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

M. Saccon et al.

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The authors would like to thank the three reviewers for their valuable comments. Most of the referee's comments were concerning the proposed reaction mechanisms and uncertainty of the methodology. Anonymous Referee #2: Referee Comment: 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 δ13C data biased towards samples with higher nitrophenol concentrations". Any idea how large could such bias be? Some

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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. Reply: The uncertainty of the isotope ratio measurements of the nitrophenols was found to be 0.3 ‰Ṙesults shown in Fig. 3 indicate that there is no systematic dependence between the concentration of a species and its isotope ratio. With the given uncertainty, it cannot be determined if there is a bias resulting from the inability of measuring isotope ratios of samples with low concentrations. This is addressed on page 13 lines 7 to 15. Indeed, the problem of bias due to the limited lower concentration range for isotope ratio measurements is not limited to nitrophenols, but is a general limitation resulting from the current state of isotope ratio measurement techniques for atmospheric VOC. We added a brief explanation to the end of the conclusions.

Referee Comment: 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. Reply: The authors understand that the measurements uncertainty of 0.3 ‰ can sometimes prevent the interpretation of differences observed between certain samples. However, differences exceeding 0.7 ‰ exceed this uncertainty within a 90 % confidence limit and the spread of the data is in the range of 4 to 8 ‰Ȧ discussion of this was added on page 8, line 17 to 23.

Referee Comment: The authors mentioned in the introduction section that nitrophe-

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nols 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 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. Reply: Primary emissions of the target compounds from vehicles were indeed mentioned in the introduction section, and were again addressed and discussed in Section 3.4. To demonstrate that the nitrophenols are found to be consistent with the hypothesis of being dominantly formed from secondary processes, this discussion was moved to Section 3.1, specifically, page 10 line 3 to page 11 line 11. The ambient isotope ratio measurements of target nitrophenols indicate that they have a delta value that is significantly more depleted in 13C, compared to the parent VOC. Given this information, primary emissions of the nitrophenols can be ruled out as a significant source. Providing strong evidence that secondary formation is, for the conditions studied here, the dominant source of the target nitrophenols is an important point for this paper. We clarified this in the conclusions (Page 23, lines 8-10).

Referee Comment: 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. Reply: A figure showing a schematic of the postulated reaction mechanism was added as Fig. 1.

Referee Comment: Page 15435, line 12. The word “close” is vague. Close by how much? Reply: A quantitative description of the relation in isotope ratio of 2-methyl-4-nitrophenol with that of the sum of the oxidation products of the photooxidation of toluene was added in 3.3 (page 17, line 1 to page 18, line 18).

Referee Comment: 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. Reply: The sampling of artifacts is indeed a problem for all PM filter sampling. Sampling artifacts were addressed in Saccon et al. (2013) a short summary of this is now added to Section 2, page 7 lines 1 to 12.

Referee Comment: 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. Reply: A description of how to estimate the isotope ratio of the nitrophenols during the initial phase of the reaction was added on page 9, lines 8 to 10. Details can be found in the cited paper by Irei et al. (2015).

Referee Comment: 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 that species is less convincing. Reply: Irei et al. (2015) has found 4-nitrophenol to be a product of toluene photooxidation, and this now is mentioned in the introduction on page 4, lines 7 to 9. Once ambient isotope ratio results of 4-nitrophenol are presented, the possibility of having toluene as a precursor as the main source of 4-nitrophenol in the atmosphere is proven to be unlikely, which now is discussed on page 10, lines 16 to 23. In addition to the low yields reported by Irei et al, the carbon isotope ratios of 4-nitrophenol derived from toluene oxidation are very different from the isotope ratios expected from reaction of benzene thus carbon isotope ratios are useful

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to differentiate between different formation mechanisms as explained in the added text.

