BIO-MONITORING STUDIES USING NUCLEAR AND RELATED TECHNIQUES FOR THE STUDY OF AIR POLLUTION IN AND AROUND THE CITY OF HYDERABAD, INDIA

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Abstract:

Passive bio-monitoring using different plant species affords a cost effective approach to studies on environmental trace element pollution. Lower plants like mosses and lichens have already been demonstrated to be effective bio monitors.

As part of our participation in the IAEA's Co-Ordinated Research Program on "Validation and application of plants as bio-monitors of trace element atmospheric pollution analyzed by nuclear and related techniques", we have carried out studies on the use of a moss (Funaria hygrometrica) and a shrub (Lanatana Camera). About 35 sampling locations covering industrial zones, locations with heavy traffic, commercial and residential areas were identified. The samples have been analyzed using ICP-MS and PIGE to provide elemental concentrations on a number of elements. Electron microscopic images of the moss show physical trapping of fine particulate matter. The data are examined with a view to assess the use of these plants as bio-monitors of toxic trace elements. The moss, available only during the monsoon, shows, on a dry weight basis, much higher levels of concentrations for many elements, than the shrub (leaves). The concentration profiles in relation to the sampling locations suggest that metallic pollution can be easily discerned. The elemental data are examined using principle component analysis. While the qualitative identification of the metallic pollutants is easier with reference to the sampling locations, it would also require complimentary information using other techniques to provide a quantitative estimate of total environmental trace element burden.

1. INTRODUCTION

As part of out participation in this CRP, we had earlier analysed a set of lower plants: mosses (Funaria sp. and Cyathodium sp.) and a set of higher plants(a weed: Parthenium hysterophorus L. and a common bushy shrub Lantana Camera L.). Samples from different locations were collected and analyzed using PIGE and ICP-OES. These studies had shown that vehicular pollution is easy to discern.

The weed Parthenium though available in plenty during the monsoon seasons and is near perennial, is identified to be a health hazard to both humans and animals and hence we discontinued the collection and study of this plant for the bio-monitoring purposes. The collections and study of Funaria and Lanatana were continued and the results obtained subsequent to the first RCM are presented.

2. METHODS

2.1. Sampling

Moss samples:

The moss Funaria is available during monsoon periods only and grows on old brick walls (without cement mortar cover). It grows as broad patches, usually on the earlier dried patches. The Funaria was sampled during the last monsoon period (July-August 1999) from different locations in the city where the growth was found to be abundant to enable the collection of 0.2-0.5 kg of sample in each location.. The plant is hand picked from about a height of 2-3 metres from the ground level. The soil bound to the basal parts (root like fibres called rhizoids) of the plant are removed to the extent possible and stored in perforated polythene bags in a fridge.

Lantana Samples:

Lantana Camera is widely distributed and is a near perennial shrub. The leaves of this plant were sampled from nearly 35 sampling locations, covering industrial estates, commercial zones with of heavy traffic, housing areas and isolated places with very little human activity. The leaves were sampled from healthy plants from a height of about 1-2 m above the ground levels. In each location, leaf samples from 4 to 5 individual plants were sampled and mixed to form a common sample. Leaves with infection or perforations were discarded. They were stored in perforated polythene bags and stored in a fridge until analysis.

2.2. Sample Preparation

Samples of the moss, cleaned from much of the soil fraction from the basal parts, were taken (100-200g portions) in a beaker and washed with DI water with agitation in an ultrasonic bath for 1 minute. Where the soil particles were still seen to be released, one more agitation cycle was repeated. The water was drained by keeping the washed mass on a plastic sieve for some time, taken in a wide mouth beaker and oven dried for 24 hours at 45-50°C. The dried samples were ground in an agate grinding assembly and stored in polythene bottles.

The composite Lantana (leaf) samples (100-200g aliquots) were also washed once with DI water for about 30 secs., drained of water by keeping on a plastic sieve and dried under conditions similar to those of the moss samples. The powdered samples were stored in polythene bottles until analysis.

2.3. Analysis of samples

The powdered sampled were digested using microwave digestion with conc.nitric acid. Multi-element analysis of these digests samples were carried out using ICP-MS (VG-PlasmaQuad III isntrument, VG Elemental, U.K), located in the Ultratrace Analysis laboratory. Proton Induced Gamma ray Emission(PIGE) analyses were carried out using the 3MV Tandetron Accelerator(High Voltage Engineering Europa, Holland) facility at the Surface and Profile Measurement lab. of our Centre.

