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Presence of Aliphatic and Polycyclic Aromatic Hydrocarbons in the Atmosphere of Northwestern Mexico City, Mexico

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During the last years, Mexico City's atmosphere has suffered significative changes in several of its climatological features due to the fast growth of the city and to the gradual deterioration of its air quality.

The most noticeable alterations are: an increase in air temperature, increase in rain precipitation and the reduction of solar radiation, produced mainly by the presence of atmospheric aerosols, particles, dusts and toxic gases originated from industrial activity (Galindo 1990), besides the emanation caused by fossil hydrocarbons combustion and the supply of natural sources.

Among the organic compounds present in atmospheric particles, the satured and aromatic hydrocarbons have outstanding importance due to their carcinogenic potential (Sawicki 1962; CBEAP 1972; Hoffman and Wynder 1977) and its formation from different photochemical reactions (Schuetzle et al. 1975; Calvert 1976; Graedel 1978).

Thus, the observed changes in the physical factors that take place in the climatic system have reached magnitudes that work as harmful agents for the inhabitants of Mexico City producing discomfort and chronic diseases of the respiratory system (Galindo 1990).

MATERIAL AND METHODS

The sampling area is located in the NW part of Mexico City, near the oil refinery "18 de Marzo", in Azcapotzalco (Figure 1), being important to note that in the zone the north is the predominant wind direction. The area shows an annual average concentration of 250 ug/m3 of total suspended particles (SEDUE 1986) related with the presence in its limits of a great diversity of industries, high vehicular movement and the settling of high population nuclei.

The sampling of atmospheric particles was made for 24 hours during January 1990, using a high volume air sampler Hi-Vol

(Sierra Instruments Inc.), which was placed 7 m above the ground level and 400 m far away from the refinery, to the north.

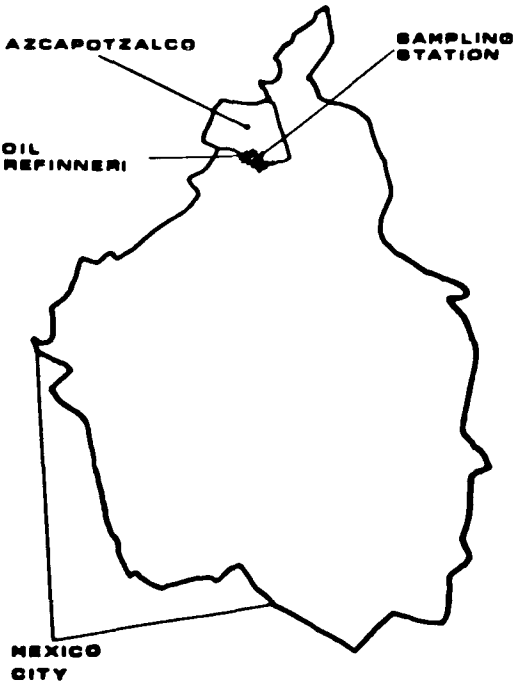

Figure 1. Sampling area in the NW of Mexico City.

The air flux through the filter was 1.2 to 1.7 m3/min., using a glass fiber filter (Gelman A/E) as collecting medium. Samples were kept in bags covered with aluminium foil in order to avoid direct sunlight. One blank filter was placed every ten samples to be analyzed.

The analytic procedure for the extraction and purification of the hydrocarbons fractions was the recommended by the Caripol-IOCARIBE Manual 1986. The filters were digested by using a solution of KOH-Methanol (5% in vol) for 3 hours, then the organic phase was extracted using hexane bidistilled (Aldrich) and purified in chromatography columns (30 cm long, 1.5 i. d.) packed with activated alumina and eluting with hexane and CH4Cl2.

The fractions of satured and aromatic hydrocarbons, were analized by capillary gas chromatography using a Hewlett Packard Model 5890 equiped with a phenil-metil silicone 5% capillary column (25 m x 0.25 mm i.d). Nitrogen was the carrier gas. Injection was performed on splitless mode at 280 ^{o}C. The oven temperature was

programed from 40 to 300 ^{o}C at 6 ^{o}C/min. Detector temperature was 300 ^{o}C. n-C28 was the internal standard for the satured fractions and a mixture of PAH's (PPH 10M from EPA, Chemical Service), containing 15 compounds, was used as an external standard for aromatic fraction.

Also, a series of blanks were carried before and after chromatographic analysis to reconfirm the presence of aliphatic and aromatic compounds.

The identification and quantification of the organic compounds were carried out by its retention time compared with an internal standard (Supelco Inc.)

RESULTS AND DISCUSSION

The determination of organic compounds in atmospheric particles has been increased lately due mainly to its carcinogenic potential and its risks for human health.

In Mexico City, 715,000 tons of particles and 505,000 tons of hydrocarbons are emitted to the atmosphere annually (INEGI 1984), making of paramount importance their determination in atmospheric samples.

