DETERMINATION OF HEAVY METAL CONTENT IN THE SOIL SAMPLE FROM THE MUNICIPAL SOLID WASTE DUMP SITE IN MASERU

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Heavy metals are mostly occurring naturally in the environment and their concentrations may be altered by anthropogenic activities such as wastes disposal. The study investigated and determined the presence of heavy metals in Ts'osane solid-waste dumping site in Maseru. Soil samples were randomly collected from the dumping site and screened qualitatively through chloride and hydroxide precipitation. Quantitative analyses of the acid leachate for few suspected heavy metals – cobalt, chromium, copper, iron, lead, manganese and zinc were done using Atomic Absorption Spectrometry resulting in concentration in the range of 0.2 to 95 μg g-1 of soil which are way above the soil's holding capacity that ranged between 0.05 and 0.225 μg g-1 of soil. Other parameters studied included the effect of pH, temperature and time of exposure to water. This revealed that prolonged exposure to water mimicking continued rainy conditions could lead to different leaching rates with copper ions demonstrating the lowest leaching rate over a period of five weeks as opposed to manganese which demonstrates about 170% on the fifth week relative to the first week, while as expected lower pH and higher temperatures favoured leaching of the metal ions. Lastly the soil-metal holding capacity was determined whereby it was shown that the soil bound lead the strongest (90%) while iron was the weakest bound (20%). The obtained values are worrisome since this dumpsite is upstream of the municipal water source for the Maseru Municipality.

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Introduction

As the world undergoes urban migration there is concomitant increase in waste generated from human activity that needs to be treated safely and effectively to avoid pollution and environmental health scares. However, solid waste remains a challenge in the Sub-Saharan Africa due to very weak efforts being made to respond to the challenges adequately despite the availability of knowledge.[1] Solid waste contains myriad of materials including paper, plastic, metals, rubber, paints, plant material, just to mention a few, the ratio and amount of which is reportedly linked to socio-economic status of the households.[2] The disposal of this waste should be carried out with care since some of these solids have a potential to leach out some hazardous materials. Consequently, municipal landfills are regarded as the sources of a wide range of compounds with environmental, wildlife and human health concern,[3] while also release greenhouse gases that contribute towards climate change.[4]

Since many different solid waste materials end up in the landfills, there is expectedly different types of chemicals that can be detected, the nature and abundance of which depend on the type of source. There are typically two types of pollutant chemicals from landfills – organic and inorganic compounds. The organic compounds that are released are suspected to have endocrine activity,[5] while the inorganic compounds that include some heavy metals that are also considered to have deleterious effects on health such causing neurodegenerative diseases such as Alzheimer's, Menkes, Wilsons,[6,7] Parkinson's, damage to liver, kidney, gastro intestinal tract, joints, and reproductive system.[8] As a consequence, heavy metals levels are regulated internationally by environmental protection agencies.[9,10]

Lesotho, a Least Developed Country landlocked by South Africa, is a signatory to some international conventions, treaties and protocols aimed at protecting the environment against contamination.[11] However, the solid waste sector is plagued with insignificant investment and poor legal framework as such it is still very rudimentary.[12] Solid waste management still relies heavily on some designated "official disposal sites" in most towns some of which are not protected hence access is not controlled for destitute people and animals such as dogs and cats that often scavenge off them.[13] This is so even in the capital city – Maseru, whose population constitutes about 23 % of the country, the solid waste is still being dumped in an old and abandoned quarry dug in the 1980s for road construction in Maseru lying about 5 km from the Maqalika reservoir, and a further kilometer or so to Caledon River, both of which are used as municipal water source.[14] This dumpsite has received a lot of attention with studies investigating its environmental and health impact.[15] However, no studies have been reported on the actual chemistry, except one study on the water quality in Caledon River showing a considerable degree of change in most physico-chemical properties attributed to human activity between upstream and downstream of the Caledon River and Maqalika stream confluence.[16]

Of the known hazardous chemicals that always find their way into the landfills is heavy metals, as such they are always a subject of study for landfill leachate as markers of landfill-linked pollution.[17] These are more serious since they do not decompose as opposed to the organic counterparts that, despite some being persistent, do end up being decomposed at some point. Despite occurring in most geological formations, exogenous heavy metals enter the environment via human activity.[18] These activities include various applications of metals in everyday life processes and utensils such as iron pots, stainless steel kitchen ware, copper cables, lead batteries, just to mention but a few. Although they are not hazardous in their intended forms, once they are disposed into the environment, they can change their chemical form through processes such as oxidation resulting in hazardous species.

