Atmospheric Pollution in the Tula Industrial Corridor studied using a biomonitor and nuclear analytical techniques

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This study deals with the application of nuclear analytical techniques to analyze trace elements in the biological monitor *Tillandsia usneoides*. Biological monitors provides an alternative advantageous way of particulate matter sampling in air pollution studies, since there is no need of special sampling devices, accumulation time can be as long as desired. *T. usneoides*, which occurs naturally throughout Mexico, was used to monitor air quality of Tula-Vito-Apasco (TVA) industrial corridor at central Mexico. This area is considered one of the critical zones of the country because of atmospheric contaminants high concentration. Particulate matter is regulated by Mexican norms, but its chemical composition is not. Plants were transplanted from a clean environment to four sites at the TVA corridor, and exposed for 12 weeks from February to April 2008. Trace element accumulation of plants was determined by Particle induced X ray Emission PIXE and Neutron Activation Analysis (NAA). Results reveal differences in trace elements distribution among sites in the TVA corridor. Furthermore, anthropogenic elements (S, V) and crustal elements (Ca) in *T. usneoides* exhibit high levels. Highly toxic elements such as Hg, As and Cr although present at trace levels, showed un enrichment relative to the initial values, when transplanted to the TVA corridor. Results show that monitoring with *T. usneoides* allows a first approximation of air sources to provide insights of the atmospheric pollution in the TVA corridor.

Keywords: PIXE; NAA; biomonitors; Tillandsia usneoides; trace elements; Mexico.

Este estudio aborda la aplicación de técnicas nucleares para analizar elementos traza en el monitor biológico *Tillandsia usneoides* (heno). El uso de monitores biológicos proporciona una alternativa ventajosa en el muestreo de material particulado en estudios de contaminación del aire, ya que no requiere dispositivos especiales de muestreo y el tiempo de monitoreo puede ser tan largo como se desee. *T. usneoides* que crece en todo el país, se utilizó para estudiar la calidad del aire del corredor Tula-Vito-Apasco (TVA) en el estado de Hidalgo. Esta área es considerada zona crítica debido a la alta concentración de contaminantes atmosféricos. Las plantas fueron trasplantadas desde un entorno limpio a cuatro sitios en el corredor de TVA y expuestas durante 12 semanas de febrero a abril de 2008. La acumulación de elementos traza en plantas sin lavar y secas se determinó por PIXE y NAA. Los resultados obtenidos revelan diferencias en la distribución de elementos traza entre los sitios del corredor TVA y muestran que el monitoreo con *T. usneoides* permite establecer una primera aproximación de fuentes de contaminantes atmosféricos.

Descriptores: PIXE; NAA; biomonitores; Tillandsia usneoides; elementos traza; México.

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1. Introduction

Due to large volumes of contaminants generated by the TVA industrial corridor this region has been classified as a critical zone. Several studies have been already carried out in this corridor [1-3]. The monitoring network in the area [4] determines and analyzes criteria pollutants and total suspended solids, but there is a lack of studies on the elemental composition of the particulate. Mexican norms only regulate concentration and size of the particulate matter, but not its composition, which according to various studies; can have adverse effects on health. The use of biomonitors is presented as a low cost option of monitoring with a sufficient level of confidence for the diagnosis of pollution in extensive regions and little infrastructure as the TVA corridor, where we find small urban and industrial areas immersed in a large rural area with agricultural activities for subsistence.

The coexistence in the area of various industries including oil, power generation, transformation and mining industry introduce in the atmosphere elements which combination could be particularly risky. The acidity of sulphur dioxide in presence of heavy metals, which are usually in the form of oxides, is a potentially dangerous combination because it favours the increasing of the oxidation state of the metal

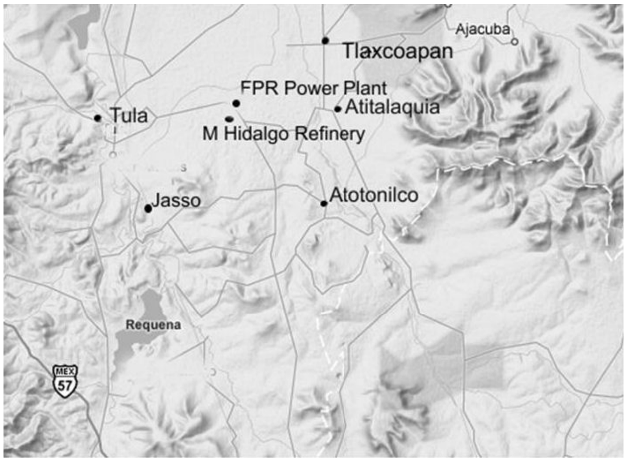

FIGURE 1. Study area.

