Potential Toxic Elements Contamination of Soils in O’Kiep, an Arid Region of Namaqualand, South Africa

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Abstract—The aim of this study was to evaluate the geochemical background and spatial distribution patterns of selected potential toxic elements (PTEs) in ten sub-surface soil samples (n=10) collected in the former copper mining area, O’Kiep. The major oxides and PTEs in the samples were identified and measured using X-ray fluorescence and X-ray diffractometer. The contaminated soils were compared to prestige soil and Soil Screening Values for All Land-Uses Protective of the Water Resource – references which can elucidate PTE contamination. The examined soils showed a high variability in the PTEs concentrations. O’Kiep soils show some degree of contamination with an average low pH of 3.5 and an Eh of 520 mV. The most abundant PTEs in the soils were S > Cu > F > Mn > Cl > Zn > Cr > V > Pb > Ni > Co. The soil type in downstream was classified as silt with a clay content of 1.1%. The mineralogical study of the soils revealed minerals such as Aluminio-silicates, Ca-silicates and Mg-silicates aggregates, with a strong similarity between the downstream and upstream samples from the mining area, while the midstream only differed by the presence of hematite. The median values of oxides contents in soils follow a decreasing order as: SiO\textsubscript{2} > Al\textsubscript{2}O\textsubscript{3} > Fe\textsubscript{2}O\textsubscript{3} > K\textsubscript{2}O. Furthermore, factors that influence the distribution and migration of PTEs in soils were largely identified as mine waste heaps and slime dams further north from the sampling sites. Excessive concentration of PTEs in O’Kiep’s soils may lead to elevated potential risks to human health and the local environment. The material of mine waste heaps is very fine and can easily migrate with wind and water erosion. Therefore, further risk assessment analyses of mine waste heaps and the mine are required in O’Kiep.

Keywords— Arid region, Copper mining, Potential Toxic Elements (PTEs), O’Kiep, Soil Contamination.

I. INTRODUCTION

Worldwide, soil contamination has increasingly been studied by various researchers including in South Africa (SA) with the support of environmental protection organisations [1]. In SA, some studies have been conducted on metals pollution in gold [2], coal [3] and diamond [4] mining areas. However, minimal studies have been reported in potential toxic elements (PTEs) of soil in copper mining areas especially in O’Kiep, SA. The area is the oldest formally proclaimed copper mining area in SA [5]. Soils can be a reservoir of large quantities of PTEs from several sources including municipal and industrial waste such as mining gangue [6]. However, the physico-chemical characteristics of the soil is a vital indicator which influences the dispersion of PTEs in contaminated areas [7]. Contaminated soils including arable land are no longer suitable for farming, since they are unable to yield healthy crops especially in O’Kiep. O’Kiep soils have been described as being highly polluted, which is indicative of significant environmental damage related to the presence of PTEs in the organic fraction, bound forms [8], with some metal recycling occurring as a result of organic matter decomposition. Soluble minerals are also being mobilised through interaction of carbonic acid and water, while relatively insoluble minerals such as quartz (SiO\textsubscript{2}) disintegrate as finer particles and the end result of weathering is soil [9]. The persistent wind in the area was also considered a health problem in this town [10].

In historic mining areas, soils are usually enriched with PTEs. These PTEs are from geochemical processes, weathering of mineralised zones and from different mining activities including disposal of mine wastes [11, 12]. According to previous reports, the mineralogical composition of soils from O’Kiep mining area includes bismuthinite, bornite, chalcocite, chalcopyrite, covellite, galena, ilmenite, magnetite, molybdenite pentlandite, pyrite, pyrrhotite, quartz, scheelite, sillimanite, sphalerite and thorite [13, 14]. In some warm climate areas including O’Kiep, where chemical weathering dominates, soils tend to be richer in clay – resulting in the localisation entrapment of some PTEs. The closed mining areas are often a source of severe environmental problems caused by the mobility of PTEs and consequently the formation of acid mine drainage [15], with chemical and biochemical reactions proceeding fastest under warm conditions [16]. Before rehabilitation of soils in historic mining areas, it is essential to establish geochemical
characteristics of metals in the soils.

