

1 Comments "...The iterative method to determine the isomer-specific branching ratios is quite
2 critical to the accuracy of the overall analysis. While I am comfortable with the description of the
3 very careful efforts to understand the sources of calibration errors, the manuscript would be
4 improved with a more extended discussion of this method and the results..."

5
6 More description of the iterative method was added to page 11 (lines 307-311) of the revised
7 manuscript. To further clarify the iterative method, we have added more detailed description and
8 a flow chart to the supplement section 3.1.

9
10 Comments "...In particular, I am intrigued by Supplement Figure S8, which shows the model-
11 determined isomer-specific branching ratios. While it seems to me that this figure contains very
12 important results, I could not find a reference to this figure in the main manuscript..."

13
14 Reference to this figure was added to the revised manuscript page 7 (line 201). Please note
15 Figure S8 is now Figure S9 because we added a new figure to describe the iterative method.

16
17
18 Comments "...In particular, Figure S8 shows that there are only two significant isomers formed
19 (1,2-IN and 4,3-IN), which is quite a different result than that reported by both the CIMSbased
20 (Paulot et al. 2009) and GC-based (Lockwood et al. 2010) previous laboratory studies. The new
21 finding suggests that the OH-initiated oxidation of isoprene is more regiospecific than these
22 previous studies indicated, which is interesting (and simplifying with respect to modeling
23 isoprene oxidation). In particular, both of the previous studies identified the various 1,4- and 4,1-
24 HNI isomer-producing reaction pathways as having minor, yet significant, branching ratios, but
25 Figure S8 indicates that they are very minor products. It would be helpful to explain what part(s)
26 of the analysis are responsible for the difference as compared to the two previous laboratory
27 studies..."

28
29 Figure S8, which is now Figure S9 in our revised supplement, shows the results of isomer
30 distribution during the SOAS field study. In comparison, the previous work by Paulot et al.
31 (2009) and Lockwood et al. (2010) are focused on experimental chamber studies.

32
33 The difference can be explained from two aspects. First, the isoprene nitrates in the field undergo
34 more oxidation degradation than in the reaction chamber. As the 1,4 and 4,1 nitrate isomers have
35 larger OH and O₃ oxidation rate constants than the 1,2 and 4,3 isomers, the 1,4 and 4,1 nitrate are
36 consumed faster in the field, making their contribution to the total IN pool smaller. The second
37 factor is 1,6-H shift of cis-1,4 and cis-4,1 RO₂ isomers and RO₂ interconversion. During the
38 SOAS field study, the NO concentration is in the range that allows a significant amount of cis-
39 1,4 and cis-4,1 RO₂ to undergo H-shift, which reduces the amount of 1,4- and 4,1- RO₂ available
40 to react with NO and form 1,4- and 4,1-nitrates. In chamber studies, however, NO concentrations
41 are in the range that force all the RO₂ radicals to react with NO, making 1,4- and 4,1-nitrates
42 more important. This is clarified in the revised manuscript on page 14 (lines 387-392).

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47
48 p. 17851 line 25: I'm not familiar with the scrubbing technique described here. Please provide a
49 reference to the method and indicate what species are being removed.

50
51 The method and citation are added to the revised manuscript on page 9 (lines 253-256).

52
53 p. 17853 line 3: Since the relative quantity $[IN]/([MVK]+[MACR])$ is the critical quantity being
54 analyzed, it would be helpful to know how much the absolute quantity ($[MVK]+[MACR]$) varied
55 in the SOAS data being analyzed here, as larger variations in the absolute value would have the
56 potential to cause more uncertainty in the relative value. Additionally, can the absolute variations
57 in $[MVK]+[MACR]$ be qualitatively explained according to expected changes in transport and
58 boundary height?

59
60 The $[MVK]+[MACR]$ measurement during SOAS has a 40% measurement uncertainty. This is
61 added to page 18 (line 507) of the revised manuscript.

62
63 The absolute diurnal concentrations of $MVK+MACR$ are more consistent with the dynamics of
64 photochemistry, with its peaking concentration at around 1:00 PM when radiation was strong,
65 and [isoprene] is large. The changes in $MVK+MACR$ concentrations are also affected by
66 transport and changing boundary layer height. Since we did not apply three-dimensional
67 transport model in this work, we were unable to quantify the influence of transport and boundary
68 layer height on the absolute $MVK+MACR$ concentrations. However, the relative concentrations
69 of IN to $MVK+MACR$ can provide some insight into the isoprene oxidation chemistry, since
70 these meteorological factors influence all three compounds. We have discussed in more detail the
71 $MVK+MACR$ diurnal profile on page 13 (lines 361-364) of the revised manuscript.

72
73
74 p. 17863 line 4: Is the 13% branching ratio OH + HNI pathway to IEPOX under the low NO
75 conditions a significant source of IEPOX in the afternoon, or does the modeling indicate that
76 ISOPOOH is still the dominant precursor of IEPOX?

77
78 During the SOAS study, the 24-hour averaged peak is around 80 ppt for isoprene nitrates and
79 300 ppt for ISOPOOH. The yield of IEPOX is 13% for isoprene nitrate oxidation and ~ 75% for
80 ISOPOOH oxidation (St. Clair et al., 2015). Therefore, ISOPOOH is still the dominant precursor
81 for IEPOX. This is now discussed in the revised manuscript on page 21 (lines 609-611).

82
83 Technical corrections

84 p. 17848 line 14: What is the solvent used in the IN solutions?

85
86 Information on the solvent (C_2Cl_4) is now added on page 5 (line 131).

87
88 p. 17851 line 14: change to “. . . , so wall loss correction was not applied to the IN
89 measurements.”

90
91 We have now re-worded the sentence on page 9 (line 240).

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95 p. 17856 equation 2: the alpha term in this equation should be defined immediately as the nitrate
96 branching ratio.

97

98 [Description of the alpha term is now added on page 14 \(line 399\).](#)

99

100 p. 17859 line 24: typo: “efficiency”

101

102 [Typo has been corrected on page 18 \(line 514\).](#)

103

104 p. 17862 line 9: typo: “different”

105

106 [Typo has been corrected on page 20 \(line 584\).](#)

107

108

109 Reference

110 St. Clair, J. M., Rivera, J. C., Crouse, J. D., Knap, H. C., Bates, K. H., Teng, A. P., Jørgensen, S.,
111 Kjaergaard, H. G., Keutsch, F. N., and Wennberg, P. O.: Kinetics and Products of the Reaction of
112 the First-Generation Isoprene Hydroxy Hydroperoxide (ISOPOOH) with OH, The Journal of
113 Physical Chemistry A, 10.1021/acs.jpca.5b06532, 2015.

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