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RESEARCH ARTICLE

Large-scale monitoring and assessment of metal contamination in surface water of the Selenga River Basin (2007–2009)

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Abstract An extensive and year-round survey was conducted to assess metal pollution in vast watershed areas of the Selenga River Basin (2007–2009), which provided baseline heavy metal database for the future management. Sources and environmental hazard and risk indices associated with metal pollution were evidenced across the countries of Mongolia and Russia (Buryatia Republic). In general, the concentrations of heavy metals in river water of Mongolia were greater than those of Russia, expect for the upstream of the Dzhida River in Russia. The spatial distribution generally indicated that metal pollution in the Selenga River was mainly associated with the activities in the Mongolian upstream regions. Similar pollution sources of metals between river water and wastewater associated with surrounding activities were found across the industrial and mining areas. Compositional patterns of metals suggested their sources were independent of each other, with hot spots in certain sites. Our measurements indicated that about 63 % of the locations surveyed (48 of 76) exceeded the critical heavy metal pollution index of 100, identifying possible harmful effects on aquatic ecosystems through metal pollution. Zinc was found to be the chemical of priority concern, as more than half of the locations exceeded the corresponding water quality guideline. Other metals including Mn, Fe, Cr, Cu, and As might be problematic in the Selenga River Basin considering the occurrence and their concentrations. Results of our extensive survey during the period of 3 years indicated that urgent action would be necessary in timely manner to improve water quality and mitigate the impact of heavy metals on aquatic environment of the Selenga River Basin.

Keywords Metals · Water quality guideline · Mining area · Industrial area · Pollution index · Selenga River Basin

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Introduction

The rapid and intensive development of East and Central Asia has brought significant environmental changes and deterioration to this region. Anthropogenic influences along with natural processes appear to be causing water quality deterioration, particularly in the lotic system of rivers (Rashid and Romshoo 2013; Stubblefield et al. 2005). The river pollution has long been associated with metals generally being originated from inland human activities followed by improper management, particularly in

Mongolia and other developing countries (Hudson-Edwards et al. 2003; Stubblefield et al. 2005).

The Selenga River, which originates in Mongolia would not be a direct source of heavy metal pollution; however, any possible pollution could have a greater impact on the nearby or downstream ecosystems, such as Lake Baikal in Russia (R. Chalov et al. 2014). The lake is the deepest and among the clearest in the world, containing about 19 % of world reserves of lake fresh water (Sinyukovich 2008). Lake Baikal is home to more than 1,700 species of plants and animals, two thirds of which can be found nowhere else in the world. It was declared a UNESCO World Heritage Site in 1996. For the Baikal region, it is extremely important to manage the water resources of the Lake Baikal to properly protect the aquatic resources. Accordingly, a special federal law, “Lake Baikal protection,” was passed on the part of Russia in 1999.

Considering the geological and geographical settings of the Selenga River Basin (Shichi et al. 2007), the assessment of the potential impacts on the state of this unique lake would be significant enough. Historically, Mongolian water reservoirs have been minimally affected by anthropogenic activities (Batoev et al. 2005; Dalai and Ishiga 2013; Inam et al. 2011; Kashin and Ivanov 2010; Pfeiffer et al. 2014; Thorslund et al. 2012). However, recently, the Selenga River Basin has been experiencing the heavy and rapid developing pressures by increased human activities (Batoev et al. 2005; Beeton 2002; Duker et al. 2005; Hofmann et al. 2014). As a consequence, vast areas of the basin have been changing dramatically, and the affected ecosystems have been under potentially serious environmental stresses (Batjargal et al. 2010; Dalai and Ishiga 2013; Jiang et al. 2014; Nriagu et al. 2012; Pavlov et al. 2008; Stubblefield et al. 2005). Importantly, the effects of potential metal pollution in the Selenga River associated with inland activities including mining operations have not been well documented. Accordingly, it is presently difficult to assess the ecological effects of anthropogenic changes in the Selenga River Basin on the state of Lake Baikal in Russia.

Spatial and temporal variations in water quality require a comprehensive monitoring program to provide a representative and/or regional assessments of potential ecological impairment. Thus, the determination of trans-boundary river pollution between Mongolia and Russia (Buryatia) should be critically important. At present, there have not been many studies conducted on heavy metals in the watercourses in other parts of Mongolia and Russia (Chebykin et al. 2010; Kashin and Ivanov 2008; Khazheeva and Pronin 2005; Khazheeva et al. 2006; Khazheeva et al. 2004; Krapivin et al. 1998); thus, comprehensive and large-scale monitoring studies should be of significant needs, particularly within the Selenga River Basin encompassing upstream (Mongolia) to downstream (Buryatia, Russia).

In the present study, we performed a large-scale monitoring survey targeting heavy metals in river water and wastewater along the Selenga River Basin. We aimed to document the following: (i) concentrations and distribution, (ii) pollution sources, and (iii) water quality assessment categorizing priority sites and/or pollutants in the Selenga River Basin. This background information of 2007–2009 baseline data of heavy metal pollution in the given area would be a valuable standing point for the upcoming pollution management of these valuable water resources.

