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RESEARCH ARTICLE

Spatial and temporal variations of sediment metals in the Tuul River, Mongolia

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Abstract

Mongolia has been a pristine environment without much pollution. Our objective is to study a section of the Tuul River to evaluate the present condition of this pristine environment. Sediment metal (Al, Fe, Mn, Cu, Zn, Pb, Ni, Cd, Hg, and Cr) concentrations and Pb-210 were sampled and analyzed. Results showed that metal concentrations are much higher at areas near the capital city and municipal sewage outlet, with enrichment factor values up to 18 for Cu, and 26 for Cr. Higher copper concentrations were found at sites about ~ 50 km downstream from the source, an indication that pollutions are spreading further down the river. Vertical metal concentration profiles indicated that pollutions could be traced back to the 1960s. Inefficient sewage treatment plants and poorly managed power plant ash ponds were major sources of metals leaking into the Tuul River. Sewage wastewater is carrying metals through Tuul River to the lower river basin. Dusts from ash ponds are airborne and transport to greater area. These findings indicate that new and alternative measures have to be enforced to prevent further pollution entering the Tuul River drainage basin and airborne dust to other broader regions of the Asia and ocean.

Keywords Metal pollution · Sediment · Aerosol · Sewage waste · Ash pond

Introduction

Mongolia is a landlocked country between Russia and China and is best known for the wealth of natural resources and pristine environment. With only 3.2 million people living in the 1.5 million sqm, this makes Mongolia the 18th largest country in the world, and one of the least populated country (NSOM 2018). Major water sources of Mongolian are rivers, lakes, marshes, and groundwater. However, for years, no water pollution management system dealing with pollution control and prevention is fully enforced in Mongolia. Reports on surface and ground waters indicated that pollutants from natural sources and anthropogenic activities may have already existed and may have led to dangerous exposure for human and animals in rural area through direct consumption without any pretreatment (Batsaikhan et al. 2018; Nriagu et al. 2012; Pfeiffer et al. 2015). Pfeiffer et al. (2015) investigated metal concentrations in ~ 300 samples of ground, surface, waste, and drinking water in north-central Mongolia, including Tuul River basin. They have found elevated concentrations of arsenic (As) in about 10% of all drinking and surface water samples exceeding WHO maximum permissible level (10 μg/L) with the maximum concentration reaching 300 μg/L. The elevated levels of metals in natural waters were mainly linked to mining and coal combustion in the study area (Pfeiffer et al. 2015). Batsaikhan et al. (2018) also found 32% of all groundwater samples from the northern part of the Ulaanbaatar city, where most Ger settlements exist,

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showed anthropogenic sources of nitrate contamination, with minimum and maximum concentrations in between 64.0 and 305.6 mg/L. Furthermore, Mongolia is one of the most important sources of Asian dust entering the atmosphere. A huge amount of Asian dust were transported to the ocean (Uno et al. 2009) and could have a detrimental effect should the local pollution become severe.

Tuul River is the main water resource of the capital city, Ulaanbaatar (UB), as well as downstream regions (Sato 2012; Zandaryaa et al. 2003). UB is the largest city and also the most important hub for commerce and industry in Mongolia. Population of the UB city is rapidly increasing in the last several decades and, currently, reaching to more than 1 million, which is close to a half of the entire country's population (NSOM 2018). Since the present and future water supply of Ulaanbaatar and surrounding regions depends completely on surface water and groundwater along the Tuul River, the condition of the Tuul River basin is of prime important not only for a majority of the population's health but also for the future socio-economic development of the country (Sato 2012). Currently, the Tuul River is suffering from anthropogenic pollution, a result of inadequate operation of Ulaanbaatar's central wastewater treatment plant during the last two decades. The river water is polluted for the most part of downstream Ulaanbaatar with concentrations of some contaminants reaching up to 20–30 times higher than drinking water standards by draining ill-treated sewage effluent from the central wastewater treatment plant (Bron and Linden 2012; Dalai and Ishiga 2013). Additionally, in the lower part of the river, heavy mineral and sedimentation pollution from gold mining near the Zaamar area also registered significant imprints on the Tuul river quality.

Despite these pollutions in Tuul River water, at present, little is known on sediment pollution in the Tuul River for both organic and inorganic contaminants (Dalai and Ishiga 2013; Thorslund et al. 2012). According to a previous work conducted on the Tuul River surface sediments (Dalai and Ishiga 2013) near the UB city, relatively lower concentration of sedimentary metals (e.g. Sr, Ni, Th, Sc, and Zr) was found, but with possible indications of anthropogenic pollutions for the toxic trace metals (As, Pb, Zn, Cu, Mn, and Cr). Here, we present the first record of metals (Al, Fe, Mn, Cu, Zn, Pb, Ni, Cd, Hg, and Cr) from twelve short sediment cores down to ~ 50 cm. Our research enables a full investigation of metal pollution status on not only spatial distributions of pristine, urban, and mining areas, but also historical variations through the last hundred year's deposition. Our approach includes (i) to identify spatial distribution of sediment metals in Tuul River sediment, (ii) to evaluate anthropogenic contribution by comparison with average composition of the upper continental crust (UCC), (iii) to establish metal vertical variations by age model from sedimentation rate determination, and (iv) to assess ecological risk by reference to sediment quality guidelines (SQG).

Study area

The Tuul River, one of the three major tributaries of the Orkhon River, is approximately 704 km long with a drainage basin covering 49,840 km^2 in Central Mongolia (Fig. 1). The average altitude of the basin is about 1,350 m above mean sea level, with an average annual precipitation of ~ 250 mm (JICA 1995). Sediments of the Tuul River consist mainly of claystones, siltstones, coal debris, and fine-grained sandstones (Dalai and Ishiga 2013). Neogene and Quaternary red to yellow clays, sands, and gravels are widely distributed in the Ulaanbaatar area and along the Tuul River valley (Dalai and Ishiga 2013; JICA 1995; Zandaryaa et al. 2003).

This study focused on a ~ 500-km stretch of the river, extending both upstream and downstream of the UB city as well as those near the Zaamar mining area. Core samples were taken at four areas, the upper (St. 1301, 1302A, B), urban (St. 1303, 1304, 1305), municipal sewage drainage (St. 1307, 1311, 1308, 1309, 1310), and gold mine (1403) (Fig. 1 and Table 1).

The upper part of the Tuul River basin, ~ 40 km upstream from the UB city, is an area mainly used for pastureland by local rancher and were considered, comparatively, less affected by human activity. Our sample sites start from Terelj (St. 1301) to Nalaikh (St. 1302A, B), where a small stream flows through Nalaikh from the south to the north before merging into the main channel of the Tuul River. Nalaikh is a coal mine, the largest in Mongolia during the last century, with a satellite town located ~ 6 km from the river. The urban and sewage drainage area of the Ulaanbaatar occupies the middle part of the river, extending from Sonsgolon (st. 1303) to Morin Davaa (St. 1305) and from Songino (St. 1307) to Altanbulag (st. 1310), respectively.

Most industries, textiles, tanning, food processing, energy production, and urban constructions are concentrated in the urban zone. Four small tributaries (Selbe, Uliastai, Tolgoit, and Gachuurt rivers) flow through the city from north to south. Air and soil pollution of Ulaanbaatar has become a main problem for residents living in the city (Allen et al., 2014; Cousins, 2019; Naidansuren et al., 2017). Population growth in combination with a major shift from rural to urban has led to major increases in the capital city's air pollution emissions (Cousins, 2019). This situation further deteriorated due to the needs to use coal, wood, and animal waste burning to provide energy and daily household heating because most of the population growth has been in the city's low-income Ger area (Cousins, 2019; Luvsan et al., 2012). This incomplete combustion has led to higher emission of atmospheric pollutants such as ash particulates and toxic gases (Batmunkh et al. 2013; Davy et al. 2011; Luvsan et al., 2012)), accumulations in soil through dry and wet deposition (Batjargal et al. 2010; Chung and Chon 2014), and transfer to the Tuul River by rain wash of soil.

