PIXE and RBS elemental analyses of tree rings from Mexico Basin forests as a record of pollution.

J. Miranda, G. Calva-Vásquez¹, C. Solís, and L. Huerta

Instituto de Física, Universidad Nacional Autónoma de México
Apartado Postal 20-364, 01000 México, D.F., MEXICO

Abstract. Particle induced X-ray emission (PIXE) and Rutherford backscattering (RBS) elemental analyses of tree rings and soils from forests around the Mexico City Metropolitan Area (MCMA) were performed. The aim was to estimate the impact of pollution on the forests. Cores from Pinus montezumae and Abies religiosa trees, in four forests around the MCMA (Desierto de los Leones, Iztapopocatépetl, Villa del Carbón and Zoquiapan) and a reference site (El Chico). Differences were observed in samples from the different forests, showing higher values in the areas closest to the MCMA. A correlation of several elements with ring width was found using cluster analysis. Additionally, soil analyses from different depths in the forests were carried out, trying to relate the elemental concentrations measured in the tree rings with cation mobility. In this case, samples taken in 1993 and 1999 were analyzed, showing elemental mobility to the various depths.

INTRODUCTION

Atmospheric pollution in the Mexico Basin started significantly around 1975, together with official measurements and reports. However, the effect on forest ecosystems has not been investigated extensively [1]. Therefore, it is necessary to study them using very sensitive and reliable methods. The Metropolitan Environmental Commission (CAM) [2] reported that total emissions in the Mexico City Metropolitan Area (MCMA) reached $2.5 \times 10^6$ ton during 1998, with 84% produced by mobile sources, 12% by area sources, 3% by point sources, and 1% by soils and vegetation. Among the main indicators of pollution are suspended particulate matter with dimensions below 10 µm (PM10), SO$_2$, and NO$_x$. The CAM predicts a general growth in the emissions for the year 2010. Thus, PM$_{10}$ would increase by 26%, SO$_2$ by 48%, and NO$_x$ by 37%. According to information provided by the Automatic Atmospheric Monitoring Network (RAMA), the North and Central regions of the Mexico Basin have larger deposits of particulate matter, which are dispersed by the dominant winds towards the SW-SWW area, while the phenomenon is inverted during the dry season. As a consequence, the forests around the Mexico Basin are affected in different ways by the pollutants emitted in the MCMA. The Environment Secretary of the local Government (SMA-GDF), reported the existence of $6 \times 10^6$ ha of conifer forests in the Basin, including several National Parks [3]. The degradation of these forested areas is apparent. Industrial emissions alter the concentration in trees and other plants of elements known as macronutrients (C, K, Ca, Mg, P, S), and micronutrients (B, Fe, Cu, Zn, Mo). Something similar occurs with other trace elements, like Cd, Co, Cr, Pb, Hg, Ni, and V. The accumulation of the elements in the trees may affect their normal development, according to elemental concentrations and toxicity [4]. The species Pinus montezumae and Abies religiosa are present in altitudes ranging between 2800 m and 3200 m above sea level. The ages of the trees in the Mexico Basin forests oscillate between 150 and 200 years, with heights around 25 m. It is important to point out that these species present well defined growth rings. Thus, it was considered as an important task to measure elemental concentrations, using particle induced X-ray emission (PIXE), in rings extracted from trees located in forests around the Mexico Basin. This technique has proven to be a very powerful tool for this kind of studies [5, 6]. The

¹ On leave from Facultad de Estudios Superiores Zaragoza, UNAM.
The purpose of this work was to identify the influence of pollutants emitted in the MCMA on the development of the trees, estimating differences among the studied forests.

MATERIALS AND METHODS

Four forests around the Mexico Basin were selected as study sites: Izta-Popo National Park, Zoquiapan National Park, Desierto de los Leones recreational area, and Villa del Carbón. Moreover, the El Chico National Park was taken as a reference site, as it is located north of the Basin, and is mostly subjected to winds that disperse pollutants coming from the Southern region. Fig. 1 shows the location of the sites.

FIGURE 1. Location of sampling sites.

