



Measurement of Cu and Zn adsorption onto surficial sediment components: New evidence for less importance of clay minerals

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ABSTRACT

Clay minerals in surficial sediment samples, collected from the Songhua River in China, were separated via sedimentation after removal of Fe/Mn oxides and organic materials; Cu and Zn adsorption onto the sediment components was then evaluated. Clay minerals were examined via X-ray diffraction and scanning electron microscopy. Clay minerals were found to consist mainly of illite, kaolinite, chlorite and an illite/smectite mixed layer. Non-clay minerals were dominated by quartz and orthoclase. The retention of Cu and Zn by clay minerals was 1.6 and 2.5 times, respectively, greater than that of the whole, untreated surficial sediment. Compared to the other critical components in sediments related to metal sorption (Mn oxides, Fe oxides and organic materials), the adsorption capacity of clay minerals was found to be relatively lower on a unit mass basis. These data suggest that, although clay minerals may be important in the adsorption of heavy metals to aquatic sediments, their role is less significant than Fe/Mn oxides and organic materials.

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1. Introduction

Because of the known toxicity and bioaccumulation potential of many heavy metals, their behavior, transport and ultimate fate in the environment, are increasingly of interest to the scientific community. It has been widely accepted that surficial sediments play crucial roles in the accumulation of heavy metals, acting both as sinks and as sources for pollutants [1–3]. Adsorption of heavy metals on sediment constituents is one of the most important reactions that determines the mobility and bioavailability of heavy metals in aquatic environments. Earlier studies have identified three of the most important geochemical components affecting metal bioavailability in aquatic systems: Mn oxides, Fe oxides and organic materials [2,4–7]. These factors are crucial for binding and adsorption of heavy metals onto the surficial sediments, as indicated by various analytical and data evaluation methods such as correlation analyses [8,9], sequential extraction [4,10,11], specific or selective extraction [5,12,13], a combination of chemical extraction and adsorption techniques [4,14] and selective extraction–adsorption–statistical analyses [15–18]. The last procedure has been applied to accurately estimate the relative roles of Fe oxides, Mn oxides and organic materials in natu-

ral surface coatings on adsorption of heavy metals, and provide significant insight into the mechanisms of the heavy metal associations with adsorptive components of heterogeneous aquatic sediments. In a previous study, we successfully applied the selective extraction–adsorption–statistical analysis method to separate Mn oxides, Fe/Mn oxides and organic materials from surficial sediments and estimate the relative roles of these three components in Cu and Zn adsorption [19].

Clay minerals in surficial sediments also affect adsorption of heavy metals, and may do so in combination with Fe, Mn amorphous oxides and organic materials, some of which may cover clay surfaces [20]. Several studies have explored the relationship between heavy metals and clay minerals, including pure clays, such as illite [21], smectite [22], kaolinite [23], vermiculite [22], rec-torite [24], and clay minerals in soil and sediment [25,26]. When compared with pure clay minerals, clay minerals isolated from soil or sediment are composed of various minerals with various crystalline structures. For example, the clay minerals in some lacustrine sediments in Mexico were predominantly composed of a Si-rich allophone and smectite, with halloysite at a lower concentration [27]. Given the range of possible clay mineral composition, the reactions between heavy metals and clay minerals in the sediments are expected to be complex. While there is an absence of critical information regarding the role of mineralogy on sediment adsorption, a better understanding of these processes may be important in understanding the manner in which heavy metals are transferred from a liquid mobile phase to a solid one. Few historical studies

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have focused on the influence of clay mineral characteristics on metal sorption. From the aspect of correction analysis, clay minerals have always been judged to be more important in dictating the adsorbing capacity of sediments [25,28], while amorphous Fe/Mn oxides and organic materials were also shown to be more important in affecting the affinity of sediments for metals through correction analysis [25,28]. However, the relative significance of clay minerals, organic materials and Fe/Mn oxides has not been quantitatively determined through correction analysis.

