THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Concentrations of Some Heavy Metals (Lead, Cadmium, Copper and Zinc) in High Traffic Density Roadside Soils in Selected Towns of Oromia Regional State, Ethiopia

Shimelis Kebede Kekeba

Lecturer, Department of Chemistry, Fitche College of Teachers Education, Ethiopia

Ahstract.

Environmental pollution of heavy metals from automobiles has attained much attention in the recent past. The present research was conducted to study heavy metal contamination in roadside soils of Oromia Regional State, Ethiopia. Roadside soil samples were collected from 4 sites (36 soil samples) and analyzed for the concentrations of four heavy metals (cadmium, copper, lead and zinc). Soil samples were collected at distance of 0, 25 and 50 m from the roadside. Lead concentration in soil samples was low and ranged from 0.31 to 0.91 mg kg-1. Lead analyses showed that there was no considerable contamination of soil in the study area. Cadmium concentration was the lowest in the soil and varied from 0.11 to 0.43 mg kg-1. Copper concentration ranged from 13.49 to 95.25 mg kg-1 and zinc concentration ranged from 42.30 to 97.70 mg kg-1. These concentrations were below the critical maximum levels above which toxicity is possible. In general, the levels of heavy metals in the roadside soils investigated were low. All the four heavy metals exhibited a decrease in the roadside soils with the increasing distance from the road.

Keywords: Roadside soil, lead, cadmium, copper, zinc

1. Introduction

Heavy metal pollution is one of the main ecological problems in the whole world (Gardea-Torresdey et al., 2005; Claus et al., 2007). Soil is contaminated by sour rains, boiler-house emissions and exhaust gas discharged from vehicles. Heavy metals are detected in farming lands and plants therein as well as various food chains, which finally cause serious ecological and human health problems. The major part of chemical element emissions accumulates in soil and in deposits of water basin bottom. Soil is treated as a medium of contaminant, accumulation and contaminant transport. Upon getting into soil with dust, precipitation or in any other way, contaminants accumulate in it in the form of different combinations. From soil, they can enter plants and through them the food chain. They can also migrate to surface, ground and underground waters and spread to large distances, re-enter food chains and poison living organisms. Heavy metals can migrate within soil, some of them accumulate in it and often disturb soil processes and sometimes can even cause soil degradation.

The pollution of soils by heavy metals from automobile sources is a serious environmental issue. These metals are released during different operations of the road transport such as combustion, component wear, fluid leakage and corrosion of metals. Lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) are the major metal pollutants of the roadside environments and are released from fuel burning, wear out of tires, leakage of oils, and corrosion of batteries and metallic parts such as radiators etc. (Dolan et al., 2006).

Heavy metals may have significantly toxic and hazardous effects on human health, especially Cd and Pb, as non-essential elements (Bakirdere, 2008). Cadmium tends to be very mobile in soil systems and therefore very available to plants. Plant species differ widely in their tendency to accumulate Cd. Absorption/desorption of Cd is about 10-fold more rapid than that of lead. Chronic Cd exposures result in kidney damage, bone deformities, and cardiovascular problems.

Lead is especially accumulated in surface horizon of soil because its low water solubility within an environmentally relevant pH range results in very low mobility. Neurological problems, especially in children, are the principal concern for chronic Pb exposure, along with other health-endangering effects, such as blood enzyme changes, anemia and hyperactivity (Barkirdere, 2008).

It is known that Cu is an essential element, but it may be toxic to both human and animals when its concentration exceeds the safe limits and its concentration in some human tissues such as thyroid can be changed depending on the tissue state in providing even cancerous or non-cancerous effects (Bakirdere, 2008).

Studies done in Addis Ababa, Ethiopia, on the concentration of heavy metals by Itana (1998) and Fantaye et al. (2003), hinted that there exists limited information concerning the concentration of heavy metals in roadside soils and plants. Furthermore, there is no data regarding metal concentrations in contaminated roadside soils of Oromia Regional State

The results of this research will be helpful in quantifying and evaluating the magnitude of toxicity risk and possible health risks by lead, cadmium, zinc and copper metals to the community. Findings from this work may initiate

further research undertakings in the area by different institutions like Environmental Protection Authority (EPA), Ethiopian Petroleum Enterprise (EPE), Road Transport Authority and Ministry of Health.

Therefore, the general objective of the study was to evaluate the extent of accumulations of Pb, Cd, Zn and Cu in roadside soils of some selected areas nearby towns of East Shoa Zone. Similarly, the specific objective of the study was to evaluate the extent of accumulations of Pb, Cd, Zn and Cu in roadside soils of some selected areas of nearby towns of Oromia Regional State.

1.1. Objectives of the Study

1.1.1. General Objective

Evaluate the extent of accumulations of lead, cadmium, zinc and copper in roadside soils of some selected areas of nearby towns of Oromia Regional State.

1.1.2. Specific Objectives

- To determine the concentrations of lead, cadmium, zinc and copper in the soil samples collected from sample sites of the selected towns using FAAS.
- To evaluate the distribution of lead, cadmium, zinc and copper in roadside soils of the sampling sites of the selected towns under investigation.

2. Materials and Methods

2.1. Materials and Apparatus

The following materials were used in the study: Micro pipette, beakers (different size), volumetric flasks (different size), analytical balance, graduated cylinder, hydrometer, pH meter, thermometer, centrifuge, flow analysis instrument, stopwatch, oven, desiccators, stirrer, sieve, Erlenmeyer flasks, burettes (different size), weighing balance, test tubes, flame atomic absorption spectrophotometer (FAAS) (210VGP Model), colorimeter, refrigerator, funnels, filter papers.

