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Chapter 14

PHOTOLYSIS RATES FOR CMAQ

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ABSTRACT

The method for calculating photodissociation reaction rates (photolysis rates) for CMAQ is described in this chapter. The description includes the photolysis rate preprocessor (JPROC) and CMAQ subroutine PHOT. JPROC produces a clear-sky photolysis rate look-up table. The look-up table consists of photolysis rates at various altitudes, latitudes, and hour angles. The look-up table is recalculated for each simulation day and is dependent upon the chemical mechanism. Within CMAQ, photolysis rates for individual grid cells are interpolated from the look-up table in subroutine PHOT. PHOT also uses a parameterization to correct the clear-sky photolysis rates for cloud cover.

14.0   PHOTOLYSIS RATES FOR CMAQ

14.1   Background

Many chemical reactions in the atmosphere are initiated by the photodissociation of numerous trace gases. These photodissociative reactions are responsible for most of the smog buildup detrimental to humans, animals, plant life and materials. In order to accurately model and predict the effects of air pollution, good photodissociation reaction rate (or photolysis rate) estimates must be made.

Photodissociation is the conversion of solar radiation into chemical energy to activate and dissociate chemical species. Examples of species that photodissociate include many important trace constituents of the troposphere such as NO_2, O_3, HCHO, CH_3CHO, HONO, the NO_3 radical, and H_2O_2 (also see Table 14.1). The simulation accuracy of the entire chemical system is highly dependent upon the accuracy of photolysis rates, which are the primary sources of radicals in the troposphere. Photolysis rates (min^{-1}), sometimes called J-values, are computed for photodissociation reaction (*i*) by

$$J_i = \int_{\lambda_1}^{\lambda_2} F(\lambda)\,\sigma_i(\lambda)\,\phi_i(\lambda)\,d\lambda \qquad (14\text{-}1)$$

where, $F(\lambda)$ is the actinic flux (photons cm^{-2} min^{-1} nm^{-1}), $\sigma_i(\lambda)$ the absorption cross section for the molecule undergoing photodissociation (cm^2 $molecule^{-1}$), $\phi_i(\lambda)$ the quantum yield of the photolysis reaction (molecules $photon^{-1}$), and λ the wavelength (nm). Absorption cross sections and quantum yields are functions of wavelength, and may also be functions of temperature and pressure; they are unique to species and reactions. Laboratory experiments measuring the absorption cross sections and quantum yields. have been conducted for many species that photodissociate in the troposphere. Actinic flux is a radiometric quantity that measures the spectral radiance integrated over all solid angles per unit area. The spherical receiving surface distinguishes the actinic flux from the more commonly measured irradiance, which is the radiance falling on a horizontal surface. Thus, the actinic flux can be called spherical spectral irradiance. The actinic flux changes with time of day, longitude, latitude, altitude, and season, and is governed by the astronomical and geometrical relationships between the sun and the earth. It is greatly affected by the earth's surface albedo as well as by various atmospheric scatterers and absorbers. Hence, correct model calculation of the temporal and spatial variation of the actinic flux is critical to obtaining accurate photolysis rates for regional and mesoscale episodic photochemical modeling.

The current approach taken for setting photolysis rates in the Models-3/CMAQ framework follows that of the Regional Acid Deposition Model (RADM) (Chang et al., 1987). It includes two stages of processing: (1) a table of clear-sky photolysis rates is calculated for specified heights, latitudes, and hours from local noon; and (2) photolysis rates are interpolated from the

table within the CMAQ Chemistry Transport Model (CCTM) based on grid cell location and the model time, and are corrected for cloud cover. This approach is computationally efficient and has been shown by Madronich (1987) to give clear-sky photolysis rates within the uncertainty of the surface-based measurements.

14.2   Preprocessor JPROC: Calculate Clear-sky Photolysis Rate Table

Preprocessor JPROC calculates a table of clear-sky photolysis rates (or J-values) for a specific date. The table is dimensioned by latitude, altitude, and time. Currently, J-values are calculated for 6 latitudinal bands ($10°N$, $20°N$, $30°N$, $40°N$, $50°N$, and $60°N$), 7 altitudes (0 km, 1 km, 2 km, 3 km, 4 km, 5 km, and 10 km), and ± 9 hours from local noon (0 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, and 8 h). There is a separate table for each photolysis reaction. In order to compute the photolysis rates using Equation 14.1, the actinic flux, absorption cross section, and quantum yield must be determined as a function of wavelength.

