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Comment on “Isotopic evidence for dominant secondary production of HONO in near-ground wildfire plumes” by Chai et al. (2021)

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Abstract. Chai et al. (2021) recently published measurements of wildfire-derived (WF) oxides of nitrogen (NO_x) and nitrous acid (HONO) and their isotopic composition. The method used to sample NO_x, collection in alkaline solution, has a known 1 : 1 interference from another reactive nitrogen compound, acetyl peroxynitrate (PAN). Although PAN is thermally unstable, subsequent reactions with nitrogen dioxide (NO_2) in effect extend the lifetime of PAN many times longer than the initial decomposition reaction would indicate. This, coupled with the rapid and efficient formation of PAN in WF plumes, means the NO_x measurements reported by Chai et al. were severely impacted by PAN. In addition, the model reactions in the original paper included neither the reactions of NO_2 with hydroxyl radical (OH) to form nitric acid nor the efficient reaction of larger organic radicals with nitric oxide to form organic nitrates ($RONO_2$).

Main text

Chai et al. present ground-based measurements of nitrous acid (HONO) and the oxides of nitrogen (NO_x) and their ^{15}N and ^{18}O isotopic abundances in air masses in the immediate vicinity of wildfire (WF) (Chai et al., 2021). Although the paper was openly reviewed by me (Roberts, 2021) and somewhat modified as a result, there are several aspects of the methodology and interpretation of the results that bear further commenting on.

The main problem with the methodology, sample collection of NO_x in alkaline solution, is a 1 : 1 interference (as N) from acetyl peroxynitrate ($CH_3C(O)OONO_2$, PAN), a ubiquitous product of VOC-NO_x photochemistry (volatile organic compound). We have known this for decades, as alkaline collection and hydrolysis has been used in a number of studies as a means to calibrate PAN sources (see for example Stephens, 1969; Grosjean et al., 1984; Grosjean and Harrison, 1985; and references in Roberts, 1990). The basis of PAN interference with NO_x collection is really not in dispute, since PAN is at least 2 orders of magnitude more soluble in water than NO and NO_2 (Sander, 2015), and its alkaline hydrolysis is extremely rapid and forms nitrite (see for example Steer et al., 1969). Nitrite of course is a main product of the aqueous reactions of NO_x and is converted to nitrate by permanganate in the method of Chai et al. (2021). Thus, any conditions that will completely collect and convert NO_x to nitrate will convert PAN to nitrate quantitatively.

Regrettably, there are no PAN measurements in this study with which to constrain this interference. However, Chai et al. argue in their reply and in their paper (Chai et al., 2021; Chai, 2021) that very little PAN would be present in the air masses they sampled due to the relative freshness of the WF emissions not having made much PAN yet and/or due to the thermal instability of PAN. The gist of this comment is that the arguments underlying two assumptions are simply not correct.

The kinetics of the thermal decomposition of PAN and related compounds are well studied (see for example the review by Kirchner et al., 1999, and the more recent work of Kabir et al., 2014). It is true that the initial reaction of

$$CH_3C(O)OONO_2 + M \rightarrow CH_3C(O)OO + NO_2 \qquad (R1)$$

is relatively rapid at 298 K as $4 \times 10^{-4}\,s^{-1}$. However, net loss of PAN only occurs if the peroxy radical is lost due to reaction with nitric oxide:

$$CH_3C(O)OO + NO \rightarrow CH_3 + CO_2 + NO_2. \qquad (R2)$$

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The other main fate of the peroxyacetyl (PA) radical is recombination with NO_2 to reform PAN:

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2. \quad \text{(R3)}$$

As a result, the loss of PAN due to thermal decomposition should be expressed as an effective net loss rate:

$$\text{Net Loss Rate} = k_1\{1 - (k_3[NO_2]/(k_3[NO_2] + k_3[NO]))\}. \quad \text{(R4)}$$

