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RESEARCH ARTICLE

# Study on heavy metal pollution in plants and soil at road side location of urban area

■ D. SARALA THAMBAVANI AND M. VIDYA VATHANA

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**SUMMARY :** In this study, *Azadirachta indica*, a commonly grown a prevalent tree in Madurai town was used to monitor the influence of the heavy metal pollution caused by traffic. Samples were collected during the period May, 2011 – March, 2012 from six different locations. The concentration of heavy metals (Fe, Mn, Zn and Cu) were determined from plant leaves using Flame Atomic Absorption Spectroscopy (FAAS). Besides, heavy metal content were examined in the surface soil (0 -20 cm) and sub-surface soil (20-40 cm), samples were collected from each location. The heavy metals determined from leaves and soil was evaluated statistically. A meaningful correlation between heavy metal concentration in plant and soil sample was observed. In addition the metal concentration in *Azadirachta indica* have been compared with critical heavy metal level and phytotoxic level in the literature. The all mean data of metal concentration in leaves were found to be below the lower limits of toxicity except Fe and Mn. According to the metal concentration in surface soil and sub-surface soil studied, the concentration of metal was found to be Fe (16.1) > Mn (9.4) > Zn (5.9) > Cu (2.3) which have been found to lie below the critical limits. Though, they were well below the critical limits, the human and other living organisms are under the risk of heavy metal pollution if they are not checked and controlled. Overall conclusion is that traffic related to heavy metal was significant to urban systems and monitoring of the metal content of plants on roadside were beneficial in multiple ways.

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**Author** for correspondence :
**D. SARALA THAMBAVANI**
Department of Chemistry, Sri Meenakshi Govt. Arts College (W), MADURAI (T.N.) INDIA
Email: sarala_dr@yahoo.in
See end of the article for **Coopted authors'**

An immense interest has been focused on the toxic effect of heavy metals in the plants as most of the soils act as sink for metals. Heavy metal pollution of biosphere is increasing drastically due to industrialization and anthropogenic activities. The contamination of soils by heavy metals is one of the most serious environmental problems and has significant implications for human health. Numerous efforts have been made to develop technologies for the remediation of contaminated soils, including *ex situ* washing with physical–chemical methods and the *in situ* immobilization of metal pollutants (Rulkens *et al.,* 1995). These methods of cleanup are generally very costly, and often harmful to properties of soil (*i.e.* texture, organic matter, micro organisms) that are desirable for the restoration of contaminated sites. The phyto-extraction of heavy metals from contaminated soils has attracted attention for its low cost of implementation and many environmental benefits (McGrath *et al.,* 1993; Salt *et al.,* 1998). Plant species behave differently regarding trace metal uptake (Maisto *et al.,* 2004). Some of them have a low uptake of the metal at very high soil concentrations (excluders); other species have high metal content in their tissues compared to a very low soil metal concentration reflecting soil metal contents/indicators (Maisto *et al.,* 2004). However, the availability of metal uptake depends on the total heavy metal content of the soil and the proportion of their mobile and bio available form which are generally controlled by the texture and the other physiochemical properties of soils (Selim and Sparks, 2001). In recent years, environmental concern for air quality has lead to intensified research on solid particles introduced into the atmospheric-planetary boundary layer. Some metals and metalloids present in airborne suspended particulate matter are potentially toxic, even at low exposure levels being carcinogenic and teratogenic in mammals (Domingo, 1994; Christensen, 1995; Chang, 1996; Hamilton, 2000; Fernandez *et al.*, 2001). Traffic emissions on roads are the main cause of heavy metal accumulation on the surrounding environment including vegetation, which might have on ecological effect on them. High lead concentration in air and soil in urban areas has been attributed to increasing number of automobiles, especially leaded petrol (Thambavani and Vathana, 2011). The metals such as Cu, Ni ,Cr and Mn are essential components of engines, clutch/transmission systems and brakes of motor vehicles while Pb, along with Zn, may be derived from motor oil. Zinc has also been recognized as being associated with tyre rubber (Ellis and Revitt, 1982; Turer *et al.*, 2001).The objective of this study is to determine the concentrations of the elements Fe, Mn, Zn and Cu in Madurai urban soils and trees, and to relate these to location within the urban environment. For example,Thambavani and Vathana (2012) described the spatial variation of heavy metals in Madurai and suggested that industry and traffic are mainly responsible for the pollution. This study will investigate the distribution of heavy metals within the soil profile to examine if they are suggestive of anthropogenic sources in urban Madurai. Although a number of studies have examined either urban soils (Lu *et al.*, 2003; Imperato *et al.*, 2003; Wilcke *et al.*, 1998) or vegetation (Kovacs *et al.*, 1982; Onasanya *et al.*, 1993). The present study has investigated heavy metals of vegetation and soil in different sites at traffic area of Madurai.

**Study area:**

Madurai is one of the inhabited cities of South India. Madurai has an area of 52 square km and is located at $9.93^0$ North, $7.12^0$ East. At present it has grown as the second largest and most densely populated city in the southern state of India namely, Tamil Nadu. For the study selected areas are highly traffic density located in the central part of Madurai. Consequently automobiles may be a source of heavy metal pollution.

