

Some trace metals content of atmospheric dusts deposition in Katima Mulilo metropolis, Namibia

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Abstract: Trace metals content of atmospheric dusts continue to attract global attention as more anthropogenic activities including urban road construction impacted on the natural metals load of airborne particulates. This study employed analytical procedures to investigate the concentrations of arsenic, cadmium, cobalt, chromium, copper, nickel, lead, vanadium, tin and manganese in atmospheric dusts deposition in Katima Mulilo metropolis, Namibia. Replicate samples were collected on five days interval under dry winter conditions from mid-August to mid-October, 2013. Samples were collected from within 40 m radius at selected locations along Katima Mulilo urban road construction and from a quite residential area; 2 km away from the road work. Processed samples were digested by EPA method 3050B followed by Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP: Perkin Elmer Optima 7000 DV) analysis. The results obtained showed that manganese recorded the highest concentration in the dusts deposition collected within the urban road construction (155.67 ± 2.52 mg/kg) and residential area (64.00 ± 2.64 mg/kg) respectively. Tin recorded the lowest concentration with mean levels of 0.60 ± 0.10 mg/kg along the road construction and 0.24 ± 0.07 mg/kg in the residential area. T-test analysis of the variations in concentrations of the trace metals were statistically significant ($p < 0.05$). However, the levels of the trace metals recorded in this study were lower than their permissible concentrations recommended by Canadian soil quality guidelines for the protection of environment and human health. There is a very strong positive inter-elemental correlations and the metals enrichment factors showed moderate enrichment. These suggested common and input from anthropogenically induced sources respectively. Single element pollution indexes of the metals showed low contaminations but the levels of arsenic, cadmium, nickel and vanadium in the atmospheric dusts deposition could become source of health concern following environmental accumulations and non-biodegradation of the trace metals. Thus, it is recommended that periodic evaluation of the trace metals content of the atmospheric dusts deposition should be sustained to monitor future accumulation.

Keywords: Atmospheric dusts deposition, anthropogenic activities, trace metals accumulation, Road construction

I. Introduction

Dry deposition pathway is a natural global process of cycling particulate matters that has always been in existence, but which is now dominated by anthropogenic matter - pollution in most urban settlements due to industrialization, automobile emissions, construction activities, power generations and domestic fuel combustions. According to the "Glossary of Atmospheric Chemistry Terms", dust consists of small, dry, solid particles projected into the air by natural forces such as wind and volcanic eruption; and by mechanical or man-made processes such as crushing, grinding, milling, drilling, demolition, shovelling, conveying, screening, bagging, and sweeping [1]. It was further stated that dust particles are usually in the size range from about 1 to 100 μm in diameter, and they settle slowly under the influence of gravity. Atmospheric deposition either in the form of wet or dry deposition have distinct characteristics in terms of associated particulate sizes, pollutant types and influential parameters. It was also submitted that atmospheric deposition is the process by which airborne particles and gases are deposited to soils, vegetation, waters, and other surfaces, either through precipitation (rain, snow, clouds, and fog) or as a result of complex atmospheric processes such as settling, impaction, and adsorption, known as dry deposition [2]. The growing dominance of urban environment with trace metals through natural and anthropogenic deposition and the potentially adverse health implications following environmental contaminations have prompted the investigations of many facets of environmental phenomena including water, soil, air and plants. Exposure to dust particles with high concentration of toxic substances, especially potentially toxic metals, poses a serious threat to human health [3]. For instance, in California, studies indicated that 5–10% of the allergenicity for atmospheric total suspended particulate matter was attributed to paved road dust emissions [4]. Consequently, the monitoring of such material has been set as a priority in risk

assessment programs in order to evaluate the risk of inhalation and ingestion of dust for humans, especially for children [5].

