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NEUTRON ACTIVATION ANALYSIS FOR THE MULTYELEMENTAL DETERMINATION AND ANALYSIS OF BIOMONITORS (*Thillandsia recurvata*) FOR THE STUDY OF POLLUTING AGENTS IN THE VALLEY OF MÉXICO

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Antecedents

The use of lichens and other vegetal species to monitor environmental pollutants is an option to evaluate the air quality in a specific region and from this conclude if there is any possible damage to the environment and human health and also could evaluate the success of the implementation of preventing and control programs.

Mexico has been developed some research studies related to bio-monitoring using pine trees and tobacco species, but these were not continuous and there are few results in the last years. Since the year 2002 the Radiological Environmental Surveillance group of the, del Instituto Nacional de Investigaciones Nucleares and the Atmospheric Monitoring System (SIMAT) part of the Environment Secretary Government of Mexico City, were collaborating in developing bio-monitoring campaigns to attend its participation in the coordinated research program of IAEA, related to studies of air pollution in several Latin American countries using nuclear analytical techniques Since the year 2002

In this work, we present results of bio-monitoring using *Thillandsia recurvata.* This make a contribution to the understanding the impact of air pollution in some vegetal species of the Metropolitan Zone of the Valley of Mexico (ZMVM). Also a data base was started to establish secondary standards and to define limits in order to diagnose possible damage to vegetation and its impact to the human health (4).

Methodology

The bromeliaceae constitute one group of the monocotyledon it has exclusive distribution in the neo tropics. The gender Thillandsia is the largest and more diverse among bomilaceae.

Thillandsia recurvata is an epiphyte that reacts to a specific environmental dynamics through observable and measurable changes

By measuring these changes when they are exposed to a polluted environment, they can absorb and accumulate heavy metals, trace elements and nutrients from the atmosphere through its foliar trichomas and to have a physiological response

In this work samples of ***Thillandsia recurvata**,* (Ruiz y Pav.) were collected at San Juan Teacalco and Teotihuacan, Estado de México, this site was considered the control point duet to its environmental conditions. The experiment was completed transplanting samples into thirteen stations distributed in the ZMVM, and belonging to Atmospheric Monitoring System (SIMAT) part of the Environment Secretary Government of Mexico City. The exposition period for these samples was from august 2002 to January 2003 (5).

At the end of the exposition period the concentration of As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb y Zn, was measured using neutron activation (NAA) analysis after a decay period of 6 to 30 days. The samples were irradiated at the nuclear reactor RA-3 in a thermal flux of 1.10^{13} cm^{-2} $.s^{-1}$, 4.5 Mw for 7 hours at the Ezeiza Atomic Centre, in Buenos Aires, Argentina (3).
The foliar concentration of chlorophyll a, chlorophyll b and feofitines was measured in leaves samples, extracted from 45 bulks taken randomly from every transplant (a total of 45 vegetables bulks for transplant point). 14 samples were taken from the foliar concentration of pigments during this experiment

The index of the foliar demand was obtained from the physics-chemical parameters: chlorophyll, feofitines, conjugated hydroperoxids with dienos and melondialdehid, which were obtained using atom absorption spectrometry (AAS) at University of Cordoba, Argentina.
Climate, environmental and anthrophic factors were associated to the data analysis in order to understand multi-factorial conditions and space-time relationship, to do this we incorporate Geographic Information Systems (SIG). Additional to this, using statistical techniques like regression and correlation analysis we found relationship between social, demographic, environmental and industrial with pollutants distribution and its concentration in bromelias.

Results

For any monitoring station physical-chemical parameters were compared for every concentration of chlorophyll-b / chlorophyll –a, feofitin-a / chlorophyll-a in $mg.g^{-1}$ and maldialdehid (MDA) in $\mu mol.g^{-1}$ in wet, weight showing differences between transplanting stations. For example in the case of Chl-b/Chl-a for ININ station (control) is 0.670, Tlanepantla station 1.592, Xalostoc 2.165 and La Presa station 2.170. These values shows that less polluted stations are those who have lower Chl-b/Chl-a value and vice-versa, this means that pigment content raises with level of air pollution that indicates that photosynthetic of pigments degradation is increases

Sitios	Chl-a mg g^{-1}FW	Chl-b mg g^{-1}FW	Feofitina-a mg g^{-1}FW	Feofitina-b mg g^{-1}FW	Chl-b/Chl-a mg g^{-1}FW	Feofitina-a/Chl-a mg g^{-1}FW	MDA (µmol g^{-1} FW)
Tlanepantla	0.156	0.191	0.248	0.171	1.225	1.592	193.361
C. Estrella	0.190	0.208	0.247	0.199	1.091	1.299	150.573
Tlalpán	0.221	0.282	0.431	0.371	1.276	1.948	148.103
UAMI	0.199	0.267	0.262	0.232	1.338	1.315	158.378
Pedregal	0.186	0.216	0.291	0.244	1.161	1.567	179.902
Chapingo	0.185	0.292	0.306	0.300	1.582	1.654	186.451
Tlahuac	0.398	0.902	0.540	0.650	2.263	1.357	216.391
Hangares	0.155	0.22	0.205	0.176	1.418	1.326	198.481
S. Agustín	0.161	0.293	0.174	0.170	1.817	1.082	283.179
Xalostoc	0.268	0.582	0.389	0.422	2.165	1.450	159.010
Merced	0.212	0.268	0.281	0.273	1.263	1.321	158.530
L Presa	0.303	0.659	0.372	0.417	2.170	1.226	179.093
Neza	0.175	0.214	0.236	0.175	1.218	1.344	140.881
ININ	0.340	0.228	0.435	0.245	0.670	1.281	148.773

