THE USE OF BIOMONITORS AND NEUTRON ACTIVATION ANALYSIS IN THE STUDY OF AIR POLLUTION OF BUENOS AIRES CITY

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Abstract

Biomonitors were used as part of a pollution study of Buenos Aires city atmosphere under the International Atomic Energy Agency Research Contract ARG 7251, from the Co-ordinated Research Programme on Applied Research on Air Pollution using Nuclear Related Analytical Techniques. Lichens were primarily selected as indicators. Two different approaches were conducted, direct sampling of *Parmotrema reticulatum*, at a few places and the use of lichen bags, filled with *Usnea sulcata* from a northern national park, and hung at different sites. Simultaneously, tree bark was tried as biomonitor. *Platanus acerifolia* and *Melia azedarach* were selected as candidates, for being the most common trees in the city, but only *P.acerifolia* was analyzed. All the samples were analyzed using instrumental neutron activation analysis at the Ezeiza Atomic Centre of the National Atomic Energy Commission. RA-3 reactor was used for the irradiations, determining: As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn. Concentration values for *P. reticulatum* compared well with values from literature. For *U. sulcata* differences were found among the tested sites and also, for some elements an increasing trend with time was observed. Enrichment factors calculated using Sc as reference and Mason's crustal average concentrations showed vehicules and refuse incineration as contributing sources to the aerosol. Tree bark from Buenos Aires and from a smaller city with mainly agricultural activities were analyzed and the results are coincident with those from lichens. This work is the first and preliminar contribution to the study of Buenos Aires aerosol using biomonitors.

1. INTRODUCTION

Air pollution studies using biomonitors are an interesting and economic alternative to those performed by means of direct measurements, especially when large areas have to be covered [1-3]. Buenos Aires urban area has aproximately 11 million inhabitants and 2.7 million vehicules, numerous industries and workshops, and varied traffic conditions and building profiles. With these characteristics it could present many of the pollution problems typical of a mega city. Its principal emission source has been considered to be vehicule circulation but, until recently, there has been no information about other emission sources and the city has no air monitoring network. Several years ago, a municipal sampling network for SO_2, NO_x, CO_2 and particles, was deactivated and since then, only isolated efforts had been done on this subject. Previous to an aerosol study conducted between 1993 and 1996, at the Neutron Activation Analysis Laboratory of the National Atomic Energy Commission, there were no trace-element data available for atmospheric aerosols. This study was conducted within an IAEA Co-ordinated Research Programme on Applied Research on Air Pollution using Nuclear Related Analytical Techniques (Research Contract ARG 7251) and it not only allowed to gather information about the aerosol elemental profile but also to know the most important types of pollution sources for the city area.

As a supplement of the direct sampling conducted at this programme, a study was began to explore the possibility of the application of biomonitors to the study of air pollution in Buenos Aires. Its results though preliminar, are the first ones for this kind of approach to aerosol studies, for the city.

Parmotrema reticulatum was suggested as a suitable biomonitor, but a survey showed that although this lichen is present at different locations of the country, it is scarce in the city. As another approach, lichen transplants were tried, using *Usnea sulcata* from a clean area at a National Park in the north of the country.

As an alternative biomonitor tree bark was considered, as tree-lined streets are very common in Buenos Aires. The municipal inventory of tree species showed *Platanus acerifolia* and *Melia azedarach* as the most common ones. *M. azedarach* has a very rough bark which offers more difficulties for sampling and sample preparation, than that of *P. acerifolia*, so this last tree species was selected.

2. SAMPLING AND SAMPLE PREPARATION

2.1. Lichens

For *Parmotrema reticulatum,* some direct sampling was conducted at different places. These samples were taken from trees at a height between 1.5 and 2 m, put into clean plastic bags and transported to the laboratory where the lichen was separated from adhering bark with plastic tweezers. Special care was taken in selecting trees of similar age, not sampling from fallen, decayed or young ones. A first cleaning operation was done to separate soil, bark particles and other lichen species, then the samples were washed with deionized water with gentle agitation and dried in oven at 40 °C for 24 hours [1]. The dried material was ground in an agate mortar with the help of liquid nitrogen to get it brittle and the material was kept refrigerated until its analysis [4].

Usnea sulcata was collected at a clean area at "El Copo" National Park (Santiago del Estero province). Nylon-mesh bags filled with the lichen were hung from trees at five sites of Buenos Aires area, but they were recovered only from three of them. Three bags were used at each site, to try exposure times of three, six and nine months.

