Environment International 73 (2014) 270–281

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

Effects of sediment geochemical properties on heavy metal bioavailability

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ARTICLE INFO

Article history:
Received 18 February 2014
 11 August 2014
Accepted 12 August 2014
Available online xxxx

Keywords:
Sediment geochemical properties
Heavy metals
Bioavailability
Toxicity assessment

ABSTRACT

As the largest container and resource of metals, sediment has a special role in the fate of metals. Factors influencing bioavailability of heavy metals in sediment have never been comprehensively considered and the sediment properties still fail to understand and even controversial. In this review, the mechanisms of sediment properties such as acid-volatile sulfides (AVS), organic matter, texture (clay, silt or sand) and geology, organism behaviors as well as those influencing the bioavailability of metals were analyzed. Under anoxic condition, AVS mainly reduce the solubility and toxicity of metals, while organic matters, Fe–Mn oxides, clay or silt can stabilize heavy metals in elevated oxidative–reductive potential (ORP). Other factors including the variation of pH, redox potential, aging as well as nutrition and the behavior of benthic organism in sediment also largely alter metals mobility and distribution. These factors are often inter-related, and various toxicity assessment methods used to evaluate the bioavailability of trace metals have been also discussed. Additionally, we expect that some novel synthetic materials like polysulfides, nano-materials, provide the substantial amendments for metals pollution in sediment.

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http://dx.doi.org/10.1016/j.envint.2014.08.010
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1. Introduction

In aquatic ecosystem, sediments are the main sink and source of heavy metals, serving as a significant role in the transportation and storage of potentially noxious metals (Alonso Castillo et al., 2013; Burton et al., 2006b; Durán et al., 2012; Superville et al., 2014). Sediment available to the river mainly from channel sources (the bed and banks of its catchment) and non-channel sources (the rainfall runoff, flooding, and the erosion of bare soil, particularly) (Wood and Armitage, 1997). Thus, sediments are heterogeneous assemblages of multitudinous sorbent phases (such as organic matter, oxide, sulfides, carbonates and clay or silt minerals), whose relative abundance depends on pH, redox conditions, hydrological regime and the depositional environment (Burton et al., 2006b). The sediments have provided more significant tools for the better clarification of the origin identification and partitioning dynamics of heavy metals than the analysis of the overlying water column as a result from discontinuity and fluctuations in water flows (Alonso Castillo et al., 2013).

Toxic metals pollution in sediment have been proved to be an increasingly global problem (Fernandes et al., 2008; Kucuksezgin et al., 2008) and is considered to pose a serious threat to the aquatic environment result from their toxicity, non-biodegradable and persistent nature, and the bio-enrichment ability in food chain (Gopinath et al., 2009; Nobi et al., 2010). Heavy metals in aquatic system are increasingly identified as important intermediate sources for subsequent the occurrence of pollution in aquatic ecosystems, even public health, due to rapid urbanization and industrialization (Alonso Castillo et al., 2013). Besides, high variation loads in heavy metal occur among impervious surfaces along with different urban land uses (Zhao et al., 2010). These elements are deposited onto sediment surfaces and immobilized through adsorption, coagulation or flocculation and incorporation into the lattice structure of minerals (e.g., Fe–Mn oxides), and precipitation by forming insoluble fractionation (such as metal sulfides) (Du Laing et al., 2009; Lin et al., 2013). Only a small portion of free metal ions, however, stay dissolved in water (Hou et al., 2013) and in comparable, more than 90% of heavy metals load in aquatic systems have been found to be related to suspended particles and sediments (Amin et al., 2009; Zahra et al., 2013; Zheng et al., 2008). Thus, the distribution of trace metals in sediment adjacent to populated areas (includes industries, mining exploitation in particular) can give us the evidence of anthropogenic influence on aquatic system and convenience in assessing the potential risks associated with human waste discharge.

Given the importance of aquatic environment, numerous studies have been focused on heavy metals pollution (Atkinson et al., 2007; Luoma and Rainbow, 2005; Saeedi et al., 2013; Simpson, 2005) and the metals geochemical nature associations in sediments (Lee et al., 2000a; Simpson et al., 2012a). In aquatic sediments, the bioavailability of metals to benthic organisms depends not only on metals chemical form (Besser et al., 2003; Riba et al., 2004; Simpson, 2005), but also sediment geochemical properties (Nobi et al., 2010; Rainbow, 2007) and varies exposure pathways of the organisms (Simpson et al., 2012b). The calculation of toxicity of metal contaminants in sediments to benthic organisms is particularly challenging due to the significant influence of the properties of the sediments (Campana et al., 2012; Costello et al., 2011; Strom et al., 2011) as well as the changes of sediment supply and post-depositional processes (Fernandes et al., 2011). The partitioning of metals between different phases is strongly influenced by sediment attributes such as pH, redox potential, particle size and its distribution, and the important metal-binding phases such as AVS, organic matter (OM) and iron and manganese oxyhydroxides (Chapman et al., 1999; Simpson et al., 2012a).

Factors influencing bioavailability of heavy metals in sediment have never been comprehensively considered and the mechanisms of solid phases binding with metals are still constricted. What's more, sediment geochemical properties are often mutual correlated, and it is not adequate to assess the metals behavior in sediment through considering just several factors among those properties. Thus, understanding their relationships requires knowledge of sediment geochemistry and organism behaviors (Hou et al., 2013; Nizoli and Luiz-Silva, 2012). To further our understanding of the influence of sediment geochemical properties on the bioavailability of metals to benthic organisms, the consideration and analysis of mechanisms turns into a necessity. Besides, know of partitioning and distribution of heavy metals in the sediments will give us insights into the source of pollution in the aquatic systems (Nobi et al., 2010; Silva et al., 2009) and the effects on aquatic biotas. Here, we comprehensively depicted for the first time the contribution of AVS, OM, sediment texture, diagenesis as well as benthic organism behavior and other drivers in affecting metals behavior, particularly bioavailability in sediment area, so as to provide further information for researches and sediment management.

2. Metal forms in sediment

It is universally accepted that a large portion of heavy metals in nonpolluted sediment present in the crystal lattice of minerals and residual fraction which constitute the bottom mud (Du Laing et al., 2009; Lin et al., 2013). When polluted, the form and distribution of heavy metals in sediment is altered. These elements in sediment mainly exist in the forms of soluble, ion-exchangeable, Fe–Mn oxides, organic matters/sulfides and carbonates (Hou et al., 2013). In consideration of characterizing the solid-phase partitioning of trace metals in sediments, sequential extraction procedures become an increasingly popular method, which employ a series of reagents to selectively extract metals associated with operationally defined fractions (Burton et al., 2005a, 2006a; Morillo et al., 2004).

