Hydrogeochemistry and Mineralogy of a River System in a Mining Region with a Cu-world-class Deposit in Mongolia

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Abstract

The present work is reporting the environmental conditions of a river (Khangal River) under the influence of one of the biggest Cu mines in the world: the Erdenet mine, located in North Central Mongolia. The results show that the Khangal River is suffering the influence of the mining works and waste accumulations of the Erdenet Cu mine. The high proportion of calcite neutralizes the acidity potential of sulfides. However, the potential toxic elements represent high environmental risk. In such alkaline conditions and in the absence of mineralogical control, elements such as Mo and As have high mobility, contaminating the ecosystem and preventing the use of water, either for consumption or for irrigation.

Keywords: Erdenet, Khangal River, Potential Toxic Elements

Introduction

Environmental degradation promoted by mining activities is most commonly associated with acid mine drainage processes. However, contamination also occurs in neutral to alkaline mine waters. Some potentially toxic elements (PTE) could show high mobility in such pH conditions.

The Erdenet is a small industrial city with over 100 thousand population in the North-Central part of Mongolia (Ziadat, Jiries *et al.* 2015) and developed along with exploring porphyry copper-molybdenum (Cu–Mo) deposit since 1974 (Battogtokh *et al.* 2014, Ziadat *et al.* 2015, Solongo *et al.* 2018, LCC Monitoring 2021). The city is located in the forest-steppe zone in the Orkhon-Selenge river basins at an altitude of 1300 m above sea level. It has an extreme continental climate characterized by the cooler in the warm season, relatively warm in the cold season with the increasing wind in the spring and autumn, leading to increased dryness and temperature fluctuations (Ziadat *et al.* 2015, LCC Monitoring 2021). The Erdenet mine (Figure 1) is one of the largest open-pit Cu mines in the world and it has been producing around 580 thousand tons of Cu and 5 thousand tons of Mo concentrates annually since 1978 (LLC, 2021, Battogtokh *et al.* 2014, Ziadat *et al.* 2015, Solongo *et al.* 2018, LCC Monitoring 2021).

Along with the production of ores, around 25 million tons of tailings are produced annually and stored north of the city, becoming sources of various environmental pollution (Ziadat, Jiries *et al.* 2015). Currently, the tailing pond contains about 800 thousand tons of mine tailings including slag and liquid. Therefore, such materials might penetrate the local river, the Kangal (Solongo *et al.* 2018). The Khangal flows from the west along with the tailing ponds and mining sites to the east and is used as a water supply by locals even

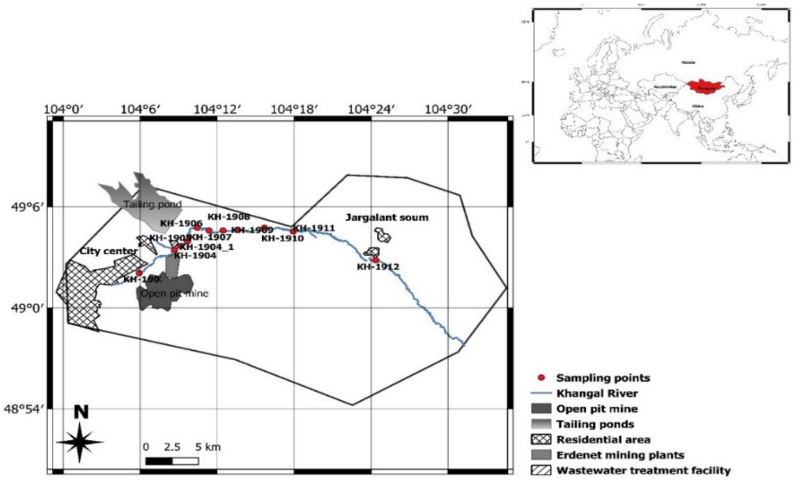

Figure 1 *Sampling points of river and sediments of Khangal River*

though the official drinking water source is the Selenge River (Battogtokh *et al.* 2014, Solongo *et al.* 2018).

