



Comparative Assessment of Trace Metal Concentrations and Their Eco-Risk Analysis in Soils of the Vicinity of Roundhill Landfill, Southern Africa

Nyika Joan*† Onyari Ednah*, Megersa Olumana Dinka** and Shivani Bhardwaj Mishra***

*University of South Africa, Department of Civil and Chemical Engineering, University of South Africa [Florida Science Campus], Cnr Christian de Wet Road and Pioneer Avenue, Johannesburg, South Africa

**University of Johannesburg, Department of Civil Engineering Science, University of Johannesburg, APK Campus 2006, Johannesburg, South Africa

***University of South Africa, Nanotechnology and Water Sustainability Unit, University of South Africa [Florida Science Campus], Cnr Christian de Wet Road and Pioneer Avenue, Johannesburg, South Africa

†Corresponding author: Nyika Joan; joashmada2011@gmail.com

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ABSTRACT

Soil is a vital media in transmitting contaminants in the environment. Contamination of soils by trace metals has received much attention due to their associated toxicity, persistence, bioaccumulation and non-biodegradability that is harmful to the ecology. This study assayed the concentrations of trace metals in topsoils of the vicinity of Roundhill landfill using inductively coupled plasma-mass spectrometry (ICP-MS) and X-ray fluorescence (XRF), compared the detection capabilities of the two techniques and determined ecological risks of the contaminants using geographical information system. Soils were collected from nine sampling sites around Roundhill landfill in the Eastern Cape and analysed for five trace metals using the two techniques. Mean concentrations of Cr, Cu, Ni and Zn determined by ICP-MS and XRF were normally distributed ($p < 0.05$) from the parametric test while no significant differences between the two datasets were established from the non-parametric test. Under-estimated elemental concentrations determined by XRF were attributed to its high detection limits, matrix effects, inter-elemental peak interferences and low sensitivity of the equipment. Correlation values of Cr, Cu and Ni showed a high degree of linearity compared to Pb. Evaluated eco-risk indices revealed low to extremely high ecological risks, posed by assessed trace elements in soils. Cr had the highest potency. Assayed trace metals were ecologically harmful to soils and their origin was linked to landfill leachate pollution.

INTRODUCTION

Soils provide many ecosystem services including vegetation support and modulating the flow of fugitive emissions, heat, nutrients and water (Wang et al. 2012). Besides, they adsorb and attenuate pollutants including trace metal elements. Consequently, trace metal pollution in soils is a growing environmental issue due to their non-biodegradability, bioaccumulation, persistence and toxicity (Zhu et al. 2018). Their entry in the food chain causes harm to organisms, including humans. The sources of these trace elements are either geogenic or anthropogenic-based. In the former, sources include pedogenesis and weathering activities on rocks while in the latter, use of agrochemicals, commercial fertilisers and unscientific disposal of waste, are the main pollution causes (Shokr et al. 2016). The distribution of trace metals in soils is dynamic and influenced by climate, soil parent material and its mobility. The rapid generation of the trace metals

due to increased industrialisation and urbanisation activities worldwide and their capacity to become bioavailable and diffuse in other environments once disposed of explains the need to accurately quantify them (Wang et al. 2012, Shokr et al. 2016).

Different analytical techniques in in-situ and at ex-situ conditions have been developed to identify and quantify such pollutants in soils. Most of these assay methods are based on spectroscopy techniques and include X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), inductively coupled plasma (ICP)- atomic emission spectrometry (AES) and ICP- mass spectrometry (ICP-MS) (Towett et al. 2013). ICP-MS/AES is common assay method based on aqua regia digestion to breakdown resistive metals and silicates in soils and have acceptable recovery and sensitivity. However, pre-conditions of sample pre-treatment before analysis that use concentrated acids are considered harsh and induce complex

matrix effects that compromise accurate analysis of trace elements (McComb et al. 2014). Therefore, XRF analysis that is multi-elemental and non-destructive is a growing alternative to aqua-regia-based methods. XRF is dependent on wavelength-dispersive electro-technology, sensitive detectors and sample excitation to assay trace elements in soils and can be carried out intrusively or in-situ (Kilbride et al. 2006). Comparisons of aqua-regia digestion methods and XRF in trace element analysis in existent studies reported close linearity in some studies (Marcos et al. 2011, Towett et al. 2013, Poto et al. 2015) while in others, there were deviations in their sensitivity and detection limits (Kilbride et al. 2006, Radu & Diamond 2009, McComb et al. 2014).

Using these techniques, trace elements can be quantified and their associated ecological risks measured using indices. Eco-risk indices reveal possible contamination in soils and the potency of specific metals to inflict environmental harm (Zhu et al. 2018). Most of the indices are derived from Hakanson's (1980) principle and are practical and quick tools to classify areas based on environmental pollution according to Wang et al. (2012). The distribution of eco-risk can be spatially represented if geographic information systems (GIS) are incorporated. According to Poggio & Vrscaj (2009), GIS tools assess interactions between released trace elements and calculated eco-risk indices with recipient environs based on processes governing contaminant distribution and spatial information on sources. These interactions are interpolations over a georeferenced space and provide a basis for environmental assessment (Wang et al. 2012). In this way, ecological risk indices are diagnostic tools that show pollution pathways. The objectives of this study were to 1) determine contaminant concentrations of topsoils in the Roundhill landfill vicinity using ICP-MS and XRF, 2) compare the detection capabilities of the two techniques and 3) determine ecological risks of the contaminants using GIS.

