

## HEAVY METALS ACCUMULATION IN ROADSIDE SOIL AND VEGETATION ALONG A MAJOR HIGHWAY IN LIBYA

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### ABSTRACT

*Levels of some heavy metals in soil and vegetation along a major highway in Libya were determined by Atomic Absorption Spectrophotometry. The concentrations of Pb, Cd, Ni, Zn, Cu, Cr and Mn in soil and vegetation all decreased with distance from the road, indicating their relation to traffic. The concentrations of the metals also decreased with depth in the soil profile indicating that the source of the metals was aerial deposition from motor vehicles. Inter-relationships between metals in the soil were highly significant ( $p < 0.05$ ) suggesting a common source for these metals. Pb and Zn were found to be deposited more than the other metals. Average values for *citrus limon* leaves were generally 30 - 65 % of those for *Olea europaea* leaves. In most cases, between 20-40% of the metals was removable by simple washing with water, indicating that a significant, but not predominant fraction of the metals is in the form of easily-removed particulate matter. Discussion of the results of this study is based on statistical treatment of the data.*

**Keywords:** Heavy metals, roadside soil, vegetation, highway

### INTRODUCTION

Many investigations in recent years have concentrated on the pollution of roadside soil and vegetation by lead from motor vehicles originating from the use of additives in petrol (Cannon and Bowles, 1962; Chow, 1970; Motto *et al.*, 1970; Page and Ganje, 1970; Ward *et al.*, 1974; Ward *et al.*, 1975; Iqbal and Qadir, 1990; Clarke, 1994; Morton-Bermea *et al.*, 2002; Bhargava *et al.*, 2003; Turer, 2005). Tetra-alkyl lead is usually added to petrol at a rate of about

0.9 g Pb L<sup>-1</sup> (Atkins, 1969), most of which gets emitted from the exhausts of motor vehicles (Clark, 1994) and eventually get deposited. Stoker and Seager (1972) reported the consumption of about 300000 tonnes of lead alkyls of which about 180000 tonnes appear in the atmosphere as emission from motor vehicles in the United States. Lead levels of 100-3000 µg g<sup>-1</sup> have commonly been reported both in soils and in the ash of plants taken near roads carrying more than 10000 vehicles per day (Cannon and Bowles, 1962; Chow, 1970; Im-

pens *et al.*, 1973; Ward *et al.*, 1974). The concentrations of lead in soil and in plants along major urban highways have been shown to decrease rapidly with distance from the roadside and with decreasing traffic density (Motto *et al.*, 1970; Page *et al.*, 1971; Ward *et al.*, 1975; Ward *et al.*, 1977; Fergusson, 1991; Sithole *et al.*, 1993; Jaradat and Moman, 1999). Some of these studies have also shown that a considerable proportion of the lead can be removed from the leaf surfaces by simple washing with water (Motto *et al.*, 1970; Page *et al.*, 1971; Ward *et al.*, 1977; Ndiokwere, 1984; Ramakrishnaiah and Somaskhar, 2003). Impens *et al.*, (1973) found that 10-20% of the lead of beet leaves collected 10-35 m from Belgian highways could be removed by washing with water.

Apart from lead, very little concern has been given to the likelihood of pollution by other heavy metals which can originate from automobiles, tyre wear and motor oils. Lagerwerff and Specht (1970) have reported the Cd content of three lubricating oils to range from 0.20 to 0.26 ppm and that of three diesel oils from 0.07 to 0.10 ppm. The Cd content of four tyres of different brands was also found to range from 20 to 90 ppm. The presence of cadmium, nickel and zinc in addition to lead in soils and grasses at roadside has hence been reported to be presumably derived from motor vehicle exhausts, tyre wear and motor oils (Cannon and Bowles, 1962; Lagerwerff and Specht, 1970; Motto *et al.*, 1970; Ward *et al.*, 1974). For a major road carrying 48000 vehicles per day, the following ranges of levels ( $\mu\text{g g}^{-1}$  dry weight) have been reported for surface soils in the interval of 8-32 m from the road: Pb, 840-140; Cd, 0.94-0.24; Zn, 162-114 and Ni, 7.4-2.4 and for grasses the levels were as follows: Pb, 51.3-18.5; Cd, 0.75-0.48; Zn, 40-30 and Ni, 3.8-1.3. Ward *et al.*, (1977) have also reported the following mean concentrations ( $\mu\text{g g}^{-1}$  dry weight) for a site carrying more than 50000 vehicles per day: Pb, 2200; Cd, 2.2; Zn, 480; Cu, 200; Ni, 105 and Cr, 80 for surface soil. For vegetation the levels were Pb, 350; Cu, 30; Ni, 3.7 and Cr, 4.

