



SENSITIVITY ANALYSIS OF A UV RADIATION TRANSFER MODEL AND EXPERIMENTAL PHOTOLYSIS RATES OF NO₂ IN THE ATMOSPHERE OF MEXICO CITY

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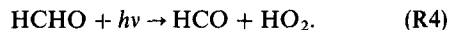
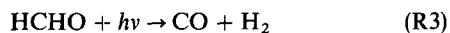
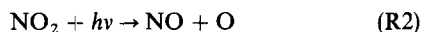
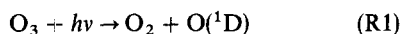
(First received 19 December 1995 and in final form 19 June 1996)

Abstract—Photolysis of key species such as nitrogen dioxide, ozone and aldehydes, are the elementary reactions leading to the formation of photochemical smog. Calculations and experimental measurements (in particular, nitrogen dioxide) of these key reactions are reported, as well as, the sensitivity of them to the ozone column, local albedo and properties of the urban aerosol layer in Mexico City. A radiation transfer model (RTM), based on the delta-Eddington approximation, was used in the calculations. The results show the importance of providing local resolution for photolysis rates by considering different local conditions within the modeling domain of air quality models. Copyright © 1996 Elsevier Science Ltd

Key word index: Nitrogen dioxide, ozone, formaldehyde, photolysis rates, Mexico City.

INTRODUCTION

Air quality models require among other parameters, of the specification of photolysis rate constants (the so-called “*J* values”) of reactions occurring in the troposphere. The most important reactions are:



These reactions take place in several regions of the solar spectra, mainly between 280 and 420 nm. The constants of dissociation of reactions (R1) and (R2) have been studied experimentally under various atmospheric conditions. In such experiments a gas mixture, placed inside a quartz tube, is exposed to UV radiation. The change of gas concentration after the reaction and the products of secondary reactions are measured following the exposure to solar radiation. The rate of reaction is determined by the time of exposure, the initial concentration of the gas, the concentration of secondary products and by the standard chemical kinetics considerations.

In this way, the rates of reactions (R1) and (R2) have been measured in the past, under several atmospheric conditions by several workers (Jackson *et al.*, 1975; Harvey *et al.*, 1977; Zafonte *et al.*, 1977; Sickles *et al.*,

1978; Dickerson *et al.*, 1982; Parrish *et al.*, 1983; Madronich *et al.*, 1983; Junkermann *et al.*, 1989; Shetter *et al.*, 1992; Brauers and Hofzumahaus, 1992). On the other hand, the calculation of *J*'s by radiation transfer models requires major simplifications which usually introduce uncertainties as large as 20% (Madronich, 1987). In these models the transfer equation is solved and the actinic flux is thus obtained (Demerjian *et al.*, 1980; Ruggager *et al.*, 1993, 1994). Recently, preliminary calculations of solar irradiance and photolysis rates for NO₂, O₃ and HCHO under Mexico City conditions were reported for the first time (Ruiz-Suárez *et al.*, 1993 a, b).

This work has three aims: (a) perform a sensitivity analysis of calculated *J*'s to changes in albedo, to load and refraction index of aerosols, and ozone column. This analysis is used to select possible scenarios for the experiments and to understand the underlying behavior of rate constants when different atmospheric conditions are present, (b) carry out an experimental program to obtain the nitrogen dioxide photolysis rates around the city and (c) adjust our model by comparing the theoretical results with these experimental measurements. In this way, more realistic routine calculations of *J*'s can be done for Mexico City.

Furthermore, an additional comparison is done against two models reported by (Madronich, 1987):

$$J = C[f^{-1} + 2A_L]E \quad (1)$$

and

$$J \approx \frac{1.35E}{(0.56 + 0.03z)\cos \theta_0 + 0.21} \quad (2)$$

where C is a constant, f^{-1} is a function of the direct and the diffuse downward light, A_L is the local albedo, z the altitude, θ_0 the zenith angle and E the irradiance.

SENSITIVITY ANALYSIS

The radiation transfer model (RTM) is designed to calculate irradiance, actinic flux and photolysis rate constants (Ruiz-Suárez *et al.*, 1993a, b). The input data for the model are: the concentration profile for some atmospheric components, the absorption and dispersion coefficients as a function of wavelength (290–400 nm), the spectral quantum efficiencies and the spectral irradiance at the top of the atmosphere (Montero, 1993). We considered an atmosphere of 50 km height, composed of air, nitrogen dioxide, ozone and aerosols. The atmosphere is divided into five layers, the first from 50 to 35 km, the second from 35 to 20 km, the third from 20 to 5 km, the fourth from 5 to 1 km and the fifth from 1 km to the surface. The optical thickness and the albedo for simple dispersion are calculated in each layer. Aerosols are considered only in the fifth layer.

We measured UV surface albedo in different parts of Mexico City and found, for asphalted surfaces, an albedo of 0.05, and for gray cement surfaces, an albedo of 0.10, in the region of UV. A value of 0.15 corresponds to forested areas (Dickerson, 1980). With

respect to the ozone column and according to the work reported by Bravo (1984), we used 240, 270, 290 and 300 DU. Dust aerosols could be formed of clay with a typical refractive index value of $1.6 + 0.005i$. On the other hand, urban aerosols are particles with high organic content and a refractive index of $1.4 + 0.005i$ could be used (Finlayson-Pitts and Pitts, 1986). The aerosol size distribution for the atmosphere of Mexico City (Fig. 1), can vary from 0.05 to $1 \mu\text{m}$ (Montañez and García-García, 1993). According to Junge (1969), the size average distribution for aerosols larger than $0.1 \mu\text{m}$ of radius can be described by

$$\frac{\Delta N}{\Delta r} = cr^\alpha \quad (3)$$

where $\Delta N/\Delta r$ is the particle concentration per size interval, r is the radius of the particles and, c and α are constants. For $r > 0.09$, Junge's functional form is satisfied for the set of analyzed data by Montañez and García-García (1993). Thus, the equation could be written as

$$\frac{\Delta N}{\Delta r} = n \left[\frac{r_0}{r} \right] \quad (4)$$

where N is the concentration of particles with radius larger than r ($r_0 = 0.05$ is the minimum value for which equation (4) is valid). The values they reported for α are: 3 for a polluted urban atmosphere, 4 for a clean urban atmosphere and 5 for a continental atmosphere, which agrees with Junge (1969) and some results found in this work.

