

Study of the elemental concentration variation of Mn, Fe, Cu, Zn and Pb in rings of growth of *Abies religiosa* and *Pinus montezumae* from Mexico Basin Surroundings

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Introduction

Dendrochemistry and dendroecological studies of the tree rings agree in the argument that the environmental factors and composition of the soil determine the elemental composition and the properties of the wood (Watmough 1999, Nabais 1999). The soil characteristics also depend on the atmospherical and hydrological conditions (Pernestal et al. 1991, Schäffer & Wilpert 2001). Those conditions are related to natural factors, as winds, rain, volcanic eruptions, and by anthropogenic factors due to human activities. Especially, anthropogenic factors have been playing an important role in the modification of the natural patterns of winds and rain as well as in the atmospherical aerosols composition since the last century.

The constituent elements of the wood can be divided in two types: the macroelements are those components of the wood presented in high concentrations (H, C, O, N), while microelements occur in low concentrations (such as Mn, Fe, Cu, Zn) (Lindeberg 2004). The microelements are necessary for physiological processes of the trees, but in high concentrations they become toxic, producing plant illness or dead (Schäffer & Wilpert 2001). For this reason, the study of metallic elements in the trees and their relationship with the environmental conditions is important for forest conservation and for human communities that still survive from the production of wood.

Mexico City is located in the center of the Mexico basin surrounded by mountainous systems in the South-West, South and East regions. The mountains surrounding the basin have forests of pines and firs in the altitudes from 2,800 m to 3200 m asl. The trees of those forests have been exposed to the prevailing atmospherical conditions in the zone which are affected especially by the emission of pollution agents by traffic and industry. Also, the Popocatepetl Volcano located 70 km South-east from the downtown of Mexico City has increased its activity since 1991. Several exhalations of gases and ashes have taken place reaching the Mexico basin. Those events have affected the atmospherical conditions significantly during the last 35 years, producing changes in the composition of aerosols and having an impact on the environment of the whole region. Also, they have affected the ecological conditions of the basin and the chemical conditions in the soils of the forests. It is expected that the effects of the changes mentioned above are recorded in the elemental composition of the growth rings of the trees (Mäkinen & Vanninen 1999).

For the elemental measurements, the PIXE (Particle Induced X-ray Emission) technique was used thanks to its capability for ppm metallic element detection in tree rings (Aoki *et al.* 1998, Vanderlei *et al.* 1999, Liao *et al.* 2000).

The first report on a dendrochemical analysis of the surrounding forest of Mexico City over the past 100 years was carried out on sacred fir (*Abies religiosa* H.B.K. et Cham) (Watmough & Hutchison 1999). The main results indicated an increment in the pollution when the city extended and the number of cars started to escalate 35 years ago. In previous studies by Miranda *et al.* (2003), tree rings series from pine and sacred fir corresponding to 1970 up to 2000 AD from forests in the Mexico basin were analyzed using PIXE in order to obtain a record of contaminants. However, they concluded that more analysis were required to validate the statistical information. Calva *et al.* (2006) continued this research with significant experimental improvements in the PIXE setup and additional measurements of Zn, Fe, Mn and Cu concentrations in tree rings of sacred fir and pine from the same forest. They concluded that the elemental concentrations may not reflect the changes in the environmental conditions due to the human activities in the basin. Moreover, the trends in the elemental concentrations of Fe and Zn can be related to the recent events of the Popocatepetl volcano.

In this work, we present a study of metallic elemental concentrations in growth rings from trees from forests of the Zoquiapan National Park (ZNP), located in the mountains east of the Mexico basin (Fig. 1). The aim of this work is to determine differences in elemental concentration among firs and pines from two different altitudes, considering that there is a different exposure to pollution and environmental conditions, particularly due to the Popocatepetl volcano eruptions.

Area of Study and Sampling

The forest at the Zoquiapan National Park (ZNP) is located in the mountains 55 km east of Mexico City. It consists mainly of pines and firs and extends from 2,450 m to 4000 m asl. The top of the mountains are covered with snow during most time of the year. The Popocatepetl volcano is located 15 km south of the ZNP. It has intensified its activity since the year 1991. There are four kinds of volcano exhalations: Dry fumes (mainly emission of sodium and potassium chlorides, sulfuric and carbon anhydrides), acid fumes (sulfuric and chloride acid), alkaline fumes (ammonia chloride) and rock fragments. The largest exhalations occurred in the periods 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 (Smithsonian, 2007; CENAPRED Mexico, 2005).

