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Atmospheric particles in the central coastal zone of the Gulf of Mexico, Laguna Verde area, Veracruz, México

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RESUMEN

Se presentan los resultados de la concentración por peso de las partículas atmosféricas recolectadas con muestreadores de bajos volúmenes en 16 estaciones de la Red del Monitoreo Radiológico Ambiental de la Central Nucleoeléctrica Laguna Verde, durante el período 1991 a 1993. Los niveles de concentración por peso de las partículas varían en un rango de promedios anuales de 22.6 $\mu g/m^3 \pm 5.0 \mu g/m^3$ a 107.8 $\mu g/m^3 \pm 3.7 \mu g/m^3$. Esta variabilidad es explicada por la ubicación de las estaciones, y las influencias naturales y antropogénicas. No fue observada variabilidad significativa en las concentraciones promedio a lo largo del tiempo. Se presentan los primeros resultados de la caracterización química del aerosol costero obtenidos por medio de Fluorescencia de Rayos X.

ABSTRACT

The results of mass concentration of atmospheric particles collected by low volume samplers in sixteen monitoring stations of the Environmental Radiological Monitoring Network from Laguna Verde Nucleoelectric Plant, from 1991 to 1993, are reported. The levels of the yearly average mass concentrations were in a range of 22.6 $\mu g/m^3 \pm 5.0 \mu g/m^3$ to 107.8 $\mu g/m^3 \pm 3.7 \mu g/m^3$. Spacial variability is explained through the location of the stations, anthropogenic and natural influences. There were no significant differences in the average concentration over time. Moreover, the preliminary results of the chemical composition obtained by X Ray Fluorescence analysis are presented.

1. Introduction

The atmosphere is made up of gases and tiny abundant solid or liquid particles or a mixture of them. The smallest electrically neutral particles (0.1 μm to 10 μm diameter) remain in the atmosphere for long periods, settling down slowly over the Earth's surface; while the largest (>10 μm in diameter) are deposited by the influence of gravity in hours or minutes, or are washed down by the rain.

In general, in unpolluted rural areas, the atmospheric particle mass concentration levels are balanced. Thus, the particles reaching the Earth's surface are substituted by the introduction of new ones from different sources. On a global scale, Junge (1963) distinguished three types of aerosol or atmospheric particles: the continental, the marine and the tropospheric background aerosols. As far as the chemical composition is concerned, the first two types contain mainly materials from the nearby surface sources. The third type represents an aged and much diluted continental aerosol. This type of aerosol is also present over the oceans. Continental and marine aerosols are mixed to some extent in coastal regions and, depending on wind direction, a continental dust plume may travel over the ocean, or sea salt may be carried inland for hundreds of kilometers.

The study of natural aerosols is especially important with regard to the base line of the atmospheric particle mass concentration, to which the anthropogenic contribution is added, and the determination of the space and time variability of the concentration.

The purpose of this paper is to present the levels of atmospheric particle (mass concentration), observed in the central coastal zone of the Gulf of Mexico, Laguna Verde area, Xalapa city and the Port of Veracruz, Veracruz State, at the Environmental Radiological Monitoring Network of Laguna Verde Nucleoelectric Facility (CNLV). The results were obtained from data collected during a three-year period, from 1991 to 1993. Some of the results are also based on the elemental chemical composition obtained by means of X-Ray Fluorescence analysis.

2. Sites of study

The Environmental Radiological Monitoring Network for atmospheric particles consists of 16 stations (Fig. 1); of these, 14 are located in the Laguna Verde Nucleoelectric Facility area, within a radius of 12.45 km; two stations are located at relatively distant communities, 60 km and 70 km away (Xalapa and Veracruz, respectively). In Table I, the number, name, key, position with respect and distance to the CNLV of the sampling stations are shown.

Laguna Verde Nucleoelectric Facility

The CNLV is located on the central coast of the State of Veracruz (19°43'30" N; 96°24'09" W). The coastal range to the west is an extension of the volcanic axis that reaches almost to the shoreline. Elevations exceeding 500 m are reached within 5 km from the coast, and higher than 1400 m within 60 km from the coast. This area is over basaltic and andesitic bedrock. The coastal soils of the area are products of eolian action and alluvial deposits.

The climate of the study area is tropical with a well defined rainy season (June to September) during which the easterly moist trade wind current prevails bringing convective rain showers. Fronts of continental polar air masses occur during the winter and the beginning of the spring and are associated with strong winds from the north and little rain. The annual precipitation is around 1300 mm, with a yearly mean temperature of 25°C. The prevailing winds are NW during autumn and winter and SW during summer.