MATERIALS AND METHODS

Study Area and Sampling

Roundhill landfill is located in Buffalo city municipality of Eastern Cape, South Africa and is situated at latitude 32°53' 13.66 S and longitude 27°37' 26.20 E (Fig. 1). The facility was commissioned in 2006 and was previously a natural grassland (Dookhi et al. 2015). It receives more than 500 tonnes of general wastes from domestic, healthcare, businesses and building sectors of the vicinity daily. The landfill has a geomembrane liner and a leachate collection system whose effectiveness has been overwhelmed by increased waste disposal at the facility. Consequently, waste is inadequately lined and covered while leachate runs off to

surroundings posing as a pollution threat (Jewaskiewitz & Dookhi 2017). The climate of the area borders the Mediterranean and humid subtropical climate characterised by an average annual temperature of 21°C, rainfall ranging between 400-100 mm/year and evaporation of 160-170 mm/month. It has clayey soils, low organic matter and low groundwater potential whereby, borehole yields are less than 1 L/s (Chigor et al. 2013).

Sampling was carried out in September 2018 and nine sampling sites around the landfill facility were selected for soil collection including a reference sample (blank) (Fig. 1). At each site, samples were collected using a soil auger and emptied in polyethylene bags for further analysis. In the laboratory, soils were oven-dried and passed through a 2 mm sieve.

ICP-MS Analysis

Analysis of contaminants using ICP-MS began with the digestion of soil samples using the aqua regia EPA method 3015a (USEPA 1998). One gram of each soil sample was placed in a reaction vessel that contained 9 mL nitric acid (65%), 2 mL hydrochloric acid (35%) and 1 mL hydrogen peroxide (30%). The reaction was allowed for 5 min before sealing the reaction vessels and placing it in a rotor for microwave digestion at 180°C for 5.5 min. Samples were then held at the same temperature for 9.5 minutes and allowed to cool after digestion. Particulates in the digestant were removed by sedimentation before collecting it in plastic containers and labelling for ICP-MS analysis. Before this analysis, each sample was diluted 1000 times with 0.1% (v/v) nitric acid prepared using deionised water (milli-Q). ICP-MS Agilent 7500ce containing an octupole reaction system was used in this study that followed the EPA method 6020B (USEPA 2014). Analysis began with configuring the instrument computer using the manufacturer's directions and setting it up using appropriate operating parameters. The instrument was tuned and allowed to equilibrate for 30 minutes before analysis. This was followed by calibration using both internal and external standards containing rhenium and rhodium, respectively. A solution containing 1% nitric acid was used as the blank to flush the ICP-MS system until a steady-state signal was acquired. Samples beyond the linear analysis range were diluted before final analysis. A mixed solution standard was prepared in the blank solution and used to correct background interferences of the equipment from the solvent, air entrainment and plasma gases. Suitable isotopes were selected to eliminate possible isobaric spectral interferences due to ion species with many atoms before analysing the samples. The analysis was done in duplicates for Cr, Cu, Ni, Pb and Zn and their final concentrations were determined using equation 1.

$$\text{Metal concentration (mgkg}^{-1}\text{)} = \frac{\text{ICP-MS Reading} \times \text{Digestate volume} \times \text{Dilution Factor}}{\text{Weight of sample digested}} \quad \dots(1)$$

XRF Analysis

About 10 g of the dried soils were ground in a pulveriser to particles sizes of 75 μm and below. The soils were emptied in crucibles and heated to 950°C for 2 h for loss on ignition (LOI) analysis to remove volatile organics. They were allowed to cool and transferred to aluminium containers for pressing in a semi-automated press. This study used the sequential XRF spectrometer (PW 2404, Phillips, Holland) that uses americium-241 and cadmium-109 isotopes for fluorescence excitation and has a detector made of silicon pin-diode. Before analysis, instrument performance was validated using a blank and two check samples that had high heavy metal levels before making adjustments on the zero level according to EPA method 6200 (USEPA 2016). The samples were placed on carriers that were previously cleaned using acetone and mounted on the equipment cassette for heavy metal analyses in triplicates through direct quantification.

Calculation of Eco-Risk Indices

Four eco-risk indices namely potential ecological risk index (PERI), cumulative risk index (CRI), toxic units (TU) and toxic risk index (TRI) were used to assess the ecological threat of trace metals to soils of the study area. PERI was calculated using equation 2.

$$\text{PERI} = T_r * \frac{C_{\text{obs}}}{C_{\text{norm}}} \quad \dots(2)$$

Where, T_r is the toxic response coefficient of a particular metal, C_{obs} is the measured concentration of given trace metal and C_{norm} is the geochemical background levels outlined by the Department of Environmental Affairs (DEA 2013). Toxic response coefficients are predefined values that account for sensitivity and toxic requirement (Pedersen et al. 1998). Elemental values of T_r used to calculate PERI in this study are given in Table 5.

