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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Dependence between the Photochemical Age of Light Aromatic Hydrocarbons and the Carbon Isotope Ratios of Atmospheric Nitrophenols” *by* Marina Saccon et al.

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Ref 1

In their study, Saccon et al. present an instructive kinetic model for estimating the stable isotope C transfer between the VOCs emitted into the atmosphere and intermediates/ end products of their oxidation, with a focus on nitrophenolic species eventually ending up in the PM. They further attempt to use the model for estimating the OH exposure of involved components, obtain sensitivities to several key assumptions andcompare

their estimates to those of earlier studies from the same group. Whereas the topic and research question here is certainly within the scope and interest for ACP, I cannot recommend this study for publication until major improvement will be done with respect to (1) clarity of introduction and description of the methods,aromatic VOC with the OH-radical (2) adding a sufficient analysis of uncertainties, and (3) refraining from using largely oversimplified model approach / evaluation framework.

i) Reply: We agree that the paper will benefit from improved clarity of the introduction and some details of the methodology and the paper will be revised accordingly. However, we do not agree with the criticism of an oversimplified model approach. The current understanding of the carbon isotope fractionation during formation of nitrophenols from aromatic volatile organic compounds (VOC) in the atmosphere is very limited. One of the intentions of this paper is to use the available limited information to restrain the range of carbon isotope ratios for nitrophenols formed in the atmosphere by reaction of aromatic VOC with OH-radicals and to identify the most important sources of uncertainty. See also ii)

Most of my general comments below are related to point (3), the specific comments touch on points (1) and (3). Regarding (1), I suggest taking the manuscript of Kornilova et al. (2016) as exemplary (also w.r.t to sentence formulation and length). I note that there is no overview of the recent literature on the subject except that offered by the same group, which has to be improved (try, for example, using search function on ACP website with the keyword “phenol” for abstract – you will find a lot).

ii) Reply: The purpose of the paper is not to provide a review on formation and reactions of atmospheric nitrophenols. The focus is on carbon isotope ratio of atmospheric nitrophenols. In the paper we point out that the information on this subject is very limited and we are not aware that we missed any literature that presents useful information on this subject. We indeed used a simplified scheme for the OH-radical reaction initiated formation of nitrophenols. We explained that the overall isotope fractionation is result of isotope fractionation at various steps of the reaction sequence. We also explained that based on the observed overall isotope ratios of nitrophenols it is not possible to identify at which step isotope fractionation occurs. With the exception of the initial reaction step, the reaction of OH-radicals with aromatic VOC, none of the isotope fractionation effects for individual reaction steps have been measured directly. Currently the possibility to derive constraints for isotope fractionation during formation of nitrophenols from experimental evidence is limited to a small set of ambient observation and laboratory measurements of the isotope ratio of nitrophenols. Consequently, it is not possible to identify at which specific step of the reaction sequence following the initial OH-radical attack isotope fractionation occurs. We explain this limitation and its principle in more detail in the revised supplement.

Regarding (2), a full analysis of uncertainties should be provided, e.g. uncertainty in derived PCA should include propagated errors in reaction rates, yields if available, isotope signatures and KIEs, deposition rates – that is, all components of the kinetic model. Since the model is rather unsophisticated and not resource-intensive, there are many available approaches (e.g. Monte-Carlo or even analytical analysis of errors). I also strongly advice to use a Monte-Carlo (or similar) approach to derive the probability densities/relationships of unknown parameters (e.g. unknown KIEs and deposition rates) that lead to observed mixing and isotope ratios. In this case, I guarantee that the authors will gain a substantially deeper insight into their research subject.

iii) Reply: It seems that the referee misunderstands the intention of our paper. We make no attempt to use a numerical model to predict the carbon isotope ratio of atmospheric nitrophenols. There are several reasons. Such numerical models currently do not exist and the development of such a model is beyond the scope of this paper. Such a model would require knowledge of the isotope fractionation in the formation of nitrophenols following the initial step (reaction of nitrophenols with OH-radicals). The results for the two “extreme “scenarios demonstrate that the range of isotope ratios predicted by these scenarios is too wide to allow meaningful predictions of nitrophenol carbon isotope ratios. However, the existing ambient observations and laboratory studies can

be used to constrain the overall isotope fractionation during formation of nitrophenols resulting in an “in between scenario”. The main purpose of our error analysis is to identify the main sources of uncertainty, which is essential for conducting useful further laboratory studies. This is clarified in the revised paper, including a more detailed analysis and explanation of error in the Supplement.

Regarding (3), current oversimplifications allow one to apply the proposed model (after correcting the formulation) only for instructive use, that is, not for evaluation of any lab of observational data. I also see no point in boldly comparing distributions of the isotope ratios/PCA for samples obtained in very different conditions, seasons, locations, etc. I have, e.g., following concerns: – Why mostly isotope ratios (but not abundances) of precursors and products are being compared?

iv) Reply: The subject of this paper are isotope ratios. The intention of the paper is to identify which type of information can be gained from isotope ratio measurements of organic compounds formed by reactions of atmospheric VOC.

