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The influence of aerosols on photochemical smog in Mexico City

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Abstract

Aerosols in the Mexico City atmosphere can have a non-negligible effect on the ultraviolet radiation field and hence on the formation of photochemical smog. We used estimates of aerosol optical depths from sun photometer observations in a detailed radiative transfer model, to calculate photolysis rate coefficients (J_{NO_2}) for the key reaction $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ($\lambda < 430 \text{ nm}$). The calculated values are in good agreement with previously published measurements of J_{NO_2} at two sites in Mexico City: Palacio de Minería ($19^\circ 25' 59'' \text{N}$, $99^\circ 07' 58'' \text{W}$, 2233 masl), and IMP ($19^\circ 28' 48'' \text{N}$, $99^\circ 11' 07'' \text{W}$, 2277 masl) and in Tres Marias, a town near Mexico City ($19^\circ 03' \text{N}$, $99^\circ 14' \text{W}$, 2810 masl). In particular, the model reproduces very well the contrast between the two urban sites and the evidently much cleaner Tres Marias site. For the measurement days, reductions in surface J_{NO_2} by 10–30% could be attributed to the presence of aerosols, with considerable uncertainty due largely to lack of detailed data on aerosol optical properties at ultraviolet wavelengths (esp. the single scattering albedo). The potential impact of such large reductions in photolysis rates on surface ozone concentrations is illustrated with a simple zero-dimensional photochemical model. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photolysis rates; Aerosols optical properties; Photochemical smog; Mexico City

1. Introduction

Mexico City is among the 10 largest cities of the world (Ezcurra and Mazari, 1998), with people exposed daily to high pollution episodes. Elevated ozone concentrations in the city routinely violate the environmental air quality standards (110 ppbv over 1 h). The city's location in the tropics (19°N) and high elevation (2240 masl) create a high-radiation environment, a condition that drives the chemistry leading to the formation of photochemical ozone. One of the key reactions in the ozone formation in the troposphere is the photodissociation of NO_2 at $\lambda < 430 \text{ nm}$.



The photolysis frequency, J_{NO_2} , of this first-order reaction (R1), depends on the solar spectral actinic flux $F(\lambda)$,

$$J = \int F(\lambda)\sigma(\lambda)\varphi(\lambda) d\lambda,$$

where $\sigma(\lambda)$ denotes the nitrogen dioxide absorption cross section and $\varphi(\lambda)$ the photodissociation quantum yield. The solar actinic flux of course depends on local optical conditions, including aerosols and gases present in the urban atmosphere. Radiative transfer models show that aerosols can either increase or decrease the actinic flux (and J_{NO_2}), depending on their detailed scattering and absorption properties at UV wavelengths (e.g., Fiocco et al., 1978; Madronich and Flocke, 1998; He and Carmichael, 1999). Calculations with various oxidant models show that these effects can vary regionally. Dickerson et al. (1997) found for the eastern US a

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substantial increase in surface O_3 production, resulting from high diffuse actinic fluxes due to scattering by non-absorbing aerosols. However, Jacobson (1998) found that in Los Angeles the presence of aerosols caused a 5–8% decrease in near-surface ozone-mixing ratios. Jonson et al. (2000) showed relatively little effect on ozone production from sulfate aerosols in Europe.

The atmosphere of Mexico City has typically even higher concentrations of optically active particles (Vasilyev, 1995; IMADA, 1997; PROAIRE, 1996) with both scattering and absorbing characteristics, and it is not clear a priori whether J values are increased or decreased. Recent measurements of particles optical properties ($\lambda = 500$ nm) in Mexico City made by Baumgardner et al. (2000) indicate that there is a strong light-absorbing component in particles with diameters less than 1 μm . These particles can modify the vertical profile of the solar actinic flux may reduce surface ozone production (Raga and Raga, 2000). In this paper we attempt to understand the relationship between photolysis rates measured at the surface, the aerosol optical properties in Mexico City, and the photochemical ozone changes. Castro et al. (1997) modeled these measurements with a delta-Eddington radiative scheme, but recent studies have suggested that such two-stream methods may be inaccurate under heavily polluted conditions (Petropavlovskikh, 1995; Dusseux, 1995), a result also confirmed by our calculations (see Section 3). Here, we compute the effect of aerosol on the radiation field using the tropospheric ultraviolet–visible model (TUV) with an accurate eight-stream discrete ordinate solver. This allows a somewhat less ambiguous attribution of the effect of aerosols on J_{NO_2} .

