The importance of considering depth-resolved photochemistry in snow: a radiative-transfer study of NO₂ and OH production in Ny-Ålesund (Svalbard) snowpacks

J.L. FRANCE,¹ M.D. KING,¹ J. LEE-TAYLOR²

¹Department of Earth Sciences, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UK
E-mail: m.king@es.rhul.ac.uk
²National Center for Atmospheric Research, PO Box 3000, Boulder, Colorado 80305, USA

ABSTRACT. Solar visible radiation can penetrate 2–30 cm (e-folding depth) into snowpacks and photo-lyse nitrate anions and hydrogen peroxide contained in the snow. Photolysis rate coefficients, J, for NO₃⁻ and H₂O₂ photolysis are presented for a melting and a fresh snowpack at Ny-Ålesund, Svalbard. Calculations of (a) transfer velocities, υ, and molecular fluxes of gaseous NO₂ from the snowpack and (b) depth-integrated production rates of OH radicals within the snowpack are presented. The results show the importance of considering the depth dependence, i.e. not just the snow surface, when modelling snowpack photochemistry. Neglecting photochemistry under the snow surface can result in an apparent larger molecular flux of NO₂ from NO₃⁻ photolysis than the melting snowpack. However, when the depth-resolved molecular fluxes of NO₂ within the snowpack are calculated, a larger NO₂ flux may be apparent in the melting snowpack than the fresh snowpack. For solar zenith angles of 60°, 70°, and 80°, the modelled molecular fluxes of NO₂ from fresh snowpack are 11.6, 5.6 and 1.7 nmol m⁻² h⁻¹, respectively, and those for melting snowpack are 19.7, 9.1 and 2.9 nmol m⁻² h⁻¹, respectively.

INTRODUCTION

Snowpack hydroxyl radicals, OH, have been implicated in the production of gaseous fluxes from snowpack to the lower atmosphere (e.g. formaldehyde and acetaldehyde (Shepson and others, 1996; Hutterli and others, 1999; Sumner and Shepson, 1999; Couch and others, 2000; Dassau and others, 2002; Grannas and others, 2002; Houdier and others, 2002; Hutterli and others, 2003, 2004; Mabilia and others, 2007) and the fluxes of many other species such as halogens, alkenes, alkyl nitrates, peroxides and organic acids (Couch and others, 2000; Boudries and others, 2002; Dibb and Arsenault, 2002; Grannas and others, 2002; Guimbaud and others, 2002; Frey and others, 2009)). Laboratory studies have demonstrated the formation of OH radicals within snowpack from the photolysis of nitrate (Honrath and others, 2000; Dubowski and others, 2002, 2001, 2002; Chu and Anastasio, 2003; Cotter and others, 2003; Anastasio and others, 2007; Jacobi and Hilker, 2007),

\[
\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-, \quad (1a)
\]

\[
\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}, \quad (1b)
\]

where h is Planck’s constant and \(\nu\) is the frequency of the radiation, and from the photolysis of hydrogen peroxide (Chu and Anastasio, 2005; Jacobi and others, 2006; Anastasio and others, 2007),

\[
\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}. \quad (2)
\]

In the presence of oxygen, formation of OH radicals within snowpack will create a radical-initiated oxidizing medium, allowing oxidation of chemicals in the snowpack. Trace organics in snowpack, suggested as palaeoclimate indicators in ice cores (Grannas and others, 2006), may be altered through photo-produced hydroxyl radical chemistry, and therefore may be unsuitable as palaeoindicators without a correction (Anderson and others, 2008).

Fluxes of gaseous NO₂ and HONO have been observed from snowpacks in Arctic and Antarctic environments (Beine and others, 1997, 1999, 2001, 2002a,b, 2003, 2006, 2008; Jones and others, 2001; Zhou and others, 2001; Honrath and others, 2002; Oncley and others, 2004; Kleffmann, 2007). Gaseous NO₂ is produced in snow through the photolysis of NO₃⁻ (Equation (1a); Honrath and others, 2000), in analogy to the liquid phase reaction (Mack and Bolton, 1999). An overall assessment of snowpack photochemistry is provided by Grannas and others (2007).

