

Comparison of Pb and Cd adsorption to the surface coatings and surficial sediments collected in Xianghai Wetland

LI Yu^{1,*}, WANG Xiao-li¹, WANG Yue¹, DONG De-ming¹, ZHANG Hua-peng¹, LI Qing-shan², LI Xing-chun^{1, 2}

(1. College of Environment and Resources, Jilin University, Changchun 130023, China. E-mail: liyuxx@mail.jlu.edu.cn; 2. Song-Liao River Basin Water Resources Protection Bureau, Changchun 130021, China)

Abstract: Surface coatings and surficial sediments were obtained in four natural waters in Xianghai Wetland in China to study the role of surface coatings and surficial sediments in controlling the transporting and cycling of heavy metals in aquatic environments. Pb and Cd adsorption to the surface coatings and surficial sediments were measured under controlled laboratory conditions (mineral salts solution with defined speciation, ionic strength 0.05 mol/L, 25°C and pH 6.0 for surface coatings; and 0.005 mol/L CaCl₂ solution, 25°C and pH 6.0 for surficial sediments). The Langmuir adsorption isotherm was applied to estimate equilibrium coefficients of Pb and Cd adsorption to the surface coatings and surficial sediments, and the component analyses of surface coatings and surficial sediments were also carried out. Correlation analyses between the maximum adsorption of Pb and Cd (Γ_{\max}) and the components in the surface coatings and surficial sediments suggested that there was a statistically significant trend for Pb and Cd adsorption (Γ_{\max}) to the surface coatings to increase with increasing in contents of Fe and Mn oxides in the surface coatings and surficial sediments. And the metal adsorption abilities of surface coatings were much stronger than those of surficial sediments, highlighting that in the same water, i.e. at the same pH and initial metal concentrations, the metals (such as lead and cadmium) in supernatant were feasible to be adsorbed by surface coatings than surficial sediments. The more importance of surface coatings than surficial sediments for adsorbing and cycling of heavy metals in aquatic environments was evidenced.

Keywords: surface coatings; surficial sediments; Pb; Cd; adsorption capabilities

Introduction

Because of toxic and bioaccumulative effects of trace metals on people's health and environments, the behavior, transport and ultimate fate of trace metals have drawn great interest. Sediments and surface coatings associated are believed to play significant roles in the cycling and bioavailability of trace metals (Vuceta, 1978; Santschi, 1997). Surface coatings, forming on surfaces of sediments, are insulating layers that must be reached and crossed before a contaminant contacts with the sediments supporting the surface coatings (Weber, 1991). There are many studies on the heavy metal adsorption characteristics of sediments (Lion, 1982; Young, 1992; Chartier, 2001) and surface coatings (Nelson, 1995; Dong, 2000; 2002), using different approaches, such as an additive model (Nelson, 1999), the use of selective extractants (Dong, 2000; 2002; 2003a; 2003b) or the use of sequential extractants (Gleyzes, 2002). But there is less report on the relative importance of sediments and surface coatings in adsorbing heavy metals in the same natural waters, and the similarities and differences of sediments and surface coatings in adsorbing trace metals. So the purpose of the work reported here is to investigate the relative contributions of surface coatings and surficial

sediments in the trace metal adsorption by thermodynamics adsorption experiments.

1 Materials and methods

1.1 Collection of natural surface coatings and surficial sediments

Four natural waters, reed pond, cattail pond, fishpond and Fulaowen pond, in Xianghai Natural Preservation Areas in Jilin Province, China, were chosen as the aquatic environments to develop natural surface coatings and to collect surficial sediments. At each field site, precleaned glass slides (4.8 cm × 7.5 cm × 0.1 cm) fixed in polypropylene racks were submerged in the water at a depth of about 40 cm for 2 weeks. When glass slides with attached surface coatings were retrieved from the waters, surficial sediments were collected at the same time. Then the surface coatings (submerged in pond water) were transported to the laboratory for chemical characterization and adsorption tests; the surficial sediments were air dried and the agglomerates were broken by hand and by using a mortar, and particles larger than 0.076 mm were removed by sieving. All further tests were performed on surficial sediments less than 0.076 mm in size.

The organic matter was measured by a method using by

Dong *et al.* (Dong, 2001) for surface coatings and by the TOC-analyzer using a TOC-V_{CPH} (Shimadzu, Japan) for surficial sediments; the metal oxides (such as iron and manganese oxides) of surface coatings were extracted by 15% HNO₃ for 24 h and those of surficial sediments were extracted by HCl-HNO₃-HClO₄, and the metals in supernatant were determined by FAAS(WYX-9004, Shenyang, China).

