Accumulation of Heavy Metals in Tarry Deposit on Leaves at Various Locations of Karachi

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Summary: In this study heavy metal accumulation in the tarry deposit on the leaves of trees growing along the busy road of Karachi city has been estimated. Samples of the tarry deposit on leaves were collected from various intersections on the busy roads of Karachi. In this study total average concentration of lead, copper, manganese, zinc, nickel and cadmium were found in the range of 0.014 - 2.547, 0.026 - 1.8, 0.285 - 4.984, 0.472 - 7.173, 0.014 - 0.265 and 0.002 - 0.027 mg/g respectively. The result shows that almost all the pollution is being generated by automobile exhaust in the urban areas of Karachi.

Introduction

Pollution from motor vehicles has become a major issue simply because of rapidly increase both in the number of vehicles in use and the distance traveled by each vehicle each year. The number of vehicles kilometers driven in UK increased by 99% during the year of 1970 – 1990. Up to the year 1997, the total vehicular driven distance from 26 million motor vehicles in UK was 480 billion km/year and it is expected that this figure have to increase upto 653 billion km by 2010 [1]. But no such data is available in Pakistan.

In industrialized cities like Karachi, vehicular emission is a major source of atmospheric pollution. The continuous rise in population, trade and industrial activities demand large transportation, which has been resulting increase in environmental problems. Recent urban expansion and increase in automobile activities has brought negative impact on roadside traders, dwellers, especially vegetation and trees. Some studies on the impact of vehicular emission on roadside plants have been reported by some workers [2-8]. Some surveys on the measurement of air pollutants, especially CO, smoke and particulate matter in Karachi city [9-13], have indicated high level of air pollutants. The uncontrolled motor vehicles emission of smoke and tarry materials has also started damaging important monuments. Tarry deposit have already started damaging plants and various sensitive species to the extent that they are dwarfed and color of leaves has changed from green to grey at some locations. The deterioration in quality of macro environment has thus exceeded the critical limit of adaptation of plants to stress situation.

Particulate type air pollutants such as ash, dirt and grit, land on the top of leaves. They do not enter the leaf but may damage it by mechanical abrasion of the surface. Particulate matter can also block out the sunlight and thereby reduce the food making ability of plant. Removal of the wax from the surface of the leaves due to tarry deposits increases the penetration of heavy metals. Foliar uptake mainly depends on the species, plant age and environmental variables. The stomata of plants growing on the roadside in the central district are blocked to the extent of 20 to 50 % depending on the locations [14]. This shows that a serious problem has arisen now in the congested part of the city.

Present study was carried out to determine the quantity of tarry deposits and concentrations of heavy metal accumulation in tarry deposit on leaves of trees, growing along the main roads of Karachi city and also obtained relative estimate of total aerial burden of metals in the materials deposited on the surface of the leaves, which serve as a sink especially for particulate matter at various intersections of Karachi city.

Results and Discussion

Analysis of tarry deposit was carried out for lead, copper, manganese, zinc, nickel and cadmium. Quantity of tarry deposits and total average concentrations of these heavy metals are presented in Table-1 and their Correlation coefficient matrix in Table-2. Figure 1 shows the comparative concentrations of tarry deposit recorded at the 23 selected sites during the year 2004 (present study),

Table-1: Concentration of Heavy Metal (along with mean and standard deviation) values estimated in the tarry deposits on leaves at 23 locations on the busy roads of Karachi city