In the work discussed here, the 1997 Ny-Ålesund (Svalbard) field measurements by Gerland and others (1999) are used to determine snowpack optical properties, and to calculate NO₂ fluxes from these snowpacks and OH production rates within the snowpacks. Gerland and others (1999) measured the broadband transmission of photo-synthetically active radiation (PAR; 400–700 nm) through snow, and the snow surface spectral albedo at different sites near the Ny-Ålesund base in May and June 1997. The two snowpacks described by Gerland and others (1999) are hereafter described as ‘fresh’ and ‘melting’. Further details of these snowpacks are given in Table 1 and by Gerland and others (1999). We present calculations, with appropriate assumptions, of photolysis rate coefficients of nitrate and hydrogen peroxide photolysis within the snowpack, using the discrete-ordinate radiative transfer code (DISORT) model, TUV-snow (Lee-Taylor and Madronich, 2002). A photolytic rate coefficient, J, for Equations (1a) and (2), respectively, is defined by the kinetic rate equations

\[
\frac{d[\text{NO}_3^-]}{dt} = -J_{1(a)}[\text{NO}_3^-] \quad (3)
\]

and

\[
\frac{d[\text{H}_2\text{O}_2]}{dt} = -J_{2(b)}[\text{H}_2\text{O}_2], \quad (4)
\]

where \(t\) is time. Photolytic rate coefficients may be calculated...
by integrating the product of the chromophore (i.e. nitrate or hydrogen peroxide) absorption cross section, \( \sigma(\lambda, T) \), the chromophore quantum yield, \( \Phi(\lambda, T) \), and the spherical irradiance, \( F(\lambda) \), over the wavelength of the irradiance, \( \lambda \), at a known temperature:

\[
J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda, T) \Phi(\lambda, T) F(\lambda) \, d\lambda.
\]

The reported values of light attenuation and albedo (Gerland and others, 1999) are used to optically characterize the snowpack for the TUV-snow model using a previously described method (e.g. Fisher and others, 2005). The depth-resolved photolysis rate coefficients of nitrate and hydrogen peroxide are then used to calculate the formation rate of OH radicals within the snowpack, and the fluxes of NO\(_2\) from the snowpack. The photolytic rate coefficients of Equations (1) and (2) depend upon the optical properties of the snowpack, described by a scattering and an absorption coefficient. Values for these coefficients may be constrained by observations of albedo, e-folding depth (characteristic distance over which the diffuse irradiance in the snowpack decays to \( 1/e \) or \( 37\% \) of its initial value (King and Simpson, 2001)) and snow density. Measurements of albedo, light transmission and density were recorded by Gerland and others (1999) for fresh and melting snowpacks. The validity of using the TUV-snow DISORT radiative-transfer coding (Lee-Taylor and Madronich, 2002) to describe photochemistry in snow was borne out in experiments by Phillips and Simpson (2005) that showed good agreement between photolysis of a chromophore within laboratory snow and predictions based on the TUV-snow model.

### METHODS

The TUV-snow model (Lee-Taylor and Madronich, 2002) employs an eight-stream pseudo-spherical, discrete-ordinates, radiative-transfer scheme (Stamnes and others, 1988). It allows optical characterization of a snowpack from knowledge of albedo and light transmission into the snowpack, without the need for knowledge of snow grain size. The optical information is used to derive a wavelength-dependent absorption coefficient for absorption by impurities within the snowpack, \( \sigma_{abs} \), and a wavelength-independent scattering coefficient, \( \sigma_{scatt} \). A detailed description of the modelling process to find values for these coefficients is given by Lee-Taylor and Madronich (2002).

