



Water Pollution Assessment of an Abandoned Copper Mine in Lasail, Sultanate of Oman

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Abstract

Abandoned mining sites are largely responsible for the release of heavy metals into water systems. This study assessed heavy metals in the water collected from the mine sumps and bore-wells of an abandoned copper mine in Lasail, northern Oman. Other physiochemical parameters of the water were also evaluated. The waters were extremely acidic with very high electrical conductivity. Aluminium (Al), boron (B), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn) and zinc (Zn) were in very high concentrations, well above the limits recommended by Oman and World Health Organisation (WHO) standards. The principal component analysis (PCA) explained 93% of the variability. The impact of mining on the water quality of Lasail area is presented and remediation measures are recommended.

Keywords: water pollution, abandoned copper mine, heavy metals, multivariate data analysis, Omans

Introduction

Industrial activities such as mineral exploitation is highly responsible for the input of toxic elements into water systems. The toxic elements are released not only at the big mining sites, but also in places of artisanal mineral exploitation (Atibu et al., 2013) and abandoned mining sites (Neiva et al., 2014). The adverse effects of abandoned mines were known to persist for decades, even after the decommissioning of mines, most often till the sulphides were completely weathered (Carvalho et al., 2009; Lopes et al., 2016). Water is one of the vital compounds for all forms of life (Valoon and Duffy, 2005). Hence, water pollution receives considerably more attention when compared to soil and air. When the concentration of the metals exceeds the retention capacity of soils, they leach into groundwater and soil solution (Zamani et al., 2012). Metals can be distinguished from other toxic pollutants, since they are non-biodegradable, and can be concentrated and accumulated throughout the food chain (Dubey et al., 2014).

Acid Mine Drainage (AMD) is one of the major environmental impacts of sulphide mines. AMD is produced mostly when pyrite ore is left exposed on the surface and thus oxidized by a combination of water, oxygen, and existing bacteria (Johnson and Hallberg., 2003). It is characterized by extremely low pH values and high concentrations of heavy metal ions, which pollute large areas and surface/groundwater systems (Foucher et al., 2001; Stylianou et al., 2014). Numerous studies have been undertaken on trace element contamination derived from mining activities in soils, plants, waters and sediments in various countries (Lee et al., 2001). However, no previous study has been carried out in Oman on water pollution due to mining activities. So, the main objective of this study was to determine the water quality of the abandoned Lasail copper mine area by evaluating the composition and concentrations of heavy metals.

Materials and methods

Study area

Lasail copper mine is located in Northern Oman (Lat. 24°16'44.1"N; Long. 56°25'43.0"E). The Lasail copper mine was one of the largest single ore deposits that operated from 1983 to 1994. The mine was abandoned in 1994, but large amounts of waste piles were left behind. The mine area includes two mine sumps and two open bore-wells. The area is arid with long summers and short winters (Months) (Ahmed and Choudri, 2012).

Sampling

Water samples were collected in the months of July 2016 and January 2017 representing summer and winter seasons. Three samples were taken in each season randomly from two mine sumps (referred to as red and yellow sump) and two open bore-wells (referred to as well 1 and well 2) situated in the study area. The coordinates for red, yellow sump, well 1 and well 2 are 24°16'25.00" N 56°26'3.88"E, 24°16'29.44"N 56°26'3.30"E, 24°16'25.33"N 56°25'58.44"E, 24°16'31.82"N 56°25'59.53"E respectively. The water samples were collected in a pre-cleaned PVC containers. The pH and Eh were measured in the field itself (Hand-held Mettler Toledo SG2). Electrical conductivity (EC) and Total dissolved solids were measured in the laboratory (Aquaread 800, Aquaread Ltd.). Heavy metals were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the samples were filtered with 0.45 µm filter paper prior to the analysis. In the ICP- OES, the measurements were repeated thrice for every sample. Control samples were collected in nearby wadis and from a well in a nearby village.

Statistical analysis

SPSS (Version 21.0 IBM, USA) was used for the data analysis. ANOVA for two samples was performed to evaluate the differences in the means between the summer and winter samples. Principal component analysis (PCA) was used as a dimension reduction tool to reduce a large set of variables to a small set that still do not affect the integrity of the in-

