PIXE MEXICO 2007

Proceedings of the XI International Conference on PIXE and its Analytical Applications
Puebla, Mexico, May 25-29,2007

The Use of Biomonitors and PIXE Analysis in the Study of Air Pollution in Mexico City

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Abstract. . An environmental study of air contamination in the Valley of Mexico is under investigation based on the use of two biomonitors: The epiphytic lichen *Flavopunctelia flaventior* and bromeliaceae *Thillandsia recurvata*, which are rather sensitive to air pollution and have a great capability to absorb and accumulate airborne mineral elements, including heavy metals. The thalli of lichen samples were collected in a controlled area, La Marquesa National Park while **bromelias** were collected in San Juan Teacalco, Estado de México. Samples were subsequently transplanted to 13 sites corresponding to 12 stations of the automatic network of atmospheric monitoring in the metropolitan area of the Valley of Mexico and a control site. This region includes urban and industrial places and one rural station. The study area is located at an altitude of 2240 m. with about 20 million inhabitants; it includes as well 3.5 million vehicles and 35,000 industries. The samples of transplanted lichen were exposed during 6 months in different seasonal periods during the year from 2002 to 2003. Pellets were prepared from ashes of the exposed lichens and bromelias. The contents of Cr, Cu, Fe, Ni, Mn, Pb, Zn and other trace elements were determined by PIXE using an external proton beam setup. This work presents the results of analysis of correlation factors between elements and main components using the Statistical Package for the Social Sciences (SPSS). The elemental distribution in the area of study and the environmental conditions are discussed.

Keywords: Biomonitor, lichen, Thillandsia, pollution, Valley of Mexico.

INTRODUCTION

Air pollution is a serious problem in many parts of the world, particularly in developing countries due to increasing urbanization, and transportation, together with growing population during recent years. This study focuses on the assessment of atmospheric pollution in Mexico City, one of the most polluted cities in the world.

Epiphytic lichens and bromeliaceae have been traditionally used as bioindicators of atmospheric pollution because they show differential sensibilities to air pollution, i.e., the most sensitive of these biomonitors tend to disappear from polluted areas whereas the most tolerant species can be seen in areas with moderate pollution emissions [1,2].

Lichens are extremely sensitive symbiotic organisms consisting of a fungus and an alga or cyanobacterium, which may react to even slightly polluted air. Lichens are biomonitors with a good accumulation capacity which allows the determination of pollutant deposition in terrestrial ecosystems, particularly of sulfur dioxide, heavy metals present in the air, etc. Epiphytic lichens have a great advantage over other plants in that there is no possibility of uptake of metals from the soil, and their morphology does not change with season. [3].

On the other hand, the bromeliaceae includes mainly epiphytic species with a slow growth and characterized because of their high tolerance to hydric stress and an extraordinary capacity to obtain water and nutrients from the atmosphere where pollutants are present. They constitute a group of plants with exclusive distribution in the neotropic making it appropriate for studies in this region.

In this work epiphytic lichens and bromeliaceae are being used as passive and active biomonitors of trace elements in the "Metropolitan Area of Mexico City" (MAMC, from its spanish abbreviation). The lichen *Flavopunctelia flaventior* (L.) Nyl and *Thillandsia recurvata* were exposed at 13 locations for atmospheric monitoring during a 6 month period.

Although several studies have shown that trace element concentrations in biomonitors may be related with particulate matter in air, and in both wet or dry depositions of pollutants over a certain time, this kind of research has not been carried out on a large scale in México so far.

METHODS

Study area and sampling

Samples of the *in*-situ lichen *Flavopunctelia flaventior*, were collected in August 2002 from tree trunks and branches of *escobilla* at a height greater than a 3000 m at "Miguel Hidalgo La Marquesa" National Park forest ecosystem situated 36.5 km from the centre of México City. On the other hand, samples of the *in-situ* bromelia *Thillandsia recurvata,* were collected from cactaceous; *Opuntia sp. (prickly pear)*and *Marginatocereus marginatus. (organ)* in San Juan Teacalco and Teotihuacan, Estado de México, a semi-arid ecosystem.