Materials and methods

Selenga River Basin

The Selenga River is the most important tributary of the Lake Baikal, which accounts for 82 % of the watershed area of the Lake Baikal (Fig. 1). It is located between 46°20′ and 53°00′, southwest, and 96°50′ and 112°50′, northeast. The length of Selenga River is roughly 943 km and holds an area of around 447,060 km^2. The Selenga River is a trans-boundary waterway in the Northeast Asia that rises in the Khangai Mountains in Mongolia and flows into the Lake Baikal in Russia. In Mongolia, the Selenga River has a water catchment of 282,349 km^2, while the catchment area in Russia is about 148,060 km^2. Most of the Selenga River rests in Mongolia (roughly 63 %) and what is left is in Russia (about 37 %). The river plays an important role mostly because 19.2 % of the total land area of Mongolia is contained by it. Its upstream quality has been deteriorated due to rapid urbanization, scarce wastewater treatment systems, and hasty mining developments in Mongolia (KEI 2008). Simultaneously, the transition from a planned economy to a market economy, inefficiently operated wastewater treatment systems, and reckless deforestation have timely increased non-point pollution sources on the lower Selenga River in Russia. Thus, the management of this river became considered as one of the important regional pollution issues in the Northeast Asia.

Sampling strategies

Water samples were collected to measure heavy metals during the summer of 2007–2009 (surveys I–III). Sampling strategies were somewhat different for each year depending on the specific purposes in timely fashion (Table 1 and Fig. 1). In brief, in the first survey (survey I) conducted in 2007, we collected samples along the Selenga River and at its main tributaries in order to acquire a general understanding of the extent of metal pollution in the Selenga River Basin. In the following year of 2008 (survey II), sampling targeted potential “hot spot” areas, which was defined herein as areas with the most significant pollution sources, based on their impacts on the aquatic ecosystem as well as on drinking water condition. For example, the mining (Zaamar) and industrial or urban

Fig. 1 Map showing the sampling sites for assessment of heavy metal pollution in the Selenga River Basin (*Red*, survey I in 2007; *yellow*, survey II in 2008; *green*, survey III in 2009; 1–76 for river water and W1–W10 for wastewater, sampling locations for wastewater given in a greater detail in Fig. S1)

(Ulaanbaatar, Gusinoozersk, Ulan-Ude, and Selenginsk) areas were considered as hot spot areas, as assigned by the Mongolian and Russian experts. Of note, these areas include point (e.g., industrial and municipal effluents) and non-point (e.g., water runoff from mining areas) sources. Finally, in 2009 (survey III), new sampling sites were added at potential hot spot areas in mining areas (Erdenet and Zakamesnk) and at several remaining industrial areas (Ulaanbaatar, Darkhan, Ulan-Ude, Gusinoozersk, and Selenginsk), to more fully investigate the most heavily influenced areas. Three years of survey efforts combined generally covered the upstream through the downstream in the Selenga River Basin, encompassing major cities and potential industrial and mining sources for heavy metal pollution. In particular, as for wastewater sampling, most of samples were collected close to the point sources such as copper mining places and/or sewer treatment plant to investigate a direct effect of metal pollution associated with known sources (Table S1 and Fig. S1).

Field and laboratory analyses

The exact location (longitude and latitude) of each sample point was measured by a GPS, and environmental observations such as surrounding activities were documented during the fieldwork (Table 1 and Fig. 1). Water samples were collected in pre-cleaned Teflon bottle from all the surveyed locations (n=86), and at some locations, wastewater samples (locations W1–W10) were additionally collected in the selected hot spot areas (Table S1 and Fig. S1). In general, the hot spot locations for wastewater sampling were situated within the kilometers (mostly about 500 m downstream of point sources), slightly varied depending on the accessibility to the sites. After collection, aliquot of 1 L water samples was filtered through a GF/C filter and kept in pre-cleaned Teflon bottles. A small amount of 60 % nitric acid (HNO_3) was added in the field as a preservative. Then, the pretreated sample bottles were stored in a cooler box and transported to the

Table 1 Sampling sites, sample type, region, and surrounding activities for large-scale heavy metal monitoring study in the Selenga River Basin conducted from 2007 to 2009

Country	River	Region	Surrounding activity	Sample type	Sample i.d.[a]		
					Survey I 2007 (*n*=27)	Survey II 2008 (*n*=34)	Survey III 2009 (*n*=25)
Mongolia	Kharaa River	Darkhan	Industrial area	River water	1	31, 32	61, 62
				Wastewater			W7
	Khangal River	Erdenet	Mining area	River water	2		63–65
				Wastewater	W1, W2		W8, W9
	Sharin Gol River	Darkhan	Mining area	River water	3, 4		66
	Selenga River	Darkhan	Others	River water	5–7		
	Ere River	Darkhan	Others	River water	8, 9		
	Delger River	Muren	Others	River water	10, 11		
	Egiyn River	Khovsgol Lake	Others	River water	12, 13		
	Tuul River	Ulaanbaatar	Industrial area	River water		26–30	58–60
				Wastewater		W3, W4	W5, W6
		Zaamar mining	Mining area	River water		33–37	
	Orkhon River	Hujirt	Others	River water		38–44	
Russia	Selenga River, Uda River	Ulan-Ude	Industrial area	River water	14–16	45–49	67–69
	Modonkul River	Zakamensk	Mining area	River water		54–57	70, 71
				Wastewater			W10
	Dzhuda River	Zakamensk	Others	River water	17		
	Selenga River	Kyakhta	Others	River water	18	50	
		Selenginsk	Others	River water	19–22	52, 53	72, 73
		Novoselenginsk	Others	River water		51	
	Temnik River		Others	River water	23		
	Chikoy River		Others	River water	24		
	Khilok River		Others	River water	25		
	Goosinoe Lake	Gusinoozersk	Others	River water			74–76

[a] Sample i.d.: locations are presented in Fig. 1 and Fig. S1

laboratory for further processes. Analytical measurements for nine metals (Mn, Fe, Ni, Cr, Cu, Pb, Cd, As, and Zn) were carried out by use of an Inductively Coupled Plasma-Atomic Emission Spectrophotometer (ICP-AES, Thermo iCAP 6500, Thermo Scientific, Waltham, MA) for surveys I and II ,and ICP-Mass Spectrometer (ICP-MS, X-7 Series, Thermo Scientific) for survey III. The detection limits for metals in ICP-MS analysis were 0.01 $\mu g\ L^{-1}$ for Ni, Cu, Pb, and Cd, and 0.1 $\mu g\ L^{-1}$ for Fe, Mn, Cr, As, and Zn, respectively.