Tab. 1. Water physiochemical analysis (Units of measurement: EC $\mu\text{S}/\text{cm}$, Eh mV, TDS mg/l, Metals mg/l)Tab. 1. Analiza fizykochemiczna wody (Jednostki pomiaru: EC $\mu\text{S}/\text{cm}$, Eh mV, TDS mg/l, Metals mg/l)

| Parameters | Sample locations | | | | | | | |
|------------|------------------|--------|-------------|--------|--------|--------|--------|--------|
| | Red sump | | Yellow sump | | Well 1 | | Well 2 | |
| | Jul-16 | Jan-17 | Jul-16 | Jan-17 | Jul-16 | Jan-17 | Jul-16 | Jan-17 |
| pH | 3.11 | 2.80 | 3.78 | 3.10 | 4.28 | 4.09 | 4.40 | 4.27 |
| EC | 21360 | 27640 | 26230 | 18730 | 11220 | 7033 | 7733 | 2256 |
| Eh | 685.30 | 423.00 | 595.90 | 375.00 | 650.00 | 236.00 | 390.00 | 230.00 |
| TDS | 14830 | 18240 | 19580 | 11450 | 9097 | 4040 | 5202 | 1491 |
| Al | 89.95 | 100.15 | 31.39 | 80.36 | 8.56 | 9.52 | 1.32 | 0.56 |
| B | 4.44 | 6.33 | 4.82 | 5.54 | 2.48 | 3.57 | 1.02 | 1.69 |
| Ca | 74.99 | 47.04 | 70.28 | 47.35 | 84.43 | 53.54 | 79.34 | 51.61 |
| Cu | 57.91 | 48.17 | 40.27 | 78.65 | 5.69 | 5.34 | 1.07 | 0.27 |
| Fe | 514.08 | 395.11 | 518.67 | 367.00 | 409.92 | 403.22 | 256.68 | 253.53 |
| Hg | 12.01 | 60.77 | 21.93 | 36.89 | 6.45 | 34.95 | 3.02 | 12.29 |
| K | 5.93 | 2.93 | 8.62 | 11.58 | 5.28 | 6.34 | 3.19 | 3.50 |
| Mg | 44.67 | 34.58 | 39.91 | 36.36 | 48.51 | 35.50 | 45.93 | 33.01 |
| Mn | 66.58 | 83.03 | 68.46 | 89.72 | 24.12 | 25.02 | 9.37 | 9.67 |
| Na | 81.56 | 166.95 | 77.29 | 184.38 | 63.03 | 128.34 | 58.99 | 95.30 |
| Si | 91.96 | 79.58 | 58.75 | 79.22 | 35.37 | 36.60 | 16.67 | 16.49 |
| Zn | 19.37 | 19.17 | 21.99 | 18.39 | 6.35 | 6.29 | 0.50 | 0.29 |

formation content in the large data set. PCA was used here to find a more meaningful basis for the data collected using variance –covariance matrix (Tabachnick and Fidell, 2007). Hierarchical cluster analysis (HCA) was performed to group the identified metals.

Results and discussion

The water samples in the mine sumps were yellow and red. The colour of water in the mine site significantly depended on the mineralogical composition of the iron oxides and oxide phases and varied between reddish (hematite) and yellow (jarosite). The water pH, Eh, EC, TDS and mean concentration of heavy metals are presented in Table 1. The results revealed that the pH was extremely acidic in the red and yellow sump water samples in the range of 2.80-3.78. The pH varied from 4.10 - 4.27 in the well water (WHO limit 6.50-8.50). The lowest values of pH can be attributed to the influence of underground water leaching the mine waste and tailings, which contain sulphides (Lopes et al., 2016). The EC values varied between 2256 $\mu\text{S}/\text{cm}$ (well 2) and 27640 $\mu\text{S}/\text{cm}$ (red sump). The pH and EC values exceeded the WHO permissible limit (400-600 $\mu\text{S}/\text{cm}$) in all samples, thus indicating the high quantities of total dissolved solids. Oman standards: Al 0.02, B 0.50, Cu 2, Fe 1, Hg 0.001, Mn 0.40, Zn 3. WHO standards Ca 75, Cu 1, Fe 0.10, Hg 0.001, Mg 50, Mn 0.5, Zn 5.

The mean concentration of Cu was very high in two mine sump water samples when compared to the Oman and WHO water standards. Similarly, the Cu concentration was high in well 1 samples, where the water was at an approximate depth of 150 m. The Cu mean concentration reached as high as 5.69 mg/l and 5.34 mg/l during summer and winter (Table 1). It appears that the chemical composition of the ground-

water was affected by the tailings water. On the other hand, water in well 2 contained comparatively lesser heavy metals concentration. This could be due to dilution of metal concentrations by rain water surface runoff, since the well head is about 1m below ground surface level. However, similar to mine sumps and well 1, the heavy metals such as Al, B, Fe, Hg and Mn exceeded the WHO and Oman standards in all the water samples of well 2. Particularly, the Fe concentration was very high. The primary and secondary minerals likely to be found in the massive sulphide ore are pyrite (FeS_2), chalcopyrite (CuFeS_2) and sphalerite (ZnS). The primary metals which tend to leach are iron (Fe), copper (Cu), and zinc (Zn) (Stylianou et al., 2014). This could be the reason for getting high concentrations of Cu, Fe and Zn in this study. Lasail deposits that belong to Volcanogenic Massive Sulphide (VMS) are very rich in these metals. Further, Al, B, Ca, Hg, Mg and Mn concentrations were very high in the mine sumps, well1 and 2 water samples.

