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UV-B exposure and atmospheric ozone: evaluation of radiative flux to changes in ambient ozone levels

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Abstract

The changes in ground level radiative flux as a function of stratospheric and tropospheric ozone changes are investigated with a delta-two stream radiation model. Ground level radiative flux are calculated for several future scenarios with tropospheric pollution levels representative of an urban center in the eastern United States. These simulations were conducted under conditions of stratospheric ozone loss based on recent satellite measurements. The calculated ground level radiative flux is found to be disproportionately affected by the tropospheric ozone levels.

1. Introduction

Anthropogenic emissions of chloroflurocarbons (CFCs) have been the major contributor to destruction of stratospheric ozone documented over the last decade. Stratospheric ozone depletion was originally associated with the polar regions of the southern hemisphere remote from heavily populated areas. However, recent analysis of data obtained from the Nimbus-7 satellite has shown a decline in the total ozone column over a majority of the globe [1–3]. This analysis has shown a significant downward trend (0.4%–0.8% a year) over the last decade for much of the northern hemisphere including the heavily populated areas of northern United States, Canada, Scandinavia, Europe, and the former Soviet Union.

Stratospheric ozone is a primary filter for ultraviolet-B radiation (UV-B). Depletion of stratospheric ozone allows more UV-B radiation to reach the earth's surface. This

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has led to trepidation about the potential impacts to human health, agriculture, and the ecological and aquatic systems [4]. UV-B has been directly linked to cataracts and skin cancers, and there is concern that UV-B may also act to depress the immune system. Based on dose–response relationships derived from animal experiments and human epidemiological studies, it is estimated that non-melanoma cancers increase at a rate of 3% per 1% decrease in stratospheric ozone, and melanomas increase at 1–2% per 1% decrease in stratospheric ozone [5]. The effects of increasing UV-B radiation are not limited to human health. Studies conducted by Cullen et al. [6] on phytoplankton have shown a significant drop in photosynthesis with increasing levels of UV-B. Similar studies conducted on cultivated crops have shown a negative impact on growth rates, photosynthesis, and flowering under increasing UV-B levels [7].

The expected regional or global increases of UV-B radiation due to the ongoing decrease in stratospheric ozone have not been substantiated. At present there does not exist a comprehensive measurement network for UV-B radiation. This lack of a UV-B monitoring network makes it impossible to document UV-B trends. In addition, the expected increase in ground level UV-B radiation is clouded by limited point ground level UV-B measurements near urban centers which have shown a downward trend over the last decade [8].

The evaluation of the potential increase in UV-B radiation is currently limited to detailed modeling efforts which utilize vertical profile measurements of atmospheric ozone. A typical ozone profile is depicted in Fig. 1. The profile can be separated into two components; the stratosphere (above 10 km) which contains approximately 90% of the total ozone and the troposphere (0–10 km).

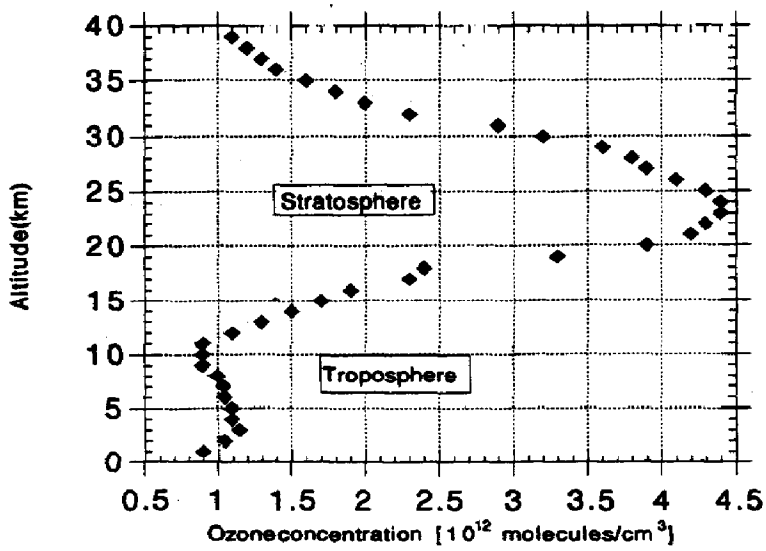

Fig. 1. Measured average ozone profile from Hohenpeissenburg Germany, 1982.

