# Heavy Metal Pollution in Water and Sediment of the Cherat River affected Zirab Coal Cleaning Plant, Mazandaran province, Iran

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## Abstract

Concentration, origin and fractionation of heavy metals in water and sediment around the Zirab Coal Cleaning Plant (ZCCP) have been investigated in this study. For this purpose, eleven water and sediment samples were collected from the Sheshrudbar (as background) Cherat and Talar Rivers as well as the ZCCP and drainages. Generally, the predominate water type in ZCCP was $Ca^{2+}$-$SO_4^{2-}$; while, in the Cherat and Talar Rivers, and also the ZCCP drainages were $Ca^{2+}$-$HCO_3^-$, $Ca^{2+}$-$SO_4^{2-}$-($HCO_3^-$) and $Ca^{2+}$-$HCO_3^-$-($SO_4^{2-}$), respectively. Water samples in the ZCCP and its direct drainages tested with a high metal load; whereas samples taken prior to the ZCCP classified as low metal water. The highest metal enrichment was detected for Cd, Cu and As in around the ZCCP and drainages that were categorized in moderate (for Cu and As) and extreme (for Cd) contamination. According to modified contamination degree, the river's sediments were classified with a very low degree of contamination, whereas the ZCCP and drainages fall into a moderate to high degree of contamination. The sequential extraction analysis results revealed that most metals before and after the ZCCP were bimodal and mainly occur in silicate and sulfide bounds as residual fraction. Whereas, the metals in the ZCCP sample included three modes with an increase of organic bound fraction. The metal mobility factor in the ZCCP sample demonstrate that the Cd, As and Cu were high mobility with high percent of occurrences in water soluble and exchangeable fraction.

*Keywords: Heavy metals pollution; Sequential extraction analysis; Coal cleaning; Mobility factor; Source identification*

## Introduction

Coal plays an important role in electricity generation, steel production, cement manufacturing and transportation as well as a source for liquid fuel production in the world. Approximately, 70% of steel production and more than 38% of the world energy are related to Metallurgical and Thermal coals, respectively.

However, coal mining and purification may lead to substantial environmental hazard such as land degradation, topography changes, environmental pollution, ecological deterioration and also human health problems. On the other hand, the chemical form of heavy metals in liquid and solid media can strongly influence their mobility, toxicity and bioavailability. As metals discharge into the fluvial environment, their partitioning occurs between sediment and water column. Further partitioning of metals occurs within the sediment chemical fractions and metal speciation in the water column with different ligands [1].

Iran is the largest coal producer in the Middle-East region with production of 1.11 million tons of coal concentrate

per year while it has 1.15 billion tons of proven reserves; around 72 percent of this is cooking coal and the rest is thermal coal. Alborz (~17%) along with Kerman (~8%) and Tabas (~75%) are the principal coalfields in Iran Alborz coalfield divided to three zones called Eastern, Central and Western zones. Applicable coal layers in the central Alborz coalfield are Karmozd, Kiasar, Goliran and Karsang and coking coals are the primary target of mining. Because of high ash contents, the exploitation coal is not suitable for used in Iranian Steel Corporation. In order to improve the coal quality, it is necessary to remove mineral matters from coal. This can be done through physical and chemical processes at the Zirab Coal Cleaning Plant (ZCCP). Annually, the process leaves about 700,000 m3 of wastewater and 400,000 tons waste that accumulated in waste dump and tailing dam. Zirab Coal Cleaning Plant is located next to the Cherat River and the effluents of this plant are discharged directly and indirectly into the river. This study was conducted to evaluate the metal contamination of the ZCCP on the Cherat River and the partitioning of metals in sediment by the sequential extraction method.

## Literature Review

Eleven sampling points were designed for evaluation of the Cherat and Talar rivers' contamination through the coal cleaning processes during June 2018 as follows: one sample collected from the Sheshrudbar Stream as a background sample that was placed upstream from the coal cleaning plant (WB), three samples from the Cherat Stream (W1, W2, and W5), three samples from the tailing dam (WP1, WP2 and WP3), two samples from plant drainages (W3 and W4) and two samples (W6 and W7) from the Talar River downstream.