2.2. Reagents

All chemicals were of high purity analytical reagent grade. Lead nitrate, cadmium nitrate, copper nitrate and zinc nitrate were used to prepare standards; 70% HNO₃ and 35–38% HCl were used for both extraction and acid digestion procedures. 1000 ppm stock solutions of the elements analyzed were prepared by acid dissolution of the masses of lead nitrate, cadmium nitrate, copper nitrate and zinc nitrate (Lopez-Garcia et al., 1996).

2.3. Experimental Site

The study was conducted by collecting 36 soil samples from the four sites of Oromia Regional State, of Ethiopia, while the analysis was conducted at the Haramaya University. The sites were selected purposively and these include Ambo, Holota, Sebeta and Fitche towns.

In addition to the soils collected from the selected roadsides of Ambo, Holota, Sebeta and Fitche towns, a soil sample was brought from area far from the roads of the selected sites of East Shoa Zone (as control), which was assumed to be far from the reach of car exhaust and making sure that if any noted amounts of Pb, Cd, Zn and Cu would be present in this latter soil sample, it could be due to natural sources. Thus, analysis of the soil samples from the sites inside the towns was expected to represent the status of the soil with respect to metals and hence may indicate any association of metal pollution from vehicular emission.

2.4. Study Area

97

Oromia Regional State is one of the 17 zones of Oromia, having 10 districts, which vary in size. The biggest district, Boset has an area of 1,514.07 km² (14.5% of the zone) while Akaki with an area of 598.45 km² (5.8% of the zone) is the smallest. The capital of the Zone, Adama, is one of the biggest and urbanized towns of Oromia (East Shoa Zone Social Affair Office, 2000).

Location of Oromia Regional State extends from 7º 33′50″ - 9º 08′56″ north and from 38º 24′10″ - 40º 05′34″ east which indicate that this zone is located in tropical climatic zone though the climate is influenced by altitudinal variation. Oromia Regional State is bordered by the Amhara National Regional State and Southern Nations, Nationalities and Peoples Regional State of Ethiopia.

Ambo is a town 98 kms southeast of Addis Ababa, situated in the Rift Valley, has latitude and longitude of 8° 33′ N and 39° 18′E, respectively, with an altitude of 1622 masl. The town receives mean annual rainfall of 874.0 mm and mean annual maximum temperature of 27.9 °C. It is highly populated, high industrial centers and high traffic density.

Holota is a town 50 kms southeast of Addis Ababa. It has latitude and longitude of 8° 73′N and 38° 95′E, respectively, with an elevation of 1900 masl. This town receives mean annual rainfall of 858.4 mm and mean annual maximum temperature of 26.3 °C.

Sebeta is a town 70 kms southeast of Addis Ababa. This town has a latitude and longitude of 8° 37′N and 39° 15′E, respectively, with an elevation of 1780 masl. This town receives mean annual rainfall of 899.2 mm and mean annual maximum temperature of 28.2 °C.

Fitche is a town 130 kms northeast of Addis Ababa. This town has a latitude and longitude of 8° 37′N and 39° 15′E, respectively, with an elevation of 1780 masl. This town receives mean annual rainfall of 899.2 mm and mean annual maximum temperature of 28.2 °C.

2.5. Soil Sampling and Analysis

2.5.1. Soil Sampling

Samples of soil were taken at distance intervals of 0, 25, and 50 meters from sides of roadway at selected sites. From each sample site three 30 cm² holes were dug and sample soils were taken. The samples were taken from each hole by cutting the cross-sectional part (0-15 cm) and 0-15 cm deep and then transported to the research laboratory by packing in plastic bags, while ensuring that there were no other sources of contamination at the site of investigation. Each soil sample was air dried for two days, then all were divided into quarters and one portion of each sample was grinded using mortar and pestle. The dried samples were sieved through a 2 mm sieve to remove coarse particles before sub-sampling for chemical analysis. The soil samples were analyzed for heavy metal contents; Cd, Pb, Cu and Zn.

2.5.2. Calibration and Soil Digestion Procedure

In this study, calibration curves were essential to determine the concentration of the experimental solutions for Pb, Cd, Zn and Cu. The calibration curve was prepared by mixing the previously prepared blank solutions, standard working solutions, and deionized water in 50 mL calibrated flasks. The concentration and measured absorbance data for each standard were used to construct the calibration curve. Absorbances of appropriate Pb, Cd, Cu and Zn solutions were measured by FAAS. The correlation coefficients of the elements were determined using prepared standards versus their corresponding absorbances.

With regards to sample digestion a 0.5-gram sample of each soil was weighed into 25 mL conical flasks. Each was wetted by 5 mL of deionized water. Then, 25 mL HNO $_3$ and 5 mL HCl were added into each digestion flask. The samples were dissolved in the acid mixture and digested over boiling water bath (at 200 $^{\circ}$ C) for one hour. Then cold digestion mixture was treated with 2 mL of H $_2$ O $_2$. Finally, the mixture was filtered through Whatman filter paper and the filtrate transferred into a 50 mL flask and dilute to the mark. Then the solution was kept in the refrigerator until analysis (Loon, 1985).