In the present study, clay minerals were separated from sediment particulates after sequential removal of Mn oxides, Fe oxides and organic materials through the application of selective extraction reagents; the adsorptive properties of clay minerals were then investigated. Previously-generated [19] isothermal adsorption data of Cu and Zn onto the surficial sediments before and after removal of Mn oxides, Fe/Mn oxides, and organic materials were re-analyzed using a nonlinear least-squares fitting (NLSF) technique by MicrocalOrigin (Version 6.0, Microcal Software, Inc., Northampton, MA, USA) to estimate the adsorption parameters of each of these three components plus residues. Finally, the adsorption capacity of each sediment component was investigated and quantitatively compared.

2. Materials and methods

2.1. Separation of clay minerals from surficial sediments

The Songhua River lies in the northeast region of China ($41^{\circ}42'–51^{\circ}38'N$ and $119^{\circ}52'–132^{\circ}31'E$). The total basin area of the Songhua River is $55.68 \times 10^4 \text{ km}^2$ (920 km long and 1070 km wide), corresponding to 44.9% of the area of northeast China and 5.8% of the entire country. The Songhua River has an average storage capacity of $851.5 \times 10^8 \text{ m}^3$, making it the third largest river system in China by water volume, exceeded only by the Yangze River and Pearl River. The sampling location was near the Linjiangmen Bridge in Jilin, China, an industrial city located in the upstream reach of the Songhua River. Jilin is situated on an open plain in the river valley, covering $27.12 \times 10^3 \text{ km}^2$ (urban area of $1.76 \times 10^3 \text{ km}^2$).

Four initial samples of surficial sediment, approximately 20 cm apart, were collected and homogenized into a single composite sample. Samples were taken to the laboratory and air-dried at ambient temperature. Agglomerates formed during drying were ground with a pestle and mortar. The dried, ground material was then sieved to remove particles larger than 0.076 mm. All further analyses were performed on sediments less than 0.076 mm in size.

The sieved sediment sample was divided into five equal portions. The first portion was sequentially extracted with H_2O_2 (hydrogen peroxide, 30%) and 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (ammonium oxalate), buffered to pH 3.0 with $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) to remove organic materials and Fe/Mn oxides. The clay minerals in the solids were separated by sedimentation according to the Schultz principle; silicate residue remained after removal of the clay minerals. The additional four sediment portions were used to obtain sediment samples representing (1) the control (no treatments), (2) after removal of Mn oxides, (3) after removal of Fe/Mn oxides and (4) after removal of organic materials, using selective extraction in isolation [19]. Briefly, selective extraction consisted of the following: 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) + 0.1 M HNO_3 (nitric acid) to remove Mn oxides; 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (ammonium oxalate) + $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) buffer solution (pH 3.0) to digest both Fe and Mn hydrous oxides; 30% H_2O_2 to selectively extract organic materials. All reagents in the extraction process were trace metal grade, purchased from Sinopharm Chemical Reagent Co., Ltd (China).

2.2. Analytical methods

Total organic carbon (TOC) in the solid particles was measured by a TOC-analyzer (TOC-V_{CPH}, Shimadzu, Japan). Pseudo-total Fe and Mn in the solid particles were digested by $\text{HNO}_3\text{--HClO}_4$, and concentrations in the supernatant were measured using flame atomic adsorption spectrometry (FAAS) (WYX-9004, Shenyang, China). Fractionation of Fe and Mn was completed using the modified sequential extraction procedure. Using this technique, all six of the operationally-defined binding fractions (exchangeable, bound to carbonates, bound to Mn-oxides, bound to Fe-oxides, bound to organic materials and residues), as well as total extractable amounts of Fe and Mn oxides, could be determined [29–31].

BET surface area was measured with a surface area and pore size analyzer (TriStar 3000, Micromeritics, USA). The clay samples were characterized by X-ray diffraction (XRD-6000, CuK α radiation) and environmental scanning electron microscopy (PHILIPS XL-30, Philips-FEI). Qualitative and quantitative analyses of the clay mineral fraction were according to the SY/T 5163-1995 method.

