

Problems in assessment of the UV penetration into natural waters from space-based measurements

Alexander Vassilkov¹, Jay Herman², Nickolay Krotkov³, Greg Mitchell⁴, and Mati Kahru⁴

¹Science Systems and Applications, Inc.; ²NASA/Goddard Space Flight Center; ³GEST Center Univ. of Maryland Baltimore County; ⁴Scripps Inst. of Oceanography, Univ. of California San Diego

ABSTRACT

Satellite instruments currently provide global maps of surface UV irradiance by combining backscattered radiance data with radiative transfer models. The models are often limited by uncertainties in physical input parameters of the atmosphere and surface. Global mapping of the underwater UV irradiance creates further challenges for the models. The uncertainties in physical input parameters become more serious because of the presence of absorbing and scattering quantities affected by biological processes within the oceans. In this presentation we summarize the problems encountered in the assessment of the underwater UV irradiance from space-based measurements, and propose approaches to resolve the problems. We have developed a radiative transfer scheme for computation of the UV irradiance in the atmosphere-ocean system. The scheme makes use of input parameters derived from satellite instruments such as TOMS and SeaWiFS. The major problem in assessment of the surface UV irradiance is to accurately quantify the effects of clouds. Unlike the standard TOMS UV algorithm, we use the cloud fraction products available from SeaWiFS and MODIS to calculate instantaneous surface flux at the ocean surface. Daily UV doses can be calculated by assuming a model of constant daily cloudiness. Both SeaWiFS and MODIS provide some estimates of seawater optical properties in the visible. To calculate the underwater UV flux the seawater optical properties should be extrapolated down to shorter wavelengths. Currently, the problem of accurate extrapolation of visible data down to the UV spectral range is not solved completely. The major difficulty is insufficient correlation between photosynthetic and photoprotective pigments of phytoplankton absorbing in the visible and UV respectively. We propose to empirically parameterize seawater absorption in the UV on the basis of available data sets consisting of seawater spectral absorption, UV-visible reflectance, diffuse attenuation coefficient, and concentrations of chlorophyll and mycosporine-like amino acids obtained in a variety of ocean waters. Another problem is the lack of reliable data on pure seawater absorption in the UV. Laboratory measurements of the UV absorption of both pure water and pure seawater are required.

Keywords: UV irradiance, radiative transfer models, seawater optical properties

1. INTRODUCTION

Increased levels of biologically harmful UV-B radiation (280-320nm) resulting from the depletion of Earth's ozone layer have been shown to affect aquatic ecosystems. One of the important effects of enhanced levels of UVB radiation is a reduction in the productivity of phytoplankton caused by inhibition of photosynthesis due to damage to the photosynthetic apparatus¹. Enhanced UVB radiation could also affect the photochemical production of carbonyl sulfide in seawater², thereby augmenting the greenhouse effect and affecting other long-term global biogeochemical cycles. Photochemical degradation of oceanic dissolved organic matter (DOM) associated with changes in UV radiation flux may affect carbon cycling. A detailed overview of the effects of UV radiation on marine ecosystems has been published recently³.

The quantitative assessment of UV effects on aquatic organisms on a global scale requires an estimate of the in-water radiation field. The total ozone and UV reflectivity measurements, from the Total Ozone Mapping Spectrometer (TOMS) satellite instruments, allow calculation of global daily UV irradiance at the ocean surface⁴⁻⁷. Estimates of UV transmission in ocean waters require knowledge of the inherent and apparent optical properties of seawater. For ocean properties, the

¹alexander_vassilkov@sesda.com; phone 1 301 867 2184; fax 1 301 867 2151; Science Systems and Applications, Inc., 10210 Greenbelt Rd., Lanham, MD, USA 20706;

²herman@tparty.gsfc.nasa.gov; phone 1 301 614 6039; fax 1 301 614 5903; NASA Goddard Space Flight Center, Code 916, Greenbelt, MD, USA 20771

⁴gmitchell@ucsd.edu; phone 1 858 534 2697; fax 1 858 534 2997; Scripps Inst. Of Oceanography, Univ. of California San Diego, La Jolla, CA, USA 92093

Coastal Zone Color Scanner flown onboard NASA's Nimbus-7 satellite and current ocean-color satellite instruments, such as Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and Moderate Resolution Imaging Spectroradiometer (MODIS) were designed to provide frequent global measurement of water-leaving radiances in the visible region. Seawater optical properties and constituents (e.g. chlorophyll concentration) are inferred from the water-leaving radiance allowing estimates of inherent optical properties (IOP) in the visible region. To calculate the underwater UV irradiance, the visible IOP should be extrapolated down to shorter wavelengths. The extrapolation requires some assumptions to be justified.

The main goal of this paper is to assess the problems of the UV penetration into ocean waters using global TOMS surface-UV and satellite ocean-color measurements. In assimilating these satellite data sets, two major problems arise: the fast radiative transfer (RT) modeling of the penetration of UV light into the water and extrapolation of water optical properties derived from the satellite visible channels to the UV spectral region. The paper discusses both problems. In section 2 we briefly discuss the satellite ocean-color sensor and TOMS data as input to the RT models. Section 3 discusses the RT models in more details as well as the parameterization of the UV optical properties. Section 4 discusses the global products, which can be created from the models.

2. SATELLITE DATA

The Level 3 spatially binned SeaWiFS and MODIS data can be used for estimates of chlorophyll concentration and seawater diffuse attenuation coefficient $K_d(490\text{nm})$. SeaWiFS also provides the daily cloud fraction data. The calibrated radiances (Level-1) over the ocean are atmospherically corrected⁸ to derive Level-2 geophysical products, e.g., normalized water-leaving radiances, chlorophyll-*a*⁹, and diffuse attenuation coefficient at 490 nm, $K_d(490)$ ¹⁰. These data are spatially binned and averaged on a 9 km global grid (Level-3) for each day. The daily gridded data is temporally averaged at 8-day, monthly, and annual periods.