In sewage drainage area, the main pollution source of the Tuul River is the Ulaanbaatar's Central Wastewater Treatment Plant (CWTP), located between Nisekh (Chingiskhaan

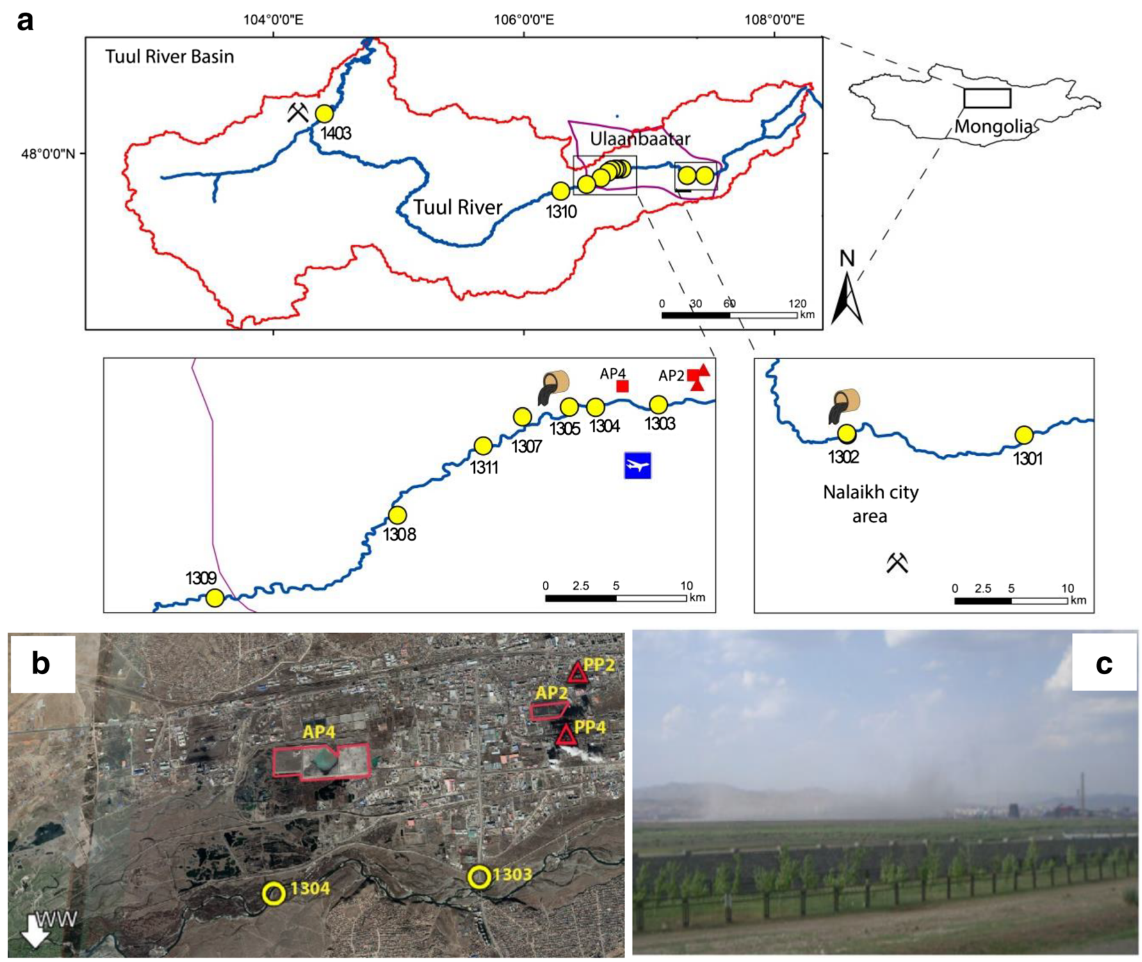

Fig. 1 **a** Study area map and site locations (yellow circles). Red symbols: locations of ash ponds (squares) and power plants (triangles); pipe: location of sewage treatment plant; blue airplane symbol: location of UB city airport. **b** Google Earth map showing location of ash ponds (AP) and power plants (PP) near the sampling sites. **c** Airborne dust aerosol from ash pond (AP4) (adopted from AQA-UB 2013)

airport) and Songino (Fig. 1). The CWTP for the Ulaanbaatar city was established back in 1964 with a designed capacity of 150,000 m^3/day wastewater. The rapid increase of population, compounded by technical, aging, and an overloading of wastewaters (245,000 m^3/day) had already led to a significant increase of treatment plant downtime (Dolgorsuren et al. 2012; Itoh et al. 2011). Consequently, river water quality had deteriorated sharply in this part of the city (especially near Bio and Shuvuu). In order to assess status and ranges of sediment pollution of the river system, we have sampled and investigated pollution status of the region down to ~ 50 km (Albanbulag) from this CWTP source.

Table 1 Study regions, site ID, location, and core length in the Tuul River

Region	ID	Location	Core length (cm)
Upstream	1301	Terelj	22
	1302A	Nalaikh1	30
	1302B	Nalaikh2	27
Urban	1303	Sonsgolon	32
	1304	Nisekh2	34
	1305	Morin davaa	36
Municipal sewage drainage	1307	Songino	20
	1311	Songino guur	46
	1308	Bio guur	20
	1309	Shuvuu	48
	1310	Altanbulag	4
Gold mine	1403	Mongol sov	36

Further downstream, the lower part of the river extends to the Zaamar gold mining area. Gold mining in Zaamar has been active since the 1970s and currently holds the largest gold production in Mongolia, with 147 tonnes produced between 1998 and 2007. Mining in Zaamar employed water sluicing method, either by mechanically dredging or by excavating gold placers with high-pressure water. Earlier studies indicated that mining activities in Zaamar area resulted in a significant increase of metal transport in the downstream Tuul

River–Selenga River–Lake Baikal water systems, especially on suspended loads rather than the dissolved form (Stubblefield et al. 2005; Thorslund et al. 2012).

Materials and methods

Sampling and pretreatment

Sampling was carried out on September, 2013, and August, 2014, at twelve locations through the Tuul River (Fig. 1). Sediments were collected by a hand-push corer to collect undisturbed samples for both vertical and surface variations. All sediments were transported to the laboratory within a few hours for further processing. Sediments were sub-sampled and sub-cored, sectioned into 1 cm with a plastic spatula and stored frozen in the polyethylene (PE) bags. Sediments were freeze-dried, and then ground to fine powder using an agate mortar and stored in PE bags until metal analyses.

Analyses of metals

In order to assess metal pollution in Tuul River sediment, we analyzed concentrations of Al, Fe, Mn, Cu, Zn, Pb, Cd, Ni, Hg, and Cr for each 4-cm depth of the cores except site 1310 which was analyzed for each 1-cm depth.