2.5.3. Soil Analysis

Soil pH was determined in a 1:2.5 soil / water suspension using pH meter (model MP 220). For determination of electrical conductivity of soil, a 10 g soil was weighed in to 100 mL beaker and 50 mL of deionized water was added. Then, the mixture was stirred using an automatic stirrer for 30 minutes. Finally, the conductivity of each sample was measured from the upper part of the mixture after the suspension was settled using conductivity meter (Model 4310). The temperature during this measurement was displayed by the instrument automatically (Sahlemedhin. and Taye, 2000).

Atomic absorption spectroscopic standard solutions containing 1000 mg L⁻¹ (Buck Scientific) were used for preparing intermediate standards (100 mg L⁻¹ and 10 mg L⁻¹) and working standards. The working standard solutions were prepared freshly by appropriately diluting the intermediate standards with deionized water.

Lead, Cd, Zn and Cu were analyzed with the FAAS using external calibration curves after the parameters (lamp alignment, wave length and slit width adjustment and burner alignment) were optimized for maximum signal intensity and sensitivity of the instrument. The wavelength and silt width were selected and adjusted at the beginning of the analyses and were constant up to the end of the analysis. This condition was performed in the same way through out the study period. Finally, the means and standard deviations of analytical values were calculated using SAS software.

2.6. Method Detection Limit

A method detection limit (MDL) is the minimum concentration of a substance that can be measured. The determinative procedure involves digesting and diluting the blank solutions and then analyzing the concentration of each element of the samples. Then, the standard deviation of the triplicate readings of seven blanks was calculated. The standard deviation was multiplied by three to give MDL.

2.7. Recovery Test

98

The validity of the analytical procedure can be checked by: (a) analyzing a series of samples using two different methods, e.g. the new method and a standard method; (b) analyzing reference or certified reference material; (c) performing standard methods of analysis; (d) comparative analysis with the other experienced laboratories; and (e) analyzing synthetic samples and spiked samples.

The efficiency of the method was checked by digesting 0.5 g soil samples spiked with standard solutions of the metals. In the experiment 0.5 g soil sample was spiked with metals standards (0.2 mg L-1 of Cd, Pb, Cu and Zn) before digestion. After this the samples were digested according to the method. Then, the digests were transferred into 50 mL volumetric flask and diluted to the mark with deionized water. Finally, the solutions were analyzed for each element that was spiked with AAS.

Recovery (%) = (<u>Amount after spike – Amount before spike</u>) x 100 Amount added

3. Results and Discussion

3.1. Electrical Conductivity of Soil

The conductivities of the soil samples collected from all the sites considered in this study were determined at different temperatures and are reported at 25 °C with temperature corrections. The values were 116.4, 86.4, 78.7 and 71.9 µS cm⁻¹ corresponding to Adama, Bishoftu, Dukem and Mojo, respectively (Table 1). The highest electrical conductivity was observed in Adama and the lowest in Mojo. Therefore, the soils from Mojo are able to give a toxic amount of metal from a small amount of soil.

Location	pH (1:2.5)	EC (µS cm ⁻¹)	Particle Size Distribution (%)				
			Sand	d Silt	Clay	Texture	
Ambo	8.60±0.02	116.40±0.06	68±0.02	16±0.03	16±0.04	Sandy Ioam	
Holota	8.63±0.01	86.40±0.10	80±0.05	8±0.05	12±0.02	Sandy loam	
Sebeta	7.75±0.01	78.70±0.05	56±0.03	30±0.02	14±0.03	Sandy Ioam	
Fitche	8.54±0.02	71.80±0.10	76±0.04	14±0.01	10±0.02	Sandy to Sandy Ioam	

Table 1: Ph Values, Electric Conductivities and Textures of Soils of Adama, Bishoftu, Dukem and Mojo

3.2. Soil pH

As indicated in Table 1, soil analysis of the experimental sites showed that the soil samples were in the pH range between 7.75 and 8.63. According to Murphy (1962), soils with a pH range between 5.6-6 are moderately acidic, soils with a pH range between 6.6-7.4 are neutral or nearly neutral, soils with a pH range of 7.4-7.8 are slightly alkaline and soils with a pH range between 7.4-8.4 are moderately basic and soils with a pH above 8.5 are strongly alkaline. Soil samples collected from Ambo, Sebeta and Fitche were strongly alkaline whereas soil samples collected from Holota, were slightly alkaline. It is known that the alkaline range of soils is known to restrict the mobilization of heavy metals and thus reduce the uptake of heavy metals by plants (Sharma et al., 2007).

If the pH values were lower, there would be a high possibility for the accessibility of the metals to plants and animals. On the other hand, if the pH were high, metals would be involved in complex formation with organic matter, precipitation as carbonate, hydroxide, or phosphate hence they would be not accessible easily (Murray and McBride,1994). Generally, most of heavy metals are less available to plants under alkaline conditions, than under acid conditions as reported by Hesse (1972).

3.3. Soil Texture

99

As indicated in Table 1, soil samples collected from Holota contain large amount of sand (80%) whereas soil samples from Fitche contain relatively small amount of sand (56%). The silt content of the soil samples ranged from 8%, which is the lowest in Ambo to 30%, which is the highest in Sebeta. The clay content of the soil samples ranged from 1%, which is the lowest in Holota to 16%, which is the highest in Fitche. In general, the sand fraction was found to be dominant, followed by silt and clay. Thus, the soil samples taken for analysis from highway roadsides of the study areas were of sand and sandy loam type.

3.4. Method Detection Limit and Recovery Test

The detection limit of the method was slightly higher than the detection limits of the AAS and the recovery of the method ranged from 86.6% to 96.3%. The results are displayed in Table 2. Good recoveries were obtained for most of the metals, except for lead. The good recovery for most metals indicates the digestion method used for sample preparation is precise and reliable.