1.2 Pb and Cd adsorption to the surface coatings

Pb and Cd adsorption to the surface coatings were carried out in solutions with defined metal speciation and six initial Pb and Cd concentrations ranging from 0.2 to 2.0 μmol/L. The Pb and Cd adsorption solutions were prepared using a minimal mineral salts(MMS) solution(Table 1). Pb and Cd speciation in the solutions was calculated using MINEQL(Westal, 1976). The calculations showed that free Pb²⁺ or Cd²⁺ ions would comprise 89% of total Pb or total Cd(Table 1). Two slides after rinsing with MMS solution were submerged into each of six 800 ml solutions with different Pb or Cd concentrations. The solutions were stirred continuously for 24 h, maintaining the pH at 6.0 ± 0.1 using 0.01 mol/L HNO₃ and NaOH (25 ± 1℃). After equilibration, slides with surface coatings were extracted into 25 ml of 15% HNO₃ for 24 h for adsorbed Pb or Cd.

Table 1 Composition of MMS solution used in metal adsorption experiments

	Component or species	Concentration, μmol/L	Concentration, mg/L
MMS medium	CaCl ₂ ·2H ₂ O	200	30
	MgSO ₄ ·7H ₂ O	140	35
	(NH ₄) ₂ SO ₄	910	120
	KNO ₃	150	15
	NaHCO ₃	10	0.84
	KH ₂ PO ₄	5	0.70
Pb speciation	Pb ²⁺	89%	
	PbSO ₄	9%	
	PbOH ⁺	1%	
Cd speciation	Cd ²⁺	89%	
	CdCl ⁺	1.5%	
	CdSO ₄	4.6%	
	CdNO ₃ ⁺	4.9%	

Pb or Cd in equilibrium solutions was measured by FAAS (WYX-9004, Shenyang, China) equipped with a graphite furnace(SML-III, Shenyang, China), and Pb or Cd in acid extracts was analyzed by FAAS (WYX-9004, Shenyang, China).

1.3 Pb and Cd adsorption to the surficial sediments

Pb and Cd adsorption to the surficial sediments were made in solutions with eight initial Pb and Cd concentrations ranging from 20.0 to 90.0 μmol/L. The Pb and Cd adsorption solutions were prepared with CaCl₂ solution of 0.005 mol/L, adjusting pH at 6.0 ± 0.1 using 0.01 mol/L

HNO₃ and NaOH(25 ± 1℃). Then, surficial sediments of 0.0100 ± 0.0001 g(less than 0.076 mm in size) were put into each of eight 50 ml solutions with different Pb or Cd concentrations, and the mixture solutions were stirred continuously for 3 h. After the experiments, the pH was readjusted to the initial value and the samples were filtered through the filter paper. It was found that the changes in pH after 3 h were small(all these adjustments were only within ±0.3 pH). Pb or Cd in initial solutions or in equilibrium solutions was measured by FAAS (WYX-9004, Shenyang, China). The amount of adsorbed Pb or Cd was calculated as the difference between the amount added initially and that remaining in solution.

1.4 Statistical analyses

Here, Pb and Cd adsorption data of surface coatings and surficial sediments were analyzed by the Langmuir adsorption isotherm, which was expressed as

Γ = \frac{\Gamma_{max} K [M^{2+}]}{1 + K [M^{2+}]}

where Γ is the adsorption of M²⁺ by the surface coatings or surficial sediments per unit weight (mg/g), Γ_{max} is the maximum adsorption of M²⁺ by the surface coatings or surficial sediments per unit weight (mg/g), K is the Langmuir equilibrium coefficient (m/g) and [M²⁺] is the concentration of Pb and Cd in supernatant in solution.

A linear-program was applied to perform the regression. Then, according to the maximum adsorption of Pb and Cd by the surface coatings and surficial sediments, the difference of Pb and Cd adsorption capabilities between the surface coatings and the surficial sediments are apparent, and the resulting information is expected to investigate whether surface coatings or surficial sediments is important for removing heavy metals from the waters.

2 Results and discussion

2.1 Characteristics of the developed surface coatings and the sampled surficial sediments

The composition of the surface coatings developed in the four natural waters in China and the composition of the surficial sediments collected in the corresponding waters are listed in Table 2. Surface coatings and surficial sediments had the same tendency in the order of the concentrations of metal oxides, i.e. following the order Fe > Mn. The content of components of surface coatings developed in different waters varied remarkably comparing with the content of components of surficial sediments. But the surface coatings developed in each body of the water were consistent from slide to slide (component concentrations varied less than 10%), allowing the use of different slides for each

characterization and for measurement of Pb and Cd bindings. The content of organic material of surface coatings was significantly more than that of surficial sediments; the content of Mn oxides of surface coatings was slightly higher than that of surficial sediments, and for the average content of Fe oxides, there was no appreciable difference between the surface coatings and the surficial sediments.

