Atmospheric
Chemistry
and Physics
Discussions

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

2 near-ground wildfire plumes."

3

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5

6 **Abstract**

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

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

9 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 ($RONO_2$).

17

18 **Main Text**

19   Chai et al., (2021) present ground-based measurements of nitrous acid (HONO) and the

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

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

22 reviewed by me (Roberts, 2021) and somewhat modified as a result, there are several aspects of

23 the methodology 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:

45

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

47

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;

50

51           $CH_3C(O)OO + NO \rightarrow CH_3 + CO_2 + NO_2$ (2)
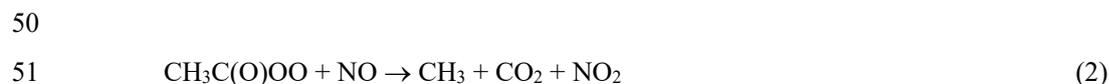
52

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   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 $\times 10^{-11}$ 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".

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

91   those of the aged categories, to argue against a significant contribution from PAN. However,

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

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

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

95   reactions of NO_3 and N_2O_5. So, PAN formation is not the only reactive nitrogen chemistry that

96   will shift $\delta^{15}N$-NOx (which is actually δ^{15}-(NOx + PAN) to lower values relative to the WF

97   signature. This other NOx chemistry needs to be considered.

98

99   **Competing Interests**

100   The author declares no competing interests.

101

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107   **References**

108
109   Chai, J., J.E. Dibb, B.E Anderson, C. Bekker, D.E Blum, E. Heim, C.E. Jordan, E.E. Joyce, J.H.
110   Kaspari, H. Munro, W.W. Walters, and M.G. Hastings, Atmos Chem Phys., 2021a.

111

112   Chai, J., et al., Reply to review of acp-2021-225, "Isotopic evidence for dominant secondary
113   production of HONO in near-ground wildfire plumes." https://doi.org/10.5194/acp-2021-225-
114   AC1, 2021b.

115

116   Grosjean, D., Fung, K., Collins, J., Harrison, J., and Breitung, E., Portable generator for on-site
117   calibration of peroxyacetyl nitrate analyzers, Anal. Chem., 56, 569-573, 1984.

118

119   Grosjean, D., and Harrison, J., Peroxyacetyl nitrate: Comparison of alkaline hydrolysis and
120   chemiluminescence methods., Environ. Sci. Technol., 19, 749-752, 1985.

121

122   Juncosa Calahorrano, J. F., Lindaas, J., O'Dell, K., Palm, B. B., Peng, Q., Flocke, F., Pollack, I.
123   B., Garofalo, L. A., Farmer, D. K., Pierce, J. R., Collett Jr., J. L., Weinheimer, A., Campos, T.,
124   Hornbrook, R. S., Hall, S. R., Ullman, K., Pothier, M. A., Apel, E. C., Permar, W., Hu, L., Hills,
125   A. J., Montzka, D., Tyndall, G. S., Thornton, J. A., and Fischer, E. V.: Daytime oxidized reactive
126   nitrogen partitioning in western U.S. wildfire smoke plumes., J. Geophys. Res., 126,
127   e2020JD033484, 2020.

128

129   Kabir, M., Jagiella, S., and Zabel, F.: Thermal stability of n-acyl peroxynitrates, Int. J. Chem
130   Kinet., 46, 462-469, 2014.

