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Comparison of lead, cadmium, copper and cobalt adsorption onto metal oxides and organic materials in natural surface coatings

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Abstract

Selective extraction techniques followed by adsorption experiment and statistical analysis were employed to estimate and compare the relative roles of metal oxides and organic substance in adsorption of Pb, Cd, Cu and Co onto surface coatings. Results indicated that metal oxides were very important sorbents for all of metal ions involved in this study, especially for Pb and Co. Furthermore, manganese oxides contributed to the absolute majority of Co adsorption regardless of concentration. But for Cu and Cd, organic materials are also very important sorbent phases, particularly for Cu, organic materials contributed to most of the Cu adsorption regardless of concentration. In addition, the analysis suggested the extraordinary predominance of Mn oxides for metal adsorption at the low concentrations. Considering the low concentration in natural water environments, Mn oxides might exert the greatest influence on the behavior of heavy metals.

Keywords: Heavy metals; Adsorption; Surface coatings; Main components

1. Introduction

Heavy metals are released into aquatic and soil environments largely from various anthropogenic activities and pose a serious threat to plants, animals and even human beings because of their bioaccumulation, nonbiodegradable properties and toxicity even at low concentrations [1,2]. Adsorption of trace heavy metals onto solid phases and associated surface coatings is considered very important in controlling heavy metal activity. In addition to the well-established effects of solution chemistry, adsorption of trace heavy metals is expected to be governed by the composition of solid phases, particularly the content of metal oxides (iron oxides and manganese oxides) and organic materials [3–7]. Iron oxides are abundant components in solid phases that have been studied extensively and are considered important sorbents for trace heavy metals [8,9]. However, recent research results indicate that manganese oxides exhibit strong adsorption ability for heavy metals in spite of the fact that concentrations of manganese oxides in solid phases are lower [10]. Main components in solid phases have diverse binding abilities for trace metals and have contrasting influence on the metal transportation and bioavailability. So the identification of the main binding sites of trace metals not only helps one understand geochemical processes but also allows one to predict the potential for remobilization, to determine the bioavailability of an element, to discriminate between sources [11] and to optimize remediation efforts.

Many techniques have been used to qualify the contribution of different sorbent phases to metal sorption in soils like sequential extraction techniques, additivity model [12] and selective extraction techniques followed by adsorption experiments and statistical analysis, etc. Traditional sequential extraction techniques removed certain components and trace metals associated with those components simultaneously. The main issue of the method is the possibility of the readsorption of the liberated metals onto the residual solid phases remaining after the extraction [2]. In the additivity model, total adsorption was predicted from the sum of contribution of individual components that were pure laboratory surrogate materials. Limitation of the method was that laboratory surrogate materials probably could not substitute the real components in the solid phases owing to the complexity of natural environments. Selective extraction techniques followed

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by adsorption experiment and statistical analysis were first applied to natural surface coatings by Dong et al. to investigate the relative adsorption contribution of different components of surface coatings for heavy metals [13]. This technique can effectively avoid the disadvantages above and may also be employed to other pollutants adsorption by surface coatings. The natural surface coatings, including biofilms and minerals associated, are thought to be the dominant determinant for the behavior of the associated composite solid and play important roles in transportation and bioavailability of heavy metals in aquatic environments [14–16].

Pb, Cd, Cu and Co are important trace heavy metals in aquatic environments. Among them, Pb and Cd are nonessential elements of environmental concern for their toxic effects on plants, animals and human beings, whereas Co and Cu were not only toxic elements but also micronutrients for plants and animals [17]. Most researches concerning the roles of components in solid phases are focused on adsorption of Pb and Cd, but Co and Cu adsorption onto solid phases was relatively fewer, especially onto the natural water surface coatings. Since the relative roles of metal oxides and organic materials were affected by the nature of trace metals itself [18] and distribution of one kind of heavy metal among the components is very different from others, the purpose of this paper is to estimate and compare the relative roles of metal oxides and organic substance in adsorption of Pb, Cd, Cu and Co onto surface coatings using selective extraction techniques followed by adsorption experiment and statistical analysis. Pb and Cd adsorption onto surface coatings was also studied in order to compare with Cu and Co on the same basis.

