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First Screening Study of Metal Content in Soil from a Mixed Waste Receptacle

Shaneel Chandra[1], Philomena Gangaiya[2], Culwick Togamana[3] and Surendra Prasad[1]

[1]*School of Biological and Chemical Sciences, Faculty of Science, Technology and Environment, University of the South Pacific, Suva, Fiji*
[2]*Wollongong City Council, Locked Bag 8821, Wollongong DC NSW 2500, Australia*
[3]*National Parliament Office, P.O. Box G19, Honiara, Solomon Islands*

Abstract

We report the first screening study for the metals copper, zinc, lead, nickel and cadmium in the Lami municipal disposal facility, in Suva, Fiji where virtually uncontrolled dumping has been carried out for over fifty years. Soil from three parts of the facility having had different degrees of usage was analysed for a range of heavy metals, and evaluated according to international guidelines. The results show copper (100 – 220 mg kg^{-1}), lead (200 – 500 mg kg^{-1}) and zinc (220 – 350 mg kg^{-1}) concentrations exceeded commonly used eco-toxicity threshold values (copper, 160 mg kg^{-1}, lead, 210 mg kg^{-1} and zinc 220 mg kg^{-1}). Moreover, there were indications that considerable leaching may have been occurring for long periods of time at the site. Overall, this study shows that even in areas with little industrialization, lack of adequate waste management controls can result in unusually high levels of contamination. The results raise concerns about the wellbeing of the communities living adjacent to the facility that depend on the adjacent marine environment for subsistence.

Keywords: *Lami, Heavy metals, Waste*

1. Introduction

Pollution of the environment with toxic metals has been attracting considerable public attention over the past few decades (Peng *et al.*, 2008; Toribio and Romanyà, 2006; Van Alsenoy *et al.*, 1993). This is evidenced by a constant stream of publications in the literature exploring heavy metal extraction (Agemian and Chau, 1976), interrelationships (Chen, 2000), fractionation in the environment (Zhang *et al.*, 2013), bioaccumulation (Mathews and Fisher, 2009) and toxicity (Ghariani *et al.*, 2010) among others. Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. Their toxicity stems from their bioaccumulative nature, making them virtually non-degradable (Reddy *et al.*, 2011). Consequently it is imperative to ensure safe disposal of wastes that have the potential to liberate heavy metals into the environment.

Industrialization and urbanization have elevated the anthropogenic contribution of heavy metals in the biosphere (Li *et al.*, 2012), and South Pacific island nations have not been spared in this regard. While globalization has created the demand for consumer products and services that generate different kinds of wastes from those produced by earlier subsistence societies, accompanying mechanisms for the safe management and disposal of resultant wastes have not kept pace with acceptable forms of control used elsewhere in the world (Morrison and Munro, 1999). Moreover, the cumulative effect of mixed dumping of such wastes over a long period of time could be quite significant. This kind of scenario exists at many waste disposal sites in Pacific Island countries and most of these sites are located in sensitive areas such as mangrove swamps, foreshore areas or riverbanks from where contamination can easily spread to other surrounding areas (Watling and Chape, 1992). However, there is no published data of detailed investigations of waste disposal sites in Pacific island countries to determine whether contamination has indeed occurred and, if so, the extent of the contamination, particularly from heavy metals. For instance, a study of the Lami waste disposal site in Suva, Fiji conducted more than a decade ago provided only a limited amount of data and pointed to the need for a more detailed investigation (Naidu and Morrison, 1994). Until its recent closure, the disposal site was the recipient of all of Suva's domestic and industrial wastes, which were disposed of together irrespective of composition. The level of industrialization in the area is not high as the economy is largely dependent on agriculture and tourism. However, numerous small to medium-scale manufacturing industries are present in the vicinity. Those utilizing the Lami disposal site for waste disposal included garment factories, food manufacturing, electroplating and mechanical works, and other commercial enterprises. No data on the composition of the wastes entering the disposal site is

available but visual observations indicate that material of an organic nature make up the bulk.