Once the bags were collected and carried to the laboratory, the lichen filling was lyophilized and ground for the analysis.

2.2. Tree bark

Tree bark samples [1, 3] were collected from trees at a height between 1.5 and 2 m. At the laboratory the samples were gently brushed to remove soil, insects or any other solid pollutants and then treated as *P. reticulatum* samples.

3. ANALYTICAL METHODS

Masses of about 150 mg were used for instrumental neutron activation analysis, doing three replicates of each sample. The samples were sealed in quartz ampoules and irradiated for five hours at the RA-3 reactor (thermal flux 3.10^{13} $cm^{-2}.s^{-1}$ and 4.5 MW) located at the Ezeiza Atomic Centre of the National Atomic Energy Commission. Once the irradiation was concluded, the ampoule contents were transferred to fresh plastic vials for counting. Two measurements were done, with decay times of 6 days and 4 weeks, for the determination of As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Rb, Sb, Sc, Sm, Ta, Th, U, Yb and Zn [5,6]. They were performed using a HP Ge detector (resolution 1.9 keV for the 1332.5 keV ^{60}Co) coupled to a Series 85 Canberra Multichannel and the elemental concentrations were calculated using a software developped at the laboratory. The accuracy of the analytical technique was tested by the analysis of standard reference materials from NIST: SRM-1572 Citrus Leaves and IAEA: V-10 Hay Powder, SL-1 and Soil -7, finding good agreement with literature values.

4. RESULTS AND DISCUSSION

P. reticulatum growing at eight different locations was analyzed and enrichment factors (EF), using Sc and Mason's crustal abundances [7] as reference, were calculated. Enrichment factor values from three representative locations figure in Table I. These are: Longchamps (L_1), a residential

TABLE I. ENRICHMENT FACTORS FOR *Parmotrema reticulatum*

L_1	Buenos Aires suburb, Longchamps
L_5	El Copo National Park, Santiago del Estero
L_6	Martín García Island Reserve

	L_1	L_5	L_6
Ba	3.4	2.3	2.9
Br	160	49	64
Ce	1.4	5.0	5.3
Cr	1.7	1.0	0.9
Cs	2.6	8.5	9.9
Eu	0.5	3.5	3.3
Fe	1.1	1.4	1.3
Hf	---	5.3	4.1
K	1.4	4.2	2.2
La	3.5	2.5	4.2
Lu	---	0.9	1.8
Na	1.2	0.9	0.8
Nd	---	4.0	4.6
Rb	2.8	2.5	4.0
Sb	63	15	17
Sm	2.9	4.0	4.4
Ta	---	1.7	1.8
Th	---	4.5	3.7
Yb	---	2.6	2.8
Zn	51	13	20

Sc was used as reference.
The absence of a value is due to the missing of the corresponding concentration.

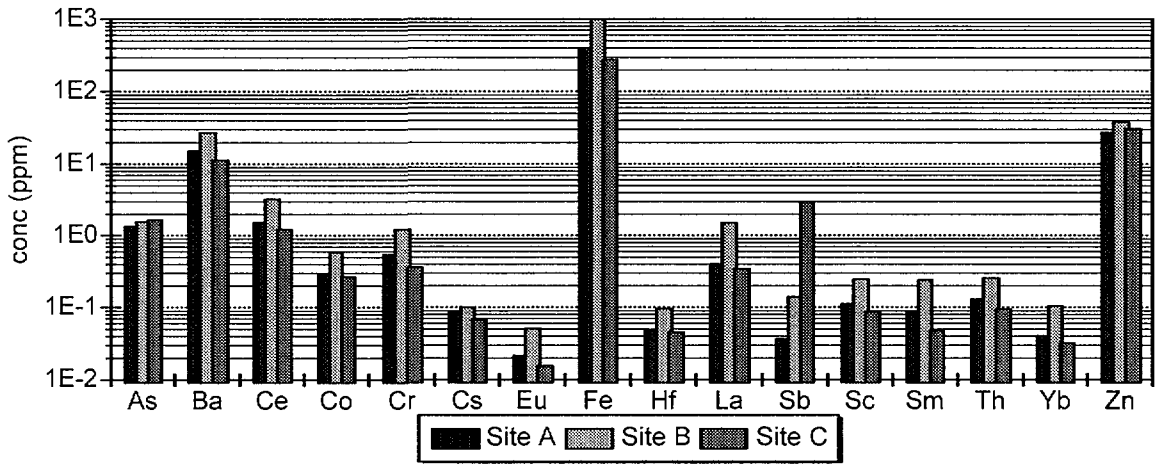

Fig 1. Usnea sulcata *concentrations for 3 months exposure.*

TABLE II. ENRICHMENT FACTORS FOR *Usnea sulcata*

site A	Buenos Aires suburb, on-storey houses, medium-low traffic
site B	Buenos Aires downtown, high buildings, high traffic
site C	Buenos Aires downtown, workshops, medium traffic

