

**Authors' response to comments on "Summertime NO<sub>x</sub> measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?" by S. J.-B. Bauguitte et al.**

We thank the two anonymous referees for constructive comments on our manuscript. We address below the referees' comments. Updated Tables, Figures, Captions and References are provided in lieu of the revised manuscript.

**Response to Anonymous Referee #1 (C6151)**

**Specific Comments**

**p. 20374 line 18:** We have included two references for the recent ARCPAC and ARCTAS missions and results, and included the following sentence to address the referee's suggestion regarding satellite BrO data product retrievals, at the end of the 4<sup>th</sup> paragraph: "*despite the recent results from the NASA ARCTAS and NOAA ARCPAC airborne campaigns which have highlighted issues with BrO retrievals from satellites (Jacob et al., 2010 and Salawitch et al., 2010).*"

**p. 20376 line 2:** The sample illumination time (cell residence time and optics geometry) was indeed unchanged between the 75W to 200W arc lamp power upgrade; however the optical alignment and focus control of the Oriel Photomax lamp housing ellipsoid mirror onto the photolysis cell were also improved, which most likely contributed to the 3-fold improvement in conversion efficiency.

**p. 20376 line 28:** "*quantitative*" has been deleted in the revised manuscript.

**p. 20377 line 12:** The 2 pptv artefact of our NO CL detector was very consistent throughout our study. The NO<sub>2</sub> artefact was somehow less stable. We quote (end of 8<sup>th</sup> paragraph in Section 3.1) a  $\pm 3$  pptv NO<sub>2</sub> artefact determination error, which is probably not conservative and may explain the reported negative NO<sub>2</sub> mixing ratios cited later on in our paper. Due to the lack of provision of an optical shutter in this version of our PLC, we could not distinguish between CL detector and PLC artefacts. See also our response to Comment 1 of anonymous Referee #2.

**p. 20378 line 15:** The authors verified that the NO+Oxidant $\rightarrow$ NO<sub>2</sub> perturbation on the NO/NO<sub>2</sub> ratios for a 14 sec transfer time is negligible (<1.5 pptv NO oxidation), assuming low summertime Ozone levels (~10 ppbv) and 4 pptv of BrO and IO as oxidants, using JPL Evaluation No 15 (Sander et al., 2006) rate constants.

**p. 20381 line 19:** We do not have the  $F(\lambda)^\downarrow$  data for the Summit 2000 study, to compare with that of Halley in the summer. In order to elucidate the factor 5 difference between the Qiu et al. (2002) actinometry measurements and our estimated in-snow  $JNO_3^-$ , we used the NCAR radiative transfer model quick TUV calculator to output  $E^\downarrow(\lambda)$  for both measurement sites. We initialised the online calculator for the conditions of the Qiu et al. (2002) results, namely lat/long/alt for Summit as per Table 2, date/time as 08/06/2000 1400GMT, O<sub>3</sub> column left at 300DU (default input). We repeated the initialisation for CHABLIS/Halley on 15/01/2005 1400GMT. The TUV modelled direct spectral irradiances ( $W m^{-2} nm^{-1}$ ), relevant to the nitrate ion photolysis range (280-320 nm), were clearly much higher in the UV end of the

spectrum for the Qiu et al. conditions, by a factor 600 at 280 nm, dropping exponentially to a factor ~3 at 320 nm; the difference between the two measurement site conditions may therefore be ample to explain the factor 5 difference between our in-snow nitrate photolysis rates.

**p. 20381 lines 26-27:** We reworded the 1<sup>st</sup> sentence of Section 2.4 as follows: “*For model calculations, we employed various data sets acquired for the period 1<sup>st</sup> January to 10<sup>th</sup> February 2005 at the Halley Research Station.*”

**p. 20382 line 2:** The words “*the extended Leighton relationship*” were replaced by “*NO/NO<sub>2</sub> ratio*”.

**p. 20382 line 3:** IO and BrO were detected above the detection limit of the LP-DOAS deployed during CHABLIS whenever the solar zenith angle was less than ~ 92°. The detection limit was 1-2 pptv (Saiz-Lopez et al. 2007a). As can be see from Figure 2, SZA was < 90° for all of the CHABLIS summertime study (24 hr daylight). We included the following sentence in Section 2.4: “*As the sun remained above the horizon (SZA<90°) throughout the CHABLIS summertime study (24 hour daylight), “night-time” IO and BrO were always above the instrument detection limit.*” See also our response to Comment 3 of anonymous Referee #2.