S. No	Locations	Pb mg/g	Cu mg/g	Mn mg/g	Zn mg/g	Ni mg/g	Cd mg/g	Terry Deposit mg/m^2
1	University Road	0.263 ±0.021	0.145 ± 0.000	0.633 ± 0.007	0.86 ± 0.028	0.066 ± 0.028	0.007 ± 0.014	6,559
2	University Petrol Pump	0.697 ± 0.049	0.353 ± 0.007	0.467 ± 0.000	0.495 ± 0.007	0.038 ± 0.007	0.002 ± 0.000	16,607
3	NIPA	0.142 ± 0.007	0.072 ± 0.007	0.423 ± 0.007	0.857 ± 0.014	0.024 ± 0.000	0.008 ± 0.021	14,229
4	Gulshan Chorangi	0.014 ± 0.028	0.026 ± 0.014	0.285 ± 0.007	0.472 ± 0.000	0.014 ± 0.000	0.013 ± 0.042	11,661
5	Sohrab Goath	0.340 ± 0.021	0.212 ± 0.000	0.864 ± 0.007	0.948 ± 0.000	0.061 ± 0.007	0.006 ± 0.071	11,952
6	Water Pump	0.741 ± 0.014	0.450 ± 0.014	1.323 ± 0.057	1.673 ± 0.014	0.184 ± 0.035	0.011 ± 0.007	7,608
7	Aisha Manzil	0.581 ± 0.028	0.295 ± 0.028	1.471 ± 0.035	1.500 ± 0.021	0.108 ± 0.007	0.012 ± 0.007	7,692
8	Husainabad	0.190 ± 0.049	0.092 ± 0.007	0.347 ± 0.035	1.261 ± 0.007	0.030 ± 0.007	0.004 ± 0.042	20,443
9	Karimabad	0.204 ± 0.092	0.104 ± 0.007	0.404 ± 0.000	0.573 ± 0.007	0.034 ± 0.028	0.006 ± 0.028	20,108
10	Liaquatabad	0.908 ± 0.099	0.396 ± 0.007	1.115 ± 0.028	0.894 ± 0.007	0.041 ± 0.028	0.005 ± 0.028	26,555
11	Dakhana	0.666 ± 0.014	0.375 ± 0.007	0.976 ± 0.021	1.940 ± 0.028	0.083 ± 0.000	0.014 ± 0.007	45,801
12	Germander	0.044 ± 0.028	0.084 ± 0.007	4.984 ± 0.014	0.771 ± 0.028	0.015 ± 0.028	0.002 ± 0.014	9,702
13	Teen Hatti	0.028 ± 0.035	0.287 ± 0.007	0.295 ± 0.000	0.964 ± 0.028	0.030 ± 0.028	0.003 ± 0.007	14,675
14	Numaish	0.435 ± 0.000	0.465 ± 0.000	1.788 ± 0.007	1.841 ± 0.028	0.094 ± 0.007	0.006 ± 0.028	9,162
15	Tibet Centre	0.622 ± 0.007	0.766 ± 0.014	1.995 ± 0.007	4.822 ± 0.000	0.166 ± 0.007	0.020 ± 0.000	23,251
16	City Court	0.423 ± 0.021	0.990 ± 0.000	2.461 ± 0.042	4.432 ± 0.035	0.144 ± 0.007	0.027 ± 0.007	21,514
17	Jamia Cloth	0.166 ± 0.014	0.169 ± 0.007	0.812 ± 0.000	0.906 ± 0.028	0.032 ± 0.007	0.005 ± 0.007	22,578
18	Tower	0.125 ± 0.028	0.055 ± 0.007	0.342 ± 0.000	0.783 ± 0.021	0.039 ± 0.007	0.017 ± 0.021	16,388
19	Buffer Zone	1.278 ± 0.057	0.632 ± 0.042	1.074 ± 0.007	1.484 ± 0.000	0.116 ± 0.028	0.008 ± 0.007	13,396
20	Kharadar	2.547 ± 0.064	1.800 ± 0.028	4.052 ± 0.028	7.173 ± 0.007	0.265 ± 0.007	0.026 ± 0.057	4,657
21	Lee Market	0.652 ± 0.021	0.392 ± 0.035	0.920 ± 0.007	1.413 ± 0.007	0.059 ± 0.007	0.005 ± 0.007	13,575
22	Jinnah Hospital	0.114 ± 0.007	0.095 ± 0.014	0.381 ± 0.021	1.082 ± 0.007	0.033 ± 0.042	0.005 ± 0.000	9,455
23	PCSIR (Control Site)	0.019 ± 0.010	0.021 ± 0.011	0.064 ± 0.010	0.098 ± 0.021	0.009 ± 0.001	0.000 ± 0.000	4,723

Table – 2: Correlation Coefficient of Metals in Tarry Deposit on Leaves

	Cu	Mn	Zn	Ni	Cd
Pb	0.870	0.440	0.710	0.789	0.465
Cu		0.566	0.928	0.884	0.700
Mn			0.576	0.490	0.354
Zn				0.871	0.809
Ni					0.725

with our previous investigation during the year 1995 [10].

Table 1 show that the maximum concentration of tarry deposit on leaves was found to be 45,801 mg/m^2 at Dakhana Chock and minimum concentration 4,657 mg/m^2 at Kharadar. Dakhana Chock is one of the busiest-intersection of Shahrah-e-Pakistan in Karachi, where traffic density is very high and mostly traffic is held up by the traffic lights. Moreover there are several automobile workshops around the Dakhana Chock and there is also a large parking place on the sides of this round about. In these workshops at Dakhana Chock a large number hundreds of automobiles are engaged in repair and maintenance, emitting black smoke. In our earlier study, at this location, tarry deposit was recorded

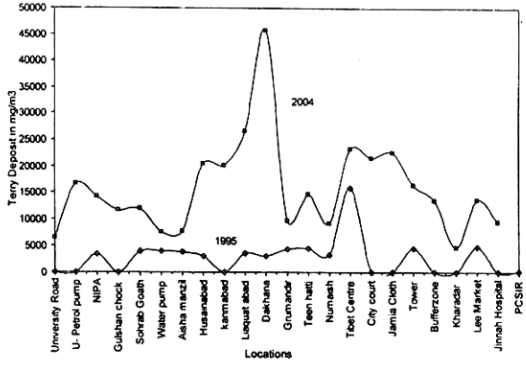

Fig. 1. Accumulation of tarry deposits on the leaves reported in 1995 and 2004 observed at 23 locations in Karachi city in this study.

