

Interactive comment on “Stable carbon isotope ratios of ambient secondary organic aerosols in Toronto” by M. Saccon et al.

Anonymous Referee #2

Received and published: 6 July 2015

General Comment: This manuscript describes measurements of stable carbon isotope ratios of five nitrophenols in the gas phase and PM from ambient Toronto, Canada. The application of the stable carbon isotope ratio measurement in atmospheric science provides insights into the gas-phase (original phase) processing of VOC oxidation and whether gas-particle partitioning has been reached by comparing gas-phase vs. particle-phase samples. The authors found that the difference in carbon isotope ratios between nitrophenols in the particle phase and gas phase is insignificant, except for a limited number of samples collected in summer, suggesting under high OH conditions photochemical formation or removal of nitrophenols can be faster than exchange between the two phases and gas-particle partitioning cannot be quickly maintained. Based on meteorology conditions and pollutant concentrations, further conclusion is

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drawn that the influence of precursor concentrations is more important than the extent of photochemical processing on nitrophenol concentrations. The application of stable carbon isotope ratio measurement is interesting and potentially important for atmospheric studies. The discussions are technically sound and the manuscript is well presented. However, I do have some reserve on the discussion and conclusions of this work.

Main Comments: 1. The authors presented results for five nitrophenols from aromatic VOC photooxidation. 4-NP and 2-me-4-NP are abundant and analyzed in most samples. However, the other three nitrophenols, 4-me-2-NP, 3-me-4-NP, and 2,6-dime-4-NP are not as abundant and only 17%, 47%, and 22% of the overall samples have enough signal to provide results. The authors admitted that this “could result in subsets of $\delta^{13}\text{C}$ data biased towards samples with higher nitrophenol concentrations”. Any idea how large could such bias be? Some discussion could be added. For example, For the three NPs from toluene photooxidation, 2-me-4-NP is more abundant; 3-me-4-NP and 4-me-2-NP are less abundant. But one could imagine the isotope ratios of the three being similar. Comparing the isotope ratio results between the three NPs, the authors may be able to provide some insights about such bias. This actually is discussed later in Section 3.3, but the authors did not effectively link the two parts there.

2. There are a number of places in this paper that the authors compare the differences between observations with measurement uncertainties. For example, comparing the measurements vs. predictions in 3.1, comparing total vs. PM phase in 3.2, comparing isotope ratios of different nitrophenols in 3.3. In many of these comparisons, the differences are not very far from the measurement uncertainties. Given the small number of available samples, it is somehow difficult to draw clear conclusions as the main flaws of this paper, substantially decreasing the potential impact of this work.

3. The authors mentioned in the introduction section that nitrophenols have been found in trace amounts as primary emissions from vehicles. But in the results and discussions, never mentioned that again. If the primary sources of the nitrophenols

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are important fractions of total nitrophenols in the area of this study, the interference can cause a large impact. The authors at least need to estimate the primary emission of nitrophenols and aromatic VOCs (benzene, toluene, and m-xylene). Then with the known yields of nitrophenols from their photooxidation, estimate the mass of the secondary nitrophenols. Only with such discussion and if the primary source is minor, the results from this paper can be reliably used. Otherwise, the entire conclusion should be doubted

Minor Comments: From page 15433, line 23 to page 15434, line 11, the authors gave a very detailed introduction of the chemical mechanism of 4-nitrophenol formation from benzene. The authors should also provide the formation mechanisms of the methyl-nitrophenols and dimethyl-nitrophenols in the similar level of detail, at least the four nitrophenols (4-methyl-2-nitrophenol, 3-methyl-4-nitrophenol, 2-methyl-4-phenol, and 2,6-dimethyl-4-nitrophenol) focused in this study. The authors may want to add a figure or a scheme that shows the general chemical mechanisms leading to the formation of the five nitrophenols from benzene, toluene, and m-xylene. It would be more intuitive than just the text description here.

Page 15435, line 12. The word "close" is vague. Close by how much?

Page 15436, line 1-3. Quartz fibre filters are known to absorb gas-phase organics. How did the author make sure only PM are collected on the uncoated filters? Also, add the collection efficiency of the coated filters (84%) and the reference in the text.

Page 15437, line 12. A equation should be provided with the estimate of isotope ratios of nitrophenol formed in the initial phase of the reaction.

Could 4-nitrophenol also be formed from toluene photooxidation? Irei et al. (2014) seems to observe 4-nitrophenol from toluene photooxidation from the H-abstraction pathway. Thus, this compound can be produced from both benzene and toluene. There is no way to differentiate the source. Then the comparison of the isotope ratios of 4-nitrophenol with only benzene does not seem appropriate. The conclusion drawn from

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that species is less convincing.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 15431, 2015.

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