The delta-Eddington two-stream radiative transfer model (Joseph et al., 1976; Toon et al., 1989) is used for computing the actinic flux. The two-stream approximations are limited in application to cases where the scatter is not highly anisotropic. In computing the actinic flux, a description of the extraterrestrial radiation, aerosol, ozone absorption, oxygen absorption in the Schumann-Runge Bands, Rayleigh scattering (WMO, 1985) and surface albedo are provided to the radiation model.

Extraterrestrial radiation is specified by a user input file. JPROC is flexible enough to use any extraterrestrial radiation data distribution specified by the user. However, the wavelength distribution of the extraterrestrial radiation data is important because this is also the distribution that will be used in the integration of Equation 14.1. Therefore, the user should choose a wavelength distribution that resolves the features that are important to the photolysis reactions of interest. A modified WMO extraterrestrial radiation data distribution (Chang, et al., 1990) is used as input to JPROC, which has a variable wavelength resolution ranging from 1 nm to 10 nm.

The O_2 and O_3 absorption cross section data are specified by user input files, but it is recommended that the most recent NASA data (DeMore et al., 1994) be used in the calculations. Vertical ozone profiles are set by interpolating seasonal profiles from a user input file, and if total ozone column data are available (such as data measured by the Total Ozone Mapping Spectrometer (TOMS) instrument aboard the sun-synchronous polar orbiting Nimbus satellite), then the interpolated vertical profiles are uniformly rescaled so that the profiles integrated total ozone column value matches the measured total ozone column data. TOMS data are archived and available at the National Satellite Service Data Center (NSSDC) in the form of digital daily maps with a resolution of 1 degree latitude by 1.25 degrees longitude. The TOMS data are averaged over each latitudinal band in JPROC. Nimbus-7 TOMS data are available for years 1978 through 1993; Meteor-3 TOMS data are available for 1991-1994; ADEOS TOMS data are available for 1996-1997; and Earth Probe TOMS data are available for 1996-1998. These data can be downloaded from site *http://jwocky.gsfc.nasa.gov*.

The albedo data given by Demerjian et al. (1980), which have been used extensively in radiative transfer models, are given as a function of wavelength and are used in the current version of JPROC. Currently, a single vertical profile of aerosol attenuation coefficients (Elterman, 1968) is used in JPROC. An effort is underway to incorporate predicted aerosol parameters from CMAQ into the photolysis rate calculations.

Several factors in JPROC depend on the vertical profiles of temperature and pressure, including ozone absorption and the absorption cross sections and quantum yields for individual photolysis reactions. JPROC interpolates seasonal profiles of temperature and pressure. We use the same vertical profile data that are used in the RADM (Chang et al., 1987).

Absorption cross section and quantum yield data are specified by the user through input files. Input files depend on the chemical mechanism selected by the user in the Program Control Processor (see Chapter 15). The original sets of cross section/quantum yield data published with the Carbon Bond Mechanism IV (Gery et al., 1989), the Regional Acid Deposition Model mechanism version 2 (RADM2) (Stockwell et al., 1990), and the SAPRC mechanism (Carter, 1990) are available for use in JPROC. However, users can deviate from these standard sets to test other data, including the revisions suggested by NASA (DeMore et al., 1994). Table 14.1 lists the photolysis reactions for the RADM2 mechanism.

14.3 Subroutine PHOT: Table Interpolation and Cloud Attenuation

Subroutine PHOT within the CCTM has two basic functions, including interpolation of the clear-sky photolysis rate table and application of a cloud correction factor to the clear-sky values. The interpolation step is fairly simple. For each grid cell, the latitude, height, and time from local noon are determined and used to interpolate clear-sky values from the photolysis rate table. The cloud correction step is a little more complicated. The method used to correct for cloud cover in PHOT was taken from RADM (Chang et al., 1987; Madronich, 1987). The correction of clear-sky values depends on whether the location is below, above, or within the cloud. The below cloud photolysis rate (J_{below}) is calculated as:

$$J_{below} = J_{clear}[1 + cfrac\,(1.6t_r\cos(\theta) - 1)] \qquad (14\text{-}2)$$

where cfrac is the cloud coverage fraction (cloud fraction is interpolated from hourly data for each grid cell), θ is the zenith angle, and t_r is the cloud transmissivity. Below cloud photolysis rates will be lower than the clear-sky values due to the reduced transmission of radiation through the cloud. The cloud transmissivity is calculated by:

$$t_r = \frac{5 - e^{-\tau_{cld}}}{4 + 3\tau_{cld}(1 - f)} \qquad (14\text{-}3)$$