The absorption of UV-B radiation is a function of the total atmospheric ozone profile. Recent investigations [9] on ground level radiative flux as related to changes in tropospheric, and stratospheric ozone have shown intriguing results. While any reductions in stratospheric ozone leads to an increase in radiation transfer to the troposphere, the presence of tropospheric ozone can reduce the radiative transfer to the surface. This mitigation effect of tropospheric ozone is enhanced due to the disproportional role of tropospheric ozone as a filter for UV-B radiation. Studies conducted by Bruhl and Crutzen [9] have shown that molecule for molecule tropospheric ozone can absorb more radiation than stratospheric ozone. This greater affinity for absorption of UV-B radiation is explained by a longer optical path length which is the result of an increase in diffuse (scattered) radiation in the troposphere.

Scattering of the UV-B radiation occurs as it encounters, molecules, aerosols, and water droplets in the atmosphere. The UV-B radiation striking the top of the earth's atmosphere is essentially parallel, however, when it reaches the lower troposphere approximately 70% of the incident beam is diffuse.

The enhanced shielding effect of tropospheric ozone on ground level radiative flux is limited to locations with elevated ozone levels. Madronich [10] has shown the potential for significant UV-B increases based on calculations utilizing total ozone column measurements taken from the total ozone mapping system (TOMS) on board the Nimbus-7 satellite for the years 1979–1989.

The focus of this study is the evaluation of the sensitivity of ground level radiative flux to changes in the tropospheric and stratospheric ozone profile. Detailed radiation flux calculations are made utilizing total column ozone trends data obtained from the Nimbus-7 satellite, and tropospheric ozone levels based on several future photochemical smog scenarios. Results representative of a metropolitan region in the eastern United States are presented.

2. Mathematical review of the radiation model

The calculations for the propagation of UV-B radiation through the atmosphere encompasses an interactive process with atmospheric constituents involving scattering and absorption of the radiation. This interactive process is depicted in Fig. 2. For absorption, stratospheric ozone is the major atmospheric constituent involved with radiative transfer, and it is the total column ozone (tropospheric and stratospheric) that determines the quantity of photons which reach the earth's surface. Scattering of UV-B radiation includes molecular or Rayleigh scattering, and scattering by clouds and aerosols.

To model the propagation of radiation throughout the atmosphere a delta-two stream method presented by Zdunkowski et al. [11] is utilized. The model solves for radiative transfer in 177 spectral intervals. The model accounts for multiple scattering by air molecules, aerosols, particles and cloud droplets [12]. The propagation of radiation (diffuse and direct) is described via three differential equations; for diffuse upward (F_1), diffuse downward (F_2), and parallel

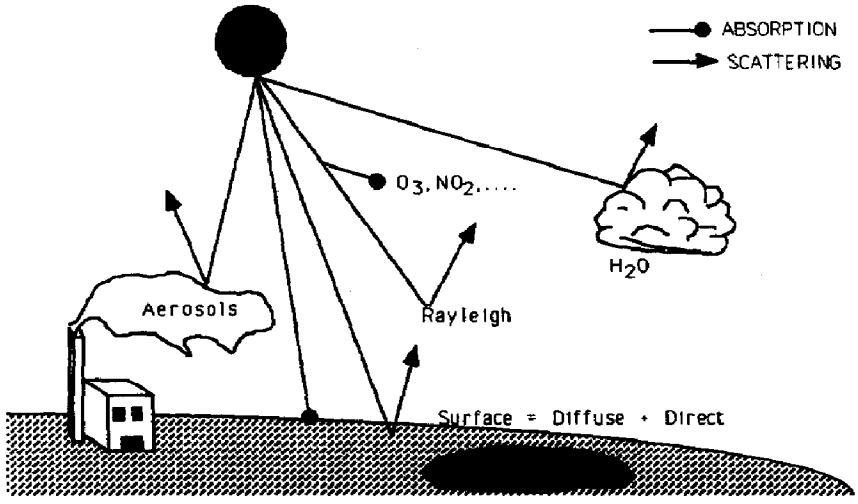

Fig. 2. Schematic, atmospheric transfer of radiation.

radiation (S).