2.3. Cu and Zn adsorption to solids

Cu and Zn adsorption onto the solid particles was measured in duplicates using the batch equilibration method [19]. Preparative experiments indicated that Cu and Zn concentrations in the sediments were 0.56 $\mu\text{mol/g}$ and 1.72 $\mu\text{mol/g}$, respectively. Adsorption of Cu and Zn onto the solid particles was measured in chemically-defined solutions with eight different Cu and Zn concentrations (15.5, 31.0, 62.0, 93.0, 124.0, 155.0, 232.5 and 310.0 μM) in order to avoid interference with existing Cu and Zn. The preparative experiments also showed that the equilibrium time for Cu and Zn adsorption to clay minerals was 16 h. However, in order to generate data that could be directly compared to our previous study results [19], a Cu and Zn isothermal adsorption period of 24 h was chosen. The adsorption solutions were prepared by diluting 15.5 mM $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ reference solutions with a minimal mineral salt (MMS) solution consisting of 200 μM $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, 140 μM $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 910 μM $(\text{NH}_4)_2\text{SO}_4$, 150 μM KNO_3 , 10 μM NaHCO_3 , and 5 μM KH_2PO_4 . The solutions were adjusted to $\text{pH } 6.0 \pm 0.1$ using 0.01 M HNO_3 and NaOH ($25 \pm 1^\circ\text{C}$). Sediment samples or clay mineral particles of 0.1 g were placed in 100 ml polyethylene tubes, followed by 50 ml of a solution containing the Cu or Zn (eight separate analyses using the eight different Cu/Zn concentrations). The particulate suspensions were stirred continuously for 24 h and filtered through 0.45- μm filters (Millipore, Billerica, MA, USA). Before filtering, the pH was re-adjusted to the initial level; changes in pH after 24 h were found to be within ± 0.5 pH units of the original. Cu and Zn concentrations in the initial or equilibrium solutions were measured by FAAS. The amounts of adsorbed Cu and Zn were calculated as the difference between the amount initially added and that remaining in the equilibrated solutions.

3. Results and discussion

The concentration of clay minerals in the sediment particles was 132.2 mg/g. The mineralogy of the clay minerals in the surficial sediments was illustrated in the XRD patterns (Fig. 1). The clay minerals in the surficial sediments consisted of illite, kaolinite, chlorite and an illite/smectite mixed layer, corresponding to 50.7%, 13.9%, 14.2% and 21.2% of total clay minerals, respectively. Residues were operationally defined as, and represented by, the solid particulates after chemically extracting Mn oxides, Fe oxides and organic materials from the sediment samples. Silicate residues were operationally defined as the solid particulates after removing clay minerals. The clay minerals were dominated by laminar and layered particles

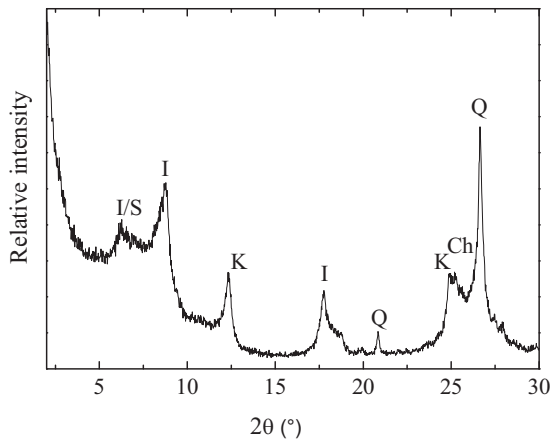


Fig. 1. X-ray diffraction spectra of the clay mineral saturated by glycol. I, S, K, Q, Ch represent illite, smectite, kaolinite, quartz, and chlorite, respectively.

with diameters of less than 5 μm , based on the morphological measurements (Fig. 2). Removal of Fe/Mn oxides and organic materials yielded “cleaner” clay minerals and silicate residue surfaces (Fig. 2). The presence of Fe/Mn oxides or organic materials on the clay or silicate residue surfaces implies a significant interaction between these components within the sediment matrix.