For underwater irradiance calculations, one needs to know both the direct and diffuse components of the surface irradiance, and the boundary conditions at the air-water interface. The TOMS standard UV data (described below) provides only the total surface irradiance (diffuse plus direct). To calculate the daily-average direct irradiance, information on average cloud fraction in each grid-cell is required. Such information is obtained from the 865nm channel of the SeaWiFS sensor. The SeaWiFS 0.85 μm cloud-albedo threshold over ocean was set at 1.1% albedo¹¹. The relation is a binary one: if the threshold is crossed, the SeaWiFS pixel (4km by 4km) is declared cloud contaminated and the cloud flag is set for that pixel. During binning, if the flag is set, that sample is considered to be 100% cloud, otherwise 0%. It should be noted that the current cloud flag also masks sun glint, high aerosols, and thin cirrus clouds.

The TOMS daily gridded (Level 3) products (ozone, reflectivity and aerosol index) are used as an input to the atmospheric radiative transfer model to generate daily global maps of the surface total (direct plus diffuse) spectral irradiance at the satellite overpass time⁵⁻⁷. To calculate daily UV exposures, it is neglected by diurnal variation of cloud and aerosol amounts. Because of the highly variable nature (temporal and spatial) of cloud cover the TOMS daily UV estimations should be averaged over periods of at least a week to obtain a good estimate of the accumulated UV exposure at a specific location⁶. It was shown that the corresponded uncertainty in the satellite estimated monthly UV exposure is less than 5%¹².

3. RADIATIVE TRANSFER MODELS

3.1 Atmospheric model

The atmospheric RT model provides the boundary conditions at the ocean surface for the underwater irradiance calculation. The radiative transfer solutions in the atmosphere and in the ocean are coupled through the contribution of photons first reflected from the ocean and then scattered back to the water by the atmosphere. However, if the ocean albedo is small enough, the atmospheric and oceanic radiative transfer problems can be treated separately. The separation of the atmospheric and oceanic RT models gives less than 10% resulting error for satellite estimation of underwater UV irradiance¹³.

Existing scheme of calculations of surface UV irradiance consists of three steps. The first step is calculation of the clear-sky surface irradiance using a lookup table pre-computed for pure Rayleigh scattering. Then the clear-sky surface irradiance is corrected for non-absorbing aerosols and clouds using a semi-empirical model on the second step. The third step is optional; it is performed if absorbing aerosols are detected. Output of the scheme is the total (direct plus diffuse) downward surface irradiance⁶. It has been shown that the scheme provides reasonable estimates of the total surface irradiance for

snow-free conditions that compares with ground-based data at 324 nm as well as schemes, which use more complicated cloud correction algorithms⁷. However, in the ocean the diffuse and direct irradiances are attenuated differently. Therefore, an independent estimation of direct and diffuse components is required at the ocean surface. We will briefly describe the existing computational scheme and mainly focus on a technique we are proposing to estimate the direct and diffuse irradiances separately.

3.1.1 Clear sky irradiance

Assuming pure Rayleigh scattering and Lambertian reflection with albedo A at the bottom of the atmosphere, the direct and diffuse downward clear-sky irradiance just above the ocean surfacels, F_{Clear} , can be calculated exactly provided the column ozone amount is known. In the operational algorithm, F_{Clear} is calculated using Beer's law for direct component and interpolation from a lookup table of diffuse/direct ratio pre-calculated for a Rayleigh atmosphere using climatological TOMS 325DU ozone and temperature profile for different solar zenith angles⁶. Estimates of A can be made from the monthly minimal Lambert equivalent surface reflectivity derived from the Nimbus-7/TOMS measurements¹⁴. For the open ocean regions $A(380nm)$ typically varies between 0.05 - 0.08. The satellite measured high-resolution extraterrestrial solar irradiance spectrum (the ATLAS-3 SUSIM data available on the Internet: http://www.solar.nrl.navy.mil/susim_atlas_data.html) is used in the computations.

3.1.2 Reduction of UV irradiance by non-absorbing aerosols and clouds

The common approach for satellite estimations of surface irradiance involves calculation of the clear-sky surface irradiance, F_{Clear} , multiplied by C_T :

$$F_{Cloud} = F_{Clear} \cdot C_T \quad (1)$$

According to the standard semi-empirical model⁶, the factor C_T is a function of the TOMS measured scene Lambert Equivalent Reflectivity (LER) at 360 nm, R_{360} , and surface albedo, A , obtained from the minimum LER climatology¹⁴. This model provides a simple algorithm for cloud correction for total irradiance on the ocean surface. To estimate the direct and diffuse irradiances separately, we propose using the fractional cloud model¹⁵, with cloud fraction estimated from the SeaWiFS data. The algorithm is as follows:

First, we estimate the cloud fraction, f by averaging SeaWiFS cloud fraction data over a model grid-cell. For completely cloud-free conditions the TOMS measured LER, R_{360} should be close to the ocean albedo and cloud correction is not required ($C_T=1$). However, due to the possible time differences between TOMS and SeaWiFS overpass (less than an hour) and natural geophysical variability in the ocean albedo and cloud amounts we have to impose a certain threshold on f for clear-sky conditions. Currently, we do not perform direct irradiance cloud correction for grid-cells with $f < 0.05$. The total irradiance is corrected if $R_{360} > A$.

