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FINAL REPORT

**ULTRAVIOLET RADIATION CLIMATOLOGY OF
THE EARTH'S SURFACE AND LOWER ATMOSPHERE**

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TABLE OF CONTENTS

ABSTRACT

1 INTRODUCTION

2 ACCOMPLISHMENTS

2.1 Re-evaluation of Spectroscopic Data for UV Modeling

2.2 Radiative Transfer Studies

2.3 Development of the Tropospheric Ultraviolet-Visible (TUV) Model

2.4 UV Climatology

2.5 TUV Model Validation

3 REFERENCES

4 TABLE

5 FIGURES

6 APPENDIX: Publications

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ABSTRACT

Ultraviolet (UV) radiation is the driving force of tropospheric chemistry and is furthermore detrimental to most living tissues. A three year modeling program was carried out to characterize the UV radiation in the lower atmosphere, with the objective of developing a climatology of UV biologically active radiation, and of photo-dissociation reaction rates that are key to tropospheric chemistry. A comprehensive model, the Tropospheric Ultraviolet-Visible (TUV) model, was developed and made available to the scientific community. The model incorporates updated spectroscopic data, recent advances in radiative transfer theory, and allows flexible customization for the needs of different users.

The TUV model has been used in conjunction with satellite-derived measurements of total atmospheric ozone and cloud amount, to develop a global climatology of UV radiation reaching the surface of the Earth. Initial validation studies are highly encouraging, showing that model predictions agree with direct measurements to ca. 5-10% at times when environmental conditions are well known, and to 10-30% for monthly averages when local environmental conditions can only be estimated remotely from satellite-based measurements. Additional validation studies are continuing.

1 INTRODUCTION

Ultraviolet (UV) radiation is a key environmental variable in the Earth's lower atmosphere and surface. Exposure to UV radiation is generally recognized as damaging to living tissues and therefore to individual organisms. Known effects include the induction of skin cancers, ocular damage, and suppression of the immune system in humans and animals, and changes in growth and morphology of both terrestrial and aquatic plants (UNEP, 1994). Indeed, our awareness of the potential dangers of increased UV radiation exposure has been a major reason for concerns about the ongoing depletion of stratospheric ozone (WMO, 1994).

A second role of UV radiation, which perhaps is less recognized by the general public but still of great importance, is that UV radiation is the fundamental driving force of atmospheric chemistry. The reason is that UV photons are sufficiently energetic to break the bonds of many relatively stable molecules, e.g., for a generic molecule AB,

and the resulting fragments (A and B above) are usually highly reactive (radicals). The reactions of these photo-fragments control the atmospheric processing and lifetimes of many compounds such as ozone, nitrogen oxides, sulfur oxides, carbon monoxide, methane, non-methane hydrocarbons, chlorofluorocarbons (CFCs) and their promulgated substitutes (HFCs and HCFCs), among others. The rates of such photo-dissociation (or photolysis) reactions are given by the coefficient J, which is directly proportional to the available UV radiation (the actinic flux), and depends on the spectroscopic properties of the dissociating molecules. Quantitative understanding of these so-called J-values is required for modeling the tropospheric chemistry associated with major environmental issues, including urban and regional photo-chemical smog formation, acidification of precipitation, the build-up of greenhouse gases, and the growth and decline of ozone-destroying substances.

Despite this well-recognized importance of environmental UV radiation, the state of knowledge of the geographical and temporal distributions of UV radiation (and of J-values) has been relatively poor. The work described here aims to provide a better understanding of the factors that control UV radiation, and to develop a global UV climatology based on numerical modeling and utilization of satellite-derived observations. This work is particularly timely because of the recent increases in the quantity and quality of ground-based UV measurements. While such point-measurements cannot possibly provide global coverage, they are of great utility for validating our modeling approach.

2 ACCOMPLISHMENTS

2.1 Re-evaluation of Spectroscopic Data for UV Modeling

We have updated the absorption cross sections and quantum yields used to calculate rate coefficients of key atmospheric photodissociation reactions. The updates were based on recent literature and, in some cases, on re-evaluations of older data. We have incorporated the new data in the Tropospheric Ultraviolet Visible (TUV) model (see Section 2.3), together with in-line documentation of the source of the data. Table 1 summarizes the reactions currently included in the TUV model. The updated spectroscopic data allow a more reliable calculation of atmospheric photodissociation reaction rates for these molecules.

We have also carried out comparisons of the effects of using different extraterrestrial irradiance measurements on the calculation of surface UV radiation. Differences in the range of 2-10% were found among commonly used data sets, and a more comprehensive evaluation is underway in association with the June 1998 Boulder intercomparison of UV measurements and models (see Section 2.5). Preliminary results from New Zealand suggest that better agreement is attained using the recent Atlas-3

spectrum (unpublished, but available publicly on the web at <ftp://susim.nrl.navy.mil/pub/atlas3>), than the SUSIM spectrum (van Hoosier et al., 1987) used by us and others in earlier studies.

