

Photolysis rate coefficient in Buenos Aires city

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Abstract

The main purpose of this study was to estimate hourly mean surface photolysis rate coefficients of nitrogen dioxide for the atmosphere in Buenos Aires city during cloud free conditions. A nine years period of Aerosol Optical Depth (AOD) was used as input data to run the TUV (Tropospheric Ultraviolet Visible) model. Results showed that monthly maxima of surface photolysis rate doubles from winter to summer. The study of a three month biomass burning period occurred at 70 km north from Buenos Aires City also showed an impact in the variable studied.

1. Introduction

Buenos Aires's urban and metropolitan area cover a surface of around 4082 km² with a population of 15 millions of inhabitants. According to Pineda Rojas and Venegas (2009) Buenos Aires City has an estimated annual emission of NO_x of 54000 ton yr⁻¹, where 46.4% is produced by mobile sources and 48.7% is produced by power plants.

In presence of sunlight the NO₂ is transformed to NO at a rate measured by the photolysis rate coefficient (j). The aim of this work is to study the variability of the surface photolysis rate coefficient for NO₂ and to describe the impact of the effect of aerosol particles on the calculation of this coefficient. A particular case of smoke cloud due to biomass burning in the delta of Paraná River, located *circa* 70 km to the NE of Buenos Aires City is analyzed.

2. Methodology

The actinic flux is determined by the solar radiation entering the atmosphere and it is modified by the presence of atmospheric gases, particles and reflections from the ground. Often, an ultraviolet radiative

transfer model is used to estimate the radiative flux throughout the atmosphere and determine the value of j . The TUV model (V.4.2) (<http://www.acd.ucar.edu/TUV>) (Madronich, 1987) was run to calculate daily spectral actinic flux and the photolysis rate coefficient values. As aerosols can absorb or scatter radiation depending on their size, the TUV model was supplied with information about particle size distribution. Aerosol optical properties (aerosol optical depth AOD, single-scattering albedo SSA and Angstrom alpha parameter a) were obtained from a nine year record (Oct/99 to Sep/08) of optical properties observed by de AERONET sun photometer located in Buenos Aires (34°34'S, 58°30'W) (Holben et al., 1998). Cloud-free days and a surface albedo of 10% were considered. The vertical profiles for air density and temperature were taken from the USSA profile for 1976 (USSA, 1976). Meteorological surface parameters were obtained from a meteorological station of the National Weather Service (Aeroparque Aero, 34°56'S, 58°42'W).

3. Results and discussion

The surface photolysis rate maxima occurred at noon (13hs) in every month (Table I). Also, the maxima value of j in January is twice the value registered in June. Standard deviation of these values varied both with month and hour. Cold months (April, May, June, July, August, September) showed the maximum hourly standard deviation at noon, while warm months (October, November, December, January, February, March) showed two maxima: in the early morning and in the late afternoon (Table 1). From February to April of 2008, several successive grassland fires took place in the north of Buenos Aires and in the south of Entre Ríos provinces and the smoke plume from these fires reached the city. The observed values of aerosol optical thickness (AOT) in 500nm during April of 2008 showed high values. Aerosol size distributions for these days had the typical pattern of burning ash transport, with maximum values in the fine mode. During March and April 2008 the increase of aerosol mass in the atmosphere of Buenos Aires city produced a diminution of the monthly mean photolysis rate coefficient value of around 2 to 6% in March and 1.5 to 3% in April.

4. Conclusions

Monthly mean values of j at noon in Buenos Aires city varied between 0.34 and 0.66 min^{-1} , according to the month of the year. The increment of the aerosol composition in the lower atmosphere diminishes the values of j .

