Prediction of Metals Bioavailability in the Soils of O'kiep, South Africa

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Abstract—Mining activities cause environmental pollution problems by contaminating nearby areas with heavy metals (HM) such as Cu, Fe, Zn and Al from overburden and leachates. HM can leach into groundwater, be transferred into rivers, and streams by surface run-off, in a form of dissolved species or as a part of suspended solids, culminating in their accumulation to toxic levels in the ecosystem downstream of the source. In view of such mobility attributed to bioavailability, the objective of this study was to assess the bioavailability and mobility of HM species in the sediments around a closed copper mine and subsequent to analysis with XRF, FTIR and a three-step sequential extraction process. Cu, Zn and Mn were predominantly bound to carbonates and could thus be easily desorbed during moisture laden periods, which will increase their bioavailability thus mobility, away from the source. The BCR fractions also showed that under oxidative reductive conditions, Fe species bound to Fe-Mn oxides, thus can be de-bonded in the presence of an acidified environment; therefore, be mobile for redistribute further downstream from the point of source and further contaminating pollutant free areas.

Keywords— Bioavailability, European Community Bureau of Reference (BCR) Sequential extraction, heavy metals, O'kiep

I. INTRODUCTION

Heavy metal (HM)-containing sediment from mining activities is a common environmental problem that pose threat to arable land and groundwater sources [1], [2]. Metal bioavailability, including transfer via numerous transportation mechanism, have led to an increase in toxic heavy metal mobility [3], thus are easily absorbed and accumulate and subsequently bioaccumulate in the food chain [2]. The presence of HM in an environment have a significant impact on plant functionality in an ecosystem as a result of their accumulation potential including toxicity with some having shown to cause cellular damage in plants and animal cells [4]. The environmental risks of metal(loid)s is primarily associated with their chemical forms or the type of their binding forms and reactivity [5], [6], with metal speciation being vital to the assessment of environmental risks, particular in various matrices such as water, dust, air, soil and sediments [3], [7]. The understanding of these risks is a prerequisite for the development of suitable remediation strategies [8]. To understand such risks, numerous extraction procedures can be used as an assessment guideline to determine mobility and availability.

Sequential extraction procedures are widely used for assessing HM fractionation, bioavailability including reactivity in soils and sediments [9], with the modified three-stage sequential extraction method being used by The European Community Bureau of Reference (BCR) as a reliable, indicative and widely accepted method, to quantify such concentration of HM interaction in the environment. In the BCR extraction, HM fractions are evaluated in three steps: exchangeable and bound to carbonates; reducible (bound to Fe–Mn oxides) and oxidisable (bound to organic matter and sulfides) [10]. Limited studies have been reported on the mobility and bioavailability of HM in O'kiep.

The objective of this study was to: (1) determine the total metal content from sediments, and compare their binding forms in representative sediment samples, (2) to evaluate metal distribution in the sediment samples using sequential chemical extraction (BCR), and (3) to characterize HM/sediment interaction using XRF and FTIR.

II. MATERIALS AND METHODS

O'kiep is a small town in the Northern Cape, South Africa and it is a well-known copper mining yielded approximately two million tons of copper [11]–[13]. Okiep located approximately 600 km from North-West of Cape Town as shown in Fig. 1.

Fig. 1: Map of study area and sampling points

A. Sediment Samples and Reagents

Sediment samples (n = 12) were collected from upstream, midstream and downstream along the dried stream bed where there was evidence of effluent flow from a closed mining area, downstream to a surrounding community. For each sampling site, the sediment samples were collected 5 cm below surface, sieved through a 2 mm mesh and stored in sterile plastic bags and transported to the laboratory. The sediment samples were milled (<100 μm), dried (25 ℃) for 24 h [2] and homogenized to make composite samples C1 – C6 (Table I) prior to analyses. All the chemical reagents used in this study were of analytical grade. Working solutions were prepared from stock standard solutions by dilution with sterile Milli-Q water (Millipore, USA). The stock standard solutions used in this study were prepared using; Acetic acid (Merck, Germany), Hydroxylamine hydrochloride (HIMEDIA, India), Hydrogen peroxide (Sigma-Aldrich, USA) and Nitric acid (Merck, Germany).

