Comparison of Photolysis Rates Using Aerosol Conditions in Mexico City

11 August 1999
Stephanie Rivale, University of Colorado
Significant Opportunities in Amtospheric and Related Science (SOARS)
National Center for Atmospheric Research (NCAR), Boulder, Colorado
Universidad Nacional Autonoma Metropolitan (UNAM), Mexico City

Scientific Mentors: Dr. Sasha Madronich and Dr. Telma Castro
Graduate Advisor: Dr. Jana Milford
Writing Mentor: Juli Rew
Community Mentor: Dr. Telma Castro

Abstract

Mexico City is plagued with both high ozone and aerosol concentrations. Ozone absorbs radiation in the ultraviolet (UV) spectrum, and aerosols can both absorb and scatter radiation in the UV spectrum. Urban chemistry models have largely neglected pollution effects on radiation. The Tropospheric Ultraviolet-Visible (TUV, version 4.0a) radiation model was compared to NO_2 photolysis rates measured in Mexico City. Because of a lack of aerosol property data at the measurement sites, aerosol optical properties measured during Project Azteca, a ground based study on the northeast slope of Mexico City, were used in the model simulations. The maximum optical depths measured during Azteca are comparable to those measured at the research sites in the basin. The model compares well to the experimental data with a maximum of 10% deviation. More comprehensive aerosol and $J(NO_2)$ measurements are needed to increase the confidence of this comparison.

1. Introduction

Since 1940, Mexico City's population has risen from 2 million to somewhere near 20 million (PROAIRE, 1996). This rapid population growth and Mexico City's unique geography have led to a severe air pollution problem. Mexico City is located at an altitude of over 2.2 km and latitude of 19°N, a situation that results in a high radiation environment. This radiation environment enhances the formation of photochemical smog, of which ozone (O_3) is the characteristic pollutant. The photolysis of NO_2:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (1)$$

is one of the most important reactions in O_3 formation (Kelly 1995). The rate constant of this reaction, $J(NO_2)$, has been measured in numerous studies and locations. (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; Shetter et al., 1992; Brauers and Hofzumahaus, 1992)

The Mexico City basin is surrounded by mountains, allowing the build-up of high local concentrations of O_3 as well as aerosols (Raga 1999 and Baumgardner 1999). Aerosols reduce visibility and are harmful to the human respiratory system if they are inhaled. Aerosols also absorb and scatter UV radiation, changing the rates of photolysis reactions, and thus influence O_3 concentrations. Dickerson et al. (1997) calculated an increase of 20 to 45 ppb O_3 due to the scattering aerosols of the Eastern U.S. Jacobson (1998) calculated a 5-8% decrease in O_3 mixing ratio in the Los Angeles basin. Wendisch et al. (1996) measured vertical profiles of aerosols and $J(NO_2)$ over Germany, and concluded that enhanced aerosol concentrations in the boundary layer reduced total irradiance and $J(NO_2)$.

In this study, we compare surface $J(NO_2)$ measurements (Castro et al., 1995, 1997) taken within Mexico City, to theoretical values calculated by the Tropospheric Ultraviolet (TUV) model using aerosol properties obtained during Project Azteca (Raga 1998). The aerosol properties used in the model are consistent with those measured over all wavelengths by Vasilyev et al. (1995).

2. Methods

2.1 $J(NO_2)$ Measurements

The theoretical $J(NO_2)$ values were compared to $J(NO_2)$ values observed at two sites in Mexico City, Palacio Minería (PM) [19° 25' 59'' N and 99° 07' 58'' W] and Instituto Mexicano del Petreóleo (IMP) [19° 28' 48'' N and 99° 11' 07'' W]. J(NO2) was measured using a variable length quartz cylindrical flow reactor (Castro et al., 1995, 1997). The PM data were taken from in 1994 from the 9th to the 13th of February, and modeled for 11 February 1994. The PM site is located downtown, surrounded by high buildings and concrete streets. The IMP data were taken in 1994 from the 23rd to the 27th of March, and modeled for 25 March 1994. IMP is located in the northern zone of the city surrounded by buildings, gardens, and asphalt streets. Both campaigns were conducted during high pollution days (500 m to 700 m visibility), but winds reduced pollution in the afternoons at IMP. Optical depths were obtained in the morning during both campaigns. The average morning optical depths in the visible region were 0.56 μm and 0.52 μm at PM and IMP, respectively.

