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AAS DETERMINATION OF LEAD AND CADMIUM IN LEAVES POLLUTED BY VEHICLE EXHAUST

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The determination of Pb and Cd in three different kinds of biological tissues, namely *Sapindus mukorossis*, *Alstonia scholaris* and *Diospyros embryopteris* collected from a national city park were carried out using atomic absorption spectrophotometry. The various tissues contain different concentrations of Pb and Cd. This phenomenon and changes in concentration with the distance to the sampling sites are discussed and compared with values reported in literature. Significant pollution is mainly due to vehicle exhaust.

KEY WORDS: Lead, cadmium, atomic absorption spectrophotometric technique, leaves, *Sapindus mukorossis*, *Alstonia scholaris*, *Diospyros embryopteris*, pollution.

INTRODUCTION

Lead and Cadmium are toxic to man. In the past two decades many environmental studies have revealed that atmospheric pollution due to automobile exhaust emission, is one of the major sources of heavy metal contamination in urban areas. This metal emission may then deposit on soil and vegetation in the vicinity to highways. Airborne Pb stems primarily from the combustion of leaded gasoline in motor vehicles, from the use of lead arsenate as a fungicide on crops and from industrial sources. Air in rural areas contains $0.1 \mu\text{g m}^{-3}$ of Pb as compared to $1-3 \mu\text{g m}^{-3}$ in urban areas. In an interesting study in Belgium, the Pb concentration on traffic-free days in air was determined to be $0.6 \mu\text{g m}^{-3}$ compared to $5 \mu\text{g m}^{-3}$ on normal days.¹ Cadmium is present as an impurity in zinc used, for example, in rubber tyres. Other major sources of cadmium pollution are industrial and waste incineration, fossil fuel combustion and treated sewage sludge. Air generally contains $1-300 \mu\text{g m}^{-3}$ of Cd, depending upon the extent of pollution of the area.²

About 10% of the petrol lead fallout occurs within 100m^3 around open roads. Considerably more lead is retained close to the roadside in urban areas, because of the interception of trees, shrubs and buildings.⁴ As some soil lead and most foliage lead originates from deposited petrol lead,⁵ this has caused much concern in thickly populated cities.

Pollution studies concerned with heavy metals around highways^{6,7} and roadside parks on plant leaves have been conducted in various countries. Ho and Tai⁸ have studied the potential use of a roadside fern, *Pteris vittata*, to biomonitor Pb and

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other aerial metal deposition, while Tam *et al.*⁹ have used the leaf of the *Bauhina variegata* plant for studying pollution due to Pb, Cd, Ni, Zn, Cu, Mn and Fe. Hibben *et al.*¹⁰ have used seven leaf crops along with their roots for the comparison of the Cd and Pb content of vegetables grown in urban and suburban gardens affected by air pollutants. The present work deals with the measurement of Pb and Cd in the leaves of three species, *Sapindus mukorossis*, *Alstonia Scholaris* and *Diospyros embryopteris* collected near the busy roadside in Lahore, the second largest city of Pakistan.

EXPERIMENTAL

Sample Collection

Three different plant leaf samples were collected from a national park (Bagh-e-Jinnah) situated near a very busy dual carriage way (Sharah-e-Quaid-e-Azam) at distances of 5, 50 and 500 feet away from the road. About 50 g of whole leaf were collected from different heights of each selected plant. After washing in deionized water the collected samples were freeze-dried at -148°C with liquid nitrogen and finally dried at 0.02 mbar pressure using a freeze drier Model Christ Beta A obtained through the IAEA. Next, each sample was ground to powder and stored in a sealed glass vessel. Caution was taken during collection, preparation and analysis of the samples to keep them homogeneous and uncontaminated.

Reagents

Stock solutions (100 mg/l) of Pb and Cd were prepared by dissolving cadmium chloride monohydrate (BDH) and lead nitrate (E. Merck) in deionized water. Standard solutions for the preparation of calibration curves were prepared by appropriate dilution of the stock solutions. Fresh working standards were prepared immediately before use. The concentration of the working standard was from 2.5 to 10 ppm for lead and 0.1 to 0.7 ppm for cadmium. Glassware was cleaned by soaking in 50% HNO_3 for 4 h and subsequently rinsed several times with deionized water. Perchloric acid (A.R. grade) and distilled nitric acid (Suprapure grade) were used for digestion of the samples.