The parameters used to derive the absorption cross section, \( \sigma_{abs} \), and scattering cross section, \( \sigma_{scatt} \), for the two snowpacks assumes an under-snow ground albedo of 0.1, no atmospheric aerosol, and stratospheric ozone columns of 325 and 375 DU (Dobson units; daily values for 19 June 1997 (melting snow) and 19 May 1997 (fresh snow), respectively). Ozone column data were taken from the NASA Total Ozone Mapping Spectrometer (TOMS) programme (McPeters and others, 1998). Earth–sun distances were calculated for the dates of the original snowpack measurements and are needed to calculate solar irradiance at the top of the atmosphere. The absorption cross section of ice was taken from Warren and Brandt (2008). Values of e-folding depths are kept constant over the wavelength range 400–700 nm, as only PAR (cumulative radiation over wavelengths from 400 to 700 nm) attenuation is reported by Gerland and others (1999). Spectral albedo data between 350 and 1300 nm are reported by Gerland and others (1999). Values are derived for \( \sigma_{abs}^+ \) and \( \sigma_{scatt}^+ \) cross sections for the two types of snowpack at 400 nm, and the values derived for \( \sigma_{abs}^- \) and \( \sigma_{scatt}^- \) at 400 nm are used to calculate photolysis rate coefficients for Equations (1a) and (2). King and Simpson (2001) show that e-folding depth varies by only \( \sim 9\% \) over the wavelength range 330–400 nm, suggesting that it is reasonable to use values of \( \sigma_{abs}^+ \) and \( \sigma_{scatt}^+ \) at 400 nm. The aqueous ultraviolet (UV) absorption cross section of hydrogen peroxide and nitrate anion decreases rapidly with increasing wavelength in the 320 nm region. The irradiance of incident solar radiation increases rapidly with increasing wavelength in this region. The product of these two functions results in a new function that peaks around 320 nm as shown by Chu and Anastasio (2005, 2008). Using values of \( \sigma_{abs}^+ \) and \( \sigma_{scatt}^- \) at 400 nm to calculate photolysis rate coefficients of nitrate and hydrogen peroxide is also consistent with previous work (King and Simpson, 2001; Lee-Taylor and Madronich, 2002; Fisher and others, 2005; Beine and others, 2006; France and others, 2007).

The TUV-snow model can predict photolysis rate coefficients at any number of depths within snowpacks with a minimum resolution of 1 mm, provided that \( \sigma_{abs}^+ \) and \( \sigma_{scatt}^- \), the snowpack density, \( \rho \), location, time, ozone column depth and sky conditions are known (Lee-Taylor and Madronich, 2002).
In this work, 30 unequally spaced separate snowpack layers, with more thin layers near the snow surface, within a 1 m deep and laterally semi-infinite snowpack slab were used. The layer spacing is the same as used by Lee-Taylor and Madronich (2002). Photolysis rate constants, $J$, are calculated for each snow layer for Equations (1) and (2). Depth-integrated photolysis rate coefficients (also known as transfer velocities), $v_i$, for the production of NO$_2$ ($v_{NO_2}$) and OH ($v_{OH}$) radical from the photolysis of NO$_3^-$ and H$_2$O$_2$ in snow, respectively, are calculated as

$$v_{NO_2} = \int_{z=0}^{z=1} f_{(1a)} \, dz,$$

$$v_{OH} = 2 \int_{z=0}^{z=1} f_{(2)} \, dz,$$

where $f_{(1a)}$ and $f_{(2)}$ are the photolysis rate coefficients for Equations (1a) and (2), respectively, and $z$ is the snowpack depth with $z=1$ m the snowpack surface and $z=0$ m the snowpack interface with the ground.