2. Materials and methods

2.1. Development and pretreatment of natural surface coatings

Nanhu Lake in Jilin province, P.R. China, was chosen as the aquatic environment to develop natural surface coatings. Precleaned glass microscope slides (5.0 × 7.5 × 0.1 cm) were fixed on polypropylene racks and submerged in the water at a depth of approximately 30 cm for a period of 2 weeks. After retrieval from the lake, glass slides with attached surface coatings were transported to the laboratory (submerged in the lake water) within 1 h. Natural surface coatings on the glass slides were scraped off and transferred into the beaker filled with MMS solution, and then stirred homogeneously for use. Prior to extraction and metal adsorption, linear relation between volume of suspension and dry weight was established for the measurement of solid quality.

2.2. Extraction of natural surface coatings

The extraction techniques of metal oxides used by Dong et al. [13] were modified and employed here for extraction of iron oxides and manganese oxides. Al oxides and Ti oxides are not considered as the primary sorbents for metals generally, whereas it could reveal the environmental background feature in the particular area [19]. Hydroxylamine hydrochloride reagents (0.02 mol/L $NH_2OH{\cdot}HCl$ + 0.01 mol/L HNO_3) extraction for 20 min was used to remove manganese oxides selectively without significant effects on the other components. 30-min sodium dithionite (0.4 mol/L$Na_2S_2O_4$, pH = 6.0) extraction was used for the removal of both iron and manganese oxides. H_2O_2 (volume ratio HNO_3:H_2O: H_2O_2 = 1.14:1.86:5) was employed to remove all metal oxides and most of organic materials [20].

2.3. Measurement of Pb, Cd, Cu and Co adsorption to natural surface coatings

Adsorption of Pb, Cd, Cu and Co onto extracted and unextracted surface coatings was undertaken in chemically defined solution (MMS) with five different metal concentrations ranging from 0.2 to 2.0 μmol/L for Pb, Cd and Cu, and 0.2 to 4.0 μmol/L for Co. The equilibration solution were prepared by dilution of 1000 mg/L $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $Co(NO_3)_2$ reference solution with ionic strength adjusted to 0.05 mol/L with $NaNO_3$. 40 mg surface coatings were added into each 800 ml equilibration solution with five different metal concentrations. Then the solution was stirred continuously with magnetic stirrers for 24 h. pH was maintained at 6.0 ± 0.1 using 0.01 mol/L HNO_3 and NaOH during the whole adsorption process. When the adsorption was completed, 0.45-μm-micropore-filter membrane was used to filter the mixture. Fe oxides, Mn oxides and adsorbed metal ions of surface coatings on the filters were extracted in the 25 ml 15% HNO_3 for 24 h and the percolate was collected for analysis. Thereafter, metal concentration in the extracts and percolate was measured with FAAS.

2.4. Statistical analyses

None of the extraction techniques could remove a single component without affecting other components, so accurate determination of metals associated with each individual component required consideration of contribution from the partial fraction of the other components removed from the surface coatings. Here, adsorption data were analyzed using nonlinear least squares fitting (NLSF) by Microcal Origin software (Version 6.0). The model used for analysis considered total adsorption (Γ_{total}) by unextracted and extracted surface coatings at a given concentration to be the sum of contribution from the three constituents (iron oxides, manganese oxides and organic materials) and the contribution of each components was

Table 1
Surface concentration of each component on unextracted and extracted surface coatings

Extractant	Surface concentration of components		
	Mn oxides	Fe oxides	Organic materials
Unextracted	1.368 ± 0.074	9.56 ± 0.07	155.7
$NH_2OH{\cdot}HCl$	0.082 ± 0.003	7.97 ± 0.06	150.1
$Na_2S_2O_4$	0.019 ± 0.003	2.64 ± 0.05	151.5
H_2O_2	–	0.22 ± 0.02	37.59

"–" below detection limit.

expressed as a Langmuir adsorption isotherm:

$$\Gamma_{\text{total}} = C_{\text{Mn}}\Gamma_{\text{Mn}} + C_{\text{Fe}}\Gamma_{\text{Fe}} + C_{\text{org}}\Gamma_{\text{org}} \tag{1}$$

$$\Gamma_i = k_i \cdot \Gamma_i^{\max}/(1 + k_i C) \tag{2}$$

Here, $C_{\text{Mn},}$ C_{Fe} and C_{org} are the surface concentration of each components (mg Fe or Mn/g and mg TOC/g) and the Γ_{i} terms are adsorption on a per quantity of material basis. $\Gamma_{\text{i}}^{\max}$ is the maximum adsorption , k_i is the Langmuir equilibrium coefficient and C is the concentration of free metal ions.