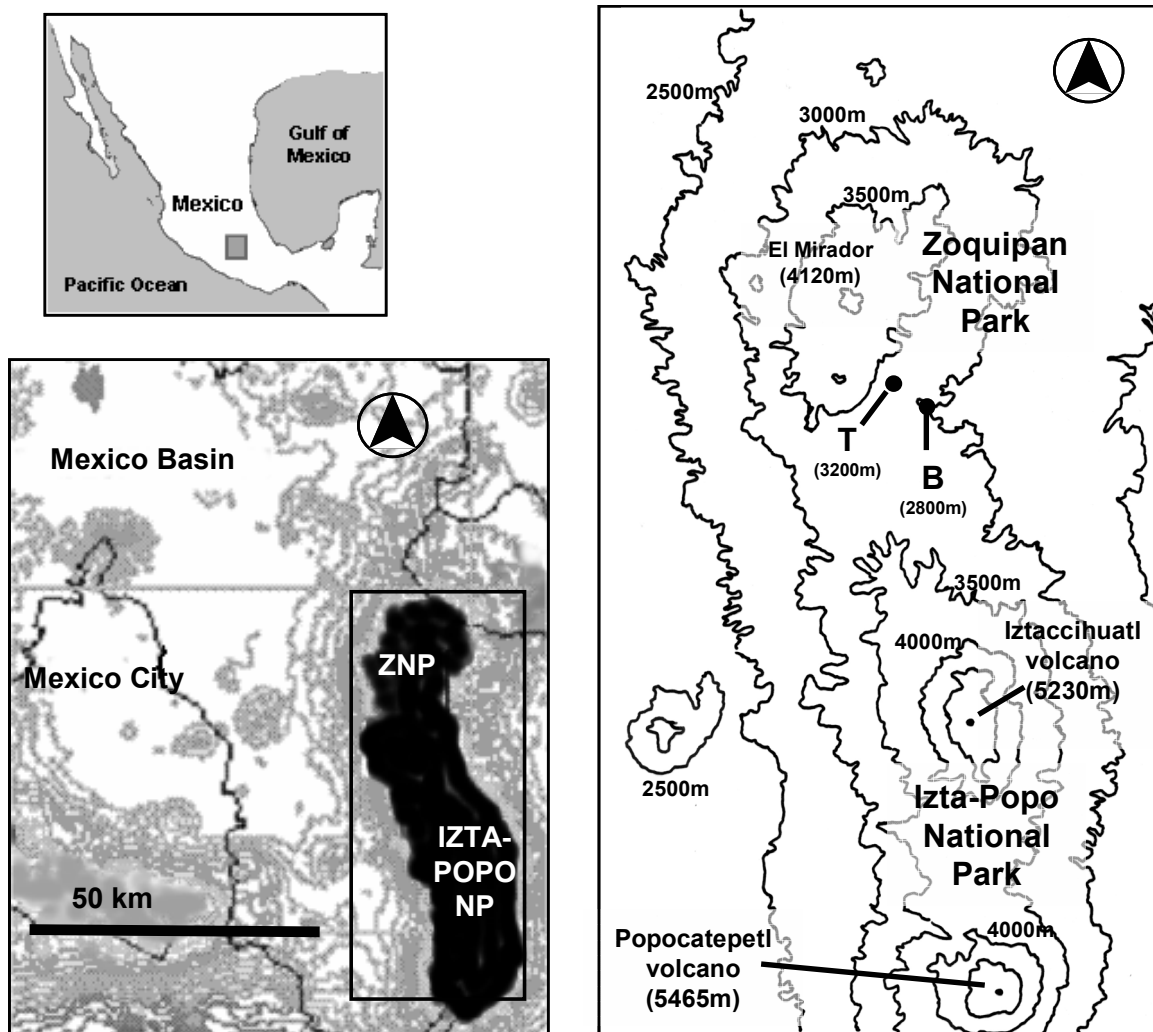


Figure 1: Map showing the location of the Mexican Basin and the Zoquiapan and Izta-Popocatepetl National Parks. The points T (top) and B (bottom) indicate the respectively sampling regions for this work.