A number of analytical techniques have been developed for quantitative determination of the heavy metals ranging from electrochemistry like electrochemical sensors,[19] screen printed sensors,[20] ion selective electrode approaches,[21] and voltammetry;[22] spectroscopy including atomic absorption/emission spectrometry and atomic mass spectrometry.[23] However, despite their efficiency and wide applications, these techniques are relatively expensive. Consequently, there has a lot of research towards development of alternative and affordable screening approaches using sensors. These techniques are mostly solution-based which still limits their application to wet chemistry and they cannot be applied in the field.[24] A simple colorimetric sensor has been reported based on silica-gel grafted with amino-compound with a potential for field application as it can be directly suspended into any water body.[25]

This study aims to explore the status of the heavy metals content of the soil sample collected at the dumpsite in Maseru and the dynamics of their release during rains as a preliminary to the study of monitoring the mobility of the leachate containing the same metal ions downstream leading to both the Maqalika Reservoir and the Caledon River that are important as a source of municipal water.

Experimental

Chemicals and Reagents

All the Analytical Reagent grade chemicals copper nitrate, cobalt nitrate, manganese nitrate, chromium (III) nitrate, ferric nitrate, lead nitrate, sodium hydroxide and nitric acid were used as is and were obtained from Merck South Africa (Johannesburg, South Africa). The distilled water was prepared in house using water still and used to prepare respective standard solutions as required. The pH measurements were made using a Hanna pH-meter (Romania).

Collection, storage and treatment of the samples

The surface (not exceeding 20 cm depth) soil samples were collected from the study area (Ts'osane dumping site – see Figure 1) by random sampling from five different areas where the soil was exposed. These soil samples were mixed to provide representative sample, about 1-kg of which was taken to the laboratory. This sample was further homogenized by grinding using mortar and pestles. The homogenized soil sample was sieved to achieve a particle size ≤ 0.250 mm and stored in a refrigerator at around 5 °C until subsequent analyses.

Treatment, extraction and analysis

For the preliminary screening experiment, 10 g portions of the samples were dissolved in 25 mL of distilled water or 6 M HNO_3 for aqueous and acid digestions respectively, and left to extract for about 30 min with shaking. The suspensions were then filtered to get rid of the soil particles. The extracts were then treated with either HCl to test for insoluble chlorides or sodium hydroxide to test for insoluble hydroxides. To achieve these, about 2 mL of the extracts were transferred into the test-tubes, subsequently HCl or NaOH was added until no sign of formation of a precipitate was observable. Thereafter the solutions were let to settle and the visual inspection was carried out.

Regarding the spectroscopic analyses, Varian Spectra AAS 100 Spectrometer (California, USA) was used for quantitative analyses of the heavy metals. First, the analytical curves of the suspected ions prepared by preparing and analysing the nitrates mixture of the individual metal ions in the range of $1 - 250$ μg mL^{-1}. These solutions were thereafter stored at the same temperature as the soil samples when not in use. The aqueous and acid suspensions of the soil sample described above were filtered and aspirated into the atomic absorption spectrometer. The actual concentrations were determined from the regression equation from the calibration curves.

Exploring the dynamics of the leaching of the heavy metals from the soil

A number of different experiments, namely, the effect of period of soaking, the effect of pH and the effect of temperature were performed using 1-g portions of the well-ground soil sample. To achieve these, the pre-weighed soil samples were suspended in the appropriate solvents and shaken for a specified period and temperature (see details in the results section). Thereafter, the suspensions were filtered and the filtrates aspirated into the spectrometer. The remaining solutions were stored in the refrigerator for further use.