2. Observations and methodology

Photolysis rate coefficients for reaction (1) were measured with a chemical actinometer during early 1994, as described by Castro et al. (1995, 1997). These observations were made on different days in three places: (1) The Palacio Minería (PM: 9–13 February, 19°25′59″N, 99°07′58″W, 2233 masl), located downtown Mexico City; (2) The Instituto Mexicano del Petróleo (IMP: 24–27 March, 19°28′48″N, 99°11′07″W, 2277 masl), located on the north side of the city and experiencing heavy vehicular traffic and industry; and (3) Tres Marias a rural site located at 50 km from the south of the city (TM: 11–15 April, 19°03′N, 99°14′W, 2810 masl). The PM measurements were carried out on days of high pollution and no clouds. Measurements at IMP were obtained with high pollution during the morning but lower pollution in the afternoons due to winds. The visibility at both locations was reported to be 500–700 m (but see below). Tres Marias measurements were taken on clear sky and an apparently clean atmosphere.

Aerosol optical depths, $\tau(\lambda)$, were determined from ground-based measurements of the attenuation of direct solar radiation. We used two Volz's Sun Photometers (models No. 107 and 673), one with three interference filters (500, 880 and 940 nm), the other with four filters (380, 500, 875 and 946 nm). For this work we only used the 380 and 500 nm wavelengths. Aerosol optical depths at these wavelengths were obtained from the solar radiation measurements via the expression (Volz, 1974)

$$\tau(\lambda) = \frac{1}{m_r} [\ln(I_0) - \ln(I, f) - (\tau_R m_a + \tau_o m_o)],$$

where I_0 denotes the extraterrestrial solar radiation at mean solar distance; I is observed solar radiation; f is a correction factor for mean Sun–Earth distance; τ_R is Rayleigh optical depth at sea level ($P_0 = 1013.25$ mb); τ_o is ozone optical depth; $\tau_o = \sigma_o \Omega$, where σ_o and Ω are, respectively, the ozone absorption coefficient and atmospheric column amount; m_r is the relative “air mass” (using Kasten formula, (Kasten, 1966)); $m_a = m_r(P/P_0)$ is the absolute optical air mass; m_o is the relative optical ozone mass; $m_r \approx m_o$ for $m_r < 2.5$ (Robinson, 1966). The values for τ_R obtained from Leckner (1978) for λ equal to 380, 500 and 880 nm were 0.453, 0.1480 and 0.0150, respectively. The value of τ_o for $\lambda = 500$ nm was calculated from an absorption coefficient of 0.03 cm^{-1} (Vigroux, 1953) and an ozone column amount of 280 DU corresponding to a mean measured value for February and March in Mexico City (e.g., McPeters et al., 1996).

Figs. 1 and 2 show the $\tau(\lambda)$ measured during the PM and IMP campaigns. At ultraviolet wavelengths (380 nm), $\tau(\lambda)$ ranged from 0.5 to 1.5. At visible wavelengths (500 nm) the range was from 0.3 to 1.2, and at near-infrared wavelengths (875 and 880 nm) the values ranged from 0.2 to 0.4. From these ranges, we estimated