Regarding the satured fraction analyzed, compounds from n-C9 to n-C28 were present, having the n-C10 and n-C11 the highest concentrations and being associated with the exhaust of gasolines used in automobiles (Figure 2).

The range of concentration of this fraction is from 1.3 to 560 ug/g (Table 1) with an average of 3 to 300 ug/g and its sources are related with: a) fermentation processes, b) gasoline and diesel emissions, c) refining of crude oil, d) turbine operations and e) tobacco smoke (Graedel 1978).

It is of importance to notice that during weekends, the concentration of the saturated compounds is remarkably lower because of the decrease of industrial activity in the area, as well as to the decrease of automobile traffic during these days (Figure 3). However, the concentration of n-C10 and n-C11 is still constant, being an indication that the activity in the oil refinery does not diminish completely during weekends.

The analyses of the aromatic fractions show the presence of 11 polycyclic aromatic hydrocarbons, mainly those from 2 to 5 benzenic rings as: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo(b) fluoranthene, Benzo(k) fluoranthene and Benzo(a)pyrene (Table 2).

The higher concentrations determined were for those with four rings (Pyrene, Chrysene), followed by those of three and two

rings (Acenaphthene, Phenanthrene and Anthracene), Figure 4.

The main origin of these PAH's is closely related with the refinement of petroleum, manufacturing of asphalt and aluminium, burning of coal and refuse, emission of automobiles and tobacco smoke (Graedel 1978).

Table 1. Aliphatic hydrocarbon compounds concentration (ug/g)

	S A M P L E S								
Carbon Number	901	902	903	904	905	906	907	908	Average
C9	11.27	10.66	2.17	7.68	16.18	1.47	1.81	N.D	7.32
C10	63.56	344.60	111.25	268.62	14.44	44.38	31.38	177.97	132.02
C11	181.75	560.65	342.83	477.03	279.32	86.53	81.03	394.32	300.43
C13	18.32	14.24	2.10	11.36	18.64	N.D	6.60	N.D	11.88
C15	3.77	2.56	2.51	3.70	4.66	N.D	N.D	N.D	3.44
C16	8.61	17.32	5.47	5.04	10.88	9.99	12.23	N.D	9.93
C17	2.22	3.57	4.87	4.68	2.16	13.13	2.02	N.D	4.66
C18	2.40	2.95	6.68	3.10	3.48	N.D	2.25	1.67	3.22
C21	3.36	3.17	4.10	5.06	5.31	N.D	N.D	1.34	3.72
C22	4.05	3.52	6.17	5.53	4.92	N.D	2.49	1.91	4.09
C23	3.75	3.02	5.77	5.05	4.93	N.D	2.49	1.41	3.84
C24	4.84	5.80	11.0	7.58	8.13	N.D	2.61	1.51	5.92
C25	3.62	3.68	14.79	14.55	9.44	N.D	2.22	N.D	6.90
C28	5.05	4.70	8.38	5.62	6.42	N.D	13.56	15.05	8.39

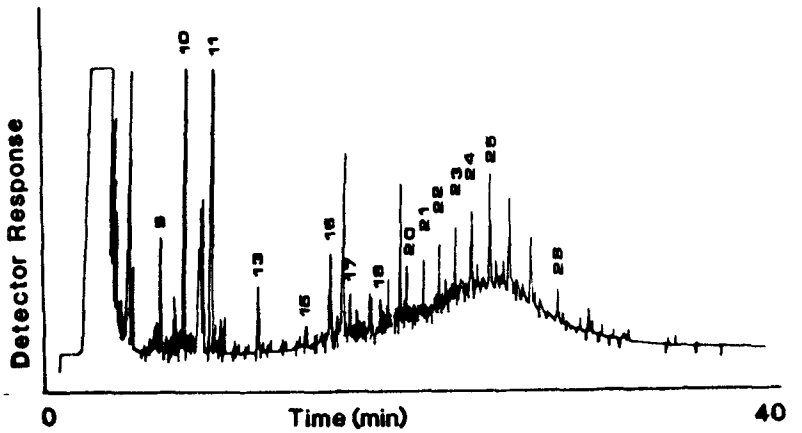

Figure 2. Gas chromatogram of aliphatic hydrocarbons in atmospheric samples.

It should also be pointed out that in most cases, these compounds are highly reactive with gases and other compounds present in the

atmosphere and they can change rapidly, e.g. Benzo(a)pyrene in the presence of high concentrations of ozone and other oxidizing agents (Lane and Katz 1977; Davies et al. 1987), being important that the study area has a high annual concentration of SO2 (> 100 ug/m3), and NOx.

