1 Comment on "Isotopic evidence for dominant secondary production of HONO in

2 near-ground wildfire plumes."

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6 **Abstract**

7 Chai et al. (2021a) recently published measurements of wild fire (WF) derived oxides of nitrogen

8 (NOx) and nitrous acid (HONO) and their isotopic composition. The method used to sample

9 NOx, collection in alkaline solution, has a known 1:1 interference from another reactive nitrogen

10 compound, acetyl peroxynitrate (PAN). Although PAN is thermally unstable, subsequent

11 reactions with nitrogen dioxide (NO_2) in effect extend the lifetime of PAN many times longer

12 than the initial decomposition reaction would indicate. This, coupled with the rapid and efficient

13 formation of PAN in WF plumes, means the NOx measurements reported by Chai et al. were

14 severely impacted by PAN. In addition, the model reactions in the original paper did not include

15 the reactions of NO_2 with hydroxyl radical (OH) to form nitric acid, nor the efficient reaction of

16 larger organic radicals with nitric oxide to form organic nitrates ($RONO_2$).

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18 **Main Text**

19   Chai et al., present ground-based measurements of nitrous acid (HONO) and the oxides

20 of nitrogen (NOx) and their ^{15}N and [18]O isotopic abundances in airmasses in the immediate

21 vicinity of wildfire (WF) (Chai, et al., 2021a). Although the paper was openly reviewed by me

22 (Roberts, 2021) and somewhat modified as a result, there are several aspects of the methodology

23 and interpretation of the results that bear further commenting on.

24   The main problem with the methodology, sample collection of NOx in alkaline solution,

25 is a 1:1 interference (as N) from acetyl peroxynitrate ($CH_3C(O)OONO_2$, PAN) a ubiquitous

26 product of volatile organic compound (VOC)-NOx photochemistry. We have known this for

27 decades as alkaline collection and hydrolysis has been used in a number of studies as a means to

28 calibrate PAN sources (see for example Stephens, 1969, Grosjean et al., 1984, Grosjean and

29 Harrison, 1985, and references in Roberts 1990). The basis of PAN interference with NOx

30 collection is really not in dispute since PAN is at least 2-orders of magnitude more soluble in

31 water than NO and NO_2 (Sander, 2015) and its alkaline hydrolysis is extremely rapid and forms

32 nitrite (see for example Steer et al., 1969). Nitrite of course is one main product of the aqueous

33 reactions of NOx and is converted to nitrate by permanganate in the method of Chai et al.,

34 (2021a). Thus, any conditions that will completely collect and convert NOx to nitrate will

35 convert PAN to nitrate quantitatively.

36   Regrettably, there are no PAN measurements in this study with which to constrain this

37 interference. However, Chai et al., argue in their reply and in their paper (Chai et al., 2021a&b),

38 that very little PAN would be present in the air masses they sampled due to the relative freshness

39 of the WF emissions not having made much PAN yet and/or due to the thermal instability of

40 PAN. The gist of this Comment is that the arguments underlying two assumptions are simply not

41 correct.

42   The kinetics of the thermal decomposition of PAN and related compounds are well

43 studied, (see for example the review by Kirchner et al., (1999), and the more recent work of

44 Kabir (2014)). It is true that the initial reaction:

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46       $CH_3C(O)OONO_2 + M \rightarrow CH_3C(O)OO + NO_2$ (1)

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48 is relatively rapid at 298K, 4×10^{-4} s^{-1}. However, net loss of PAN only occurs if the peroxy

49 radical is lost due to reaction with nitric oxide;

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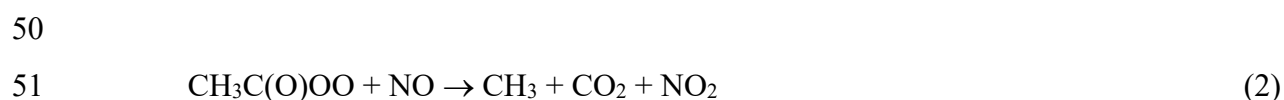
51       $CH_3C(O)OO + NO \rightarrow CH_3 + CO_2 + NO_2$ (2)

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

54

55       $CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2$ (3)

56

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

58 net loss rate;

59

60       $\text{Net Loss Rate} = k_1\{1-(k_3[NO_2]/(k_3[NO_2] + k_3[NO]))\}$ (4)

61

62 This introduces a dependence of the loss rate on the ratio [NO$_2$]/[NO] shown in Fig. 1. NOx

63 measurements from the Chai study itself correspond to lifetimes as long as 8 hours, clearly long

64 enough for PAN to persist at ground level, and to be mixed throughout the daytime planetary

65 boundary layer (PBL). This aspect of PANs chemistry has considerable experimental support,

66 (see for example Roberts et al., 2007), and is one of the reasons why PANs are universally

67 observed at ground level. In fact, the only instances in which ground level PAN concentrations

68 over the continent reach very low levels, essentially zero, are nighttime periods under very stable

69 nocturnal boundary layers with local sources of nitric oxide (see for example Roberts et al.,

70 2002). Daytime PAN levels are more characteristic of the entire daytime PBL because of the

71 relatively long lifetime and PBL mixing times on the order of a few hours. The other major gas

72 phase losses of PA radical involve reaction with HO$_2$ or RO$_2$ radicals and have similar rate

73 constants to Reactions (2&3), 1- 2 ×10^{-11} cm^{3}molec^{-1}s^{-1}, so will only be important when NOx

74 levels are below 100 pptv or so. It should also be noted that other photochemical loss processes

75 for PAN (photolysis, reaction with OH) are quite slow compared to thermal decomposition

76 (Talukdar et al., 1995) and will not impact PAN in this environment. So, it is possible that that

77 the Chai et al., (2021a) results from young nighttime plumes could have been had very low to no

78 PAN contributions, but all the other sampling instances will have had substantial contributions

79 due to PAN.