Water samples were collected in 1liter polyethylene bottles. All the sample bottles were soaked in 10% nitric acid and rinsed with deionized water three times prior to use. The bottles were rinsed twice with surface water before filling. Two sets of water samples were collected, one was used to determine major anions and cations and the other for heavy metal analysis [2]. Water samples for heavy metal analysis were filtered through 0.45μm Millipore membranous filters. The filtered samples were preserved by acidifying with concentrated ultra-pure nitric acid to pH<2 and stored at 4°C in 250ml polyethylene bottles. Electrical conductivity and pH of water samples were determined by a portable digital pH meter and conductivity meter in situ. The concentration of Na and K were determined by a flame photometer, Ca and Mg by EDTA titration, Cl using the Mohr method, sulfate by turbidimeter method and bicarbonate by HCl titration in the geochemistry laboratory at Shiraz University. The cationic and anionic change balance (CBE ± 10%) is added proof to the precision of the data.

Sediment samples were collected using polyethylene spade from the upper 3-5cm of the riverbed and tailing dam, then packed in plastic bags and kept cool in an ice box (4°C) during transportation to the laboratory. They were dried at room temperature (25-30°C) and analyzed for total organic carbon (TOC), then sieved and the portion finer than 0.63μ was chosen for chemical analysis. The TOC was determined with the infrared spectroscopy. Grain size and textural analysis were carried out by a combination of sieving (2-0.063 mm) and Hydrometer (<0.063 mm) methods. Sequential extraction analysis was carried out on three sediment samples for determination of chemical species of element and to predict the mobility and bioavailability of these elements in polluted sediments. Finally, all heavy metals in sediment and water samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at the Amdel Laboratory in Australia. Digestion of International References Materials and blanks were prepared and analyzed following the same procedure (Amdel Laboratory, Australia) and analytical errors were estimated at less than 10% for most of the elements.

The statistical analysis of the measured parameters in water and sediment samples was carried out using *SPSS*. The probability distribution of the dataset was investigated prior to statistical analysis using the Kolmogorov–Smirnov methods. It can be seen that most of the parameters in datasets display non-normal distribution. Hierarchical cluster analysis (*HCA*) was used for the categorization of stations in two datasets. Cluster analysis was carried out by using between group linkage methods with Euclidean distance as an interval and standardized with maximum magnitude of 1 as the transformation [3].

The descriptive statistics including mean, maximum, minimum, median, coefficient variation and standard deviation along with Maximum Contaminant Level (MCL) of elements in drinking water (EPA, 2018), drinking water quality guideline (WHO, 2017) and the average natural content of elements in world stream waters for various physicochemical parameters and metal contents in water samples are given in Table 1. The water temperature ranged from 18.5 To 23.3°C. The river water is categorized as neutral to alkaline by pH values between 7.18 and 8.27. Electrical Conductivity (EC) varies from 365 to 1350 μs/cm with an average of 781 μs/cm. EC values in all samples are lower than WHO standard for drinking water (1500 μs/cm). Total dissolved solids (TDS) ranged from 306 to 1078 mg/l with a mean value of 729 mg/l. TDS in drainage of tailing dam are exceeded by the WHO guideline value (1000 mg/l). Coefficient of Variation (CV) for EC and TDS were more than 20 %, illustrating the probable occurrence of anthropogenic factors.

The average concentration of major cations (mg/l) indicates that $Ca^{2+}>Mg^{2+}>Na^+>K^+$ in river water, while in the wastewater discharges from the ZCCP, the trend changes to $Ca^{2+}>Na^+>Mg^{2+}>K^+$. The mean values of anions (mg/l) displays the following decreasing order $HCO_3^->SO_4^{2-}>Cl^->CO_3^{2-}$ in river samples, while in the ZCCP, it changes to $SO_4^{2-}>HCO_3^->Cl^->CO_3^{2-}$. The sulfate and sodium ions in the tailing dam are incredibly high due to using NaOH in coal washing processes and also the presence of oxidized sulfate minerals, such as pyrite and marcasite (Moore and Esmaeili, 2012). Chloride, sodium, potassium, magnesium and carbonate ions in all of water samples are below both guideline values. Sulfate and bicarbonate ions in analysis samples 3 and 5 exceeded the WHO guideline values, respectively. The high concentration of these parameters were observed within and around the coal cleaning plant.

