

Final author reply to the editor

The first part of this document is the response to each of the reviewers' comments and the second part lists all other changes that have been made to the manuscript.

PART 1: REVIEWERS COMMENTS

The reviewers' comments and our responses are labelled. Text from the manuscript is in quotations and with changes highlighted in blue.

REVIEWER 1

Comment:

This study fills an important information gap about HONO sources and sinks in the polar boundary layer at a snow-covered coastal site, a key question for the oxidative properties of the polar atmosphere. Thus, the manuscript is clearly in the scope of ACP. The study presents new data and the manuscript is structured adequately with respect to the aim of the manuscript. In my opinion the manuscript is suitable for publication after one point has been corrected.

The only real concern I have is that the authors invoke in section 4.1 (paragraph which starts at line 295) very high levels of organic matter at Halley by referencing Calace et al. (2005) and Antony et al. (2011) to explain the flux density measured during the field campaign, whereas Legrand et al. (2013) clearly demonstrated that these studies overestimate the organic matter content significantly. Instead, Legrand et al. (2013) reports much lower levels of about 10-20 ppbC of dissolved organic carbon at inner continental sites as well as near coastal sites (see also Figure 3 for HULIS species). Thus, the contribution of the production mechanism via R10 and R11 are likely too limited to explain the observed HONO flux.

On the other hand, concerning the organic matter content which should be low at both sites, snow at Halley and Dome C might not be so different, what might allow to do a first order estimation of the Halley HONO flux density via the Halley NO_x flux measured during the CHABLIS campaign and the HONO to NO_x production rate ratio measured in the Dome C snow photolysis experiment described by Legrand et al., 2014. Such an exercise could give a hint whether the, to a few hours limited, HONO flux measurements conducted within this study would be representative or not.

Response:

We added a discussion of the findings of Legrand et al. (2013) in the text, including that the organic content of the snow could not be as high as initially suggested. We have done the calculation suggested and included it in the text:

'...marine sources associated with sea-spray. [Legrand et al. \(2013\)](#) have highlighted that these studies could overestimate the organic matter content due to their sampling method and measurement technique. They suggest that the organic matter at coastal Antarctic sites could be lower, comparable to inland sites like Dome C (3 – 8 µg L⁻¹). [Legrand et al. \(2014\)](#) suggest that this could still lead to significant HONO production. Assuming Dome C and Halley snow have similar organic content, a HONO flux density can be estimated based on the HONO:NO_x

emission ratio measured in a laboratory study of Dome C snow (Legrand et al., 2014) and the measured NO_x flux density at Halley (Bauguitte et al., 2012). The HONO:NO_x ratio is temperature dependent; the highest temperature studied by Legrand et al. (2014) is -13°C which is below the Halley air temperature for the flux measurement period. An emission ratio of 0.77 and NO_x flux density of $7.3 \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$ give a HONO flux density of $5.6 \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$, close to the measured value. NO₂ has been measured...'

Comment: The method sections 2.2. and 2.4 are rather long considering that both methods (LOPAP and flux calculations) are already reported in literature. For the sake of the straightness of the manuscript, the authors might consider to shorten these topics considerably in the main manuscript and to detail them in a supporting text. On the other hand, the manuscript is not too long, as it is, therefore I leave the decision to the authors.

Response: We have decided to leave the method section as is. ACP's manuscript guidelines require methodological details to be part of the main text; they should not appear as supplement.

Comment: Figure 5 (line 201) is addressed for the first time before Figure 4 (line 205) is addressed for the first time. Therefore figure 4 and 5 might be inversed in their order.

Response: Figures 4 and 5 have now been reversed in order.

Comment: Please let the reader know where the data of this study will be available.

Response: The data will be available at the UK Polar Data Centre. This is now stated in the manuscript.

REVIEWER 2

Comment:

This paper reports the results of a field measurement study assessing the sources and contribution of HONO to oxidation capacity of the Antarctic boundary layer at a coastal (ie, sea level altitude) location. This remains a persistent challenge and key issue in understanding within- and above-snowpack atmospheric chemical processing. The paper combines field measurement results from a challenging environment with derivation of vertical flux using the gradient flux approach, and simple calculations to assess the contribution of HONO to OH formation.

The results are similar to those reported from other comparable locations, and advance quantitative understanding of the importance of HONO at this location; they go some way to unpicking conflicting results (from HONO measurements likely over-estimated previously) at this location.

The measurements appear to have been carefully performed with appropriate corrections and blanks etc, and are described at an appropriate level of detail. The analysis presented is carefully considered. Use of species measurements from previous campaigns (i.e. different years) is made, but this is unavoidable and appropriately noted / caveated. The paper is well written and clearly presented.

I recommend the paper is accepted for publication, subject to the authors considering the corrections / suggestions outlined below.