– What is the point of using rate coefficients for 298K only (see the comment to P9L8)? v) Rate constants for 298 K have been used by Kornilova et al. (2016) for determining PCA based on isotope ratios of light aromatic VOC. Comparison of precursor and reaction product derived PCA is an important part of this paper. To avoid inconsistency in this comparison we use the same rate constants. Furthermore, 298 K with is within a few K of the temperature for the laboratory studies of the isotope ratio of nitrophenols formed by the OH-radical initiated reaction of toluene. Thus the results of our conceptual model can directly be compared with these results.

– Why distributions of PCA for all samples (instead of only those observed in rainy days) are being compared? Why do you not scale wet removal rates according to precipitation rates? vi) Reply: Again, there is a misunderstanding. We do not try to predict the impact of dry or wet removal by using removal rates. One of the findings of this paper is to demonstrate that wet or dry removal processes, which cause very little isotope fractionation compared to chemical reactions (see below) still can have a strong indirect impact on the isotope ratios of reaction products if they have a strong impact on the atmospheric residence time of the reaction products. – What are the grounds for comparing precursor and products from samples collected in different years/seasons? vii) Reply: The precursor data are taken from the cited paper by Kornilova et al. (2016). Details of sampling for nitrophenols are presented in Saccon et al. (2015). The sampling periods are given in these two publications. For the precursor sampling started in fall 2009 and the last samples were collected in Sept. 2010. Nitrophenol samples were collected between March 2009 and August 2012. These sampling periods are not identical but they overlap. Moreover, in both papers it is explained that average and standard deviations of the measurements are, within the statistical uncertainties, representative for the study period and area. Moreover, the paper of Kornilova et al. includes a comparison of their VOC concentration measurements with measurements at two other locations in Toronto and it is concluded that there is no statistical significant difference. We see no reason to repeat details already presented and discussed in publications that are very easily (published in ACP) available for all readers interested in those details.

Since the environmental data on observational conditions (e.g. temperature, back-trajectory analysis) are available, you should compare the samples arriving from the same catchment areas, on the days with similar temperatures, precipitation rate, etc. Model calculations should account for these parameters, too. Without such clustering of the data, no consistent evaluation of your results is possible! I encourage the authors to address all the points raised (as opposed to the initial review where some of my comments were neglected) and wish good luck with improvements.

viii) We agree that detailed numerical model simulations either using Lagrangian Trajectory type models or large scale Eulerian chemical tracer models and comparison with observations may provide some further insight. However, to our knowledge, no models allowing prediction of the carbon isotope ratios of nitrophenols in the atmosphere exist

and development of such a numerical model is not the subject of the paper.

General comments P6L2-4: “Atmospheric reactions” is a vague term, you imply “removal by OH” (or extend the model with other radicals). Please provide a reference (or a brief conceptual description) on how the impacts of atmospheric mixing and dilution are singled out (I estimate it as nearly impossible here). Reply: The principles and references of using VOC isotope ratios to differentiate between mixing and reactions are presented and discussed in literature cited on page 5, L6-7 and L15-16. We see no need to repeat this about 10 lines later.

P8L16-17: Since you also show the results for the “mass-balance” calculations, please present the formulation or elucidation on how they are performed. What do you imply with “straightforward”, do you mean “disregarding yields, KIEs, etc.”? Reply: Mass balance is an established concept in isotope ratio calculations, moreover details can be found in the cited references by Irei et al. and explanations are given between P8L17 and P9L3.

P9L8: Table 1 lists rate coefficients for taken for given temperature (e.g. 298K for benzene kOH). You argue that the uncertainties associated with these reaction rates are small. The change in kOH for benzene is about 720K, which is comparable to the relative uncertainty in " (6.1same rate coefficient for the samples that were taken in different seasons, for which 20K variations in average daily temperatures are certainly realistic. I am concerned that you oversimplify the kinetics model (also the ratio between the reaction rate coefficients for initial VOC and intermediates changes!) and you cannot apply it for evaluating the observational data. The same applies to other (environmental) parameters which are available for sampling locations; you should use these (per sample) to drive the kinetics of the model properly. Reply: We can only repeat that the approach suggested by the referee is entirely different from the conceptual approach in our paper. The revised introduction explains the difference between our conceptual approach and complete numerical model simulations. The use of a fixed temperature is based on our approach to interpret the isotope ratio data sets based on averages and variance, not individual data points. (see also v) in general reply to comments).

