XA9952950

AIR POLLUTION BIOMONITORING IN ARGENTINA, APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE STUDY OF BIOMONITORS

MARÍA LUISA PIGNATA [1] AND RITA R. PLÁ [2]

[1] Cátedra de Química General. Facultad de Ciencias Exactas, Físicas y Naturales. Universidad Nacional de Córdoba. Avda. Vélez Sársfield 299, 5000 Córdoba, Argentina.
[2] Comisión Nacional de Energía Atómica (CNEA), Unidad Radioquímica, Sector Técnicas Analíticas Nucleares. Avda. Libertador 8250, 1429 Buenos Aires, Argentina.

Abstract

The assessment of baseline levels of atmospheric pollutants and the identification of polluted areas is a complex problem, as pollutant contents at a certain geographical location is usually a combination of contributions from various diverse sources, including long-range transport. Elemental chemical characterization of atmospheric pollutants is thus of great importance and Neutron Activation Analysis has proved to be a powerful technique for multielemental determination of trace elements in biomonitors and aerosols.

The general objective of this project is to study the use of biomonitors, specially lichens, for evaluating pollutant levels over a wide geographic area of Argentina and for establishing baseline values and assessing time trends.

Two lichen species (Usnea sp. and Ramalina ecklonii (Spreng.) Mey. & Flot) have been identified as suitable monitors of air pollution, with potential regional application at the central area of the country (province of Córdoba) and pilot studies have been initiated to test the practicability of sampling and sample collection. An area of approximately 40,000 km^2 will be covered by a sampling network, using in situ growing lichens. The distribution maps for the two selected species are already drawn and sampling of local soils will also be conducted.

Current efforts at the Neutron Activation Analysis laboratory are put on assessing, for the selected lichen species, the influence of sample preparation methods on trace element concentrations. The use of other analytical techniques will allow the evaluation of the bioindicator chemical response and its relationship to different atmospheric quality levels.

Source identification and apportionment will be done by statistical fingerprinting of the elemental concentrations, as sources of pollution are characterized by being composed of different mixtures of elements in different proportions. In this way and as a long-term objective, regional maps will be drawn showing the geographical distribution of certain air pollutants and of emission sources. The study of biomonitor physiological response will contribute to identify location of major pollution sources and predict environmental long-term changes.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

1.1. Introduction

Unlike the situation present in other countries of the region, in Argentina it is difficult to have access to information about the levels of pollutants. This is due, on one hand, to the lack of a national official institution that measures levels and records data, and on the other hand, to the scarce attention the problem has drawn from the political area [1]. However, despite the urban-industrial growth shown in recent years, the absence of a serious environmental event in most urban areas in Argentina is attributable to its favourable situations (both geographical and climatic) rather than to low levels of emission of toxic compounds.

Argentina is a country containing markedly different ecologies, resources, population densities and land use systems. Many areas in the region are seriously damaged by various anthropogenic activities, such as agriculture and cattle raising, mining and industrial activities, threatening the quality of life in the concerned areas. For an objective assessment of the impact that industrial, mining or agricultural activities may have on the environment, there is a need for reliable information on the environmentally relevant concentrations of elements and chemical compounds that might serve as reference levels in these studies. At present, in Argentina there is no information on base levels and/or natural levels of such analytes.

Regarding fixed emission sources of air pollutants, in Argentina there is not either an adequate and unique national law that regulates these emissions but an array of different regulations, enforced only at some provinces or cities, which represents a serious problem for people and industries. Besides, there have been some individual and isolated actions for the pollution control that have not produced the desired results due to failures in the control proceeding and the difficulty or impossibility of carrying out police reports or start legal proceedings in order to punish those responsible for the emissions [1].

In urban areas, traffic represents a serious problem whose consequences have not yet been assessed in their real dimensions. It was only in recent years that legislation on these emissions has been in force, but the control policies are not quite appropriate. Regarding emissions released from traffic, the data gathered by the National Consultant of Vehicular Transport at the end of 1994 showed that 22% of all cars nationwide were not fit to run. Among the main problems found in these cars were release release of black fumes which have a high content of soot, lead, hydrocarbons and residues non-volatiles coming from fuel pirolysis. Vehicle emission of these products is not controlled in Argentina [1].

It is well known that direct measurements of pollutants in various compartments of the environment (e.g. air, water, and soil) require enormous efforts as to investments in infrastructure and manpower and often sophisticated sampling and numerous analytical methodologies should be developed and applied.

