Open Access Journal of Chemistry
Volume 2, Issue 2, 2018, PP 29-37

Method Verification of Total Digestion Technique for the Determination of Nine Heavy Metals in Soil Using Flame, Graphite Furnace and Cold Vapor, Coupled With Atomic Absorption Spectrometer

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ABSTRACT

In this study a method of quantitative analysis for the determination of total heavy metals in soils by atomic absorption spectroscopy (flame, graphite furnace and cold-vapour options) using USEPA method 3052 sample digestion technique was evaluated and applied. Method parameters such as linearity, accuracy, repeatability, limit of detection, limit of quantification and robustness were assessed using laboratory fortified soil for all heavy metals studied. The results showed satisfactory average recoveries for all metals (65% - 107%) and good linearity in terms of regression co-efficient greater than or equal to 0.997. Repeatability was also verified with relative standard deviation values all less than 10%. Thus, the method was deemed satisfactory and effective, and was used for the intended purpose of heavy metal determinations in surface soils of twenty (20) public parks in Greater Accra Region, Ghana. The results from the monitoring study demonstrated the contributions of anthropogenic activities as sources to heavy metal contamination in the study area as a result of industrialization and urbanization. With mercury ranging from 0.001 – 0.094 mg/kg, cadmium (0.12 – 0.50 mg/kg) and even higher concentrations of lead observed (11.28 – 628.31 mg/kg) confirming the use of leaded fuel in the study area. The abundance order of the heavy metals in surface soils for this study was Fe >> Mn > Zn > Cr > Pb > Cu > Ni > Cd > Hg.

INTRODUCTION

To properly assess metal hazard in soils, it is necessary to first of all evaluate the sample preparation technique in order to calculate the screening levels (Chen and Ma, 1998). In such evaluations, the duration required for total metal recovery may be known.

The use of mineral acid digestion and thermal decomposition steps may result in analyte losses, incomplete recoveries, and/or sample contamination (Chen and Ma, 1998; Kubrakova, 1997; Nieuwenhuize et al., 1991; Quevauviller et al., 1993).

Currently, four USEPA digestion techniques are available for sample preparation. These include method 3050 (hot-plate; HNO_3-HCl), method 3051 (microwave; HNO_3), method 3051A (microwave; HNO_3-HCl) and method 3052 (microwave; HNO_3-HCl-HF) (Chen and Ma, 1998). Among the four methods, only method 3052 involves a total decomposition technique; however, the other three methods (also known as total recoverable method) have become common for sample preparation for metal analyses (Chen and Ma, 1998; Sawhney and Stilwell, 1994). For trace elemental analysis like this study, the sample preparation technique is very critical. And to gain both optimized concentration of all dissolved metals and instrument detection limits, the USEPA method 3052 sample preparation technique was adopted for this study.

For the determination of metals, atomic absorption spectroscopy (AAS) plays a very important role. However, due to sensitivity of trace analysis in matrices such as soil and sediments, the traditional flame AAS may not be appropriate at that level of detection. It is therefore imperative to use other means in conjunction with AAS in order to achieve those sensitivity levels. In such cases, the graphite furnace or hydride generation options with the AAS come in very handy. Another atomization technique incorporated in AAS analysis for mercury determination is known as cold-vapor method. This provides a relatively sensitive approach for mercury determination than the traditional flame atomic absorption mercury analysis.

Since the furnace methods for mercury are not recommended due to the extreme volatility of mercury, which has a significant vapor pressure even at room temperature, the cold vapor atomic absorption technique for mercury has received the greatest attention (Shrader and Hobbins, 2010). These then informed our choices of metal determinations in this study.

According to the International Standardization Organization (ISO) 17025:2005, it is a mandatory requirement for an analytical laboratory to demonstrate its competence in methods of analysis. These methods of analysis could be international, standard, journal methods or even an in-house laboratory developed method. In all methods cases, the laboratory shall demonstrate its capability in analysis.

Specifically, for in-house developed method, validation is compulsory for laboratory accreditation towards ISO 17025. Validation is performed to provide evidence that a method is fit for the purpose for which it is to be used. Method validation is therefore a requirement of accreditation bodies, and must be supported and extended by method performance verification during routine analysis (analytical quality control and on-going method validation) (Huber, 2007). Thus, even for international and standard methods, verification is a must for quality assurance purposes.