2.2 Modeling Conditions and Assumptions

The modeling study used input parameters typical for Mexico City. United States Standard Atmosphere (USSA) temperature and air density profiles were used (USSA 1976). This resulted in a surface air column of 778 mbar at the elevation of Mexico City (2.2 km). The USSA O_3 profile was used above the boundary layer scaled to 280 Dobson Units (DU), and a homogenous concentration of 150 ppb was assumed within the boundary layer contributing 11.2 DU, resulting in a total ozone column of 291.2 DU. This is consistent with values reported in Juárez et al. 1994. The boundary layer was assumed to be constant at a height of 1.2 km above the surface. This is an average approximation of the daily fluctuation of the boundary layer. Uniform aerosol concentrations were assumed within the boundary layer. All aerosols above the boundary layer were ignored. Both NO_2 and SO_2 absorption were ignored. The model was run for cloudless skies and a ground albedo of 10%.

2.3 Aerosol Data

The optical properties, optical depth, single scattering albedo, and asymmetry factor (τ, ω_o and g, respectively), used in this study were obtained during Project Azteca (Raga 1998). Project Azteca was a ground-based aerosol study on the northeast slope of Ajusco 450 m above Mexico City from November 3-17 in the dry season.

The absorption coefficients, C_{abs}, were obtained using a soot photometer in the green spectrum (550 nm). Absorption coefficients are a function of wavelength, and in this modeling simulation the absorption coefficients were assumed to have an inverse

wavelength dependence. Both the total scattering coefficient, C_{scat}, and backscatter coefficients, b, were measured using a three-wavelength nephelometer. The nephelometer measured at blue (450 nm), green (550 nm), and red (700 nm) wavelengths. The extinction coefficient, C_{ext}, was computed as the sum of C_{abs} and C_{scat}.

$$C_{ext} = C_{scat} + C_{abs} \qquad (2)$$

Optical aerosol properties for 15 November 1997 were used. Variations of maximum and average observed scattering coefficients were used. See Table 1. for test cases.

Optical depth was calculated from the extinction coefficient ignoring the altitude dependence.

$$\tau = \int C_{ext} dz \qquad (3)$$

Single scattering albedo was computed as the ratio of C_{scat} to C_{ext}.

$$\omega_o = \frac{C_{scat}}{C_{ext}} \qquad (4)$$

The asymmetry factor was computed from a backscatter coefficient measured at 180°. This resulted in an asymmetry factor of 0.126. This value is low due to the fact that backscattering was not measured at every angle or integrated over 180°. Modeling test studies show that $J(NO_2)$ is not highly sensitive to the asymmetry parameter (Rivale 1998).

3. Results and Discussion

Figure 1 compares the PM data to theoretical values obtained using the variations of the maximum aerosol optical properties obtained on November 15, 1997 during Project Azteca. The model results for case 1 (maximum scattering and absorption coefficients) agree well with the measurements until noon with a maximum difference of 23% between the PM data and case 1, and a factor of 2.4 maximum difference between the PM data and the no-aerosol case. At PM, the surface results range 30% from a near noon minimum of 0.0067 for case 1 to a near noon maximum of 0.0096 for the no aerosol case. Figure 2 compares the IMP data with maximum aerosol properties. The IMP data compares to the modeling results similar to the PM data. As with the PM results, the data agrees best with the maximum aerosol properties (case 6). At IMP, the surface results range 25% from a near noon minimum of 0.0075 for case 1 to a near noon maximum of 0.01 for the no aerosol case. There is maximum difference of 17% between the IMP data and case 1, and a maximum difference of 98% between the IMP data and the no-aerosol case.

Figure 3 compares the PM data to theoretical values obtained using variations of average aerosol data for the same day of the Azteca project. The average aerosol properties resulted in lower optical depths and higher single scattering albedos (more scattering environment). This resulted in higher surface $J(NO_2)$ values, but did not

enhance surface values beyond the no-aerosol case. There is a factor of 1.2 maximum difference between the PM data and case 6, and a factor of 2.4 maximum difference between the PM data and the no-aerosol case. Figure 4 compares the IMP data with average aerosol properties. During the mid-morning, there is a maximum difference of 57% between the PM data and case 6, and a maximum difference of 98% between the PM data and the no-aerosol case.

