

Temporal and spatial trends studied by lichen analysis: atmospheric deposition of trace elements in Mexico

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Ball moss on *Tillandsia recurvata* (Bromeliaceae), collected in an area previously identified as unpolluted, was transplanted to thirteen bio-monitoring sites in the downtown and metropolitan areas of Mexico City (which cover a surface of 9,560 km²) during the periods August 2002 – January 2003 and July 2003 – Octubre 2003. A total of 52 lichens (weighing 300 g) were transplanted to each place. Two were analysed as zero or reference, El Chico National Park, a location 100 Km upwind from the city and the remaining 26 were hung in nylon net bags in order to be able to collect two transplanted tree month, out of every season over a one-year period. The concentrations were measured by the quantitative PIXE method based on an external beam facility. The atmospheric deposition for trace elements was inferred by its concentration in lichen samples collected in 2002 from 13 sites in Mexico and compared with data from a similar survey in 2003. The concentration of Cr, Cu, Co, Fe, Mn, Ni, Pb and Zn and other elements was determined for each sample. Maps for each element were drawn after a geostatistical estimate of the metal concentration in the sample was made. Maps were drawn for all elements with the estimated values. Geographical distribution patterns were obtained for the different metals, reflecting the contribution of natural and antropogenic emission sources. The deposition patterns of V, As, Se, Cd and Pb are substantially influenced by long-range transport from other parts of Mexico City. For Cr, Fe, Co, Ni, and Cu, the deposition patterns are largely determined by contribution from point sources within Mexico and in the metropolitan area. The lichen data for Br and, in part, Se reflect an airborne supply from the environment. Contributions to trace element concentrations in lichen sources other than atmospheric deposition are identified and discussed. The Spatial and temporal variations in the distribution of metal concentration are discussed.

Keywords: Bio-monitoring; lichens; atmospheric contamination; PIXE analysis.

Líquenes del tipo *Tillandsia recurvata* (Bromeliaceae) se colectaron en un área no contaminada y posteriormente fueron transplantados en 13 estaciones para biomonitorio en la ciudad de México cubriéndose una superficie de 9,560 km² durante los períodos de agosto de 2002 a enero de 2003 y de julio de 2003 a octubre del mismo año. Fue un total de 52 líquenes (300 g) transplantados en cada sitio. Algunos líquenes fueron tomados como referencia, éstos provenientes del parque nacional “El Chico” localizado 100 km al norte de la ciudad de México, y protegidos con bolsas de “nylon” fueron transplantados anualmente. Las concentraciones de elementos de interés se determinaron por la técnica PIXE. La deposición de elementos traza fue determinada por sus concentraciones en los líquenes colectados en 13 sitios de la ciudad de México durante 2002 y éstas fueron comparadas con otro estudio similar realizado en 2003. Los elementos analizados entre otros en cada muestra fueron Cr, Cu, Co, Fe, Mn, Ni, Pb y Zn. Con base a las concentraciones en las muestras se elaboraron mapeos para todos los elementos detectados y así se determinó su distribución geográfica de deposición de cada uno reflejando ésta tanto la contribución natural como la debida a la actividad antropogénica. Los patrones de deposición para V, As, Se, Cd y Pb son básicamente determinados por los mecanismos de transporte de largo alcance. Para Cr, Fe, Co, Ni y Cu, la deposición la establece fuentes de emisión específicas dentro de la ciudad de México así como en el área metropolitana circundante. Los datos para Br y parcialmente para Se, reflejan una contribución aerotransportada en el entorno. Se identificaron fuentes adicionales a la atmosférica para las concentraciones de los elementos traza. Finalmente se discute la tendencia de deposición tanto espacial como temporal de los elementos metálicos.

Descriptores: Biomonitorio; líquenes; contaminación atmosférica; análisis PIXE.

PACS: 92.60.Sz; 32.30.Rj; 78.70.En

1. Introduction

The goal of this work is, first of all, to present a regional map for the presence and displacement of heavy metals in the Mexico City atmosphere and their effect on adjacent forests, and secondly to establish the method's reliability using lichens versus the conventional sampling method, which, as mentioned above, uses specialized equipment.

Atmospheric pollution in Mexico City is a consequence of a high population growth, and of the fact that it has not been possible to carry out any appropriate social planning; this has led to an excessive concentration of all types of urban-industrial activities and, therefore, the city now faces

serious environmental problems due to physical, economic, and social factors.

The Mexico Valley Metropolitan Area (ZMVM) is located at 19°20' north (Latitude) and 99° 05' west (Longitude) and it has an average altitude of 2,240 meters above sea level. At this altitude, the oxygen content in the air is about 23% less than at sea level. This means that the internal combustion processes from vehicles and industries will be less efficient and will generate greater quantities of pollutants. The ZMVM has a surface area of 9560 km², the average altitude is 3,200 meters, and some mountains exceed 5,400 meters in height. The predominant meteorological systems establish, basically, two climatic periods during the year: the “rainy

season” from June to October, characterized by tropical marine air with a high content of humidity, and the “dry season”, which is identified with low relative humidity. It is a subtropical high-altitude climate with temperatures that oscillate between 5.3°C to 26°C, with dominant winds blowing from northwest to southwest. The geographical location of the ZMVM and its characteristic environment has a decisive influence on air quality in that zone.

