Response to Reviewer 3

In this manuscript the authors present the ground-based measurement results of concentrations and isotopic ratios ($^{15}N/^{14}N$ and $^{18}O/^{16}O$) of NO_x and HONO in the wildfire smoke plumes in the Western U.S. With a simple box model, they are able to use the data to assess the relative importance of pathways of HONO formation and loss in the smoke plumes. The research approach is innovative and is capable of providing insights into HONO formation mechanisms, although its low method sensitivity limits its applications to air masses with relatively high levels of NO_x and HONO, such as urban atmosphere and wildfire plumes. The paper contains valuable and useful information and thus should be published. I do have some concerns and comments below that need to be addressed before the manuscript is accepted for publication.

We are grateful for the helpful comments from Reviewer 3. Below are the point-to-point response to the reviewer's comments in blue text.

There were simultaneous real-time measurements of HONO, NO_x and other relevant parameters during the study, as stated in the manuscript and published in Kaspari et al. (2021). I suggest the authors to validate the denuder sampling methods by comparing the concentrations of NO_x and HONO with those by Kaspari et al. (2021) and to address the comments by Referee #1 regarding potential interference from PAN on NO_x sampling by denuders. It is critical to prove the methods used to be accurate and reliable before any significant conclusion can be made.

Thank you for the comments and suggestions. Indeed, comparison between the real time measurement and our sample collection is key to ensure accuracy of our offline quantification for both concentration and isotopic composition. During the FIREX fire lab experiment, we applied the same method to quantify the HONO and NOx isotopic composition (Chai et al., 2019). The HONO concentrations captured with our annular denuder system (ADS) were well compared with 4 other high time resolution concentration measurement techniques, including mist chamber/ion chromatography (MC/IC), open-path Fourier transform infrared spectroscopy (OP-FTIR), cavity enhanced spectroscopy (CES), and proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF). In the same work, the NOx concentration collected in the permanganate impinger was verified by real-time measurement with a chemiluminescence NOx analyzer. In addition, our NO_x collection technique has been verified with real-time NOx concentrations in on-road, near-road and urban background environments (Wojtal et al., 2016; Miller et al., 2017). These agreements verify complete capture of HONO and NO_x associated with biomass burning emissions using our technique, which preserve the isotopic signatures without isotopic fractionation during the sampling process.

Based upon the reviewer's suggestion, we added lines 196-206 and lines 233-236 in the main text and Figure S3 in the supplemental materials.

lines 196-206: "Note that complete collection of HONO and NO_x have been verified in various environments including biomass burning emissions. During the FIREX fire lab experiment, we applied the same method to quantify the HONO and NO_x isotopic composition (Chai et al., 2019). The concentrations of HONO captured with our annular denuder system (ADS) well compared with 4 other high time resolution concentration measurement techniques, including mist chamber/ion chromatography (MC/IC), open-path Fourier transform infrared spectroscopy (OP-FTIR), cavity enhanced spectroscopy (CES), and proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF). In the same work, the NO_x concentrations collected in the permanganate impinger was verified by real-time measurement with a chemiluminescence NO_x analyzer. In addition, our NO_x collection technique has been verified with real-time NO_x concentrations in on-road, near-road and urban background environments (Wojtal et al., 2016; Miller et al., 2017). These agreements verify complete capture of HONO and NO_x associated with biomass burning emissions using our techniques, which preserve the isotopic signatures without isotopic fractionation during the sampling process."

lines 233-236: "The concentration results for the ADS collected [HONO] agree well with that measured via MC/IC in real-time and averaged over the ADS sampling periods (Fig. S3). The good agreement between these techniques sampling the same plumes near the ground, and previous agreement with other HONO and NO_x observation methods suggest the concentrations are accurate (see also Section 2.3)."

To address reviewer #1's comment on possible PAN interference with NOx, we added text in lines 236-248 and lines 294-304. Please also refer to our response to Reviewer #1's comments.

lines 236-248: "It is important to also consider possible interference of peroxyacetyl nitrate (PAN) with NO_x collected in the alkaline permanganate solution for biomass burning conditions (Jaffe and Briggs, 2012). There is minimum PAN formed in fresh biomass burning (BB) emissions and young smoke of less than half an hour, based upon previous lab and field measurements, as well as modeling studies (Stockwell et al., 2014; Yokelson et al., 2009; Alvarado et al., 2010, 2015). In aged BB plumes in the upper troposphere, PAN can form rapidly at low temperatures and act as a temporary NO_x reservoir, reaching a maximum PAN/NO_y ratio of 0.3 (comparable to NO_x/NO_y) within ~2 to 4 hours of aging after emission (Yokelson et al., 2009; Liu et al., 2016; Akagi et al., 2012). Though we note that these results are all from airborne measurements. There are no ground-level measurements for PAN in BB plumes during WE-CAN or FIREX-AQ, nor from other field studies, to the best of our knowledge. PAN is thermally unstable in the boundary layer during summertime, and its main loss process in the atmosphere is thermal decomposition to release NO_2. The lifetime of PAN is on the order of 1 hour or less at 20 °C and above (Talukdar et al., 1995; Fischer et al., 2010). We therefore expected PAN in near-ground air to maintain low levels or less due to photochemistry and thermal decomposition. Thus, given the short lifetime and the sample integration time of over 40 min to 2 hours' timescale, PAN is unlikely to interfere with our NO_x results."