In the present study, the four-step sequential extraction method established by Tessier et al. (1979) in sediment is introduced to determine and fractionate heavy metals chemical fractions (Hou et al., 2013; Peng et al., 2009; Tessier et al., 1979). This extraction method then divides the heavy metals into five fractions via four steps: extractable and exchangeable (F1), carbonate bound (F2), iron and manganese oxides bound (F3), organic matter bound (F4) and residual metal (F5). The descending order of bioavailability of the heavy metals in sediments may be based on the metal fractionation ($F1 > F2 > F3 > F4 > F5$ in general), and most spiked metals preferential adsorb onto phases that apt to exchangeable and reducible. Normally, the exchangeable fractions of metals can be used to evaluate the extent of environmental bioavailability of sediment component (Jones et al., 2008). Whilst the residual fraction, which associated with anthropogenic or geogenic components, represents the more stable metal forms (Saeedi et al., 2013).

Nowadays some novel extraction methods emerge around us. The modified Community Bureau of Reference (BCR) three-step sequential extraction procedure has been used to the study of metals in soils or sediment (Pueyo et al., 2008). Besides, the technology of diffusive gradients in thin-films (DGT) can efficiently determine labile species of metals in soil or sediment and thus better predict the assimilation of these elements by living beings (Davlson and Zhang, 1994; Simpson et al., 2012b). Different popular sequential extraction procedures are depicted as follows in Table 1.

3. Influence factors for metals bioavailability in sediment

What influence the metals bioavailability and toxicity in sediments and waters can be enumerated as the following: (1) solid phases, especially metal binding phases, such as AVS, particulate organic carbon, iron and manganese oxyhydroxides (Campana et al., 2012; Simpson and Batley, 2007); (2) aquatic phases, i.e., overlying and pore water physical–chemical attributes, such as pH, redox potential (Eh), hardness/salinity, and ligand complexes; and (3) sensitivity and behavior of benthic organisms, e.g., taxa, lifestyle (such as bioturbation, burrowing), and prior exposure history (Chapman et al., 1999).

Table 1
Characteristics of popular sequential extraction procedures.

Sequential name	Extraction steps needed	Extracted metals species	Reference
Modified BCR	Three steps	Exchangeble and weak acid soluble fraction; Reducible fraction; Oxidizable fraction; Residual fraction.	Pueyo et al. (2008)
Tessier	Four steps	Extractbale/exchangeable fraction; Carbonate fraction; Iron and manganese oxides fraction;OM fraction; Residual fraction.	Tessier et al. (1979)
Diffusive Gradients In Thin-film (DGT)	One-off	Labile species (bioavailable)	Davlson and Zhang (1994)

Correlations between geochemical phases, which potentially involved in trace metal trapping and previously observed for total organic carbon (TOC), AVS, and Fe, are expected (Keene et al., 2010; Machado et al., 2010; Nobi et al., 2010). Alternatively, sediment texture, mineralogical composition and physical–chemical transport are also the factors affecting the distribution and accumulation of heavy metals in sediment (Buccolieri et al., 2006; Marchand et al., 2006). Thus, the accumulation of heavy metals depends on the geochemical properties of sediments and significant variations of their concentration are related to habitats (Nobi et al., 2010).

3.1. Solid phases

3.1.1. Sulfides: acid volatile sulfides (AVS)

Operationally, AVS is defined as the determination of sulfides concentration volatilized by the additional reagent of 1 N HCl and mainly consists of iron and manganese sulfides (De Jonge et al., 2011; Di Toro et al., 2005). In anaerobic sediments, sulfate reduction, initiated mainly by sulfate reductive bacteria (SRB), can lead to the formation of AVS (Campana et al., 2012; De Jonge et al., 2011). The equilibrium concentration of AVS in sediment is the result of the balance of both the rate at which its production and the rate at which its loss by oxidation or diffusion, the supply of SO_4^{2-}, the rate of SO_4^{2-} reduction and organic matter decomposition, and the redox status of sediments that all could affect AVS concentrations (Hou et al., 2013).

The circumstances giving rise to the formation and the distribution of AVS in aquatic sediments are very complex as a result of seasonal and spatial variations in physical–chemical properties of the pore water (Hernández Crespo et al., 2012). The distribution of AVS concentrations varies temporally and spatially (Campana et al., 2009) and the values of AVS increase with sediment depth (Chen et al., 2006; Fang et al., 2005). At the surface sediment top, its low values can be attributed to the exposure of bio-irrigation (bioturbation) and the permeation of oxygen from surface waters, which create aerobic oxidation of the sulfides and thus lower the AVS levels (Campana et al., 2005; Nizoli and Luiz-Silva, 2012). But the lower levels of AVS and Fe observed in deeper layers may be accounted for by the replacement of reactive Fe and AVS by stable or crystalline fractions within deeper sediment, such as pyrite (Hernández Crespo et al., 2012).

Reactive sulfide species, including aqueous sulfides, poorly crystalline FeS, mackinawite, greigite and pure trace metal sulfide minerals, are thought to be important to trace metal binding and partitioning under anoxic conditions (Burton et al., 2005b; Morse and Rickard, 2004). The reduction of SO_4^{2-} formulation can be depicted as:

$$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O \qquad (1)$$

When Fe^{2+} exists in anoxic sediments, the reduction of SO_4^{2-} may cause the formation of poorly crystalline FeS (Burton et al., 2006a):

$$Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^- \rightarrow FeS + 4H_2O. \qquad (2)$$

Fe and Mn sulfides constitute an important part of AVS-metal precipitations in the sediment. Lowest labile Fe and Mn concentrations were found in the more oxic sediment surface layers and this may emphasize the importance of Fe and Mn oxide precipitation near the sediment–water interface, which can reduce metals mobility. For an instance, as a result of Fe and Mn (hydro)oxides on the root surface, the "root plaque" can act as a physical barrier for mobile metals in the sediment, resulting in a lower susceptibility to metal toxicity (Teuchies et al., 2012).

The chemical basis of AVS bind with metal ions is the occurrence of displacement between iron in iron monosulphides (FeS(s)) and divalent metals (Me^{2+}) to form more insoluble metal sulfides (Fang et al., 2005; Hernández Crespo et al., 2012; Machado et al., 2010; Nizoli and Luiz-Silva, 2012):

$$Me^{2+} + FeS(s) \rightarrow MeS(s) + Fe^{2+}. \qquad (3)$$

Based on this reaction mechanism, Zn and Cu can be accumulated as authigenic sulfide minerals or form discrete sulfide mineral phases such as covellite (CuS) and sphalerite (ZnS) (Martin et al., 2003). The generation of AVS and its mechanism of action with heavy metals are depicted in Fig. 1.

