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AIR POLLUTION IN THE ATMOSPHERE OF THE TOLUCA VALLEY, MEXICO

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ABSTRACT

Air samples from the Toluca Valley atmosphere were analyzed by neutron activation technique and atomic absorption was used for Pb determination. Total suspended particulate matter was also determined. On fiber glass filters, the samples were collected and treated with hot concentrated nitric acid and hydrogen peroxide. Pb, Cr, V, Cl, Br, Mn and Ce were measured. The concentration of suspended solids reached values between 90 and 130 $\mu g/m^3$. These results show that particles found in the air were mainly from vehicle fuel combustion exhaust.

RESUMEN

En la atmósfera del Valle de Toluca se determinaron algunos elementos mediante la técnica de activación neutrónica y Pb por absorción atómica. También se determinaron las partículas suspendidas totales. Las muestras se colectaron sobre filtros de fibra de vidrio, para el análisis de los elementos se realizó un tratamiento químico con HNO_3 y H_2O_2. Mediante este procedimiento se detectaron los elementos: Pb, Cr, V, Cl, Br, Mn y Ce. La concentración de los sólidos suspendidos fue entre 90 y 130 $\mu g/m^3$. En los resultados se nota que la mayoría de los contaminantes en los diferentes sitios de muestreo provienen de la combustión vehicular.

INTRODUCTION

Since the middle of this century, human activities have affected the chemical constitution of the atmospheric air, anthropogenic emissions contribute to increase the polluting compounds in the environment. Many studies have been carried out in order to quantify the content of some elements emitted into the atmosphere (Dams *et al.* 1970, Cook 1977, Alpert and Hopke 1981, Salazar *et al.* 1981, Paringo *et al.* 1990, Castellanos *et al.* 1991, Salazar 1993, Villalobos-Pietrini *et al.* 1995).

Heavy metals are among the most important atmospheric pollutants and they are thoroughly distributed in the atmosphere, lithosphere and hydrosphere. Although their natural concentrations rarely reach harmful levels, they can be dangerous to human health and to the environment at high concentrations (Ariens *et al.* 1981).

Environmental preservation has been a main concern of the mexican government and citizens in recent years. At present, several cities have atmospheric pollution problems due to their rapid development (López-Portillo 1982). The Toluca area is particularly characterized by the composition of the chemical particles in its air. This is due to the increase of the industrial activities, the nature of the fuels used and to a significant growth in its population.

Toluca is located 60 km NW of Mexico City, 2689 m above sea level. The climate of the region is temperate and humid, with rain in summer and winter precipitation lower than 5%. The annual precipitation average is about 800 mm and temperatures oscillate between 12° and 18° C all year round.

Pollutant emissions in the Toluca area are produced by hydrocarbon combustion and chemical industrial processes. A study undertaken in 1983 by the Panamerican Center of Human Ecology and Health (1984), a regional organism, reported that atmospheric particulate matter emissions were 1079 ton/year, 46% of which originated from vehicles emissions (Sánchez-Meza 1987).

In the present research, atmospheric air was monitored from some areas located in Toluca; a rural area was also considered as part of the regional atmospheric monitoring program. The main purpose was to identify the contents of particles suspended in the atmosphere, utilizing neutron activation analysis (NAA) and Pb by atomic absorption (AA) techniques. The sampling periods were 8 and 9 months between 1992 and 1993, at San Pedro

Totoltepec and Vía Alfredo del Mazo station, six and five months at Toluca Hospital and the Departament of Justice building, respectively.

MATERIALS AND METHODS

Four stations were considered in this study : the Toluca Hospital Station (A) and the Department of Justice building (B), both are located in the city, with a relatively low vehicular flow. San Pedro Totoltepec (C) is a rural zone considered as a control area for vehicular transit and VÍa Alfredo del Mazo (D), located in the peripheral industrial zone, has a heavy vehicular transit. The sampling sites are indicated on **figure 1**.