As the case with many urban areas, Katima Mulilo city may also has some vulnerable areas plagued with consistently elevated concentrations of pollutants, particularly heavy metals pollution. Within the last decade, the city has been expanding, including the construction of new buildings and commercial areas, increasing number of vehicles and very recently, mass construction of urban roads. These developmental indices are significant sources of atmospheric emission and deposition; which are critical factors in trace metals contamination of urban environment because of trans-boundary air pollution, which could affect even the most remote area. Heavy metals may accumulate in surface dust from atmospheric deposition via sedimentation, impaction and interception [6], and the control of emission and deposition of atmospheric dust constitute a significant challenge in urban areas. More worrisome; heavy metals pollution represents a global challenge to both public health and environmental sustainability because of their non-biodegradability and geo-accumulation. Some studies have indicated that urban surfaces received heavy metals deposit from multiple sources including municipal wastes incineration, vehicular emissions, industrial wastes as well as coal and fuel combustion [7]. In recent times, the increasing urban road and other infrastructural development in many expanding communities has added to the array of anthropogenic activities, hitherto identified as point source of trace metals emission into the atmosphere. Urban street soils can easily become re-suspended with adhered particulates into the atmosphere and then deposited back onto the surface soil within or at another location depending on the wind velocity. Thus, studies on trace metals contamination in urban soils could assist in developing strategies to protect urban environments and human health against long-term accumulation of heavy metals [8]. Due to the diverse effects of trace metal elements, the importance of their quantification in wet and dry atmospheric depositions has been shown by several authors [9 - 11].

The amount of anthropogenically derived metals has increased continuously since the beginning of the industrial revolution, and the awareness and concern about associated environmental and health risks have risen sharply over the last few decades [12, 13]. It has been reported that some metals absorbed on ambient air suspended particulate produced tissue damage of the lungs [14]. The health effects of toxic metals in air and dust from atmospheric deposited dust on humans is better appreciated if one consider the fact that an active person typically inhales 10,000 L to 20,000 L of air daily [15]. Under rigorous physical exercise, the rate of inhalation increases; thus increasing the chances of inhaling air-borne particulates. Apart from the direct human health problems, adverse effects of airborne pollutants may also include the capability to contaminate exposed foodstuffs.

Thus, investigation of Katima Mulilo atmospheric deposition for heavy metals content is particularly necessary because during winter, the populace is exposed to sever dusts. The region has a semi arid to arid climate which fosters the transfer of huge amount of suspended particulate matters from one place to another during dry, windy seasons. The more the atmospheric dusts are contaminated with heavy metals, the more the exposed populations are at risk of the adverse health effects associated with such metal toxicities. Furthermore, atmospheric deposition is one of the major media through which heavy metals find their way into soil, surface and underground water via rainfall, which may eventually enter the food chain. Therefore, this study was undertaken with the aim of assessing some trace metals content of atmospheric deposited dust within Katima Mulilo urban road construction.

II. Materials And Method

2.1 Study Area

This study is carried out in Katima Mulilo, the capital city of Zambezi Region, Namibia. It is located on latitude 17°30'00"S and longitude 24°16'00"E based on the World Geodetic System (WGS) 84 coordinate reference system. Katima Mulilo urban settlement is currently undergoing tremendous road network and other infrastructural transformations characterized with diverse and high human activities. This trend of urbanization has great implication for anthropogenic pollution, especially dust emissions and particulates into the atmospheric. Furthermore, the region has a semi arid to arid climate which fosters the transfer of huge amount of suspended particulate matters form one place to another during dry, windy seasons. According to Namibia 2011 population and housing census preliminary result, Katima Mulilo urban has a population of 28,200 and a total land area of 32 Sq.Km [16]. Vehicular traffic congestion is also on the increase and this has been associated with the release of particulates into the environment. Consequently, the monitoring of environmental pollution indicators such as heavy metals in atmospheric deposited dust become necessary to check unintended exposure of the populace.

2.2 Sample Collection

Samples of atmospheric dusts deposition were collected on five days interval under dry winter conditions from mid- August to mid-October, 2013. Samples were collected by placing high-density

polyethylene bucket (20 cm diameter) on an elevated tripod stand (1m) above the ground surface to minimize contamination from resuspended particles generated by traffic induced and natural wind. The bucket method was selected in this study because it has been successfully used in similar studies [17], and in the National Atmospheric Deposition Program (NADP), at more than 200 sites in the US [18]. Sample collectors were mounted each sampling day between 8h00 and 18h00. This duration was chosen to cover the peak of high anthropogenic activities in the study area. Separate pre-cleaned buckets were used for sample collections along Katima Mulilo urban road construction and residential area respectively. A total of ten replicate samples were collected from within 40 m radius at selected locations along the road and similar samples were collected from the residential area, about 2 km away from the road construction to assess the effect of the road construction activities on the metals content of the atmospheric deposited dust within the vicinity of the urban road. The residential area chosen is completely devoid of the intense anthropogenic activities within the vicinity of the road construction. At the end of each sampling day, dust deposited were carefully transferred into clean pre-labelled polyethylene bags, fasted properly at the opening with cellophane and kept prior to bulking at the end of sampling period before further processing.

