

***Interactive comment on* “Small HONO emissions from snow surfaces at Browning Pass, Antarctica” by H. J. Beine et al.**

H. J. Beine et al.

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Anonymous Referee #1

Authors presented measurement results of HONO flux in Antarctica, which was surprisingly small from sunlight-exposed snowpack containing significant levels of nitrate and mostly at acidic pH. Interpretations have been attempted by considering the forms of nitrate in different types of snowpack and the availability of organics that would further react with NO₂, the assumed primary product of nitrate photolysis. In the aged snowpack, reaction and neutralization of produced HONO by sea salt components may, at least in part, explain the lack of observable HONO flux. However, the interpretation based on NO₂-photosensitized organic interaction for the fresh snow is highly speculative and is not consistent with some laboratory and field observations. In fact, the

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production of HONO from nitric acid/nitrate photolysis does not require the presence of organic compounds (e.g., Zhou et al., 2003; Ramazan et al., 2004). Furthermore, relatively high HONO concentrations were observed at South Pole (Dibb et al., 2004), where organic contents were expected to be low. The lack of satisfactory explanation for the field observations really calls for laboratory investigations into HONO formation mechanisms in snowpack, as suggested by the authors in the last sentence.

The Anonymous Referee #2 has done a great job in pointing out many mistakes and inconsistencies that I found. There is no need to repeat the specific comments.

Anonymous Referee #2

General comments:

The paper describes first selective gas phase measurements of nitrous acid in Antarctica with a highly sensitive instrument. Gradient measurements show very low fluxes of HONO from the snow surface, although the conditions are favorable for the photochemical formation, based on the generally accepted photolysis of nitrate/HNO₃ in the snow. Thus, these gradient measurements clearly demonstrate that the mechanism of HONO formation from snow surfaces is clearly not at all properly understood, which should be the major outcome of the present study.

The authors try to explain the different observations (i.e. no HONO formation on aged and fresh snow, and some HONO production after the surface was windblown) by considerations of the state of nitrate in snow and by an alternative photochemical HONO formation pathway, which was proposed in a recent laboratory study. However, the discussion is all of a highly speculative nature. For example, it is not at all clear why HONO formation is not observed for fresh snow. The authors claim that nitric acid is adsorbed on fresh snow, however, especially for adsorbed nitric acid photochemical HONO formation would be expected based on the observations from laboratory studies. In addition, the different proposed states of nitrate in snow seem to be very speculative (see special comments). Thus, the discussion should mainly highlight the

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existing lack of knowledge in the formation mechanism.

Response to the general issues raised by the reviewers:

Clearly, a thorough review of the literature can only lead to the conclusion that the processes producing HONO from surfaces in the atmosphere are little understood. As noted by both reviewers, this paper then does not pretend to solve the aspects relevant to ice, but rather shows that the picture may in fact be even more complex than currently thought, and attempts to propose ideas that, if implemented, may help improve our understanding of the mechanisms and our ability to predict HONO production rates from nitrate photolysis in snow.

The main idea that we put forward is that the location, or state, of nitrate in snow is crucial to its reactivity. This is supported by laboratory data reported in the literature. For example, Dubowski et al. (2002) obtain a HONO quantum yield for nitrate photolysis at 313 nm and 263 K of 0.0015. This was obtained by studying hard-pressed ice pellets (density = 0.9 !) made from 10 mM NaNO₃ solution flash-frozen in liquid N₂. It is legitimate to argue that this is not a good mimic of natural snow, both regarding the concentration of nitrate and the physical state of the medium, and it is legitimate to wonder whether such a quantum yield may be applied to natural snow. Dubowski et al. themselves compare their value to another one of the same process obtained using submillimeter ice films sprayed with KNO₃ solution, which was 0.0048. They conclude that the experimental protocol and the morphology of the system should influence the value of the quantum yield. Obviously, if the experimental protocol influences the value, a different value should be obtained for natural samples, and different natural samples having different morphologies and different locations/chemical states of nitrate should show different quantum yield values. We are performing calculations of expected HONO yields from the values of Dubowski et al. simply because they are the only ones available. The discrepancy between calculations and experiments serves to illustrate that HONO production in snow may come from processes different from those in a hard pressed ice pellet made from flash frozen highly concentrated solutions.

