

1 The authors present a combination of laboratory and field measurements of isoprene nitrates plus
2 related compounds. They use a 0-D chemical model to interpret the data in terms of constraints
3 on isoprene nitrate formation and fate in the atmosphere. This paper is well written and makes a
4 valuable contribution to our developing understanding of isoprene nitrate chemistry in the
5 atmosphere. It should be published. Comments and suggestions are listed below, and are
6 generally minor.

7
8 **Thank you.**
9

10 17857, 25: You could still have some IN production from $\text{NO}_3 + \text{isoprene}$ in the NBL. NO is not
11 so high at night that it would dominate NO_3 loss. The ratio of the rate coefficients
12 $k(\text{NO}_3 + \text{NO})/k(\text{NO}_3 + \text{isoprene})$ is about 37. Fig 6 shows that NO_x at midnight was around 0.6
13 ppb, but this is almost all NO_2 , NO at midnight averaged <10 ppt. On the other hand isoprene
14 was >2 ppb at midnight. Based on that, isoprene + NO_3 would be 5-6 times faster than $\text{NO} +$
15 NO_3 at that time. Would this affect your interpretation of the diurnal IN cycle? Would the CIMS
16 detect any of the $\text{NO}_3 + \text{isoprene}$ nitrates with the daytime products, or no?

17
18 The CIMS would detect the hydroxynitrates (IN) from NO_3 reaction with isoprene near ground.
19 Our IN raw data during the SOAS study was interpreted with an IN isomer distribution estimated
20 by a 0D model. Within this model, IN production from NO_3 chemistry was also included,
21 besides IN formation from the $\text{OH} + \text{isoprene}$ pathway. Therefore, we have already considered
22 the IN formation from NO_3 chemistry in our data analysis. This is clarified on page 16 (lines
23 456-461) of the revised manuscript.

24
25 17848, 15-28. Please discuss why you believe it is reasonable to use the sensitivity for 4,3-IN as
26 a surrogate for all other beta INs (aside from 1,2). And likewise using cis/trans-1,4 for cis/trans-
27 4,1.

28
29 The CIMS sensitivities toward alkyl alcohol and alkyl nitrates are both around 5 orders of
30 magnitude smaller than its sensitivity toward the isoprene hydroxynitrates. Hence, it is the
31 combination of the OH group and the nitrate group, as well as their relative positions that has the
32 dominant influence on the CIMS sensitivity, which will affect how the molecule binds with the
33 iodide ion, while the structure of the carbon backbone would have little effect. For the IN
34 isomers, the relative positions of the OH group and the nitrate group are α, β position, trans- α, δ
35 position and cis- α, δ position. We assume the same sensitivity can be applied to isomers within
36 each structural group, namely β -isomers, trans- δ isomers and cis- δ isomers. This assumption is
37 consistent with our observation of identical sensitivity for 1,2-IN and 4,3-IN isomers when water
38 is not added to the CIMS. For the case with water addition to CIMS, the smaller sensitivity of
39 1,2-IN was caused by the smaller amount of 1,2-IN available for detection, as 1,2-IN is lost
40 inside the instrument, rather than from a fundamental difference in the ionization efficiency of
41 1,2-IN. Primary nitrates (δ -IN, 3,4-IN, and 2,1-IN) and secondary nitrate (4,3-IN) are not as
42 likely to be affected by water (Hu et al., 2011). We have now clarified these assumptions on
43 page 7 (lines 174-184) of the revised manuscript.

44
45 17854, 5. Some significant assumptions had to be made for the instrumental sensitivities for the
46 various IN isomers. Only a couple isomers were actually synthesized and calibrated directly, and

47 the derived sensitivities for those range over a factor of 7. These were then used to estimate the
48 sensitivity for other IN isomers. Given that, I find it hard to believe that the reported 15%
49 uncertainty for IN measurements is even close to realistic.

50
51 While the sensitivities of the IN isomers vary greatly, the relative contribution of each isomer to
52 the total pool of IN is well understood from the theoretical work on the formation of isoprene
53 RO₂ and experimental studies that measured MVK and MACR formed simultaneously with IN
54 in isoprene oxidation. The measurement uncertainty for IN comes from 1) the measurement
55 uncertainty for each individual isomer obtained in our calibrations and 2) the uncertainty in the
56 relative abundance of each isoprene nitrate, caused by uncertainty in the kinetics data of the
57 LIM1 mechanism (Peeters et al., 2014). 15% uncertainty is associated with instrument
58 calibration only, and the IN measurement uncertainty is around 23%, with both factors
59 considered. We have provided a more detailed discussion on the estimated IN data uncertainty in
60 supplement section 5 and error propagation is clarified on page 12 (lines 329-339) of the revised
61 manuscript.

62
63
64 17849, 20-25. Do we know that 1,2-IN is the only isomer affected by humidity in this way? If
65 that's not the case would that affect your interpretation of the field data? Likewise (17854, 13)
66 do we know that 1,2 is the only isomer affected by inlet loss?

67
68 Hu et al. (2011) suggests that primary and secondary organic nitrates do not undergo hydrolysis
69 under neutral condition, but hydrolysis in neutral pH is efficient for tertiary nitrates. Given the
70 fact that the 1,2-IN is the only tertiary nitrate and the short residence time for the ion-molecule
71 reaction, we do not expect the other nitrates to be affected by humidity. We have discussed the
72 humidity sensitivity of IN isomers on page 7 (lines 184-193) of the revised manuscript.