Application of biomonitors has several advantages compared to the use of direct measurements of pollutants, related primarily to their permanent and common occurrence in the field, the easy of sampling and trace element accumulation. Furthermore, biomonitors provide a measure of integrated exposure over a certain period of time, are present in remote areas and no expensive technical equipment is involved in their collecting [2-3].

Up to present time, environmental biomonitorig for elemental deposition has not been widely applied in Argentina. The present project is intended to address this issue by applying Neutron Activation Analysis, one of the nuclear analytical techniques available at the Argentine Atomic Energy Commission.

Related to the application of bimonitors, studies were begun in 1993 at the University of Córdoba referred to the response of some lichen species to air pollutants, being the aim their use for establishing atmospheric quality levels at urban areas. Up to now, work has been oriented mainly to the evaluation of physiological damage caused by air pollutants on different Argentine lichen species, for studying their response to the cited pollutants. The results show different grades of sensibility and/or tolerance of some of these species to urban atmospheric pollutants, of both vehicular traffic and industrial origin (see Table I).

For these urban studies, lichen species were transplanted from non-polluted areas to those which atmospheric quality was being evaluated [19]. Transplants had to be used because for the majority of our country cities, lichen species are scarce. This may be due to urban microclimatic conditions or atmospheric pollution problems, as well as for native tree species being replaced with introduced ones for urban forestation. Thus, transplantation allows us to evaluate the effects of the atmospheric pollution on lichens in areas where they are not present. However, the application of this method to complex situations such as urban environments requires a combination of chemical-physiological measurements on the transplanted organisms and an adjusted experimental design. Naturally, the transplantation of lichens to an urban environment does not make it possible to evaluate the toxic effects of a determined compound or element. On the contrary, the lichen response is associated with effects potentially synergetic, additive or antagonist of different pollutants under certain environmental conditions such as temperature, humidity, winds, solar radiation and different grades of atmospheric stability.

From 1997 on, part of our work was oriented to the study of heavy metal biomonitoring using AAS on lichen transplants. *Usnea* sp. was used for a study in the province of Córdoba, being the homonymous city included in the sampled area, and Fe, Co, Cu, Ni and Mn were determined. Lichen samples from a rural environment, were exposed for three months, placed at 3 m height, on wooden poles at each sampling site ($n=3$). Within the area, sampling points were distributed on a grid, each 10 km ($n=30$) and distant at least 100 m from streets and 300 m from high transit routes.

In order to evaluate the potential existence of differences for the deposition of those quantified heavy metals and considering the city of Córdoba as a particulate and gaseous pollutant emitter, sampling points were grouped considering each one's distance from the city. Sampling points were divided into four categories: 1: less than 10 km from the city center, 2: at 20 km, 3: at 30 km, 4: more than 40 km from city center. Variance analysis showed, for the studied metals, non-significant differences between groups. Significant correlation was observed for Co/Fe ($r = 0.66$) and Ni/Mn ($r = 0,45$). For the other metal pairs significance was low.

In the same way, physiological parameters didn't show any differences among groups, except for the ratio dried to fresh weight which presented higher values for category 1, decreasing the value while increasing distance from the city.

Based on the comparison between basal and transplant samples, it was found that all quantified metal concentrations were higher for the transplants, although only Fe and Ni showed significant differences. ANOVA comparison of metal concentration values of lichen transplants show higher Fe concentrations for rural areas while Ni was higher for urban areas.

Principal component analysis (PCA) was used to obtain an overview of the data and to identify possible sources. In this work, 80% of the variability in the analyzed metals was explained by three components. Fe and Co were associated in the first component; the second was defined by Ni and Mn concentrations inversely related, and the third one was represented by Cu.

The application of Neutron Activation Analysis to biomonitors was begun at the Ezeiza Atomic Centre (Argentine Atomic Energy Commission) on 1994 as part of an IAEA Co-ordinated Research Programme on applied research on air pollution using nuclear related techniques [20]. Instrumental NAA was used for the determination of 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. *Parmotrema reticulatum* samples from different urban and rural locations were analyzed and enrichment factors calculated. Three elements (Br, Sb and Zn) were found to be enriched with respect to average crust composition, corresponding the highest values to Buenos Aires area. Lichen transplants were tried at three sites in Buenos Aires, using *Usnea sulcata* from a northern national park. The chosen sites had different characteristics: site A: residential suburb with medium to low traffic, site B: downtown location with high traffic and site C: downtown location with some workshops and medium vehicle circulation and three different exposure times (3, 6 and 9 months) were tried at each site. For nearly all the determined elements, site B showed higher concentration values and a marked increasing tendency with time; for Sb the greatest values corresponded to C site. The enriched elements suggested vehicle circulation and refuse incineration as potential emission sources for the Buenos Aires city area.