Anonymous Referee #3: Referee Comment: The interpretation of the isotope ratio data is predicated on the concept that nitrophenols present in the atmosphere are formed from one reaction pathway, the gas-phase reaction between benzene (or toluene or xylene) and the OH radical; for example: on page 15433 lines 15-20 it is stated ". . .the aromatic VOC can undergo photo-oxidation with the OH radical. . .", on page 15435 line 5 it is stated ". . .nitrophenols are formed from one reaction pathway and are specific to the aromatic VOC + OH reaction"; whilst on page 15439, line 10 it is stated that "Formation of nitrophenols from aromatic VOC is the result of a gas phase reaction sequence. . ..". There is a substantial body of previous work that indicates a potential substantial role for a range of aqueous-phase chemistry in the production of nitrophenols from mono-aromatic precursors. This includes the potential that a portion of nitrophenol measured in the gas phase has re-partitioned back into the gas phase following reaction pathways through the aqueous phase, e.g. through a phenol emitted precursor or a phenol intermediate. The authors have briefly highlighted some of this literature in the second and third paragraphs of the Introduction. In the fourth paragraph of the Introduction (starting p15434, line 12) the authors also refer to primary sources of nitrophenol to the atmosphere from traffic exhausts. So why, having referred to these other sources and reaction pathways to nitrophenol formation, do the authors indicate that their measurements can be interpreted in the context of a single gas-phase reaction of aromatic with OH? Indeed there appears to be a direct contradiction in the opening lines of the Introduction between page 15433, lines 15-20 where it is stated that nitrophenols are dominantly produced by gas-phase reaction with OH, and line 24 where it is stated that 4-nitrophenol has several proposed formation pathways in both gas and aqueous phases. Reply: While there are several different possible sources for atmospheric nitrophenols, the overall evidence points strongly towards secondary production as dominant source (revised discussion…). We eliminated statements that could be interpreted as a priory assumptions about the sources of nitrophenols and added more detailed explanations (introduction page 4 line 12-20, discussion page 11, line 20 to page 12 line 13 and conclusions page 23, lines 10-12) to clarify that this is not an a priory assumption but a conclusion that is evaluated based on the available overall evidence and the measurements presented here.

Referee Comment: Similarly, on page 15441, line 18, it is stated that “The three methyl nitrophenol isomers we studied are formed from the same precursor following the same initial reaction step, the addition of an OH radical to the aromatic ring of toluene” – this seems to be an assertion, rather than based on direct evidence, for samples collected from the atmosphere (as opposed to a controlled chamber study); the authors themselves cite in the introduction that methyl nitrophenols have been noted to be emitted to the atmosphere from direct emissions from vehicle exhausts. The authors do return to the issue of atmospheric nitrophenols derived from direct emissions rather than via atmospheric oxidation of mono-aromatic VOC, but this is not until the second and third from last paragraphs of the Results and Discussion section, and the direct emissions are largely dismissed as not being important. More clarity on the authors’ interpretation in the context of only a gas-phase OH reaction is needed earlier on in the Introduction and during the Results sections. Reply: We rearranged the parts of the paper dealing with conclusions about possible sources into one part early in the discussion to avoid confusion between conclusions drawn from the observations and a-priory assumptions and added a discussion of the possible role of all currently known sources of the target compounds (page 10, line 3 to page 12, line 13). Referee Comment: This reader’s attempt to interpret analysis in the context of this sole gas-phase formation pathway was not helped by some unclear phrasing in the description of chemical reactions. As examples. . .(1) on page 15437, lines 13 & 20, and on p15438, line 15, the phrase “initial phase of the reaction” is used. What is meant here by a “phase” (in a kinetic sense) of a reaction? I don’t think the authors mean the formation of a transition state in a reaction? The nitrophenol formation pathways are multi-reaction sequences. Perhaps by “phase” the authors mean the first, and/or rate-determining, reaction of a multi-reaction scheme? In each case, the text needs to make clear what chemical reaction is the subject. (2) Likewise, on page 15435, line 12, it is not clear to which reaction the phrase

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“sum of all reaction products” refers – the generation of a nitrophenol from an aromatic involves more than one reaction. (3) And, again, on page 15435, line 12, I could not work out what actual reaction or reaction(s) are being referred to in the sentence “This allows for a first order prediction of the dependence between isotope ratios of reaction products and photo-chemical precursor processing in the atmosphere”. The understanding of the authors’ work would benefit from a schematic of the chemical reaction sequence their study provides information on. Reply: We changed “initial phase of the reaction” to “secondary products formed from unprocessed emissions” to clarify the meaning. The “sum of all reaction products” means exactly what it says, all products of the reaction, which can easily be derived from a mass balance. We added an explanation to clarify this (page 6, lines 3-9). This is based on the cited paper by Irei et al., 2015 A figure with the reaction scheme has been added. Referee Comment: P15443, lines 18-26: Some analysis of results is undertaken with respect to wind direction during a sample collection, but there is little detail on the stability of a wind direction during a sample collection. There is only the sentence “Only samples with a relatively stable wind direction during sampling were used for the analysis”; what criteria actually defines “relatively stable wind direction” and how many samples were retained and excluded from analysis after application of the sample selection? Is this analysis in fact based on only a minority of samples? Reply: A clarification of how many samples and what was classified as a “stable wind direction” was added on page 19, lines 16 to 118.

Referee Comment: Technical comments: P15434, l11: The citation to Hamilton et al. 2005 doesn’t look like a correct citation here. Reply: The reference was corrected to Harrison et al., 2005.

Referee Comment: P15442, l23: Better to phrase as “the values actually observed for. . .” Reply: Done.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C6760/2015/acpd-15-C6760-2015-

supplement.pdf

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