Data analysis

In order to best characterize heavy metal data for river water and wastewater, different data analysis techniques were applied. First, the results of metal concentrations are presented by survey (Fig. 2), considering the series of yearly sampling: screening (in 2007), hot spot monitoring (in 2008), and potential sources (in 2009), then summarized (original data presented in Tables S2–4 of Supplemental Materials). Second, the surrounding activities potentially associated with metal pollution, categorized by industrial, mining, and other areas, were scrutinized for source identification, where compositional analysis and principal component analysis (PCA) were applied using SPSS 12.0 (for Windows, SPSS Inc., Chicago, IL). Exploratory factor analysis was performed by varimax rotation, which minimized the number of variables with a high loading on each component, facilitating the interpretation of PCA results.

Heavy metal pollution index

Environmental hazard and risk assessment was conducted by comparing concentrations of target metals with corresponding water quality guidelines (Mongolian National Standard (MNS) 1998; Russian National Standard (RNS) 2010). Data in the present study was also compared with previously documented data in the Selenga River Basin (Chebykin et al. 2010; Krapivin et al. 1998; Li and Zhang 2010) to evaluate

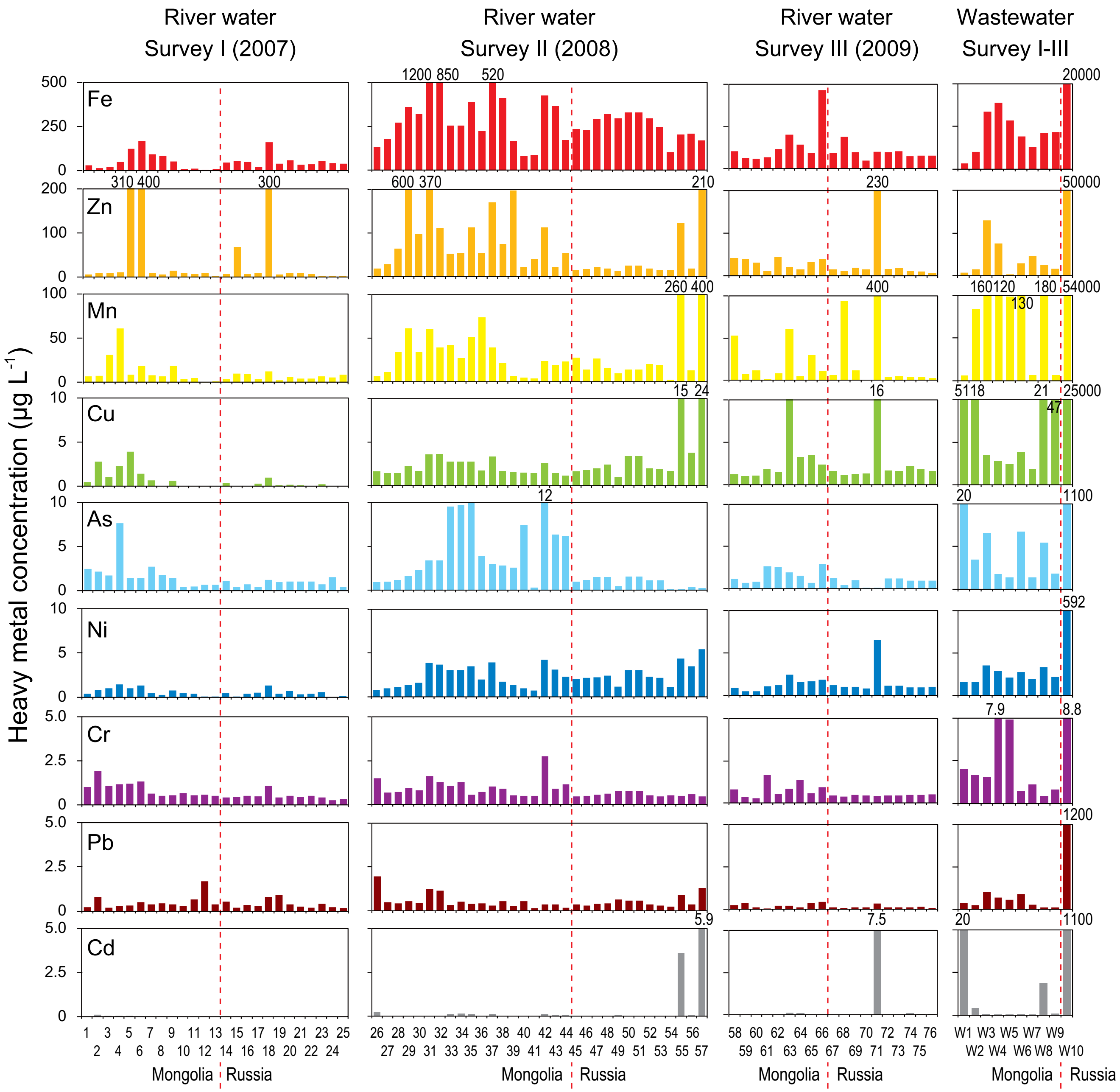

Fig. 2 Concentrations of metals in river water (n=76) and wastewater (n=10) from the Selenga River Basin of Mongolia and Russia from 2007 to 2009 (site numbers are present in Fig. 1)

