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FORMALDEHYDE IN RAIN WATER IN MEXICO CITY ATMOSPHERE

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RESUMEN

Se llevó a cabo la cuantificación del formaldehído en agua de lluvia colectada en las instalaciones de la Universidad Nacional Autónoma de México durante las épocas de lluvia de 1981 y 1982, obteniéndose un total de 71 muestras.

Los resultados señalan que la concentración promedio registrada de 0.479 ± 0.19 mg/l es mucho más alta que las citadas por diferentes autores para atmósferas marítimas o costeras. El programa estadístico "tabulación cruzada" aplicado a los resultados indicó una correlación lineal entre las concentraciones de CH_2O, las horas de insolación y la hora en la cual se inicia la lluvia.

Las altas concentraciones de CH_2O en agua de lluvia señalan que existen otras fuentes generadoras de formaldehído además del proceso de oxidación del metano que normalmente se lleva a cabo siendo las emisiones producidas por los vehículos de combustión y el enorme consumo de combustóleo los candidatos obvios para las fuentes adicionales de CH_2O en la atmósfera de la Ciudad de México.

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ABSTRACT

Measurements of formaldehyde in rain water were performed at the National University of Mexico during the rainy seasons of 1981 and 1982. A total of 71 samples from storms and prolonged rains were analyzed. The results obtained throughout this study gave an average of 0.479 ± 0.19 mg/l, much higher than those reported in rain water by different authors for maritime and clean coastal air. The statistical program "cross tabulation" applied to CH_2O concentrations, indicated a linear correlation only between the CH_2O concentrations, sunshine hours and the time when precipitation began. The high CH_2O values found in rain water indicated a much greater source than that provided by the methane oxidation. Motor vehicles emissions and the huge combustion of fuel oil are the obvious candidates for the additional CH_2O sources in the atmosphere of Mexico City.

INTRODUCTION

It has been demonstrated that aliphatic aldehydes are constituents of rural and urban atmosphere (Cleveland *et al.*, 1977); even in remote marine areas concentrations of 7.9 ± 0.9 ppb in air and 0.0004 ± 0.0002 mg/l in rain water have been reported by Zafiriou *et al.* (1980). However, in urban polluted atmospheres formaldehyde is an important product of photochemical reactions and consequently its concentration is much higher than that found in clean air (Grosjean, 1982). The CH_2O measurements in air have been used, among other air contaminants, to evaluate the levels of photochemical smog. Likewise, its determination in rain water has permitted to estimate the rate of CH_2O removal from the atmosphere (Thompson, 1980).

Despite the great importance that formaldehyde has in atmospheric photochemistry of polluted atmospheres, relatively few formaldehyde studies have been reported in rain water. However, urban formaldehyde measurements have shown that the principal sources are likely to be gasoline engines (Barber and Lodge, 1963), diesel engines (O'Donnell, 1970) and a variety of incomplete combustion processes. In addition to its injection into the atmosphere by direct emissions, formaldehyde is known to be formed from hydrocarbon precursors, by ozonolysis and hydroxyl radical reactions.

The concentrations are the result of the kinetic balance between sources and sinks, which consist largely of photolysis and radical reactions (Calvert *et al.*, 1972).

Some of the formaldehydes forming reactions that have been postulated are:

$$\begin{array}{rlcccc}
\text{Olefin} & + \text{O} & \longrightarrow & \text{R} & + & \text{RCHO} \\
\text{HC} & + \text{O}_3 & \longrightarrow & \text{RO}_2 & + & \text{RCHO} \\
\text{HC} & + \text{OH} & \longrightarrow & \text{RO}_2 & + & \text{RCHO} \\
\text{HC} & + \text{RO}_2 & \longrightarrow & \text{RO}_2 & + & \text{RCHO}
\end{array}$$

where:

HC = hydrocarbons

RO_2 = peroxiradicals and

RCHO = aldehydes

reactions that occur in polluted atmospheres.

Preliminary air pollution studies carried out in Mexico City showed that photochemical smog is formed in sunny days. In one of these studies the pH of the precipitation collected in short events was measured. The results indicated the presence of acid rain which is related to atmospheric precursors such as SO_2 and NO_X which are photochemically transformed in strong acids (Báez and Padilla).