## EXPERIMENTAL METHODOLOGY

In the present study, stratified regular sampling method was adopted for soil sample collection as in geo-assessment of the variables estimated, the stratified regular sampling is more suitable because this kind of sampling draws homogenous error (Burges *et al.*, 1981). Six different sampling stations were selected and samples were collected at 0-20 cm depth top, 40-60 cm depth bottom using, plastic spatula after removing the debris, rock pieces and physical contaminants. Similarly, plant samples of dominant tree species such as *Azadirachta indica* were collected from urban roadsides. The samples were stored in polyethylene bags then treated and analyzed separately. Fe, Mn, Zn and Cu were included for study because they might be expected to be present at enhanced levels along roadsides. They have been investigated in recent years in a number of studies (Albasel and Cottenie, 1985; Burguera and Burguera, 1988; Bergkvist *et al.*, 1989; Garcia-Miragaya *et al.*, 1981; Onasanya *et al.*, 1993; Pichtel *et al.*, 1997; Tam *et al.*, 1987; Turer *et al.*, 2001). Therefore, heavy metal elements such as Fe, Mn, Zn and Cu were selected for this study.

**Sample preparation and analysis:**

500 g of each air dried composite sample was ground separately to pass through a 2mm sieve. About 5 g of the homogenized sample from each group was ground into fine powder using agate mortar and pestle and further dried in hot air oven at $70^0$C for 72 hrs to constant weights (ISO, 1995). Exactly 1 g from each of these finely ground soil samples were weighed out using an electronic balance into properly cleaned 250 ml beaker.

Digestion was performed by adding 12ml of aqua regia (3:1, v/v. concentrated HCl to concentration $HNO_3$) into the beaker covered with watch glass on a hot plate for 3h at $110^0$ C. After evaporation to near dryness carefully, the sample was diluted with 20 ml of 2 per cent (v/v with water) nitric acid and transferred into a 100 ml volumetric flask after filtering through Whatman no. 42 filter paper and diluted to 100 ml with double distilled water (Chen ana Ma, 2001 and Hseu *et al.*, 2002) and used for chemical analyses. Similarly, the samples of the plants were washed with distilled water to clean off the soil particles and dust and therefore they provide a measure of the elemental concentrations of plant tissue. Washed plant tissue samples were dried in an oven at $60^0$C for 48 hr, then they were ground in a milling machine. Heavy metal analysis was carried out for both soil and plant with the flame atomic absorption spectrophotometer in the following wavelength Fe-248.3 nm, Mn-279.5 nm, Zn-239 nm and Cu-324.8 nm. Statistical analysis was made for the data sets. Comparison of mean heavy metal concentrations along roadside locations were made for tree leaves and soils using the standard deviation. Correlation analysis to study the association between heavy metal concentrations in tree leaves and soil were made using the pearson correlation coefficient. The association between metals in soil was also investigated using Pearson correlation. Similarly, the association between heavy metal concentration in soil and leaves was also investigated.

## EXPERIMENTAL FINDINGS AND DISCUSSION

The experimental findings of the present study have been presented in the following sub heads:

**Heavy metal concentrations in urban tree leaves at different traffic density roadside area:**

Table 1 shows that the mean concentration of Fe, Mn, Zn and Cu in all the leaf samples at the sampling site 1 was 685.4, 1030, 549.7 and 31.1 mg/kg, respectively. The heavy metal concentration in the sampling site 1 ranged between Fe (669-697), Mn (1026-1049), Zn (539-558) and Cu (25-39). Cu variation coefficient was the highest over all for the plant species and Mn had the smallest variation co-efficient at sampling site 1.

At sampling site 2, the mean concentration of heavy metals such as Fe, Mn, Zn and Cu were found to be 1069, 76.4, 12.58 amd 20.16 mg/kg, respectively. The concentration of heavy metals such as Fe, Mn, Zn and Cu ranged between