The substances emitted by the volcano 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.

The contaminant agents emitted by the Mexico City pollution are transported towards the forests through winds and rain (Miranda *et al.* 2004). The predominant winds during the year blow from the north, where winds that blow from south occur only few days in a month. Therefore we expect more environmental impact in the forests in the south-east and southern mountains, due to higher concentration of pollution agents, than in the ZNP forests. For this study two predominant tree species in those forests were chosen: the Montezuma pine, *Pinus montezumae* (Lamb. var. Lindleyi), and the sacred fir, *Abies religiosa* (H.B.K. et Cham). The pine is a tree resistant to changes in the environment while the sacred fir is more sensitive.

The samples were collected at two different sites and altitudes in the ZNP. The first one, called "bottom" (B), is located at 19°20.8'73" N / 98°40'41" W and at an altitude of 2800 m asl.

The second one, called “top” (T), is located at 19°20′55” N / 98°40′11” W and at 3100 m asl. The coordinates of these places were obtained using a GPS Magellan (SportTrak Pro).

In each site the sampling was done by selecting six trees of each species randomly. In both places the environmental conditions were similar. The average height and the diameter of the pine trees are 24 m and 2.25 m, respectively, while for the sacred fir average values are 30 m and 3.5 m. The age of the pine trees is around 80 years. The sacred fir trees are older. 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 few 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 (1975). The widths of each ring were measured with a vernier caliper and the position was marked in the frame.

PIXE analysis

For the elemental composition analysis of the cores, Particle Induced X-ray Emission Spectroscopy, PIXE, was used. 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. Only the rings corresponding to the last 35 years of each core were analyzed. 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. A 7.5 μm Kapton window and a helium gas flux around the target were used to reduce proton beam dispersion and absorption of emitted X-rays. The sample surface was located in a distance of 10 mm from the beam exit window and the proton energy at the sample surface was 3.0 MeV. The X-rays generated in the target were registered by a LEGe detector with a resolution of 150 eV placed at 135° from the incident beam direction. To enhance the X-rays detection of heavy elements, a 38 μm aluminum absorber was placed in the LEGe detector window. For the X-ray detector efficiency calibration and elemental quantification, compressed pellets of NIST SRM 1573a tomato leaves were used as reference material. With this experimental setup (Calva *et al.* 2006), 840 measurements were carried out in the set of 24 trees.

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

The average tree ring widths of the six trees, for both tree species, are shown in figure 2. The tree ring widths depend mainly on water availability and display a high similarity among the species. Pine is a rapid growing tree while sacred fir is more sensitive to available water. The major eruption periods of Popocatepetl Volcano since the increase of its activity (1995, 1996, 2003 and 2004), are indicated in this figure by dashed lines (Smithsonian 2007).