	Site A			**Site B**			**Site C**		
	A_3	A_6	A_9	B_3	B_6	B_9	C_3	C_6	C_9
Ba	7.0	9.8	10.5	5.7	6.5	4.8	6.8	0.8	0.9
Br	292	412	407	182	109	191	314	295	370
Ce	5.1	3.5	3.1	4.9	3.1	3.3	5.1	3.5	3.0
Co	2.3	2.5	2.5	2.0	2.0	2.0	2.7	2.6	2.6
Cr	1.1	2.0	2.8	1.1	1.8	1.4	0.9	1.2	1.8
Cs	3.9	4.6	4.4	2.2	2.9	2.8	5.7	7.5	8.2
Eu	3.5	3.9	2.6	3.7	2.4	2.6	3.3	3.5	4.4
Fe	1.6	1.3	1.2	1.8	1.3	1.3	1.5	1.2	1.5
Hf	3.1	4.6	3.6	2.8	5.0	3.6	3.9	3.8	5.5
K	4.6	8.4	5.3	5.7	2.3	3.3	16	30	62
La	2.5	3.2	3.5	4.4	3.0	3.2	3.0	3.0	2.8
Lu	1.5	1.9	2.3	0.2	2.1	2.3	3.8	1.9	2.8
Na	1.4	3.0	2.9	1.1	1.2	0.7	3.9	2.6	9.5
Rb	3.1	6.3	3.4	2.5	1.8	1.4	2.9	4.8	5.2
Sb	36	118	152	63	99	77	3773	5381	5918
Sm	2.9	2.4	2.4	3.6	2.6	2.8	2.1	2.1	1.9
Ta	2.3	2.0	1.3	1.3	0.9	1.3	2.4	4.0	2.9
Th	3.6	2.3	2.4	3.1	3.4	2.9	3.4	3.6	2.3
Yb	2.4	1.5	1.7	2.8	2.2	2.0	2.4	2.0	1.7
Zn	76	197	179	48	44	42	112	166	430

Sc was used as reference.
For each site, subindices 3, 6 and 9 are for three, six and nine month of exposure.

neighborhood of Buenos Aires southwestern suburbs, El Copo National Park (L_5) in Santiago del Estero province (1200 km north of Buenos Aires) and Martín García Island (L6), a reservation area on the Río de la Plata river. Three elements were found to be enriched with respect to the average crust composition (considering as enriched those values higher than 10). The higher values were those of the Buenos Aires sample and the enrichment of Br, Sb and Zn, suggests vehicule exhausts and refuse incineration as pollution sources [6]. These results are in agreement with what was expected on potential sources, but local soils will have to be analyzed in order to recalculate EF. The obtained elemental concentrations, compared well with other values from literature [1, 8].

The *Usnea sulcata* bags were recovered at three places: site A: a southwestern suburb of Buenos Aires, with one storey-houses with gardens and medium to low traffic; site B: a downtown location with extense park areas and high buildings and high vehicule circulation and site C, also downtown, but by a printing workshop and with medium traffic. For nearly all the determined elements, site B showed greater concentration values than the other two sites and also, looking at the results of 3, 6 and 9 months of exposure, a marked increasing tendency with time. For Zn, the three sites exhibit a similar performance and incresing tendency. As for Sb, site C has a much higher value than the other two locations. The differences obtained for site B were expected, in accordance to its characteristics. As for site C, some elements exhibit higher values than for site B, and this can be

TABLE III. *Platanus acerifolia* BARK ELEMENTAL CONCENTRATIONS (JUNIN SAMPLES)

