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STUDIES USING NUCLEAR AND COMPLEMENTARY NON-NUCLEAR ANALYTICAL TECHNIQUES FOR BIO-MONITORING OF AIR POLLUTION

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Abstract

A set of lower and higher plants have been analysed for their trace element contents. The plants are; a moss (Funaria sp.), a bryophyte (Cyathodium sp.), a weed (Parthenium hysterophorus L.) and a common bushy shrub (Lantana Camera L.). The trace element concentrations have been determined using INAA, PIGE and ICP-OES. The data are examined with a view to assess the use of these plants as bio-indicators of toxic trace metal pollutants in ambient air. The moss and the bryophyte samples show much higher accumulation levels for many elements, but are seasonal. The other two plants, due to their perennial nature, can be used for bio-montoring purposes, almost throughout the year.

1. SCIENTIFIC BACKGROUND

Human beings, plants and animals are directly exposed to contaminants in the ambient air and the pollutants enter the organisms through various pathways. Many plant and animal species are known to accumulate these trace elements from terrestrial and aquatic environments. While air particulate analysis is able to indicate the particulate bound fraction, the pollutants present in gaseous forms at the moment of sampling of the air particulates can escape detection. Some plants when exposed to both particulate and gaseous pollutants have been shown to absorb them through precipitaion or physical trapping and serve as indicators as to the level and type of these metallic pollutants.

The term bio-indicator may be used to represent plant species that are susceptible to the presence of pollutants and the absence of these plant species (alternately, a reduction in their population) can be qualitatively used to identify the extent of pollution. An operational definition is given [1] that , "bio-indicators (i.e. biomonitors) are organisms which can be used for the recognition and quantitative determination of anthropogenically induced environmental factors". In biomonitoring using plants, a distinction has to be made between active and passive chemical monitoring. Active bio-monitoring includes the exposure of well defined plant species to controlled conditions while the passive monitoring refers to the observation or chemical analysis of indigenous plants.

From the analytical point of view, due to bioaccumulation in plants, the concentrations of many elements being at elevated levels, the analytical uncertainties would be much lower when compared to the direct analysis of air particulate material or gaseous contaminants in air. Also from the point of view of sampling, passive bio-monitoring is much easier, quantity of samples can be larger and needs no special equipment. Thus bio-monitoring through plants offers a viable technique to recognize the presence and quantitatively estimate (anthropogenically introduced) metallic contaminants in ambient air.

2. SCOPE OF OUR PROJECT WORK

Atmospheric pollution (particulate and chemical) levels in many Indian cities are alarmingly high with TSP far exceeding the WHO limits. Vehicular pollution contributes more than 80% of the pollutants of various kinds. In addition, industrial pollution is also significant in many cities as many industries tend to be located within or around major cities only.

One of the major objectives of our Centre, the National Centre for Compositional Characterisation of Materials (CCCM), set up in Hyderbad by the Department of Atomic Energy, is to provide validation support to national programmes through the development of standardised analytical methodology, personnel training and issue of reference materials in environmental and biological (health related) studies. Towards this end, the Centre is equipped with several analytical instruments covering nuclear, spectrochemical, electrochemical and chromatographic techniques. Hyderabad, a fast developing metropolis, is also experiencing a rapid decline of air quality. We have taken up studies earlier, towards the determination of inorganic toxic trace elements in ground water and lake waters in Hyderabad. Our participation in this CRP, is to establish the role of bio-monitoring through plants as a means to assess the air quality, initially in the local (Hyderabad City) level and then expand to other areas through our own studies and with the help of other institutions (mainly for sampling).

3. METHODS

3.1. Selection of plant species

We have chosen the passive bio-monitoring approach through chemical analysis of some widely distributed plant varieties. In the first year the we laid emphasis on identifying the plant species and sampling locations, pertaining mainly to vehicular pollution.

Moss: (Funaria sp.)