$$\frac{dF_1}{d\tau} = \alpha_1 F_1 - \alpha_2 F_2 - \alpha_3 S/\cos\theta$$

$$\frac{dF_2}{d\tau} = \alpha_2 F_1 - \alpha_1 F_2 + \alpha_4 S/\cos\theta$$

$$\frac{dS}{d\tau} = -(1 - \varpi g^2) S/\cos\theta \tag{1}$$

where τ is the optical thickness which includes absorption by ozone and scattering by molecular species, clouds, and aerosols and θ is the solar zenith angle. The coefficients of Eq. (1) are defined as follows:

$$\alpha_1 = 2(1 - \varpi)(1 - \beta_0)$$

$$\alpha_2 = 2\varpi\beta_0$$

$$\alpha_3 = (1 - g^2)\varpi\beta(\theta)$$

$$\alpha_4 = (1 - g^2)\varpi(1 - \beta(\theta), \tag{2}$$

where ϖ is the albedo for a single scattering event defined as

$$\varpi = k_s/\{k_s + k_a\} \tag{3}$$

and k_S and k_a are the coefficients for scattering and absorption, respectively. In addition, $\beta(\theta)$ and β_0 are the backward scattering coefficients for parallel and diffuse light and g accounts for the anisotropic scattering by aerosols and cloud droplets.

In the above equation $\beta(\theta)$ and β_0 are approximated as follows for aerosols and clouds:

$$\beta_0 = \frac{3}{8}(1 - g)$$

$$\beta(\theta) = \frac{1}{2} - \frac{3}{4}\frac{g}{1+g}\cos\theta . \tag{4}$$

For molecular scattering both the coefficients are set equal to 0.5.

The boundary conditions for the solution set to Eq. (1) are

$$F_2(\tau = 0) = 0$$

and

$$F_1(\text{surface}) = A_S(\theta)S(\text{surface}) + A_S F_2(\text{surface}) \tag{5}$$

where A_S is the surface albedo.

The monochromatic energy flux or irradiance $E(\lambda)$ is approximated via the solution of Eq. (1) by the formula [12]:

$$E(\lambda) = \int_{\theta}\int_{\phi} L(\lambda, \theta, \phi)\cos\theta \sin\theta \, d\phi = S/\cos\theta + 2(F_1 + F_2) \tag{6}$$

where $L(\lambda, \phi, \theta)$ is radiance per wavelength from the zenith angle θ and azimuth angle ϕ.

The results are then integrated over the wavelengths categorized for UV-B (280–320 nm). The majority of the spectral data utilized in the model calculations were obtained from De More et al. [13]. In addition to the UV-B levels, a dose rate for erythemal induction defined by the action spectra listed in Fig. 3 was calculated as described by Madronich [10];

$$R = \int_{\lambda} E(\lambda)A(\lambda)\,d\lambda \tag{7}$$

where $A(\lambda)$ is the erythemal function (Fig. 3).

3. Illustration of disproportional role of tropospheric ozone

To demonstrate the disproportional effect of tropospheric ozone as a filter for UV-B radiation, radiative flux calculations were made utilizing the ozone profile in Fig. 1. The sensitivity of radiative flux to changes in the ozone profile can be expressed by the radiation amplification factor (RAF). A RAF is defined as the percent increase in ground level radiative dose resulting from each 1% decrease in the total ozone column. RAFs based on noon time UV-B radiation levels were calculated by

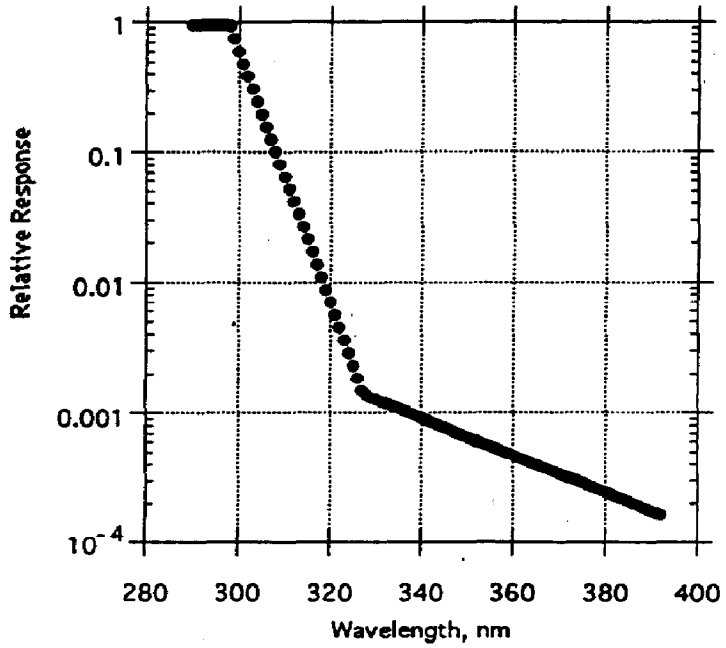

Fig. 3. Action spectra for erythemal dose.

