

We made a number of changes to improve the clarity of the paper. In addition to changes in the introduction we added more detailed error analysis, estimates of the possible role of condensed phase reactions and more details about the numerical integration of the differential equations in the revised Supplement. This also allowed removing some details of error analysis and uncertainty discussions from the paper itself.

Specific changes and replies to referee's comments are below.

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 and compare 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. We added more detailed explanations in the 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. To further clarify uncertainties of our mechanistic model predictions we include a more detailed error analysis in the revised 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 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, backtrajectory 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 7% upon temperature changes by 20K, which is comparable to the relative uncertainty in " (6.1%). Then, you use the same 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 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 δ -value from molecular ratios. You could use starting composition (or emission) of 0‰ for C_{pre} and see how the effective fractionation builds up in all compartments (which is commonly used in models studying using sink fractionation; the errors associated with this approach are marginal in the used range of some 40‰ V-PDB). Then, you state that you derive δ -values from concentrations of isotopologues. How are the concentrations of C_{pre} initialised in the model, also using ¹³C/¹²C ref. ratio of unity?

In any case, I am very concerned that kinetics in your model are erroneous, because you mix molecular and atomic entities whilst simulating fractionation in each step. That would not be a problem should each simulated species bear only one C atom. But, for instance, toluene possesses seven C atoms, so one reaction of ¹³C-substituted isotopologue transfers one ¹³C and six ¹²C atoms to the products, which in turn define molecule concentrations used to calculate further reaction steps. If in Eqs. 6-9 you use R_{st}=1 for defining C_{pre}, then you react ¹³C-isotopologues several times faster (whilst ¹²C/¹³C are still formulated for molecular counts) and simulate incorrect mixing ratios as well. If not, you overestimate the fractionation by some 6%, 7.2% and 8.6% for species bearing 6, 7 and 8 C atoms, respectively, in every reaction escorted by fractionation.

At this point, I see no sense reviewing the derived δ -values and PCA; first the kinetic model should be formulated properly.

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 by adding more details in the supplement.

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_kpre product, and I am concerned that this does not lead to unambiguous results. Please, comment on that.

Reply: We do not understand the purpose of this comment. Our statement in no way implies that fractionation will be insignificant. On the contrary, in the case of small yields (due to branching reactions) the isotope fractionation cannot be constraint by mass balance considerations and as stated, the overall fractionation is determined by Eq.10 (P12, L13), which exactly explains that only the overall effect can be seen in the isotope ratio of the second generation product. This is not the consequence of how the model is formulated, but due to the fact that the isotope ratios of first and second generation product cannot be constraint by mass balance considerations. In the revised version we further clarify the principle that only the overall impact of the intermediate steps can be seen in the isotope ratio of the second generation product.

P15L14-17: In what terms do you measure the consistency and imply that it full? The model uses toluene emission $\delta^{13}\text{C}$ typical for its major source; sink fractionation will expectedly enrich leftover “ambient” toluene in ^{13}C . Statistically speaking, the maximum $\delta^{13}\text{C}$ of toluene (-7.7‰) 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 100% of processed toluene; admitting a 0.5‰ error in $\delta^{13}\text{C}$ of toluene (taking -8.2‰ instead) will yield some 96% processed of originally about 2.25 nmol/mol of toluene. That 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 100% toluene processing is simply wrong. The dependence between PCA and the fraction of toluene processed is an exponential function asymptotically approaching, but never reaching 100 %. This is well established and also is shown in Figure 3. For some reason the referee seems to think that our calculations create values exceeding 100% processing of toluene. In the revised manuscript we add some explanations to Figure 3 to clarify that it clearly shows that 100% toluene processing can be approached asymptotically, but never reached or exceeded.

It 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. We deleted the qualifier “fully” since it is not necessary.

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. Carbon 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 % of the measured atmospheric isotope ratios of 4-nitrophenol. We do not understand the suggestion of estimating uncertainty. The purpose of our argument is an explanation of the considerations used to constrain uncertainties based on the necessity that any scenario needs to be able to explain the entire observed range of isotope ratios, not only the average or individual subsets of the observations. In the revised manuscript a more detailed explanation of the considerations used to constrain possible scenarios based on atmospheric observations and laboratory experiments is given in the supplement.