Mosses and other lower plants have been established to accumulate in them heavy metals (in considerable quantities) which have been correlated to atmospheric trace element levels [2]. Thus we have collected a common moss Funaria, which grows as dark green patches on old brick walls and in cool, shady areas, from several locations. The plant body is erect and consists of a slender central axis bearing green, flat leaf like expansions. The basal part of the axis gives rise to many rhizoids (root loke structures). Considerable amounts of base soil or wall materials adhere to the rhizoids. This moss specie grows in abundance, only during the rainy season, but Hyderabad receives rains (though somewhat less) both during the south-west and north-east monsoon periods and the moss can be sampled over a period of 4-6 months with a gap of two months between the two monsoon periods. Sample amounts ranging from 0.5-2 kg were collected (including the sub-soil adhering to the moss), from different locations.

Bryophyte: (Cyathodium sp.)

This lower plant has been sampled from Bombay, which receives copius amounts of rain but only during the north-west moonsoon. The sample were collected along the walls of a storm water drainage in a housing colony and along a nearby motor way with heavy traffic. This is found growing along with the patches of Funaria, but has a fluorescent green colour and grows like a carpet covering the walls. This variety appears to be nearly absent in Hyderabad. Nearly 0.5 kg of the fresh plant was collected almost free from the sub-soil.

Weed (Parthenium hysterophorous L.)

The Parthenium, is an imported weed! This is native of West Indies and tropical north and south Americas. But it is found throughout India in many cities and villages and possesses a tendency to be a perennial weed. The plant usually grows to height of 1 to 1.5m. Parthenium is also found throughout Hyderabad, abundant along the roadways. This plant is known to cause contact dermatitis to some sensitized individuals. We have carefully sampled the leaves of this plants at different locations, along a motor way (over 1km. stretch), inside housing colonies and from remote places far away from motor traffic.

A shurb (Lantana Camera L.)

This bushy plant is widely distributed and is grown as a fence but is also found as a wild growth in many places. It is a perennial shrub, with older parts woody and the leaves leathery and covered with cuticular hair. The leaves of this plant have been sampled along motor ways and in housing colonies. The plant grows to 1-2m in height with thick foliage and many branches

The leaves of Parthenium and Lantana plants have been sampled 1 foot above the ground level. Nearly 0.2- 0.5 kg of fresh leaves, without any visible infection, were collected in a sampling area from several individual plants.

3.2. Sample preparation

The top green, leafy portion of the moss was cropped with a scissor and washed with DI water and washed three times with DI water using an ultrasonic bath until the water was clear from dirt or suspended matter. The bryophyte and the leaves of Parthenium and Lantena were also cleaned with DI water and ultrasonification. They were individually dried, under cover, inside a hot air oven at 40-50° C. The dried matter was ground to a fine powder using a agate grinding assembly and stored in polythene bottles.

3.3. Sample analyses

Preliminary multielement analysis of these samples were carried out using Proton Induce Gamma Emission (PIGE) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) at our Centre. IAEA reference sample IAEA-140/TM, Fucus, (Sea Plant Homogenate) was used for validation of the analytical methods.

3.3.1. Analysis with PIGE

The PIGE analyses were carried out using the 3MV Tandetron accelerator facility at the Surface and Profile measurement lab. of our Centre. The powdered samples (ca. 300 mg aliquots) were mixed with pure graphite powder and pelletized. The pellets were irradiated using a proton beam and the ensuing gamma rays were counted using a portable HPGe detector. The concentrations of F, N, Na, Al, Si, P and Cl were determined using suitable standards. The details of the PIGE analyses are given in Table I.

3.3.2. Analyses with ICP-AES

The ICP-AES (JY 38 system) analyses were carried out after microwave digestion of the samples. Both open microwave digestions (500 mg. sample, HNO3 and hydrogen peroxide) and closed microwave digestion in PTFE bombs (100-200mg, HNO3) were carried out. The digests were suitably diluted with DI water and analysed using standard addition calibration procedure.