**p. 20384 line 16:** The model derived NO<sub>x</sub> lifetime ( $\tau$ ) is independent of the BLH. The derived flux however does need to be scaled with BLH. See our response to Comment 5a and 5b of anonymous Referee #2 for a discussion of summertime BLH at Halley.

**p. 20393 lines 15-17:** The authors agree that “the halogen oxidation influencing the isotopic nitrate signature in the snowpack” is not a major focus of this paper. We have removed the last sentence of the Abstract, and the last sentence of the Conclusions. We added the following paragraph in the Introduction following the (Morin et al., 2008 and references therein): “*They also confirmed that NO<sub>x</sub> emissions from snow play a large role on the budget of NO<sub>x</sub> and nitrate in polar regions at the regional scale, and that NO<sub>x</sub> oxidation by halogen oxides is happening at a very large scale in the Antarctic and in the Arctic. In addition, Morin et al. (2009) recently showed that such NO<sub>x</sub> emissions not only occur from snow on ice sheets but also from snow on sea ice, as inferred from the  $\delta^{15}N$  of aerosol nitrate over the frozen Weddell Sea.*”

In our Discussion, we included the two following paragraphs:

“*The link between NO<sub>x</sub> emissions from snow and local oxidation by halogens and heterogeneous loss to BrNO<sub>3</sub> was also clearly demonstrated using a very different approach, namely isotopic measurements of nitrate both in the Arctic and Antarctic (Morin et al., 2008; Morin et al., 2009).*”

and “*It seems clear from this study that, in coastal Antarctica, the impact on NO<sub>x</sub> lifetime and partitioning is also significant, although this impact is highly dependent on atmospheric dynamics. For instance, Legrand et al. (2009) found no evidence of active halogen chemistry at the French Dumont d’Urville Research Station in coastal Antarctica, where air masses are mostly brought from the Antarctic Plateau through katabatic flow.*”

The authors' intention is to highlight the fact that the nitrate isotopes studies by Joel Savarino and Samuel Morin have come to very similar conclusions to this study, but from a different approach, and therefore strengthen our argument.

**p. 20399 (Table 1):** This is not possible for the reason given in our response to the 'p. 20377 line 12' comment. We included the sentence "*The reported NO<sub>2</sub> artefact is the combined CL (NO<sub>x</sub>) analyser and PLC artefact.*" in the caption of Table 1 to clarify.

**p. 20403 (Fig. 3):** The authors agree with the referee that systematic errors are more appropriate than 2 $\sigma$  standard errors in Figure 3. Standard error bars have been replaced in Figure 3 by uncertainty/systematic error bars; NO<sub>x</sub> uncertainty was taken as the root sum of squares (rss) of NO and NO<sub>2</sub> uncertainties, 1.3 and 3.3 pptv respectively (as per Table 1).

Uncertainty for modelled NO<sub>x</sub> arise from the input parameters of Equation 2, namely observed NO<sub>x</sub> and  $E(\text{Nitrate})^\dagger$ , and to a lesser extent errors propagated from the mathematical fitting method employed in Equation 3.  $E(\text{Nitrate})^\dagger$  could be as high as 20% near noon on a few days with fully clear skies as discussed in Section 2.3.2 on in-snow  $J(\text{Nitrate})^\dagger$ . Observed and modelled NO<sub>x</sub> therefore agree within combined uncertainties.

Figure 3 caption and Section 3.2 were reworded to reflect the above.

See also our response to Comment 5a of anonymous Referee #2.

**p. 20404 (Fig. 4):**

10 minute averaged wind speeds ( $v$ , in  $\text{m s}^{-1}$ ) are now plotted with the turbulent diffusivity  $K$  against the right-hand axis in panel b of Figure 4.

As recommended by the referee, we evaluate the  $\frac{\partial \text{NO}_x}{\partial z}$  precision by analysing the

random noise (2 $\sigma$  precision) of our NO<sub>x</sub> data for solar noon on 4<sup>th</sup> February 2005, when low NO<sub>x</sub> gradients (<1.6 pptv  $\text{m}^{-1}$ ) and high diffusivities were experienced.

$\frac{\partial \text{NO}_x}{\partial z}$  is a differential measurement and therefore does not suffer from instrumental artefacts (discussed in Section 2.1); measurement accuracy is not an issue in the present evaluation.