2.2 Radiative Transfer Studies

Theoretical studies were carried out to improve the accuracy of radiative transfer methods for the calculation of UV radiation levels at the surface and in the lower atmosphere.

In one study, we showed that the delta-scaling method, commonly used to simplify the calculation of scattering by aerosols and clouds, must be used with some caution. In particular, more accurate results for the actinic flux are obtained if the delta-scaled direct solar beam is not un-scaled at the end of the calculation (as is often done). A paper describing this work was published in the *Journal of Geophysical Research* and is attached in the Appendix.

We have improved the treatment of scattering at low sun conditions by a novel application of the pseudo-spherical technique. This method is equally applicable to two-stream and discrete ordinate methods, and is highly efficient computationally. We compared the results with a fully-spherical isotropic scattering model, with satisfactory agreement for most practical situations. In the same study, we noted that some errors can arise due to the curvature of the Earth's atmosphere even at high sun conditions, if plane-parallel and pseudo-spherical methods are used. A draft manuscript describing this work is attached in the Appendix. A short report on this study was also published in the DOE/ACP monthly newsletter, and is included in the Appendix.

We have studied the enhancement of UV absorption by clouds, which results from the increases in photon pathlengths due to scattering by cloud particles. In heavy cloud (e.g., cumulus nimbus) our results indicate that even small amounts of absorber (e.g., interstitial ozone and/or aerosols) can effectively reduce UV transmission. A paper

describing this work (accepted, Journal of Geophysical Research) is attached in the Appendix.

We have resolved a controversy on the enhancement of the actinic flux in droplets. Several earlier studies contained subtle errors, due (in one case) to the failure to account for the index of refraction of water, or (in another study) incorrectly averaging over the impact parameters of photons incident on droplets. A paper describing this work is in preparation.

2.3 Development of the Tropospheric Ultraviolet-Visible (TUV) Model

We have developed a comprehensive framework, the Tropospheric Ultraviolet-Visible (TUV) model, for the calculation of UV radiation and related quantities at any point in the atmosphere. The model uses updated spectroscopic data (see Section 2.1) and is based on state-of-the-science radiative transfer theory (see Section 2.2). It is written in Fortran (77 and 90 compatible) and was implemented on Unix platforms (however, friendly users have ported it to PC and MacIntosh platforms without unusual difficulties). Highlights of the model include:

- Extensive in-line documentation.
- Calculation of scattering by air molecules (Rayleigh scattering), by clouds and aerosols (Mie scattering); absorption by O_2 , O_3 , SO_2 , NO_2 , and particles (clouds and aerosols); wavelength-dependent surface albedo.
- Lyman-alpha and Schumann-Runge parameterization for stratospheric calculations.
- Pseudo-spherical correction for atmospheric curvature.
- Selectable solvers for the equation of radiative transfer (very fast two-stream, slower but arbitrarily accurate multi-stream discrete ordinates).
- High flexibility for customization, including user-controlled wavelength and altitude gridding.

The current public release of the model (version 3.9) is available to the scientific community at <http://acd.ucar.edu/models/open/tuv/tuv.html>. Version 4.0 is undergoing final testing and is available by contacting the author (sasha@ucar.edu).

2.4 UV Climatology

The TUV model was used to calculate the global distribution of UV radiation in the lower atmosphere, using as inputs values of atmospheric ozone and clouds measured from satellite-borne instruments. A sample of the results is given in Figure 1, in which monthly integrals of erythemal (sun-burning) radiation at the surface are presented. The effects of latitude, season, cloudiness, and ozone distributions are clearly seen. Black areas indicate regions where insufficient input data were available during that time period, due to downtime of the satellite instrument. The calculations and analysis of the global UV distributions for the other years of the satellite record are now being completed and will be available to the user community in electronic format.

We have also developed a technique for estimating the global distribution of actinic fluxes and photolysis rate coefficients (J-values) at the surface, based on satellite-derived input data. A manuscript describing this method has been submitted for publication (Geophysical Research Letters) and is given in the Appendix.

2.5 TUV Model Validation

The evaluation of the TUV model is ongoing, but results to date are highly encouraging. Figure 2 shows the performance of the model in cloud-free, pollution-free conditions, by comparing TUV model predictions against observations obtained by one of the world's leading UV measuring groups (Dr. R. McKenzie and colleagues, of NIWA/Lauder, New Zealand). Agreement to ca. 5% or better is noted over a wide dynamic range of UV irradiances. The synergistic benefits of this type of studies cannot be overstated: As a result of comparisons to our model results, the NIWA group identified and solved some

(relatively minor) calibration problems, while detailed spectral comparisons helped us decide that the newer Atlas-3 spectrum of extraterrestrial irradiance was probably more accurate (in the UV range) than the spectrum we had used earlier.