CRI was calculated using equation 3.

$$\text{CRI} = \sum_{i=1}^n \text{PERI} \quad \dots(3)$$

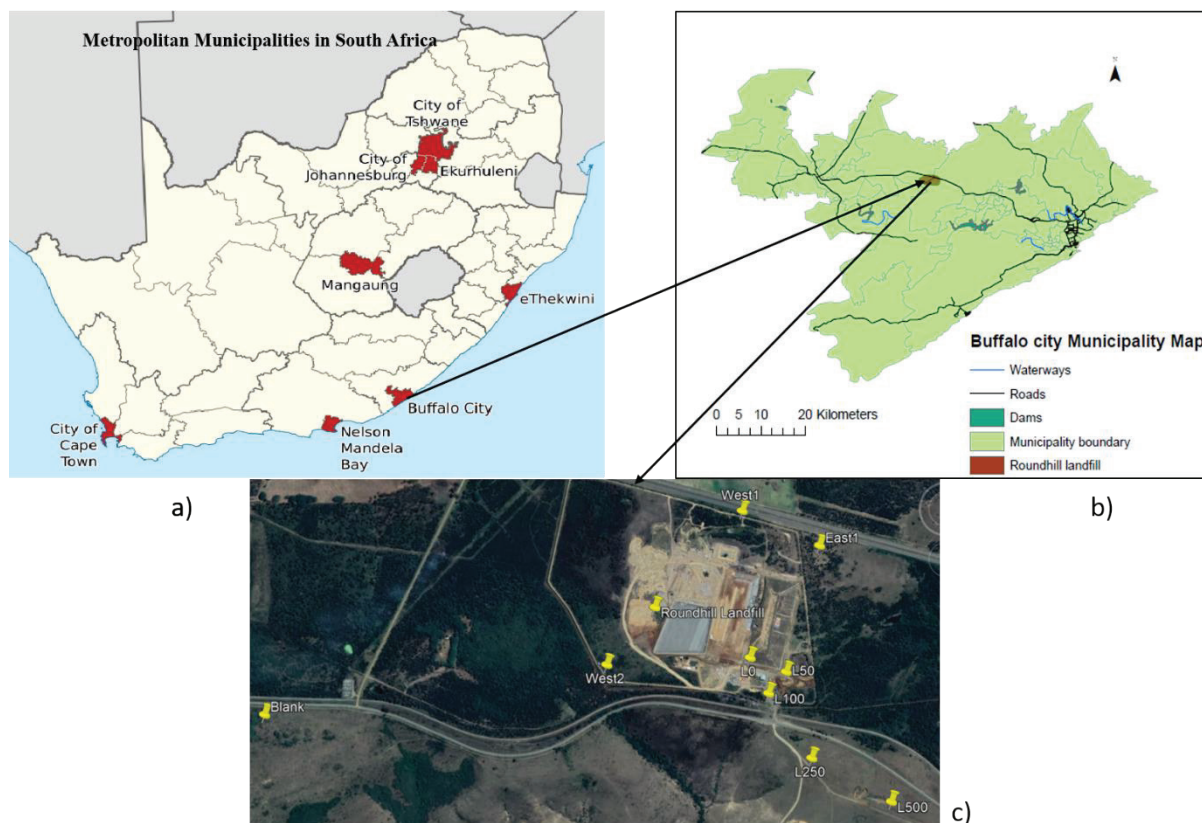


Fig. 1: Map of the study area and the distribution of sampling sites in relation to the landfill site.

Where, n is the number of trace metals assayed and PERI is the potential ecological risk index of each metal.

TUs of individual metals at various sampling sites were calculated as relationships of observed metal concentration at each sampling site to predetermined probable effects level (PEL) as shown in equation 4.

$$TU = \frac{C_{obs}}{PEL} \quad \dots(4)$$

Where, PEL is the probable effects level of individual metal, which is defined as the lower limit of chemical concentrations, which is affiliated to negative biological effects (Pedersen et al. 1998). PEL values of assayed elements used in this study were as shown in Table 5 and are derived from studies by Pedersen et al. (1998) and Zhu et al. (2018).

TRI assessed the integrated toxic risk using both PEL and threshold effect level (TEL) of heavy metals using equation 5.

$$TRI = \sqrt{\left(\frac{C_{obs}}{TEL}\right)^2 + \left(\frac{C_{obs}}{PEL}\right)^2} \quad \dots(5)$$

Where, TEL is the threshold effects level, which is defined as the upper limit of soil chemical concentration that has no-effect data (Pedersen et al. 1998). TEL values used in this study were as documented by Zhu et al. (2018) and are presented in Table 5. Results of the above indices are categorised as given in Table 1.