TABLE I: DESCRIPTION OF SAMPLES

Sample Name	Sample description	Latitude	Longitude
C1	Upstream	-29.5956707	17.888709
C2	Upstream	-29.597764	17.883976
C3	Slime dams*	-29.5818611	17.876694
C4	Midstream	-29.5961502	17.879916
C5	Tailings*	-29.5964278	17.879167
C6	Downstream	-29.582329	17.87114194

*Potential sources of heavy metals

B. Experimental Procedure

A modified BCR sequential extraction procedure was used to analyse the binding forms of HM in the sediment samples. The analyses were conducted according to the following standard methods namely; 1) fraction 1: acid soluble HM bound to carbonates which are susceptible to cation exchange, 20 fractions 2: reducible HM bound to Fe–Mn oxides and fraction 3: oxidisable HM bound to organic matter and sulfides [6], [10]. Each stage, the extractant were analysed using a Thermo iCAP 6000 series (Thermo Scientific, USA) ICP-AES, with NIST

traceable standards being used for calibration and quality control. The calibration curve acceptance criteria of R2> 0.9995 was used, with the instrument conditions set at: RF Power of 1350 W, Carrier gas (Argon) at 0,65 L/min, Aux gas (Argon) at 1.0, Micromist Nebuliser at 2 mL/min and 1 mg/L of Yttrium internal standard. Mineralogical analyses were performed according to Stellenbosch University's internal standard method, to determine major component analyses with X-Ray Fluorescence (XRF) Spectrometer and to determine the binding groups in the sediment samples using Fourier Transform Infrared Spectroscopy (FTIR).

III. RESULTS AND DISCUSSION

A. Bioavailability and Metal Mobility

Bioavailability of HM in the sediments was examined by a BCR sequential method to quantify the redistribution or partitioning of the metals including their various chemical binding forms, i.e. adsorbed (with exchangeable sites), reducible and oxidisable - see Table II. It was evident that HM in the sediments of the O'kiep are entrapped within the sediment in different binding forms of varying strength, which is indicative of metal reactivity in the sediments. This can be utilised to assess the risk of HM dispersion and subsequently uptake including mobility within an ecosystem.

TABLE II: BCR SEQUENTIAL RESULTS

Sample name	Al	Cr	Mn	Fe	Cu	Zn	Σ
	Fraction 1: exchangeable fraction (mg/kg)						
C1-F1	185.9	0.6	154.6	2.5	5103.5	139.0	5586.1
C2-F1	687.6	1.0	62.7	325.1	1685.3	33.4	2795.1
C3-F1	1265.5	4.4	127.5	137.5	956.7	85.0	2576.6
C4-F1	664.5	4.5	27.0	427.8	6013.0	25.8	7162.7
C5-F1	3763.2	10.2	69.0	2677.6	13628.3	1105.8	21254.1
C6-F1	427.4	10.1	29.3	502.9	258.2	16.6	1244.5
	Fraction 2: reducible fraction (mg/kg)						
C1-F2	186.5	4.8	39.0	263.2	21.9	7.8	523.2
C2-F2	196.4	5.2	6.3	213.3	9.4	2.3	432.9
C3-F2	126.4	7.5	0.8	49.5	7.8	1.6	193.5
C4-F2	840.7	8.7	7.1	5904.3	666.0	4.7	7431.4
C5-F2	92.6	4.2	1.6	11552.2	210.0	14.5	11875.3
C6-F2	205.7	7.9	12.4	494.4	63.5	3.4	787.3
	Fraction 3: oxidisable fraction (mg/kg)						
C1-F3	3001	5	3	147	726	36	3919
C2-F3	704	4	21	2345	194	8	3276
C3-F3	304	4	2	87	13	3	412
C4-F3	165	12	2	187	64	4	435
C5-F3	221	4	2	144	40	4	414
C6-F3	504	8	2	157	133	5	809

Slime dams (sample C3) and mine tailings (sample C5) were considered to be potential sources of HM as indicated by the high presences of HM, with sample C5 being a greater threat due to the proximity to a densely populated residential area. Sample C5 also had a stronger smell (sulphurous smell) which was observed during sampling, with dark, fine grains, as a result of the mined ore being processed by froth flotation in the past [15]. HM in samples C4 and C5 could be as a result of HM physical mobility, i.e. erosion, owing to finer particle size and other mineralogical characteristics of the sediments collected at these sites [16].

Fraction 1: BCR sequential method indicated that, HM that were weakly adsorbed onto the solid surface of the sediment, i.e. bounded to carbonates with weak electrostatic bonds, could be easily influenced by the change in the ionic composition of the matrices, and are thus prone to be exchangeable and remobilized downstream of the source point. [17]. The results showed that samples C5 (mine tailings) had the highest total exchangeable HM with sample C3 having the lowest exchangeable heavy metals in the sediments. Sample C5, also showed a higher Cu concentration (13628.3 kg.kg-1) which was indicative of the high mobility of metal, in comparison to other metals. The total HM extracted in all the sediment samples collectively using the BCR method decreased in the order of Cu> Al> Fe> Zn> Mn> Cr.