where f is the scattering phase function asymmetry factor (assumed to be 0.86) and τ_{cld} is the cloud optical depth. We have replaced the cloud optical depth equation in RADM with one taken from Stephens (1978). The original RADM equation for τ_{cld} required an estimate of the cloud droplet radius, which is not readily available. In RADM, the cloud droplet radius was assumed to be 10µm. The empirical formula for τ_{cld} from Stephens (1978):

$$\log(\tau_{cld}) = 0.2633 + 1.7095 \ln[\log(W)] \tag{14-4}$$

is only a function of liquid water path (W), where W=LΔz (g/m^2), L is the liquid water content (g/m^3), and Δz is the cloud thickness. The above cloud top factor (F_a) is calculated as:

$$J_{above} = J_{clear}[1 + cfrac(\alpha_i(1-t_r)\cos(\theta)] \tag{14-5}$$

This equation allows for enhancement of photolysis rates above the cloud due to the reflected radiation from the cloud. It also includes a reaction dependent coefficient (α_i) which allows for further above cloud enhancements (Chang et al., 1987). Within the cloud, the cloud correction factor is a simple linear interpolation of the below cloud factor at cloud base to the above cloud factor at cloud top. Once computed, the below, above, and within cloud factor are used to scale the clear sky photolysis rates to account for the presence of clouds. In the current implementation, all cloud types (including clouds composed of ice crystals) are treated the same using the above outlined procedure.

14.4 Summary

The current method for calculating photolysis rates in CMAQ, which was derived from RADM, uses a preprocessor to compute a look-up table and a subroutine within the chemistry transport model to interpolate J-values and apply a cloud-cover correction. Other approaches and enhancements are being developed and tested. One enhancement to be added in the future is the dynamic link between aerosol predictions and photolysis rate calculations. Another is to replace the two-stream model with a more comprehensive multi-stream radiative transfer model (Stamnes et al., 1988). Other absorption cross section and quantum yield data will be added or updated using the DeMore et al. (1997) revisions.

14.5 References

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Table 14-1. RADM2 Photolysis Reactions (Adapted from Stockwell et al., 1990.)

Reaction	Description
$O_3 + h\nu \rightarrow O_2 + O^1D$	Ozone Photolysis to O^1D
$O_3 + h\nu \rightarrow O_2 + O^3P$	Ozone Photolysis to O^3P
$NO_2 + h\nu \rightarrow NO + O^3P$	Nitrogen Dioxide Photolysis
$NO_3 + h\nu \rightarrow NO + O_2$	Nitrate Photolysis to NO
$NO_3 + h\nu \rightarrow NO_2 + O^3P$	Nitrate Photolysis to NO_2
$HONO + h\nu \rightarrow OH + NO$	Nitrous Acid Photolysis
$HNO_3 + h\nu \rightarrow OH + NO_2$	Nitric Acid Photolysis
$HNO_4 + h\nu \rightarrow HO_2 + NO_2$	Pernitric Acid Photolysis
$H_2O_2 + h\nu \rightarrow OH + OH$	Hydrogen Peroxide Photolysis
$HCHO + h\nu \rightarrow H + HCO$	Formaldehyde Photolysis to Radicals
$HCHO + h\nu \rightarrow H_2 + CO$	Formaldehyde Photolysis to Molecular Hydrogen
$CH_3CHO + h\nu\ (+2O_2) \rightarrow CH_3OO + HO_2 + CO$	Acetaldehyde Photolysis
$CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$	Acetone Photolysis
$CH_3COC_2H_5 + h\nu \rightarrow ACO_3 + ETH$	Methyl Ethyl Ketone Photolysis
$HCOCHO + h\nu \rightarrow HCHO + CO$	Glyoxal Photolysis to Formaldehyde
$HCOCHO + h\nu \rightarrow 2CO + H_2$	Glyoxal Photolysis to Molecular Hydrogen
$CH_3COCHO + h\nu \rightarrow ACO_3 + HO_2 + CO$	Methyl Glyoxal Photolysis
$HCOCH=CHCHO + h\nu \rightarrow 0.98HO_2 + TCO_3 + 0.02ACO_3$	Unsaturated Dicarbonyl Photolysis
$CH_3OOH + h\nu \rightarrow CH_2O + OH + HO_2$	Methyl Hydrogen Peroxide Photolysis
$CH_3ONO_2 + h\nu \rightarrow 0.2ALD + 0.8KET + HO_2 + NO_2$	Organic Nitrate Photolysis
$C_3H_4O + h\nu \rightarrow products$	Acrolein Photolysis