P10L13-16: Firstly, partitioning rate is not the decisive factor determining overall chemical loss of total nitrophenols if the loss in the PM phase is fast; partitioning (as an equilibrium process) acts merely as a scaling factor here. Secondly, there are reported important aqueous-phase losses of PM nitrophenols (see, e.g., doi:10.5194/acp-16-4511-2016), thus I conclude that this assumption requires further assessment for adequacy. Reply: To our knowledge there are no studies of the chemical removal rate for nitrophenols in PM. The cited paper presents reaction of reactive phenols in aqueous solutions in the aqueous phase under conditions somewhat similar to atmospheric conditions in fog or cloud water. In the study (Yu et al., 2016) the loss rate of phenol (C6H5OH) due to reaction with OH in the aqueous phase under simulated sunlight conditions is 0.05 h-1. The authors also state that in their study the oxidant concentration is about a factor of 7 higher than for fog water at midday in winter at Davis (CA). The resulting loss rate in the condensed phase for these conditions would thus be approximately 7x10-3 h-1. It can be expected that for phenol, similar to nitrophenols, most of the phenol will be in the gas phase. Consequently the loss rate for the total atmospheric phenol concentration will be in the range of 10-3 h-1. The gas phase loss rate for phenol due to reaction with OH for a global average [OH] radical concentration of 106 cm-3 is approximately 0.1 h-1. This is a factor of 100 faster than the condensed phase removal rate. Nitrophenols are substantially less reactive than phenol, for example the gas phase reaction rate constant of 4-nitrophenol with OH radicals is approximately a factor 80 slower than the reaction rate constant for phenol + OH. When using this as scaling factor for the reactivity of 4-nitrophenol in the condensed phase the loss rate for 4-nitrophenol due to reaction in the condensed phase is in the range of 10-5 h-1, not surprisingly again a factor 100 slower than the average loss rate of nitrophenol due to reaction with OH in the gas phase. There are large uncertainties in this estimate since the oxidant concentration in particulate matter in Toronto may be very different from that in fog at Davis. However, it is unlikely that this can compensate for the by a factor of 100 slower losses in the condensed phase. The revised manuscript includes

an explanation that based on current knowledge the contribution of aqueous phase reactions is negligible.

P11L14-16: The convenience here unfortunately messes up model formulation. I do not understand practical reasons for using different isotope standard ratio – as it is bound to atomic 13C/12C ratio – and retrieving final $\_valuefrommolecularratios.Youcouldusestartingcomposition(oremission)of0\ forCpreand$ $PDB).Then, youstatethatyouderive\_valuesfromconcentrationsofisotopologues.Howarethe$ $substitutedisotopologuetransfersone13Candsix12Catomstotheproducts, whichinturndefin$ $9youuseRst = 1fordefiningCpre, thenyoureact13C -$ $isotopologuesseveraltimesfaster(whilst12k/13karestillformulatedformolecularcounts)and$

Reply: In our calculations the heavy isotopologues contain only one 13-C atom, this is justified since for small molecules the probability of multiple 12-C-atoms being replaced by 13-C atom is negligible. The conversion of molecular ratios into atom based ratios and vice versa is trivial, if the number of carbon atoms in the reactant and in the product is identical it is not even necessary. Simple example: Toluene and methylnitrophenols have all seven carbon atoms. The probability that one of the seven carbon atoms is a 13-C atom therefore is 7-times the probability of one C atom being a 13-C atom. However, when converting the abundance of the heavy isotopologue containing one 13-C atom into atom based ratios the concentration the molecular concentration ratio has to be divided by 7 since only one of the seven atoms is a 13-C atom. When expressing isotope ratios in δ-notation a calculated change in δ between reactant and product is independent of the reference point. Only when expressing the isotope ratio relative to a defined reference point such as V-PDB the δ-value of the reactant has to be considered. The result will still be independent of the absolute ratio of the abundance of 13-C atoms in carbon, which is the intention of the use of δ-notation. In the revised manuscript this is briefly clarified, but we see no reason to explain textbook level principles of δ-notation in great detail.

P12L8-11: Small yields do not imply that there will be insignificant

fractionation caused by the dependence of the yields on the isotope substitution (because you do not know how large the KIE is). In other words, in Eqs. 6-9 you can probe only the combinations of Yint$_k preproduct, and I am concerned that this does not lead to unambiguous results. Please, comm$
$We do not understand the purpose of this comment. Our statement in no way implies that fraction$

P15L14-17: In what terms do you measure the consistency and imply that it full? The model uses toluene emission $_13C typical for its major source; sink fractionation will expectedly enrich leftover “ambient'' tol$
in Kornilova et al. (2016) is an extreme outlier (outside Q3+3*IQR, actually nearing Q3+5*IQR). Using the model calculation, that is above 100instead) will yield some 96That is above the maximum (nearing Q3+IQR) observed by Kornilova et al. (2016). Now, does this amount of toluene produce phenols/POM in the model at comparable to the observed values? Answering this question for all samples will make comparison adequate (I may use consistent, too), otherwise one cannot consider results in Figs. 3 (and similar) suitable for model evaluation. Read, you need to show (in addition to isotope ratios) that the mixing ratios of intermediates/phenols/POM correspond those of precursor VOCs calculated from the fractionations predicted by the model. Reply: Again we have difficulties to understand this comment. Indeed, the reaction of toluene with OH-radicals will result in toluene enriched (relative to emissions) in 13-C. This principle has been discussed in detail by a substantial number of publications, including the one by Kornilova et al. (2016). Statistically speaking the maximum isotope ratio reported by Kornilova et al. (2016) may be considered to be an outlier (when using simple parametric statistics). However, the statement that it would require more than 100It seems that the referee suggests a comparison of concentrations predicted by our calculations with observations. We made no attempt to predict concentrations and did not present any calculated concentrations since the focus of this paper is the isotope ratio and its dependence on photochemical processing. P18L17-P19L2: Causation does not imply correlation. Reply: We do not understand the purpose of this statement. In a very general sense the referee's statement is true.