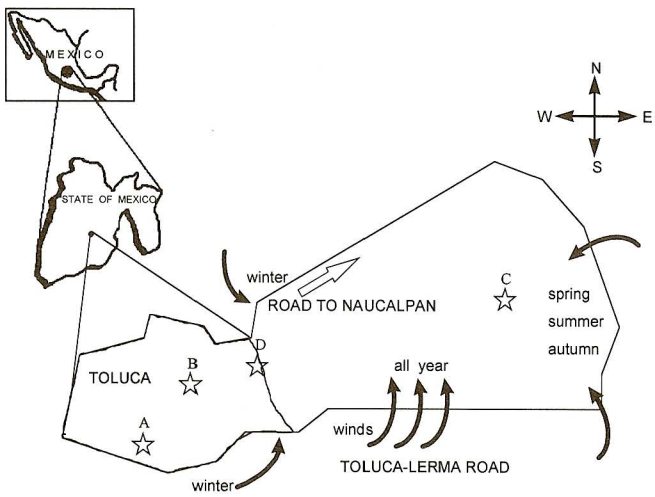

Fig. 1. Map of Toluca city and sampling stations

Wind currents remain the same along the year and do not blow from the industrial zone to the city.

Air samples were collected on glass fibers of 0.5 μm pore size filters. A manual atmospheric monitoring system equipped with a high volume sampling pump (model GMWL-2000-H) was operated continuously during 24 hours. The pump flow rate was 1.056 m^3/minute (NTE-CRP-002 1988)before and after sampling The filters were previously desiccated for 24 hours. The total particle samples were collected, treated chemically and analyzed to find some elements that permitted the air quality determination.

In this aspect, glassware was submerged in 30% HNO_3 solution for 24 hours. Afterwards, they were rinsed with deionized water and dried at 110°C for 3 hours. However, a previous chemical treatment for element determination in the filters was required.

The total filter area was 444 cm^2 and the central fraction (16 cm^2) from each was cut and placed in 250 mL flasks with 25 mL of concentrated HNO_3 and 1 mL of hydrogen peroxide solution and left at reflux for 4 hours with continuous stirring. After filtration, a 50 mL volume solution was obtained by evaporation and homogenized. The chemical treatment was carried out on all samples including filters without exposure, which were taken as blank.

Qualitative and quantitative analyses were determined by NAA (Travesi 1975) to identify the elemental composition and its amount in the sample filters, respectively. Standard solutions containing each element detected in the samples were prepared. Three different solutions were aliquoted in 1 mL each and the first solution was used as standard. The second solution contained the unexposed filter. The last one contained the sample. All samples and standard solutions were put in small polyethylene viales and inserted into irradiation containers. They were all irradiated simultaneously.

The Triga Mark III Mexico Nuclear Reactor was used to irradiate the samples. Some samples were irradiated for 5 minutes and other for 10 hours in the pneumatic irradiation system (SINCA) and the fixed irradiation system (SIFCA) positions, respectively, depending on the nuclear characteristic of the elements. Thermal neutron flux was approximately 10^{12} - 10^{13} neutrons.cm^{-2}/s.

Different periods for the sample decay were used, depending on the radioisotope. The isotopes of short half life were measured after irradiation. To determine the radioactivity, a hyperpure germanium solid-state detector was used. Its active area is 2231 mm^2, with a relative efficiency of 20%. The energy resolution, (FWHM) was 1.90 keV at 1332 keV gamma ray energy. The calibration system was accomplished with ^{204}Tl (70.84 keV), ^{22}Na (511 and 1274.5 keV) and ^{137}Cs (662 keV) isotopes.

On the other hand, a 2380 Perkin-Elmer atomic absorption spectrophotometer (Beauty 1982) was used for Pb determination. Lead standard solutions (1 and 5 mg/L) were prepared for calibration.