The words validation and verification have been used interchangeably. However, there exists a difference between these terms. In method validation, especially initially developed method, all parameters pertaining to analytical methods have to be evaluated.

These parameters include linearity, matrix effect, and limit of quantification, specificity, accuracy, precision, reproducibility, robustness and ruggedness. However, in method verification, key or essential parameters have to be assessed in order to demonstrate preparedness and capability. This is especially true for international and standard methods where validated results already existed, and thus thorough method validation is not a requirement under laboratory accreditation to ISO 17025. This notwithstanding, if any major aspect of the international or standard method is being modified, then full method validation would be required.

Thus, for this study in which USEPA 3052 standard method for sample preparation couple with AAS – flame, AAS – graphite furnace and AAS – cold vapor options were considered for heavy metals determination; method verification was fully considered.

MATERIALS AND METHODS

Reagents and Apparatus

Certified Reference Materials, which were individual metal standards of Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Mercury (Hg), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn), were purchased from Sigma Aldrich, certified to be within ± 0.5% of the reported value (1000 mg/L). And for dissolution of metals in soil; nitric acid, hydrochloric acid and hydrofluoric acid were of ultra-pure trace-metal grade purchased from Fisher Scientific. Deionized water used for dilution was laboratory made of ultra-pure grade.

A Milestone START D, 630 watts system microwave with carousel capable of carrying 10 vessels was used for soil sample metal digestion. And for the determination of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn; Varian model AA240/GTA120 Atomic Absorption Spectroscopy equipped with flame and graphite furnace options was used, whilst Cold-Vapour Atomic Absorption Spectroscopy from Varian model VGA77 was used for Hg contents in soil determinations.

Sample Processing and Fortification

Beach soil samples were collected into zip lock plastic bags and transported to the laboratory for sample processing. For processing, soil samples were transferred into Pyrex beaker and placed in an oven overnight at 150^{o}C. The dried soil samples were then sieved through 2mmstainless steel sieve with the aid of a mechanical shaker, and foreign materials were removed. To verify the sample preparation techniques for the metal preparation, processed beach soil were fortified with analytes of interest (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) at three different concentration levels (1.0 mg/kg, 10.0 mg/kg and 100.0 mg/kg) and for Hg (0.001 mg/kg, 0.010 mg/kg and 0.10 mg/kg) and processed using the digestion technique (USEPA Method 3052) as used for the samples in this study.

Sample Digestion

USEPA method 3052 was employed for sample preparation for the selected heavy metals analysis. Two types of analyses were carried out respectively; one after a known amount of the metal standards of interest was added (spiked/fortified sample) and the other without the addition of the metal standards (matrix blank sample).

Soil samples of 0.5 ± 0.01 g were weighed into Teflon microwave vessels, and 9 mL of concentrated HNO_3 and 4 mL concentrated HF were added.

These vessels were then sealed after all initial visible reactions were ceased in a fume hood, and were placed into the microwave system. The vessels were connected appropriately, and the power settings for the microwave oven rose steadily over 45 min to 120 psi at 100% power, and then held constant at this pressure for 10 min. The vessels were allowed to cool and depressurized, and were then vented and opened.

The digest was then filtered with the aid of filter paper and polypropylene funnel into 100 mL volumetric flask, and 20 mL of 10% HNO_3 in deionized water was used to rinsed the vessel onto the filter paper, and finally made up to the mark with ultra-pure deionized water.

Each was then transferred into plastic sample bottles with caps, labeled accordingly, and stored until further processing.

Instrumentation

A Varian model AA240/GTA120 atomic absorption spectrometer equipped with an element hollow cathode lamp operated at a current recommended by the lamp and instrument manufacturer, an automatic background correction device and a computerized read-out, coupled with flame and graphite furnace options, and an automated flow injection analysis system (FIAS) adaptable to the AAS was used for (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) determinations.

A set of analyte calibration metal standard solutions (0.2, 0.4, 0.8, 2.0, 5.0 and 10.0 µg/mL) were prepared from serial dilutions of the prepared analyte stock solutions, into 100 mL volumetric flask and making up to the mark with ultra-pure deionized water.

