Distributions, fluxes, and toxicities of heavy metals in sediment pore water from tributaries of the Ziya River system, northern China

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Abstract The distributions and mobilities of metals in pore water strongly influence the biogeochemical processes and bioavailabilities of metals at sediment–water interfaces. Heavy metal concentrations were measured in pore water samples from the Shaocun River (SR), the Wangyang River (WR), and the Xiao River (XR), tributaries of the Ziya River system, northern China. The aim was to assess heavy metal contamination in the system and the associated environmental risks. The mean Cd, Cr, Cu, Ni, Pb, and Zn concentrations in all three tributaries were 0.373, 57.1, 37.7, 20.4, 14.0, and 90.6 µg/L, respectively. The calculated Cd, Cr, Cu, Ni, Pb, and Zn diffusion fluxes in the rivers were −0.427 to 0.469, −71.8 to 42.5, 3.16 to 86.6, 5.29 to 14.0, 7.24 to 19.0, and −204 to 21.9 µg/(m² day), respectively, showing that the pore water was a source of most of the metals to the water column. Only Cu and Pb in the XR and Cu in the WR exceeded the final chronic value recommended by the US Environmental Protection Agency, but the metals in the WR sediment could have caused toxic effects.

These results are likely to be useful to the authorities responsible for sustainable river management.

Keywords Pore water · Heavy metals · Ziya River · Diffusion fluxes

Introduction

The contamination of aquatic systems with heavy metals has become an important worldwide problem requiring urgent action because of the toxicities of heavy metals and their abilities to accumulate in biota. Once a metal is released into the aquatic environment, a portion of the metal will be transferred to sediment through being adsorbed onto suspended matter and the sedimentation of the suspended matter (Cortecci et al. 2009, Zwolsman et al. 1993). Metals in sediment will be present in both the particulate phase and the dissolved phase (i.e., in the pore water), and these phases will interact with each other and with the overlying water at the sediment–water interface. The distributions and mobilities of metals in pore water play important roles in the overall cycling of metals at the sediment–water interface (Davis and Galloway 1993, Donahoe and Liu 1998). In particular, the fraction of a metal in the pore water is generally considered to be the main bioavailable fraction in the sediment, although only a very small amount of a heavy metal will be present in the dissolved state in pore water (Ankley et al. 1991, Hall 1996, Suresh et al. 2011, Wenholz and Crunkilton 1995). If the concentration of a metal in the pore water is higher than the concentration in the overlying water column, the concentration gradient between the pore water and the overlying water will cause the dissolved metal to be transported from the sediment to the overlying water (Ciceri et al. 1992, Lyons and Fitzgerald 1980, Sakellari et al. 2011). In order to understand the mobility

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and toxicity of metals in the river ecosystem, it is very important to understand the heavy metal fluxes that occur at the sediment–water interface (Blasco et al. 2000, Costello et al. 2015).

Intensive industrial and agricultural activities in a densely populated river basin can lead to enormous amounts of nutrients and heavy metals entering the riverine ecosystem (Kucuksezgin et al. 2008). The Haihe Basin is located in the political, economic, and cultural center of China. The Ziya River system (ZYS), which is a major water system in the Haihe Basin, has been significantly contaminated by heavy metals due to industrial development and rapid urbanization. Previous studies have already reported high metal contents in the sediments from the ZYS (Tang et al. 2015, Tang et al. 2014, Tang et al. 2013). The sediments of the ZYS have been considered to be high ecological risk due to heavy metals. However, until now, there have been few studies focused on the processes through which contaminants are released from sediment in the ZYS to the overlying water through the sediment–water interface.

Dissolved metals in pore water are potential sources of pollution because they can be liberated into the overlying water through complex and dynamic processes. Therefore, three typical tributaries of the ZYS characterized by different wastewater sources were selected to (1) investigate the concentrations of heavy metal in sediment pore water; (2) examine the diffusion fluxes of trace metals between the pore water in surface sediment and the overlying water; (3) assess the toxicities of trace elements in the pore water. The results will allow a better understanding to be gained of the role of sediments as a source or sink for metals in the ZYS and, consequently, to allow a better understanding to be gained of the influence of metals in the sediments on water quality in the ZYS..