However, it is a widely used scientific tool to use causation in order to predict functional dependencies. Testing the existence of possible correlations is a widely used tool to identify possible dependencies.

The fact that Scenario 3 “fits” the data best does not imply that it is the correct one. A first argument for that is indicated by you on L20-22 – I am concerned that one cannot adequately compare precursor and product based on the data collected in different years! At least, you need to show comparisons for samples (pairs precursor VOCs -ensuing nitrophenols) with very similar air catchment area (e.g. by means of back-trajectory analysis). Taking into account that you have introduced simplifications like T-independent reaction rates etc. (see the comment to P9L8), your calculation approach is merely instructive but cannot be applied to any lab/observational data. Reply: The laboratory experiments used for comparison were not only conducted at constant T, but also at temperatures very close to the temperature we used in the calculations. For reply to comments on comparison of data from different years see vi) above. For reply to comments on using constant T see reply to P8L9 and v). The revised manuscript also explains in more detail that the available experimental evidence only allows constraining the impact of the entire reaction sequence following the reaction of the precursor with OH (as outlined already in Eq. 10).

P21L12-19: The line of discussion is unclear here. One of the major factors affecting the chain of conversions is the reaction of phenols with OH and potential associated KIE. You conclude that the latter cannot be ruled out, however you do not attempt to estimate the uncertainty associated with it (e.g. based on the KIE expected from functional analysis of the reaction mechanism proposed). Reply: The reasoning is simple. The carbon the isotope fractionation in the formation of 4-nitrophenol from benzene may be lower than for alkyl substituted nitrophenols since one of the intermediate steps will only result in a secondary isotope effect. Therefore using a lower overall KIE it is possible to create a scenario where the measured average isotope ratio agrees with the predicted isotope ratio. However, using a scenario with such a small

KIE cannot explain the lowest 30 P24L21-22: Please provide references/calculations supporting that KIEs in dry/wet removal processes are typically smaller than those of chemical kinetics. Dry deposition implies diffusivity/reactivity at the stomatal level, that is, including surface kinetics that may proceed with fractionations of comparable magnitude (I agree that massdependent diffusion effects for larger molecules like toluene are small). Wet deposition includes aqueous/heterogeneous chemistry, where, e.g., equilibrium/solubility IEs may play role. Reply: From our reply to the comment on P10L13-16 it is obvious that, based on current knowledge, liquid phase chemical loss reactions of nitrophenols will be extremely slow (a liquid phase loss rate of 10-4 h-1 corresponds to a residence time of more than one year). Consequently chemical reactions in solution cannot explain the average atmospheric residence time of nitrophenol deduced from isotope ratios. Moreover, the isotopic evidence supports the assumption that removal processes for atmospheric nitrophenols are dominated by processes resulting in, compared to chemical reactions, negligible isotope fractionation. The revised manuscript discusses this in more detail.

P26L18-20: I do not see how small fraction of phenols in the particle phase imply small loss rate (as you balance unfitting PCA with deposition term, the problem is ill-defined here). “Deposition processes” imply washout with rain (incl. aqueous/heterogeneous chemistry) and diffusivity/reactivity at the stomatal level, i.e. processes neglected in your model approach. See also the comment to P10L13-16. Reply: The average residence time of atmospheric PM is typically at the lower end of the derived range of 6 days to two weeks. This finding can be explained by the observation that only a small fraction of nitrophenols is in the PM phase, which allows an atmospheric residence time for nitrophenols exceeding the residence time of PM. In the revised manuscript this part is rephrased to clarify our reasoning. Specific comments P2L5: “... oxidation of aromatic VOCs by OH radicals”. Since it is established that the oxidation of atmospheric VOC in the atmosphere is dominated by reaction with OH there is no reason to point out this specific detail in the abstract. P2L10-11: “included knowledge of KIEs...” -> “takes into account the KIEs” (or reformulate) changed P2L12: “these values” -> “model parameters” (or reformulate the sentence) “These values” is better, “model parameters” would imply that fundamental kinetic rate constants or KIEs are specific for model calculations. P2L15: Remove “normal” (or explicate why only the KIEs with ">1 should be used?) Agreed, in this context “normal” is unnecessary.

P2L18-22: Split the sentence into two and reformulate the last one, e.g. “Our results suggest that the mass balance-based model should not be used for predicting the OHexposure of nitrophenols from their C isotope ratios”. Agreed

P3-8: The introduction and description of the methods in Sects. 1-3 are sloppy and are hard to follow, also due to poor usage of terminology (well-established in cited literature however). May references are doubled or vague, e.g. “precursor” and “reactant” on P11L10 may (or may not) refer to the same entity, use of “secondary” (e.g. on P3, P6, P8) is not clear to me. “Product” is used often without specifying “of what”, which flaws the line of argumentation for a process involving multiple conversion steps. These sections require to be improved, e.g. usage of “precursor VOC”, “product SOA”, clear relationship between the two is required, otherwise the Reader will be lost (I am dealing isotope kinetics and acquainted with works of Rudolph’s lab, however you got me lost in Sects. 1-3). I suggest adding a conceptual graphic (a flow-chart, e.g. a rework of Fig. 1 fused with Table 2) for all steps involving the interconversions of C from emission of VOCs to formation of POM, including typical $_13Csignatures, stepsinvolvingsignificantKIEsandyields/branchingratiosimportantfornit$
$Intherevisedversiontheintroductionanddescriptionoftheconceptualmodelismodifiedinorde$

P3L14-16: Stable carbon isotope ratios; also P5 and further: you may like to state in the beginning of the manuscript that you are communicating on the stable isotope C ratios only. Reply: In the revised manuscript “carbon isotope ratio” is explicitely stated whenever this is not obvious from the context.