At the start of each metal analysis, the system was optimized with the selection from library the correct analyte and wavelength; and the automatic background corrections done. With the least calibration standard, the solution bottle was connected to the system and the time-controlled programme started.

And it was ensured that the signal of the blank calibration solution was negligible as compared to the lowest standard solution; and the response of the instrument to zero signal adjusted accordingly. The measurement with each standard calibration solution was repeated at least thrice, and the three values which fell within acceptable ranged, averaged by the instrument Spectra A software. And a linear plot with analyte concentration as abscissa and the corresponding signal values as ordinate was generated by the instrument Spectra A software.

Likewise, each prepared labeled test sample solution bottle was connected to the system, with the flame or graphite furnace option, and the time-controlled programme started to record the signal and the corresponding concentration calculated. Similarly, each measurement was repeated at least thrice and the signal and corresponding concentrations recorded. However, where the concentration of analyte exceeds the calibration range, the test solution was diluted appropriately and factored into its concentration calculations.

For mercury; Hg analysis, a Varian model VGA77 atomic absorption spectrometer equipped with an element hollow cathode lamp operated at a current recommended by the lamp and manufacturer, an automatic background correction device and a computerized read-out; coupled with cold-vapor generator, and an automated flow injection analysis system adaptable to the AAS was used.

A flow-controlled argon stream was used as an inert carrier to transport Hg vapor into the cell. Time-controlled addition of tin (II) chloride reducing solution in combination with automatic start of the read signal of the spectrometer was in place.

In both calibration and test solution measurements for Hg; the AAS and the cold-vapor generator were set up according to the manufacturer’s instructions, wavelength of 253.7 nm, correctly adjusted quartz cell, the gas flow, and the reaction time and flow rate of tin (II) chloride solution were all optimized to achieve acceptable sensitivity.

Real Soil Samples for Heavy Metal Monitoring

Surface soil samples for the present study were collected from public parks situated in the nation's capital of Ghana for the period September, 2013 and March, 2015; at quarter-yearly intervals. In all, 20 public parks from two industrialized metropolitan cities in Greater Accra region of Ghana; namely, Tema and Accra were monitored for heavy metal contaminations.

Tema Metropolis sampling sites include Sakasaka Park (5^o 37' 51.31'' N, 0^o 0' 51.47'' W); Oninku Park (5^o 38' 29.75'' N, 0^o 0' 5.36'' E); Mantse Park (5^o 39' 32.62'' N, 0^o, 1' 37.24'' E); Mantey Park (5^o 38' 27.74'' N, 0^o 0' 11.69'' W); Macho Park (5^o 37' 40.94'' N, 0^o 0' 43.33" W); Chemu Park (5^o 38' 27.74" N, 0^o 0' 11.69" W); Community 8 Park (5^o 40' 0.32" N, 0^o 0' 46.32" W); Mandela Park (5^o 41' 26.50" N, 0^o 1' 34.18" W); Kofi Nimo Park (5^o 41' 56.11" N, 0^o 1' 19.33" W) and Community 5 Children's Park (5^o 38' 31.10" N, 0^o 0' 34.25" W).

Those of Accra Metropolis comprise Mantse Agbo Naa (5^o 32' 2.65" N, 0^o 12' 41.88" W); Ndafa Park (5^o 32' 7.55" N, 0^o 14' 7.53" W); Dome Community Park (5^o 39' 3.94" N, 0^o 14' 10.26" W); Dansoman Railways Park (5^o 32' 55.22" N, 0^o 15' 59.48" W); Adenta Community Park (5^o 42' 28.83" N, 0^o 9' 35.44" W); Teshie Salem Park (5^o 34' 43.49" N, 0^o 6' 45.48" W), Nungua Methodist Park (5^o 36' 12.47" N, 0^o 4' 10.01" W), La Anglican Park (5^o 33' 26.41", 0^o 9' 36.51" W) and the Efua Sutherland Children's Park (5^o 33' 18.47" N, 0^o 11' 57.28" W).

Depending on the size of the park, 16 to 30 evenly spaced sampling points in a grid plan format were sampled at random. The 16 – 30 sampling points from a park, collectively weighing 1 kg of surface soil were collected using a small garden spade and transferred into zip-lock polypropylene sampling bags, labeled and sealed accordingly.