Materials and methods

Study area

The ZYS is in Hebei Province, the economy of which has rapidly developed in recent years. Rapid urbanization and the development of heavy industries have caused water bodies in Hebei Province to become significantly polluted. Hebei Province is lacking in water resources, and the deterioration of water quality has exacerbated the effects of this shortage. The ZYS watershed covers an area of 2747 km², and 70 % of the long-term mean annual precipitation of 550 mm falls between July and September.

The study was focused on three important but heavily polluted rivers, the Shaocun River (SR), the Wangyang

River (WR), and the Xiao River (XR), which are tributaries of the ZYS. A map of the study area is shown in Fig. 1. These rivers are mainly subject to continuous point-source inputs of pollutants in domestic and industrial wastewater effluents, and these sources have caused the water quality to deteriorate and the sediment in the rivers to become polluted. A field investigation revealed that the dominant sources of pollutants are tannery wastewater effluents to the SR and pharmaceutical wastewater effluents to the WR. Sewage and industrial wastewater effluents are significant sources of pollutants to the XR. The SR, WR, and XR receive 28, 30, and 290 Mm³/a of wastewater effluents, respectively, each year.

Sample collection and analysis

Samples were collected at one sampling station on each of the SR, WR, and XR. The locations of the sampling sites are shown in Fig. 1. Three groups of sediment columns were taken at random from each station, and three cores of undisturbed sediment were collected in each group using a hand-held polyvinyl chloride corer with a diameter of 8 cm and a length of 60 cm. Sediment samples were collected in a manner designed to minimize any disturbance to the sediment–water interface (Kalnejais et al. 2015). The cores were collected with at least 15 cm of overlying water and 20 cm of sediment columns. The cores were stored in a 4 °C walk-in refrigerator and brought back to the laboratory as soon as possible after they had been collected.

In the laboratory, the overlying water samples were collected from 10 cm above the sediment–water interface at each sampling point (Azcue et al. 1996) using a syringe and a silicone tube that had been decontaminated by immersing it in nitric acid. The cores of every group were treated in one of three ways: one core from each sampling station was used to determine the vertical distribution of heavy metals. And, the top 10 cm of this core was divided into 1-cm slices, and the remainder of the core was divided into 2-cm slices. Another core from each sampling station was used to determine the diffusive fluxes of heavy metals, and the top 5 cm of this core was divided into 0.5-cm slices, and the remainder of the core was divided into 1-cm slices. The third core from each sampling station was used to determine the toxicity of the surface sediment, and the top 5 cm of the sediment core was taken as whole to extract pore water. All sub-samples of the sediments were centrifuged at 4000 rpm for 30 min to separate pore water. Each overlying water and pore water sample was filtered through a cellulose membrane containing 0.45-μm pores, preserved by adding ultrapure nitric acid, and stored at 4 °C until heavy metal analysis.

The concentrations of Cd, Cr, Cu, Ni, Pb, Zn, Ca, and Mg were measured by inductively coupled plasma-mass

Fig. 1 Map of the of the study area in the Ziya River system, with the sediment sampling sites indicated on the Shaocun River, Wangyang River, and Xiao River

spectrometry (ICP-MS) (7500a, Agilent, USA) (detection limit 0.015–0.120 $\mu\text{g/L}$) and inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 2000DV, PerkinElmer, USA) (detection limit 0.001–0.030 mg/L). Laboratory quality control consisted of the analysis of black and triplicate samples. The precision of the method was acceptable (the relative standard deviation was <5 %). The results of all indices were the average of the three parallel samples of pore water and overlying water, respectively.

