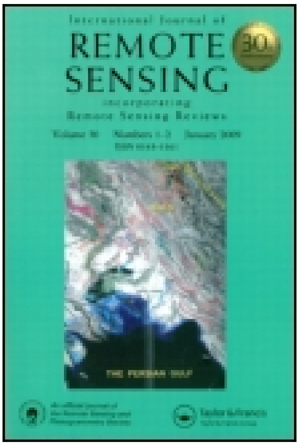

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Ozone and solar UV-B radiation: monitoring of the vitamin D synthetic capacity of sunlight in Kiev and Antarctica

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Vitamin D synthesis is a well-known beneficial effect of solar UV-B radiation. Theoretical calculations showed the significant effect of the stratospheric ozone layer thickness on the vitamin D synthetic capacity of sunlight. During 2003–2004 permanent monitoring of solar UV radiation, using an *in vitro* model of vitamin D synthesis, was carried out in Kiev (50°23′ N, 30°32′ E) and in the Antarctic at the Vernadsky station (65°15′ S, 64°16′ W). Simultaneously, ozone layer thickness in the Antarctic was measured with a Dobson spectrometer. The results obtained confirm the known dramatic seasonal effect on the vitamin D synthetic capacity of sunlight. In addition, for the first time, a significant increase in the efficiency of vitamin D synthesis was revealed at the Vernadsky station in October under low ozone conditions.

1. Introduction

The unprecedented event of the occurrence of a major, sudden stratospheric warming over Antarctica, which resulted in the Antarctic ozone hole split in September 2002, intensified scientific interest in ozone changes and induced solar UV variability (Varotsos 2002, 2003)

Variations in solar (UV radiation due to clouds and aerosols have a comparable effect on UV-B (280–315 nm) caused by variations in stratospheric ozone that hinder accurate detection of mid-latitude UV-B trends. To reveal ozone depletion under conditions of opaque atmosphere when clouds and aerosols attenuate solar UV flux like a grey filter, a UV-B measuring device should possess two independent parameters. One should respond to the integral intensity of UV-B radiation and the other should be exclusively sensitive to the short wavelength variations in the solar UV spectrum related to ozone depletion. The desired spectral selectivity is intrinsic in the 'D-dosimeter', which is based on an *in vitro* model of vitamin D synthesis.

It is known that vitamin D_3 plays an essential role in calcium homeostasis. In addition, vitamin D_3 is acknowledged now as a critical hormone that helps regulate the health of more than 30 different tissues, from the brain to the prostate (Holick and Jenkins 2003). Being one of the body's many control systems, vitamin D plays a crucial role in regulating cell growth, the immune system and blood pressure, and in the production of insulin, brain chemicals and bone. Recently, vitamin D and its metabolites have been proposed as a protective factor for several types of cancer (Grant 2002).

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The UV-B portion of sunlight converts provitamin D_3 (7-dehydrocholesterol, 7-DHC) in skin into previtamin D_3. Once formed, previtamin D_3 is converted thermally into vitamin D_3. Dramatic seasonal and latitudinal effects on the vitamin D synthetic capacity were revealed using an *in vitro* model of vitamin D synthesis (ethanol solution of 7-DHC) and High Performance Liquid Chromatography (HPLC) analysis (Webb *et al.* 1988). In view of the remarkable difference between the absorption spectra of provitamin and previtamin D_3 (figure 1), UV absorption spectroscopy is more suitable for the *in situ* monitoring of previtamin D photosynthesis *in vitro* (Terenetskaya 2000).

2. Methods

To check the sensitivity of previtamin D photosynthesis to the thickness of the ozone layer, UV solar spectra were calculated using the standard radiation transfer (RT) model (Bird and Riodtran 1986). For calculation of previtamin D accumulation, the calculated solar spectra were used as input data in the photoreaction mathematical model (Galkin and Terenetskaya 1999).

For solar UV monitoring the provitamin D_3 solutions in ethanol (C=20 μg ml^{-1}) were exposed in rectangular quartz cuvettes of 0.5 cm thickness directly to the Sun's rays. Additionally, in the Antarctic the solution was exposed in spherical quartz cuvettes to measure global UV irradiance (figure 2). The cuvettes with 7-DHC solutions were exposed three hours per day around noon (local time). The solution absorption spectra were recorded within 230–330 nm by the UV spectrophotometer (Perkin&Elmer Lambda 25) before and after an exposure and were processed further with a computer for concentration analysis.