Materials and Methods

Eleven sites along the Khangal River were chosen for surface water and sediment sampling (Fig 1). The samples were collected in July 2019 during the warmest season of the year. River water were collected and temperature and pH were measured on-site using a portable multi-parameter meter (Horiba U51), which was calibrated according to the manufacturer's instruction. Water samples were filtered through a 0.45 µm membrane, acidified with HNO_3 and maintained in refrigerated conditions until the further analyses. Sulfate and other major ions for water samples were analysed by ion chromatography (Dionex ICS3000, USA) and metals measured by inductively coupled plasma mass spectrometry (NeXION 300Q, Perkin Elmer, UK). The sediment samples were taken from the uppermost layer of the profile (0–10 cm) using a plastic dipper and a polyethylene bag. Bulk sediment samples were dried at 60 °C, milled, thoroughly homogenized, and two size fractions were obtained: <2 mm and <2 µm. Total concentrations of metals were determined in <2 mm size fractions by inductively coupled plasma mass spectrometry (ICP-MS, NeXION 300Q, Perkin Elmer, UK) and inductively coupled plasma optic emission spectrometry (ICP-OES, Optima 7300DV, Perkin Elmer) at the SGS International Laboratory in Ulaanbaatar, Mongolia. The precision and accuracy of the analyses were checked with the certified reference materials (GBM 901-5, OREAS 501c and NIST2705). The mineralogy of the sediment was studied by X-Ray diffraction in the XRD Lab of University of Minho, Portugal in two size fractions. A mineralogical bulk composition for <2 mm was obtained in the interval 3 to 65 °2θ. The finest fraction (<2 µm) was analysed from oriented aggregates in the interval of 3 to 35 °2θ in order to identify clay and associated minerals.

In order to give proper assessment of the degree of contamination in river sediment, attempts were made to calculate the pollution load indexes (PLI) using the Tomlinson, Wilson *et al.* (1980) approach. The PLI represents the number of times by which the metal concentration in the sediments exceeds the average natural background, and gives a summative indication of the overall level of metal toxicity in a particular sample. We used the average continental crust concentration (Hans and Wedepohl 1995) as a reference background to calculate the PLI as follows:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \ldots CF_n)^{1/n} \quad (1)$$

Where, n is the number of metals (n = 12 in this study). PLI<1 implies that the site is free from contamination whilst, PLI = 1 implies to base line level of pollution and PLI> 1 = deterioration of site quality. The CF represents the individual impact of each trace metal on the sediments obtained using the equation:

$$CF = C_n / C_{ref} \tag{2}$$

Where C_n represents metal concentration in the studied environment and C_{ref} being the background concentration in the environment. Then, CF values were interpreted as follows: CF < 1 low contamination, 1 < CF < 3 moderate contamination, 3 < CF < 6 considerable contamination, 6 < CF very high contamination.

Results and Discussion

Khangal river hydrochemical characteristics

The pH of Khangal River's water was neutral to weak alkaline (pH 7.3 - 8.4), which is high compared to other mine area that possibly receive contribution from mining activities. The concentrations of total dissolved solids is high as indicated by electrical conductivity values that range between 2.28 and 10.1 mS/ cm, and hardness are in range of 4.87 - 19.2 mg-Eq/L. The detailed chemical compositions of the Khangal river's samples are presented in Table 1.

Total dissolved solids and hardness were increased by 52% and 35.6%, respectively since 1973 Battogtokh *et al* (2014), suggesting that pollution increased due to the mining activity. The cation composition of all samples was dominated by Na^+, Ca^{2+}, and Mg^{2+}; the anion composition was overall dominated by HCO_3^- and SO_4^{2-}. Almost all parameters, especially SO_4, Ca, Na, K, HCO_3^- Sr, and Ni were higher at the sampling site KH-1904-1. This site represents special conditions, namely it is stagnant water located at the industrial area and near leakage water from the tailings pipe of the Cu processing plant. The upstream characteristics of Khangal River were previously reported as dominated by sulfate ion but it has now changed to bicarbonate and downstream is dominated by sulfate ions. This is maybe due to seasonal variations in input of sulfate ions. The increased concentration of sulfate in downstream could be related with the oxidation of sulfides in the Erdenet Cu-Mo mine tailings.