Geo-statistical Analysis

The spatial analyst tool of ArcGis 10.3 was used in spatial interpolation of assayed pollutants and calculated indices

of various sampling points. Inverse Distance Weighted (IDW) method, which takes a plug point as a core point of determining weighted averages for an entire area within a specified radius was used to represent pollution extent (Yan & Li 2011). The method applied inverse proportioning between known concentrations and was represented using equation 6.

$$Z = \frac{\sum_{i=1}^n \frac{1}{(D_i)^p} Z_i}{\sum_{i=1}^n \frac{1}{(D_i)^p}} \quad \dots(6)$$

Where, Z is the interpolated value, Z_i is the sample value of i which = 1, 2, ... n , D = distance and p = distance's power as described by Yan & Li (2011).

Statistical Analysis

Descriptive statistics including the average (avg), standard deviation (SD), kurtosis and skewness of topsoils were applied to explain differences of ICP-MS and XRF elemental concentrations. The t-test assessed significant differences in the means of identified heavy metals for the two methods. The method has been used to compare differences in heavy metal concentrations obtained by XRF and ICP-MS successfully (Ahmed et al. 2012, Maliki et al. 2017). The Kolmogorov-Smirnov (K-S) test, which is an empirical distribution function (EDF) where theoretical and test distribution functions are compared was used in assessing normality or non-normality of the data (Ghasemi & Zahediasi 2012). The method is preferred due to its high sensitivity compared to alternatives such as Shapiro-Wilk test, D'Agostino Pearson omnibus test, Anderson-Darling test and Jarque-Bera test (Oztuna et al. 2006). Mann Whitney U-test, a non-parametric was used to compare if sample means of the two methods were equal. The test was used to complement t-test by show-

Table 1: Criteria to classify calculated ecological risk indices.

Index Method	Values	Ecological risk level	Reference
PERI	≤40	Low	Sun et al. (2015)
	40 < PERI ≤80	Moderate	
	80 < PERI ≤160	High	
	160 < PERI ≤320	Very high	
	>320	Extremely high	
CRI	<150	Low	Zhu et al. (2018)
	150-300	Moderate	
	300-600	Considerable	
	≥600	Disastrous	
TU	<4	Non-toxicity	Gao et al. (2018)
	>6	Acute toxicity	
TRI	<5	No toxic risk	£
	5≤TRI<10	Low risk	
	10≤TRI<15	Moderate toxic risk	
	15≤TRI<20	Considerable toxic risk	
	≥20	Very high toxic risk	

ing differences in the spread for data that did not have normal distribution after the K-S test. To determine the correlation between heavy metal concentrations obtained by the two methods, linear regression analysis was applied. This analysis resulted in a linear model shown in Equation 7 that reduces the square difference between the regression line and the dependent variable (Kilbride et al. 2006).

$$y = mx + c + \epsilon \quad \dots (7)$$

Whereby, y is XRF concentration, m is the slope, x is the ICP-MS concentration, c is the y -intercept of the regression line and ϵ is the residual.

Generally, ≥ 0.7 value of determination coefficient (R^2) represented the significant relationship of concentrations obtained from the two assay methods, while a value of 1.0 depicted an ideal case with no data scattering (Towett et al. 2013). These analyses were done using XLSTAT software at $p < 0.05$ significance level. Regressed data was subjected to a quality analysis using the USEPA (1998) criteria based on their determination coefficients and as shown in Table 2.

RESULTS

Concentration of Contaminants

Statistical comparisons of ICP-MS and XRF for the identified elements were as given in Table 3. Average concentrations of all elements obtained by ICP-MS were higher compared

to those of XRF, which revealed under-estimations of the latter. A comparison of SD values of elemental concentrations obtained from the two techniques showed a similar trend of closeness in the variability of values except for Pb. However, a comparison of SD values among identified elements showed a large spread where Cr and Cu had the highest and lowest values, respectively. Skewness, SD and kurtosis values for the two methods had the same tendency whereby values of Cr, Cu, Ni and Zn were nearly similar while those of Pb differed significantly.

Comparison ICP-MS and XRF

Results of K-S test, t-test and Mann Whitney U-test at $P < 0.05$ were as shown in Table 4. K-S results showed normal distribution for all the elements except Pb. The results of the Mann Whitney U-test showed a similar trend where P values of Cr, Cu, Ni and Zn were higher than 0.05 and corresponded to no differences in the two data sets, while Pb had significant differences. The means of the two data sets except Pb were found to be equal from the t-test.

To assess the data quality from the two methods, regression analysis was carried out and R^2 values calculated as shown in Figs. 2 and 3. Determination coefficient values of Cr, Cu and Ni were above 0.8, which indicated that the results of the two methods were statistically similar for the concentrations of these elements. Zn had an R^2 value of 0.7 and concentration levels obtained with the two methods were statistically different, but within the acceptable limit

Table 2: Criteria to categorise regression data quality based on R^2 values (USEPA 1998).