3. Results

The UV solar spectra were calculated for different ozone layer thicknesses. As an example, the calculated spectra for the solar zenith angle (SZA)=54°43′ that correspond to 12:00 local time (16:00 GMT) at the Antarctic Vernadsky station on 22 October 2004 are shown in figure 3, depending on the stratospheric ozone.

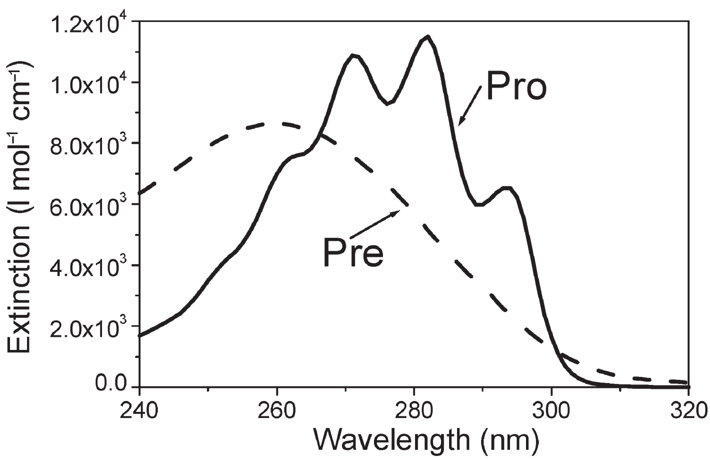

Figure 1. UV absorption spectra of vitamin D photoisomers. Pro, initial provitamin D; Pre, photosynthesized previtamin D.

Figure 2. Exposure of provitamin D_3 solution in spherical and quartz cuvettes at the Vernadsky station in Antarctica.

The time-dependencies of previtamin D accumulation were calculated using these spectra (with tenfold magnification of the UV intensity) as the input data in the mathematical model describing the photoreaction kinetics (figure 4). As can be seen from figure 4, not only is the rate of previtamin D accumulation dependent on the ozone layer thickness, but its maximum achievable concentration is decreased significantly with increasing thickness of stratospheric ozone layer. Moreover, whereas the photoreaction rate is dependent on the integral UV intensity, the maximum achievable concentration of previtamin D is dictated solely by the spectral position of the short-wave edge of the solar spectrum. This spectral selectivity

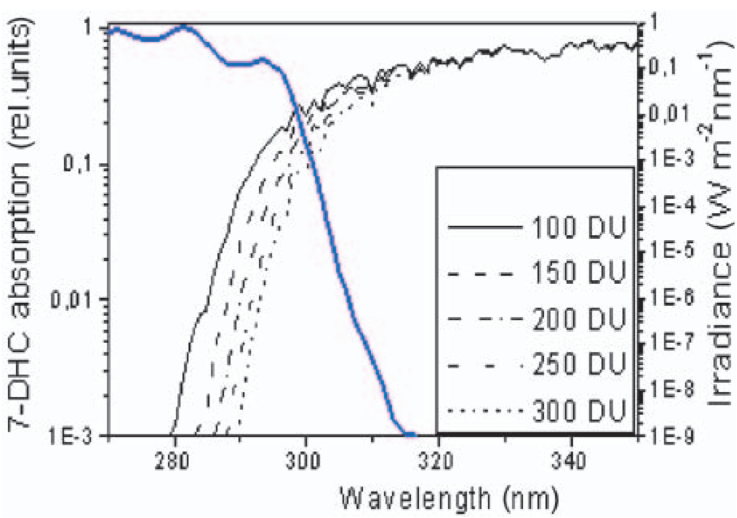

Figure 3. Calculated solar UV spectra for SZA = 54°43′ for different thicknesses of the stratospheric ozone layer in relation to provitamin D absorption spectrum (on the left).