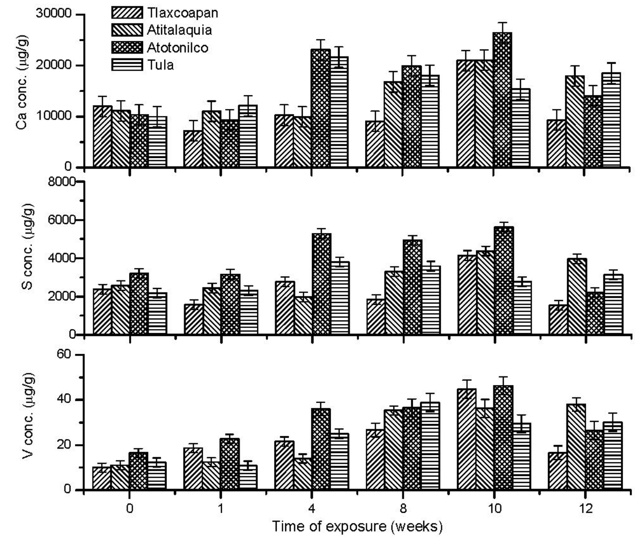

FIGURE 2. Concentration of Ca, S and V (μg/g) in *T. usneoides* determined by PIXE at 0, 1, 4, 8, 10 and 12 weeks of exposure.

species through a solubility process. It is therefore necessary to know the elemental composition of the particulate matter in the area. In this way, it will be possible to know which elements are present and their concentrations in order to design strategies of analysis to assess the potential damage that could cause the combination of various inorganic pollutants.

Basic receptor models allow the determination of the emitting sources of pollutants [5,6]. The construction of these models is performed using filters or biomonitors which collect the air particulate matter in the area of interest. An advantage of biomonitors relies on the ability of plants to retain and to incorporate elements which are not possible to collect using standardized filter methods. Biomonitors are not only an indication of the zone atmospheric conditions, but also are able to preserve the fingerprint of the anthropogenic activity. They can collect potentially toxic elements whose presence could be considered as low risk due to their low concentration, but whose combined effect could be potentially dangerous [7,8]. In other words, the presence of isolated concentrations of traces elements could be considered not risky, but their simultaneous presence could have a synergistic effect and become dangerous. Therefore it is necessary to know the concentration of elements in the particulate matter, even that of those in very low concentrations.

Among the biomonitors employed to analyze trace element's atmospheric pollution, *T. usneoides* shows up as a very adequate option for the TVA corridor. It grows very well in dry climatic conditions like those of the study area and also is widespread in the region. It has been also validated by the International Atomic Energy Agency (IAEA) [7] as a suitable biomonitor; therefore it can be used to determine the air quality in remote areas where the use of filters is expensive. The determination of the elemental composition in the air particulate matter, either at toxic level or at potential toxic levels, requires very sensitive techniques where no sample or minimal sample preparation is required. The multi-elemental capability of the technique is highly recommended in order to reduce cost in the analysis. Nuclear analytical techniques such as PIXE and NAA met all these requirements. Combining them a large number of chemical elements can be determined.

Therefore, the objective of this work is to employ nuclear analytical techniques to explore the behaviour of *T. usneoides* as active biomonitor in this remote area of high industrial activities, where the use of filter can be expensive. This work was particularly focused on the determination of Ca, S, V, As, Hg and Cr. It is already known the presence in the zone of the first three elements due to the oil refinery, thermoelectric power plant and cement industries [1,2,9]. In the case of the last three elements, they may also be present in the area. Mercury emissions to the atmosphere have been associated with incineration and fossil fuel combustion [10]. Arsenic and Cr are generated from industrial activities. The presence of these contaminants could only be potentially toxic, but it is desirable to be able to detect them due to their high toxicity. Moreover, Hg usually is not reliable determined when air particulate matter sampling is carried out by filters because it is volatilized; therefore it is particular interesting to study whether or not *T. usneoides* could be a more suitable option for Hg sampling.

2. Material and Methods

Study area

TVA industrial corridor is located in Hidalgo at the central region of Mexico. Important sources of atmospheric contamination such as the oil refinery, two plants for electricity generation, lime and cement production industries, among others industrial activities are located there. Four sites around the refinery and Power plant were chosen: Tlaxcoapan, Atitalaquia, Atotonilco and Tula (Fig. 1). The area is characterized by a semi-arid climate with an annual average rainfall of 600 mm and an average temperature between 16 and 17°C. Slow winds (<2 m s^{-1}) are predominantly from northeast.

