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OCCURRENCE OF ARSENIC IN THE RIVERBED SEDIMENTS OF THE SELENGA RIVER SYSTEM

Orgilbold MYANGAN*, Masayuki KAWAHIGASHI*,

Nobuhide FUJITAKE, Bolormaa OYUNTSETSEG***,**

Viacheslav V. KHAKHINOV ** and Hiroaki SUMIDA *******

Abstract Over the past few decades, anthropogenic activities have concentrated in the transboundary Selenga River basin, especially in the two-thirds of it located in the Mongolian territory. In this study, we measure the concentration of arsenic (As) in riverbed sediments and the mobilization and accumulation of this metalloid in sediments of the Selenga River system. Higher concentrations of As were detected in the sediments collected from the Orkhon River system than those from downstream of Selenga River in Russia. The observed difference indicates that the Orkhon River watershed is highly affected by anthropogenic activities involving soil excavation. In particular, high concentrations of As (3.6–4.9 mg kg^{-1}), in comparison with the average for the entire Selenga River system (2.8 mg kg^{-1}), were detected in sediment samples collected downstream of gold mining areas and near Darkhan City. Around this city, As pollution might be related to the combustion of coal with high As content. Gold mining is a main source of As pollution in rural areas. Notably, the content of fine fractions in sediment samples collected downstream of the Zaamar mining area was half that measured in samples collected upstream of it. However, no correlation was observed between As concentration and fine particle content in sediment samples collected throughout the whole research area, suggesting that the proportion of fine particle sediments is not a controlling factor in As distribution in the riverbed. Heavy and coarse particles released by mining sites seem to quickly deposit on the riverbed near their source. However, fine particles can co-precipitate at river junctions due to changes in water quality. These deposition processes can limit the extent to which As pollution can spread in a large area, but redissolution of As from secondary minerals is now recognized as a key factor in the widespread groundwater As contamination observed around the world.

Key words: transboundary river, gold mining, metalloid, As adsorption, soil erosion

* Department of Geography, Tokyo Metropolitan University.
** Graduate School of Agricultural Science, Kobe University, Kobe 6570013, Japan.
*** Department of Chemistry, National University of Mongolia, Ulaanbaatar, Mongolia.
**** Baikal Institute of Nature Management, SB of the Russian Academy of Sciences.
***** College of Bioresource Sciences, Nihon University, Fujisawa, Kanagawa 2520880, Japan.

1. Introduction

Arsenic (As) is a ubiquitous element present in the atmosphere, soils, rocks, natural waters, and organisms. It ranks as the 20th most abundant element in the environment (Gorny *et al.* 2015). The valence of As, a metalloid, varies across the values −3, 0, +3, and +5, depending on environmental conditions. In the natural environment, As(III) is a stable form in As-containing minerals, such as arsenopyrite and As-rich pyrite, under chemically reductive conditions. On the other hand, As(V) is the dominant form under oxidative conditions (Nicholas *et al.* 2017). Oxidation of As leads to the dissolution of As-containing minerals into water, resulting in the release of As ions into the aquatic phase (Zhao *et al.* 2017; Drahota *et al.* 2009). Most of the environmental As contamination is the result of natural processes, such as weathering of minerals, biological activities, and volcanic emissions. However, anthropogenic activities, like mining, combustion of coal, and the use of arsenical pesticides and herbicides, alter As dynamics on the earth's surface (Yurkevich *et al.* 2012).

Arsenic toxicity is the result of its carcinogenicity, mutagenicity, and teratogenicity (Qiu *et al.* 2017). Exposure to As through breathing, consumption of contaminated food and/or water, and occupational contact leads to serious effects on human health. Long-term exposure to low doses of As has been linked to skin, liver, lung, and bladder cancers (Abdul *et al.* 2015; Ziegler *et al.* 2017). Over 130 million people worldwide are at risk of diseases related to the presence of As in drinking water in concentrations exceeding the World Health Organization's (WHO) standard limit of 10 ppb (Even *et al.* 2017). Large aquifers characterized by As concentrations exceeding 50 ppb have been reported in parts of Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam, and southern and northern USA (Smedley and Kinniburgh 2002). Localized As contamination associated with anthropogenic activities has been confirmed in many areas and countries around the world. Localized problems related to As contamination are reported in a number of countries, and such instances appear to be on the increase with many new cases surfacing over time (Smedley and Kinniburgh 2002).

The Selenga River is a transboundary waterway that ultimately flows into Lake Baikal in Russia. Two-thirds of the river's watershed falls in the Mongolian territory and one-third falls in that of Russia. Large-scale mining operations have been set up in the upper reaches of the watershed of the river, especially in Mongolia. Furthermore, large tracts of the mid reach of the same watershed have been recently reclaimed for agricultural activities. People who have settled along the river are now facing a critical pollution problem associated with the development of modern anthropogenic activities.