The samples were collected in paper bags, and rinsed with distilled water in order to eliminate dust, subsequently they were dried at open air. Representative samples of 300 g fresh weight of both species are introduced in plastic nets and transplanted to 13 atmospheric monitoring stations (urban, industrial, rural and natural woodlands, Fig. 1): Industrial: Tlanepantla (TLA), La Presa (LPR), San Agustín (SAG), Xalostoc (XAL); Urban: Merced (MER), Hangares (HAN), Pedregal (PED), Tlalpán (TPN), Cerro de la Estrella (CES), Iztapalapa (IZT); and rural and natural woodlands: Tlahuac (TAH), Chapingo (CHA), Nezahualcoyotl (NTS).

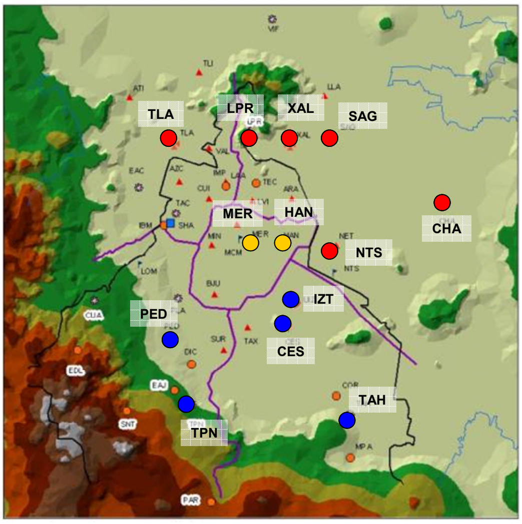

FIGURE1. Atmospheric monitoring stations in MAMC.

Two extra representative samples (of both biomonitors) were transplanted to the control site in ININ in order to have a non polluted reference. The samples were at the 13 sites during a six month period from August 2002 to January 2003. Once the samples were removed from the sites, representative 1 g subsamples are ashed at 400°C during 24 hours using a graphite furnace. After incineration they were dried and 0.1 g samples from the plant material were taken to produce pellets and their water content was determined (DW/FW ratio) for both lichen and bromeliacea exposed at the 13 stations.

PIXE and RBS in air were performed simultaneously using the external proton beam set up located at the 3 MV Pelletron tandem accelerator at the Instituto de Física, UNAM. The proton beam was collimated to 1.5 mm dia. with a 8 μm Al window. The sample surface was located at 10 mm from the beam exit window and the proton energy at the sample surface was 3.0 MeV. The X-rays generated in the sample were registered by a LEGe detector placed at 135^o from the incident beam direction. To enhance the X-rays detection of heavy elements, a 155 μm aluminum absorber was placed at the LEGe detector window. In contrast, for light and major elements a Si-pin detector 135^o from the incident beam direction with a He flux and a Ta collimator of 0.5 mm dia. was used. Backscattered protons were registered simultaneously by a surface barrier detector inside a capsule under vacuum at 135^o from the incident beam direction. The protons reach this detector passing through a 3.5 μm Mylar window along a cylindrical collimator with a 1.5 mm diameter aperture and 5 mm length. For the X-ray detector efficiency calibration and elemental quantification, compressed pellets of NIST SRM 2704 and 2711 sediments and SRM1573*a* tomato leaves as well as AIEA336 and AIEA482 of lichen were used as reference materials.

The matrix composition of oxygen for each sample was determined from the backscattered protons. The X-ray peak counts in the PIXE spectra were obtained using the QXAS code. The elemental concentration in each sample was determined using PIXEINT program for thick target analysis considering an oxides matrix. The uncertainties in elemental concentration were estimated among 8% to 12% for major and trace elements respectively.