Analytical method including sample digestion procedures and instrumental analyses for Al, Fe, Mn, Cu, Zn, Pb, Cd, Ni, and Hg was described in (Huang and Lin 2003). In brief, dry sediments (~ 0.25 g) were digested in a Teflon-lined digestion vessel using a CEM microwave (MARS 6). Digested solution was stored in PE vials for analyses. Metals were determined using Hitachi ZA3700 (graphite: for Cu, Pb, Cd) and Perkin Elmer A200 (flame: for Al, Fe, Mn, Zn, Ni) atomic absorption spectrometer. For mercury analysis, sediments were digested in tracer pure 6 N nitric acid (Merck) for 4 h at 90 °C. Mercury determination was conducted using Hg Analyzer (Hiranuma HG-400). Accuracy of the analysis was determined by total dissolution of the NIST-2709 Standard Sediment. Relative standard deviations were better than 5% for most metals. Chromium in the sediment was determined separately from other metals at the University of Minho, Portugal. Grind sediment samples (0.5 g) were digested by aqua-regia (ultrapure HNO_3:HCl, 3:1) in microwave digester (MDS 2000, CEM) and then analyzed by inductively coupled plasma optic emission spectrometer (Optima 8000, Perkin-Elmer). Analytical accuracy was checked by NIST-2702 Standard sediment material and agreed with the certified value within 3%.

Geochronology

Sedimentation rate for a 1304 core sample was measured using the Pb-210 method by alpha counting its daughter, Po-210 (Lin et al. 2000; Nittrouer et al. 1979). A Po-209 spike (Isotope Products Lab, CA) was added to approximately 5 g of dry sediment. Samples were leached by concentrated HNO_3, filtered, dried, and re-dissolved in HCl. After adjusting pH, Po isotopes were plated on silver planchet (23 mm, United Mineral). Polonium activities were determined using EG&G Ortec 576A silicon surface barrier detectors connected to a Seiko EG&G Multi-channel analyzer (7800). Counting errors were usually less than 5%. Sedimentation rate calculation was based on the steady-state distribution of Pb-210 in sediments:

$$\frac{\mathrm{dA}}{\mathrm{dt}} = D\frac{d^2A}{dZ^2} - \omega\frac{dA}{aZ} - \lambda_{Pb}A = 0 \tag{1}$$

where A is the activity of Pb-210; t is the elapse time; D is the particle mixing coefficient; ω is the sedimentation rate; Z is the depth; and λ_{Pb} is the decay constant of Pb-210.

Pb-210 activity in sediments is a combination function of sediment mixing, addition of Pb-210 from new sedimentation, and decay from the parent nuclide to Pb-210 (Eq. (1)). Assuming mixing is insignificant, and then Eq. (1) was reduced to

$$-\omega\frac{dA}{aZ} - \lambda_{Pb}A = 0 \tag{2}$$

which has the solution

$$A(Z) = \mathrm{A}_0\exp[-(\lambda_{\mathrm{Pb}}/\omega)Z] \tag{3}$$

where $A(Z)$ is the activity of Pb-210 at depth Z and A_0 is the initial activity. Apparent sedimentation rates were calculated by applying Eq. (3) to the log-linear portion of the excess Pb-210 distribution since Pb-210 dating sediments assume steady-state deposition, with an exponential decrease of activity from radioactive decay.

Results and discussion

Spatial variations of metals in sediments

Analytical results of metals in sediment core samples are presented in Table 2 with mean concentrations, concentration ranges (maximums and minimums) and compared with average concentrations of upper continental crust (UCC) (Wedepohl 1995) in Table 2 and Fig. 2. Distributions of Al, Fe, Mn, Zn, Cu, Cd, Ni, Hg, and Cr in the Tuul River sediments (Fig. 3) show large variations both spatially and vertically.

Aluminum and iron concentrations (Fig. 2) in the Tuul River sediments were in the range of 2.9–8.3 % and 0.7–3.3 %, respectively. High concentrations of Al were observed mostly in sediments from urban and sewage drainage area (average concentrations, 5.4–7.2%) with some exceptions found upstream (> 6.6%, St. 1301) and downstream (> 6.1%, St. 1403) sediments. Lower

Table 2 Average metal concentrations (mean ± 1sd) (range) in four regions (upstream, urban, municipal sewage drainage, and gold mine) sediments

Metal	UCC[a]	Upstream (n = 19)	Urban (n = 27)	Municipal sewage drainage (n = 39)	Zaamar gold mine (n = 9)
Al (%)	7.7	4.5 ± 1.2 (2.9–6.6)	6.6 ± 0.7 (5.7–8.3)	5.8 ± 1.2 (3.1–7.3)	5.6 ± 0.4 (5.1–6.1)
Fe (%)	3.1	2.1 ± 0.3 (1.6–3.0)	1.6 ± 0.8 (0.83–3.3)	1.8 ± 0.6 (0.71–3.0)	2.5 ± 0.4 (1.9–3.1)
Mn (μg/g)	527	515 ± 65 (370–640)	423 ± 122 (222–705)	459 ± 145 (189–795)	582 ± 115 (395–717)
Zn (μg/g)	52	62 ± 9 (42–74)	43 ± 28 (20–130)	67 ± 43 (22–216)	47 ± 10 (35–64)
Pb (μg/g)	17	20 ± 4 (12–27)	20 ± 6 (15–34)	21 ± 6 (11–34)	16 ± 3 (11–21)
Cu (μg/g)	14	33 ± 32 (4.9–108)	5.6 ± 6.4 (1.3–29)	16 ± 17 (1.8–62)	20 ± 5 (14–27)
Cd (μg/g)	0.102	0.06 ± 0.01 (0.03–0.09)	0.015 ± 0.003 (0.011–0.020)	0.052 ± 0.037 (0.006–0.13)	0.075 ± 0.012 (0.057–0.090)
Ni (μg/g)	18.6	39 ± 8 (23–51)	35 ± 13 (15–54)	33 ± 7 (20–51)	39 ± 6 (32–48)
Hg (μg/g)	0.06	0.02 ± 0.01 (0.002–0.03)	0.014 ± 0.013 (bdl–0.038)	0.025 ± 0.029 (bdl–0.16)	0.016 ± 0.006 (0.008–0.027)
Cr (μg/g)	35	34 ± 39 (8–113)	13 ± 13 (4–35)	78 ± 86 (10–429)	29 ± 7 (18–37)

[a] *UCC*: upper continental crust average (Wedepohl 1995); n: number of samples; *bdl* = below detection limit

concentrations of Al were found mostly in sediments in both sides of the Ulaanbaatar city, e.g., Nalaikh1-St. 1302A (3.1 ± 0.2%) and Altanbulag-St. 1310 (3.2 ± 0.0%). The lowest concentration of Fe in sediment was found at St. 1303 (average, 1.0 ± 0.1%, and range 0.8–1.2%), a site in the urban area. The highest concentration of iron was found at St. 1403 (2.5 ± 0.4% (1.9–3.1%)) from gold mining area (Table 2).

Relatively high concentrations of Cu, Ni, Zn, Pb, and Cr were found not only in downstream sediments near the sewage drainage outlet but also in sediments upstream near the coal mining area. Up to 82 ± 65 μg/g Zn, 0.030 ± 0.043 μg/g Hg, and 98 ± 123 μg/g Cr were found at downstream sewage station 1309 (Shuvuu), 49 ± 6 μg/g Ni and 0.095 ± 0.042 μg/g Cd at urban station 1305 (Morin davaa), 582 ± 115 μg/g Mn at goldmine station 1403 (Mongol sov), and 75 ± 17 μg/g Cu at upstream coal mine station 1302A (Nalaikh1). These are higher than those lower values found in the middle stream urban area sediments near the UB city, with average values 23 ± 1 μg/g Zn, 0.008 ± 0.014 μg/g Hg, 13 ± 13 μg/g Cr, 20 ± 2 μg/g Ni, 277 ± 87 μg/g Mn, 2.0 ± 0.4 μg/g Cu, and 0.015 ± 0.003 μg/g Cd. A higher concentration of Cu (57 ± 3 μg/g) found at St. 1310 (Altanbulag) is slightly lower than the highest concentration (75 ± 17 μg/g) at the upstream coal mine St. 1302A (Nalaikh 1) (Fig. 2).

