

Interactive comment on “Importance of biogenic precursors to the budget of organic nitrates during BEARPEX 2009: observations of multifunctional organic nitrates by CIMS and TD-LIF” by M. R. Beaver et al.

Anonymous Referee #2

Received and published: 27 February 2012

This paper is scientifically very interesting. It addresses the issue of the apportionment of NO_y in a polluted region with strong biogenic emissions. Previous work using the TD-LIF showed a very large contribution of alkyl nitrates (AN) to the total NO_y and importantly that this could explain what was previously known termed the “missing NO_y”. However the TD-LIF only measures the sum of AN and not the individual species. This paper brings new insight by measuring some of the AN species derived from isoprene oxidation. I think the paper should be accepted for ACP subject to some minor revisions detailed below.

C281

There are several places in the paper, which refer to the CIMS measuring speciated AN. (e.g. page 329, lines 12-15). Whilst the *m/z* ratios measured for some species can be reasonably assigned to some specific compounds, some can only be assigned to groups (e.g. the sum of hydroxynitrates isomers (ISOPN) and the sum of MVKN and MACRN). I think this needs to be made much clearer upfront and the text modified so as not to be misleading.

What is the impact of the uncertainty in the CIMS data of 40% on the conclusions?

There should be some discussion in section 3.2 of the effect on the budget calculation of only including the VOCs measured at the site.

p. 328, l. 1. Need a reference or more details of what is B3LYP/6-31G9(d) level of theory.

p. 330. The discussion in which the measurements of isoprene nitrates are compared to previous measurements is a bit misleading, since only a limited number of ISOPN were measured before and thus to compare concentrations with total ISOPN is not comparing like with like.

p. 331, l. 26-27. This sentence about assuming an alpha value of 0.15 is confusing. What exactly was this alpha value assumed? From Table 1, can the reader take this to be for the formation of secondary AN from primary AN?

p. 332, l. 4. Where does this value of 41% come from. Table 1 gives a value of 36% for isoprene.

p. 334, l. 18. The fact that monoterpene emissions are temperature dependent means that they “can” be emitted at night (not “are”).

p. 334, l. 26. Suggest this sentence is part of the previous paragraph and the new paragraph is started by the next sentence.

p. 335, l. 15. Please provide a reference/comment as to why the CIMS only measures

C282

the gas phase.

Table 2. and Figures 3 and 4. Figure 3 captions refers to Table 2 for the organic nitrate species observed by the CIMS and yet that table only gives m/z , with no explanation. Only becomes clear later in the text. The letters in the last column of Table 2 needed to be referenced to Figure 4 as they are meaningless.

Figure 5. It would be interesting to see other m/z ratios (structures given in Figure 4) plotted in Figure 5.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 319, 2012.