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.

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 OH exposure 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). Many 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 $\delta^{13}\text{C}$ signatures, steps involving significant KIEs and yields/branching ratios important for nitrophenols (with probed parameters highlighted therein, for example). Each compartment should be uniquely defined and referred to in the manuscript. Moreover, assumptions probed later in scenarios (i.e. which KIEs are neglected/added in which steps) should be shown.

Reply: In the revised version the introduction and description of the conceptual model is modified in order to clarify the intention of this paper. The suggested table would not serve this purpose since the intention of this paper is not an attempt in numerical modeling of the concentrations and carbon isotope ratios of atmospheric nitrophenols and thus would increase the risk that a reader interprets the paper as an attempt in numerical model predictions.

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 explicitly 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” 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 ^{13}C .

Reply: Changed to: “due to the depletion in ^{13}C relative to the isotope ratio of the precursors.

P4L11: Do you mean **singly substituted** ^{13}C -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. leftover 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 $\int[OH]dt$ of the precursor VOC (Rudolph and Czuba, 2000). However, Eq. 4 is only a valid approximation if the differences in PCA are small compared to the average PCA. Otherwise EQ.4 will underestimate the average of χ_0 .

P6L17-20: Can you explicate, why the relationship is more complex and why the δ_{13C} of subsequently produced SOA/nitrophenols is (expected to be) not affected by this?

Changed to: “However, due to the simultaneous formation and removal of the reaction products the relation between the carbon isotope ratio of the reaction product and the extent of photochemical processing is more complex than the simple relation between the carbon isotope ratio of the precursor and $\int[OH]dt$ as described by Eq. 3.

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 8% of the time/cases” (should comply with P9L18).

Reply: Changed to “for 8 % of all reactions”

P10L5-6: Can you comment on what fractionations (or their uncertainties) may be expected in the rest of the cases (20% is a perceptible fraction to be influential should KIEs be comparable or larger than that in the reaction with OH)?

Reply: 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 function 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 “reasonable 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 % to 20 % range and error in the KIE of 0.5 ‰ (see Figure S3 for details) is...”

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 30% of ...” or specify 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. We do not fully understand “how deposition rate is simulated” but we added some more details in the supplement.

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.1&2: Using “x 1000%” is redundant (you have indicated above that _ and " are expressed in per mil). Avoid using “x” instead of correct multiplication sign (e.g. bullet).
Reply: Eq. 2 gives the correct result in ‰. “x” is widely used in publications in ACP as multiplication sign. No reason to make changes.

P7L3: Remove “approximately”
Changed to: “..are between 2 ‰ and 3 ‰...”

P7L9: “... based on nitrophenols formation and removal in the atmosphere ...”
Reply: The sentence is correct and clear in its present form.

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 is moved to supplementary material, which allows to add a more detailed explanation of the rationale 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%. 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 the linear approximation. c 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 '% of the time' use '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 % of the time (Bejan et al., 2007). Since an OH radical is being added to the ring, fractionation typical for reaction at the 6 aromatic ring is expected to occur for 80% of the loss reactions.

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 k_{12} nor k_{13} is identical to the experimentally determined rate constant. The fact that for mostly all practical applications $k_{12}=k_{OH}$ 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, this important consideration is clarified and explained in more detail in the revised manuscript and the supplement.

Page12Line13: This is no equation

Changed " $KIE_{for=..}$ " where " KIE_{for} 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 ‰. This 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'

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**Dependence between the Photochemical Age Light Aromatic Hydrocarbons and the
Carbon Isotope Ratios of Atmospheric Nitrophenols**

Saccon, M.¹, Kornilova, A.¹, Huang, L.², Rudolph, J.¹

Affiliation:

1. Centre for Atmospheric Chemistry
York University
4700 Keele St.
Toronto, ON.
M3J 1P3
2. Climate Research Division
Atmospheric Science & Technology Directorate
STB, Environment & Climate Change Canada
4905 Dufferin St.
Toronto, ON.
M3H 5T4