**Table 1: Heavy metal concentrations (mg/kg) in urban tree leaves at different traffic density roadside area**

| Sampling Site | Item | Fe | Mn | Zn | Cu |
|---|---|---|---|---|---|
| Site 1 | Min | 669.0 | 1026.0 | 539.0 | 25.0 |
| | Max | 697.0 | 1049.0 | 558.0 | 39.0 |
| | Mean | 685.4 | 1030.0 | 549.7 | 31.1 |
| | Median | 686.0 | 1038.0 | 550.5 | 29.5 |
| | SD | 7.7 | 7.5 | 6.2 | 4.1 |
| | CV | 0.012 | 0.007 | 0.012 | 0.14 |
| Site 2 | Min | 1062.0 | 65.0 | 306.0 | 14.0 |
| | Max | 1075.0 | 84.0 | 318.0 | 28.0 |
| | Mean | 1069.0 | 76.4 | 312.6 | 20.2 |
| | Median | 1070.0 | 78.0 | 313.0 | 20.0 |
| | SD | 3.9 | 6.4 | 3.6 | 4.2 |
| | CV | 0.004 | 0.087 | 0.012 | 0.22 |
| Site 3 | Min | 639.0 | 49.0 | 107.0 | 17.0 |
| | Max | 660.0 | 67.0 | 119.0 | 26.0 |
| | Mean | 650.0 | 59.5 | 112.8 | 21.0 |
| | Median | 650.5 | 60.5 | 113.5 | 20.5 |
| | SD | 5.3 | 5.6 | 3.6 | 2.92 |
| | CV | 0.0084 | 0.098 | 0.33 | 0.15 |
| Site 4 | Min | 2058.0 | 95.0 | 112.0 | 24.0 |
| | Max | 2077.0 | 110.0 | 130.0 | 36.0 |
| | Mean | 2068.0 | 101.1 | 120.8 | 30.1 |
| | Median | 2069.0 | 100.0 | 120.5 | 30.5 |
| | SD | 5.7 | 4.5 | 5.9 | 3.9 |
| | CV | 0.003 | 0.046 | 0.051 | 0.133 |
| Site 5 | Min | 913.0 | 53.0 | 104.0 | 14.0 |
| | Max | 928.o | 67.0 | 120.0 | 27.0 |
| | Mean | 918.9 | 60.3 | 111.8 | 20.0 |
| | Median | 918.0 | 60.5 | 110.5 | 20.0 |
| | SD | 4.5 | 4.6 | 5.7 | 4.1 |
| | CV | 0.005 | 0.079 | 0.053 | 0.215 |
| Site 6 | Min | 224.0 | 7075.0 | 2305.0 | 16.0 |
| | Max | 237.0 | 7099.0 | 2321.0 | 25.0 |
| | Mean | 229.5 | 7089.0 | 2312.0 | 19.7 |
| | Median | 229.5 | 7091.0 | 2311.0 | 19.5 |
| | SD | 3.6 | 7.6 | 4.8 | 2.7 |
| | CV | 0.016 | 0.001 | 0.002 | 0.14 |

1062-1075, 65-84, 306-318 and 14-28, respectively. On comparing the co-efficient of variation, Cu was found be maximum and Fe was lowest at sampling site 2. The mean concentration of Fe, Mn, Zn and Cu in all the leaf samples at the sampling site 3 was 650, 59.5, 112.8 and 21mg/kg respectively. The heavy metal concentration in the sampling site 3 ranged between Fe (639-660), Mn (49-67), Zn (107-119) and Cu (17-26), respectively. The variation co-efficient of Cu was the highest and Fe had the lowest variation co-efficient at sampling site 3. At sampling site 4 the mean concentration of heavy metals such as Fe, Mn, Zn and Cu in the plant leaf was 2068, 101.1, 120.8, and 30.1 mg/kg, respectively. The heavy metal concentration in the same sampling site ranged between Fe ( 2058-2077), Mn (95-110), Zn (112-130) and Cu ( 24- 36) . Cu variation co-efficient was the biggest for the plant species and Fe had the minimum variation of co-efficient at sampling site 4. The mean concentration of heavy metals such as Fe, Mn, Zn and Cu at sampling site 5 were found to be 918.9, 60.3, 111.8 amd 20 mg/kg, respectively. For the heavy metals such as Fe, Mn, Zn and Cu the concentration ranged between 913-928, 53-67, 104-120 and 14-27, respectively. The co-efficient of variation at sampling site 5 for Cu was found be maximum and for Fe it was minimum. Similarly at sampling site 6, the mean concentration of Fe, Mn, Zn and Cu in all the plant species was 229.5, 7089, 2312 and 19.7, respectively. The concentration of heavy metals such as Fe, Mn, Zn and Cu ranged between 224-237, 7075-7099, 2305-2321 and 16-25, respectively. At sampling site 6 the Cu variation of co-efficient was the highest and Mn had the lowest co-efficient of variation.

The heavy metal concentration in the tree leaves at the sampling site 1 was found to be in the order of Mn (1030.0) > Fe (685.4) > Zn (549.7) > Cu (31.1). At sampling site 2, the metal concentration was in the order of Fe (1069.0) > Zn (312.6) > Mn (76.4) > Cu (20.2). The results revealed that the heavy metal concentration at the sampling site 3 was found to be in the order of Fe ( 650.0) > Zn (112.8) > Mn (59.5) > Cu (21.0). It has been found that the concentration of heavy metals in the tree leaves at the sampling site 4 was in the following order of Fe (2068.0) > Zn (120.8) > Mn (100.0) > Cu (30.5). Similarly at sampling site 5 and 6 the heavy metal concentration in the plant leaves was found to be in the order of Fe (918.9) > Zn (111.8) > Mn (60.3) > Cu (20.0) and Mn (7089.0) > Zn (2312.0) > Fe (229.5) > Cu (19.7), respectively. In the plant leaf, the heavy metal concentration of Mn (1030.0 $S_1$) and (7089 $S_6$) was found to be maximum. The concentration of Fe (1069.0 $S_2$), (650.0 $S_3$), (2068 $S_4$) and (918.9 $S_5$) was maximum in these sites. The reason for the maximum concentration of Fe is due to the automobiles emission which cause iron contribution to the environment from urbanization. Manganese is also an essential element for plants and animals. Its uptake is being controlled metabolically. Soil derives manganese from the parent material and its content in the rocks are higher than the concentration of other micronutrients apart from (Smith, 1990). In general, the concentration of iron in plants from polluted area was higher. Thus, plants collected from polluted area were more affected by pollution, emitting more iron into the environment and to the soil. The concentration of iron in the plant was high as compared to other elements. The high iron amount in the aerial parts was also due to the foliar absorption from the surrounding air. Iron deficiency in plants produces

