CSIRO Publishing The South Pacific Journal of Natural and Applied Sciences, **34**(1), 21-28, 2016
www.publish.csiro.au/journals/spjnas 10.1071/SP16003

Study of Heavy Metal Fractionation in the Lami Municipal Disposal Facility, Fiji

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Abstract

This work reports the first screening study of the bioavailability of heavy metals such as copper, zinc, lead and nickel in the Lami municipal disposal facility, Suva, Fiji where virtually uncontrolled dumping had been carried out for over fifty years. The soil samples from three parts of the facility were collected and the potential for mobility into the surrounding marine environment was assessed according to international guidelines. The results showed high levels of Pb in Site A (109.0 mg kg^{-1}) and that Zn was the predominant metal across Sites B and C with 550.7 mg kg^{-1} and 206.8 mg kg^{-1}, respectively. Ni was present in the least amount with the highest value 8.7 mg kg^{-1}. In addition, Cu, Pb and Zn concentrations exceeded commonly used eco-toxicity threshold values. Moreover, there were indications that considerable leaching of the studied heavy metals may have been occurring for long periods of time at the sites. Overall, this study showed that even in areas with little industrialization, lack of adequate waste management controls could result in unusually high levels of heavy metals contamination of the soil. The results raise concerns about the wellbeing of the communities living adjacent to the Lami municipal disposal facility that depend on the adjacent marine environment for their subsistence.

Keywords: *Lami disposal facility, Heavy metals, Bioavailable fraction*

1. Introduction

In the past few decades, extensive attention has been devoted globally to the incidences of heavy metal pollution (Huang *et al.*, 2016; Peng *et al.*, 2008; Toribio and Romanyà, 2006). Works on fractionation in the environment (Zhang *et al.*, 2013), bioaccumulation (Mathews and Fisher, 2009) and toxicity (Ghariani *et al.*, 2010; Reddy *et al.*, 2011; Saito, 2004) have regularly been reported among others. The heavy metals are significant environmental pollutants. Thus, their toxicity is a problem of increasing concern for ecological, evolutionary, nutritional and environmental reasons (Nagajyoti *et al.*, 2010). Their toxicity, exacerbated from bioaccumulation, renders heavy metals 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.

To be able to assess the risk of heavy metal toxicity to flora and fauna, it is essential to determine the levels of metals present in soils as it provides a snapshot of the extent of metal enrichment of a sphere of the physical environment. Though measurements of the total amount of contaminants like heavy metals in soil are used for risk assessment, they do not adequately reflect the actual hazards to living organisms, since heavy metals are physically and chemically associated with soils and sediments (Yoon *et al.*, 2016). Thus, an alternative approach largely used to estimate the degree of heavy metals contamination and their potential risks linked to the increase in their concentrations is to study the bioavailability of the heavy metals in the soils and sediments (Pereira *et al.*, 2015).

The Tessier sequential extraction method of determining the bioavailable fraction of the heavy metals in soils and sediments has widely been accepted as an important tool providing insights into the environmental behavior of potentially toxic elements (Roig *et al.*, 2016; Tessier *et al.*, 1979). The chemical speciation of heavy metals has been associated with different fractions such as: the exchangeable fraction (F1) that is affected by changes in the solution ionic composition and the carbonate fraction (F2) that is highly susceptible at lower pH levels. The F1 and F2 fractions are considered to be the most mobile and easily available for plants (Singh *et al.*, 2016). Other fractions are; reducible (F3), oxidizable (F4) and residual (F5) fractions. Metals from these fractions under natural conditions generally do contribute to bioavailability and thus do not enter into the food chain over a reasonable span of time (Tessier *et al.*, 1979).

The present work reports levels of copper, zinc, lead and nickel in the bioavailable fraction of soils from the Lami municipal waste receptacle. Recently, we have published our findings of the Lami municipal facility for total metals (Chandra *et al.*, 2015). Thus, the present report augments that of our previous study and presents an immediate snapshot of the risk status of the heavy metals (Cu, Zn, Ni and Pb) to the sites and surroundings.