The 2 $\sigma$  precision of 1 Hz measurement over a 9 minute sampling period at one sampling height (see Section 2.2) for NO and NO<sub>2</sub> is  $\pm 11.6$  and  $\pm 38.8$  pptv respectively, improving to  $\pm 0.5$  and  $\pm 1.7$  pptv for a 9 minute average. The

$\frac{\partial \text{NO}_x}{\partial z}$  precision for two 9 minute NO<sub>x</sub> measurements (two heights) is  $\pm 2.5$  pptv  $\text{m}^{-1}$

in rms. This threshold is represented by the horizontal dashed line in panel a of Figure 4. Most of the NO<sub>x</sub> gradient measurements for 1<sup>st</sup> Feb. and 4<sup>th</sup> Feb. 2005 fall below this threshold, as rightly pointed out by the referee. We filtered out NO<sub>x</sub> gradients below 2.5 pptv  $\text{m}^{-1}$  in the product of  $\frac{\partial \text{NO}_x}{\partial z}$  and  $K$  in panel c of Figure 4.

We also evaluated the uncertainty/confidence level in our diffusivity estimates using the sonic anemometry array deployed North and South of the CASLab for this purpose (Figure 1), and report a  $\pm 3\%$  uncertainty for  $K$ .

We reworded the Abstract sentence: "*This emission rate compares to directly measured values ranging from 2.1 to 12.6  $\times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  made on 3 days at the end of the study period.*"

We also reworded the last paragraph of Section 4.2 discussing our measured NO<sub>x</sub> flux and (now) uncertainties, updated Figure 4 and its caption and Table 2 to reflect the above comments and corrections.

## Technical Comments

**p. 20377 line 8:** Palladium misspelling corrected

**p. 20384 line 16:** We included “*Assuming a 100 m summertime boundary layer mixing height ...*”

See also our response to Comment 5b of anonymous Referee #2.

**p. 20386 line 9:** We reworded this sentence as follows: “*For Reactions 4 and 5, we assumed a constant 3 pptv IO and 3 pptv BrO **mixing ratio**, consistent with the DOAS summertime observations conducted by Saiz-Lopez et al. (2007a) during CHABLIS.*”

## Response to Anonymous Referee #2 (C9019)

### **Comment 1 - section 2.1**

In Table 1, we reported 1 $\sigma$  random errors for the two chemiluminescence channels. We acknowledge that combining systematic and random errors to express a limit of detection is misleading. In distinguishing systematic and random errors, the authors aimed to clarify that although our chemiluminescence detectors had good precision, ie low random noise and hence NO<sub>x</sub> detectability, like most chemiluminescence analysers our system suffered from artefacts and potential interferences which affected its measurement accuracy. We have acknowledged this fact when appropriate in the manuscript (eg Section 3.1 and Section 6.1). To avoid further confusion, we have now removed the last row in Table 1, and quote 2 $\sigma$  random errors (95% confidence level). We reworded the paragraph defining the instrumental detection limit as follows:

*“The instrumental limit of detection was estimated from the two sigma standard error determined when averaging the 1Hz NO and NO<sub>2</sub> data to one minute means.”*

Regarding comments on the HONO and HNO<sub>4</sub> interference, the authors acknowledged the lack of characterisation of the optical/photolytic HONO interference of their photolytic converter, a matter well published, but a challenging experimental test due to the requirement to produce gas-phase HONO in a free molecular NO<sub>2</sub> calibration stream.

As for HNO<sub>4</sub>, we consider this would be a minimal interferent to our measurements for the following reasons: i) the optical interference is known to be negligible (see Plate 1 of Ryerson et al. 2000); ii) the air sample thermal management of our photolytic converter (cell cooling, short residence time) is specifically aimed at minimising this interference and that of PAN.

In the above response, we acknowledge that the level of detectability of our instrumentation, based on precision / random errors, is suitable for low level NO<sub>x</sub>,

with an uncertainty/accuracy reflecting both systematic errors and potential interferences.

### **Comment 2 - Section 2.2.3**

We feel that the text in Section 2.2.3 already fully spells out the methodologies used in prior studies and this paper. We therefore have made no further changes.

### **Comment 3 - Section 2.4**

We have amended the text in this section. See response to Comment “**p. 20382 line 3**” of anonymous Referee #1.

### **Comment 4 - Section 3.1**

Regarding the below detection limit NO<sub>2</sub>, see response to Comment 1.