**Table 2 : Relationships among heavy metal concentrations in tree leaves (n=12)**

| Sampling site | Elemental pair | Correlation co-efficient (r) |
|---|---|---|
| Site 1 | Fe –Mn | -0.178 |
| | Fe – Zn | 0.186 |
| | Fe – Cu | -0.590 |
| | Mn –Zn | 0.100 |
| | Mn – Cu | 0.015 |
| | Zn - Cu | -0.053 |
| Site 2 | Fe –Mn | 0.027 |
| | Fe – Zn | 0.450 |
| | Fe – Cu | 0.133 |
| | Mn –Zn | -0.032 |
| | Mn – Cu | -0.149 |
| | Zn - Cu | -0.059 |
| Site 3 | Fe –Mn | -0.179 |
| | Fe – Zn | -0.397 |
| | Fe – Cu | -0.035 |
| | Mn –Zn | -0.220 |
| | Mn – Cu | -0.330 |
| | Zn - Cu | 0.007 |
| Site 4 | Fe –Mn | 0.035 |
| | Fe – Zn | -0.024 |
| | Fe – Cu | 0.505 |
| | Mn –Zn | 0.092 |
| | Mn – Cu | -0.073 |
| | Zn - Cu | -0.242 |
| Site 5 | Fe –Mn | 0.375 |
| | Fe – Zn | -0.268 |
| | Fe – Cu | 0.297 |
| | Mn –Zn | -0.440 |
| | Mn – Cu | 0.062 |
| | Zn - Cu | -0.594 |
| Site 6 | Fe –Mn | -0.376 |
| | Fe – Zn | 0.065 |
| | Fe – Cu | -0.348 |
| | Mn –Zn | -0.135 |
| | Mn – Cu | 0.224 |
| | Zn - Cu | 0.3923 |

chlorosis, however its high concentration also affects plant growth (Sakolnik, 1984). Iron together with hemoglobin and ferridoxin plays a central role in metabolism.

Most of the elemental pairs at sampling site 1 were correlated with each other (Fe–Zn, Mn–Zn, Mn–Cu). The elemental pairs Fe – Mn, Fe – Cu and Zn – Cu were negatively correlated with each other but Fe–Cu elemental pair was negatively correlated with each other significantly (-0.59). Because the heavy metal concentration of leaves were mainly dependent on air pollution and those of topsoil were largely dependent on soil parent materials and solid waste. The elemental pairs such as Fe – Mn, Fe – Zn, and Fe – Cu were correlated with each other at sampling site 2 (Table 2). At the same sampling site, Mn – Zn, Mn – Cu and Zn – Cu elemental pair were negatively correlated but not significantly. It has been observed that at sampling site 3, except the elemental pair Zn – Cu (0.007) all the other elemental pairs Fe – Mn, Fe –Zn, Fe – Cu, Mn – Zn and Mn–Cu were negatively correlated with each other but not significantly. At sampling site 4, Fe – Mn, Fe – Cu and Mn - Zn elemental pairs were positively correlated with each other. Positive and significant correlation was found between Fe – Cu (0.505). The elemental pairs such as Fe – Zn, Mn – Cu and Zn – Cu were negatively correlated with each other. The results revealed that the elemental pairs at sampling site 5 were correlated with each other ( Fe – Mn, Fe – Cu and Mn – Cu ). The elemental pairs Fe – Zn, Mn – Zn and Zn – Cu were negatively correlated with each other but Zn – Cu elemental pair was negatively correlated with each other but significantly (-0.594). At sampling site 6, the following elemental pairs were positively correlated Fe – Zn, Mn – Cu and Zn – Cu. But the elemental pairs Fe – Mn, Fe – Cu and Mn – Zn were negatively correlated with each other.

In terms of toxicity to plants (Table 3) with exception to Fe and Mn, the mean values observed in leaves in sampling sites of all other metals lied at the margin of, or below the lower limits of toxicity as reported by Alloway and Ayers (1993).

**Metal distribution in the soil profile:**

As noted in Table 4 the mean heavy metal concentrations were significantly high in the top soils compared to the other layers which is in accordance to a number of studies that revealed enrichment of top soil (Imperato *et al.*, 2003; Burguera and Burguera, 1988).