131

132   Kirchner, F., Mayer-Figge, A., Zabel, F., and Becker, K. H.: Thermal stability of peroxynitrates,
133   Int. J. Chem. Kinet., 31, 127-144, 1999.
134
135   Roberts, J.M., The atmospheric chemistry of organic nitrates, Atmos. Environ, 24A, 243-287,
136   1990.
137
138   Roberts, J.M., Flocke, F., Stroud, C.A., Hereid, D., Williams, E.J., Fehsenfeld, F.C., Brune, W.,
139   Martinez, M., and Harder, H.: Ground-based measurements of PANs during the 1999 Southern
140   Oxidants Study Nashville intensive, J. Geophys. Res., 107, 10.1029/2001JD000947, 2002.
141
142   Roberts, J.M., Marchewka, M., Bertman, S.B., Sommariva, R., Kuster, W.C., Goldan, P.D.,
143   Williams, E.J., Lerner, B.M. and Fehsenfeld, F.C.: Measurements of peroxycarboxylic nitric
144   anhydrides off the coast of the northeast United States during the New England Air Quality
145   Study, (NEAQS) 2002, J. Geophys. Res., 112, D20306, doi:10.1029/2007JD008667, 2007.
146
147   Roberts, J.M. Review comment on acp-2021-225, "Isotopic evidence for dominant secondary
148   production of HONO in near-ground wildfire plumes." https://doi.org/10.5194/acp-2021-225-
149   RC1
150
151   Talukdar, R. K., Burkholder, J. B., Schmoltner, A.-M., Roberts, J. M., Wilson, R. R., and
152   Ravishankara, A. R.: Investigation of the loss processes for peroxyacetyl nitrate in the
153   atmosphere: UV photolysis and reaction with OH, Journal of Geophysical Research, 100, 14163-
154   14173, 1995.
155
156   Sander, R.: Compilation of Henry's law constants (version 4.0) for water as solvent, Atmos.
157   Chem. Phys., 15, 4399-4981, 2015.
158
159   Stephens, E.R., The formation, reactions, and properties of peroxyacyl nitrates (PANs) in
160   photochemical air pollution, Adv. Environ. Sci., 1, 119-146, 1969.
161
162   Steer, R. P., Darnall, K. R. and Pitts, J. N. Jr.: The base-induced decomposition of
163   peroxyacetylnitrate, Tet. Lett. 43, 3765-3767, 1969.
164

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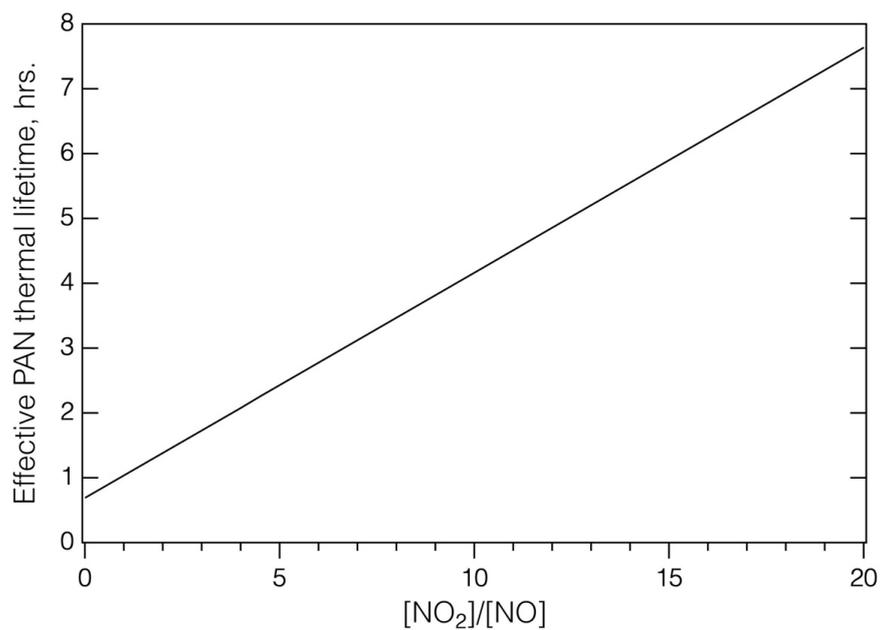
Figure 1. The effective PAN thermal lifetime at 298K as a function of $[NO_2]/[NO]$ based on Reactions (1-3).