Gerland and others (1999) reported snow thicknesses for some of their melting-snow pits of 0.48 and 0.78 m where PAR transmission through the snowpack was measured. For modelling in this work, we use a 1 m thick snowpack to ensure an optically semi-infinite snowpack (Lee-Taylor and Madronich, 2002). The minimum snowpack depth to ensure an optically semi-infinite snowpack was discussed by Gerland and others (1999) and suggested from a review of literature to be 50 cm for the snowpacks studied in this work. The issue of minimum depth for semi-infinite snowpack has also been investigated by France (2008) who found the molecular flux (and depth-integrated production rate) from Equation (2) was independent of snowpack depth provided the snowpack is thicker than three e-folding depths, i.e. -0.3 m for the melting snowpack (and 0.18 m for the fresh snowpack). Thus, whether the snowpack thickness is 0.3, 0.48, 0.78 or 1 m makes a negligible (<3%) difference to the flux of material from the snowpack. The irradiance of light in the snowpack decays exponentially with depth below the first few cm. For melting-snowpack thicknesses less than 0.3 m, the albedo of the ground underlying the snowpack will become significant in determining snow surface albedo. Melting snowpacks less than 0.3 m thick are not considered here, as the main aim is to show the importance of considering photochemistry at depth within the snowpack.

For calculating photolysis rate coefficients (Equation (5)), the absorption cross section for hydrogen peroxide was taken from Chu and Anastasio (2005), and the nitrate absorption cross section from Burley and Johnston (1992), for consistency with our previous studies (Simpson and others 2002; Fisher and others 2005; France and others 2007; Beine and others 2008). The temperature-dependent quantum yields used to calculate nitrate and hydrogen peroxide photolysis rate coefficients are taken from Chu and Anastasio (2003, 2005, respectively). The snowpack modelling in this study uses snowpack temperatures from Gerland and others (1999) (Table 1).

The predicted molecular flux of NO$_2$, $F_{NO_2}$ (NO$_2$), from the snowpack to the atmosphere, owing to nitrate photolysis within the snowpacks, is

$$F_{NO_2} (NO_2) = | NO_3^- | v_{NO_2} = | NO_3^- | \int_{z=0}^{z=1} f_{(1a)} \, dz,$$

assuming that all the NO$_2$ formed from the photolytic reaction (Equation (1)) can escape the snowpack. Depth-integrated production rates of OH radicals are calculated for Equations (2) and (1), respectively:

$$F_{H_2O_2} (OH) = [H_2O_2] v_{OH} = [H_2O_2] \int_{z=0}^{z=1} f_{(2)} \, dz,$$

$$F_{NO_3^-} (OH) = [NO_3^-] v_{NO_3^-} = [NO_3^-] \int_{z=0}^{z=1} f_{(1a)} \, dz.$$
of H$_2$O$_2$ from deposition following gas-phase generation in the atmosphere, whereas nitrate is associated with precipitation and deposition. Surface snow concentrations of H$_2$O$_2$ in snow vary seasonally, with large values in spring and small values in winter. Seasonal variation of the concentration of H$_2$O$_2$ in surface snow results in a depth dependence of H$_2$O$_2$ concentrations. Here a value of 4 nmol cm$^{-3}$ in snow (invariant with depth) is considered, and later in the discussion the small effect of a concentration–depth dependence on molecular fluxes out of the snowpack.

The molecular fluxes (or depth-integrated production rates), calculated by Equations (8–10), are linearly proportional to the snowpack concentration of nitrate and hydrogen peroxide. Thus, the reader can adjust the molecular fluxes reported in this paper for their values of the concentration of nitrate or hydrogen peroxide in the snowpack by simply dividing the molecular flux (or depth-integrated production rate) by the concentration of nitrate or hydrogen peroxide used here and multiplying by preferred values of concentration of nitrate or hydrogen peroxide in their snowpack.

RESULTS

The values of scattering and absorption coefficients (Table 1) are within the range of other studies (e.g., $\sigma_{\text{abs}} = 0–8$ (Lee-Taylor and Madronich, 2002), 4.3–37 (Beine and others, 2006) and 0.7–1 (Fisher and others, 2005); and $\sigma_{\text{scatt}} = 1.1–30$ (Lee-Taylor and Madronich, 2002), 1–6 (Beine and others, 2006) and 1–5 (Fisher and others, 2005)). The fresh Ny-Ålesund snowpack is optically most similar to Arctic spring wind-blown snowpack (King and Simpson, 2001), and the melting Ny-Ålesund snowpack is optically transitional between coastal maritime Antarctic wind-blown (Beine and others, 2006) and Arctic summer melting snowpack (Grenfell and Maykut, 1977).