Total suspended particles (TSP) were also determined for the samples taken in each of the four places. Some parameters for suspended solids calculation were considered, such as environmental temperature, atmospheric pressure and filters weighed before and after sampling. In order to obtain the TSP concentration, the following equation was used:

$$TSP = \frac{Wf - Wi}{Vs} x 10^6 \qquad \text{and} \qquad Vs = F(t)$$

Where: TSP = total suspended particles
Wi = inicial weight
Vs = air volume at standard conditions
F = pump flux
t = time in minutes
Wf = final weight

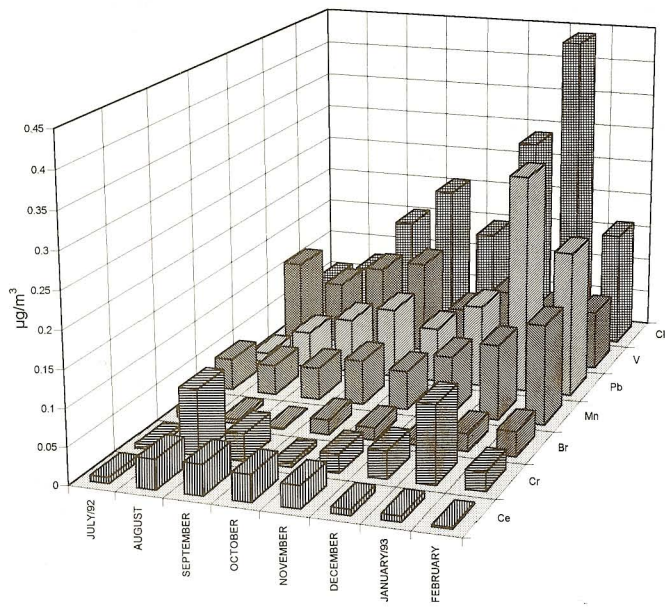

Fig. 2. Element concentrations detected in sampling station A during July-92 to February-93

RESULTS AND DISCUSSION

Table I shows some typical nuclear properties of the elements measured by neutron activation analysis, such as gamma ray energy, half life, irradiation time, etc.

The following figures show the results obtained from the solutions of filters determined by neutron activation and atomic absorption techniques.

At station A (**Fig. 2**), V, Cl, Br, Mn, Ce, Pb and Cr elements were detected. Mn values tended to increase from July to February while Ce values tended to decrease from August to February. A slight augmentation of Br in January and February was noted and since V stayed almost constant during all sampling periods, it is supposed that most elements found in the filters were from fossil fuels. This has been reported in the literature where neutron activation analysis was used to determine some elements in gasoline (Iturbe *et al.* 1995). Some Cl was observed in July-October and again in November to February-93. The Cr greatest values were obtained in August-92 and January-93 and Pb highest concentration was defined during the months of July, January and February; these concentrations were 0.113, 0.302 and 0.201 µg/m^3, respectively. It can be said that, at this sampling place, few pollutants were detected during all the sampling months, but an appreciable increase of almost all elements was noted during the last three months.

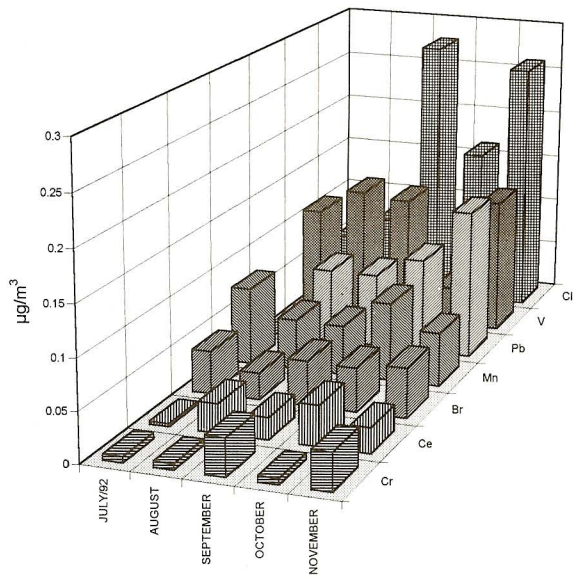

Fig. 3. Element content found in station B during July-92 to November-93

In regard to station B, **figure 3** shows the Ce, Mn, Br, Cl, V, Cr, and Pb concentrations from July to November. This place is also a urban zone with similar vehicular flow than station A. Cl reached values of 0.277 and 0.260 µg/m^3 during September and November, but these concentrations decreased in July. On the other hand, 0.013 to 0.150 µg/m^3 of lead were screened during July and November. Lower amounts of Br were detected during the sampling period, their concentrations varying between 0.005 and 0.044 µg/m^3. The detected elements showed variations between 0.003 and 0.270 µg/m^3. A tendency to an augmented concentration was observed in the last three months, especially for the elements of anthropogenic origin.