The possible hazards arising from pollution of the environment by heavy metals have surfaced more recently, and the toxicity of some of these metals toward humans especially children when exposed to them from the atmosphere, water or food has been well documented (Browning, 1969; World Health Organisation, 1972; Page and Bingham, 1973; Mahaffey, 1977; Smith, 1994). Vehicle exhausts, as well as several industrial activities, emit these heavy metals (Lagerwerff and Specht, 1970; Solomon and Hartford, 1976; Bower *et al.*, 1978; Reeves and Brooks, 1983; Turer, 2005; Guan Dong-sheng and Pert, 2006) so that soils, plants and residents along roads with heavy traffic loads are subjected to increasing levels of contamination with heavy metals (Welch and Dick, 1975; Harve and Underdal, 1976; Ward *et al.*, 1977; Harrison *et al.*, 1981; Ho and Tai, 1988; Jaradat and Moman, 1999; Delmas *et al.*, 2002; Bhargava and Gupta, 2003)

Although substantial work has been carried out in Europe and the United States on lead distribution with distance from roads, and the trends expected are well established, so far as we are aware data for other metals is more restricted, and there are no previous studies of this type from Libya.

With the rapid increase in the number of motor vehicles on Libya's roads recently, and as a consequence of a boost in commercial and industrial activities, considerable amounts of some heavy metals are likely to be emitted regularly as long as the nearby sources remain active. Hence the need to initiate monitoring. This paper reports the concentrations of lead, cadmium, zinc, copper, chromium, nickel and manganese in soils and in the leaves of two trees collected at various distances from a major highway in the Tripoli region of Libya. The heavy metal content of soils as a function of depth was also reported.

## MATERIALS AND METHODS

### Collection and Preparation of Samples

The area selected for the study is a two dual carriage highway about 15 km from Tripoli city centre and runs eastward. It carries an average of 30700

motor vehicles per day. This site was selected for this study because it links two major port cities (Tripoli and Misurata) and it has a comparatively high traffic density. There are also no major road intersections to cause a significant decrease in the traffic density. In addition, it is far away from any possible sources of heavy metal pollution except for automobile emissions since; there is neither a residential nor industrial area in the proximity.

Leaf samples from two species of trees, *Citrus limon* and *Olea europaea*; and their associated soils were taken at distances of 1 m, 20 m and 50 m from the edge of the road.

Samples of leaves (90-120 g) were taken at approximately 2-3 m height and divided into two parts. Samples of topsoil (0-5 cm) were also collected at the bases of the trees, at a position within 1 m of the tree. At each sampling location, 5 samples of soil were collected randomly in about one metre square area and bulked together to give one sample (2-3 kg). In order to determine whether heavy metals have been translocated down the soil profile, samples were collected from greater depths at various distances from the edge of the road along the highway. The samples were transported immediately to the laboratory in polythene bags. One part of the leaf samples was washed by rinsing several times in deionised distilled water and left to drain dry at room temperature. The washed and unwashed samples were then dried in an oven (Gallenkamp, Model OV-445) at 80°C for 12 h and milled (Hammer mill, Model C680, Glen Creston, Middlesex, UK) to pass a 1.0-mm round-holed sieve. The mill was thoroughly cleaned between samples. Samples of the powder (2-3 g) were accurately weighed into pyrex tubes with constriction near the top; and digested with concentrated HNO<sub>3</sub> and HClO<sub>4</sub> (70%) in a multi-place digestion block (Techne Dri-Block DB-4, Techne (Cambridge) Ltd, UK). The digest was diluted with deionised distilled water and then filtered through Whatman No 42 filter paper. The soil samples were first air dried and sieved through a 2 mm nylon sieve. A portion of the

