The Role of Natural Attenuation in the Decrease of Metal Concentration in a River Polluted by AMD Released from Sungun Mine (NW of Iran)

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Abstract

The self-purification potential of rivers contaminated by Acid Mine Drainage (AMD) released from the tailings dump of the Sungun mine (NW of Iran) and the bioaccumulation potential of suspended and floating algae in the rivers were studied. By moving away from the mine and via contact of AMD with limestone pebbles in the riverbed,metal concentrations decrease due to the increase in pH. Dilution due to mixing with other stream brunches also has a considerable effect on natural attenuation. The population density of algae illustrated an adverse relationship with metal concentration and algae showed a high capacity to bioaccumulate metals.

Keywords: Natural attenuation, Metal pollution, Surface water Pollution, Algae bioaccumulation

Introduction

Mining has been identified as one of the major sources of metal pollution in surface water (Gao *et al.* 2022). Acid mine drainage (AMD) is attributed to mining for minerals such as Cu. AMD enters nearby freshwaters and has substantial adverse effects on aquatic biodiversity, reducing the value of the water for agricultural, recreational or industrial uses, and making it unsafe for human consumption (Tripole *et al.* 2006). Some AMD is treated naturally through increasing the pH, which causes precipitation of oxide and hydroxide minerals which effectively adsorb metals and metalloids in AMD (Chikanda *et al.* 2021). Using organisms is a valid method for estimating the existence of metals and their availability in an aquatic system. Algae have the ability to accumulate metals within their organs (Hamidian *et al.* 2016) and they have proven to be reliable indicators for monitoring metals in aquatic environments (Ali *et al.* 2021). Besides, algae are the first link in the aquatic environments food chain and as such any effect on them has ripple effects on subsequent members of the food chain or trophic levels (Abirhire and Kadiri 2011). Shamshad *et al.* (2015) tested four freshwater algae for their bioaccumulation capacity for cadmium (Cd), chromium (Cr) and lead (Pb) in a controlled environment. The results indicated that the removal of metals was higher with low levels of metals in aqueous solutions. The results of a study by (Bakatula *et al.* 2014) demonstrated that algal biomass could be used as an efficient biosorbent for the treatment of trace element-bearing wastewater.

Sungun copper mine is a porphyry copper-molybdenum mine located in NW of Iran. The main environmental and social challenge in this area is high levels of metal pollution because of mining activities, which affected the surface water and aquatic organisms. In this research, the amount of pollution in surface water by metals are evaluated. The potential of natural attenuation and the bioaccumulation potential of algae are also studied to help decision makers and authorities in conducting future remediation scenarios.

Study area

Sungun copper mine, as the largest open-cast copper mine in the NW of Iran, has been exploited since 2008 (Nasrabadi *et al.* 2009). This valuable porphyry deposit is located on the international metallurgical belt called Alp Himalaya in East Azarbaijan province, 105 kilometers northeast of Tabriz, NW of Iran and has been known for almost one billion tons of sulfide copper ore reserve (Rezaei *et al.* 2020). Ilgineh basin is the main basin in the area, in which Sungun and Pakhir Rivers are the permanent rivers, flowing in this area and the ore deposit is located between them. Mine tailings which are deposited in Pakhir valley are drained by Pakhir River at the foot of the tailings. This drainage causes dissolution of minerals, such as malachite Cu_2 (CO3) $(OH)_2$ and azurite Cu_3 $(CO3)_3(OH)_2$, releasing metals and producing acid mine drainage (AMD) (Aghili *et al.* 2018) (Fig. 1).

Materials and methods

Nine surface water points were sampled in winter 2019 and summer 2020 and collected in pre-cleaned plastic bottles to evaluate the quality of surface water and the concentration of toxic metals (Hg, Zn, Mn, Al, Ag, Ni, Pb, Fe, Cu, Cr, Cd and B) in Sungun copper mine area (Fig. 2). Sampling was done from the branches of Ilgineh river, which is the main limited drainage system of the mine, and also from the beginning of Ilgineh itself. The suspended algae and algae floating in the depth of 1 to 15 cm of water were collected at the sampling stations in order to investigate the existence of microorganisms in the surface water. One litre (1L) polyethylene (PET) containers were used for sample storage. They have been rinsed three times then filled completely and then sealed to avoid interfering reactions with the air. Then they were acidified to pH < 2 using concentrated reagent-grade HNO3 and were stored on ice until analysis. Physicochemical parameters were measured in situ such as temperature (°C), EC, TDS and pH using a HI98194 multi-parameter probe. PET containers with few cc of formaldehyde to fix the samples for algae samples and one-liter containers for other samples, were used.

