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Comment on acp-2021-225

Anonymous Referee #3

Referee comment on "Isotopic evidence for dominant secondary production of HONO in near-ground wildfire plumes" by Jiajue Chai et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-225-RC3, 2021

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.

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.

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.

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.

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

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.

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.

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

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

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

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.