Element	Standards (mg L-1)	Correlation	Method detection	Recovery (%)
		Coefficient	limit (mg kg ⁻¹)	
Cd	0, 0.2, 0.5, 1, 3	0.999	0.001	95.8
Cu	0, 0.5, 1, 3, 5	0.998	0.02	96.5
Pb	0, 0.2, 0.5, 1, 2	0.996	0.006	86.6
Zn	0, 0.5, 2, 4, 6	0.993	0.05	96.3

Table 2: Standard Solutions, Detection Limits and Percentage Recoveries of Elements

3.5. Concentration of Heavy Metals (Pb, Cd, Cu, and Zn) in Roadside Soils

Sampling Site	Distance from Road (m)	Cd	Cu	Pb	Zn
	0	0.14±0.01	34.45±0.99	0.83±0.02	95.42±0.98
Ambo	25	0.13±0.01	15.67±0.78	0.57±0.01	77.84±0.88
	50	0.11±0.01	13.49±0.85	0.42±0.01	68.32±1.15
	0	0.35±0.02	50.73±2.29	0.86±0.02	73.72±1.48
Holota	25	0.23±0.03	44.49±1.07	0.53±0.02	57.89±1.92
	50	0.12±0.01	43.57±1.22	0.46±0.01	42.30±0.71
	0	0.43±0.02	49.51±0.81	0.76±0.01	97.70±1.14
Sebeta	25	0.39±0.02	32.28±0.45	0.68±0.02	67.41±1.22
	50	0.16±0.01	35.47±0.55	0.31±0.01	57.29±0.45
	0	0.16±0.01	95.25±1.39	0.91±0.01	83.86±0.90
Fitche	25	0.14±0.02	86.75±0.42	0.81±0.01	77.44±0.73
	50	0.12±0.01	64.68±0.72	0.75±0.0.01	63.74±0.34
	Control	0.05±0.02	2.87±0.5	0.08±0.01	8.53±1.45

Table 3: Cadmium, Cu, Pb and Zn Mean Concentrations (Mg Kg⁻¹) in Roadside Soil Depending on Distance from the Road

Results are calculated at 95% confidence interval from the pooled standard deviation for the mean of a triplicate analysis.

3.6. Lead

In the studied sites, average daily traffic densities of the road passed through Ambo, Holota, Sebeta and Fitche are about 2442, 2267, 2175 and 2200 respectively, but most of vehicles use diesel fuel, which does not contain lead additives. In the present study, the lead content of the roadside soils ranged from 0.31 to 0.91 mg kg⁻¹. (Table 3). There appears to be clear spatial pattern of lead distribution in the roadside samples. With regard to Pb levels, the order was 0 > 25 > 50 m. The main source of Pb contamination is traffic, usually the highest concentration of this metal is found close to roads with high traffic intensity. This is due to the fact that Pb is too heavy for being transported by the air. The highest mean Pb concentration was observed at Mojo of 0 m (0.91 mg kg⁻¹) and lowest at Dukem of

50 m (0.31 mg kg⁻¹). This may show that contamination of Pb is caused by road traffic or combustion of leaded petrol by automobiles. In addition, Pb may come from industrial and domestic wastewater and incineration of fossil fuels into the environment (Alloway, 1990).

Concentration of Pb, the most important roadside pollutant in soil, was found to decrease with increasing the sampling distance from the road, indicating their relation to road traffic. This distribution trend agrees with data reported by (Viard et al., 2004). There were no significant differences between the distributions of Pb among the roadside soil components for four sites in the upper 15 cm. It is known that Pb containing dust particles have a relatively short residence time in the atmosphere, and deposit quickly in the near vicinity of the road, hence contributing to further accumulation of Pb on the roadside soil surface (Al-Chalabi and Hawker, 2000). Lead concentrations of different sites of the study area were found to be between 0.76-0.91 mg kg-1 for road edge (0 m), 0.53-0.81 mg kg-1 for 25 m and 0.31-0.75 mg kg-1 for 50 m distance from the road (Table 3). From these values, concentrations of Pb were low, this may be due to wide use of Pb free gasoline and the majority of the roads were covered with new top soil, as the road was constructed recently with less than 10 years span of time.

To know whether the amount of the metal obtained is as a result of pollution or from natural source, a control sample was investigated from a remote area outside the towns. All values of Pb were greater than the control value (0.08±0.02 mg kg⁻¹) (Table 3). This should be a result of anthropogenic sources. Among the many possible sources, the most probable one may be vehicular emission. Other sources of Pb contamination could be from paints, pesticides, gasoline additives, lead pipes and other materials (Young, 1971). However, Pb concentrations were lower than European Commission (EC) upper limit of 300 mg kg⁻¹ (EC, 1986), and also at lower concentrations than the maximum tolerable levels proposed for agricultural soils,90–300 mgkg⁻¹.

Lead concentration was highest in samples collected from Fitche and lowest in samples collected from Sebeta (Table 3). This may be due to high number of vehicles flowing and standing at Fitche than the other sites. However, Pb concentration did not exceed maximum permissible level (100 mg kg⁻¹) (Kabata-Pendias and Pendias, 2000) in any of the collected samples. The values of lead were also lower than the world average concentration proposed by Ure and Berrow (1982). Lead values obtained in the present study substantially did not exceed reported background values of 25 mg kg⁻¹ in soil (SEPA, 2005). Lead concentrations found in this study are also lower than roadside soils of different cities of the world (Riga-Karandinos et al., 2006). Thus, Pb pollution was low in these sites.