A style point: personally I find the terminology “amount fraction” somewhat jarring – “mixing ratio” preferable. We need to make our manuscripts accessible as well as precise ! But this is up to the Editor and journal...

Response: ACP expects authors to follow IUPAC terminology. "Amount fraction" (short for "amount-of-substance fraction") are the terms recommended in the IUPAC Green Book. Mixing ratio is an ambiguous term and therefore best avoided (e.g., it can refer to mass, volume and amount fractions, or even mass or amount per volume of air). We have therefore kept the term "amount fraction".

Comment: R4 is termolecular and should include the third body M – line 31 and subsequently in the manuscript.

Response: R4 has been amended to include M.

Comment: L51 are reactions “accelerated” by sunlight – consider phrasing.

Response: This has been rephrased as follows:

‘The uptake of NO₂ on such organics is greater in the presence of sunlight (George et al., 2005)’

Comment: L81 / L232 it would be possible to estimate the magnitude of potential PNA interference – using the previous data for HO₂ and NO₂ to estimate [HO₂NO₂]_{ss} and hence the interference contribution. This might usefully be added to the discussion.

Response: The average steady state HNO₄ amount fraction was calculated as 0.05 pmol mol⁻¹. Legrand et al. (2014) suggest 100 pmol mol⁻¹ of HNO₄ would lead to an overestimate by 15 pmol mol⁻¹ HONO. The interference is therefore insignificant and below the detection limit of the LOPAP. This will be included in the manuscript:

‘The LOPAP’s response to HNO₄ has been investigated in both the laboratory with an HNO₄ source and in the field at Dome C by placing a heated tube at the instrument inlet to decompose HNO₄. Both showed that the LOPAP partially measures HNO₄ as HONO [with approximately 100 pmol mol⁻¹ HNO₄ leading to an interference of 15 pmol mol⁻¹](#), but further investigation is needed to systematically quantify this effect (Legrand et al., 2014).’

‘As a further check on this interference, the steady-state concentration of HNO₄ was calculated. The method for this is detailed in Appendix B. Again the concentrations of HO₂, NO₂ and OH from the CHABLIS campaign were used. The average steady-state amount fraction was 0.05 pmol mol⁻¹. Using the estimate of Legrand et al. (2014), this suggests that the interference is likely <0.01 pmol mol⁻¹, well below the detection limit of the LOPAP.’

‘Appendix B: Calculation of HNO₄ steady state concentration

The steady state concentration of HNO₄ was calculated using Eq. B1. The reactions and their rate coefficients are listed in Table B1.

Loss of HNO₄ via photolysis was also included in the calculation (HNO₄ + hν → products). The rate coefficient, J(HNO₄), was derived from the TUV radiation model as described in the main text.’

$$[\text{HNO}_4] = \frac{k_{\text{B1}}[\text{HO}_2][\text{NO}_2]}{J(\text{HNO}_4) + k_{12} + k_{\text{B2}}[\text{OH}]} \quad (\text{B1})$$

Table B1. Rate coefficients used in calculation of the HNO₄ steady state concentration

<i>k</i>	Values	Reaction	Ref.
<i>k</i> _{B1}	$k_0 = 1.4 \times 10^{-31} \left(\frac{T}{300K}\right)^{-3.1} [\text{M}] \text{ cm}^3 \text{ s}^{-1}$ $k_\infty = 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ $F_c = 0.4$	HO ₂ + NO ₂ + M → HNO ₄ + M	
<i>k</i> _{B2}	$3.2 \times 10^{-13} \text{ e}^{\left(\frac{690K}{T}\right)} \text{ cm}^3 \text{ s}^{-1}$	HNO ₄ + OH → H ₂ O + NO ₂ + O ₂	Atkinson et al. (2004) IUPAC (last accessed: 2022-03-08)
<i>k</i> ₁₂	$k_0 = 4.1 \times 10^{-5} \text{ e}^{\left(\frac{-10650K}{T}\right)} [\text{M}] \text{ cm}^3 \text{ s}^{-1}$ $k_\infty = 6.0 \times 10^{15} \text{ e}^{\left(\frac{-11170K}{T}\right)} \text{ s}^{-1}$ $F_c = 0.4$	R12	

Comment: L113 the key assumption of LOPAP is that HONO is effectively entirely removed in coil 1, but that the abundance of interferents is effectively unchanged – so that subtraction of coil 2 signal from coil 1 signal results in just HONO.

Response: The fact that this is an assumption has been emphasised in the text:

‘The interferences ~~should~~ are assumed to be taken up to the same small extent in both channels so that the HONO amount fraction can be calculated by subtracting the signal in channel 2 from that in channel 1’

Comment: L139 How did the 15 min height change compare with the (liquid) residence time of the LOPAP – were the data used for flux calculations adjusted / truncated for the delay from instrument residence time between gas intake and absorption signal response.