With respect to other studies performed in Argentina, having to do with trace/element deposition using lichens as biomonitors, Calvelo *et al.* [21] in the Nahuel Huapi National Park, North-Western Patagonia, an area covered mainly by *Nothofagus* forests, can be mentioned. The elemental composition of six lichen species was analyzed using INAA, from pristine areas of Nahuel Huapi National Park, from urban and periurban areas of a small, non-industrial city (Bariloche). For each species the mean concentration values and the minimum- maximum intervals of elements are lower in periurban areas than in urban ones. In pristine areas, in general fruticose lichens tend to have lower elemental concentrations than foliose lichens of the same collection site.

Having as a goal to enlarge these studies to other regions of the country, the present CNEA and University of Córdoba joint project, signifies an opportunity of combining experience and efforts. Having into account that environmental pollution is an issue of ever increasing concern in Argentina, this project gives the opportunity of adding a nuclear analytical technique such as neutron activation analysis to those already employed at the University of Córdoba such us AAS, and chemical determinations of sulphur and physiological parameters. These techniques, will produce valuable information on trace element concentration in biomonitors and their relationship to different air quality levels. Moreover, it will allow to obtain information on the distribution of trace elements on a wide area (something not easily done by direct aerosol sampling), and to detect potential emission sources. The study of biomonitors´ physiological response will be contribute to identify location of major pollution sources and predict environmental long-term changes.

1.2. Objectives

1.2.1. General objective

The general objective of this Project is to study the use of biomonitors, especially lichens, to evaluate pollutant levels over a wide geographic area of Argentina and to establish baseline values and to assess time trends.

1.2.2. Specific objectives

To identify one or more suitable biomonitors of air pollution with potential regional application, in order to use them for general environmental monitoring throughout the country or region.

To initiate pilot studies to test the practicality of the selected sampling, sample collection and analysis procedures

To create regional maps showing the baseline levels of selected elements, environmental pollutants and biomonitors' physiological state, which allow identification of major pollution sources, analyzing both its spatial and temporal variation.

To obtain information about the ability of different lichen species growing in the same location to accumulate metal ions and to expose, by means of their response, both the presence of pollution sources and the existence of environmental changes on long-term trends.

To improve ability to apply advanced statistical tools for the recording and evaluation of multiparameter environmental data sets.

2. METHODS

2.1. Study Area

The study area is the central part of the Argentine Republic, it is a quadrilateral area whose four corners are at the following coordinates: to the West, 31° 25′ 21″ S, 65° 24′ W; to the East, 31° 41′ 15″ S, 62° 38′ 34″ W; to the North, 30° 36′ S, 64° 15′ W; to the South, 32° 48′ S, 64° 10′ 12″ W. The study area is 40,000 km^2. The country surface is 3,761,274 km^2, of which 2,791,810 km^2 correspond to the American continent and the remaining 969,464 km^2 belong to Antarctica and the Austral Islands. Land morphology of study area is highly variable, ranging from a mean altitude of about 250 m in the southeast to more than 2,500 m to the mid-west. There are cities (high and medium sized) and many small villages in the area; industrial plants, mainly metallurgical, petrochemical, chemical, food, vegetable oil and cement, are mostly located in the center and south where the highest population density is recorded.

West of the study area lie the Pampeanas Hills that are a series of three somehow paralleled ranges, with North- South direction and separated by longitudinal valleys. The highest hill of the group is Cerro Champaquí (2,790 m.a.s.l.). As for its fitogeography, there are three regions: the "Chaqueña" province (Western and Eastern Chacos), The "Espinal" province (thorny bushes) and the "Pampeana" province. The Western Chaco shows different faces such as xerophile woods, bushes and high pastures. Lichens here are adhered to tree trunks and rocks. The Espinal fitogeographic province is disappearing at present from the region and it is scarce in the north- eastern plains. The continuous extinction of the native flora is the result of transformation processes caused by the expansion of cattle breeding and agriculture. This area shows important climatic changes ranging from North to South. The dominant vegetation is open xerophile and non-perennial woods and bushy steppes. Only lichens adhered to trunks are found here. The Pampeana fitogeographic province is also called Estepa Pampeana and is characterized by the predominance of grass steppes that are modified by weather variations. This area also shows lack of trees and is made up of fertile soil that has favored the development of the major agricultural activities of the region. Only lichen species adhered to tree substrates are found in this region in some patches [22].