consistency with other studies (Table 2). Metals were prioritized by comparing the median and highest values to corresponding guidelines (Table 3) and arranged according to degree of pollution levels. The heavy metal pollution index (HPI) was calculated by use of the obtained data and guidelines to identify the potential contaminated areas, say above the critical pollution limit (viz, HPI> 100) (Prasad and Bose 2001; Venkata Mohan et al. 1996). HPI model is given as:

$$Q_i = (M_i - I_i) / (S_i - I_i) \times 100 \qquad (1)$$

$$\mathrm{HPI} = \sum W_i Q_i \qquad (2)$$

Where Q_i is a subindex of the ith parameter and M_i is the monitored value of metal of the ith parameter. I_i is the ideal/baseline value of ith parameter and W_i is the unit weightage ($1/S_i$). S_i is the standard value of ith parameter. The critical pollution index value is 100 (Reza and Singh 2010). In this study, HPI was calculated by use of the mean value of three water quality criteria as the standard values (S_i) including Mongolian, Russian, and US EPA metals guidelines for aquatic life protection (Fig. S2).

Table 2 Summary of concentrations of selected metals in river water of the Selenga River Basin obtained from this study and previous reported data (min-max or mean±SD)

Regions	Sample type	Sampling year	No.	Metals (µg L^{-1})					References
				Mn	Cr	Cu	Cd	Zn	
Kharaa River	River water	2007–2009	5	23±25	1.2±0.5	2.2±1	0.03±0.01	110±150	This study
Khangal River	River water	2007–2009	4	26±26	1.2±0.6	7.6±9	0.10±0.04	19±10	
Sharin Gol River	River water	2007–2009	3	34±25	1.1±0.1	1.9±0.7	0.04±0.02	20±15	
Selenga River (Mongolia)	River water	2007–2009	3	12±6	1.1±0.4	2.0±2	0.03±0.02	240±210	
Ere River	River water	2007–2009	2	12	0.53	0.33	0.010	11	
Delger River	River water	2007–2009	2	4.2	0.62	0.015	0.015	8.3	
Egiyn River	River water	2007–2009	2	0.76	0.54	<DL	0.005	6.5	
Tuul River	River water	2007–2009	12	34±22	0.81±0.7	1.8±0.7	0.06±0.07	99±160	
Orkhon River	River water	2007–2009	7	15±9	1.0±0.8	1.6±0.5	0.04±0.04	75±63	
Selenga and Uda River	River water	2007–2009	11	21±20	0.51±0.1	1.2±0.8	0.02±0.02	19±17	
Modonkul River	River water	2007–2009	6	180±200	0.50±0.06	10±9	2.8±3	100±100	
Dzhuda River	River water	2007–2009	1	3.4	0.49	0.32	0.02	8.7	
Selenga River (Russia)	River water	2007–2009	11	9.4±6	0.60±0.2	1.4±1	0.02±0.01	41±87	
Temnik River	River water	2007–2009	1	3.6	0.48	2.2	0.080	11	
Chikoy River	River water	2007–2009	1	3.8	0.49	1.8	0.060	9.7	
Khilok River	River water	2007–2009	1	2.8	0.53	1.6	0.050	6.4	
Goosinoe Lake	River water	2007–2009	3	3.4±0.5	0.50±0.03	1.9±0.3	0.06±0.02	8.9±2.0	
Boroo Gold mine area	Ground water	2009	29	86±205	na	6.1±8.3	0.069±0.11	18±21	Inam et al. (2011)
Mouth of Selenga River	River water	na	24	47±35	na	12±6	1.0±0.6	6.0±4.4	Khazheeva et al. (2006)
Selenga River delta	River water	2001	9	12±4	30±10	33±12	na	260±140	Khazheeva et al. (2004)
Ulaanbaatar	Well water	2011	129	0.12–177	na	na	<0.02–0.69	<0.1–690	Nriagu et al. (2012)
Tuul and Orkhon rivers	River water	2005–2008	11	59±120	na	2.0±1.1	na	4.4±2.1	Thorslund et al. (2012)

<*DL* below detection limit, *na* not analyzed or not available

Results

In survey I, the concentrations and a large-scale distribution of metals in surface water in the Selenga River Basin were determined (Fig. 2 and Table S2). Greatest concentrations were observed near Darkhan and downstream of the Sharingol River and Khara River for Mn, Cu, As, and Cd, and in the Selenga River Basin at sampling locations 7 and 8 in the Mongolian section, Ulan-Ude, and Mongolian-Russian border for Zn and Fe. Elevated concentrations were mostly found at the locations in the Mongolian section (upstream regions), while lesser degree of contamination was obvious at the locations in the Russian section (downstream). The results presumably reflected the influences of increasing discharges of metals from local industrial and mining activities mainly originating from the upstream regions of the Selenga River Basin.

In survey II, the monitoring of hot spot areas (Fig. 2 and Table S3) revealed sources of heavy metal pollution both in Mongolia and Russia. In particular, the greatest concentrations of metals for Fe, Zn, and Mn were found near Ulaanbaatar, Zaamar, Darkhan, and upstream of Orkhon in Mongolia. The Russian section generally showed lesser degree of heavy metal pollution compared to the Mongolian section, but several locations at Ulan-Ude and Zakamensk had concentrations that were comparable to those in Mongolia. In particular, elevated concentrations of Mn, Pb, and Cd found in the upstream section of the Dzhida River indicated an independent source of metals originating in Russia.

In survey III, potential sources of metals were investigated more thoroughly (Fig. 2 and Table S4). In particular, the greatest concentrations of all nine target metals were measured in wastewater collected at location 81 (Zakamensk, Russia). Ulaanbaatar, Erdenet, and downstream of the Sharingol River in the Mongolian section also were found to be severely contaminated with some of these metals in general. In the Russian section, the rivers at Ulan-Ude and Zakamensk showed the greatest concentrations of Mn, Pb, and Cd compared to other areas. In general, several hot spots not identified in survey I were newly recognized from survey III.