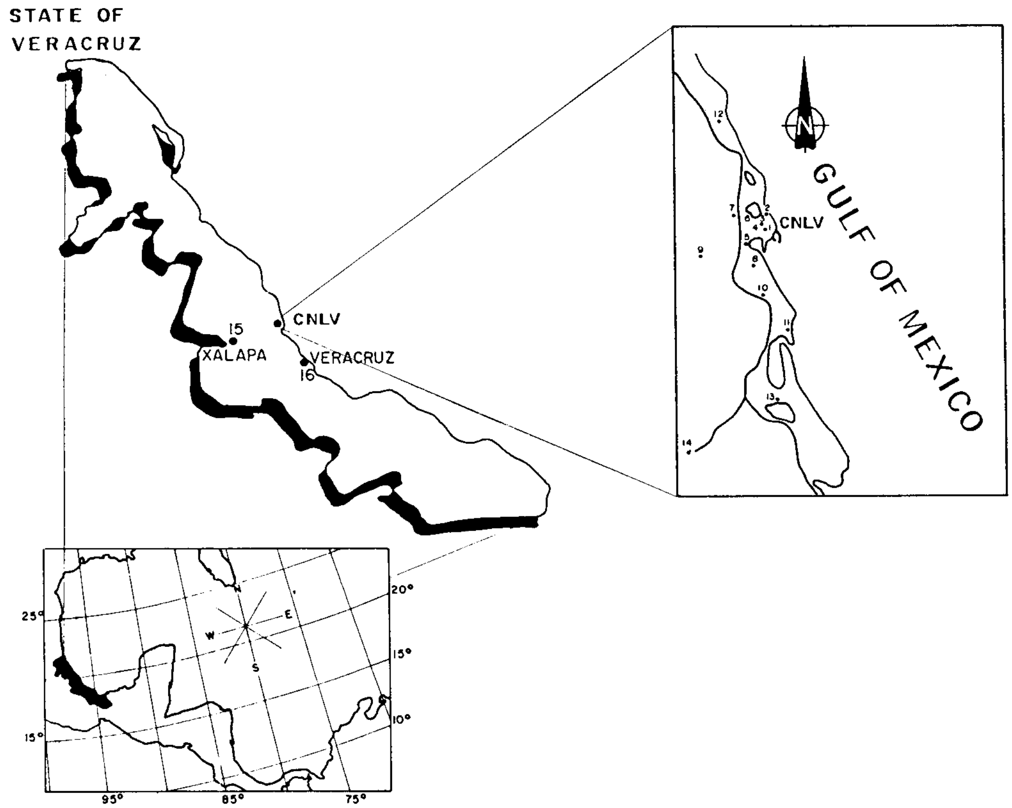


Fig. 1. Location of the sites and monitoring stations, Laguna Verde area, Veracruz State, Mexico.

Veracruz

The city of Veracruz (19°11'N; 96°08'W) lies on the coast of the Gulf of Mexico, some 70 km from the nuclear plant (Fig. 1). It has a flatland topography.

The climate is similar to that of Laguna Verde except that precipitation is higher (around 1695 mm), with a yearly mean temperature of 25.3°C. Veracruz city had a total population of about 300.3 thousand inhabitants in 1990. The main activities are commerce and shipping, as well as the railroad transportation of the goods (INEGI, 1993a).

Xalapa

The capital city of Veracruz State (19°32'N; 96°52'W), 60 km to the west of the nuclear plant is at an average altitude of 1400 meters above sea level (masl). The topography of the city and its sorroundings is mountainous. Its main elevation, Cerro del Macuiltépetl (1460 masl), is found in the middle of the urban area. The climate varies between subhumid warm with summer rains, to subhumid temperate with winter precipitation mainly in the form of drizzle from cold front passages. The annual rainfall is around 1421 mm with a yearly mean temperature of 19.1°C. Xalapa city has a population of about 300 thousand inhabitants, being the commercial and services its main activities (INEGI, 1993b).

Tabla I. Number, name, key stations, sector and distance respect to CNLV.

NUMBER	NAME	KEY	POSITION	DISTANCE (km)
1	DOMO	DM	WNW	0.30
2	ESTACION CLIMATOLOGICA	EC	NNE	0.96
3	LAGUNA VERDE	LV	NNW	0.99
4	LAGUNA SALADA	LS	WSW	1.40
5	SAN CARLOS	SC	SW	1.40
6	SUPERVISORES	SP	NW	1.50
7	MONTE CARMELO	MC	WNW	2.00
8	POZO C	PC	SSW	2.50
9	ARROYO AGRIO	AG	WSW	3.00
10	EL VIEJON	EV	S	3.60
11	VILLA RICA	VR	S	4.80
12	PALMA SOLA	PS	NNW	6.00
13	EL FARALLON	EF	S	9.20
14	TINAJITAS	TN	SSW	12.45
15	XALAPA	XAL	WSW	60.00
16	VERACRUZ	VZ	SSW	70.00

3. Experimental methods

Sampling

The particulate matter in air samples was obtained drawing 50 l/min of air with low volume samplers Model LV-1 (F and J Specialty Products, Inc.), with Whatman filters EPM-2000 of 5 cm diameter and 0.3 μm pore size. The sampling is performed continuously during seven days in each station (MLDMA, 1994). To quantify the mass concentration of atmospheric particles, the filters were weighted under controlled conditions of humidity and temperature, before and after exposure. The total air volume was determined with the flow and the sampled time, corrected to reference conditions. The mass concentrations are reported in $\mu g/m^3$ (CFR 40, 1990) and must be interpreted as weekly averages.

Chemical Analyses

Analysis were carried out with X-Ray Fluorescence Spectrometry. This technique was selected because it allows elemental chemical quantitative and qualitative analysis without destroying the sample. It has the advantage that the sample can be kept to do other studies based on it or for future reference. Ten filters from EC station (representative of the coastal zone) were analyzed.

The X- Ray Fluorescence Spectrometry analysis were performed using a Philips Model PW 1410 with Tungsten tube of 2700 W, with analyzer crystals of LiF (200) and PET; employing fixed conditions for elements with $Z<19$ and $Z>19$ (Bertin, 1970) in combination with the flow proportional and scintillation detectors, for angular intervals from 7° to 146° two-Theta (White and Johnson, 1970).

Sample preparation consisted of cutting a circle 4 cm in diameter, avoiding folding which was set over a pure cellulose plate as a filter holder, with a mylar cover to prevent discharge on the window of the X-Ray tube.