Tables 1–3 summarize the results of the sensitivity analysis for (R1), (R2) and (R4) with the RTM model

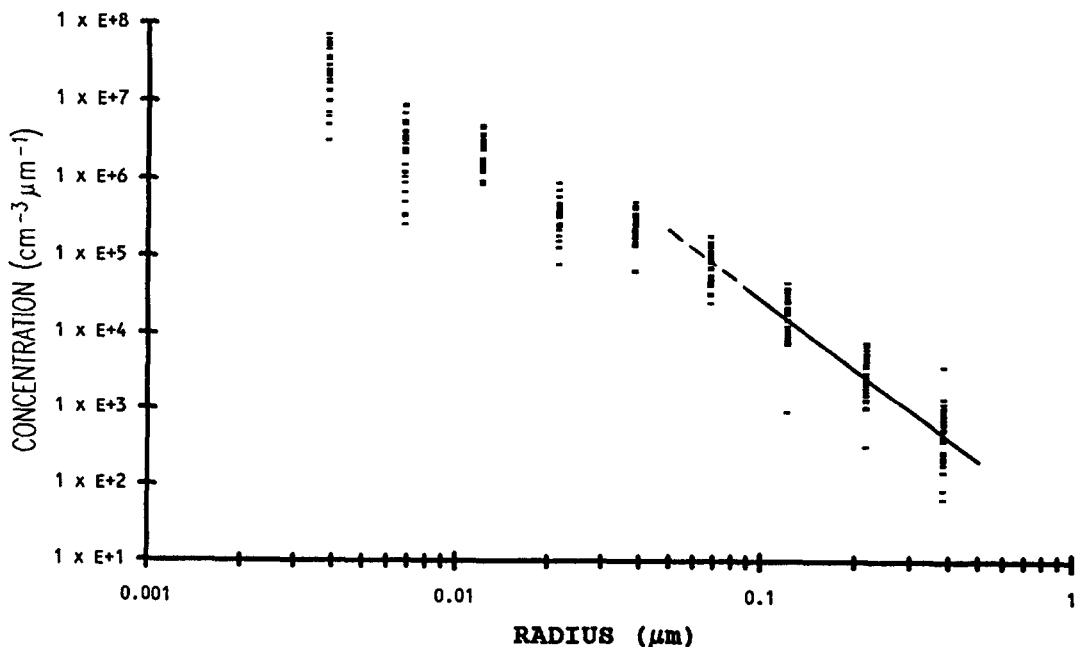


Fig. 1. Aerosols size distribution in Mexico City (Montañez and García-García, 1993).

Table 1. Sensitivity of ozone photolysis rates to changes in albedo, ozone column, refraction index and aerosol load

		Dobson units				Dobson units				Dobson units				R index
		240	270	290	300	240	270	290	300	240	270	290	300	
a	0.05	25.7	2.2	-11.8	-23.1	49.9	25.8	12.6	6.7	47.8	24.1	11.0	5.2	1.4
l		47.6	24.1	11.1	5.4	49.3	25.2	11.1	6.2	48.8	25.0	11.8	6.0	1.6
b	0.10	39.9	14.3	0.0	-6.6	63.6	37.3	22.8	16.4	61.1	24.1	21.0	14.7	1.4
e		60.5	34.9	20.8	14.6	62.9	36.7	22.2	15.9	62.3	36.3	21.9	15.6	1.6
d	0.15	54.4	26.5	11.2	4.4	77.6	49.0	33.3	6.7	74.9	46.9	31.4	24.5	1.4
o		73.8	46.1	30.8	24.1	76.9	48.4	32.7	25.8	76.1	47.9	32.3	25.4	1.6
		$\alpha = 3$				$\alpha = 4$				$\alpha = 5$				

to changes in the above-mentioned parameters and a zenith angle of 6.88, which corresponds to summer solstice at 1 pm in Mexico City. The small boxes in the matrix contain percentage changes related to the reference case (albedo 0.10, refraction index $1.4 \pm 0.005i$, 290 DU and $\alpha = 3$), which represent a mean urban albedo, mean annual ozone column with the mean urban ozone included and high pollution case.

Table 1 shows that the ozone photolysis constant decreases 12% when the surface albedo is decreased from 0.10 to 0.05 and increases 11% when moving to an area out of the city with albedo 0.15. As we can see, a change of approximately 23% in the values of the ozone rate constants may be obtained when moving from one part of the city to another maintaining all the other parameters the same. Nitrogen dioxide and formaldehyde have similar behavior as ozone (Tables 2 and 3). With respect to the ozone column, it can be observed that the ozone photolysis constant decreases almost 7% when passing from 290 to 300 DU (which represents the annual maximum at Mexico City latitudes) and increases 40% when going from 290 to 240 DU (annual minimum and clean atmosphere). Formaldehyde and nitrogen dioxide are less sensitive to these changes. Moreover, under these conditions a change on the aerosol refractive index from 1.4 (organic) to 1.6 (dust) leads to an increase of almost 20% in the ozone photolysis rate constant. Other scenarios may be analyzed; winds strong enough to swap away the smog layer (270 DU and $\alpha = 4$), may lead to an increase of 37.3%. With the dominant presence of dust aerosols, the increase may be smaller (36.7%). Under similar conditions but with a more reflective surface, such as is found southwest of the city, the ozone photolysis rate may increase by 48.4%.