Due to the noxious effects of atmospheric formaldehyde it was considered important to measure its concentrations in rain water during the wet seasons of 1981 and 1982 at the campus of the University of Mexico. Nevertheless the University is located in one of the cleanest residential areas at the south of the city, this area is influenced by the prevailing northeast winds that carry on into the zone a great amount of air pollutant emitted by the industrial and downtown areas, besides, an average traffic density of 30 000 vehicles/day which is a common rate at the University campus during working days.

EXPERIMENTAL

Rain samples were collected in a 0.38 m^2 stainless steel funnels, draining into 2 litres polyethylene bottles, mounted in an iron frame 1.5 m above ground to minimize splash. The apparatus was rinsed before sampled collection with deionized water and covered with aluminum foil which was removed few minutes before the precipitation event.

Samples were collected at the end of the precipitation, except when it was raining at night, in this case the samples were collected early in the morning. It was attempted to sample in rain-event bases.

Rainfall, rainrate, pH, temperature, relative humidity, insolation hours and total global solar radiation were recorded. The analyses were performed as soon as it was possible. At daytime, samples were analyzed within an hour after the end of precipitation or when a sufficient amount was accumulated, night falls were analyzed in the morning. No corrections were applied for conceivable losses.

In this study, the analytical method first reported by Nash (1953) was used; acetyl acetone, ammonium and formaldehyde form the colored condensation product diacetyl dehydro-lutidin (DDL) which is determined by spectrophotometry at the maximum absorption at 412 nm. This method, as has been reported by Klippel and Warneck (1978), has negligible interferences by higher aldehydes, not only because their absorption spectra are shifted, but because they react much more slowly.

In order to apply cross tabulation it was necessary to divide the measured values in groups. The CH_2O concentrations were segmented in 5 groups (from 0.6 mg/l to 1.17 mg/l). The pH values were divided in 4 (4.4 to 8.10), rainrate in 5 (from 0.5 mm to 45.5 mm), raining starting time in 6 (from 10 hours to 22.30 hours), temperature in 4 (from 13.6°C to 22°C), global solar radiation in 5 (from 440 J m^{-2} day^{-1} to 2 852 J m^{-2} day^{-1}) and finally the sunshine hours in 8 groups (from 0 hours to 9.5 hours).

RESULTS AND DISCUSSION

A total of 71 samples from storms and prolonged rains were analyzed between June and September of 1981 and from June to September of 1982.

In Table 1, the formaldehyde (CH_2O) concentrations in rain water collected during the selected seasons at the University of Mexico,

Mexico City sampling station are tabulated. From this table it can be noted that in 1981 the monthly average concentrations were rather uniform but in 1982 the average values were somewhat higher and less uniform. The results obtained throughout this study are much higher than those reported by different authors. Our values were in the range of 0.16 to 1.17 mg/l with an average of 0.48 ± 0.19 mg/l for the two seasons.

Klippel and Warneck (1978) found CH_2O concentrations in rain water at several sampling sites in Western Europe, in the order of 0.141 ± 0.048 mg/l in Deuselbach and Ireland, and 0.111 ± 0.059 mg/l in very clean air in Ireland. They reported that the CH_2O average concentrations found, are the same for rural, continental and coastal clean air conditions.

Table 1

Formaldehyde in precipitation at University of Mexico City. (1981 - 1982).

Date	Concentration mg/l	pH	Rainfall (mm)	Rainfall (time)
1981				
June				
16	0.90	5.3	7.5	14.00
17	0.42	5.0	0.1	16.00
18	0.36	5.0	6.7	11.30
22	0.49	6.8	17.0	17.42
23	0.34	4.4	15.4	15.10
24	0.62	5.6	0.3	12.30
30	0.44	6.7	1.2	18.20
Arith. mean	0.51 ± 0.18	5.54 ± 0.83	6.88 ± 6.51	---
July				
01	0.47	6.4	1.3	10.30
02	0.47	5.7	2.5	10.00
06	0.55	6.8	37.1	16.45
07	0.32	6.6	0.4	18.07
08	0.53	4.6	8.4	14.45
09	0.22	4.9	45.5	16.32
14	0.58	5.3	0.1	15.00
21	0.32	5.5	6.3	18.12
22	0.36	6.1	6.4	17.40
23	0.47	6.7	1.6	18.00
27	0.52	5.7	22.7	14.10
Arith. mean	0.41 ± 0.13	5.81 ± 0.69	11.99 ± 14.53	---

(Cont. Table 1)