The ZMVM has around 30 thousand industries, namely, chemistry, iron and steel foundries, textiles, mining, plastics, paper, nutrition, asphalt, oils, cement, petrochemistry and its associate refinement, besides approximately 3 million automobiles. These sources generate annually at least 5 million tons of atmospheric pollutants such as nitrogen oxides, sulfur dioxide, carbon monoxide, heavy metals etc.. Around 70% of the pollution is caused by vehicles. The emissions mentioned are relatively constant all year long, so that variations for concentrations of pollutants in air are directly related to prevalent meteorological conditions. In fact, the valley is affected by a well-established pattern of movement of air masses during most of the year. Now it has the advantage of using nuclear techniques, whose capacities make it possible to measure small variations in concentrations, so that, a correlation can be established between those variations and meteorological changes. The importance of this evaluation lies in the fact that *this could indicate a deterioration of natural environmental conditions, in addition to the risks to human health and therefore the quality of life of the population. Such an environmental evaluation can also be, indirectly, an important index of economic risks.*

To determine air quality in the ZMVM, an atmospheric system for environmental surveillance is used that is intended to watch over and to evaluate the state of air quality, related to the pollutants that, according to established norms, should serve as a “reference”, measuring meteorological variables. Another purpose is to maintain the population informed as well as evaluating the impact of actions for preventing and controlling higher levels of contamination and thus to protect



FIGURE 1. Typical facilities for environmental monitoring of metropolitan network where lichens were.

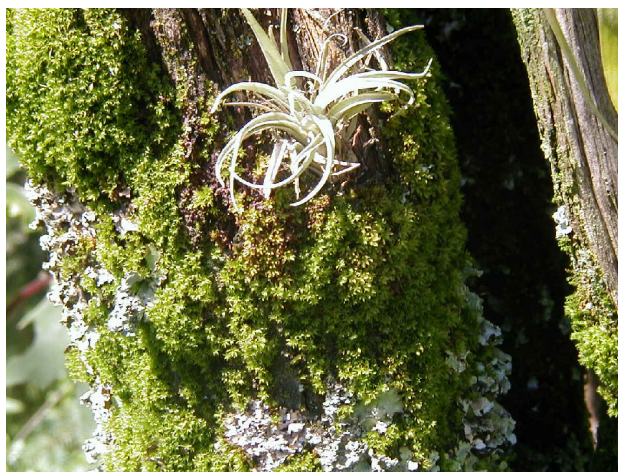


FIGURE 2. The figure shows the *Tillandsia recurvata* (Bromelaceae) “in situ” that for sampling purposes, was later transplanted.

the population’s health and improve the environmental conditions. Each environmental monitoring site has the equipment necessary to take the measurements of pollutants derived from the most significant activities in the region. The equipment makes it possible to analyze specific gases of ozone, nitrogen oxides, dioxide of sulfur, monoxide of carbon and aerosol-particles from the breathable fraction (PM10 - 2.5) (Fig. 1). The environmental monitoring network operates 24 hours per day, 365 days per year, for which reason it is possible to maintain a constant surveillance of spatial and temporal behavior for “reference” pollutants and to inform the population opportunely about the condition of the air quality through the Metropolitan Index of Air Quality (IMECA).

There is thought to be another viable alternative for quality surveillance of the air in the ZMVM, namely biological monitoring using the lichen transplant technique, using these as a biological means of detection (bio-monitoring) for these purposes, particularly for heavy metals. Lichens are recognized for their capacity to capture and accumulate metal ions from the atmosphere, so that it have been a valuable geological and biological indicator for different types and grades of environmental contamination [1,2]. These abilities are due to their metabolic properties, slow growth rate and longevity, which make it possible to incorporate water, dissolved minerals and metallic micro-particles. Lichens absorb mineral nutrients, beyond their physiological needs, mainly from wet and dry precipitation on *lichen talo* surfaces [3,4].

The use of lichens as bio-monitors in environmental contamination, over the last few years, has been developed extensively in many countries such as Canada, England, Israel, Brazil, Argentina, Chile, etc. *Tillandsia usenoides* (L.) is very efficient at capturing atmospheric mercury in the surroundings of *chlor-alkali* plant in Rio de Janeiro, Brazil. It had already been used previously to evaluate the fluoride contained in rain water and Hg dispersed in urban areas. In Colombia, air heavy metal deposition in the industrial-

ized valley of Cauca is evaluated using *Tillandsia-recurvata* as a contamination indicator. In Argentina “*T. Capillaris*” has been used to evaluate the atmospheric quality and heavy metal distribution on wide country’s central region, considering it to be a good bio-index for air quality with advantageous properties such as its metal accumulation capacity and its fast physiological changes, and very useful as sensitivity indicators.

Here the use of one species of lichen, “*Tillandsia recurvata*” (“epífita”), is described, a species with slow growth and an extraordinary capacity to obtain water and nutrients from the atmosphere. According to considerations and definitions from Ref. 5 due to the characteristics of the bio-monitors used for the present study, this use can be placed in the category of regional space bio-monitoring using local species, because it seeks to explain, over a brief, recent period, differences related to concentration values and pollutant types, both found in organisms coming from different zones, as a function of emission sources and meteorological conditions existing in the zone studied.