### **Section 3.4**

A brief quantitative comparison between summertime Halley, Neumayer and Summit NO<sub>x</sub> diurnal cycles is included at the end of this section in the following paragraph:

*“This diurnal variation is in line with that reported for summertime NO<sub>x</sub> measurements at Neumayer, another coastal Antarctic site, with NO<sub>x</sub> maxima of ~25 pptv at around 19:00 GMT (Jones et al. 1999; Weller et al. 1999). Similarly, Honrath et al. (2002) report NO<sub>x</sub> diurnal cycles at Summit for summer 1999 and 2000, with maximum median values of ~40 and ~60 pptv respectively. “*

### **Comment 5**

#### a) Section 4.1/4.2

Neither Equation 2 nor 3 invoke any assumption regarding BLH.

With regards to uncertainties of  $\alpha$  and  $\tau$ , we have included the following paragraph at the end of Section 4.1: *“Uncertainties for modelled NO<sub>x</sub>,  $\alpha$  and  $\tau$ , arise from the combined uncertainties of the input parameters of Equation 2, namely observed NO<sub>x</sub> and  $E(\text{Nitrate})^\downarrow$ , and to a lesser extent errors propagated from the mathematical fitting method employed in Equation 3. The minimum uncertainty for observed NO<sub>x</sub> is ~15%, as showed by the systematic error bars for the highest mixing ratios in Figure 3. Uncertainties for  $E(\text{Nitrate})^\downarrow$  could be as high as 20% near noon on a few days with fully clear skies as discussed in Section 2.3.2 (in-snow  $J(\text{Nitrate})^\downarrow$ ). Observed and modelled NO<sub>x</sub> therefore agree within the above combined uncertainties.”*

See also our response to Comment “**p. 20403 (Fig. 3)**” of anonymous Referee #1.

b) 1) The 70 m average boundary layer height quoted by Jones et al (2008) was an annual average, not a summertime average. During the summer, the boundary layer height will on average be higher than during the rest of the year, due to convection. It is therefore entirely reasonable to assume a 100 m summertime boundary layer height for Halley, as done also in the study of Bloss et al. (2010).

2) We re-iterate that  $\alpha$  and  $\tau$  are estimated independently of BLH in Eq. 2.

The referee’s suggestion in exploring sensitivities introduced by a BLH varying between 40 and 110 m is therefore only relevant for the linear scaling of the product  $\alpha E(\text{Nitrate})^\downarrow$ , to express the mean NO<sub>x</sub> flux. We included this statement: *“This emission rate would scale linearly with a changing boundary layer height.”* in Section 4.2.

Furthermore, we must note that the 40 and 110 m BLH is an annual range, and may not be experienced during the summertime months.

Although we agree with the referee that a logical step would be to combine the chemical and physical approaches in a model including key aspects of both, this would be a major task and go well beyond the scope of the present paper.

c) Snow produced  $\text{NO}_x$  flux variability is driven by both the  $\text{NO}_x$  gradient and the meteorology ( $K$  diffusivity) as per Equation 1. As showed by  $K$ , in panel b) of Fig. 4, the meteorology varied greatly over the 1-5 Feb. 2005 period. We have now included wind speed in panel b) of Fig 4. See also our response to Comment “**p. 20404 (Fig. 4)**” of anonymous Referee #1 for the error analysis and reporting of our  $\text{NO}_x$  flux measurements.

### Comment 6

a) The 3 pptv for IO and BrO are perfectly valid mixing ratios for a sensitivity assessment, regardless of being close to the 1-2 pptv detection limit of the DOAS instrument employed for the Halley XO measurements (Saiz-Lopez et al. 2007a). Small mixing ratios (few pptv) have significant impact on atmospheric composition, which is what we are illustrating strikingly in Fig 5.

We made this clearer by amending the text in Section 5.2 as follows:

*“Even with the low concentrations of IO and BrO observed during summertime CHABLIS, the production of halogen nitrates appears to be the most significant sink for  $\text{NO}_x$ , as indicated by the black and grey lines in Figure 5. “*

b) We thank the referee for correctly pointing out the short thermal decomposition lifetime of  $\text{HNO}_4$ . This fact has clearly been overlooked in our study and we have corrected our manuscript as follows.

In the Abstract, we deleted the statement “, with a potential smaller contribution from  $\text{HNO}_4$  formation and uptake”.