Date	Concentration mg/l	pH	Rainfall (mm)	Rainfall (time)
1981				
August				
03	0.66	4.6	19.8	14.43
04	0.38	6.1	3.7	18.33
05	0.42	6.5	0.7	16.40
10	0.50	4.8	0.1	17.30
12	0.30	7.4	3.4	18.18
13	0.43	5.3	3.3	19.20
20	0.37	6.8	2.0	23.20
24	0.17	6.3	6.7	18.30
26	0.41	7.3	1.1	21.30
27	0.29	4.5	22.6	16.00
28	0.67	5.3	0.3	11.30
Arith. mean	0.42 ± 0.14	5.90 ± 1.01	5.79 ± 7.51	–––
September				
01	0.36	6.3	3.8	18.30
02	0.55	5.0	15.2	16.00
03	0.46	5.4	20.2	18.10
07	0.55	6.3	21.4	16.40
17	0.50	5.6	1.0	17.10
23	0.26	8.1	2.2	18.00
28	0.47	4.9	3.4	20.40
29	0.25	5.2	29.9	13.50
30	0.56	5.1	29.6	14.45
Arith. mean	0.44 ± 0.11	5.77 ± 0.96	14.08 ± 11.13	–––
1982				
June				
14	0.41	6.5	3.0	19.00
23	0.73	6.5	4.3	11.10
28	0.19	4.9	37.9	21.00
29	0.25	4.7	7.5	20.45
30	1.17	7.1	1.8	13.50
Arith. mean	0.55 ± 0.36	5.94 ± 0.96	10.9 ± 13.63	–––
July				
02	0.32	7.2	10.9	15.25
06	0.72	6.2	2.3	14.30
08	0.35	6.4	3.5	15.00
12	0.43	6.9	18.7	17.00
13	0.67	6.3	6.2	14.30
15	0.76	5.6	3.3	14.50
19	0.45	6.6	2.1	21:00
21	0.34	7.5	0.8	19.35
26	0.37	5.8	2.3	18.35
27	0.42	5.4	11.6	16.30
Arith. mean	0.48 ± 0.16	6.39 ± 0.65	6.17 ± 5.47	–––

(Cont. Table 1)

Date	Concentration mg/l	pH	Rainfall (mm)	Rainfall (time)
1982				
August				
02	0.48	6.8	6.6	19.50
03	0.41	5.7	1.2	16.30
09	0.28	6.4	11.6	18.40
10	0.16	7.2	20.1	18.45
11	0.60	7.4	1.0	16.38
12	0.85	6.9	0.1	13.00
16	0.78	7.4	0.1	19.00
18	0.34	6.5	0.6	18.55
19	0.49	4.8	23.2	15.30
24	0.45	7.4	0.2	21.00
25	0.31	6.7	4.3	20.55
30	0.37	6.9	1.7	20.40
Arith. mean	0.46 ± 0.19	6.67 ± 0.74	5.89 ± 7.79	–––
September				
08	0.64	5.7	4.5	16.20
13	0.78	6.3	0.8	21.00
20	0.95	7.4	0.2	14.25
21	0.53	7.7	0.2	16.20
22	0.64	7.2	2.5	13.50
Arith. mean	0.71 ± 0.14	6.86 ± 0.74	1.64 ± 1.66	–––
Arith. mean 1981-1982	0.48 ± 0.19	6.11 ± 0.92	8.13 ± 10.32	16.67 ± 2.84
Minimum	0.16	4.40	0.10	10.00
Maximum	1.17	8.10	45.50	23.20

Zafiriou *et al.* (1980) reported measurements of CH_2O in the gas phase and in rain, at remote maritime site in the central Ecuatorial Pacific, Enewetok Atoll, the rainfall analysis averaged 0.0079 ± 0.0019 mg/l, values close to their detection limit of 0.0015 mg/l.

Thompson (1980) determined at Woods Hole, Massachussets, a midlatitude coastal site, CH_2O in rain water. The range reported was from 0.0084 to 0.245 mg/l with an average value of 0.087 ± 0.057 mg/l, close to the concentration of 0.111 mg/l reported by Klippel and Warneck (1978).