The above results lead us to carry out a series of experiments in order to measure the photolysis constants of the (R1)–(R4) reactions in several Mexico City places. The second part of this work reports only experimental data for nitrogen dioxide.

EXPERIMENTAL SECTION

A full description of the experimental set up is given elsewhere (Castro *et al.*, 1995), here a brief description is

provided. A constant flow of diluted NO_2 (45.3 ppm) in nitrogen (ALPHAGAZ) was passed through a cylindrical quartz reactor and measured with an NO_x monitor. Exposure time was controlled by covering part of the reactor tube from sunlight. All gas tubing was made of teflon covered with black tape. The reactor was supported by a metal frame (30 cm high) painted black. Underneath the frame a black cloth was placed extending about 2 m each side. Simultaneous recording of the outputs from the NO_x monitor an UV radiometer, a J termopar and a pressure transducer placed at the end of the reactor, were made every minute from 7 to 10 h depending on the measurement period using an A/D card in a PC.

Measurements at the Estadio Olimpico

The Estadio Olimpico is located at the University Campus, south of Mexico City ($19^\circ 19' 50''$ north latitude, $99^\circ 11' 03''$ longitude and 2280 m above sea level) and it is surrounded by trees, gardens and volcanic lava. The surface albedo we considered was 0.13 (Finlayson-Pitts and Pitts, 1986; Dickerson, 1980). The measurements were carried out on 30 November, 1, 3 and 4 December 1993. There were clear skies during these days with exception of the last day, which was partially foggy. The solar zenith angle in this site was 41.66° at 12:30 h (local time).

The experimental values of $J(\text{NO}_2)$ (solid triangles) and the Eppley irradiance measurements (solid line) at the Estadio Olimpico are shown in Fig. 2. We observe that the minimum and maximum values in both curves are well correlated. However, after 13:30 the curves show a displacement, which could be caused by the presence of a roof structure (increasing the local albedo) near to the experiment and the cosine response of the radiometer with zenith angle. This construction was located 70 m southeast of reactor axis, which in turn was oriented perpendicular to the sun trajectory plane during the day. In this location the reactor and the radiometer were placed on the top of a mobile laboratory, the instruments and the roof structure were almost on the same plane. At large zenith angles, particularly in the afternoon, the horizontally placed reactor tube would get more light than the upward facing radiometer window. Therefore, the radiation measurements would drop faster than the J values. As it is observed from the displacement of the curves.

Theoretical values of the nitrogen dioxide photolysis constants were calculated in clear sky conditions, 2240 m above sea level, regional albedo of 0.13 for $\lambda < 410$ nm, 290 DU (the mean ozone column at this latitude is 270 DU but 20 DU are added to account for the impact of urban ozone which in 1989 was found to contribute with 18 DU (Juárez *et al.*, 1994), $\alpha = 3$ and refractive index of $1.4 + 0.005i$).

In general, direct light as well as downward and upward diffuse light are considered when calculating J 's. However, in order to compare with the experimental values, the upward diffuse light is not considered in the calculations.

Table 2. Sensitivity of nitrogen dioxide photolysis rates to changes in albedo, ozone column, refraction index and aerosol load

	Dobson units						R index						
	Dobson units			Dobson units									
	240	270	300	240	270	300							
a	0.05	-8.22	-8.43	-8.56	-8.63	-8.74	-8.80	-9.22	-9.42	-9.55	-9.61	1.4	
l		-6.96	-7.16	-7.29	-7.35	-7.35	-7.29	-7.29	-7.29	-7.35	-7.35	-7.35	1.6
b	0.10	0.38	0.15	0.0	-0.07	0.27	0.04	0.04	0.04	-0.10	-0.17	-0.56	1.4
e		1.33	1.12	0.98	0.91	0.69	0.46	0.46	0.31	0.25	-0.25	-0.48	1.6
d	0.15	9.17	8.92	8.76	8.68	9.14	8.89	8.73	8.73	8.80	8.31	8.07	1.4
o		9.86	9.62	9.47	9.40	9.56	9.31	9.15	9.15	9.08	8.63	8.39	1.6
													$\alpha = 3$
													$\alpha = 4$
													$\alpha = 5$

Table 3. Sensitivity of formaldehyde photolysis rates (reaction R4) to changes in albedo, ozone column, refraction index and aerosol load

	Dobson units						R index								
	Dobson units			Dobson units											
	240	270	300	240	270	300									
a	0.05	-0.95	-5.87	-8.92	-10.39	1.03	-3.76	-6.72	-8.10	-8.10	-0.05	-4.78	-7.71	-9.07	1.4
l		-1.19	-5.81	-8.67	-10.01	1.15	-3.65	-8.67	-8.00	-8.00	0.41	-4.34	-7.28	-8.65	1.6
b	0.10	8.70	3.33	0.0	-1.56	9.68	5.20	1.96	0.45	0.45	9.28	-4.78	0.90	-0.60	1.4
e		7.52	2.49	-0.62	-2.08	10.55	5.30	2.05	0.54	0.54	9.75	4.55	1.33	-0.17	1.6
d	0.15	18.64	12.79	9.17	7.48	20.15	14.44	10.91	-8.10	-8.10	18.94	13.28	9.79	8.16	1.4
o		16.55	11.09	7.72	6.14	20.25	14.53	10.99	9.34	9.34	19.42	13.75	10.24	8.61	1.6
															$\alpha = 3$
															$\alpha = 4$
															$\alpha = 5$