Figures 1 and 2 show surface and depth-integrated photolysis rate coefficients, $J$, and transfer velocities, $v$, for Equations (1a) and (2) versus solar zenith angles 0–90° for both snowpack types at Ny-Ålesund based on the assumptions discussed. In Figure 1, the surface photolysis rate coefficients are larger for the fresh snow than for the melting snow, but in Figure 2 the transfer velocities are larger for the melting snow than for the fresh snow. Using the surface photolysis rate coefficients (Fig. 1) instead of the depth-integrated photolysis rate coefficients (Fig. 2) can lead to errors in calculation of the fluxes of NO$_2$ from the snowpack. Considering only the surface photolysis rate coefficients to calculate NO$_2$ fluxes will lead to the false conclusion that the fresh Ny-Ålesund snowfall will produce a larger flux than the melting snowpack. The authors consider this issue a result that demonstrates the importance of modelling photolysis rate coefficients for a whole snowpack rather than considering just the surface snow layer. A similar argument can be constructed for the depth-integrated production rates of OH radicals.
Depth-integrated production rates of OH radicals from the photolysis of NO$_3$/$CO$ and H$_2$O$_2$ are shown in Figure 3. Hydroxy radical production from H$_2$O$_2$ photolysis is over 100 times larger than from NO$_3$/$CO$ photolysis, as has been shown by Chu and Anastasio (2005) for surface OH production and by France and others (2007) for depth-integrated OH production rates at other snowpack sites. The results plotted in Figure 3 show that depth-integrated OH production rates are larger within the melting snowpack than within the fresh snowpack.

The molecular fluxes of gaseous NO$_2$ from melting and fresh snowpack at Ny-Ålesund for solar zenith angles of 30–90° solar zenith angles are shown in Figure 4. For solar zenith angles of 60°, 70° and 80°, the modelled fluxes of NO$_2$ from the fresh snowpack are 11.6, 5.6 and 1.7 nmol m$^{-2}$ h$^{-1}$, respectively, while for the melting snowpack they are 19.7, 9.1 and 2.9 nmol m$^{-2}$ h$^{-1}$, respectively.

**DISCUSSION**

For the two snowpacks considered here, the predicted fluxes of NO$_2$ from the snowpack to the atmosphere are comparable with values of NO$_x$ observed in other snowpack studies (Table 2). Maximum fluxes of NO$_x$ above the snowpack have been measured to be ~40 nmol m$^{-2}$ h$^{-1}$ at Alert, Canada (Beine and others, 2002a,b), 30 nmol m$^{-2}$ h$^{-1}$ at South Pole (Oncley and others, 2004) and 13 nmol m$^{-2}$ h$^{-1}$ at Neumayer, Antarctica (Wolff and others, 2002). The maximum solar zenith angle was 68° for the South Pole campaign and approximately 60° for the Neumayer and Alert studies.