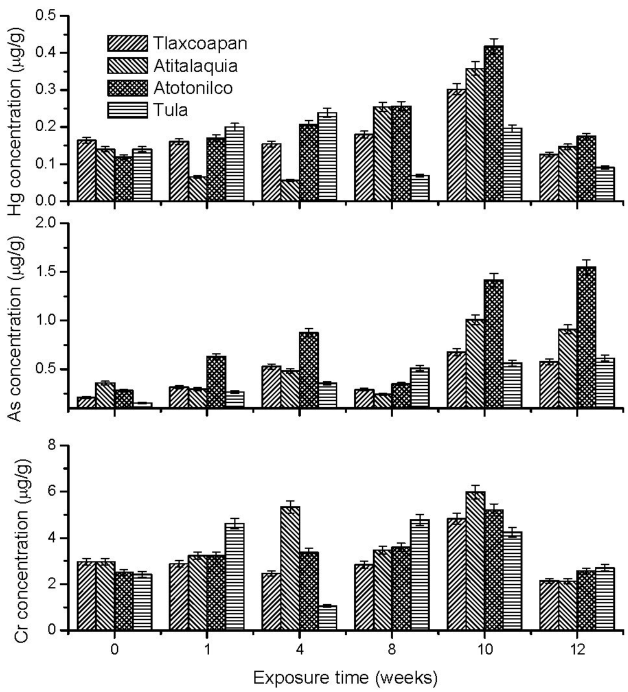

FIGURE 3. Concentration of Hg, As and Cr (μg/g) in *T. usneoides* determined by AAN at 0, 1, 4, 8, 10 and 12 weeks of exposure.

Sampling campaign

T. usneoides plants were collected in an unpolluted control site and transplanted to the four studies sites. Plants were hanged in artificial trees at 3 m above the ground. Samples of *T. usneoides* were removed from the monitoring sites after 1, 4, 8, 10, 12 weeks of exposure. Sampling was performed during the dry season from February to April 2008.

3. PIXE analysis

Fifty mg of dried samples (three replicates) of *T. usneoides* in presence of an aliquot of Indium were digested using nitric acid (Merck Suprapure 65%) in a microwave oven. Indium was used as an internal Standard. After digestion, 5 μL were deposited on 4 μm Prolene substrate until dryness. Analytical blanks were processed in the same way. For quality control, reference materials such as peach (NIST-SRM No 1547) and spinach (NIST-SRM No 1570a) were prepared in the same way as described for samples. Standard solutions with known concentrations of different elements and with In as an internal standard were prepared for calibration. Samples were analyzed at the Institute of Physics on the NEC Pelletron accelerator 9SDH wich, were bombarded with protons of 3 MeV to produce characteristic X-rays from the atoms in the samples. X-rays were detected with a Ge detector (Canberra) with an energy resolution of 155 eV at 5.9 keV. Quantification was performed using the GUPIX code [11].

NAA analysis

Standard solutions of known concentrations of various elements were placed at irradiation rabbits containing sugar to ensure that standards and samples have the same irradiation geometry. After freezing drying, about 200 mg of the sample were deposited at the irradiation rabbit. Same procedure was followed for the SRM-IAEA 336 epiphytic lichen. Samples were irradiated at the TRIGA-MARK III nuclear research reactor at the National Institute of Nuclear Research in México using a neutron flux of 1.3×10^{13} n cm^{-2} s^{-1} during 20 hours. After a decay time of 5 days they were counted for 2 h on top of the detector in a gamma-ray spectrometry system consisted of an EG&G Ortec HPGe p-type coaxial detector with a resolution (FWHM) of 1.72 keV at the 1332.5 keV photopeak of ^{60}Co and a relative efficiency of 25% with respect to a standard NaI(Tl) detector.

4. Results and discussion

PIXE analysis

The determination of Ca, S, and V was carried out by PIXE after digestion of the samples. These elements were detected in all analyzed samples and their quantification was carried out by the comparator method. Table I shows the Kα line used for the quantification of each element along with the sensitivity, detection limit achieved in 5 min of irradiation, accuracy tested on standard reference materials and the range of concentration found in samples.

For the three elements, detection limits and accuracy (which all can be improved with longer irradiation time) are very suitable for the reliable determination of these elements by PIXE. Moreover, the lowest concentration found in the analyzed samples for each element is at least 5 times of the LOD, ensuring the validity of the reported value.