2. Experimental

Regarding sampling and sample preparation, biomonitoring was carried out by using ball moss or *Tillandsia recurvata* (Bromeliaceae, see Fig. 2) for two periods, from August, 2002 to January, 2003 and from July to October, 2003.

The lichen substrate was obtained from “*pine-oyamel*” and “*bromelias*” forest at 3070 m (altitude). The forest is located in a non polluted area approximately 70 km north-east of the ZMVM in an arid zone in the cactus substrate. Then lichens were transplanted to the sampling places. At each site, two sampling transplants were suspended. The additional two lichen transplants from the set were at the same time separated and prepared for analysis to provide reference values.

In Fig. 3 we indicate the location of the thirteen sites on the ZMVM map: Tlalnepantla (TLA), La Presa (LPR), San Agustín (SAG), Xalostoc (XAL), Nezahualcoyotl (NTS), Chapingo (CHA), Merced (MER), Hangares (HAN), Pedregal (PED), Tlalpán (TPN), Cerro de la Estrella (CES), Iztapalapa (IZT).

Zona Norte:

- Tlalnepantla
- La Presa
- San Agustín
- Xalostoc
- Nezahualcoyotl
- Chapingo

Zona Centro:

- Merced
- Hangares

Zona Sur:

- Pedregal
- Tlalpan
- C. de la Estrella
- UAM-Iztapalapa
- Tláhuac

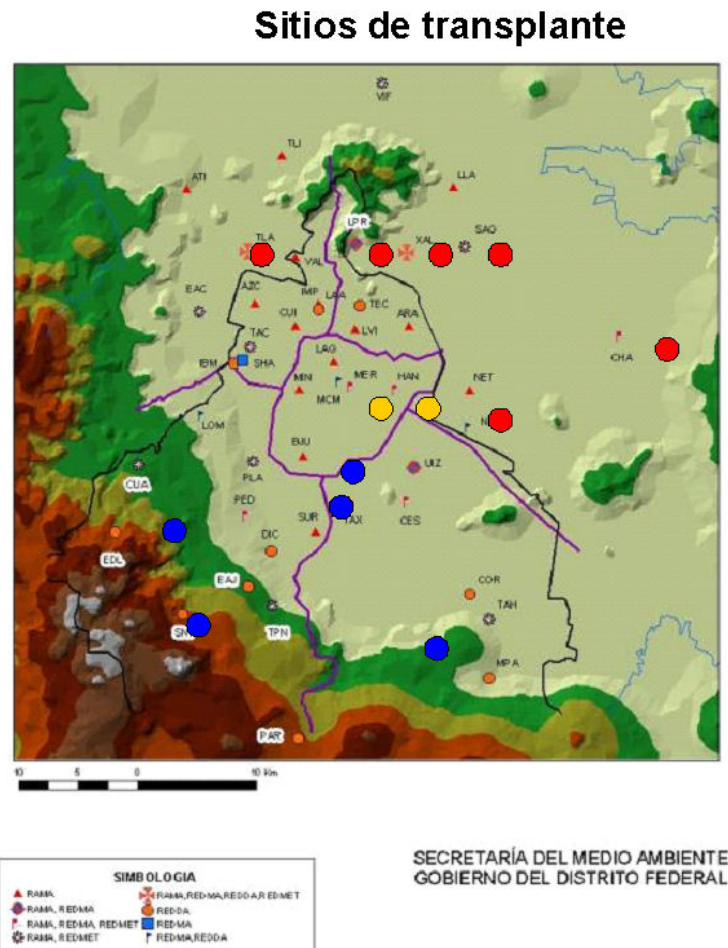


FIGURE 3. Localization map of sampling sites in Mexico City.



FIGURE 4. Figure shows part of sample preparation process for PIXE analysis; it is the cryogenic mill.

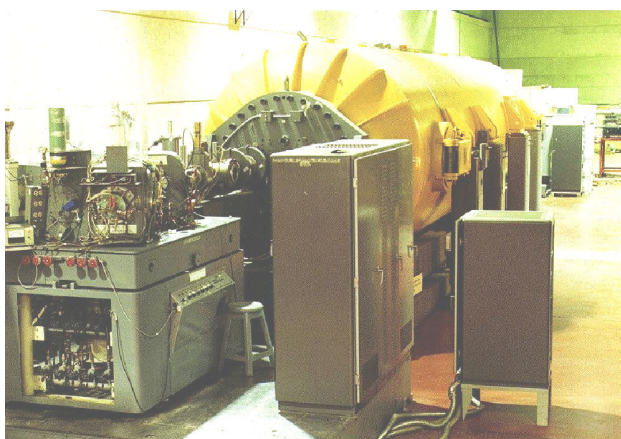


FIGURE 5. View of room of Tandem Van de Graaff Accelerator (EN) at the ININ.

Laboratory samples were cleaned, weighed and made brittle by immersion in liquid nitrogen and finally crushed and ground. About 0.5 - 0.7g of dry lichen powder was used to make sample pellets for PIXE analysis. Some samples were incinerated for 24 h at 400°C, to improve the yield for PIXE (counts / mass-charge) for heavy elements at low concentrations.