2.3 Sample pretreatment

Replicate samples of the atmospheric deposited dusts collected along the urban road construction and from residential area were respectively pooled together, weighed and ground thoroughly to ensure homogeneity, then filtered through 75 μm sieve. This sieve size was chosen because it satisfactorily process the particles classified as dust. The International Standardization Organization (ISO 4225), described dust as small solid particles, conventionally taken as those particles below 75 μm in diameter, which settle out under their own weight but which may remain suspended for some time [19]. According to the "Glossary of Atmospheric Chemistry Terms", dust particles are usually in the size range from about 1 to 100 μm in diameter, and they settle slowly under the influence of gravity [1]. Dust deposits collected in this study are those that settled slowly on their own, under the influence of gravity and thus, fit into the above two classifications. The sieved dust were packaged in clean, pre-labelled polyethylene bags, fasted and conveyed to Analytical Laboratory Services, Windhoek Namibia, for further processing and analyses. All materials used for holding samples, homogenization and sieving were pre-cleaned to minimize the potential of cross contamination.

2.4 Sample digestion

The atmospheric deposited dust samples were digested according to EPA method 3050B for Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES) analysis. A known amount (1.00g) of each sieved sample was transferred into a digestion vessel and 10 mL of 1:1 nitric acid (HNO_3) was added, mixed thoroughly and covered with a watch glass. Then, the samples were heated to 90°C and refluxed at this temperature for 10 minutes after which they were allowed to cool for 5 minutes under room temperature. Thereafter, 5 mL of concentrated HNO_3 was added to each, covered and refluxed again at 90°C for 30 minutes. Then, the solutions were allowed to evaporate without boiling to approximately 5 mL each and cooled again for 5 minutes. This was followed by the addition of 2 mL of deionised water plus 3 mL of 30% hydrogen peroxide (H_2O_2) to each. The vessels were covered and heated just enough to warm the solutions for the peroxide reaction to start [20]. This was continued until effervescence subsided and the solutions were cooled. The acid-peroxide digestates were covered with watch glasses and heated until the volume reduced to approximately 5 mL again. Then, 10 mL of concentrated hydrochloric acid (HCl) was added to each, covered and heated on a heating mantle, then refluxed at 90°C for 15 minutes. After cooling, each digestate was filtered through Whatman No. 41 filter paper into a 100 mL volumetric flask and the volume made to the mark with deionised water [20].

2.5 Sample analysis

Ten (10) mL of each digestate was taken and mixed with equal volume of matrix modifier [20] and then analyzed using ICP-OES for the levels of lead, arsenic, chromium, cobalt, nickel, cadmium, copper, vanadium, manganese, iron and tin.

1.6 Data analysis

Data generated from triplicate analyses were subjected to treatment of mean and standard deviation, inter-elemental correlation as well as t-test at $P > 0.05$ error protection to determine the significance of data variation between sample locations.

2.7 Assessment of site contamination

In this study, site contamination was assessed using the criteria of Single Element Pollution Index (SEPI), Combined Pollution Index (CPI) [21], and soil Enrichment Factor (EF) [22]. Each of these assessment criteria was calculated using the following equations.

$$SEPI = \frac{\text{Soil metal concentration}}{\text{Soil permissible limit of the metal}} \text{----- (1).}$$

$$CPI = \frac{\text{Soil metal concentration/Its Soil PMC}}{\text{Number of the metals investigated}} \text{----- (2).}$$

$$EF = \frac{C/Fe(\text{sample})}{C/Fe(\text{earth crust})} \text{----- (3).}$$

Where PMC is the permissible maximum concentration used, C/Fe (sample) is the ratio of the metal to Fe concentration of the sample and C/Fe(earth crust) is the ratio of the metal to Fe concentration of the earth crust. The earth's crust Fe concentration used in this study was the value reported by the Mineral Information Institute [23].

III. Results And Discussion

3.1 Concentrations of the trace metals

Table 1 presents the concentrations (mg/kg) of arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), tin (Sn) and manganese (Mn) determined in atmospheric deposited dusts in Katmia Mulilo, Namibia during dry winter condition from mid- August to mid-October, 2013. The results obtained showed that manganese recorded the highest concentration in both the samples collected along Katima Mulilo urban road construction (155.67±2.52 mg/kg) and residential area (64.00±2.64 mg/kg) respectively. Tin recorded the lowest concentration in both sampling areas with mean levels of 0.60±0.10 mg/kg along the road construction and 0.24±0.07 mg/kg in the residential area. The relative mean concentrations of the trace metals (Fig. 1) investigated in this research showed significantly ($P < 0.05$) elevated levels in the atmospheric deposited dusts collected along the road construction than the samples collected in the residential area located 2 km away. This has significant implication for the trace metal inputs from the construction works and other anthropogenic activities along the urban road. Although, the results obtained showed lower levels than the permissible concentrations of the trace metals recommended by the Canadian soil quality guidelines for the protection of environmental and human health [24], Appendix I; accumulations in the environment is possible and people traversing the road as well as living within its vicinity are exposed to this potentially contaminant-bearing dust via inhalation, dermal contact, ingestion and absorption.