2. Methodology

2.1. Field Conditions

Located one kilometer to the West of the capital city Suva, the Lami municipal disposal site sits on the South coast of Viti Levu, the largest island in the Fiji archipelago (Figure 1). It is a rectangular-shaped area of approximately 0.2 km^2 and had been used as the waste disposal site since 1947. Mangrove forests surround the site, with the Southern side being on the coastline fronting the Suva Harbor. Until its closure in 2004, the disposal site was the recipient of domestic as well as industrial wastes from the greater Suva that 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 of Lami municipal disposal facility. Those that utilized the disposal site for waste disposal included garment factories, food manufacturing, electroplating and mechanical work industries as well as other commercial enterprises. At the time of sampling, no data on the composition of the wastes entering the disposal site was available but visual observations indicated that material of an organic nature make up the bulk (Chandra *et al.*, 2015).

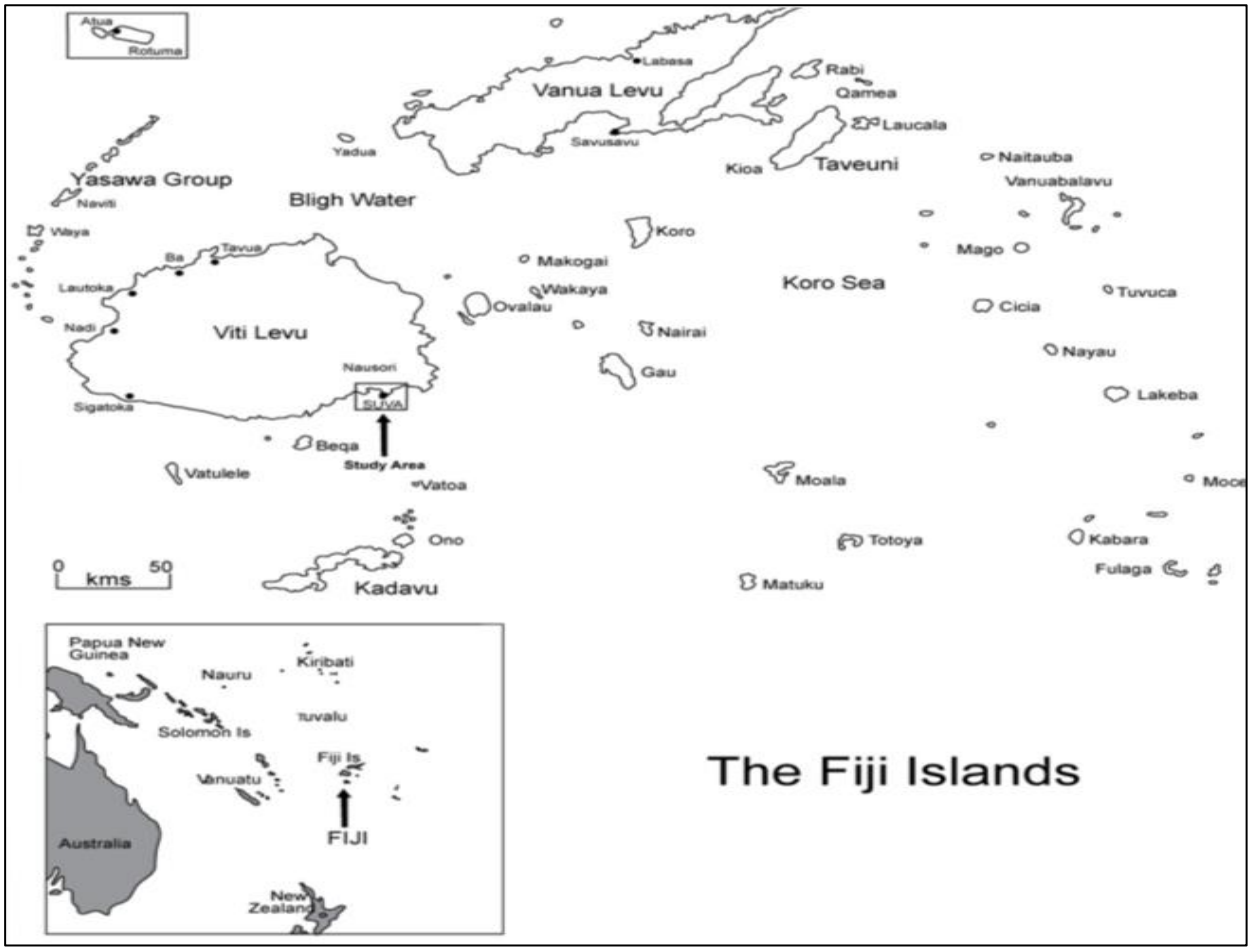

Figure 1. Map of the Fiji islands showing the Lami disposal facility (Gangaiya *et al.*, 2011).

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 ^{o}C (FMS, 2002). Such warm, wet conditions are conducive for waste decomposition and leachate formation (Koshy *et al.*, 2007; Fan *et al.*, 2006). The parts of the disposal site that had lately been in use are the Southern, Western and Central areas. The 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 through to other parts of the facility by transport trucks. Some areas of the disposal facility had previously not been in use for many years which led to a variety of plant life on them (Chandra *et al.*, 2015).

2.2. Sampling Sites

Three sampling sites were selected based on degree of usage. Site A reportedly had not been used for at least 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 dumping had ceased for about a year. Vegetation consisted mostly of creepers and weeds. The soil-like cover in Site C 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 facility.

2.3. Soil Sample Collection and Preparation

Soil collection and treatment followed the protocol of Chandra *et al*. (2015). Within each site, a 9 m^2 area was marked off and further divided into 1 m × 1 m blocks (total of nine blocks). From each block, three samples of surface material were collected to make a composite 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