Arsenic concentrations in surface waters, riverbed sediments, and soils of the Selenga River system have been recently documented and published (Hofmann *et al.* 2010, 2015; Inam *et al.* 2011; Thorslund *et al.* 2012; Batjargal *et al.* 2010; Nriagu *et al.* 2012). High concentrations of As were detected in areas of Mongolia surrounding the sites where anthropogenic activities are concentrated. Here the concentration references are Mongolia's drinking water standard (10 ppb) and the country's permissible limit (6 mg kg^{-1}) in surface soils (Batjargal *et al.* 2010; Nriagu *et al.* 2012). The high measured concentrations of As indicate that accumulation or enrichment of As in the tributaries of the river and on the surface soils of its watershed is occurring. An extraordinarily high concentration of As (508 ppb) was detected in the ash basins of the thermal power plant of Darkhan City (Hofmann *et al.* 2010). The average concentration of As in the top soils of

Ulaanbaatar was 14 mg kg^{-1}, which is above the legally permissible level (Batjargal *et al.* 2010). These observations are related to the high content of As in coal, which is the main fuel used in power plants supplying energy to Mongolian cities (Batjargal *et al.* 2010). In Central Mongolia, the main source of coal is the deposits in Baganuur and Nalaikh, which are characterized by high As contents (i.e., over 100 mg kg^{-1}) (WHO 2005).

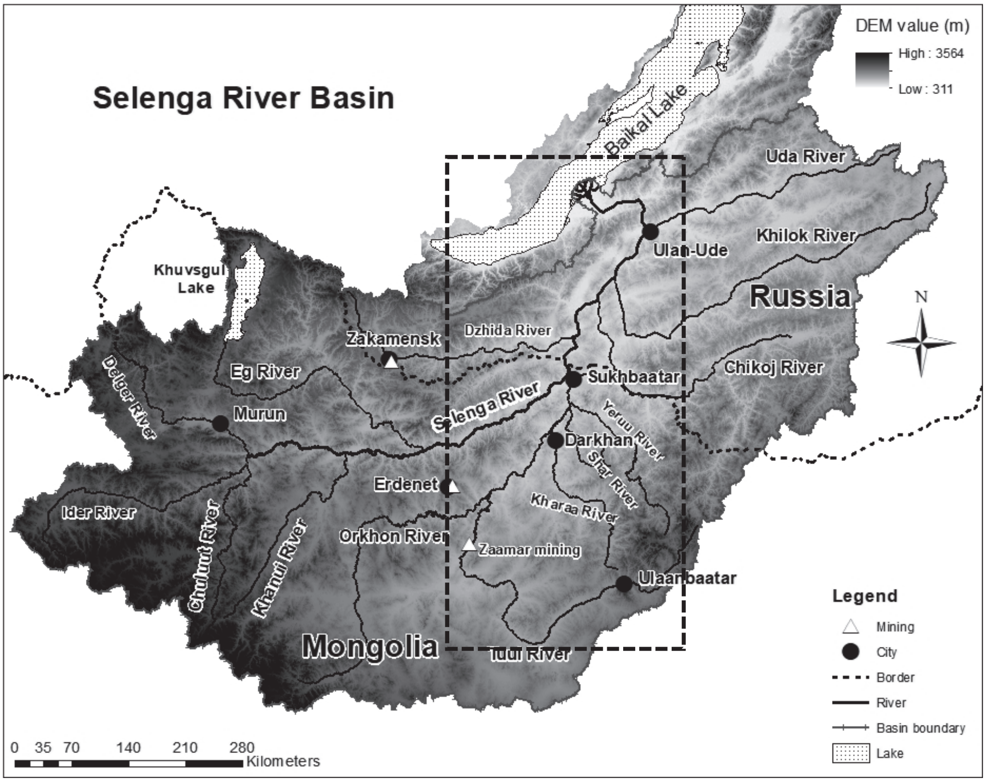

Fig. 1 Elevation map showing locations of tributary rivers, large cities and large mining areas in trans-boundary Selenga River basin. Flow direction of rivers is from northern Mongolia to Lake Baikal in Russia. The dashed square box corresponds to the current study area shown in Fig. 2.

By contrast, only few sources of As pollution are present in the downstream section of the Selenga River watershed that falls in Russia's territory. The concentration of dissolved As was actually lower in the (downstream) Russian tract of the Selenga River than in Mongolia's (Nadmitov *et al.* 2014). The average concentration of As in top soils of Ulan-Ude City, which is the biggest city in the Russian section of the river watershed, was 2.6 mg kg^{-1} (Kasimov *et al.* 2016). This concentration is lower than that measured in the soils of Mongolia's capital, Ulaanbaatar City (11 mg kg^{-1}). Data from these studies suggest that any sources of As pollution are regulated by factors that are different from those that determine pollution from heavy metals.