Table 2 Concentrations of organic material and metal oxides in surface coatings and in surficial sediments

Sample sources	Organic material ^a ,		Fe oxides ^b ,		Mn oxides ^c ,	
	mg/g		mg/g		mg/g	
	Surface coatings	Surficial sediments	Surface coatings	Surficial sediments	Surface coatings	Surficial sediments
The reed pond	128.31	20.36	2.94	11.88	0.52	0.30
The cattail pond	96.32	23.15	5.03	14.44	0.59	0.38
The fish pond	317.47	6.10	43.81	28.99	2.99	0.62
Fulaowen pond	> 1080.00	19.71	40.44	25.36	1.95	0.64

Notes : ^a Quantified by measuring the total organic carbon(TOC); organic material in the surface coatings was firstly quantified by measuring the chemical oxygen demand(COD), then according to the result of previous study(Li, 2003), and the COD value was transformed into the TOC value; ^b quantified by measuring the total content of Fe; ^c quantified by measuring the total content of Mn

2.2 Comparison of the metal adsorption capabilities of surface coatings and surficial sediments

Langmuir adsorption isotherm is well-known empirical equation used to describe rules of trace metals adsorption from liquid phase to solid phase. In this study, adsorption of Pb and Cd to different surface coatings and surficial sediments were carried out at pH 6.0 and 25℃, and the estimated Langmuir parameters for Pb and Cd adsorption to surface coatings and surficial sediments are shown in Table 3. Pb adsorption was approximately one order of magnitude greater than that of Cd for surficial sediments in average, but the ratio for surface coatings is only 5, differing from what previously obtained(Dong, 2001). This suggested that Pb is adsorbed more strongly than Cd studied by both surface coatings and surficial sediments. Pb and Cd were strongly adsorbed by surface coatings, approximately four and sixteen times stronger than by surficial sediments, respectively, implying that the surface coatings is more important than the surficial sediments for transporting and cycling of heavy metals in aquatic environments.

According to the Langmuir parameter Γ_{max} (Table 3) and the components in the surface coatings and surficial sediments (Table 2), the maximum adsorption of Pb follows an order of increase with increasing of the content of Mn oxides in the surface coatings, and that of surficial sediments is a little different from surface coatings, in descending order with increasing content of organic material in the surficial sediments. But for the maximum adsorption of Cd, surface

coatings and surficial sediments have the similar tendency, in increasing order with increasing content of Fe oxides.

Table 3 Estimated Langmuir parameters for Pb and Cd adsorption to surface coatings and surficial sediments collected from the different natural waters in Xianghai Wetland based on linear regression analysis

Sample sources	$\Gamma_{max Pb}$, mg/g		$\Gamma_{max Cd}$, mg/g	
	Surface coatings	Surficial sediments	Surface coatings	Surficial sediments
The reed pond	93.24	29.61	4.39	3.62
The cattail pond	79.57	36.69	6.11	2.96
The fish pond	298.39	61.92	129.48	3.64
Fulaowen pond	238.69	34.76	107.91	4.90

2.3 Comparison of correlation analyses between Γ_{max} and components in the surface coatings and surficial sediments

It has been found that metal oxides, especially iron and manganese oxides, and organic material are very important components of the surface coatings and surficial sediments for their capacities of adsorbing trace metals (Vuceta, 1978; Santschi, 1997; Dong, 2001). However, there remains some uncertainty about understanding the respective role of these three components in controlling the adsorption of trace metals. In this study, the correlation analyses between the Langmuir parameter(Γ_{max}) and the contents of components in the surface coatings and surficial sediments were undertaken to investigate the statistical trend for Pb and Cd adsorption to the different components, and therefore, the difference of the metal adsorption abilities between the surface coatings and the surficial sediments could be explained from the view of statistical analyses. The results of the correlation analyses (Table 4) revealed that for surface coatings, the higher adsorption of Pb by Mn oxides and the higher adsorption of Cd by Fe oxides were statistically significant, respectively, and the adsorption of Pb and Cd by organic material was statistical insignificant. While, for the surficial sediments, the adsorption of Cd was dominated by Mn oxides, with less roles attributed to adsorption by Fe oxides and organic material, and the adsorption of Pb was dominated by Fe oxides. There is one thing must be made clearly that the more content of organic material, the less adsorption of Pb to the surficial sediments, although the correlation between $\Gamma_{max Pb}$ and organic material within the surficial sediments was significant. In a word, compared with organic material, metal oxides were relative important for adsorption of heavy metals to both surface coatings and surficial sediments from the view of statistical analyses, implying that the results of the correlation analyses of developed surface coatings and that of sampled surficial sediments were similar to each other.