2.3.1.Sample Digestion

200-300 mg aliquots of the powdered sample were taken in Parr PTFE digestion vessels(45 ml volume). 3ml of concentrated nitric acid was added. The digestion was carried out for 3 minutes at high power (650 watts). Upon cooling, the digest was later taken in standard flasks, diluted to 25 ml with DI water. Appropriate blanks were also prepared in the same way. The digests of the Lantana samples were always clear but digests of Funaraia showed some sediment on standing indicating some unattacked soil fractions clinging to samples despite the wash cycle. Only clear supernatant portions of the Funaria digests were analyzed.

2.3.2. Analysis using ICP-MS

The Lantana and the funaria digests were suitably diluted with high purity water obtained using a Milli-Q water system and analyzed using external calibration procedure. NIST Multi-element standards 3171A (mix A1) and 3172A(mix B1) were used. NIST SRM Oyster 1566a tissue was used for validating the analytical procedure. Rh and Re were used as internal standards for the analysis.

2.3.3. Analysis using PIGE

The analysis of some the Funaria and Lantana samples were carried out using PIGE. The powdered sample (ca. 300 mg) was mixed with high purity graphite powder and pelletized. The pellets were irradiated using a proton beam and the ensuing gamma spectra were recorded, using a HPGe detector.

3. RESULTS AND DISCUSSION

The elemental data obtained on the Lantana and Funaria samples are given in Tables I and Table II respectively. As is seen the concentrations in Funaria are much higher than the Lanatana indicating the ability of the moss samples to accumulate the trace elements.

3.1. Lantana samples

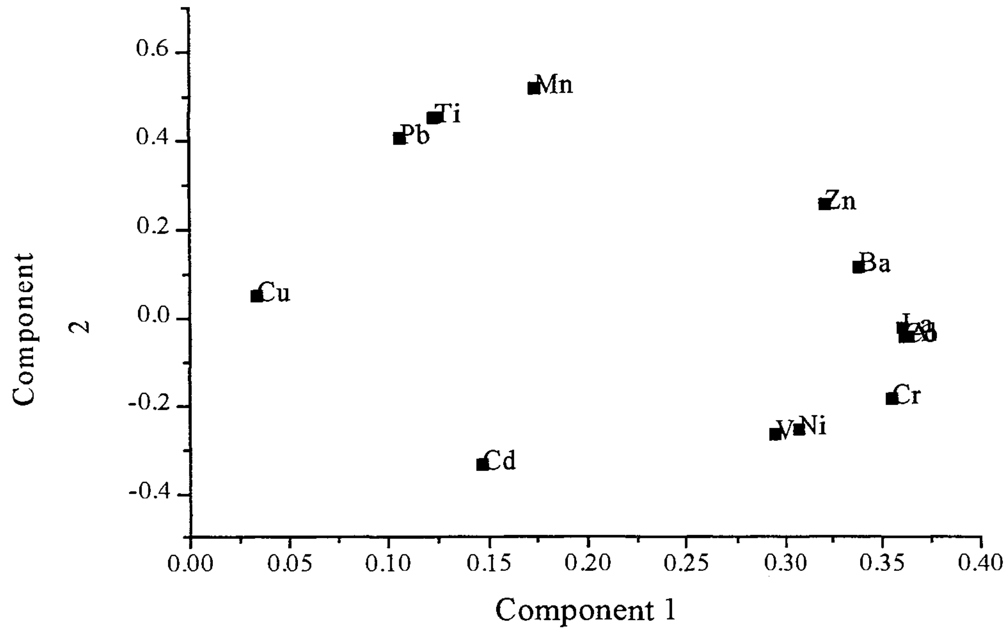
3.1.1. Local Variations and exposure

The variations within a sampling locality were studied and are given for two locations (JDM2,JDM 4 and Pattancheru 2 and 3) in Table III. As is seen, variations of concentrations on many elements seem to be very small within a locality. Also given in Table III, are the results on the Lanatana samples collected near a foundry (JDM3), which show considerably enhanced levels of concentrations for all the elements. JDM 2 and JDM4 are about 500m away from this location. This would essentially suggest that the exposure to and accumulation of trace elements in Lantana is within a restricted zone.