Most studies on As contamination focus mainly on the metalloid's concentration in ground and river waters, comparing it to the governmental legal limit for human health, since these reservoirs supply water for human consumption and/or irrigation. However, less attention has been paid to the fate of As present in riverbed sediments of freshwater systems. After exposure of rocks and/or sediments to air, As in primary minerals can be oxidized, causing the As hitherto locked in the solid phase to become susceptible to release in water. This oxidation process can occur as a consequence of land surface erosion or artificial excavation. The As released from primary minerals then contaminates the aqueous environment (Fendorf *et al.* 2010), although As presence and concentration in water may be affected by the metalloid's adsorption to, or coprecipitation with, oxides and hydroxides of aluminum (Al), iron (Fe), and/or manganese (Mn) (Cai *et al.* 2017). During in-stream processes, the dynamics of the secondary minerals play an important role as As sinks or sources of contamination by this element, either by lowering the concentration of As in water or by acting as agents of As release into the water. Physical and chemical properties of river water, such as pH, redox potential, the presence of organic matter, and ionic strength, can control the fate of As complexes in tributary systems.

This study aimed to reveal potential sources of As pollution in the Selenga River system and to clarify As contamination dynamics through the transportation and accumulation of this metalloid, as inferred from the distribution of As concentrations in riverbed sediments from the upper section of the watershed in Mongolia to Lake Baikal in Russia, with particular attention paid to the composition and particle size of suspended sediments. An understanding of As dynamics in this system is important to assess the risk of future As pollution in the Selenga River basin.

2. Materials and Methods

Study area

The Selenga River, which is the largest river system in the drainage basin of Lake Baikal, contributes over 50 % of the annual water inflow of the lake and covers 82 % (447,060 km^2) of the drainage basin (Fig. 1). The largest freshwater delta, with an area of 5,000 km^2, has developed by sedimentation of suspended particles at the mouth of the Selenga River (Chalov *et al.* 2015). The Selenga River delta, which is mainly comprised of a huge wetland area, is critically important, and its environment needs to be protected from pollution caused by the upstream release of contaminants.

The river discharge peaks twice a year. The first peak occurs during the snow melting season, around May. The second peak occurs in late summer during July, August, and September, due to heavy rainfall. More than half of the yearly precipitation (60–70 %) concentrates in the summer months. The average water discharge of the Selenga River is 28.7 km^3 year^{-1}, as measured at a meteorological station located close to the Selenga River delta (Lychagin *et al.* 2017).

The part of the Selenga River basin located in the Mongolian territory comprises the first-order tributary Orkhon River and the second-order tributaries Tuul, Kharaa, Shar, Yeruu, and Buir Rivers (Fig. 1). Three major Mongolian cities—Ulaanbaatar, Darkhan, and Erdenet—are located in the Tuul, Kharaa, and Orkhon River basins, respectively. These are very important centers in Mongolia, politically, economically, and culturally (Karthe 2017; Malsy *et al.* 2016). More than half of the Mongolian population lives in these cities. Ulaanbaatar, which has developed in the

Tuul River basin, has a population of approximately 1.5 million, and large factories and industrial complexes are located in this city. Darkhan City, the second largest city in Mongolia, is located in the Kharaa River basin. Iron metallurgy, leather tanning, and meat processing industries are concentrated in this urban area. Erdenet City, the third largest city in the country, is connected to the Orkhon River through a small tributary. In Erdenet, the largest copper and molybdenum mining company in Mongolia is based. Most gold mines are concentrated near tributaries of the Orkhon River, although the largest-scale gold mining operation in the country has been established in Zaamar, which is located in the Tuul River valley (Fig. 1). Intensive and expanding farming operations have been established in the Selenga River basin, particularly in the watersheds of the Kharaa and Shar Rivers. The environment of the biggest river system of Mongolia has, therefore, deteriorated because of urbanization, scarce wastewater treatment systems, rapid mining development, and expansion of agricultural areas in the northern part of the country.

Within the Russian portion of the study area, the tributaries of the Selenga River are located, called Dzhida, Khilok, Chikoj, and Uda (Fig. 1). Ulan-Ude City, which is the capital city of the Russian Republic of Buryatia, is located in the lower section of the Selenga River basin (Fig. 1). This city is the largest, population-wise, in the section of the Selenga River basin in the Russian territory, and it is also the area's largest industrial center. Zakamensk, a town located in the Dzhida River basin, has been a source of heavy metal pollution due to large-scale wolfram–molybdenum mining and processing, which have been conducted in the area since the 1970s (Törnqvist *et al.* 2014). Few studies have been performed on As distribution and dynamics in the area of the industrial complexes located in the Selenga watershed in Russia.

Sediment sampling procedure

Sediment samples were collected in sampling stations in mid-August in 2013, 2014, and 2015 (Fig. 2), when the highest precipitations were recorded for this area. The sediment samples were collected using a sediment sampler (Rigousha, Tokyo, Japan) at sampling sites with high water level, or using a shovel at sites where the water was shallow. The sediments of the riverbed have never been of uniform size, but they are characterized by a wide range of sizes, from boulder to fine silt particles. To understand the dynamics of As in the river environment, sediments that could be transported by the water flow, in other words, those with relatively small particle sizes, ranging between that typical of clay and that of sand (below 2 mm in diameter), were mainly collected. The distribution area of the fine sediments at the sampling site was also taken into account by checking the river bottom condition with a rod and walking. After they were collected from the riverbed, sediment samples were immediately transferred to a plastic bag to minimize exposure to air, and the bags were tightly closed to reduce the risk and extent of sample oxidation. The samples thus collected were then kept in a refrigerator during the travel and transported to Japan for analysis.