Unlike other metals, Pb concentration showed less variability between minimum of 16 ± 1 μg/g (St. 1303, Sonsgolon) and maximum of 24 ± 6 μg/g (St. 1305, Morin davaa). Higher chromium concentrations 98 ± 123 μg/g were found at sewage St. 1309 (Shuvuu).

Anthropogenic pollution

The extent of sediment pollution was evaluated using the crustal enrichment factor (EF) (Chen et al. 2007; Huang and Lin 2003; Morillo et al. 2004; Palanques et al. 2017; Qiao et al. 2013). Metal concentrations were normalized relative to the reference element from crust (Wedepohl 1995). The EF is defined as:

$$\mathrm{EF} = \frac{(X/\mathrm{Al})_{\mathrm{sediment}}}{(X/\mathrm{Al})_{\mathrm{crust}}} \quad (4)$$

where $(X/\mathrm{Al})_{\mathrm{sediment}}$ and $(X/\mathrm{Al})_{\mathrm{crust}}$ are the ratios of metal (X) to the Al in sediment sample and average continental crust, respectively. EF < 1 indicates no enrichment, EF = 1–3 is minor enrichment, EF = 3–5 is moderate enrichment, EF = 5–10 is moderately severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment, and EF > 50 is extremely severe enrichment (Chen et al. 2007). Variations of aluminum% were found in between stations indicating grain size changes within the study sites. In order to avoid the grain size effect, metal concentrations were normalized by aluminum% and were compared to the crust metal concentrations to evaluate metal enrichment (Eq. 4).

Large variations in metal enrichment factors (EFs) were found in our study environments (Table 3). Relatively higher EF values (up to 5.9 for Zn, 3.0 for Pb, 11 for Cu, 4.1 for Hg, and 26 for Cr) were found in sediments near the municipal sewage drainage outlet, which received huge amounts of metallic and nutrient pollutant discharged from nearby industrial plants and poorly treated CWTP wastewater. Chromium had the highest EF values among metals in this study. Chromium EF values were frequently larger than ten (range, 0.32–26; average, 3.7), which indicates a higher degree of Cr pollution. Zinc (0.52–5.9), Cu (0.14–11), and Hg (0.02–4.1) also showed relatively higher EF values. Cadmium and Ni exhibited the lowest EF values among metals studied.

Our results demonstrated that one of the major sources of metals entering the Tuul River sedimentary system is the poorly treated effluent discharge from the UB city Central Wastewater Treatment Plant. The CWTP is designed to receive and to

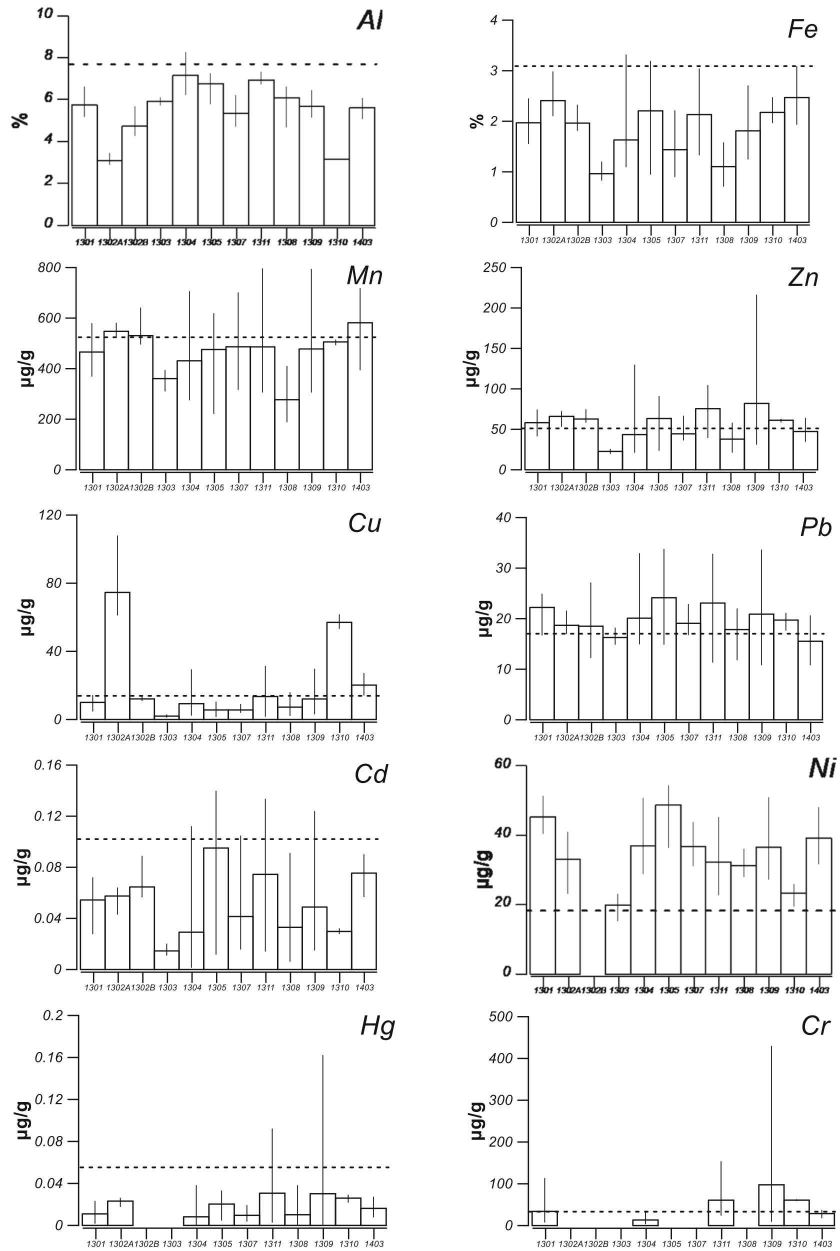

Fig. 2 Average metal concentrations (bar) and concentration ranges (vertical line) in sediments at 12 study stations. Horizontal dashed lines are average corresponding upper continental crust concentrations

process industrial wastewater before draining to the Tuul River. Two of the major industries in the City, leather and wool, use chromium salts to separate fur and leather. These wastewaters were supposed to channel to the CWTP after pretreatment at Khargia Industrial Waste Water Treatment Plant (IWTP) for further treatment. Additionally, tanneries, wool, and cashmere industries in the region used over 30 chemicals for routine processing. The Khargia IWTP was built in 1972, with a designed chemical and biological purification capacity of 13,000 m^3/day. In the last decade, however, Khargia IWTP, accepted only 7,000–8,000 m^3/day of wastewater because of poor technical and operation conditions of this pretreatment facility. Consequently, huge amounts of untreated industrial wastewater were channeled directly into the CWTP and later discharged into the Tuul River without further treatment, resulting in an increasing degree of polluted wastewater discharged directly into the environment, Tuul River, groundwater, and soil (Bron and Linden 2012). Furthermore, volume of municipal wastewater from the UB city has dramatically increased in recent decades due to large population growth that negatively affected the cleaning efficiency of CWTP to less than ~ 70% of its original capacity, which, in turn, led to a release of higher concentrations of metals and other pollutants into the Tuul River (Bron and Linden 2012). In addition, our results show a dramatic increase of Cr concentration in Tuul River sediment (Fig. 2) with increasing distance from the source downstream to St. 1309 (Shuvuu). This shows that dissolved Cr in the river water has been carried downstream by the river to at least ~ 30 km in distance. Very high