3. Results and discussions

3.1. Surface concentration of each component on unextracted and extracted surface coatings

The composition of unextracted and extracted surface coatings was listed in Table 1. Unit of surface concentration of components is mg (Mn or Fe or TOC) /g (surface coatings). The concentrations of components in unextracted surface coatings followed the order organic materials > Fe oxides > Mn oxides and content of Fe oxides is about seven times higher than Mn oxides. $NH_2OH{\cdot}HCl$ removed 94% of Mn oxides, but also removed 16% of Fe oxides and very lithe organic materials. $Na_2S_2O_4$ removes nearly all of the Mn oxides and 72% of the Fe oxides. Similarly, $Na_2S_2O_4$ extraction has very little effect on the organic materials. H_2O_2 removes about 76% of organic materials and nearly all of the Fe oxides and Mn oxides. Above all, each extractant could remove target materials effectively with fewer effects on the other components.

3.2. Comparison of relative contribution of metal oxides and organic materials to Pb, Cd, Cu and Co adsorption

The results of adsorption of Pb, Cd, Cu and Co onto unextracted and extracted surface coatings are shown in Fig. 1. As shown in Fig. 1, experiment data of Pb, Cd, Cu and Co adsorption onto unextracted and extracted surface coatings were very close to the curves fitted, which suggested that methods used in this paper