Present studies indicated that AVS might play a dominated role in deeper layers of sediments (about >20 cm) with regard to metal activity (He et al., 2011; Hou et al., 2013; Huo et al., 2013; Louriño-Cabana et al., 2011; Nasr et al., 2013; Zhuang and Gao, 2014). As sulfide phases exhibit low solubility in anoxic sediment, AVS concentrations are considered sufficiently high to bind cationic metals and lower the final chronic effects threshold to benthic invertebrates (Besser et al., 2004; Nizoli and Luiz-Silva, 2012). For an instance, a case study indicated that in sulfide spiked sediment, Copper was bond with AVS, causing lower toxicity to juveniles of the epibenthic amphipod, *Melita plumulosa* without oxidation (Simpson et al., 2012a). Also, compared to that of containing high AVS level in West Bearskin and Columbia sediments, the Florissant sediment with lower AVS concentration (<0.01 μmol/g) caused significant amphipods mortality (Besser et al., 2004).

Moreover, numerous studies have suggested exploit the relationship of AVS and simultaneously extracted metal (SEM) for assessing toxicity (Garcia et al., 2011; Hou et al., 2013; Ribeiro et al., 2013; Simpson et al., 2012a; Yang et al., 2013). Based on the chemical basis, this has created a condition that the content of AVS and SEM are promulgated as a measure of sediment quality (Burton et al., 2006b, 2007; Hernández Crespo et al., 2012; Li et al., 2010). The relationship SEM/AVS < 1(or [SEM-AVS] < 0) is a stoichiometrically determined proposal to predict the low or non-potential bioavailability of metals (Lee et al., 2000b; Nizoli and Luiz-Silva, 2012). Based on SEM–AVS model, the metal mobility is expected to increase if SEM exceeds AVS (Machado et al., 2010; Nizoli and Luiz-Silva, 2012; Teuchies et al., 2012), revealing that the fixed metal ability of reactive AVS reach saturation (De Jonge et al., 2009). On the other hand, the reactive sulfides (AVS) in excess compared to SEM make the metals unavailable to the biota (Han et al., 2005; Oueslati et al., 2010).

But some studies observed that benthic animals could accumulate metals even when SEM < AVS, since it necessarily alluded to the potential mechanisms including the ingestion of contaminated food, heterogeneity of geochemistry around animals' microhabitats, adsorption to surface membranes, or differences in behavior of animals (Ahlf et al.,

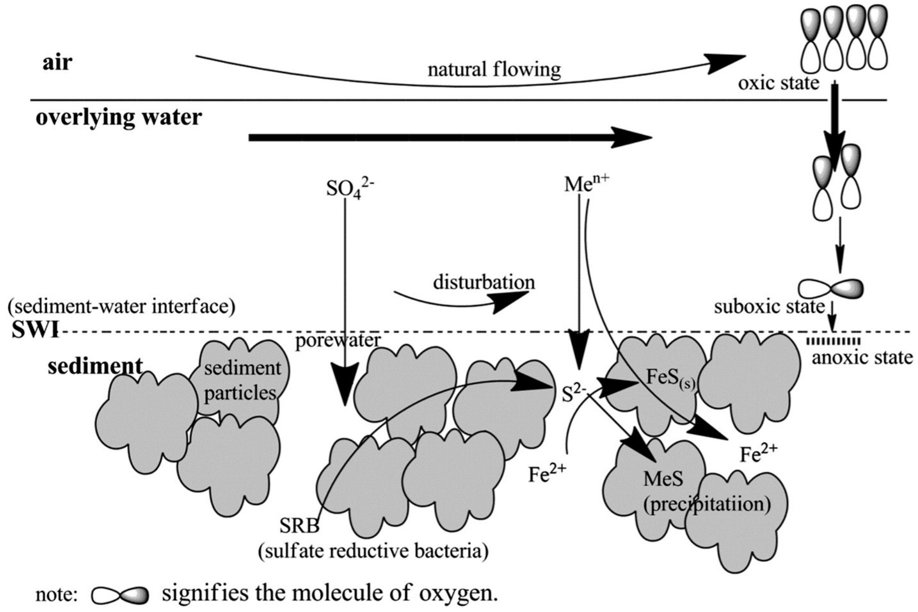

Fig. 1. The AVS mechanism of action: the transformation of SO_4^{2-} from overlying water to sediment pore water and its fate during the metabolism SRB in pore water with heavy metal ions. The arrows indicate the migratory direction of materials and its thickness reflects the amount or extent of materials. Me^{n+} represents the n-valence metal ion; The irregular shapes stand sediment particulates.

2009; De Jonge et al., 2009; Lee et al., 2000a). Some studies still found no relevance between AVS and metal concentrations in pore water (De Lange et al., 2008; Hernández Crespo et al., 2012). As a matter of fact that the poorly crystalline FeS is thermodynamically labile, levels of AVS (mainly FeS) were insignificant for binding metals under oxidative condition (Burton et al., 2006a). The oxidation of AVS under aerobic conditions, caused by the irrigation of organism burrows (Campana et al., 2013; Simpson et al., 2012a,b) and the oxygen mass transfer, can reduce the metal immobility capacity of sediments (Teuchies et al., 2012),and then overemphasize the significance of metal-sulfide binding. Additionally, it is presently not appropriate for the use of the Tessier et al. (1979) sequential extraction procedure to fractionate AVS–metals (e.g., Pb, Zn and Cu) to any single operationally defined fractions due to their insolubility in extraction reagent (Simpson et al., 2012a).

Hence, AVS seems turn out to be an insignificant variable in describing variation in metal accumulation when the emergence of oxygen. And, the relationships of equilibrium partitioning between AVS and metals become inappropriate for benthic organisms that construct oxic/suboxic micro-environments near burrow walls within sulfidic sediments.

3.1.2. Organic fraction

Organic matter (OM) originates from varies resource such as a derivative of plant, animal detritus and its fecal matter, and even artificial organic materials comprising subsurface aquatic systems (Hong et al., 2010). The enhanced deposition of OM to coastal waters has been related to the intensive use of agricultural fertilizers, the growth of population and the increasing urban and domestic sewage inputs of sedimentary matter. The organic material is quickly transferred below the more diagenetically active zone and thus suffers less degradation (Fernandes et al., 2011). SOM, often operationally quantified as TOC, is an important amendment phase for metal-binding in oxidized sediments (Besser et al., 2003). SOM is a considerably complex and heterogeneous component initially ascribing to the physical, chemical, and especially the microbial evolution of biopolymeric materials, which are further decomposed to fulvic and humic acids, kerogen, and even black carbonaceous materials via various degrees of diagenetic processes (Hong et al., 2010). The vertical profile of TOC distribution shows an increase in the upper layer of sediment core but a decrease in the lower portion (Fernandes et al., 2011).

Low to medium molecular weight OM can provide dissolved ligand for metals to form soluble complexes, while the macromolecule fraction can reduce the metals availability (Du Laing et al., 2009). Since SOM is believed to serve as a principal geo-sorbent for hydrophobic organic contaminants in soils and sediments, its characterization has been regarded as a vital effort for understanding and evaluation of the fate of trace metals in contaminated sediment and for successful remediation object (Hong et al., 2010). The formation of complexes between organic matter and metals is shown in Fig. 2.