The bioavailability and mobility of PTEs in surface soils was examined in O’Kiep by Moncho [17] with application of sequential extraction analyses. Characterising the factors affecting bioavailability, leaching and toxicity of metals and metalloids in soil to water sources is of paramount importance. Although, metals and metalloids are significant natural components of all soils where their presence in the mineral fraction comprises a storage of potentially-mobile species that have a negative influence on soil geochemistry and groundwater quality [18, 19].

In SA, attention has been drawn to the mining industries and its adverse effects on the environment and posing potential health risk to communities such as those at O’Kiep. Copper contamination of the whole region is the result of processing of copper ores from a closed metalliferous mine. Produced waste material from this mine was stored in the numerous heaps and in the tailing ponds. Rehabilitation of the mine including copper oxide ore dumps and extensive slime dams remains a challenge and as part of the program are earmarked for redistribution and reprocessing [10]. The present past land use of this site is well known for copper mining. However, the mining activity ceased in 2007 and the area has been under slow but systematic rehabilitation ever since [10]. The mineralogy and geochemistry of this soil was never examined. The main objectives of this study were: 1] to characterise spatial distribution of trace elements in soils of the historic O’Kiep copper mining area in Namaqualand; and 2] to evaluate site-specific geochemical background concentrations of these elements in the mine soils as the geochemical and mineralogical studies of the soils will elucidate contamination by PTEs such that effective reclamation and remediation actions are developed.

II. MATERIALS AND METHODS

A. Sample collection

Soil samples (n =11) were collected in O’Kiep [29°35’45” S, 17° 52’ 51” E] (38.63 km²) located in the Namaqualand region, Northern Cape, SA. This area is described as arid with a temperature of 37°C with an estimated evaporation rate which greatly exceeds the precipitation, highlights both the aridity and water scarcity of the area [20, 21]. This high evaporation rate, which significantly exceeds the rainfall, highlights water scarcity and the dryness of the area. Soil samples were collected as per field soil sampling guidelines by mean of haphazard, judgement, probability and analysis of soils method described by Gregorich and Carter [22] and Schoeneberger [23]. The sampling site was cleared of litter, of living plants and surface rocks prior to sample collection. The sub-soil was sampled from a spolic and transportic soil layer at a subsurface depth of approximately 30 to 100 cm [24]. All samples were collected in August 2017 during the wet season and sampling points were marked using a Global Positioning System (GPS) as shown in Fig. 1.

To assess soil samples variation, all samples were taken every 150 to 200 m from upstream to downstream area of the mining site. A total of ten potentially contaminated soils were collected namely, OCM1 and OCM2, samples representing a composite of four sub-samples collected in a 5 m x 5 m grid, upstream; [OCM3, OCM4, OCM5, OCM6 (near mine waste heaps)] (midstream) and OCM7, OCM8, OCM9 and OCM10 (downstream) were compared to pristine soil sample (S1P) (prestige) collected 5 km away from sampling site by means of a Draper 24414 steel auger [23, 25, 26]. Subsequently, about 1 kg was sampled, then homogenised by mortaring into a composite sample which was air-dried and sieved using a 2-mm polyethylene with fraction remaining on the sieve being weighed to determine the percentage of coarse fragments. The samples were bagged into sterile polythene zipper top bags to prevent contamination and transported to the laboratory for further analysis.

B. Soil Sample Analyses

1) Soil type and texture

As According to soil guide of SA, the soil texture and type in arid regions consist of different principle of soils with special sub-soil characteristics relating to pedogenic accumulation and having an orthic topsoil characteristics comprising of groups namely calcic and silicic constituents [27].

2) Paste preparation for pH and Redox (Eh) determination

Saturated pastes created by slurrification of the soil and water using a 1:2 ratio, were prepared with soils from each of the eleven sub-soil sample composites. The pastes were prepared in 500 mL polypropylene bottles according to Sobek (1978). The soils were allowed to wet by capillary action before being stirred to a thin paste with a spatula. The spatula was rinsed with deionised water before stirring each sample. Prior to the measurement of pH and Eh using an EXSTIK II® EC500, the instrument was calibrated.
3) Laboratory Methods

The soil samples were analysed at the University of Cape Town, Department of Geological Sciences, SA, using X-ray fluorescence (XRF) and X-ray diffractometer. The details of sample preparation, instrumental techniques for each method are described by Beckhoff [29] and Compton [30].