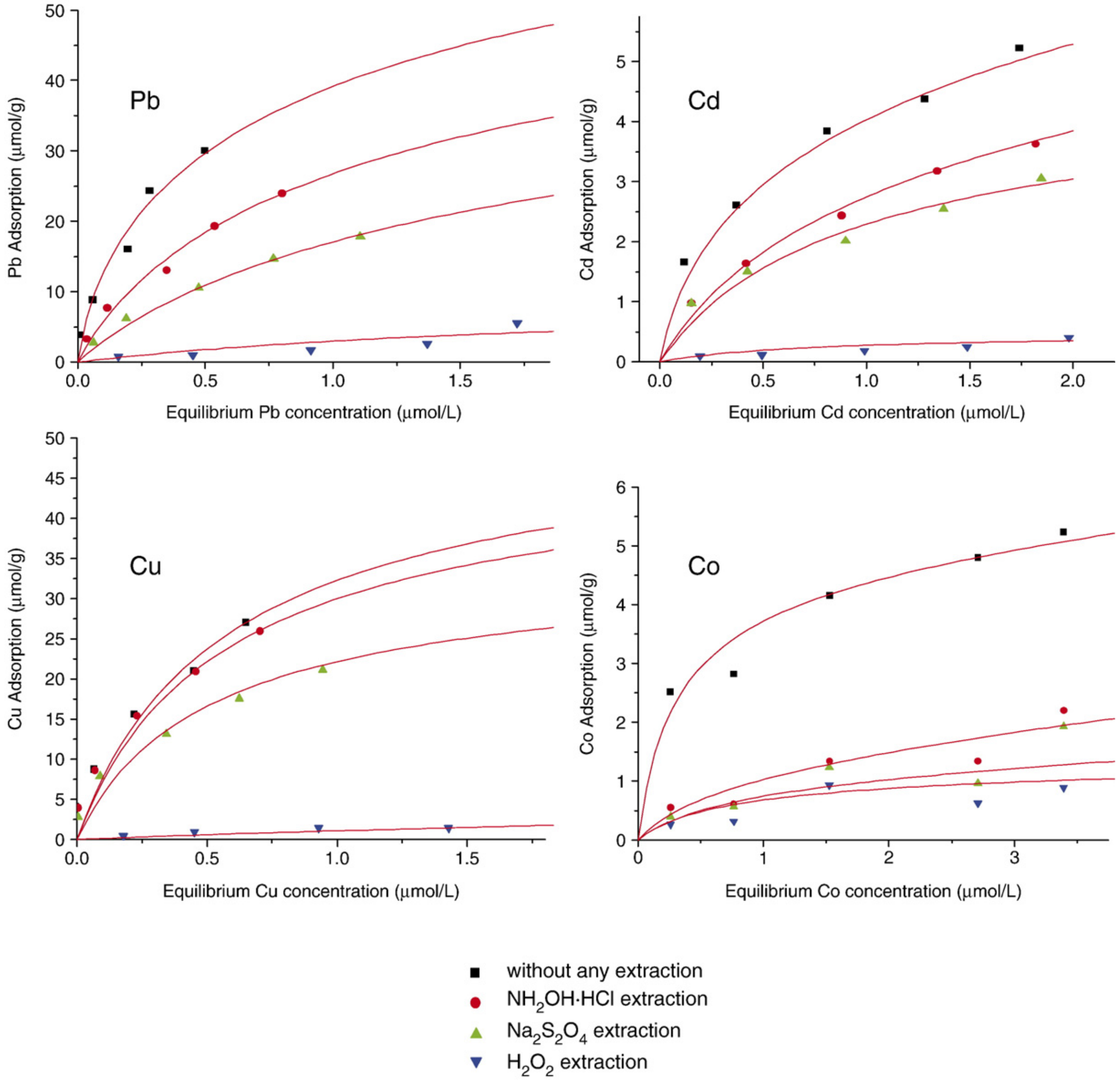

Fig. 1. Pb, Cd, Cu and Co adsorption to surfaces coatings before and after extraction. Curves were obtained from nonlinear least squares fitting of the isotherm.

Table 2
Estimated Langmuir parameters for Pb, Cd, Cu and Co adsorption to metal oxides and organic materials

Parameters	Pb	Cd	Cu	Co
$\Gamma_{\mathrm{Mn}}^{\max}$	8.289	0.9391	1E−4	1.977
$\Gamma_{\mathrm{Fe}}^{\max}$	2.469	1.1880	2.491	0.3274
$\Gamma_{\mathrm{org}}^{\max}$	0.2547	0.0214	0.158	2.056
K_{Mn}	15.31	9.56	1E−7	4.211
K_{Fe}	2.251	0.0655	1.384	0.1172
K_{org}	0.4631	1.2943	2.403	0.0019
R	0.9910	0.9946	0.9802	0.9812

provide a reliable estimate of Langmuir parameters of each component. Adsorption capacity of unextracted surface coatings for four kinds of heavy metals was as follows: Pb > Cu ≫ Cd > Co. Accordingly, it can be deduced that Pb and Cu was easier to transfer into solid phases from water with lower transportation capacity compared with Co and Cd.

The estimated parameters for each component using NLSF analysis on the basis of surface coatings composition data and adsorption data for unextracted and extracted surface coatings are listed in Table 2. The relative contribution of components to total observed Pb, Cd, Cu and Co absorbed to unextracted surface coatings based on the C_i and the estimated $\Gamma_{\max}$ and K were depicted in Fig. 2. As shown in Fig. 2, the iron oxides, manganese oxides and organic materials played important roles in adsorption of Pb, Cd, Cu and Co onto surface coatings. For Pb, the contribution from components followed the order Mn oxides > Fe oxides > organic materials at lower equilibration concentrations (<0.1 μmol/L). When the concentration of equilibration solution was greater, contribution from Fe oxides surpassed that from Mn oxides, but organic materials exerted least part of adsorption similarly. In brief, metal oxides exerted most of the contribution to Pb adsorption with less part from organic materials, which agreed with the results gained by Dong et al. [13]. Sequential extraction had been used to qualify the contribution of different sorbent phases to Pb sorption and a similar conclusion was made [19]. The distribution of Cd among surface coating components estimated by NLSF analysis is quite different from that of Pb. Besides the contribution of metal oxides to Cd adsorption, organic materials are important sorbent phases to Cd adsorption. However, at the low Cd concentration (<0.2 μmol/L), the greatest contribution to Cd adsorption was still from Mn oxides. For Cu, the regression analysis indicated that organic materials exerted the greatest influence on Cu binding, followed by a less contribution from Fe oxides in the whole concentration range. However, the