OM, especially fine particles, has a significant influence on trace metals solubility and bioavailability in sediment. These fine particles come mainly from benthic invertebrate fecal material, biofilms and the decay of aquatic macrophytes (Wood and Armitage, 1997). Metals solubility variation depends significantly on sediment size carried OM. Solubilization efficiencies increased in decreasing particle size compared to coarse particles of the sediment samples, as a result of the larger interaction area of unit amount of particles with lower diameter in fine grains (Guven and Akinci, 2013). For example, in Buckhorn sediment (OC = 17.7%), Cu and Cd solubilization was lower compared to that with ashed (OC = 10.4%) but higher than that of Ruban sediment (OC = 21.9%) due to the extremely high affinity of Cu to OM (Zhong et al., 2012, 2013). Fine particles were readily to be suspended and the concentration of particulate organic matter in the river had a positive relation to the amount of sediment in suspension during flooding (Tesi et al., 2013).

In the fine sediments, particulate organic carbon phases are well considered for their binding of metals, and its concentrations have been demonstrated to reduce the solubility and toxicity of many metals (Besser et al., 2003; Di Toro et al., 2005; Strom et al., 2011). Fine sediments with greater particulate organic carbon concentrations so often have elevated metal concentrations as a result of their affinity for metals (Strom et al., 2011). It is widely recognized that sediments fraction less than 63 μm in size are the most important for the adsorption and transport of metals, with relation to their larger surface area and special geochemical composition. Metals toxicity to benthic organisms were unconspicuous for sediments with higher concentrations of fine particulate organic carbon (<63 μm sediment in particular). Sediment guidelines based on the <63 μm sediment fraction are thus effective for

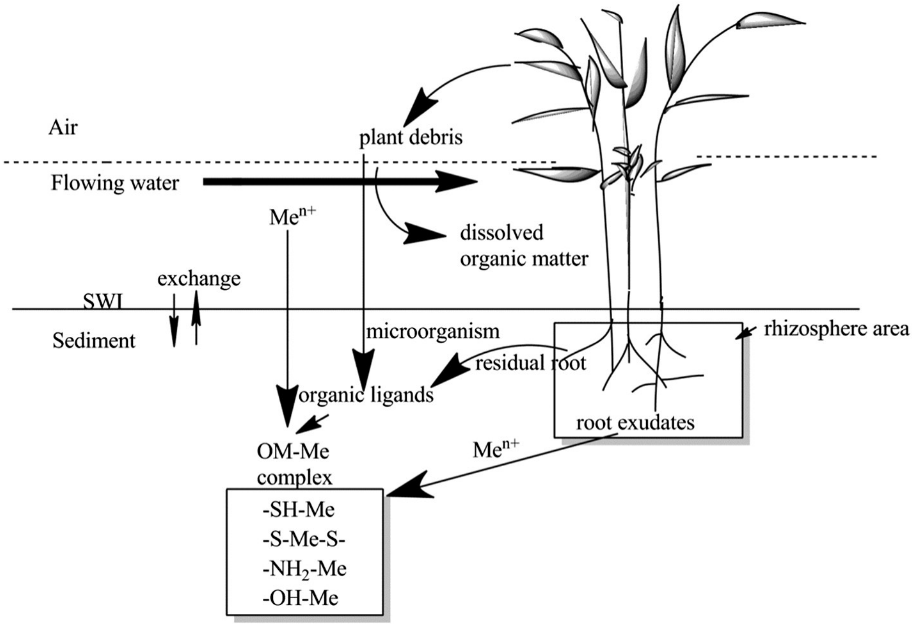

Fig. 2. Organic matter originated from aquatic system forms the complexes with heavy metal ions, via diverse ligands or perssads.

predicting the sub-lethal threshold of copper in sediments with varying attributes (Campana et al., 2013; Sadeghi et al., 2012; Zhao et al., 2010).

As the major component of the organic matter from marine sediments (Won-Wook and C., 1976), humic substances are the mainly metal binding material and, the sediment with greater humus concentrations in sediment will have higher metals content (Besser et al., 2003; Fernandes et al., 2011). For an instance, compared to natural treatment, amendment of specific sediments with humus substantially increased the partitioning ratio of Cd and Cu between sediment and pore water (Besser et al., 2003). The concentration of accumulate metal in organic-rich sediment is balanced by the partitioning of these metals to the organic solid phase. No adverse effects on organisms would occur in the high-humus treatment. The most probable mechanism for this reduction of bioavailability of aqueous metals in humus treatments is the formation of metal complexes with organic ligands (Besser et al., 2003; Correia and Costa, 2000; Craven et al., 2012; Playle et al., 1993). Besides, some studies also indicated the sorption of metals to the "organic" fraction, was significantly correlated with the content of sediment organic carbon (Burton et al., 2006b; Machado et al., 2010). Situations where an excess ΣSEM levels compared to AVS levels have been emphasized as evidence that factors such as OM other than AVS should be considered to account for metal bioavailability and toxicity risk.

In general, survival and growth of benthic organisms were both affected by sediment varies properties, with influences being significantly lower in sediments having greater organic carbon concentrations. For example, the mean growth of *T. deltoidalis* during the 41d test period was greatly enhanced with increasing OC content (Campana et al., 2013). Metal accumulation in benthic invertebrates was strong significantly correlated with sediment metal concentrations normalized for loss on ignition (LOI), which weighed up the measure of organic matter content and appeared to significantly explain a part of the variation in metal accumulation (De Jonge et al., 2009). Toxic effects of metal like Cr are unlikely occurred in freshwater sediments containing substantial content of OM (Besser et al., 2004). Moreover, some results highlight the function of SOM in regulating benthic communities and distributions of individual species and biomass (Jyväsjärvi et al., 2012), this may be related to the feeding habits of organisms and food distribution in sediment. Microorganisms live in the rhizosphere of wetland plants produce exopolymers to detoxificate Cu and reduce its availability, and in comparable, carbon dioxide produced during aerobic breakdown of OM can enhance the release of metals via decalcification (Du Laing et al., 2009).

However, the decomposition process of higher organic matter may lead to the lower value of pH due to the production of humic acid (Nobi et al., 2010), which would increase the metal release. Although metals binding with the organic matter are considered to be stable, it is obliged to note that these metals may be run out over time because of organic matter degradation. Given that the binding characteristics of heavy metals with SOM can be markedly changed by modification of SOM properties, enhancement or ultimate stabilization in their overall bioavailability within the geo-sorbent media may be possible (Hong et al., 2010).