III. RESULTS

The abundant major oxides of soil samples are presented in Fig. II.

![Fig. 2. Major Oxides at various sampling points](image)

### Table I: Potential Toxic Elements compared within Soil screening values (SSV) adopted from Waste Act 59 of 2008.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Co (mg/kg)</th>
<th>Mn (mg/kg)</th>
<th>V (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>F (mg/kg)</th>
<th>S (mg/kg)</th>
<th>Cl (mg/kg)</th>
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<tr>
<td>Streams</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>OCM1</td>
<td>53.2</td>
<td>74.5</td>
<td>1080</td>
<td>39.8</td>
<td>26.9</td>
<td>615</td>
<td>38.0</td>
<td>69.4</td>
<td>1412</td>
<td>2613</td>
<td>116</td>
</tr>
<tr>
<td>OCM2</td>
<td>33</td>
<td>63</td>
<td>591</td>
<td>27</td>
<td>10</td>
<td>353</td>
<td>58</td>
<td>63</td>
<td>665</td>
<td>687</td>
<td>116</td>
</tr>
<tr>
<td>OCM3</td>
<td>122</td>
<td>267</td>
<td>935</td>
<td>47</td>
<td>16</td>
<td>385</td>
<td>64</td>
<td>53</td>
<td>652</td>
<td>790</td>
<td>116</td>
</tr>
<tr>
<td>OCM4</td>
<td>28</td>
<td>51</td>
<td>225</td>
<td>0</td>
<td>-5</td>
<td>254</td>
<td>46</td>
<td>51</td>
<td>642</td>
<td>790</td>
<td>121</td>
</tr>
<tr>
<td>OCM5</td>
<td>29</td>
<td>56</td>
<td>495</td>
<td>25</td>
<td>-5</td>
<td>197</td>
<td>50</td>
<td>47</td>
<td>671</td>
<td>528</td>
<td>108</td>
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<tr>
<td>Average</td>
<td>52.8</td>
<td>124.3</td>
<td>503</td>
<td>24.8</td>
<td>13.0</td>
<td>288</td>
<td>38.5</td>
<td>51</td>
<td>616</td>
<td>676</td>
<td>116</td>
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<tr>
<td>SSV</td>
<td>20</td>
<td>240</td>
<td>16</td>
<td>91</td>
<td>300</td>
<td>740</td>
<td>6.5</td>
<td>150</td>
<td>30</td>
<td>40000</td>
<td>52000</td>
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</table>

IV. DISCUSSION

A. Paste and leachates physical parameters

The O’Kiep soil samples were dark brown in colour, weakly altered with an average paste pH of 3.4 determined to be fairly acidic. This was attributed to the presence of sulphidic minerals in the host rock that was undergoing oxidation thus acidifying the paste to sulphuric acid. However, the presence of pH buffering minerals such as Alumino-silicates, Ca-silicates and Mg-silicates in such soil samples plays a significant role in mitigating the effects of acidic forming constituents and slurred leachates [32, 33]. As expected the measured paste Eh values were higher in the all soil sample with an Eh of 518 mV (max) being indicative of a highly oxidative environment. The soil redox potential and pH directly and indirectly influences all chemical processes undergone by a soil sample, and consequently, it can also determine the behaviour of PTEs in that soil sample. The combined effect of pH and Eh on the mobility of PTEs is complex and is highly species specific. The solubility of the PTEs that can occur as free hydrated cations generally increases with a decreasing pH [34, 35], which will facilitate their mobility due to an increased concentration gradient.