There is ample evidence to suggest that exposure to even low concentrations of heavy metals over long periods of time cause adverse effects (Kobayashi, 1971). Accordingly, in this work, we present the results of heavy metal levels assessment in selected sites in the recently-decommissioned Lami waste disposal site. The study was undertaken with an aim to provide more extensive information and to determine the extent of contamination using international environmental contamination criteria (Singh *et al.*, 2010). This study should also be of considerable interest to other countries where uncontrolled dumping exists as to the nature and extent of environmental consequences that could arise.

2. Methodology

2.1. Field Conditions

The Lami disposal site is located one kilometer to the west of the city of Suva, on the south coast of Viti Levu, the largest island in the Fiji archipelago. It is situated around 8.1416° S, 178.4419° E on the map, and is an almost rectangular- shaped area of approximately 0.2 km^2. It has been used as a disposal site since 1947. Mangrove forests surround the site, with the Southern side being on the coastline fronting the Suva Harbor. During its use, the site also lacked lining material or any other containment mechanism to protect the surrounding environment from leachates emanating from the disposal site. Being located on the windward side of the main island Viti Levu, the site receives considerable amounts of rain. Rainfall data computed from Fiji Meteorological Service measurements indicates annual average rainfall varies from 1000 - 2000 mm annually, and temperatures range from 22 - 32 ^oC (FMS, 2002). Thus, the warm, wet conditions are conducive for waste decomposition and leachate formation (Koshy *et al.*, 2007). The parts of the site that have most recently been in use are the southern, western and central areas. Dumped material was leveled using a bulldozer and layers of new soil piled on the disposed matter to allow for containment of odor and to facilitate access to other parts of the facility by transport trucks. Some areas of the Lami disposal site had previously not been in use for many years, leading to soil-like material supporting a variety of plant life.

2.2. Sampling Sites

Sampling was done between June and August of 2001. Owing to uncertainty regarding the usage of all areas of the Lami disposal site, coupled with the indiscriminate dumping pattern that was adopted at the site, visual cues such as extent and type of vegetation cover had to be used as indicators of recent use. Figure 1 shows the sampling site locations within the facility. Three sites were selected. Site A reportedly had not been used for five years and represented an area that had some opportunity for waste mineralization. The ground had a soil-like cover although this was not uniform and was characterized by small channels and drains bisecting the area. Vegetation of approximately 1 m height was also present. Site B was a still active area and little mineralization of waste material was evident although some vegetation cover was present. In Site C, the waste disposal had ceased for a year. Vegetation consisted mostly of creepers and weeds. The soil-like cover here was thin, discontinuous, and where present, was sandy and had a significant amount of gravel in it. The selection of sites of such varying stages of usage facilitated an assessment of the heavy metal levels across the disposal site.

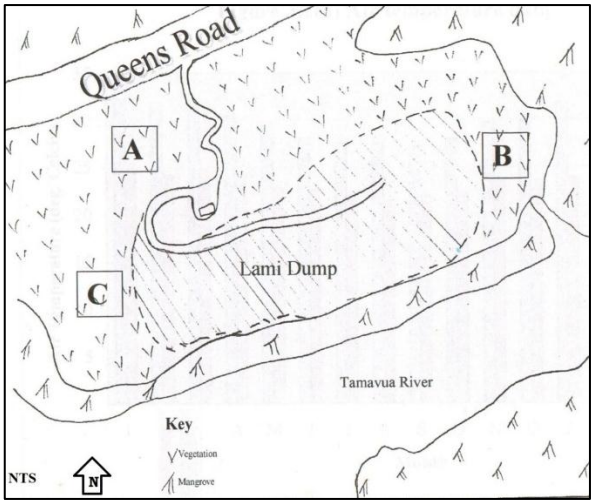

Figure 1. Unscaled map showing sampling locations within the waste disposal site.