In Section 5.2, we reworded the following paragraph:

*“ $\text{HNO}_4$  formation (green line) offers a potentially more efficient loss process with a mean  $\text{NO}_x$  lifetime of the order of 20 hours, still significantly longer than that derived from the observations. Once sequestered in the  $\text{HNO}_4$  reservoir, further aerosol uptake and hydrolysis is required to ultimately remove  $\text{NO}_x$ . However,  $\text{HNO}_4$  can undergo both photolysis and thermal decomposition of  $\text{HNO}_4$  prior to aerosol uptake. Using the radiative transfer model described in Saiz-Lopez et al. (2008), we estimate a maximum noon-time  $J\text{HNO}_4$  value of  $5.05 \times 10^{-6} \text{ s}^{-1}$ , corresponding to a photolysis lifetime greater than 2 days, which is therefore negligible. Using the termolecular reaction and equilibrium constants for Reaction 3 from the JPL Evaluation Number 15 (Sander et al., 2006), and the mean diurnal temperatures and pressures for summertime CHABLIS, we compute  $\text{HNO}_4$  lifetimes to thermal decomposition ranging from 8 to 15 minutes. This proves that during our study, the  $\text{HNO}_4$  reservoir was too thermally labile to play a significant role in  $\text{NO}_x$  sequestration and further loss.”*

We removed references to  $\text{HNO}_4$  in Section 5.3 and Section 5.4.

In the Conclusion, we added the following paragraph:

*“We found the  $\text{HNO}_4$  heterogeneous loss channel for  $\text{NO}_x$  to be negligible in the relatively warm summertime, although it may play a more significant competing role in the colder springtime.”*

- c) We agree with the referee that our computed NO<sub>x</sub> lifetime should be put into context with that measured at other polar sites. We have included the following paragraph in Section 5.1:

*“Ridley et al. (2000) and Beines et al. (2002) did not derive NO<sub>x</sub> lifetimes from their respective measurements at Alert. However, the pronounced diurnal cycle of NO<sub>x</sub> concentrations reported by Ridley et al. (2000), with noon-maximum, may suggest NO<sub>x</sub> lifetimes shorter than 4 hours (Evans et al., 2003). Davis et al. (2004) report enhanced NO<sub>x</sub> lifetimes at South Pole. Although NO<sub>x</sub> concentrations at South Pole are much more elevated than at Halley (up to 800 pptv), Davis et al. report box modelled NO<sub>x</sub> lifetimes (with loss to HO<sub>x</sub> and HNO<sub>4</sub>) as function of NO<sub>x</sub> concentration; for concentrations below ~170 pptv, their estimated NO<sub>x</sub> lifetimes remain constant at ~8 hour.”*

#### **Comment 7 - Section 6.1. NO/NO<sub>2</sub> ratios**

See our response to Comment 1 for a justification of our error analysis treatment.

#### **Comment 8 – Section 7 – Discussion**

- a) The first paragraph of the discussion was reworded as follows:

*“We showed that our observed mean NO<sub>x</sub> diurnal cycle can be reproduced using a simple chemical steady state NO<sub>x</sub> analysis. A credible estimate for the mean NO<sub>x</sub> emission rate from snow was derived. Employing up-to-date kinetics data and known NO<sub>2</sub> oxidation mechanisms, we identified and verified viable NO<sub>x</sub> chemical loss pathways leading to short NO<sub>x</sub> lifetimes.”*

- b) we reworded the 1<sup>st</sup> sentence of the 3<sup>rd</sup> paragraph as follows:

*“Our NO<sub>x</sub> lifetime study identified apparent NO<sub>2</sub> oxidation loss pathways involving halogen nitrates, and their aerosol uptake.”*

- c) we removed reference to the Evans et al. (2003) HNO<sub>4</sub> study.

- d) Ditto

- e) NO/NO<sub>2</sub> and O<sub>3</sub> production: we agree that our original statement is misleading and reworded the sentence as follows:

*“however in coastal regions the halogens tend to mitigate this effect **leading to a reduced NO<sub>x</sub> lifetime and a reduction in the NO/NO<sub>2</sub> ratio.**”*

HO<sub>2</sub> plus NO does not contribute significantly to NO→NO<sub>2</sub>; we estimate this to be <2% (see Section 6.2). Bloss et al. (2010) also confirm in their modelling study the O<sub>3</sub> loss regime. Lowering the O<sub>3</sub> production rate is exactly what we infer, and what referee #2 implies when concluding his comment. This is also exhibited by the low O<sub>3</sub> mixing ratios observed in the summer in coastal Antarctica (Helmig et al, 2007).

#### **Comment 9 – Conclusion**

- a) reference to HNO<sub>4</sub> has been deleted  
b) “*impurities*” has been substituted with “*ions*”

#### **Other comments –References citation**

Evans et al. (2003) has been added to the references list (updated list below).