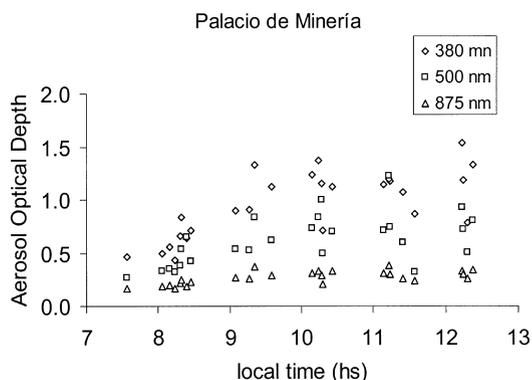


Fig. 1. Aerosol optical depths, $\tau(\lambda)$, using ground-based measurements of the attenuation of direct solar radiation at Palacio de Minería, Mexico City.

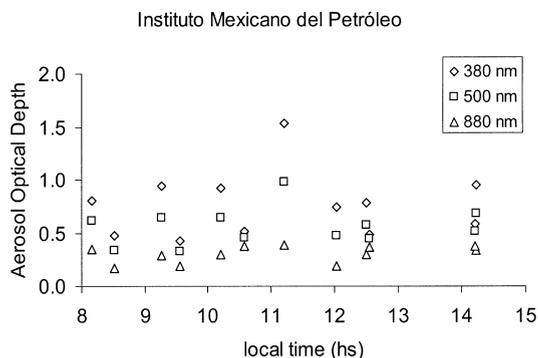


Fig. 2. Aerosol optical depths, $\tau(\lambda)$, using ground-based measurements of the attenuation of direct solar radiation at IMP.

an average value for optical depths at PM to be 1.0, 0.6 and 0.3 for 380, 500 and 875 nm, respectively, while at IMP values were 0.5 and 0.3 at 500 and 880 nm, respectively. In our TUV model calculations, we used an optical depth of 1.0 at 380 nm, while for other wavelengths we use the common form $\tau(\lambda) \sim \tau(380 \text{ nm}) (380/\lambda)^\alpha$ where $\alpha \sim 2.0$ was estimated from photometer data at different wavelengths.

Additional estimates of aerosol optical properties are available from the Project Azteca measurements taken during two weeks in November 1997 (Baumgardner et al., 2000). The scattering coefficient ranged from a minimum of $3.12 \times 10^{-5} \text{ m}^{-1}$ to a maximum of $3.98 \times 10^{-4} \text{ m}^{-1}$, with an average value of $1.42 \times 10^{-4} \text{ m}^{-1}$. The corresponding values for the absorption coefficient were $0.48 \times 10^{-5} \text{ m}^{-1}$, $5.89 \times 10^{-5} \text{ m}^{-1}$ and $2.23 \times 10^{-5} \text{ m}^{-1}$, respectively (Raga et al., 2000). These values translate into a range of single scattering albedo from 0.40 to 0.99. Since no measurements of the vertical profiles of particle optical properties have been made in Mexico City, we used the surface values throughout the boundary layer, which was taken to be 1200 m deep and constant in time (see, for example, Perez-Vidal and Raga, 1998). Using this height, the above total (scattering + absorption) coefficients imply optical depths in the range of 0.12–0.55 at 500 nm.

Table 1
Assumed aerosol optical properties at 380 nm

Case	$C_{\text{scat}} (\text{m}^{-1})$	$C_{\text{abs}} (\text{m}^{-1})$	$C_{\text{ext}} (\text{m}^{-1})$	τ	α	ω_0^a
1	3.98×10^{-4}	5.89×10^{-5}	4.57×10^{-4}	0.55	0	0.87
2	1.42×10^{-4}	2.23×10^{-5}	1.64×10^{-4}	0.20	0	0.87
3	na	na	na	1.0	2	0.95
4	na	na	na	1.0	2	0.80

^a Assumed independent of wavelength over the spectral region relevant to J_{NO_2} .