The rather uniform occurrence of CH_2O in rain water in maritime regions indicate a source such as the oxidation of methane (MO) by radicals (Shearer, 1969; Levy, 1971). Sellers (1965) considers that the atmospheric loss rate of CH_2O due to rainout would be 1.15×10^{-5} gr cm^{-2} $year^{-1}$ for 0.142 mg/l CH_2O in rain water, this amount corresponded roughly to all CH_2O produced by MO if the Warneck (1975) OH concentrations were adopted. Taking into account that the rate of photodecomposition of CH_2O is much greater than the MO, with a photodissociation life time for CH_2O in the atmosphere about 5×10^{-4} s (Calvert *et al.*, 1972) and a mixing ratio of 1 ppb in the lower atmosphere, Klippel and Warneck (1978) estimate a loss rate of 3×10^{-4} gr cm^{-2} $year^{-1}$. In order to balance a loss of this magnitude, much greater sources than those provided by the MO would be required. The average concentration at 0.48 ± 0.19 mg/l determined in our rain water samples was 100 times higher than those reported by Zafiriou *et al.* (1980) for remote maritime sites, indicating that alternative sources, others than the methane oxidation, such as motor vehicles emissions and the huge consumption of fuel oil are the obvious candidates for the injection of CH_2O into the atmosphere of Mexico City.

Relative frequencies were calculated for CH_2O concentrations measured in rain water during the wet seasons of 1981 and 1982 (Figure 1). The CH_2O values were grouped into class intervals of 0.20 to 0.60 mg/l for 1981 and from 0.25 to 1.09 for 1982, in which the highest frequencies percentages corresponded to 0.42 and 0.46 mg/l respectively. Figure 1, also shows the relative frequency histogram for the combined 1981 - 1982 CH_2O values, again the highest frequency percent corresponded to 0.46 mg/l close to the arithmetic mean of 0.48 ± 0.19 mg/l.

pH values in rain water ranged from 8.1 to 4.4 with an average of 6.1, 36 percent of the samples was bellow 5.7 (acid rain) while only 15 percent of them was above 7 pH units indicating the possible neutralization of rain water by alkaline particles emitted in great amounts into the Mexico City atmosphere by the cement and lime processing plants.

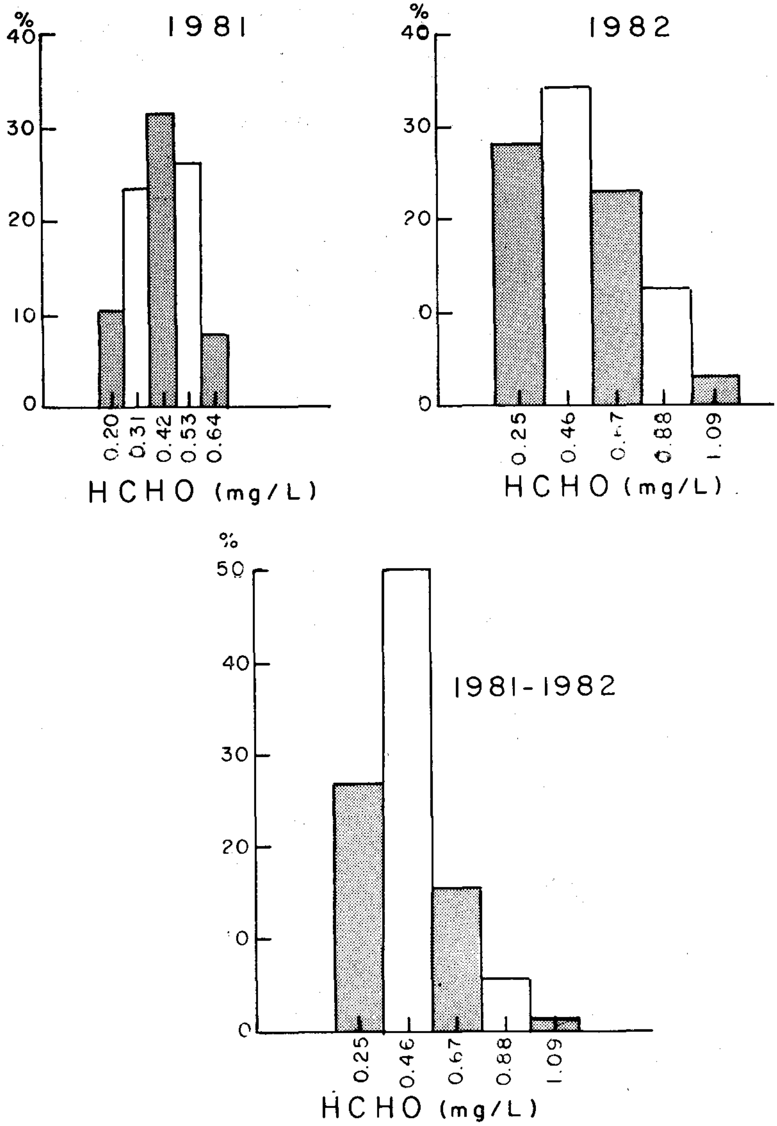

Fig. 1. Distribution of the CH_2O levels in rain water samples taken at the University of Mexico sampling station.