Five trees from every forest and each one of the Pinus and Abies species were selected to extract 40 cm long cores, 5 mm in diameter, using a Pressler drill. Additionally, samples of soils from every forest were collected at depths ranging from 0 to 120 cm, in 15 cm steps, in 1993 and 1999. Tree cores were cut to show a flat surface, using glass tools, while soil samples were palletized. PIXE analyses were performed with external beam setup at the 3 MV Pelletron accelerator, Instituto de Física, UNAM [7]. A 3 MeV proton beam was the primary radiation. A Canberra LEGe detector was used to measure contents of heavy elements, while an Amptek Si detector provided data about lighter elements. Calibration of the detection systems was carried out with pellets of IAEA Lake Sediment SL-1 reference material. The computer code GUPIX [8] was used to obtain quantitative results, while the NIST tomato leaf reference material was employed to check analytical accuracy. Rutherford backscattering (RBS) with a 0.7 MeV He beam helped to determine the matrix composition for the soils and the wood in the tree cores. Also, ring thicknesses were determined with the WinDENDRO [9] computer code, from digitized images of the tree cores.

RESULTS AND DISCUSSION

First, elemental concentrations measured in tree rings are considered. In general, elements S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, and Zn were detected, with eventual appearances of As, Br, Rb, Sr, Y, Zr, and Pb. RBS provided information mainly on C, N, and O. As an example, Fig. 2 shows the results for a Pinus core from the Iztapopocatepetl site. Although the uncertainties do not allow a definite conclusion, a growing trend is observed in several elements, like Cr, Mn, Fe, and Cu, which are normally related to human activities. A similar phenomenon was observed by Watmough and Hutchinson [10] in sacred fir tree rings from the Desierto de los Leones site. To estimate the reproducibility of the measurements, Fig. 3 displays data for two different cores from the Iztapopocatepetl National Park. There, S concentrations are plotted as a function of time. It can be seen that the data have a very similar behavior. However, in this case there is not a trend observed in the data, except for a few peaks in the concentrations. It should be noted that the peak in 1992 is in agreement with the highest pollution indices measured in Mexico City [1].

It is also of interest to identify some kind of correlation among the different elements and the width of the tree rings. To carry out this task, the application of cluster analysis, with the 1-r Pearson correlation and Ward’s method of amalgamation [11] is useful to present the results in a graphical form. Thus, Fig. 4 shows a dendrogram for a Pinus core from the Iztapopocatepetl forest. There, a linkage is found among the ring width and the elements Cl, K, Ca, and Mn. This is expected, as these elements are usually associated to the growth of living organisms. It should be pointed out, also, that a correction in the rings width due to volume increase in the trees is done by the WinDENDRO program. Additionally, groups of elements possibly anthropogenic are identified, including Ni, Ti, Cu, and S in one group, and Fe, Cr, Zn, and V in another.
The effect of pollution can be observed when comparing the Desierto de los Leones site, which is very close to the MCMA, with the reference site, El Chico. Both sites are chosen as they are extreme situations: the former is expected to be the most affected due to its proximity to the urban area. The elemental concentrations measured in the cores are averaged along the thirty years of interest. The results are shown in Figs. 5 and 6. There, the elemental contents are higher in Desierto de los Leones, as a result of human influence, polluting the environment in this forest. This is supported by the fact that winds in the Mexico Basin tend to accumulate the pollutants in the Southwestern area, so this forest receives a very strong influence of the anthropogenic emissions.

FIGURE 2. Elemental concentrations in a Pinus montezumae core from the Iztapopocatépetl site, as a function of the year corresponding to each ring.

FIGURE 3. Concentration of S in tree rings from two cores extracted at the Iztapopocatépetl site.

FIGURE 4. Dendogram based on data obtained in the analysis of a core taken from Pinus montezumae at the Iztapopocatépetl site.

FIGURE 5. Mean elemental concentration in tree rings (corresponding to 30 years), from cores extracted at the Desierto de los Leones and El Chico, for the most abundant elements.

Also, Ca concentrations measured in soil samples extracted in 1993 and 1999 are given in Fig. 7. These results correspond to the Iztapopocatépetl National Park. The data show similar contents near the surface, but they are very different in the deepest regions. This is because there is a higher cation mobility in the shallower layers, as was shown with measurements of this variable. Therefore, an accumulation of Ca was observed in the 1999 samples.
CONCLUSIONS

The results presented in this work represent only examples of the advances obtained in the study of tree rings and soils from the Mexico Basin forests. The effects of pollution were observed in several cases, although more analyses are required in order to validate statistically the information obtained until now. The consideration of official pollution records is still pending, as well as the explanation of the role of elemental mobility in soils in the tree rings.

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REFERENCES


10. Watmough, S.A.; Hutchinson, T.C. Change in the dendrochemistry of sacred fir close to Mexico City over the past 100 years. Environmental Pollution 104 (1999) 79-88.