Almost all the digests, especially those of Funaria and parthenium samples, had some undigested material (mostly silica) and in such cases the clear supernatant layer was used for analysis.

4. RESULTS AND DISCUSSION

Elemental concentrations for elements determined using PIGE and ICP-AES in the IAEA Sea plant homogenate sample are given in Table II, showing fairly good agreement.

The values of the trace elements, determined in these plant samples, are given in Table III. The values are given in mg/kg (ppm) units on dry weight basis and are average values of 2 or 3 independent determinations with variations well within 5% RSD. Aluminium was determined both using PIGE and ICP-AES to assess the inter-technique agreement. A typical PIGE spectrum is shown in Fig.1.

Among the samples collected within the Hyderabad city, the moss samples have shown much higher concentrations of trace elements compared to other varieties. Funaria (M), the moss sampled on a old wall near a dusty road with fairly high traffic, showed considerably elevated values of Al, Na, P, Si, Cr and Pb. The other moss sample Funaria (SB) also showed high values of Pb and Cr. Both these samples were collected at a level of 1.5-2m above the ground level. In other reported studies also, mosses have been known to exhibit considerably elevated levels of concentrations of many heavy metals, taken up either through precipitation (rain) and through trapping of atmospheric dust and this has been attributed to ion-exchange properties of moss [1]. High values of nickel was noticed in the Parthenium weed samples. Aluminium values by PIGE are marginally higher than those obtained using ICP-OES after chemical digestion, indicating that some of the aluminium is bound to the undissolved silica fraction (found in almost all digests).

The parthenium leaf samples, Par(M), Par(C) and Par(V), represent those samples from along a busy main road (2-3 metres from the road on either side), those inside a housing colony located along this main road (500m interior) and those samples from nearly 1.5 km. away from the road in agricultural fields, respectively. The decrease in the lead content as one moves away from the traffic, illustrated in Fig.2, is indicative of the extent of lead pollution caused through vehicular traffic. In addition. the levels of Pb, as expected, were higher in plant samples (Funaria and Parthenium) collected along busy roads. Lead appears to be bound to fine dust particles and this very fine dust adhered to the surface of the leaves were not removed even by ultrasonic cleaning. A rough association of aluminium and lead, also shown in Fig.2, in these plants, may be indicative of the lead associated with atmospheric dust, kicked up by vehicular traffic. The analysis of the shrub Lantana Camera sampled from the same location as sample PAR(C) also showed similar Pb content, even though the aluminium content was lower.

The concentrations of many trace elements in the bryophyte (Cyathodium sp.) collected from two localities in Bombay are much higher than even the Funaria samples from Hyderabad. Inter species different apart, with respect to uptake of trace elements, these numbers can be taken to represent the pollution levels in Bombay, which are expected to be higher than Hyderabad.

An interesting aspect is the high concentrations of fluorine in all the samples. F is usually considered a gaseous component and its source in all these samples is not clear.

5. FUTURE WORK

In addition to the above plants, it is proposed to include samples of some tree leaves which can be sampled in summer as well. Samples from areas, polluted by the presence of different industries, are planned to be collected, with a sampling frequency of once in two months. It is also planned to collect air particulates, from locations affected by industrial and vehicular pollution, along with the plant samples, with a view to correlate the two.

Due to high levels of construction activity in the Hyderabad region, it will perhaps be difficult to obtain samples of the moss Funaria in future. Efforts are now underway to grow this plant on bricks and translocate them in polluted areas and harvest the moss later after a specific period of exposure.

We plan to procure a cryo-ball mill with PTFE / KEL-F liners to homogenize the samples to ensure contamination free sample preparation. PIXE and ICP-MS techniques, are planned to be used in subsequent studies to extend the elemental coverage and to provide cross validation of results.

