Effects on the Elemental Concentration in Tree Ring Growth due to Popocatepetl Volcano Exhalations

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Abstract. The Popocatepetl volcano has increased its activity since the year 1991 affecting the environmental conditions of its surroundings. The concentration of Z > 12 elements were measured on pine tree rings from forests in Paso de Cortés, located at 6 km from the volcano’s crater. The analysis was done by simultaneous PIXE-RBS using an external proton beam on tree rings of Pinus montezumae. In order to understand the effects originated by eruptions in those near forests this study provides information about the elemental concentration in pines of this region during the years from 1974 to 2004. The tree rings composition exhibit an increment tendency for P, S and K concentrations since 1991 while a Zn decrement is observed. The metallic elements Mn, Fe and Cu do not present significant variation or a clear behavior with the time. These results indicate that changes in the pines elemental compositions are more related to gaseous volcanic exhalations of the Popocatepetl than to its ash emissions.

Keywords: PIXE, Popocatepetl, tree ring, dendrochemistry, pine, volcano, environment

INTRODUCTION

The Popocatepetl volcano (5465 m asl) is located 70 km Southeast from the downtown of Mexico City. It has increased significantly its activity since 1991. Several exhalations of gases, dust and ashes have taken place reaching the Mexico Valley and the city of Puebla. Those events have affected the atmospherical conditions in the surroundings, producing changes in the composition of aerosols and having an impact on the environment of the whole region. They have also affected the ecological conditions in the soils.

The soil characteristics and environmental factors where the trees grow determine the composition and properties of the wood. Dendrochemistry studies can be used to obtain the elemental composition of the tree rings and make a register of the concentration variations in the rings throughout the years. It is expected that the effects due to changes in soil are recorded in the elemental composition of the tree ring growth [1,2].

In order to understand more about the induced effects by eruptions in forests surrounding the Popocatepetl, we present a study of the Z > 12 elemental concentration in tree rings from pines of forests at Iztapopocatepetl National Park during the last 30 years, using PIXE technique in air.

EXPERIMENTAL

Area of study and sampling

The forests at Iztapopocatepetl National Park (Izta-Popo NP) are located in a region occupied by the volcanoes Iztaccihuatl and Popocatepetl. The Iztaccihuatl is located 15 km north from the Popocatepetl. Those forests are around 65 km east of Mexico City and consist mainly of pines and firs which extend from 2,450 m to 4000 m asl. The tops of these volcanoes are covered with snow during most of the year. The Popocatepetl has intensified its activity since the year 1991 and the largest exhalations occurred in the periods [3,4]: December 1994 – August 1995 (Volcanic Explosivity Index, VEI 2), March 1996 – November 2003 (VEI 3), May 2004
(VEI 2) and January 2005 – January 2006 (VEI 2), when gases and ashes emitted reached Mexico City.

The substances emitted by the volcanic fumes are incorporated to the ecosystem, mainly through the melt water from the glaciers on top of Popocatepetl and the adjacent mountains. The water from the slopes of the mountains forms the streams of the mountains hydrological system.

For this study pines of *Pinus montezumae* (Lamb. var. Lindleyi) were considered because they are one of the predominant tree specie in those forests. The samples were collected during year 2005 in the narrow valley formed between the two volcanoes in a region called Paso de Cortés (98°38'24"W / 19°05'10"N / 3660 m asl) 6 km from the Popocatepetl crater. This place is a natural crossing pass from Mexico Valley to Puebla Valley. Figure 1 shows the location of the Iztapopocatepetl NP and the sampling area. The sampling was done by selecting trees randomly. The average height and the diameter of the pine trees are 24 m and 2.25 m, respectively. The age of the pine trees is around 80 years. From each tree, two cores were extracted with a 5 mm diameter and 35 cm in length stainless steel Pressler drill at breast height (1.5m). The extracted cores were placed in a wood frame and dried at 50°C for 48 hours. Those extractions were done trying to produce as little damage as possible to the tree. The identification of the tree rings in the cores was carried out according to the criteria given by Fritts [5].