In Figure 2, the graphs of the CH_2O concentration values versus the time when rain occurred are shown. These graphs show that the highest concentrations were measured in rain water collected around 12.30 to 13.30 hours, with a marked decrement in samples collected during the evening and during night. It is also noted that in 1982 higher CH_2O concentrations were obtained. There is at present no apparent explanation for this increment, but it would be attributed to the constant increase of the air pollution levels in the Mexico City air.

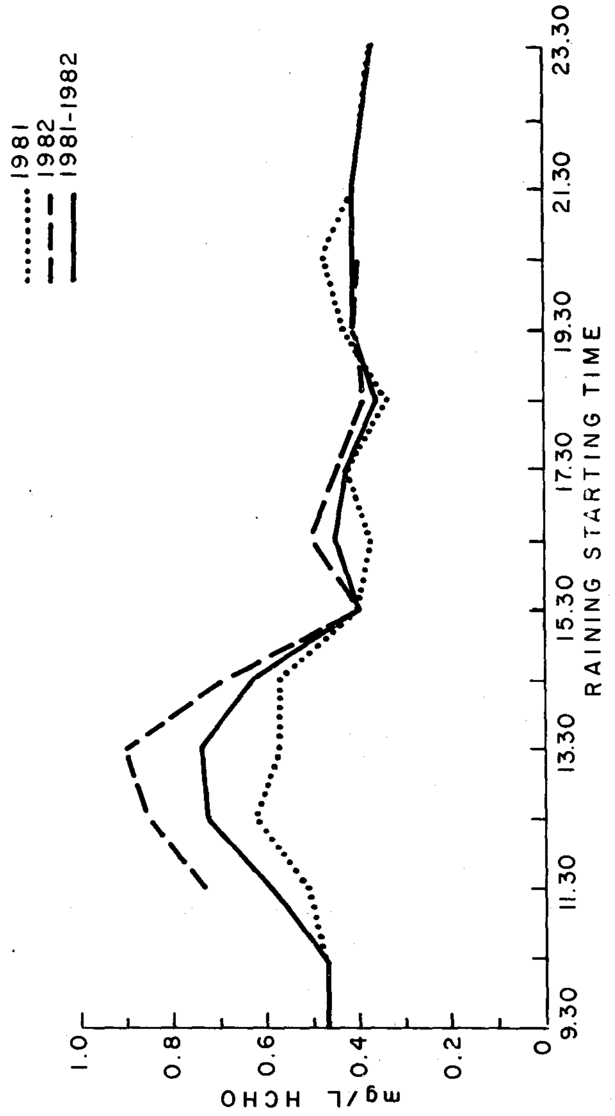

Fig. 2. Relationship between CH_2O levels in rain water and raining starting time.

In Table 2, the data of the general weather conditions observed in the days rain samples were collected are tabulated. Data of temperature, relative humidity, global solar radiation and sunshine hours plus pH, rain volume and raining starting time were used to apply the statistical program "cross tabulation" to determine if there were significant differences (X^2) and a linear correlation (R) between these and the CH_2O concentrations (Table 2).