sieved sample was then ground in a porcelain mortar to pass 300-mesh. Accurately weighed soil samples (3 g) were digested with a 1:1 mixture of concentrated HNO<sub>3</sub> and HF. The solutions were taken to dryness over a water bath. The digestion was repeated and the residues were dissolved in 5% HNO<sub>3</sub>, filtered and diluted to volume. The plant and soil extracts were then assayed for the metals by atomic absorption spectrophotometry (Perkin Elmer Model 2380 AAS) with deuterium arc background correction where necessary. Concentrations were in most cases sufficiently high to obviate the need for preconcentration procedures. The instrument, capable of performing calibration and repetitive measurements, was programmed to take measurements every 0.5 s and print the average concentration. The results were obtained on Perkin Elmer PRS-10 Printer Sequencer. For quality assurance the measurements were also taken in the absorbance mode and the calibration data were subjected to least square treatment using a personal computer. All analyses were conducted in triplicate. For each run, a triplicate sample and three blanks were carried through the procedure. An analytical spike recovery was done by adding increasing amounts of the metals determined to an aliquot of the digested sample. A matrix spike recovery was also completed for each of the digestion procedures used by adding a known amount of an analyte to the pre-digest sample, which was then digested. Recoveries were between 96% and 110% with coefficient of variation between 2% and 7%. Instrument performance was checked using quality control standards and results were in agreement with the control data to within 5%. To assess the precision of the overall procedure, 6 replicate analyses of two different samples of both plant and soil were conducted, the results agreed to within 5%. During the measurements, the sample uptake capillary and the nebulizer system were periodically cleaned using a brass wire, and the burner slot cleaned with razor blade. Solutions of single standards were prepared from stocks (T. Baker, UK) and mixed as appropriate for a single analysis run and individual standard calibration curves were constructed for a visual check for linearity. The

data obtained were subjected to statistical analyses using the Statgraphics Statistical Graphics Version 6.0. Differences in the concentrations of the metals for the samples were analysed for significance by the t-test method

## RESULTS AND DISCUSSION

The heavy metal concentrations in unwashed leaves sampled from *Citrus limon* and *Olea europaea* trees along the highway are presented in Table 1 and those of surface soils from the same locations are shown in Table 2. Each value is the mean of three replicate samples  $\pm$  standard deviation. In most cases there is a clear pattern of decreasing metal concentrations with distance from the edge of the highway for both plants and soils. The metal content data from this study has been subjected to simple linear correlation analysis to examine the variation of the metal concentrations in the samples. The results of these analyses for the heavy metals in *Olea europaea* are presented in Table 3 in the form of correlation coefficients. All the metals except Cd correlate negatively with the distance of sampling from the roadside. This indicates decreasing metal concentrations with increasing distance and therefore their relation to traffic. The metals showed a more pronounced decrease in their levels from 1m to 20m compared to from 20m to 50m. With regards to inter-metal relationships Pb was found to correlate positively

with all the metals except Cd. Cd however correlates with Zn, Cu and Mn.

The results of simple correlation analysis of the metals in *citrus limon* with distance are given in Table 4 in the form of correlation coefficients.

**Table 2: Mean concentrations of heavy metals (mg g<sup>-1</sup> dry weight) in surface soil (0-5cm) collected at distances from the roadside**

Metal	1m	20m	50m
Pb	296 $\pm$ 24	31 $\pm$ 1	14 $\pm$ 0.7
Cd	3.4 $\pm$ 0.4	1.1 $\pm$ 0.1	0.96
Zn	47 $\pm$ 4	30 $\pm$ 0.8	17 $\pm$ 0.8
Cu	15 $\pm$ 3	7 $\pm$ 0.4	5.6 $\pm$ 0.3
Ni	3.4 $\pm$ 0.7	5.5 $\pm$ 0.2	4.9 $\pm$ 0.4
Cr	11 $\pm$ 0.3	12 $\pm$ 0.6	12 $\pm$ 1
Mn	89 $\pm$ 11	80 $\pm$ 1	65 $\pm$ 4

1m, 20m and 50m indicate the distances from the roadside at which samples were collected.