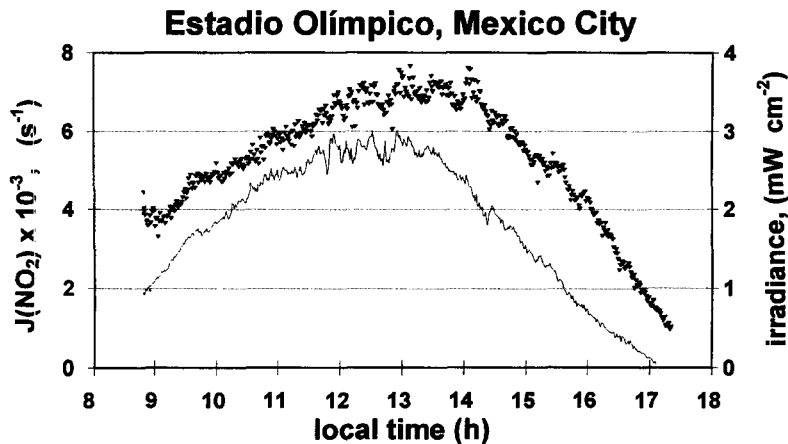


Fig. 2. Experimental values for $J(\text{NO}_2)$ and readings in the Eppley radiometer as a function of time (continuous line), Estadio Olímpico, Mexico.

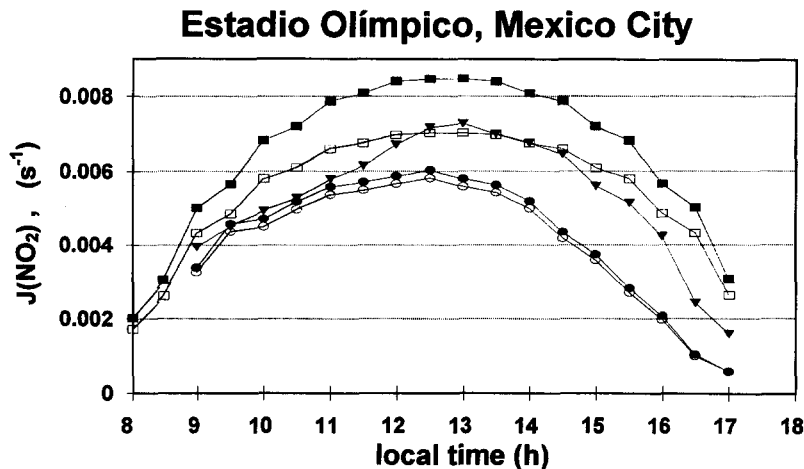


Fig. 3. Comparison between experimental and theoretical values of the nitrogen dioxide photolysis constant at the Estadio Olímpico; (a) experimental (solid triangles); (b) calculated (solid squares), (c) calculated without the contribution of upward diffuse light (empty squares); (d) calculated with equation (1) (solid circles) and (e) calculated with equation (2) (empty circles).

Figure 3 shows experimental values in intervals of 30 min (solid triangles), the values calculated with all contributions, direct, upward and downward light (solid squares) and the ones calculated without the contribution of the upward diffuse light (empty squares). Values calculated with equation (1) are also shown (solid circles), where f is calculated with our model (Montero, 1993) and E is the UV irradiance measured *in situ* with the Eppley radiometer. It is clear that the best agreement between experimental and theoretical J values is the one corresponding to empty squares (without upward diffuse light). Both Madronich models agree well with the experimental values before noon and strongly underestimate the experimental values of $J(\text{NO}_2)$ whereas the RTM model with all light contributions yields in general larger values for $J(\text{NO}_2)$.

Measurements at the Palacio de Minería

The experiment was carried out on the roof of the Palacio de Minería, located downtown Mexico City ($19^\circ 25' 59''$

north latitude, $99^\circ 07' 58''$ longitude and 2233 m a.s.l.). It is surrounded by buildings and concrete streets. The surface albedo considered for this place is 0.10. The measurements were carried out on 9–13 February 1994, days of high contamination (visibility between 500–700 m), clear sky (except day 11 which had few high cirrus clouds). The zenith angle in this period was 34.06° at 12:30 h (local time). The concentration of particles with diameters of 0.4–1 were also registered at this place.

Figure 4 shows the $J(\text{NO}_2)$ experimental values (solid triangles) and the Eppley measurements (with intervals of 1 min). As in Fig. 2, the curves are in good correlation, but compared to the irradiance curve (continuous line) a displacement is noticeable between 14:00 and 16:00 h. This behavior can be explained by the presence of large buildings located southeast of the radiometer. Although these buildings did not obstruct the direct sun light arriving to the reactor they had influence on the photolysis constant measurements (the multiple reflections from these buildings and structures may increase the diffuse light reaching the

reactor compared to that arriving at the flat surface of the radiometer).

Theoretical values of $J(\text{NO}_2)$ were calculated for the following conditions: regional albedo of 0.10, ozone column of 290 DU, aerosols refractive index of $1.4 + 0.005i$ and $\alpha = 3$. Upon analyzing the aerosol concentration (Fig. 5) we find that this value of α is in good agreement with the value presented by Montañez and García-García (1993).

Figure 6 shows the $J(\text{NO}_2)$ experimental values (solid triangles), the calculated ones (solid squares), and the calculated values without the contribution of the upward diffuse light (empty squares). The solid and empty circles are the values calculated with Madronich's formula and Madronich's parameterized formula, respectively. Again Madronich models agree well with the experimental values before noon and in this location agreement with the experimental

data was better. It can be seen that our model overestimates the J 's, especially during the first hours of the day and in the afternoon, when attenuated or modified light arrives to the reactor (the presence of buildings are not accounted for in the model).