NAA analysis

Some pollutants such as As, Hg and Cr, present in air particulate matter usually are at very low concentrations. Therefore it is difficult to measure them accurately by PIXE. In those cases, NAA is more adequate because of its high sensitivity. These three elements were then determined by NAA instrumentally and, as well as in PIXE, using the comparator method. Table II shows the gamma energy line used for the quantification of each element along with the sensitivity, detection limit calculated from the matrix's background, accuracy tested on standard reference materials and the range of concentration found in samples.

For the three elements, the gamma line used for quantification is the strongest one from the gamma spectrum. Due to the irradiation-counting scheme and the resolution of the detector employed these lines are free of interferences. The sensitivity values and the detection limit in each case were very good, although these value can be improved varying the irradiation-counting scheme. Arsenic and Cr were detected in all samples and for these elements the accuracy values were very good. Mercury was detected in most of the samples. However, accuracy value is not reported since it was not detected in the reference material.

TABLE I. Characteristics of PIXE analysis.

	Calcium (%)	Sulfur (%)	Vanadium (μg/g)
Kα (keV)	3.691	2.308	4.952
Limit of detection	10.0	6.0	0.5
Accuracy on Peach Leaves (NIST-SRM-1547)	*(1.56 $\pm$ 0.02) 95 %	**(0.2) 93%	*(0.37 $\pm$ 0.03) 91 %
Accuracy on Spinach Leaves (NIST-SRM- 1570a)	*(1.527 $\pm$ 0.041) 95%	**(0.46) 94%	*(0.57 $\pm$ 0.03) 91 %
Range on samples	1.0-2.6	0.2-0.5	6-23

*NIST-SRM certified concentration value **NIST-SRM reference values

TABLE II. Characteristics of NAA analysis.

	Arsenic	Mercury	Chromium
Gamma energy (keV)	559.1	279.2	320.1
Sensitivity (counts/ μg)	51004	23734	5917
Limit of detection (μg/g)	0.08	0.14	0.4
Accuracy (%) on Epiphytic lichen (IAEA-SRM-336)	*(0.63) μg/g 93%	*(0.20) μg/g No detected	†(1.06) μg/g 97%
Range on samples	(0.1 – 1.8) μg/g	(0.07^a – 0.53) μg/g	(1 – 9) μg/g

*IAEA-SRM recommended concentration value. †IAEA-SRM information concentration value. ^{a}Critical limit.

The concentration range found in the analyzed samples was above the detection limit for arsenic and chromium and around the detection limit for Hg. Sometimes the determined concentration for mercury in samples was about half of the detection limit but the peak was very well defined, this means that it was at the critical limit, which was selected to be the lower extreme in the concentration range found in samples. In general, the determination of this elements under the irradiation-counting conditions selected are excellent for Cr, very good for As and good for Hg. Perhaps this scheme should be optimized to improve the results for Hg, but the purpose of this work, which it was to prove whether or not *T. usneoides* incorporates Hg was achieved.

T. usneoides behaviour

Figure 2 shows the concentration of Ca, S and V elements in *T. usneoides* at 0, 1, 4, 8, 10 and 12 weeks of exposure in the four studied sites. It was already known from previous studies of the region using filters that the particulate matter in the air of the area has important amounts of these elements [3]. The fact that these elements increase their concentration in *T. usneoides* using the active sampling shows that this plant takes these elements from the air particulate matter and it can be used as a biomonitor of the region. The maximum accumulation point was reached at week 10, which is in agreement with other authors [12]. Atotonilco showed the highest accumulation levels relative to the other sites. The reduction in absolute concentration values observed by week 12 may be due to a slight rain in the region which removed mainly the elements adsorbed to the biomonitor surface.

Figure 3 shows the same accumulation trend for As, Hg and Cr indicating that although at low concentrations, these elements are also present in the air particulate matter of the zone, which is potentially very risky due to their high toxicity. Further studies are required to investigate the chemical species in which these elements are present, since their toxicity level depends very much on this point.

These results are very interesting because the filter analysis by PIXE of the PM_{10} in the area did not revealed the presence of any of these 3 elements, either because they were volatilized from the filter or they were in the filter but the determination conditions were not enough to detect them. In any case this work proves that the usage of *T. usneoides* is a suitable sampling method for the determination of As, Hg and Cr in the PM_{10} of the TVA corridor.

5. Conclusions

Active biomonitoring using *T. usneoides* has been used for the first time in the TVA industrial corridor, where relatively little work has been reported related to particulate matter composition. Biomonitoring combined with nuclear analytical techniques allowed to confirm the presence of high amounts of elements such as Ca, S and V in the atmosphere of the region as reported by previous reports. Biomonitoring also provided new information about the presence of toxic elements such as Hg, Cr and As in the TVA corridor.

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