For the rest of the grid-cells with $f > 0.05$, an effective cloud reflectivity, R_C , is derived from the TOMS LER, ocean albedo, A , and cloud fraction, f , using the following expression:

$$R_C = \frac{R_{360} - (1 - f)A}{f} \quad (2)$$

The R_C is converted to the effective optical depth of the cloud portion of the grid-cell, τ_C using parameterizations based on the radiative transfer calculations¹⁶. This allows calculation of the direct irradiance under the cloud, $F_{C,direct}$.

The grid-averaged direct irradiance is estimated using the following equation:

$$F_{direct} = fF_{C,direct} + (1 - f)F_0 \quad (3)$$

where F_0 is direct irradiance at the surface for a clear sky and $F_{C,direct}$ is estimated from the equation of direct beam attenuation:

Finally, the diffuse irradiance is calculated as a residue between the total and direct components:

$$F_{Diffuse} = F_{Clear} C_T - F_{Direct} \quad (4)$$

where F_{Clear} is estimated from equation (1), F_{Direct} is estimated from equation (3), and C_T is estimated from the standard semi-empiric model with replacement of R_{360} by R_C . For cloud fraction close to 100% the method reduces to the standard TOMS LER method^{4,6,7} with additional direct/diffuse irradiance partition.

3.1.3 Correction for absorbing aerosols

An additional correction is needed in the presence of absorbing aerosol plumes, where UV irradiance reduction is stronger. The correction is performed using the TOMS aerosol index and a semi-empirical conversion factor, which is a function of aerosol height^{5,6}. The aerosol plumes in tropics and at large distances from their sources are usually located between 3 and 4 km altitude, and are repetitive at a given location from year to year.

3.2. Radiative transfer in the ocean

Given the TOMS estimate of the surface UV irradiance, and assuming isotropic angular distribution of the diffuse downward radiance at the ocean surface, any appropriate radiative transfer scheme can be applied to model light penetration into the ocean. There are two basic requirements for those schemes. The RT scheme should be fast enough to compute the spectral UV penetration into the ocean on a global scale for reasonable time. The RT scheme should have a sufficient accuracy at biologically significant optical depths. However, the accuracy of the current optical measurements of the most fundamental inherent optical properties IOP of seawater (scattering, absorption coefficients, and phase function) is normally about 10%, and the errors of extrapolation of these properties into UV spectral region has yet to be estimated. The current errors in IOP make it reasonable to use less sophisticated radiative transfer schemes for the purpose of operational satellite mapping of underwater UV fields. The accurate models^{17,18} are very important for testing faster operational algorithms.

3.2.1 Fast radiative transfer scheme

The first model¹⁹ for an assessment of underwater UV radiation and biodoses was developed in 1979. In this model it was assumed that the irradiance is attenuated exponentially in the ocean: $E_\lambda(z) = E_\lambda^0 \exp(-K_d z)$, where E_λ^0 and $E_\lambda(z)$ are spectral irradiances just below the ocean surface and at depth, z (we use different notation E for irradiances within the ocean to distinguish them from the atmospheric irradiances, F). This simple formulation of the radiative transfer in the ocean widely used²⁰ requires an a-priori knowledge of K_d in the UV spectral region. In general, K_d cannot be extrapolated from the visible region for use in the UV wavelengths. The coefficient K_d depends on the angular structure of the light field and, thus, on depth (even for a homogeneous ocean), and on seawater inherent optical properties (IOPs). Therefore, there is no a-priori reason to expect that K_d values in the UV region will vary in the same manner with the angular structure of the light field and depth as in the visible region. The problem of correlation between spectral values of the diffuse attenuation coefficient has been carefully discussed²¹.

To calculate UV underwater irradiances, an approximate RT model should have a capability to account for the angular structure of the light field. This capability is of importance because the direct and diffuse solar fluxes attenuate essentially different. One of the approximate RT schemes having this capability is the Quasi-Single Scattering Approximation (QSSA)²². The QSSA model has a simple analytical formulation, yet enabling us to address the dependence of K_d on the angular distribution of the light field in the ocean. The QSSA is based on the strong absorption with highly anisotropic scattering of seawater²². It assumes: (a) single scattering in the upward direction; (b) multiple scattering in the downward direction in accordance with delta-function. The approximation assumes the exponential direct-beam transmittance: $T_b = \exp(-\Gamma z/\mu)$, where $\Gamma = a + b'_b$ is the effective attenuation coefficient, a is the absorption coefficient, b'_b is the fraction of backscatter in the upward direction, and μ is the cosine of the zenith angle of incident beam. The fraction of backscatter in the upward direction is exactly equal to the backscattering coefficient, b_b , in the case of normal incident beam, i.e. $\mu = 1$. In-water zenith angles are limited by the angle of total internal reflection. Accounting for this fact, and the small contribution of backscatter to total attenuation of light, we assume that $b'_b \equiv b_b$. The spectral irradiance at depth, z , can be written as a sum of the direct solar radiation and the integral of surface radiance over spherical angles from the diffuse radiation, both attenuated by water^{13,23}. A flat ocean surface is assumed and the water column is assumed to be vertically homogeneous.

The accuracy of the QSSA was estimated by comparison with the accurate RT calculations for the simplified models of the ocean. Its accuracy becomes better for lower values of the single scattering albedo. Using the results¹⁷ for direct solar illuminating the ocean surface, it was found that the relative error of the QSSA within the optical depth range of 10 was less than 7% for the single scattering albedo $\omega=0.2$. For the single scattering albedo $\omega=0.9$, which is not the case in the UV, the QSSA error was 17% for the optical depth $\tau=5$ and 49% for the optical depth $\tau=10$. To estimate the errors of the QSSA in case of diffuse illumination, Monte-Carlo calculations were conducted for an isotropic angular distribution of incident radiance on the ocean surface²⁴. For a single scattering albedo $\omega=0.6$, the QSSA error was less than 35% in the optical depth region $\tau<10$. In all cases the errors were less at smaller optical depths.

