seawater show undersaturation with respect to known trace metal solid phases (Schindler, 1967; Hem, 1972, 1976). Even for interstitial waters of *oxic* sediments, in which trace metals have longer residence times than in the bulk solution and are thus more apt to approach a state of equilibrium with solid phases in the sediments, trace metals are still undersaturated with respect to their least soluble compounds (Carignan, unpublished results). Hence, since solubility equilibrium with pure solids seems unlikely for trace metals under oxic conditions in natural waters, adsorption by solid surfaces has been suggested as an important mechanism for controlling certain trace metal concentrations (Schindler, 1975). Possible substrates for adsorption include clays, organic matter, as well as iron, manganese, aluminum and silicon hydrous oxides.

Oakley *et al.* (1981) have recently proposed a model based on adsorption processes to describe and predict trace metal partitioning among various geochemical phases in aquatic sediments. The adsorption of a trace metal M onto the various substrates of the sediment can be characterized in a simplified manner by:

$$M + S(1) \overset{K_A(1)}{=} MS(1) \qquad (1)$$

$$M + S(2) \overset{K_A(2)}{=} MS(2) \qquad (2)$$

$$\circ \qquad \circ$$

$$\circ \qquad \circ$$

$$M + S(k) \overset{K_A(k)}{=} MS(k) \qquad (3)$$

$$K_A(k) = \frac{[MS(k)]}{[M]\,[S(k)]} \qquad (4)$$

where K_A (k) is considered as an apparent overall (or average) equilibrium constant and [M], [S(k)] and [MS(k)] represent, respectively, the concentration of dissolved trace metal, the number of sites available for adsorption on the substrate k (i.e. Fe oxyhydroxides, Mn oxides, humic acids, etc.), and the concentration of trace metal adsorbed onto the substrate k. Mathematically, this model is similar to those used to calculate the distribution of a dissolved trace metal among a mixture of ligands.

Necessary input data for such competitive adsorption models would include, according to equation (4) (Luoma & Davis, 1983): (i) the abundance of each of the k components in the natural sediments and their binding capacities (number of sites); and (ii) the binding intensities (K_A) of each component. The determination of component concentrations relies, for the most important sinks (metal oxyhydroxides, specific organic substances, carbonates, etc.), upon chemical extraction techniques. Methods to measure the binding capacity of individual components have been reviewed by Luoma & Davis (1983), but such techniques cannot be applied to determine the binding capacity of a particular component in a multicomponent system such as natural sediments. Stability constants have been determined mostly in well-defined media, for the adsorption of trace metals onto various substrates potentially present in natural sediments (Loganathan & Burau, 1973; Murray, 1975; Davis & Leckie, 1978; Farrah & Pickering, 1979; Swallow *et al.,* 1980; Balistrieri & Murray, 1982; Millward & Moore, 1982); however, as discussed below, extension of these constants to complex systems is difficult at the present time.

In extrapolating the stability constants obtained in simple well-defined systems to natural sediments, one should realize that the complexity of natural systems can lead to some divergence as several key parameters can influence these 'constants'. The temperature in natural systems (~ 4–20 °C) can differ appreciably from that for the laboratory experiments (≃ 20–25 °C). Reactions in the natural systems proceed for much longer times than in the well-defined systems for which equilibrium is usually assumed to be attained within minutes or hours. Surface area and porosity of solid phases will influence their adsorption characteristics. For example, Crosby *et al.* (1983) have identified significant differences in surface area and porosity between fresh and aged iron oxyhydroxides, and between those derived from Fe(III) and Fe(II) sources. Most laboratory studies involve the precipitation of high Fe(III) concentrations (much higher than in natural waters) while natural iron oxyhydroxides are more commonly derived from the oxidation of Fe(II) (Crosby *et al.*, 1983). Studies over wide ranges of metal concentrations in well-defined systems suggest that the surfaces of some metal oxyhydroxides comprise various binding sites, the binding energy of which may vary be more than one order of magnitude (Benjamin & Leckie, 1981a, b). This can result in a variation of the stability 'constants' with surface coverage. Competitive interaction of high concentrations of cations for adsorption sites can also influence the stability 'constant' value for adsorption of a given metal ion. Dissolved ligands may compete with the solid phases for binding a metal ion and thus reduce its adsorption. Alternatively, the complex formed may adsorb strongly onto some solid phases and thus enhance the metal adsorption.

Few studies have tried to compare theoretical investigations or adsorption experiments in well-defined media with adsorption in natural systems; such comparisons should provide information about the possible extrapolation of results obtained in simple controlled systems to multicomponent systems such as natural sediment. Lion *et al.* (1982) have compared the adsorption of Cd, Cu and Pb onto oxic estuarine sediments before and after extracting the sediments with chemical reagents. Changes in the Cd and Pb adsorption (vs pH) behavior after specific extractions suggested that iron and manganese oxides, and organic matter were important phases in these estuarine sediments for adsorbing these metals. These results were consistent with the partitioning obtained for these metals in the same sediments using a sequential extraction procedure.