Deionized distilled water (DDW) was used to prepare all solutions. Analytical grade magnesium chloride, sodium acetate, acetic acid, sodium dithionate, sodium citrate, citric acid, hydroxylamine hydrochloride, hydrogen peroxide, nitric acid, hydrochloric acid and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma Aldrich (USA). Metals standard solutions were purchased from Spectrosol (Australia), while all acids were purchased from Univar (USA). All chemicals were used without further purification. Ultra-high purity acetylene gas was purchased from BOC Gases (Fiji).

2.5. Analytical Methods and Quality Control

In the present study, 4 g soil samples were subjected to extraction with cold EDTA following the modified Tessier method reported previously (Agemian and Chau, 1976). The extraction using 40 mL of a 0.05 M EDTA solution (pH 4.8) was performed in 50 mL screw-capped high-density polypropylene centrifuging tubes. The centrifuge tubes were placed on an end-to-end mechanical shaker and shaking was continued for 3 h at room temperature. The contents were then centrifuged at 2000 revolutions per min for 20 min. The clear supernatants were treated and subjected to analysis of heavy metals as per our published procedure (Chandra *et al.*, 2015). The extracted heavy metals were subsequently analyzed using a Perkin Elmer 3110 flame atomic absorption spectrometer (AAS).

For quality control, the AAS instrument was calibrated daily prior to analyses using standard solutions of the metals to be analyzed. The 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 DDW and monitored in the continuous output mode. The statistical significance of all correlation coefficients at the 95% confidence level was tested using Student's t-test.

3. Results and Discussion

Fractional determination of heavy metals in soil is necessary since their behavior in the environment i.e. mobility, bioavailability to plants and remobilization potential strongly depend on their specific chemical forms or ways of binding (Ma and Rao, 1997). Weak acids or complexometric agents are generally used for

extracting heavy metals fraction that is referred as the bioavailable fraction.

Moreover, heavy metals associated with the exchange complex on the soil solid phase are in direct equilibrium with those in the soluble soil solution phase, and therefore constitute the most readily bioavailable fraction of total amount (McLaughlin *et al.*, 2000). Thus, determining this fraction using EDTA as extracting agent presents the actual bioavailable concentrations (fractions) of heavy metals that can potentially leach into the environment.