However, in cases where sampling points amounts over 1 kg, the conical sample reduction formula was applied; and homogeneous 1 kg soil sample was collected.

The samples collected from each sampling site were transferred into individually clean containers and air dried. Each soil sample was thoroughly mixed and sieved through 2 mm mesh and labeled.

RESULTS AND DISCUSSION

Method Verification

The performance of the standardized procedure of soil digestion, preparation and analysis for the selected heavy metals using flame, graphite furnace and cold vapor technique were verified evaluating the linearity, recoveries, reproducibility, limits of detection (LODs) and quantification (LOQs) and robustness.

These were done in order to demonstrate that the performance parameters specified in the method have been met with the matrices to which the method is being applied. The results are as listed in Table 1.

Linearity

Linearity was determined for the instrumental response. The range of concentration studied was0.2 – 10.0µg/L analyzing reference standard solution at six concentration levels (0.2, 0.4, 0.8, 2.0, 5.0 and 10.0 µg/L). The linear calibration curves were obtained by plotting the absorbance for each metal analyte versus its concentration. Each metal showed good linearity for the AAS analysis in the studied working range, with regression co-efficient (R^2) greater or equal to 0.997 (Table1).

Accuracy

Accuracy was determined by comparing the measured concentration with the known/spiked concentration values and was expressed as percentage recovery. Table 1 shows the average recoveries of all the metals investigated in this study. The average recoveries for the metals studied were generally satisfactory ranging from 65% – 107% (Table 1).

Repeatability

Repeatability of results expressed as relative standards deviation of replicates of spiked soil samples gave very good values, all less than 10% (Table 1). Good reproducibility for all metal determination was also realized.

The limit of quantification was obtained by multiplication of the standard deviation by a factor of 10. These were then used to determine the differences in statistical significance between low level analytes responses and the combined uncertainties in both the analyte and the background measurement. Table 1 shows the various method determination limits of the studied metals.

Robustness

To determine the robustness of the method, other soil types were taken through the digestion and instrumental analysis. Clay, silt, loamy types of soil and sediment were investigated. Recovery test of the analytes of interest in these soil types and sediments (60% - 95%) proved very successful.

Thus, the preparative technique and analytical procedures involved in USEPA Method 3052 couple with atomic absorption spectrometer flame, graphite furnace and cold-vapour techniques in this study were demonstrably reproducible. The method was therefore deemed satisfactory and effective for intended purpose of the metal determinations in this study.

Table1. *Summary of Method Verification Parameters for Metals Analysis*

Metals	Experimental Value N = 6, (mg/kg)	Expected Value (mg/kg)	% Recovery	RSD (%)	MDL (mg/kg)	Linearity R^2
Cd	0.97 ± 0.05	1.0	97.0	5.2	0.005	0.998
	9.58 ± 0.62	10.0	95.8	6.5		
	94.15 ± 5.09	100.0	94.2	5.4		
Cr	0.65 ± 0.03	1.0	65.0	4.6	0.01	0.997
	6.74 ± 0.52	10.0	67.4	7.7		
	77.41 ± 6.54	100.0	77.4	8.4		
Cu	0.81 ± 0.02	1.0	81.0	2.5	0.02	0.997
	7.78 ± 0.22	10.0	77.8	2.8		
	87.4 ± 7.39	100.0	87.4	8.5		
Fe	1.07 ± 0.08	1.0	107.0	7.5	0.10	0.997
	9.92 ± 0.54	10.0	99.2	5.4		
	92.5 ± 8.16	100.0	92.5	8.8		
Mn	0.91 ± 0.08	1.0	91.0	8.8	0.01	0.999
	9.24 ± 0.23	10.0	92.4	2.5		
	101.56 ± 8.64	100.0	101.6	8.5		
Ni	0.87 ± 0.07	1.0	87.0	8.0	0.01	0.998
	8.04 ± 0.31	10.0	80.4	3.9		
	93.99 ± 7.49	100.0	94.0	8.0		
Pb	0.97 ± 0.05	1.0	97.0	5.2	0.01	0.997
	9.62 ± 0.22	10.0	96.2	2.3		
	99.16 ± 6.55	100.0	99.2	6.6		
Zn	0.96 ± 0.08	1.0	96.0	8.3	0.01	0.999
	9.50 ± 0.73	10.0	95.0	7.7		
	91.20 ± 5.90	100.0	91.2	6.5		
Hg	0.0007 ± 0.0003	0.001	65.2	9.5	0.001	0.997
	0.0068 ± 0.0012	0.010	68.0	9.1		
	0.071 ± 0.007	0.100	70.7	9.9		