6. CONCLUSIONS

The preliminary studies carried out using these four plant varieties have shown that the observed concentrations of some elements, particularly Pb, Al, Si and Cr values, can be attributed to air pollution caused by vehicular movement. The moss (Funaria sp.) and the bryophyte Cyathodium appear to be very promising plants, for use in identifying trace metal pollution (cumulative) in the ambient air, but both the plants are seasonal. The Parthenium and Lantana plants, being near perennial, can be sampled over longer durations and used for the study of exposures to trace metal pollutants.

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Table I. Proton Induced Gamma Ray Emission (PIGE) Analysis

Element	Gamma Ray Energy (keV)	Reaction
F	110	$^{19}F(p,p_1\gamma)^{19}F$
	197	$^{19}F(p,p_2\gamma)^{19}F$
Na	440	$^{23}Na(p,p_1\gamma)^{23}Na$
Al	1013	$^{27}Al(p,p_2\gamma)^{27}Al$
Si	1273	$^{29}Si(p,p_1\gamma)^{29}Si$
P	1266	$^{31}P(p,p_1\gamma)^{31}P$

Experimental Conditions:

Proton Energy	3/4 MeV
Beam Current	5-10 nA
Incidence	Normal
Detector	Portable HPGe (40%)
Position of Det.	90° to beam direction

Table II. Analysis of IAEA RM Sea Plant Homogenate using PIGE and ICP-AES
(n=2, dry weight , values in mg/kg unless indicated otherwise)

Element	**Technique**	**Conc.**	**IAEA values.**
Al	PIGE	1041	1184 (919-1449)
Mg	PIGE	8400	9070(8190-9950)
Na	PIGE	3.8%	3.2%(2.54-3.8%)
Cr	ICP-AES	10	10.4(9.6-11.2)
Mn	ICP-AES	52.2	56.1(53.7-58.5)
Cd	ICP-AES	0.5	0.537(0.50-0.574)
Pb	ICP-AES	2.0	2.19(1.91-2.47)
Fe	ICP-AES	1138	1256(1221-1291)
Zn	ICP-AES	50.5	47.3(45.3-49.3)

Table III. Trace element concentrations in the plants from some locations.
(in mg/kg, unless indicated otherwise,dry weight basis)

Element[a]	Par(M)	Par(C)	Par(V)	Tul.	Fun(M)	Fun(SB)	Lan	Cya(ASN)	Cya(ST)
Al(PIGE)	180	60	nd	138	3800		133	0.63% (?)	1530 (?)
Al(ICP-OES)	102	81	15	128	2885	535	38	1.56%	3625
Pb	15	10	1.5	1.2	28.2	10	8.1	55	38
Ni	143	128	360	62	24	18	63	102	31
Mn	16.7	17.1	59	33	21.4	50	64	476	111
Cu	3.5	4.3	21.2	11	15.1	17.1	8.5	48.3	24.1
Cr	0.97	0.30	<0.1	<0.1	8.8	3.1	<0.1	64.3	16.4
Si	nd	nd	nd	0.44%	11.58%	nd	0.82%	14.3%	4.10%
P	0.62%	0.57%	nd	0.49%	0.79%	nd	0.50%	0.61%	0.61%
F	483	374	nd	685	0.77%	nd	256	402	254
Na	336	194	nd	1.58%	0.96%	nd	222	0.52%	0.24%
N	8.73%	6.05%	nd	4.09%	2.36%	nd	3.89%	2.28%	3.26%
Cl	4.96%	3.9%	nd	3.68%	nd	nd	1.4%	2.5%	2.9%

(a) Al,Si,P,F,Na,N and Cl were determined using PIGE.