Table 1. Photosynthetic pigment analysis in *Thillandsia recurvata leaves corresponding to biomonitoring points*

Alteration in pigment composition was related to atmospheric pollutants in a classic way (Wolfenden et al., 1988) having since then a wide spread tool to determine the damage produced by pollutants (Darrall y Jagger, 1984; y Agrawal, 1994).

These plants are characterized by its capacity to absorb through foliar trichomas, water and solved salts, showing an effective substitution of the root in bad habitats and often dry.

In the active photosynthetic tissue of superior plants among others chlorophyll-a, chlorophyll-b, carothenoids and feofitines are found. Not only pigment content in absolute terms could be affected by the pollutants, also its relative proportions. For example some preferment chlorophyll-a diminution relative to chlorophyll-b (also implies reduction in the a/b relation) could be an indicative of damaged leaves by photo-oxidation and reduction of this quotient was found by effect of the metals and other pollutants.
Other index of damage is the feofitinization index ($A_{435}/_{415}$). When absorbency relation to this wavelength suffers diminution, this implies that there was a degradation process from chlorophyll to feofitins. The absorbency index $A_{430}/_{665}$ nm has similar meaning.

Chlorophyll-a absorbs light radiation, especially around two maxims or peaks located at wavelength of 430 and 665 nm. In this case $A_{430}/_{665}$ is an estimation of the proportion between total pigments to chlorophyll-a.

Quantify of photosynthetic pigments like chlorophyll-a, chlorophyll-b, feofitines and malondialdehid has been traditionally used (MDA, González y Pignata, 1994) as complement to visible damage evaluation in vegetation affected by atmospheric pollutants interacting with some other kind of stress (González et al., 1996; Carreras et al., 1998).

SITIOS DE TRANSPLANTE		**CONCENTRACION ELEMENTAL (ppm) EN *Thillandsia recurvata***							
ZONA	**ESTACION**	**As**	**Cr**	**Co**	**Fe**	**Na**	**Sb**	**Se**	**Zn**
NORTE	TLA	2.25	19.13	3	7292	2896	2.1	1.27	412
	SAG	1.1	14.9	2.2	6674	3785	0.66	0.6	93
	XAL	1.39	18.3	2.5	7682	3524	1.25	0.8	212
	CHA	1.11	16.3	2.6	7195	3389	0.63	0.8	79
	LPR	1.9	16.3	2.4	6713	2631	0.86	1.43	140
	NET	2	16.1	2.7	7501	5762	0.92	0.66	73
CENTRO	MER		15.5	2.1	6399	2851	1.13	0.9	114
	HAN	1.05	17.3	2.4	7048	2862	1.14	0.8	170
SUR	PED	1.26	15.17	2.2	6654	1611	1.15	0.7	70
	TPN	1.29	17.24	2.4	7310	1954	1.06	0.9	71
	CES	1.37	19.2	3.3	7004	2227	0.87	0.7	73
	TAH	1.15	15.7	2.4	6613	2876	0.84	0.8	80
	UIZ	1.84	21.7	3	8778	2502	1.1	0.9	81

Table No.2 Analysis of some trace elements in *Thillandsia recurvata leaves* using NAA

They are from industry, metallurgic, air, and soil origin, showing differences between sampling stations.