4. Results and Discussion

The annual average mass concentrations of atmospheric particles at each sampling station during the period of study are shown in Figure 2. A variance analysis was applied to these concentrations, by means of a Tukey test to 95% confidence level, in order to determine statistically spacial and temporal differences.

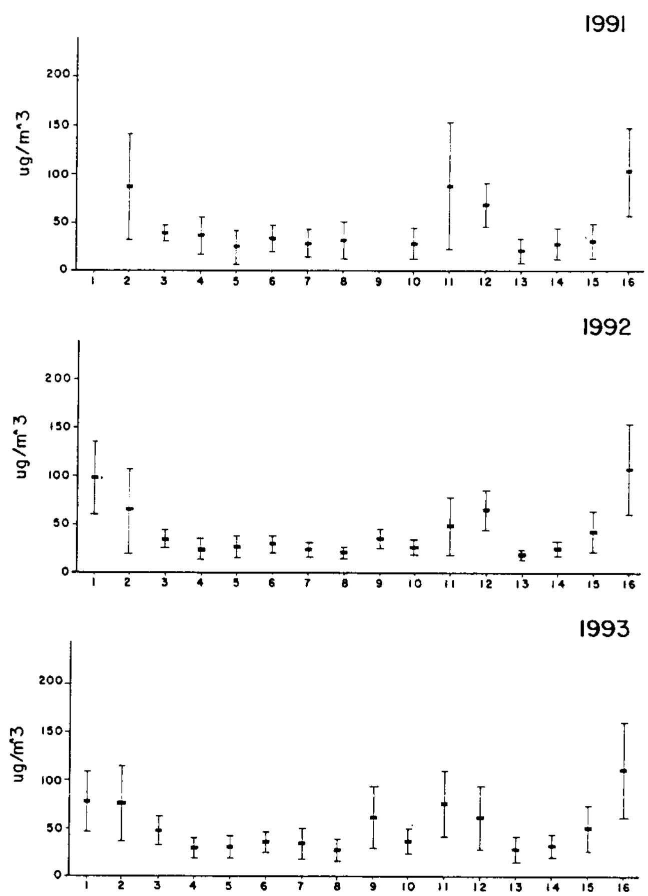


Fig. 2. Annual average mass concentrations and standard deviations of atmospheric particles, monitoring stations network of the CNLV (1991- 1993).

With regards to spacial differences, three groups of stations were obtained, one with low (< 50μg/m3) value mass concentrations, other with intermediate (from 50 to 100 $\mu g/m^3$) mass concentrations (Group 2) and a third one with more elevated mass concentrations (>100 $\mu g/m^3$), as shown:

Station		Average Mass Concentration	Homogeneous Group	
Key	Number	($\mu g/m^3$)		
EF	13	22.6	*	Group 1
PC	8	26.6	*	
SC	5	27.4	*	
TN	14	28.5	*	
MC	7	28.7	*	
LS	4	29.9	*	
EV	10	30.6	*	
SP	6	32.9	*	
LV	3	40.3	* *	
XAL	15	41.5	* *	
AG	9	48.2	* * *	
PS	12	64.9	* * *	Group 2
VR	11	70.6	* *	
EC	2	75.9	* *	
DM	1	88.0	* *	
VZ	16	107.8	*	Group 3

It is important to point out that most of the Laguna Verde area stations are located in rural-coastal zones with surrounding green areas, mainly consisting of grassland, live oaks of medium height and mangroves (IBUNAM, 1972). Almost all Laguna Verde monitoring stations, with the exception of four, constituted Group 1. Be noted that Xalapa's monitoring station (XAL), even through it belongs to an urban area presents a particle mass concentration similar to the one in the rural-coastal area (<50 $\mu g/m^3$). Apparently these results are related to the characteristics of the city of Xalapa, which consists of steep topography with elevations of 1200 to 1460 masl, high density of green areas, precipitation all year long and low industrialization (Tejeda y Acevedo, 1990). Furthermore, the monitoring station is on the side of the city's highest elevation, namely Macuiltépetl hill (1460 masl). The green areas are 300 hectares (8%) of a total of 3562 hectares of urban settlings equivalent to 6.5 m2 of green area per inhabitant (Dredge, 1996). Frequent rains are recorded as can be observed in Table II. These natural and anthropogenic conditions seem to influence the results of this monitoring station, and even when doing Tukey's test it belongs to group 1 (rural-coastal stations). The difference of the particle mass concentration compared to the first stations in their group seem to reflect the contribution of anthropogenic sources typical of urban areas.

Table II. Xalapa's city precipitation 1951-1980. Comision Nacional del Agua (Personal communication).

Month	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Monthly precipitation (mm)	43.3	47.4	48.6	60.0	103.4	314.5	231.3	175.4	259.7	120.2	67.7	46.5
Rainy days/month	13.8	12.8	14.1	12.5	13.6	21.2	20.0	18.3	21.6	18.3	16.0	14.9

The Group 2 stations (PS, VR, EC and DM) belonging to the Laguna Verde area, have anthropogenic and/or natural (eolian effect) influences. The more notable characteristics of these stations are:

PS station is located along the Federal highway 180 Veracruz-Nautla with heavy vehicular traffic and activities related to a food market that disposes of various waste materials. Moreover, the station is near to the shoreline where sand dunes are located. In this area the eolian effects are significant.