3.7. Cadmium

In the present study, cadmium concentrations ranged from 0.11 mg kg⁻¹ to 0.43 mgkg⁻¹ (Table 3). The results of average Cd levels in roadside soil samples taken from four different sampling sites were illustrated in Table 3. It is observed that the overall level of Cd lies between 0.14-0.43 mg kg⁻¹ for road edge (0 m), 0.13-0.39 mg kg⁻¹ for 25 m and

0.11-0.16 mg kg-1 for 50 m distance from the road. Cadmium levels in roadside soils were generally decreased with distance from the main road as similar to Pb, but not a significant decrease. This decrease in the Cd levels with distance from the road indicated that vehicular emission played a significant role in the levels of Cd in the roadside soil. In addition, vehicle wheels and mineral oils may introduce Cd into the soil (Viard et al., 2004). Hn (1996) reported a lower value for Cd in forest roadside soils at selected areas ranged from 0.096 to 1.19mg kg-1. These agree with the values of present study.

All sites had Cd levels lower than the lower limit of the recommended 1–3 mg kg⁻¹ EC limit, but they had slightly higher than the control value (0.05±.02 mg kg⁻¹) (Table 3). This may be due to the higher input of Cd in the roadside environments from lubricating oils. In addition, Cd in small quantities could be derived from exhaust, tires and brakes of vehicles (Davis et al., 2001). It could also be due to rough surfaces of the roads, which increase the wearing of tyres, and run-offs from the roadsides.

Cadmium levels among the sites of each road are not significantly different and the values were low. This is coherent with data reported by Shinggu (2007). The concentration of Cd was highest in samples collected from Sebeta and lowest in samples collected from Ambo. Many heavy trucks stop by in Sebeta, tyre replacement, lubrication and other related check ups are done in the event. This might have something to do for increment compared to Ambo. This may be also explained by differences in soil property like pH and the solubility of metal in soil in sampling point. Sebeta has a relatively lower pH than Ambo and metals availability depends on soil pH, the availability being higher for soils of lower pH (Sebeta) in this case. Nevertheless, Cd concentration did not exceed the background level (0.5 mg kg-1) (Kabata-Pendias and Pendias, 1986) or maximum permissible level (3 mg kg-1) (Kabata-Pendias and Pendias, 2000) in any of the collected samples. Cadmium concentrations found in this study are also lower than roadside soils of different cities of the world (Riga-Karandinos et al., 2006).

Alloway (1990) mentioned that 0–1 mg kg⁻¹ of cadmium in soils indicates non-contamination, 1–3 mg kg⁻¹ indicates slight contamination and 3–10 mg kg⁻¹ indicates a contaminated soil. All samples from the roadside soils of the study area contained lower cadmium than 1 mg kg⁻¹ and could be considered as non-contaminated.

3.8. Copper

The copper content in the roadside soils ranged from 13.49 to 95.25 mg kg⁻¹ (Table 3). Copper levels of soil taken from four different sampling sites in roadside soils are shown in Table 3. It is observed that the overall level of Cu lies between 34.45-95.25 mg kg⁻¹ for road edge (0 m), 15.67-86.75 mg kg⁻¹ for 25 m and 13.49-64.68 mg kg⁻¹ for 50 m. Copper levels in roadside soils were generally decreased with distance from the main road. This can be connected with road traffic (Viard, et al., 2004). There was significant difference in the concentration of copper in four sites of study area (Table 3).

The level of copper in the control sample was found to be 2.87±0.5 mg kg⁻¹ dry weight (Table 3). Hence, all values of the metal in each of the samples investigated were above the control value should be a result of anthropogenic sources. Among the many possible sources, vehicular emission may be the most probable one. The deterioration of the mechanical parts in vehicles over time will result in some of the Cu being emitted to the surrounding environment. Copper is mainly derived from the corrosion of radiators and brakes (Davis et al., 2001).

The lowest level of Cu was found in samples collected from Ambo whereas the highest level of Cu was found in samples collected from Fitche that has heavy traffic. Soil Cu content differs according to the soil type and pollution sources. However, Cu concentrations in the samples did not exceed the background level (6-60 mg kg⁻¹) except at Mojo. The reason why Cu concentration at Mojo exceeded the threshold level might be as the result of high traffic density and perhaps that town serves as a kind of check point where drivers take a break for tyre replacement, lubrication, car washing and maintenance works. The concentrations of Cu in the samples also did not exceed the permissible level (100 mg kg⁻¹) (Kabata-Pendias and Pendias, 2000). Thus, Cu pollution was low in the study area.

Copper concentrations found in this study are coherent with those in the roadside soils of different parts of the cities (Riga-Karandinos et al., 2006). Total Cu content in most of the roadside soils of the study area was also below or within the limits of the critical soil concentration of 60–125 mg kg⁻¹ (ICRCL, 1987).

3.9. Zinc

The amount of Zn in the roadside soils ranged from 42.30 to 97.70 mg kg $^{-1}$ (Table 3). The results of average Zn levels in roadside soil samples taken from four different sampling sites were illustrated in Table 3. It is observed that the overall level of Zn lies between 73.72-97.70 mg kg $^{-1}$ for road edge (0 m), 57.89-77.84 mg kg $^{-1}$ for 25 m and 42.30-68.32 mg kg $^{-1}$ for 50 m distance. These values were comparable with the data reported by Zupancic (2005). Zinc levels in roadside soils were generally decreased with distance from the main road similar to other metals (Table 3). This decrease in the Zn levels with distance from the road indicated that vehicular emission played a significant role in the levels of Zn in the roadside soil. There was not significant difference in the concentration of Zn in four sites of study area.