It should be noted that certain conditions specific for UV spectral region justify the application of the QSSA to the radiative transfer problem in the water:

- (a) ω is normally less than 0.7 in the UV spectral region and gets smaller at short wavelengths, which are more biologically effective;
- (b) only small optical depths play a significant role in biological applications of the underwater UV calculations. For optical depths $\tau<5$, the QSSA error is less than 20% even for high solar zenith angles²⁴. All these considerations should permit the use of the QSSA for calculations of biologically significant parameters from the underwater UV irradiance.

3.2.2. Model of seawater inherent optical properties (IOPs)

The QSSA makes use of the absorption coefficient, a , and the backscattering coefficient, b_b . The total IOPs are the sums of the IOP of the pure seawater and the three major scattering and absorbing water substances:

$$a(\lambda) = a_w(\lambda) + a_{DOM}(\lambda) + a_{ph}(\lambda) + a_p(\lambda), \quad b_b(\lambda) = b_w(\lambda) + b_p(\lambda) \quad (5)$$

where subscripts w , p , ph and DOM denote the pure seawater, the suspended particulate matter (SPM), the phytoplankton pigments, and dissolved organic matter (DOM), respectively.

For a long time, the pure seawater IOPs were usually obtained from a 1981 paper²⁵. According to recent findings²⁶, the pure water absorption coefficient is significantly below the consensus values²⁵ in the wavelength range 380 – 500 nm, about 2 times lower than the old value at 380nm. A recent paper²⁸ suggests that the most reliable combination of absorption data is data²⁶ for 380 to 700 nm and data²⁹ for 196 to 320 nm. The gap between the data sets, 320 to 380 nm is filled by linear interpolation (Fig. 1). It is clear from the discussion²⁸ that additional laboratory measurements and ocean validation are needed over the entire UV range.

The SPM backscattering coefficient and the DOM absorption coefficient can be used in the conventional form:

$$a_{DOM}(\lambda) = a_0 \exp[-S(\lambda - \lambda_0)] \quad , \quad b_p(\lambda) = b_0 (\lambda / \lambda_0)^{-m} \quad (6)$$

where m is the backscatter wavelength ratio exponent, S is the DOM spectral slope. The DOM spectral slope $S=0.014 \text{ nm}^{-1}$ was commonly accepted for the visible spectral region³⁰. A more recent study³¹ showed that the DOM spectral slope should be made slightly greater in the UV spectral region: $S=0.017 \pm 0.001 \text{ nm}^{-1}$. Recent measurements have showed that the DOM spectral slope can increase with photodegradation of colored DOM and can vary within a rather wide range from 0.01 to 0.03 nm^{-1} for clear waters³². Unfortunately, these variations of the DOM spectral slope have not been parameterized. Therefore, an average value of the DOM spectral slope for the UV spectral region $S=0.017 \text{ nm}^{-1}$ is recommended. The parameter m may vary in a wide range depending on the optical type of seawater. Fortunately, the SPM backscattering coefficient, b_0 , is normally much less than the total absorption coefficient, a , in the UV spectral region. An average estimate of the parameter $m=1$ is recommended³³.

In Case 1 ocean waters, where re-suspension of sediments or coastal and terrestrial influences are negligible, it has long been recognized that the bulk optical properties are strongly correlated with the photosynthetic pigment mass concentrations of the water³³. The quantitative absorption coefficient data combined with photosynthetic pigment mass as estimated by chlorophyll-*a* provide the basis for visible region optical model parameterizations^{34,35}. The phytoplankton pigment absorption is commonly expressed through chlorophyll-*a* concentration, C , and the chlorophyll-specific absorption coefficient:

$$a_{ph}(\lambda) = C a_{ph}^*(\lambda, C) \quad (7)$$

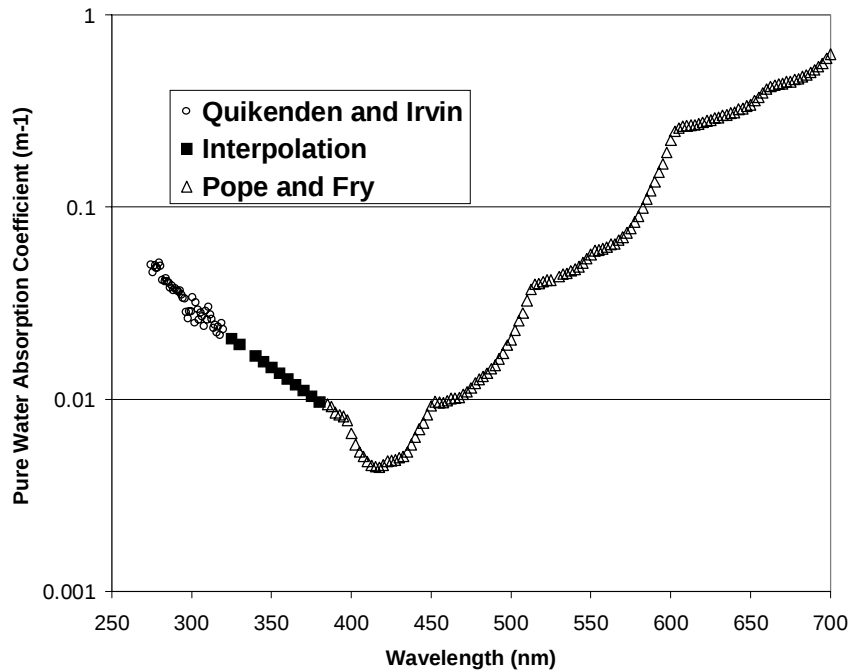


Fig. 1. Data for laboratory determinations of pure water absorption²⁹ in the UVB region, and data²⁶ for the UVA and visible regions. As recommended²⁸, interpolation between the two data sets is made to approximate the absorption from 320-380 nm.