The study area includes the city of Córdoba, the 2nd largest city of Argentina, which faces problems with air pollution mainly during wintertime. Preliminary studies have shown that the most important factor contributing to urban air pollution in Córdoba City is the emissions from mobile sources (85% of total emissions); the downtown area is the most seriously affected due to high traffic density. This situation is worsened by its topography. The city is at 31°24' S and 64°11' W. It is at 440 m.a.s.l., and surrounded by hills, with a population of 1,198,000 inhabitants (according to a 1991 census).

As for sampling, the chosen area will be divided according to a square pattern, each square of 50 by 50 km (25 sampling points in the area). Lichen and soil samples will be taken at each intersection point. At them, the collection sites will be located at least 500 m from major routes and highly populated areas, and at least 300 m from street with lower traffic density.

2.2. Sampling collection

Two lichen species will be used: *Ramalina ecklonii* (Spreng.) Mey. & Flot and *Usnea* sp.. They are present in the study area but they are not evenly distributed as they represent different environments or fitogeographic provinces. *R. ecklonii* is found in tree trunk substrates, whereas *Usnea sp.* is found in rocks. The two of them are fruticose species. This characteristic enables a better separation of the lichen thallus from the substrate when collecting samples and avoids further handling of the samples previous to their analysis.

Lichen samples will be collected from the tree barks (*R. Ecklonii*) and from the rocks (*Usnea* sp.) preferably at open forest sites. To determine element composition, three independent pools will be collected at each sampling site. Each will consist of 30 to 40 individual samples randomly taken from an area of 100 by 100 m. Individual samples will be cleaned of any soil or other material adhered to them, and then placed and packed in plastic bags. Disposable plastic gloves will be used when handling samples in order to avoid any contamination [3].

For the rest of the chemical determinations, 50- 60 individual lichen samples will be collected from the same sampling sites, randomly taking them from an area of 100 by 100 m. They will make up a starting pool. At each biomonitoring point, further soil samples will be taken.

2.3. Chemical Methods

2.3.1. Sample preparation and analysis

To carry out their analysis by INAA, the lichens will be separated from the bark substrate with nylon tweezers. Lichens will be ground and homogenized in an agate mortar with the aid of liquid nitrogen to increase lichen brittleness and then freeze dried for 24 h. Masses of about 200 mg will be sealed in high purity quartz ampoules for their irradiation, together with two certified reference materials, NIST 1633b Coal Fly Ash and NIST 1547 Peach Leaves [23-24]. The irradiations will be done at the RA-3 reactor of the Ezeiza Atomic Center (Argentina National Atomic Energy Commission), of thermal flux 3.10 13 cm^{-2}. s^{-1} and 4.5 Mw, during 5 hours. Instrumental Neutron Activation Analysis will be performed, measuring twice after 6 and 30 day decay, for medium and long- lived nuclides (Table II). The measurements will be carried out using Ge HP detectors (30 % efficiency, 1.8 keV resolution for the 1332.5 keV ^{60}Co peak) coupled to both a Canberra Series 85 multichannel analyzer and to an Ortec 919 buffer multichannel module plus Gamma Vission software for data acquisition. Concentrations for the determined elements (As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, La, Lu, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn) will be calculated using a software developed at the laboratory [20].

To carry out their analysis by AAS, 1 g samples will be treated in the same manner as above. After being ground, they will be reduced to ashes at 650°C for 4 hours. The ashes will be digested with HCl (18%): HNO_3 (3:1) at mild heat; the solid residue will be separated by centrifugation. Finally, all the material will make up a volume of 50 ml with Milli Q and will be analyzed by spectrophotometry of atomic absorption with a Buck Spectrophotometer Model 210-VGP, in order to determine the concentration of metals. Likewise, blanks of the digest will be prepared and analyzed [25].