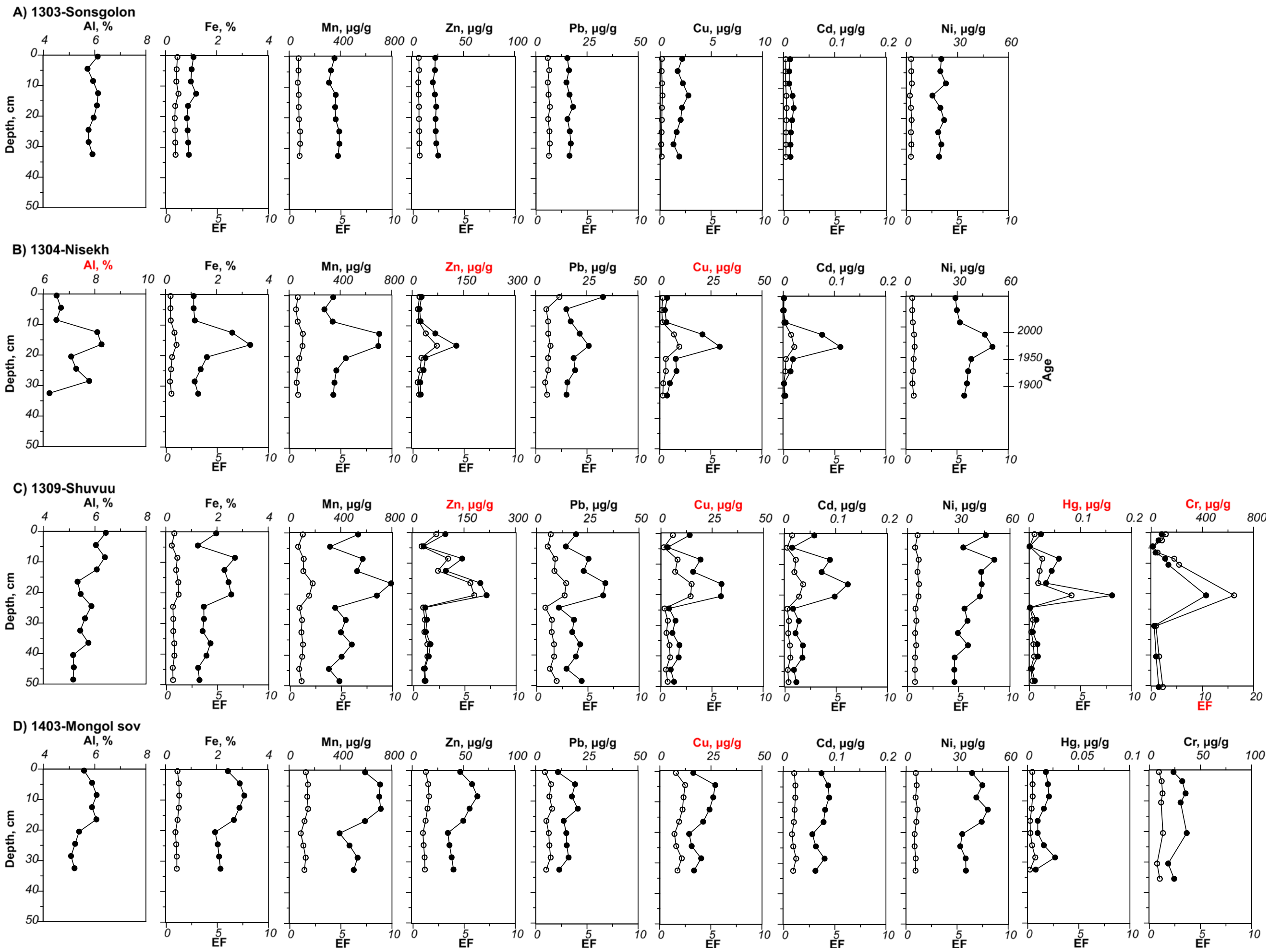

Fig. 3 Vertical metal concentration profiles in Tuul River sediment. (● concentration; ○ crustal enrichment factor). Different scale *X*-axes for some higher value were labeled by red

concentrations of other metals, Zn, Mn, Pb, and Hg, which also appeared at stations near the municipal sewage drainage outlet (Table 2), also supported that the CWTP has been the source of pollution in the region. The combined failures of both waste treatment plants, the CWTP and IWTP, are not only unable to prevent pollutants entering the Tuul River, but instead, are channeling large amounts of pollutants into this major water source of the region.

Pollutants through wastewater treatment plants are not the only source of pollution entering the Tuul River. Sediments upstream of the Tuul River also show a moderate degree of metal contamination with EF values slightly less than those in the municipal sewage drainage area (the highest EF values: up to 3.6 for Zn, 3.3 for Pb, 18 for Cu, 1.2 for Hg, and 6.4 for Cr) (Table 3). The upstream region, as represented by three upstream sites (St. 1301, 1302A, and 1302B), has been considered relatively pristine before. However, metal contamination levels in this part of the Tuul River were significantly higher than we had previously expected. The only possible source of pollution in this section of the Tuul River is Nalaikh city (Fig. 1). Nalaikh city was established in the 1960s for workers of Nalaikh coal mine industry which was one of the largest coal mining sites of Mongolia until it was shut down in the late 1990s. Nowadays, despite the closing of coal mining industry in Nalaikh, population in the area remains at approximately 30,000. Mine wastes as well as city sewage have been drained into the Tuul River with only very limited pretreatment in local treatment plant until 2015, when the sewage system was connected to CWTP of Ulaanbaatar. Cu concentration of 75 ± 17 μg/g and EF values (13 ± 3) reached the highest level at the upstream St. 1302A site (Table 1).

Lead EF values show a unique feature that most values are higher than 1 for all study areas (upstream, urban, municipal sewage drainage, mining), and varied within a very narrow range (average, 1.3–2.1, Table 3). This unusual slightly higher EF value indicates that the source of sedimentary Pb in the Tuul River basin is most likely from atmospheric deposition of automobile emissions of leaded gasoline (Mohiuddin et al. 2010). Concentrations and EF values at the Zaamar gold mine

Table 3 Average enrichment factors (EF) (range), and pollution characters of the Tuul River sediments

	Zn	Pb	Cu	Cd	Ni	Hg	Cr	Pollution characters
Upstream	2.2 (1.1–3.6)	2.1 (1.0–3.3)	5.0 (0.47–18)	1.1 (0.37–1.6)	1.3 (1.0–1.9)	0.60 (0.049–1.2)	1.7 (0.47–6.4)	Moderate pollution, relatively high EF
Urban	0.94 (0.45–2.3)	1.4 (0.91–2.3)	0.43 (0.12–1.9)	0.52 (0.02–1.8)	0.73 (0.34–1.3)	0.38 (0.06–0.64)	0.47 (0.13–0.93)	Background level, low EF
Municipal sewage drainage	1.8 (0.52–5.9)	1.7 (0.71–3.0)	1.9 (0.14–11)	0.67 (0.08–1.8)	0.81 (0.46–1.1)	0.64 (0.02–4.1)	3.7 (0.32–26)	Moderate to severe pollution, high EF
Zaamar gold mine	1.2 (1.0–1.6)	1.3 (0.89–1.6)	1.9 (1.4–2.5)	1.0 (0.80–1.2)	1.0 (0.84–1.1)	0.40 (0.21–0.74)	1.0 (0.84–1.2)	Background level, low EF

area, however, show less pollution with lower metal concentrations in river bed sediment, as well as low EF values (Table 3).