The table shows relatively limited numbers of significant correlations between the metals and distance of sampling. Only Pb correlated negatively with distance. This suggests that the concentration of Pb decreased with distance and indicates its relation to traffic. However, this is not the case for

**Table 1: Mean concentrations of heavy metals  $\pm$  standard deviation (mg g<sup>-1</sup> dry weight) in Unwashed leaf samples collected at distances from the roadside**

Metal	<i>Olea europaea</i>			<i>Citrus limon</i>		
	1m	20m	50m	1m	20m	50m
Pb	148 $\pm$ 13	38 $\pm$ 6	24 $\pm$ 3	23 $\pm$ 2	15 $\pm$ 2	10 $\pm$ 0.6
Cd	0.7	0.6 $\pm$ 0.1	0.5 $\pm$ 0.1	0.6	0.6	0.7
Zn	41 $\pm$ 3	16 $\pm$ 3	12 $\pm$ 1	25 $\pm$ 3	20 $\pm$ 0.4	26 $\pm$ 1
Cu	11 $\pm$ 1	5 $\pm$ 1	5 $\pm$ 0.7	7 $\pm$ 0.3	6 $\pm$ 0.4	6 $\pm$ 0.5
Ni	4 $\pm$ 0.9	2 $\pm$ 0.1	0.92	2 $\pm$ 0.2	1.2	1.5 $\pm$ 0.1
Cr	4 $\pm$ 0.7	2 $\pm$ 0.3	2 $\pm$ 0.4	2 $\pm$ 0.1	2 $\pm$ 0.1	3 $\pm$ 0.2
Mn	26 $\pm$ 2	15 $\pm$ 3	16 $\pm$ 1	8 $\pm$ 0.1	10 $\pm$ 0.5	11 $\pm$ 0.1

1m, 20m and 50m indicate the distances from the roadside at which samples were collected.

**Table 3: Correlation coefficients for heavy metals in *Olea europaea* and with relation to distance from the roadside**

Metal	Distance	Pb	Cd	Zn	Cu	Ni
Pb	-0.8028					
Zn	-0.8478	0.9921	0.6712			
Cu	-0.7717	0.9365	0.7698	0.9628		
Ni	-0.8648	0.8056		0.8205	0.7449	
Cr	-0.7187	0.8698		0.8259	0.7848	0.9157
Mn	-0.6613	0.9333	0.7009	0.9292	0.9415	0.6656

Only correlations where  $p < 0.05$  are quoted

**Table 4: Correlation coefficients for heavy metals in *Citrus limon* and with relation to distance from the roadside**

Metal	Distance	Pb	Cd	Zn
Pb	-0.9263			
Cd	0.8748			
Cr	-0.9449		0.9258	0.8088
Mn	0.8502	-0.9694		

Only correlations where  $p < 0.05$  are quoted

the other metals. The change in the metal concentrations with distance from the roadside was rather inconsistent. The inconsistent change in the metals levels on *citrus limon* leaves with distance from the roadside compared to *olea europaea* leaves could be attributed to the smooth surface allowing much of the deposited particulates to be washed off by rain. Many authors have documented the distribution of heavy metals in soils, vegetation and the atmosphere along transects originating for busy highways. These studies have found clearly defined gradients of lead contamination beside roadways, and some have also shown generally less-defined gradients of other metals, including cadmium, chromium, copper, nickel, vanadium and zinc. The results presented here are in agreement with the results of earlier studies (Motto *et al.*, 1970; Page *et al.*, 1971; Ward *et al.*, 1975; Ward *et al.*, 1977; Ndiokwere,