Procedure

The method of Piper and Jackson¹¹ was used for the digestion of samples with slight modification of the glass apparatus, which is semi-closed and consists of a thermostat, reaction flask, condenser, "U" tube and ice bath. To avoid cross-contamination, each sample was digested in a separate set of apparatus. About 0.3 g of each of the samples, 3 ml of conc. HNO_3 and 0.5 ml of conc. HClO_4 were added to the reaction flask followed by heating at $50\text{--}70^{\circ}\text{C}$ till most of the sample had dissolved. Complete dissolution was achieved by raising the temperature to about 150°C and the final volume was made up to 10 ml in a measuring flask. In

Table 1 Instrumental atomic absorption spectrophotometer conditions

Parameter	For Pb	For Cd
Atomization	Flame	Flame
Lamp current	7.5 mA	7.5 mA
Wave length	283.3 nm	228.8 nm
Slit	1.3 nm	1.3 nm
Atomizer	Air-C ₂ H ₂	Air-C ₂ H ₂
Oxidant (air)	1.66 kg/cm ²	1.00 kg/cm ²
Fuel (C ₂ H ₂)	0.3 kg/cm ²	0.25 kg/cm ²
Burner height	7.5 mm	7.5 mm

Table 2 Measurement of Pb and Cd concentrations in various plant leaves

Plant	Sample No.	Distance (feet)	Pb $\mu\text{g/g}$ dry weight basis	Cd $\mu\text{g/g}$ dry weight basis
<i>Sapindus mukorossis</i>	1	5	31.2 \pm 1	22.69 \pm 0.20
	2	50	35.0 \pm 2	7.17 \pm 0.01
	3	500	16.6 \pm 1	4.49 \pm 0.25
<i>Alstonia scholaris</i>	4	5	206.3 \pm 2	1.59 \pm 0.01
	5	50	233.0 \pm 2.5	5.30 \pm 0.31
	6	500	313.5 \pm 3	7.13 \pm 0.01
<i>Diospyros embryopteris</i>	7	5	292.4 \pm 0.5	1.64 \pm 0.03
	8	50	241.6 \pm 4	1.50 \pm 0.02
	9	500	222.6 \pm 1	1.66 \pm 0.05

case of incomplete dissolution, the process of cooling to 100°C, addition of 0.2 ml conc. HNO₃ and reheating to about 150°C was repeated. The destruction time was different for each sample. Each sample solution was prepared in triplicate, while the blank solution was prepared under the same conditions without the leaves.

Instrumentation

The measurements were carried out in triplicate for each prepared solution with a polarized atomic absorption spectrophotometer (Hitachi Model Z-8000) under instrumental conditions recorded in Table 1. The absorption signals during the atomization steps were recorded by computer and printer. This instrument has a detection limit for Pb from 2 to 12 ppm, and for Cd from 0.1 to 0.6 ppm. Under usual experimental conditions, the relative error for Pb is 0.5–1%, and for Cd 0.5%

RESULTS AND DISCUSSION

The concentration of Pb and Cd in the leaves of three plants are given in Table 2 on a per microgram dry weight basis. *Sapindus mukorossis* has apparently accumulated a much smaller amount of lead as compared to the two other species,

although they originate from the same sampling area. The opposite trend was shown for cadmium with the same species. This kind of differences has also been observed for Pb by Furr *et al.*¹² while Robert and Green¹³ have mentioned that tobacco leaves can concentrate 10-fold higher amounts of Cd than other plants when grown on contaminated soil. Actually a wide variety of conditions can affect the level of heavy metals that may be toxic to plants or taken up by vegetation and eventually consumed by humans. Different plant and tree species in the environment can thus accumulate metals at varying concentrations.