P3L22: It is unclear, which “secondary processes”, please define. Also concerns “secondary phenols” on P5 (“secondary pollutants”), P8 (“secondary phenols”), etc. Reply:

In the revised manuscript “precursor”, “first generation product (or intermediate)” and “second generation product” is used and reactions (if specific for one of these) are identified as “reaction of precursor” etc.

P3L22-23: Isotope ratios cannot be depleted; species can be depleted in 13C. Reply: Changed to: “due to the depletion in 13-C relative to the isotope ratio of the precursors.

P4L11: Do you mean singly substituted 13C-containing species? Reply: Change to “isotopologues containing one 13-C atom”

P4L12-13: Please be precise about the reservoirs you imply (also further), i.e. left-over atmospheric burden becomes enriched. Reply: Changed to “and the remaining compound becomes. . .”

P5L5,7-10: What is “ambient species”, is it VOCs, intermediates or ensuing (nitro) phenols? Which “ambient precursor” and emissions of what are implied? Please use clearer terminology, e.g. like in Kornilova et al. (2016). Same concern about the definitions on P6. Please use “precursor VOC”, “product SOA/nitrophenols”, etc. to avoid ambiguities. Reply: Changed to “of a VOC with emissions as only relevant source” and “the PCA of this VOC..”

P6L8-10: Unclear, please reformulate or provide how “minimum contribution” is quantified. Reply: Changed to: In the case of mixing air masses containing VOC with different photochemical ages Eq. 3 still is a very good approximation for the concentration weighted average $\int[OH]dtoftheprecursorVOC(RudolphandCzuba,2000).However,Eq.4isonlyavalidapproxi$

P6L17-20: Can you explicate, why the relationship is more complex and why the $_13Cofsubsequentlyproduced SOA/nitrophenolsis(expectedtobe)notaffectedbythis?Changed$
$“However,duetothesimultaneousformationandremovalofthereactionproductstherelationb$

P7L8: You do not really present different mechanisms, rather different assumptions on KIEs (e.g. you do not introduce any new pathways or C transfer). Reply: Changed to “

a mechanism” and "Different scenarios based on a range of KIEs will be discussed”

P9L11: It is not “presently proposed” however not “known” (cf. caption to Fig. 1, where it is correct). Reply: Changed to “The reaction sequence resulting . . .. proposed by . . .”

P9L19: “... occurs in remaining 8Reply: Changed to “for 8

P10L5-6: Can you comment on what fractionations (or their uncertainties) may be expected in the rest of the cases (20Reply: We added “Reaction at the alkyl group or the phenolic OH result in a much lower KIE than for addition to the aromatic ring and therefore their contribution to the KIE is negligible”

P10L17-18: Reformulate, e.g. “There are also some reactions for which no laboratory measurements of rate constants are available”. Reply: Changed to: “Reaction rate constants for which no laboratory measurements are available are estimated on the following principles.”

P11L4: Please use present tense and clearly communicate about the assumptions made in the current study (please check throughout the manuscript). That is, “In this study, it is assumed that phase partitioning is fast ...” Reply: Present tense is used for description of the conceptual model in the revised manuscript.

P11L9: I suggest numbering (or recapping) the assumptions referred to here (in contrast to all assumptions mentioned heretofore). Reply: We do not agree; it is clear from the context which assumptions are referred to.

P11L10: Are “reactant” and “precursor” (3 and 4 lines below) the references to the same entity? Reply: Precursor is used only for the VOC emitted into the atmosphere (here the light aromatic VOC). Reactant is used in a general meaning for any compound undergoing a reaction, independent whether the compound is precursor, first generation (intermediate) or second generation product. The revised manuscript is checked to make sure that this is followed consistently.

P12L12: You imply isotope fractionation? Reply: yes, corrected

P12L13: Please explain how Eq. 10 is obtained (and what does the variable x mean, or never use "x" for multiplication). Elucidate how Eq. 10 reduces the number of scenarios that have to be considered. What is the initial number of scenarios? Reply: See our reply to comment on P12, L8-11.

P13L1: Specify which diff. equations you imply (I guess, Eqs. 6-8). It will be useful to present the solution in the manuscript (or in an Appendix). Reply: From the context it is obvious which set of differential equations is meant. We do not understand the comment "It will be useful to present the solution in the manuscript (or in an Appendix).". The differential equations were solved by numerical integration and the results of this integration are presented in various graphs and tables.

P13L2: Which KIE is implied? Reply: Changed to clarify the purpose of the scenarios to: "To understand uncertainties arising from the assumptions made to estimate KIEs which have not been determined experimentally different scenarios are used."