The heavy metal concentration in the surface soil at the sampling site 1 was found to be in the order of Fe ( 14.7 ) > Mn (10.1) > Zn (4.4) > Cu (1.9). In the sub-surface soil the heavy metal concentration at the same sampling site was in the following order Zn (2.05) > Mn (1.71) > Fe (1.6 ) > Cu ( 0.9 ). At sampling site 2, the metal concentration was in the order of Fe (14.4) > Zn (7.2) > Mn ( 5.4) > Cu (5.0). The results shows that in the sub-surface soil the heavy metal concentration at the sampling site 2 was found to be in the order of Fe ( 7.2 ) > Zn ( 4.2 ) > Cu ( 2.3 ) > Mn ( 1.2 ). It has been found that the concentration of heavy metals in the surface soil at the sampling site 3 was in the following order of Fe (18.1) > Mn (8.9 ) > Zn ( 7.1 ) > Cu ( 2.2 ) and in the sub-surface soil the heavy metal concentration was found to be in the order of Fe (7.1 ) > Mn ( 2.5 ) > Zn ( 2.0 ) > Cu ( 0.9 ). The heavy metal concentration at sampling site 4 in the surface soil was in the order of Fe ( 21.6 ) > Mn ( 6.7 ) > Zn ( 6.1 ) > Cu ( 2.4 ).The results implies that in the sub-surface soil the concentration of heavy metal was in the following order Zn ( 12.3 ) > Fe (11.6) > Cu ( 6.2 ) > Mn ( 1.1 ). At sampling site 5 in the surface and in sub-surface soil the heavy metal concentration were found to be in the order of Mn (16.3 ) > Fe ( 11.9 ) > Zn ( 5.9 ) > Cu (2.3) and Zn ( 8.9 ) > Fe ( 6.6 ) > Cu ( 3.4 ) > Mn (1.3 ) respectively. The heavy metal concentration in the surface soil and sub-surface soil at sampling site 6 was in the order of Fe (15.7 ) > Mn ( 9.1 ) > Zn ( 4.9 ) > Cu ( 1.6 ) and Fe ( 3.0 ) > Zn ( 2.5 ) > Mn ( 1.4 ) > Cu ( 0.9 ), respectively. On comparing, the heavy metal concentration in the surface soil iron was found to be maximum in all five sampling site except ($S_5$) { Fe [14.7 ($S_0$)], [ 14.4 ($S_2$)], [ 18.1 ($S_3$)], [22.4 ($S_4$)] and [ 15.7 ($S_6$)]}. The concentration of Mn [ 16.3 ( $S_5$ )] was maximum in these sites.

**Table 3: Metal concentrations in tree leaves and toxicity levels (mg/kg)**

| Sampling site | Item | Fe | Mn | Zn | Cu | Sources |
|---|---|---|---|---|---|---|
| Site 1 | Mean | 685.4 | 1030.0 | 549.7 | 31.1 | This study |
| Site 2 | Mean | 1069.0 | 76.4 | 312.6 | 20.2 | This study |
| Site 3 | Mean | 650.0 | 59.5 | 112.8 | 21.0 | This study |
| Site 4 | Mean | 2068.0 | 101.1 | 120.8 | 30.1 | This study |
| Site 5 | Mean | 918.9 | 60.3 | 111.8 | 20.0 | This study |
| Site 6 | Mean | 229.0 | 7089.0 | 2312.0 | 19.7 | This study |
| | All data-Mean | 936.7 | 1402.7 | 586.6 | 23.7 | This study |
| Critical heavy metal level | --- | 50 – 200 | 300 – 500 | 80 – 200 | 100 | --- |
| Normal level | ---- | 30 -300 | 50 – 500 | 15 – 150 | 3 - 20 | Alloway and Ayers, 1993 |
| Phytotoxic level | ---- | 10 – 200 | 300 – 500 | 500 – 1500 | 25 - 40 | Alloway and Ayers, 1993 |