DM station is located close to the main entrance of the CNLV buildings (offices, parking area, workshops, and energy generation units) in front of a gravel-pebble semiconsolidated parking area, where airborne particles are generated by mechanical effect. It has been observed that the positions of the buildings relative to each other create a wind tunnel effect which results in the picking up and resuspention of a great number of particles.

VR and EC stations have the peculiarity of being situated a few meters from the coast (80 and 30 meters, respectively). VR station is located in a fishermen's village, close to the beach beside the single accessway to it (sand road), with a few houses and vegetation surrounding it. EC station is located in the NNE part of CNLV; bordering the Gulf of Mexico, under the direct influence of the coastal aerosol.

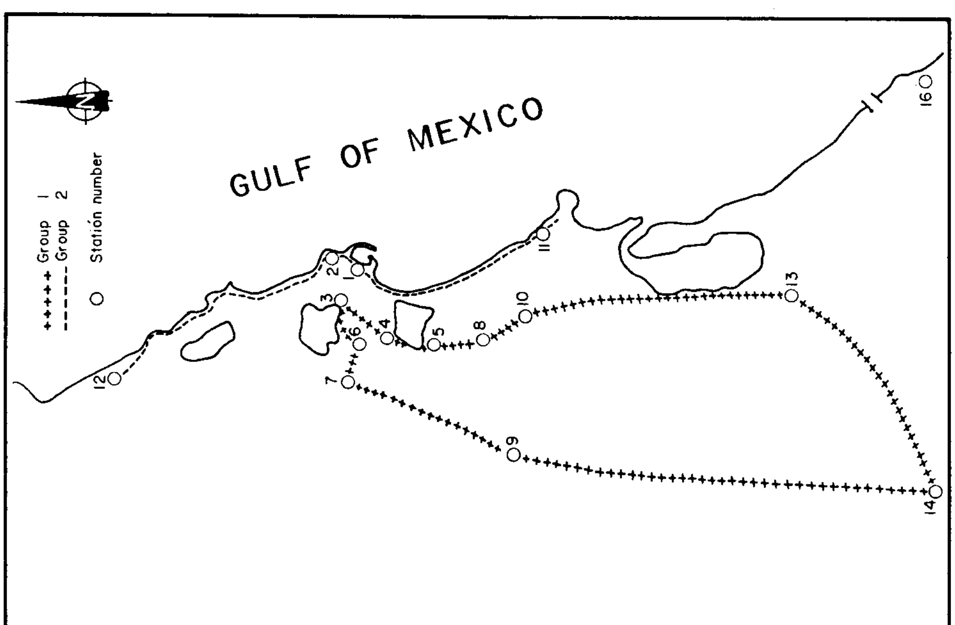


Fig. 3. Spacial distribution of atmospheric particles by homogeneous mass concentrations group, Laguna Verde area. (Groups 1 and 2).

VZ station (Group 3), with a higher average concentration (>100 μg/m3), is located in the NE of Veracruz city, in a great anthropogenic and natural influence zone. Anthropogenic influence is due to its proximity to maritime loading and unloading areas (docks), where heavy vehicular traffic such as lorries and railway cars is common. On the other hand, the main natural influence is recorded during the season of the "nortes" (north winds), since there are sand dunes, whose components are carried towards the VZ station.

In Figure 3, the Laguna Verde area is shown, where the stations with homogeneous results are grouped together: Groups 1 (>22 μg/m^3 to 50 μg/m^3) and Group 2 (>51 μg/m^3 to <100 μg/m^3). In this figure, it is clear that stations near to the coast line (Group 2, or with some anthropogenic influence) present higher mass concentrations than those stations relatively far from the coast (Group 1).

To determine differences over time, the variance analysis was applied to the weekly weight concentrations of the atmospheric particles. No statistical differences were observed. However it has been observed that during the rainy season (summer) low mass particle concentration is generally shown and that during the dry season (fall and winter), and/or high intensity winds, high concentrations are shown (Fig. 4). This observation, was positively confirmed when the seasonal correlations between meteorological parameters and particle mass concentrations were

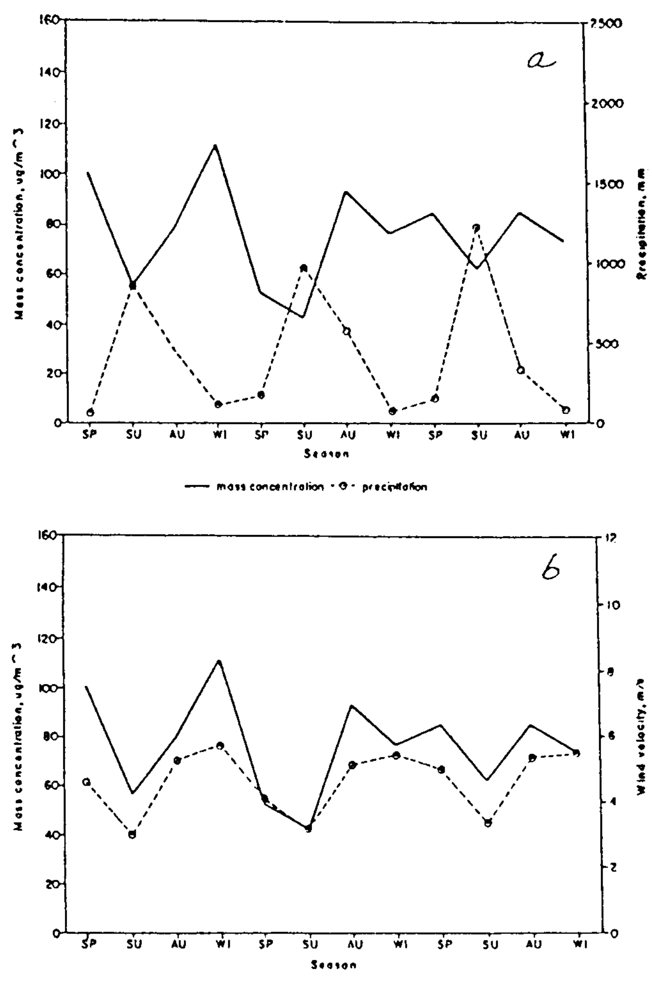


Fig. 4. Seasonal relationships between precipitation and atmospheric particles (a), wind intensity and atmospheric particles (b), EC station, Laguna Verde area (1991-1993).