B. Major Oxides and Potential Toxic Elements

The pristine soil (S1P) had a sandy texture (2.5 – 5.4 %clay) with the clay including quartz, microcline, muscovite-2M albite and calcian. The average pH and Eh values of S1P was 8.1 and 178 mV, respectively. These Eh values indicated that S1P might have been slightly contaminated due to the accumulation processes of Fe$^{3+}$ and S$^{2-}$, even at distances far away from the source [36], which was attributed to wind conditions with contamination being via air deposition, as the S1P had a high PTEs concentration (mg/kg): F (640), Cr (63) and Pb (30), values which were not within Soil Screening Values (SSV) ascribed to a PTE free soil as defined by Waste Act 59 (200). The most abundant oxides were (wt%): SiO$_2$ (75.8) > Al$_2$O$_3$ (11.2) > K$_2$O (5.08), and Fe$_2$O$_3$ (2.41). However, it was noticed that other PTEs such as Zn, Cu, Ni, Co, Mn, V, S and Cl, were all within the SSV – an observation attributed to the absence of industrial activity in the location where S1P sample was collected, as further evidenced by the high pH (8.1) and the relatively low S content; an indication that acid-forming potential is probably low for the sample [37].

The composite sample OCM1 (source) which was within a 100 m distance of sampling point (OCM2) from the closed metalliferous mine, both defined as upstream in Table I, Fig. 1. OCM1 showed average SiO$_2$ of 63.1 wt% (high), which increased in the upstream and downstream up to 72.7 wt% and 79.3 wt%, respectively due to the presence of oxide minerals and sulphidic silicate that are present in several forms in O’Kiep [32]. Also, the high SiO$_2$ content indicated active degradation including weathering of silicate minerals [38]. Localised hydrothermal alteration of hyperssthene around sulphide grains is a conspicuous feature in altered host rock. On the other hand, oxides such as Fe$_2$O$_3$, MgO and CaO present in all the soil samples are usually degraded via mineral carbonation mechanisms [32, 38]. Ca-silicates comprise minerals such as albite, calcian, anorthite and soda while Mg-silicates include phlogopite-1M and serpentine while Fe-silicates include goethite [32]. Also, Alumino-silicates such as microcline, orthoclase and microline were also detected upstream. Furthermore, on the surface, the oxide ore comprised of azurite, chrysocolla and malachite; hence up to 4453 mg/kg (average) of Cu. However, the OCM1 displayed pyrrhotite-chalcopyrite ore characteristics similar to the classic magmatic mafic to ultramafic copper-nickel cobalt bodies [10]. Another observation was (see Table I) the presence of Fe$_2$O$_3$, Al$_2$O$_3$, K$_2$O and Fe$_2$O$_3$, which are normally formed during weathering process and/or events [38].

All measured PTEs in the upstream samples, i.e. Pb, Zn, Cu, ...
Ni, Co, Mn, Cr, V, F, S and Cl, were present in high concentrations (mg/kg): 137, 109, 4453, 101, 46.5, 316, 110, 106, 1293, 8595 and 135, respectively. Clifford and Barton [39] reported that O’Kiep’s soil is rich in bornite Cu₉FeS₄; as evidenced by the high concentration values of S and Cu. From the literature reviewed, it was reported that distance from the pollution source and weather-related matters, play significant roles in the exposure to metalloids and metals [40]. PTE concentrations in the upstream showed that contaminant concentrations were higher near the close metalliferous mine and Fe-silicates include hematite. It was also noted that the average pH of 3.0 and Eh of 492 mV, which favoured hematite over goethite weathering, as observed in the study of Schwertmann [41] are pronounced in the presence of clay minerals [41], as observed in this study. The average pH and Eh values for midstream values were from 3.4 and 518 mV, respectively with SiO₂ and K₂O decreasing to 53.8 and 1.72 (wt.%), respectively; while Al₂O₃ and Fe₂O₃ increased to 14.9 and 10.6 (wt.%), respectively; a phenomena attributed to the wash-out effect of the suspended solids by mostly wind rather than moisture erosion, even when the samples were collected during the wet season. Such observations were also supported by the slope of the waste rock heap dump, which is not vegetated, further supporting waste heap weathering processes due to climatic conditions in this arid region. Additionally, acidity of the soil samples increases with the mobilisation of PTEs in soils, as some are potentially acid forming, posing a risk of acid metalliferous drainage (AMD) [42-51] formation in this area after washed out event and subsequent contamination of groundwater [21].