1984; Sithole *et al.*, 1993; Ho and Tai, 1988; Jaradat and Moman, 1999; Bhargava *et al.*, 2003; Imperato *et al.*, 2003; Luilo and Othman, 2003; Guan Dong-sheen and Pert, 2006). Among the metals determined, lead is the greatest pollutant of the plants and soils. The source of lead contamination has been attributed to the use of lead tetra-alkyl additives to improve the octane rating of petrol in order to increase engine efficiency and petrol economy, while decreasing engine wear due to engine 'knock'. Most of the added lead in the petrol gets emitted through the automobile tailpipe, at a rate of  $0.07 \text{ g km}^{-1}$  (Cantwell *et al.*, 1972) accounting for some 40% of emitted automobile particulates (Atkins, 1969). Clarke (1994), also reported that about 70% of the lead added to petrol is emitted from the exhausts of motor vehicles, mainly as mixed halides. It has been suggested that the emit-

ted automotive lead particulates are not absorbed by plants but that they exist as coatings on leaf surfaces of which a considerable amount can be removed by simple washing (Motto *et al.*, 1970; Page *et al.*, 1971; Ward *et al.*, 1977; Ndiokwere, 1984; Ramakrishnaiah and Somasekhar, 2003). In this study, the washed samples showed significantly (Table 5) lower levels of the metals except Cd than the unwashed samples for *Olea europaea*.

For the *Citrus limon*, differences were significant (Table 6) for only Pb and Zn although the values for some of the metals were lower for washed samples.

In most cases the washed samples contained 60-80 % of the metal levels of the unwashed sam-

**Table 5: Comparison of Heavy Metals Concentration in Unwashed and Washed Leaves of *Olea europaea* taken at 1m from roadside**

Heavy metal	Mean concentration (mg g <sup>-1</sup> )	
	Unwashed	Washed
Pb	148.65a	91.85
Zn	41.00a	25.98
Cu	11.27b	8.67
Ni	4.29b	1.53
Cr	4.19a	1.48
Mn	26.33a	18.57
Cd	0.73	0.63

a) Indicates significantly higher value ( $P < 0.01$ ) as compared with the washed sample according to t-test.

b) Indicates significantly higher value ( $P < 0.05$ ) as compared with the washed sample according to t-test.

ples. This indicates that a significant fraction of the metals especially lead and zinc is in the form of easily-removed particulate matter. This observation supports that of Impens *et al.* (1973) who found that 10-20 % of the lead of beet leaves collected 10-35 m from Belgian highways could be removed by washing. Ward *et al.* (1975) also reported that 10-30 % of the lead of three species of vegetation collected 1-12 m of the edge of a

**Table 6: Comparison of Heavy Metals Concentration in Unwashed and Washed Leaves of *Citrus limon* taken at 1m from roadside**

Heavy metal	Mean concentration (mg g <sup>-1</sup> )	
	Unwashed	Washed
Pb	23.43a	12.59
Zn	25.88a	13.34
Cu	7	6.7
Ni	1.84	2.15
Cr	2.22	2.22
Mn	7.88	6.46
Cd	0.6	0.55

a) Indicates significantly higher value ( $P < 0.005$ ) as compared with the washed sample according to t-test.

b) Indicates significantly higher value ( $P < 0.05$ ) as compared with the washed sample according to t-test.

New Zealand State Highway could be removed by washing with water. Flanagan *et al.* (1980) reported that washing with distilled water can remove up to 50 % of lead on leaves of bramble and rhododendron collected 5 m from a main road in a rural district of the Strathclyde region. Although the other heavy metals studied are not found in petrol, their concentrations on or in the plants and in the soils appear to follow a similar distribution pattern to lead. The amounts concerned are however much smaller. This suggests the presence of these metals in other components of motor vehicles.

Lower metal concentrations were generally observed on *citrus limon* leaves than on *olea europaea* leaves. Although the metal concentrations were higher for *olea europaea* compared with *citrus limon* for all the metals, the differences were significant (Table 7) for only Pb, Zn, Cu and Mn. Average values of Pb, Zn, Cu and Mn for *citrus limon* were 16, 63, 62 and 30 % respectively of those for *olea europaea* at the same location. For Ni, Cr and Cd they were 43, 53 and 82 % respectively.