It is well known that the chlorophyll-specific absorption coefficient depends on chlorophyll concentration due to, for example, pigment packaging effect. This dependence has been parameterized for the visible range³⁵: $a_{ph}(\lambda, C) = A(\lambda)C^{-B(\lambda)}$, where the functions $A(\lambda)$ and $B(\lambda)$ are tabulated for the visible region.

The UV region particle absorption is more complicated, since there may be strong accumulations of detrital pigments with UV absorption^{36,37}. More recently, the importance of strongly absorbing mycosporine amino acids (MAA) indicates that this region of the spectrum is not easily modeled based only on proxies of bulk photosynthetic pigments, such as chlorophyll-a. Phytoplankton synthesize a variety of compounds that absorb radiation in the UV-B and UV-A regions of the spectrum and which could affect the response of the cell to UV radiation. In vivo absorption in the UV-A and UV-B shows a wide range of values, with peaks of absorption between 320 and 350 nm and a maximum between 330 and 335 nm³⁸. For all surface samples, the average in vivo pigment-specific UV absorption was larger than absorption in the blue. The overall variance was high, demonstrating that the absorption in the UV is not due to the major photosynthetic pigments and that the UV-absorbing compounds, such as MAA, vary independently. This suggests including a term, a_p , in Eq. 5, which is independent of the term describing the phytoplankton pigment absorbance.

However, for the UV region there is still no parameterization of both phytoplankton pigment and MAA absorbance. Because of lack of the UV parameterization, a rather simple model of the chlorophyll-specific absorption coefficient was chosen¹³. The model assumes $B(\lambda)=0$ in the UV and adopts the chlorophyll-specific absorption coefficient from data³⁸. The average for all-stations spectrum was accepted to be the chlorophyll-specific absorption coefficient in the model. Additionally, the model neglects the term, a_p , in Eq. 5 assuming it can be described through phytoplankton pigment absorbance. Basically, the model is a simple extension of the Case 1 water model³⁴ to the UV region.

The model¹³ allows an extrapolation of the water absorption and scattering coefficients measured or retrieved from satellite measurements in the visible (400 – 600 nm) into the UV spectral region (290 – 400 nm). The model contains three input

quantities: a_0 , b_0 , and C . These parameters are to be estimated from available satellite data sets. First, the chlorophyll concentration is the standard SeaWiFS and MODIS product. To determine other quantities, the Case 1 water model³⁴ is assumed. According to the model, the DOM absorption at 440 nm is 20% of the total absorption of pure seawater and pigments. This assumption determines the most important parameter a_0 . To estimate the backscattering coefficient, the standard SeaWiFS product of the diffuse attenuation coefficient and the model of the diffuse attenuation coefficient³⁹ can be used. Estimates of the DOM absorption coefficient play the major role in calculations of the UV penetration into seawater because backscatter is much less than absorbance in the UV. The largest uncertainty is from the way the model of seawater IOPs is constructed. That is, because (1) DOM absorption is estimated as 20% of the sum of pure seawater and chlorophyll absorption and (2) SPM absorption is calculated using a constant relationship with chlorophyll. These two problems should be addressed in further studies.

Coastal waters are normally referred as Case 2 waters in which IOPs are uncorrelated. The above model cannot be directly applied to those waters. However, independent retrieval of absorption coefficients of DOM and phytoplankton pigments has been suggested⁴⁰⁻⁴³. Given the DOM absorption coefficient in the visible region, it can be extrapolated into the UV region. The SPM backscattering coefficient can also be retrieved using analytical algorithms⁴¹⁻⁴³.

4. RESULTS

The biological effect of UV radiation is typically described by action spectra. A large number of action spectra, $A(\lambda)$, has been proposed for various biological effects of UV radiation in marine environment⁴⁴⁻⁴⁶. The biological daily UV doses can be calculated by convolution of UV irradiance spectra- $E_\lambda(z)$ with $A(\lambda)$ and integrating over the time of the day:

$$D(z) = \int_{290}^{400} dt \int E_\lambda(z, \theta_0(t)) A(\lambda) d\lambda \quad (8)$$

Comparisons of the simulated dose with measured one were done¹³ for the action spectrum for unshielded DNA⁴⁷. It was found that calculated daily doses were in a good agreement with surface measurements⁴⁸ and underwater measurements⁴⁹.

Using the above-described model, monthly global maps of DNA doses at selected depths and 10% penetration depths defined for UVB irradiance and DNA doses were created¹³. The main features of the averaged DNA dose map are determined by latitude dependence of the surface UV irradiance. The latitude dependence of the DNA dose is clearly apparent in all oceans. Some features of the DNA dose map are due to cloudiness structure. For example, the cloudiness effect on the DNA dose was observed in the Mediterranean Sea - where clear-sky conditions remained for more than a week, resulting in DNA dose values characteristic of equatorial regions. It is interesting that the latitudinal distribution of both total ozone and the optical properties of ocean waters are not seen on the global DNA dose map. The effects of ozone amount and seawater optical properties are almost masked by cloudiness effects, indicating that latitudinal dependence of the UV irradiance and cloudiness are the major factors affecting the underwater DNA dose. Exceptions to this will be in ocean or coastal areas of large local turbidity.

An important measure of a biologically weighted dose is the depth at which the dose is reduced to 10% of its surface value. This is the approximate depth over which biological damage due to UV effects takes place for a particular mechanism. The 10% depth depends on the action spectrum used in calculations of UV dose rates. The larger the spectral slope of an action spectrum is, the smaller the 10% penetration depth. This is because seawater absorbs more strongly in the short-wave region, therefore, shorter wavelength radiation penetrates into seawater less than longer wavelength radiation.