3,017 mg/m^2 [10]. Figure 1 clearly indicate that the concentration at this site is five fold higher concentrations. This increase in concentration may be due to the increase in traffic density during past years.

Table-1 shows the concentration of metals in tarry deposit. The range of total average concentration of lead, copper, manganese, zinc, nickel and cadmium in tarry deposit was found to be in the range of 0.014 - 2.547, 0.026 - 1.8, 0.285 - 4.984, 0.472 - 7.173, 0.014 - 0.265 and 0.002 - 0.027 mg/g respectively.

Among all these elements, higher concentration of lead found at Kharader, Bufferzone, Lee market, Tibet centre, Liaquat Abad, Aisha Manzil, Water Pump and University Petrol Pump. At Kharader, Lee market, Tibet centre, Liaquat Abad, Aisha Manzil and Water Pump the higher concentration of lead may be due to the higher traffic density, whereas at Bufferzone Bridge, concentration of lead may be higher due to the traffic congestion, as at this site the road is narrow and congested and during the period of survey civil work was under progress. At University Petrol Pump, the higher concentration of lead may be due to careless handling of the Petrol Pump workers.

The highest concentration of lead was recorded 2.547 mg/g at Kharadar. Most of the lead present in the atmosphere of urban areas is in the form of aerosols and particulate matter. Particulate emitted from defective vehicles comprises of smoke, unburned fuel and tarry material due to in-appropriate mixing of gasoline with lubricant in two stroke engines and their impact on vegetation in city streets is simply distressing [15]. The highest concentration of lead found at this site may be due to vehicular traffic. The main source of Pb is gasoline, which contains 0.5 to 0.8 g/l of Pb. Depending upon the number of vehicles plying on the road as well as on meteorological conditions; the level of Pb in air varies from 1.5 to 3μ g/m^3. Lead from petrol is not only inhaled from the air but also absorbed indirectly through its lingering presence in soil and dust [16]. It is a non-degraded pollutant and it not only accumulated in the body but can also modifying itself as it moves through biological cycles and food chain [17].

The highest concentration of zinc present in tarry deposit on leaves may be due to the fact that most of the vehicles (60%) are using old and out dated tyres. These tires are prone to tear off quickly as compared with new tyres and add more particles in the atmosphere, as zinc is the component of tyre, whereas copper and manganese are the component of engine [18]. The average concentration of lead, copper, manganese and zinc are of same order of magnitude. Lead is used as antiknocking agent in petrol, copper is used for engine parts, and manganese and zinc are the components of tyres and motor oil [19]. The sources of Cd are diesel and lubricating motor oils, tyres and galvanized parts of the vehicles. Diesel oil contains 0.07 to 0.1 ppm of Cd, whereas lubricating oil contains 0.26 ppm. The wear and tear of automobile tyres, which contain 20 to 90 ppm cadmium, is a main source of Cd pollution [16].

Table II presents the matrix correlation for all the variables. Correlation coefficient determines the behavior of two related variables and the extent of their relation, denoted by "R". Negative values of "R" show the negative correlation coefficient, whereas positive values show perfectly positive correlation coefficient relation. The correlation Coefficient is statistically significant when the values are above + 0.5. The Table clearly shows that the values are positive and approximately all the values are above + 0.5.

Lead in the form of tetraethyl lead acetate is used as antiknocking agent in petrol. It shows good relationship with Cu, Zn, Ni and Cd. The sample of tarry deposit were collected from busy congested

roads, therefore the source of tarry deposit may be vehicular traffic. Lead is antiknocking agent in petrol and copper is the component of engine; hence both are directly related in automobiles and have good agreement in correlation coefficient matrix. Manganese shows the lowest correlation co-efficient with all the metals studied. Although it is the component of tyres, but the values show that the correlation of manganese with other metals is not statistically significant. Zinc shows good agreement of correlation co-efficient with Ni and Cd, but its highest correlation was found 0.928 with copper. Nickel is also the component of tyres and motor oil. It shows significant relation with Pb, Cu, Zn and Cd. The source of these metals may also be the motor vehicles.

Thus Table II shows that the correlation coefficient between Pb, Cu, Mn, Ni and Cd are statistically significant and source of these elements in the tarry deposit on leaves may be the same as vehicular traffic.