2.3. Soil Sample Collection and Preparation

Within each site, a 9 m^2 area was marked off and further divided into 3 m × 3 m blocks. From each block, surface soil was collected to make a composite soil sample of about 1 kg. Any visible litter was removed and the samples left to air-dry in the laboratory for 14 days. The samples were then ground using mortar and pestle and sieved through a 0.5 mm nylon sieve. The sieved samples were manually homogenized by shaking and placed into acid pre-washed plastic bags for analysis.

2.4. Reagents and Equipment

Analytical grade ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma Aldrich (Australia), while respective metal stock solutions (1000 mg/L) were purchased from Spectrosol (USA), while all mineral acids were purchased from Univar USA). All chemicals were used without further purification. Ultra

high purity acetylene gas was purchased from BOC Gases (Fiji). Deionized water was used to prepare all solutions. Using the respective metal stock solutions, working standards of each metal were prepared using the linear range outlined by the instrument manufacturer's (Perkin Elmer) guidelines. These were: Cu (1.0 – 5.0 mg L^{-1}), Zn (0.2 – 1.0 mg L^{-1}), Pb (5.0 – 20.0 mg L^{-1}), Ni (0.5 – 2.0 mg L^{-1}) and Cd (0.5 – 2.0 mg L^{-1}). In each instance, 100 mL solutions of five working standards not exceeding the specified linear range were prepared in 10% nitric acid.

2.5. Analytical Methods

To extract the total amounts of heavy metals, a mixture of nitric (HNO_3), perchloric ($HClO_4$) and sulphuric (H_2SO_4) acids in the ratio 10:2:1 was adopted. This method has been previously reported for extracting metals (Yoshigae *et al.*, 1998). It is appropriate, being the strongest acid mixture to be able to efficiently extract metals from all possible fractions of soil, particularly as it is dominated by HNO_3 which particularly targets the organic fractions.

For extraction of metals, 1 g of ground soil sample was accurately weighed and digested using a 25 mL mixture of HNO_3-$HClO_4$-H_2SO_4 (10:2:1) acids, while being heated on a hotplate. When perchloric acid fumes were observed and the acid volume had reduced, 20 mL of deionized water was added and the mixture was further boiled for 15 min before being allowed to cool to room temperature. The mixture was filtered through Whatman No**.** 541 filter paper, washed several times and the filtrate and washings diluted to a final volume of 50 mL. These were analysed for Cu, Zn, Cd, Ni and Pb using a Perkin Elmer 3110 flame atomic absorption spectrometer. Statistical significance of all correlation coefficients at the 95% confidence level was tested using Student's t-test. Uncertainties associated with the slope and *y*-intercepts of all linear plots used for calibrations, as well as all mean value comparisons were expressed as confidence intervals at the 95% level.

3. Results and Discussion

3.1. Total Heavy Metal Levels in Soil

In determining total heavy metal content in the soil, an acid mixture of HNO_3-$HClO_4$-H_2SO_4 in the ratio 10:2:1 was employed to digest soil samples. The results of the heavy metal analysis for all three sites are presented in Table 1 and sorted by metal in Figure 2. From these results, it is evident that site A contained the lowest levels of heavy metals of all three sites. The levels of metals at the remaining two sites varied, with site B having a higher concentration of Zn of all three sites, as was observed for the metal in the bioavailable fraction.

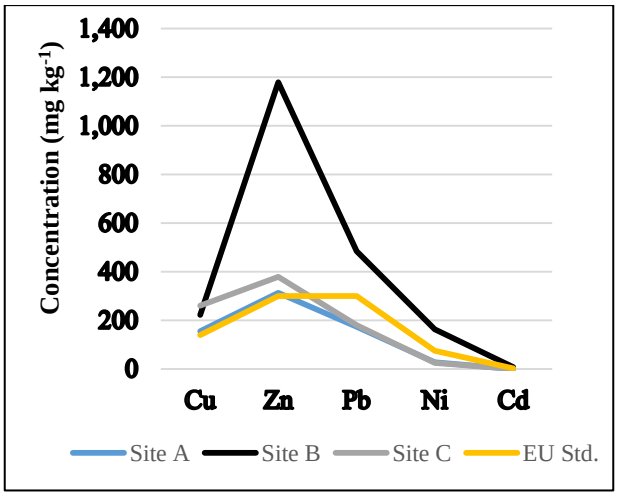

Figure 2. Heavy metal levels sorted by type and site.