Horizontal distribution of the 10% DNA dose depth is primarily determined by bio-optical properties of ocean waters. However, the angular structure of the light incident on the sea surface determined by cloudiness structure and solar zenith angle also affects the 10% DNA dose depth. This is because of the dependence of the diffuse-attenuation coefficient on the angular structure of the in-water light field. The 10% UVB irradiance depth is normally greater than the 10% DNA-dose depth. This is due to the fact that the integral over UVB irradiance is mainly determined by the longer wavelength part of UVB spectrum as opposed to the DNA dose that is mainly determined by shorter UVB wavelengths. The seawater is an effective filter of the shorter UV wavelengths.

A sensitivity study^{13,50} showed that knowledge of the absorption coefficient of pure seawater is crucial in estimates of the UV penetration depth. The 10% UVB penetration depth calculated from the extrapolated new absorption coefficients²⁷ is about 20% greater than that calculated from the old coefficients²⁵. It is instructive to estimate how variations in the DOM

absorbance affect the UVB penetration depth. Calculations were conducted for two cases. In the first one, no DOM absorption was assumed. The case represents upper limit values of the penetration depth. In the second case, it was assumed that the DOM absorption at 440 nm is 20% of the total absorption of pure seawater and pigments³⁴. The result demonstrates the significant effect of the DOM absorption on the UVB penetration depth. For example, the DOM absorption reduces the maximum penetration depth from 19.9 m to 15.8 m for most probable chlorophyll concentration of 0.1 mg/m³. The sensitivity study highlights the importance of accurate knowledge of the pure water absorption coefficient and a fraction of DOM absorption.

5. CONCLUSIONS

Problems in assessment of the UV penetration into oceanic waters on a global scale and some possible solutions were considered. Global mapping of the underwater UV irradiance creates challenges for models combining RT computations with assimilation of satellite data. The uncertainties in physical input parameters become more serious because of the presence of absorbing and scattering quantities affected by biological processes within the oceans. We summarized the problems encountered in the assessment of the underwater UV irradiance from space-based measurements, and propose approaches to resolve the problems.

We have developed a RT scheme for computation of the UV irradiance in the atmosphere-ocean system. The scheme makes use of input parameters derived from satellite instruments such as TOMS and SeaWiFS or MODIS. The atmospheric part of the model generates spectral direct and diffuse irradiance on the sea surface that are inputs to the underwater part of the RT model. The major problem in assessment of the surface UV irradiance is to accurately quantify the effects of clouds. Unlike the standard TOMS UV algorithm, we use the cloud fraction products available from SeaWiFS and MODIS to calculate instantaneous surface irradiance at the ocean surface. Daily UV doses can be calculated by assuming a model of constant daily cloudiness.

The in-water radiative transfer model is based on the QSSA that is simple, computationally fast, and yet enables the angular distribution of the light field to be addressed. To calculate the underwater UV irradiance the seawater optical properties should be extrapolated down to shorter wavelengths. Currently, the problem of accurate extrapolation of visible data down to the UV spectral range is not solved completely. The major difficulty is insufficient correlation between photosynthetic and photoprotective pigments of phytoplankton absorbing in the visible and UV respectively. Empirical parameterization of seawater absorption in the UV should be done in the future on the basis of available data sets consisting of seawater spectral absorption, UV-visible reflectance, diffuse attenuation coefficient, and concentrations of chlorophyll and mycosporine-like amino acids obtained in a variety of ocean waters. Another problem is the lack of reliable data on pure seawater absorption in the UV. Laboratory measurements of the UV absorption of both pure water and pure seawater are required. We have developed a simplified model of seawater IOPs allowing the extrapolation of the absorption and backscattering coefficients to the UV spectral region provided their values in the visible region are known. Values of the absorption and backscattering coefficients in the visible region are estimated from the SeaWiFS standard products by using the Case 1 water model.

The sensitivity study has shown that the main parameters controlling levels of the most harmful UV-B radiation underwater for clear sky conditions are the solar zenith angle, water bio-optical properties and total ozone. Attenuation of UV-B irradiance and DNA dose rate with water depth is primarily controlled by the seawater absorption coefficient and its spectral dependence. An influence of the seawater backscatter on the attenuation of UV irradiance is considerably less. Changes in the angular distribution of the surface radiance due to aerosol load or clouds may result in an irradiance increase (or decrease) at a given depth for large solar zenith angles.

The main spatial features of the monthly maps of underwater DNA dose are determined by the SZA and cloudiness. The seawater IOPs and total ozone effects are less significant for the spatial distribution of the DNA dose. The spatial distribution of the 10% DNA dose depth is mainly determined by the spatial structures of chlorophyll. Cloudiness effects and latitude dependence of the 10% DNA dose are also observed due to the effect of the angular distribution of the light incident on the sea surface in the in-water UV irradiance attenuation

ACKNOWLEDGEMENTS

The work was supported by the NASA Contract 916-15-1 and TOMS project.