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Ramazan et al., and Zhou et al. observe HONO production from nitrate photolysis on surfaces in the presence of adsorbed water vapor. One characteristic of their systems is that nitrate is adsorbed on the surface from the gas phase, and is thus readily available on the surface, and reaction products can readily desorb to the atmosphere.

From our data, we argue that in aged snow, even if nitrate is available on the surface, HONO, if formed, may not be able to be easily released to the atmosphere, either because of cage effects or of secondary reactions. This suggestion, although clearly speculative, is reasonable, and does not contradict the observations and interpretations of Dubowski et al., Ramazan et al., and Zhou et al. that explicitly or implicitly imply that the physical and chemical environment of nitrate is important. The interaction between nitrate and other ions in aged snows is discussed in greater detail in a further paragraph below (discussion of 4.4).

We also argue that in fresh snow, the absence of organics may explain the lack of HONO production. That organics can indeed very efficiently produce HONO from NO₂ (that could come from nitrate photolysis) is gaining support. A recent study (Stemmler et al., 2006, Nature, 440, 195) shows that natural humid acids, presumably close in structure to compounds found in coastal Antarctica, can lead to strong photo-enhanced emissions of HONO when exposed to NO₂. This supplements the work of George et al. (2005) on model molecules and adds considerable credibility to the necessity of organics to produce HONO.

The reviewer mentions that HNO₃ is adsorbed in fresh snow and thus should lend itself to processes similar to those observed by Ramazan et al. and Zhou et al. that led to significant HONO production. This is a legitimate remark. However, HNO₃ can certainly be adsorbed, but we also say that it can be dissolved in the ice lattice, where it easily forms a solid solution (Thibert and Domine, 1998). If, where the snow formed, gas phase HNO₃ was 30 ppt and T=-40°C, then dissolved HNO₃ would be about 3 μM, the value typically measured for fresh snow. Hence we conclude that nitrate in fresh snow may very well not have been readily available for surface reaction, but rather

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trapped in the ice lattice where it would be unreactive. Thus the high reactivity of nitrate on surfaces observed by others may not be applicable to our system.

In summary, we conclude that our mechanism is indeed speculative, but the strong point we wish to make is that HONO production from nitrate does strongly depend on its physical (surface or volume) and chemical (ice or salt) environment. Therefore, results obtained in laboratory ices that are incredibly different from natural snow, or on glass surfaces may simply be inapplicable to our natural system. We have attempted to understand the physical and chemical environment of nitrate in snow, because we believe that there lays the key to understand our measurements. Of course, here we do not control all the variables and we do acknowledge that there is a large degree of speculation in our discussion. We propose to add or explain further the above points in the discussion of the revised version. And we will suggest – in the conclusions - that further experiments where the nitrate environment is controlled would be of crucial value to clarify these issues.

Special comments:

Abstract, page 616, lines 10-12:

This sentence is not clear, see discussion above and results on HONO formation from recent laboratory studies on glass surfaces (Zhou et al., 2002, 2003, Ramazan et al., 2004).

“In fresh snow, the NO₃⁻ ion is probably present as dissolved or adsorbed HNO₃ and yet, no HONO emissions were observed.”

We wholeheartedly share the reviewer’s concern; this is exactly the matter at hand: The individual pieces of information from field, lab and model experiments do not combine to a complete picture. This sentence in the abstract is intended to point out this discrepancy, and we therefore decided to retain it as is. (see general reply above).

Chapter 2.1, page 618, lines 1 + 5: If the container is 20 m away from the measurement

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site, the sampling lines should be at least 20 m (here, 15 m given...).

A couple of typos were corrected in this section:

We sampled HONO at 25 and 150 cm above the snow surface, using two independent 2.5 cm (I.D.) light-shielded inlet lines of 20 m length at flow rates of 13 L min⁻¹ to feed the sample into the container where the instrument was placed. The samples were taken from this flow through ca. 50 cm of 1.58 mm (I.D.) tubing at 3 L min⁻¹. The total residence time in the inlet lines was ca. 45 s. Both inlet lines were identical, and no null-gradients between the two inlets were detected.