Vertical distributions and historical variations

Vertical profiles of metal concentrations and EF values displayed various degrees of variation at the study regions (Fig. 3), including the urban (St. 1303 and St. 1304), the municipal sewage outlet (St. 1309), and the Zaamar gold mining area (St. 1403).

Deposition of metals in sediments showed clear historical change, especially at stations near the Ulaanbaatar city (St. 1304 and St. 1309), but less in the gold mining area (St. 1403). For St. 1303, at the eastern perimeter of the UB city, metal concentrations were low and with almost no vertical variation. Higher concentrations of metals in surface sediments near the upstream coal mine area did not reach the UB city perimeter. This clearly demonstrates that most of the area in the upper Tuul River remains relatively unpolluted recently.

At the site near UB city, St. 1304, high metal concentrations peaks appeared at depth between 11 and 20 cm, with the highest values at ~ 15 cm from the sediment/water interface (Fig. 3b). In the uppermost ~ 11 cm, however, little metal concentration variation was found. Enrichment factors and metal concentrations (Fig. 3b) remained relatively low in the upper 11-cm sandy sediments, but rapidly increased toward the fine and black sediment layer in the middle and lower sections (12–20 cm) (Fig. 4). This indicates that supply of polluted metals to the area was abruptly overlaid by a layer of coarser material at the top (~ 10 cm). The reason for this abrupt change of metal deposition is due to river gravel extraction operations by construction companies, which occupied this part of the Tuul River to extract gravel between 2000 and 2007 for emerging construction needs in the UB city. Huge amounts of crustal and sandy materials were flushed and deposited at the surrounding Tuul River. According to reports by the Ministry the Environment and Tourism, gravel extraction at this area was terminated in 2007, but some companies and private miners still worked until early 2010s. This supports a rapid drop of metal concentration and enrichment factor at the upper 10-cm sediments. By excluding this top 10-cm sediment, and the assumption that the decrease of metal concentration (~ 12.5 cm) coincided with the year 2000 when gravel extraction started, the sedimentation rate calculated at site St. 1304 is 0.177 cm/year (Fig. 4). Using this age model, ages of major sediment layers in core 1304 were calculated and illustrated in Fig. 3 b.

Concentrations of Zn, Mn, Cu, Pb, Cd, and Ni (highest values at 16.5-cm depth) started to increase at a depth of ~ 20 cm (Fig. 3b). Based on our Pb-210 age model calculation, extra metals started to increase from the early 1960s and peaked at around late 1970s to 1980s. Since no observable higher metal concentration was detected at site 1303 (Fig. 3a), the source of metal was most likely located between these two stations: St. 1303 and St. 1304. The most reasonable source of metal entering the Tuul River near

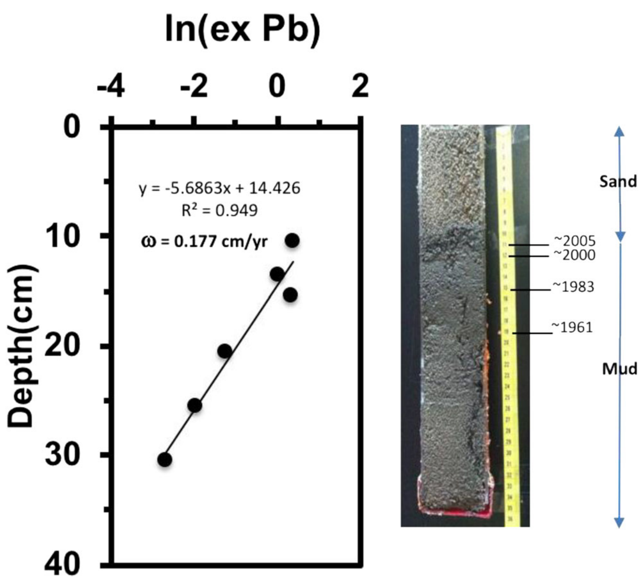

Fig. 4 Age model for 1304 core based on excess Pb-210. Note sediment grain size changes from top sand layer to lower muddy sediments

St. 1304 is the open ash ponds for the coal-fired power plants (Fig. 1). Two coal-fired power plants (PP2 and PP4), established in 1961 and 1983, respectively, in our sampling area supply ~ 60% electricity of the UB city. PP2, PP4, and ash ponds are nearby our sampling sites. As shown in Fig. 3 b, higher metal concentration entering the Tuul River sediment at St. 1304 coincided with the establishment of PP2 and its ash pond (Fig. 1). Usage of the largest coal-fired power plant (PP4) of the UB city and its ash ponds (AP4) in 1983 matched very nicely with metals entering the site sediment further increasing metal concentrations to their highest level in the 1980s (Figs. 1 and 3b). These open ash ponds located on the western part of the UB city, therefore, are one of the main sources of metal-enriched particulate matter to nearby environments, including both river sediments as well as the atmosphere (Fig. 1). According to the air quality agency of UB city (AQA-UB 2013), more than 10,000 tons of ash particles became airborne by wind-blowing per year (Fig. 1c)

Another major source of pollutant was wastewater processing and its direct draining into the Tuul River. At the downstream area of the sewage outlet (core 1309, ~ 30 km downstream), higher degrees of metal concentration variations (Fig. 3c) have been observed. High concentrations of metal peaks were found at depth between 10 and 20 cm in St. 1309 (Shuvuu) for all studied metals with maximum concentrations reaching 2.7% for Fe, 793 μg/g for Mn, 30 μg/g for Cu, 216 μg/g for Zn, 0.12 μg/g for Cd, 51 μg/g for Ni, 0.16 μg/g for Hg, and 429 μg/g for Cr, respectively. The enrichment factors also increased to the highest levels ever found in this study, with EF values of Zn, Pb, Cu, Hg, and Cr equal to 5.9, 2.9, 3.0, 4.1, and 26, respectively (Fig. 3). Furthermore, the appearance of zig-zag features on the vertical profiles of metal concentrations and EF values at St. 1309 indicated that degrees of anthropogenic inputs may have varied considerably with time at this site. Our results show that sources of metal pollutant at this downstream site included industrial, construction, and coal-fired power plant ash. These metal pollutants were either directly entering the River by ash winnowing into or indirectly by channeling through wastewater treatment plants. Waste treatment plants, CWTP and IWTP, were designed to reduce pollutants entering the River. However, either malfunction or insufficient design rendered a worsening of the River system. Due to insufficient cleaning operation of the CWTP, inefficiently treated waste and sewage water, containing various amounts of inorganic (and organic pollutants also), have been pouring into the River for the last several decades irregularly. The combined effect of various degrees of ash ponds entering the River and frequent but irregular malfunction of the treatment plants were the cause for the irregular pattern of metal deposition observed. In addition, construction materials entering the river system could have diluted metal deposition in river by a large amount of coarse-grained sand from mechanical sieving during gravel and sand extraction processes near the site.

Metal concentrations and EF values in the gold mining area (St. 1403, Fig. 3d) increased only slightly, as compared to those larger peaks found at the polluted sites. For most metals (Fe, Mn, Zn, and Cd), maximum concentrations appeared with a broader peak at ~ 10 cm, with up to 3.1% Fe, 717 μg/g Mn, 64 μg/g Zn, and 0.090 μg/g Cd, respectively. When comparing with those UB city polluted samples (e.g., 1304 and 1309), the lesser degree of metal pollution and historical variation at site 1403 indicated that the degree of enhancement for anthropogenic metal pollution in the Zaamar gold mining area along the Tuul River was much lower.