Site B also had slightly higher metal levels than site A, with the exception of Cu. Site C, meanwhile had metal levels intermediate between sites A and B, with the exception for Pb. The value of Pb (485 mg kg^{-1}) at this site was extremely high, quite likely as a consequence of localized Pb-bearing wastes in this area.

3.2. Comparison with International Contamination Guidelines

A comparison of heavy metal levels with internationally accepted guidelines (Singh *et al.*, 2010) can allow for determining if the site is contaminated. Such a comparison between the standards defined and adopted within the European Union (EU) countries and those found in the sites in this study as shown in Table 1 is presented in Figure 2. Notably, at all three sites, the levels of Cu and Zn exceeded those accepted by the EU as contaminant levels. For Pb, sites B and C contained higher than EU-specified levels, with site C posing as an area of particular concern. Nickel was highest in site B (163 mg kg^{-1}), and exceeded EU contaminant guideline (75 mg kg^{-1}) for the metal, while Cd levels in sites B and C also remained higher than the EU limits (Table 1).

The high incidence of the remaining heavy metals, particularly Pb across the three sampling sites is a concern. It may be the result of dumping of Pb-containing wastes, especially batteries that are used in large numbers in island countries including Fiji. The lack of any proper disposal facilities for these batteries means that they eventually find their way into waste disposal facilities. Site B, which was the active dumping receptacle at the time of sampling had high levels of Cu, Zn, Pb, Ni and Cd. This may be due to inputs of heterogeneous waste at the site, which would have had the least period of metal export from the soil via processes such as uptake by plants growing in the

area (Borghei *et al.*, 2011). Based on the data obtained, we suggest that in the Lami disposal site, heterogeneous waste dumping has been a larger source of heavy metals than that present in the soil from its parent material. This observation is based on metal concentration trends evident across the three sites where the levels tend to decrease with greater disuse of the active dumping regions. Given that metal loss from soil through processes such as plant uptake (Chen *et al.*, 2003), leaching from soil (Rabajczyk, 2011) and migration through soil sub-layers (Varank *et al.*, 2011) has been well-documented, it is extremely likely that with time, metal levels would be significantly attenuated in a site, and either be lost to the surroundings or accumulate in lower soil strata (McBride *et al.*, 1997). In the Lami disposal site, a combination of these processes may be likely, particularly due to the discharge of unchecked and untreated leachate from the facility being allowed to permeate into the surrounding mangrove areas. Generally, the results obtained are not unexpected for a waste disposal site that has been the recipient of all categories of waste including those that might have contained appreciable amounts of heavy metals. Even if the original waste materials were not appreciably contaminated with heavy metals, their eventual decomposition would result in a less bulky residual material that is enriched in components such as heavy metals that resist decomposition (Rabajczyk, 2011; Varank *et al.*, 2011).

Table 1. Total heavy metal concentrations in soil in the disposal facility at different sites.

	Concentration (mg kg^{-1})			
Metal / Site	A	B	C	European Union Standards for soil (Singh *et al.*, 2010)
Cu	156.4 ± 55.8	223.4 ± 54.9	261.4 ± 12.8	140
Zn	312.9 ± 66.1	1179.9 ± 375.6	379.3 ± 164.6	300
Pb	173.7± 36.2	485.4 ± 204.5	180.4 ± 100.7	300
Ni	28.2 ± 13.4	163.1 ± 59.6	25.1 ± 10.4	75
Cd	<LOD[a]	8.5 ± 0.6	<LOD[a]	3

[a]Denotes concentration is below limit of detection. The ± values denote the standard deviation of three measurements.