Major anions and cations in meq/l were plotted on the Piper Diagram Piper, 1944 The results show that the water samples were categorized calcium bicarbonate ($Ca^{2+}$-$HCO_3^-$) in the Sheshrudbar Stream (backgroud area) and the Cherat River, while calcium sulfate ($Ca^{2+}$-$SO_4^{2-}$) was found in the ZCCP drainage and the Talar River. Water samples from the ZCCP fall in a sulfate rich zone. The diamond section of diagram was also demonstrated by gradually mixing the ZCCP drainage with the waters from the Cherat River [4].

The statistical summary of metal contents along S, P, TOC and grain size in the investigated sediment samples are given in Table 2. Based on Granulometry Analysis and the USDA Classification, sediment samples were mainly composed of fine grains (clay and silt) in the drainage of ZCCP, which is categorized in Clayey Loam.

Whereas, Sediment samples from the Talar and Cherat Rivers were placed in the Loam and Sandy Loam categories, respectively (Fig. 4a). The sediments were neutral to weak-medium alkaline with pH ranging from 6.2 to 9.1 (Mean=7.7). The highest pH was observed in the TS3 sample that was collected from the output of the ZCCP. The total organic carbon ranges from 3.5 to 33% with a mean of 14.1% in sediment samples. Similar to the pH, the higher TOC values were found in the drainage and downstream from the plant. The mean content of TOC was 5% distal to the plant, while it was 25% around the plant, revealing extreme organic matter contents in the ZCCP wastewater.

The major and trace elements (mg/kg) showed wide variations with Al, 56,3000 – 69,500; Fe, 24,300 – 59,823; As, 9.6 – 29.7; Cd, 0.1 – 3.1; Cr, 54 – 124.1; Cu, 24.2 – 69.5; Co, 10.8 – 28.4; Mn, 605 – 1,377; Ni, 33.0 – 75.4; Pb,16.3 – 27.54; Zn, 70.0 – 113.0; P, 100 – 842; S, 350 – 13,486. Coefficient of variation (CV) was used as an index for spatial variability trace elements. Low CV indicates a relative stability of element concentration versus high CV, which indicates the presence of an external factor; either geogenic or anthropogenic [5].

## Conclusion

Generally, the concentration of Si, Al, Pb and Zn in the sediment varied by a CV<20%. This indicates that the concentration of these metals remains fairly stable across the sampling sites and Al would be a good choice as a normalizer for the computation of pollution indices (CV=8%). The widest coefficient of variations (CV>20%) were observed for S, Cd, P, Cu, As, Co, Mn, Ni, Fe and Cr, respectively.

## References

1. Abrahim G, Parker R. Heavy-metal contaminants in Tamaki Estuary: Impact of city development and growth, Auckland, New Zealand. Environ Geo. 2002;42:883-890.

2. Baran A, Tarnawski M. Assessment of heavy metals mobility and toxicity in contaminated sediments by sequential extraction and a battery of bioassays. Ecotoxicology, 2015;24(6):1279-1293.

3. Caboi R, Cidu R, Fanfani L, et al. Environmental mineralogy and geochemistry of the abandoned Pb-Zn Montevecchio-Ingurtosu mining district, Sardinia, Italy, Chron. Reche Min. 1999;534:21-28.

4. Dang Zh, Liu C, Haigh MJ, et al. Mobility of heavy metals associated with the natural weathering of coal mine spoils. Environ Poll. 2002;118:419-426.

5. Equeenuddin Sk, Tripathy S, Sahoo PK, et al. Hydrogeochemical characteristics of acid mine drainage and water pollution at Makum Coalfield, India. J Geochem Expl. 2010;105:75-82.