Diffusive fluxes

The diffusive fluxes of the trace elements from the sediment to the water column were calculated from the concentration gradients found in the pore water samples using Fick's first law of diffusion (Berner 1984):

$$F = \phi \cdot D_s \cdot \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (1)$$

where F is the diffusive flux, ϕ is the porosity of the sediment–water interface, D_s is the molecular diffusion coefficient, and $\left(\frac{\partial C}{\partial x} \right)_{x=0}$ is the concentration gradient found at the sediment–water interface. The D_s is calculated from the empirical equations (Ullman and Sandstrom 1987):

$$D_s = \phi D_0 (\phi < 0.7) \quad (2)$$

$$D_s = \phi^2 D_0 (\phi > 0.7) \quad (3)$$

where D_0 is the diffusion coefficient in water. The values for D_0 for each metal are taken from Li and Gregory (1974). The concentration gradient was estimated from the pore water profiles, with the assumption that the gradient across the sediment–water interface is one-dimensional and can be approximated as the linear fitting slope of the

concentration of metal in the sediment–water interface (Kalnejais et al. 2015, Sherman et al. 1994).

Pore water toxicity analysis

The interstitial water quality was examined for each metal using a water quality index, the interstitial water criteria toxicity unit (IWCTU), defined as:

$$IWCTU_{Me} = \frac{[Me]_{i.w.}}{FCV_{Me}}, \quad (3)$$

where $[Me]_{i.w.}$ is the dissolved metal (Me) concentration and FCV_{Me} is the hardness-dependent final chronic value for the metal (Lourino-Cabana et al. 2011, Sterckeman et al. 2000). While the $IWCTU_{Me}$ exceeds 1, it implies that there is a risk of toxicity to aquatic organism. The method for calculating FCV_{Me} is presented in Table 1 (EPA. 2002).

The Nemerow index (NI) was also used to estimate the pore water quality, and it was calculated as shown in Eq. 4:

$$(NI) = \sqrt{\frac{(IWCTU)_{\max}^2 + (IWCTU)_{\text{mean}}^2}{2}}. \quad (4)$$

Five grades of toxic impact were used: no impact, slight impact, moderate impact, strong impact, and serious impact, with NI values of <1, 1–2, 2–3, 3–5, and >5, respectively (Liu et al. 2003).

Statistical analysis

The data were analyzed using SPSS 19.0 for Windows software. Pearson correlation coefficients were used to assess the relationships between the heavy metal concentrations in the pore water. Origin Pro 8.0 software was used to plot the data. One-sample t tests ($p \leq 0.05$) were used to assess the differences between groups of data. All of the results used were averages of the results found from analyzing three parallel sediment core samples.

Table 1 Final chronic values (FCVs) for the metals based on the dissolved metal concentration

Metal	FCV
Cd	$[1.101672 - 0.041838 \ln(\text{hardness})][e^{0.7852 \ln(\text{hardness}) - 3.490}]$
Cu	$0.960[e^{0.8545 \ln(\text{hardness}) - 1.465}]$
Ni	$0.997[e^{0.8460 \ln(\text{hardness}) + 1.1645}]$
Pb	$0.791[e^{1.273 \ln(\text{hardness}) - 4.705}]$
Zn	$0.986[e^{0.8473 \ln(\text{hardness}) + 0.7614}]$

Results and discussion

Spatial and vertical distributions of the heavy metals in the pore water

The Cd, Cr, Cu, Ni, Pb, and Zn concentrations in the pore water samples from the SR, WR, and XR varied both spatially and vertically, as shown in Fig. 2. The metals followed different spatial and vertical distribution trends from each other and at the different sites because different types of wastewater contain different mixtures of metals and other pollutants. The mean concentrations were gained by averaging the values of heavy metal in all depths. And, the mean Cd, Cr, Cu, Ni, Pb, and Zn concentrations in all three tributaries were 0.373, 57.1, 37.7, 20.4, 14.0, and 90.6 $\mu\text{g/L}$, respectively.

In terms of the spatial variability, the results showed that the pore water in the SR samples contained high mean concentrations of Pb (17.1 $\mu\text{g/L}$) and Zn (105 $\mu\text{g/L}$), whereas the pore water in the WR samples contained high mean concentrations of Cd (0.488 $\mu\text{g/L}$), Cr (78.3 $\mu\text{g/L}$), Cu (50.8 $\mu\text{g/L}$), and Ni (23.2 $\mu\text{g/L}$). The metal concentrations in the pore water decreased in the order $\text{Zn} > \text{Cr} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cd}$ in the samples from the XR and the WR, but in the order $\text{Zn} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Ni} > \text{Cd}$ in the samples from the SR. It can be assumed that the metal concentrations in all three tributaries were predominantly controlled by the metals being released in contaminated wastewater in the ZYS area, which suffers from a severe shortage of water. The main sources of water to the SR, WR, and XR are sewage and other wastewater discharges, and different types of wastewater will supply different patterns of trace metal pollution and result in different trace metal patterns in sediment (Tang et al. 2015).