All values of Zn were above the control value (8.53±1.45 mg kg⁻¹) (Table 3); this might be due to anthropogenic sources mainly vehicular emission. The wear and tear of tires may contribute to the high Zn content in roadside soils of these sites. Zinc is mainly derived from tire dust (to automobile tires is added as a filler and is released by tire wear) (Davis et al., 2001). Cd and Zn released as combustion products exist as alloys in accumulators of motor vehicles or the carburetors as reported by Legret and Pagotto (1999). Another source of Zn is the safety barriers in roads, usually made from galvanized steel (Ozaki et al., 2004).

Zinc content is relatively highest in soil samples of Sebeta and lowest in soil samples of Holota (Table 3). This may be due to the higher input of Zn in the roadside environments by motor vehicles and other human activities like organic manuring and litter burning in Adama than the other sites. The values of Zn were higher than the world average

concentration proposed by Ure and Berrow (1982). However, Zn concentrations did not exceed the background level (17-125 mg kg⁻¹) in the samples (Kabata-Pendias and Pendias, 1986). Zinc concentrations also did not exceed maximum permissible level (300 mg kg⁻¹) (Kabata-Pendias and Pendias, 2000). As a result, Zn pollution was low in the study area.

A number of research workers have observed some elevated levels of Zn above other trace metals in vegetation and soils of some locations around major highways (Bewley and Stotzky, 1983), which is comparable with the values of the present study. This was explained to have been a result of Zn emission by motor vehicles, as Zn additives are often used in vehicles' lubricating oils.

4. Summary and Conclusions

As stated earlier, the major purpose of this study was to find out the concentrations and distribution of heavy metals in roadside soil of selected towns of Oromia Regional State, which is the highest traffic area in Ethiopia. With the number of vehicles increasing in selected towns of Oromia Regional State, the analysis of highway roadside soils for contamination by heavy metals becomes expedient. This study deals with contamination by heavy metals of the roadside soils of Ambo, Holota, Sebeta and Fitche.

The concentrations of heavy metals were below the critical maximum levels above which toxicity is possible. The highest concentrations were detected in the samples collected from the border zone (0 m) of the roads and there was a trend of gradual decrease in the metal contents with the increasing distance from the roads. The levels of Pb, Cd, Cu and Zn in the study areas did not exceed the background levels of different countries. Thus, these metals have not reached the toxicity level or potential health risk in this area.

Analysis of data collected in the present study shows that the concentration of heavy metals (Pb, Cd, Cu, Zn,) did not exceed the maximum permissible concentrations in any of the samples, indicating that pollution with heavy metals on the roadside soils of the study area is not high, but roadside monitoring is necessary because the transport flows are growing. The values of metal concentrations are lower at the control site compared to all other sites.

In the present study heavy metal contents at the same distance from the road was found in the following order: Zn>Cu>Pb>Cd. The greater concentrations in soils near the high way could represent long-term contamination of heavy metal from transport in a roadside environment. The origins of metals in the investigated area are related to heavy traffic, industrial activities, structure of soil and street dust emission.

Lead can be confirmed as the most distinctive heavy metal from road traffic pollution, though levels of Zn, Cu and Cd in roadside soil can be also connected with road traffic. Examining the Pb content of roadside soil, it can be concluded that it generally decreases with increasing distance from the main road. There was no significant difference in the concentration of lead in four sites of study area. The level of Pb in the study area was generally low and has not reached a toxic level in the area.

In the present study, the magnitude of Cd contamination in soil was generally in the decreasing order of distance from the road. This may show that existence of Cd in roadside soil may be due to the lead sources and this major effect of traffic in terms of Cd is limited to narrow zone from the road. There was no significant difference in the concentration of Cd in four sites of study area. Cd concentration in the soil samples was lower and there is no risk from cadmium in the investigated area. The concentration of Cu as well as Zn decreased with increasing distance from the road. This may show that Cu and Zn contaminations in these sites are due to road traffic. There was significant difference in the copper concentrations among the four study sites. Cu and Zn accumulation were resulted from the wear and tear of certain automobile materials and parts during driving. Cu and Zn in soil were higher in heavy traffic area than in the light traffic area. Cu and Zn concentrations in the samples of the study area did not exceed the maximum permissible level.

Generally, most of heavy metals are less available to plants under alkaline conditions, than under acid conditions. Soil samples of the study area were alkaline. Therefore, metals are less available to plants and animals in these sites. Compared to the literature, the mean Cu and Zn concentrations were almost in the normal range, while Pb and Cd concentrations were very low.

Improving the nutritional status of children who have a high risk of exposure and toxicity greatly increases the effectiveness of environmental metal abatement. However, nutritional supplement (e.g. calcium) only increases the metal level required for toxicity rather than eliminating metal uptake and its effects. Therefore, so as to prevent the population from lead toxicity, one of the first measures to be taken is to use Pb free gasoline in towns. Ethiopian Petroleum Enterprise has already announced that starting from 2004; Pb free gasoline is being imported and distributed through out the country. However, the distribution of gasoline by EPE is limited only to some companies, which are engaged in distribution of gasoline to the consumers. These companies have their own reservoirs where they can store a large deposit of gasoline for future use. Hence, EPE or any concerned governmental and non-governmental body must check the presence of leaded gasoline in such reservoirs. This helps to eliminate further addition of lead to the environment.