The visibility data largely conflict with the more direct aerosol measurements. Applying Koshmeider's relationship to visible ranges of 500–700 m for both PM and IMP, yields attenuation coefficients of $6\text{--}8 \times 10^{-3} \text{ m}^{-1}$, or vertical optical depths of 7–9 in a well-mixed 1.2 km boundary layer. It is unclear to what extent this apparent discrepancy is due to observational methods, or to more physical reasons such as near-surface stratification of primary pollutants.

The aerosol data described above are rather limited, and there is some question as to whether they are sufficiently representative to allow comparison of measured and calculated J values. Therefore, we used a range of aerosol optical properties based on the Project Azteca measurements (Cases 1 and 2 in Table 1) and on photometer data (Cases 3 and 4). For Cases 1 and 2, the use of values obtained at 500 nm for all other wavelengths may underestimate UV optical depths. Both the maximum and the average cases have a single scattering albedo $\omega_0 = 0.87$, probably fortuitously given the large variability observed by Raga et al. (2000). Cases 3 and 4 are based on measurements on days overlapping with those of the J_{NO_2} measurements, and the 380 nm data should be of more direct import. However, no independent estimate of ω_0 is available, and the two cases represent plausible bracketing values, 0.80–0.95. The asymmetry factor was 0.6 for all cases.

The modeling methodology included two components, the tropospheric ultraviolet model (TUV) (e.g., Madronich and Flocke, 1998) and the chemical kinetics model (KINMOD). The TUV model uses an eight-stream discrete ordinates approximation (Stamnes et al., 1988) to solve the radiative transfer equation in a layered atmosphere. The effect of aerosols on J values was examined with the TUV model. For this purpose, aerosols were added in the boundary layer of the city, which we approximated as being of 1200 m high and constant in time. No horizontal variation in aerosols was considered, in effect making this TUV calculation a one-dimensional problem. Additional model assumptions included cloudless skies, 10% ground albedo, and vertical profiles for air and temperature from the United States Standard Atmosphere (USSA, 1976) appropriate for annual means at 45 N. To account for local (pollutant) ozone, we

maintained a constant O₃ column of 280 DU above the PBL, and added 150 ppb of ozone to the PBL, for a total column amount of 291.2 DU, comparable with earlier estimates (Juárez et al., 1994). Note that the ozone amounts have only minor effects on J_{NO_2} , but are significant for other photolysis reactions. The KINMOD model, as used here, is a zero-dimensional (box) model in which chemical concentrations at a single location are integrated forward in time, from specified initial conditions, to predict concentrations (e.g. of ozone and other species) at a later time (Ruiz-Suarez et al., 1993). The time integration is carried out numerically with the LSODE solver, Hindmarsh (1980) version of Gear's method. For the present purposes, we used the highly simplified organic/NO_x mechanism (HC/NO_x) suggested by Seinfeld and Pandis (1997) with O(¹D) quenching added. This mechanism, although unable to represent in detail the complexity of the myriad of pollutants present in Mexico City, does contain the main known features of the photochemistry of NO_x and hydrocarbon that ultimately leads to urban smog formation. Furthermore, the use of a box model neglects horizontal inhomogeneities in both emissions and environmental state (e.g. winds, humidity, radiation) and thus cannot capture the spatial variability in ozone formation in different sectors of the city.

These very strong simplifications and multiple choices for initial conditions, imply that the results of the simulations should be viewed as illustrating the importance of perturbed J values on the photochemistry, but do not necessarily represent actual or predicted concentration of ozone at any specific time or location. Initial chemical conditions are based on observations reported by Baez et al. (1989, 1995) for formaldehyde and NO, NO₂ and O₃ (see Table 2).

3. Results

The measured and calculated values of J_{NO_2} are shown in Figs. 3–5. The diurnal cycle predicted by the model is symmetric, while morning observations appear systematically lower, for reasons that may be site-specific, e.g. possible reflections from buildings at the PM site, or the afternoon wind noted for the IMP site.