As presented in Table 2, the concentrations of dissolved metals and As in the Khangal river water are 933 – 1444 µg/L for Sr, 3.23 – 97.6 µg/L for Mn, 0.7 – 2.66 µg/L for Ni, 34.1– 73.3 µg/L for Mo, 7.88–11.1 µg/L for U, 0.52–4.29 µg/L for V, 1.24–3.2 µg/L for As, and 0.07–2.18 µg/L for Pb. While, the concentrations of Cd (<0.13 µg/L) and Sn (<0.03 µg/L) are comparably low. The mean concentrations of dissolved elements in the water samples were

***Table 1** Major ions and selected physical-chemical parameters of the Khangal River samples (mg/L)*

Sample	T (°C)	pH	EC, mS/cm	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
KH-1903	10.5	7.53	2.28	279	9.8	16.2	81	48.3	29.9	43.4	1.4
KH-1904	15.9	7.30	2.97	360	19.5	9.1	150	84.2	38.8	49.2	7.2
KH-1904-1	20.3	7.50	10.1	1320	8.2	3.4	450	371	7.8	229	84.9
KH-1905	16.5	7.68	3.00	424	10.0	7.8	78	75.5	37.9	46.4	2.9
KH-1906	15.2	7.65	3.32	409	13.7	8.4	180	106	43.1	47.5	2.5
KH-1907	16.2	7.61	3.25	365	13.6	9.2	187	98.6	42.2	44.7	2.5
KH-1908	16.9	7.86	3.17	354	9.7	6.6	128	75.2	39.3	41.2	2.2
KH-1909	17.8	7.95	3.16	180	20.7	13.9	306	92.6	42.5	45.0	2.5
KH-1910	18.6	8.04	3.08	311	16.1	9.3	206	88.9	41.9	46.8	2.7
KH-1911	18.9	8.05	3.00	262	16.8	13.1	227	85.4	40.8	46.2	2.6
KH-1912	20.6	8.40	2.96	201	21.1	9.5	263	81.0	38.5	51.2	2.9

***Table 2** The trace metals concentration of the Khangal River samples (µg/L); bdl – below detection limit.)*

Sample	Cu	Mn	Sr	V	Ni	Mo	As	Cd	Sn	Sb	Pb	U
KH-1903	bdl	bdl	933	1.37	bdl	34.1	1.24	0.08	0.01	0.13	0.07	8.27
KH-1904	22.3	97.6	1267	1.55	2.09	73.3	3.20	0.13	0.02	0.39	0.22	7.88
KH-1904(1)	20.9	129	1540	bdl	88.2	0.85	0.06	0.28	0.07	0.03	0.48	0.52
KH-1905	11.3	50.6	1054	1.72	1.27	44.7	1.95	0.08	0.01	0.25	0.05	8.18
KH-1906	4.49	29.3	1444	0.52	2.66	68.5	1.75	0.10	0.003	0.20	0.18	11.1
KH-1907	4.96	10.5	1360	1.92	1.89	60.7	1.83	0.11	0.02	0.18	0.20	10.3
KH-1908	3.19	3.23	1105	0.93	0.77	60.1	2.05	0.10	bdl	0.21	0.50	9.94
KH-1909	2.29	4.17	1290	1.24	2.01	60.4	1.97	0.13	0.03	0.23	0.09	10.7
KH-1910	7.29	5.15	1230	2.68	2.10	61.5	2.30	0.10	0.02	0.24	2.18	10.2
KH-1911	11.7	5.06	1200	1.92	1.78	58.1	2.16	0.11	0.014	0.25	0.13	10.0
KH-1912	3.42	8.53	1286	4.29	1.71	50.9	2.51	0.10	0.016	0.32	0.17	9.80

decreased by following order Sr>Mo>Mn>U >Cu>As>V>Ni>Pb>Sb>Cd>Sn. Increases in concentration of As, Pb and U in the Khangal River were evident along the mining area and further downstream. In contrast, the concentrations of Cu and Mo in the river water decreased from the upstream to downstream, suggesting the possible precipitation into the sediments or other attenuation processes, such as dilution (Santos *et al* 2012). These dissolved elements should be closely related to the mining activities as the mine tailings discharge potentially toxic elements, thus polluting water resources as referred for other mining systems (Guo *et al.* 2013)