In terms of the vertical variability, the concentrations of Cd, Cr, Pb, and Zn in the XR pore water generally increased with depth increased and reached a maximum at 8 to 15-cm depth and then decreased, except for the Cu concentrations, which decreased as the depth increased. The Cr, Cu, and Ni concentration maxima in the WR pore water were found at 15-cm depth, and the Cd, Pb, and Zn concentration maxima were found at 10-cm depth. The concentrations of most of the metals in the SR pore water varied slightly, and the highest concentration was founded between 15- and 20-cm depth, except for Zn, which concentration was varied dramatically in all depths. Most of the metals were found at low concentrations in the top layers of the sediment (which correspond with the oxic zone), and higher metal concentrations were found in the deeper layers corresponding with the sub-oxic zones, and these results were similar to the results of other studies (Campanha et al. 2012, Couture et al. 2010, Santos-Echeandia et al. 2009).

Fig. 2 Spatial–vertical distributions of metals concentrations in the pore water sediments samples from XR (a), WR (b), and SR (c)

Table 2 Cd, Cr, Cu, Ni, Pb, and Zn concentrations in sediment pore water from the Xiao River, the Wangyang River, and the Shaocun River and other water bodies in China and other regions

Site	Maximum concentration (µg/L)						Reference
	Cd	Cr	Cu	Ni	Pb	Zn	
Xiao River, China	1.53	162	61.8	32.2	40.3	252	This study
Wangyang River, China	1.35	257	77.3	35.9	30.8	174	This study
Shaocun River, China	0.779	86.2	123.1	32.2	47.8	281	This study
Xiangjiang River, China	16.7		43.9		74.5	417	Han et al. (2013)
Liao River, China	0.9		5.7		2.22	59.5	Deng BL (2011)
Songhua River, China			154	167	357	56	Zhu et al. (2011)
Liao River, China	1.24	30.1	17	10.3	18.2	27.8	Bu et al. (2014)
Delûe River, France	7		16.5	11.9	115.6	112.1	Lourino-Cabana et al. (2011)
Meuse River, The Netherlands	0.135		5.597	12.74	6.84	27.73	Van Den Berg et al. (1999)
Tagus estuary, Portugal	6.5		10.7		28.5	915	Santos-Echeandía et al. (2010)
Dose Lake, USA	0.9	13	2	38.2	14.9		Balistrieri et al. (2003)
river Leie, Belgian	0.16		3	8.7	1.3	46	Gao et al. (2006)
Great Salt Lake, USA		3.3	50.7	22.1	1.8		Carling et al. (2013)

The trace metal concentrations found in the present study were compared with those determined in other areas (Table 2). It can be observed that the concentrations of most metals in the ZYS were higher than the contents in other regions. The concentrations of the trace metals, particularly Cr and Zn, were higher in the ZYS samples than what have been found in other Chinese riverine sediment pore water samples. The Cu, Ni, and Zn concentrations were higher in ZYS pore water than in pore water from rivers in other parts of the world, whereas the Cd and Pb concentrations were lower in ZYS pore water than in pore water from rivers in other parts of the world. The high concentrations of metals in pore water indicated that as a region with industrial development and rapid urbanization, the ZYS has been polluted by artificial activities.