**Table 4 : Mean heavy metal concentration (mg/kg) of soil profile in traffic area of Madurai**

| Sampling site | Soil layer | Item | Fe | Mn | Zn | Cu |
|---|---|---|---|---|---|---|
| Site 1 | 0 – 20 cm | Min | 14.2 | 9.5 | 4.0 | 1.4 |
| | | Max | 15.1 | 10.7 | 4.8 | 2.4 |
| | | Mean | 14.7 | 10.1 | 4.4 | 7.9 |
| | | Median | 14.8 | 10.1 | 4.4 | 1.9 |
| | | SD | 0.28 | 0.39 | 0.23 | 0.31 |
| | | CV | 0.019 | 0.040 | 0.054 | 0.174 |
| | 20 – 40 cm | Min | 1.0 | 1.0 | 1.5 | 0.4 |
| | | Max | 2.1 | 2.3 | 2.6 | 1.3 |
| | | Mean | 1.6 | 1.7 | 2.1 | 0.9 |
| | | Median | 1.6 | 1.8 | 2.1 | 0.9 |
| | | SD | 0.35 | 0.37 | 0.35 | 0.27 |
| | | CV | 0.232 | 0.228 | 0.175 | 0.320 |
| Site 2 | 0 – 20 cm | Min | 13.9 | 4.7 | 6.3 | 4.4 |
| | | Max | 14.9 | 6.1 | 7.9 | 5.7 |
| | | Mean | 14.4 | 5.4 | 7.2 | 5.0 |
| | | Median | 14.5 | 5.3 | 7.4 | 5.1 |
| | | SD | 0.30 | 0.43 | 0.52 | 0.36 |
| | | CV | 0.022 | 0.084 | 0.075 | 0.075 |
| | 20 – 40 cm | Min | 6.5 | 0.7 | 3.6 | 1.6 |
| | | Max | 7.8 | 1.9 | 4.8 | 2.8 |
| | | Mean | 7.2 | 1.2 | 4.2 | 2.3 |
| | | Median | 7.3 | 1.2 | 4.3 | 2.3 |
| | | SD | 0.39 | 0.35 | 0.37 | 0.3 |
| | | CV | 0.057 | 0.301 | 0.091 | 0.155 |
| Site 3 | 0 – 20 cm | Min | 17.6 | 8.5 | 6.3 | 1.6 |
| | | Max | 18.6 | 9.4 | 7.8 | 2.7 |
| | | Mean | 18.1 | 8.9 | 7.1 | 2.2 |
| | | Median | 18.1 | 8.9 | 7.2 | 2.2 |
| | | SD | 0.30 | 0.26 | 0.48 | 0.35 |
| | | CV | 0.018 | 0.031 | 0.069 | 0.167 |
| | 20 – 40 cm | Min | 7.6 | 2.0 | 1.5 | 0.5 |
| | | Max | 8.7 | 3.0 | 2.4 | 1.3 |
| | | Mean | 8.1 | 2.5 | 1.9 | 0.9 |
| | | Median | 8.7 | 2.5 | 2.0 | 0.9 |
| | | SD | 0.34 | 0.30 | 0.24 | 0.25 |
| | | CV | 0.044 | 0.127 | 0.127 | 0.288 |
| Site 4 | 0 – 20 cm | Min | 20.7 | 5.9 | 5.3 | 1.9 |
| | | Max | 22.4 | 7.2 | 6.9 | 2.9 |
| | | Mean | 21.6 | 6.7 | 6.1 | 2.4 |
| | | Median | 21.6 | 6.7 | 6.2 | 2.5 |
| | | SD | 0.47 | 0.36 | 0.53 | 0.33 |
| | | CV | 0.023 | 0.056 | 0.089 | 0.142 |
| | 20 – 40 cm | Min | 10.8 | 0.6 | 11.8 | 5.6 |
| | | Max | 12.3 | 1.6 | 12.7 | 6.7 |
| | | Mean | 11.6 | 1.1 | 12.3 | 6.2 |
| | | Median | 11.8 | 1.1 | 12.3 | 6.3 |
| | | SD | 0.47 | 0.31 | 0.28 | 0.33 |
| | | CV | 0.042 | 0.291 | 0.023 | 0.055 |

*Contd…Table 1*

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| | | | | | | |
|---|---|---|---|---|---|---|
| Site 5 | 0 – 20 cm | Min | 11.4 | 15.4 | 5.4 | 1.7 |
| | | Max | 12.6 | 16.9 | 6.5 | 2.4 |
| | | Mean | 11.9 | 16.3 | 5.9 | 2.3 |
| | | Median | 11.9 | 16.3 | 5.9 | 2.3 |
| | | SD | 0.39 | 0.43 | 0.34 | 0.34 |
| | | CV | 0.034 | 0.028 | 0.059 | 0.156 |
| | 20 – 40 cm | Min | 5.9 | 0.7 | 7.7 | 2.7 |
| | | Max | 7.2 | 1.8 | 8.9 | 3.8 |
| | | Mean | 6.6 | 1.3 | 8.4 | 3.3 |
| | | Median | 6.7 | 1.4 | 8.9 | 3.4 |
| | | SD | 0.39 | 0.34 | 0.39 | 0.32 |
| | | CV | 0.060 | 0.282 | 0.048 | 0.102 |
| Site 6 | 0 – 20 cm | Min | 15.0 | 8.5 | 4.0 | 1.0 |
| | | Max | 16.3 | 9.9 | 5.7 | 2.2 |
| | | Mean | 15.7 | 9.1 | 4.9 | 1.6 |
| | | Median | 15.8 | 9.1 | 5.1 | 1.7 |
| | | SD | 0.44 | 0.45 | 0.51 | 0.36 |
| | | CV | 0.027 | 0.051 | 0.108 | 0.236 |
| | 20 – 40 cm | Min | 2.5 | 0.9 | 2.0 | 0.6 |
| | | Max | 3.5 | 1.8 | 2.9 | 1.3 |
| | | Mean | 3.0 | 1.4 | 2.5 | 0.9 |
| | | Median | 3.0 | 1.4 | 2.5 | 0.9 |
| | | SD | 0.307 | 0.27 | 0.26 | 0.21 |
| | | CV | 0.107 | 0.208 | 0.108 | 0.226 |

The reason for the maximum concentration of Fe is due to the automobiles cause iron contribution to the environment from urbanization. The auto body rust and engine parts are releasing iron to the environment. Motor oil is tending also to accumulate metals as it comes in contact with surrounding parts as the engine runs, so oil leaks becomes another pathway by which metal is entering the environment. Since the heavy metal does not degrade naturally, accumulation of high concentration in soils can be toxic to organisms living in surrounding environments (Olajire and Ayodele, 1996). As Mn, in the environment being abundant in the earth's crust (Adriano, 2001; Dixit *et al.,* 2002).