Abbreviations:

Par: Parthenium Hystophorus L.., M,C,and V represent sampling locations
Tul: Tulasi
Fun: Moss Funaria. M and SB represent sampling locations
Lan: Lantana Camera L.
Cya: Bryophyte Cyathodium sp. ASN and ST represent sampling locations in Bombay.

nd: not determined

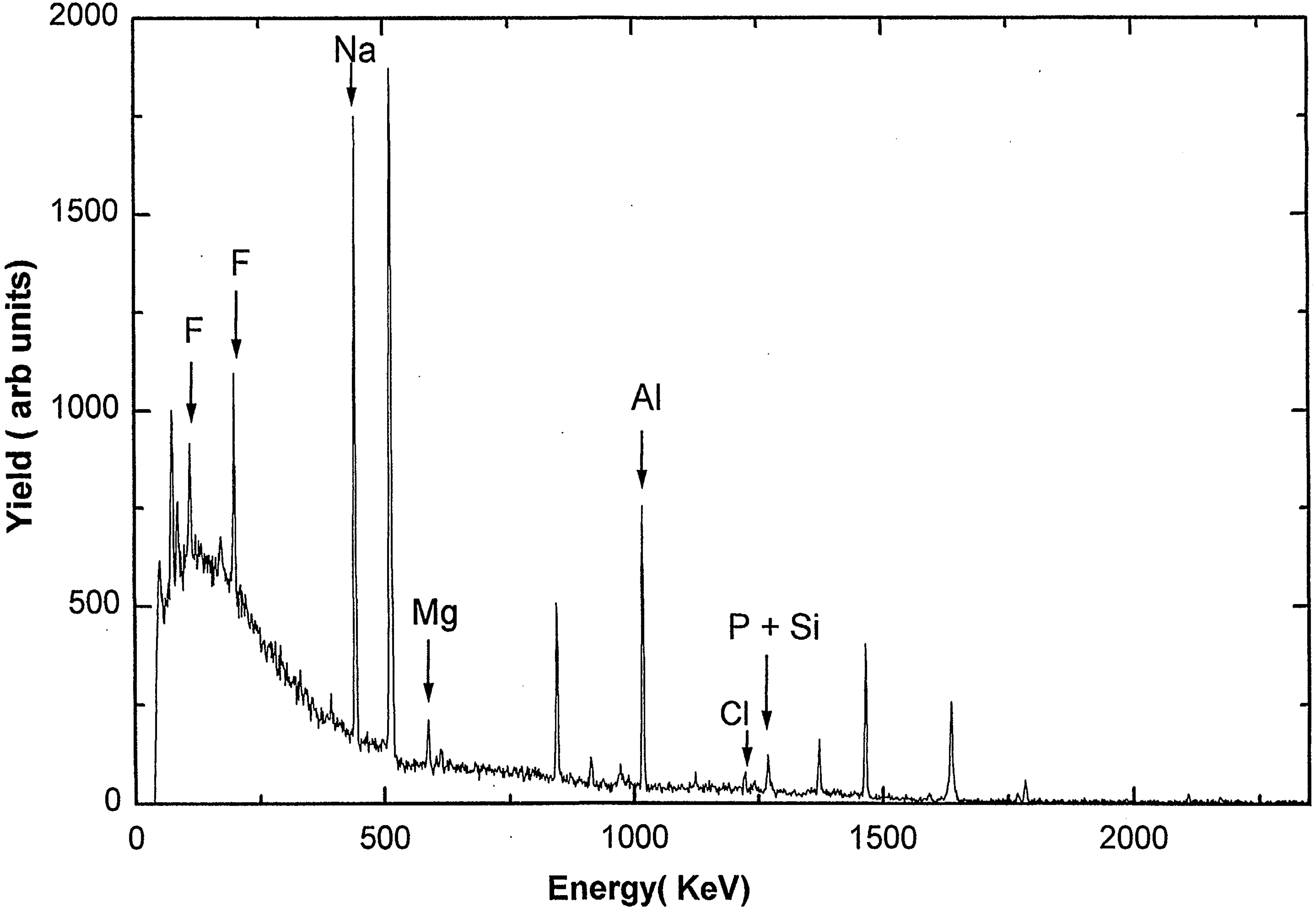

Fig.1.PIGE spectrum of Bryophyte Cyathodium Sp. (E_p = 3 MeV)

