

## ***Interactive comment on “Snow optical properties at Dome C, Antarctica – implications for snow emissions and snow chemistry of reactive nitrogen” by J. L. France et al.***

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France et al., Dome C – Snowpack Optics Reply to Referees:

Firstly we would like thank all three referees for constructive and helpful comments along with their general praise of the manuscript, it is always a pleasure to receive supportive comments. As there are no long and detailed responses required within the reply to referees, each review will be treated in turn within this one document.

Reviewer 1.

The referee has separated their points and questions with numbering, we will maintain

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the numbering for the responses and take each point in turn.

Minor comments:

“1) Should parenthetical references be listed chronologically? e.g. pg 11962, line 4, Davis et al 2001 should come in the list before Davis et al 2004.”

1. This has now been fixed, and references are in chronological order in the final manuscript.

“2) This is really a matter of style, but I would remove the preambles at beginning of sections 3 and 4 (where you essentially say “this is how we split up these sections”). To me, as I’m reading, it is apparent how you are splitting up the sections, so I think this is superfluous.”

2. We would prefer to keep the small pre-ambles before the results and discussion sections in the finalised document. We do agree that when reading the whole manuscript it feels a little superfluous, however, many people may not read the whole paper and will skim read to the sections of personal importance. We feel these kind of pre-ambles act as a very useful guide to what information is found within each section.

“3) I’d rephrase page 11974 line 4 to: “The measured e-folding depths are  $\_3$  times longer than the 3.7 cm at 320 nm previously calculated by Wolff et al. (2002)”

3. We completely agree that the reviewer suggested text reads more clearly, and the text has been changed accordingly.

“4) Page 11978 line 6: Is “smoothen” a word? I think smooth would fit there just as well”

4. The word “smoothen” has been removed.

Minor questions:

“1) How long does each set of measurements take? Just wondering if you get a change

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in SZA during the timeframe of the measurements, or any other conditions that would affect your values?”

1. Each set of albedo measurements for a site takes about 10 minutes from the first measurement being taken to the last measurement. The measurements are taken around the solar noon to minimise any solar zenith angle variation effects and at Dome C the overhead sky conditions were very stable. The in-snow irradiance measurements are not affected by solar zenith angle change as the light regime is totally diffuse within the snowpack at the depths at which the measurements are made and the measurements are completed within 20 minutes. The most time consuming aspect of the experiments are the digging of the snowpit and the packing / unpacking of the equipment.

“2) Do you have any feeling for how the BC vs HULIS component of absorption may change if you get farther away from the Dome C base? I'd think there would be a fairly substantial local BC source there. Perhaps farther out, where things might be more representative of "background", the HULIS component is even greater compared to BC?”

2. The black carbon concentration in the two surface snows are 1 ng g<sup>-1</sup> and 2 ng g<sup>-1</sup> for the hard snowpacks (The black carbon and HULIS absorption cross-sections have been refitted more robustly for the final manuscript for each snowpack layer and show a small decrease in the amount of black carbon required). Warren et al., (2006) showed that the black carbon in snow before the base was established was 0.6–1.4 ng g<sup>-1</sup> relative to 3.3 ng g<sup>-1</sup> in present surface snow near the base. Therefore we believe our optical properties are not too effected by the presence of the base. The following test has been added to the paper.

“The concentrations of black carbon estimated for the surface snowpack layers is 1–2 ng g<sup>-1</sup>, comparable to the black carbon concentrations measured by Warren et al., (2006) for the same snowpack locality. Warren et al., (2006) measured 3.3 ng g<sup>-1</sup> of

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black carbon for snowpack contaminated by emissions from the base, and 0.6–1.4 ng g<sup>-1</sup> for snowpack formed pre-development of the Concordia station.”

The discovery of the absorption requiring a HULIS like component was a slight surprise, to our knowledge there are no measurements of HULIS on remote Antarctica – though some are planned, thus it is hard to comment. HULIS in Antarctic snow is definitely an area for further study.

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Reviewer 2:

Changes regarding scientific quality:

“The largest flaw in the manuscript is a lack of comprehensive literature review. The citations are largely 'in house' British Antarctic Survey manuscripts, and the authors failed to include prior investigations into the topic and furthermore to discuss some of the limitations in their methods that are highlighted by some recent radiative transfer studies of snow pack. In particular, the limitations and challenges of accurately measuring and modeling reflectance from polar snow packs as discussed in the following manuscripts should be provided at a minimum: (See reference list in reviewer's comments)”

We have added all the references suggested by the reviewer and the introduction has been extended, especially with reference to reflectivity and nitrate loss.

Presentation Quality:

“The authors should return to the draft and review their use of acronyms, and the introduction of the acronyms. Clearly, due to their familiarity with Antarctic research, they fail to properly present a few key locations:”

The over-use of acronyms in the paper without proper definition has been addressed. Each acronym now has a definition alongside the first occurrence in the manuscript.

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“Some other inconsistencies: page 11971, the range of BC is provided as 0-13 ng g<sup>-1</sup>, whereas in the discussion is 2-6 ng g<sup>-1</sup> page 11976, define and provide a reference to ISCAT Table 2, the headings in the last two columns are illegible.”