	Range	Mean (n=8)	Std. Dev.
As	0.044 - 0.54	0.28	0.20
Ba	65 - 116	88	17
Br	1.3 - 6.5	3.1	1.7
Ce	0.44 - 1.57	0.70	0.38
Co	0.226 - 0.368	0.28	0.06
Cr	0.12 - 0.96	0.49	0.24
Cs	0.008 - 0.13	0.06	0.04
Eu	0.011 - 0.026	0.017	0.005
Fe	97 - 770	340	190
Hf	0.011 - 0.16	0.072	0.043
K	1674 - 3907	2668	652
La	0.11 - 0.72	0.34	0.19
Na	98 - 574	246	143
Rb	1.12 - 4.27	2.08	0.99
Sb	0.004 - 0.12	0.72	0.04
Sc	0.03 - 0.244	0.110	0.061
Sm	0.023 - 0.132	0.064	0.031
Th	0.032 - 0.24	0.113	0.057
Yb	0.012 - 0.069	0.030	0.018
Zn	6.3 - 18.7	12.4	3.9

Concentrations in ppm.

related to the presence of workshops in the area. Figure 1 shows the elemental concentrations for the three sites, for the bags corresponding to three months of exposure.

For all the results, enrichment factors were calculated to explore the source of the elements that had been determined, specially those showing rapid increase with time of exposure. The results are in Table II and it can be seen that those elements related to soil, as Fe and rare earths, are not enriched; Br, Sb and Zn appeared enriched as in the *P. reticulatum* experiment, signaling the same polluting sources.

The analytical methodology for tree bark was adjusted analyzing eleven samples of *Platanus acerifolia* from Junín, a city with mainly agricultural and cattle raising activities, 250 km from Buenos Aires. The elemental concentration ranges, average concentration and standard deviation are in Table III. Some samples from Buenos Aires were also analyzed and the results are in Table IV, together with those of a Junín sample. These bark samples were taken at sites with different characteristics: B_3: downtown with heavy traffic and high buildings; B_4: downtown, with medium traffic and low buildings; B_8: suburbs, with high vehicule circulation and low buildings and B_9: similar to B_8 but with medium traffic; the Junín sample (B_{11A}) represents a site with low buildings and medium traffic. The values for B_9 are, for nearly all the elements, out of Junín concentration ranges (Table III); for Cr, Sb and Zn, also B_3 and B_4 concentrations, exceed the upper limit of the range. Enrichment factors were calculated for these concentrations finding similar results to those obtained with lichens.

5. CONCLUSIONS

The results for the two lichen species are coincident on pointing to soil, vehicules and refuse incineration as contributors to atmospheric aerosol and similar results were achieved by a more extensive study with aerosol direct sampling. Vehicles were already suggested to be the most

TABLE IV. *Platanus acerifolia* BARK CONCENTRATIONS

B_3 Buenos Aires downtown, high buildings, high traffic
B_4 Buenos Aires downtown, low buildings, medium traffic
B_8 Buenos Aires suburbs, low buildings, high traffic
B_9 Buenos Aires suburbs, low buildings, medium traffic
B_{11A} Junín, low buildings, medium traffic

	B_3	B_4	B_8	B_9	B_{11A}
As	0.201	0.348	0.160	0.630	0.152
Ba	111	57	110	208	80
Br	2.337	3.843	1.366	7.587	1.692
Ce	0.733	1.473	0.299	4.21	0.605
Co	0.390	0.501	0.342	0.936	0.326
Cr	1.33	1.67	0.341	3.72	0.398
Cs	0.045	0.081	0.019	0.267	0.063
Eu	0.0128	0.0217	0.0086	0.068	0.0151
Fe	430.3	630.3	122.1	1628.1	320.5
Hf	0.055	0.187	0.027	0.426	0.065
K	995	1332	2473	------	2595
La	0.515	1.006	0.171	0.0050	0.408
Na	156.3	380.7	108.6	907.1	196.3
Rb	1.55	2.26	1.55	5.58	1.49
Sb	0.209	0.148	0.039	0.276	0.065
Sc	0.0772	0.1744	0.0362	0.0318	0.1008
Sm	0.0539	0.1217	0.0028	0.0858	0.0586
Th	0.0752	0.1574	0.0404	0.570	0.1120
Yb	0.0246	0.0507	0.0139	0.140	0.0220
Zn	45.4	46.2	7.17	39.0	12.9

Concentrations in ppm

polluting source for the city which has daily values of CO concentration up to 18 ppm. With respect to refuse incineration, although it is prohibited within the city limits, more than 100 dumpsites have been reported at the suburbs, in what is called Great Buenos Aires area.

This work is only a preliminar one and more samples as well as local soils, have to be analyzed, but its results allowed to evaluate potential biomonitors, for a future monitoring network for Buenos Aires, or any of the other cities in the country with pollution problems. Also, through this study, it has been possible to obtain the first results on Buenos Aires aerosol using biomonitors.

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