80   The magnitude of this contribution could be quite large due to rapid a formation of PANs

81 in WF plumes and the fact that long PAN lifetimes mean that formation of PANs aloft will

82 impact the ground due to mixing. As indicated by the references quoted by Chai et al, (2021a)

83 and other relatively recent papers, PANs formation is often rapid in WF plumes, so PAN/NOx

84 can reach or exceed 1 within ½ -to-several hours. For example: Alvarado et al., (2010) observed

85 40% conversion of WF NOx to PAN within a few hours, Juncosa Callahorrano (2020) found

86 PAN/NOx averaged more than 1 after 1 hr of processing during one of the same projects as Chai

87 et al. So, we can conclude with considerable confidence that production of PAN from WF NOx

88 likely impacted airmasses that authors have termed as "young daytime", and certainly impacted

89 the airmasses that have been categorized as "mixed" and "aged". There are ground-level

90 measurements of PAN and oxides of nitrogen in the Boise, Idaho urban area during the 2017 WF

91 season (McClure, and Jaffe, 2018), and they show that PAN levels are a substantial fraction of

92 odd-nitrogen, and are certainly significant relative to NOx.

93   Chai et al. (2021a&b) use the results of their ^{15}N-NOx measurements, particularly those

94 of the aged categories, to argue against a significant contribution from PAN. However, their

95 conceptual model does not take into account the other NOx chemistry that we know to be taking

96 place in this environment: reaction of NO_2 to form HNO_3 from OH +NO_2, the formation of

97 organic nitrate species $RONO_2$ from reaction of RO_2 radicals with NO, and nighttime reactions

98 of NO_3 and N_2O_5. So, PAN formation is not the only reactive nitrogen chemistry that will shift

99 δ^{15}N-NOx (which is actually δ^{15}-(NOx + PAN) to lower values relative to the WF signature. This

100 other NOx chemistry needs to be considered.

101   The community engaged in ^{15}N isotopic analysis appears to be left with a conundrum:

102 why don't ^{15}N signatures, from NOx + PAN and other reactions of NOx, match their current

103 understanding of the effects of photochemistry? As with many such situations, this is an

104 opportunity to learn and refine our understanding of ^{15}N cycling in atmospheric photochemistry.

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106 **Code Availability**

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

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109 **Author Contribution**

110   This work was the product of the sole author.

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112 **Competing Interests**

113   The author declares no competing interests.

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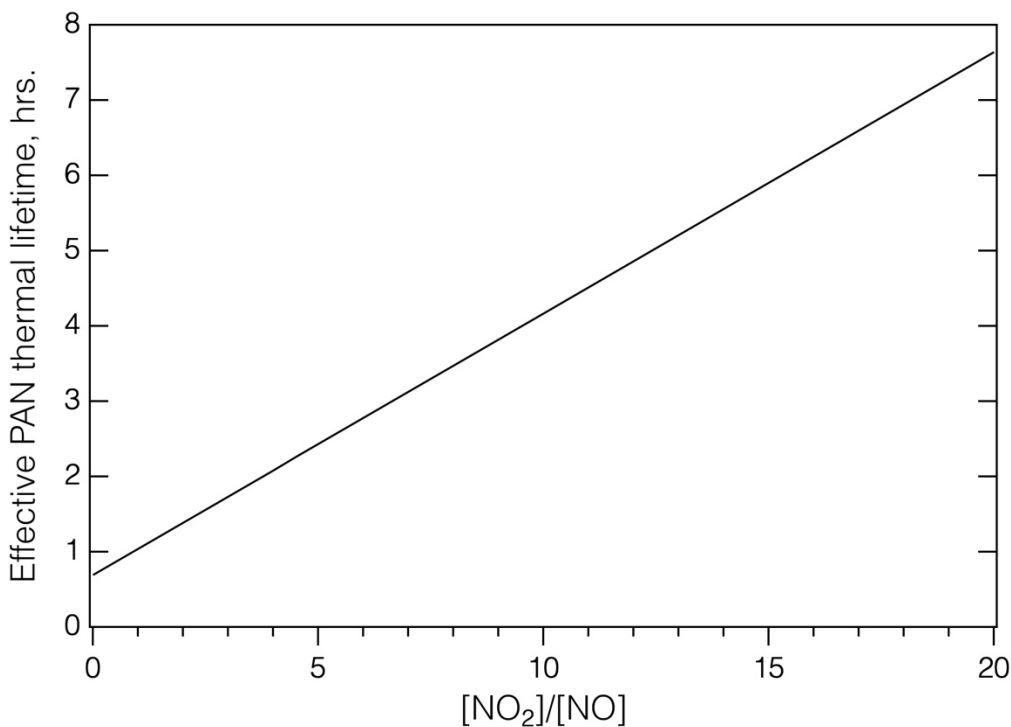
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185   Figure 1. The effective PAN thermal lifetime at 298K as a function of $[NO_2]/[NO]$ based on
186   Reactions (1-3).