When comparing the means of these metals between summer and winter, the metals such as Al, B, Cu, Fe, K, Mn, Si and Zn are not significantly different, indicating no seasonal variation. Ca, Hg, Mg and Na are significantly different (ANOVA for two samples; $P < 0.05$). The difference could be due to the temperature variation and monsoonal precipitation. No significant contamination observed in the control water samples taken from the nearby areas

Principal Component Analysis (PCA)

In this study, variance - co-variance matrix was applied as all the variables have the same unit of measurement. The rotation of the principal components was performed by the Varimax orthogonal rotation option. Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were applied to assess suitability

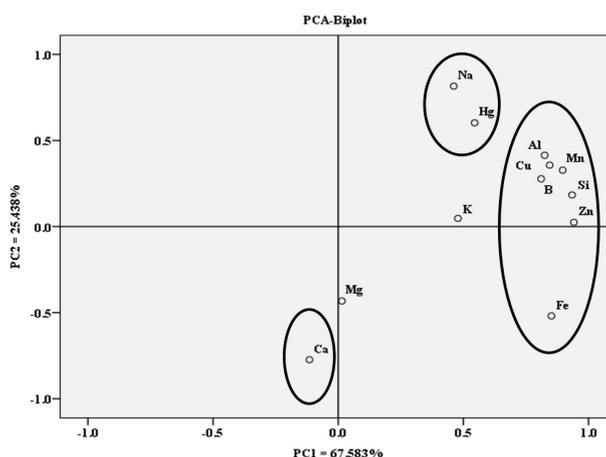


Fig. 1. PCA biplot showing the grouping of 12 heavy metals. PC1 and PC2 show 93.021% of variability.

Rys. 1. Analiza PCA dla 12 metali ciężkich. PC1 i PC2 wykazują 93,021% zmienności

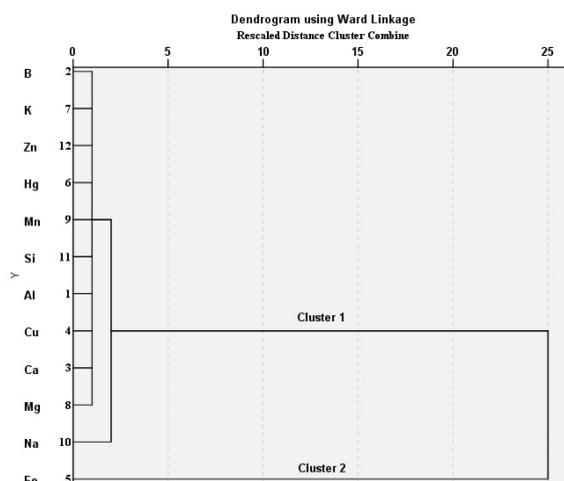


Fig. 2. Hierarchical dendrogram of the potential toxic elements obtained by the Ward-distance clustering method

Rys. 2 Hierarchiczny dendrogram potencjału pierwiastków toksycznych uzyskany metodą grupowania na odległość Warda

ity of data for PCA (PCA – Principal Component Analysis).

The PCA shows two principal components for the heavy metals which explain 93.021% of the total variance. Zn, Si, Mn, Fe, Cu, Al and B were closely associated with the first component (PC1), explaining 67.583% of total variance (Figure 1), and PC1 was the most important component. PC1 confirmed that these elements were from anthropogenic sources such as mining activities, since these metals are closely associated with Cu. However, PC2 comprised of Na, Ca and Hg explained 25.438% and Ca is negatively related to Na and Hg. Thus, it can be concluded that these metals are influencing the overall water quality in Lasail mining area.

Hierarchical Cluster Analysis (HCA)

HCA was performed to group the identified metals into clusters. Two clusters were identified based on the concentration of metals. Al, B, Ca, Cu, Hg, K, Mg, Mn, Na, Si and Zn were in the first cluster. Fe alone in the second cluster (Figure 2). The metals in the same cluster have close similarities in concentration. Metals in the first cluster were from anthropogenic sources. Whereas, Fe was from both anthropogenic and lithologic sources.

Conclusion

The water in the mine sumps and wells were characterised as extremely acidic with very high electrical conductivity and high heavy metal concentrations. The very high concentration of iron and acidity are typical features of acid mine drainage and there is a possibility of metal transportation and formation of acidic ponds. The greatest concern is about the Hg contamination level, as it was approximately 60,000 times higher than those of the Oman and WHO limits. Cu and Fe concentrations were approximately 39,500 times higher than those of the standard limits. Therefore, proper remediation measures should be taken to cleanse the area to avoid further ground water contamination. PCA results revealed Zn, Si, Mn, Fe, Cu, Al B, Na and Hg are responsible for the poor and unacceptable quality of water in the Lasail area.

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