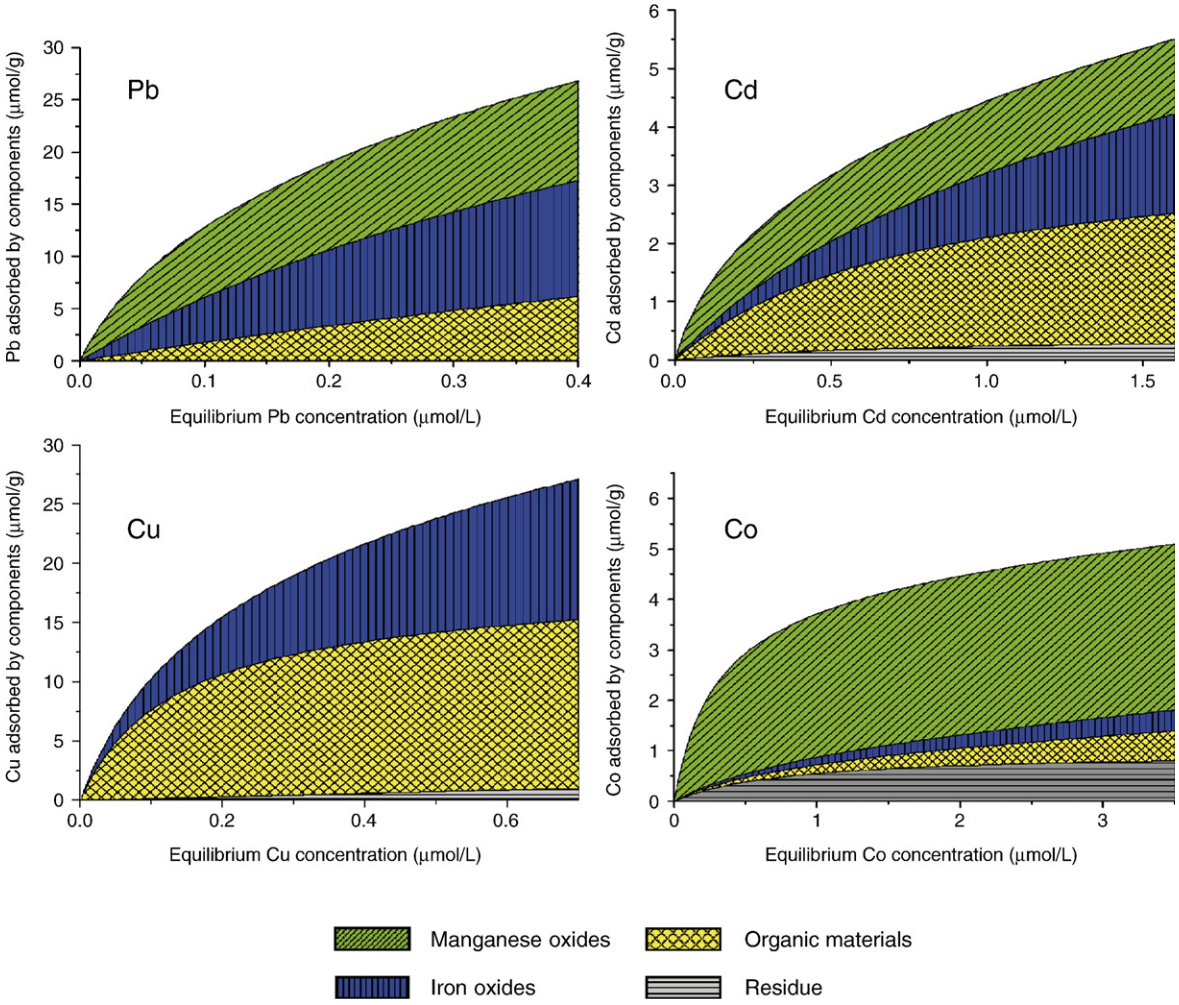

Fig. 2. Estimated Pb, Cd, Cu and Co adsorption to components of unextracted surface coatings based on the nonlinear squares fitting of the isotherm.