	AS	BA	BR	CE	CO	CR	CS	EU	FE	HF	LA	LU	NA	ND	RB	SB	SC	SE	SM	TA	TB	TH	U	YB	ZN
AS	**1**																								
BA	0.42	**1**																							
BR	0.45	-0.25	**1**																						
CE	0.40	0.12	0.52	**1**																					
CO	0.54	0.41	0.24	**0.60**	**1**																				
CR	0.47	0.57	0.03	**0.62**	**0.80**	**1**																			
CS	0.36	0.55	0.02	**0.68**	0.46	**0.65**	**1**																		
EU	0.41	0.40	0.29	**0.83**	0.59	0.57	**0.87**	**1**																	
FE	0.53	0.58	0.21	**0.79**	0.59	**0.82**	**0.89**	**0.86**	**1**																
HF	0.33	0.59	-0.05	**0.67**	**0.68**	**0.90**	**0.81**	**0.74**	**0.91**	**1**															
LA	0.58	0.46	0.27	**0.79**	**0.78**	**0.77**	**0.77**	**0.80**	**0.79**	**0.76**	**1**														
LU	0.45	0.28	0.20	**0.86**	0.56	**0.66**	**0.81**	**0.87**	**0.85**	**0.77**	**0.80**	**1**													
NA	0.20	-0.30	**0.85**	0.37	0.02	-0.21	**0.10**	0.33	0.14	-0.16	**0.09**	0.08	**1**												
ND	0.22	-0.04	0.06	0.14	0.09	-0.16	0.21	0.26	**0.07**	-0.11	0.01	0.25	0.30	**1**											
RB	0.27	0.33	0.00	0.32	0.34	0.25	**0.60**	**0.65**	0.46	0.45	**0.62**	0.46	0.17	0.18	**1**										
SB	0.33	0.51	0.12	-0.05	0.15	0.40	-0.04	-0.19	0.18	0.13	0.14	-0.14	-0.18	-0.46	-0.35	**1**									
SC	0.50	0.45	0.27	**0.88**	**0.65**	**0.71**	**0.89**	**0.90**	**0.91**	**0.83**	**0.88**	**0.92**	0.18	0.23	0.54	-0.03	**1**								
SE	0.39	0.03	-0.03	-0.08	0.06	0.23	-0.15	-0.31	0.00	-0.04	0.08	-0.02	-0.25	0.06	-0.11	0.45	-0.06	**1**							
SM	0.47	**0.62**	0.05	**0.74**	**0.72**	**0.74**	**0.90**	**0.89**	**0.87**	**0.84**	**0.90**	**0.82**	0.03	0.23	**0.67**	-0.02	**0.93**	-0.09	**1**						
TA	0.59	-0.22	0.54	**0.61**	0.58	0.44	0.24	0.46	0.43	0.36	0.48	0.58	0.33	0.18	0.17	-0.20	0.46	0.13	0.33	**1**					
TB	0.32	0.02	0.34	0.18	0.03	0.23	-0.04	0.05	0.24	0.12	0.15	0.26	0.09	-0.21	-0.04	0.43	0.09	0.54	-0.07	0.28	**1**				
TH	0.39	0.44	0.06	**0.86**	**0.65**	**0.78**	**0.86**	**0.85**	**0.89**	**0.88**	**0.86**	**0.92**	-0.04	0.15	0.51	-0.04	**0.95**	-0.01	**0.93**	0.43	0.06	**1**			
U	0.01	0.14	-0.09	0.29	0.16	0.31	0.22	0.21	0.28	0.46	0.28	0.36	-0.36	-0.56	-0.02	0.00	0.32	-0.35	0.23	0.16	-0.03	0.38	**1**		
YB	0.55	**0.62**	0.18	**0.75**	**0.81**	**0.76**	**0.78**	**0.84**	**0.83**	**0.82**	**0.86**	**0.73**	0.09	0.19	0.54	0.06	0.89	-0.13	**0.95**	0.40	-0.13	**0.87**	0.26	**1**	
ZN	0.38	0.13	0.40	0.02	0.12	0.31	-0.26	-0.27	**0.08**	0.00	0.07	-0.16	0.02	-0.52	-0.41	**0.87**	-0.12	0.56	-0.21	0.12	**0.63**	-0.14	0.02	-0.09	**1**

Table No. 3 Pearson's correlation matrix

ELEMENTOS	COMPONENTES PRINCIPALES					
	1	2	3	4	5	6
Sc	**0.967**					
Sm	**0.956**	-0.167	-0.145	0.151		
Th	**0.949**		-0.124		-0.161	
Fe	**0.939**	0.106				0.187
Yb	**0.933**				0.155	-0.253
La	**0.925**	0.104				
Eu	**0.912**	-0.281	0.140		0.134	0.134
Lu	**0.901**			-0.107	-0.271	0.205
Hf	**0.889**		-0.325	-0.119		
Cs	**0.877**	-0.224	-0.147		0.111	0.229
Ce	**0.853**		0.315	-0.263		
Cr	**0.818**	0.385	-0.258		-0.112	-0.149
Co	**0.761**	0.168				-0.518
Rb	0.573	-0.381		0.259		0.211
As	0.572	0.422	0.314	0.308		-0.228
Zn		**0.974**	0.113		0.138	
Sb		**0.879**	-0.229	0.116	0.349	
Tb	0.127	**0.674**	0.278		-0.216	0.536
Se		**0.659**		0.497	-0.469	0.111
Na	0.119	-0.151	**0.852**		0.450	
Br	0.235	0.252	**0.845**	-0.230	0.314	
Ta	0.526	0.125	0.566	-0.215	-0.421	-0.282
Ba	0.526	0.214	-0.550	0.377	0.392	
U	0.310		-0.409	**-0.758**		
Nd	0.145	-0.482	0.406	**0.627**	-0.196	

Table No.4 Analysis of main components

Descriptive statistic was calculated for all the elements and transplant stations, so the variation coefficients (CV), Pearson's correlation factors, and also the elemental distribution maps elaborated.

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