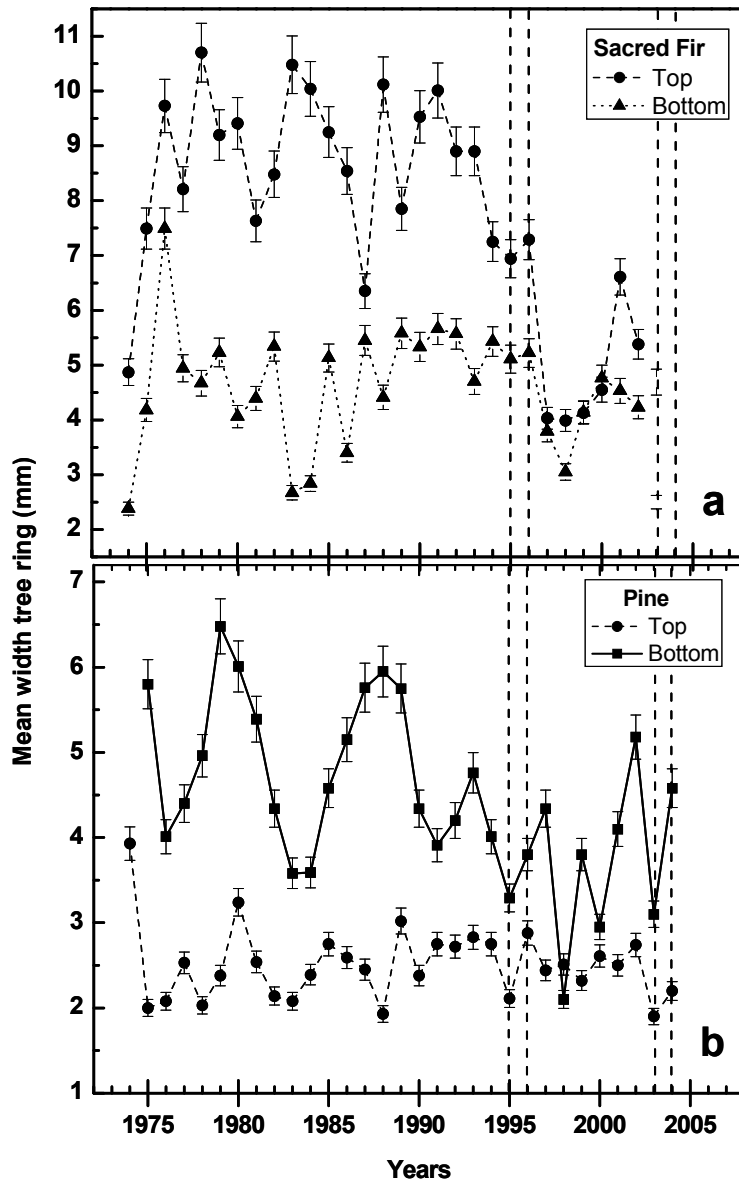


Figure 2: Average ring width of the years, 1974 to 2004, (a) for the sacred fir and (b) for the pine. The dashed lines indicate the years of the major exhalations of the Popocatepetl Volcano (1995, 1996, 2003, 2004).

By PIXE measurements the elements K, Ca, Mn, Fe, Cu and Zn were observed in all the analyzed rings. Other elements only detected in traces were Ti, V, Cr, Ni, Br, Sr, Rb and Pb. In this work, special interest was placed on the metallic elements Mn, Fe, Cu, Zn and Pb. The first four elements are considered to be important for physiological processes in the tree, while the last one is an indicator for environmental pollution.

The average elemental concentrations of Mn, Fe, Cu, Zn and Pb for the rings corresponding to the same year were calculated for the trees of the same species. The average concentrations for the sacred firs and pines, related to the last 35 years, for the sites B and T are shown in figure 3 and 4 respectively. We considered that a real variation corresponds to a change higher than 50% of the mean elemental content. The major exhalations of Popocatepetl Volcano are indicated in those figures by the dashed lines.