3.1.3. Sediment texture: clay minerals and silt

Sediment texture has closely association between sediment particle size distribution, specific area, and consolidation processes over time (Sutherland et al., 2007). Minerals, mainly evolved from geological weathering, significantly influence the attachment process on which the bacterial sulfur oxidation system depend. In the process of attachment, the bacteria alternatively prefer specific sites of crystal imperfections but do not attach the whole mineral surface (Rohwerder and Sand, 2007). Silt and clay of mineral have particularly important influence on the transport and storage of heavy metal within fluvial sediments. Montmorillonite are the main composition of clay minerals in sediment and suspended particulate matter, and the soil or sediment containing montmorillonite clay are recognized as good adsorbents owing to the existence of varies active sites such as the surface- and ion-exchange sites (Saeedi et al., 2013).

Fe and Mn oxides, the main component of minerals, are significant scavengers of trace metals and these elements can be consequently accumulated in oxic interfacial sediments (Sutherland et al., 2007). Because of their large surface area, the "Fe–Mn oxide controlled factor" is considered predominant sorbent and found to have high significant positive loadings on metals like Fe, Cr, Mn, Ni and TOC (Fernandes et al., 2011). Fe and Mn oxyhydroxides, which diagenetic enriched during the process of the reductive dissolution of Fe and Mn oxides under redox cycling, can also influence the metal fluxes and its mobilization like Zn and Cu in coastal sediments (Fernandes et al., 2011; Sutherland et al., 2007). This process can be explained by the following reaction equations (for example Fe, the same as Mn):

$$Fe_2O_3 + 2e^- + 4H^+ \rightarrow 2Fe^{2+} + 3H_2O \tag{4}$$

$$Fe^{2+} + 1/4O_2 + 3/2H_2O \rightarrow 2H^+ + FeOOH_{(s).} \tag{5}$$

However, the expected vertical profiles of Fe and Mn in pore water were not easily obtained at present, owing to its rapid establishment after sediment disturbance (Fernandes et al., 2011).

A fine fraction of minerals play significant roles in the quality of water and sediment, especially in the adsorption of metals (De Jonge et al., 2009), and even the degree of metals accumulation in biological tissues. A case study decades ago shown that in the fine sediment (<70 μm granulometric fraction) collected from the mining and smelting complex in Rouyn–Noranda, Quebec, Cu, Pb, and Zn was notably against accumulated in tissues of E. Complanata by amorphous iron oxy-hydroxides (Tessier et al., 1984). The fine-grained fraction in sediment, compared to coarse particles, generally contains greater concentrations of trace metals because of their larger surface area and higher cation exchange capability (Fernandes et al., 2011; Huang et al., 2012; Kucuksezgin et al., 2008; Lu et al., 2005; Sadeghi et al., 2012; Strom et al., 2011; Zhao et al., 2010). By reason of trigonal or hexagonal smooth crystal surfaces, larger quartz particles in the coarse sediment are unable to supply sufficient interaction area for the bacteria, resulting in the lower sulfur oxidation in the system and then higher solubility of metals (Guven and Akinci, 2013). Besides, the fine particles (such as clay) in sediments are often closely associated with organic matter and exist in the form of organic-mineral complexes (Won-Wook and C., 1976). These fine particles adsorb active metals from the water phases and carry them diagenetically to the bottom sediments.

Moreover, fine sediment has the ability to the recognition of sediment sources, transport, and deposition processes (Fernandes et al., 2011). For these reasons, heavy metals accumulation in systems dominated by riverine inputs depends on the migration and transportation of these elements along with the lattices of detrital minerals (e.g., clays or silt) (Sadeghi et al., 2012; Sutherland et al., 2007). Further, on the basis of the role of fine grains on heavy metals, the particle size distribution in sediment sample may also have a significant impact on the concentration of these metals (Huang et al., 2012). Each class of grain size has its own characteristics (such as specific area, shape, minerals composition) and influences the consequent interaction with heavy metal concentrations. Thus, we should clearly emphasize the necessity for considering particle size distribution during the resuspension event in controlling the transportation of heavy metal concentrations.

The suspension and deposition of fine sediment result from the ecology of running waters have been widely reported (Burton et al., 2006a; Huang et al., 2012). In extreme cases, however, small grain size enriched in sediment may also worse the aquatic system. In the water column during resuspension, fine sediments may increase turbidity, weaken the light intensity, reduce primary productivity and even smother the entire aquatic ecosystem as well as the alteration of channel morphology. With the increase percentage of fine substrate, the difference between fish assemblages in relation to activities (i.e., riffles, runs) decreased largely owing to a decline in riffle taxa (Wood and Armitage, 1997).

3.2. Aquatic phase parameters

3.2.1. pH

The value of pH is used to weigh the acidity or alkalinity in sediment or water column and strongly influence the solubility of trace metals. High pH values promote adsorption and precipitation while low pH can actually weaken the strength of metal association and impede the retention of metals by sediments (Belzile et al., 2004; Guven and Akinci, 2013).

In general, the value of pH is observed to exhibit a increasing trend with minor fluctuations from surface to bottom and is found the sulfate productions had positive correlation on the pH decreases (Fernandes et al., 2011; Guven and Akinci, 2013). A decrease in pH resulted from the release of H^+ into pore water causes a secondary release of heavy metals. The reaction equation can be depicted as (Peng et al., 2009):

$$MS_2 + (15/4)O_2 + (7/2)H_2O \rightarrow M(OH)_3 + 2SO_4^{2-} + 4H^+. \tag{1}$$

Low pH can reduce the negative surface charge of organic matter, clay particles and Fe–Mn–Al oxides, and especially solubilize sulfides (Du Laing et al., 2009). In the coarse sediment system, the Eh–pH (Morse and Rickard, 2004) changes may contribute to the relatively low transform of sulfur and the leaching mechanism of metals from sediment is explained by the following reactions (Guven and Akinci, 2013):

$$S^0 + H_2O + 3/2O_2 \rightarrow H_2SO_4 \tag{2}$$

$$H_2SO_4 + (\text{Sediment} - \text{Metal}) \rightarrow (\text{Sediment} - 2H^+) + \text{Metal} - SO4^{2-}. \tag{3}$$

On the other hand, the relative high pH can slower the reduction rate of SO_4^{2-} through the inhibition of both activity and growth of SRB, but the sorption capacity of clay minerals increases with an increasing pH, due to the formation of stable hydroxide complexes and precipitate with metals (Hou et al., 2013). A study reported that the high pH under different hydrological regime may be interpreted by the alkaline geologic formations which originated from the second geological era and runoff generation (Sadeghi et al., 2012). However, there is no obvious variation of pH in sediment or soil due to the presence of carbonates, which are considered as effective buffer agent (Du Laing et al., 2009).