Chapter 2.1, page 618, line 12: Please specify the pH of the sampling solution, since interferences are known for instruments, which sample HONO under alkaline conditions (see for example: Spindler, et al., 2003, Atmos. Environ., 37, 2643-2662.).

The information on the pH value was added:

“... briefly; gaseous HONO was trapped quantitatively in a 10-turn glass coil sampler using 1-mM phosphate buffer (pH 7).”

*Possible interferences to our HONO method are discussed by Amoroso et al., Atmospheric Environment, 40, 1949-1956, **2005***

Since the reviewer cites Spindler's paper, he is concerned about possible interferences from SO₂ and NO₂;



*Mixing ratios for SO₂ and NO₂ in Antarctica (near Terra Nova Bay [Ianniello, et al., Gradient Measurements of Inorganic Acids and Ions Above a Snow Surface at Terra Nova Bay, Antarctica . . . , Eos Trans. AGU, 81(48), Fall Meet. Suppl., 169, **2000**.]) are 50 pptv and up to 20 pptv, respectively, during springtime. Using Spindler's equations (at positive temperatures, since our wet sampling system was indoors) at the two pH*

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values;

at pH 10

$$K20(T) = (1.06 \pm 0.90) \exp[-(2833 \pm 2000) K/T]$$

and at pH 4.5

$$K22(T) = (1.5 \pm 1.8) \times 10^6 \exp[(950 \pm 300) K/T]$$

we can calculate the maximum concentration of the [NO₂-SO₃] complex in solution as 1.8 10⁻²⁰ [mol/L] at pH 10 and 1.6 10⁻¹⁴ [mol/L] at pH 4.5.

Our sampling system works at pH 7; hence the concentration of the complex might be estimated as somewhere on the order of 10⁻¹⁷ [mol/L]. Assuming, however, a theoretical “worst case”, the liquid concentration of the complex in the sampling solution was 10⁻¹⁴ [mol/L], and all of it would produce NO₂⁻, and thus interfere with our measurements. Typical liquid NO₂⁻ concentrations in our sampling system were on the order of 10⁻⁹ [mol/L], this interference was thus ca. 5 orders of magnitude smaller, and presented no concern.

Chapter 2.1, page 618, line 14: Change UV-vis absorption to vis absorption, since the used dye absorbs light around 540 nm.

Changed in the ms.

Chapter 2.1, page 619, lines 2-8: The calculation of the minimum detectable difference in the HONO concentration between the two different heights should be calculated individually, since this value can be significantly higher than the detection limit of the instrument of 0.5 ppt. For example, when the difference between two values around 3 ppt (see Figure 2a) is considered, the minimum detectable difference in the HONO concentration will be higher than 1 ppt. This will probably also affect the calculation of the minimum detectable fluxes (see Figure 2c).

Surely there are many different ways that a minimum detectable difference between

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the two measurements may be defined; the reviewer would apparently like to see a definition based on the %-precision of each individual measurement at the two heights.

We are, however, not convinced that this would clarify our analysis and help our interpretation.

First; most commonly a detection limit is defined as some measure of the precision (e.g. 3σ) at the blank level (\pm an offset taking accuracy into account). The same reasoning holds for the difference between the two individual measurements; it can be considered 'detected' when it is larger than the uncertainty of the blank. Most of our HONO mixing ratios were around 1 pmol/mol; we defined a practical method detection limit for their difference.

Second, our analysis in Table 1 would become totally illegible if we applied a variable detection limit for the fluxes.

Chapter 2.2, page 620, line 5: It should be: King and Simpson, 2001 (see list of references).

Changed in the ms.

Chapter 3.1, page 622, lines 1-2: Can the authors estimate the relative importance of the sources of NO (nitrite photolysis vs. NO₂ photolysis)? In contrast to the statement by the authors, most of the NO might be formed by the photolysis of NO₂, because of the much higher quantum yield for the NO₂ channel (R1) compared to the nitrite channel (R2) in the photolysis of nitrate and the short photolytic lifetime of NO₂.