Apparent overall equilibrium constants (K_A) for the adsorption of Cd, Cu, Ni, Pb and Zn onto natural iron oxyhydroxides have been calculated with equation (4) using field data (Tessier *et al.*, 1984b); [MS(K)] and [S(k)] were obtained by extracting the oxic sediment samples with a reducing agent, and [M] was measured in the associated pore waters collected *in situ*. These data were compared with equilibrium constants obtained for the adsorption of the trace metals onto iron oxyhydroxides in well-defined media. The field data were found to be consistent with laboratory experiments and with theory. Both the influence of pH on adsorption and the binding strength sequence (i.e. Pb > Cu > Zn > Cd > Ni) observed for the field data agreed with theory. At high sediment pH values, the partitioning of Cd, Ni and Zn between the pore waters and the natural iron oxyhydroxides was similar to those reported in the literature for the adsorption of these metals at low surface coverage onto amorphous iron oxyhydroxides in a simple electrolyte. Deviation from this simple model, however, was observed for Cu and Pb, presumably due to the competitive action of dissolved ligands present in the interstitial water. At low sediment pH values, the adsorption was much higher than predicted by the simple model, and could be explained by the formation of ternary complexes with the iron oxyhydroxide surface.

As an alternative to metal partitioning models, methods have been suggested for fractionating the sediment physically and/or chemically. The sediment may be fractionated physically, according to grain size or by density gradient separation, and the individual fractions analysed separately. Alternatively, sequential extractions with appropriate reagents can be devised to leach successive fractions of the metals 'selectively' from the sediment samples. Many such experimental procedures have been proposed and applied to a wide variety of suspended or surficial sediments from streams and lakes. Some limitations of the extraction techniques are discussed briefly below.

Metal partitioning determined by chemical extractions: limitations of the methods

To extract sediment-bound metals selectively from a particular phase or component, one may choose among a wide variety of different reagents (see Table 1 for a partial list). The reagents fall naturally into classes of similar chemical behavior, for example: concentrated inert electrolytes, weak acids, reducing agents, complexing agents, oxidizing agents and strong mineral acids. The extractants can be used in sequential fashion; representative examples of this type of approach are shown in Table 2. Note that each of these procedures was designed for use with *oxic* sediments. A number of methodological points should be considered concerning these extraction procedures. It would be unrealistic to think that one could select a sequence of reagents that would extract the individual fractions in order without influencing the other sediment constituents. Any sequential extraction procedure will unavoidably suffer from a certain lack of selectivity, as has been shown theoretically (Sigg *et al.,* 1984) and experimentally. Experimental verification of extraction selectivity has been carried out by using pure solids or known geochemical phases (Rapin & Förstner, 1983), or by determining various parameters (inorganic and organic carbon, sulphur, X-ray diffraction) either in the extracts and/or in the residual sediment remaining after the various extractions (Tessier *et al.,* 1979; Rapin & Förstner, 1983). These various techniques have shown that the selectivity of most of the procedures presently in use is generally acceptable for sulphide-poor (oxic) surface sediments; for sulphide-rich (anoxic) sediments, however, selectivity deteriorates markedly (Campbell & Tessier, 1984; Rapin *et al.,* 1986).

Table 1. Methods for the extraction of metals from major chemical phases in sediments (examples). After Förstner (1982), with modification.

adsorption and cation exchange:	
$BaCl_2$-triethanolamine (pH 8.1)	Jackson (1958)
$MgCl_2$	Gibbs (1973)
ammonium acetate (pH 7)	Engler *et al.* (1977)
carbonate phases:	
CO_2-treatment of suspension	Patchineelam (1975)
acidic cation exchanger	Deurer *et al.* (1978)
NaOAc/HOAc-buffer (pH 5)	Tessier *et al.* (1979)
reducible phases (in approximate order of release of iron):	
acidified hydroxylamine (+0.01 M HNO_3)	Chao (1972)
ammonium oxalate buffer	Schwertmann (1964)
hydroxylamine-acetic acid	Chester & Hughes (1967)
dithionite-citrate buffer	Holmgren (1967)
organic fraction (incl. sulphides):	
H_2O_2-NH_4OAc (pH 2.5)	Engler *et al.* (1977)
H_2O_2-HNO_3	Gupta & Chen (1975)
organic solvents	Cooper & Harris (1974)
0.1 M $NaOH/H_2SO_4$	Volkov & Fomina (1974)
Na-pyrophosphate	Stover *et al.* (1976)
diethylenetriaminepentaacetic acid (DTPA) – NaOAc (pH 7)	Khalid *et al.* (1981)

Table 2. Examples of sequential extraction procedures[1].