3.2.2. Heavy metals concentration and their chemical forms

In sediment, total metals concentration can indirectly reflect both logical mineralogy and even the beginning or nature of sediments (Alagarsamy, 2006; Gopinath et al., 2009; Nobi et al., 2010). In general, metal accumulation in aquatic biotas has a significantly correlation with total metal concentrations in the sediment, which appear to be the most important variable parameter in environment. Consistence with the more solubility of metals causing by low pH, studies have suggested that the metal concentration in suspended and bed sediments can be sensitive predictor of contaminants in hydrological systems (Chao et al., 2009; Sadeghi et al., 2012). With an increase concentration of metals in the water column and sediment, the adsorption capacity of both sediment and suspended particulate matter for metals rises (Saeedi et al., 2013). Previous studies observed that metal bioaccumulation increased linearly with the total concentrations of sediment metal, immunized to AVS, or pore water metal concentrations (De Jonge et al., 2009; Simpson et al., 2012b).

However, the total concentration of heavy metals is not always concerned with its toxic effects and its bioavailability (Hernández Crespo et al., 2012). A study indicated there was no single significant correlation between metal accumulation and its concentration in the pore water (De Jonge et al., 2009). Besides, other paper found that the survival of organism was substantially greater instead despite of high measured Cd concentration in sediment (Besser et al., 2003). Moreover, the transformation between metals species may be occurred when these elements load increase. As for Cu and Pb, for example, their "organic" fraction transformed to the "carbonate" fraction with their loading of increasing (Burton et al., 2006b). Determination of total metals concentrations in sediments, thus, has little access to effectively calculate the capability for its mobilization (Alonso Castillo et al., 2013; Lee et al., 2000a; Tan et al., 2013), since the bioavailability of heavy metals determined by their chemical species (Hernández Crespo et al., 2012; Ibragimow et al., 2013).

Recently, studies focusing on the bioavailability of heavy metals are shifted from the total metal concentrations to their chemical species (Dacera and Babel, 2012; Han et al., 2014; Lee et al., 2011; Moreda-Piñeiro et al., 2012). The chemical forms of heavy metals in ambient are defined as five fractions: exchangeable, carbonate, iron–manganese oxides, organic matter and residual (Tessier et al., 1979). It is known that heavy metals ions, instead its particles, can be accumulated by living beings and heavy metals existing in these fractionations can be entered into the water phase in the form of ion states, which organisms can readily ingest them by metabolism (Amato et al., 2014; Simpson et al., 2013). The distribution of different species indicates the bioavailability and migration of heavy metals in sediment (Huo et al., 2013). The fractions of exchangeable, carbonate and Fe–Mn oxides (sometimes include metal sulfides, especially in aerobic condition), due to their weak binding with heavy metals, are readily available by organisms, accompanied by its toxicity (Baumann and Fisher, 2011; Campana et al., 2013; Kelderman and Osman, 2007). Once adsorbed onto the plane of crystal, or inducing the formation of metal sulfides/complex with OM, heavy metals are immobilized and less available is accepted (Gustavsson et al., 2013). Hence, when it comes to the bioavailability and toxicity of heavy metals, their chemical forms should be considered.

3.2.3. Redox potential

It is generally acknowledged that sediment oxidative–reductive potential (ORP) is also an important parameter controlling heavy metal mobility (De Jonge et al., 2012b,c; Kalantzi et al., 2013; Kelderman and Osman, 2007; Peng et al., 2009). ORP is a measure for the electron availability and promises the prediction of the stability and bioavailability of heavy metals in sediment or soil. On the basis of oxygen content, the redox zones of sediments usually can be stratified vertically into three classes: the oxic (oxygen reduction), the suboxic (nitrate, manganese, and iron reduction), and the anoxic (sulfate reduction and methanogenesis) (Di Toro et al., 2005; Strom et al., 2011). The distinction between these three layers is important for metal bioavailability. It varies from high to low when the redox status in soil or sediment changes from aerobic to anerobic condition during disturbation, flooding, for example.

The increasing ORP in sediment will facilitate the oxidization rate of sulfides and the degradation of organic compounds correspondingly, accelerating the liberation of the adsorbed/complexing heavy metal (Peng et al., 2009). For example, the Cd bound to organic sulfide, which is accepted as a stable metal form, dropped from 65% to 30% and transform to a more mobile form with ORP in sediment increase (Kelderman and Osman, 2007; Zoumis et al., 2001). Some recent researches have examined the influence of redox potential on Cu and Zn accumulation in *Tubifex tubifex* with relation to the hydrological regime (Hernández Crespo et al., 2012; Speelmans et al., 2010). Also, some studies have demonstrated that various redox conditions result in substantial different the physical–chemical properties of SOM (Hong et al., 2010) and sulfides (Hernández Crespo et al., 2012).

Accordingly, the heavy metal performs release and fixation in seasonal period with the annual variations of ORP in sediment (Bostick et al., 2001; Nizoli and Luiz-Silva, 2012). These phenomena are very useful and significant for studying, especially in some seasonally flooding rivers. For an instance, approximately 18 t of Zn in Mulde reservoir transferred from sediment into water, only due to the oxidization of flooding (Zoumis et al., 2001). Thus, oxidation and disturbation of sediment should be avoided for decreasing the release of metal from sediment in the dredging process of river or lake (Peng et al., 2009). What's more, the increased redox potential inhibits activity of anaerobic SRB and even promotes the growth of nitrate-reducing, sulfide-oxidizing bacteria (NR-SOB), which can then oxidizes sulfide compounds through nitrate reduction (Chen et al., 2013). So, oxygen availability seems to be the critical indicator of organisms' diversity (Jyväsjärvi et al., 2012).

3.2.4. Salinity

The relative high salinity can inhibit the growth and activity of SRB by increasing cell osmotic pressure and repressing metabolic enzymes, and thus affected the reduction of SO_4^{2-} and the decomposition of organic matter in sediment, resulting in increasing metals bioavailability (Hou et al., 2013; Nizoli and Luiz-Silva, 2012). Also, the increase of salinity was related to an enhancement in the content of major cations (e.g., Na, K, Ca, Mg) that compete for the sorption sites with heavy metals and decreased the binding of metals to humic acids (Du Laing et al., 2009). When soluble chloride complexes enforced, the mobility of trace metals was improved.

3.2.5. Nutrients

The greater nutritional content, or the concentrations of nitrite and ammonia, which were positively proportional to the content of particulate material, bacteria activity (ammonification–nitrification) or ionic exchange (Tesi et al., 2013), may increase the occurrence of dietary exposure to metals (Casado-Martinez et al., 2009; Simpson, 2005; Strom et al., 2011). Nitrate in nutrition can result in the increase of redox potential as a thermodynamically electron acceptor (Chen et al., 2013). Moreover, in normal conditions, a more significant role of OM and reactive sulfides was observed compared to the station with more eutrophicated conditions (in which a vital function of AVS could be expected) (Machado et al., 2010). Sedimentary OM in oligotrophic sites is more important for the structure of macro-invertebrate assemblages while eutrophic basins might supply food resources instead of OM (Jyväsjärvi et al., 2012). This appearance may result in the higher metal accumulation in poor nutrition of aquatic environment. So the pollution of heavy metals in oligotrophic condition should be received more attention just like eutrophication issue.