P14L14: Define the "mechanistic models" (or name the corresponding scenarios). You refer to only one model earlier (P13L21). Reply: Changed to "Mechanistic model". In the revised manuscript it is clarified that there are different scenarios for one mechanistic model.

P14L19: Consider reformulation ("shape of dependence"?) Reply: Changed to: " ..shape of the curve describing .."

P15L6: Define "quasi steady state". If you mean that production is equilibrated with loss, specify the interval. Reply: Quasi steady state is established terminology in reaction kinetics and a widely used concept, which requires no further explanation.

P16L 1-7: This paragraph is not scientific. Which and how large are "some" uncertainties? What "reasonalble errors" are you referring to? Reply: "some" is unnecessary and is removed, the uncertainties used in the calculations are explained in the caption of Figure S3. This is clarified by replacing reasonable by the uncertainties used in the

calculation: ".. for relative uncertainties of the rate constants in the 10

P19L19-22: You do show in this study (also in Table 5 referred) anything about the effect of branching of intermediates. Reply: Branching in the reaction sequence following the reaction of the precursor with OH is the reason why mass balance based considerations cannot be used to constrain the isotope ratio of specific reaction products. See also reply to comment on P12L8-11.

P21L17-19: Reformulate "lowest ... ratio is significantly higher than 30specify how you set significance levels. Reply: "significantly" changed to "by more than the measurement error"

P22L14-15: Bias in PCA is expressed in per mil (wrong units, not PCA?) Reply: Changed to "The resulting average bias in PCA corresponds to an uncertainty of less than 0.5 ‰ in carbon isotope ratio . . ." P23L 2: Which carbon isotope ratio is implied? Reply: Clarified: "carbon isotope ratio of nitrophenols"

P25L11-14: Please show (within Eqs. 6-9, for example) how deposition term is simulated (even if it is proportional to reaction rate with the OH). Also, I suggest investigating whether not OH sink-proportional rate and/or presence of KIEs in deposition processes changes the shape of PCA distribution similarly to that currently obtained. Reply: The principle of the combined impact from removal by OH and other loss processes is discussed in more detail in the supplement of the revised manuscript.

P25L23: Do you mean "a range of derived PCA will be more realistic"? Reply: No, the realistic situation, especially in an urban environment, is clearly that VOC with a range of PCA contribute to the actual observations.

P27L12-14: This consistency does not imply unambiguity (see the comment to P29L14-15). Also, you may like to note potential reductions in nitrophenols due to aqueous phase chemistry (see the comment to P10L13-16). Reply: It is a fundamental scientific principle to test a hypothesis by trying to falsify a prediction resulting from the hypothesis. Failure to falsify the hypothesis supports the hypothesis, but we are aware (and expect that the reader will also be aware of this) that this does not exclude alternative explanations. However, as explained in our reply to comment on P10, L13-16, based on current knowledge the rate of chemical loss of nitrophenols in the aqueous phase is too slow to compete with gas phase reactions. The residence time of raindrops in the atmosphere is very short compared to the removal by chemical reaction in the aqueous phase. Consequently, nitrophenols dissolved in rainwater will be removed by wet deposition and not by chemical reaction. For molecules with the molecular mass of nitrophenols isotope fractionation due to mass dependent differences in diffusion rate or solubility will be negligible compared to chemical reactions.

P28L21: “increasing reactivity” of what? Reply: Clarified: “reactivity of the secondary pollutant”

P28L22-P29L1: In this study, you have not shown that you can unambiguously differentiate between impacts of local emission and long-range sources (cf. previous paragraph), so you cannot state that. Reply: Based on the context it is obvious that the timescales which can be probed by isotope ratio measurements of nitrophenols depend on the reactivity of precursor. To clarify this we added: “depending on the reactivity of the precursor”. Different VOC react with different rates and it is unnecessary to reiterate in great detail the rather trivial point that VOC with atmospheric residence time in the range of weeks are not suitable to probe processes with timescales in the range of hours. P29L14-15: You cannot state that, as you have not studied KIEs in removal effects but only conjectured that KIEs in deposition processes are small. Reply: Rephrased since it is indeed a more general principle: “Loss processes such as physical processes based on diffusion or solubility or chemical reactions such as secondary isotope effects which cause only very small isotope fractionation can still have a strong indirect impact on the carbon isotope ratio of nitrophenols if they play a major role in determining the atmospheric residence time of nitrophenols.” Technical comments P2L17: effects (not one unknown IE was tested?) Changed

P3L12-14: Reformulate, e.g. “In specific identified reactions, carbon isotope ratio of the product can be linked...” Changed

P4 Eqs.12: Using “x 1000‰' is redundant (you have indicated above that $_and”areexpressedinpermil).Avoidusing“x''insteadofcorrectmultiplicationsign(e.g.bullet).I
Eq.2givesthecorrectresultin$^{\Omega}$x''iswidelyusedinpublicationsinACPasmultiplicationsign.No

P7L3: Remove “approximately” Changed to: ”..are between 2 ‰ and 3 ‰$. . .''P7L9 :
“...basedonnitrophenolsformationandremovalintheatmosphere...''Reply :
Thesentenceiscorrectandclearinitspresentform.

P10L22: Consider reformulation (use of “direct reaction to position” is vague and uncommon). Reply: P10 L22 (or any line nearby) does not contain the cited phrase.