N=Number of Replicates; RSD=Relative Standard Deviation; MDL=Method Detection Limit

LOD and LOQ

Limit of detection and quantification for all studied metals were investigated. To do this, ten reagent blanks (without sample soil) were prepared following the digestion and preparative method. These were aspirated and the signal intensities were recorded. From these, the mean and standard deviations were calculated, and the limit of detection estimated from the equation:

$$Y_{ld} = Y_{blank} + 3sd \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Y_{ld} is the limit of detection, Y_{blank} is the mean from the ten reagent blanks aspirated and sd is the standard deviation.

Real Samples Monitoring

The verified method as above was applied to routine soil monitoring analysis of heavy metals from surface soil samples collected during the period September, 2013 to December, 2014 from 20 selected public parks situated in the Tema and Accra Metropolises of the Greater Accra Region of Ghana.

Figure 1, 2 and 3 depict the distribution of selected heavy metals on surface soil samples collected from the twenty public parks situated in Greater Accra region. Across the public parks, the usual suspects of heavy metals abundance were realized. Iron, Mn, Cu, Pb, Cr and Zn were detected in all samples collected at varying concentrations.

Lead, Pb

The use of leaded fuels in the study area was observed. The highest value (628.31 mg/kg) was recorded from public park in Tema Metropolis, GRTE1.MAN Park (Fig. 1). Tema is an industrial city with several manufacturing companies and a refinery. Thus, these high levels of Pb observed on surface soils of these parks, are as a result of atmospheric deposition from their polluted atmosphere. This clearly demonstrates that industrialization may lead to the negative influence of the atmosphere; thereby contaminating surface soils in the area as a result of atmospheric fallout. A mean Pb concentration of 92.18 ± 133.82 mg/kg was observed across public parks studied. This then gives an indication of vast variation in mean concentrations of Pb on surface soils in this study. The lowest mean Pb concentration was recorded from GRAC2.LAA Park (11.28 mg/kg). This park is close in proximity to the sea, and also is not near any industrial activities, which might influence Pb deposition on its surface soil. GRAC2.LAA Park is also partly covered by grass on its surface soil which could all account to it recording the lowest mean Pb concentration in its surface soil.

Zinc, Zn

Another heavy metal in this study that showed significant differences in mean concentrations across selected public parks was Zn. It recorded mean concentration of 128.55 ± 81.48 mg/kgspanning from 39.69 mg/kg (recorded from GRAC10.ATO Park, a non-industrial area) to 333.04 mg/kg at GRTE1.MAN Park, a heavily populated and high vehicular traffic zone.

This also goes to buttress the earlier point that industrialization may lead to the negative influence of an atmosphere which will then lead to the contamination of surface soils in an area as a result of atmospheric deposition.

Chromium, Cr

Again, among the most occurring heavy metals in this study was Chromium. It was detected in all selected public parks studied, with concentrations ranging from 20.11 mg/kg recorded in surface soil from GRAC7.NDA Park to 339.39 mg/kg at GRTE3.MAS Park in a highly industrial area, and average values of 108.92 ± 82.88 mg/kg.

Zinc and Cr are essential or trace elements, but in excess can be extremely harmful or may bring distress to the human body (Food and Nutrition / Institute of Medicine, 2001).

Therefore, the presences of Zn and Cr in surface soils of public parks where people have most of their outdoor activities need to be monitored continuously in order to have an informed decision about the parks.