The TM site's cleaner atmosphere offers the opportunity to compare model and measurements under relatively well-defined conditions, that is, without the additional uncertainties related to modeling large aerosol loading. In the afternoon, measured values are comparable to and even exceed the theoretical no-aerosol values. The ~10% excess may well be due to instrument/model calibration issues, thus suggesting possibly even greater J_{NO_2} reductions at the PM and IMP sites, to the extent that the same instrument and model were used. But in view of the unexplained lower values in the morning,

Table 2
Parameter values used in KINMOD model

Total pressure	582 Torr
Temperature	293 K
Relative humidity	50%
<i>Initial conditions</i>	
[RH] ₀	$3.00 \times 10^{13} \text{ mol cm}^{-3}$
[NO] ₀	$7.52 \times 10^{11} \text{ mol cm}^{-3}$
[NO ₂] ₀	$7.52 \times 10^{11} \text{ mol cm}^{-3}$
[O ₂] ₀	$3.96 \times 10^{18} \text{ mol cm}^{-3}$
[M]	$1.49 \times 10^{19} \text{ mol cm}^{-3}$
[HCHO] ₀	$7.52 \times 10^{11} \text{ mol cm}^{-3}$

such small differences should be viewed with caution, as they are comparable to the uncertainties in both measurements and calculations. Many sources of error are possible in both the model and the measurements, and the agreement found for the TM afternoon measurements is consistent with our view that these are not excessive, perhaps on order of ~10% in view of Fig. 5. These TM measurements add credibility to our clean-sky calculations for the other two sites.

The PM and IMP observations are persistently lower than clean-sky values, e.g. for noontime, by factors of 0.81 at PM and 0.86 at IMP (but 1.0 + 0.9 at TM). Even stronger reductions are observed at other times, especially in the morning. A range of different assumptions about the aerosols is consistent with such reductions. If photometer-derived optical depths are used, a single-scattering albedo in the range 0.8–0.95 (Cases 4 and 3 in Table 1) must be invoked to explain the reduction of the observed values from the theoretical clean-sky values. Calculations based on the Project Azteca aerosol data give similar results, with Cases 1 and 2 bracketing most of the measurements. This suggests that the aerosol absorption optical depths, $\tau(1 - \omega_0)$, fall between ca. 0.05 and 0.15 at wavelengths weighted by the NO₂ photodissociation spectrum.

The aerosol-related reductions in J_{NO_2} , by ca. 20% at PM and 15% at IMP, are consistent with Raga et al. (2000) results. They determine that the presence of highly absorbing aerosols in Mexico City leads to a reduction between 18 and 21% in photolysis rates for NO₂ and ozone at surface. Recently, Jauregui and Luyando (1999) presented climatological evidence that solar radiation within Mexico City is 21.6% lower than in rural areas surrounding the city, and they attribute this to the presence of urban atmospheric pollutants. The importance of local conditions (albedo and pollution) on the experimental J_{NO_2} can be seen in Fig. 6, e.g. for the same zenith angles the J values are different (Castro et al., 1997).

Fig. 7 shows the sensitivity of calculated J_{NO_2} values to a few assumptions. Relative to the clean-sky case (thick

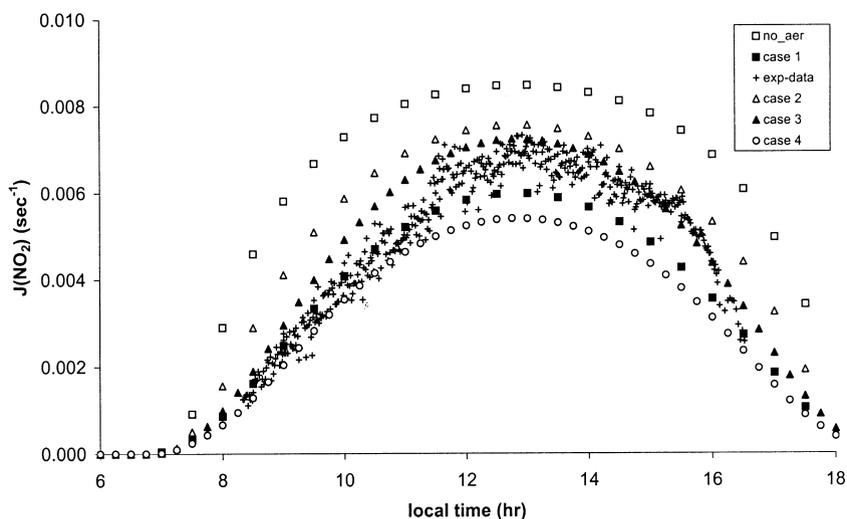
J(NO₂) for MAX aerosol conditions at Palacio Minería on 11 Feb 94