The modelled fluxes of NO$_2$ leaving the snowpack using the TUV-snow model for the fresh and melting Ny-Ålesund snowpacks at a solar zenith angle of 60° are 11.6 and 19.7 nmol m$^{-2}$ h$^{-1}$ respectively. Thus, the magnitude of modelled NO$_x$ fluxes above Ny-Ålesund snowpack is consistent with previous measurements at other sites. The actual molecular flux of NO$_2$ from the snowpack may be affected by secondary processes, such as photolysis of NO$_2$ before venting from the snowpack or snow microphysics preventing the release of NO$_2$ from the snowpack. Boxe and others (2003, 2005, 2006) showed that emission rates of gaseous NO$_2$ from irradiated ice (containing nitrate anions) increase with increasing ice temperature. Gaseous emissions of NO$_2$ are partially controlled by mass transfer, and hence the morphology, of polycrystalline ice (Boxe and others, 2006). Laboratory experiments by Boxe and others (2003, 2005) showed that photolysis of nitrate in polycrystalline ice produces large NO$_2$ emissions above an ice temperature of ~8°C. Boxe and others (2006) could not reproduce the [NO$_2$]/[NO] ratio in field measurement studies, but Boxe and others (2003, 2005, 2006) did demonstrate that there may be some loss of photogenerated NO$_2$ in snowpack. NO$_2$ loss in snowpack is minimal at higher ice temperatures. Both snowpacks considered here have temperatures greater than ~8°C, and the comparative nature of this work means the loss of photogenerated NO$_2$ is not critical for the main result. The availability in the Arctic environment of NO$_x$ from snowpack emissions has been shown to have a substantial impact upon the oxidative capacity of the lower troposphere, especially in the spring (Morin and others, 2008).

Previous work has shown that UV radiation penetrates deeper into warmer, wetter snows with larger grain sizes than into colder, drier, smaller-grained snowpacks, so wetter snowpacks have larger photolysis rate coefficients at depth.
The melting snowpack has a higher measured liquid water content than the fresh snowpack (Gerland and others, 1999), and as expected has a lower value of \( C_27 \) than the fresh snowpack, as liquid water effectively increases snow grain size (Warren, 1982). The measured electrical conductivities of the fresh and melting snowpacks from Ny-Ålesund are similar within the top 10 cm of snowpack (Gerland and others, 1999). Photochemistry occurs mainly in the top 10 cm of the snowpack, so it is speculated that ionic chemical concentrations in the two snowpacks are similar, supporting the assumption that the concentrations of nitrate and hydrogen peroxide have similar values in each snowpack. The assumption that the concentrations of nitrogen and hydrogen peroxide have similar values in each snowpack is not critical here, as our aim is to demonstrate the effect of considering photolysis at depth in the snowpack. The large difference in absorption between the two snowpacks is probably due to depositional accumulation of coloured, non-ionic chemicals (e.g. black carbon or humic material) as the snowpack ages. The older, melting snowpack, having had longer to accumulate such absorbers, will thus have a higher value of \( \sigma_{\text{abs}} \). The presence of absorbers in snowpack has been shown to cause a climatic feedback loop, leading to further melting of the snowpack due to lowering of the surface albedo, and thus increasing the absorption of solar radiation (Qian and others, 2009). The TUV-snow model uses a monochromatic black carbon absorber to determine the absorption coefficient, which is a good first approximation to Svalbard soil with its high coal content (France, 2008).

An interesting result of this work is the comparison between surface photolysis rate coefficients and depth-integrated photolysis rate coefficients. The origin of the larger depth-integrated photolysis rate coefficients in the melting snow, and of the larger surface photolysis rate coefficients in the fresh snow, is shown in Figure 5. The large value of albedo and the shorter e-folding depth in the fresh snow give larger values of surface photolysis rate coefficients, but little penetration into the snowpack compared to the melting snowpack. The photolysis rate coefficient--depth profiles for the two snowpacks are equal at approximately 2 cm (nitrate) and 5 cm (hydrogen peroxide) depth in the snowpack. The value of the fresh-snowpack photolysis rate coefficient decreases faster with depth than the melting-snowpack photolytic rate constant. Integration of the photolysis rate coefficient over the depth for the snowpacks results in a larger flux of the melting snowpack than of the fresh snowpack. Therefore, snowpack photolytic emission fluxes should always be calculated using depth-integrated photolysis rate coefficients, not just surface photolysis rate coefficients.