Response: The average response time of the LOPAP (90 % of final signal) was (8.0 ± 1.5) min. All LOPAP data was shifted to account for the time delay, including the flux data. This is now stated in the text:

'...at the instrument inlet. The detection limit ($3\sigma_{\text{blank}}$) was $0.26 \text{ pmol mol}^{-1}$ for the measurement period. The average response time (90 % of final signal change) was $(8.0 \pm 1.5) \text{ min}$.'

'The elevator is depicted in Fig. 3. The LOPAP data were shifted to account for the time delay ($(17 \pm 2) \text{ min}$) between gas intake and the observed absorption signal. This is determined from the average of all abrupt concentration changes (start/stop of blanks) and defined as the time between concentration change and the 50 % response of the instrument.'

Comment: L198 what albedo assumed for the TUV calculations.

Response: 0.95, this has been included in the text:

' F is the actinic flux derived from the TUV radiation model over the wavelength range 300 to 1200 nm using measured ozone column density, a surface albedo of 0.95, and assuming clear sky conditions (Madronich and Flocke, 1999; Lee-Taylor and Madronich, 2002).

Comment: L291 worth commenting on the snow surface age vs porosity (ie fresh snow or subject to many weeks freezing or...)

Response: This is now mentioned in the text as a factor to consider when evaluating wind pumping:

'... suggesting such wind pumping does occur at Halley. The degree of wind pumping will be affected by snow permeability, which is related to snow porosity (Waddington et al., 1996). During this measurement period the snow was fresh and therefore more porous and likely more permeable than aged snow.'

Comment: Fig 7 – caption - not sure that $P_{\text{ss}}(\text{HONO})$ makes any assumption about the nature of the source.

Response: This is true, the figure caption has been amended:

'HONO production calculated from Eq. (8), $P_{\text{ss}}(\text{HONO})$.'

Comment: Table 3 – what is y ?

Response: Amount fraction, this has been included in the table caption:

'Observations of HO_x concentrations and NO_x amount fractions (y) made during the CHABLIS campaign at Halley'

Comment: L371 the comparison of HONO and NO_x lifetimes is useful – previous Halley work has shown the NO_x lifetime is significantly reduced from halogen nitrate photolysis (Bauguitte et al. 2011), this will be quite different from that estimated due to NO₂ + OH alone – and may improve agreement with the observed HONO:NO_x ratio?

Response: This reduction in the NO_x lifetime does bring the HONO:NO_x lifetime ratio closer to the measured ratio. This is now discussed in the text:

‘... the steady-state conditions are not fulfilled. However, Bauguitte et al. (2012) found that the NO_x lifetime was reduced by halogen processing (BrNO₃ and INO₃ formation and heterogeneous uptake). A reduced NO_x lifetime would improve the agreement with the observed HONO:NO_x ratio.’

Comment: L385 – HOI and HOBr are not primary sources of OH – they reflect HO_x cycling, as they form from HO₂+XO, so in terms of OH sources they are really similar to HO₂ + NO. Suggest the table compares either primary OH sources (HONO, O¹D) or all OH sources (including HO₂ + NO etc) or (best) all HO_x sources – HONO, O¹D, HCHO, but excluding recycling such as HO₂+NO, HO₂+XO.

Response: The table has been updated to include both primary OH sources and HO_x recycling sources with the distinction between the two made clear in the table and caption:

Table 4. Maximum and average HO_x production by primary HO_x sources (HONO, O₃, formaldehyde (HCHO) and hydrogen peroxide (H₂O₂)) and HO_x recycling at different Antarctic (Halley and Dome C) and Arctic (Barrow) locations.

Location	OH source	Maximum OH production / pmol mol ⁻¹ h ⁻¹	Average OH production / pmol mol ⁻¹ h ⁻¹
Halley (this campaign)	O ₃	31	12
	HONO	12	5
Halley (CHABLIS campaign, Bloss et al. (2007))	O ₃	62	
	HCHO	10	
	H ₂ O ₂	<10	
	HOI	89	
	HOBr	14	
	HO ₂ + NO	13	
Dome C (Kukui et al., 2014)	HONO	298	194
	HCHO	50	28
	H ₂ O ₂	28	12
	O ₃	23	4
	HO ₂ + NO	157	112
Barrow (Villena et al., 2011)	HONO	90	
	O ₃	3	

PART 2: OTHER CHANGES TO THE MANUSCRIPT

Snow nitrate data

The main change that has been made to the manuscript is that snow nitrate concentration data for the measurement campaign are now available. This had not been measured initially due to Covid-19 related delays in the lab work. The addition of this data does not change the overall conclusions of this study.

Including this has led to changes to the following sections:

Abstract

'The measured flux density is ~~at the upper limit of the~~ close to the calculated HONO production rate from photolysis of nitrate present in the snow.'