Regarding the scope of our work objectives as outlined previously, the analysis of the “atmospheric” elements captured by lichens is basic. This elementary analysis was carried out by the nuclear analytical technique PIXE (Proton Induced X-ray Emission) technique, whose main advantages are 100% reliability and precision in parts per million (ppm). The sample preparation is relatively simple and the quantity required for analysis is around $\mu\text{g}/\text{cm}^2$. However, as the PIXE technique tests only the top 10 to 50 micrometers of the sample, it is very important that the volume irradiated by the ion beam be representative of the whole lichen sample. Therefore, it is necessary to grind the sample to a fine pow-



FIGURE 6. Scattering vacuum chamber used for applications of PIXE, DIXE, PIGE, RBS and NRA.

der (preferably with particle size smaller than 1-2 micrometers, (see Fig. 4) and then pressed into pellets.

The basic physical principle of the applications of PIXE consists in atomic fluorescence induced by ionized sample atoms, producing spectra of characteristic X-rays, which permit identification and quantification of the elements with an atomic number higher than 12. Measuring intensities of characteristic X-ray lines, one can determine concentrations down to approximately 1 ppm. Sample irradiation is usually performed by means of 2-3 MeV protons produced by an ion accelerator, and X-ray detection is usually done by energy dispersive semiconductor detectors such as Si(Li) or High Purity Germanium detectors. PIXE technique is often used for quantitative analysis in geology, archaeology, biology, materials science and environmental pollution.

The samples were irradiated by using a 3 MeV proton beam from the ININ EN Tandem Accelerator (Fig. 5). The samples belonging to the August, 2002 – January, 2003 period were analyzed with an external probe and a Si(Li) detector placed at 135° with respect to the laboratory system. The charge transported by the beam was collected at the target. The samples from the July, 2003 – October, 2003 period were irradiated inside a scattering vacuum chamber (Fig. 6)

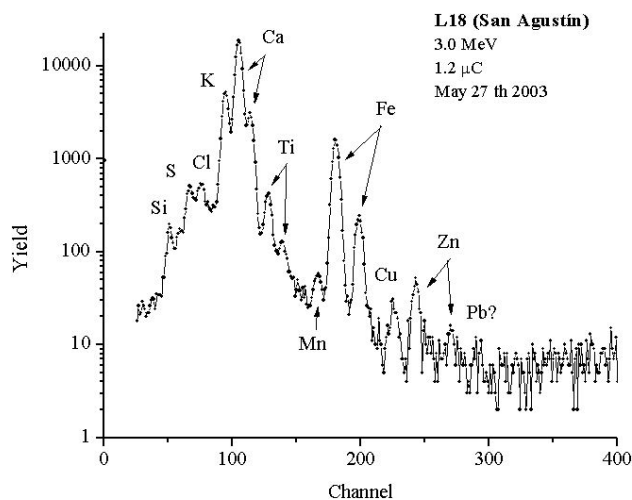


FIGURE 7. X-Ray spectrum from San Agustín site (non-ash sample) corresponding to dry period.

whose residual pressure was 5×10^{-5} torr. A previously calibrated “chopper” was used to measure the charge on the samples. A hiperpure Ge detector in this case was used. It is

important to notice that all the samples from the second period were toasted. Figures 7 and 8 shows typical spectra from the San Agustín site, belonging to both periods.

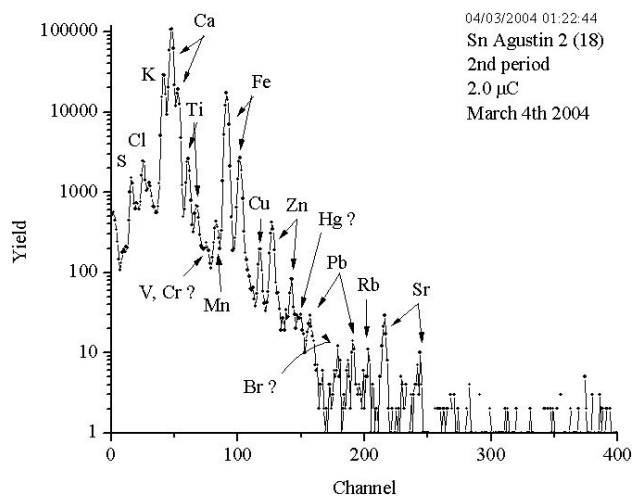


FIGURE 8. X-Ray spectrum from San Agustín site (ash sample) corresponding to rainy period.

TABLE I. Table shows sample-concentrations ratio element/calcium (for each sampling site), for non-ash samples during first period. Calcium average concentration (dry weight) was 0.712% and calculation error for concentration, in all cases, was not greater than 10%.