4. Conclusions

The model showed good agreement with experimental measurements of $J(NO_2)$. The model shows better agreement when maximum aerosol optical depths were used. Project Azteca was conducted on a slope above the city, while the photolysis measurements were taken downtown. Larger aerosol concentrations would be expected downtown. This might explain the deviation between experimental J-values and the model using average aerosol property data. Simultaneous photolysis rate and aerosol property measurements would increase the confidence of this comparison.

Acknowledgments

I would like to thank Dr. Telma Castro for help and guidance throughout this project, Dr. Graciela Raga and Dr. Darrel Baumgardner for providing aerosol data and hosting my visit to UNAM, and Dr. Sasha Madronich for his patience and guidance throughout my participation in SOARS. I also thank Tom Windham, Beverly Johnson and the rest of the SOARS staff for the extra effort that made my summer in Mexico possible. I would also like to thank Juli Rew and Marie Boyko for great on-line editing. Finally, I cannot express enough my appreciation to Dr. Telma Castro (who also served as my community mentor), José Carlos Jimenez and the rest of the students at UNAM for their kindness throughout my stay in Mexico. I would also like to thank NSF for the funding that made the opportunity possible.

References

Baumgardner, D., G.B. Raga, G. Kok, J. Ogren, I. Rosas, A. Báez and T. Novakov. On the evolution of aerosol properties in Mexico City. *Submitted to J. Geophys. Res.* 1999-08-17

Brauers, T. and A. Hofzumahaus. Latitudinal variation of measured NO2 photlysis frequencies over the Atlantic Ocean betweeen 50°N and 30°S. *J. Atmos. Chem.,* **15**, 269-282, 1992.

Castro, T., L.G. Ruiz-Suárez, C. Gay, M. Helguera and J.C. Ruiz-Suárez. Direct measurements of NO_2 photolysis rates for Mexico City. *Atmosfera*, **8**, 137-142, 1995.

Castro, T., L.G. Ruiz-Suárez, J.C. Ruiz-Suárez, M. Molina and M. Montero. Sensitivity analysis of an UV radiation transfer model and experimental photolysis rates of NO_2 in the atmosphere of Mexico City. *Atmos. Env.* **31**, 609-620, 1997

Dickerson, R.R., D. H. Stedman and C.A. Delany. Direct measurements of ozone and nitrogen dioxide photolysis rates in the troposphere. *J. Geophys. Res.* **87**, 4933-4946, 1982.

Dickerson, R., S. Kondragunta, G. Stenchikov, K. Civerolo, B. Doddridge and B. Holben. The impact of aerosols on solar UV radiation and photochemical smog. *Science,* **278,** 827-830, 1997.

Harvey, R. B., D.H. Stedman and W. Chameides. Determination of the absolute rate of solar photolysis NO_2. *J. Air Pollut. Control Ass.* **27**, 663, 1977.

Jackson, J.O., D. H. Stedman, W. Chameides, R.G. Smith, L.H. Hecker and P.O. Warner. Direct NO2 photolysis rate monitor. *Rev.Sci. Instrum.* **46**, 376-378, 1975.

Jacobson, M. Studying the effects of aerosols on vertical photolysis rate coefficient and temperature profiles over an urban airshed. *J. Geophys. Res.* Vol. **103,** No. D9, 10,593-10,604, 1998.

Juárez A., C. Gay, and J.L. Bravo. Influence of urban ozone in the measurements of the total ozone column in Mexico City. *Atmófera*, **8**, 35-43, 1994.

Kelly, P., R.R. Dickerson, W.T. Luke, and G.L. Kok. Rate of NO_2 photolysis from the surface to 7.6 km altitude in clear-sky and clouds. *Geophys. Res. Letters*, **22**, 2621-2624, 1995.

Madronich, S., D.R. Hastie, B.A. Ridley, and H.I.Shiff. Measurement of the photodissociation coefficient of NO2 in the atmosphere: I. Method and surface measurements. *J. Atmos. Chem.,* **1**, 3-25, 1983.

Parrish, D.D., P.C. Murphy, D.L. Albritton, and F.C. Fehsenfeld. The measurement of the photodissociation rate of NO2 in the atmosphere. *Atmos. Env.*, **17**, 1365-1379, 1983.

PROAIRE. Programa para Mejorar la Calidad del Aire en el Valle de México. *Departamento del Distrito Federal, Gobierno del Estado de México, Secretaría del Medio Ambiente Recursos y Pesca y Secetaría de Saud. México*, 1996.