done, EC and VZ stations were considered to be representative of the coastal aerosol (Table III). To validate this seasonal behaviour, these relationships were repeated for Groups 1 and 2. Figure 5 and Table III, show the behavioral and correlation factors. On Table III it can be observed that the intensity of the wind and the rain show highly significant level correlations for the stations EC and VZ. For Group 2 significant levels drop to 0.05% and for Group 1 there is not a statistical significance. For the stations in Group 1 the vegetations seems to play an important role.

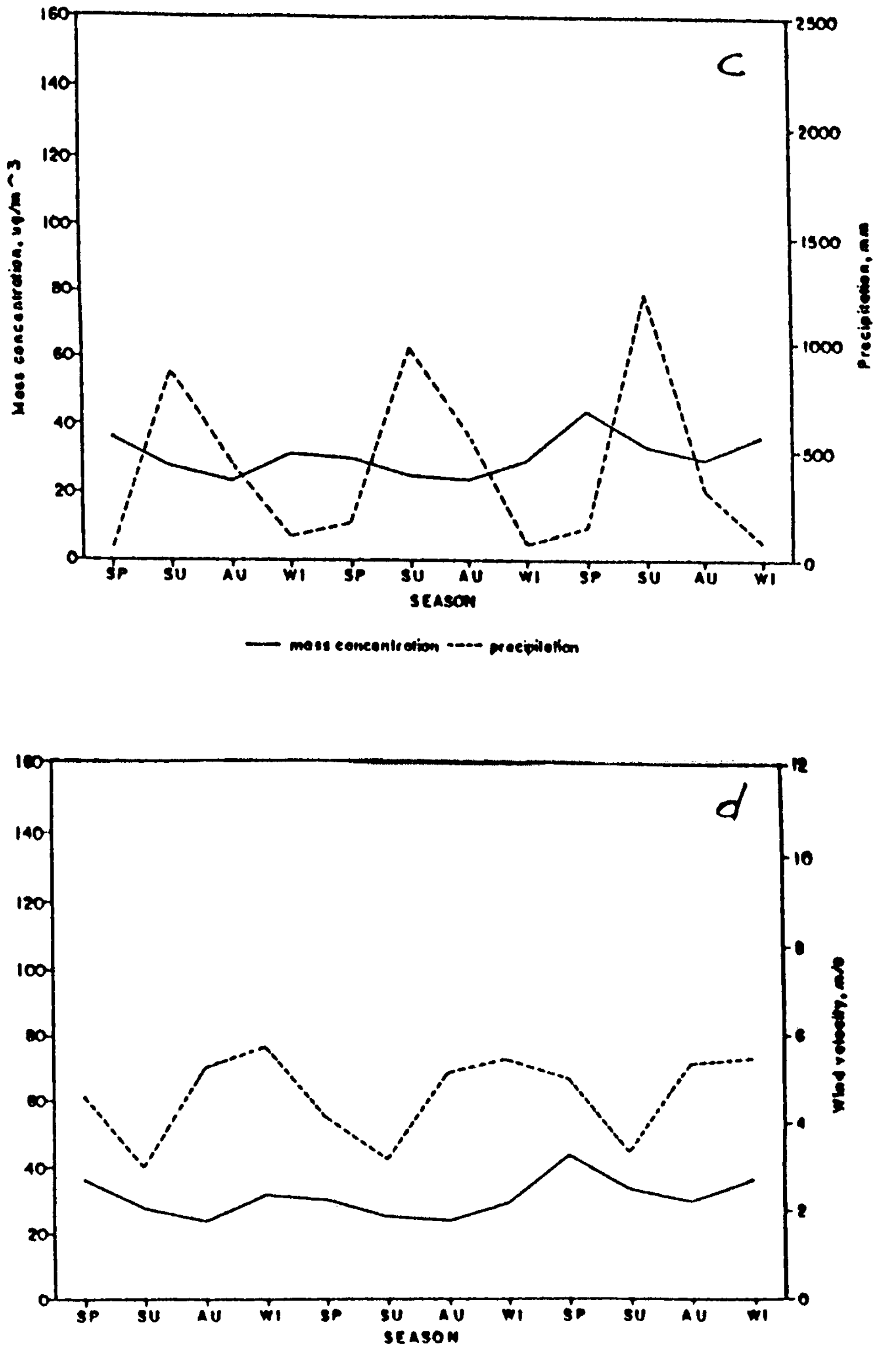
Table III. Seasonal correlation factors between mass concentration of atmospheric particles and meteorological parameters, EC and VZ stations, Group 1 and Group 2 (1991-1993).