Fraction 2: Furthermore, for fraction 2 of the BCR, which involved the mobilisation of HMs bound to an amorphous Fe-Mn oxides constituents including hydroxides, which simulate reductive mobility conditions, indicated that a large quantity (11875.3 kg.kg-1) of HMs downstream (sample C5) of the source with the largest contribution being attributed to Fe. The concentration of metals bound to the Fe-Mn oxides in all the sediment samples collectively, decreased in the order of Fe> Cu> Al> Mn> Zn> Cr.

Fraction 3: HMs assessed which are bound to natural organic matter which bioaccumulate in living organisms [18], and which are largely bound to sulphides thus prone to redistribution under oxidation conditions, were largely immobile, with the dominant species being Zn (3001 kg.kg-1), which is prone to oxidation. Accordingly, the concentration of metals prone to oxidation decreased in the order of Al> Fe> Cu> Zn> Cr> Mn.

Generally, the concentration of Al, Cu and Fe indicated a higher extractability in the sediment and thus higher mobility and risk (Table III) in the O'kiep environment. In all the sediment samples, Cu, Zn and Al were predominantly bound to carbonates and were hypothesised to be readily mobilized as previously reported [3]. Cr was determined to be the least bioavailable HM as shown by its low acid solubility and oxidisability [17], [19]. Sample C1, C4, C5, and C6 indicated that under reductive conditions, i.e. condition associated with acid mine drainage (AMD), immobile Fe bounded to Fe-Mn oxides including hydroxides, could easily degrade and thus become bioavailable.

TABLE III: Risk And Mobility Of Heavy Metals

Heavy Metals	Less Risk (Low mobility)		High Risk (High mobility)
Al			■
Cr	■		
Cu			■
Fe		■	
Mn		■	
Zn	■		

Risk Assessment Code (RAC), previously reported by Jain [20], can therefore be used as a criterion to quantitatively determine the risk of HM contamination in an environment, by evaluating the percentage of the total metal content present in individual sediment fractions, as determined by the BCR. Organic matter bound HMs were therefore determined to pose the highest risk to the OCD population [21] due to the weak electrostatic binding mechanism of the HMs, with HM contaminants source points (slime dams and tailing stream) being considered to constitute a high risk thus environmental health problem. Generally, the mobility and bioavailability of total HMs in the sediments decreased in order of exchangeable> reducible> oxidisable, HMs."

B. FTIR Spectroscopy

The FTIR spectra (Fig. 2 and 3) are indicative of functional groups within the range of 4000 – 1500 cm-1 whereas spectra between 1500 to 400 cm-1 presents the fingerprint region. Spectra bands between 3000 and 3730 cm-1 attributed to the hydroxyl group (-OH) were more prominent in samples C1 and C4, with symmetric and asymmetric vibrations being observed at 997 cm-1 for samples C1, C2 and C4 and at 1016 cm-1 for samples C3 and C5. Sample C5 was associated with a high concentration of silicates and quartz functional groups [22]. The peaks observed in all samples at 517 cm-1 and between 766 and 790 cm-1 can be assigned to the Si-O-Si functional group [23].
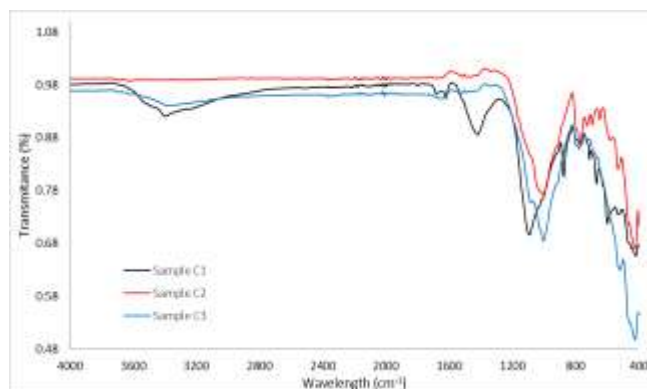