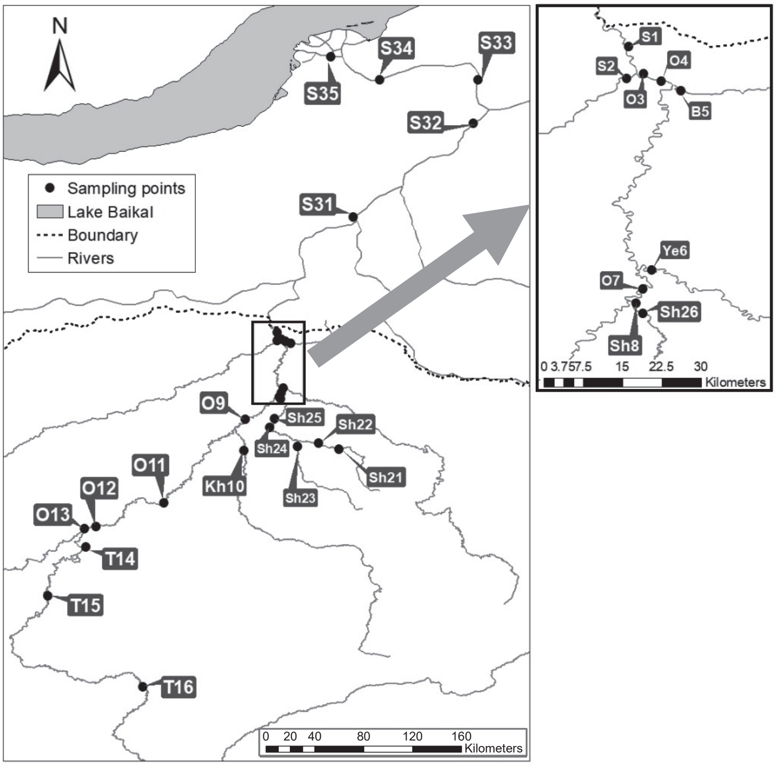

Fig. 2 The map showing geographic locations of sampling points of this study area in the Selenga River basin. Sampling numbers between 1–16 are followed pervious publication (Myangan *et al.* 2017) and those samples were taken during Aug 2013. Sediment samples, which are indicated by Sh21–Sh26, were taken during Aug 2015 in the Shar River watershed. Sediment samples in downstream of Selenga River, Russian territory, which are indicated S31–S35, were taken during Aug 2014. The area in the black square line magnified to the right-hand map.

Sample preparation and analysis

Before analysis, the riverbed sediment samples were freeze-dried. The dried samples were sieved through a 2 mm sieve to remove the present stones. The sieved sediments were finely powdered using a ceramic mortar for chemical digestion and, subsequently, subjected to complete combustion to determine elemental contents. Approximately 500 mg of powdered sediment samples was correctly weighed in a Pyrex® glass tube and digested for more than 12 hours in a 4 : 1 volumetric mixture of concentrated nitric and perchloric acid (4 mL and 1 mL, respectively) in an aluminum block heater kept at 155°C. Notably, this procedure is a modification of the method described by Twyman *et al.* (2005). The digested solutions were analyzed to determine As concentration in the sediment samples using ICP-AES with a hydrogen generator.

The proportion of fine-sized particles, consisting of silt and clay, in the sediment was determined after separation of sediment particles by sieving through a 20 μm mesh.

3. Results and Discussion

Concentration of As in Riverbed Sediments

The concentrations of As in riverbed sediments of the Orkhon–Selenga River system (Selenga River System) are presented in Fig. 3. These concentrations ranged between 1.01 and 4.87 mg kg^{-1}, with an average concentration of 2.84 mg kg^{-1}. The average concentration of As in the Selenga River (2.04 mg kg^{-1}) was lower than that measured in the Orkhon River (3.38 mg kg^{-1}). In fact, As concentration in the Orkhon River was higher than that in the Selenga River at most sampling sites. The Orkhon River itself and/or its watershed is a main contributor to the As contamination detected in riverbed sediments in the entire river system. Changes in water quality of the Orkhon River accompanied by As concentration variations in the sediment can be attributed to land use distribution in the watershed of this tributary of the Selenga River. As concentration in the sediments of the Orkhon River increased along the river course. In particular, As concentration was 2.29 mg kg^{-1} upstream of the merging point between the Orkhon and Tuul Rivers (O13) and 4.79 mg kg^{-1} downstream of it (Fig. 3). The upper course of the Orkhon River is probably less affected by As contamination because of the low level of anthropogenic activity in the relevant watershed compared to the middle and lower courses of the river, even though the largest Cu–Mo mining area is actually located in the upper watershed of the Orkhon River. In fact, one might expect the transportation of As only to take place for short distances from the mining area, because