Trace metal	Level of data quality	Statistical requirement	Inference
Cu	Definitive	$R^2 \geq 0.8$	Relationship $y=x$ acceptable
Cr			
Ni			
Zn	Quantitative Screening	$R^2 = 0.7$	Relationship $y=mx + c$ acceptable
Pb	Qualitative screening	$R^2 < 0.7$	No relationship in data sets

Table 3: A comparison of average concentrations, standard deviation, kurtosis and skewness values of top soils obtained by for ICP-MS and XRF.

	Cr	Cu	Ni	Pb	Zn
Avg-ICP (mgkg^{-1})	2197	246.67	535.56	104.96	244.89
Avg-XRF (mgkg^{-1})	2044.56	239.56	497.33	104	175.56
SD-ICP	2159.9	101.77	219.09	84.52	161.23
SD-XRF	2147.98	107.92	205.79	172.03	134.45
Kurt-ICP	8.5	3.38	-0.75	-0.43	7.06
Kurt-XRF	8.56	3.3	-0.62	1.4	7.25
Skew-ICP	2.88	1.89	0.57	1.53	1.58
Skew-XRF	2.9	1.64	0.73	0.52	1.6

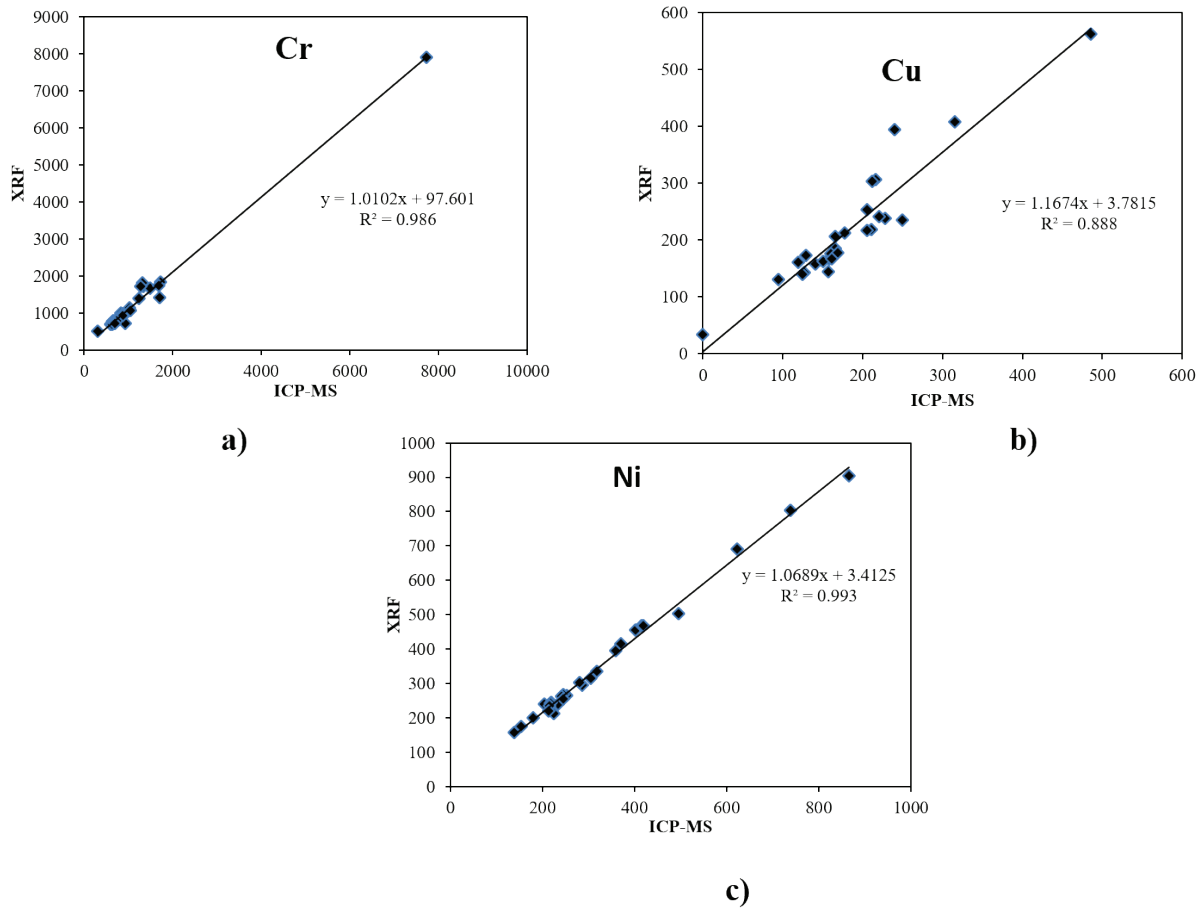


Fig. 2: Regression lines and equations for a) Cr, b) Cu and c) Ni.