Gravels used in road constructions are mined from rock sites previously enriched with diverse metal elements. These no doubt, contributed immensely to the elevated trace metals concentration recorded in the atmospheric dusts deposition collected along the urban road works. The road works as observed were associated with heavy airborne particulates emission into the atmosphere and some of the particulates do not travel far before being deposited via sedimentation under gravity. Thus, it is possible for most of the contaminant-bearing atmospheric dusts to sediment closer to the point source, as the case in this finding. Furthermore, higher vehicular activities and machineries occurring at the construction site are important factors in the increased dusts emission and deposition along the road. Multiple sources of particulates emission via burning of heavy duty oils, wear and tear of brake pads, tires and vehicle body due to friction abound along the road construction and these have significant effects on trace metals release into the atmosphere. This assertion corroborates the finding that major atmospheric pollution sources were industrial emissions, automobile emissions and wind blown soil dust [25]. It was also reported that suspended particulates are introduced into the atmosphere from a variety of natural and antropogenic sources; the latter being more predominant in the urban and industrial areas [26]. Research has also identified that some of the well known anthropogenic processes contributing to airborne particulate pollution include transportation, industrial activities, fuel combustion and agricultural activities [27-29].

3.2 Pollution indexes

The Single Element Pollution Indexes (SEPI) of the trace metals in the atmospheric dusts deposition (Fig. 2) indicated low contamination ($SEPI \leq 1$) based on the established guideline [21] classified in Table 2. However, arsenic showed the most SEPI of the atmospheric dusts with indexes of 0.442 and 0.308 while tin showed the least (0.012 and 0.005) within the road work and residential area respectively. Apart from arsenic, the SEPI of vanadium, cadmium and nickel could also present future concern with the atmospheric dusts deposition because these elements are environmentally persistent, accumulative and non-biodegradable. Human exposures to trace metal elements have been noted with great concern, particularly because of the classification of some (e.g, As, Cd, Cr, Ni) as a potential carcinogens. Carcinogenic substances are those that induce tumors (benign or malignant), increase their incidence or malignancy or shorten the time of tumor occurrence when they get into

the body through inhalation, injection, dermal application or ingestion [30]. These metals apart from acute or chronic poisoning can be transferred to next generation and have potential toxicity from the viewpoint of public health [31].

The Combined Pollution Index (CPI) of the trace metals in the atmospheric dusts deposition (Fig. 3) was less than one (1) which indicates that within the road work and residential area, the average levels of the metals are below the selected standards but does not necessarily indicate that there are no anthropogenic sources of enrichment over background level, and suggested single metal contamination [32]. Thus, continuous monitoring of the trace metals in the atmospheric dusts may be an important way to check geo-accumulation and prevent unintended exposure of the populace to the toxicity effects of the elements.

3.3 Enrichment Factors

The enrichment factors of the trace metals in the atmospheric dusts deposition showed that within both the road work and residential area, the values suggested moderate enrichment based on established environmental site quality criteria [22], presented in Table 3. The current values of the atmospheric dusts enrichment factors within the road work varied between 4.82 to 4.87 while in the residential area, the result varied between 4.84 to 4.87 which were approximately at the peak limit ($2 < EF < 5$) for moderate enrichment. This level of trace metal enrichment in an environment is related to input from anthropogenically induced sources. The enrichment factor was used in this study to assess the level of contamination and the possible anthropogenic impact on the health of the atmospheric dusts deposition along Katima Mulilo urban road construction. Comparisons were made to background concentrations in the earth's crust using Fe as reference element following the assumption that its content in the crust has not been disturbed by anthropogenic activities, and it has been chosen as the element of normalization because natural sources (98%) vastly dominate its input [33]. Furthermore, iron was proposed as an acceptable normalization element in the calculation of enrichment factors since its distribution was not related to other heavy metals [34]. In this study, iron concentration of the atmospheric dusts deposition (Fig. 4) were indeed far higher than the level obtained for any of the other trace metals; both within the road work and residential area. However, the iron contents of the dusts deposition at the road work was significantly ($p < 0.05$) higher which has implication for inputs from anthropogenic sources.