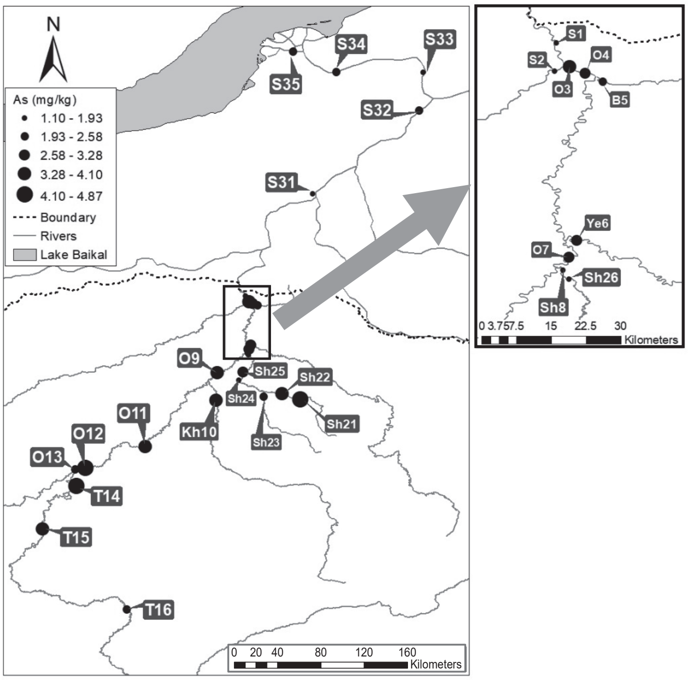

Fig. 3 Concentration of arsenic in the riverbed sediments of the Selenga River system. The area in the black square line magnified to the right-hand map.

of the systems put in place to minimize the leakage of pollutants during metal extraction and purification operations.

Large tract of placer gold mining areas distributes downstream of the Tuul River valley (Figs. 1 and 4). A high level of activity involving the use of heavy machinery for the extraction of gold exists in this region, and the area where these activities take place is currently expanding in size. The concentration of As in riverbed sediments sharply increased downstream of the Zaamar placer gold mining area (4.1 $mg\,kg^{-1}$) with respect to the value of 2.4 $mg\,kg^{-1}$ measured in sediment samples collected upstream of it (Figs. 3 and 4). However, the highest concentrations of As in the riverbed sediments are still lower than those measured in the soils of surrounding areas (13 $mg\,kg^{-1}$), which are mainly composed of alluvial sediments contaminated by ore sediments excavated from the Zaamar mining region (Jarsjö *et al.* 2017). The average soil concentration of As in the Zaamar region also exceeds the maximum permissible level of As (6 $mg\,kg^{-1}$) in Mongolian soils, due to the geochemical characteristics of the local basement rock. The most abundant As ore mineral is arsenopyrite, FeAsS, which is present in the sulfide ores associated with sediment-hosted Au placer deposits (Smedley and Kinniburgh 2002; Goldfarb and Groves 2015). Intensive gold mining activities are a main source of As release from sulfide sediments. In particular, such activities cause As mobilization through water dissolution after As-containing minerals get exposed to air, resulting in As oxidation. On the other hand, the processes involved in mine closure and in the reclamation of excavated sites also lead to a considerable loss of soil and sediments from the mining areas. Jarsjö *et al.* (2017) found that the rate of release of contaminated soil (5.9 $kg\,m^{-2}\,day^{-1}$) from a mining area was much higher than that associated with natural soil erosion (0.16 $kg\,m^{-2}\,day^{-1}$) in the Zaamar area. A banking area obtained after reclamation of an excavated mining site is characterized by loose soil, high variability of soil texture, with high concentrations of heavy metals and metalloids in sediments, and very low plant density.

Elevated concentrations of As (3.6–4.9 $mg\,kg^{-1}$) in riverbed sediments were observed in the upper reaches of Shar River (Fig. 5). These high As contents (Sh21 and Sh22) are probably the result of intensive gold mining activities taking place in the mountainous region of the Shar River watershed (Fig. 5). This region is the main source of riverbed sediments through surface runoff and also release of As contaminants of primary minerals provided from weathering rocks processed in the Khentii Mountain Range. Most of the tributaries of the Orkhon River (the Tuul, Kharaa, Shar, and Yeruu Rivers) originate from the Khentii Mountain Range in Northern Mongolia. Several types of gold deposits occur in this mountainous region, with high levels of geogenic heavy metals and metalloids like As detected (Hofmann *et al.* 2015). Headwater zones of tributaries are intensively affected by gold mining activities. The constant distribution of relatively high As concentrations in the riverbed sediment samples collected along the Orkhon River and its tributaries (O9, Kh10, O11, O12, and T14) is the result of the expansion of these mining activities in the rivers' watersheds (Fig. 3).