Sediment quality and mineralogy: The results of the analyses of potentially toxic elements in surface sediments from the Khangal River is given in Table 3. Concentrations of total elements at sites KH-1904(1) were much higher than other sites as already observed and discussed for water. The increase in Cu and Mo concentration from the second sampling point may be due to the infiltration of water from the tailing pond, which stores Cu concentrate tailings, into the river. Trace elements were arranged in the following order: Cu > V > Zn > As > Pb > Ni > Mo > Co > U > Cd. Cu concentration in sediment was higher than other metals as a consequence of direct activities in this mining area.

The calculated CFs, Cd, and PLI are presented in Table 4. The contamination factor indicates a difference in the contamination levels for some PTE. Except for the KH-1906 and KH-1910 samples, the PLI index is greater than 1, indicating an anthropogenic origin of metal contamination. From the CF values, stream sediments are heavily contaminated with Cu and Mo, the main components of the ore materials from the Erdenet mine. The CF of As in sediments also indicated by high contamination. In other world contexts, high concentrations of As in sediments have been be attributed to anthropogenic activities such as treatment from the fertilizers and arsenical pesticides industries (Fu *et al.* 2014), treating of wood by exhausting copper arsenate and tanning about some chemicals especially arsenic sulfide (Baeyens *et al.* 2007). However, there are practically no such industries in Erdenet. Therefore, such pollution is should be associated with the mining industry. Indeed, As is closely associated with ores containing metals such as Cu and Pb (ATSDR 2007). The contamination factors for all PTE with exception of Cu, Mo, and As indicated low to moderate contamination degree for other sampling points. The C_d and PLI of sediments samples did not vary between samples. The contamination degree of the sampled points varies, but all points except KH-1906 are found to be very highly contaminated. The accumulation of PTE such as Cu, Mo, and As in the Khangal River is directly related to the operation of the Erdenet

Mining Corporation, but this pollution may be transmitted in several ways. In the fall and spring, when precipitation is low, the white dust from ore dumps and tailings is carried away by the wind and could pollute the soil (Banzragch *et al*. 2018, Chonokhuu *et al*. 2019). This further leaches to the surface water by the runoff of rainwater resulting in the increase of the concentrations of elements in sediments.

The other reason for the contamination of sediments is a leakage from the tailing's impoundment and the temporary storage of tailing materials which discharges from the rock piles with subgrade ore materials. The temporary storage area is located outside of the tailing dam, a few tens of meters away from the Khangal River. It is used for holding tailing materials when the water-recirculation system requires maintenance. There is overflow of the discharge water in the storage due to the strong rainfall resulting in the flooding to Khangal River (Battogtokh *et al*. 2014).

The mineralogy is in accordance with the ore deposit paragenesis and with the geology of the region. Therefore, pyrite was identified by XRD in agreement with the volcano-sedimentary nature of the Erdenet mine. Calcite is one of the most abundant

Table 3 *Concentrations of potential toxic elements in surface sediments from the Khangal River, mg/kg*