Table 4 Correlation coefficients (r) between Γ_{\max} and the contents of components in the surface coatings and surficial sediments obtained from different natural waters

		Organic material, mg/g		Fe oxides, mg/g		Mn oxides, mg/g	
		r	p	r	p	r	p
Surface coatings	Γ_{\max} Pb, mg/g	0.5649 ^a	> 0.10	0.9823 ^a	0.01	0.9986 ^a	0.001
	Γ_{\max} Cd, mg/g	0.6387 ^a	> 0.10	0.9969 ^a	0.001	0.9731 ^a	0.01
Surficial sediments	Γ_{\max} Pb, mg/g	0.7531 ^b	0.01	0.6469 ^c	0.05	0.6129 ^d	0.10
	Γ_{\max} Cd, mg/g	0.6217 ^d	0.10	0.5700 ^b	0.10	0.6724 ^b	0.05

Notes: ^a $n = 4$; ^b $n = 10$; ^c $n = 9$; ^d $n = 8$

3 Conclusions

The transform of Langmuir adsorption isotherm was employed to describe Pb and Cd adsorption to surface coatings and surficial sediments, which sampled in Xianghai Wetland in China. The results showed that the Langmuir adsorption isotherm was suitable to describe Pb and Cd adsorption both to the surface coatings and surficial sediments at the confidence level of $p = 0.01$. In the same natural water, the contents of organic material and Mn oxides of surface coatings were greater than those of surficial sediments, and those of Fe oxides were similar to each other. The correlation analyses between the Langmuir parameter (Γ_{\max}) and the contents of components in the surface coatings and surficial sediments revealed that there was a statistically significant trend for Pb and Cd adsorption (Γ_{\max}) to the surface coatings to increase with increasing in contents of Fe and Mn oxides in the surface coatings and surficial sediments. The metal adsorption capabilities of surface coatings were much stronger than those of surficial sediments, indicating the relative importance of surface coatings for transporting and cycling of heavy metals in aquatic environments.

References:

Chartier M, Mercier G, Blais J F, 2001. Partitioning of trace metals before and after biological removal of metals from sediments[J]. *Water Research*, 35 (6): 1435—1444.

Dong D, Nelson Y M, Lion L W *et al.*, 2000. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: new evidence for the importance of Mn and Fe oxides [J]. *Water Research*, 34(2): 427—436.

Dong D, Li Y, Hua X, 2001. Investigation of Fe, Mn oxides and organic material in surface coatings developed in different natural waters [J]. *Microchemical Journal*, 70: 25—33.

Dong D, Hua X, Li Y *et al.*, 2002. Lead adsorption to metal oxides and organic material of freshwater surface coatings determined using a novel selective

extraction method[J]. *Environmental Pollution*, 119: 317—321.

Dong D, Derry L A, Lion L W, 2003a. Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials[J]. *Water Research*, 37: 1662—1666.

Dong D, Hua X, Li Y *et al.*, 2003b. Cd adsorption properties of components in different freshwater surface coatings: The important role of ferromanganese oxides[J]. *Environmental Science and Technology*, 37: 4106—4112.

Gleyzes C, Tellier S, Astruc M, 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures [J]. *Trends in Analytical Chemistry*, 21(6—7): 451—467.

Li Y, Liu J, Dong D *et al.*, 2003. The ratios of COD to TOC in organic materials in the natural surface coatings [J]. *Science Technology and Engineering*, 3(5): 479—481.

Lion L W, Altmann R S, Leckle J O, 1982. Trace-metal adsorption characteristics of estuarine particulate matter: Evaluation of contributions of Fe/Mn oxides and organic surface coatings[J]. *Environmental Science and Technology*, 16: 660—666.

Nelson Y M, Lion L W, Shuler M L *et al.*, 1995. Lead distribution in a simulated aquatic environment: Effects of bacterial biofilms and iron oxide [J]. *Environmental Science and Technology*, 29: 1934—1944.

Nelson Y M, Lion L W, Shuler M L *et al.*, 1999. Lead binding to metal oxide and organic phases of natural aquatic biofilms [J]. *Limnology and Oceanography*, 44 (7): 1715—1729.

Santschi P H, Lenhart J J, Honeyman B D, 1997. Heterogeneous processes affecting trace contaminant distribution in estuaries: The role of natural organic mater[J]. *Marine Chemistry*, 58(1—2): 99—125.

Vuceta J, Morgan J J, 1978. Chemical modeling of trace metals in fresh waters: Role of complexation and adsorption [J]. *Environmental Science and Technology*, 12(12): 1302—1308.

Weber W J, McGinleys P M, Katz L E, 1991. Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport[J]. *Water Research*, 25(5): 499—528.

Westall J C, Zachary J L, Morel F M M, 1976. MINEQL., a computer program for the calculation of chemical equilibrium composition of aqueous systems [Z]. Tech Note 18, Department of Civil Engr Mass Inst of Tech, Cambridge, MA.

Young L B, Harvey H H, 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments[J]. *Geochimica et Cosmochimica Acta*, 56: 1175—1186.

(Received for review March 9, 2004. Accepted July 16, 2004)