Element	Thillandsia recurvata, no ash sample (22/11/04)				First Period (FP)			Concentrations ratio: Element / Ca							
	Aerop	Chapingo	Estrella	Hanga	La Presa	Merced	Metepec	Neza	Oxto	Pedre	Sn Agus	Tlahuac	Tlalpan	Tlane	UAM
Si	0.66	1.65	0.80	0.85	1.40	0.98	0.82	0.95	0.98	0.80	1.19	0.78	1.25	0.66	1.73
P		0.063									0.047	0.036	0.047		
S	0.142	0.183	0.135	0.296	0.169	0.158	0.269	0.165	0.146	0.224	0.287	0.222	0.125	0.210	0.242
Cl	0.079	0.113	0.113	0.158	0.163	0.075	0.123	0.391	0.069	0.116	0.168	0.121	0.073	0.091	0.114
K	0.835	0.628	0.621	0.639	0.781	0.507	1.058	1.167	0.695	0.664	0.711	0.458	0.635	0.643	0.801
Ca	1.000	1.000	1.000	1.000	1.00	0.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ti	0.082	0.147	0.093	0.075	0.143	0.113	0.089	0.082	0.086	0.111	0.119	0.084	0.151	0.070	0.172
V		0.007	0.003	0.006		0.005		0.006	0.005	0.008	0.006			0.004	0.011
Cr		0.007	0.002	0.004			0.003	0.003							0.005
Mn	0.033	0.017	0.022	0.028	0.024	0.023	0.031	0.039	0.06	0.021	0.023	0.044	0.027	0.022	0.025
Fe	0.805	1.703	0.855	0.729	1.396	1.144	0.892	0.919	0.950	1.040	1.213	0.845	1.662	0.671	1.875
Co		0.014	0.008	0.009		0.18		0.017	0.015		0.026	0.012	0.046	0.015	0.022
Ni											0.010		0.012	0.004	
Cu	0.032	0.047	0.021	0.027	0.028	0.016	0.063	0.021	0.029	0.046	0.050	0.022	0.051	0.020	0.058
Zn	0.038	0.033	0.029	0.030	0.046	0.029	0.048	0.021	0.016	0.052	0.034	0.033	0.053	0.044	0.062
Ge	0.015		0.005	0.008											0.008
Br													0.035		
Rb				0.035			0.051	0.032							0.063
Sr		0.094													
Mo	0.256	0.236	0.177			0.211							0.288	0.206	
Pb		0.082													

Ca no ash (NA) 7120 ppm (average)

3. Results

The X-ray spectra for the lichen samples were analyzed by using a GUPIX code (GUELPH University, Canada); the criteria applied are described in Ref. 6. To obtain the parameter values that the GUPIX code requires in order to carry out spectra analysis, the following reference material was used: iron foil, 0.005" thick, from Reactor Experiment Inc. Cat 815. Precision of the calculated concentrations was no greater than 10%.

Tables I and II contain the results (concentrations in ppm) belonging to the periods studied with ash and non-ash samples for the same lichen type, *Tillandsia recurvata*. Note that since Table I shows the sample concentration ratios referred to calcium in each sampling site, and calcium concentration is approximately constant, the absolute concentration in each case can be obtained, with good precision, by multiplying by the average concentration corresponding to calcium, 7120 ppm.

Table II shows, in the same way, sample concentration ratios referred to calcium; so, in this case, to obtain the absolute concentration, it must be multiplied by 7029 ppm.

Because calcium variation from the first to second period was minimal, only "-1.28%", in order to detect a possi-

ble variation of concentration for the second sampling period with respect to the first one, the ratios of corresponding concentrations were taken whenever possible. Table III contains the variations obtained. If we suppose that the variation in percentage coefficients from Table 3 with a value of around 100 (because we are considering low concentrations of ppm), indicates a tendency regarding concentration variation, then we can say that for Silicon, Manganese, Iron, Cobalt and Copper, their concentrations increase to nearly double and that of Sulfur decreases to nearly half. Similarly by the same approach, for the remaining elements we can establish that they do not show a well-defined tendency for these concentrations due to their high variability.

An analysis was carried out using statistical χ^2 for Table I ("dry season") with two classification factors: element analyzed and sampling site. For all sampling places, Ti, Mn, Cu and Zn were the elements with the least variability in concentration (less than 7.5% of K which was the greatest). Now sampling places with a variation in concentration (less than 8.1% with respect to Neza, which was the greatest), regarding all elements analyzed at the site, were La Estrella (South), La Presa (North), Oxtó (North), Pedregal (South) and San Agustín (North).

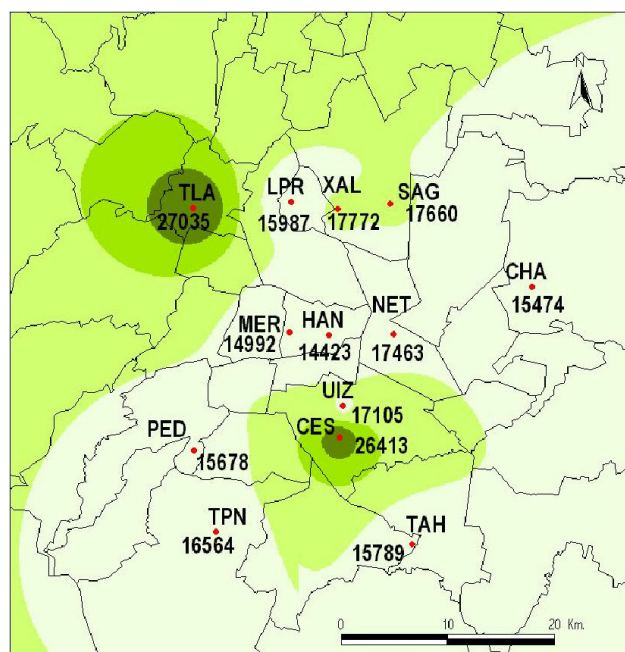
TABLE II. Table 2. Table shows sample-concentrations ratio element/calcium, for ash samples for second period. Average Calcium concentration was 0.703%.