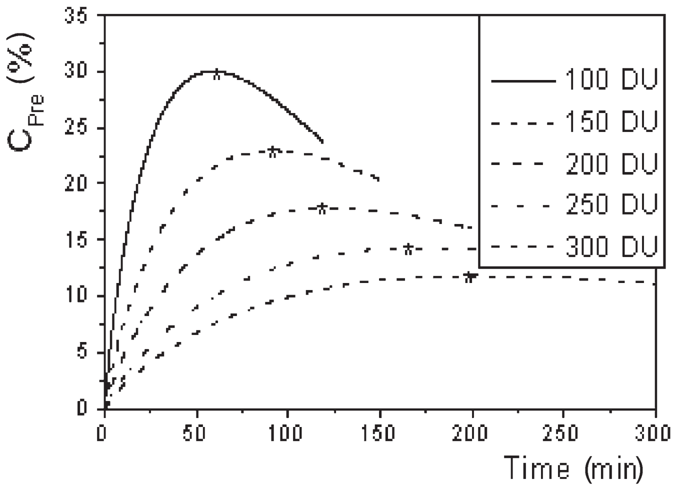

Figure 4. Calculated kinetics of previtamin D photosynthesis with different ozone layer thicknesses (asterisks indicate the maximum achievable concentration of previtamin D).

provides a way for the detection of ozone depletion under conditions of opaque atmosphere.

UV monitoring in Kiev was carried out during April – October, 2003. Comparison of experimental and calculated (cloudless sky, 300 DU (Dobson units) ozone) concentrations of accumulated previtamin D is shown in figure 5.

In the Antarctic two cuvettes (rectangular and spherical) with the same 7-DHC solution were exposed simultaneously. A remarkable difference between direct and global solar UV radiation is demonstrated clearly in figure 6 by the corresponding spectral changes (curves 2 and 3).

4. Conclusions

Endogenous synthesis of vitamin D under UV solar irradiation is widespread in the biosphere and inherent in most animals and plants. Although sunlight has long been

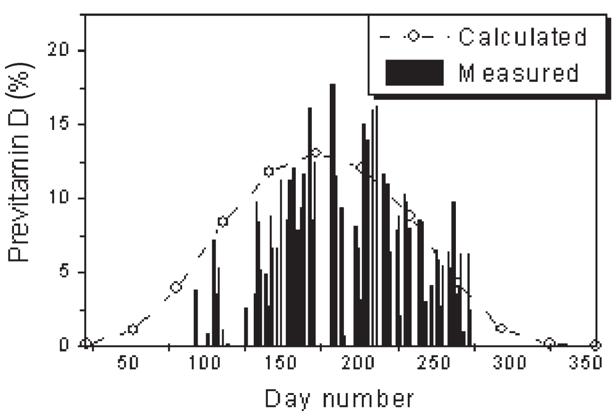

Figure 5. Seasonal changes of the vitamin D synthetic capacity of sunlight in Kiev. Columns, experimentally measured concentrations of previtamin D; dotted line, calculated data.

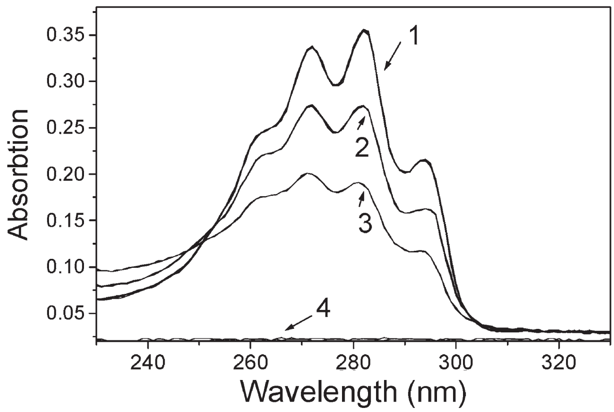

Figure 6. Absorption spectra of 7-DHC in ethanol recorded in the Antarctic on 5 December 2003. 1, before exposure; 2 and 3, after three hours of exposure (2, rectangular cuvette; 3, spherical cuvette; 4, zero line).

recognized as the main source of vitamin D_3 for humans, the sharp decrease in provitamin D absorption within the range 282–305 nm implies extreme sensitivity of vitamin D synthesis to the most changeable UV-B part (280–315 nm) of the solar spectrum. A dramatic influence of ozone layer thickness on the vitamin D synthetic capacity of sunlight has been revealed by both numerical calculations and experimental studies in the Antarctic using an *in vitro* model of vitamin D synthesis.

Acknowledgements
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