Raga, G., D. Baumgardner, and J. Ogren. The direct radiative forcing by Mexico City aerosols on downwind climate, 9th Symp. of the IAMAS Commision on Atmospheric Chemistry and 5th Scientific Conf. of the Intl. Global Chemistry Project, August 19-25, 1998, Seattle, WA.

Raga, G.B., D. Baumgardner, G. Kok, I. Rosas. (1999) Some aspects of boundary layer evolution in Mexico City, *Atmospheric Environment, in press*.

Rivale, S. Photolysis rates in the polluted boundary layer of Mexico City. SOARS Report. 1998.

Shetter, E.R., H.A. McDaniel, A.C. Cantrell, S. Madronich, and J.G. Calvert. Actinometer and epply radiometer measurements of the NO2 photolysis rate coefficient during Mlopex. *J.Geophys. Res.,* **97**, 10349-10359, 1992.

Sickles, J.E. II, L.A. Ripperton, W.C. Eaton and R.S. Wriht. Nitrogen dioxide photolytic radiometric and meteorological field data. EPA-600/7-78-053, EPA, Research Triangle Park, North Carolina, 1978.

U.S. Standard Atmosphere, National Oceanic and Atmospheric Administration, National Aeronautics and Space Administration, United States Air Force, Washington, D.C. 1976.

Vasilyev et al. Spectral optical properties of the polluted atmosphere in Mexico City. *J. of Geophysical Research.* **100**, pp. 26,027-26,044, 1995.

Wendisch, M., S. Mertes, A. Ruggaber and T. Nakajima. Vertical Profiles of Aerosol and Radiation and the Influence of a Temperature Inversion: Measuremets and Radiative Transfer Calculations. *J. of Appl. Meteorol.*, **35**, 1703-1715, 1996.

Zafonte, L., P.L. Rieger, and J.R. Holmes. Nitrogen dioxide photolysis in the Los Angeles atmosphere. *Envir. Sci. Technol.* **11**, 483-487, 1977.

Figure Captions

Table 1. is a summary of all aerosol property conditions run in the model in addition to the no-aerosol cases. The scattering, absorption, and extinction coefficients are observations or some variation of the observations made on 15 November 1997 during Project Azteca. The resulting optical depths, τ, and single-scattering albedos, ω, are also given.

Figure 1. compares TUV results surface $J(NO_2)$ using maximum aerosol data to measurements made at Palacio Minería. The case study conditions are given in Table 1.

Figure 2. compares TUV results surface $J(NO_2)$ using maximum aerosol data to measurements made at IMP.

Figure 3. compares TUV results surface $J(NO_2)$ using average aerosol data to measurements made at Palacio Minería.

Figure 4. compares TUV results surface $J(NO_2)$ using average aerosol data to measurements made at IMP.

Conditions for case studies

	Case condition	Cscat	Cabs	Cext	τ	ω
case 1	MAX values	3.98E-04	5.89E-05	4.57E-04	0.548	0.871
case 2	50% Cabs(max)	3.98E-04	2.95E-05	4.27E-04	0.512	0.932
case 3	10% Cabs(max)	3.98E-04	5.89E-06	4.04E-04	0.485	0.985
case 4	50% Cscat(max)	1.99E-04	5.89E-05	2.58E-04	0.310	0.771
case 5	10% Cscat(max)	3.98E-05	5.89E-05	9.87E-05	0.118	0.403
case 6	AVE values	1.42E-04	2.23E-05	1.64E-04	0.197	0.866
case 7	50% Cabs(ave)	1.42E-04	1.12E-05	1.53E-04	0.184	0.928
case 8	10% Cabs(ave)	1.42E-04	2.23E-06	1.44E-04	0.173	0.986
case 9	50% Cscat(ave)	7.10E-05	2.23E-05	9.33E-05	0.112	0.761
case 10	10% Cscat(ave)	1.42E-05	2.23E-05	3.65E-05	0.044	0.389

Table 1.