Fig. 3. Comparison between experimental and theoretical values of nitrogen dioxide photolysis rate at Palacio de Minería (PM), Mexico City. Experimental values (+ + +), calculated using TUV model for Case 1 (■ ■ ■), Case 2 (△ △ △), Case 3 (▲ ▲ ▲) and Case 4 (○ ○ ○). Noaerosols included in the boundary layer (□ □ □).

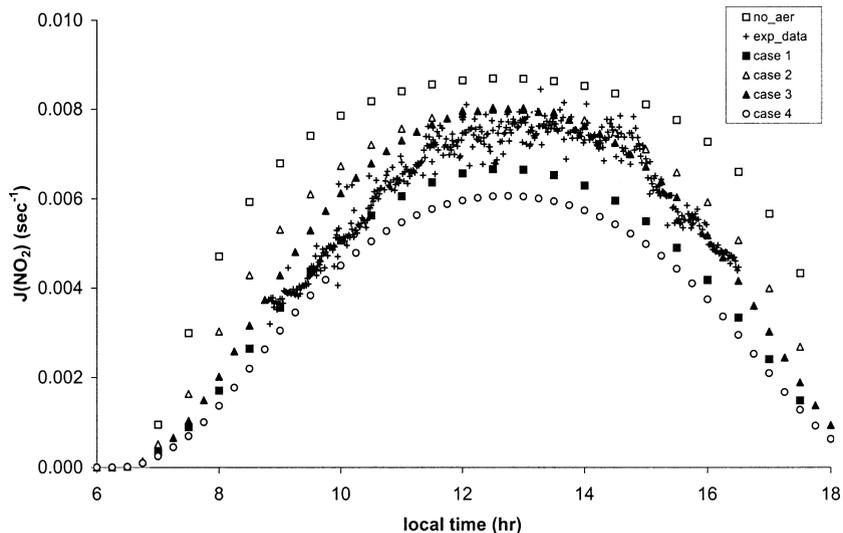
J(NO₂) for aerosol conditions at IMP on 25 Mar 94

Fig. 4. Comparison between experimental and theoretical values of nitrogen dioxide photolysis rate at Instituto Mexicano del Petróleo (IMP), Mexico City. Experimental values (+ + +), calculated using TUV model for Case 1 (■ ■ ■), Case 2 (△ △ △), Case 3 (▲ ▲ ▲) and Case 4 (○ ○ ○). No aerosols included in the boundary layer (□ □ □).

curve), the presence of 30 ppb of NO₂ (e.g., see Table 2), distributed uniformly over the 1.2 km boundary layer height cause a reduction in surface J_{NO_2} values of about 7% (thin curve); absorption by tropospheric ozone (not shown) has even less effect. Aerosols affect both the magnitude and the shape of the vertical profile of the

actinic flux. Scattering tends to enhance the actinic flux above and within the aerosol layer. On the other hand, surface values depend mainly on the absorption component. For example, in Fig. 7 the curves shown for absorbing aerosols have the same value of the absorption optical depth, $(1 - \omega_0)\tau \sim 0.2$, but differ by a factor of