REFERENCES

1. W.F. Vincent and J.J. Neale, "Mechanism of UV damage in aquatic organisms," *The Effects of UV Radiation on Marine Ecosystems*, Eds. S.J. de Mora, S. Demers, and M. Vernet, Cambridge Univ. Press, pp. 149-176, 2000.
2. R.G. Zepp and M.O. Andreae, "Factors affecting the photochemical production of carbonyl sulfide in seawater," *Geophys. Res. Lett.*, **21**, pp. 2,813-2,816, 1994.
3. S. de More, S. Demers, and M. Vernet (Eds.) *The effects of UV radiation in the marine environment*, p. 324, Cambridge Univ. Press, Cambridge, 2000.
4. J.R. Herman, P.K. Bhartia, Z. Ahmad, and D. Larko, "UV-B radiation increases (1979-1992) from decreases in total ozone," *Geophys. Res. Lett.*, **23**, pp. 2117 – 2120, 1996.
5. N.A. Krotkov, P.K. Bhartia, J.R. Herman, V. Fioletov, J. Kerr, "Satellite estimation of spectral surface UV irradiance in the presence of tropospheric aerosols 1. Cloud-free case," *J. Geophys. Res.*, **103**, pp. 8779-8793, 1998.
6. J.R. Herman, N. Krotkov, E. Celarier, D. Larko, and G. Labow, "The distribution of UV radiation at the Earth's surface from TOMS measured UV-backscattered radiances," *J. Geophys. Res.*, **104**, pp. 12059-12076, 1999.
7. N.A. Krotkov, J.R. Herman, P.K. Bhartia, V. Fioletov and Z. Ahmad, "Satellite estimation of spectral surface UV irradiance 2. Effects of homogeneous clouds and snow," *J. Geophys. Res.*, **106**, 2001.
8. H. R. Gordon, and M. Wang, "Retrieval of water-leaving radiance and aerosol optical thickness over the oceans with SeaWiFS: a preliminary algorithm," *Appl. Opt.*, **33**, pp. 443-452, 1994.
9. J. E. O'Reilly, S. Maritorena, B. G. Mitchell, D. A. Siegel, K. L. Carder, S. A. Garver, M. Kahru, and C. McClain, "Ocean color chlorophyll algorithms for SeaWiFS," *J. Geophys. Res.*, **103**, pp. 24937-24953, 1998.
10. J. L. Mueller and C. C. Trees, Revised SeaWiFS prelaunch algorithm for the diffuse attenuation coefficient $K_d(490)$, *Case Studies for SeaWiFS Calibration and Validation, Part 4, NASA Tech. Memo. 104566*, vol. 41, edited by S. B. Hooker and E. R. Firestone, 18-21, 1997.
11. K. Arrigo and C. McClain, Cloud and ice detection at high Latitudes for Processing CZCS imagery, SeaWiFS Algorithms, Part I, *NASA Tech. Memo 104566*, vol. 28, 38pp, 1995.
12. T.J. Martin, B.G. Gardiner, and G. Seckmeyer, "Uncertainties in satellite-derived estimates of surface UV doses," *J. Geophys. Res.*, **105**, pp. 27005-27011, 2000.
13. A.P. Vasilkov, N. Krotkov, J.R. Herman, C. McClain, K. Arrigo, and W. Robinson, "Global mapping of underwater UV irradiance and DNA-weighted exposures using TOMS and SeaWiFS data products," *J. Geophys. Res.*, 2001, (accepted).
14. J.R. Herman and E. Celarier, "Earth surface reflectivity climatology at 340 to 380 nm from TOMS data," *J. Geophys. Res.*, **102**, pp. 28003-28011, 1997.
15. M.L. Nack, and A.E.S. Green, "Influence of clouds, haze and smog on the middle ultraviolet reaching the ground," *Appl. Opt.*, **13**, pp. 2405-2415, 1974.
16. J.R. Herman, E. Celarier, and D. Larko, "UV 380nm reflectivity of the Earth's surface, clouds and aerosols," *J. Geophys. Res.*, **106**, pp. 5335-5351, 2001.
17. C.D. Mobley, B. Gentili, H.R. Gordon, Z. Jin, G.W. Kattawar, A. Morel, P. Reinersman, K. Stamnes, and R.H. Stavn, "Comparison of numerical models for computing underwater light fields," *Appl. Opt.*, **32**, pp. 7484-7504, 1993.
18. Z. Jin and K. Stamnes, "Radiative transfer in nonuniformly refracting layered media: atmosphere-ocean system," *Appl. Opt.*, **33**, pp. 431-442, 1994.
19. R.C. Smith and K.S. Baker, "Penetration of UV-B and biologically effective dose-rates in natural waters," *Photochem. Photobiol.*, **29**, pp. 311-323, 1979.
20. C.R. Booth and J.H. Morrow, "Invited review: The penetration of UV into natural waters," *Photochem. Photobiol.*, **65**, pp. 254-257, 1997.
21. N.K. Hojerslev, "Yellow substance in the sea," *The Role Of Solar Ultraviolet Radiation In Marine Ecosystems*, Ed. by J. Calkins, Plenum Press, pp. 263-281, 1982.
22. H.R. Gordon, "Simple calculation of the diffusive reflectance of the ocean," *Appl. Opt.*, **12**, pp. 2803-2804, 1973.
23. N.A. Krotkov and A.P. Vasilkov, Theoretical model for prediction of ultraviolet radiation in the atmosphere-ocean system, *IRS'92: Current Problems in Atmospheric Radiation, Proc. IRS 1992*, A. DEEPAK Publ., pp. 555-558, 1993.
24. A.P. Vasilkov, O.V. Kopelevich, N.A. Krotkov, S.V. Sheberstov, V.I. Burenkov, and S.V. Ershova, "A model for calculations of ultraviolet radiative transfer in waters of the Arctic Seas," *Oceanology*, **39**, pp. 192-201, 1999.
25. R.C. Smith and K.C. Baker, "Optical properties of the clearest natural waters," *Appl. Opt.*, **20**, pp. 177-186, 1981.
26. R.M. Pope and E.S. Fry, "Absorption spectrum (380-700 nm) of pure water. II. Integrating cavity measurements," *Appl. Opt.*, **36**, pp. 8710-8723, 1997.
27. F.M. Sogandares and E.S. Fry, "Absorption spectrum (340-700 nm) of pure water. I. Photothermal measurements," *Appl. Opt.*, **36**, pp. 8710-8723, 1997.