This introduces a dependence of the loss rate on the ratio $[NO_2]/[NO]$ shown in Fig. 1. NO_x measurements from the Chai et al. study itself correspond to lifetimes as long as 8 h, clearly long enough for PAN to persist at ground level and to be mixed throughout the daytime planetary boundary layer (PBL). This aspect of PAN chemistry has considerable experimental support (see for example Roberts et al., 2007) and is one of the reasons why PANs are universally observed at ground level. In fact, the only instances in which ground-level PAN concentrations over the continent reach very low levels, essentially zero, are nighttime periods under very stable nocturnal boundary layers with local sources of nitric oxide (see for example Roberts et al., 2002). Daytime PAN levels are more characteristic of the entire daytime PBL because of the relatively long lifetime and PBL mixing times on the order of a few hours. The other major gas phase losses of PA radicals involve reactions with HO_2 or RO_2 radicals and have similar rate constants to Reactions (2) and (3), 1–$2 \times 10^{-11}\,cm^3\,molec^{-1}\,s^{-1}$, so these will only be important when NO_x levels are below 100 pptv or so. It should also be noted that other photochemical loss processes for PAN (photolysis, reaction with OH) are quite slow compared to thermal decomposition (Talukdar et al., 1995) and will not impact PAN in this environment. So, it is possible that the results of Chai et al. (2021) from young nighttime plumes could have been had very low to no PAN contributions, but all the other sampling instances will have had substantial contributions due to PAN.

The magnitude of this contribution could be quite large due to rapid a formation of PANs in WF plumes and the fact that long PAN lifetimes mean that formation of PANs aloft will impact the ground due to mixing. As indicated by the references quoted by Chai et al. (2021) and other relatively recent papers, PAN formation is often rapid in WF plumes, so PAN/NO_x can reach or exceed 1 within a half to several hours. For example, Alvarado et al. (2010) observed 40 % conversion of WF NO_x to PAN within a few hours, and Juncosa Callahorrano et al. (2020) found PAN/NO_x averaged more than 1 after 1 h of processing during one of the same projects as Chai et al. So, we can conclude with considerable confidence that production of PAN from WF NO_x likely impacted air masses that authors have termed as "young daytime" and certainly impacted the air masses that have been categorized as "mixed" and "aged". There are ground-level measurements of PAN and oxides of nitrogen in the Boise, Idaho, urban area during the 2017 WF season (McClure and Jaffe, 2018), and they show that PAN levels are a substantial fraction of odd nitrogen and are certainly significant relative to NO_x.

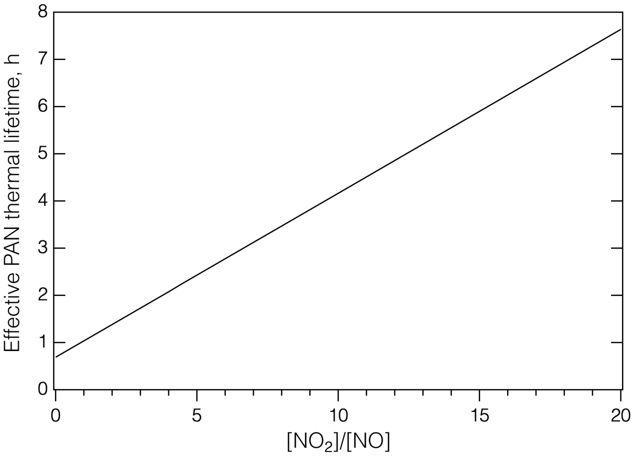

Figure 1. The effective PAN thermal lifetime at 298 K as a function of $[NO_2]/[NO]$ based on Reactions (1)–(3).

Chai et al. (2021) and Chai (2021) use the results of their ^{15}N-NO_x measurements, particularly those of the aged categories, to argue against a significant contribution from PAN. However, their conceptual model does not take into account the other NO_x chemistry that we know to be taking place in this environment: reaction of NO_2 to form HNO_3 from OH $+NO_2$, the formation of organic nitrate species $RONO_2$ from reaction of RO_2 radicals with NO, and nighttime reactions of NO_3 and N_2O_5. So, PAN formation is not the only reactive nitrogen chemistry that will shift $\delta^{15}N$-NO_x (which is actually δ^{15}-(NO_x + PAN) to lower values relative to the WF signature). This other NO_x chemistry needs to be considered.

The community engaged in ^{15}N isotopic analysis appears to be left with a conundrum: why do ^{15}N signatures, from NO_x + PAN and other reactions of NO_x, not match their current understanding of the effects of photochemistry? As with many such situations, this is an opportunity to learn and refine our understanding of ^{15}N cycling in atmospheric photochemistry.

Code availability. There was no code used in this manuscript aside from common data plotting software.

Data availability. No data sets were used in this article.

Competing interests. The contact author has declared that there are no competing interests.

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