Throughout these 3 years of surveys in the Selenga River Basin, we found that most rivers were polluted by Fe, Zn, and

Table 3 Median and maximum concentrations of metals and toxic units compared to water quality criteria (Mongolia, Russia, and US EPA) in river water of the Selenga River Basin

Metal	Country	Median value				Maximum value			
		Concentration ($\mu g\ L^{-1}$)	Toxic unit[a]			Concentration ($\mu g\ L^{-1}$)	Toxic unit		
			Mongolia[b]	Russia[c]	US EPA[d]		Mongolia	Russia	US EPA
Fe	Mongolia	130	nv	1.3		1,200	nv	12	1.2
	Russia	99	nv			330	nv	3.3	
Zn	Mongolia	37	3.7	3.7		600	60	60	4.0
	Russia	15	1.5	1.5		300	30	30	2.0
Mn	Mongolia	18		1.8	nv	73		7.3	nv
	Russia	9.5			nv	400	4.0	40	nv
Cu	Mongolia	1.6		1.5		21	2.1	21	2.0
	Russia	1.6		1.6		24	2.4	24	2.4
As	Mongolia	2.2				12	1.2	2.5	
	Russia	1.0				1.6			
Ni	Mongolia	1.1				4.2			
	Russia	1.1				6.6			
Cr	Mongolia	0.85				2.8		2.8	
	Russia	0.48				1.1		1.1	
Pb	Mongolia	0.38				2.0			
	Russia	0.30				1.3			
Cd	Mongolia	0.023				0.20			
	Russia	0.020				7.5	1.5	1.5	30

Blank: toxic unit value <1.0

nv no criteria value

[a] Median and maximum concentrations of metals ($\mu g\ L^{-1}$)/various water quality guidelines ($\mu g\ L^{-1}$)

[b] Water quality criteria for Mongolia ($\mu g\ L^{-1}$): Zn, 10; Mn, 100; Cu, 10; As, 10; Ni, 10; Cr, 50; Pb, 10; Cd, 5 (MNS 1998)

[c] Water quality criteria for Russia (Baikal region) ($\mu g\ L^{-1}$): Fe, 100; Zn, 10; Mn, 10; Cu, 1; As, 5; Ni, 10; Cr, 1; Pb, 6; Cd, 5 (RNS 2010)

[d] US EPA CCC value (chronic, $\mu g\ L^{-1}$): Fe, 1,000; Zn, 150; Cu, 10; As, 150; Ni, 52; Cr, 11; Pb, 2.5; Cd, 0.25 (US EPA 2006)

Mn, in that order (Fig. 3). While Ni, Pb, and Cd were found to be least contaminated groups of metals across the upstream to downstream regions, when compared to the water quality guidelines of Mongolia (MNS 1998) and Russia (RNS 2010) (Table S5). The most polluted reach among Mongolian rivers in terms of numbers of metals that exceeded guidelines was the Tuul River near Ulaanbaatar City, followed by the Kharaa River near Darkhan City, as well as reaches of the Orkhon, Sharingol, Khangal, and Ere Rivers, where about half of target metals exceeded the corresponding guidelines (MNS 1998). In Russia, most rivers were found to be polluted with Mn, Zn, and Cu, but less so by Ni, Cr, Pb, Cd, and As, considering the guidelines. The most polluted Russian rivers were the Modonkul River near the Zakamensk mining area, followed by the Selenga River near Kyakhta City, Novoselenginsk, Ulan-Ude, and Selenginsk. Overall, metal concentrations obtained in the present study seemed to be comparable to the previously reported ones in other regions of the Selenga River Basin (Table 2) (Inam et al. 2011; Khazheeva et al. 2004; Khazheeva et al. 2006; Nriagu et al. 2012; Thorslund et al. 2012). However, extremely elevated concentrations at certain locations such as Modonkul River for Mn, Cu, and Zn which far exceeded the corresponding guidelines indicated previously unidentified hot spots which might need urgent management.

Discussion

Sources and distribution

Compositions of target metals (Fe, Zn, Mn, Cu, As, Ni, Cr, Pb, and Cd) were examined using box-plots (Fig. 3) of individual variables in three different areas (industrial, mining, and other sectors) and the result showed varying compositions. Compositions of metals clearly indicated different patterns within mining areas, while relative proportions seemed to be similar in industrial and other sectors for the following metals:

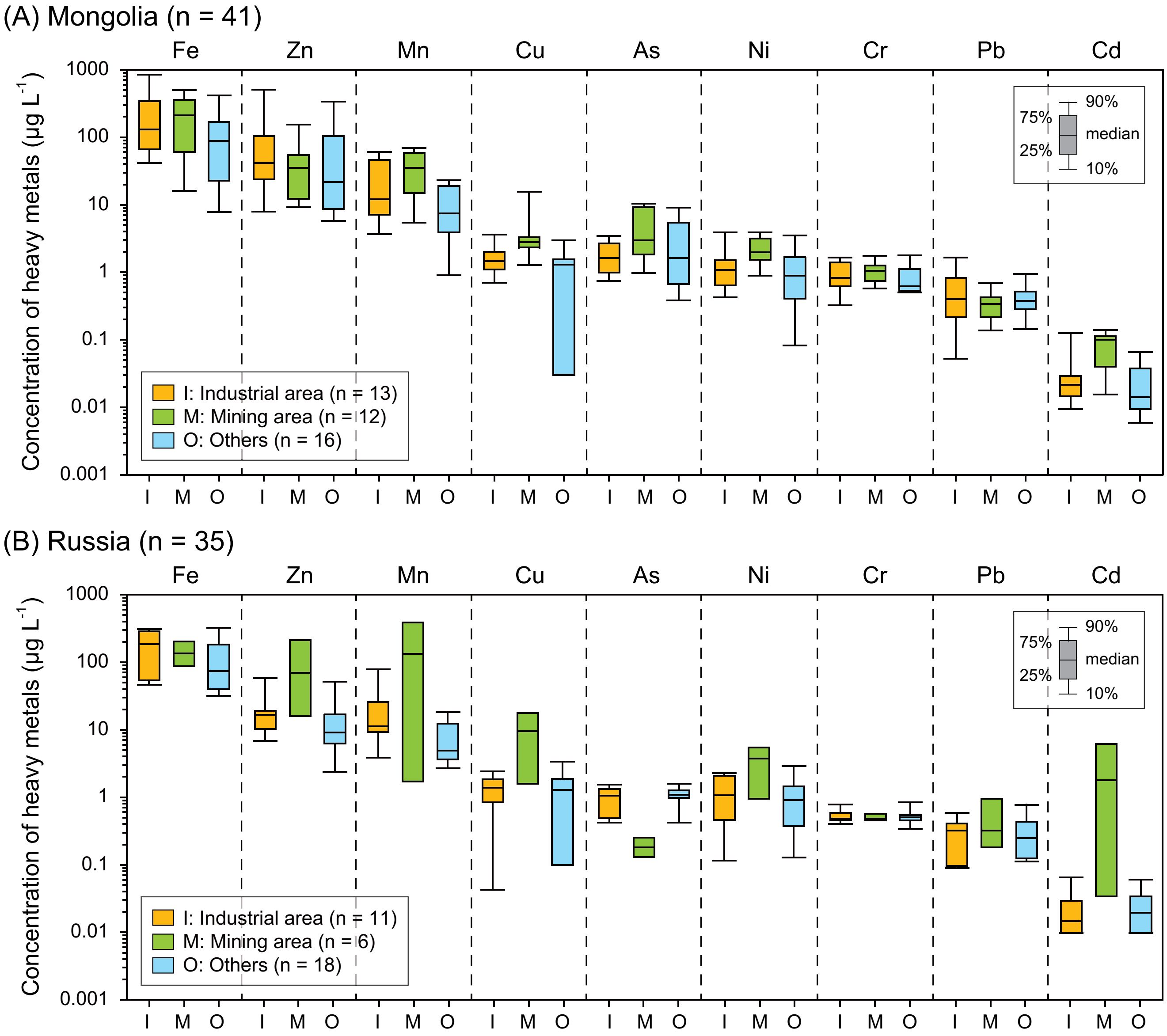

Fig. 3 Box-plots for concentrations of metals in river water samples (*n*=76) collected from industrial area, mining area, and other areas of the Selenga River Basin of **a** Mongolia (*n*=41) and **b** Russia (*n*=35)

Fe, Mn, Cu, As, Ni, and Cd. Specific compositions could be affected by various factors, such as common and continuing sources, and would not necessarily appear as similar within these general categories. For example, as for mining areas, considering the differences in mining intensity and operations, such compositions might be different within each country.

To identify specific sources for heavy metal pollution in the rivers of the Selenga River Basin, the profiles of individual metals from in the given areas were compared by use of PCA (Fig. 4). The plot of principal components facilitated the clustering of the locations into major groups. Two principal components were extracted, together explaining approximately 55 % (PC1, 34 %; and PC2, 21 %) of the total variances in heavy metal concentrations. Based on the weight of the contribution of each variable in the PCA, it can be seen that all variables are positively associated with the first component (PC1). However, variables for Cd, Cu, and As are negatively associated with the second component (PC2).

Metals were split into three groups distinguished by contamination trends according to their different activities (industrial, mining, and other areas). Especially, both industrial and other sectors were positively associated with the first component (PC1) but not for the second component. The major group of lesser polluted locations was clearly associated with Fe, Zn, and Cu, indicating common metal sources. Some other highly polluted locations for river waters allocated in a separate group encompassed Cd, Cd, and As (mining area) and Fe, Zn, and Pb (industrial area). The group of metal compositions

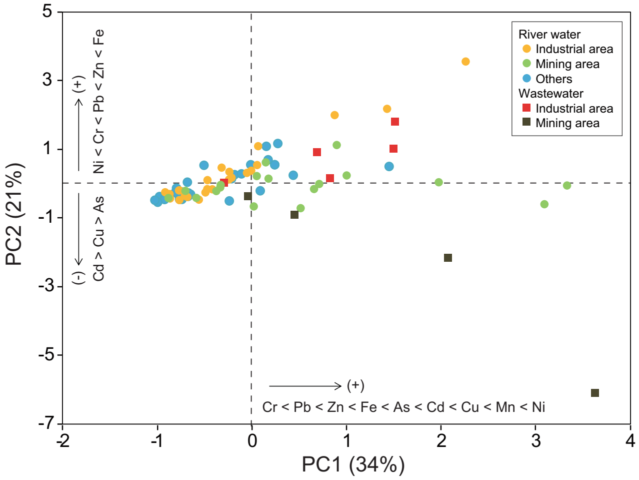

Fig. 4 Results for principal component analysis (PCA) of metals composition in river water and wastewater samples collected from the industrial, mining, and other areas of the Selenga River Basin

in river water was clearly associated with those of wastewater. These results indicated that the metal contamination of river water generally reflected discharging sources such as wastewater.