Step	Method			
	1	2	3	4
I	$MgCl_2$	NH_4OAc	NH_4OAc	$NH_2OH \cdot HCl/HNO_3$
II	NaOAc/HOAc	$NH_2OH \cdot HCl/HNO_3$	$NH_2OH \cdot HCl$	$NH_2OH \cdot HCl/HOAc$
III	$NH_2OH \cdot HCl/HOAc$	$(NH_4)_2C_2O_4/H_2C_2O_4$	H_2O_2/HNO_3	$Na_2S_2O_4$
IV	H_2O_2/HNO_3	H_2O_2/HNO_3	$Na_2S_2O_4$	$KClO_4/HCl/HNO_3$
V	$HF/HClO_4$	HNO_3	HF/HNO_3	HF/HNO_3

[1] method 1: Tessier *et al.* (1979); method 2: Förstner (1982); method 3: Engler *et al.* (1977); method 4: Chao & Theobald (1976).

Once the reagents have been selected, there remains a decision as to the order in which they are to be employed. The precise sequence of extractants may vary considerably, particularly with respect to the oxidation of the organic matter present in the sediment (Table 2). This step may follow the reduction procedure (methods 1, 2 and 4) or may be introduced between two reduction steps (method 3). For a given set of reagents, the sequence used will influence the partitioning obtained. During the procedure, there is a potential problem related to readsorption (Rendell *et al.,* 1980) in that when a metal is liberated with a given reagent it may readsorb onto the remaining solid phases; i.e. the extraction procedure itself may cause a shift in the metal distribution pattern. Precipitation reactions may also be a problem, particularly if sodium hydroxide is used to remove the organic fraction. Even with a given set of reagents and a given extraction sequence, the exact experimental conditions employed to extract the different metal fractions may influence the metal distribution. For example, the ratio of extractant to sediment may be important, as may be the contact time between the sediment and the extractant.

In addition to these analytical problems, there is also a potential problem in preserving sample integrity between sampling and analysis. Sample pretreatment (e.g., wet storage at 1–4 °C, freezing, freeze-drying, air-drying) influences the distribution of metals obtained by a sequential extraction procedure (Campbell & Tessier, 1984; Rapin *et al.,* 1986); methods involving the drying of the sediment have especially marked effects. As expected, the effects of pre-treatment are more important for anoxic samples than for oxic.

It follows from these methodological considerations that the partitioning of a metal among various fractions, as obtained by a sequential extraction procedure, necessarily will be *operationally defined.*

Physico-chemical factors influencing particulate trace metal availability

Despite the methodological problems discussed above, partial extractions of sediments have provided significant insight into the physico-chemical factors influencing the bioavailability of particulate trace metals. Many studies have shown that trace metal levels in various benthic organisms are best related not to total metal concentrations in the adjacent sediments, but rather to relatively easily extracted fractions (Luoma & Bryan, 1978; Langston, 1980; Diks & Allen, 1983; Tessier *et al.,* 1984a). Of particular relevance are those studies where surficial sediment samples and specimens of benthic invertebrates have been collected at sites located along gradients in metal concentration in the sediments (Table 3). These studies consistently show that prediction of the trace metal levels in benthic organisms is improved when the trace metal concentrations extracted from the sediments are normalized with respect to the iron (hydrous oxide) and/or organic content of the sediments. Multiple regression analyses of a large data set involving measurements of Ag, Cd, Co, Cu, Pb and Zn in

Table 3. Prediction of trace metal availability to benthic organisms from sediment characteristics. Some examples from *in situ* studies.

Organism	Metal	Best predictor in the sediment	Reference
Scrobicularia plana	Pb	[Pb]/[Fe] extracted with 1 N HCl ($r = 0.99$)	Luoma & Bryan, 1978
Scrobicularia plana	Hg	[Hg] extracted with HNO_3/organic content (%) ($r = 0.80$)	Langston, 1982
Scrobicularia plana	As	[As]/[Fe] extracted with 1 N HCl ($r = 0.96$)	Langston, 1980
Macoma balthica	Hg	[Hg] extracted with HNO_3/organic content (%)	Langston, 1982
Elliptio complanata	Cu	[Cu]/[Fe] extracted with $NH_2OH \cdot HCl$ ($r = 0.97$)	Tessier *et al.*, 1984a
Anodonta grandis	Cu	[Cu]/[Fe] extracted with $NH_2OH \cdot HCl$ ($r = 0.92$)	Tessier *et al.*, 1983

Scrobicularia plana, Nereis diversicolor and in various sediment extracts (together with measurements of other sediment characteristics) have led to similar conclusions (Luoma & Bryan, 1982). In this latter study, the concentrations of metals extracted from the sediments with HCl or HNO_3 generally explained the largest percentage of the total variation in the metal concentrations in both deposit-feeding organisms. Interestingly, the concentrations of iron, manganese, humic acids, carbonates or total organic carbon (depending on the metal and the organism) in the sediments also explained a significant percentage of the total variation. All these constituents are potential sinks for trace metals in the sediments.