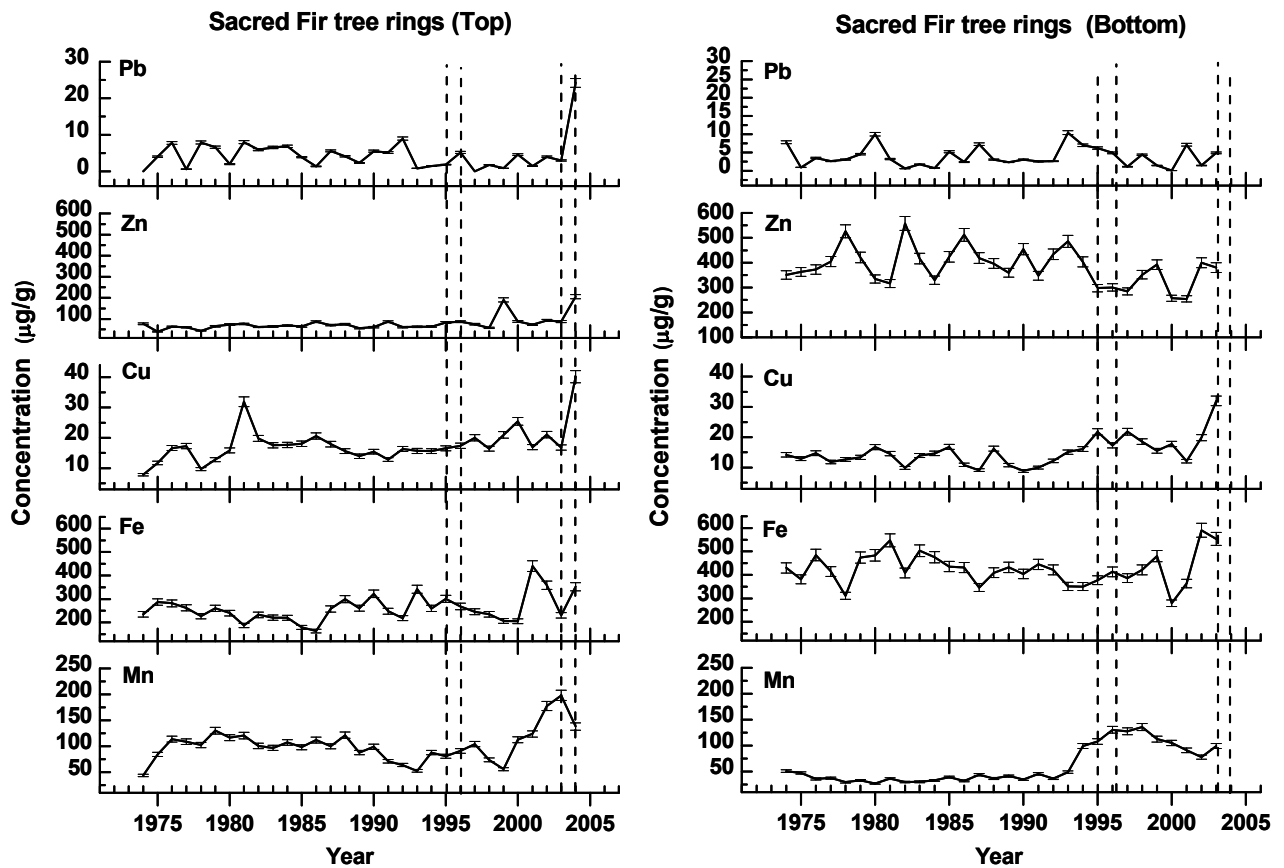


Figure 3: Average concentrations of Mn, Fe, Cu, Zn and Pb for *Abies religiosa* in relation to the time for sampling sites top and bottom. The dashed lines indicate the years of the major exhalations of Popocatepetl volcano.

A comparison among the mean values of Mn, Fe, Cu, Zn and Pb for both tree species and for the bottom and top sites is shown in figure 5. The average values were calculated by a multifactor ANOVA statistical analysis considering a confidence range of 95% and a Tukey HSD proof. The error bars indicate the total variance of the average values.