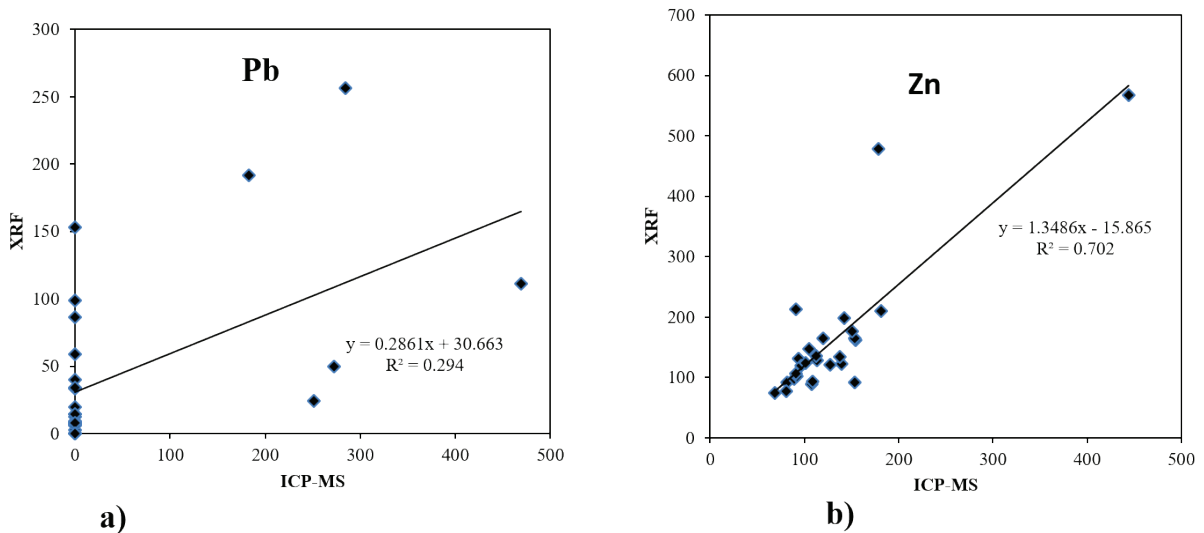


Fig. 3: Regression lines, determination coefficients and regression equations for a) Pb and b) Zn.

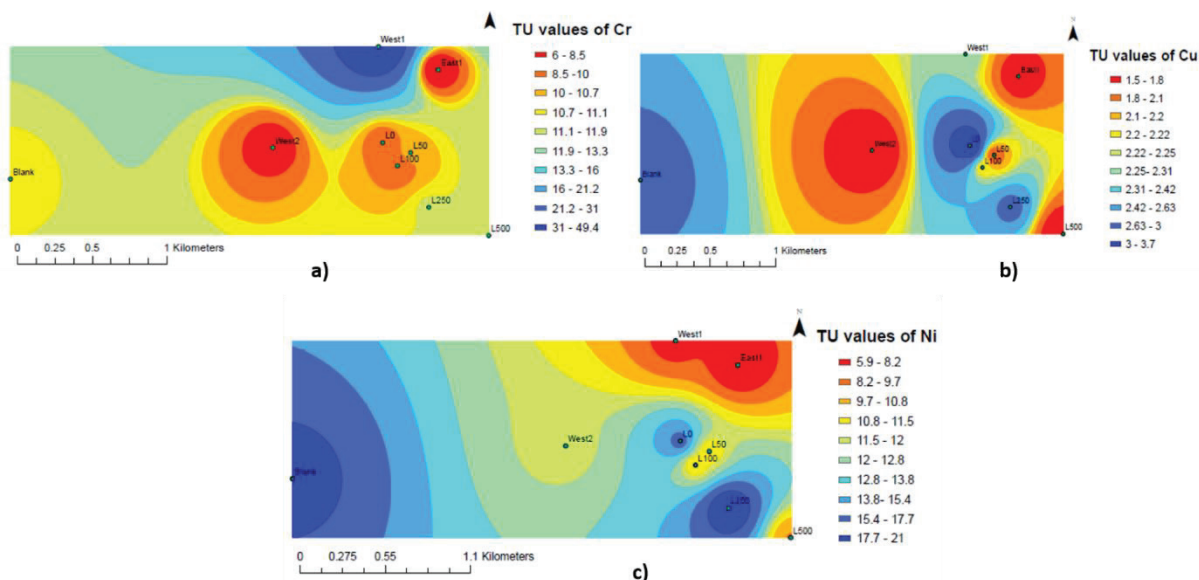


Fig. 4: Toxic Units (TU) of a) Cr, b) Cu and c) Ni.

Table 4: P values for K-S, Mann Whitney U-test and t-test of heavy metals concentrations at 95% significance level.

Variable	K-S test	Mann Whitney U-test	t-test
Cr	0.324	0.254	0.77
Cu	0.518	0.122	0.19
Ni	0.744	0.469	0.6
Pb	<0.0001	0.001	0.02
Zn	0.518	0.250	0.25

($y=mx + c$). Pb had R^2 value <0.7 and its concentrations were statistically different. Regression lines of Cr, Cu and Ni showed ideal linear regression models ($y=x$) of concentrations obtained with the two methods. The regression line of Zn showed a significant and acceptable relationship of data obtained from the two methods, though with some deviations. The regression line of Pb had significant deviations in concentrations of the two methods.