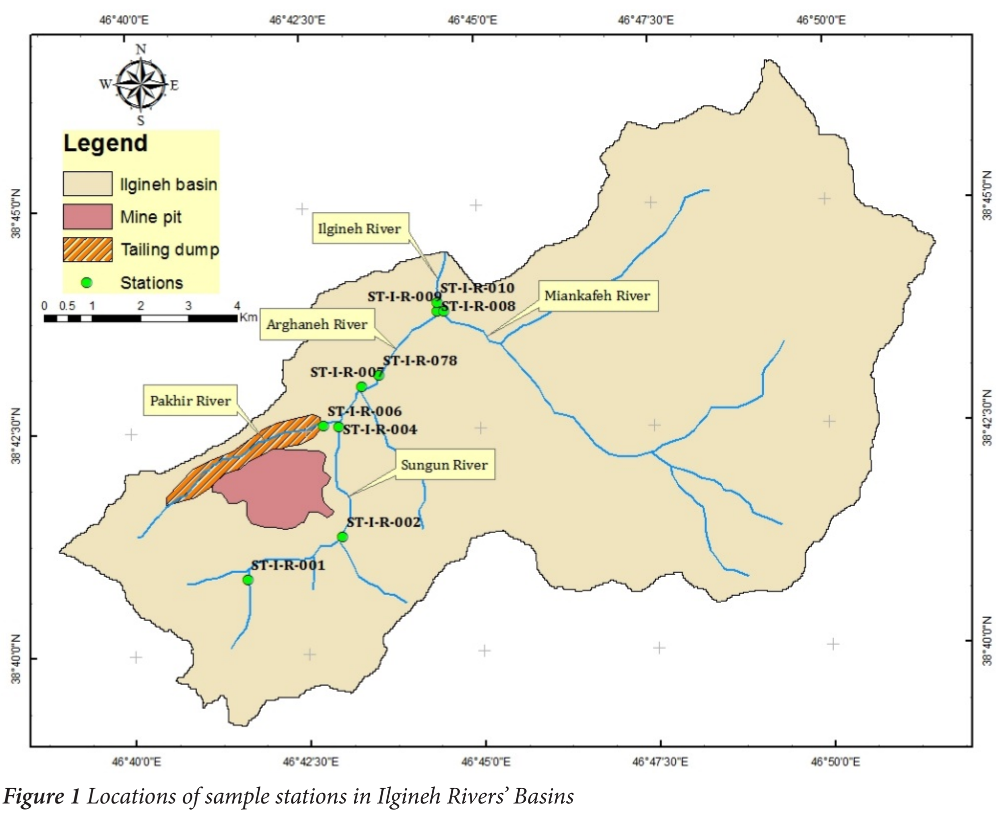

***Figure 1** Locations of sample stations in Ilgineh Rivers' Basins*

The samples were then transported to the laboratory. The titrimetric method was used to determine the carbonate and bicarbonate concentrations. Analytic jena_specord200 device was used to quantify the phosphate, nitrite, nitrate and fluorine. All the metals were measured using an atomic absorption device (Jene_vairo06 analytical model). The algae samples were prepared according to the standard methods (Abirhire and Kadiri 2011) and then transferred to the soil science laboratory of Tabriz University to study their population and bioaccumulation capacity for metals. Bio-concentration factor (BCF) is one of the indices that shows the direct absorption of chemical compounds by living organisms through the water they are living in (Barron 1995). In addition, the amount of the bio-concentration factor can indicate the ability of the intended organisms to remediate the pollutants (Sasmaz *et al.* 2008). BCF is obtained using the following equation (Chiou 2003):

$$BC = \frac{\text{(Concentration of pollutant in living organisms)}}{\text{(Concentration of pollutant in river water)}}$$

Results and discussion

Based on the obtained results, temperature, pH, TDS, TSS, ES and turbidity as well as TH, CH, NCH, nitrite, nitrate, phosphate, BOD and COD for all stations in Ilgineh basin in warm and cold seasons were obtained. The distribution of the concentration of 12 metals (Hg, Zn, Mn, Al, Ag, Ni, Pb, Fe, Cu, Cr, Cd and B) was analyzed in samples from cold and warm seasons (Tables 1-2). The concentrations of boron, chromium, silver, nickel and lead in in cold and warm seasons were below the detection limit. In this research, the highest concentration of metals is related to the stations that have the shortest distance from the tailings dump as in previous studies in this area (Aghili *et al.* 2018; Azizi *et al.* 2021; MollapirirLivari 2013)

There is a direct relationship between low pH and high concentration of Cu, Mn and Zn. The concentration of these elements increases with the decrease of pH in stations ST-I-R-006 and ST-I-R-007. However, the pH increases toward the downstream, due to the reaction of the water with the existing limestone of the river bed (Fig. 3).