P16L11: Reformulate “ambient studies”. Clarified: “atmospheric studies”

P25L7: Reformulate (“dominant fresh emissions”) Changed: “Nevertheless, a general consequence of the mixing of aged air with fresh emissions of light aromatic VOC is the absence of very low values for 4-nitrophenol derived PCA. In contrast values close to zero can be expected for the precursor derived PCA in the cases where fresh emissions dominate.”

P20L3 | P21L6,8 | P23L12,20 | P24L18 | P25L7,9,17 | P28L15,20: Add or correct the use of commas. Reply: In the revised manuscript the use of commas is checked.

Consider using help from a native English speaker w.r.t. to proper use of articles. Since you generally use long complex sentences with many participles, please use hyphens for half-compound words, e.g. -derived, -based, -specific, etc.

Ref 2 The paper presents a methodology to establish relationships between the stable carbon isotope ratios of the nitrophenols (as products of the photo-oxidation of light aromatic VOC) and the extent of their chemical processing as well as of the precursors. This is a further contribution to the systematic source, mechanistic and ambient investigations using isotopes as useful additional information to increase the understanding of the atmospheric processes. The novelty consists in showing the advantage to provide better insight into the formation of secondary products by using the isotopic information of the secondary organic pollutants rather than those of the precursors. Therefore the paper is highly suitable to be published in the journal. The paper contains yet some weak points which need to be improved before publishing.

General comments The authors present the potential for using the concepts presented in this study, on the other hand they fairly caution what uncertainties still remain. The complexity of possible sources for the isotopic fractionation (such as the weight of different reaction channels, partitioning between gas phase and aerosol particles), as well as the questions raised when determining PCA based on the mixing and isotopic ratio measurements are more than extensively discussed. Also the assumptions made in the three mechanistic models are sound and the results give a good sensitivity to understand reaction steps for the aromatic photo-oxidation. Unfortunately, there are too many points in the manuscript, where repetitions or sentences making no sense obstruct the understanding of complex features (examples are given below). The work is too good to risk to make the reader hostile due to these dissonances. Generally, the paper needs to be editorially thoroughly revised. Moreover, there are some erroneous references, interrupting the thread of reflection. All figure and table references should be checked once more.

Reply: We agree, the paper will be revised thoroughly and the paper itself shortened substantially by moving details of uncertainty analysis as well as the discussion of the different scenarios to the supplementary material. This will also include renumbering of figures and tables.

Specific comments The linear approximation approach starting on Page17Line19 should be better described. Is the regression analysis done for all data or only for a limited PCA range? The authors might consider including at least in Figure 3 the line fitted to the Scenario 3 data, it would make easier understanding the Section 3.5. Some questions related to this are presented in the following:

Reply: This part will be moved to supplementary material, which will allow to add a more detailed explanation of the rational behind the linear approximation. The lower end of the linear range is set to a PCA of zero, the upper end is defined such that in this range no data point from the calculations deviates from the calculations by more than 0.5‰.The advantage of a substantial linear range is an easy interpretation of isotope ratios for mixtures of air masses with different PCA. We will add a more detailed explanation in the revised manuscript.

Page23Lines1-3: It is not clear what this sentence means: 'While there is an effectively linear dependence between PCA and carbon isotope ratio for a range of approximately 5 to 8 ‰ for the mechanistic models (Fig. 3, Table 2), eventually the slope of the dependence of carbon isotope ratio on PCA begins to decrease substantially (Fig. 3).' Also Table 2 should be Table 3 (?)

Reply: Changed: "For a range of 5 to 8 ‰ the dependence between PCA and carbon isotope ratio for the model scenarios can be described by a linear approximation (Fig. 3, Table 3). Above this range the slope decreases substantially and the dependence can no longer be approximated by a linear function."

Page36Table3: It is not clear what the footnotes mean: 'b Upper end of linear range where exact calculations deviate more than 0.5 From exact calculations. Reply: Changed: "b Upper end of a the range where a linear fit with a PCA of zero as lower end does not deviate by more than 0.5 ‰ from the result of the numerical integration. c result of numerical integration for a PCA of zero."

Editorial revisions: Page4Line12: it should be ' Normal KIE, that is when epsilon is positive, ...' (>0) Changed

Page6Lines2-3: it should be either 'addition of carbon isotope ratio measurements' or 'combination of mixing ratio with carbon isotope ratio measurements' Changed

Page9Line2: the authors suggest that kOH is equal k12. Replace k12 in Eq.5 with kOH

Changed

Page9Lines17-19 and Page10Lines3-4: Reformulate. Instead of ”probability for the reaction channel’ Changed

Page10Lines2-6: Reformulate, maybe split in more sentences. Changed: Similarly, the main gas phase loss process of nitrophenols is expected to be through reaction with the OH radical, occurring through an OH addition to the ring greater than 80

Page11Lines3-8: Move to the partitioning part, before the paragraph starting on Page10Line17. Changed

Page11Lines16-17: It is not clear what this sentence means: ’ These carbon isotope ratios represent the difference between the carbon isotope ratios of precursor emissions and reaction products.’ Changed: “The thus calculated carbon isotope ratios represent the difference between the carbon isotope ratios of precursor emissions and reaction products. For comparison with atmospheric measurements these isotope ratios have to be corrected using the carbon isotope ratios of the precursor emissions”.