Table 2

Weather conditions at University of Mexico Campus during raining season

Date	Air temperature °C	Relative humidity %	Total radiation $J/cm^2/day$	Sunshine hours	Wind direction	Wind speed m/s
1981						
June						
16	16.0	81.7	1856	5.0	———	———
17	16.4	70.6	954	7.0	N–NW	1.2
18	14.6	83.3	617	0.0	Calm	0
22	16.3	76.0	1495	3.8	Calm	0
23	15.5	74.6	975	7.0	N–NW	0.8
24	17.0	69.0	1866	6.0	N–NE	1.4
30	16.1	72.0	701	0.0	N–NW	1.9
Arith. mean	15.98 ± 0.70	75.31 ± 5.05	1209 ± 487	4.11 ± 2.80	———	———
July						
01	15.4	74.8	912	0.0	Calm	0
02	14.9	74.5	980	6.2	Calm	0
06	17.0	71.2	1531	6.4	E–NE	0.8
07	15.8	74.6	1583	2.8	E–SE	0.4
08	16.4	73.8	1183	2.0	N–NW	0.8
09	16.1	73.1	1895	5.7	N–NW	1.3
14	16.0	72.4	1524	0.0	E–NE	0.4
21	17.9	65.8	1853	5.8	E–SE	0.4
22	17.9	68.7	2390	6.7	E–SE	0.8
23	17.5	63.6	2059	7.7	E–NW	0.6
27	16.9	75.5	1336	3.0	E–NE	0.6
29	17.6	67.4	2026	7.0	N–NW	1.4
Arith. mean	16.61 ± 0.96	71.28 ± 3.78	1606 ± 436	4.44 ± 2.63	———	———

(Cont. Table 2)

Date	Air temperature °C	Relative humidity %	Total radiation J/cm²/day	Sunshine hours	Wind direction	Wind speed m/s
1981						
August						
03	13.6	73.7	1757	5.9	N–NE	0.4
04	21.6	61.5	2023	6.6	Calm	0
05	18.8	63.1	1925	6.6	N–NW	0.6
10	19.4	62.1	2045	7.5	N–NW	0.2
12	18.8	62.3	1987	5.0	N–NW	0.3
13	18.7	67.8	1709	0.6	E–NE	0.4
20	21.4	50.6	1115	3.0	N–NW	0.4
24	21.4	68.9	1918	6.4	N–NE	0.4
26	18.4	69.8	675	0.1	N–NW	0.9
27	16.6	83.3	440	0.2	Calm	0
28	14.9	78.9	890	1.3	E–SE	0.4
Arith. mean	18.50 ± 2.49	67.45 ± 8.65	1498 ± 572	3.93 ± 2.79	–––	–––
September						
01	19.2	63.6	1751	5.1	N–NE	0.3
02	20.2	69.3	1315	6.0	N–NW	0.5
03	19.8	67.9	1818	6.2	N–NE	0.2
07	17.5	71.7	1567	5.1	N–NE	0.4
17	17.8	56.6	1245	2.8	N–NE	0.4
23	22.0	59.1	1529	4.6	N–NW	0.8
28	20.0	57.1	1030	5.0	–––	–––
29	19.0	60.2	970	0.8	N–NW	0.6
30	17.1	56.5	1056	1.9	N–NE	0.4
Arith. mean	19.18 ± 1.46	62.4 ± 5.56	1364 ± 299	4.17 ± 1.78	–––	–––

(Cont. Table 2)

Date	Air temperature °C	Relative humidity %	Total radiation J/cm^2/day	Sunshine hours	Wind direction	Wind speed m/s
1982						
June						
14	19.6	58.3	2796	8.0	N–NE	0.8
23	20.5	64.2	1903	3.9	SE	0.9
28	19.4	61.8	2033	5.5	NW	---
29	17.1	69.2	2096	3.8	N–NE	0.8
30	16.3	73.9	1646	0.4	S–SW	0.8
Arith. mean	18.58 ± 1.6	65.48 ± 5.50	2095 ± 383	4.32 ± 2.48	---	---
July						
02	16.3	63.6	2159	7.2	E–NE	1.6
06	16.9	65.5	1776	4.8	E–NE	0.8
08	16.4	64.9	2179	6.8	E–SE	1.0
12	14.9	66.9	2194	5.8	NE	1.0
13	17.7	64.3	2229	6.0	NW	1.1
15	16.4	67.7	1829	4.3	NW	1.2
19	14.2	61.1	2684	7.6	NW	1.4
21	17.4	55.7	1951	4.6	NE	1.4
26	17.0	74.0	1360	7.0	E	0.6
27	15.0	71.8	2357	6.5	N–NE	1.3
Arith. mean	16.22 ± 1.10	65.55 ± 4.89	2072 ± 344	6.06 ± 1.10	---	---

(Cont. Table 2)