Determination of the adsorption capacity of the soil for the heavy metals

To achieve this, the soil sample was treated with 6 M HNO_3 and rinsed thoroughly with water until the pH of supernatant liquid was neutral. Thereafter this soil was air-dried to a constant mass. To three 10-g portions of this soil sample, 25 mL of 100 μg mL^{-1} solution of the six-component standard mixture was added and allowed to equilibrate for a week (7 days), thereafter filtered and analysed appropriately. The absorbances of the original 100 μg mL^{-1} and the resulting filtrate post adsorption experiment

were compared to evaluate the extent of adsorption capacity for each metal ion by the soil sample.

Results and Discussions

Profiling of the solid waste dumpsite

Figure 1 is the satellite picture of part of Maseru map showing the dumping site and the surrounding residential area as well as a run-off stream leading to the Maqalika municipal water reservoir (top left corner). As can be seen, this site is located in the middle of a densely populated residential area as well as being upstream of the Maqalika reservoir (the flow is from South-East to North-West), which makes it a pollution concern threat.
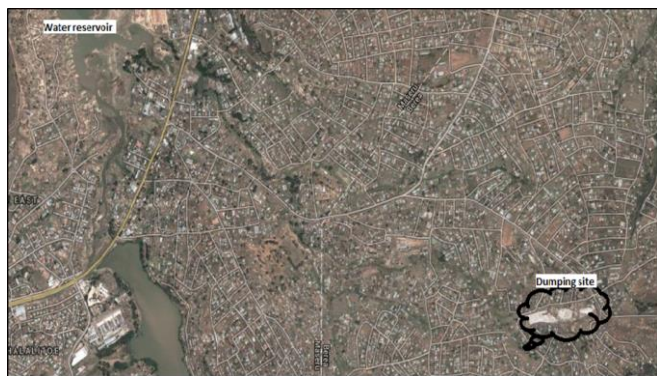

Figure 1. The satellite map of Maseru showing the Maqalika Reservoir and the dumpsite

Qualitative screening of the presence of heavy metals using wet chemistry

Most hydroxides and chloride salts of heavy metal ions precipitate out of their respective aqueous solutions. These therefore present an easier way of qualitatively testing presence of heavy metal ions by hydroxide and chloride precipitation and assessing the colour of the precipitates formed thereof. Table 1 shows the results obtained during the precipitation reaction of the nitric acid digestion extracts precipitated with chloride ions and sodium hydroxide. These precipitates were identified by comparison with the colours of the precipitates from the known reagents that would be likely to be present in the soil sample.

Table 1. The chloride and hydroxide precipitates and their colours for different metal ions.

Medium	Colour of precipitate		Possible/expected metal ion
	after HCl	after NaOH	
HNO_3	White	White, grey, rust red, dark	Pb^{2+}, Fe^{3+}, Mn^{3+}, Zn^{2+}
HNO_3	White	White, rust red, Grey	Pb^{2+}, Fe^{3+}, Mn^{3+}, Zn^{2+}
HNO_3	White	Rust red, dark brown	Pb^{2+}, Fe^{3+}, Mn^{3+}, Zn^{2+}
H_2O	White	White	Zn^{2+}, Pb^{2+}
H_2O	White	White	Zn^{2+}, Pb^{2+}
H_2O	White	White	Zn^{2+}, Pb^{2+}

Efforts to separate these precipitates for further analysis were not very successful since the precipitates were only partially separated.

Total acid digestion and quantitative analysis of the samples

This being a preliminary study, only a few metal ions using an atomic absorption spectrophotometry were analysed. Individual standards were prepared in the concentration range of 1 - 250 µg mL^{-1} of each ion as appearing in Table 2.

Table 2. Some analytical data obtained from the calibration curves of the different metal ions.