**PIXE analysis**

For the elemental composition analysis of the cores the PIXE technique was performed in air using the external proton beam setup located the 3 MV Pelletron tandem accelerator at the Instituto de Física, UNAM. The best conditions to analyze the tree cores were established in a previous work [6]. Only the rings corresponding to the last 30 years of each core were analyzed (period from 1974 to 2004). The proton beam was collimated to a rectangular area of 0.5 x 3 mm² to ensure that the beam is irradiating inside each ring area. The proton energy at the sample surface was 3.0 MeV. The X-rays generated in the target were registered by a LEGe and an AmpTek Si-PIN detectors placed at 135° from the incident beam direction. For the X-ray detector efficiency calibration and elemental quantification, compressed pellets of NIST SRM 1573-a tomato leaves were used as reference material. The X-ray peak counts in the PIXE spectra were obtained using the AXIL code. The elemental concentration in each tree ring was determined using the PIXEINT program for thick target analysis considering C and O contents of wood. The uncertainties in elemental concentration were estimated to be 8% to 14%. The detection limits of the system for elements with 19 < Z < 30 were between 4 μg/g and 20 μg/g.

**RESULTS AND DISCUSSION**

The average tree ring widths for the collected cores samples for every year are shown in figure 2. These widths vary along the years around a stable value of 1.75 mm. Only for year 2004 a fall in the width is observed.

By PIXE measurements the elements P, S, Cl, K, Ca, Mn, Fe, Cu and Zn were observed in all the analyzed rings as mayor constituents. All of them are considered to be important for physiological processes in the tree. Other elements only detected in traces were Ti, V, Cr, Ni, Br, Sr, Rb and Pb. Figure 3 shows the average concentration variation for P, S, Cl and K. These elements are related to gaseous volcano exhalations. From 1991 a notorious increment tendencies on S and K are observed, while for P only a slight rise is observed. Cl has three separated points from the rest of the measurements for the years 1974, 1978 and 2004. But in general, the other Cl
measurements maintain variations around 2000 μg/g. The presence of these large variations has not been related to any specific event yet.

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**FIGURE 2.** Average ring width of the years 1974 to 2004. The dash line indicates the year when Popocatepetl volcano increases its activity.

The increase on the amount of S and K can be related to dry fumes (mainly emission of sodium and potassium chlorides, sulfuric and carbon anhydrides) and to acid fumes (sulfuric and chlorine acid).

Figure 4 shows the average concentration variation for Mn, Fe, Cu and Zn. These metallic elements are mainly related to ashes and rock fragments exhalations. The Mn exhibits large variation during the period of 30 years considered. However these oscillations are around a value of 90 μg/g. In the case of the Fe and Cu concentrations show small fluctuations during the period of time considered in the measurements. Their oscillations maintain around steady values of 815 μg/g and 35 μg/g respectively for Fe and Cu. Only the Cu concentration has an isolated large variation in 2001. It seems to be a random fluctuation because the concentrations for the following years moved again to the same mean steady value. The Zn concentration presents a clear amount decrease from 1971 to 1982, and regular variations with a very slight diminution tendency since 1983. The slight diminution of Zn can be associated with the increments observed in the amount of S and K. These two elements can inhibit the absorption of Zn in the plant or been substituting the Zn atoms in some metabolic substances of the tree.

For the most recent years 2003 and 2004 large variations in some analyzed elements have been observed (increment of K and Fe; diminution of Cl, P and Mn). The explanation of these deviations can be done in terms of the tree physiology [7]. The inner rings are composed by died cells which have suffered

**FIGURE 3.** Average concentrations of P, S, Cl and K for years from 1974 to 2004. The dash line indicates the year when Popocatepetl volcano increases its activity. These elements are related to gaseous fumes.
FIGURE 4. Average concentrations of Mn, Fe, Cu and Zn for years from 1974 to 2004. The dash line indicate the year when Popocatepetl volcano increase its activity. These elements are related to ashes emissions.

a mineralization process during several years, doing they chemical composition more stable. The recent tree rings are the mainly live and most dynamic part of the wood. They present high elemental mobility because the main water and nutrients flow from the soil through them. Due to these effects, the youngest rings become more chemically unstable and the elemental concentration measurements can not be considered conclusive to establish a behavior well related to the volcano.

The notorious Zn decrease before 1991 can be related to the wood formation too. The suggested inhibition of Zn absorption reduces its mineralization process in the late inner rings, generating an effect of less Zn for rings grown even before 1991.

CONCLUSIONS

The tree rings composition exhibit an amount increment tendency for P, S and K, with a Zn decrement since 1991, when the Popocatepetl increased its volcanic activity. In general, the behaviors observed on the concentration for metallic elements Mn, Fe and Cu are variations around a steady mean value along time. In some cases they do not present a clear tendency with time in order to make estimations of any possible change for the future. These results indicate that for pines from forests at Iztapopopopopopopopo NP the changes in tree rings elemental compositions are more related to gaseous volcanic exhalations of the Popocatepetl than to its ashes emission.

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REFERENCES