The determination of the remaining chemical parameters will be done according specific techniques. In all cases each sample (one sample per site, each consisting of several thalli) will be carefully cleaned in order to eliminate dust deposited on the thallus surface. The thalli will be shredded (using a blender with a blade) to achieve homogeneity and then freeze dried. All determinations will be done by triplicate for each of three sub-samples taken from the starting pool.

Sulphur content will be determined according to González and Pignata [9] by the acidic suspension method with barium chloride; malondialdehyde (MDA) content will be determined following González *et al.* [6]. Chlorophylls and phaeophytins will be determined according to González and Pignata [9-10] and Carreras *et al* [18] and hydroperoxy conjugated dienes (HPCD) concentration, according to Levin and Pignata [4]. For each sample point and based on chemical data, a pollution index (PI), already statistically evaluated, will be calculated. For *R. Ecklonii*, it will be calculated according to the equation cited by González and Pignata [7] and for *Usnea sp.* according to what was cited by Carreras *et al.* [18].

2.4. Data Analysis

The results obtained will be analyzed by correlation, multiple regression and multivariate analysis techniques.

To draw distribution maps, SPANGIS 7.0 and ERMAPPER 5.5, programs for image processing and geochemical mapping, will be used. Both programs are at the Geological Atomic Unit at CNEA, Ezeiza Atomic Center.

3. RESULTS

The study area was set considering that several agricultural and cattle breeding as well as industrial activities are carried out in the same region. The highest population density is recorded there too, that corresponds to the central area of the country. The access ways to the different sites, the diversity of environments and the available facilities were considered. The layout design for sampling collection was chosen bearing in mind the diversity of environments in the area. It was made on the basis of a study of lichen species present in the study area; *Usnea* sp. and *Ramalina ecklonii* (Spreng.) Mey & Flot was set as the lichens to be used. For their election, these species were previously tested as good biomonitors of air pollution; besides the following characteristics were also considered: their distribution, abundance and easiness of collection.

The effect of sample preparation for INAA has been studied testing dried and freeze-dried samples. Based on the sample transformations after irradiation and hence the difficulties in changing them to fresh vials for measurement, lyophilisation prior to irradiation was adopted. *Usnea* sp., due to its characteristics, presented for grinding, so a test was conducted in order to explore the possibility of discarding the medullar fraction of thallus. In order to study the influence of the material grinding, two batches of ground material were prepared for the two lichen species and three replicates from each batch were analyzed.

INAA techniques as well as those for the quantification of some elements by AAS were adjusted and improved in these samplings.

4. PLANS FOR FUTURE WORK

New samples will be taken again from the same sites considering last year's results in order to carry out a temporary follow up study. At those points where situations need to be analyzed in a more detailed way, the sampling scale will be decreased in order to increase the number of biomonitoring sites so as to represent the region more accurately. Likewise, the study area could be widened as from the second year.

Chemical analysis as well as the analysis and interpreting of results will be completed and the protocols for the methods described for sampling collection and preparation and analysis will be written.

REFERENCES

[1] MORETTON, J., GUASCHINO, H., AMICONE, C., BELETZKY, V., SÁNCHEZ, M., SANTORO, V., NOTO, B., "Contaminación del Aire en Argentina: aspectos generales, legislación y situación en Capital Federal y provincia de Buenos Aires", Ediciones Universo, Buenos Aires (1996) 1-127.

[2] STEINNES, E., Biomonitors of air pollution by heavy metals. In "Control and fate of Atmospheric Trace Metals", (PACYNA, J.M, OTTAR, B. Eds.), Kluwer Academic Publishers, Dordrecht (1989) 321-338.

[3] SLOOF, J.E, Environmental Lichenology: Biomonitoring trace-element air pollution, Thesis, Interfacultair Reactor Instituut, Technische Unversiteit Delft (1993).

[4] LEVIN, A.G., PIGNATA, M.L., *Ramalina ecklonii* (Spreng.) Mey. and Flot. as bioindicator of atmospheric pollution in Argentina, Can. J. Bot., **73** (1995) 1196-1202.

[5] GONZÁLEZ, C.M., PIGNATA, M.L., Diferente respuesta química de dos especies liquénicas a contaminantes atmosféricos emitidos por tránsito vehicular e industrias, XXV Jornadas Argentinas de Botánica, Mendoza, Argentina, Actas (1996) 135.

[6] GONZÁLEZ, C.M., CASANOVAS, S.S., PIGNATA, M.L., Biomonitoring of air pollution in Córdoba, Argentina employing *Ramalina ecklonii* (Spreng.) Mey. and Flot., Env. Pollut., **91** (1996) 269-277.