The values of the quantum yield for R1 and R2 used in this study are

R1, $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$, $\Phi = 0.003\text{-}0.004$ (see figure 5 in the paper) based on temperature-dependent quantum yield from Chu and Anastasio (2003)

R2 $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}$, $\Phi = 0.0015$ Dubowski et al. (2002), note earlier Dubowski work recorded a value of 0.0045 for this channel.

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The photolysis rate $J(\text{NO}_3^-)$ depends on the product of the nitrate absorption cross-section, σ , the quantum yield, Φ , and the actinic flux, F , integrated over wavelength. For channels R1 and R2 the cross-section and actinic flux are the same, only the wavelength invariant quantum yield is different for the two channels. Thus $J(\text{NO}_3^-)$ will appear to vary linearly with the value of quantum yield chosen.

There is not a big difference between the two channels, i.e. a factor of 2-3. Note that the uncertainty in the quantum yield for channel R2 is about a factor of 3. Thus if channel 1 were 100% efficient in producing NO by the photolysis of nitrate, followed by photolysis of NO_2 , then the channel R1 may be up to a factor of 2 faster than channel 1.

The referee's suggestion that the NO needed for mechanism 2 may come from the photolysis of NO_2 , which is produced by R1, is an interesting idea. However, the authors speculate that R2 may be more important in producing NO than R1 for the following reasons

1) If production of NO from snow and ice were efficient by initially following channel R1 then there would be little or no $\text{NO}_2(\text{g})$ from snow or ice. Laboratory and field experiments suggest that the photolysis of nitrate in snow and ice produces NO_2 . If this NO_2 were efficiently photolyzed to produce NO then there would be no measurable NO_2 .

2) Mechanism 2 in the original text suggests that OH and NO radicals recombine in "solution". The photolysis of nitrite produces NO and O^- in close proximity (probably in some sort of solvent cage of water molecules). The O^- radical anion may rapidly react with the abundant water to produce the OH radical and hydroxide anion. Thus the photolysis of nitrite may produce OH and NO radicals in close proximity, possibly in a solvent cage, and this may favor rapid recombination. In contrast, the NO_2 photo-produced from R1 has a photolytic lifetime of about 10^2 s in the snowpack at Browning Pass ($\text{SZA}=70^\circ$), i.e. time to diffuse away from its solvent cage where a hydroxyl radical

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may be formed from the O^- radical anion formed in R1.

To conclude the referee's suggestion is interesting, but would not produce a vastly faster photolysis rate for formation of NO. Controlled laboratory experiments, possibly with isotopic labeling, are needed to confirm or deny these suggestions.

Chapter 3.1, page 622, lines 15-21: In contrast to the statement by the authors, the estimated HONO production (using the quantum yield for (R2) from the study of Dubowski et al.) might not represent the upper limit, if mechanism 3) is significant. In this case, a significant fraction of the NO₂ formed by reaction (R1), might be converted into HONO.

The referee is quite correct, But there is a presently a lack of photophysical and organic chromophore abundance data with which to estimate a flux of HONO for mechanism 3. The paragraph was extended;

“Thus, we consider the photolysis of nitrate to produce nitrogen dioxide as a measure of snowpack photochemistry, and photolysis of nitrate to produce nitrite as an estimation of the upper limit of HONO production. If mechanism 3 is significant, however, a fraction of NO₂ formed in reaction (1) might be converted to HONO. A flux for that case, however, cannot presently be estimated because of the lack of photo-physical and chromophore abundance data.”

Chapter 3.1, page 622, lines 8-9: In the study of George et al., HONO formation on bulk substrates was studied (it was not an aerosol study).

The sentence was corrected.

Chapter 3.1, page 622, line 14: Mechanism 1) does not require nitrogen oxide, since HONO is formed by the direct photolysis of nitrate followed by the protonation of nitrite.

The referee may have misunderstood the line “These mechanism (1-3) all require nitrogen oxides and the sources of these nitrogen oxides is thought to be the photolysis of nitrate”. Mechanism 1 talks about the photolysis of aqueous phase nitrite, NO₂⁻. Chemically, nitrite is an oxide of nitrogen.

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Chapter 3.2, page 623, line 10: It should be: Chu and Anastasio (2003), see list of References.

Changed in the ms.