1 Abstract

2 Concepts were developed to establish relationships between the stable carbon isotope ratios
3 of nitrophenols in the atmosphere and photochemical processing of their precursors, light aromatic
4 volatile organic compounds. The concepts are based on the assumption that nitrophenols are
5 formed dominantly from the photo-oxidation of aromatic VOC. A mass balance model as well as
6 various scenarios based on the proposed mechanism of nitrophenol formation were formulated and
7 applied to derive the time integrated exposure of the precursors to processing by OH-radicals
8 ($\int[\text{OH}]dt$) from ambient observations taken between 2009 and 2012 in Toronto, Canada. The
9 mechanistic model included the possibility of isotopic fractionation during intermediate steps,
10 rather than during the initial reaction step alone. This model ~~included knowledge of~~takes into
11 account kinetic isotope effects for reaction of the precursor VOC with the hydroxyl radical and
12 their respective rate constants, as well as carbon isotope ratio source signatures. While many of
13 these values are known, there were some, such as the kinetic isotope effects of reactions of ~~the~~
14 ~~intermediate compounds~~first and second generation products, which were unknown. These values
15 were predicted based on basic principles and published laboratory measurements of ~~normal~~-kinetic
16 carbon isotope effects and were applied to the mechanistic models. Due to uncertainty of the
17 estimates based on general principles three scenarios were used with different values for isotope
18 effects that were not known from laboratory studies. Comparison of the dependence between
19 nitrophenol carbon isotope ratios and $\int[\text{OH}]dt$ with published results of laboratory studies and
20 ambient observations was used to narrow the range of plausible scenarios ~~of the~~for the mechanistic
21 model. ~~The results also suggests that and to eliminate the~~ mass balance based models do not
22 adequately describe as useful formulation of a the dependence between nitrophenol carbon isotope
23 ratios and $\int[\text{OH}]dt$.

1

2 1 Introduction

3 Secondary organic aerosols (SOA) in the atmosphere, formed from the photo-oxidation of
4 both anthropogenic and biogenic volatile organic compounds (VOC) are poorly understood.
5 Products formed from these reactions are only partly known and beyond the composition of SOA,
6 little is ~~also~~ known about its atmospheric processing. It has been proposed that the use of
7 concentration measurements in conjunction with stable carbon isotope ratio measurements can be
8 used to gain insight into this topic (Goldstein and Shaw, 2003; Rudolph, 2007; Gensch et al., 2014).
9 The compounds of interest in this study are nitrophenols, which have been proposed to be formed
10 specifically from the gas phase photo-oxidation of aromatic VOC (Forstner et al., 1997; Atkinson,
11 2000; Jang and Kamens, 2001; Hamilton et al., 2005; Sato et al., 2007). Once toluene, for example,
12 is emitted from its anthropogenic sources, it is expected to react according to the proposed reaction
13 mechanism (Forstner et al., 1997) to produce methylnitrophenols (Fig. 1). By being formed
14 specifically from identified reactions, the stable carbon isotope ratio of the product can be linked
15 back to the precursor and its source. ~~Additionally~~Based on observations in the laboratory (Irei et
16 al., 2011), methylnitrophenols were found to have an average isotope ratio that is close to the
17 isotope ratio of the sum of all products calculated from mass balance. ~~observations in the laboratory~~
18 ~~(Irei et al., 2011)~~. The aqueous phase production of nitrophenols, specifically 4-nitrophenol, has
19 also been proposed to be formed through a reaction pathway with the NO₃ radical (Hermann et al.,
20 1995; Harrison et al., 2005). This pathway has been proposed to be a quite significant source of 4-
21 nitrophenol in the presence of clouds with high liquid water content but has been modelled to
22 contribute less than 2 % when the liquid water content is low (Harrison et al., 2005). Ambient
23 measurements in the Toronto area (Saccon et al., 2015) indicate that nitrophenols are dominantly

1 ~~formed from secondary processes~~second generation products due to their ~~depleted stable carbon~~
2 ~~isotope ratio~~depletion in ¹³C relative to the carbon isotope ratio of the precursor.