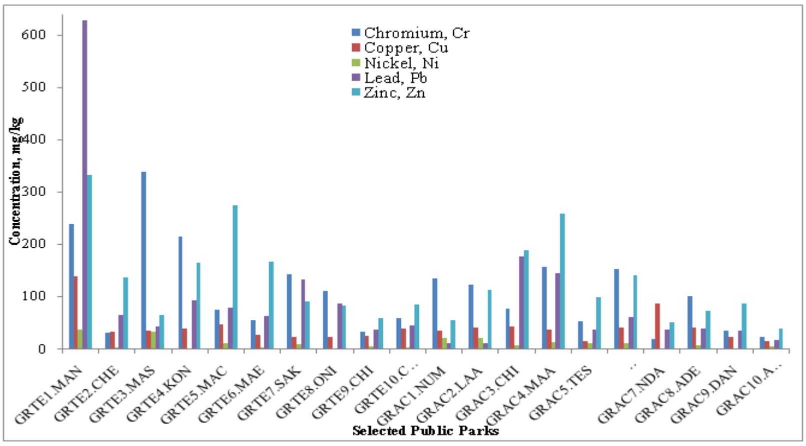

Fig1. Distribution of Cr, Cu, Ni, Pb and Zn across the Selected Public Parks in the Study

Copper, Cu

Copper was recorded in all surface soils analyzed (Fig. 1). Its concentration ranged from 14.27 mg/kg in the surface soil on GRAC5.TES Park to 138.85 mg/kg recorded from GRTE1.MAN Park in Tema Metropolis, with a mean concentration of 40.28 ± 27.86 mg/kg.

Copper is used in making several metal products, including old pipelines, coinage, ear-rings, and are also used together with other metals as alloys in motor tires and parts of vehicles. It is also registered by the EPA of Ghana in the pesticide industry for fungicide formulations to control cocoa diseases (EPA

Ghana, 2015). Thus, the occurrence of Cu in the surface soil samples across public parks could be attributed to atmospheric deposition as a result of its several uses in nature.

Nickel, Ni

High concentrations of Ni are harmful to human health and the environment (Shivhave and Sharma, 2012). Nickel contamination was observed in surface soils of 18 public parks out of the 20 parks investigated (Fig. 1). The concentration ranged from 0.92 mg/kg realized from GRAC9.DAN Park in the Accra Metropolis to 36.95 mg/kg recorded from Public Park in the Tema Metropolis (GRTE1.MAN Park). Even though natural contribution of Ni on these parks cannot be ruled out, the high level of Ni on GRTE1.MAN Park could also be attributed to Ni contamination as a result of waste incineration in this area. A mean concentration of 11.31 ± 10.22 mg/kg was observed indicating large differences in Ni concentration across the public parks studied.

Iron, Fe and Manganese, Mn

Iron concentrations ranges from 4536.10 mg/kg to 14498.15 mg/kg (Fig. 2) with mean concentration of 10475.51 ± 3178.21 mg/kg. Manganese followed with concentrations ranging from 109.24 mg/kg to 1641.49 mg/kg (Fig. 2). A Mean value of 419.87 ± 364.68 mg/kg was observed for Mn. This mean value gives an indication of the vast variation in mean concentrations for Mn in this study.

The relatively high values of Fe and Mn than other metals in this study were expected. This could be attributed to their natural abundance in the earth crust of the area of study. However, even higher values of Fe than this study were recorded by Ackah (2012), who observed a range of 1331.7 – 85688.7 mg/kg as mean concentrations for Fe.

Ackah also observed comparable values for Mn concentrations (23.7 – 1066.0 mg/kg) in his study of selected heavy metals in cocoa farms soils of the Western Region of Ghana (Ackah, 2012).

Cadmium, Cd and Mercury, Hg

The least occurring heavy metal in the study was Cd, with mean concentrations ranging from 0.12 mg/kg to 0.50 mg/kg (Fig. 3), and an average value of 0.34 ± 0.20 mg/kg was observed. About50% of the public parks surface soil samples recorded Hg contamination (Fig. 3), this ranged from 0.001 mg/kg to 0.094 mg/kg with average concentration of 0.04 ± 0.04 mg/kg.

Apart from the fact that Hg has no biological importance to the body, it is toxic, which can cause lung damage, and permanently damage the brain, kidneys and developing fetuses (Martin and Griswold, 2009) even at low concentrations. Thus, its presence in surface soil samples from public parks where adults as well as children whose organs are not fully developed have their outdoor activities could be detrimental.

The abundance order of the heavy metals in surface soils studied was Fe >> Mn > Zn > Cr > Pb > Cu > Ni > Cd > Hg.