[7] GONZÁLEZ, C.M., PIGNATA, M.L., Effect of pollutants emitted by different urban-industrial sources on the chemical response of the transplanted lichen *Ramalina ecklonii* (Spreng) Mey. and Flot. (1998). Toxicol. Env. Chem., (1998) In Press.

[8] GONZÁLEZ, C.M., ORELLANA, L., CASANOVAS, S.S., PIGNATA, M.L., Environmental conditions and chemical response of a transplanted lichen to an urban area, J. Env. Management, (1998) In Press.

[9] GONZÁLEZ, C.M., PIGNATA, M.L., The influence of air pollution on soluble proteins, chlorophyll degradation, MDA, sulphur and heavy metals in a transplanted lichen, Chem. and Ecol., **9** (1994) 105-113.

[10] GONZÁLEZ, C.M., PIGNATA, M.L., Chemical response of the lichen *Punctelia subrudecta* (Nyl) Krog transplanted close to a power station in a urban-industrial environment, Env. Pollut., **97** (1997) 195-203.

[11] GONZÁLEZ, C.M., PIGNATA, M.L., Transplante de *Canomaculina pilosa* (Stizen.) Elix & Hale a una región urbano-industrial de la ciudad de Córdoba, Argentina: evaluación de la respuesta química a contaminantes atmosféricos emitidos por distintas fuentes, Tercer Encuentro del Grupo Latino Americano de Liquenólogos (Glal-3), San Pablo, Brasil, Actas (1997) 27.

[12] CAÑAS, M.S., ORELLANA, L., PIGNATA, M.L., Chemical response of the lichens *Parmotrema austrosinense* and *P. conferendum* transplanted to urban and non-polluted environments, Ann. Bot. Fennici, **34** (1997) 27-34.

[13] CAÑAS, M.S., PIGNATA, M.L., Variación temporal de pigmentos y productos de peroxidación en *Parmotrema uruguense* (Kremplh.) Hale transplantada a sitios urbanos y a su ambiente natural, Tercer Encuentro del Grupo Latino Americano de Liquenólogos (Glal-3), San Pablo, Brasil, Actas (1997) 28.

[14] CAÑAS, M.S., PIGNATA, M.L., Temporal variation of pigments and peroxidation products in the lichen *Parmotrema uruguense* (Kremplh.) Hale transplanted to urban and non-polluted environments, Symbiosis, **24** (1998) 147-162.

[15] CARRERAS, H.A., PIGNATA, M.L., Correlación entre contaminantes atmosféricos y parámetros químicos cuantificados en *Usnea* sp., XXV Jornadas Argentinas de Botánica, Mendoza, Argentina, Actas (1996) 132.

[16] CARRERAS, H.A., PIGNATA, M.L., Variación en la respuesta química de *Usnea* sp. a contaminantes atmosféricos de la ciudad de Córdoba en diferentes épocas del año, Xi Jornadas Científicas de la Sociedad de Biología de Córdoba, Córdoba, Actas (1997) 44.

[17] MARTÍNEZ, G.J., PIGNATA, M.L., Evaluación estadística del biomonitoreo del aire con *Usnea sp.* en relación a datos del Sistema de Monitoreo del Aire en la ciudad de Córdoba, XVIII Reunión de la Asociación Argentina de Ecología, Buenos Aires, Argentina, Actas, (1997) 81.

[18] CARRERAS, H.A., GUDIÑO, G.L., PIGNATA, M.L., Comparative biomonitoring of atmospheric quality in five zones of Córdoba city (Argentina) employing the transplanted lichen *Usnea* sp., Env. Pollut., (1998) In Press.

[19] MARTIN, M.H., COUGHTREY. P.J., "Biological monitoring of heavy metal pollution", Land and Air Pollution Monitoring Series (MELLANBY, K., Ed.), Applied Sci. Publ. London, (1982).

[20] PLÁ, R.R., MORENO, M.A., ADLER, M., The use of biomonitors and NAA in the study of air pollution of Buenos Aires city BioMAP. Lisboa, Portugal, (1997), Book of Abstracts, 4.5. To be published in IAEA TECDOC series.

[21] CALVELO, S., BACCALÁ, N., ARRIBÉRE, M., RIBEIRO GUEVARA, S., BUBACH, D., Concentrations of biological relevant elements of foliose and fruticose lichens from Nahuel Huapi National Park (Patagonia), analyzed by INAA, Sauteria (1997), In Press.