Measurements at the Instituto Mexicano del Petróleo (IMP)

The experiment was located on the roof of the Geophysics department in the IMP located north Mexico City ($19^\circ 28' 48''$ north latitude, $99^\circ 11' 07''$ longitude and 2277 m a.s.l.) surrounded by buildings, gardens and asphalt streets. The regional albedo considered for this place is 0.10. The measurements were carried out during 23–27 March 1994. There were clear skies during these days, high pollution during the mornings (visibility between 500 and 700 m) but low pollution during the afternoons due to winds. The

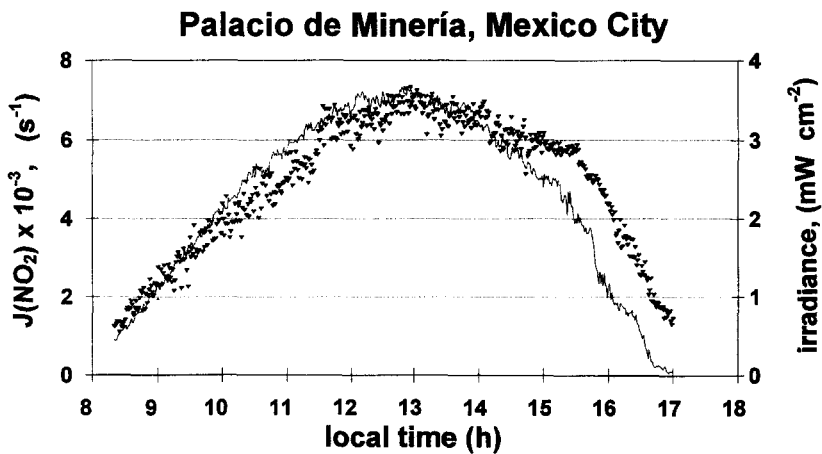


Fig. 4. Experimental values of $J(\text{NO}_2)$ and Eppley radiometer readings as function of the time, 10–13 February 1994, Palacio de Minería, Mexico City.

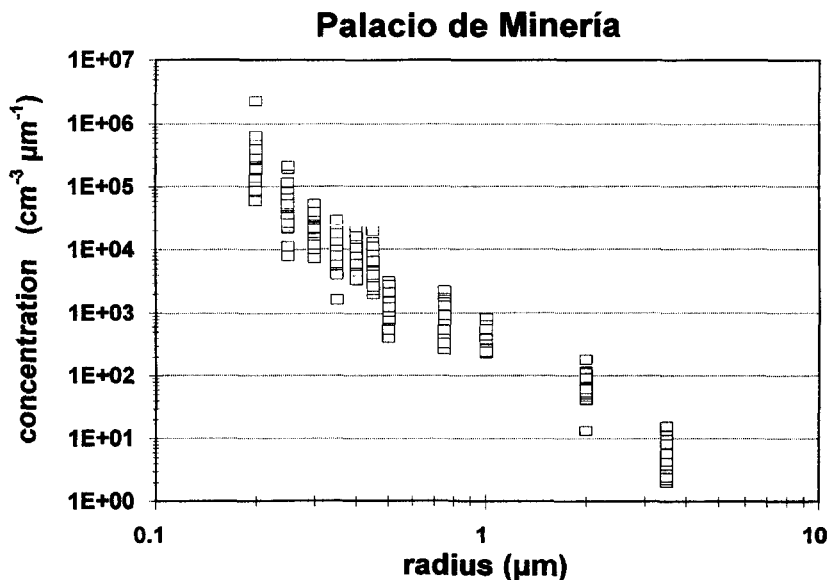


Fig. 5. Particle concentration profile, Palacio de Minería, Mexico City.

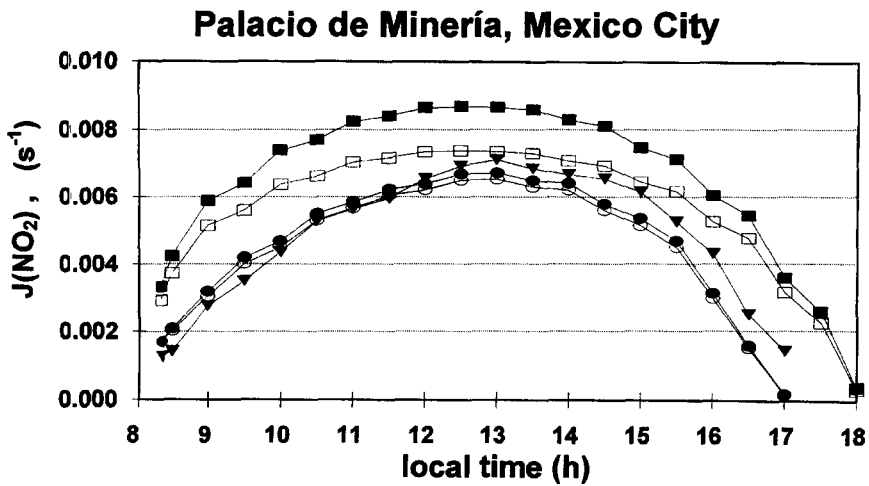


Fig. 6. Experimental and theoretical values of the nitrogen dioxide photolysis constant at the Palacio de Minería; (a) experimental (solid triangles); (b) calculated (solid squares); (c) calculated without the contribution of upward diffuse light (empty squares); (d) calculated with the equation (1) (solid circles); and (e) calculated with equation (2) (empty circles).