Ion	R^2	Average abundance (µg g^{-1})		Relative abundance*
		Water digestion	HNO$_3$ digestion	
Co	0.9978	$0.005 \pm ND^{\#}$	0.294 ± 0.012	63
Cr	0.9989	0.020 ± 0.004	0.359 ± 0.007	18
Cu	0.9899	0.082 ± 0.004	9.087 ± 0.052	110
Fe	0.9977	0.206 ± 0.013	95.702 ± 0.039	466
Pb	0.9969	0.044 ± 0.001	9.419 ± 0.021	214
Mn	0.9987	0.495 ± 0.036	8.111 ± 0.024	16
Zn	0.9992	0.096 ± 0.006	0.376 ± 0.075	4

* Ratios of concentration after HNO$_3$ and aqueous extractions
$^{\#}$ The confidence interval not determined due to the low magnitude of the concentration.

The linearity of the response versus concentration was determined for respective analytes. Analysis of regression was performed to obtain the linearity for each of the analytes. Table 2 shows the analytical data from the calibration curves of the respective standards as well as the calculated concentration of the analytes.

As can be seen from Table 2, acid digestion yields more than 10 times the aqueous digestion. This indicates that most metals occur in a relatively water insoluble state. However, it must be noted that the fact that aqueous digestions still yields analysable amounts of the ions, is a cause for concern given that the sampled site is upstream of the water supply to the Maseru Municipal water reservoir (Maqalika Dam). In addition to this, even without leaching, these metals could still be washed as fine suspension of the soil during rains. It would be interesting to identify the possible sources for these ions, although the levels were considerably low compared to the other ions. As expected the abundances of iron and copper were the highest. This can be explained since these are the most common metals used in most domestic tools and electrical wiring of houses. The higher increase following acid digestion could be attributed to the digestion of the metal pieces or some oxides that were not soluble in the distilled water.

Since the soil sample was obtained directly from the solid waste dump, it was not important to compare the obtained values to those stipulated in the guidelines for the occurrence of these ions in both soil and water respectively. Their concentration in the soil obtained upstream was not detectable indicating that the obtained amounts were attributable to the solid waste being dumped in this site.

The effect of time of soaking the sample with distilled water to mimic water moisture

Having established the levels of the heavy metals in the sample, the next task was to investigate the effect of natural rainfall and moisture on leaching of these ions. To achieve this, 5 different soils samples were obtained and soaked in distilled water over a period ranging from one to five weeks. Thereafter, the samples were filtered appropriately before being analysed. Figure 2 shows the effect of soaking time on the leaching of these metal ions relative to day seven (after a week of soaking the samples since day 1 did not yield much).
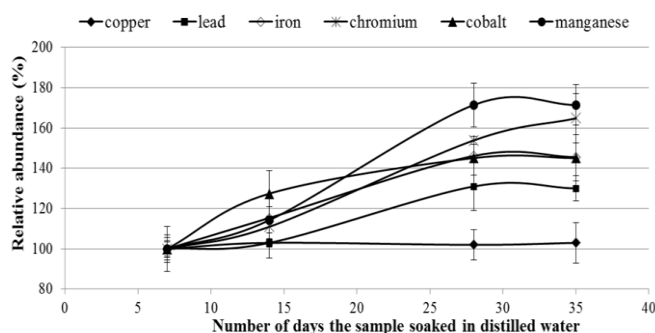

Figure 2. The effect of soaking time on the release of metal ions in the distilled water

Before dwelling in the interpretation of these results, it is worth noting that the observed trend was constructed using absorbance values not the actual concentrations. The trend shows that Cu (II) is a bit insensitive of the soaking time, while other ions are quite sensitive. This would suggest that these ions would be highly mobile as they dissolve more as they are subjected to water for extended period of time, thus posing more environmental risk than copper which is comparatively less mobile.