Relationships between the heavy metal concentrations

A high correlation coefficient for the relationship between two metals means that they are likely to share common sources (Suresh et al. 2011). The relationships between the heavy metal concentrations in the pore water samples were analyzed using the Pearson correlation coefficients (see Table 3). For the XR samples, the Pb concentrations correlated well with the concentrations of Cd ($r=0.713$, $p<0.01$), Cr ($r=0.952$, $p<0.01$), and Cu ($r=0.544$, $p<0.05$), and the Cr and Cd concentrations also correlated well ($r=0.745$, $p<0.01$). The Ni concentrations did not correlate well with the concentrations of

any of the other metals in the XR samples. In the WR samples, significant positive correlations ($p<0.01$) were found between the Cd and Pb concentrations, and good

Table 3 Pearson correlation coefficients for the relationships between the concentrations of the metals analyzed in samples from the Xiao River, the Wangyang River, and the Shaocun River

Site	Cd	Cr	Cu	Ni	Pb
Xiao River					
Cr	0.745 ^a				
Cu	0.051	0.493			
Ni	0.412	−0.117	−0.283		
Pb	0.713 ^a	0.952 ^a	0.544 ^b	−0.186	
Zn	−0.034	0.230	0.541 ^b	−0.439	0.381
Wangyang River					
Cr	0.092				
Cu	0.496	0.759 ^a			
Ni	0.302	0.551 ^b	0.637 ^b		
Pb	0.860 ^a	0.064	0.418	0.139	
Zn	−0.076	−0.010	0.097	−0.110	−0.248
Shaocun River					
Cr	0.300				
Cu	0.500	−0.229			
Ni	0.607 ^b	0.563 ^b	0.136		
Pb	0.780 ^a	0.300	0.270	0.687 ^a	
Zn	0.182	0.262	−0.143	0.048	0.153

^a Correlation significant at the 0.01 level (2-tailed)

^b Correlation significant at the 0.05 level (2-tailed)

Fig. 3 Fluxes of dissolved metals at the sediment–water interface in the three water bodies of the ZYS

positive correlations were also found between the Cr, Cu, and Ni concentrations. The Cd, Ni, and Pb concentrations in the SR samples positively correlated, indicating that the spatial distributions of these metals were controlled by common local inputs and similar dispersion processes at the SR sampling site. No correlations were found between the concentrations of Zn and the other metals in the SR samples, suggesting that Zn contamination in the SR might have different origins from contamination with the other metals.

The significant positive correlations of Cd, Cr, and Pb in XR may be interpreted as the high enrichment factor (EF) values of these three metals in XR sediments, which indicated that the three metals in the sediments had anthropogenic origins (Tang et al. 2015). Moreover, the Cd, Cr, and Pb in the sediments of XR may come from similar sources (domestic

sewage and industrial wastewater) (Tang et al. 2015). However, hydrodynamics, biogeochemical progress, and environmental conditions also influenced the partitioning behavior and distribution of metals between pore water and solid phase in the sediments (Eggleton and Thomas, 2004). In addition, the Cd and Pb concentrations significantly positively correlated in all three tributaries ($p < 0.01$), which may be because that they are both typical anthropogenic metals, and human activities control their concentrations in the sediments of the ZYS (Quinton and Catt 2007).

Diffusive fluxes of the heavy metals from the pore water to the overlying water

The diffusive fluxes from the sediment pore water to the overlying water were calculated to estimate the risks of

Table 4 Fluxes of dissolved metals in the three rivers in the Ziya River system that were studied: the Xiao River, the Wangyang River, and the Shaocun River; and in rivers in other regions

	Fluxes of dissolved metals ($\mu\text{g}/(\text{m}^2\cdot\text{d})$)						Reference
	Cd	Cr	Cu	Ni	Pb	Zn	
Xiao River	−0.427	−71.8	86.6	5.29	7.24	−41.4	This study
Wangyang River	0.469	7.39	3.16	13.7	7.86	21.9	This study
Shaocun River	0.258	42.5	33.6	14.0	19.0	−204	This study
Meuse River, The Netherlands	0.038			3.656	−5.5	7.60	Van Den Berg et al. (1999)
Deule River, northern France	6.04		12.0	−0.45		64.7	Lourino-Cabana et al. (2012)
Rupel River, Belgium	0.3		5	10		372	Leermakers et al. (2005)
Scheldt River, France and Belgium	2.00		9.53	15.48	27.25	138.8	Gao et al. (2006)
Bang Pakong River, Thailand	0.3	0.2	58	2.7	4.0	41	Cheevaporn et al. (1995)
Elbe River, Germany	0.8	0.4	131	27.5	6.81	63	Petersen et al. (1995)
Odiel River, Spain		0	483	580		9810	Blasco et al. (2000)
Caper, Brazil		0	35				Campanha et al. (2012)
Rturarg, Brazil		0	6302				Campanha et al. (2012)
Rgrande, Brazil		0.5	0.2	0.3	−3.491		Campanha et al. (2012)