In riverbed sediment samples collected in the mid and lower reaches of the Shar River (Sh23–Sh26), relatively low concentrations of As (1.6–2.6 $mg\,kg^{-1}$) were measured with respect to the river's upper reaches (Fig. 5). The decrease in As concentration in these samples is the consequence of the mixing of the relevant sediments with uncontaminated suspended solids (SS) originating from the surface soil and resulting from intensive agricultural land use in the surrounding areas. The mid and lower reaches of this river are dominated by open steppe and lowland landscape, with significant terracing, which is a transition of two main landscapes

(Theuring *et al.* 2015). The main soil type of continental dry grasslands is Kastanozems, which is highly susceptible to cultivation leading to soil erosion The areas dedicated to intensive farming activities have been expanding in Northern Mongolia, resulting in an increase in surface soil erosion and an enhancement of SS release into waterways.

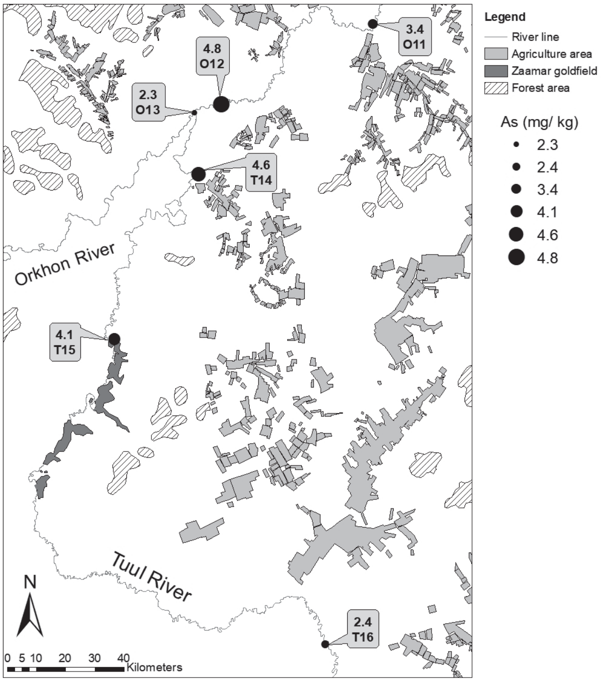

Fig. 4 Concentration of As in the riverbed sediments of downstream of Tuul River.

A slightly elevated concentration of As (3.87 mg kg^{-1}) was detected in the riverbed sediment of the Kharaa River (Kh10) compared to the average concentration of As measured in sediment samples collected along the Selenga River system (2.84 mg kg^{-1}) (Fig. 3). The Kh10 sampling site was located near Darkhan City. A high number of comprehensive studies have been carried out in the Kharaa River basin (Hofmann *et al.* 2010; Inam *et al.* 2011; Pfeiffer *et al.* 2015; Theuring *et al.* 2015; Hartwig *et al.* 2016), which were spurred by the development taking place in the region, where has been addressed as special importance in the sector of industry, mining, agriculture, and animal husbandry. Although As concentration in surface water was mostly observed to fall within the 1–10 μg L^{-1} range (Hofmann *et al.* 2010), extremely high concentrations of this metalloid, reaching up to 508 μg L^{-1}, were detected in several ash basins of the thermal power plant in Darkhan City. Based on the high As concentration measured, coal combustion is speculated to be a point source of As contamination in solid and liquid phases in the Kharaa River. In Central Mongolia, the main source of coal is the deposits in Baganuur and Nalaikh, which are known to be characterized by high As content (over 100 mg kg^{-1}) (WHO 2005).

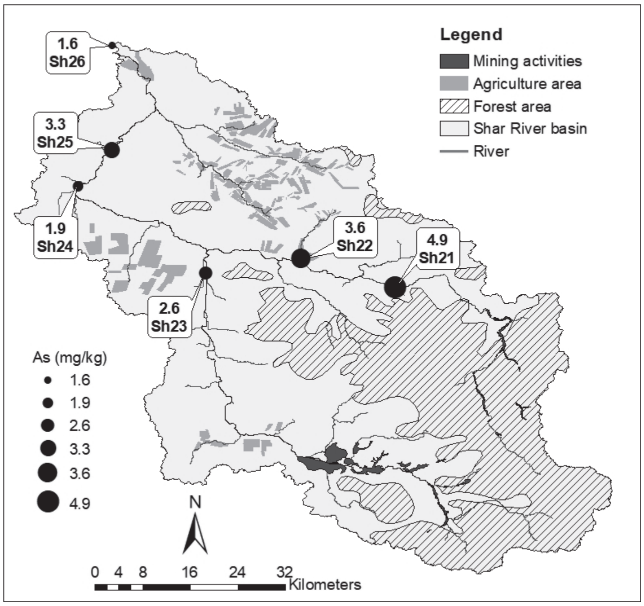

Fig. 5 Concentration of As in the riverbed sediments of the Shar River.

Gold mining activities have been considered the main source of As contamination in the upper reaches of Kharaa River. Several large gold mines (including the Boroo and Gatsuurt mines) are located in this area's mountainous region. In the tailing dam of the Boroo gold mine, the average As concentration in sediment samples was 4.42 mg kg^{-1} (Inam *et al.* 2011). Notably, an exceptionally high concentration of As (49.98 mg kg^{-1}) was detected in rocks of Gatsuurt gold mine locating along Kharaa River (Pfeiffer *et al.* 2015).