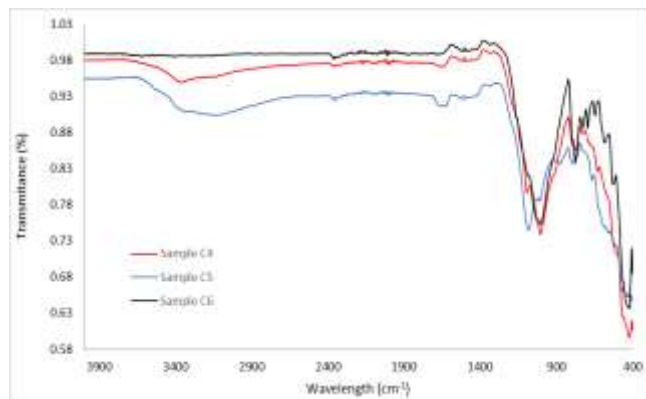Fig. 2: FTIR spectra of sample C1, C2 and C3

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Fig. 3: FTIR Spectra of sample C4, C5 and C6

The XRF chemical compositions (Table IV) of all the samples indicated the presence of inorganic silicate minerals, such as clay and quartz, with predominant SiO2, Fe2O3, Al2O3 and traces of MgO, Cr2O3 and MnO. The dominant minerals represent in the samples (70.2% - 83.4%) for C2-C6 were only accounted for being 52% in sample C1. Sample C4 showed a higher Fe2O3 composition (3.84%), compared to downstream, i.e. sample C6, which further supports the hypothesis that the appreciable concentration of HM in sample C4 is primarily due physical mobility from sample C4. Although the toxic compounds (HMs) were not recorded in the investigated samples, ICP-AES analyses indicated a high copper concentration in sample C1 and thus the lower silicate mineral composition observed.

TABLE IV: CHEMICAL COMPOSITION BY XRF ANALYSIS

Chemical composition (wt.%)	Sample name					
	C1	C2	C3	C4	C5	C6
SiO$_2$	26.06	79.50	44.05	50.82	11.25	78.35
Al$_2$O$_3$	7.16	9.91	10.87	11.91	2.12	9.13
Fe$_2$O$_3$	3.91	1.66	23.29	16.18	58.11	3.84
MgO	1.30	0.15	1.51	0.93	1.38	0.31
Cr$_2$O$_3$	0.11	0.12	0.13	0.13	0.03	0.19
MnO	0.06	0.03	0.08	0.05	0.05	0.05

IV. CONCLUSION

Slime dams and mine tailings were considered to be potential sources of HM, with mine tailings being identified a greater threat to the community of the OCD due its proximity to a residential. Primarily, Cu, Zn and Al bound to carbonates by a weak electrostatic interaction, were determined to be readily mobilizable and bioaccumulative in the sediments studied. Under reductive conditions, immobile Fe bounded to Fe-Mn oxides including hydroxides, could degrade and thus become bioavailable. Overall, mobility and bioavailability of HM in the OCD sediments samples decreased in order of exchangeable> reducible> oxidisable with a high inorganic material, such as clay and quartz, being observed in the sample studies.

REFERENCES

[1] Z. Ding, Q. Wang, and X. Hu, "Extraction of heavy metals from water-stable soil aggregates using EDTA," *Procedia Environmental Sciences*, vol. 18, pp. 679-685, June 2013. https://doi.org/10.1016/j.proenv.2013.04.092

[2] A. Sungur, M. Soylak, E. Yilmaz, S. Yilmaz, and H. Ozcan, "Characterization of heavy metal fractions in agricultural soils by sequential extraction procedure: the relationship between soil properties and heavy metal fractions," *Soil and Sediment Contamination: An International Journal*, vol. 24, no. 1, pp. 1-15, May 2015. https://doi.org/10.1080/15320383.2014.907238

[3] H. Altundag, S. Doganci, M. S. Dundar, and E. Altintig, "metal fractionation using the bcr sequential extraction procedure with regard to carpark dust samples from sakarya, turkey," *Feb-fresenius environmental bulletin*, p. 2764, 2016.

[4] G. S. Simate and S. Ndlovu, "Acid mine drainage: Challenges and opportunities," *Journal of Environmental Chemical Engineering*, vol. 2, no. 3, pp. 1785-1803, September 2014. https://doi.org/10.1016/j.jece.2014.07.021

[5] Y.-H. Xu, J.-H. Huang, and H. Brandl, "An optimised sequential extraction scheme for the evaluation of vanadium mobility in soils," *Journal of Environmental Sciences*, vol. 53, pp. 173-183, March 2017. https://doi.org/10.1016/j.jes.2016.02.019

[6] M. Žemberyová, J. Bartekova, and I. Hagarova, "The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins," *Talanta*, vol. 70, no. 5, pp. 973-978, December 2006. https://doi.org/10.1016/j.talanta.2006.05.057

[7] P. M. Thanh, B. Ketheesan, Z. Yan, and D. Stuckey, "Trace metal speciation and bioavailability in anaerobic digestion: A review," *Biotechnology advances*, vol. 34, no. 2, pp. 122-136, March 2016. https://doi.org/10.1016/j.biotechadv.2015.12.006