heavy metals being released from the river sediment. The top 5 cm of sediment cores were divided into 0.5-cm slices, and the remainder of the core was divided into 1-cm slices to obtain the concentration profiles at the sediment–water interface. The diffusive fluxes are shown in Fig. 3. All of the metals in the WR were found to diffuse from the sediment to the overlying water, and Cu was found to have the highest diffusive flux from the sediment to the overlying water in all three tributaries. The mean diffusive fluxes of Cd, Cr, Cu, Ni, Pb, and Zn in the SR were 0.258, 42.5, 33.6, 14.0, 19.0, and $-204 \mu\text{g}/(\text{m}^2 \text{ day})$, respectively, meaning that the net Cu, Cr, Cd, Pb, and Ni fluxes were from the pore water to the overlying water and that the net Zn flux was from the overlying water to the sediment. The mean diffusive fluxes of Cd, Cr, Cu, Ni, Pb, and Zn in the WR were 0.469, 7.39, 3.16, 13.7, 7.86, and $21.9 \mu\text{g}/(\text{m}^2 \text{ day})$, respectively, meaning that the net fluxes of all six metals were from the pore water to the overlying water. The mean diffusive fluxes of Cd, Cr, Cu, Ni, Pb, and Zn in the XR were -0.427 , -71.8 , 86.6 , 5.29 , 7.24 , and $-41.4 \mu\text{g}/(\text{m}^2 \text{ day})$, respectively, meaning that the net Cd, Cr, and Zn fluxes were from the pore water to the overlying water.

We found that Cu, Ni, and Pb were being released to the overlying water in all of the rivers studied, so they may negatively affect surface water quality and pose health risks. Heavy metals in pore water in the WR were found to pose the greatest ecological risk, and all of the metals had diffusion rates of >0 , probably because the highest concentrations of most of the heavy metals were

found in the WR pore water samples. The release fluxes of some of the heavy metals, especially Cr, in the SR were very high, even though the SR pore water samples did not contain the highest concentrations. The results indicated that the sediments have become important pollution sources of heavy metals in the SR due to the discharge of leather industry wastewater in recent decades (Tang et al. 2015).

The fluxes found in our study are compared with fluxes found in other places in Table 4. The fluxes we found were generally close to those found in other polluted rivers around the world, including the Meuse River in the Netherlands (Van Den Berg et al. 1999), the Deule River in France (Lourino-Cabana et al. 2012), and the Bang Pakong River in Thailand (Cheevaporn et al. 1995). Flux calculations can suffer serious errors because of the presence of hydroxides and oxides and the occurrence of bioturbation, bioirrigation, and resuspension caused by wave action and shipping activities (Van Den Berg et al. 1999). Therefore, the actual net diffusion of

Table 5 Hardness-dependent final chronic value (FCVMe) determined for Cd, Cu, Ni, Pb and Zn in pore water of the Xiao River (XR), the Wangyang River (WR), and the Shaocun River (SR)

River	CaCO_3 (mg/L)	FCV_{Cd}	FCV_{Cu}	FCV_{Ni}	FCV_{Pb}	FCV_{Zn}
XR	396	2.85	36.7	503	14.5	335
WR	376	2.74	35.2	482	13.5	321
SR	296	2.30	28.7	394	10.0	262

Table 6 Toxic unit analysis results for the dissolved metals in sediment in the three rivers in the Ziya River system that were studied: the Xiao River (XR), the Wangyang River (WR), and the Shaocun River (SR)