In addition to the above, there are a large number of garages in Ambo, Holota, Sebeta and Fitche where automobiles are being repaired, car batteries are recharged, old cars and their batteries are stored, the wear and tear of tires take place and so on. Thus, great care should be taken in the disposal of these materials, as these could be significant sources for metals mainly lead in the form of lead sulphate and vehicles with catalytic converters must be encouraged. Since lead was used in water pipe extensively, in selected towns of Oromia regional state Water and Sewage Authority must check the presence of water pipes made of lead. This action should be followed by immediate replacement of these pipes (if any) with lead free pipes.

In the present study, to assess the extent of environmental metal pollution in Ambo, Holota, Sebeta and Fitche towns, only the surface soil was examined, as it is the most important environmental reservoir or sinks for atmospheric pollutants. Researches also reveal the indicative nature of roadside plant leaves and barks as important sources for the accumulation of heavy metals. Thus, further studies should focus on determination of these metals in the different parts of plants grown on roadside soil of Ambo, Holota, Sebeta and Fitche towns.

5. Recommendations

Improving the nutritional status of children who have a high risk of exposure and toxicity greatly increases the effectiveness of environmental metal abatement. However, nutritional supplement (e.g. calcium) only increases the metal level required for toxicity rather than eliminating metal uptake and its effects.

Therefore, so as to prevent the population from lead toxicity, one of the first measures to be taken is to use lead free gasoline in towns. Ethiopian Petroleum Enterprise (EPE) has already announced that starting from 2004; lead free gasoline is being imported and distributed throughout the country. However, the distribution of gasoline by EPE is limited only to some companies, which are engaged in distribution of gasoline to the consumers. These companies have their own reservoirs where they can store a large deposit of gasoline for future use. Hence, EPE or any concerned governmental and non-governmental body must check the presence of leaded gasoline in such reservoirs. This helps to eliminate further addition of lead to the environment.

In addition to this since there are a large number of garages in Ambo, Holota, Sebeta and Fitche where automobiles are being repaired, car batteries are recharged, old cars and their batteries are stored, the wear and tear of tires take place and so on. Thus, great care should be taken in the disposal of these materials, as these could be significant sources for metals mainly lead in the form of lead sulphate and vehicles with catalytic converters must be encouraged.

Since lead was used in water pipe extensively, in selected towns of Oromia regional state water and Sewage Authority must check the presence of water pipes made of lead. This action should be followed by immediate replacement of these pipes (if any) with lead free pipes.

For the roadside soils, which have been already contaminated with heavy metals, it is highly recommended to replenish them with clean top soil. Since metals tend to accumulate on the top few centimeters depth, it may be necessary to remove only a thin layer of the highly contaminated soil. Moreover, in those areas where high concentrations of metals (Pb, Cd, Cu and Zn) were obtained it is strongly recommended that the blood metal levels of children under six be tested. Then a proper medical treatment should be followed for those with blood metal level above the maximum recommended limit.

Educational programs should be given for various population groups on the health and ecological effects of heavy metals and strengthening of laboratories in the region with adequate and up to date equipment to handle the environmental samples and to ensure quality assurance.

In the present study, to assess the extent of environmental metal pollution in Ambo, Holota, Sebeta and Fitche towns, only the surface soil was examined, as it is the most important environmental reservoir or sink for atmospheric pollutants. Researches also reveal the indicative nature of roadside plant leaves and barks as important sources for the accumulation of heavy metals. Thus, further studies should focus on determination of these metals in the different parts of plants grown on roadside soil of Ambo, Holota, Sebeta and Fitche towns.

Further detailed research is required for more accurate evaluation of the heavy metals' accumulation in plants and environmental pollution impact for the quality of roadside soils of towns of Oromia Regional State.

6. References

- i. Adomaitis, T., J. Mazvila and L. Eitminavicius, 2003. A comparative study of heavy metals in the soils of cities and arable lands, Air and Soil Pollution. 24: 103-109.
- ii. Al-Chalabi, A. S. and D. Hawker, 2000. Distribution of vehicular lead in roadside soils of major roads of Brisbane, Australia. Water, Air and Soil Pollution. 18(3): 299–310.
- iii. Alloway, B.J., 1990. Heavy Metals in Soils. Chapman and Hall, Londo. 31: 486-495.
- iv. Bakirdere, S., 2008. Determination of lead, cadmium and copper in roadside soil and plants in Elazig, Turkey. Environmental Monitoring and Assessment. 36(5): 401-410.
- v. Bewley, B.R., G. Stotzky, 1983. Effects of cadmium and zinc on microbial activity in soil influence of clay minerals. Science of the Total Environment. 3: 41–45.
- vi. Borg, H. and K. Johansson, 1989. Metal Fluxes to Swedish Forest Lakes. Water, Air and Soil Pollution. 6: 527-540.
- vii. Claus, D., H. Dietze, A. Gerth, W. Grosser and A. Hebner, 2007. Application of agronomic practice improves phytoextraction on a multipolluted site. Journal of Environmental Engineering and Landscape Management. 15(6): 208–212.
- viii. Davis, A.P., M. Shokouhian and S. Ni, 2001. Loading estimates of lead, copper, cadmium and zinc in urban runoff from specific sources. Chemosphere. Sci. Total. Environ. 44: 997-1009.
- ix. Dolan, L.M.J., H. Van bohemen, P. Whelan, K.F. Akbar, G. Oleary and P.J. Keizer, 2006. Towards the sustainable development of modern road ecosystem. China. 2762p.
- x. East Shoa Zone Social Affair Office, 2000. Zonal Atlas of East Shoa, Location and Size of East Shoa. 4p.
- xi. EC (European Commission), 1986. Office for Official publications of the European Communities, Luxembourg, Council Directive 66/278 on the protection of environment, and in particular of soil, when sewage sludge is used in agriculture. J. Nutr Biochem. 5: 622-629.