Thus establishing the local variations within a plant species is important prerequisite to identify 'local hot spots' and establish the source and the area likely to be affected by the source.

3.1.2. Principal Component Analysis (PCA) of the elemental concentrations

PCA is a powerful multivariate statistical approach for the study of associations among the variables; in addition in can also help infer 'independent causal factors' which can be used to account for the dispersion in the data set. The multi-elemental data obtained on the Lanatana samples from different locations were examined using PCA, which suggested 4 'factors' to account for the variability; however the first two components account for nearly 70% of the total variance. The plot of the eigen vector coefficients of the first two components is given in Fig.1.



The Communalities, i.e., the fraction of variance accounted for by each component for the given set of variables (elements) is given in Table IV. The first component alone accounts for nearly 80-95% of the total variance of Al, Cr, Co, Ba and La; it also accounts for 61% ,67% and 74% of the variances of V, Ni and Zn respectively. This information, in association with the plot given in Fig would suggest that the 'soil fraction' could be the dominant factor. Only a fraction of Pb and Cd are associated with this component.

The coefficients of the first and second components suggest an association of Ti,Mn and Pb with the second component accounting for 39%, 52% and 32% of the total variance of these elements. The first and third component suggest an association of V, Pb and Cd with the third component accounting for 20%,36% and 56% of the variances associated with these elements. The physical factors that would account for the suggested association of Ti,Mn and Pb; and V,Pb and Cd are not apparent, in this juncture. Further, copper is not accounted for in any of first three factors and a fourth component accounts for nearly 87% of the variance in copper.

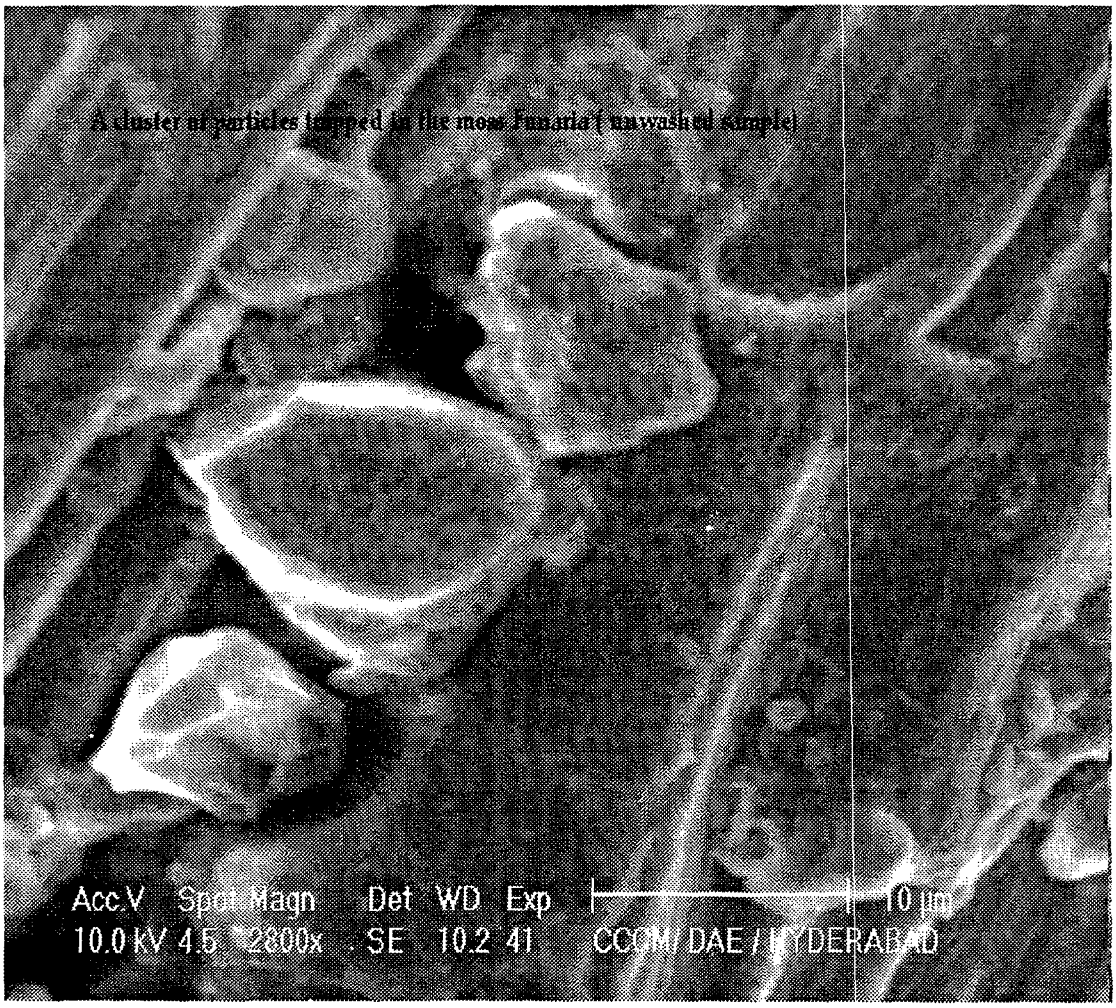
The plot of the 'component scores' on the first two components of the Lanatana samples from different locations are given in Fig. showing areas of high metallic pollution. The cluster of other sample points can be used to establish the base values of the concentrations of the elements (in Lantana) and locations where significant deviations occur can be probed for possible sources of pollutants.

