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A solid-phase chemical actinometer film for measurement of solar UV penetration into snowpack

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ABSTRACT

A solid-phase actinometer system suitable for measuring 295–400 nm solar light intensity and penetration into snowpack has been developed and field-tested. Snow and atmospheric chemists are concerned with ultraviolet light irradiance as this spectral range has been linked to NO_x and ·OH radical formation within snowpack. The actinometer, prepared as thin films, consists of 2-nitrobenzaldehyde (2NB) dispersed in a polymethylmethacrylate (PMMA) matrix. The concentration of 2NB at the film surface decreases due to ultraviolet light exposure and is quantified using attenuated total reflectance infrared spectroscopy (ATR-IR); either relative or absolute light intensity can be determined. The films are inexpensive, physically robust and can be easily deployed in cold-weather environments that are inhospitable to electronic instrumentation or liquid actinometer systems. Measurements of light penetration into seasonal snowpack near Barrow, Alaska, were made in 2007 and 2008. E-folding depths of 8–26 cm were observed, depending on snow conditions; alternatively, the depth of snow required to attenuate 75% of solar UV-A incident on the snowpack surface was found to range from <5 cm for aged snowpack to 15 cm for snowpacks undergoing annual melting. The variation in penetration depth is dependent on the recent history of the snowpack and is likely to determine the extent of photochemical transformations occurring within the snowpack.

1. Introduction

Snowpack has recently been recognized as an active medium for photochemical processes. Snowpack is a porous non-uniform medium that allows considerable air exchange with the overlying atmosphere and may act as either a sink or source of atmospheric species. Fluxes of photochemically produced species in snowpack are known to perturb the chemistry of the overlying atmospheric boundary layer (Grannas, et al., 2007; Honrath, et al., 1999; Sumner and Shepson, 1999) and it has been proposed that photochemical reactions in snowpack and polar ice may play a significant role in the transformation of persistent, bioaccumulative and toxic substances in these regions (Klan and Holoubek, 2002).

Environmental fluxes of photochemically-generated species and photochemical reaction rates are dependent on the intensity and spectral distribution of incident light. Quantitative studies of solar irradiance and attenuation beneath the surface of snowpacks are necessary in order to assess the likely significance of photochemical reactions that have been examined under laboratory conditions, to determine rates of snowpack photochemical processes from field concentration measurements and as a parameter for incorporating snowpack reactions into models of tropospheric composition. Both direct measurement and modeling approaches have been reported.

Light attenuation within snowpack is a complex process that is dependent on a number of site-specific conditions. Long wavelength radiation tends to be absorbed, whereas visible and ultraviolet radiation is scattered by individual snowgrains. In the top few centimeters of snowpack, incident light may be back-scattered and upwelling radiation may escape (Kuhn and Siogas, 1978; Lee-Taylor and Madronich, 2002; Simpson, et al., 2002). In this near-surface region, the actinic flux within the snowpack is dependent on the incident angle of the radiance and is affected by factors such as the solar zenith angle, the orientation and regularity of the snowpack surface and the extent to which the radiance is already diffuse due to atmospheric scattering. Below the top few centimeters, multiple scattering events leave the radiance with little directional memory. For optically homogenous snowpack, the attenuation of intensity in this region is described by the Bouguer–Lambert law (Barkstrom, 1972):

$$I(d) = I(d')e^{-\kappa(\lambda)\left(d-d\prime\right)} \tag{1}$$

where $I(d)$ and $I(d')$ are the irradiances at depths d and d' and $\kappa(\lambda)$ is the asymptotic flux extinction coefficient at wavelength λ. Previous

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studies of solar attenuation, such as Simpson et al. (2002), have reported the asymptotic *e*-folding depth $\varepsilon(\lambda)$ instead of $\kappa(\lambda)$, where

$$\varepsilon(\lambda) = \frac{1}{\kappa(\lambda)} \qquad (2)$$

which corresponds to the depth of snow that attenuates diffuse light to 1/*e* of its incident intensity. The *e*-folding depth cannot simply be interpreted as the depth at which intensity is 1/*e* of surface intensity, as Eq. (1) only applies below the near-surface boundary, i.e. after the contribution from directly-propagated downwelling radiation becomes negligible. Stratification within the snowpack, which results from multiple snowfall and wind events, melting and refreezing cycles, and snow crystal metamorphism, means that $\varepsilon(\lambda)$ is likely to vary with depth. Additionally, snowpack at some sites may include a significant concentration of optically absorbing material which would reduce $\varepsilon(\lambda)$. Lee-Taylor and Madronich (2002) note that field measurements, interpreted in light of attenuation models, are required to characterize optical penetration of real snowpacks.

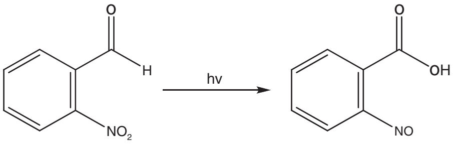
Snow and atmospheric chemists are primarily concerned with fluxes of UV-A (315–400 nm) and UV-B (280–315 nm) light as these are linked to NO_x formation by nitrate photolysis (Qiu, et al., 2002) and ·OH radical formation by peroxide photolysis (Chu and Anastasio, 2005). Some groups have made wavelength-specific measurements of the *e*-folding depth; the asymptotic e-folding depth is independent of wavelength through the visible region but decreases by 25% from 460 to 310 nm (King and Simpson, 2001). Several measurements of UV irradiance in ice (King and Simpson, 2001; Perovich and Govoni, 1991) and snowpack (Beaglehole, et al., 1998; King and Simpson, 2001; King, et al., 2005; Phillips and Simpson, 2005) have been reported and these show good agreement to the results obtained by theoretical radiative transfer models. In light of these studies, it has been proposed that measurements of a small set of parameters – surface irradiance and albedo, snowpack e-folding depth and impurity content – are sufficient to enable calculation of light intensities within the snowpack (Lee-Taylor and Madronich, 2002; Phillips and Simpson, 2005).