Additional TUV model validation is being carried out in association with an international intercomparison of spectral actinic flux radiometers and chemical actinometric measurements, which took place in Boulder, Colorado in June 1998. This measurement campaign included both clear and cloudy days, thus providing fairly stringent model-testing conditions. TUV model results have been submitted to the intercomparison referees, however at this date we do not know the extent of agreement/disagreement due to the "blind" nature of the intercomparison. A workshop on the results is planned for the spring of 1999.

The TUV model also participated in a number of model-model intercomparisons. Excellent agreement was found between TUV and other models that treat in detail multiple scattering (Koepke et al., 1997). Among these models, TUV is the only one that was classified in the "fast" category. The TUV model also participated in an intercomparison organized in the framework of the European Cooperation on Scientific and Technical Research (COST). Of the 13 models entered by 11 research groups, TUV was used by NCAR, the Belgian Royal Meteorological Institute, and the University of Thessaloniki. A preliminary evaluation shows good performance by the TUV model.

Finally, we have undertaken comparisons of our satellite-derived UV-climatology, with UV measurements obtained at a number of monitoring stations around the world and reported to the World UV and O₃ Data Center (WUVODC) in Toronto, Canada. Results are shown in Figure 3. These comparisons are much more challenging than those for specific days discussed above, because they are subject to the full variability of UV radiation levels from uncharacterized cloudiness, pollutants, and local perturbations (e.g., shadows and reflections). Another important difference is that the measurements refer to a single geographical point, while the satellite-derived ozone and cloudiness refer to a

foot-print of several thousand square kilometers. Furthermore, the data reported to the WUVODC are (so far) not cosine-corrected, which would increase the instrument signal by about 2-7% (Bais et al., 1998) and thus bring them into closer agreement with our calculations. Despite these difficulties, reasonably good agreement is noted in Figure 3. The slight over-estimation at the Northern Hemisphere sites may be due, at least in part, to the effects of local pollution in reducing the measured values.

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Table 1: Photolysis reactions included in the Tropospheric Ultraviolet Visible (TUV) model.

Reaction	$J, s^{-1} (a)$	Evaluation ^(b)
$O_3 \rightarrow O_2 + O(^1D)$	4.667E-05	1,2
$O_3 \rightarrow O_2 + O(^3P)$	4.914E-04	1,2
$NO_2 \rightarrow NO + O(^3P)$	1.029E-02	1,2
$NO_3 \rightarrow NO + O_2$	2.464E-02	1,2
$NO_3 \rightarrow NO_2 + O(^3P)$	1.940E-01	1,2
$N_2O_5 \rightarrow NO_3 + NO + O(^3P)$	3.636E-09	2
$N_2O_5 \rightarrow NO_3 + NO_2$	5.336E-05	2
$HNO_2 \rightarrow OH + NO$	2.276E-03	2
$HNO_3 \rightarrow OH + NO_2$	8.439E-07	2
$HNO_4 \rightarrow HO_2 + NO_2$	6.038E-06	2
$H_2O_2 \rightarrow 2 OH$	8.695E-06	2
$CH_2O \rightarrow H + HCO$	3.751E-05	1,2
$CH_2O \rightarrow H_2 + CO$	5.385E-05	1,2
$CH_3CHO \rightarrow CH_3 + HCO$	6.800E-06	1
$CH_3CHO \rightarrow CH_4 + CO$	2.675E-11	1
$CH_3CHO \rightarrow CH_3CO + H$	0.000E+00	1
$C_2H_5CHO \rightarrow C_2H_5 + HCO$	2.360E-05	1
$CHOCHO \rightarrow \text{products}^{(c)}$	8.544E-05	1
$CH_3COCHO \rightarrow \text{products}$	1.223E-04	1
$CH_3COCH_3 \rightarrow \text{products}$	8.595E-07	1
$CH_3OOH \rightarrow CH_3O + OH$	6.565E-06	1
$CH_3ONO_2 \rightarrow CH_3O + NO_2$	1.204E-06	1
$CH_3COONO_2 \rightarrow \text{products}$	9.355E-07	1
$ClOO \rightarrow \text{products}$	2.621E-19	2
$ClONO_2 \rightarrow Cl + NO_3$	4.912E-05	2
$ClONO_2 \rightarrow ClO + NO_2$	1.031E-05	2
$CCl_2O \rightarrow \text{products}$	8.620E-23	2
$CCl_4 \rightarrow \text{products}$	1.992E-22	2
$CH_3CCl_3 \rightarrow \text{products}$	7.710E-23	2
$CH_3Cl \rightarrow \text{products}$	3.559E-25	2
$CClFO \rightarrow \text{products}$	4.874E-23	2
$CF_2O \rightarrow \text{products}$	1.149E-24	2
$CF_2ClCFCl_2$ (CFC-113) $\rightarrow \text{products}$	4.784E-24	2
CF_2ClCF_2Cl (CFC-114) $\rightarrow \text{products}$	2.718E-25	2
CF_3CF_2Cl (CFC-115) $\rightarrow \text{products}$	8.075E-28	2
CCl_3F (CFC-11) $\rightarrow \text{products}$	4.557E-23	2