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Table 1. Monthly mean values and standard deviation of surface photolysis rate coefficient from 6 to 20 hs (local time of Buenos Aires, UTC-3). Unit: min⁻¹.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|----|---------------|---------------|---------------|---------------|---------------|---------------|
| 6 | 0.006 ± 0.005 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 |
| 7 | 0.087 ± 0.017 | 0.036 ± 0.011 | 0.010 ± 0.006 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 |
| 8 | 0.239 ± 0.023 | 0.167 ± 0.022 | 0.108 ± 0.018 | 0.053 ± 0.013 | 0.019 ± 0.007 | 0.005 ± 0.002 |
| 9 | 0.394 ± 0.021 | 0.330 ± 0.023 | 0.265 ± 0.025 | 0.181 ± 0.025 | 0.110 ± 0.018 | 0.071 ± 0.007 |
| 10 | 0.515 ± 0.017 | 0.464 ± 0.020 | 0.403 ± 0.025 | 0.314 ± 0.030 | 0.228 ± 0.024 | 0.176 ± 0.012 |
| 11 | 0.597 ± 0.012 | 0.556 ± 0.016 | 0.499 ± 0.024 | 0.410 ± 0.031 | 0.321 ± 0.025 | 0.269 ± 0.015 |
| 12 | 0.644 ± 0.009 | 0.610 ± 0.014 | 0.555 ± 0.023 | 0.465 ± 0.031 | 0.375 ± 0.024 | 0.325 ± 0.015 |
| 13 | 0.660 ± 0.008 | 0.629 ± 0.013 | 0.573 ± 0.024 | 0.480 ± 0.032 | 0.389 ± 0.024 | 0.341 ± 0.015 |
| 14 | 0.647 ± 0.008 | 0.618 ± 0.014 | 0.557 ± 0.026 | 0.457 ± 0.034 | 0.363 ± 0.024 | 0.318 ± 0.014 |
| 15 | 0.604 ± 0.010 | 0.573 ± 0.016 | 0.505 ± 0.029 | 0.394 ± 0.036 | 0.296 ± 0.024 | 0.255 ± 0.013 |
| 16 | 0.525 ± 0.013 | 0.491 ± 0.020 | 0.412 ± 0.033 | 0.289 ± 0.037 | 0.192 ± 0.022 | 0.158 ± 0.009 |
| 17 | 0.409 ± 0.015 | 0.367 ± 0.024 | 0.277 ± 0.036 | 0.153 ± 0.033 | 0.075 ± 0.014 | 0.055 ± 0.003 |
| 18 | 0.256 ± 0.014 | 0.208 ± 0.025 | 0.120 ± 0.031 | 0.035 ± 0.016 | 0.005 ± 0.003 | 0.001 ± 0.000 |
| 19 | 0.100 ± 0.007 | 0.061 ± 0.015 | 0.015 ± 0.011 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 |
| 20 | 0.009 ± 0.002 | 0.001 ± 0.001 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 |
| | 7 | 8 | 9 | 10 | 11 | 12 |
| 6 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.002 ± 0.003 | 0.019 ± 0.005 | 0.024 ± 0.003 |
| 7 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.012 ± 0.010 | 0.070 ± 0.021 | 0.128 ± 0.012 | 0.134 ± 0.010 |
| 8 | 0.006 ± 0.003 | 0.031 ± 0.014 | 0.105 ± 0.030 | 0.218 ± 0.033 | 0.291 ± 0.014 | 0.294 ± 0.014 |
| 9 | 0.076 ± 0.010 | 0.136 ± 0.031 | 0.250 ± 0.040 | 0.370 ± 0.032 | 0.435 ± 0.012 | 0.439 ± 0.013 |
| 10 | 0.186 ± 0.017 | 0.260 ± 0.040 | 0.378 ± 0.040 | 0.486 ± 0.028 | 0.541 ± 0.010 | 0.547 ± 0.009 |
| 11 | 0.283 ± 0.020 | 0.357 ± 0.041 | 0.467 ± 0.036 | 0.561 ± 0.024 | 0.608 ± 0.008 | 0.618 ± 0.006 |
| 12 | 0.342 ± 0.020 | 0.415 ± 0.040 | 0.516 ± 0.032 | 0.599 ± 0.020 | 0.642 ± 0.008 | 0.656 ± 0.004 |
| 13 | 0.362 ± 0.020 | 0.433 ± 0.038 | 0.527 ± 0.030 | 0.604 ± 0.019 | 0.646 ± 0.009 | 0.665 ± 0.004 |
| 14 | 0.342 ± 0.021 | 0.412 ± 0.038 | 0.502 ± 0.030 | 0.577 ± 0.020 | 0.622 ± 0.010 | 0.647 ± 0.006 |
| 15 | 0.282 ± 0.021 | 0.352 ± 0.038 | 0.439 ± 0.031 | 0.515 ± 0.021 | 0.565 ± 0.013 | 0.598 ± 0.009 |
| 16 | 0.186 ± 0.019 | 0.253 ± 0.035 | 0.335 ± 0.030 | 0.413 ± 0.024 | 0.472 ± 0.016 | 0.514 ± 0.012 |
| 17 | 0.076 ± 0.012 | 0.127 ± 0.024 | 0.195 ± 0.025 | 0.271 ± 0.025 | 0.339 ± 0.019 | 0.392 ± 0.016 |
| 18 | 0.006 ± 0.003 | 0.025 ± 0.008 | 0.060 ± 0.013 | 0.112 ± 0.019 | 0.177 ± 0.020 | 0.238 ± 0.016 |
| 19 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.001 ± 0.001 | 0.012 ± 0.006 | 0.043 ± 0.012 | 0.086 ± 0.011 |
| 20 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.006 ± 0.003 |