The concentration of As in sediment samples collected at the Ye6 site of the Yeruu River was 2.79 mg kg^{-1}, a value close to the average concentration of As in sediment samples collected in the Selenga River system (2.84 mg kg^{-1}) (Fig. 3). The Ye6 sampling site is near the point where the Yeruu River and the Orkhon River merge. The landscape along the Yeruu River is similar to that found along the Kharaa and Shar Rivers, and it comprises mainly areas dedicated to intensive farming and gold mining. No large mining operations have been set up in this watershed, but only small artisanal gold mines. The As concentration in sediment samples collected along the Yeruu River is higher than that measured in the samples collected in the lower reaches of the Shar River. The area dedicated to agriculture in the Yeruu River basin is relatively small, resulting in lower surface soil erosion than that occurring in the Shar and Kharaa River basins. As a consequence, the lower contribution of suspended sediments to the Shar River causes the concentration of As in riverbed sediments to remain relatively high.

Relationship between As concentration and particle size composition

The proportion of fine and coarse particles in the various sediment samples are presented in Fig. 6. The fine particle (<20 μm) content in riverbed sediments ranged from 3.6 % to 69.2 %, with an average value of 22.5 %. A high variation in particle composition was observed in sediment samples collected in the Orkhon River basin compared to that determined for samples collected in the lower section of the Selenga River basin. Spatial variations of the fine fraction contents in the riverbed sediments are influenced by hydrological factors, such as channel bed slope and river discharge, in the research region. Chalov *et al.* (2015) concluded that suspended sediment transport dominated in the upper section of the Selenga River basin, whereas transport of riverbed sediments is considerable in the lower section of the Selenga River (up to 50 % of total transport). High proportions of fine particles were mainly observed at the junctions of two tributaries (48.4 and 69.2 % in sediment samples collected at O12 and O4 sites, respectively). The presence of such high contents of fine particles in the riverbed sediment can be attributed to the coprecipitation and aggregation of fine particles as suspended sediments caused by the mixing of water with different properties from the two tributaries.

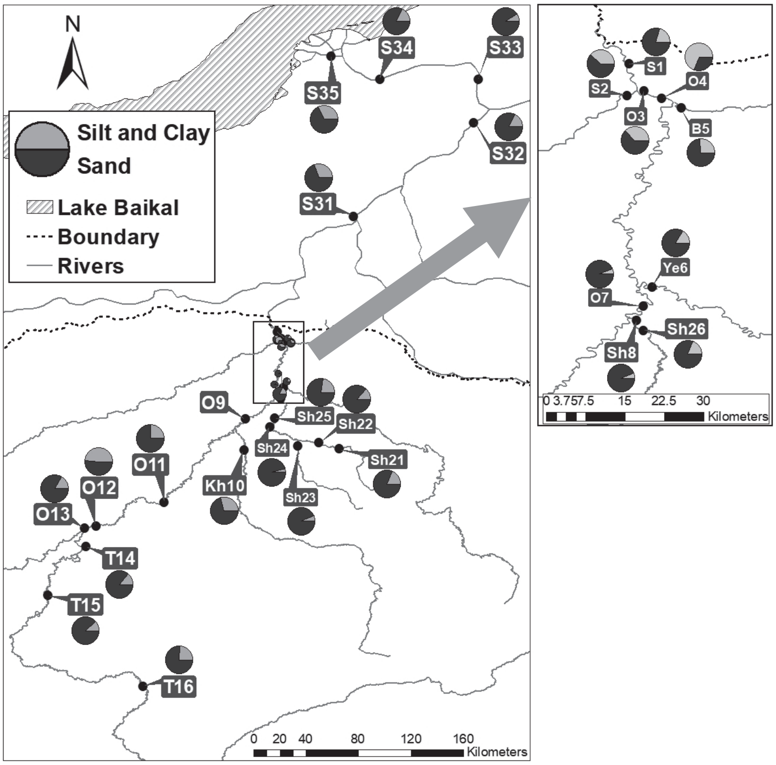

Fig. 6 The rate of fine and coarse fractions in the riverbed sediments of the Selenga River system. The area in the black square line magnified to the right-hand map.

The concentration of As in sediment samples was not significantly correlated with fine particle content (Fig. 7(a)). However, a significant positive correlation between Zn concentration (Myangan *et al.* 2017), which is representative of heavy metal presence in the research area, and the fine particle content in sediment samples was confirmed by the data reported in Fig. 7(b).

These data indicate that the fine particle fraction in sediments is a controlling factor in the accumulation of heavy metals in riverbed sediments. By contrast, in the river system, mobilization of As with sediments does not seem to have a significant correlation with the fine-sized fraction. However, indigenous As in primary minerals characterized by large particle size can disturb the mentioned lack of a relationship between As concentration and particle size. The presence of As in the fine fractions might originate from the dissolution of As as As(V) in $HAsO_4^{2-}$ or $H_2AsO_4^-$, after strong adsorption onto iron oxyhydroxides, hydroxides, and oxides and aluminum and manganese hydroxides (Sengupta *et al.* 2018). These adsorption reactions suggest that riverbed sediments could be a possible source and/or sink of As and could be responsible for the reduction in the concentration of dissolved As to nontoxic levels in the surface waters of the rivers. Naturally high contents of As in the coarse fraction of sediments as a primary mineral might enhance the As concentration in the riverbeds (Jarsjö *et al.* 2017).