***Table 1** Concentration of toxic metals in water samples during the cold season (mg/L)*

Cu	Mn	Cd	Zn	Hg	Al	Fe	Stations
0	0	0.0044	0.12	0	0.0124	0.1	ST-I-R-001
0	0	0	0	0	0.0115	0	ST-I-R-002
0.42	0.74	0.0072	0.41	0.107	0.0142	0.23	ST-I-R-004
70.47	21.17	0.0517	3.2527	0.416	0.0174	0	ST-I-R-006
63.1	21.52	0.0493	3.322	0.31	0.0113	0	ST-I-R-007
0.38	0.56	0.0086	0.774	0	0.0106	0.32	ST-I-R-078
0	0	0.0042	0	0	0.0113	0	ST-I-R-008
0	0	0	0	0	0.0134	0	ST-I-R-009
0.29	0	0.0037	0	0	0.0123		ST-I-R-010

***Table 2** Concentration of heavy and toxic metals in water samples during the warm season (mg/L)*

Cu	Mn	Cd	Zn	Hg	Al	Fe	Stations
0.23	0.15	0.026	0	0	0.05	0.046	ST-I-R-001
0.35	0.18	0.007	0	0	0.084	0.12	ST-I-R-002
3.03	0.22	0.003	0.087	0	1.07	5.32	ST-I-R-004
50.1	24.22	0.4	1.33	0	41.66	5.67	ST-I-R-006
40.75	21.72	0.032	1.22	0	40.5	4.74	ST-I-R-007
1.14	3.68	0.033	0	0	0.022	0.5	ST-I-R-078
1.64	2.35	0.023	0	0	0.029	0.1	ST-I-R-008
0.15	0.13	0.006	0	0	0.014	0.18	ST-I-R-009
0.85	1.84	0.014	0	0	0.019	0.34	ST-I-R-010

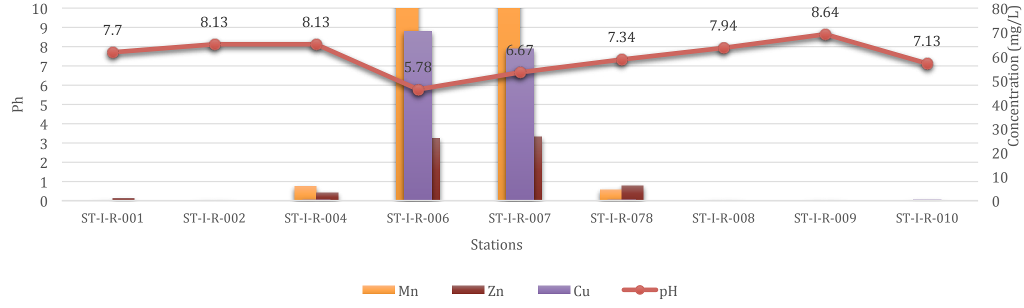

***Figure 2** Changes in concentrations of Cu, Mn and Zn according to pH*

Water samples taken in the cold season from the Ilgine River at the sampling depth of 1 to 15 cm illustrates the absence of algae population in the cold season. In the warm season, most of the algae in the Ilgineh basin waters are cyanobacteria and diatoms. The effect of copper as the main pollutant in Ilgineh basin on the population density of algae demonstrates that the highest population density of microorganisms occurs at station ST-I-R-004, which is before the Sungun and Pakhir Rivers' adjoining in which, there is not high concentrations of Cu. Increasing concentrations of metals such as Cu is observed due to the passage of Pakhir River through the tailing dumps in the Pakhir Valley. As a result, the concentration of algae in the next stations declines to zero. However, there is a peak in station ST-I-R-009, which is due to the joining of the Miankafeh River the impact of dilution (Table 3)

The bioaccumulation potential of Cu, Cd, Mn and Zn as the main pollutants in the rivers in the area was investigated in the algae samples floating on the surface of the rivers of Ilgineh basin (warm season). In station ST-I-R-001 located in Sugun River, where no tailings have been discharged, the bioaccumulation of metals is low (263.12 mg/kg). The concentrations of the analysed metals in river water in this station are also low. After moving downstream and joining the Pakhir River, which is passing through the tailing dumps, accumulation of metals in algae increases considerably. So that the highest amount of accumulation in algae for Cu, Cd, Mn and Zn elements in station ST-I-R-08 is 16761.07, 14.7, 104.89 and 1358.57 mg/kg, respectively. With the increase in the amount of pollution and biological accumulation of these elements in the algae, their population density decreases from 103 numbers per mL in station ST-I-R-001 to 36 numbers per mL in station ST-I-R-008, which means that there is an adverse relationship between them (Fig. 3) (Fig. 4).