73
74 For inlet loss, we have conducted new experiments and found the inlet loss to be around 5% on
75 average for all the isomers, and our data has been corrected for the 5% inlet loss. This is
76 described on page 8 (line 213) of the revised manuscript.

77
78
79 17851, 16-28. Was the sample stream humidified for the field measurements as it was for the lab
80 data? If not, how do you correct for humidity-dependent losses of the various isomers?

81
82 The sample was humidified during the field measurement with the same conditions used in the
83 lab experiments. This information is added on page 9 (line 219) of the revised manuscript.

84
85
86 Fig. 7 is well done. The diurnal trend in gamma shows nicely how the fractional importance of
87 RO₂ + NO versus other RO₂ sinks varies during the day. It may also be worth pointing out that
88 the calculated IN production rate (Fig 7b) is not as peaked in the morning as the RO₂ loss rate to
89 RO₂ + NO (Fig 7a) or gamma. And that this is because the RO₂ concentrations are still quite
90 low at that time. Right?

91

92 Right. When the γ value peaks around 6 AM to 8 AM, the isoprene and OH concentrations are
93 relatively low. Therefore, the nitrate production rate is limited by the availability of RO₂. In the
94 afternoon, while only a fraction of RO₂ will react with NO to form organic nitrates, the total
95 amount of isoprene RO₂ is higher due to higher isoprene and OH concentrations. Therefore, the
96 IN production rate does not have an abrupt decrease in the afternoon as the γ value does. This is
97 further clarified in the revised manuscript on page 14 (lines 407-412).

98
99
100 Fig 8, 17859-17860. You consider the possibility of fast photolysis to explain the day time IN
101 decrease. Could heterogeneous losses / deposition be playing a role?

102
103 Aerosol formation may be a small sink for IN, but the C5 hydroxynitrate is unlikely to undergo
104 efficient aerosol uptake (Surratt et al., 2010) due to its small molecular weight. Field
105 observations during SOAS suggest that the isoprene-derived SOA components were associated
106 with IEPOX and more oxidized organic nitrates, not the first-generation hydroxynitrates (Lee et
107 al., 2015; Xu et al., 2015). Therefore, we did not consider aerosol uptake as a major factor for the
108 overestimation of [IN]/([MVK]+[MACR]) ratio in the afternoon. This is discussed on page 22
109 (lines 663-666) of the revised manuscript.

110
111 17849, 1-8. It seems this method could be used as a check on the relative sensitivities for all IN
112 isomers. Is it just that 4,3 and 1,2 are the only ones detected with enough signal for the purpose?

113
114 The small abundance of the other isomers makes it more difficult to obtain reliable quantification
115 through this method. Therefore, the sensitivity was obtained by synthesizing a standard. This
116 discussion is added to the revised manuscript on page 6 (line 171-173).

117
118
119 17853, 5. Should say “partially cancel the influence of dilution” or “reduce the influence”.
120 Transport could easily affect MVK+MACR differently than INs, just based on differing lifetimes
121 and concentrations in the residual layer, advected air masses, etc.

122
123 The change has been made on the revised manuscript on page 10 (line 289).

124
125 17853, 11-18. Need a description or at least a mention and citation for the other measurements
126 used (PTR, GC).

127
128 Citation for PTR and GC measurements have been added to the revised manuscript on page 11
129 (line 295 and line 297).

130
131 17854, 13-18. Reported 9% IN yield is “in the 4-14% range of IN yields determined from
132 previous experiments (...) but is more consistent with determinations from the higher end of the
133 range”. Actually it seems to be exactly in the middle.

134
135 We have made the adjustment on the revised manuscript on page 12 (line 342).

136
137

138 References

139

140 Hu, K. S., Darer, A. I., and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of
141 atmospherically relevant organonitrates and organosulfates, *Atmospheric Chemistry and*
142 *Physics*, 11, 8307-8320, 10.5194/acp-11-8307-2011, 2011.

143 Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., D'Ambro1, E. L., Lutz, A., Hallquist, M., Lee, L., Romer,
144 P., Cohen, R. C., Iyer, S., Kurten, T., Hu, W. W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Xu,
145 L., Ng, N. L., Wild, R. J., Brown, S. S., Koss, A., Gouw, J. d., Olson, K., Goldstein, A. H., Seco, R.,
146 Kim, S., McAvey, K., Shepson, P. B., Baumann, K., Edgerton, E. S., Nguyen, T. B., Wennberg, P. O.,
147 Liu, J., Shilling, J. E., and Thornton, J. A.: Highly functionalized particle-phase organic nitrates
148 observed in the Southeastern U.S.: contribution to secondary organic aerosol and reactive
149 nitrogen budgets, in preparation, 2015.

150 Peeters, J., Müller, J.-F., Stavrakou, T., and Nguyen, V. S.: Hydroxyl Radical Recycling in Isoprene
151 Oxidation Driven by Hydrogen Bonding and Hydrogen Tunneling: The Upgraded LIM1
152 Mechanism, *The Journal of Physical Chemistry A*, 118, 8625-8643, 10.1021/jp5033146, 2014.

153 Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P.,
154 Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary
155 organic aerosol formation from isoprene, *Proceedings of the National Academy of Sciences of*
156 *the United States of America*, 107, 6640-6645, 10.1073/pnas.0911114107, 2010.

157 Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the
158 southeastern United States using high-resolution aerosol mass spectrometry: spatial and
159 seasonal variation of aerosol composition and sources with a focus on organic nitrates,
160 *Atmospheric Chemistry and Physics*, 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015.

161