Effect of pH of the leaching of the metal ions

We have observed that these metals are released more in acidic pH values attributed to the reduction of the electron density in the binding sites of the soil. To establish the effect of pH, 6 different solvent mixtures were prepared by spiking with either HNO_3 or NaOH to obtain different pH levels. Different soil samples were thereafter soaked for a 7-day period before the analysis. Figure 3 shows the effect of pH on the leaching of the metals relative to the original solution whose pH was measured to be 6.3.
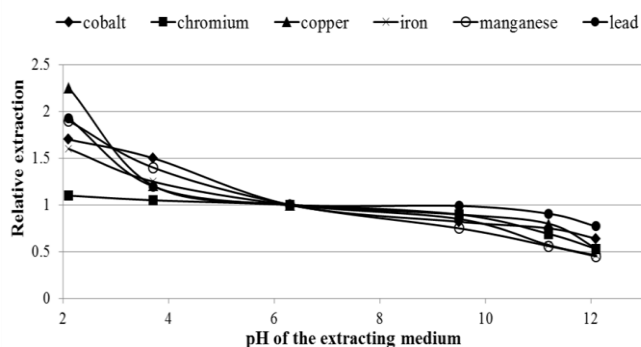

Figure 3. The effect of pH of the solvent on leaching of the metal ions measure relative to pH 6.3, the pH of the original sample after suspension in 25 mL of water.

As it was expected, all the ions seemed to dissolve more in acidic medium. However, chromium seemed less soluble as its value remained almost unchanged despite the pH variation. Dissolution of copper on the other hand increased the most at pH value of 2.1. This could infer that there was more copper in the sample that had not dissolved fully at the pH of 3.7, hence an increase as the pH was decreased further. This arguably could be due to ion exchange behaviour between the metal ion and the hydronium ions under acidic media.[26] Regarding the drop in extraction as pH increases, this can easily be explained in terms of the decreasing solubility of the metal ions in basic medium. Most of heavy metals produce relatively insoluble hydroxides hence this would reduce their solubility in the basic conditions.

Effect of temperature on the leaching of the metal ions

Temperature is one of the universally known factors that affect solubility of materials. Figure 4 shows the effect of varying temperature on the leaching of the metal ions. The figure is plotted with the absorbances recorded relative to the extraction at room temperature (24 °C), following a continuous shaking for 30 min.

It is evident from Figure 4 that these ions are all more soluble as the temperature increases although only slightly with only lead showing 12 % increase at about 55 °C relative to the room temperature (24 °C). Since temperature, in nature, does change by this magnitude, especially in the presence of moisture, these results may not necessarily have a major bearing on the natural environment.
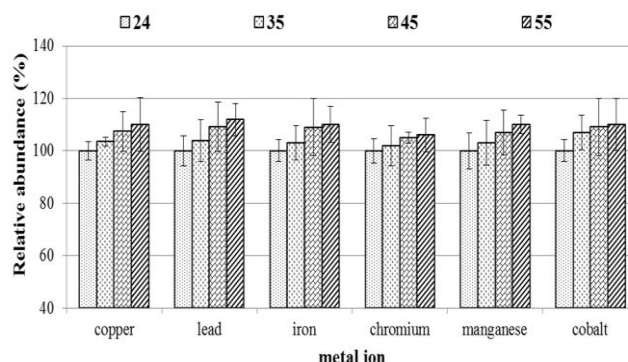

Figure 4. The effect of temperature of water on extractability and leaching of the metal ions.