3.3. Biological attributes of the benthic species

Sediment dwelling benthic organisms such as polychaetes, bivalves and amphipoda as well as other varies microorganisms are the most frequently used biomonitors (Campana et al., 2013; De Jonge et al., 2011; Lee et al., 2000b; Paller and Knox, 2010; Tan et al., 2013). The variation of attributes of benthic organisms can be significantly correlated with the quality modification of the sediment or overlying water, and can in turn influence the fate of materials in sediment. Bacterial and animal frequent activities and energetic electron acceptors in the surface layer of the sediments, together lead to the oxidation of organic matter (Fernandes et al., 2011). Based on different types of final electron acceptors (e.g., aerobic, anoxic, and obligate anaerobic conditions), microbial metabolic processes can alter the characteristics of SOM (Hong et al., 2010). Besides, major reactions in redox process including denitrification, Mn (IV) and Fe (III) reduction as well as sulfate reduction are catalyzed by benthic microorganisms (Du Laing et al., 2009).

Organisms' behaviors, including feeding mode, burrowing and feeding depth as well as irrigation habits all can affect its metal exposure pathway (Lee et al., 2000a). In sediment, the relationship between AVS and metal accumulation of aquatic invertebrates is highly determined on its feeding behavior. These benthic creatures that reside in the surface sediments can build a oxidation microenvironment (e.g., burrowing, irrigation) (Simpson et al., 2012a) and thus maintain a much lower level of AVS than that of the bulk sediment (Campana et al., 2012). For deposit or detritus feeders, which represent a large portion of benthic invertebrates, grain phases may be the major route of metal exposure. Like marine polychaetes, which predominately feeding on the particle sediment, accumulated metals affected by minor influence of dissolved metals in pore water (Hernández Crespo et al., 2012). The amphipod, *M. plumulosa*, ingest large quantities of deposit during their foraging for food and dietary exposure to metals may elicit toxicity effects to itself (Simpson and King, 2004; Simpson et al., 2012a). The bivalves, such as *Tellina deltoidalis* (Campana et al., 2013), can maintain these particles within their digestive tracts for a long time through the filteration of particulates from the sediment–water interface (Lee et al., 2000a).

However, some benthic bivalves are also recognized as the deposit feeders and accumulated metal via a combination of both dissolved and particulate exposure routes (Campana et al., 2012; Simpson et al., 2012b). For those benthic organisms feeding on deposit, the combination of dissolved and solid particle phases may the mechanism of self-regulation to avoid external toxicity. Additionally, the sipunculan worms, *P. arcuatum*, indiscriminately ingest sediment particles rather than dissolved metals (Tan et al., 2013). Thus, decrease in growth of benthic organisms was inevitably recognized as the dietary exposure to sediment-bound metal (Campana et al., 2013). In concentration–response relationship measurements, the less than 15 μg/L for *M. plumulosa* and 50 μg/L for *N. spinipes* in dissolved Cu phases was entirely attributed to particulate exposure (Campana et al., 2012). Nevertheless, these thresholds are not always the right guidelines for sediment or water qualities. The threshold may be overly conservative, for sediment containing the important metal binding phases such as AVS, and especially for those organisms receives most of its exposure metals from dissolved phases (i.e., the overlying water) other than the deposit alone (Strom et al., 2011).

Meanwhile, these organisms decomposition of labile organic matter stimulate the microbial activities near the dead organisms, and then increase the availability of this labile fraction. These processes may also facilitate the metal mobilization from these organic phases and threaten to the growth and survival of organisms. But, some studies found that the organisms decomposed the availability of labile organic materials, especially sedimentary residues, decreased copper mobilization owing to the formation of copper-sulfide phases (Simpson and Batley, 2007; Simpson et al., 2012b; Stockdale et al., 2010). So the sediment factors influencing metal accumulation should be comprehensively considered when assessing toxicity to the benthic biota. What's more, the efficiency of metals assimilation from different sediment phases also depends on the organism physiology (e.g., gut passage or residence time, gut chemistry). Therefore, dietary uptake, coupled with sediment metal binding phases and organisms regulatory mechanisms, will better explain toxic effects to benthic organisms and the reason why metal bioaccumulation was closely related to extractable, sediment particle metals than to porewater metals.

3.4. Hydrological kinetic conditions

Hydrological kinetic conditions include the physical disturbance (including the flooding, runoff) (Atkinson et al., 2007; Petersen et al., 2011), organic matter diagenesis or sedimentation (Fernandes et al., 2011) and sediment resuspension (Breckel et al., 2005) that all can influence the remobilization of heavy metals. The term sedimentation has approximately been widely related to the deposition of fine sediments, which have a whole range from coarse sand to clay (Burton et al., 2006b; Kucuksezgin et al., 2008). Sedimentation process modifies the sediment substrate by changing its surface conditions and the volume of fine particles within the hyporheos. These fine grains settle down ultimately through its gravity, carrying heavy metals from liquor to the bottom of solid sediment, and frequently consolidate the lower sediments. So the water content of pore water during this process is increasingly fall off as well as the decrease of metal solubility, especially in higher clay content sediment. Particulates deposition protects the buried organic matters from contact with the main potential oxidants such as oxygen, nitrate and sulfate, which are found in the liquid phases (Fernandes et al., 2011). In the process of deposition, sediment density gradually increases because of the pressure, and the occupied anoxic state is further beneficial for the decomposition and humification of SOM (Hong et al., 2010).

Besides, suspended sediment containing heavy metals is a nonpoint source pollutant, and its variations in transport are usually hard for us to demonstrate due to its rapid change (Sadeghi et al., 2012). Physical processes (such as water current, anthropogenic disturbance) and benthic organism activities (e.g., burrowing, irrigation) can lead to sediment resuspension, altering the partitioning of metal between sediment–water and its speciation in the dissolved phase. For example, sediment disturbances enhanced the release of heavy metals and bioturbation caused by benthic organism arouse metal release from pore water and iron and manganese in overlying waters, increasing the metals bioavailability (Atkinson et al., 2007). In suspended sediment, understanding the particle size distribution and concentration may pave the way for well knowing the concentration and distribution of metals. Particulates adsorb or bind metals and transport together following the hydrological kinetics. For an instance, in various runoffs, heavy metal concentration is correlated with suspended sediment content (Sadeghi et al., 2012; Saeedi et al., 2013). Besides, Carmen's result indicated that flooding (resulting in more reduced conditions) minimized the availability of metals duo to the biodegradation of fresh organic matters and the production of sulfides (Hernández Crespo et al., 2012).