Data analysis

The concentration of metal and other trace elements in lichen in bromelias from each sampling station was used to construct a series of distribution maps with the aid of a mapping program. The differences among zones determined by the mapping procedure were also checked by variance analysis.

RESULTS AND DISCUSSION

Table 1 shows concentration results obtained with PIXE analysis in the lichen and bromelia transplants after exposure for a 6-month period. It is interesting to recall the origin of the different elements. Structural elements such as O, P, S, Si and Ca are macronutrients and K, Ca and Cl are electrolytic elements, important component of lichens. Elements correlated to native soil (Al, Fe, P, Si, Rb) reflect the effect of air dust particles brought by the wind to the transplants during the dry spring and summer weather. S, Cl, Cr, Cu and Pb come from industrial processes sources and vehicle exhausts.

Descriptive statistics were performed and Pearson´s correlation coefficients were calculated for all the elements, positive correlation >0.75 with DW/FW, developing seven principal component analysis that minimize the variance between them. Figs. 2 and 3 show maps of the geographical distribution of heavy metals (Mn and Zn) in lichen and bromelia.

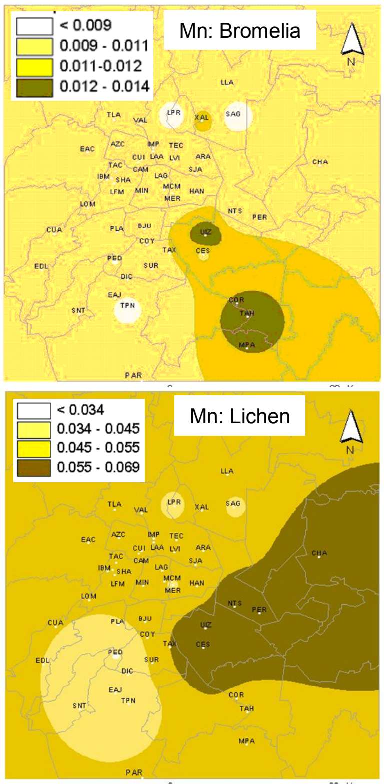

FIGURE 2. Geographical distribution of Mn.

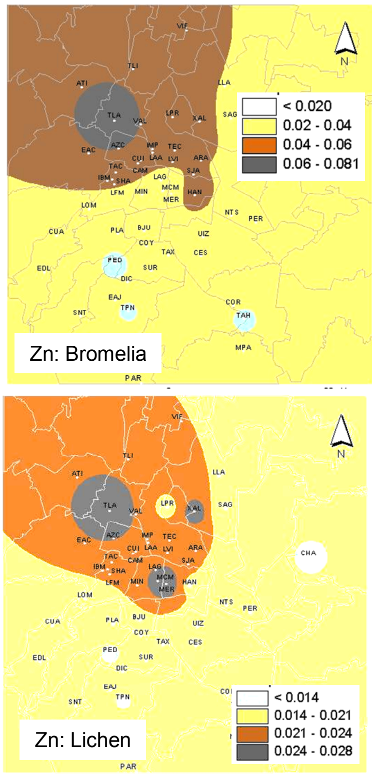

FIGURE 3. Geographical distribution of Zn.

The distribution patterns of Mn show high levels around non-industrial areas like the East and Southeast and it may partly be derived also from the upper soil layer, blown off by wind. The distribution of Mn suggests a soil origin, in spite of other works that have found correlation of this element with Zn [4]. It is remarkable that the levels of this element are different for the two kinds of samples.

The levels of Zn measured in the survey area are associated mainly with the metal-working industries whereas the abrasion of motor vehicles tires may be a second source of emission (Fig. 3) [5,6]. Another possible source could be linked to the use of Zn compounds as foliar nutrients for agriculture.

Fe is mainly associated to coarse atmospheric particles; it is generally deposited in the neighborhood of the emission sources. The content of Fe in transplanted lichens is explained mainly by soil particle input, though higher levels observed at northeast stations are due to the influence of car industries that may contribute with some iron-containing particles.