CCl_2F_2 (CFC-12) $\rightarrow$ products	1.699E-24	2
CF_3CHCl_2 (HCFC-123) $\rightarrow$ products	4.045E-24	2
CF_3CHFCl (HCFC-124) $\rightarrow$ products	4.331E-26	2
CH_3CFCl_2 (HCFC-141b) $\rightarrow$ products	5.730E-24	2
$\text{CH}_3\text{CF}_2\text{Cl}$ (HCFC-142b) $\rightarrow$ products	3.503E-26	2
$\text{CF}_3\text{CF}_2\text{CHCl}_2$ (HCFC-225ca) $\rightarrow$ products	9.452E-24	2
$\text{CF}_2\text{ClCF}_2\text{CHFCl}$ (HCFC-225cb) $\rightarrow$ products	6.763E-26	2
CHClF_2 (HCFC-22) $\rightarrow$ products	5.564E-28	2
$\text{CH}_3\text{Br} \rightarrow$ products	3.462E-22	2
$\text{CHBr}_3 \rightarrow$ products	1.714E-06	2
$\text{BrONO}_2 \rightarrow \text{Br} + \text{NO}_3$	4.473E-04	2
$\text{BrONO}_2 \rightarrow \text{BrO} + \text{NO}_2$	1.095E-03	2
CF_2Br_2 (Halon-1202) $\rightarrow$ products	3.915E-09	2
CF_2BrCl (Halon-1211) $\rightarrow$ products	1.367E-14	2
CF_3Br (Halon-1301) $\rightarrow$ products	6.686E-23	2
$\text{CF}_2\text{BrCF}_2\text{Br}$ (Halon-2402) $\rightarrow$ products	6.526E-22	2
$\text{O}_2 \rightarrow \text{O} + \text{O}$	3.664E-27	1
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(^1\text{D})$	1.960E-24	2
$\text{HO}_2 \rightarrow \text{OH} + \text{O}$	1.237E-21	2

(a) Typical photolysis rate coefficient at sea level, solar noon on 21 March, equator, 300 Dobson units, continental aerosols, no clouds, surface albedo of 10%, computed with pseudo-spherical two-stream radiation scheme.

(b) 1 = Evaluation by PIs; 2 = evaluation by De More et al. (1997).

(c) Includes all possible products.

Figure 1: Monthly erythemal irradiances at the Earth's surface for 1985, computed with the TUV model using ozone and cloud reflectivity data from satellite-borne instruments (Total Ozone Mapping Spectrometer, TOMS, aboard the Nimbus-7 satellite).

ERYTHEMAL SPECTRAL EXPOSURE (kJ/m²) FOR 1985

June

May

April

March

February

January

July

August

September

October

November

December

ERYTHEMAL SPECTRAL EXPOSURE (kJ/m^2) FOR 1985

ERYTHEMAL IRRADIANCE, $\mu\text{W cm}^{-2}$
at Lauder, New Zealand (45°S), cloud-free skies

Figure 2: Comparison of TUV model predictions and measured UV erythemal irradiances, for Lauder, New Zealand (45°S), cloud-free conditions. Several days of data are included. The variations in irradiance are due mostly to variations in the solar elevation and in the overhead ozone column.

Figure 3: Comparison of daily erythemal irradiances predicted by the TUV model using satellite-derived input data for ozone and cloud cover, with measurements obtained by Brewer spectroradiometers at a number of locations. All values are given as monthly averages.

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APPENDIX: Publications

Zeng, J., Madronich, S., and Stamnes, K., A note on the use of the two-stream delta-scaling approximation for calculating atmospheric photolysis rate coefficients, J. Geophys. Res., 101, 14525-14530, 1996.

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Mayer, B., Fischer, C., and Madronich, S., Estimation of surface actinic flux from satellite (TOMS) ozone and cloud reflectivity measurements, Geophys. Res. Lett., submitted, 1998.

Zeng, J., Petropavlovskikh, I., Kunasz, P., and Madronich, S., Modeling surface and tropospheric UV radiation and photolysis rates with the pseudo-spherical approximation, 1998, in revision.*

(*) Manuscript was submitted to J. Geophys. Res. Due to the departure from NCAR of three of the co-authors, we were unable to meet the deadline for submission of the revisions. The revised paper will be re-submitted in the near future.