Table 1
Changes in the atmospheric ozone profile and the related sensitivity of ground level UV-B: Percentage change in profile and UV-B with respect to the base case depicted in Fig. 1

Trop (%)	Start (%)	Total column (%)	UV-B (%)	RAF
00.0	− 20	− 18.7	+ 13.1	0.7
− 50.0	0.0	− 3.7	+ 3.6	1.0
50.0	0.0	+ 3.7	− 3.4	0.9
− 20.0	− 20.0	− 20.0	+ 14.8	0.7

independently changing the tropospheric and stratospheric components of the profile. The results are listed in Table 1.

Consider first the case where the stratospheric ozone level is reduced by 20%. This represents an 18% decrease in the total ozone column. As a result of this decrease in stratospheric ozone the UV-B flux at the earth's surface increases by 13% producing a RAF of 0.70. Contrast this situation to the case where the tropospheric profile is decreased by 50% (a 3.7% decrease in the total column ozone). This decrease in tropospheric ozone increases the ground level UV-B by 3.6% and the resulting RAF is 0.97. The difference in these RAFs highlights the disproportional role of tropospheric ozone as a filter of UV-B radiation. When ozone is increased in the troposphere the radiative flux reaching the earth's surface is decreased. Proportionally the

tropospheric component of the total ozone column has a greater effect on the radiative flux reaching the earth's surface.

4. The UV-B scenarios

The sensitivity of ground level UV-B fluxes and erythemal dose rates to changes in the vertical ozone profile is studied under several potential regional scale scenarios for the eastern half of the United States. To analyze the effects of ozone changes on ground level UV-B all other environmental conditions such as clouds, and concentrations of aerosols and other radiatively important trace gas species were held constant. This sensitivity procedure for ozone was validated by WMO [14] where it was shown that changes in ground level UV-B as a function of atmospheric ozone is nearly independent of other environmental conditions. Owing to the lack of ozone profile measurements the vertical distribution of ozone measured at Hohenpeissenburg Germany (47°N) was used in this study. The profile was then adjusted using the ratio of the integrated profile to the averaged ozone column amounts measured from the Nimbus-7 satellite for the eastern half of the United States. The total ozone column measurements for 40°N for the spring equinox of 1991 were used. The optical properties utilized for aerosols and clouds are detailed in [12]. A surface albedo of 10.5% was used.

To evaluate the range of potential UV-B exposures due to changes in both stratospheric and tropospheric ozone levels four scenarios were studied. In the first scenario (case 1/base case) the stratospheric ozone profile was as described above, and the tropospheric ozone profile was that calculated using a three-dimensional regional scale photochemical model (STEM-II) [15]. In this study the tropospheric ozone profile used in case 1 is that calculated for a regional scale ozone episode which occurred in June 1984. From this simulated episode the model calculated profile representative of tropospheric loading for an east coast metropolitan area was chosen.

The remainder of the scenarios represent potential UV-B exposures for the year 2010. For each of these scenarios the stratospheric ozone profile is decreased from the base case (case 1) by projecting the present trends in total column ozone loss to the year 2010. A decrease of 4% per decade was used based on the recent analysis by Stolarski et al. [2] for the mid latitudes of the northern hemisphere (Fig. 4).

Three different tropospheric profiles were used. In Case 2, the tropospheric ozone profile was held constant simulating no change in photochemical smog conditions over the next several decades. Case 3, the tropospheric ozone profile for the year 2010 was calculated using the STEM-II model taking into account estimates of future emissions, changes in water vapor and temperature, and an increase in UV-B flux to the top of the troposphere (for photochemical oxidant calculations) based on present estimates of climate change. The perturbations from the base case included a 33% increase in NO_x emissions, a 25% decrease in SO_2 emissions, a 3 K change in surface temperature, and 20–27% increase in the water vapor column for the lower troposphere [16]. These perturbations are consistent with present