3.3. Quality Control of Data

Various methods of quality control were adopted in the study to ensure reliability of measurements and generation of representative data. The spectrophotometer was calibrated daily prior to each set of analyses, using standard solutions of the metals to be analyzed. Periodic assessment of instrument drift was undertaken by analyzing standards intermittently between samples. In between each sample aspiration, the instrument was permitted to flush out the preceding sample by allowing continuous stream of distilled water, and monitored in the continuous output mode.

In order to gain an insight into intra-sample variability (further compounded by limitations on the use of the strong hydrofluoric acid), samples were analyzed in triplicate. The results from these analyses are included in Table 1 and presented as the mean and the standard deviation among the replicates. Furthermore, the limit of detection was determined and spiked recovery analysis was carried out as quality control measures. The limit of detection value for each metal is presented in Table 2. Here, limits of detection for Pb was the highest (at 7.8 and 5.0 mg kg^{-1}, respectively) among those for the metals, with Zn being the lowest (0.7 mg kg^{-1}).

Table 2. Quality control of data, listing the limit of detection (total) of metals detectable and percentage recovery.

Metal	Limit of detection (mg kg^{-1})	Percentage recovery (%)[*]
Cu	1.3	104
Zn	0.7	72
Pb	7.8	110
Ni	4.3	41
Cd	2.0	102

[*]The percentage recovery refers to the amount recovered following spike of the sample with metal standard.

To isolate any matrix effects, studies were carried out by spiking some pre-analyzed samples with variable aliquots of 50 – 100 mg L^{-1} standard solution of each metal as per published procedure (Wragg *et al.*, 2011) to arrive at final concentrations within the standards' calibration range. The spiked samples were then mineralized using the same digestion procedures as were applied to the non-spiked samples, and therefore subjected to the entire treatment and analysis protocol.

Such treatment of the introduced aliquot ensures that any losses within the sample treatment or loss through matrix effects is detected (Momen *et al.*, 2006). The results obtained for spiked recoveries are also presented in Table 2. Cu, Pb and Cd showed good recoveries, confirming there was no significant matrix interference for these metals in the samples. However for Ni and Cd, the extremely low recovery values suggest that there may be matrix effects affecting the response of the method. Common types of interference from within the matrix include those from anions, with the anions resulting in the formation of compounds of low volatility, which may reduce the rate of atomization of the analyte in atomic absorption spectrometry and hence low recovery.

3.4. General Discussion

The heterogeneity in metal distributions found at all three sites in the Lami disposal site, even over short distances, has serious implications for future management of these sites. Thus, any contamination assessment at such a site requires a very intensive sampling program at shorter distances to ensure that all contamination hotspots are captured.

Based on the EU guidelines, this site would be declared as heavily contaminated and requiring extensive clean up. Furthermore, the Lami disposal site's hazardous location close to the harbor area may necessitate clean-up in future before any re-use. High concentrations of heavy metals in biota in the vicinity have been reported (Naidu and Morrison, 1994). Thus, there is a possibility that the metals studied may be leaching out into the marine environment.

4. Conclusion

In this study, the concentration profiles of Cu, Zn, Pb, Ni and Cd in the Lami municipal site were established. The total concentrations of these metals were high enough to exceed international accepted guidelines for polluted sites. Cu and Zn are of concerning amounts across all three sites. On the other hand, in the active disposal section and that disused over a year, Pb was present in high amounts exceeding European Union pollution standards. The heterogeneity of the disposal method at the facility was also an overriding factor that appeared to be strongly influencing the localized hotspots of metals encountered at various sites. Further work through biomonitoring of the site may be essential in the long term to ensure an accurate picture of the risks posed is established.

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Correspondence to: S. Chandra

Email: shaneel.chandra@usp.ac.fj