It is well known that high Ni concentrations are indicative of the use of fossil fuels or the presence of power plants or metallurgical industries located in the the northern part of MAMC. Miranda *et al.* have always found Ni associated to S and V, tracers of fuel oil [7].

TABLE 1. Elemental concentrations by PIXE for *Thilandsia* and lichens. Average uncertainty is 12%. Dry weight basis

Biomonitor	S	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
Thilandsia	%	%	μg/g	%	%	μg/g	μg/g	μg/g	μg/g
SAG	0.513	0.137	106	442	1.83	43	106	286	34
VAL	0.560	0.138	97	529	1.84	41	97	533	55
LPR	0.409	0.098	141	431	1.33	32	141	474	26
NTS	0.557	0.175	52	636	2.12	52	52	249	33
TLA	0.604	0.138	73	552	1.68	56	73	810	67
TPN	0.403	0.101	100	383	1.28	37	100	201	20
PED	0.402	0.099	63	343	1.27	32	63	187	24
CHA	0.619	0.189	80	682	2.41	58	80	261	26
TAH	0.485	0.127	2	529	1.73	38	2	197	23
CES	0.424	0.141	2	673	2.02	43	2	264	24
IZT	0.471	0.123	20	607	1.91	49	20	247	31
HAN	0.424	0.127	23	535	1.87	42	23	513	44
MER	0.445	0.098	36	448	1.52	34	36	337	34
Lichen									
SAG	0.069	0.040	53	88	0.54	152	53	177	32
VAL	0.080	0.048	962	122	0.67	14	962	264	38
LPR	0.067	0.050	93	88	0.52	14	93	208	18
NTS	0.110	0.050	59	110	0.55	19	59	194	35
TLA	0.093	0.056	85	110	0.57	20	85	276	47
TPN	0.073	0.046	83	93	0.53	17	83	144	35
PED	0.065	0.053	109	95	0.54	16	109	142	34
CHA	0.078	0.064	126	114	0.65	17	126	136	29
TAH	0.081	0.061	103	134	0.68	21	103	175	39
CES	0.061	0.046	40	114	0.60	20	40	169	34
IZT	0.079	0.055	105	139	0.66	21	105	205	32
HAN	0.067	0.047	75	114	0.64	18	75	208	33
MER	0.057	0.044	55	107	0.59	17	55	276	39

Lichens are very efficient accumulators of Pb, through aerosols, particulate metal fallout or acid rain. Pb is bound to insoluble anionic sites, accumulated extracellularly and concentrated in the cellular structure. Once bound, it is not easily removed by rain or winds.

The assessment of S content in lichens provides a good estimation of the atmospheric SO_2 concentration in rural, suburban and urban sites. Sulfur dioxide is a by-product of coal or fuel oil combustion, many industrial processes and vehicle exhausts. The high concentrations of S measured in biomonitors transplanted to the far surroundings of the industrial areas point towards the transport of sulfur-containing particles derived from the combustion of heavy fuel oil

The lichen *Flavopunctelia flaventior* and bromelia *Thillandsia recurvata* survey show, in relative terms, a general idea of the state of the atmosphere in relation to the pollutants: S, Fe, Ni, Cu, Zn, Pb and Mn in the MACM area, although it is still hard to point out the exact sources that reach the lichen thalli in the study area.

The main results can be summarized as follows: Although the content of the elements measured is still low, the distribution pattern indicates the areas where the highest pollution levels are most probable.

Most studies implementing the technique of lichen and bromeliad transplantation to monitor air pollution carried out for rather long periods provides important information about the anthropogenic activity in a relatively short period of time.

ACKNOWLEDGMENTS

Authors acknowledge support from projects IAEA ARCAL LX RLA/7/01 (2003-2005) and IAEA ARCAL RLA/2/013 (2007-2009) and technical assistance from R. Ramos, A. Retama, K. López, F. Jaimes, G. Valentín and R. Benítez, A. Fernández, as well.

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