[22] CABRERA, A.L., Fitogeografía de la República Argentina, Bol. Soc. Arg. Bot., **14** (1971) 1-42.
[23] DE BRUIN, M., VAN WIJK, P.M., Trace-element patterns obtained by INAA as a basis for source identification, Journal of Radioanalytical and Nuclear Chemistry, Articles **123** (1988) 227-238.
[24] DE BRUIN, M., VAN WIJK, P.M., VAN ASSEMA, R., DE ROOS, C., The use of multi-element concentration data sets obtained by INAA in the identification of sources of environmental pollutants. Journal of Radioanalytical and Nuclear Chemistry, Articles **112** (1987) 199-213.
[25] PFEIFFER, H.N., BARCLAY-ESTRUP, P., The use of a single lichen species, *Hypogimnia physodes*, as an indicator of air quality in Northwestern Ontario. Bryologist. **95** (1992) 3-41.

TABLE I. DIFFERENTIAL RESPONSE TO AIR POLLUTANTS OF SEVEN SPECIES OF LICHENS IN CÓRDOBA PROVINCE, EVALUATED ON THE BASIS OF CHEMICAL PARAMETERS QUANTIFICATION.

Lichen species	Chemical response to emission sources		References
	Traffic	Industries	
Ramalina ecklonii	Sensitive	Tolerant	Levin & Pignata [4] González & Pignata [5] González *et al.* [6] González & Pignata [7] González *et al.* [8]
Punctelia microsticta	Tolerant	Sensitive	González & Pignata [9] González & Pignata [5] González & Pignata [10]
Canomaculina pilosa	Sensitive	Sensitive	González & Pignata [11]
Parmotrema austrosinense	Tolerant	Not evaluated	Cañas *et al.* [12]
P. conferendum	Sensitive	Not evaluated	Cañas *et al.* [12]
P. uruguense	Sensitive	Not evaluated	Cañas & Pignata [13] Cañas & Pignata [14]
Usnea sp.	Sensitive	Sensitive	Carreras & Pignata [15] Carreras & Pignata [16] Martínez & Pignata [17] Carreras *et al.* [18]

TABLE II. NUCLEAR PARAMETERS FOR THE DETERMINED RADIONUCLIDES

A) First Measurement

Element	Isotope	Half-live	Gamma ray energies (kev)
As	^{76}As	26.3 h	559.1
Ba	^{141}Ba	12.0 d	496.3
Br	^{82}Br	35.3 h	554.3, 776.5
Hg	^{197}Hg	64.1 h	77.4
K	^{42}K	12.36 h	1524.7
La	^{140}La	40.23 h	1596.2, 328.8, 487.0
Lu	^{177}Lu	6.74 d	208.3
Na	^{24}Na	15.02 h	1368.6
Nd	^{147}Nd	10.99 d	91.1
Rb	^{86}Rb	18.7 d	1076.6
Sb	^{122}Sb	2.72 d	564.0
Sm	^{153}Sm	46.7 h	103.2
U	^{239}Np	2.35 d	277.7, 228.1
Yb	^{175}Yb	4.19 d	396.3

B) Second Measurement

Element	Isotope	Half-live	Gamma ray energies (kev)
Ce	^{141}Ce	32.5 d	145.4
Co	^{60}Co	5.27 a	1173.2, 1332.4
Cr	^{51}Cr	27.72 d	320.0
Cs	^{134}Cs	2.06 a	795.8
Eu	^{152}Eu	13.4 a	1408.0
Fe	^{59}Fe	44.5 d	1099.2, 1291.6
Hf	^{181}Hf	42.4 d	482.2
Hg	^{203}Hg	46.6 d	279.2
Gd	^{153}Gd	242 d	103.2
Nd	^{147}Nd	10.99 d	91.1
Rb	^{86}Rb	18.7 d	1076.6
Sb	^{124}Sb	60.2 d	1691.0
Sc	^{46}Sc	83.8 d	889.3, 1120.5
Se	^{75}Se	119.8 d	136.0, 264.7, 400.7
Ta	^{182}Ta	115.0 d	1221.4
Tb	^{160}Tb	72.1 d	879.4
Th	^{233}Pa	27.0 d	311.9
Zn	^{65}Zn	243.8 d	1115.5