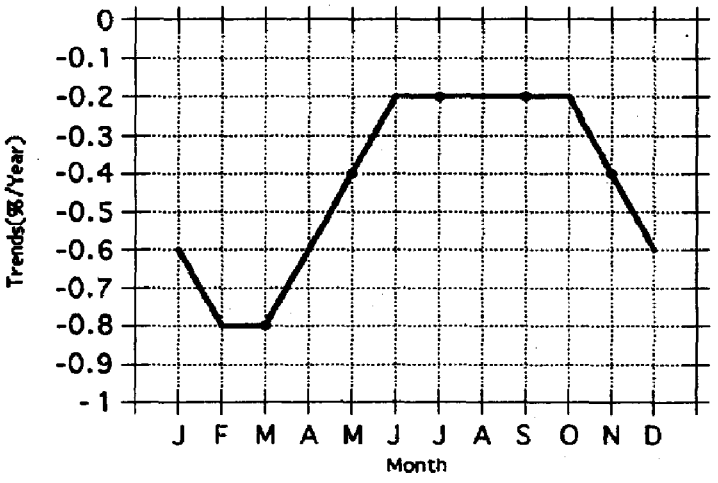

Fig. 4. Trends in the change in total column ozone as a function of season expressed in units of percentage change per decade. Trends based on analysis of Toms data (adapted from [3]).

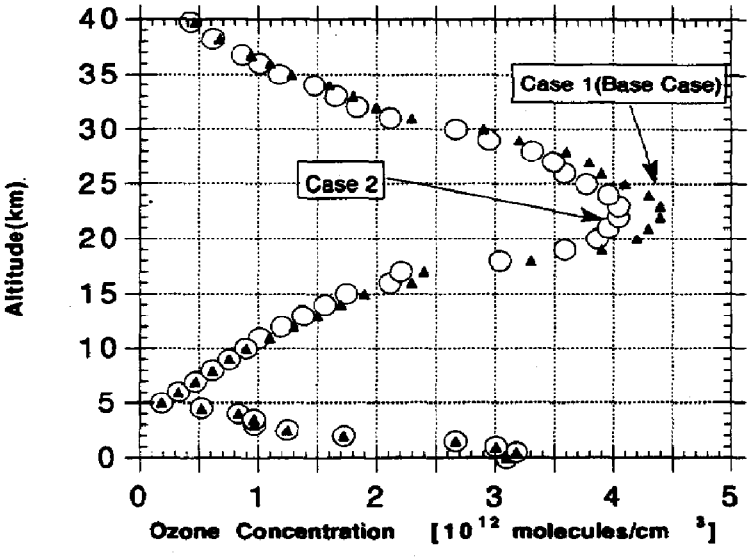

Fig. 5. Vertical ozone profiles. (Case 1) Base Case; (Case 2) stratospheric reduction.

climate change scenarios (Intergovernmental Panel on Climate Change, 1990), while those for the emissions are estimated from EPA [17].

The final scenario (Case 4) represents the maximum potential exposure to UV-B. The tropospheric profile is that estimated for pre-industrial conditions based on a calculation by Roemer [18]. This condition represents the "best case" air pollution scenario in the sense that anthropogenic emissions are essentially eliminated and tropospheric ozone is reduced to levels associated with a pre-industrial era. These four

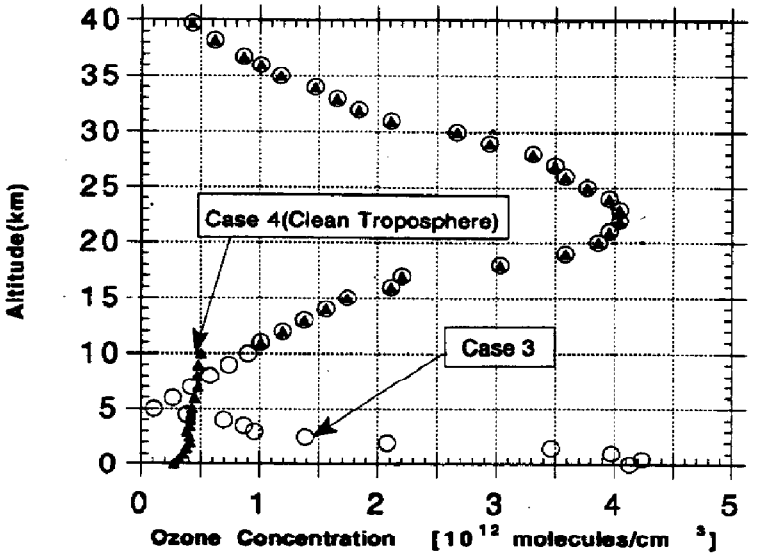

Fig. 6. Vertical ozone profiles. (Case 3) Stratospheric reduction: tropospheric increase; (Case 4) stratospheric reduction: tropospheric reduction.