3.4 Correlation analysis of the trace metals concentration

Inter-elemental correlation analyses of the trace metals content of the atmospheric dusts deposition (Table 4) indicated very strong positive correlation. Co and Cd as well as Pb and Cr showed perfect correlations between the sampling areas, which suggest common source of anthropogenic input of the trace metals. The trend of this inter-elemental correlation reflects the possible aerial deposition of dust emitted from the urban road construction sites onto the residential area, thus transferring adhered trace metal contaminants. It has been reported that trans-boundary air pollution is a major source of exposure to trace metals and because of their persistence and potential for global atmospheric transfer, pollutants emitted into the atmosphere from a particular source could affect even the most remote areas [35](Ubwa et al., 2013).

IV. Conclusion

The results of this study revealed significant presence of arsenic, cadmium, cobalt, chromium, copper, lead, nickel, vanadium, tin, manganese and iron in the atmospheric dusts deposition within Katima Mulilo urban road work and residential areas. Although, the results obtained showed lower levels than the permissible concentrations of the trace metals recommended by the Canadian soil quality guidelines for the protection of environmental and human health; accumulations in the environment is possible and people traversing the road as well as living within its vicinity are exposed to this potentially contaminant-bearing dust via inhalation, dermal contact, ingestion and absorption. In this context, children are reported more vulnerable because of their higher absorption rate of trace metals and higher hemoglobin sensitivity than adults. The single element pollution index of the trace metals showed low contamination. However, the SEEPI values of arsenic, cadmium, nickel and vanadium recorded in the atmospheric dusts may become a great source of concern following accumulation in the environment and more also, that these elements are classified as potential carcinogen. All the trace metals showed very strong positive correlation which suggested common sources of anthropogenic inputs. The trace metals enrichment factors of the atmospheric dusts indicated moderate enrichment, which is also related to input from anthropogenically induced sources. Thus, it is recommended that periodic evaluation of the trace metals content of the atmospheric dusts deposition should be sustained to monitor future accumulation. Furthermore, obvious sources of emission of airborne particles such earth removal and filling with imported gravels in urban road construction should be done along with immediate water spraying to suppress dusts prior to asphaltting. This will go a long way in reducing human exposures to some contaminant-bearing dusts emitted into the atmosphere via anthropogenic activities.

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Table I. Concentrations (mg/kg) of some heavy metals in atmospheric deposited dust in Katima Mulilo Town

Trace metal	Roadside deposition	Residential area deposition
As	5.30 ^a ±0.20	3.70 ^b ±0.10
Cd	1.83 ^a ±0.21	0.47 ^b ±0.20
Co	5.03 ^a ±0.25	1.27 ^b ±0.06
Cr	5.57 ^a ±0.31	3.60 ^b ±0.10
Cu	4.33 ^a ±0.15	2.73 ^b ±0.15
Ni	8.53 ^a ±0.12	2.57 ^b ±0.21
Pb	2.17 ^a ±0.21	1.40 ^b ±0.17
V	25.33 ^a ±2.31	5.40 ^b ±0.26
Sn	0.60 ^a ±0.10	0.24 ^b ±0.07
Mn	155.67 ^a ±2.52	64.00 ^b ±2.64

Within rows, t-test of paired means indicated significant difference at p < 0.05

Table II. Contamination criteria based on Single Element Pollution Index (SEPI) [22] and soil Enrichment Factor (EF) [36]

Single Element Pollution Index		Enrichment Factor	
Classification	Degree of contamination	Classification	Degree of enrichment
SEPI ≤ 1	Low	EF < 2	Deficient to minimal
1 < SEPI ≤ 3	Moderate	2 < EF < 5	Moderate
SEPI > 3	High	5 < EF < 20	Significant
		20 < EF < 40	Very high
		EF > 40	Extremely high

Table III. Enrichment factors of the trace metals metals in atmospheric deposited dust in Katima Mulilo

Trace metal	Roadside deposition	Residential area deposition
As	4.86	4.86
Cd	4.83	4.86
Co	4.86	4.87
Cr	4.85	4.87
Cu	4.86	4.87
Ni	4.82	4.87
Pb	4.86	4.86
V	4.87	4.86
Sn	4.84	4.86
Mn	4.84	4.84

Table IV. Inter-elemental correlation analysis of the trace metals in atmospheric deposited dust in Katima Mulilo metropolis