Although we feel that we have cited all relevant studies conducted by various research groups both in the Arctic and Antarctic alike, we have included two recent publications suggested by the referee and a third reference suggested by a co-author.

## Updated Tables

	NO	NO <sub>2</sub>
NO sensitivity, Hz/pptv	4.2	2.5
Background count rate, Hz	300-400	300-400
Reaction chamber vacuum, Torr	10	10
Detector flow-rate, std L min <sup>-1</sup>	1	1
Artefact, pptv	-2	-6
NO <sub>2</sub> photolytic CE, %	N/a	55-60
Limit of detection, based on precision/random noise, 2σ standard error, pptv	±2.0	±6.0
Accuracy based on systematic errors (<20 pptv NO <sub>x</sub> ), pptv	±1.3	±3.3

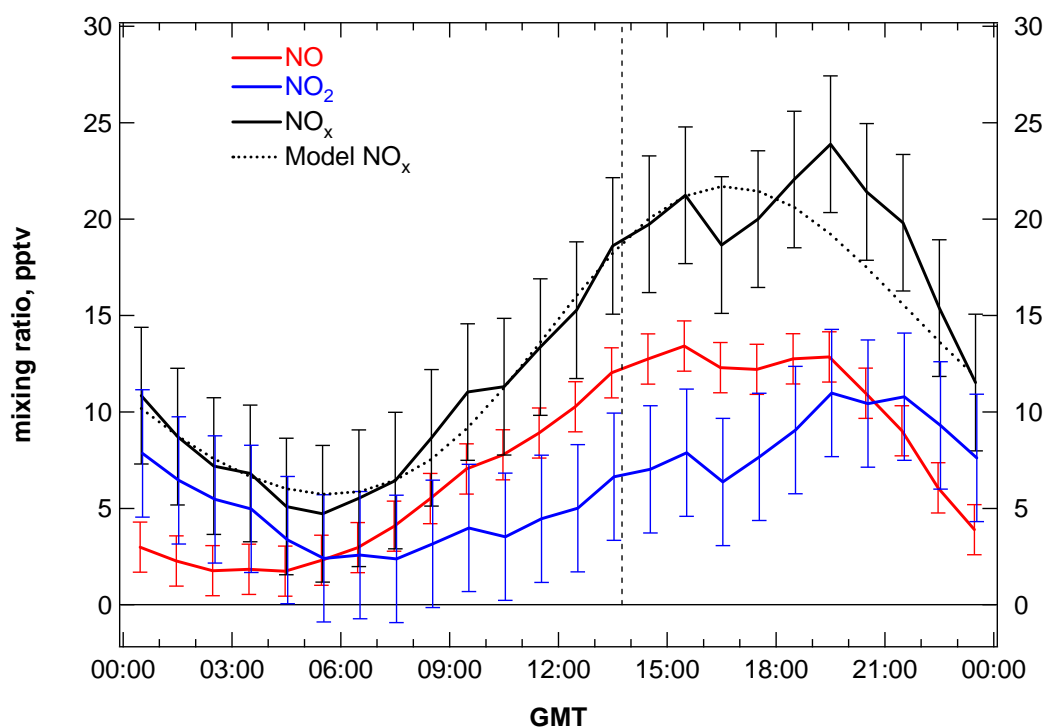
**Table 1** : Summary of CL detector performance parameters, and nominal precision and accuracy of one minute NO<sub>x</sub> mixing ratios below 20 pptv. The NO<sub>2</sub> systematic error includes the contribution due to the systematic error in NO. The reported NO<sub>2</sub> artefact is the combined CL (NO<sub>x</sub>) analyser and PLC artefact.

Location	Date	NO <sub>x</sub> flux, molec cm <sup>-2</sup> s <sup>-1</sup>	Reference
<i>Antarctic measurements</i>			
Neumayer 70°39'S, 8°15'W, 42 m	5-7 <sup>th</sup> Feb. 1999	~3 (+0.3/-0.9) × 10 <sup>8</sup> (noon maxima)	Jones et al, 2001
South Pole 2835 m	26-30 <sup>th</sup> Nov. 2000	3.9 ± 0.4 × 10 <sup>8</sup> (average over period)	Oncley et al., 2004
Halley V 75°35'S, 26°40'W, 37 m	2 <sup>nd</sup> Feb. 2005	12.6 × 10 <sup>8</sup> (noon maxima) 7.3 × 10 <sup>8</sup> (0705-1505 GMT mean)	This Study (Figure 4)
<i>Arctic measurements</i>			
Summit, Greenland 72°36'N, 38°30'W, 3200 m	5 <sup>th</sup> June-3 <sup>rd</sup> July 2001	2.5 × 10 <sup>8</sup> (daily average)	Honrath et al., 2002
Alert, Nunavut, Canada, 82°30'N, 62°18'W, 220 m	9-25 <sup>th</sup> April 2000	≥ 6.7 × 10 <sup>8</sup> (noon maxima)	Beine et al., 2002