$J(\text{NO}_2)$ for aerosol conditions at Tres Marias on 15 Apr 94

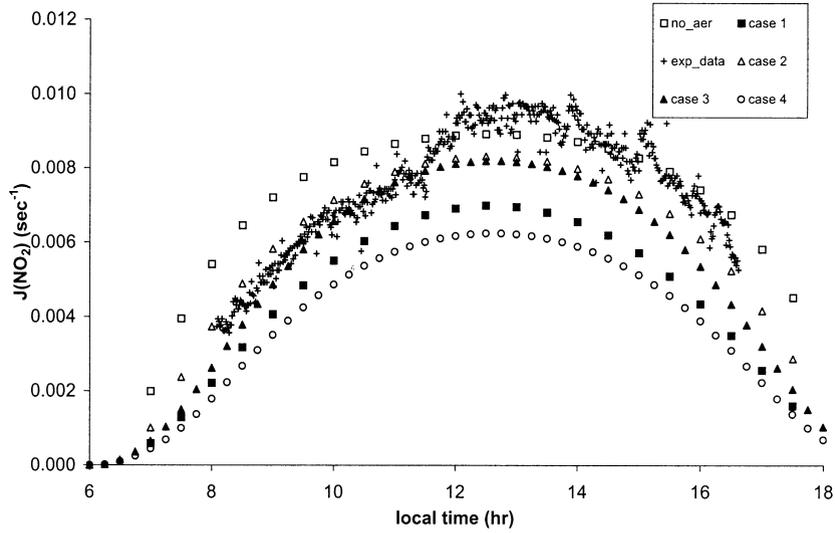


Fig. 5. Comparison between experimental and theoretical values of nitrogen dioxide photolysis rate at Tres Marias, Morelos, México. Experimental values (+ + +), calculated using UV model for Case 1 (■ ■ ■), Case 2 (△ △ △), Case 3 (▲ ▲ ▲) and Case 4 (○ ○ ○). No-aerosols included in the boundary layer (□ □ □).

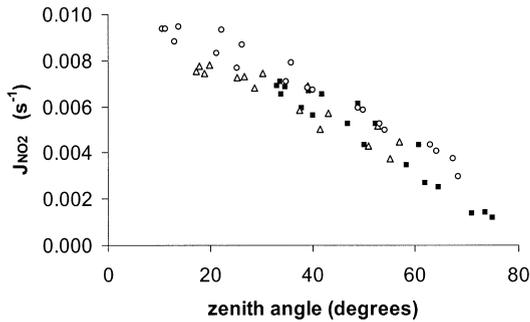


Fig. 6. J_{NO_2} vs. zenith angle. Palacio de Minería (■ ■ ■), Instituto Mexicano del Petróleo (△ △ △) and Tres Marias (○ ○ ○).

two in the values of the scattering optical depth ($\omega_0\tau$). Such an increase in scattering at constant absorption may be illustrative of the effect if increasing relative humidity, since, to first approximation, the absorption depends on the presence of constituents such as soot and organic carbon, but much less on the amount of water. Finally, Fig. 7 shows the effect of using an approximate two-stream method (delta-Eddington) to calculate J_{NO_2} , for the high scattering case. Substantial errors can arise under such polluted conditions, and multi-stream methods are preferred (eight-stream discrete ordinates was used here).

Fig. 8 illustrates the effect of reductions in photolysis rates of NO_2 , O_3 and HCHO on photochemical smog