**Relationship among heavy metals concentration in top soil (0 -20 cm) and sub-surface soil (20 – 40 cm):**

Table 5 shows that the all the elemental pairs in the surface soil at sampling site 1 were negatively correlated with each other. Though they were negatively correlated but not significant. In the sub-surface soil, the elemental pairs such as Fe – Mn, Fe – Zn, Mn – Zn and Mn – Cu were positively correlated with each other and the elemental pairs Fe – Cu and Zn – Cu were negatively correlated but not significantly. At sampling site 2 in the surface soil the elemental pairs Fe – Mn and Mn – Cu were positively correlated but Mn – Cu pair was positively correlated significantly (0.515). The elemental pairs such as Fe–Zn, Fe – Cu and Mn – Zn were negatively correlated with each other. Mn – Cu and Fe – Zn in the sub-surface soil were positively correlated with each other but the elemental pair Mn – Cu was positively and significantly (0.539). The result shows that in the surface soil at sampling site 3, except the elemental pair Mn–Cu ( -0.12) all other pairs were positively correlated with each other. The elemental pair Fe – Mn was positively significant ( 0.672 ) (Table 5).

In the sub-surface soil at sampling site 3 except Zn – Cu (0.305) all other elemental pairs were negatively correlated but Fe – Mn was negatively significant (-0.583). It had been found that at the sampling site 4 in the surface soil the following elemental pairs were positively correlated with each other Fe – Mn, Fe – Zn, Fe – Cu and Mn – Zn. The elemental pair Mn – Cu and Zn – Cu were negatively correlated but Mn – Cu was negatively significant (-0.635 ). The sub-surface soil of sampling site 4 reveals that the except Zn – Cu elemental pair all others were positively correlated with each other. The Fe – Cu ( 0.567) and Mn-Zn (0.531) elemental pairs were positively significantly

**Table 5: Relationship among heavy metals concentration in top soil (0 -20cm) and sub-surface soil (20 – 40 cm)**

| Sampling site | Elemental pair | Soil layer | |
|---|---|---|---|
| | | Surface soil (0 – 20 cm) | Sub-surface soil (20 – 40 cm) |
| Site 1 | Fe – Mn | -0.376 | 0.404 |
| | Fe - Zn | -0.063 | 0.145 |
| | Fe – Cu | -0.379 | -0.009 |
| | Mn – Zn | -0.242 | 0.397 |
| | Mn – Cu | -0.169 | 0.349 |
| | Zn – Cu | -0.158 | -0.182 |
| Site 2 | Fe – Mn | 0.392 | -0.305 |
| | Fe - Zn | - 0.839 | 0.156 |
| | Fe – Cu | -0.292 | -0.363 |
| | Mn – Zn | -0.358 | -0.273 |
| | Mn – Cu | 0.515 | 0.539 |
| | Zn – Cu | -0.0022 | -0.0178 |
| Site 3 | Fe – Mn | 0.672 | -0.583 |
| | Fe - Zn | 0.440 | -0.175 |
| | Fe – Cu | 0.250 | -0.018 |
| | Mn – Zn | 0.110 | -0.163 |
| | Mn – Cu | -0.128 | -0.374 |
| | Zn – Cu | 0.185 | 0.304 |
| Site 4 | Fe – Mn | 0.104 | 0.019 |
| | Fe - Zn | 0.208 | 0.108 |
| | Fe – Cu | 0.228 | 0.567 |
| | Mn – Zn | 0.062 | 0.531 |
| | Mn – Cu | -0.635 | 0.035 |
| | Zn – Cu | -0.152 | -0.189 |
| Site 5 | Fe – Mn | 0.522 | -0.176 |
| | Fe - Zn | -0.394 | 0.062 |
| | Fe – Cu | 0.781 | -0.022 |
| | Mn – Zn | 0.038 | -0.292 |
| | Mn – Cu | 0.318 | -0.073 |
| | Zn – Cu | -0.109 | 0.618 |
| Site 6 | Fe – Mn | 0.325 | 0.694 |
| | Fe - Zn | 0.069 | 0.104 |
| | Fe – Cu | -0.112 | 0.603 |
| | Mn – Zn | -0.374 | 0.307 |
| | Mn – Cu | -0.048 | 0.310 |
| | Zn – Cu | -0.368 | -0.243 |