On the other hand, field and laboratory studies have shown that the use of glass or quartz filters underestimate the PAH's concentrations (Grosjean 1983; Lee et al. 1980), mainly due to two processes: volatilization and chemical reactions of the compounds over the filters.

It was also observed that during the volatilization of PAH's of low molecular weight, a division takes place between gas and particle phases, depending on the temperature (Yamasaki et al. 1982; Cautreels and Cauwenberghe 1978). The chemical reactions are mainly photochemical, thermic and the formation of the so called artifact compounds (NAS 1983; Grosjean et al. 1983).

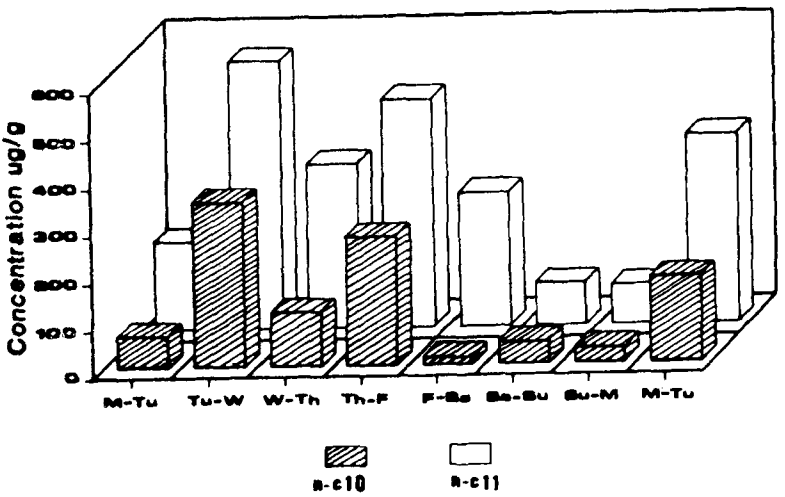

Figure 3. Weekly variation of satured hydrocarbons concentrations in NW Mexico City.

As the present research is the first in which PAH's were identified and quantified in Mexico City's atmosphere, it is considered that their concentration would be higher and that their presence represents a high risk for human health, specially because of its carcinogenic potential.

Undoubtedly, their presence also contributes in a significant way to the change of the climatic conditions, as well as to the gradual deterioration of air quality and to the increase of respiratory and pulmonary illnesses.

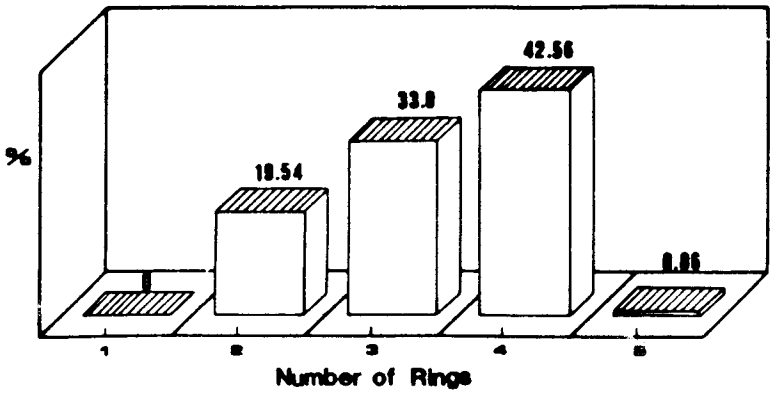

Figure 4. Percentage composition of polycyclic aromatic hydrocarbons in atmospheric samples.

Table 2. Polycyclic aromatic hydrocarbon compound concentrations (ug/g)

	S A M P L E S								
Compounds	901	902	903	904	905	906	907	908	Average
Acenaphthylene	1.14	N.D	N.D	N.D	N.D	N.D	N.D	N.D	1.14
Acenaphthene	7.20	13.04	18.87	N.D	10.50	1.89	N.D	2.44	8.99
Fluorene	N.D	N.D	2.19	N.D	N.D	N.D	N.D	N.D	2.19
Phenanthrene	3.92	2.37	3.88	N.D	2.52	1.29	N.D	1.37	2.56
Anthracene	N.D	N.D	N.D	0.18	N.D	N.D	20.38	N.D	10.28
Fluoranthene	2.99	3.11	3.98	0.63	3.50	1.41	0.56	0.43	2.08
Pyrene	0.34	40.48	0.11	0.46	0.54	12.01	9.46	0.12	7.94
Benzo(a)anthracene	1.02	0.64	N.D	0.43	N.D	0.20	N.D	N.D	0.57
Chrysene	N.D	N.D	N.D	N.D	N.D	N.D	17.41	9.25	13.33
Benzo(k)fluoranthene	N.D	N.D	0.10	N.D	0.29	N.D	N.D	N.D	0.20
Benzo(a)pyrene	N.D	N.D	0.52	0.44	0.37	N.D	N.D	N.D	0.44

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