The maximum Cu and Zn adsorption capacities of surficial sediments significantly decreased after the surficial sediments were treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_2\text{-H}_2\text{C}_2\text{O}_2$ and H_2O_2 (Table 1). The values of Cu and Zn adsorption on solid particulates were calculated using NLSF methods. The values presented in Table 1 represent saturated conditions, and are therefore higher than the experimentally-derived values of Cu and Zn adsorption determined previously [32]. The quantity of clay minerals obtained through the sedimentation method was limited, leading to a lower concentration of solid particulates in the adsorption suspension and, consequentially, to a lower solid-to-liquid ratio. These conditions

may have induced higher adsorption of Cu and Zn onto solid particulates in the present study.

Data obtained under the experimental conditions of the present investigation indicate that the affinity of clay minerals for Cu and Zn is significantly greater than that of the surficial sediments themselves, specifically 1.5 and 2.5 times, respectively. This enhancement is due, in part, to the much higher BET surface area of clay minerals, which is approximately five times greater than that of original surficial sediments (Table 2). Previous studies have clearly indicated that BET surface area plays a crucial role in adsorption; the larger the surface area of the solid particles, the stronger the adsorption capacity [8,31]. However, the surface charge of the solid phase particles is also important, with a greater surface charge resulting in a greater affinity for adsorption [33]. The illite/smectite mixed layer consisted of an expandable clay mineral; the surface charge of these clay minerals was relatively larger than that of the surficial sediments.

Although the adsorption properties of Mn oxides, Fe oxides and organic materials were previously studied through selective extraction–adsorption–statistical analysis [19], the adsorption capacities of these three components were re-estimated in order to generate data that would be directly comparable in the present investigation of clay minerals. The reanalysis, using different data processing and modeling techniques, produced the adsorption isotherms shown in Fig. 3. In order to draw the isothermal curves, data from the current study (Table 1), and partial data from the earlier study (Table 2 from [19]), were used. The applied model considered total adsorption of Cu and Zn by unextracted and extracted sediments at a given Cu and Zn concentration (Γ_{total}) to be the sum of the contributions from Mn oxides, Fe oxides, organic materials and residues, as expressed by the Langmuir adsorption isotherm:

$$\Gamma_{\text{total}} = \sum_{i=1}^4 C_i \frac{\Gamma_i^{\text{max}} K_i [\text{metal}]}{1 + K_i [\text{metal}]}, \quad (1)$$