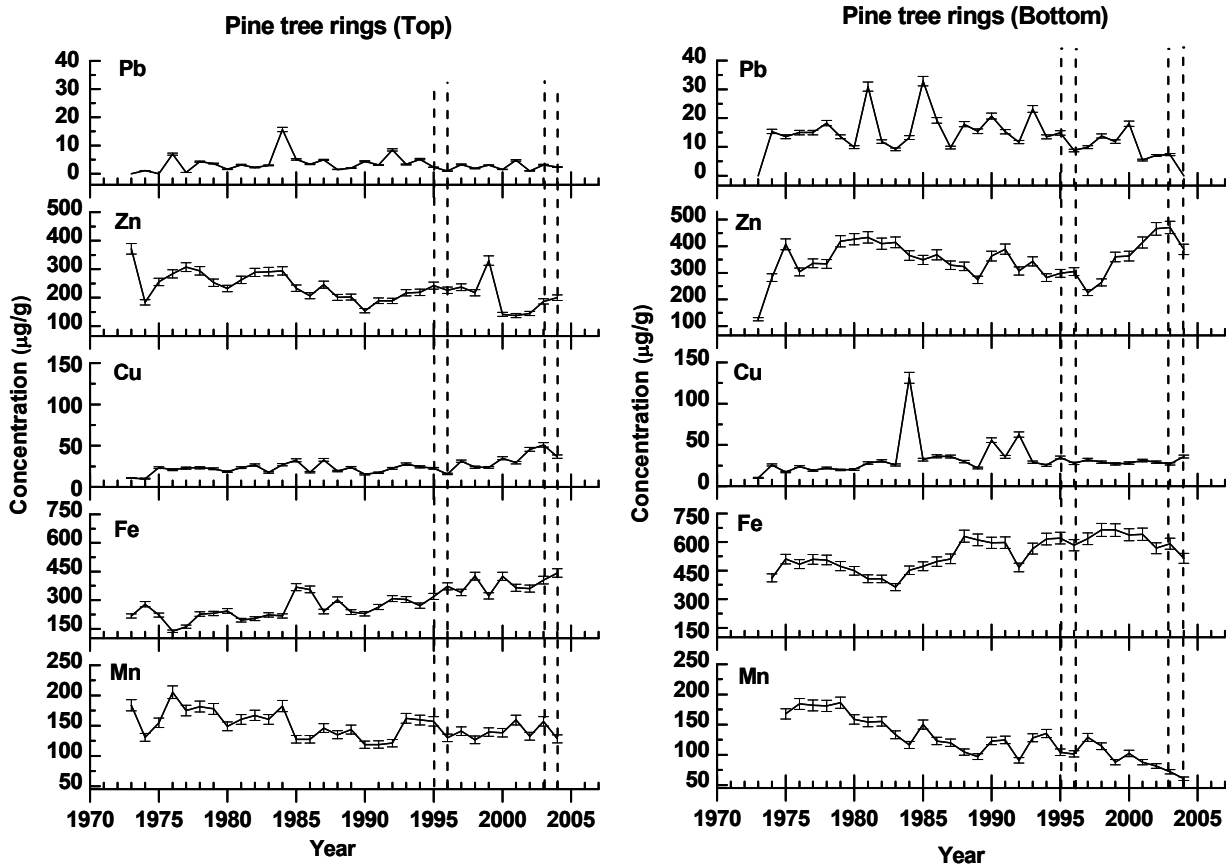


Figure 4: Average concentrations of Mn, Fe, Cu, Zn and Pb for *Pinus montezumae* in relation to time for sampling sites top and bottom. The dashed lines indicate the years of the major exhalations of Popocatepetl volcano.

Discussion

For sacred fir trees (Fig. 2), we observed larger width for the top site (average 8.5 mm) compared to the bottom site (average 5 mm.). The difference in ring widths may be attributed to the fact that sacred firs on top are older. Nevertheless, the distinctly decreasing trend (average 6 mm) in the ring widths on the top site after 1994 is correlated with the increasing Popocatepetl volcano activity and the modification of water conservation pattern due to a loss of available water. A similar (but slighter) diminution trend may be observed for the bottom site (average 4 mm).

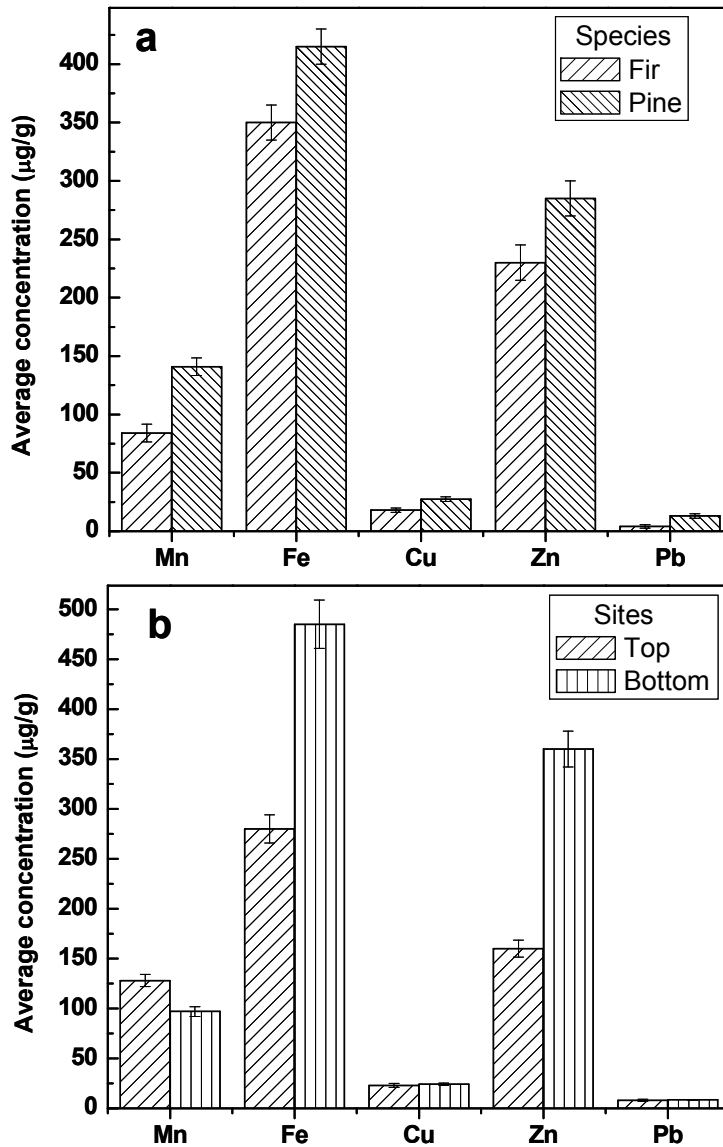


Figure 5: Comparison of the total average concentration of Mn, Fe, Cu, Zn and Pb among (a) species and (b) sampling sites. Error bars indicate the total variance.