Sample	Cu	Mn	Sr	V	Ni	Mo	As	Cd	Pb	Zn	Co	U
KH-1903	74.1	649	684	155	30	9.93	53.6	0.16	24.8	72.4	15.9	2.21
KH-1904	254	537	660	125	19.6	15.7	40.5	0.10	21.7	59.5	12.8	1.3
KH-1904(1)	2094	474	353	77.2	13.7	128	62.4	0.54	73.2	227	12.7	1.71
KH-1905	163	711	740	84.7	16.1	56.9	110	0.10	28.2	61.8	13.1	1.14
KH-1906	137	570	590	73	17.3	8.8	0.5	0.091	19.1	54	12	1.16
KH-1907	174	667	715	77.1	17.4	17.9	48.9	0.096	20.3	62.9	13.5	1.32
KH-1908	100	674	701	55.5	13.3	7.7	29.6	0.057	16.9	46.7	10.8	0.94
KH-1909	49	716	679	83.5	13.4	4.51	44.3	0.06	13.8	54	11.5	1.09
KH-1910	27.1	583	568	49.3	13	4.36	42.8	0.05	11.7	37.7	10.2	0.68
KH-1911	187	620	749	89.3	18.7	16.1	40.7	0.12	21.4	69.7	12.3	1.28
KH-1912	62.3	702	864	107	23.8	4.99	45.6	0.092	17.1	66.6	15.4	1.32

Table 4 *Contamination factors (CF and Cd), the pollution load index (PLI) and pollution rate of sediments sample*

Sample	CF												C_d	PLI
	Cu	Mn	Sr	V	Ni	Mo	As	Cd	Pb	Zn	Co	U		
KH-1903	5.2	1.2	2.2	2.9	1.6	7.1	26.8	1.6	1.5	1.4	1.4	0.9	53.7	1.63
KH-1904	17.8	1.0	2.1	2.4	1.1	11.2	20.3	1.0	1.3	1.1	1.1	0.5	60.9	1.48
KH-1904(1)	147.	0.9	1.1	1.5	0.7	91.5	31.2	5.3	4.3	4.4	1.1	0.7	289.6	2.06
KH-1905	11.4	1.4	2.3	1.6	0.9	40.7	55.0	1.0	1.7	1.2	1.1	0.5	118.7	1.56
KH-1906	9.6	1.1	1.9	1.4	0.9	6.3	0.2	0.9	1.1	1.0	1.0	0.5	25.9	0.98
KH-1907	12.2	1.3	2.3	1.5	0.9	12.8	24.5	0.9	1.2	1.2	1.2	0.5	60.5	1.44
KH-1908	7.0	1.3	2.2	1.1	0.7	5.5	14.8	0.6	1.0	0.9	0.9	0.4	36.3	1.12
KH-1909	3.4	1.4	2.2	1.6	0.7	3.2	22.2	0.6	0.8	1.0	1.0	0.4	38.5	1.17
KH-1910	1.9	1.1	1.8	0.9	0.7	3.1	21.4	0.5	0.7	0.7	0.9	0.3	34.0	0.94
KH-1911	13.1	1.2	2.4	1.7	1.0	11.5	20.4	1.1	1.3	1.3	1.1	0.5	56.5	1.53
KH-1912	4.4	1.3	2.7	2.0	1.3	3.6	22.8	0.9	1.0	1.3	1.3	0.5	43.1	1.43

minerals, which reflects the lithology of the Permian Khanui Group volcanics, composed of alkali-rich trachyandesite. The mineralogy of the fine fraction is dominated by calcite, mica and quartz. Among clay minerals there is a 14 Å phase, kaolinite, and traces of smectite. Goethite was detected in trace or small proportions. Therefore, beside traces of goethite, other iron oxyhydroxides and high proportions of clay minerals known by their ability to retain PTE were not detected. Such an absence may contribute to dispersion of contamination along the river.

Conclusion

The Khangal River is suffering the influence of the mining works and waste accumulations of Asia's largest Cu mine. In addition to the beneficiation processes, the high proportion of calcite should contribute to neutralize the acidity potential of sulfides in the ore paragenesis. However, PTE represent high environmental risk. Water pH was in the range of 7.30-8.40. In such alkaline conditions and in the absence of mineralogical control, namely by adsorption at the surface of iron oxyhydroxides and smectite, the elements such as Mo and As have high mobility, contaminating the ecosystem and preventing the use of water, either for consumption or for irrigation.

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