**Table 7: Comparison of Heavy Metals Accumulation on leaves of *Olea europaea* and *Citrus limon* taken at 1m from roadside**

Heavy metal	Mean concentration (mg g <sup>-1</sup> )	
	<i>Olea europaea</i>	<i>Citrus limon</i>
Pb	148.66a	23.43
Zn	41b	25.88
Cu	11.28b	7
Ni	4.29	1.84
Cr	4.19	2.22
Mn	26.33a	7.88
Cd	0.73	0.6

- a) Indicates significantly higher value ( $P < 0.002$ ) as compared with the other plant according to t-test.  
 b) Indicates significantly higher value ( $P < 0.02$ ) as compared with the other plant according to t-test.

Since the accumulation of metals on or in vegetation may originate from dust raised by motor vehicles and wind, and from their uptake from the soil these lower levels may indicate a lower adhesion of particulate matter to *citrus limon* and or a lower tendency for this plant to take up metal from the soil. This could then be attributed to the glossy nature of the upper surface of *citrus limon* leaves as against the rough nature of the upper surface of *olea europaea* leaves. Wedding *et al.* (1977) in a laboratory experiment reported gross deposition on rough pubescent leaves to be greater than on smooth, waxy leaves.

In so far as the change in concentration of a metal with distance from the source could be one diagnostic method to identify the source of a heavy metal, a change in concentration with depth would also indicate surface pollution from a source. Variations in the concentrations of heavy metals in soil profiles are normally not consistent and readily interpreted, because a number of factors can influence the level of a metal in a soil profile, including the nature of the parent material, the organic content of the soil,

the clay content, the pH, the rainfall, microbial activity and the extent of pollution (Fergusson, 1991; Alloway, 1994). Unchanging concentrations would show that irregular metal levels were a function of the soil type. The distribution of the heavy metals in the soils taken at different distances from the highway and at different depths is shown for Pb, Cu, Zn, Cd, Cr and Mn in Fig. 1. The figures for the other metals studied are not presented because the metals distribution was far less definite.

Information regarding the relationships between metal contents in the soil, and in relation to distance from the roadside and to depth was derived from correlation analysis. Table 8 presents results for the correlations significant at 0.05 or less probability level. Apart from Cr and Ni, the concentrations of the metals in the soils correlate negatively with the distance of sampling, which indicates their relation to traffic.

Although the levels of the metals at the top surface soil were mostly higher than sub-surface soil, there was no apparent relationship for the metal concentrations with the depth of sampling except for Zn and Ni. In most cases the values of the metals either rise or fall with increase in depth. However, Pb and Zn indicated a clear fall in their concentrations with increase in the depth of sampling (Fig 1). Whereas Zn was found to be negatively correlated with depth ( $r = -0.4973$ ,  $p < 0.002$ ) Ni was positively correlated with depth ( $r = 0.3451$ ,  $p < 0.05$ ).

This observed relationship for Ni in the present investigation indicates that the vertical distribution of Ni in the soil at various distances from the roadside did not seem to be related to airborne contamination. This observation parallels that of Yassoglou *et al.* (1978), but contradicts that of Ward *et al.* (1977) who reported that motor vehicle traffic is responsible for the build up of Pb, Cd, Zn, Cu, Cr and Ni in soils and vegetation along a motorway in New Zealand. However, in general, the results suggest that the distribution pattern of the metals in the soil profiles could be