Assessment of ecological risk

With Tuul River sediment metal concentrations and EF factors reaching a high degree of pollution, we initiated an ecological risk assessment of sediment quality based on the SQG guideline (Burton 2002) (Fig. 5). Smith et al. (1996) introduced two assessment parameters, the threshold effect levels (TEL) and possible effect levels (PEL), for the protection of aquatic organisms. Both TEL and PEL values are plotted in Fig. 5. If value exceed the TEL limit, health of the biota in the environment could be affected. If value exceed the PEL limit, biota health condition in the environment will be adversely affected (MacDonald et al. 2000; Smith et al. 1996).

Our results (Fig. 5) show that most metals are below TEL values; however, SQG values and variability (bar length) for samples near the sewage outlets (St. 1304-1309) were higher than other regions. Cr and Ni values are exceptionally high, with some values exceeding PEL limit. Most Cd and Hg values are lower than TEL and PEL. Cu, Zn, and Pb values are slightly higher, with some sites near the sewage outlet reaching TEL limits (e.g., Zn in St. 1309 are higher than TEL limit).

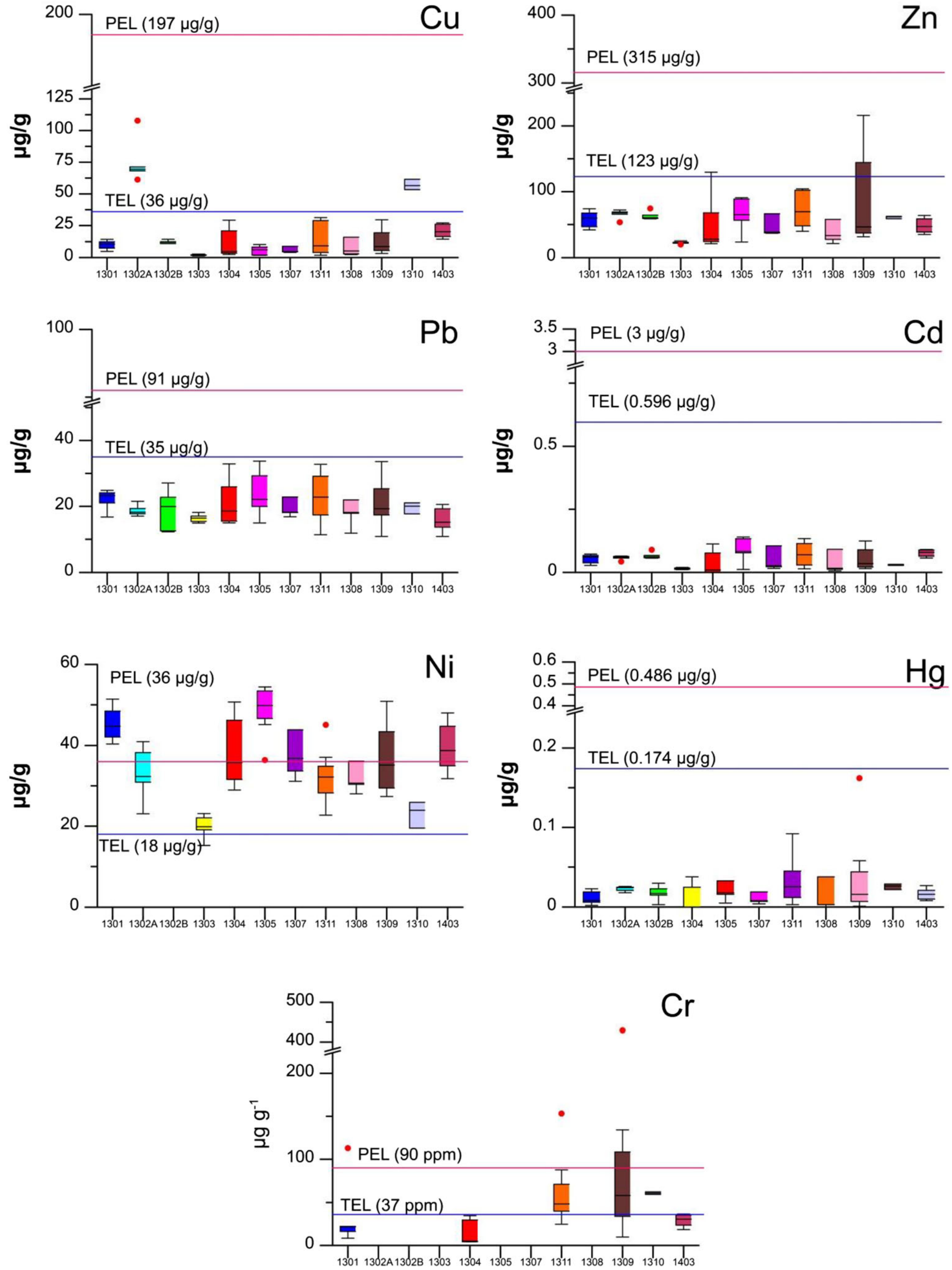

Fig. 5 Tuul River sediment metal concentrations with corresponding TEL (threshold effect levels) and PEL (probable effect levels) values. Small red circles are outliers

Ni concentration (average 37 µg/g, range 15–70 µg/g) exceeded TEL (18 µg/g) at all sites and those at 1301 and 1305 are even higher than PEL limit. This pattern suggested that regional Ni background levels were low and that the increase in the upper and middle reaches represented anthropogenic pollution from urban areas and industries of nearby cities. Zinc concentrations in the Shuvuu area (1309) exceeded the TEL (123 µg/g) (Fig. 5). The appearances of higher Hg values at sewage outlet site also indicated that extra mercury entered the River and reached high values exceeding environmental guideline.

Chromium contents are higher in the urban and sewage drainage area, with samples (St. 1311, 1309, and 1310) exceeding the TEL (37 µg/g) level considerably. Furthermore, several samples of 1311 and 1309 cores (108–450 µg/g) exceeded PEL (91.3 µg/g), up to ~ 5 times more. These higher SQG values indicated a potential impact on biota health (Fig. 5). Tanning leather is one of the most important industries in Mongolia, which is the most likely source of the elevated Cr levels in the study environment. These results clearly demonstrated that Cr from tanneries are discharging a high amount of waste. Most importantly, the CWTP's failure to properly process wastewaters and draining into the Tuul River basin is raising a serious problem for the Tuul River ecosystem. Our results show values exceeding the SQG environmental guideline values. Proper measures have to be implemented before further deterioration of the Tuul River ecosystem.

Conclusion

The distribution, enrichment, and accumulation of metals (Al, Fe, Mn, Cu, Zn, Pb, Ni, Cd, Hg, and Cr) in sediments of Tuul River, Mongolia, were investigated. Results show that signs of pollution existed in the study environment, with large spatial variations of copper, mercury, zinc, and chromium concentrations in the Tuul River sediments, particularly in areas near the Ulaanbaatar city. Natural variation was superimposed by anthropogenic-derived metals for both at the upper river near the UB city, and even to some parts downstream. High levels of metals were found in surface sediments near the sewage treatment plants. Some metal concentrations exceeded the level that could be categorized as toxic to aquatic biota health. Vertical metal concentration profiles show unusual accumulation of metal pollution traced back to the 1960s, reaching the highest level when coal-fired power plants were used to power the UB city. Furthermore, open ash ponds of nearby power plants are most likely the continuous source of metals entering the river sediment and becoming airborne.