3.2. Funaria Samples

3.2.1. Physical Trapping of particulate matter in Funaria:

As mentioned earlier, a lot of soil fraction is adhered to the Funaria and it not easily removed. The scanning electron microscopic image given in Fig.2 shows the trapping of such particulate matter in Funaria.

Fig.2. SEM image of soil particles trapped in a Funaria moss sample.



As is seen these particles are of about 10 microns or lower in size. The X-ray spectra obtained on these particles partciles show that they are essentially composed of Si, Al and oxygen indicating that they are mainly soil particles. A typical x-ray spectrum obained on one such particles is given in Fig.3.

Energy Dispersive X-ray Spectrum of a typical trapped particle (in Funaria)

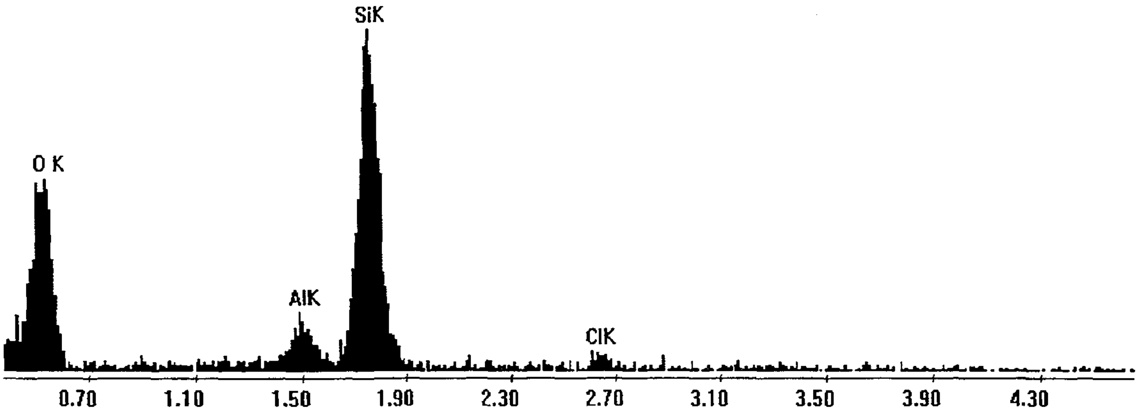


Fig.3 :EDXRF spectrum of a typical soil particle trapped in Funaria

The images of the washed samples of Funaria show a typically smaller density if trapped particles and also of smaller sizes, indicating that the washing cycle is able to remove particles of larger size.

The effect of washing on the elemental concentrations on the Lantana samples was studied. Leaves of lantana collected from a single plant, near a foundry in an industrial area, visibly covered by dust, were analyzed with and without washing them. The washing resulted in a reduction of nearly 20% in the concentrations of Al, Ti, V, Cr, Sr, Ba and Pb but showed almost no change in rest of the elements, suggesting either 'in situ' biological levels these elements or substantial fine soil fraction still adhering to the leaf surface. Analysis using multivariate statistical approaches like PCA can help elucidate such information.