Date	Air temperature °C	Relative humidity %	Total radiation J/cm^2/day	Sunshine hours	Wind direction	Wind speed m/s
1982						
August						
02	17.6	67.3	1802	4.8	NW	–––
03	15.7	68.2	1704	2.7	NW	1.3
09	17.4	61.9	2284	7.3	SE	1.2
10	16.4	69.0	2091	5.4	NE	–––
11	15.6	68.6	2115	5.4	NE	–––
12	15.2	62.9	1954	5.9	N	–––
16	17.4	53.2	2852	9.5	SE	–––
18	16.7	62.6	1844	6.3	NE	0.9
19	15.6	72.0	1895	4.6	NE	–––
24	17.3	59.5	2034	6.2	E	–––
25	18.4	59.5	2590	7.9	NW	0.9
30	17.9	57.0	2470	6.0	N	1.0
Arith. mean	16.77 ± 1.01	63.47 ± 5.39	2136 ± 334	6.0 ± 1.65	–––	–––
September						
08	16.1	64.1	1143	2.0	NW	1.0
13	16.9	65.6	1703	3.5	W	0.9
20	15.3	60.6	1677	4.0	NW	–––
21	16.7	53.9	1363	2.5	N	–––
22	15.9	68.3	1292	1.2	NE	–––
Arith. mean	16.18 ± 0.57	62.5 ± 4.97	1436 ± 220	2.64 ± 1.01	–––	–––
Arith. mean 1981-1982	17.249 ± 1.83	66.728 ± 6.97	1697.268 ± 533	4.659 ± 2.41	–––	–––
Minimum	13.60	50.60	440	0.00	–––	–––
Maximum	22.00	83.30	2852	9.50	–––	–––

From Table 3 it can be observed that the X^2 values indicated only significant differences between CH_2O concentrations and raining starting time, and sunshine hours, the first of the two being more significant. On the other hand, a low linear correlation (R) between the CH_2O concentration and the considered parameters was found with the exception of raining starting time whose Pearson's factor was 0.46.

These results were expected because the CH_2O is formed in greater quantities during the most intensive solar radiation hours (Zafiriou *et al.*, 1980), then when raining was at morning or early evening an increase in the CH_2O concentrations in rain water was measured.

Table 3

Statistical analysis of formaldehyde and environmental factors

		X^2	R[a]	G[b]	P_E
Dependent variable:	Concentration of CH_2O (mg/l)				
Independent variable:	pH	14.5	0.02	12	> 0.05
	Rain volume (mm)	16.0	0.28	16	> 0.05
	Raining starting time	44.0	0.46	20	< 0.05
	Temperature (°C)	10.3	0.27	12	> 0.05
	Relative humidity (%)	11.2	0.18	12	> 0.05
	Solar radiation ($J/cm^2/day$)	23.7	0.16	16	> 0.05
	Sunshine hours	36.9	0.25	16	< 0.05

a. Pearson's R.
b. Degrees of freedom.

It could be considered that the lack of correlation between the CH_2O concentrations and the other parameters is due to:

a. The formaldehyde in rain water must originate from the incorporation of CH_2O into clouds during rain formation (rainout) or scavenging during rainfall (washout). It is assumed that cold trapped CH_2O is gaseous and not in aerosol (Klippel and Warneck, 1978).

b. The diurnal variation of CH_2O is only about 30% because both its sources and sinks are proportional to the UV solar flux. For the same reason the concentration of formaldehyde is almost independent of cloud cover. However, its lifetime increases with increasing cloud cover (Zafiriou *et al.*, 1980). The lifetime is about two hours under clear sky in tropical regions during summer as it was our case, when most of the samples were taken.

c. Rapid formaldehyde photolysis in the troposphere greatly diminishes any contribution of long range transport.

d. The estimated CH_2O removal is only a small portion of the column production and the measurement integrate over 24 hours during which it rained only a small fraction of time.

SUMMARY

Formaldehyde has been measured in precipitation at an urban polluted area, the high values found indicate that formaldehyde could not have been formed solely by methane oxidation.

The CH_2O measurements in rain water that were carried out in this study were mainly used as an index of the CH_2O levels present in the atmosphere, but considering that most of the events occurred in the evening and during the night, the values found were a little lower than those expected because at the end of insolation hours part of the CH_2O is decomposed.

This high values could be explained through CH_2O emissions by anthropogenic sources such as motor vehicles and fuel oil consumption that are the most important sources of hydrocarbon emissions into the atmosphere of Mexico City.

The authors consider that the results obtained in this study must be supported by further measurements of formaldehyde in rain water and air. At present a program in this direction has been initiated.

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