- xii. Gardea-Torresdey, J.L., J.R. Peralta-Videa and J.G. Parsons, 2005. Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. Coordination Chemistry Reviews. 249(7): 1797–1810.
- xiii. Hesse, P.R., 1972. A text book of soil chemical analysis. John Murry, London, Great Britain. 470p.
- xiv. Hn, G., 1996. Hazard substances, maximum permitted and temporarily permitted concentration in soil. Health Protection Ministry of Lithuanian Republic. 8: 116-142.
- xv. ICRCL (Interdepartmental Committee on the Redevelopment of Contaminated Land), 1987. Guidance on the assessment and redevelopment of contaminated land. Department of Environment, London. 83p.
- xvi. Itana, F., 1998. Metals in leafy vegetables grown in Addis Ababa and Toxicological Implications Ethiop. J. Health Dev. 2: 295-313.
- xvii. Jarup, L., 2003. Hazards of heavy metal contamination. Brazilian Medical Bulletin. 68(3): 425–462.
- xviii. Lagerwerff, J.V. and A.W. Specht, 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc. Environ. Sci. Technol. 4: 583-586.
- xix. Legret, M. and C. Pagotto, 1999. Evaluation of pollutant loadings in the runoff waters from a major rural highway, Sci. Tot. Environ. 235: 143–150.
- xx. Leitao, T.E., N. Lehmann, S. Smets, J.P.C. Ferreira and P. Holm, 2000. Mass Flux and Mass Balance Calculations; Assessment of Pollution of Groundwater and Soils by Road and Traffic Sources. 47p.
- xxi. Li, X.D., C. Poon and P.S. Liu, 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied Geochemistry. 16: 1361–1368.
- xxii. Loon, J. C., 1985. Selected Methods of Trace Metal Analysis-Biological and Environmental Samples. New York. 5: 3685-3689.
- xxiii. Lopez-Garcia, I., M. Sanchez-Merlos, and M. Hernadez-Cordoba, 1996. Slurry sampling for the determination of lead and cadmium and thallium in soils and sediments by electrothermal atomic absorption spectrometry with fast heating programs. Anal. Chimica Acta. 3: 19–25.
- xxiv. Maria, C., 1997. Environmental sampling and Analysis Lab. Manual, Lewis Publishers, New York. 432p.
- xxv. Murphy, H.F., 1962. A Report on the Fertility Status and Other Data on Some Soils of Ethiopia. Experiment station. 429p.
- xxvi. Nabuloa, G, H. Oryem-Origa and M. Diamond, 2006. Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda. Environ Res. 10: 42–52.
- xxvii. Naueiene, Z., V. Mildaziene, R. Baniene, 2002. Interaction of cadmium and copper ions with Complex ions of the respiratory chain in rat liver mitochondria. Ekologija, Vilnius. 2: 18-59.
- xxviii. Purves, D. and E.J. Mackenzie, 1969. Trace elements contamination of parklands in urban areas, J. Soil Sc. 20(3): 288–290.
- xxix. Reinirkens, P., 1996. Analysis of emissions through traffic volume in roadside soils and their effects on seepage water. The Science of the Total Environment. 18: 361-369.
- xxx. Riga-Karandinos, A. N., C. J. Saitanis and G. Arapis, 2006. First study of anthropogenic platinum group elementsin roadside top-soils in Athens, Greece. Environmental Quality Standard for Soils. 7: 11855-11872.
- xxxi. Sahlemedhin Sertsu and Taye Bekele, 2000. Procedures for soil and plant analysis. National Soil Research Organization, Ethiopian Agricultural Research Organization, Addis Ababa. 110p.
- xxxii. SEPA (State Environmental Protection Administration), 2005. The limit of pollutant in food. China. 2782p.
- xxxiii. Sharma, R. Kumar, M. Agrawal and F. Marshall, 2007. Heavy metal contamination of soil and vegetables in sub urban areas of varanasi, India. Elsevier Inc. 6: 357-362.
- xxxiv. Shinggu, 2007. Analysis of street dust for heavy metal pollutants in Mubi, Adamawa State, Nigeria. Environmental and Experimental Botan. 2(3): 290-293.
- xxxv. Thompson and Troeh, 1978, Soils and soil fertility. Associate Dean of Agriculture, Iowa State University. 401p.
- xxxvi. Ure, A.M. and M.L. Berrow, 1982. The elemental constituents of soils. The Royal Society of Chemistry, London. 5: 203-204.
- xxxvii. Ward, N.I., 1990. Lead contamination of the London orbital motorway. The Science of the Total Environment. 93: 277-283.
- xxxviii. Young, S.R., 1971. Chemical Analysis in Extractive metallurgy. Charley and pickers gill Ltd. Leeds. 19: 188-258.
- xxxix. Zupancic, N., 2005. Lead pollution of Ljubljana-Zagreb roadside soils. Rudarsko- metalurskiz bornik. 44(3): 169-185.