28. E.S. Fry, "Visible and near ultraviolet absorption spectrum of liquid water: comment," *Appl. Opt.*, **39**, pp. 2743-2744, 2000.
29. T.I. Quickenden and J.A. Irvin, "The ultraviolet absorption spectrum of liquid water," *J. Chem. Phys.*, **72**, pp. 4416-4428, 1980.
30. A. Bricaud, M. Babin, A. Morel, and H. Claustre, "Variability in the chlorophyll-specific absorption coefficients of natural phytoplankton: analysis and parameterization," *J. Geophys. Res.*, **100**, pp. 13321-13332, 1995.
31. O.V. Kopelevich, S.V. Lutsarev, and V.V. Rodionov, "Light spectral absorption by yellow substance of ocean water," *Oceanology*, **29**, pp. 409-414, 1989.
32. A. Vodacek, and N.V. Blough, Seasonal variation of CDOM in the Middle Atlantic Bight: terrestrial inputs and photooxidation, *Ocean Optics XIII, Proc. SPIE*, edited by S. G. Ackleson and R. Frouin, vol. 2963, 132-137, 1997.
33. H.R. Gordon and A. Morel, *Remote assessment of ocean color for interpretation of satellite visible imagery: a review*, Springer-Verlag, New York, p. 114, 1983.
34. A. Morel, "Optical modeling of the upper ocean in relation to its biogeochemical matter content (Case I waters)," *J. Geophys. Res.*, **93**, pp. 10749-10768, 1988.
35. A. Bricaud, M. Babin, A. Morel, and H. Claustre, "Variability in the chlorophyll-specific absorption coefficients of natural phytoplankton: analysis and parameterization," *J. Geophys. Res.*, **100**, pp. 13321-13332, 1995.
36. B.G. Mitchell and D.A. Kiefer, "Variability in pigment specific particulate fluorescence and absorption spectra in the northeastern Pacific Ocean," *Deep-Sea Res.*, **35**, pp. 665-689, 1988.
37. H.M. Sosik and B.G. Mitchell, "Light absorption by phytoplankton, photosynthetic pigments, and detritus in the California Current System," *Deep-Sea Res.*, **42**, pp. 1717-1748, 1995.
38. M. Vernet, Brody E.A., Holm-Hansen O., and Mitchell B.G. The response of antarctic phytoplankton to ultraviolet radiation: absorption, photosynthesis, and taxonomic composition. *Ultraviolet Radiation in Antarctica: Measurements and Biological Effects*. Antarctic Research Series. v.62. p.143-158, 1994.
39. H.R. Gordon, "Can the Lambert-Beer law be applied to the diffuse attenuation coefficient of ocean water?," *Limnol. Oceanogr.*, **34**, pp. 1389-1409, 1989.
40. K.L. Carder, F.R. Chen, Z.P. Lee and S.K. Hawes, "Semianalytic moderate-resolution imaging spectrometer algorithms for chlorophyll *a* and absorption with bio-optical domains based on nitrate-depletion temperatures," *J. Geophys. Res.* **104**, pp. 5403-5421, 1999.
41. F.E. Hoge and P.E. Lyon, "Satellite retrieval of inherent optical properties by linear matrix inversion of oceanic radiance models: an analysis of model and radiance measurement errors," *J. Geophys. Res.*, **101**, pp. 16631-16648, 1996.
42. S. A. Garver and D.A. Siegel, "Inherent optical property inversion of ocean color spectra and its biogeochemical interpretation: 1. Time series from the Sargasso Sea," *J. Geophys. Res.*, **102**, pp. 18607-18625, 1997.
43. A.P. Vasilkov, A retrieval of coastal water constituent concentrations by least-squares inversion of a radiance model, *Proc. 4th Conference on Remote Sensing for Marine and Coastal Environments*, Orlando, 17-19 March 1997, Vol. 2, pp. 107-116, 1997.
44. R.C. Smith and J.J. Cullen, "Effects of UV radiation on phytoplankton," *Rev. Geophys.*, **33**, pp. 1211-1223, 1995.
45. J.J. Cullen and P.J. Neale, Biological weighting functions for describing the effects of ultraviolet radiation on aquatic systems. *Effects of Ozone Depletion on Aquatic ecosystems*, Ed. D.-P. Hader, 97-118, 1997.
46. P.J. Neale, Spectral weighting functions for quantifying the effects of ultraviolet radiation in marine ecosystems. *The Effects of UV Radiation on Marine Ecosystems*, Eds. S.J. de Mora, S. Demers, and M. Vernet, Cambridge Univ. Press, 73-100, 2000.
47. F.E. Quate, B.M. Sutherland and J.C. Sutherland, "Action spectrum for DNA damage in alfalfa lowers predicted impact of ozone depletion," *Nature (Letters to Nature)*, **358**, pp. 576-578, 1992.
48. J.D. Regan, W.L. Carrier, H. Gucinski, B.L. Olla, H. Yoshida, R.K. Fujumura, and R.I. Wickland, "DNA as a solar dosimeter in the ocean," *Photochem. Photobiol.*, **56**, pp. 35-42, 1992.
49. P. Boelen, I. Obernosterer, A.A. Vink, and A.G.J. Buma, "Attenuation of biologically effective UV radiation in tropical Atlantic waters measured with a biochemical DNA dosimeter," *Photochem. Photobiol.*, **69**, pp. 34-40, 1999.
50. A.P. Vasilkov and Krotkov N.A. "Modeling the effect of seawater optical properties on the ultraviolet radiant fluxes in the ocean," *Izvestiya, Atmos. Ocean. Phys.*, **33**, pp. 349-357, 1997.