The data collected was compared with the control site (PCSIR Laboratories Complex, Karachi) shows that almost all the pollution (70 %) is being generated by vehicular emissions. During the year 1970 to 2000, the total number of vehicles increased from 0.084 million in 1970 to 2.184 million in 1990 and upto 6.453 million in the year 2000 [19, 20]. Many of these vehicles are not well maintained and properly tuned. As such the emission of pollutants from these vehicles is much higher then the well maintained vehicles. Therefore, special attention should be given to check periodically the road worthiness of vehicles especially in metropolitan areas in order to control the pollution from automobiles.

Experimental

Twenty three samples of tarry deposit from leaves on the trees were collected from various intersections of main roads of Karachi city, where traffic density was very high. The samples were collected in the month of November and December 2004.

About 10 to 15 leaves were collected from each tree. The samples of the tree leaves were taken from different height and size. Leaf area was measured by using a graph paper. Tarry deposits on the leaves were removed and washed with petroleum ether in a tarred dish with the help of brush. Samples of tarry materials were gently refluxed with 2M Nitric acid for 30 minutes. After cooling the flask, the contents were filtered, through Whattman 42 filter paper into a graduated flask and diluted to the mark for the analysis. All glass-ware were extensively socked in diluted HNO_3 and rinsed twice with distilled water. The analysis of Cu, Mn, Zn and Ni were carried out by flame (FAAS), whereas Pb and Cd were carried out by flameless (ETÀAS) Atomic Absorption Spectrophotometer (Hitachi Z-800), using standard addition method. All reagents used for the preparation of samples for analysis were of ultra high purity grade. BDH, Spectrosol standard stock solutions were used for calibrations. The purity of distilled water used for the preparation of all the reagents and calibration standards was equivalent to ASTM specification type II reagent water [21].

Conclusions

The data collected shows that almost all the pollution in the environment of Karachi is being generated by automobile exhaust. Growing number of vehicles, leaded gasoline consumption and poor conditions of roads are the major causes of high concentration of tarry deposit and heavy metals level in the environment of Karachi.

References

1. J. Colls, Air Pollution- An Introduction, Spon Press, London. pp. 309 (1997)
2. M. A. A Beg, A. H. K. Yousufzai and S. N. Mahmood. *Pak. J. Sci. Ind. Res.*, **30**, 60 (1978)
3. F. Ismail and S. Ahmad, *J. Botany*, **16**, 117 (1984).
4. M. T. Mehmood and M. Z. Iqbal, *Pak. J. Sci. Ind. Res.*, **32**, 752 (1989).
5. N. Qadir and M. Z. Iqbal, *J. Envir. Studies*, **39**, 95 (1991).
6. M. Z Iqbal, M. Shafiq and S. F. Ali, *Turkish J. Botany*, **18**:475 (1994).
7. M. Z Iqbal and A.D. Siddiqui, *J. Environmental Studies*, **5**:67 (1996).
8. F. Khalid, M.Z. Iqbal and M.S. Qureshi, *Envir. Sci*, **4**, 213 (1996)
9. A. H. K. Yousufzai, M. A. A. Beg, S. N. Mahmood, *Pak. J. Sci. Ind. Res.*, **30**, 60 (1987).
10. A. H. K. Yousufzai, D. R. Hashmi, F. Ahmad and K. Durrani. *Pak. J. Sci. Ind. Res.*, 2001, **44**; 29 (2001).
11. S. S. H. Zaidi CENTO Panel on Regional

Aspect of Environmental Pollution. Tehran Report No: SCB /71/1/DIS, 52-29 (1972).
12. A. H. Chotani, M. P. Zakaullah, Z. Raza, *Pak. Acad. Sci.*, 39 (1975).
13. A. H. K. Yousufzai, M. A. A. Beg, S. N. Mahmood, Pak. J. Sci. Ind. Res., **34**, 52 (1991)
14. M. A. A Beg and Z. I. Shams, *Pak. J. Sci. Ind. Res.*, **32**, 395 (1989).
15. S. Verlag, The Natural Environment and Bio-Geochemical Cycle, Environmental Chemistry. Vol.1, Part a, PP 119 (1980).
16. I. H. Qureshi, *Proc. Pakistan Aced, Sci*, **37**: 109 (2000).
17. A. H. K. Yousufzai, *Pak. J. Sci. Ind. Res.*, **34**, 167 (1991).
18. M. W. Howard, B. Bruce, B. Sarah, H. Nancy *Envir. Res.* **34**:64-76 (1984).
19. M. J. Duggan and S. Williams, *The Science of the Total Environment*, **7**:91 (1977).
20. Anon, Federal Bureau of Statistics, Economics and Urban Advisory Wing, Government of Pakistan, Islamabad, Pakistan (2000).
21. Eton, Methods of preparation of reagent grade water, 1080C, Standard Methods for Examination of Water and Waste Water, APHA, 19th ed. pp. 1 (1995).