lines 294-304: "We note again that, although no near-ground PAN measurements in BB plumes are available, the isotopic results also suggest that PAN interference is not important to the δ^{15}N-NO_x results. For aged smoke, we would expect δ^{15}N-NO_x to decrease from that in fresh emissions due to partial transformation of NO_x to additional oxidized N products (e.g., PAN), as well as isotopic exchange between NO_x and these oxidized species; both processes will leave ^{15}N depleted in NO_x and ^{15}N enriched in PAN (Walters and Michalski, 2015). If PAN existed at significant concentrations that were 1) comparable with NO_x in the atmosphere, and 2) completely collected in the permanganate solution, then the δ^{15}N would reflect the overall δ^{15}N of NO_x + PAN in the final reduced permanganate solution. In this case, we would expect that aged smoke would not shift from the δ^{15}N-NOx range of young smoke, because δ^{15}N shifts in both PAN and NO_x could offset each other. However, our observed δ^{15}N-NO_x mean values for both aged daytime and nighttime smoke are significantly ($p<0.05$) lower than that of the young smoke, a good indicator of a lack of PAN interference on the isotopic results (see also Miller et al. (2017))."

The authors reported that nitrate photolysis plays only a minor role (<5%) in HONO formation in daytime aged smoke, while heterogeneous NO_2-to-HONO conversion contributes 85-95% to total HONO production, followed by OH+NO (5-15%). This finding is in line with what we would expect from our current understanding in HONO chemistry in the environments with moderately elevated NO_x levels. However, it should be pointed out that HONO can be produced by different mechanisms in different NO_x concentration regimes. Extensive field and laboratory studies in the past 30 years have shown that the HONO budgets can be well predicted and constrained by the reactions of NO and NO_2 in the high-NO_x environments. However, other mechanisms, such as photolysis of surface nitric acid and particulate nitrate, may play an important role in the low-NO_x environments. The real-time measurement data reported by Kaspari et al. (2021) (and also the time-series plot in Figure S3) showed very high concentrations of HONO (up to 6 ppb) and NO_2 (over 40 ppb) in bands of smoke plumes, in contract to very lower concentrations in the background air outside the plumes. Due to the long sampling times (2-12 hours for HONO and 0.75 – 2.5 hours for NO_x) required for the concentration and isotopic measurements, the "averaged" data may not be representative of wildfire smoke plumes, especially when there were significant dilution by background air in the "aged" plume. Cautions should be taken in interpreting the skewed averaged data.

Thank you for raising this point. We acknowledge previous works' findings that under low NOx conditions, nitrate photolysis is an important source of HONO. As the reviewer pointed out, our sample integration time is much longer than real-time concentration measurements, and our samples may contain both wildfire smoke plumes as well as background air. As such, our results obtained from the combination of modeling and field observation represent the average relative importance of R2 - R4 for HONO production. Techniques for measuring isotopic composition of HONO and NO_x with higher time resolution will be required to characterize the temporally and spatially varied secondary HONO formation mechanism. To clarify this point, we added text in lines 373-381:

"However… it should be noted that the result represents our best estimate of the average relative importance of R2 - R4 for HONO production during our HONO sampling periods (2-10 hours) for the aged daytime plumes. Due to the long sample integration time, we expect our samples were influenced by both aged smoke and near-background air when the smoke was very diluted. Under the NO_x–limited condition (low NO_x <1 ppbv) in the remote background air, nitrate photolysis is expected to be the major secondary HONO source (Ye et al., 2016; Zhou et al., 2011), which cannot be ruled out by our results. Isotopic measurement techniques with higher time resolution will be required to achieve real-time quantification of the HONO budget."

The manuscript contains two appendixes and a supplement, and it summarizes the key reactions with isotopic fractionation information in a figure. This unusual presentation style is sometime jumpy and confusing. I suggest that some reorganizations of the manuscript should be made to smooth the flow of data presentation and discussion and to made it easier to read.

Thank you for the suggestions. We reorganized the manuscript by adding reactions R1-R7 in the introduction text, which should make it easier for readers to follow, as suggested by Reviewer 2 as well. In addition, we changed the titles of Appendix A to make it more informative.