GROUP	r	SIGNIFICANCE LEVEL		r	SIGNIFICANCE LEVEL	
	WIND INTENSITY	5 %	1%	PRECIPITATION	5%	1%
GROUP 1	0.14	-	-	-0.39	-	-
GROUP 2	0.60	*	-	-0.64	*	-
GROUP 3 (VZ)	0.72	*	*	-0.80	*	*
EC	0.76	*	*	-0.70	*	*

*significance level

Regarding wind direction, records from the Climatological Station of the CNLV were analyzed, it was observed that two directions are frequently recorded: NNW and SW. The first prevailing during autumn and winter, and the second during summer; while during spring, the dominant component varies between the two mentioned above. Figure 6 shows the wind rose from Laguna Verde area from 1979 to 1994 (Mancilla and Pérez, 1996).

Analyzing the seasonal periods that show higher elevation of particle concentration mass (spring, fall and winter) and the direction of the dominant winds, it was noted that during spring the dominant winds were S-SW and NNW, for fall NNW and SW and for winter NNW. According to the location of the stations close to the coast line (PS, EC, DM, VR), these seem to be influenced as much by the south winds as from the north winds that touch the coast line. The stations in Group 1, even though they are not very far from the coast seemed to be influenced by the special characteristics of the area with regards to the mass of the particle observed. These special characteristics include the vegetation mainly consisting of grassland and medium height trees which act as a barrier for airborne particles. Additionally, the orography, that is shown in sectors SW-SSW-S of the area in question, even though it is not of significant height (<300 masl), seems to be a factor.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Mass concentration, ug/m^3
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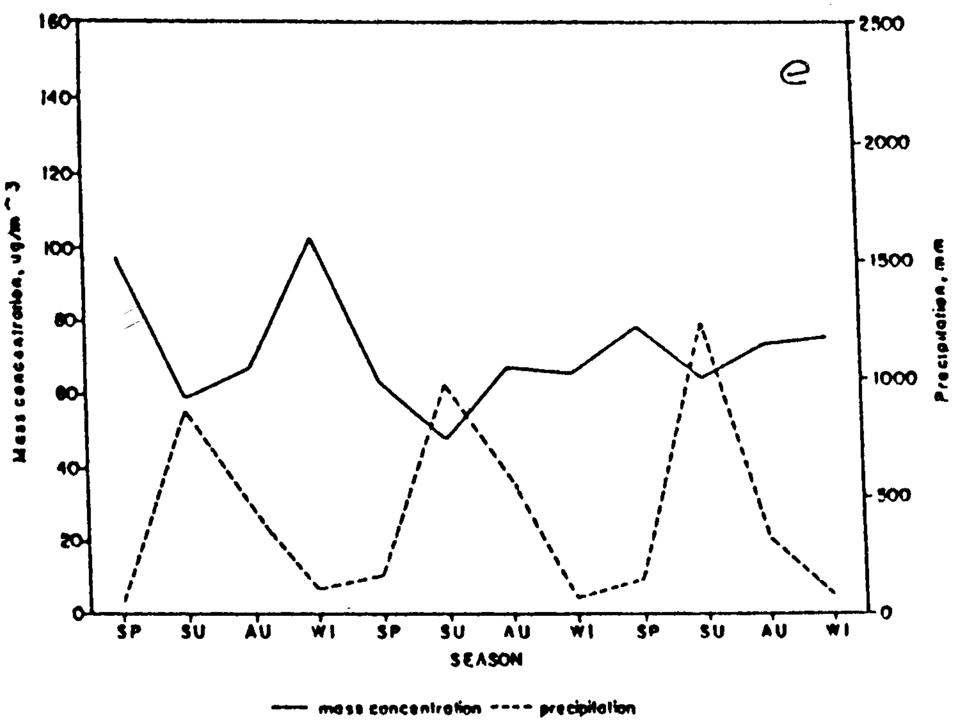
Figure 5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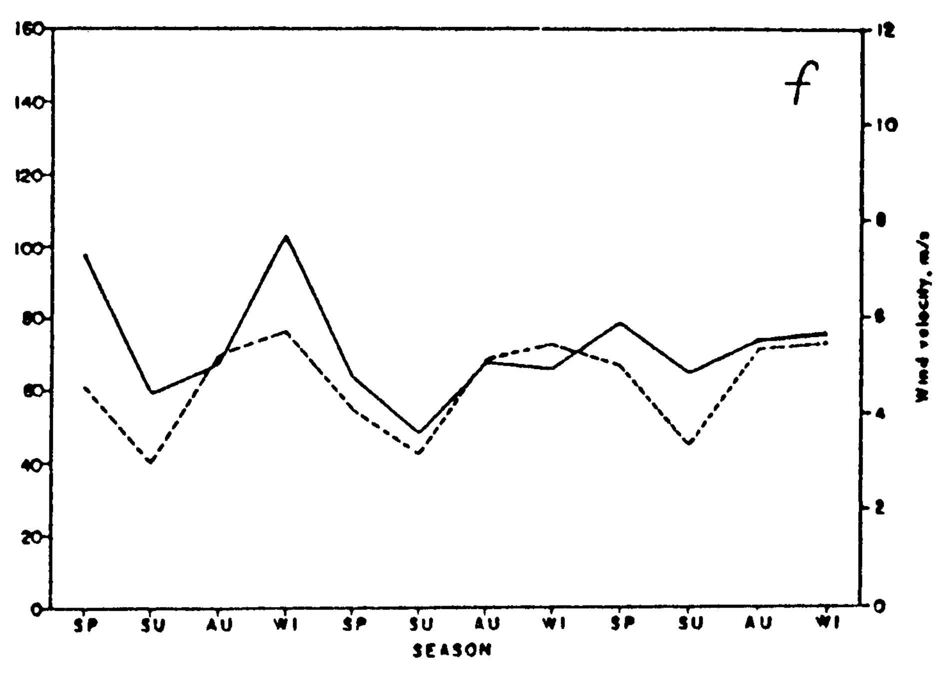
— mass concentration ---- precipitation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Wind velocity, m/s
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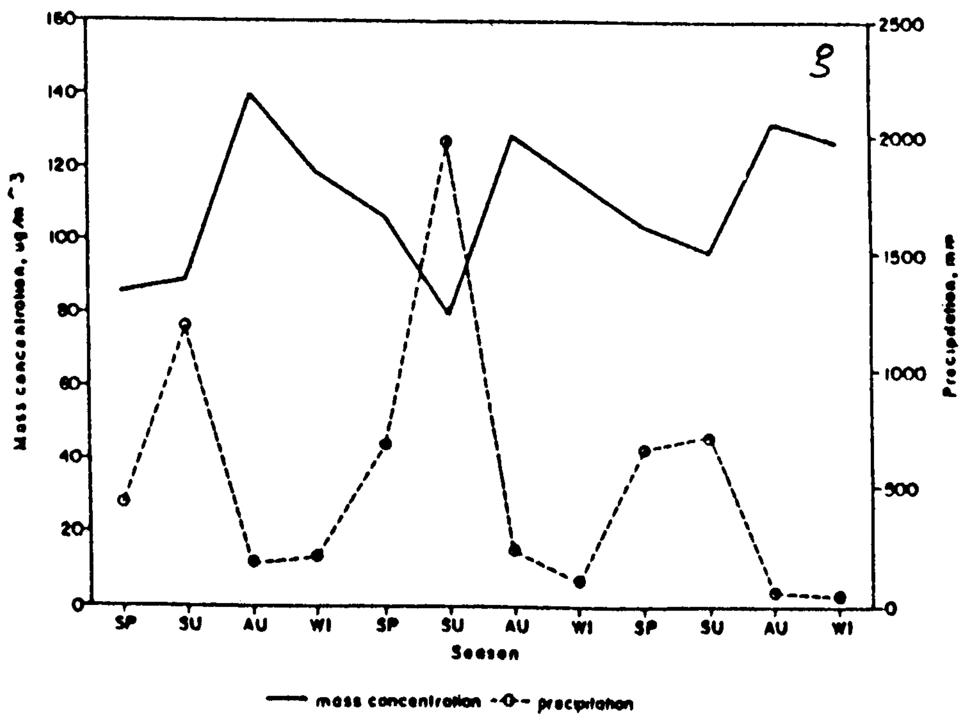
Fig. 5