Future work:

The second phase of our work under the CRP has suggested that local variations in the elemental concentrations in the plants are smaller and samples collected from locations with identifiable pollution sources have significantly higher concentrations. But the dispersal of these metallic pollutants seem to be within a 'restricted zone' around the source. It is planned to establish this 'zone of dispersal' around the some of the locations already studied. Atmospheric dust forms the predominant form of air pollution in Hyderabad and the particles trapped in Funaria show a size distribution of 10 microns or less. Thus another activity that is planned is to collect these fine particulate matter so as to examine feasibility of using these plants to study the elemental concentrations in these fine fractions.

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Table II. Elemental Concentration in Funaria from some locations.

Element	K-Nag	CPalli	M-Ali	Lguda	Nachr	Secbd	Seri	CCCM	Pchr
Al	506	335	388	878	1112	1080	810	1600	1000
Ti	76	91	124	141	56	88	45	159	113
V	7.1	11.6	4.9	5.9	5.9	5.5	5.4	1.3	10
Cr	5.6	3.6	3.8	4.9	8.1	7.1	6.2	7.4	8.7
Mn	43	27	41	34	70	57	50.6	82	51
Co	1.1	0.33	0.93	1.0	1.7	2	1.4	3.6	2.4
Ni	3.4	2.2	3.4	4.1	10.7	5.7	6.2	5.2	5.3
Cu	5.0	4.0	5.2	7.3	7.6	10.6	4.5	6.5	9.9
Zn	46	29	49	86	104	165	102	44	230
As	3	8.6	9.1	8.5	2.2	2.6	2.2	2.2	2.8
Cd	0.25	0.14	0.25	0.35	0.35	0.4	0.16	0.07	0.11
Sb	0.03	0.03	0.26	0.12	0.02	0.08	0.04	0.01	0.16
Ba	43	34	40	74	77	116	88	41	65.3
La	8.0	26	14.4	8.1	10.3	13.7	11.3	34.8	5.2
Pb	14.4	10	8.6	420	27	39	19	10	13

Description:

Knag, Cpalli, M-Ali: Residential Areas

Lguda : Residential colony, near Railway workshop

Nachr: : Industrial Estate, ferrous&non-ferrous industry

Secbd : Area in the middle of city, heavy traffic location

CCCM : Behind our laboratory

Seri : near an Aluminum works factory

Pchr : Industrial area, mainly organic/pharmaceutical industry

Table III: Variation in elemental concentrations in two locations (Lantana)

Element	**Location: Industrial Estate 1**			**Industrial Estate 2**	
mg/kg	**JDM 2**	**JDM 4**	**JDM 3**	**PCH 2**	**PCH 3**
Al	49.2	35.5	**154**	39	35
Ti	14.9	16.7	**20.2**	16	17
V	0.34	0.7	**6.8**	0.2	0.2
Cr	0.74	0.95	**3.6**	1.3	0.8
Mn	8.2	13.5	**18.1**	9.9	10.9
Co	0.09	0.09	**0.25**	0.14	0.12
Ni	1.4	1.5	**2.4**	1.7	2.6
Cu	4.0	3.1	**4.4**	4.2	4.5
Zn	13.4	15.2	**25.6**	15.2	14.2
Ba	13.3	8.4	**16.7**	21.5	19.1
Pb	1.8	2.7	**30.1**	1.5	1.2

JDM3 Collected near a foundry.
JDM2 and 4 are about 500 m away from this location.
PCH3 and PCH2 are Lantana samples collected in another industrial estate.
(all are composite samples)

Table IV. Communalities of the elemental variables in the PCA of the Lantana data

Element	Component 1	Component 2	Component 3
Al	**0.942**	0.003	0.03
Ti	0.109	**0.394**	0.011
V	**0.614**	0.136	**0.199**
Cr	**0.901**	0.065	0.005
Mn	0.208	**0.518**	0.046
Co	**0.932**	0.004	0.046
Ni	**0.674**	0.126	0.076
Cu	0.008	0.004	0.026
Zn	**0.737**	0.126	0.008
Ba	**0.817**	0.025	0.125
La	**0.926**	0.001	0.026
Pb	0.08	**0.318**	**0.356**
Cd	0.154	**0.216**	**0.557**