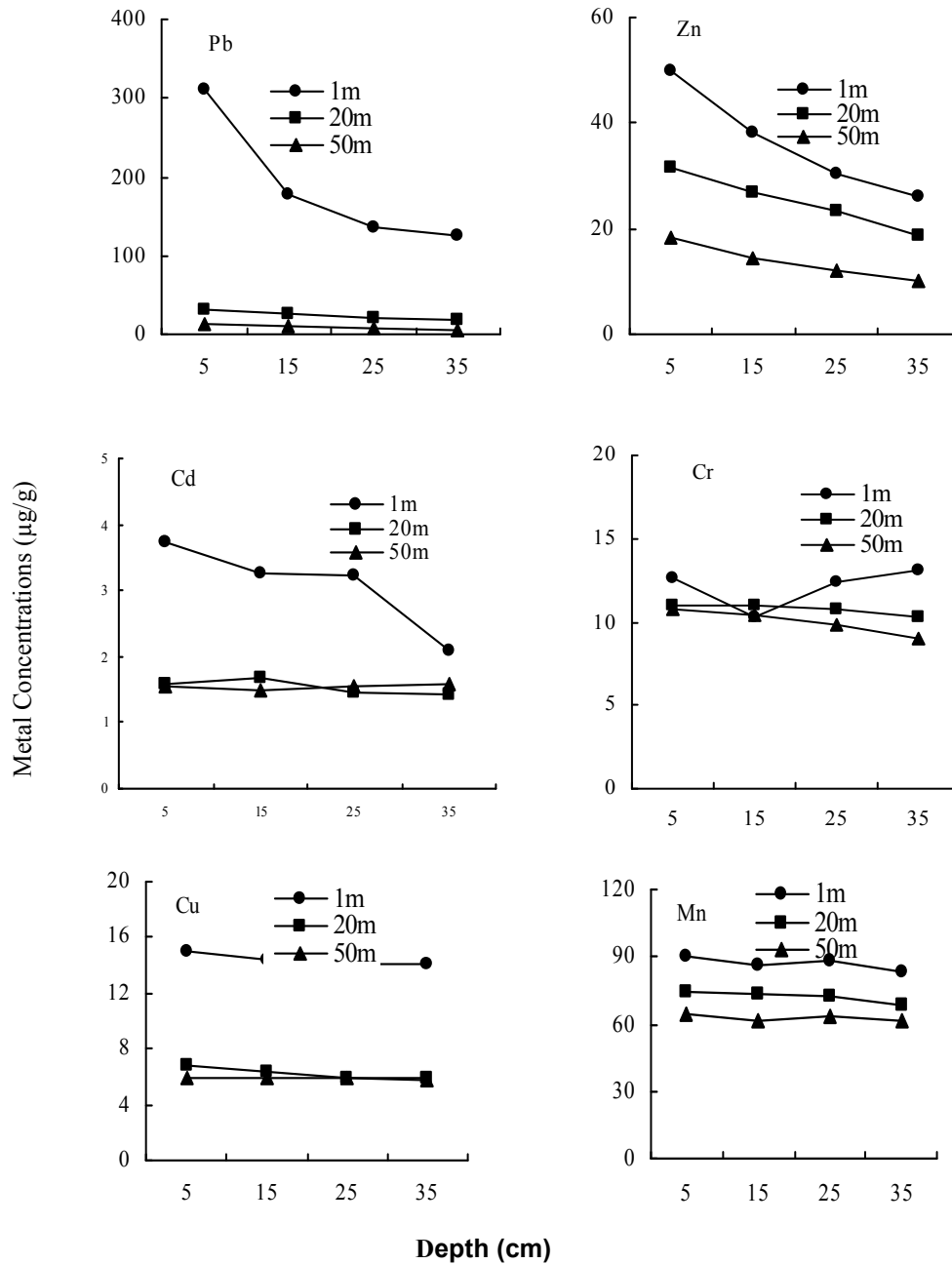


Fig 1. Concentrations (µg/g) of Pb, Cd, Cu, Zn, Cr and Mn in soil profiles



related to atmospheric input, the main source being vehicular emissions.

This is because most pollutants are added to the soil surface, and only when the amounts deposited are high is there any significant transfer of the pollutant down the profile by leaching (Chow, 1970).

With regards to soil properties, positive correlations have been reported to exist between some heavy metals and organic matter, and some heavy metals and clay content for a soil type (Fergusson, 1991). pH, organic and clay contents were determined for the soils; and an attempt was made to find any correlations between the concentrations of the metals and the soil properties.