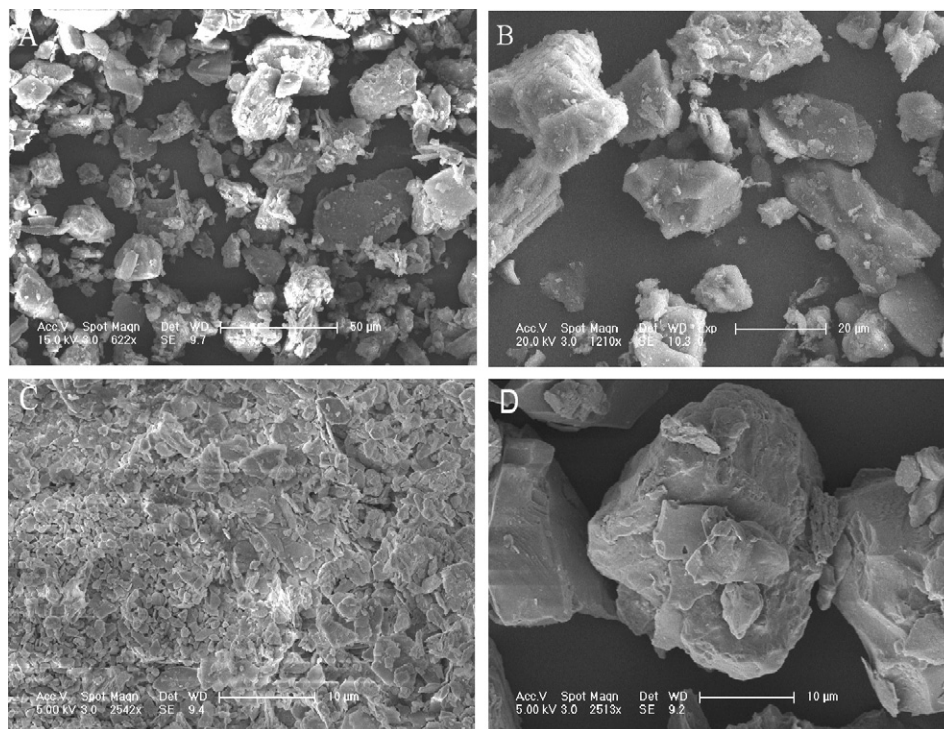


Fig. 2. Scanning electron micrograph of the surficial sediments (A), residues (B), clay minerals (C), and silicate residues (D).

Table 1
Langmuir parameters of Cu and Zn adsorption onto surficial sediments before and after selective extraction treatments and clay minerals and silicate residues.

Parameters	Sediments untreated	Clay minerals	Silicate residues	Sediments treated with NH ₂ OH·HCl	Sediments treated with (NH ₄) ₂ C ₂ O ₄	Sediments treated with H ₂ O ₂
Cu						
Γ_{\max} ($\mu\text{mol/g}$)	96.55 (4.83)	154.23 (17.62)	60.97 (6.29)	62.12 (3.03)	36.54 (4.23)	58.64 (3.21)
K ($1/\mu\text{mol}$)	0.014 (0.0016)	0.84 (0.37)	0.017 (0.0048)	0.016 (0.0021)	0.0088 (0.0023)	0.014 (0.0020)
Correlation coefficient r	0.9826	0.9603	0.9751	0.9980	0.9904	0.9935
Zn						
Γ_{\max} ($\mu\text{mol/g}$)	26.81 (0.64)	68.11 (3.06)	23.26 (2.55)	22.31 (1.23)	16.13 (2.10)	21.60 (1.27)
K ($1/\mu\text{mol}$)	0.029 (0.0026)	0.012 (0.0013)	0.018 (0.0062)	0.011 (0.0015)	0.0093 (0.0025)	0.011 (0.0016)
Correlation coefficient r	0.9938	0.9972	0.9600	0.9921	0.9849	0.9908

Numbers in parentheses are standard deviations. Γ_{\max} is the maximum adsorption of heavy metals by particulate samples, and K is the Langmuir equilibrium coefficient.

Table 2
Total organic carbon, Fe and Mn contents as well as BET surface area of solid samples.

Element	Sediments untreated	Clay minerals	Silicate residues	Sediments treated with NH ₂ OH·HCl	Sediments treated with (NH ₄) ₂ C ₂ O ₄	Sediments treated with H ₂ O ₂
C ($\mu\text{mol/g}$)	1049.91 (110.45)	236.23 (23.82)	210.59 (11.09)	1014.32 (103.11)	1005.71 (85.75)	313.82 (12.17)
Fe ($\mu\text{mol/g}$)	437.65 (6.71)	158.03 (5.21)	49.87 (1.67)	65.19 (2.03)	2.02 (0.30)	83.42 (4.42)
Mn ($\mu\text{mol/g}$)	7.32 (0.29)	2.55 (0.16)	1.09 (0.12)	1.47 (0.55)	0.35 (0.08)	2.67 (0.16)
BET (m^2/g)	16.8	91.2	13.9	20.8	19.7	29.9

Numbers in parentheses are standard deviations.