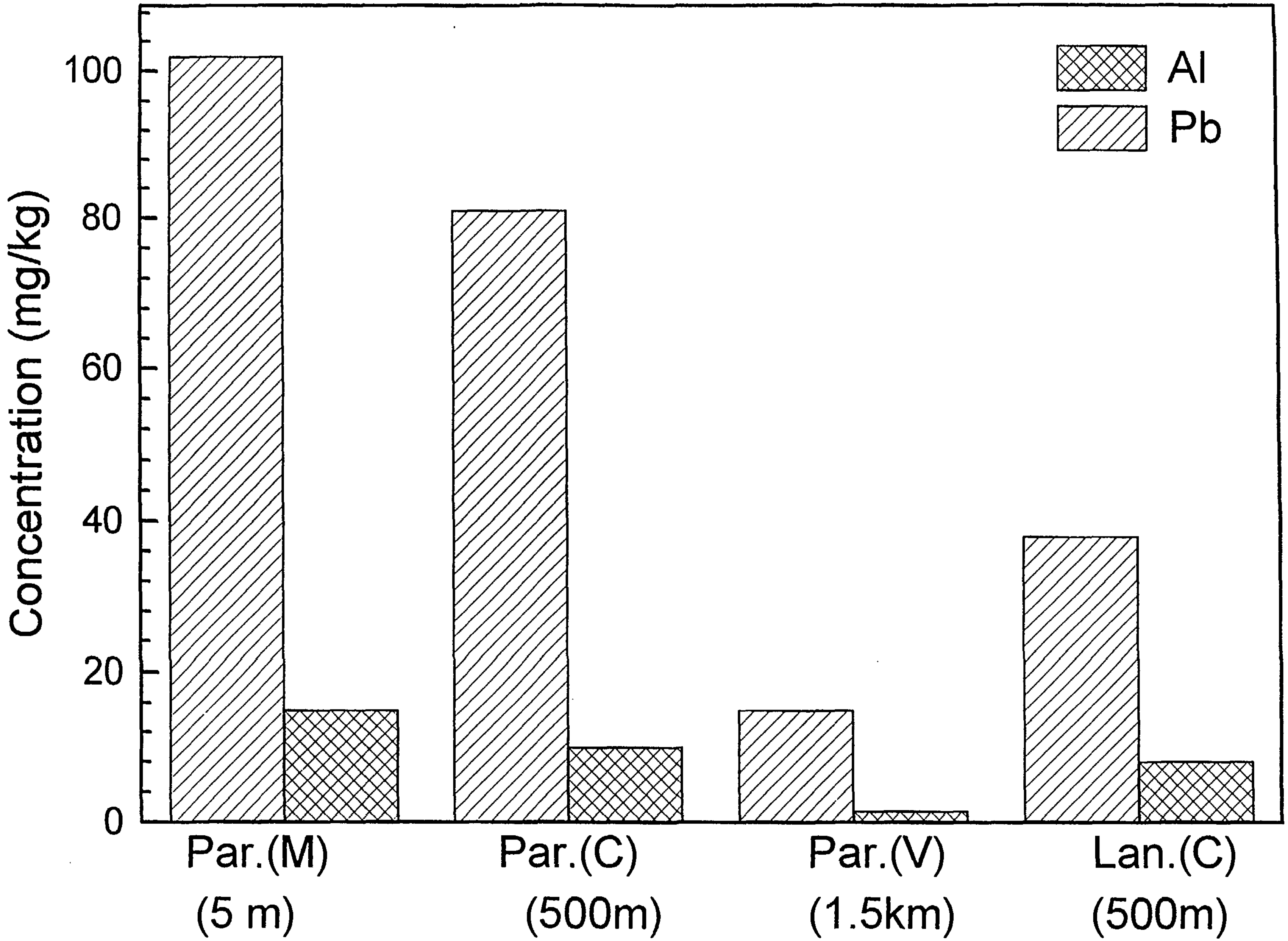

Fig.2. Aluminium and Lead Concentrations in relation to vehicular traffic