Table 2
Noon time UV-B and UV-erythemal weighted fluxes for the following scenarios: (1) base case; (2) stratospheric reduction; (3) stratospheric reduction, tropospheric increase; (4) stratospheric reduction, tropospheric reduction. DU (Dobson Units) = 2.69×10^{16} molecules/cm^2

Case	Integrated profile (DU)	UV-B W/m_2	Erythemal W/m_2
1	328	2.481	0.124
2	305	2.595	0.134
3	311	2.558	0.131
4	279	2.805	0.154

scenarios are utilized to generate atmospheric ozone profiles, which are depicted in Figs. 5 and 6. These profiles were used to calculate the ground level radiative flux.

5. Results

The results from the simulations are summarized in Table 2. The values for UV-B and ultraviolet (UV) erythemal weighted induction are integrated noon time values. Comparing scenarios 1 and 2 it is found that a decrease in stratospheric ozone of 8%, which is a 6.9% change in the total column increases the noon time UV-B at the surface by 4.6% and increases in the erythemal dose by 8.4%. The resultant RAFs are 0.661 and 1.206 for UV-B and erythemal dose, respectively. The erythemal weighted

UV results compare closely with spectral measurement obtained by McKenzie et al. [19] who determined a 1.25 ± 0.20% in erythemal induction for every 1% reduction in total ozone at 40°S.

Simulations 2, 3, and 4 reflect the impact of changing tropospheric ozone on the ground level UV-B flux. For each of these simulations the stratospheric ozone levels are those estimated for the year 2010 and reflect a decrease of 4% per decade from the present values. Comparison of simulations 2 and 3 show the effect of increasing tropospheric ozone on UV-B exposure. It is found that a 13.4% increase in the tropospheric ozone levels, which represents a 1.8% increase in the total column ozone (stratospheric and tropospheric), reduces the ground level UV-B flux by 1.4% and erythemal dose by 2.4%. This produces RAFs of 0.784 and 1.31 for UV-B and erythemal induction, respectively.

Comparison of simulations 2 and 4 shows the changes of radiative exposure under conditions of photochemical smog reduction. For this simulation the total ozone column is reduced by 8.5% resulting in an increase in UV-B flux by 8.1% and an increase in the erythemal dose rate by 14.9%. The RAFs are 0.941 for UV-B and 1.74 for erythemal dose. These RAFs are significantly higher than the RAFs calculated under stratospheric ozone changes (Cases 1 and 2).

The computed RAFs from these simulations highlight the disproportional impact of tropospheric ozone as a filter of UV-B radiation. With respect to ground level radiative flux, increases in tropospheric ozone can offset the effects due to stratospheric ozone and total ozone reductions. This effect was demonstrated by Bruhl and Crutzen [9] based on the analysis of the Hohenpeissenberg ozone profile data from 1968 to 1982. Similar effects are expected for any strong UV-B absorbing tropospheric species (e.g., SO_2, NO_2, and aerosols). For example, Liu et al. [28] revealed that the potential increases of ground level UV-B as a result of stratospheric ozone loss can be offset by aerosols concentrations formed from the emissions of sulfur dioxide in industrialized countries.

6. Conclusions

An increased human health risk associated with UV-B radiation appears eminent in light of recent trends in global total ozone measurements. Results presented in this paper demonstrate that UV-B exposure is a strong function of the air quality of the region. In those areas with elevated tropospheric ozone levels (essentially those developed industrialized regions of the mid-latitudes in the northern hemisphere) the potential health risk to UV-B exposure becomes masked, and UV-B exposure is reduced due to the role of tropospheric ozone as a filter of UV-B. However, as the air quality of these regions is improved by the implementation of successful emission reduction policies, the alternate risk to UV-B radiation will carry increasing weight under the negative trends of stratospheric ozone concentrations.

An accurate assessment of the exposure levels of UV-B requires a well designed long-term UV-B monitoring network, and continued use of models. The models used in such studies should take into account changes in stratospheric and tropospheric

composition. In the troposphere the trends in SO_2, aerosols, and NO_2 should be considered simultaneously with ozone. Furthermore, more specific scenarios which take into consideration the impact of the phase out of CFCs on stratospheric ozone levels should be evaluated.