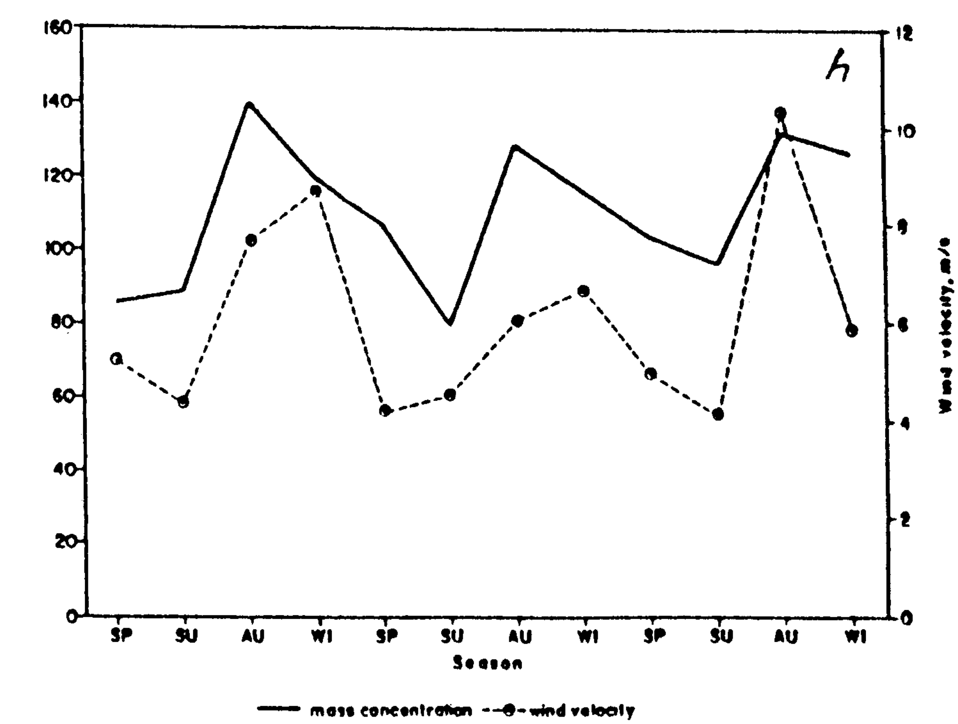


Fig. 5. Seasonal relationships between precipitation and wind intensity with the mass concentrations of atmospheric particles. Group 1 (c, d); Group 2 (e, f); Group 3 (g, h).

At VZ station, the same pattern of winds shown in Figure 6 is observed, combined at times with E components. This can influence mass concentration particles, because the Gulf of Mexico and dunes are located to the E and N. At VZ station a direct contribution is also observed.