To justify the structure of our manuscript a little bit more, the first appendix presents a current state of HONO pathways and budget quantification based upon concentration; and the second appendix presents our parameterization of the N and O isotopic fractionation associated with the major HONO pathways. We put these detailed calculations in the appendices so as to simplify the flow of the main text. Lastly, we have also modified the title of the manuscript to be more detailed to clarify the key findings of the work.

Page 6 line 165: the minimum detection limit of 0.07 mM seems too high. It should be 0.07 µM.

Thank you for catching the typo. We have corrected this in the main text.

Page 14 equations (A1) and (A2): what are R and P in the equations? Is R for the rate of production/loss? From the expression of (A2), P should be the fraction of OH-NO reaction to the total HONO production. All the terms in equations should be defined in the text.

Thank you for the suggestions. We have defined all the terms in the main text (lines 469 and 474 respectively):

"…, where $R_{emission}$, $R_{production}$ and R_{loss} are rate of emission, production and loss respectively."

"…the ratio of R2 to the total HONO production (P_{OH+NO})…"

Page 15 equation (A4): Since the sampling was conducted on the ground stations, ground surface should be considered in S/V; it may be important for the heterogeneous HONO production near the ground, especially during the night.

Thank you for the suggestions. We agree that ground surface is very important during the night for HONO production. Given the large particle loadings, it is hard to quantify the overall S/V. However, we added the discussions on this point in the text in lines 515-516:
"ground surface is also expected to play an important role in nighttime HONO production given our ground sampling location", and added a reference (Tuite et al., 2021)…"

Page 16 equation (B3): Should the equation be as follows?

$1/\Upsilon_l = 1/\alpha + 1/\Gamma_b$

The calculations in lines 393-494 do not make sense.

Thank you for catching the typo in the equation (now line 549). We have corrected the typo in equation (B3). In fact, we calculated the fractionation factor with the correct equation in our original work. Our apologies for the typo!

Figure 5: How do you define the fraction of remaining HONO upon photolysis (F_{rp})? For a daytime aged plume arrived at the site from tens km away, >99% of the original HONO would be photolyzed

within a few hours during the transport. So with <1% of HONO remaining upon photolysis, >15% of R4 contribution may still be possible.

We defined f_{cp} as remaining HONO fraction from secondary production as a result of photolysis, and we modified the sentence in lines 355-358:
"We quantify the remaining HONO fraction from secondary production, f_{rp}, to represent HONO that has been produced but not yet photolyzed. Thus, the daytime $\Delta\delta^{15}N_{HONO-NOx}$ for aged smoke was simulated as a function of f_{rp} following a Rayleigh-type isotopic fractionation scheme (Fig. 5)".

As the lifetime of HONO during the day is less than an hour due to photolysis, we expect almost all HONO in the aged smoke were produced from secondary pathways. Thus, we conducted simulations of $\delta^{15}N$ under two sets of mechanisms (M1 and M2) by incorporating the estimated isotopic fractionation factors of all the major formation and loss reactions (R1-R4). By using our field-measured values as constraint on the modeling results, we solve f_{cp} for each daytime aged sample. We found that inclusion of nitrate photolysis (R4) would require very fast HONO photolysis, and this will result in very low f_{cp} ,<0.01, <0.006 and <0.002 for 5% R4, 10% R4 and 15% R4 respectively, in order to reproduce the two highest $\Delta\delta^{15}N_{HONO-NOx}$. This suggests the larger nitrate photolysis contributes to HONO production, the less likely the observed HONO levels (hundreds pptv) can be maintained.

In addition, as the reviewer has pointed out, our sample integration time is much longer than real-time concentration measurements. We responded to this question in the reviewer's second point, and we added text in lines 373-381 to clarify this point:
"However, there are two limitations to the modeling results. First, as the $^{15}N/^{14}N$ fractionation associated with R3, R6 and R7 are not distinguishable with our current parameterization (Appendix B.1.2 and B.2.2), we cannot rule out the potential importance of heterogeneous NO_2-to-HONO conversions (R6 and R7) in daytime. Second, it should be noted that the results represent our best estimate of the average relative importance of R2-R4 for HONO production during our HONO sampling periods (2-10 hours) for the aged daytime plume. Due to the long sample integration time, our samples were influenced by both aged smoke and near-background air when the smoke was very diluted. Under the NO_x–limited condition (low NO_x <1 ppbv) in remote background air, nitrate photolysis is expected to be the major secondary HONO source (Ye et al., 2016; Zhou et al., 2011), which cannot be ruled out by our results. Isotopic measurement techniques with higher time resolution will be required to achieve real-time quantification of the HONO budget."

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