The average concentration of Pb, Zn, Cu, Ni, Cr, Co, V and S decreased in the midstream samples to (mg/kg) 53.2, 74.5, 98.0, 26.9 and 2613 respectively, while the averaged concentrations of Mn, F, and Cl increased, i.e., to (kg/mg): 613, 1424 and 143, respectively. This could be the consequence of a large quantity of mine waste heaps near midstream sampling site, with further PTE distribution due to anthropogenic activities and persistent wind conditions. The Pb, Cu, Cr and F concentrations were also not within the SSV in the midstream samples, while high concentration of Cr in the midstream samples could be ascribed to trans-boundary chromium discharge in drains from mine waste heaps in to the area; an indication that Cr leached into the subsoil. The Cr percolation may vary through the processes of reduction and oxidation than other PTEs [52]. PTEs found in the midstream samples were in the order of S > F > Cu > Mn. and These metals are important to monitor since they are capable of decreased vegetation due to the risk of bioaccumulation which will further facilitate soil erosion and possibly lead to groundwater contamination [21, 53]. Similar results were obtained by Moncho et al. [8] while predicting metals bioavailability in the top-soils in O’Kiep. For the downstream samples, the pH was 3.8 while the Eh was 531 mV, respectively. Further decrease of the concentrations of PTEs Pb, Zn, Cu, Ni, Co, Mn, Cr, V, F, S and Cl, was recorded (mg/kg): 52.8, 124.5, 503, 24.8, 13.0, 298, 59.5, 51.0, 610, 678 and 116; respectively; the concentrations of Pb, Cu, Cr and F were however all above the SSV, while the concentrations of Zn, Ni, Co, Mn, V, S and Cl were within the SSV guidelines. The solubility of the PTEs that can occur as free hydrated cations generally increases with decreasing pH [34]. Generally, the excessive concentration of PTEs in O’Kiep may lead to elevated potential risks to human health and the local environment [53] including any groundwater sources. Metals in soil can be adsorbed onto specific sites at low concentrations. It is hypothesised that little rainfall as experienced in O’Kiep can result in very limited percolation thus accumulation of salts, including the PTEs [16]. However, the content of the mobile fractions depends on the soil texture and characteristics [54]. The presence of Co, Ni, Zn, Co, Cr and V is associated with ilmenite and Ni, Cr, F associated with magnetite, which are the most common minerals in O’Kiep and they weather easily [55]. On the other hand, the presence of V, Zn, Cu, Ni and Co, are assoacted with biotite and apatite; however, these PTEs are unusual and forms a significant example of magmatic sulphide conglomerates found in O’Kiep [56] and other surrounding areas of Namaqualand. These results are similar to those reported in a study by Rozendaal and Horn [10], which focussed on the slag chemistry of the O’Kiep soil.

V. CONCLUSION

This study has provided an important reference information for the vulnerability of soils with regard to PTE mobility thus contamination from mine waste heap and mining activity in O’Kiep. The soils in O’Kiep are highly contaminated with average pH and Eh of 3.4 and 518 mV, respectively, with the most abundant potential toxic elements (PTEs) being (mg/kg): S (2965), Cu (1455), F (1125), Mn (425), Cl (133), Zn (97), Cr (87), V (80), Pb (67), Ni (45) and Co (28). The lower the pH, the higher the mobility of the PTEs. The extent of soil contamination and its effect on surrounding agro-ecosystems, all the way to the food chain, have received limited attention in O’Kiep. The bioaccumulation of these PTEs in food crops or even in vegetation, has never been explored, but as observed from various literature sources, it can cause long-term cumulative human and environmental health effects, as other diseases related to heavy metal contamination can ensue especially when these concentrations exceeds the Soil Screening Values levels. Currently, the elevated mobility and bioavailability of PTEs in soils of O’Kiep are of great concern in the area. The adequate protection and restoration of soil ecosystems contaminated by PTEs require remedial procedures especially in O’Kiep, whereby risk of groundwater contamination is high.

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Ms. Innocentia Erdogan is currently a Lecturer at Cape Peninsula University of Technology in the Department of Chemical Engineering and graduated with a Master’s Degree in Chemical Engineering. Her Masters’ dissertation looked at the application of biological reactors for the treatment of beverage industry wastewater. Ms. Erdogan holds a PhD candidate at the School of Chemical and Minerals Engineering, North West University. Her PhD focuses on species dispersion form a metalliferous mine drainage from waste rock associated with metal mining and biological passive remediation techniques to reduce the pollutants in acid mine drainage.