Most measurements of UV attenuation and *e*-folding depth have utilized an instrumental approach, where a representative sample is removed from the snowpack for measurement (Beaglehole et al., 1998) or a fiber optic probe is buried in a snowpit with previously excavated surface snow (King and Simpson, 2001) or inserted into existing snowpack (Fisher et al., 2005). Instrumental measurements typically measure the downwelling irradiance incident on the detector only, then scale this measurement to determine the total actinic flux — a reasonable approach, as solar radiation in snowpack is isotropic at depths greater than a few centimeters. These techniques generate a large body of data with detailed time profiles and wavelength dependency, but tend to be costly and require extensive disturbance of the snowpack. Further, the electronic equipment required for field measurements may be vulnerable to the extreme low temperatures encountered in polar regions. For these reasons, it is valuable to consider techniques based on chemical actinometry as an alternative to instrumental measurements.

Actinometers are chemical systems used to determine light exposure, based on measuring the extent of a well-characterized photochemical reaction after timed exposure to a light source. This provides a built-in integration of light exposure over time, and – in the absence of optical filters – integration over wavelength. In order for a photochemical system to be suitable for use as an actinometer, it must absorb light in the spectral region of interest and have a well-defined, wavelength-independent quantum yield across the range. Liquid-phase actinometer systems are widely used when investigating liquid phase photochemical reactions, as an optically transparent reaction vessel can be filled with the actinometer solution and the irradiance of light incident on the vessel measured directly. For snowpack measurements, the total actinic flux, which includes both upwelling and downwelling diffuse light, is measured; this can be advantageous when using the actinometer to determine photon fluxes in a concurrent photochemical experiment. However, most liquid-phase actinometer systems utilize water as the solvent and are unsuitable for use in arctic environments where the temperature routinely drops well below 0 °C.

Liquid-phase actinometer systems suitable for arctic use have been used for measuring the photodissociation rate constant of hydrogen peroxide (Galbavy et al., 2007a) or nitrate (Qiu et al., 2002; Galbavy et al., 2007b) in Greenland snowpack using acetonitrile ($T_f = -43.8$ °C) as the solvent. In these measurements, flame-sealed glass tubes containing an actinometric solution were buried in snowpack and exposed to ambient light for up to 24 h before excavation. In both the hydrogen peroxide actinometer and the nitrate actinometer (which employs a variation of the solar UV actinometer developed by Jankowski et al., 2000), ·OH radicals formed in the primary process are scavenged with benzene, producing phenol which is subsequently quantified in the laboratory by HPLC chromatography. Qiu's original method required sealed tubes of actinometer solution to be transported to the field, deployed, stored for the remainder of the field study and returned to the laboratory for analysis which presented logistical challenges when measurements were made at remote locations. The chemical trapping system is complex and Qiu et al. report that side reactions involving ·OH interaction with the acetonitrile solvent resulted in the underreporting of photolysis rate coefficients when samples are exposed for extended periods. Furthermore, they noted that the quantum yield of the actinometer and the efficiency with which ·OH is trapped were likely to show temperature dependence and identified these as areas for future work. Chu and Anastasio (2003) quantified the temperature dependence of the quantum yield for nitrate photolysis; Galbavy et al. (2007b) conducted a detailed study on the nitrate actinometer, including field measurements, laboratory calibrations of the actinometer solutions to account for competing processes and solvent interactions, and calculations of the predicted photolysis rates based on the quantum yields and absorption cross-sections. Their work demonstrated that the earlier limitations of liquid actinometers in arctic conditions could be successfully overcome. In their most recent publication, Galbavy et al. (2010) reported the successful use of 2-nitrobenzaldehyde (2NB) actinometer solutions in both water and acetonitrile, at temperatures ranging from −20 °C to 30 °C. They confirmed that the molar absorptivity and quantum yield for this reaction were essentially independent of temperature, and that the reaction proceeded efficiently in either solvent. The study also utilized actinometer solutions contained in stoppered quartz tubes and/or water-ice pellets, and found that, while the rate of the photochemical reaction was affected by the nature and geometry of the sample, these methods of exposing the actinometer to solar irradiation were suitable for field use.

An alternative approach, which is complementary to the use of liquid-phase actinometers, is to utilize a solid-phase actinometer system. These are potentially more physically robust and easier to handle in the field than liquid samples. In a recent review (Kuhn et al., 2004), reported actinometer systems are categorized by phase, and the extent to which they have been tested and applied is evaluated. While the majority of developed actinometer systems are solution-based, there are solid-phase actinometers that may be suitable for solar UV measurements in polar regions. The photoisomerization of 2NB to 2-nitrosobenzoic acid (NBA), which occurs similarly either in solution or in the solid phase, appears to meet our requirements.



(3)

This photoisomerization reaction was first noted by Ciamician and Silber (1900), and has been considered many times since (Laimgruber