Conditions for case studies

	Case condition	Cscat	Cabs	Cext	τ	ω
case 1	MAX values	3.98E-04	5.89E-05	4.57E-04	0.548	0.871
case 2	50% Cabs(max)	3.98E-04	2.95E-05	4.27E-04	0.512	0.932
case 3	10% Cabs(max)	3.98E-04	5.89E-06	4.04E-04	0.485	0.985
case 4	50% Cscat(max)	1.99E-04	5.89E-05	2.58E-04	0.310	0.771
case 5	10% Cscat(max)	3.98E-05	5.89E-05	9.87E-05	0.118	0.403
case 6	AVE values	1.42E-04	2.23E-05	1.64E-04	0.197	0.866
case 7	50% Cabs(ave)	1.42E-04	1.12E-05	1.53E-04	0.184	0.928
case 8	10% Cabs(ave)	1.42E-04	2.23E-06	1.44E-04	0.173	0.986
case 9	50% Cscat(ave)	7.10E-05	2.23E-05	9.33E-05	0.112	0.761
case 10	10% Cscat(ave)	1.42E-05	2.23E-05	3.65E-05	0.044	0.389

Table 1.

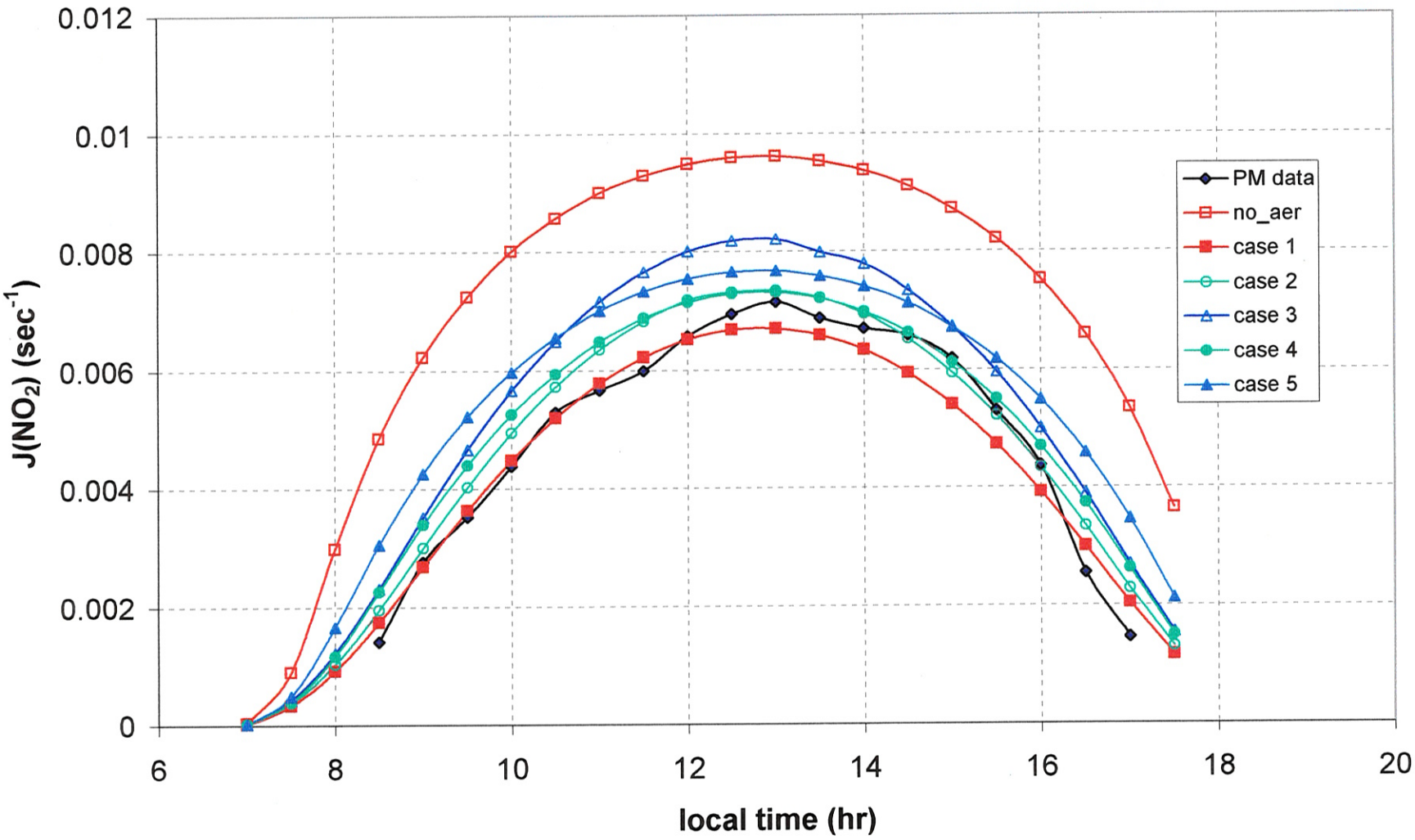
J(NO2) for MAX aerosol conditions at Palacio Mineria on 11 Feb 94
J(NO2) (sec-1)
0.012
0.01
0.008
0.006
0.004
0.002
0
6
8
10
12
14
16
18
20
local time (hr)
PM data
no_aer
case 1
case 2
case 3
case 4
case 5

Figure 1.