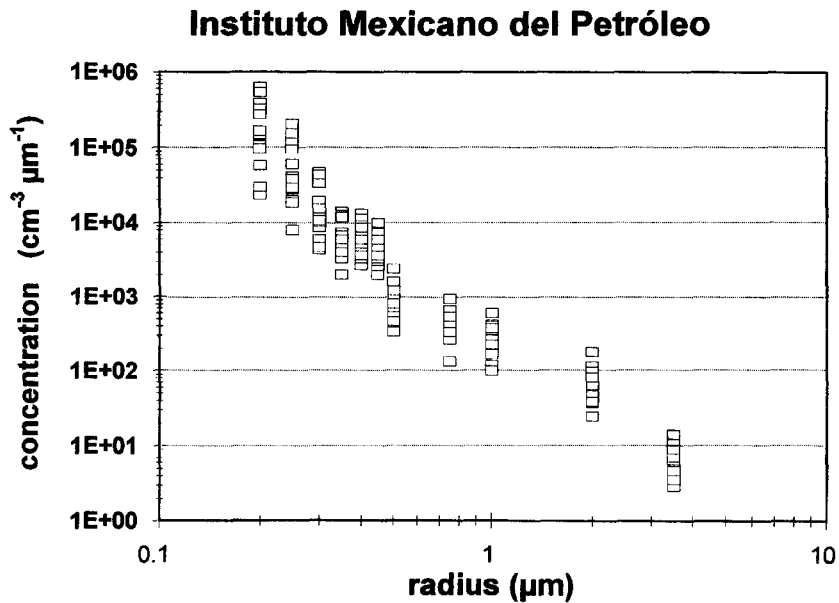


Fig. 7. Particle concentration profile, Instituto Mexicano del Petróleo, Mexico City.

zenith angle was 17.90° at 12:30 h (local time). The particle concentration profile is shown in Fig. 7.

Figure 8 shows the $J(\text{NO}_2)$ experimental values (solid triangles) and the irradiances. The curves are correlated well, although a small displacement is observed in the afternoon.

The $J(\text{NO}_2)$ theoretical values were found with the following conditions: regional albedo of 0.10, ozone column of 290 DU, particle refraction index of $1.4 + 0.005i$ and $\alpha = 3.24$. Figure 9 shows the experimental data (solid triangles) and the calculated ones.

Measurement at Tres Marias, Morelos, Mexico

Tres Marias is a town near Mexico City (19° 03' north latitude, 99° 14' longitude and 2810 m a.s.l.). The landscape is mainly grassland, trees and pines. The considered regional surface albedo was 0.15 (Finlayson-Pitts and Pitts, 1986). Measurements were carried out on 11–15 April 1994. There were clear skies and a clean atmosphere. The zenith angle was 11.13° at 12:30 h (local time). Figure 10 shows particle profile here.

As in the other experiments, Fig. 11 shows the $J(\text{NO}_2)$ the experimental values (solid triangles) and the measured

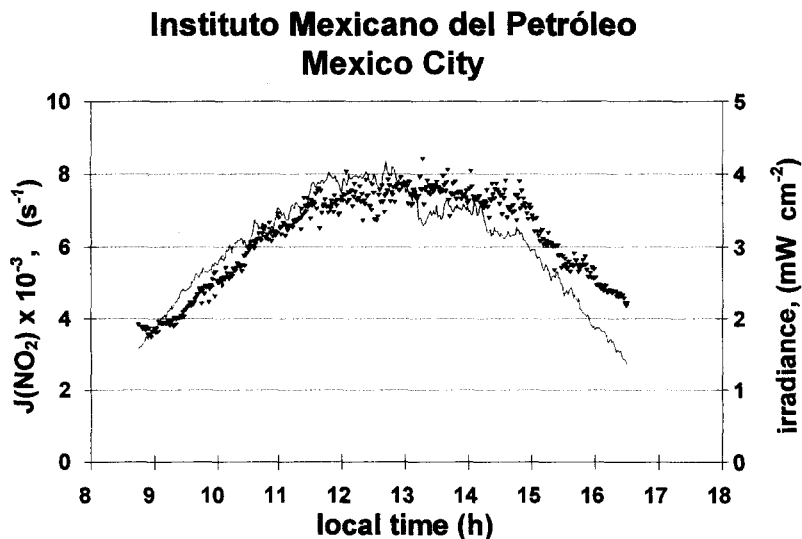


Fig. 8. Experimental values of $J(\text{NO}_2)$ and readings from the Eppley radiometer as function of time, 24–27 March 1994, Instituto Mexicano del Petróleo, Mexico City.

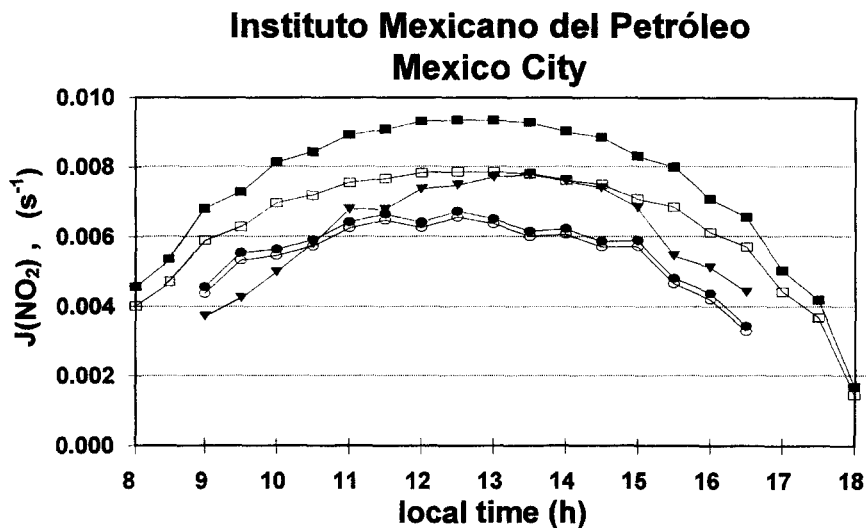


Fig. 9. Comparison of the experimental and theoretical values of the nitrogen dioxide photolysis constant at the IMP: (a) experimental (solid triangles); (b) calculated ones (solid squares); (c) calculated without upward diffuse light (empty squares); (d) calculated with equation (1) (solid circles); and (e) calculated with the equation (2) (empty circles).

irradiance. The theoretical values of $J(\text{NO}_2)$ were calculated with the following conditions: ozone column of 270 DU, particle refraction index of $1.6 + 0.005i$ (dust) and $\alpha = 3.6$.