Our findings demonstrate that inefficient sewage treatment plants and ash ponds are major sources of metals leaking into this study Tuul River environment. The finding of the ash pond as a source of polluted airborne particles as well as sediments also indicates this pollutant could further propagate to a wider distance, particularly to other parts of Asia. This finding indicates that new and alternative measures have to be enforced to prevent further pollution entering the Tuul River drainage basin and to other parts of Asia and the ocean.

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References

Allen RW, Gombojav E, Barkhasragchaa B, Byambaa T, Lkhasuren O, Amram O, Takaro TK, Janes CR (2013) An assessment of air pollution and its attributable mortality in Ulaanbaatar, Mongolia. Air Qual Atmos Health 6(1):137–150

AQA-UB (2013) Air quality of Ulaanbaatar city and performed works to reduce air pollution (in Mongolian). Air Quality Agency of Ulaanbaatar city, Ulaanbaatar http://aprd.ub.gov.mn/images/pdf/Nacha_tailan/Nacha_tailan_nom_2013.pdf

Batjargal T, Otgonjargal E, Baek K, Yang J-S (2010) Assessment of metals contamination of soils in Ulaanbaatar, Mongolia. J Hazard Mater 184(1):872–876

Batmunkh T, Kim YJ, Jung JS, Park K, Tumendemberel B (2013) Chemical characteristics of fine particulate matters measured during severe winter haze events in Ulaanbaatar, Mongolia. J Air Waste Manage Assoc 63(6):659–670

Batsaikhan N, Lee J, Nemer B, Woo N (2018) Water resources sustainability of Ulaanbaatar City, Mongolia. Water 10(6):750

Bron J, Linden Wvd (2012) Tuul River basin: integrated water resources management. Assessment report. ISBN 978-99962-4-535-0, Ulaanbaatar, Mongolia

Burton JG (2002) Sediment quality criteria in use around the world. Limnology 3(2):65–76

Chen C-W, Kao C-M, Chen C-F, Dong C-D (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 66(8):1431–1440

Chung S, Chon H-T (2014) Assessment of the level of mercury contamination from some anthropogenic sources in Ulaanbaatar, Mongolia. J Geochem Explor 147(Part B):237–244

Cousins S (2019) Air pollution in Mongolia. Bull World Health Organ 97(2):79–80

Dalai B, Ishiga H (2013) Geochemical evaluation of present-day Tuul River sediments, Ulaanbaatar basin, Mongolia. Environ Monit Assess 185(3):2869–2881

Davy PK, Gunchin G, Markwitz A, Trompetter WJ, Barry BJ, Shagjjamba D, Lodoysamba S (2011) Air particulate matter pollution in Ulaanbaatar, Mongolia: determination of composition, source contributions and source locations. Atmos Pollut Res 2(2): 126–137

Dolgorsuren G, Chagnaa N, Gerelchuluun J, Puntsagsuren C, Linden Wvd (2012) Tuul River basin integrated water management plan. ISBN 978-99962-4-553-4. Ministry of Environment and Green Development, Ulaanbaatar

Huang K-M, Lin S (2003) Consequences and implication of heavy metal spatial variations in sediments of the Keelung River drainage basin, Taiwan. Chemosphere 53(9):1113–1121

Itoh M, Takemon Y, Makabe A, Yoshimizu C, Kohzu A, Ohte N, Tumurskh D, Tayasu I, Yoshida N, Nagata T (2011) Evaluation of wastewater nitrogen transformation in a natural wetland (Ulaanbaatar, Mongolia) using dual-isotope analysis of nitrate. Sci Total Environ 409(8):1530–1538

JICA (1995) The study on water supply in Ulaanbaatar and surroundings. JICA. http://www.open_jicareport.jica.go.jp/pdf/11227733_01.pdf

Lin S, Huang K-M, Chen S-K (2000) Organic carbon deposition and its control on iron sulfide formation of the southern East China Sea continental shelf sediments. Cont Shelf Res 20(4):619–635

Luvsan M-E, Shie RH, Purevdorj T, Badarch L, Baldorj B, Chan CC (2012) The influence of emission sources and meteorological conditions on SO2 pollution in Mongolia. Atmos Environ 61:542–549

MacDonald DD, Ingersoll CG, Berger T (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39(1):20–31

Mohiuddin KM, Zakir HM, Otomo K, Sharmin S, Shikazono N (2010) Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. Int J Environ Sci Technol 7(1):17–28

Morillo J, Usero J, Gracia I (2004) Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 55(3): 431–442

Naidansuren E, Dondog A, Erdenesaikhan B, Byambanyam E (2017) Heavy metal pollution near a tannery in Ulaanbaatar, Mongolia. J Health Pollut 7(16):2–11

Nittrouer CA, Sternberg RW, Carpenter R, Bennett JT (1979) The use of Pb-210 geochronology as a sedimentological tool: application to the Washington continental shelf. Mar Geol 31(3):297–316

Nriagu J, Nam DH, Ayanwola TA, Dinh H, Erdenechimeg E, Ochir C, Bolormaa TA (2012) High levels of uranium in groundwater of Ulaanbaatar, Mongolia. Sci Total Environ 414:722–726

NSOM (2018) Web page of National Statistical Office of Mongolia. http://www.en.nso.mn/index.php. Accessed Feb. 2018

Palanques A, Lopez L, Guillén J, Puig P, Masqué P (2017) Decline of trace metal pollution in the bottom sediments of the Barcelona City continental shelf (NW Mediterranean). Sci Total Environ 579(Supplement C):755–767

Pfeiffer M, Batbayar G, Hofmann J, Siegfried K, Karthe D, Hahn-Tomer S (2015) Investigating arsenic (As) occurrence and sources in ground, surface, waste and drinking water in northern Mongolia. Environ Earth Sci 73(2):649–662

Qiao Y, Yang Y, Zhao J, Tao R, Xu R (2013) Influence of urbanization and industrialization on metal enrichment of sediment cores from Shantou Bay, South China. Environ Pollut 182(Supplement C):28–36

Sato H (2012) Mongolia: the water situation in Ulaanbaatar. Social System Review. https://www.cgu.ac.jp/albums/abm.php?f=abm00000294.pdf&n=Mongolia%EF%BC%9A+The+Water+Situation+in+Ulaanbaatar.pdf

Smith SL, MacDonald DD, Keenleyside KA, Ingersoll CG, Jay Field L (1996) A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. J Great Lakes Res 22(3):624–638

Stubblefield A, Chandra S, Eagan S, Tuvshinjargal D, Davaadorzh G, Gilroy D, Sampson J, Thorne J, Allen B, Hogan Z (2005) Impacts of gold mining and land use alterations on the water quality of central Mongolian rivers. Integr Environ Assess Manag 1(4):365–373

Thorslund J, Jarsjo J, Chalov SR, Belozerova EV (2012) Gold mining impact on riverine heavy metal transport in a sparsely monitored region: the upper Lake Baikal Basin case. J Environ Monit 14(10):2780–2792

Uno I, Eguchi K, Yumimoto K, Takemura T, Shimizu A, Uematsu M, Liu Z, Wang Z, hara Y, Sugimoto N (2009) Asian dust transported one full circuit around the globe. Nat Geosci 2:557–560

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59(7):1217–1232

Zandaryaa S, Borhculuun U, Munkhtuya S (2003) Reserves, consumption and contamination of groundwater in Ulaanbaatar, Mongolia. Atlas Urban Geol 14:445–488

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