Nitrate and hydrogen peroxide concentrations vary with season and depth within the snowpack. Here the concentration–depth profile of nitrate and hydrogen peroxide is considered constant. France and others (2007) undertook a sensitivity study of the effect of three different concentration–depth profiles on the calculated molecular fluxes (and depth-integrated production rates) using the same model used here. They showed that for hydrogen peroxide photolysis the differences in calculated depth-integrated production rates of hydroxyl radical were negligible when comparing (1) a concentration–depth profile of hydrogen peroxide from a field study, (2) a constant surface concentration of hydrogen peroxide, invariant with depth, and (3) a constant concentration of hydrogen peroxide averaged over the equivalent of two e-folding depths, but invariant with depth. They repeated the calculation for nitrate photolysis using three comparable concentration–depth profiles and noted that agreement between the three calculations was within a factor of two, i.e. a much smaller uncertainty than the natural variation in concentrations of nitrate in surface snow at Ny-Ålesund, as reported by Beine and others (2003). The depth dependence of the nitrate or hydrogen peroxide has little effect on the flux (or depth-integrated production rate) because the concentration of hydrogen peroxide or nitrate may only decrease by a factor of four over the depth of a snow pit, whereas the spherical solar irradiance will decrease exponentially with depth (a few cm below the surface).

To test the sensitivity of depth-integrated production rates to the initial values of albedo and e-folding depth, the depth-integrated production rate of OH radicals in the melting snowpack was recalculated using 90% of the original albedo and 110% of the original e-folding values to generate a lower value of \( C_27 \) and \( \sigma_{\text{abs}} \), and 110% of the original albedo and 90% of the original e-folding values to generate upper values of \( \sigma_{\text{abs}} \) and \( \sigma_{\text{scat}} \). These newly derived values were used to calculate upper- and lower-limit depth-integrated rates for OH radical production from \( \text{NO}_x \) and \( \text{H}_2\text{O}_2 \) photolysis. The resulting uncertainty is insensitive to solar zenith angle, and

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<tr>
<th></th>
<th>Ny-Ålesund, Svalbard (modelled, SZA 60°)</th>
<th>Neumayer, Antarctic (Jones and others, 2000)</th>
<th>Summit, Greenland (Hornath and others, 2002)</th>
<th>South Pole (Oncley and others, 2004)</th>
<th>Alert, Canada (Beine and others, 2002a,b)</th>
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<tr>
<td>Melting</td>
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<td>Fresh</td>
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<tr>
<td>( F_{\text{NO}_2} ) ((\text{nmol m}^{-2} \text{h}^{-1}))</td>
<td>19.7</td>
<td>11.6</td>
<td>13</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>( [\text{NO}_2^-] ) ((\text{nmol cm}^{-3}))</td>
<td>1</td>
<td>1</td>
<td>0.65*</td>
<td>4</td>
<td>4†</td>
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<tr>
<td>Maximum SZA during campaign (°)</td>
<td>56</td>
<td>49</td>
<td>68</td>
<td>66</td>
<td></td>
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*Wolff and others (2002); †Dibb and others (1998); ‡Dibb and others (2004); Hutterli and others (2004); †Simpson and others (2002).
equal to ±8%. Thus, fortuitously, a 10% error on both albedo and e-folding depth results in approximately a 10% error in depth-integrated production rates (fluxes).

CONCLUSIONS

Calculated depth-resolved photolysis rate coefficients of NO₃⁻ anions and H₂O₂, along with depth-integrated OH production rates and molecular fluxes of NO₂, for melting and fresh snowpacks at Ny-Ålesund show the importance of using a depth-resolved method to model photolysis rate coefficients in snowpack, rather than considering only the surface photolysis rate coefficients. The depth-integrated photolysis rate coefficients are greater for melting snow than for fresh snow. This study shows the importance of always considering the photochemistry of the total snowpack, not just of the snow surface.

Modelled fluxes from the two snowpacks, of NO₂ due to NO₃⁻ photolysis, at appropriate solar zenith angles are of the same order of magnitude as NOX fluxes measured at other snowpack sites. Hydroxyl radical production from both snowpacks is dominated by H₂O₂ photolysis.

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