Element	Thillandsia recurvata, ash sample				Second Period (SP)			Concentrations ratio: Element / Ca							
	Aerop	Chapingo	Estrella	Hanga	La Presa	Merced	Metepec	Neza	Oxtó	Pedre	Sn Agus	Tlahuac	Tlalpan	Tlane	UAM
Si	1.62	1.46	1.30	1.74	1.67	1.70	1.41	1.19	1.41	1.70	1.62	2.45	1.56	1.64	1.56
P	0.028	0.091	0.062	0.070			0.077		0.064	0.064	0.057	0.110	0.061	0.065	0.054
S			0.09	0.18	0.09		0.19		0.15	0.07	0.13	0.15			0.14
Cl	0.010	0.062	0.058	0.097	0.107	0.089	0.045	0.020	0.031	0.042	0.144	0.054	0.030	0.045	0.217
K	0.417	0.635	0.71	1.021	0.912	0.929	0.573	0.402	0.489	0.719	0.869	0.897	0.543	0.456	1.353
Ca	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ti	0.93	0.184	0.179	0.179	0.175	0.172	0.164	0.141	0.147	0.230	0.176	0.338	0.200	0.154	0.145
V	0.01	0.00	0.01		0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02			
Cr			0.00			0.01		0.00		0.00					
Mn	0.045	0.055	0.042	0.064	0.049	0.049	0.052	0.039	0.121	0.049	0.054	0.055	0.08	0.038	0.070
Fe	2.04	1.78	1.54	1.88	1.84	1.85	1.66	1.60	1.46	2.27	1.67	2.76	2.01	1.50	1.48
Co	0.028	0.023	0.020	0.024	0.022	0.024		0.021	0.026	0.033	0.036	0.53		0.027	0.022
Ni			0.01		0.01	0.00	0.00								
Cu	0.123	0.044	0.085	0.072	0.075	0.039	0.080	0.077	0.047	0.034	0.063	0.043	0.051	0.057	0.050
Zn	0.143	0.045	0.062	0.07	0.068	0.038	0.070	0.054	0.043	0.030	0.062	0.042	0.040	0.085	0.042
Ge									0.01						
Br															
Rb				0.037								0.048			
Sr	0.053							0.055		0.042			0.079		
Mo	0.209	0.200	0.161			0.270	0.174	0.28		0.142			0.152	0.199	0.252
Pb															

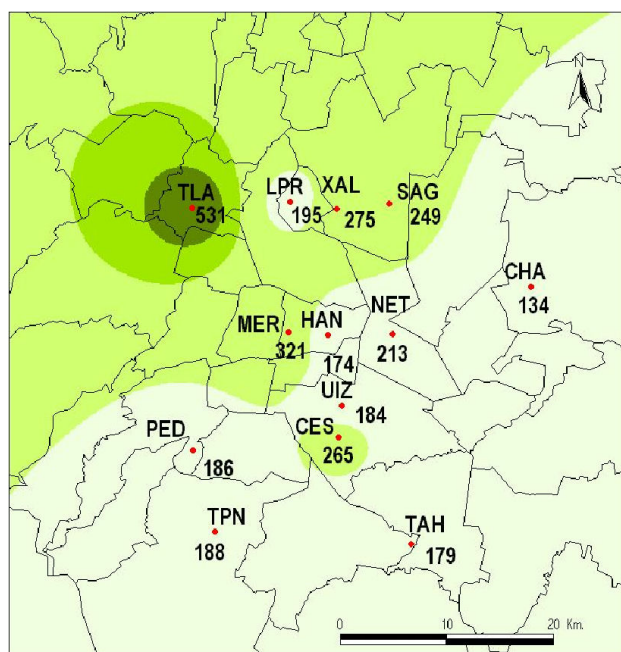
Ca ash (A)7029ppm(average) Variation : $(A/NA - 1) \% = -1.28\%$

TABLE III. Table shows ratio Second Period / First Period concentration variation. Last column contains variation percentage coefficients [standard deviation (STD)/average (AVG)].