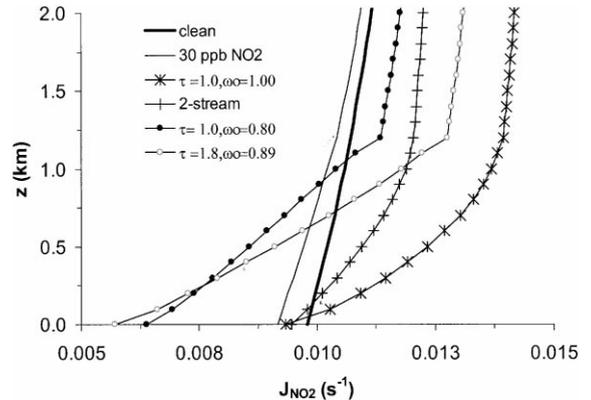


Fig. 7. J_{NO_2} values for Mexico City, calculated with the TUV model for a solar zenith angle = 30° , boundary layer height of 1.2 km, ground albedo of 10%. An 8-stream discrete ordinates method was used, except as noted. Values for a clean atmosphere (no pollutants) are given for reference by the thick curve. The effect of 30 ppb of gaseous NO_2 (no aerosols) is shown by the thin curve. The effect of scattering aerosols is given by the curve marked with (*) for calculations with eight-streams, and compared with the results using an approximate two-stream method (delta-Eddington), marked with (+). The effect of absorbing aerosols is shown by the curves marked with circles: the two cases have the same absorption optical depth, $\tau(1 - \omega_0) \sim 0.2$, but different scattering optical depths $\tau\omega_0$, 0.80 (● ● ●) and 1.60 (○ ○ ○).

formation. KINMOD simulations of ozone production were made using the no-aerosol J values (solid curve), and with Case 1 J values (dotted curve). The results show

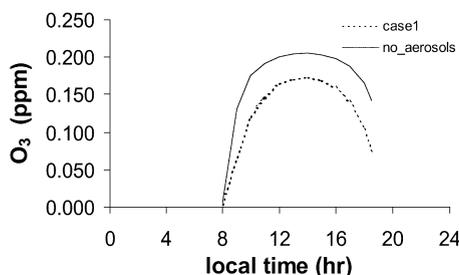


Fig. 8. Ozone concentrations predicted by KINMOD using photolysis rates (NO_2 , O_3 and HCHO) computed with no aerosols (thin solid curve) and with Case 1 aerosols (dotted curve).

a reduction of ozone concentrations by ca. 20%, or about 30–40 ppb. These reductions are for the surface, where UV reductions are greatest, but clearly the formation of ozone throughout the PBL is limited by the availability of UV radiation, which in turn is controlled by primary and secondary aerosols.

4. Conclusions

The measured and calculated values of J_{NO_2} for Mexico City are in fair agreement if allowance is made for the scattering and absorption of solar radiation by boundary layer aerosols. The effect of such aerosols is substantial, leading to reductions of J_{NO_2} of 10–30%. Such reductions in J_{NO_2} (and in J values for other photochemical reactions) have profound impacts on local air quality. Specifically, according to our calculations, surface O_3 concentrations in Mexico City could be higher by several tens of ppb if the incident solar UV radiation were not attenuated by aerosols.

Moreover, it may be expected that, because of the reduced photoreactivity near emission sources (i.e. in the city), larger amounts of unreacted (or partly reacted) nitrogen oxides and hydrocarbons will be advected to surrounding extra-urban regions, and may ultimately contribute more to global scale tropospheric chemistry.

Our result, that aerosols in Mexico City generally lead to reductions in local ozone production, is consistent with reductions (though much smaller) noted for Los Angeles (Jacobson, 1998), but of sign opposite that for aerosols characteristic of the Eastern US (Dickerson et al., 1997). Such variability is a good illustration of an effect that is potentially large, but considerable care must be taken to predict even its sign.

It must be emphasized again that our conclusions are based on the relatively few available measurements of optical properties of Mexico City aerosols, and on very simple zero-dimensional modeling of the effects of reduced J values. More comprehensive measurements of aerosol optics are needed, preferably complemented by

direct measurement of the radiation field (e.g., spectral actinic flux or irradiance) and appropriate UV radiation modeling. An analysis of the temporal and spatial patterns of high aerosol loading events is needed to assess the prevalence of the conditions discussed here. Finally, detailed three-dimensional modeling is needed to evaluate the changes in air quality (due to aerosol–radiation interactions) on scales covering both the urban area and the surrounding regions to which the partly unreacted air parcels may be transported.

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