Overall, the present study indicated that sources of metals in Mongolia and Russia seemed to be independent each other and that their distributions reflected mostly local surrounding activities. Thus, water resources management should be flexible and well-planned for each location. The following recommendations are put forth: (i) to build and update the wastewater treatment plants, (ii) to strengthen water source protection, and (iii) to improve the user fees charged in industrial and other areas in both countries. For mining areas, (i) comprehensive land use planning, (ii) strict pollution discharge systems and improvement of in situ treatment facilities in Mongolia and Buryatia (Russia) at Zakamensk, (iii) construction of sedimentation ponds, (iv) restoration of mining areas, and finally (v) increased public education about these issues are needed.

Comparison to water quality guidelines

The Mongolian, Russian, and US EPA's surface water quality guidelines for the nine target metals in river water were compared to the obtained data in the present study (Table 3 and Table S5) (MNS 1998; RNS 2010; US EPA 2006). Of note, the data for metals were compared in accordance with the Mongolian and Russian water quality guidelines, and three metals (Ni, Pb, and Cd) were found to be below and/or close to the standard values (Table S5). Occurrences of Zn exceeding the water quality guidelines were often observed in most of the rivers of Mongolia including the Kharaa River, Khangal River, Sharin Gol River, Selenga River, Ere River, Tuul River, and Orkhon River. Exceedances for Zn were also observed in the Uda River, Modonkul River, Selenga River, and Temnik River in Russia. No comparison could be made for Fe because the corresponding guideline has not been set in Mongolia. There are considerable difference gaps between Mongolian and Russian water quality guidelines. These differences need to be resolved and should be taken into account in transboundary management cooperation of the Selenga River Basin between the two countries.

The excessive use of metals over the past few decades has resulted in an overall increase of concentrations in aquatic ecosystems of this region. Clearly, guideline values have an important role in the local environment to ensure proper management of water resources. In each country, water quality guideline values mostly depend on the specified environment conditions (natural and geological backgrounds) and socioeconomical settings (anthropogenic activities and its progress). In the case of the Selenga River Basin, water use is designated for both fishery and water supply. Each use has slightly different values for water quality guidelines (for the protection of aquatic life or for drinking waters) in either Mongolia or Russia (Baikal region). However, we suggest that it would be preferable to use one water quality guideline for each metal that could be universally applied.

Risk assessment

The HPI calculated by use of the metal concentrations and surface water quality guidelines of Mongolia, Russia (Baikal region), and US EPA (CCC value) was utilized for risk assessment of metals in the Selenga River Basin (Fig. 5). The critical pollution index value is 100, above which the overall pollution level should be considered unacceptable for an aquatic ecosystem (Prasad and Bose 2001; Venkata Mohan et al. 1996). Based on the mean HPI, 31 and 17 sites in the Selenga River Basin were found to be above the critical value of 100, in Mongolia and Russia, respectively. Furthermore, ten critical areas were identified including in Mongolia: the Tuul River at Ulaanbaatar and Zaamar areas, the Khangal River at Erdenet, the Kharaa River at Darkhan, upstream of the Orkhon River, and in the Selenga River. In Buryatia, Russia, areas of critical concern include the Modonkul River at Zakamensk, the Selenga River at Kyakhta near to the Mongolian-Russian border, and the Uda River at Ulan-Ude. In addition, three potentially critical areas were identified in the Sharingol and Kharaa rivers at Darkhan in Mongolia, and one location in Buryatia (Russia) in the Selenga River after the confluence of the Dzhida River.

The values of HPI in the Selenga River Basin were generally in good agreement with the degree of populations in surrounding cities, indicating that occurrences of metal pollution were directly related with human activities (Fig. 5). We strongly recommended that these areas of concern be addressed and that one surface water quality guideline for