No significant correlations were found between the metals and the soil properties. However, with regards to the relationships between metal contents in the soil profile, positive inter-metal correlations were detected (Table 8). All the metals except Cr and Ni were found to be associated with each other. However, Cr was slightly correlated with Cu ( $r=0.3316$ ,  $p < 0.05$ ) and Ni with Zn ( $r=0.3828$ ,  $p < 0.002$ ).

These results suggest the parallel deposition of the metals from a common source and not a function of soil type. This source is most proba-

bly automobiles, as no other major sources can be identified. This observation has been reported by other authors (Ho and Tai, 1988; Jaradat and Moman, 1999). It appears from the levels of the metals in the soil profiles close to the highway that the metals have not been translocated very far down the profile. This observation has been reported for lead by other authors. Motto *et al.* (1970) in their results on soil profiles close to highway carrying 12000-55000 vehicles per day showed limited downward movement of lead. Chow (1970) reported soil lead levels at distances of 7-30 m from a highway carrying 56000 vehicles per day to be distinctly high in the 0-5 cm layer whereas background levels were found in the 5-10 cm and 10-15 cm layers. Page and Ganje (1970) studied lead levels in regions of high traffic density at distances of more than one mile from major highways and found that lead levels in the 2.5-15 cm were close to the background values. A comparable situation occurs for lead in this study where a significant drop in the level down the soil profile occurs from  $297.44 \text{ mg g}^{-1}$  in the top 0-5 cm down to  $171.15 \text{ mg g}^{-1}$  in the 5-15 cm section.

The results of this study indicate that automotive emissions are responsible for the accumulation of some heavy metals in soils and in or on plants along the highway. The source of the lead is with-

**Table 8: Correlation coefficients for metals in soil and with relation to distance from roadside and to depth of sampling**

Metal	Distance	Depth	Pb	Cd	Cu	Zn
Pb	-0.7540					
Cd	-0.7013		0.9200			
Cu	-0.7938		0.8755	0.8954		
Cr					0.3316	
Zn	-0.8225	-0.4973	0.8704	0.7993	0.7316	
Mn	-0.9345		0.8768	0.8658	0.9048	0.8880
Ni		0.3451				0.3828

*Only correlations where  $p < 0.5$  are quoted.*

out doubt from petrol to which has been added lead and this has been well reported. The sources of the other metals, which have been documented as roadside contaminants, are less well defined than that of lead. The fact that the other heavy metals appear to follow a similar distribution pattern to lead is therefore not obvious. However cadmium has been reported to occur in rubber because of the mineralogical association of cadmium with zinc, and zinc compounds are used in vulcanizing (Fergusson, 1991). Undoubtedly Lagerwerff and Specht (1970) attributed their cadmium concentrations of 20-90 mg g<sup>-1</sup> found in car tyres to the use of zinc-diethylcarbonate in the process of vulcanisation. Tyre wears could therefore contaminate plants and soils adjacent to highways. Cadmium and zinc have also been reported to occur together in lubricating oils as constituents of additives such as zinc-dithiophosphates (Lagerwerff and Specht, 1970). Certain components of automotive engines, chassis and piping contain copper and manganese while nickel and chromium are usually used in chrome plating. Some of the metals presumably derive from the wear of metallic automobile parts containing these metals. It is not surprising then that the other heavy metals appear to follow a similar distribution pattern to lead.

In general, the concentrations of the metals obtained in the soils in this study are considerably lower than the critical or 'trigger' concentrations for heavy metal contaminants in soils used in some countries (Alloway, 1994; Guan Dongsheng and Pert, 2006). Nevertheless, the reduction of the maximum permitted amount of lead in petrol to 0.15 g Pb L<sup>-1</sup> currently, and the gradual introduction of lead-free petrol for automobiles with catalytic converters should be encouraged since this has led to a decrease in the degree of urban lead contamination in many regions. The emissions of lead in 1990 were about 30% of what they were in 1975 in the UK (Fergusson, 1991; Clarke, 1994). Above all, it is suggested that growing of plants meant for consumption should be restricted to distances farther away from the roadside.

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