Formatted: Superscript

3 The carbon isotope ratio of a species, which will be referred to as the delta value ($\delta^{13}\text{C}$), is
4 defined using Eq. 1, where $(^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}$ is the internationally accepted Vienna-Peedee Belemnite
5 (V-PDB) value of 0.0112372. Since differences in isotope ratios between species are small, delta
6 values are expressed in per mille notation. Limited studies using the carbon isotope ratio of
7 atmospheric trace components, including several aromatic VOC and nitrophenols ~~in SOA~~, have
8 been applied to differentiate between sources and to trace components back to the precursor,
9 respectively (Moukhtar et al., 2011; Kornilova et al., 2013; Saccon et al., 2013). The concept to
10 derive information on photochemical processing of trace constituents from isotope ratios is based
11 on the kinetic isotopic effect (KIE) which describes the dependence of the rate constant of a
12 reaction on the atomic mass of isotopologues. In this work, the KIE will be referred to as ϵ (Eq.
13 2), where k_{12} and k_{13} are the rate constants for ~~the~~¹²C only and one¹³C containing
14 ~~species~~isotopologues, respectively. Normal KIE, that is when ϵ is ~~larger than one~~positive, is
15 exhibited when a compound reacts in the atmosphere and the remaining compound is ~~becomes~~
16 enriched in heavier isotopes, for example ~~the~~¹³C ~~isotopes~~. Like delta values, ϵ is also expressed in
17 per mille notation.

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}}{(^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}} \times 1000\text{‰} \quad \text{Eq. 1}$$

$$\epsilon = \frac{k_{12} - k_{13}}{k_{13}} \times 1000\text{‰} \quad \text{Eq. 2}$$

18

1 Among other factors The concentration of a species in the atmosphere will, ~~among other~~
2 ~~factors,~~ depend on its reactivity and the time that it has been exposed to reactants. For many VOC
3 and semi-volatile organic compounds (SVOC) the most important reactant is the OH radical, and
4 the time integrated OH radical concentration is often referred to as the photochemical age (PCA).
5 The combination of laboratory experiments and ambient measurements can allow the
6 determination of the PCA of a specific component in SOA. The PCA ~~of a species~~ for an air mass
7 has been previously used to quantify the extent of processing of a precursor using the hydrocarbon
8 clock by using mixing ratios of VOC (Parrish et al., 1992; Jobson et al., 1998, Jobson et al., 1999;
9 Kleinman et al., 2003; Parrish et al., 2007). A more recently developed method uses the carbon
10 isotope ratio of an ~~ambient species~~ atmospheric VOC with emissions as only relevant source, the
11 KIE and the isotope ratio source signature to determine the PCA of this VOC. This approach ~~and~~
12 is often referred to as the isotope hydrocarbon clock (Rudolph and Czuba, 2000; Rudolph et al.,
13 2003; Thompson, 2003; Stein and Rudolph, 2007; Kornilova, 2012, Kornilova et al., 2016). The
14 PCA of a species can be calculated using Eq. 3, where $\delta^{13}\text{C}_{\text{pre}}$ is the carbon isotope ratio of the
15 measured ambient precursor, $\delta^{13}\text{C}_0$ is the carbon isotope ratio of the emissions, and $\int[\text{OH}]dt$ is the
16 time integrated OH concentration (PCA). ~~However, it~~ has been shown that the concept of
17 ascribing a photochemical age to an air mass (Parrish et al., 1992) is only meaning-ful if all
18 ~~individual air parcels~~ VOC emissions that contribute to the observed VOC mixing ratios have been
19 subject to an identical extent of processing. In case of mixing air masses with VOC emissions
20 having been subject to different extent of processing the concept of a photochemical age of an air
21 mass has to be replaced by the concept of a photochemical age of an individual VOC (Kornilova
22 et al., 2016). It has been shown by Rudolph and Czuba (2000) that VOC carbon isotope ratio
23 measurements can be used to determine the concentration weighted average of the photochemical

1 age of individual VOC provided the variability of the carbon isotope ratio of emissions is small
2 compared to the change in carbon isotope ratio resulting from atmospheric removal reactions.