Determination of the adsorption capacity of the soil

To explore the adsorption capacity of the soil, a pre-acid extracted soil was rinsed with conspicuous amount of distilled water to remove as much acid as possible. Thereafter this sample was air-dried to a constant mass. This would give a measure of how much of each metal ion the soil can hold before its leaching could occur, if the washing of the sediment is ignored. Three 10.0 g portions of the air-dried samples were weighed and soaked with respective 25-mL aliquots of 100 $\mu g\ mL^{-1}$ solution of the six-component standard mixture and allowed to equilibrate for a week (7 days), thereafter filtered and analysed appropriately. Figure 5 shows the adsorption capacity of the soil for the individual metal ions relative to the 100 $\mu g\ mL^{-1}$ standard solution.
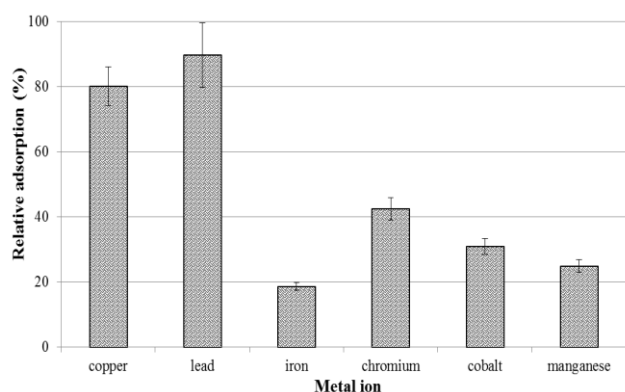
Figure 5. The adsorption capacity of the sample soil for different metal ion standard solution.

As is apparent from figure 5, the soil has a very high adsorption capacity for lead (almost 90 %) followed by copper (80 %) ions with a very low adsorption capacity of iron and manganese (around 20 %). Despite this good adsorption capacity, one cannot make a strong assertion that this adsorption capacity is attributable to the natural soil that exists in this dumpsite but could be a result of other materials that are known to be good adsorbents of metal ions such as chicken feathers, animal skins/fur, rubbers materials as well as plant material that are visible on the site.[27] The observed trend could be due to ion exchange behaviour that leads to selective adsorption on lead and copper more than the other ions that could be too weakly bonded to the "active sites" of the adsorbent materials. With or without any exogenous agents mentioned above, soils rich in clays reportedly demonstrate a relatively higher ion exchange capacity than those with less clay content, thus will show higher heavy metal ion uptake than a poorer soil.[26]

However, the actual quantitation of the ions reveals that the actual adsorption capacity of the soil ranged from 0.225 µg g^{-1} of soil for Pb and 0.05 µg g^{-1} for Mn. This therefore suggests that the levels detected for these compounds when using acid digestion (between 0.29 and 95 µg g^{-1} of soil) are far beyond the soil's holding capacity. Hence this is a call for concern regarding the mobility of these ions downstream during rains.

Conclusion

The study was able to determine the presence of some heavy metals in the solid waste dumpsite with concentrations ranging from 0.2 to 95 µg g^{-1} of soil sample. The fact that these metals are detectable with the water treatment at room temperature suggests that these metals can easily leach into the dumpsite leachate hence a potential hazard to the downstream biota as well as the Maseru Municipal water supply which is downstream to this site. Clearly iron is the most abundant followed by copper, possibly due to the common use of these two metals domestically in appliances such as electrical cables (copper) and steel products (iron). The other metals are in relatively lower levels since they are not as predominantly used. Interestingly lead, was even higher than copper at 9.419 and 9.087 µg g^{-1} of soil respectively. This could be possibly coming from the car batteries that are also disposed into the dumpsite. Another striking observation was the high level of

manganese with 8.111 µg g^{-1} of soil. Manganese is used mainly in the manufacture of iron and steel alloys as an ingredient in various products such as batteries, glass and fireworks, bleaching and disinfection products in the permanganate form, as an oxidant for cleaning, fertilizers, varnish and fungicides and as livestock feeding supplements, just to mention a few (WHO, 2011).[28]

The study of the adsorption capacity revealed that these ions already are above the adsorption capacity of the soil, suggesting that, notwithstanding the simple wash off during rains, most of the soil is oversaturated and cannot hold these ions when it rains. The next phase of this study will be to assess the presence of some of these ions in the stream that runs off this side although it runs mostly during rainy weather. Another issue is the difficult accessibility of this area due to the fact that it runs through the residential area. Either way there is need for more protection of this site since further dumping will certainly increase the concentrations beyond the holding capacity of the soil thus increasing the severity of the environmental hazard it already poses.

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