***Table 3** Population density of algae in warm season sampling stations of Ilgine Basin*

Samples	Depth for sampling	Cyanobacteria (%)	Diatom (%)	Average algae per ml
ST-I-R-001	0 – 15 cm	0	100	4
ST-I-R-002	0 – 15 cm	0	100	3
ST-I-R-004	0 – 15 cm	0	100	13
ST-I-R-006	0 – 15 cm	0	100	5
ST-I-R-007	0 – 15 cm	0	0	0
ST-I-R-078	0 – 15 cm	0	0	0
ST-I-R-008	0 – 15 cm	0	0	0
ST-I-R-009	0 – 15 cm	0	100	4
ST-I-R-010	0 – 15 cm	0	0	0
ST-I-R-001	Floating algae	34%	66%	103
ST-I-R-078	Floating algae	28%	72%	50
ST-I-R-008	Floating algae	42%	58%	36
ST-I-R-009	Floating algae	0	100%	60

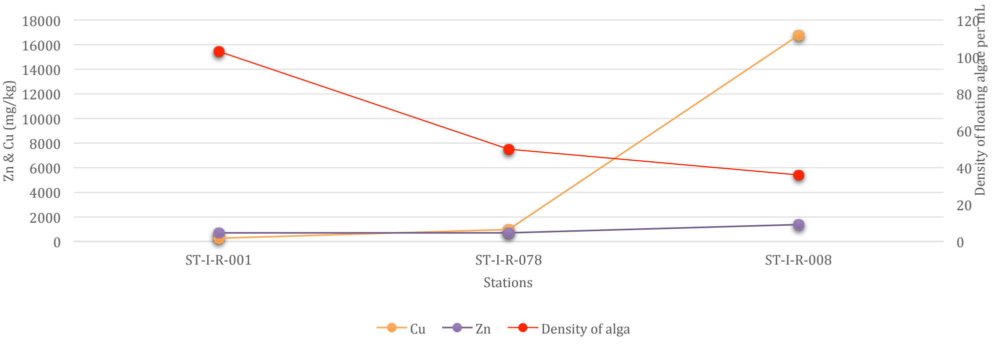

***Figure 3** Cu and Zn bioaccumulation in floating algae (mg/kg)*

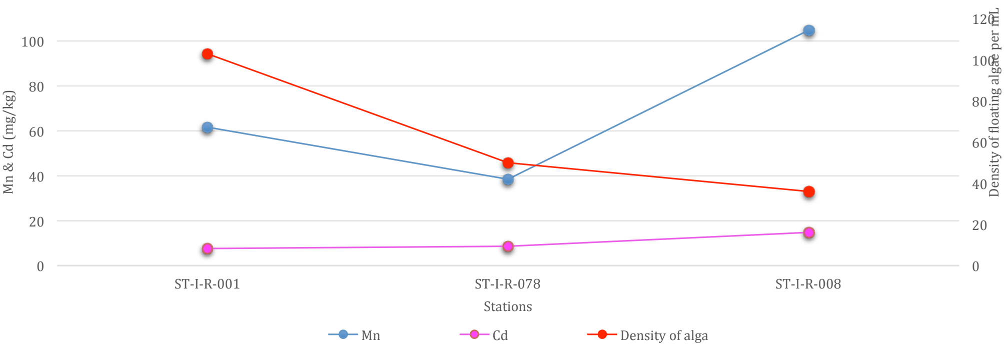

***Figure 4** Mn and Cd bioaccumulation in floating algae (mg/kg)*

Bio-concentration factors indicate high accumulation of metals in algae. According to the results, copper has the highest bioaccumulation potential among the main pollutants in the study area (Tab. 6).

Conclusions

Cu, Mn and Cd were recognized as the main pollutant metals in Ilgineh Basin. The highest amount of pollution was found near the tailings in Pakhir Valley, but there is an inverse relationship between pH and the concentration of metals in water samples due to the reaction with the limestones of the riverbed. The water temperature and the concentration of pollutants affect the amount of blue - green algae and diatoms in the study area. Algae have been affected by mining activities, so that in the stations with high concentration of metals, their population density becomes zero. There is an increase in bioaccumulation of metals in algae and decrease in metals concentrations in river water by moving downstream in Ilgineh Basin. The process of self-purification in this basin is highly active and is influenced by the limestone bed of Ilgineh river, the dilution of pollutants due to water entering from sub-branches such as Miankafeh River and the role of algae. It is recommended to use a suitable impermeable surface to prevent the infiltration of precipitation into the tailings as the main source of pollution is related to tailling dumps. Besides, it is suggested

***Table 4** Bioconcentration factor (BCF) for elements copper, cadmium and manganese in sampling stations*

BCF (Mn)	BCF (Cd)	BCF (Cu)	Stations
411.2	289	-	ST-I-R-001
10.45	259	2550	ST-I-R-078
44.63	639	-	ST-I-R-008

to investigate the ability of each species in bioaccumulation by cultivating different algae species in the study area.

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