3 The carbon isotope ratio of the emissions of many important anthropogenic VOC
4 precursors has been previously measured and their uncertainty typically is below 1 ‰ (Czapiewski
5 et al., 2002; Rudolph et al., 2002; Rudolph, 2007, Gensch et al, 2014). The change in VOC mixing
6 ratios due to reaction with OH-radicals can be described by Eq. 4, where χ_{amb} and χ_0 are the mixing
7 ratios of the ambient precursor and the mixing ratio that would be observed in the absence of
8 reaction with OH-radicals, respectively. Consequently a combination of carbon isotope ratio
9 measurements and concentration measurements allows separating between the impact of
10 atmospheric reactions and changes in source strength or atmospheric mixing and dilution.

$$\delta^{13}C_{pre} = \delta^{13}C_0 + k_{12}\epsilon \int [OH]dt \quad \text{Eq. 3}$$

$$\chi_{amb} = \chi_0 \exp(-k_{12} \int [OH]dt) \quad \text{Eq. 4}$$

11
12 Comparison of the difference between χ_0 and χ_{amb} with the ambient concentrations of the
13 products of the photochemical reactions of VOC will provide insight into the yield of the secondary
14 pollutants from the reaction. ~~However, in the case of mixing air masses containing VOC with~~
15 ~~different photochemical ages, Eq. 4 will underestimate χ_0 and only provides information of the~~
16 ~~minimum contribution from emissions, although Eq. 3 still is a very good approximation for the~~
17 ~~concentration weighted average $\int [OH]dt$ of the precursor VOC. In the case of mixing air masses~~
18 ~~containing VOC with different PCA Eq. 3 still is a very good approximation for the concentration~~
19 ~~weighted average $\int [OH]dt$ of the precursor VOC (Rudolph and Czuba, 2000). However, Eq. 4 is~~
20 ~~only a valid approximation if the variability in PCA is small compared to the average PCA.~~
21 ~~Otherwise Eq. 4 will underestimate the average of χ_0 (Rudolph and Czuba, 2000). Consequently,~~

1 yield estimates derived from combining results derived from Eq. 3 and 4 with measured ambient
2 concentrations of reaction products will be an upper limit. In principle this limitation can be
3 avoided by using the carbon isotope ratio of the reaction product to derive $\int[\text{OH}]dt$ since the
4 average of $\int[\text{OH}]dt$ derived from carbon isotope ratios of the reaction products will be weighted
5 according to the concentration of the products, which will accumulate as result of the
6 photochemical reaction of the precursor. ~~However, due to simultaneous formation and removal of
7 the reaction products the relation between the carbon isotope ratio of the reaction product and the
8 extent of photochemical processing is more complex than the simple relation between the carbon
9 isotope ratio of the precursor and $\int[\text{OH}]dt$ as described by Eq. 3. However, the relation between
10 the carbon isotope ratio of the reaction product and the extent of photochemical processing is more
11 complex than the simple relation between the carbon isotope ratio of the precursor and $\int[\text{OH}]dt$
12 described by Eq. 3.~~

13 The reported carbon isotope ratio measurements of nitrophenols in the solid and the gas
14 phase by Saccon et al. (2015) have shown that, although the average isotope ratios are consistent
15 with laboratory studies, a significant number of delta values are ~~approximately between~~ 2 ‰ to 3
16 ‰ lower than predicted from mass balance. This difference cannot be explained by the uncertainty
17 of the carbon isotope ratios of precursor emission or measurements error. However, a simple mass
18 balance only considers the KIE for the first step of the reaction mechanism, shown in Fig. 1, ~~and~~
19 ~~it~~ must be accepted that further fractionation can occur in reaction steps following the initial
20 reaction of the aromatic VOC with the OH-radical. In this work, we will present calculations using
21 a mechanisms based on formation and removal of nitrophenols from the atmosphere that describe
22 the dependence between photochemical processing of light aromatic hydrocarbons and the carbon
23 isotope ratio of nitrophenols, which are products of atmospheric reactions of light aromatic

1 hydrocarbons. ~~The mechanisms~~Different scenarios using a range of isotope fractionation effects
2 for a simple mechanistic model will be discussed using the carbon isotope ratios of nitrophenols
3 published by Saccon et al. (2015) and the laboratory studies published by Irei et al. (2015). From
4 this comparison, the magnitude of isotope fractionation effects following the initial reaction of
5 light aromatic VOC with OH-radicals can be constraint. PCA derived from nitrophenol carbon
6 isotope ratios will be compared with PCA derived from carbon isotope ratios of the precursors
7 (Kornilova et al., 2016).