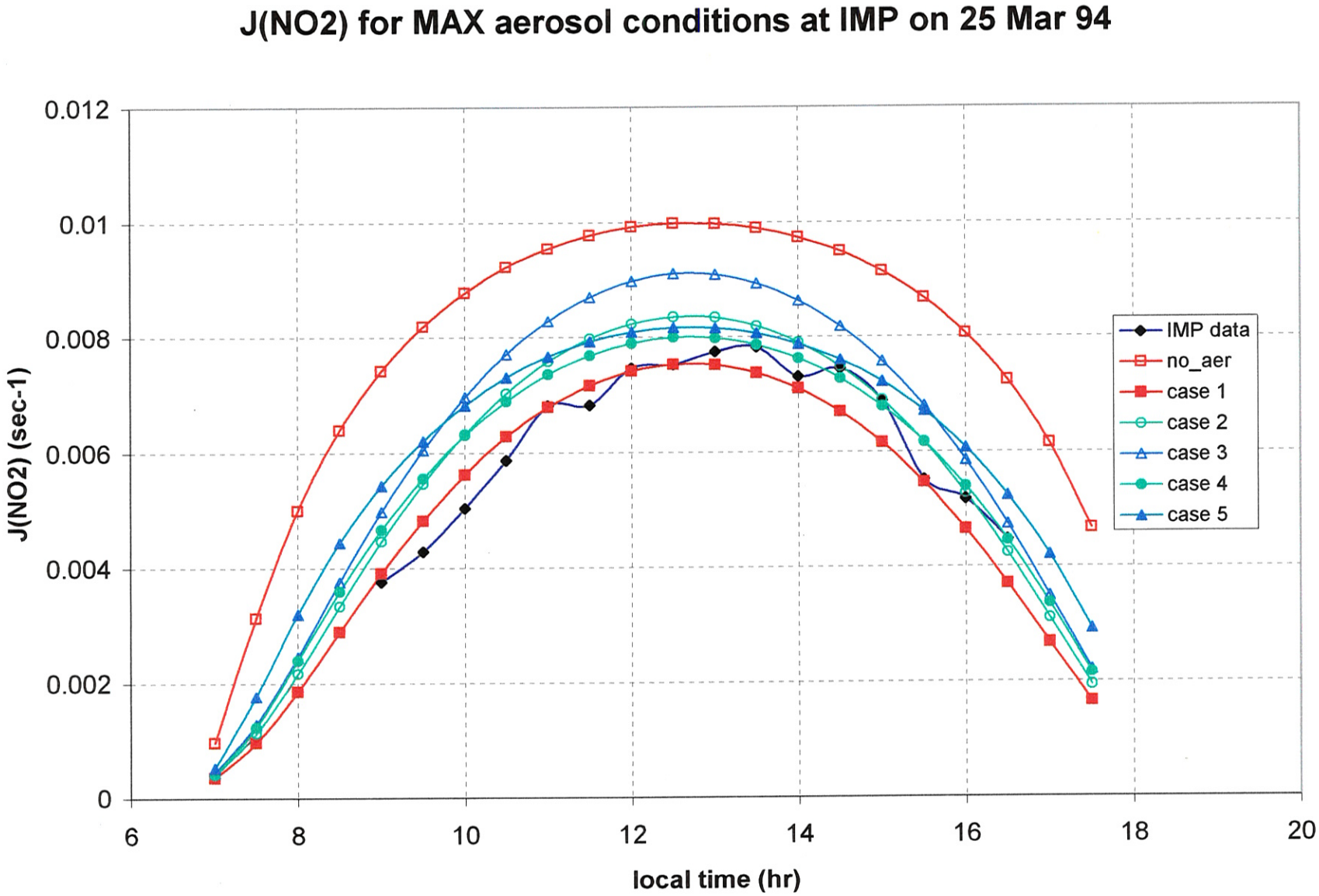
J(NO2) for MAX aerosol conditions at IMP on 25 Mar 94
J(NO2) (sec-1)
0.012
0.01
0.008
0.006
0.004
0.002
0
6
8
10
12
14
16
18
20
local time (hr)
IMP data
no_aer
case 1
case 2
case 3
case 4
case 5

Figure 2.