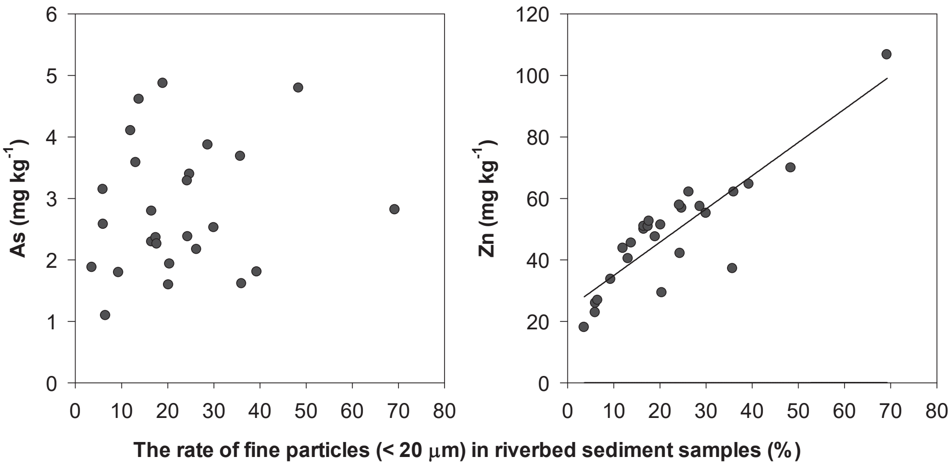

Fig. 7 Relationships between the fine fractions and (a) arsenic and (b) zinc in riverbed sediments of the Selenga River system. Concentrations of Zn in riverbed sediments were referred from Myangan *et al.* (2017).

A trend of increasing As concentration in sediments was confirmed in the Zaamar mining area, from 2.4 mg kg^{-1} (T15) to 4.1 mg kg^{-1} (T14) (Fig. 4), despite the dominance of the coarse fraction at the T14 site (Fig. 6) and an almost equal concentration of Zn at the two sites (Fig. 3). These observations suggest that coarse particles characterized by a high concentration of As, which are released from the Khentii Mountain Range, make an important contribution to the increase in As concentration measured in the bottom sediment. Jarsjö *et al.* (2017) found slightly elevated concentrations of As in sandy-textured soils (15 mg kg^{-1}) compared to soils with a finer texture (13 mg kg^{-1}) sampled from the Zaamar mining area, in locations near the present study area. Baljinnyam *et al.* (2014) also reported the existence of a relationship between As and Zn concentrations in sediments sampled along the Tuul River. In particular, As sediment concentration increased from 10.2 mg kg^{-1} in sites upstream of the Zaamar gold mining area to

50.5 mg kg^{-1} in sites downstream of it; on the other hand, Zn sediment concentration decreased from 57.3 mg kg^{-1} to 20.6 mg kg^{-1} in the same region. In the present study, a reciprocal relationship was also found to exist in the Shar River watershed between the concentrations of As and Zn in riverbed sediment samples collected in the upper versus the lower section of the watershed (Fig. 5). The reciprocal relationship between the concentration of As and that of major heavy metal suggests that a specific behavior of As should be taken into account against environmental pollution due to mining in this area.

4. Conclusion

Arsenic concentration in riverbed sediment samples collected in the Selenga River system was highest in sites downstream of gold mining areas, indicating that gold mining is likely to be the main source of As contamination, probably as a consequence of the in-depth excavation of soils and rocks. As concentration in riverbed sediments did not display any relationship with the proportion of fine-sized mineral particles observed in the same sediments, which is usually a controlling factor in the transportation of pollutants, including heavy metals. Primary minerals of coarse size, on the other hand, contribute to the total concentration of As in the riverbed sediments. Coarse particles characterized by a high As concentration may be released from primary minerals as a consequence of the placer gold mining activities that take place in Northern Mongolia. Those coarse particles quickly deposit after entering into the water stream due to their high density and weight. Coarse particles, therefore, only travel short distances as water-suspended solids, and the primary minerals transported downstream as coarse particles do not reach the lower section of the Selenga River, which is located in the Russian territory.

In the area that follows the point where two tributaries merge, riverbed sediments tend to display a higher proportion of fine-sized particles. The change in water properties that takes place downstream of a river junction, as a consequence of the mixing of the waters from two different tributaries, promotes the aggregation and coprecipitation of SS particles. Dissolved As can be trapped in these SS aggregates during the precipitation process, resulting in a greater concentration of As observed in sediments located downstream of river junctions. These deposition processes can prevent As pollution from spreading to the lower reaches of the river. However, redissolution of As in these sediments should also be evaluated, as it may cause further downstream contamination.

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