estimated contribution to Cu adsorption by Mn oxides was negligible. It has been proven by other related studies that Cu^{2+} is more prone to chelate with organic materials than other metals and only Cu can form inner-sphere chelate with organic materials at lower pH value. In addition, a similar conclusion was made using stripping voltammetry [21]. These reports were all in agreement with our results using extraction techniques–adsorption experiment–statistical analysis. The greatest contribution to total Co was from Mn oxides, followed by a very small part from Fe oxides and organic materials in the whole Co concentration range. The content of Co associated with Mn oxides was 3–5 times higher than the sum of Co bound to Fe oxides and organic materials. Some other studies have been undertaken to qualify the relative roles of components in controlling the adsorption of Co in the sediments and soils and the results also indicated that most of the element Co adsorbed on surface coatings was bound to metal oxides other than to additional sorbents. Clilds et al. have also reported that transportation of Co in soils is very correlative with Mn oxides, but not with Fe oxides. So strong affinity of Mn oxides for Co probably resulted from a special mechanism as isomorphous replacement; Co seems to replace Mn by deoxidizing Mn ions on the surface of the crystal [17,21].

Above all, Fe oxides, Mn oxides and organic materials play important roles in controlling the sorption of Pb, Cd, Cu and Co onto surface coatings, but relative contributions of components to various metals is distinct owing to the dissimilar element character. Metal oxides (including Fe oxides and Mn oxides) were very important sorbents for all of metal ions involved in this study, especially for Pb and Co; metal oxides contributed to the majority of their adsorption. However, for Cd and Cu, organic materials were also important sorbents for metal adsorption. Particularly for Cu, the organic materials played more important roles for Cu adsorption than other components.

In addition, Mn oxides exerted greatest influence on Pb, Cd and Co binding at the low metal concentration despite its low relative abundance in surface coatings. According to the estimated Langmuir parameters in Table 2, predominance of Mn oxides with respect to metal binding at low concentration range might result from a relatively higher K value and $\Gamma_{\max}$. In other words, Compared with Fe oxides and organic materials, Mn oxides tend to approach the maximum adsorption at low concentrations; Furthermore, maximum adsorption of Mn oxides was higher than other components, which might lead to a greater contribution to metal adsorption of Mn oxides at low concentration despite of low surface concentration.

3.3. *Comparison of adsorption ability of components for various metals*

As described above, the adsorption contribution of each component was determined not only by the nature of the component (K and $\Gamma_{\max}$) itself but also by its relative surface concentration (C_i) on the surface coatings in contrast with other components. Contrary to the adsorption contribution, here the adsorption ability was used to estimate the metal adsorption to per unit mass of component and was calculated using only K and $\Gamma_{\max}$. Adsorption of Pb, Cd, Cu and Co onto three components of surface coatings on such a per quantity of materials basis is shown in Fig. 3.

For Pb, Cd and Co, adsorption ability of three components all decreased in the order: Mn oxides > Fe oxides > organic materials. For Pb, the adsorption ability of Mn oxides was about one order of magnitude greater than that of Fe oxides and nearly two orders of magnitude than organic materials. For Cd and Co, adsorption ability of Mn oxides is about one order of magnitude greater than that of Fe oxides and organic materials, but adsorption capacity of Fe oxides is higher than organic materials greatly for Cd and yet adsorption ability of Fe oxides for Co were very close to that of organic materials. Furthermore, when the metal concentration was relatively lower, adsorption ability of Mn oxides was significantly higher than the other components. The significance of Mn oxides in metal adsorption process might attribute to, at least partly, the complex mineralogical structure of Mn oxides (Mn oxides generally exist in several oxidation states; it forms nonstoichiometric oxides with variable valency states). On the other hand, Fe forms a more limited number of oxyhydroxide minerals [11]. In addition, Mn oxides can exhibit a low pH point of zero charge and can develop large negative surface charges over the pH range of interest in most natural waters, which can also explain the strong scavenging capacity of Mn oxides in part [21].