Acknowledgments

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References

[1] J.R. Herman, R. Hudson, R. McPeters, R. Stolarski, Z. Ahmad, X.Y. Gu, S. Taylor and C. Wellemeyer, A new self-calibration method applied to TOMS and SBUV back scattering ultraviolet data to determine long-term global ozone change, J. Geophys. Res., 96 (1991) 7531–7545.

[2] R.S. Stolarski, P. Bloomfield, R.D. McPeters and J.R. Herman, Total ozone trends deduced from Nimbus 7 TOMS data, Geophys. Res. Lett., 18 (1991) 1015–1018.

[3] X. Niu, J.E. Frederick, M.L. Stein and G.C. Tiao, Trends in column ozone based on TOMS data dependence on month latitude and longitude, J. Geophys. Res., 97 (1992) 661–669.

[4] EPA, Ultraviolet Radiation and Melanoma With a Special Focus on Assessing the Risks of Stratospheric Ozone Depletion, EPA400/1-87/001D, Office of Air and Radiation US Environmental Protection Agency, Washington, DC, 1987.

[5] J.T. Scotto, T. Fears and J. Fraumeni, Incidence of non-melanoma skin cancer in the United States, NIH#82-2433, 1981.

[6] J.J. Cullen, P.J. Neale and M.P. Lesser, Biological weighting function for the inhibition of phytoplankton photosynthesis by ultraviolet radiation, Science, 258 (1992) 646–650.

[7] A. Teramura and J. Sullivan, Effect of ultraviolet radiation in soybean yields and seed quality, Environ. Poll., 53 (1988) 416–469.

[8] J.G. Scotto, Cotton, F. Urbach, D. Berge and T. Fears, Biologically effective ultraviolet radiation: surface measurements in the United States, Science, 239 (1988) 762–764.

[9] C. Bruhl and P.J. Crutzen, On the disproportionate role of tropospheric ozone as a filter against solar UV-B radiation, Geophys. Res. Lett., 16 (1989) 703, 706.

[10] S. Madronich, Implications of recent total atmospheric ozone measurements for biologically active ultraviolet radiation reaching the earth's surface, Geophys. Res. Lett., 19 (1992) 37–40.

[11] W.G. Zdunkowski, R.M. Welch and G. Korb, An investigation of the structure of typical two stream methods for the calculation of solar fluxes and heating rates in clouds, Atmos. Phys., 53 (1980) 147–167.

[12] C. Bruhl and P.J. Crutzen, Scenarios of possible changes in atmospheric temperatures and ozone concentrations due to man's activities, estimated with a one-dimensional coupled photochemical climate model, Climate Dynamics, 2 (1988) 173–203.

[13] W.B. De More, R.T. Watson, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, M.J. Molina and A.R. Ravishankara, Chemical kinetics and photochemical data for use in stratospheric modeling, Jet Prop. Lab. Publ., 82–57, NASA, Pasadena, CA, 1982.

[14] WMO, Scientific Assessment of Stratospheric Ozone: 1989, Volume I, World Meteorological Organization. Global Ozone Research and Monitoring Project, Report No. 20, 1989.

[15] G.R. Carmichael, L.K. Peters and R.D. Saylor, The Stem-II regional scale acid deposition and photochemical oxidant model. An overview of model development and applications, Atmos. Environ., 25A (1991) 2077.

[16] K. John and G.R. Carmichael, Potential impacts of global climate change and increased anthropogenic emissions on regional tropospheric ozone cycles, in: Transactions of the Tropospheric Ozone and the Environment II: Effects, Modeling and Control, ed. R.L. Berglund (TR-20, Air and Waste Management Association, Pittsburgh, 1992), pp. 439–458.

[17] EPA, National Air Quality and Emissions Trends Report 1990, EPA-450/4-91-023, Technical Support Division, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, NC, 1991.

[18] M.M. Roemer, Ozone and the greenhouse effect, TNO R 91/227, 1991.

[19] R.L. McKenzie, W.A. Matthews and P.V. Johnston, The relationship between erythemal UV and ozone, derived from spectral irradiance measurements, Geophys. Res. Lett. 18 (1991) 2269–2272.

[20] S.C. Liu, S.A. McKeen and S. Madronich, Effects of anthropogenic aerosols on biologically active ultraviolet radiation, Geophys. Res. Lett., 18 (1991) 2265–2268.