Ecological Risk Indices

The concentrations of trace elements obtained by ICP-MS, which was a superior method compared to XRF were used to calculate ecological risk indices of study area soils. Potential ecological risk indices of trace elements at various sampling sites are given in Table 5. The values of PERI due to Cr were high in all sampling sites and depicted extremely high ecological risk except for the reference sample (Blank) that had a very high risk. PERI values of Cu ranged between 50

and 126, which was classified as moderate to high ecological risk while Ni, Pb and Zn reported low ecological risk and had values <40 with a few exceptions. Cumulative Risk Index (CRI) was calculated as 430.28, which correlated to the considerable ecological risk of the trace elements in sampled soils.

Spatial representation of various toxic units (TU) of assayed heavy metals at various sampling points was as shown in Fig. 4 and 5 (a-b). Toxic units of trace metals decreased in the order of $Cr > Ni > Cu > Pb > Zn$. Acute risk due to Cr and Ni contamination was evident at all sampling points that had TUs values ≥ 6 . Non-toxicity by Cu, Pb and Zn, however, was reported in all sampling points whose TUs values were <4.

Toxic risk index (TRI) that considers PEL and TEL assessed the risk of trace metals in soils to the ecology of the area and results were spatially distributed as shown in Fig. 5c. TRI ranged between 13 and 113, which represented moderate to very high toxic risk. The highest levels of TRI were found in West 1 sampling site that had the highest concentrations of Cr, which confirmed the high toxicity affiliated with the element.

DISCUSSION

Reproducibility results of XRF and ICP-MS analyses in this study were dependent on the element being quantified, although the former technique underestimated assayed trace elements concentrations. Underestimation was possibly due to differences in equipment sensitivity in the two methods.

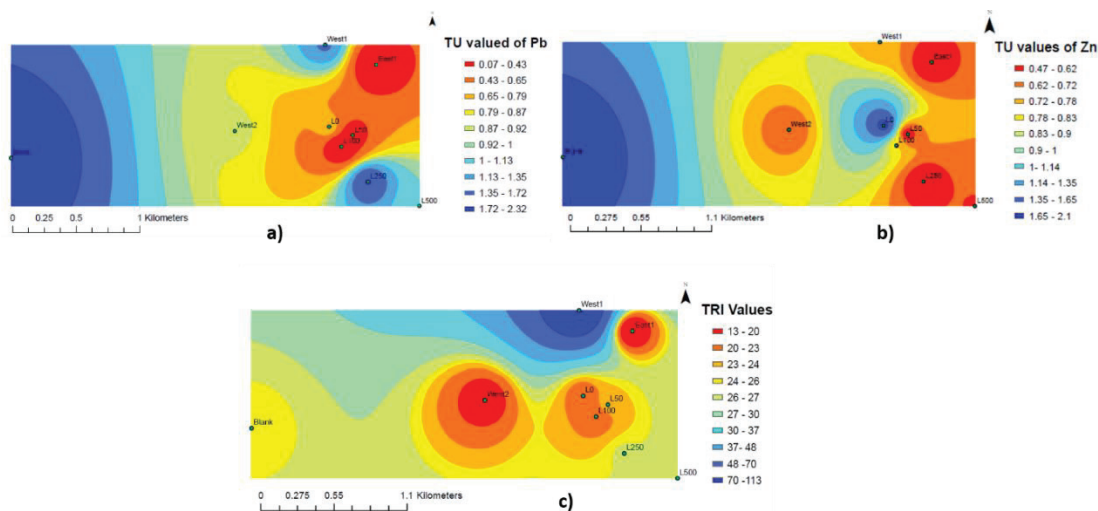


Fig. 5: Toxic units of a) Pb, b) Zn and Toxic Risk index (TRI) values at various sampling sites.

Table 5: Calculated potential ecological risk index (PERI) and cumulative risk index (CRI) values.

	PERI					CRI
	Cr	Cu	Ni	Pb	Zn	
L0	528.31	95.94	17.65	64.00	2.36	430.28
L50	433.54	127.50	15.21	21.53	1.99	
L100	514.46	64.38	10.26	8.38	0.61	
L250	425.85	74.69	10.29	1.83	0.88	
L500	553.85	94.69	19.85	47.85	0.53	
West1	560.92	50.63	9.14	27.80	0.69	
West2	2430.46	79.38	6.90	38.25	0.83	
East1	349.23	50.94	11.05	24.63	0.73	
Blank	287.38	55.63	5.58	1.90	0.56	
Normal concentrations	6.5	16	91	20	240	
T_r	2	5	2	5	1	
PEL	160	110	43	110	270	
TEL	52	19	16	30	120	

XRF has low sensitivity and high detection limits to trace metals in low concentrations while the sensitivity of ICP-MS is high and enhanced by aqua regia digestion (Chen & Ma 2001, Lin 2009). The low sensitivity in XRF explained the differences in skewness and kurtosis results of the two methods, particularly in Pb. These findings disagreed with another comparative study that confirmed no differences in mean concentrations of Pb analysed by XRF and ICP-MS (Merkey et al. 2008). Parametric and non-parametric results of Cr, Cu, Ni and Zn ratified the effectiveness of the two methods and a similar trend was reported in a trace element analysis of soils obtained from Malaysian states (Ahmed et al. 2012) and sub-Saharan Africa (Towett et al. 2013).