where for each of the four components, C_i is the total concentration of the extractable component ($\text{mg metal or organic carbon g}^{-1}$) in the solids [19]; the fraction term represents its adsorption ability ($\text{mg per g metal or per g organic carbon}$). In the fraction term, Γ_i^{\max} is the maximum adsorbed Cu or Zn by component i , and K_i is the Langmuir equilibrium constant. The Cu or Zn adsorption data on unextracted and extracted solid particles were fitted using a multiple data sets fitting technique. Before fitting, Γ_i^{\max} and K_i were set as shared parameters, and were initialized on the assumption that each component had the same adsorption ability. Iterative mode runs were conducted until X^2 was not reduced (the fitting converged) or X^2 did not change in three iterations (the fitting did not converge). X^2 was used to represent the deviations of the theoretical curves from the experimental data. Adsorption isotherms of Mn oxides, Fe oxides and organic materials in the surficial sediments, under the same basis (i.e., without considering the effect of the relative concentration of each component) are shown in Fig. 3. The adsorption capacity of residues (clay minerals and silicate residues) was much lower than those of the other three components, indi-

ating the adsorption capacity of residues was negligible when compared to Fe/Mn oxides and organic materials.

This calculated adsorption capacity of residues (mixed solid particles including both clay minerals and silicate residues) was an indirect estimate, based on the statistical analysis of previous isothermal adsorption data [19] and the empirical residue adsorption data presented here. Residue capacity (expressed as adsorption capacity of clay minerals and silicate residues) is also illustrated in Fig. 3. Our results show that adsorption capacities of clay minerals and silicate residues were all greater than that of residues. The amount of Cu adsorbed on clay minerals was about two times greater than that of residues, and the amount of Cu on silicate was approximately one times greater than that of residues. The differences among the Zn adsorption capacities of three solid samples were less substantial, but still reflected the same relative adsorption order: clay minerals > silicate residues > residues. These results were partially due to the interactions between clay minerals and silicate residues (Fig. 2). Smaller particles were clearly seen on the surfaces of the larger residual particles (Fig. 2D). However, once clay

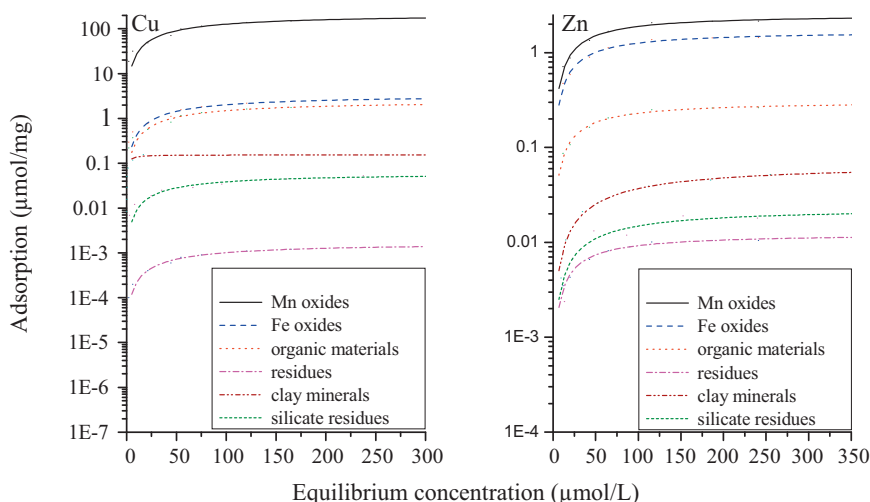


Fig. 3. Cu and Zn adsorption onto components of surficial sediments on a unit mass basis.

minerals were removed via chemical treatment, the surfaces of the silicate residue particles were generally free of adhering materials, suggesting that the clay minerals either coated or disperse between the silicate residuals. The effective surface areas of these two solids increased in parallel with the separation of clay minerals from silicate residues. Accordingly, available contact area of heavy metals and solids increased, thus favoring higher adsorption capacities. Conversely, after removal of Fe/Mn oxides and organic materials, the reticular surface structure of the solid particles weakened (Fig. 2C and D); this providing additional evidence that clay mineral and silicate residue surfaces were coated with Fe/Mn oxides and organic materials. The Fe/Mn oxides and organic materials claimed some of the surface contact area, reducing available space and interfering with adsorption of heavy metals to clay minerals and silicate residues. The adsorption capacity of residues, based on the statistical estimation analysis, was underestimated. The effects of the Fe/Mn oxides and organic materials on experimental adsorption capacity of clay minerals and silicate residues, however, were negligible due to the removal of these coated Fe/Mn oxides and organic materials through chemical treatment.