On the other hand, the rings widths of the pine trees from the top site (average 2.5 mm) are smaller than at the bottom site (average 4.5mm). A periodic variation is observed before 1994 that may be related to periodic variations of precipitation. The rings widths display a diminution trend with large variations after 1994. This behavior corresponds to the ring width trend of sacred fir for the same period. Sacred fir at the bottom site and the pine at the top site seem to be more resistant to the modifications in the water pattern since both species are located at a more favorable altitude.

For sacred fir tree rings (Fig. 3), it is observed that the Pb mean contents do not change significantly among the top and the bottom sites. A similar behavior has been observed for the mean Cu contents. Nevertheless the mean Fe and Zn contents are higher in the tree

rings of the bottom site, while the Mn mean values are higher for the top site. We may expect that the soils of the bottom site are richer in Fe and Zn due to natural downwash and for this reason these trees may incorporate higher rates of these elements in their cores. In the case of Mn, the lower amounts may indicate a higher acidity in soil in the bottom site by comparison to the top site. In the case of Zn, there is a slight higher trend for the top site but at lower altitude larger variations are observed without a particular trend. Nevertheless, a higher trend in the contents of Pb, Cu, Fe and Mn is observed in the rings of 2000 for both sites. This effect is more obvious for Mn in 1994 for the bottom site and may represent a change in the soil acidity (Watmough 1999). Considering that the volcanic eruptions give rise to an enrichment of metallic compounds in the soil (Miranda, Zepeda & Galindo, 2004; Pearson *et al.* 2005), the increase can be related to the Popocatepetl activity during this period.

For the Pine trees (Fig. 4); Pb, Zn, Cu and Fe mean contents are higher for the bottom than at the top site. The Mn mean values from the top are higher than those from bottom site. Pb and Zn contents on the other hand present larger variations than other metallic contents. An increase for Fe and Cu is observed at the top site in 1995, while the Zn contents increase after 2000 at the bottom site. In contrast, Mn contents decrease at the bottom site after 1980. The higher content of metals in the pine trees in relation to the sacred fir trees is likely due to the fast growth of this species. Nevertheless, the pines seem to be more resistant to volcanic eruption effects, since the elemental increasing trends are slighter than for sacred fir.

In figure 5 it is observed that the mean metal contents are higher for the pine than for the sacred fir trees, this may be related to the faster growth of the pine trees. On the other hand, higher mean Fe and Zn contents are observed for the bottom site, what is in contrast to the top site. This agrees with higher contents of these elements in the soil of the bottom site. On the contrary, Mn mean values are lower for the bottom site probably due to higher acidity of this soil. Cu and Pb do not show any significant difference between the top and the bottom site.

Conclusions

In the ring widths a decreasing trend in the growth of pine and sacred fir trees in the Zoquiapan National Park (ZNP) is observed, which starts in 1994 when Popocatepetl volcano increased its activity. Sacred fir trees display a higher sensibility to the effects of the volcano eruptions, since an increasing trend is observed for the Fe, Mn and Cu contents in tree rings from 1994 onwards in the PIXE results.

On the other hand, the mean values of metal contents (including Pb) are generally higher for pine trees, probably due to the fast growth of this species. Pine trees present higher resistance to the eruption effects since no obvious enrichment of metallic contents can be observed in the rings from 1994.

Zn and Fe contents in the rings are higher in trees from the bottom site. This behavior may be the result of a soil that is richer in these elements. In general, Mn mean contents are lower for the bottom site, probably due to the higher acidity of this soil.

No correlation between the measured elemental concentrations of metals and major human activities, such as the reduction of lead content in the gasoline in 1984 or the closure of the major oil refinery in Mexico City in 1991, has been observed

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