correlated. At sampling site 5, in the surface soil the elemental pairs Fe – Mn, Fe – Cu, Mn – Cu and Mn – Zn were found to be positively correlated with each other. Fe – Mn ( 0.522 ) and Fe – Cu ( 0.781 ) elemental pairs were positively significantly. The elemental pairs Fe – Zn and Zn – Cu were negatively correlated. The elemental pairs existed in the sub-surface soil such as Fe – Mn, Fe – Cu, Mn – Zn and Mn – Cu were negatively correlated with each other. But Fe – Zn and Zn – Cu were positively correlated. The Zn – Cu was positively correlated significantly (0.618 ). The elemental pairs Fe – Mn and Fe – Zn in the surface soil at sampling site 6 were positively correlated with each other. At the same sampling site the elemental pairs such as Fe–Cu, Mn – Zn, Mn – Cu and Zn – Cu were negatively correlated with each other. At sampling site 6 the elemental

**Table 6 : Metal concentration in surface soil (0-20 cm), sub-surface soil (20-40 cm) and toxicity levels (mg/kg)**

| Sampling site | Soil layer | Item | Fe | Mn | Zn | Cu | Sources |
|---|---|---|---|---|---|---|---|
| Site 1 | (0-20cm) | Mean | 14.7 | 10.1 | 4.4 | 1.9 | This study |
| | (20-40cm) | | 1.6 | 1.7 | 2.1 | 0.9 | This study |
| Site 2 | (0-20cm) | Mean | 14.4 | 5.4 | 7.2 | 5.0 | This study |
| | (20-40cm) | | 7.2 | 1.2 | 4.2 | 2.3 | This study |
| Site 3 | (0-20cm) | Mean | 18.1 | 8.9 | 7.1 | 2.2 | This study |
| | (20-40cm) | | 8.1 | 2.5 | 1.9 | 0.9 | This study |
| Site 4 | (0-20cm) | Mean | 21.6 | 6.7 | 6.1 | 2.4 | This study |
| | (20-40cm) | | 11.6 | 1.1 | 12.3 | 6.2 | This study |
| Site 5 | 0-20cm) | Mean | 11.9 | 16.3 | 5.9 | 2.3 | This study |
| | (20-40cm) | | 6.6 | 1.3 | 8.4 | 3.3 | This study |
| Site 6 | (0-20cm) | Mean | 15.7 | 9.1 | 4.9 | 1.6 | This study |
| | 20-40cm) | | 3.0 | 1.4 | 2.5 | 0.9 | This study |
| | All data (0-20cm) | | 16.1 | 9.4 | 5.9 | 2.3 | This study |
| | All data (20-40cm) | Mean | 6.4 | 1.5 | 5.2 | 2.4 | This study |
| Critical heavy metal level | ---- | ----- | 50 | 1500-3000 | 300 | 50-125 | J.E. Fergusson *et al.* (1990), Kabata-Pendias and Pendias, 1992 |
| Phytotoxic level | ----- | ----- | ---- | ------ | 300 | 100 | WHO |

pairs Fe – Mn, Fe – Zn, Fe – Cu, Mn – Zn and Mn – Cu in the sub-surface soil were positively correlated with each other and Fe – Mn ( 0.694 ) and Fe – Cu ( 0.603 ) were positively significantly. The elemental pair Zn–Cu was negatively correlated with each other (Table 5).

In terms of critical heavy metal concentration level to surface and sub-surface soil in all the sampling sites the mean concentration values for all the heavy metals lied below the critical limit reported as by Fergusson (1990) (Table 6).

**Conclusion:**

Heavy metal concentrations have been presented for trees, surface soil and sub-surface soil for high density traffic area of Madurai. Among the six different sampling sites studied, the extent of metal pollution particularly Fe and Mn were found to be highest in the plant leaves which was influenced more by heavy traffic. In terms of soil, the heavy metal concentrations both in the surface and sub-surface soil were found be within the critical heavy metal level. The results of the statistical analysis also suggested that the vehicular traffic emission represents the most important metal contamination source in the Madurai city on soil and in plant leaves. People generally use herbal medicine for prolonged period of time to achieve desirable effects. Prolong consumption of such herbal medicine might reduce chronic or subtle health hazards. Thus, the present findings indicate that the medicinal plant or plant parts used for different diseases must be checked for heavy metals contamination in order to make it safe for human consumption. Although the concentration of heavy metals in *Azardiracta indica* was below the critical level, however for local or pharmaceutical purposes, it should be collected from area not contaminated with heavy metals. From the present study, it is concluded that *Azardiracta indica* growing in polluted area has high, iron, and manganese concentration and therefore the use should be avoided in there is fair chance to finding this plant in unpolluted areas. It is required to enforce legal practices like controlling the entry of vehicles to the heavy traffic areas and imposing transit taxes.

**Coopted** Authors' :

**M. VIDYAVATHANA**, Department of Chemistry, Sacs M.A.V.M.M Engineering College, MADURAI (T.N.) INDIA

Email : vidhyanagaraj_1973@yahoo.com

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