3.1. Bioavailable (EDTA-Extractable) Heavy Metals

To determine the bioavailable fraction of the heavy metal levels in the soil samples, EDTA extraction was performed and the extracts were analyzed using AAS. The results obtained are presented in Table 1, and depicted as a pie chart in Figure 2. The results presented herein represent the mean of > 20 samples per site, and the errors represent the confidence intervals at the 95% level.

3.1.1. Metal Levels Within Sites

In Site A, Pb (50.23%) existed as the predominant metal followed by Cu and Zn, while Ni was below the limit of detection. In Site B, Zn (65.27%) was predominant followed by Pb, Cu and Ni. In Site C, Zn was again the dominant heavy metal (51.58%) followed by Pb, Cu and Ni, respectively (Table 1 and Figure 2). It is evident that the metals Cu, Zn and Pb were present at all three sites under study and in greater amounts than that of Ni. Greater Pb abundance at Site A is most likely due to high Pb-loaded waste disposal over time, such as that from battery factories. The Lami municipal disposal site has been the receptacle for such wastes from two companies in Fiji. Parent material effects on the levels of the remaining three metals however cannot be ignored.

Figure 3 presents plotted metal concentrations by site. High levels of Zn (550.7 mg kg^{-1}) at Site B, as well as that of Cu (206.8 mg kg^{-1}) at Site C stand out and could most likely reflect the disposal indifference of heterogeneous wastes in these particular regions of the disposal facility, leading to the absence of a discernible pattern of metal distribution in each site. The highest levels of Zn (550.7 mg kg^{-1}) in Site B suggests there are possible localization of metals arising from concerted disposal of particular Zn bearing wastes such as batteries (Biswas *et al.*, 2015). Adding to this possibility is the foreign soil (carted from a variety of areas within and beyond Suva) that had been used to cover the active dumping sites. Therefore, it is quite likely that such widely-sourced soils with a variety of characteristics and compositions, both of the heavy metals from parent material as well as sporting various fractions that bind these metals in their unique ways may also have been contributing to hotspots of metals in certain areas (Ma and Rao, 1997).

Table 1. Metal concentration in the bioavailable fraction of the soil at different sites within the disposal facility and correlation coefficient (*R*) values obtained between metal levels in the bioavailable fraction and the total metal concentration as obtained from previous study (Chandra *et al.*, 2015). *N* represents the number of results applied in correlation analysis.

Metal	Sites and Concentration (mg kg^{-1})			*R*	*N*
	A	B	C		
Cu	73.1 ± 29.5	91.8 ± 41.6	28.6 ± 223.1	0.9587	20
Zn	32.0 ± 13.4	550.7 ± 225.0	206.8 ± 101.4	0.9716	24
Pb	109.0 ± 27.6	192.4 ± 63.1	160.1 ± 94.3	0.9109	22
Ni	< LOD[a]	8.7 ± 3.2	5.4 ± 2.4	0.9389	22

The ± values reflect the standard deviation of three measurements per analysis.

[a]Below limit of detection.

3.1.2. Metal Levels Across Sites

The concentration profiles of Cu, Zn, Pb and Ni in the bioavailable fraction of soil from the Lami municipal waste facility were established and the data is presented in Figure 3. Three sites, A (disused over five years prior to sampling), B (in active use at time of sampling) and C (disused over a year, thus representing an intermediate between Sites A and B) were sampled. At Site A, Pb was present in the highest amount (109.0 mg kg^{-1}) while Zn was present in the highest amount (550.7 mg kg^{-1}) in the site of active disposal (Site B). In Site C, Zn was of the highest concentration (206.8 mg kg^{-1}). Overall, Ni was present in the least amount across all three sites.