The range of Black Carbon concentrations in the snowpack is quoted as 1 – 5 ng g<sup>-1</sup> (improved fitting of the absorption cross-sections has lowered the required black carbon concentrations) as this is the variation in black carbon concentrations between the snowpack layers. The range of 0 – 13 ng g<sup>-1</sup> of black carbon is the range when considering the uncertainty in determining the amount of BC from the experimental results including the experimental uncertainty. Both are valid expressions of the data, and we would prefer to keep the data expressed in the manner currently presented. The text has been altered in the final manuscript to make it clearer.

Table 2 has been reformatted to a legible state.

The required ISCAT reference has been added along with a definition of the acronym.

“Lastly, the discussion of uncertainties of the irradiance measurements themselves lacks detail. At a minimum, the values presented in Fisher (2005) should be presented again for reference. Furthermore, some more details regarding the data acquisition would be important for repeatability. For instance, on page 11965 it is not important that a Panasonic Toughbook was used, but it would be interesting to know more about the integration time of the measurements, and overall acquisition parameters. What Ocean Optics spectrometers were used? How was the data post-processed?”

There is now extra detail added into the manuscript regarding the uncertainties on the measurement process, including the details from Fisher et al., (2005). Details regarding the data acquisition process have been included, along with information about the post-processing procedure for both reflectance and in-snow irradiance measurements.

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Reviewer 3.

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Comments:

“The rate of nitrate photolysis is dependent on the quantum yield of photodegradation and yet there is some uncertainty in this value, as raised by the authors (p11969). Did the authors therefore attempt a sensitivity analysis by varying values of  $\Phi$  based on the range of lab-based measurements? Furthermore, is it likely that the model output (re: NO<sub>2</sub>flux) will be strongly influenced by this parameter and, if so, do the range of model values e.g. min max lines in Fig 5, reflect different QY.”

The authors have not considered a sensitivity analysis of the nitrate quantum yield as we believe that the phenomenological quantum yield ( $\Phi$ ) determined by Chu and Anastasio (2003) to be the most appropriate. There is a brief section in the manuscript discussing the alternative quantum yields that have been recently proposed for the photolysis of nitrate and the following text is now in the final manuscript.

“The temperature-dependant quantum yield of reaction 1 on ice and the absorption cross-section of nitrate in aqueous solution are both taken from Chu and Anastasio (2003). The quantum yield reported in Chu and Anastasio (2003) broadly agrees with the work of Dubowski et al., (2002) and Burley and Johnston (1992) and is considered a good phenomenological representation of the photolysis of nitrate in snow and ice. Other available quantum yield data for 308 nm photolysis of nitric acid on ice films of  $0.92 \pm 0.26$  (Zhu et al., 2010) seem extremely high compared with previous data (Warneck and Wurzinger, 1988; Zellner et al., 1990; Dubowski et al., 2002; Chu and Anastasio, 2003), but if correct would increase the NO<sub>2</sub> production by a factor of  $\sim 400$ .”

As for wavelength independent values of the quantum yield, which is true for the quantum yield of nitrate, it would be straightforward for other scientists to still use the data presented within this work if they wish to consider a different quantum yield to the Chu and Anastasio (2003) values used for the calculations through a simple scaling factor. The error bars for Figure 5 are a reflection of the differences in the measured nitrate profiles at Dome C, not a reflection of quantum yield uncertainty.

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“Figure 6. The figure legend describes dotted lines to illustrate the min max NO<sub>2</sub> fluxes, but these aren’t present on the figure (not in my PDF version anyway).”

Figure 6 has now been fixed for the final manuscript.

References: Burley, J. D., and Johnston, H. S.: Ionic mechanisms for heterogeneous stratospheric reactions and ultraviolet photoabsorption cross-sections for NO<sub>2</sub><sup>+</sup>, HNO<sub>3</sub>, and NO<sub>3</sub><sup>-</sup> in Sulfuric-Acid, *Geophys. Res. Lett.*, 19, 1359-1362, doi:10.1029/92GL01115 1992.

Chu, L., and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, *J. Phys. Chem. A*, 107, 9594-9602, 10.1021/jp0349132, 2003.

Dubowski, Y., Colussi, A. J., Boxe, C., and Hoffmann, M. R.: Monotonic increase of nitrite yields in the photolysis of nitrate in ice and water between 238 and 294 K, *J. Phys. Chem. A*, 106, 6967-6971, 10.1021/jp0142942, 2002.

Warneck, P., and Wurzinger, C.: Product quantum yields for the 305-nm photodecomposition of nitrate in aqueous solution, *The Journal of Physical Chemistry*, 92, 6278-6283, 10.1021/j100333a022, 1988.

Warren, S. G., Brandt, R. E., and Grenfell, T. C.: Visible and near-ultraviolet absorption spectrum of ice from transmission of solar radiation into snow, *Appl. Opt.*, 45, 5320-5334, 10.1364/AO.45.005320, 2006.

Zellner, R., Exner, M., and Herrmann, H.: Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H<sub>2</sub>O<sub>2</sub> at 308 and 351 nm in the temperature range 278–353 K, *J. Atmos. Chem.*, 10, 411-425, 10.1007/bf00115783, 1990.

Zhu, C., Xiang, B., Chu, L. T., and Zhu, L.: 308 nm Photolysis of Nitric Acid in the Gas Phase, on Aluminum Surfaces, and on Ice Films, *The Journal of Physical Chemistry A*, 114, 2561-2568, 10.1021/jp909867a, 2010.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 11959, 2011.

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