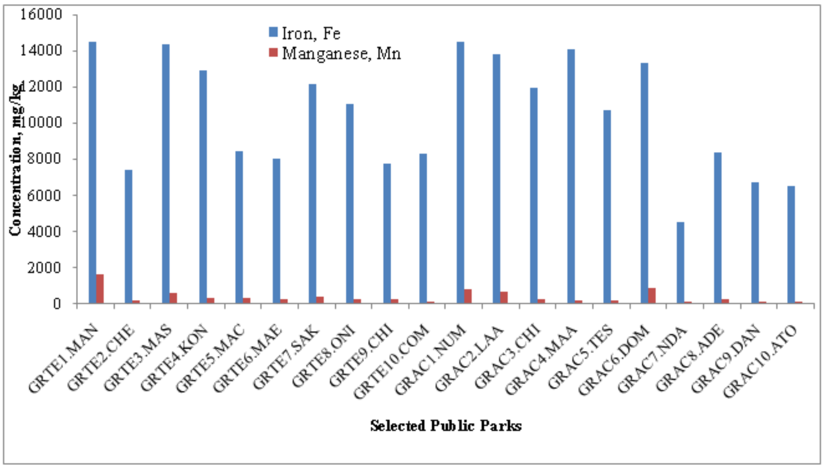

Fig2. *Distribution of Fe and Mn across the Selected Public Parks in the Study*

CONCLUSION

The method as used for heavy metals preparation and analysis in this study (USEPA method 3052) coupled with atomic absorption spectroscopy flame, graphite furnace and cold-vapor analysis was an international method. Thus, thorough method validation was not a requirement; however, demonstration of the effectiveness of the method needs to be verified. This was successfully demonstrated for Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn using laboratory fortified soil samples. The results showed satisfactory average recoveries for all metals (65% - 107%), and good linearity in terms of regression co-efficient greater than or equal to 0.997. Repeatability was also verified with relative standard deviation values all less than 10%. Thus, the method was deemed satisfactory and effective for the intended purpose of heavy metal determinations in this study.

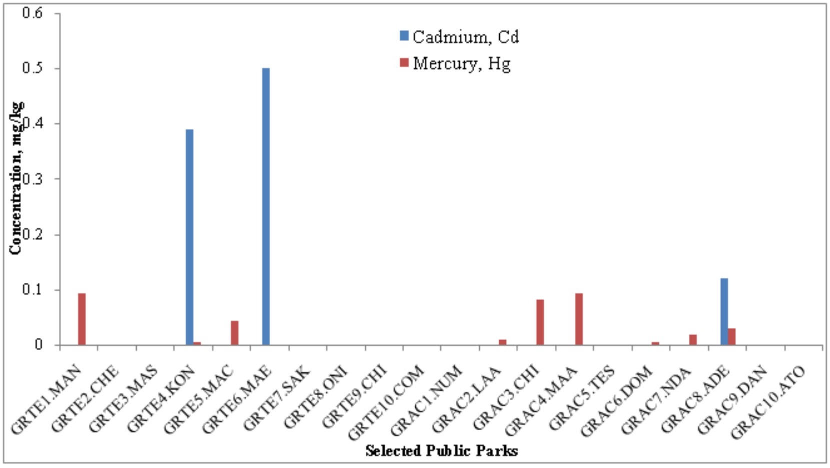

Fig3. *Distribution of Cd and Hg across the Selected Public Parks in the Study*

The results from heavy metal determination in surface soil of public parks investigated showed the usual suspect of earth crust metals abundance of the study area, iron and manganese.

However, the results also demonstrated by far the contributions of anthropogenic activities as sources to heavy metal contamination in the study area as a result of industrialization and urbanization. With mercury ranging from 0.001 – 0.094mg/kg, cadmium (0.12 – 0.50 mg/kg), and even higher concentrations of lead observed (11.28 – 628.31 mg/kg) confirming the use of leaded fuel in the study area.

The abundance order of the heavy metals in surface soils for this study was Fe >> Mn > Zn > Cr > Pb > Cu > Ni > Cd > Hg.

ACKNOWLEDGMENTS

Special thanks to the Metallic Contaminants Laboratory, Ghana Standards Authority; for the immense laboratory support. Our gratitude also goes to the head of stores of the Ghana Standards Authority for his support and cooperation throughout the entire research.

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