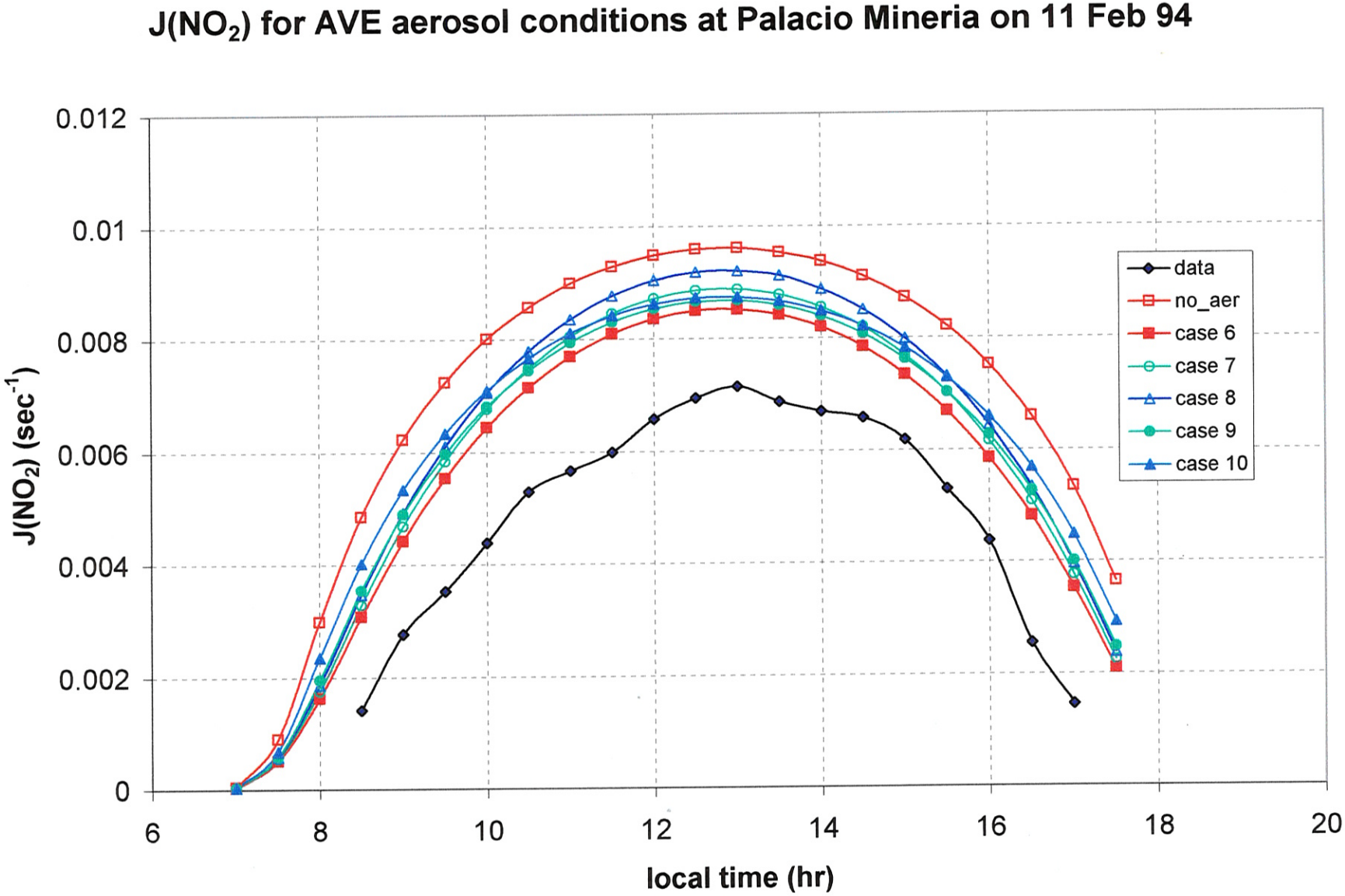
J(NO2) for AVE aerosol conditions at Palacio Mineria on 11 Feb 94
J(NO2) (sec-1)
0.012
0.01
0.008
0.006
0.004
0.002
0
6
8
10
12
14
16
18
20
local time (hr)
data
no_aer
case 6
case 7
case 8
case 9
case 10

Figure 3.