The adsorption properties of the same components for different metals varied remarkably as shown in Fig. 3. The adsorption ability of Mn oxides for four kinds of metals followed the order: Pb > Co > Cd > Cu; furthermore, the adsorption ability of Mn oxides for Pb was five times higher than that for Co and about one order of magnitude greater than that for Cd. Indeed, a number of studies using different methods have identified preferential associations of Pb with Mn oxides in contaminated environments [7]. As described above, the preferential associations of Co with Mn oxides might result from special mechanism as isomorphous replacement. The adsorption ability of Fe oxides for metal ions followed the order: Pb ≈ Cu ≫ Cd > Co. Here adsorption capacity for Pb was close to that for Cu, but 1 order of magnitude higher than that for Cd and Co. Moreover, adsorption ability of Fe oxides for Cd was greater than that for Co greatly. The adsorption capacity of organic materials for various metals was in the same order of magnitude, but varied evidently for different metals. At

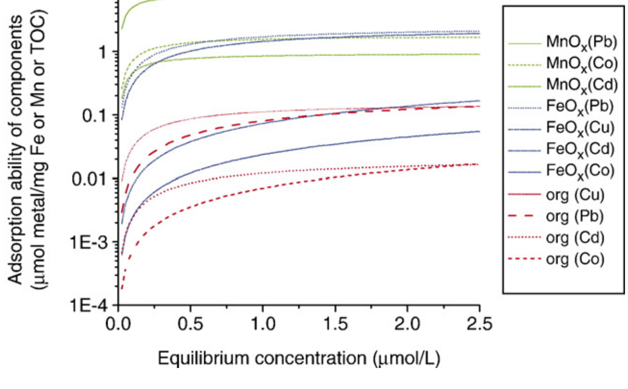

Fig. 3. Pb, Cd, Cu and Co adsorption per unit mass of components of surface coatings.

the lower metal concentration (<1.2 μmol/L), associations of Cu with organic materials was more significant than that of Pb, but just the opposite at higher concentration (>1.2 μmol/L). So organic materials might have greater influence on the transportation and bioavailability of Cu in contrast with Pb considering the low metal concentration in the natural water environments. Additionally, association of Cd and Co with organic materials was smaller than the other metal largely. Stability constant of complex was generally used to estimate the complexing capacities of humus with metals in the soils and sediments. Stability constant of fulvic acid with metal decreased in the order $Cu^{2+} > Pb^{2+} > Co^{2+}$ [21], which was in accordance with adsorption ability of organic materials for Cu, Pb and Co as described above. Study about the adsorption ability of humic acid extracted in the sediment of Altamahaha River for metal indicated that adsorption ability for Pb and Cu was close to each other, but higher than Co and Cd, which also agreed with result presented in this paper.

To sum up, adsorption ability of components for Pb, Cd and Co decreased in the order: Mn oxides > Fe oxides > organic materials. Affinity of each kind of heavy metals for the same component is very different due to the dissimilar element character. In addition, the order of adsorption ability of Pb, Cd, Cu and Co onto the various components is inconsistent, which might indicate that different sorption mechanisms occurred simultaneously rather than only one sorption mechanism works in the sorption process of heavy metals onto components.

4. Conclusion

Selective extraction techniques followed by adsorption experiment and statistical analysis were used here to estimate and compare the relative roles of main components (Fe oxides, Mn oxides and organic materials) for adsorption of Pb, Cd, Cu and Co onto natural surface coatings. Metal oxides were very important sorbents for all kinds of metal ions, especially for Pb and Co. Furthermore, manganese oxides contributed to absolute majority of Co adsorption regardless of concentration. But for Cu and Cd, organic materials are also very important sorbent phases, particularly for Cu, organic materials contributed to most of Cu adsorption regardless of concentration. In addition, the analysis suggested the extraordinary predominance of Mn oxides for Pb, Cd and Co adsorption at the low concentrations and very strong adsorption ability of Mn oxides for them over iron oxides and organic materials at the whole concentration range. Considering the low concentration in natural water environments, Mn oxides might exert the greatest influence on the behavior of heavy metals. In addition, adsorption ability of Mn oxides for metals followed the order: Pb > Co > Cd > Cu. Adsorption ability of Fe oxides and organic materials followed the order, respectively, $Pb \approx Cu \gg Cd > Co$ and $Cu \geq Pb \gg Cd > Co$.

Acknowledgements

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