**Table 2:** Summary of NO<sub>x</sub> flux measurements in Arctic and Antarctic studies



## Updated Figures



**Figure 3** : Hourly mean diurnal cycle of NO (red), NO<sub>2</sub> (blue) and NO<sub>x</sub> (black) for 1<sup>st</sup> January to 10<sup>th</sup> February 2005, compiled from the one minute pollution-filtered master dataset. Error bars are systematic errors (uncertainties from Table 1). The dotted black line (Model NO<sub>x</sub>) corresponds to the Steady State NO<sub>x</sub> calculations (see text). The vertical dashed line indicates local noon, 13:45 hrs.

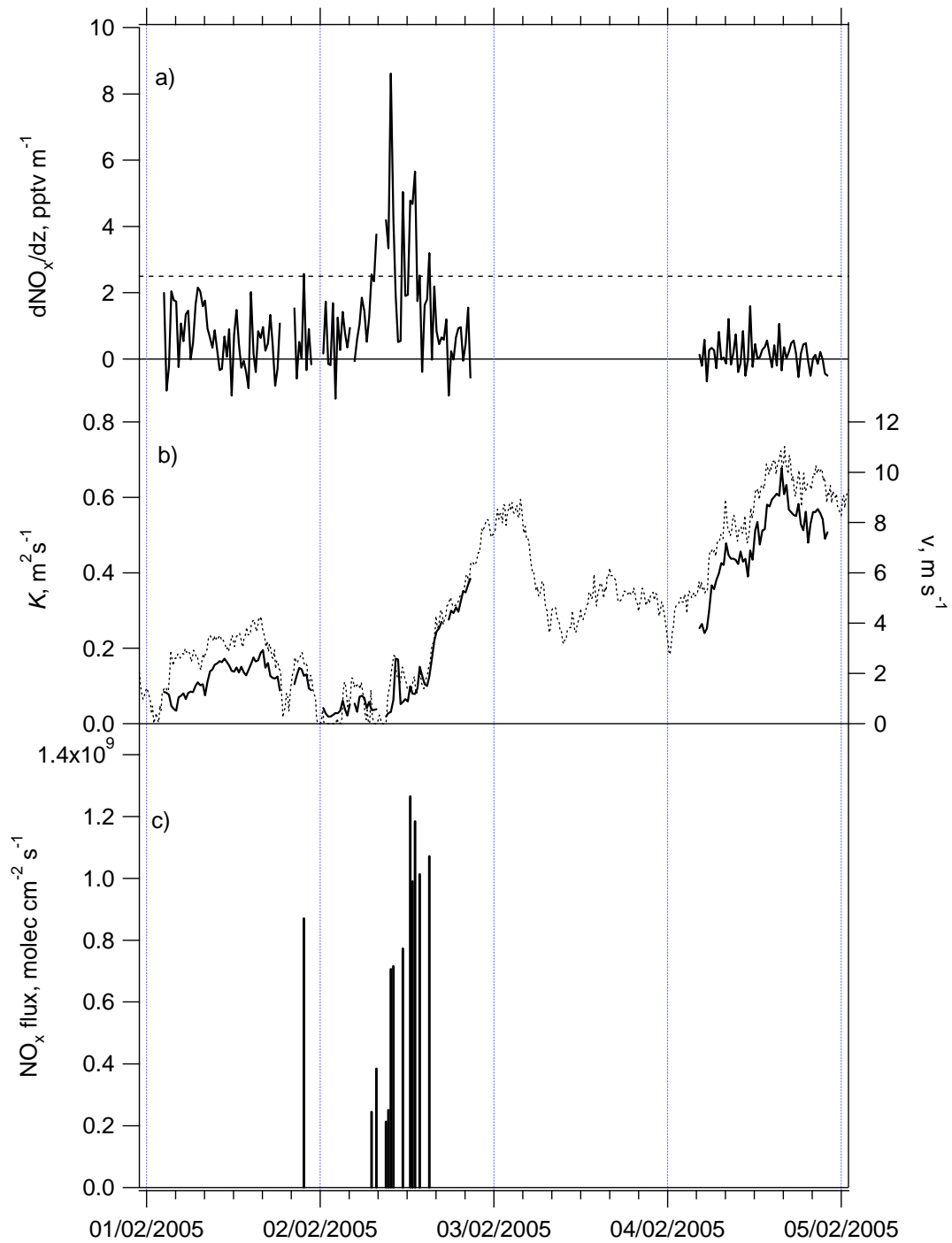


Figure 4: a) 20 minute averaged  $\text{NO}_x$  gradients ( $\frac{\partial \text{NO}_x}{\partial z}$ ) estimated from the 1.5 and 6 m high inlets  $\text{NO}_x$  measurements; the horizontal dashed line ( $2.5 \text{ pptv m}^{-1}$ ) corresponds to the  $2\sigma$  precision of the gradient measurements; b) 20 minute averaged surface diffusivities ( $K$ ) estimated from the friction velocities  $U_*$  at 4 m height (solid line, left-hand axis), and 10 minute averaged wind speeds (dotted line, right-hand axis); c) 20 minute averaged  $\text{NO}_x$  fluxes expressed as the product  $\frac{\partial \text{NO}_x}{\partial z} \times K$ , filtered for gradients less than  $2.5 \text{ pptv m}^{-1}$  detection threshold.  $\text{NO}_x$  gradient were not measured during 3<sup>rd</sup> Feb. 2005 due to instrument downtime/maintenance.

## Updated/Added References

Bloss, W. J., Camredon, M., Lee, J. D., Heard, D. E., Plane, J. M. C., Saiz-Lopez, A., Bauguitte, S., J.-B., Salmon, R. A., and Jones, A. E.: Coupling of HO<sub>x</sub>, NO<sub>x</sub> and halogen chemistry in the Antarctic boundary layer, *Atmos. Chem. Phys.*, 10, 10187–10209, doi:10.5194/acp-10-10187-2010, 2010.