Although the statistical analysis underestimated the adsorption capacity of residues, and the experimental adsorption capacities of clay minerals and silicate residues were shown to exceed that of residues, the affinities of clay minerals and silicate residues for trace metals on a unit mass basis were, nevertheless, significantly lower than those of Mn oxides, Fe oxides or organic materials. These results suggest that sediment-associated clay minerals, while playing a significant role in the adsorption of heavy metals, were not as important as Mn oxides, Fe oxides and organic materials. It is likely, however, that the relative impacts of these four sediment components on adsorption capacity will vary with the particular aquatic environment. Additional studies on other lentic and lotic systems with different physical and chemical conditions, including metal valences, will provide further insight into the importance of site-specific factors on heavy metal bioavailability.

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References

- [1] J. Vuceta, J.J. Morgan, Chemical modeling of trace metals in fresh waters: role of complexation and adsorption, *Environ. Sci. Technol.* 12 (1978) 1302–1308.
- [2] L.W. Lion, M.L. Shuler, W.C. Ghiorse, Trace metal interactions with microbial biofilms in natural and engineered systems, *CRC Crit. Rev. Environ. Contam.* 17 (1988) 273–306.
- [3] P.H. Santschi, J.J. Lenhart, B.D. Honeyman, Heterogeneous processes affecting trace contaminant distribution in estuaries: the role of natural organic matter, *Mar. Chem.* 58 (1997) 99–125.
- [4] L.W. Lion, R.S. Altmann, J.O. Leckle, Trace-metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings, *Environ. Sci. Technol.* 16 (1982) 660–666.
- [5] L.B. Young, H.H. Harvey, The relative importance of manganese and iron oxides and organic matter in the adsorption of trace metals by surficial lake sediments, *Geochim. Cosmochim. Acta* 56 (1992) 1175–1186.
- [6] J.V. Headley, J. Gandrass, J. Kuballa, K.M. Peru, Y. Gong, Rates of adsorption and partitioning of contaminants in river biofilms, *Environ. Sci. Technol.* 32 (1998) 3968–3973.
- [7] D. Perret, J.F. Gaillard, J. Dominik, O. Atteia, The diversity of natural hydrous iron oxides, *Environ. Sci. Technol.* 34 (2000) 3540–3546.
- [8] F. Wang, J. Chen, Relation of sediment characteristics to trace metal concentrations: a statistical study, *Water Res.* 34 (2000) 694–698.
- [9] J. Lin, S. Chen, The relationship between adsorption of heavy metal and organic matter in river sediments, *Environ. Int.* 24 (1998) 345–352.
- [10] B. Jones, A. Turki, Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, North-east England, *Mar. Pollut. Bull.* 34 (1997) 768–779.
- [11] M. Chartier, G. Mercier, J.F. Blais, Partitioning of trace metals before and after biological removal of metals from sediments, *Water Res.* 35 (2000) 1435–1444.
- [12] A. Turner, Trace metal contamination in sediments from U.K. estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides, *Estuarine Coast Shelf Sci.* 50 (2000) 355–371.
- [13] A. Turner, G.E. Millward, S.M.L. Roux, Significance of oxides and particulate organic matter in controlling trace metal partitioning in a contaminated estuary, *Mar. Chem.* 88 (2004) 179–192.
- [14] R. Fujiyoshi, T. Okamoto, M. Katayama, Behavior of radionuclides in the environment: 2. Application of sequential extraction to Zn(II) adsorption studies, *Appl. Radiat. Isot.* 45 (1994) 165–170.