Element	VariationRatio: (SP/FP - 1)															Average(AVG)	STD	STD/AVG%
	Aerop	Chapingo	Estrella	Hanga	La Presa	Merced	Metepec	Neza	Oxto	Pedre Sn	Agus	Tlahuac	Tlalpan	Plane	UAM			
Si	1.47	-0.11	0.62	1.05	0.19	0.74	0.73	0.24	0.44	1.14	0.36	2.15	0.25	1.49	-0.10	0.71	0.644	90.7%
P		0.43										0.22	2.03	0.31		0.75	0.861	115.3%
S			-0.34	-0.38	-0.49			-0.31	0.01	-0.69	-0.54	-0.34			-0.41	-0.39	0.192	49.7%
Cl	-0.87	-0.45	-0.49	-0.38	-0.34	0.19	-0.63	-0.95	-0.56	-0.64	-0.14	-0.56	-0.59	-0.51	0.91	-0.40	0.454	113.4%
K	-0.50	0.01	0.19	0.60	0.17	0.83	-0.46	-0.66	-0.30	0.08	0.22	0.96	-0.14	-0.29	0.69	0.09	0.501	533.6%
Ti	1.36	0.25	0.92	1.37	0.23	0.51	0.84	0.72	0.72	1.07	0.47	3.01	0.33	1.20	-0.16	0.86	0.741	86.5%
V		-0.40	1.93			0.56		-0.01	0.57	0.66	0.41					0.53	0.726	136.6%
Cr				0.74					-0.26							0.24	0.706	289.6%
Mn	0.35	2.25	0.91	1.27	1.05	1.15	0.67	-0.02	3.65	1.30	1.35	0.24	0.76	0.75	1.74	1.16	0.898	77.3%
Fe	1.53	0.05	0.80	1.58	0.32	0.62	0.86	0.74	0.54	1.18	0.38	2.27	0.21	1.23	-0.21	0.81	0.660	81.9%
Co		0.63	1.32	1.68		0.34		0.21	0.70		0.35	3.37		0.83	-0.03	0.94	0.996	105.8%
Cu	2.87	-0.08	3.00	1.69	1.64	1.37	0.27	2.69	0.66	-0.28	0.26	0.94	0.01	1.85	-0.13	1.12	1.138	101.8%
Zn	2.72	0.37	1.16	0.91	0.49	0.32	0.44	1.53	1.71	-0.41	0.83	0.26	-0.26	0.92	-0.32	0.71	0.839	118.1%
Mo	-0.18	-0.15	-0.09			0.28								-0.47	-0.04	-0.11	0.244	225.0%



● Sitios de Monitoreo
Thillandsia
Fe
14423 - 17576
17576 - 20729
20729 - 23882
23882 - 27035



● Sitios de Monitoreo
Thillandsia
Cu
134 - 233
233 - 333
333 - 432
432 - 531

FIGURE 10. Concentration distribution map for copper.

FIGURE 9. Concentration distribution map for iron at ZMVM. Inside written aside, sampling site name.

The same previous analysis for Table II (“rainy season”) showed that Ti, V, Cr, Co and Ni were elements with smaller variability (smaller than 6.2% with respect to Mo, which the

greatest). In this case, the places La Estrella and Pedregal both in the South had the smallest variability in concentration for all elements detected there (less than 17.5% with respect to the UAM, which was the greatest).

It was also possible to establish well-defined maps of concentration surface distribution for each element. Figures 9 and 10 show corresponding maps for iron and copper. The sampling site, acronym, and corresponding concentration in ppm are given, and a darker color indicates a higher concentration. In this representation, a comparison of color and shape establishes or not a possible correlation between elements deposited in the same area, as is the case of iron and copper in Tlalnepantla. For example, see "Tla" in these same figures.

4. Discussion

The analysis of Table I indicates that, during the dry season, the element deposition of Ti, Mn, Cu and Zn was practically uniform in all sampling places and that in the places La Estrella, La Presa, Oxtó, Pedregal and San Agustín, deposition of all elements analyzed was constant, independently of meteorological conditions. For the rainy season, it can be said that deposition of Ti, V, Cr, Co and Ni was uniform for all places and that for Estrella and Pedregal alone, elementary deposition did not vary as a function of meteorological conditions. Comparing these results, we can established that, throughout the year studied in all places, Ti deposition was constant and that the elementary deposition in the places La Estrella and Pedregal were practically unaltered by meteorological conditions.

From the analysis of Table III, it could be said that, if pollutant sources are considered to be practically constant all year long, then meteorological conditions for the rainy season favor the deposition of Si, Mn, Fe, Co and Cu, and at the same time do not favor S deposition.

Regarding the presence and concentration of the elements analyzed, then according to Tables I and II, it can be said that Ca, K and Fe appear with high concentrations partly because these elements are essential for lichen metabolism. During the dry season, only at Chapingo was 583 ppm of Pb found; this concentration is generally higher than those reported in polluted areas as 25.1 - 44.1 ppm [4]; 22-594 ppm; 35-246 ppm [7]; 30.8-43.8 ppm [2]; 30.7-222.1 ppm [7].

The levels obtained for Copper and Zinc have a maximum of 1005 ppm, compared with calculated concentrations for non-polluted places, where the maximum is 398 ppm [6]; thus the existence of an accumulation process of metals can be established in the lichens.

For the periods studied, cadmium was not detected, although there are some antecedents for the existence of this element in Mexico City; previously it has been reported an interval of 0.05-0.646 ppm.

The interval of concentrations obtained for chromium, 14 to 70 ppm is higher, in many cases, than those reported for

polluted areas: 9.0-14.0 ppm [4]; 4.1 ppm [2]; 23.7 ppm [8]; 2.4-8.5 ppm and 5.4-14.5ppm [7] and 4.9 ppm [9].