Quantitative relationship of Zn and non-relationship of Pb concentrations from regression analysis could be attributable to underestimations of XRF, which is a function of its sensitivity at low concentrations and inter-element interferences (Towett et al. 2013). XRF's detection limits vary from sample to sample based on the anode's X-ray range, the sample composition, the mass of an element, counting time and tube voltage and some of these aspects could have compromised precise concentration measures in this study (Poto et al. 2015). Furthermore, XRF's detection limits differ based on the analyte being assayed, the strength of the excitation source, chemical and physical matrix effects (Makinen et al. 2005). Some of the aspects are difficult to standardize and could have led to the

observed differences. Two studies that reported poor linearity of Pb in comparative XRF and ICP-MS analysis attributed the trend to these XRF equipment flaws (Potts et al. 1995, Kilbride et al. 2006). Under-estimation of concentrations by XRF was attributed to K and L line inter-elemental line interferences and overlaps, which reduce the equipment's detection intensity of the element (Stonach 2007). These interferences lead to overlapping spectrums that are predominant if assayed samples have arsenic and decrease fluorescence intensity causing underestimation of Pb (USEPA 1998).

ICP-MS was a more sensitive and superior contaminant analysis method over XRF in this study. Other publication agreed with this suggestion and highlighted the advantages of ICP-MS to be lower detection limits, reduced matrix effects and no inter-elemental peak overlaps (Ahmed et al. 2012, Towett et al. 2013, McComb et al. 2014). The results differed from those of a study in Maddison, USA, that suggested that XRF had greater sensitivity of both major and trace elements (Herner et al. 2006).

Ecological risk indices showed different potency levels of the assayed elements. Cr had the highest PERI and TU values. The trend could arise due to anthropogenic enrichment of soils of the study area with landfill leachate from wood preservation, metallurgy, varnish, leather and electroplating wastes (Bini et al. 2008). In China, accumulation of Cr in landfill vicinity soils was attributed to the unscientific disposal of solid waste used in industrial processes such as electroplating and the construction industry (Cheng et al. 2014). High values of the indices for Cr compared to other trace elements even in the reference sample could point to its source as lithologic in addition to landfill leachate contamination. A study in urban soils of Beijing reported high PERI values of Cr compared to other elements and attributed it to natural origin from rocks in addition to the accumulation of untreated solid wastes in the area (Wang et al. 2012). CRI results of the current study that showed considerable eco-risk and differed from a study in soils of Yangcaogou region of China, which had CRI levels between 75.07 to 98.61 corresponding to the low ecological risk posed by trace metals (Jiang et al. 2014). However, a great contribution to the CRI was from Cr, which suggested the high potency of the element as reported in another eco-assessment of soils from Caofeidian region of China (Zhu et al. 2018).

Accumulation of consumer and industrial by-products at the landfill could be attributable to acute toxicity by Cr and Ni-based on their TU values. Permenter et al. (2011) attributed the accumulation of Cr and Ni in soils to disposal of stainless steel, chrome pigments, plating and alloy-containing solid waste. This dominance of Cr and Ni toxicity in this study agreed with an eco-risk evaluation study of soils

from Bangladesh, where all TU values of sampling sites were >6 (Islam et al. 2015). Soils of the area had moderate to very high toxic risk based on TRI values. The results of this index differed from a related study of Chinese soils that reported a low-risk TRI range of 3.08-8.25 (Zhu et al. 2018).

CONCLUSIONS

Concentrations of Cr, Cu, Ni, Pb and Zn in this study were assayed using ICP-MS and XRF and the results of the former were used to calculate eco-risk indices. Cr had the highest concentration compared to other trace elements. Concentrations determined using XRF for all elements were under-estimated in comparison with ICP-MS, which could be attributed to the low sensitivity, high detection limits and inter-elemental interferences during XRF analysis. These underestimations were reflected in the regression analysis that showed deviations and qualitative relationship in XRF-ICPMS datasets of Pb and Zn, respectively, although Cr, Cu and Ni had ideal relationships. Eco-risk indices showed that Cr had the highest potential ecological risk based on the PERI and TU values and compared to other elements. This trend could arise from landfill leachate generated from wood preservation, metallurgy, varnish, leather and electroplating wastes. Lithologic sources of trace elements were suggested based on the high TU values of Cu, Ni, Pb and Zn in the reference sampling site. Moderate to high toxic risk was deduced from TRI values at various sampling sites. Calculated risk indices and their spatial representation revealed ecological risk from assayed trace elements in soils of Roundhill landfill vicinity, which was possibly linked to leachate pollution.

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