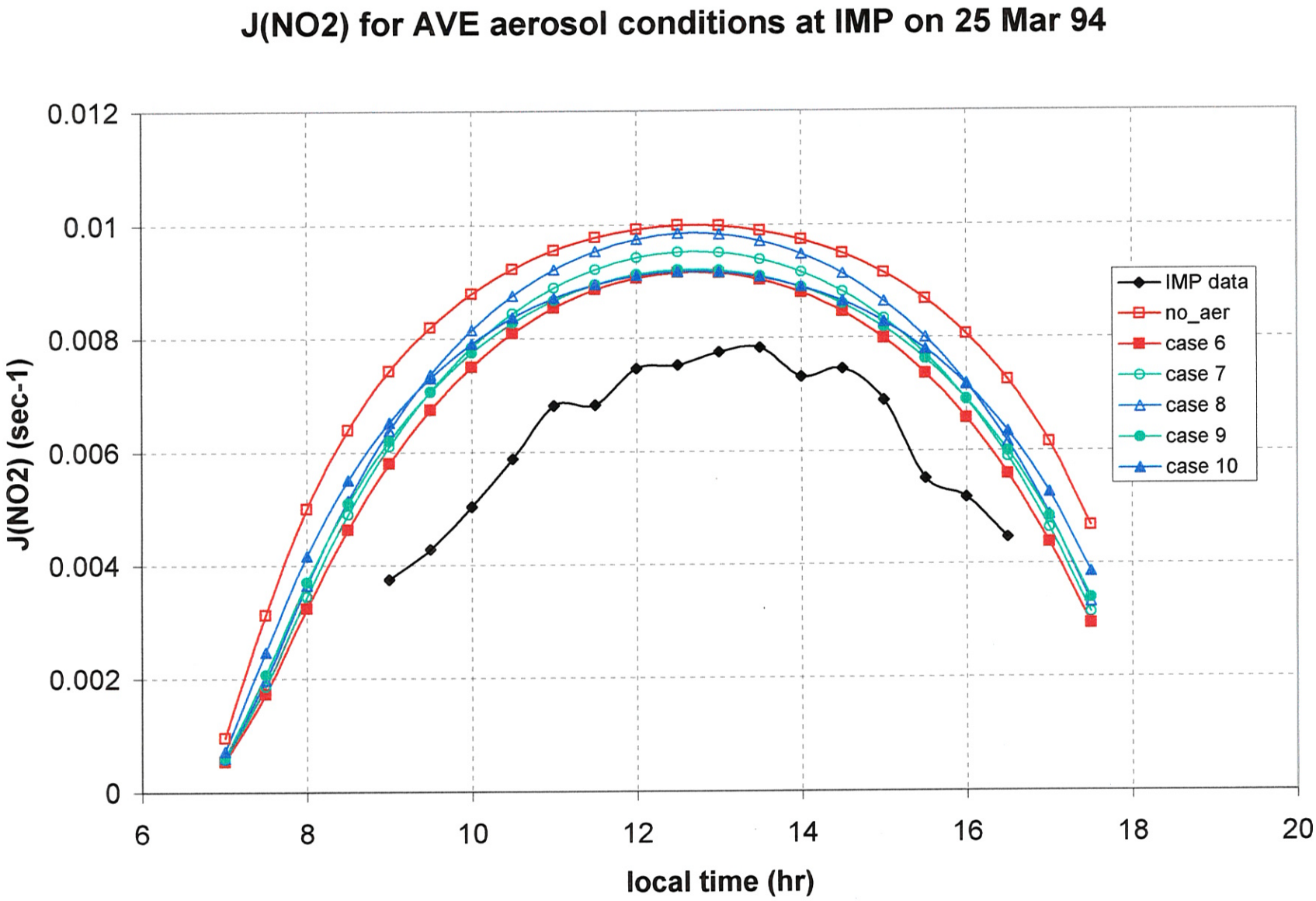
J(NO2) for AVE aerosol conditions at IMP on 25 Mar 94
J(NO2) (sec-1)
0.012
0.01
0.008
0.006
0.004
0.002
0
6
8
10
12
14
16
18
20
local time (hr)
IMP data
no_aer
case 6
case 7
case 8
case 9
case 10

Figure 4.