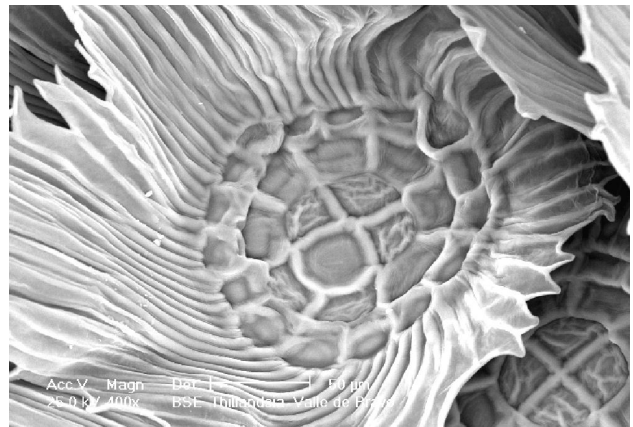
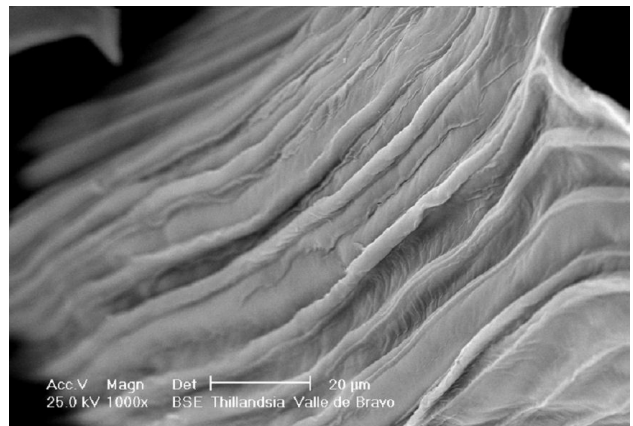
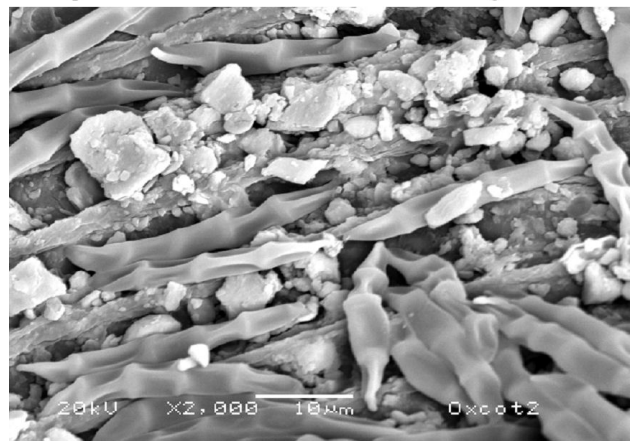


FIGURE 11. Image obtained by scanning electronic microscopy technique (SEM), showing TILLANDSIA RECURVATA morphology.



Sample of valle de bravo monitoring in SITU



Sample in high traffic area monitoring in transplant

FIGURE 12. TILLANDSIA RECURVATA images obtained by SEM that show the difference between.

In the literature, concentrations for iron from 360 to 1900 ppm have been reported as characteristic for lichens' elementary content [9]. Other authors have reported values for different species of lichens and sites, for example, in Davos, Switzerland, from 156 to 1094 ppm, while rural regions have shown from 648 to 3221 ppm and semi-urban areas, from 559 to 2785 ppm.

Since the interval of iron concentrations obtained was 4777 to 19400 ppm in Mexico City, one can say that there was in this case well-defined iron accumulation. This is in agreement with values reported by Garty and Amman [7] in relation to the fact that some lichen species are capable of accumulating great quantities of iron in urban as well as in rural areas (Figs. 11 and 12).

The highest measured concentration for calcium was 7120 ppm, which is more than one reported as average for *T. Recurvata* for its basic elementary composition of 3800 ppm [9]. Something that should stand out is that the calcium concentration of either ash and non-ash samples is practically the same.

For potassium, the concentrations obtained were from 2820 to 9510 ppm. The elementary potassium in lichens varies between 1,000 and 8,000 ppm, presenting a great deficiency for its capture from the substratum, so that its concentration and behavior are regulated mainly by atmospheric conditions. So for the present case, concentration values for potassium show a slight atmospheric accumulation.

It has also been observed that potassium in some species is intra-cellular in the free state so that it is of easily diffused

in lichens. Laboratory studies have checked that a flow of potassium exists to the outside of the cell in the presence of metals such as Copper and Lead, while for Ca, Mg, Sr and Zn, this flow is not so important.

5. Conclusions

Using the PIXE technique, it was possible to establish a spatial and temporal distribution of atmospheric deposition for certain elements; in this sense, it can be considered an appropriate technique to achieve such purposes. Bio-monitoring has been demonstrated to be an appropriate tool for estimating atmospheric quality levels, and it is regularly used in many developed countries. Bio-monitoring is a direct alternative technique that is more accessible for the countries in the region, because of its relatively low cost, applicable in different contexts and large extensions where monitoring is required. This last point is of importance in cities with low resources for environmental monitoring.

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