Overall, there was an absence of any discernible patterns of the studied heavy metals distribution across the three sites, suggesting localized hotspots arising from concentrated sectional disposal may be playing a greater role in influencing metal concentrations in the facility. However, the muted levels of metals in Site A do suggest a degree of remineralization likely to be setting in. Generally, metal levels across sites increased in the order: A < C < B. In general, the low levels of metals at Site A are possibly reflecting the longer period of inertia the site had from active waste disposal. Such a hiatus may have caused the setting in of soil mineralization, that has been associated with metals release (FAO, 2005).

The higher concentrations of metals at Sites B and C appear to be reflective of the active usage of the areas until recently. Here, it is likely that with a lower extent of remineralization, these sites are still transitioning to metal re-assimilation within the various soil fractions (Singh *et al.*, 2016).

3.2. Correlation Between Metals in Total Amount and Bioavailable Fractions

Very recently, we have published the total amounts of metals (Cu, Zn, Pb, Ni and Cd) across the three sites (Chandra *et al.*, 2015). For comparison, the results from the earlier study have been correlated (*R*-values) with metal levels in the bioavailable fraction of the soil and presented in Table 1. With the exception of Cd (indeterminable owing to bioavailable fraction metals being below detection – thus not considered further in this work), all metals showed a statistically significant correlation as is evidenced in Table 1. All stated correlations were subjected to a test of significance at the 95% confidence level according to published procedure (Miller and Miller, 2010) and were deemed to be valid.

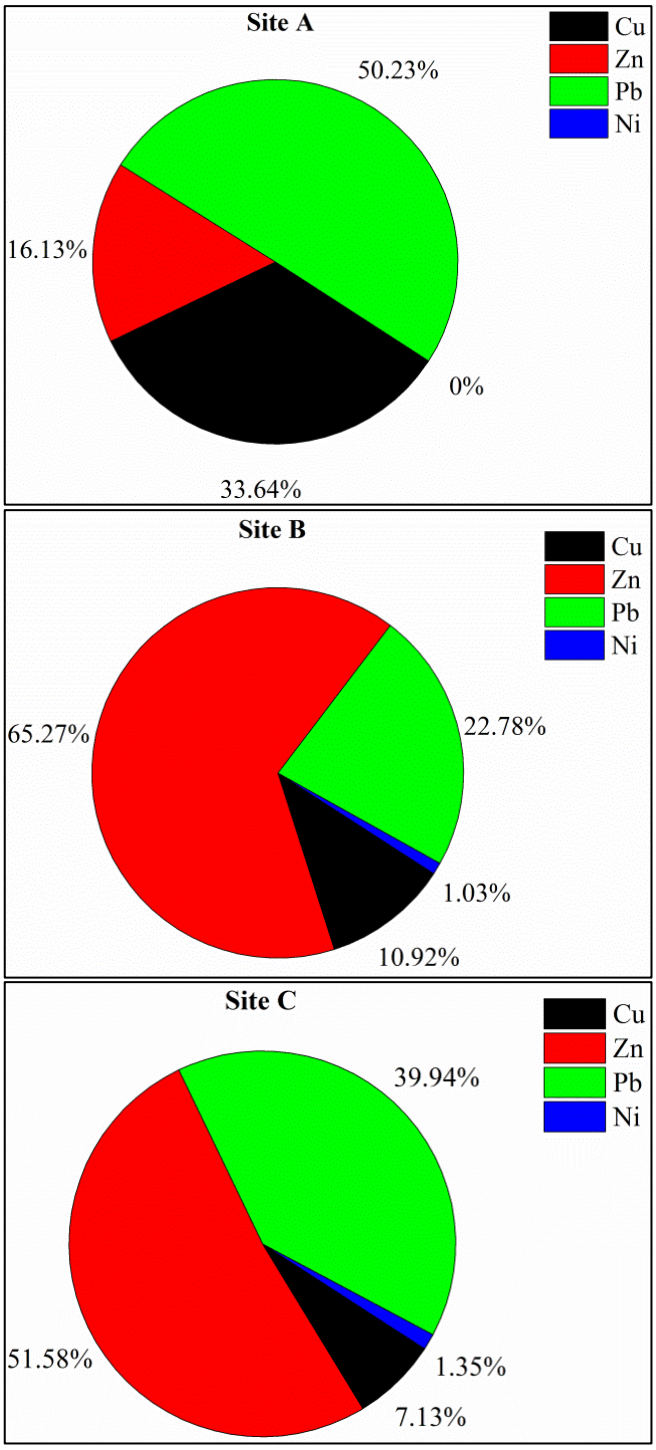

Figure 2. Pie chart showing proportional representation of bioavailable heavy metals by site.