River	Cd		Cu		Ni		Pb		Zn		Σ IWCTU	NI	Impact grade
	Cd ($\mu\text{g/L}$)	IWCTU _{Cd}	Cu ($\mu\text{g/L}$)	IWCTU _{Cu}	Ni ($\mu\text{g/L}$)	IWCTU _{Ni}	Pb ($\mu\text{g/L}$)	IWCTU _{Pb}	Zn ($\mu\text{g/L}$)	IWCTU _{Zn}			
	Cd ($\mu\text{g/L}$)	IWCTU _{Cd}	Cu ($\mu\text{g/L}$)	IWCTU _{Cu}	Ni ($\mu\text{g/L}$)	IWCTU _{Ni}	Pb ($\mu\text{g/L}$)	IWCTU _{Pb}	Zn ($\mu\text{g/L}$)	IWCTU _{Zn}			
XR	0.207	0.073	41.2	1.12	20.1	0.040	15.6	1.07	83.2	0.248	2.55	0.870	NO
WR	0.430	0.157	49.5	1.41	28.6	0.059	7.37	0.542	88.0	0.274	2.52	1.05	Slight
SR	0.074	0.032	16.6	0.579	8.6	0.022	9.97	0.993	109	0.415	2.87	0.759	NO

Data in bold when violating the corresponding water quality criteria recommended by EPA (2002)

each metal from the sediment to the dissolved phase in the surface water is probably much lower than that reported in Table 4.

Toxic unit analysis of the pore water

The dissolved phase concentration of a contaminant in interstitial water in sediment reflects the contaminant's activity and is a good surrogate for the bioavailable concentration (Burgess et al. 2013). It has previously been observed in several studies (Gaillard et al. 1986, Lourino-Cabana et al. 2011) that metal concentrations in pore water reach maxima in the surficial sediment layers (~1–3 cm deep). The surface sediment (0–5 cm) interstitial water was collected from samples from the rivers that were studied and analyzed so that the metal toxicities in the XR, WR, and SR could be estimated.

The FCV values of the selected metals (Cd, Cu, Ni, Pb, and Zn) were determined (Table 5), and the IWCTU index was calculated from Eq. (3) for each metal at every site. We found that the IWCTU values for Cu and Pb in the surface sediment in the rivers that were studied exceeded the appropriate water quality criteria recommended by the US Environmental Protection Agency (Table 6). The IWCTU_{Cu} values for the XR and WR were >1, as was the IWCTU_{Pb} value for the XR. Two indices, the total IWCTU and the NI, both combining the results for multiple metals, were used to estimate the pore water quality. The total IWCTU and NI values showed that the interstitial water was not seriously contaminated with the metals studied in any of the three rivers, but a high NI value, slightly higher than 1, was found for the WR sediment, showing that the heavy metals in the WR sediment pose risks of inducing toxic effects.

These findings were not the same as the potential ecological risk (PER) of sediments. Previous research (Tang et al. 2015) has reported that Cd in the sediments of XR showed serious PER, and Pb in WR showed higher PER.

The difference indicated that it was not accurate to estimate the sediment quality only depending on the chemical composition of sediments. Bioavailability and speciation of metals in the sediments should be considered. The previous results showed that the toxicity of pore water corresponded well to sediment toxicity (Schubauer-Berigan and Ankley 1991). The metal toxicity in sediments is directly related to the concentration in pore water, which is also influenced by the characteristics of sediments and pore water, such as pH, hardness, acid volatile sulfide (AVS), and organic matter (OM) (Crommentuijn et al. 1997). Therefore, it should be known that bioassay is very necessary to comprehensively assess heavy metal contamination in the sediments of aquatic ecosystem in future studies.

Conclusions

The distributions, fluxes, and toxicities of Cd, Cr, Cu, Ni, Pb, and Zn in sediment pore water were investigated in three tributaries of the ZRS with different wastewater sources. The mean Cd, Cr, Cu, and Ni concentrations in the pore water were higher in samples from the WR, which receives pharmaceutical wastewater discharges, than in the samples from the XR and SR. The diffusive fluxes indicated that sediments in the WR and SR acted as sources of metals to the water columns in these rivers. The total IWCTU and NI values showed that the interstitial water was not seriously contaminated with the studied metals in any of the three rivers, which was inconsistent with the PER of sediments due to heavy metals. Therefore, bioassay will be very necessary to comprehensively assess heavy metal contamination in the sediments of aquatic ecosystem. The information provided by this study will be useful in identifying the metal pollution status of the rivers in the ZYS and in similar watersheds in northern China and would allow for effective management strategies to be developed.

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