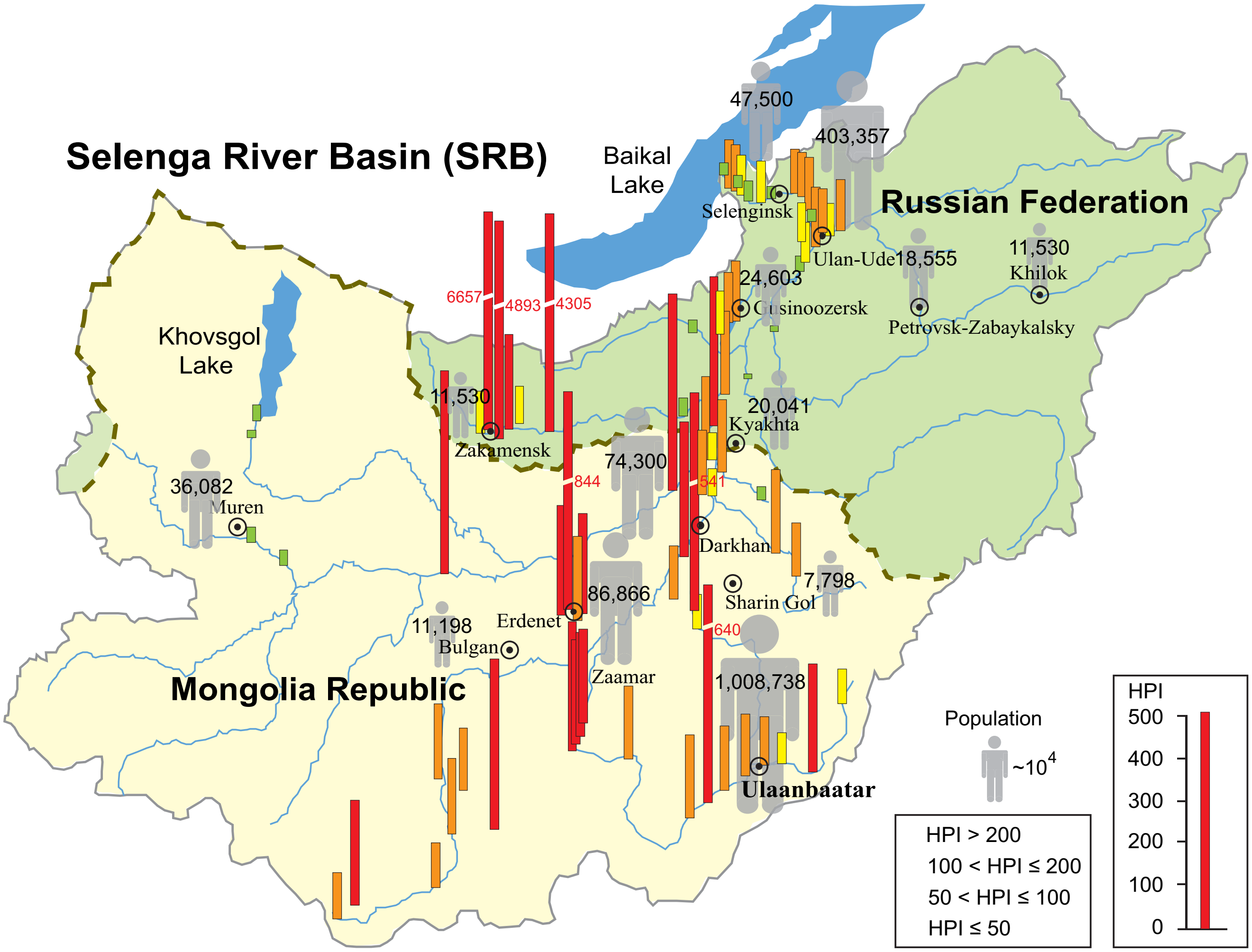

Fig. 5 Mean values of heavy metal pollution index (HPI) for the protection of aquatic life in the Selenga River Basin compared to the Mongolian and Russian water quality guidelines and US EPA CCC values (chronic) (water quality guidelines are present in Table 3)

aquatic life protection be developed for each metal for the entire Selenga River Basin in the near future.

Priority heavy meals

The evaluation of priority metals was proposed based on the comparison to the corresponding guidelines, i.e., analysis of the degree of exceeding the Mongolian and Russian guidelines (Table 3). According to the median values of metals, numerous exceedances were observed for Zn in relation to Mongolian and Russian guidelines and for Cu with respect to Russian guidelines in Mongolia and Buryatia (Russia). In addition, several exceedances were observed for Fe and Mn in the Mongolian section of the river. Some of the highest values of metals exceeded Mongolian and Russian guidelines as well as US EPA guidelines for Zn and Cu. Arsenic in Mongolia and Mn and Cd in Buryatia (Russia) were priority heavy metals exceeding Mongolian and Russian guidelines, and finally Mn, Fe, and Cr concentrations sometimes exceeded Russian guidelines in both countries.

Based on the degree and frequency of exceeding guidelines, the order of priority among these metals would be as follows: Zn>Cu>Fe>As in Mongolia and Zn>Mn>Cu≈Cd in Russia (Table 3). The somewhat different order of priority among these metals found in the present study can be simply explained by the different mining operation intensities in each country. Of note, the hydrological characteristics of rivers could play an important role in the reduction of metal loadings along the Selenga River Basin.

The possibility of potential effects caused by heavy metal pollution should be further identified as the accumulated metals in sediments and aquatic ecosystems could be a threat to both aquatic and benthic organisms. Of note, couple of previous studies pointed out significant pollution caused by mercury (Hg) in the given area, although Hg was not included as target metal in the present study. For example, the elevated concentrations of Hg in sediments were recently reported near the mining sites in the Tull and Orkhon River (Brumbaugh et al. 2013). In addition, the detectable concentrations of Hg in fish muscle collected from the Selenga River Basin indicated continuing input of mercury-related sources (Komov et al. 2014). Those studies discussed that sources of Hg in the Selenga River Basin could be attributable to the mining activity and/or atmospheric deposition (Brumbaugh et al. 2013; Komov et al. 2014). In anyhow, the addition of the present extensive metal pollution data into the precedent heavy metal database (Pavlov et al. 2008; Brumbaugh et al. 2013) enabled us to find priority chemicals for the future management in the given area, yet more comprehensive studies should be of additional needs.

Conclusion

Due to the rapid and intensive development in the Selenga River Basin in Mongolia and Russia, the river pollution caused by metals has been attracting public attention over the past decades. Heavy metals have the potential to impact on aquatic communities as well as human health. In general, the metal concentrations in surface waters of the Mongolian area were greater than those in the Russian section, except for the case of Zakamensk. The patterns of the trans-boundary pollution could not be simply explained by the hydrological dilutions and/or assimilative capacities of the river basin; rather, the pollutions predominantly would reflect a local condition at this time. From the sampling and analysis, Mn, Zn, and Cu were found to be present in most rivers in the Selenga River Basin. The Cd was prevalent in Mongolian waters, while Cr was present in most rivers of Russia. In terms of site-specific characteristics, the most polluted rivers were found to be the Tuul at Ulaanbaatar and the Zaamar mining areas in Mongolia and the Modonkul at Zakamensk. Our analysis indicated that metal sources were independent of each other and their distributions reflected local activities in both countries. Thus, water resource management should implement immediate and well-planned actions to reduce pollution in areas of concern accordingly. Overall, our study indicated that heavy metal input in the rivers is threatening the entire aquatic lotic system in the Selenga River Basin. Finally, there is an urgent need to develop common water quality guidelines for the waters of the trans-boundary system of the Selenga River in order to monitor and conduct adequate water management measures.

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