TABLE I. NUCLEAR PROPERTIES OF ELEMENTS MEASURED BY NEUTRON ACTIVATION ANALYSIS

Element	Radioisotope produced (n,γ)	Gamma energy (MeV)	Half life	Irradiation time	Decay time	Counting time
Br	^{83}Br	0.62	36 h	5 min	18 h	1 h
Cl	^{38}Cl	1.64	38 min	5 min	5 min	10 min
Ce	^{140}Ce	0.15	32 d	3 h	7 d	2 h
Cr	^{51}Cr	0.32	27.8 d	1 h	7 d	1 h
Mn	^{56}Mn	0.85	2.6 h	2 min	1.5 h	20 min
V	^{52}V	1.43	3.8 min	2 min	2 min	5 min

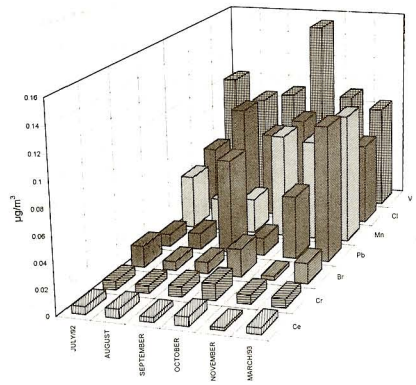

Fig. 4. Element composition determined at station C during July-November-92 and March-93

Results shown in **figure 4**, (San Pedro Totoltepec, station C) point out a notable difference in almost every element concentration from the samples obtained in July-92 and March-93. Some elements such as Mn, Cl, V and Pb slightly tended to increase during September, October, November and March. V kept a constant concentration during almost all the months monitored.

At station D, all elements detected from July to March tended to increase in October-92, January, February and March-93; the highest Pb concentration was obtained during this period and this is due to the high vehicular flow and also to climatic conditions in winter, when low temperature prevails, thus causing the gas dispersion to be slow. In **figure 5** we observe that Cl, V, Pb, Mn and Br concentrations, elements used in the gasoline employed for vehicular combustion, tended to increase.

In general, Mn, Br, Cl, V, Cr and Pb increased in several sampling areas. We can therefore conclude that the origin of these elements

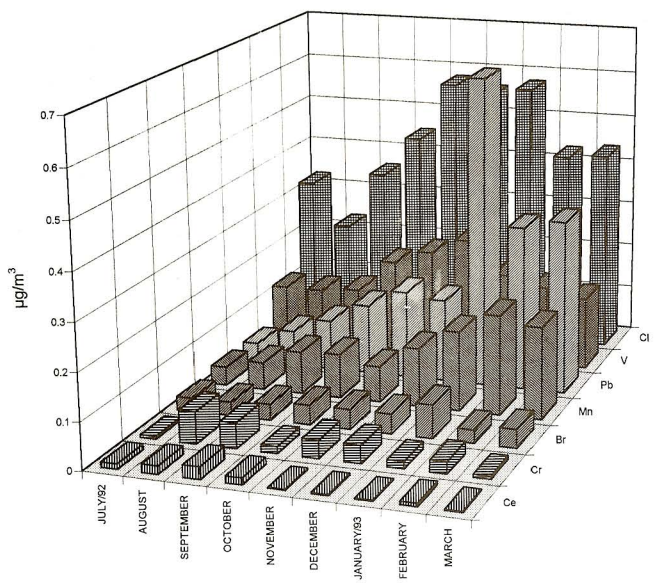

Fig. 5. Element concentration found in sampling station D during July-92 to March-93

are the various types of fuels used in vehicles. The prevailing winds come mostly from the west and practically none of the pollutants produced by the factories arrives to the city.