Chapter 4, Figure 2: In Figure 2, the total field campaign is shown and from Figure 2c, the nearly nonexistent HONO fluxes become obvious. However, when looking at Figure 2a more closely, a clear diurnal variation of the HONO concentration is discernible (see for example days 325-330). Thus, it would be helpful to show the concentrations of HONO and the corresponding irradiation in more detail for a shorter period. From such a figure a correlation of HONO with the irradiation is expected (compare Figures 2 and 5). This would demonstrate the photochemical sources of HONO, which should be discussed in the paper. For example, could this diurnal variation be explained by a gas phase source, if no fluxes from the snow surface are observed?

We agree with the reviewer that it is important to show that there actually is a relationship between the observed HONO mixing ratios and the incoming irradiance. The following figure shows our data for the period that the reviewer suggest; DOY 325 – 330.

See the figure at

<http://www.oasishome.net/docs/acpd-2005-0380-reply-figure1.pdf>

Figure 1. *Detail; timeseries of irradiance, HONO mixing ratios (down, up), and Δ_{HONO} for DOY 325-330.*

A diurnal noon time maximum, correlated with the insolation can be discerned in the HONO mixing ratios at the two heights with some goodwill. The maximum diurnal variation observed here is 1 pmol/mol. Our methods, however, are not accurate enough to see whether their difference (and hence, the fluxes) are correlated as well in the example shown..

Chapter 4.1, page 624, lines 8-9: In the study of Dibb et al. mixing ratios of up to 70 ppt

(not 30 ppt) were observed (probably caused by the non-selective sampling method, i.e. mist chamber).

The value was corrected.

Chapter 4.4, pages 626-627: The discussion about the origin of nitrate in snow is not clear. For example, in Figure 4a an excellent correlation of NO_3^- and Na^+ with no significant intercept is observed for aged snow, which is explained by the reaction of nitric acid with existing sea salt in snow. However, this can only explain the excellent correlation, if the ratio of deposited sea salt to nitric acid is almost constant and independent of time, i.e. if sea salt and nitric acid have a common origin. Otherwise, there should be a significant lower correlation or a negative intercept in Figure 4a, since the concentration of Na^+ is much higher than that of nitrate (only a small portion of the existing sea salt is replaced by nitric acid in the snow). In addition, from the lower correlation of nitrate with Na^+ in Figure 4b the presence of adsorbed HNO_3 in fresh snow was proposed. However, the lower correlation is most probably simply caused by the lower ion concentration for fresh snow. The correlation would also be significantly lower for aged snow, if only the low concentration data were plotted in Figure 4a. In addition, since the slopes are very similar for aged and fresh snow (0.05 vs. 0.08) the state of nitrate is probably not as clear as proposed by the authors in this section.

Only the main features of snow chemistry relevant to HONO emissions are mentioned in this paper. The numerous chemical data deserve a separate paper with much more detailed discussions. The legitimate questions brought up by the reviewer can be briefly addressed here, however.

First of all, let us assume that during our campaign, the processes generating sea salt aerosol and transporting them to our site remain essentially constant. Then sea salt at our site will have a constant size distribution. Between production and deposition, sea salt will undergo surface attack by HNO_3 , producing NaNO_3 , and resulting in constant Na^+ and NO_3^- fluxes to the snow. Of course, conditions will vary as sea spray intensity

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will vary, and wind speed and direction will vary. But the $\text{Na}^+/\text{NO}_3^-$ ratio will depend on the surface to volume ratio of the aerosol (i.e. on its size distribution) and on the rate of attack of HNO_3 . This mechanism implies that:

We do expect a zero intercept. A negative intercept would mean that some sea salt could reach our site before being attacked by HNO_3 . This is not possible as there is a finite, non-zero transport site.

If we suppose for example that during transport the surface of aerosols is saturated with NO_3^- , then we do expect a constant ratio. Other hypotheses can be made to explain the correlation that does not require a common origin for sea salt and HNO_3 . All that is needed is a constant interaction between sea salt and HNO_3 , as proposed.