Evans, M. J., Jacob, D. J., Atlas, E., Cantrell, C. A., Eisele, F., Flocke, F., Fried, A., Mauldin, R. L., Ridley, B. A., Wert, B., Talbot, R., Blake, D., Heikes, B., Snow, J., Walega, J., Weinheimer, A. J., and Dibb, J.: Coupled evolution of BrO<sub>x</sub>-ClO<sub>x</sub>-HO<sub>x</sub>-NO<sub>x</sub> chemistry during bromine-catalyzed ozone depletion events in the arctic boundary layer, *J. Geophys. Res.*, 108, No D4, 8368, doi:10.1029/2002JD002732, 2003.

Helmig, D., Johnson, B., Oltmans, S.J., Neff, W., Eisele, F., and Davis, D.D., Elevated ozone in the boundary-layer at South Pole. *Atmos. Environ.*, 42, 2788-2803, 2008.

Jacob, D. J., Crawford, J. H., Maring, H., Clarke, A. D., Dibb, J. E., Emmons, L. K., Ferrare, R. A., Hostetler, C. A., Russell, P. B., Singh, H. B., Thompson, A. M., Shaw, G. E., McCauley, E., Pederson, J. R., and Fisher, J. A., The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission: design, execution, and first results, *Atmos. Chem. Phys.*, 10, 5191–5212, doi:10.5194/acp-10-5191-2010, 2010.

Legrand, M., Preunkert, S., Jourdain, B., Gallée, H., Goutail, F., Weller, R. and Savarino, J.: Year round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica, *J. Geophys. Res.*, 114, D20306, doi:10.1029/2008JD011667, 2009.

Morin, S., Savarino, J., Bekki, S., Gong, S., and Bottenheim, J. W., Signature of Arctic surface ozone depletion events in the isotope anomaly ( $\Delta^{17}\text{O}$ ) of atmospheric nitrate, *Atmos. Chem. Phys.*, 7, 1451–1469, 2007.

Morin, S., Savarino, J., Frey, M. M., Dominé, F., Jacobi, H.-W., Kaleschke, L., and Martins, J. M. F., Comprehensive isotopic composition of atmospheric nitrate in the Atlantic Ocean boundary layer from 65°S to 79°N, *J. Geophys. Res.*, 114, D05303, doi:10.1029/2008JD010696, 2009.

Salawitch, R. J., et al. (41 co-authors), A new interpretation of total column BrO during Arctic spring, *Geophys. Res. Lett.*, Vol. 37, L21805, doi:10.1029/2010GL043798, 2010.