Page11Lines17-18: It should be ’The rate constants k13 for different isotopologues can be calculated from rate constants and the KIE.’ Reply: Strictly speaking neither k12 nor k13 is identical to the experimentally determined rate constant. The fact that for mostly all practical applications k12=kOH is justified within the uncertainty of the rate constant measurement is a different point, which has been explained in other parts of the paper.

Page12Lines10-11: ’... and it cannot be distinguished if the isotope fractionation occurs during formation of the intermediate or the final product.’ This is an important statement; make it as an independent sentence. Changed, we want to point out that this important consideration is explained in more detail in the revised manuscript.

Page12Line13: This is no equation Changed “ KIEfor=..” where “KIEfor represents the total isotope fractionation during formation of nitrophenols following the initial reaction of the precursor with the OH-radical.”

Page13Lines7-8: Change the order of the two equations to make it consistent with the previous sentences. Changed

Page18Lines4-7: Reformulate, maybe like this: ’Saccon et al. measured the NP isotopic ratio with an accuracy of 0.5... based on the regression analyses, this would translate in...’ Changed: “The estimated accuracy of the nitrophenol carbon isotope ratio measurements published by Saccon et al. (2015) is 0.5 ‰Ṫhis corresponds to uncertainty in . . ..”

Page18Lines12-17: Give also the average values, since Figure 3 contains only the medians. Therefore it is difficult to find in the plot the average PCA values presented in Table 4. Reply: Figure 3 is already quite busy. Figure 3 also only serves as an example showing the dependence of the isotope ratios and PCA for toluene and the reaction products. The average PCA is given in Table 4 and any reader interested in details about the statistics of the precursor isotope ratios can find them in the cited paper by Kornilova et al.

Page21Lines1-5: The authors might consider to rephrase the following due to repetitions: ’However, for the conditions of the laboratory studies reported by Irei et al. (2015) a model with such an additional isotope fractionation for the formation of nitrophenols from reaction of the intermediate would predict methylnitrophenol isotope ratios for the 7 laboratory measurements reported by Irei et al. (2015),5 which are on average by 2.5 ‰ lighter than the measured values.’ Isn’t it : ’2.5 ‰ lighter than the modelled values.’ Changed: ’However, for the conditions of the laboratory studies reported by Irei et al. (2015) a model with such an additional isotope fractionation for the formation of nitrophenols from reaction of the intermediate would predict carbon isotope ratios on average by 2.5 ‰ methylnitrophenol isotope lighter than the measured values. ...? Page23Line10: Replace ’Figure 7’ by ’Figure 4’. Changed

Page24Line23: Replace ’nitrophenols but physical’ by ’nitrophenols. Physical ’ Changed

Page25Line1: Replace ' nitrophenols in aged air masses' by 'nitrophenols from aged air' masses Changed

Page25Lines8-14: Reformulate. The sentences are too complicated. For instance, the second sentence could look like this: 'The calculation formalism considers that the 4-nitrophenol depositional loss rate is the n-fold of the chemical removal rate by reaction with the OH-radical. This of course doesn't mean that deposition is dependent upon the OH-radical concentration.' Changed: "This is the consequence of the delay in formation of nitrophenols following precursor emissions. Details on how PCA are impacted by the influence of aged air masses depends on details of mixing as well as the possible removal rate of nitrophenols by deposition (Fig. S4b). The 4-nitrophenol depositional loss rates used for the calculations are relative to the removal of 4-nitrophenol by reaction with the OH-radical. Details of the impact of changes in the ratio between deposition rate and reaction rate with OH-radicals are also shown in Figure 4." (The revised manuscript presents a revised Figure S4). Page35Table2: Reformulate footnote g. The expression makes no sense. Changed: Estimated on the assumption that reaction proceeds primarily through an addition pathway (Atkinson et al., 1980). The kinetic isotope effect for addition of OH-radicals to an aromatic ring are based on the kinetic isotope effects reported by Anderson et al. (2004). Page44Figure5: The numbers representing the n-times of the chemical loss are too small. Supplement Page1caption Figure S4: replace ' for mixing air masses with' by ' for mixing air masses characterized by ' Changed

References Kornilova, A., Saccon, M., Huang, L., Rudolph, J.: Stable carbon isotope ratios of ambient aromatic volatile organic compounds, Atmos. Chem. Phys., 16, 111755-11772, 2016. Saccon, M., Kornilova, A., Huang, L., Moukhtar, S., Rudolph, J.: Stable carbon isotope ratios of ambient secondary organic aerosols in Toronto, Atmos. Chem. Phys., 15, 10825-10838, 2015. Yu, L., Smith, J., Laskin, A., George, K.M., Cort Anastasio, C., Laskin, J., Ann M. Dillner, A.D., Zhang,Q.: Molecular transformations of phenolic SOA during photochemical aging in the aqueous phase: competition among

oligomerization, functionalization, and fragmentation, Atmos. Chem. Phys., 16, 4511–4527, 2016

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-976, 2018.