It is also worthwhile to note the effect of washing on the final determination of Pb and Cd in the leaf samples. According to Backhaus and Backhaus¹⁴ more information on the specificity of Pb binding and the mode of Pb action in foliage tissue would be needed. From their preliminary experiments on Cd and Pb binding in exposed needles, it can be concluded that a considerable amount of the total Cd and Pb load is strongly bound to unidentified non-soluble tissue constituents, whereas only a small part can be attributed to surface contamination. According to Tam *et al.*⁹ washing had little effect on reducing the leaf Pb content. This indicated that a large portion of Pb present in their leaves was non-washable and the insoluble fraction was ionically bound to the cuticular membrane or cell walls of the leaves. Although Hibben *et al.*¹⁰ have used unwashed leaves in their work on the comparison of Cd and Pb contents of vegetable crops grown in urban and suburban gardens, they have also reported that rinsing of the harvested leaves did not reduce the Cd levels. We have, therefore, preferred in the present study to wash the leaves mildly prior to their freeze-drying and acid digestion, assuming that it has no significant effect on the final determination of the Pb and Cd content of the leaves.

There is no apparent relationship of the Pb and Cd levels recorded in Table 2 with the distance of the sampling sites from the roadside. The values of Pb in *Sapindus mukorossis* rise and fall with an increasing distance from the roadside. An increase in both the values of Pb and Cd with increasing distance is shown by the leaves of *Alstonia scholaris*. The values of Pb in *Diospyros embryopteris* and of Cd in *Sapindus mukorossis*, however, show the expected decreasing trend with increasing distance. Such variations can be explained if the site of sample collection is kept in mind. This site is, in fact, surrounded by roads from all sides. Some of the sampling points, though away from the Shahrah, are near to other roads. The prevailing wind, which changes its direction over the year can thus increase the deposition of toxic metals on tree leaves from all directions. Therefore, a linear decrease in Pb and Cd values with increasing distance cannot be expected in all the collected samples in a limited space of Bagh-e-Jinnah, covering an area less than 1 km². Harrison *et al.*⁷ have also concluded that 90% of the Pb emissions are dispersed by the atmosphere away from the immediate vicinity of the road.

It is also interesting to observe the variations in the concentration of Pb and Cd accumulated in different plant species studied by various workers (Table 3). Although variation in concentration values is expected due to e.g., differences in species in these studies, the values of Pb in the present work are especially high in the leaves of *Alstonia scholaris* and *Diospyros embryopteris*. Similarly, the increased

Table 3 Comparison of Pb and Cd concentrations in different plants under various conditions

<i>Plant type (location)</i>	<i>Study condition</i>	<i>Pb µg/g dry weight basis</i>	<i>Cd ug/g dry weight basis</i>	<i>Reference</i>
<i>Bauhina variegata</i> leaves (Hong Kong)	Urban park near busy road	74	—————	9
Vegetable leaves (New York)	City environment	7.89 ^a	1.315 ^a	10
<i>Zostera marina</i> leaves (Denmark)	Coastal areas	4.6	2.3	15
Vegetables (Tehran)	Domestic waste water for irrigation	0.705 ^a	0.475 ^a	16
Standing crop (North West England)	0.5 m from roadside	947	—————	17
Spirogyra (Norway)	Lake Invanhoe	368	—————	18
Hydrilla (Norway)	Lake Invanhoe	248	—————	18
<i>Sapindus mukorossis</i> leaves (Lahore)	Urban park near busy road	27.6 ^b	11.45 ^b	Present work
<i>Alstonia scholaris</i> leaves (Lahore)	Urban park near busy road	250.9 ^b	4.67 ^b	Present work
<i>Diospyros embryopteris</i> leaves (Lahore)	Urban park near busy road	252.2 ^b	1.6 ^b	Present work

^aCalculated average values.^bAverage of 27 determinations.

concentration of Cd in the leaves of *Sapindus mukorossis* is also rather prominent in the present results.

CONCLUSION

The present study reveals that Pb and Cd contamination of roadside parks due to heavy traffic is significant. Because Bagh-e-Jinnah in Lahore city is surrounded by heavy vehicular traffic and because the number of such community gardens is increasing, we believe it is essential to learn more about such contamination. Regular monitoring of Pb levels in leaves could serve as an inexpensive and simple biomonitor of atmospheric pollution caused by automobiles.

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