Recent studies have also shown the importance of fine grain suspended sediment in the transport of heavy metals through fluvial systems (Chao et al., 2009; Sadeghi et al., 2012). During resuspension, for example, the speciation of Cu, Zn, and Pb in suspended particle matter transformed from stable to labile fractions and their concentrations are higher in the upper of water column than the lower part (Kucuksezgin et al., 2008). Nevertheless, previous studies showed a decrease adsorption of metal onto suspended particulate matter for its increasing concentrations (Huang et al., 2012). This opposite result possibly be explained by the “particles concentration effect”, which defined as the downward trend in metal partition coefficients when the suspended particulate matters increases (Kucuksezgin et al., 2008)

3.5. Other factors: temperature, geographic position, adsorption time

Apart from the factors above, many studies have revealed that sediment temperature, geographic position and adsorption time (or aging) are also well correlated with heavy metal concentrations.

The geographical distribution of climatic zone has its own specific characteristics in the matter of behavior of heavy metals in sediment. In the summer region of temperate climate, where has an ascending temperature in water, it favors the activity of sulfate-reducing bacteria, thus increasing the rate of SO_4^{2-} reduction and, subsequently, the production of AVS (Campana et al., 2009). While in tropical district, there is no variation between seasonal temperature not decisively contributing to the AVS dynamics, but just a seasonal fluctuation of sulfate (SO_4^{2-}) with highest content in winter (Nizoli and Luiz-Silva, 2012). Besides, climatic regime (i.e., temperature gradient) can regulate the dynamics behavior of metal precipitation or solubilization via affecting pH and ORP (Lau, 2000; Nizoli and Luiz-Silva, 2012). Sediment temperature, closely associated with lake depth, also accommodates the abundance and species composition of profundal macro-invertebrate (i.e., Benthic Quality Index) (Jyväsjärvi et al., 2009; Jyväsjärvi et al., 2012).

Adsorption time is a factor to be considered in distribution and partitioning of metals. For example, aging can redistribute the adsorbed metals to the interior stability of sorption sites of organic and mineral substrates (Burton et al., 2006b). The prolonged aging of metals in sediment or soils has been demonstrated to be a major factor in determining their availability: the exchangeable and carbonate fractions decrease while the refractory fractions (organic and residual phase) increase (Guo et al., 2011; Jones et al., 2008; Peng et al., 2009; Zhong et al., 2012). So it is essential to allow an adequate aging period following trace metal spiking to sediments, especially with regard to the bioavailability of heavy metals.

4. Methods for evaluating the bioavailability and toxicity of heavy metals

Generic relationships between bioaccumulation and toxicity of metals are not yet understood. To develop an efficient and effective management protocols to control metals spill, information collected from the present study can be used as baseline data for future monitoring of heavy metal pollution (Nobi et al., 2010).

Many assessment models about metals toxicity have been established and applied to evaluate the toxicity of metals to biota, but some limitations of these methods simultaneously accompanied. Past decades had widely applied SEM–AVS model to the prediction of metal toxicity to organism, but lack of consideration of the impacts of OM, Fe–Mn oxides on metals. Besides, SQGs based on metals in pore water may overestimate the toxicity of some cationic metals to biota, especially in high OM sediments, due to considering only the influence of inorganic ligands complexation (Besser et al., 2003). Still, SQGs are fail to predict how toxicity thresholds change for different sediment types and different test species (Ahlf et al., 2009; Strom et al., 2011), and only collect acute effects data other than chronic effects, which are more sensitive and more appropriate for the prediction of the risks posed by to contaminated sediments (Mann et al., 2009). Equilibrium partitioning model (EqP model), which limits to the relationship between the toxic effects and divalent metal ions in anoxic condition, ignores the dietary exposure route of organism and sulfides even acting as a direct cause of toxicity to organism (Hernández Crespo et al., 2012). In addition, establishing the effects threshold in water-only for benthic invertebrates can be inappropriate and difficult (Campana et al., 2012; Spadaro et al., 2008). Similarly, the less than 63 μm OC-normalized approach is overly conservative for sediment containing AVS (Strom et al., 2011).

To accurately estimate the initial chronic effects, a much better effects to understand the factors affecting metabolically available metal content will be necessary. A potential approach is the application of biotic ligand models, which explicitly allow for the effects of complexation on bioavailability, or to employ sampling or analytical measures that evaluate the lability of metal ion complexes into consideration (Besser et al., 2003). Therefore, the (SEM–AVS)/f_{OC} model may be a more appropriate measurement for predicting a low risk of negative biological effects when sediments apparently contain both AVS and OM (De Jonge et al., 2012a; Di Toro et al., 2005; Machado et al., 2010). The technique of DGT may also become increasingly conductive to provide spatially resolved information on metals bioavailability in sediments, particularly in the sediment–water interface and deeper pore waters (Simpson et al., 2012b; Strom et al., 2011). Establishing the models of metal bioavailability that explicitly consider the pools of AVS, OM, iron and manganese oxides and even biota as phases influencing toxicity is not only a necessity but a good prospect if possible.

5. Conclusions and expectations

As a result of its complex nature, sediment geochemical properties affecting the bioavailability of heavy metals must be comprehensively considered and even analyzed, and this will be the focus for the next studies. Consideration of chronic responses of organism and mechanisms that relate to toxicity and bioaccumulation is the next step needs to improve, particularly with regard to the elucidation of links between long-term dietary exposures to metals and adverse effects correspondingly. In modifying or preventing metal pollutions in the harbor area, we should comprehensively consider the pathway of metals discharge and the following adverse influences on the nearby environment, ecosystem, and even public health, rather than a single source of metal emissions (Lin et al., 2013).

Recently, rapid assessments of metal bioavailability in sediment based on the measurement of coelomic fluid metal content, have been established and can be effective access to the evaluation of metal bioavailability in sediment (Tan et al., 2013). Besides, the application of metal isotopes recently receives attention for the discrimination between the spiked metals and background metals in the field of influence of aging on heavy metals bioavailability in sediment (Zhong et al., 2012, 2013). Latest years studies have focused on the application of polysulfides to insolubilize metals, which are based on S-metals binding and have achieved increasingly positive effects (Kim et al., 2011; Oh et al., 2012; Shafaei-Fallah et al., 2011). The application of these potential poly-sulfides, therefore, provides us an efficient and applicable potential way to make heavy metals in sediment insoluble and further decrease the lethal bioavailability on biotas. Further, based on the mechanism of interaction of fine particles with heavy metals, emerging nano-materials can be introduced to the treatment of metals pollution in sediment. This remediation of sediment pollution will be deeply improved via the application of these approaches.

Acknowledgments

The project is financially supported by the National Natural Science Foundation of China (51179068, 51039001).

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