Figure 12 shows the experimental and calculated values for $J(\text{NO}_2)$.

Figures 13 and 14 show the experimental data obtained during the complete set of experiments, vs time and zenith angle, respectively. In particular, the data shown in Fig. 14 are in good agreement with those reported elsewhere (Demerjian *et al.*, 1980; Dickerson, 1980; Shetter *et al.*, 1992).

Figure 14 shows results from all local time at 15 min intervals. It can be seen the important role of local condi-

tions (albedo and pollution levels) on the experimental $J(\text{NO}_2)$. Moreover, landscape plays an important role since part of the apparent dispersion on the results is due to the lack of symmetry on the radiation field.

CONCLUSIONS

Experimental and theoretical photolysis rate constants for NO_2 , O_3 and HCHO , under Mexico City atmospheric conditions, are reported in this work. These constitute the first group of values obtained

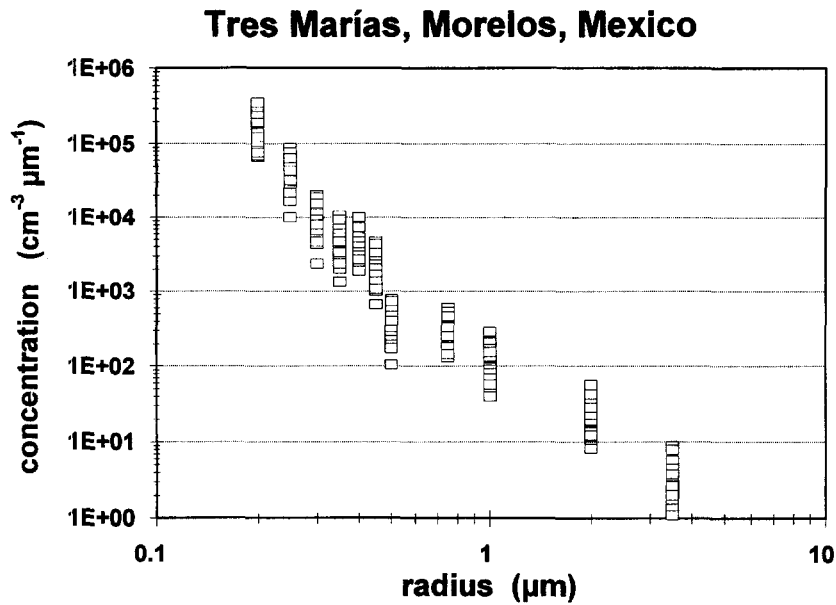


Fig. 10. Particle concentration profile, Tres Mariás, Morelos, Mexico.

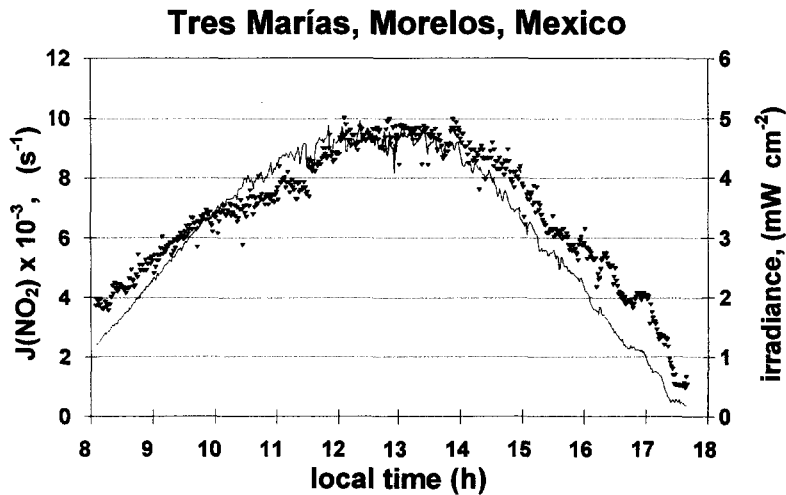


Fig. 11. Experimental values of $J(\text{NO}_2)$ and readings from Eppley radiometer as function of the time (continuous line), 12–15 April 1994, Tres Mariás, Morelos, Mexico.

under real conditions which clearly could be used in air quality models (AQM) for the city. Our radiation transfer model for Mexico City was calibrated by direct comparisons with experimental photolysis rates of nitrogen dioxide. In all cases the higher $J(\text{NO}_2)$ values provided by the model at sunrise and sunset could be explained by the fact that currently the model does not consider the presence of high mountains to the east, south and west of the city. The west

mountains are much nearer to the city than the east ones. The model is oblivious to the presence of the mountains; the reactor gets more diffuse light than the zenith facing radiometer, thus, this one, it is more sensitive to the presence of mountains and buildings. This fact may also explain the better agreement of Madronich models with the experimental values before noon and the strong underestimation in the afternoon as J is a function of E . The results show the

