The vitamin D synthetic capacity of sunlight: *In situ* monitoring and model calculation

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In appropriate dose solar UV radiation is beneficial for people, specifically due to production of vitamin D3 in skin from its precursor 7-dehydrocholesterol. Vitamin D3, traditionally perceived as the main regulator of calcium homeostasis, is now acknowledged as one of the body's many control systems.

But the UV overdose may result in detrimental health effects (sunburn, accelerated ageing of the skin, skin cancer), and because of that, when calculating biologically effective solar UV irradiance, in most cases the CIE erythema action spectrum is widely used as biologic weighting function for estimation of biological activity of solar UV radiation.

However, in view of significant difference between the action spectra of CIE erythema and vitamin D synthesis the beneficial vitamin D synthetic capacity of sunlight cannot be correctly estimated from these data. At the same time to weigh the risks and benefits of sun exposure it is necessary to determine moderate exposures that provide adequate vitamin D nutrition for people but prevent skin cancer.

With due regard to the essential role of vitamin D3 for human health we examined the possibility of use an in vitro model of vitamin D synthesis for simplified estimation in situ of provitamin D3 photoconversion into previtamin D3 from the UV absorption spectra similar to a number of chemical UV dosimeters as, for instance, polysulphone film, that measured an accepted UV dose by the absorbance decrease at the fixed wavelength. The large-scale linear correlation (R=0.99) was found on a clear summer day in Nea Michaniona (40.47N, 22.85E) between concentration of accumulated previtamin D3 and maximum absorbance decline in the initial provitamin D3 absorption spectrum at 282 nm. However, long-term observations in Kiev (50.38 N, 30.53 E) carried out over three years during April-September showed worse (R = 0.77) correlation, and a source of ambiguity of such indirect estimation of previtamin D3 concentration is discussed in detail.

In our opinion, the difference in the latitude of Kiev (50.38 N) and Nea Michaniona (40.47 N) together with variable ozone and weather conditions has essential effect on the short wavelength edge of solar UV spectrum that is closely linked to the rate of irreversible photodegradation of previtamin D3 causing rather large scatter in the Kiev data compared with those ones from Greece.

In addition, taking into account the widespread of natural synthesis of vitamin D in biosphere under solar UV irradiation that induces synthesis of vitamin D from its precursor, we have introduced new algorithm for direct calculation of the vitamin D effective irradiance. Based on the First Law of Photochemistry: “Light must be absorbed for photochemistry to occur” and keeping in mind that photobiological effects are initiated by photochemistry, a straightforward procedure for calculation the vitamin D synthetic capacity of sunlight has been developed using solar UV spectra as input data to the reaction model of previtamin D photosynthesis. Performed calculations demostrate critical dependence of previtamin D3 accumulation on stratospheric ozone, season, latitude, and cloudiness.

There are good grounds to believe that direct calculation of the vitamin D synthetic capacity of sunlight using solar spectra together with the photoreaction model is favoured over commonly used calculations based on the in vivo vitamin D action spectrum, especially in view of the fact that the vitamin D3 action spectrum is based only on the work of a single laboratory unlike the erythemic response which was developed and validated in ~20 laboratories.

Comparison of experimental and simulation data conforms to recent findings on Europe’s darker atmosphere in the UV-B and implicates practical certainty of presented algorithm for global mapping of biologically active (antirachitic) solar UV radiation. In our opinion, this algorithm is useful for direct estimation of the vitamin D synthetic capacity of

sunlight and provides a means for introduction of new UV 'D-index' on daily UV forecasts in addition to commonly used erythemal UV index.

Geochemistry and hydrology of a small catchment: fogs as an important part of the wet deposition

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The present paper deals with an importance of wind driven low clouds and fogs on the geochemistry and water balance of small forested watersheds situated in the mountainous headwater regions of the Czech Republic. The importance of the fog and cloud water droplet deposition in seacoast and mountaintop areas has been recognized for a long time. This portion of the wet deposition is rather ephemeral and terrible difficult to measure, but clouds and fogs was proved as an important delivery mechanism for atmospheric particles, gases, and liquid water from the near surface atmosphere onto the forest canopy. This contribution is concerned especially with advected fogs, that are wind-borne such orographic and other clouds that envelop mountain-tops. This type of fog wets vegetation (in harmony with radiation fogs) and unlike radiation fogs, because of the associated winds, can bring large amount of water and dissolved ions to the earth´s surface. The main goals of the present paper are to: (i) introduce the small experimental watersheds established in the headwater regions of the Czech Republic in order to evaluate their water balance and geochemistry; (ii) evaluate the time and space variation of the fog characteristics (especially the duration and frequency of occurrence; liquid water content and horizontal visibility); (iii) assess the water and mass balance of the selected experimental catchments taking into account the input of water and matter delivered to the basin via low clouds and fogs; and (iv) describe new techniques for fog water collection, i.e. ground-level cloud water sampler designs will be introduced. Mountainous ecosystems of the headwater region in the Czech Republic are frequently immersed in wind-driven clouds and this condition is believed to lead to significant deposition of water beyond that measured by incident rain gauges. In order to study the input of water and matter from wind driven low clouds and fogs on the water balance and chemistry of mountainous forested catchments, three experimental watersheds were established: (1) the Liz basin (Sumava Mts. – southern Bohemia; 0,99 km^2, 828 – 1073 m a.s.l., brown podzolic soil, moldanubic crystallinicum, paragneiss, prevailing type of tree: spruce aged up to 120 years); (2) the Uhlirska basin (the Jizerske hory Mts. – northern Bohemia; 1,87 km^2, 774 – 870 m a.s.l., brown podzolic soil, podzol, peat, Variscan igneous rocks of granite massif of the Krkonose-Jizerske hory crystalline complex, biotitic gneiss,prevailing type of tree: spruce aged up to 80 years); (3) the Modry potok basin (the Giant Mts. – north-eastern Bohemia; 2,62 km^2, 1010 – 1554 m a.s.l., ferrous humic podsole, brown podzolic soil, rocks of metamorphic aureole of Variscan granite pluton, mica schist,prevailing type of tree: spruce and dwarf pine 62 % and meadow 38 % of the area). These experimental catchments are situated in the main massifs of the Bohemian border mountains. They differ especially in the level of anthropogenic impacts on vegetation cover. While the Liz catchment represents a relatively healthy productive forest in a clear landscape, the Uhlirska basin is situated in a formerly heavily polluted region of the so-called "Black Triangle". The Modry potok basin in the Giant Mts. represents the original spruce forest in the lower part of the basin and the artic-alpine tundra with dwarf pine covers the upper part above the timberline. Based on the model predictions and on the water balance of the forest canopy the annual occult (deposited from low clouds and fogs) precipitation totals were estimated by the 10 % of the annual falling (rain and snow) precipitation total in the Sumava Mts., by 10 – 15 % in the Jizerske hory Mts., and even more than 20 – 25 % in the Giant Mts. An analysis of a statistical study of fog characteristics since 1960 till the time being was worked out. A fog water chemistry study carried out over the 16-years period proved high acidity of fog water and high values of