	As	Cd	Co	Cr	Cu	Ni	Pb	V	Sn	Mn
As	1.0000									
Cd	0.9004	1.0000								
Co	0.8984	1.0000*	1.0000							
Cr	0.9988	0.9205	0.9187	1.0000						
Cu	0.9980	0.9263	0.9246	0.9999	1.0000					
Ni	0.9198	0.9989	0.9987	0.9378	0.9430	1.0000				
Pb	0.9988	0.9209	0.9191	1.0000*	0.9999	0.9382	1.0000			
V	0.8795	0.9990	0.9992	0.9016	0.9081	0.9957	0.9021	1.0000		
Sn	0.9558	0.9885	0.9878	0.9689	0.9726	0.9945	0.9692	0.9806	1.0000	
Mn	0.9591	0.9867	0.9859	0.9718	0.9752	0.9932	0.9720	0.9782	0.9999	1.0000

Data with asteriks (*) showed perfect inter-elemental cor

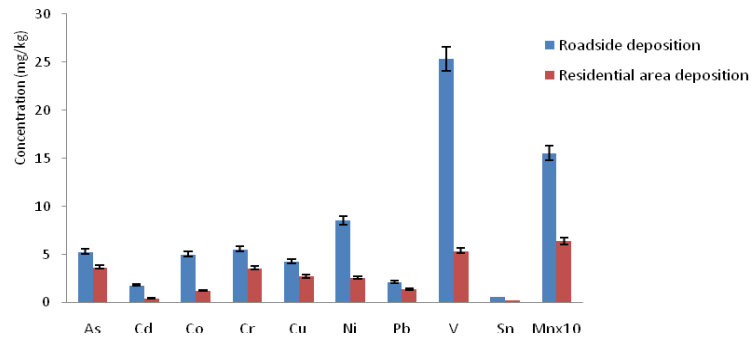


Figure 1. Relative mean concentrations (mg/kg) of some heavy metals in atmospheric deposited dusts in Katima Mulilo

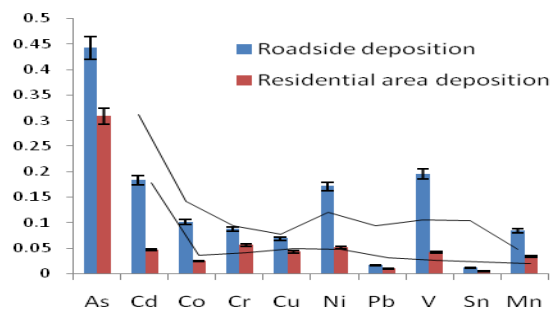


Figure 2. Single element pollution index of the heavy metals in atmospheric deposited dust in Katima Mulilo

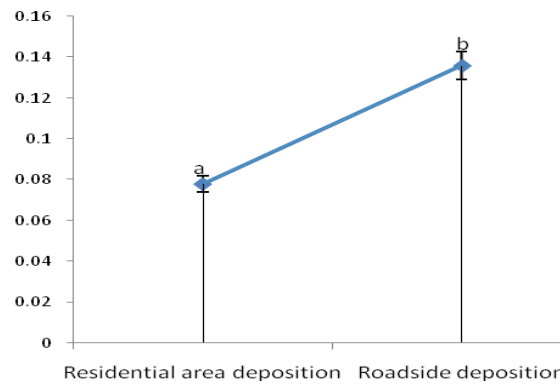


Figure 3. Combined element pollution index of the heavy metals in the atmospheric deposited dust

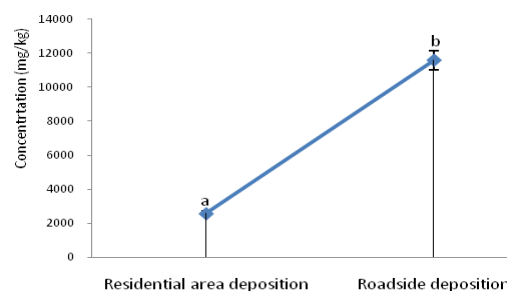


Figure 4. Iron concentration (mg/kg) of atmospheric deposited dust In Katima Mulilo

Appendix I

Canadian Soil Quality Guidelines for the Protection
of Environmental and Human Health

Trace metal	Residential/parkland MPC (mg/kg)
As	12
Cd	10
Co	50
Cr	64
Cu	63
Ni	50
Pb	140
V	130
Mn	1800*

MPC = Maximum Permissible Concentration

* = USEPA, 2004