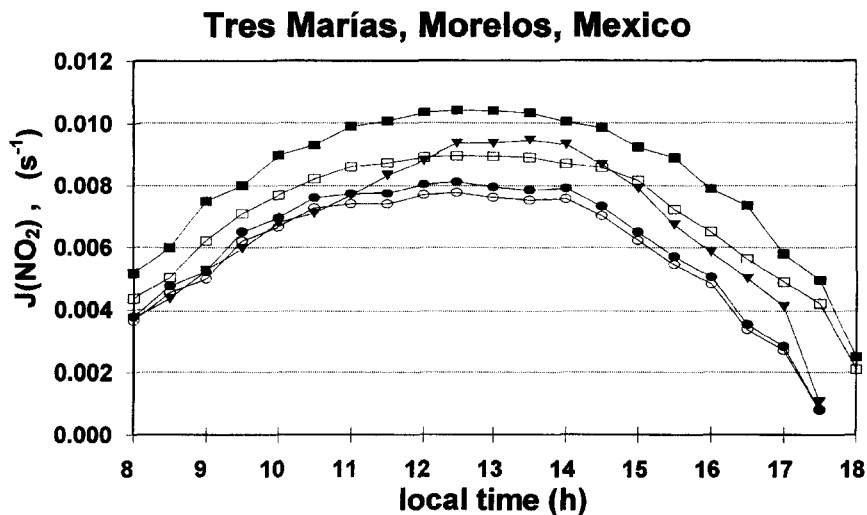


Fig. 12. Comparison of the experimental and theoretical values of the nitrogen dioxide photolysis constant at Tres Mariás, Morelos: (a) experimental (solid triangles); (b) calculated (solid squares); (c) calculated with no upward diffuse light (empty squares); (d) calculated with equation (1) (solid circles); and (e) calculated with equation (2) (empty circles).

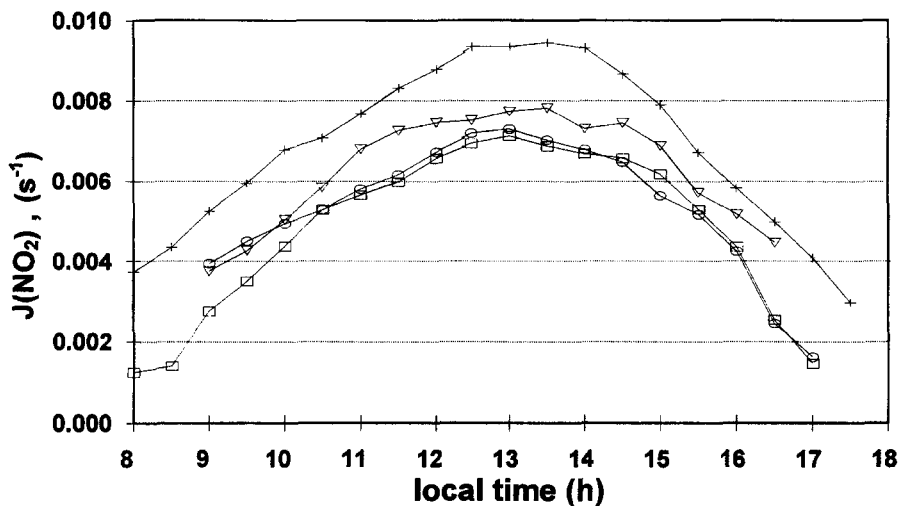


Fig. 13. Experimental values of $J(\text{NO}_2)$ in four different locations in Mexico. Estadio Olímpico (circles), Palacio de Minería (squares), Instituto Mexicano del Petróleo (triangles), Tres Mariás (crosses).

importance of providing local resolution for photolysis rates by considering different local conditions within the modeling domain of an AQM. Our calculations also show that ozone photolysis is more sensitive to local conditions than NO_2 photolysis. Experimental measurements for ozone are under way.

Acknowledgements—The authors wish to thank Dr Carlos Gay for his comments, and also to Bertha Mar and Alfredo Rodríguez for his help in the experimental part and Agustín Muhlia and Vidal Valderrama for his help in obtaining the aerosol records. This work was supported by Programs PAPID and PADEP of UNAM and Instituto Mexicano del Petróleo.

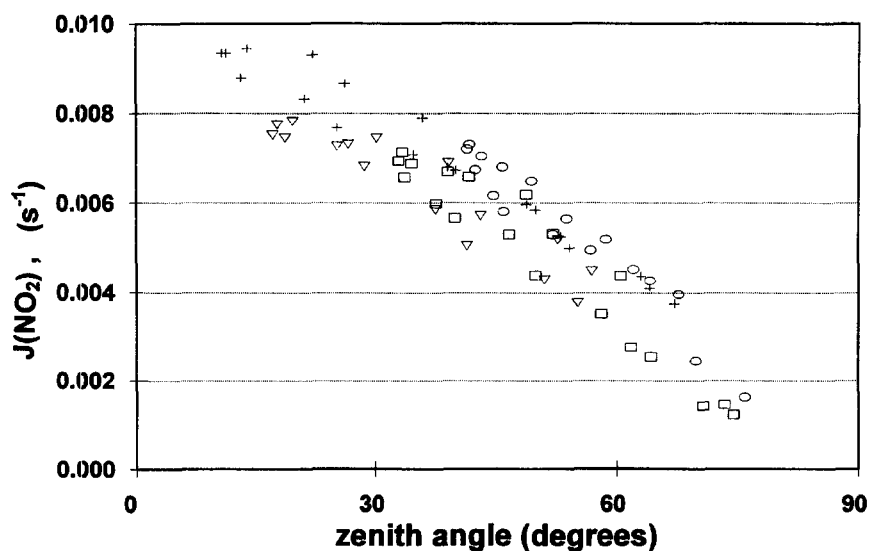


Fig. 14. $J(\text{NO}_2)$ vs zenith angle. Estadio Olímpico (circles), Palacio de Minería (squares), Instituto Mexicano del Petróleo (triangles), Tres Marias (crosses).

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