- [15] D. Dong, X. Hua, Y. Li, Z. Li, Lead adsorption to metal oxides and organic material of freshwater surface coatings determined using a novel selective extraction method, *Environ. Pollut.* 119 (2002) 317–321.
- [16] D. Dong, L.A. Derry, L.W. Lion, Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials, *Water Res.* 37 (2003) 1662–1666.
- [17] D. Dong, X. Hua, Y. Li, J. Zhang, D. Yan, Cd adsorption properties of components in different freshwater surface coatings: the important role of ferromanganese oxides, *Environ. Sci. Technol.* 37 (2003) 4106–4112.
- [18] Y. Li, X. Wang, S. Guo, D. Dong, Cu and Zn adsorption onto non-residual and residual components in the natural surface coatings samples (NSCSs) in the Songhua River, China, *Environ. Pollut.* 143 (2006) 221–227.
- [19] Y. Li, X. Wang, G. Huang, B. Zhang, S. Guo, Adsorption of Cu and Zn onto Mn/Fe oxides and organic materials in the extractable fractions of river surficial sediments, *Soil Sediment Contam.* 18 (2009) 87–101.
- [20] D.A. Laird, P.Y. Yen, W.C. Koskinen, T.R. Steinhilmer, R.H. Dowdy, Sorption of atrazine on soil clay components, *Environ. Sci. Technol.* 28 (1994) 1054–1061.
- [21] C. Poinsot, B. Baeyens, M.H. Bradbury, Experimental and modeling studies of Cs adsorption on illite, *Geochim. Cosmochim. Acta* 63 (1999) 3217–3227.
- [22] D. Malferrari, M.F. Brigatti, A. Laurora, S. Pini, L. Medici, Sorption kinetics and chemical forms of Cd (II) sorbed by thiol-functionalized 2:1 clay minerals, *J. Hazard. Mater.* 143 (2007) 73–81.
- [23] M. Gräfe, B. Singh, M. Balasubramanian, Surface speciation of Cd (II) and Pb (II) on kaolinite by XAFS spectroscopy, *J. Colloid Interface Sci.* 315 (2007) 21–32.
- [24] G. Zhang, X. Yang, Y. Liu, Y. Jia, G. Yu, S. Ouyang, Copper (II) adsorption on Carcorite and effect of static magnetic field on the adsorption, *J. Colloid Interface Sci.* 278 (2004) 265–269.
- [25] Y. Kim, K. Kim, H.D. Kang, W. Kim, S.H. Doh, D.S. Kim, B. Kim, The accumulation of radiocesium in coarse marine sediment: effects of mineralogy and organic matter, *Mar. Pollut. Bull.* 54 (2007) 1341–1350.
- [26] F.A. Vega, E.F. Covelo, M.L. Andrade, P. Marcet, Relationship between heavy metals content and soil properties in mine soils, *Anal. Chim. Acta* 524 (2004) 141–150.
- [27] C.J. Warren, D.L. Rudolph, Clay minerals in basin of Mexico lacustrine sediments and their influence on ion mobility in groundwater, *J. Contam. Hydrol.* 27 (1997) 177–189.
- [28] G. Bianchini, R. Laviano, S. Lovo, C. Vaccaro, Chemical-mineralogical characterization of clay sediments around Ferrara (Italy): a tool for an environmental analysis, *Appl. Clay Sci.* 21 (2002) 165–176.
- [29] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
- [30] N. Belzile, P. Lecomte, A. Tessier, Testing re-adsorption of trace elements during partial chemical extractions of bottom sediments, *Environ. Sci. Technol.* 23 (1989) 1015–1020.
- [31] K.C. Yu, L.J. Tsai, S.H. Chen, S.T. Ho, Chemical binding of heavy metals in anoxic river sediments, *Water Res.* 35 (2001) 4086–4094.
- [32] D.C. Seo, K. Yu, R.D. DeLaune, Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: batch and column experiments, *Chemosphere* 73 (2008) 1757–1764.
- [33] K.G. Bhattacharyya, S.S. Gupta, Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu (II) from aqueous solution, *Purif. Technol.* 50 (2006 Sep) 388–397.