Depending on the main route for accumulation of trace metals in the benthic organism of concern, at least three mechanisms could explain an inverse relationship between metal concentrations in the organism and the concentration of a potential sink in the sediments (See Table 3).

Mechanism 1. If it is assumed that the major route for accumulation of trace metals in the organism involves the digestive system, and that acidic and/or reducing conditions prevail in the intestinal tract, one can envisage the simultaneous solubilization of both the cations (Fe, Mn, Ca) and the trace metals associated with some sinks (e.g., Fe/Mn oxides). The cations thus released could then compete with the trace metals for uptake sites in the digestive system and reduce their uptake (cf. Luoma & Bryan, 1978).

Mechanism 2. If it is again assumed that accumulation of trace metals occurs predominantly via the digestive system, but that conditions prevailing within the gut (pH, pϵ, residence time) are such that the sink remains unchanged during the digestion, then the unreacted sink could compete with the uptake sites in the intestinal tract for the solubilized trace metals.

Mechanism 3. Alternatively, the main route for accumulation of the trace metals may involve not the ingestion of particulate material but rather the uptake of dissolved trace metals (e.g., via the gills and mantle). In this case, the protective role of the sink could be explained by invoking adsorption in the *external* medium as the principal factor controlling the dissolved trace metal concentrations to which the organisms are exposed. Clearly, as the concentration of adsorbing substrate increases, the concentration of dissolved trace metal will decrease (see equation (4)).

It is thus important to realize that a strong dependence of trace metal accumulation in a benthic organism upon sediment characteristics, such as those shown in Table 3, does not imply that the main route of entry of trace metals is necessarily via ingestion of particulate metals; it can be explained by a control through adsorption reactions of the dissolved trace metal concentrations in the solution to which the organisms are exposed. For example, in the case of the filter-feeders, *Elliptio complanata* and *Anodonta grandis,* for which such a dependence was evident (Table 3), high levels of trace metals were found associated with the gills and mantle (Tessier *et al.,* 1983, 1984a). The gills and mantle contributed a large proportion of the total metal body burden, suggesting that uptake of dissolved trace metals is an important route of accumulation of these elements. These two organs are indeed physiologically remote from the digestive system of the organisms, are in contact with large amounts of water necessary for feeding and respiration, and have large surface areas. Relatively high concentrations (and high contributions to the metal body burden) of Hg and As have also been reported in the gills and mantle of the deposit feeder, *Scrobicularia plana* (Langston, 1980, 1982).

Conclusions/recommendations

The biological significance of sediment-bound trace metals is complex and still poorly understood. The accumulation of trace metals by aquatic organisms is influenced by a great number of physico-chemical and biological factors that should be quantitatively characterized.

The importance of particulate trace metal partitioning in influencing the accumulation of trace metals in various benthic organisms has been pointed out in laboratory experiments and, in a few cases, in field experiments (e.g., Luoma & Bryan, 1982). However, there is presently no satisfactory method for determining unambiguously the partitioning of particulate trace metals in natural sediments. Although empirical studies (e.g., using chemical extractants) can give valuable information concerning important sinks in natural sediments, a need exists, if generalizations are to be produced, to develop theoretical models for describing trace metal partitioning in sediments, and to verify their adequacy in predicting trace metal behavior under *natural conditions.*

In particular, the processes that control trace metal partitioning in oxidized sediments should be identified and determined quantitatively, since oxidized sediments are of particular importance in a biological context (Luoma & Davis, 1983). If impacts on the environment are to be predicted, the processes and factors that control the scavenging of trace metals by the sediments and their release to the overlying water under changing environmental conditions must be understood.

In addition to the physico-chemical factors mentioned above, biological factors are also involved in the uptake of trace metals by aquatic organisms; their importance must be assessed if the dependency of trace metal levels in the biological organisms on the metal concentrations in the sediments and/or the water is to be modelled adequately. For example, the time response of the trace metal levels in the organisms to variations in environmental trace metal concentrations and partitioning should be determined. The route of entry of trace metals (water, food, sediments, endocytosis) should be determined for benthic organisms. The role of macro- and microscopic structures (gills, mantle, mucus and granules) in the uptake/accumulation/excretion of trace metals should be clarified and the biological variability introduced by factors such as age and sexual condition should be quantified.

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