The results of X-Ray Fluorescence analysis are shown in Table IV. In general, the elements obtained in higher proportions were: Fe, Cl, S, K and Ti; in lesser proportions Mn and Zn, and only traces of Br and Cr. With these results, it is not possible to determine the origin of the atmospheric aerosol. Assuming that the particulates emitted to the atmosphere by mechanical activities settle out very near to their sources, particularly for the litophile elements. We can supposed that Fe, Ti and Cr have a crustal source, K, Mn and Zn could have both a crustal and marine origin and Cl, S and Br have a marine origin (Andreae, 1986; Suzuki and Tsunogai, 1988; Injuk *et al.*, 1992). The authors with the CNLV support continue working with several techniques to confirm these assumptions.

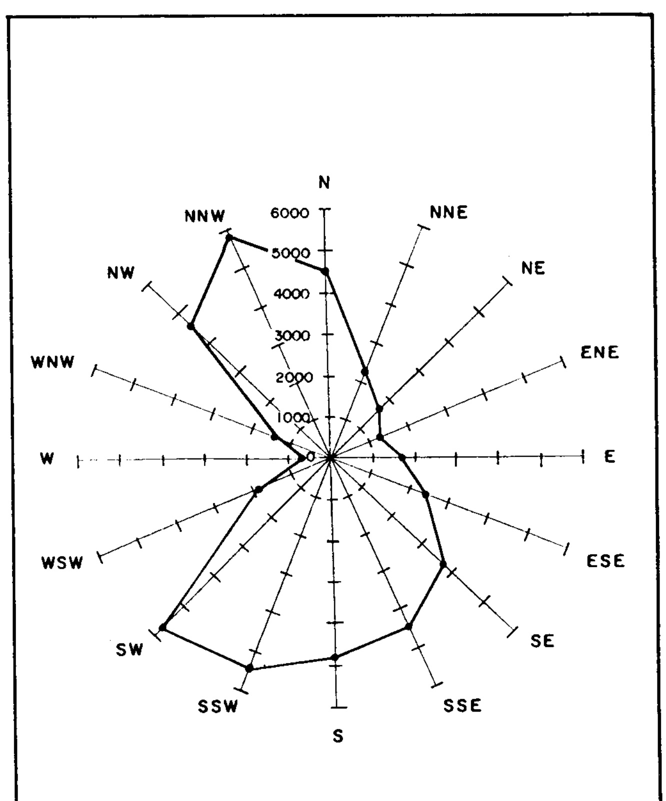


Fig. 6. Wind rose of Laguna Verde, total frequency 1979-1994. (From Mancilla and Pérez, 1996).

Table IV. Chemical elements in coastal atmospheric particles, X Ray Fluorescence analysis (EC station).

FILTER	ATOMIC NUMBER >19	ATOMIC NUMBER <19
1	Fe>K>Ti>Zn>Mn>Br> Cr traces Ca? traces	Cl>S>Al
2	Fe>K>Ti>Mn>Zn>Ca>Br>Cr traces	Cl>S>Al
3	Fe>K>Ti>Mn y Zn>Cr traces Ca? traces	Cl>S
4	Fe>Ti>K>Zn>Mn>Br Ca? traces	Cl>S
5	Fe>K>Ti>Zn>Mn>Cr traces Ca? traces	Cl>S
6	Fe>Ti>Mn>Zn probably, Pd? traces	Cl>S
7	Fe>Ti>Zn>Mn>K Sr probably traces. Nb?, Ca? traces.	Cl>S
8	Fe>K>Ti>Zn>Mn>Br traces. Ca? traces.	Cl>S
9	Fe>K>Ti>Zn>Mn>Br traces. Ca? traces	Cl>S
10	Fe>K>Ti>Zn>Br>Mn. Ca? traces.	Cl>S

5. Conclusions

The atmospheric particle mass concentration levels obtained at the central coastal zone of the Laguna Verde area, Xalapa and Veracruz have an annual average concentration that ranges from 22.6 $g\mu/m^3 \pm 5.0\ \mu g/m^3$ to 107.8 $\mu g/m^3 \pm 3.7\ \mu g/m^3$.

The spacial variability could principally be explained by the location of the sites: rural-coastal zone (from 22.6 $\mu g/m^3$ to 48.2 $\mu g/m^3$); coastal zone (from 64.9 $\mu g/m^3$ to 88.0 $\mu g/m^3$); and urban-coastal zone (107.8 $\mu g/m^3$), as well as by natural and anthropogenic influences.

The present study shows that the measurements performed in the rural-coastal zone (Group 1) are of the same order of magnitude as the values observed for typical mass concentrations of tropospheric aerosols in rural continental zones, 30-50 $\mu g/m^3$ (Warneck, 1986).

It is important to note that coastal stations (Group 2 and 3) are directly affected by the north and south winds. In the other stations this contribution is less notable as the relationships show.

The vegetation and the orography play an important role, since atmospheric particles in this zone are mostly mechanically generated (local sources). The most important meteorological factors influencing the aerosol mass concentration are the rate of precipitation (washout) and the wind intensity (eolian effect).

The variance analysis indicate that there is no significant difference for the years studied. This is supported by the fact that the particle mass concentration levels obtained could be considered as the natural atmospheric aerosol from the central coastal zone of the Gulf of Mexico; mainly in those zones where limited or no anthropogenic influences are present. Natural processes may be more important than antropogenic activities in causing the observed mass concentration.

The X-Ray Fluorescence analysis showed in higher proportions Fe, Cl, S, K and Ti; in lesser proportions Mn and Zn, and only traces of Br and Cr. With these results, is not possible to determine the origin of the atmospheric aerosol. For these reasons the authors continue working with several analytical techniques with the support of the CNLV.

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