Second, the reviewer argues that for aged snows, the correlation would be lower if only the low concentration data were plotted in Figure 4a. This is an excellent comment and it is absolutely correct. A detailed inspection of the chemical data reveals that the low concentration values came mostly from older hard windpacks that had been exposed by wind erosion. Our suggestion, which clearly has a speculative character, is that those hard windpacks were formed in winter, when the Ross sea was frozen, there was less sea salt in the air and obviously less (photochemically produced) HNO_3 . Since the conditions producing sea salt aerosols were different and HNO_3 concentrations were different, the $\text{Na}^+/\text{NO}_3^-$ ratio was different. Since these layers were hard windpacks, they had a low permeability and could not be ventilated (see details in Domine et al., 2004) and fractionated sea salt could not be deposited during our campaign. However, despite the sound basis for this comment, we argue that these layers formed only a small proportion of outcropping layers, and thus had little impact and do not represent a strong enough case to alter our conclusion that by and large, Na^+ and NO_3^- are well correlated in aged snows, which can be explained by sea salt attack by HNO_3 during spring.

Third, we believe that the interaction between sea salt and HNO_3 that is responsible for

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the correlation could not take place in fresh snows. There, NO_3^- is present as adsorbed and dissolved HNO_3 (not just adsorbed) and there is thus less potential for interaction, hence a much lower correlation. We may even speculate that if we had enough data for falling snow, the correlation would be close to zero.

Finally, we refrain from comparing the slopes of the correlations for aged and recent snows. First, the slope of the recent snows is not robust, in that it is changed significantly if only a few points are deleted, and second the “similarity” in the slopes (are 2 values differing by 60 % similar?) could simply be fortuitous.

Chapter 4.6, page 629, line 12: $J(\text{NO}_3^-)$ was refined by the ratio of the modelled and measured irradiance at 350 nm. However, since nitrate photolysis is most important around 300 nm (see for example Burley and Johnson) and since the diurnal variation of the irradiance is different between 300 and 350 nm, a wavelength near 300 nm should be used for the calculations.

The referee is not correct. There are two points to explain the referee’s error:-

Nitrate photolysis in polar snowpacks is most sensitive to irradiance around 320–325 nm. The photolysis rate $J(\text{NO}_3^-)$ depends on the product of the nitrate absorption cross-section, σ , the quantum yield, Φ , and the actinic flux, F , not just the cross-section. Figure 1 plots the variation of the product, $\sigma\Phi F$ versus wavelength for the solar zenith angles 60° , 65° , 70° , 75° and 80° for a snowpack in Browning Pass. The photolysis rate constant, J , is equal to the area under the graph. The product clearly peaks around 320–325 nm, not 300 nm.

Secondly the diel variation of normalized irradiance at 300 nm is different to the diel normalized irradiance at 350 nm, but the diel variation in normalized irradiance between 325, 350, 375 and 400 nm is not very different at all. To illustrate this we have calculated surface normalized irradiances for a cloud-free atmosphere at Browning Pass on the 17th November. The diel variation of the irradiance for each wavelength is normalized to unity at noon to highlight the variation. Figure 2 displays these calculations.

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Experimental irradiance values at 350nm are used in the paper as opposed to 325nm owing to the superior signal-to-noise ratio at 350nm as opposed to 325nm on the field spectrometer.

See the figure at

<http://www.oasishome.net/docs/acpd-2005-0380-reply-figure2.pdf>

Figure 2. The wavelength dependence for the product $\sigma\Phi F$, which clearly peaks at 320 nm not 300nm. The colored plots represent different solar zenith angles. Note how with setting sun (increasing solar zenith angle) the peak moves from 320nm to 325nm, as the atmospheric slant path increases.

See the figure at

<http://www.oasishome.net/docs/acpd-2005-0380-reply-figure3.pdf>

Figure 3. The normalized diel variation of monochromatic surface irradiance at Brown-ing pass. The variation with time is similar for the wavelengths 325, 350, 375 and 400nm but different for 300nm.

Chapter 5.2, page 631, line 25: Details referred to in Figure 2 are hard to identify (see also below). Technical corrections/suggestions Figure 2: No detail is discernible in Figure 2. Thus, the figure might be separated into two larger figures (for example Figure 2a separated from Figures 2b and c) leading to a more detailed presentation of the data.

A more detailed figure with part of the data (as shown above for DOY 325 – 330) will be included in the revised ms.

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