Cr might be produced by the tannery industry in the city. These factories use this element in their process and it is supposed that it might form volatile compounds. Cr was detected in low concentrations, having a fluctuation that did not surpass 0.05 µg/m³ during the sampling period.

The highest metallic limit exposition for chromium II and III is 0.5 mg/m³ and for chromium IV in compounds such as chromic acid, dichromate and zinc chromate the limit is 0.05 mg/m³.

The lethal dose of lead for humans was calculated to be about 0.5 g. Concerning the exposure for this element when combined as lead tetraethyl and tetramethyl components of gasoline the limit is 0.07 mg/m³.

The highest Pb value was 0.665 µg/m³ which does not surpass the standard exposure limit.

In regard to manganese, it is mainly used in the steel and battery industry. Sometimes it is used in diet supplements as well. The exposure limit in air was found to be 5 mg/m³ and 0.2 mg/m³ for the manganese compounds used as additives in gasoline.

The exposure limit for vanadium vapors is 0.05 mg/m³ and 0.5 mg/m³ for vanadium dust. For bromine and chlorine, the permissible limits are 0.11 mg/m³ and 1 g/m³, respectively (Dreisbach 1984).

Pb and Cr concentrations in the samples did not surpass the permitted limit values described in the Technical Ecological Norm of Mexico which reports the concentration of some elements considered dangerous to the atmosphere (NTE-CRP-002 1988).

Ce was not considered to be an anthropogenic pollutant, rather, it is reported (Travesi 1975) to be an athmospheric natural constituent when analyzed by neutron activation.

On the other hand, **figure 6** shows the total suspended particles concentration in samples collected at the A and D stations during August-92 to March-93. At station A, a slight increment of these particles was observed mainly during November to January, with the highest concentration seen in the latest. This is due perhaps to the winter season when no rain falls and the temperature is normally below 0 °C in the mornings. In station D, this concentration was higher than 120 µg/m³ during the whole sampling period except for November. This zone has a high vehicular flow almost all the time, in comparison with station A, where the vehicular transit is low. At this sampling site, the average of total suspended particles during the months considered was less than 100 µg/m³.

These results lead us to conclude that, in the downtown area, the concentration stayed almost constant, while it increased at the surroundings due to the constant vehicular flow and the proximity to the industrial area. In regard to bromine (1992-1993), Nova gasoline was used for vehicular transport and its analysis by Iturbe *et al.* (1995) revealed a significant Br concentration. It is supposed that Br combines with partially burned organic hydrocarbons, thus forming some volatile compounds which are not trapped by the filters and are emitted to the atmosphere.

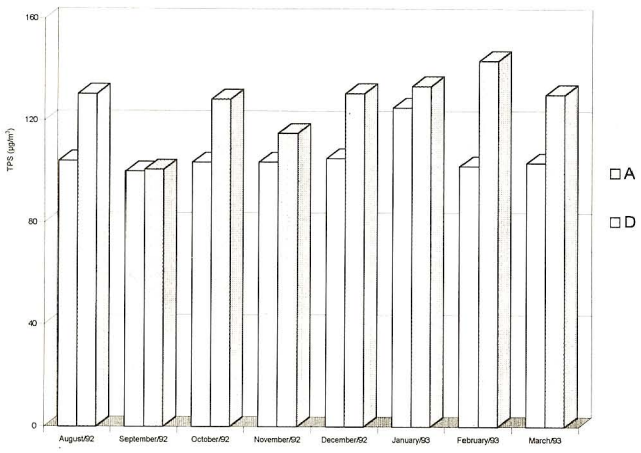

Fig. 6. Concentration of total suspended particles from A and D stations

In all sampling areas, the low Br values obtained confirm this supposition.

The neutron activation analysis technique for environmental samples offers high sensibility compared with conventional techniques and provides qualitative and quantitative multielemental analysis.

The results for environment total suspended particles were lower than the limit value reported by the Technical Ecological Norm (NTE-CRP-002 1988), which is 260 $\mu g/m^3$. However, it is important to continue this monitoring since a tendency for some elements to increase during certain seasons was observed.

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