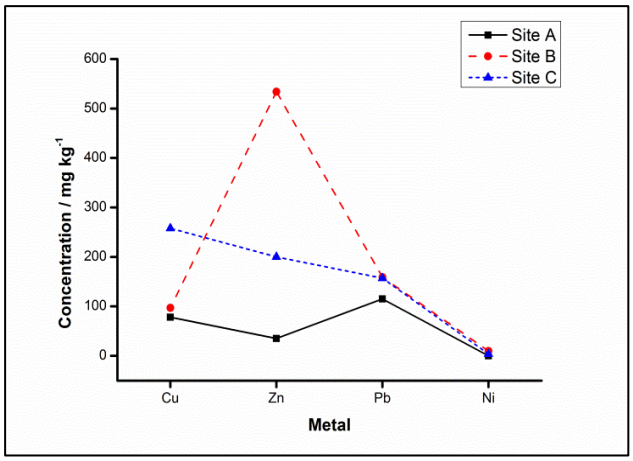

Figure 3. Proportional representation of heavy metal levels in the bioavailable fraction by site.

3.3. Quality Control of Data

Various methods of quality control were adopted in the study to ensure reliability of representative data. Firstly, in order to gain an insight into intra-sample variability, the samples were analyzed in triplicate, and the variation among replicates is included as standard deviation associated with each reported measurement in Table 1. Furthermore, two statistical approaches were considered to ensure a robust identification regime for outliers from the data sets. The first was to identify the normality of the data in each set and isolate the measurement farthest in the data set from the mean, subjecting it to a Grubb's test (Miller and Miller, 2010). Through this process, no measurement was found to be beyond the confidence limits. Then, an additional quality measure was adopted that recognizes the possible outliers which in turn lead to severely widened range of acceptable values and thus influence the acceptance of the suspected datum (Leys *et al.*, 2013). In this method, the median absolute deviation was used as an indicator of confidence limits. The data obtained through this filtration protocol is presented in Table 2. This approach has enabled the removal of affected datum from some data sets in Sites B and C.

Furthermore, the determination of the limit of detection (LOD), defined as the analyte concentration giving a signal equal to the blank signal plus three standard deviations of the blank was made (Miller and Miller, 2010). Based on this approach, the LOD value for each metal studied was determined and is presented in Table 2 and discussion has been made with reference to these limits (*vide supra*).

4. Conclusion

It appears that the heterogeneity of the disposal method at the Lami disposal facility is a dominant process in influencing the localized hotspots of metals encountered at various sites. Overall, the waste facility at Lami presented a grave risk to the adjacent environment through the high concentrations of the studied metals in the bioavailable fraction of the soil. These high levels of the metals Cu, Zn and particularly Pb encountered across the sites, coupled with free flowing and untreated leachate poses significant risk of metals mobility. 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.

Acknowledgement

The authors wish to thank the Institut de Recherché pour le Developmente and the SPREPPOL Fund that enabled the corresponding author to carry out this research.

Table 2. The median absolute deviation concentration range (mg kg^{-1}) for each metal by site and the LOD for each metal (mg kg^{-1}).

Metal / Site	A	B	C	LOD
Cu	-95.1 to 78.6	-1.3 to 170.2	-127.1 to 672.2	0.85
Zn	5.9 to 62.4	109.4 to 853.1	-48.7 to 523.2	0.98
Pb	73.2 to 159.9	-74.0 to 386.3	-101.0 to 380.8	2.44
Ni	< LOD[a]	-5.5 to 22.7	0.9 to 6.9	1.86

[a]Below limit of detection.

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