Methods

The following has been added to 2.3 Ancillary measurements:

'Surface snow samples were collected from the top 3 cm of snow in the clean air sector on 6, 25, and 31 January 2022. The samples were collected using clean sampling procedures (wearing clean room suits, gloves and masks) and transferred into 50 mL polypropylene tubes with screw caps (Corning CentriStar), which had been rinsed with UHP water and dried in a class 100 clean laboratory in Cambridge prior to field deployment. The samples were transported back to the UK at -20°C where they were melted and analysed for major ions including nitrate using Dionex Integrion ICS-4000 ion chromatography systems with reagent-free eluent generation. A Dionex AS-AP autosampler was used to supply sample water to 250 µL sample loops on the cation and anion instruments. Anion analyses were performed using a Dionex Ionpac AG17-C (2 µm, 2 x 50 mm) guard column and AS17-C (2 x 250 mm) separator column. A 3.5 – 27 mM potassium hydroxide eluent concentration-gradient was used for effective separation of the analytes. Calibration was achieved using a range of calibration standards prepared from Sigma-Aldrich standards (1000 µg g⁻¹) by a series of gravimetric dilutions. Measurement accuracies were evaluated using European reference materials ERM-CA408 (simulated rainwater) and CA616 (groundwater) and were all within 5 %. The LOD was 2 ng g⁻¹.'

Discussion: 4.1 HONO formation mechanisms

'~~Daily nitrate mass concentrations in surface snow were measured during the CHABLIS campaign; the mean value for January to February is (47.1±17~~ As detailed in section 2.3, the surface snow nitrate mass fraction was measured; the mean value is (78.2 ± 18) ng g⁻¹ (Jones et al., 2011). A yield of 100% gives a HONO production rate of ~~3.7 × 10¹² m⁻² s⁻¹~~ 1.9 × 10¹² m⁻² s⁻¹ at a light intensity corresponding to local noon, ~~just above~~ below the maximum measured flux density of 3.4 × 10¹² m⁻² s⁻¹. However, the yield is unlikely to be as high as 100 %.

There are two product channels for nitrate photolysis (reactions R6 and R8); if it is assumed that all nitrite produced in R6 is converted to HONO, $Y(\text{HONO})$ would be 10% because R8 dominates over R6 by a factor of 9 (Chu and Anastasio, 2003). This gives a noon HONO production rate of only $(0.37 \pm 0.30) \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$ ($0.19 \pm 0.13) \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$. This is lower than the measured flux density, see Fig. 7.'

Figure 7

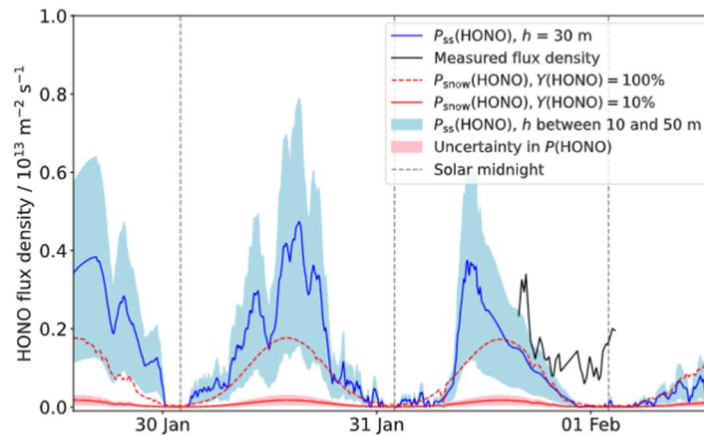


Figure 7. HONO production calculated from Eq. (8), $P_{ss}(\text{HONO})$. The blue filled region is the production expected for mixing heights of 10 m and 50 m. The HONO production from snow nitrate photolysis, $P_{snow}(\text{HONO})$, is plotted assuming a HONO yield of 100% and 10%. The uncertainty in this, from z_e , $w(\text{NO}_3^-)$ and the photolysis quantum yield, is represented by the red filled region. The measured flux density is also plotted. The production of HONO through reaction of OH + NO (R4) is not shown as its contribution would be $< 10^{11} \text{ m}^{-2} \text{ s}^{-1}$.

Conclusions

'A HONO flux density of 0.5 to $3.4 \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$ from the snow was measured which is ~~at the upper limit of the~~ **close to the** estimated HONO production from nitrate photolysis suggesting this reaction is a driver of HONO release from the snow.'

Change to $P(\text{HONO})$ labels

The only additional change is that in sections 4.1 and 4.2 $P(\text{NO}_y)$ and $P(\text{HONO})$ are used for the production of NO_y and HONO from photolysis of snow nitrate and have now been replaced with $P_{snow}(\text{NO}_y)$ and $P_{snow}(\text{HONO})$ for clarity.