[8] H. Zhang, J. Yu, and S. Zhou, "Spatial distribution of As, Cr, Pb, Cd, Cu, and Zn in the water and sediment of a river impacted by gold mining," *Mine Water and the Environment*, vol. 33, no. 3, p. 206, September 2014. https://doi.org/10.1007/s10230-013-0254-4

[9] S. M. Shaheen and J. Rinklebe, "Geochemical fractions of chromium, copper, and zinc and their vertical distribution in floodplain soil profiles along the Central Elbe River, Germany," *Geoderma*, vol. 228, pp. 142-159, September 2014. https://doi.org/10.1016/j.geoderma.2013.10.012

[10] A. Sungur, M. Soylak, and H. Ozcan, "Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability," *Chemical Speciation & Bioavailability*, vol. 26, no. 4, pp. 219-230, Jan. 2015. https://doi.org/10.3184/095422914X14147781158674

[11] B. Cairncross, "History of the THE OKIEP COPPER DISTRICT Namaqualand, Northern Cape Province South Africa," *Mineralogical Record*, vol. 35, no. 4, p. 289, 2004.

[12] C. E. Clarke, S. G. le Roux, and A. N. Roychoudhury, "The role of evaporation on the formation of secondary Cu-hydroxy minerals in the

arid Namaqualand soil system of South Africa," *Applied Geochemistry*, vol. 47, pp. 52-60, Aug. 2014. https://doi.org/10.1016/j.apgeochem.2014.05.013

[13] T. N. Clifford and E. S. Barton, "The O'okiep Copper District, Namaqualand, South Africa: a review of the geology with emphasis on the petrogenesis of the cupriferous Koperberg Suite," *Mineralium Deposita*, vol. 47, no. 8, pp. 837-857, Dec. 2012. https://doi.org/10.1007/s00126-012-0403-x

[14] S. Stats South Africa, "Statistics South Africa," Statistical release P0441, 2011.

[15] C. Beale, "Copper in South Africa-Part 1," *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 85, no. 3, pp. 73-80, March 1985.

[16] M. H. Mian and E. K. Yanful, "Erosion characteristics and resuspension of sub-aqueous mine tailings," *Journal of Environmental Engineering and Science*, vol. 6, no. 2, pp. 175-190, March 2007. https://doi.org/10.1139/s06-040

[17] M. Schintu et al., "Heavy metal accumulation in surface sediments at the port of Cagliari (Sardinia, western Mediterranean): Environmental assessment using sequential extractions and benthic foraminifera," *Marine pollution bulletin*, vol. 111, no. 1, pp. 45-56, Oct. 2016. https://doi.org/10.1016/j.marpolbul.2016.07.029

[18] K. Nemati, N. K. A. Bakar, M. R. Abas, and E. Sobhanzadeh, "Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia," *Journal of hazardous materials*, vol. 192, no. 1, pp. 402-410, Aug. 2011. https://doi.org/10.1016/j.jhazmat.2011.05.039

[19] A. Manyatshe, " Mapping the dispersion of inorganic contaminants in surface water in the vicinity of Potchefstroom". M.S. thesis, Dept. Chemical. Eng., North-West Univ., Potchefstroom, South Africa, 2017.

[20] C. Jain, "Metal fractionation study on bed sediments of River Yamuna, India," *Water Research*, vol. 38, no. 3, pp. 569-578, Feb. 2004. https://doi.org/10.1016/j.watres.2003.10.042

[21] M. A. M. Abdallah, "Chemical speciation and contamination assessment of Pb and V by sequential extraction in surface sediment off Nile Delta, Egypt," *Arabian Journal of Chemistry*, vol. 10, no. 1, pp. 68-75, Jan. 2017. https://doi.org/10.1016/j.arabjc.2012.06.001

[22] N. Junakova, J. Junak, and M. Balintova, "Reservoir sediment as a secondary raw material in concrete production," *Clean Technologies and Environmental Policy*, vol. 17, no. 5, pp. 1161-1169, June 2015. https://doi.org/10.1007/s10098-015-0943-8

[23] M. A. Habila, Z. A. ALOthman, A. M. El-Toni, J. P. Labis, and M. Soylak, "Synthesis and application of Fe 3 O 4@ SiO 2@ TiO 2 for photocatalytic decomposition of organic matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-MS analysis," *Talanta*, vol. 154, pp. 539-547, July 2016. https://doi.org/10.1016/j.talanta.2016.03.081