8 **2 Materials and Method**

9 The experimental method used in this work is described in detail by Saccon et al. (2013),
10 which is based on methods developed by Moukhtar et al. (2011) and Irei et al. (2013). The results
11 of the carbon isotope ratio measurements have been presented by Saccon et al. (2015) and we
12 therefore will only briefly describe the experimental procedure. Sample collection was done at
13 York University in Toronto, Canada using 20.32 cm x 25.4 cm quartz fiber filters (Pallflex®
14 Tissuquartz™ filters – 2500 QAT – PallGelman Sciences) on high volume air samplers (TE-6001
15 from Tisch Environmental Inc.) equipped with PM2.5 heads. Uncoated quartz filters were used to
16 collect particulate matter (PM) alone, with an average sampling time of one to three days, and
17 filters coated with XAD-4™ resin were used for the collection of gas phase and PM, with an
18 average sampling time of one day. Filter samples were collected between March 2009 and August
19 2012. The analysis of the filters included extraction in acetonitrile, and HPLC separation and solid
20 phase extraction were used as sample clean-up steps. Concentration measurements were done
21 using a HP 5890 GC equipped with a HP 5972 mass spectrometer; carbon isotope ratio

1 measurements were done using a Micromass Isoprime IRMS (Isomass Scientific, Inc.). Method
2 performance characteristics are given in Saccon et al. (2013) and Saccon et al. (2015).

3 **3 Determination of PCA**

4 Laboratory experiments studying the carbon isotope ratios of secondary particulate organic
5 matter (POM) formed by the gas phase oxidation of toluene showed that the $\delta^{13}\text{C}$ value of total
6 secondary POM can be approximated by mass balance (Irei et al., 2006, 2011). However,
7 compound specific measurements also indicate that in some cases detailed mechanistic
8 considerations are required to explain the observed $\delta^{13}\text{C}$ values of secondary phenols that are lower
9 than expected from mass balance alone (Irei et al., 2015).

10 **3.1. PCA from Mass Balance**

11 Mass balance calculations allow a straightforward determination of the dependence
12 between ~~the~~ $\delta^{13}\text{C}$ of the total of secondary POM and ~~the~~ PCA. This requires the assumption that
13 in the atmosphere the carbon isotope ratio of the gas phase reaction products is identical to the
14 carbon isotope ratio of secondary POM as observed in laboratory studies (Irei et al., 2006, 2011).
15 Furthermore, for compound specific carbon isotope ratio measurements it also has to be assumed
16 that the carbon isotope ratio of the individual products is representative for the carbon isotope ratio
17 of all secondary POM. In this case the dependence between PCA of the precursors and the product
18 isotope ratio (Eq. 5) can be derived from Eq. 3 and Eq. 4. Here, k_{OH} is the averaged rate constant
19 of all isotopomers of the precursor reacting with OH and for practical purposes, is equal to k_{12} .

$$\delta^{13}C_{\text{prod}} = \frac{\delta^{13}C_o - \exp(-k_{\text{OH}} \int [\text{OH}] dt) (\delta^{13}C_o + k_{12\text{OH}} \epsilon \int [\text{OH}] dt)}{1 - \exp(-k_{\text{OH}} \int [\text{OH}] dt)} \quad \text{Eq. 5}$$

20

1 It should be noted that, similar to the conventional hydrocarbon clock, in the case of mixing of air
2 masses with different PCA, the PCA from Eq. (5) is a combination of the PCA of the individual
3 air masses, which is not always easy to interpret. Equation 5 also neglects possible isotope
4 fractionation resulting from loss of secondary POM. The values for rate constants, carbon isotope
5 ratio of precursor VOC emissions and kinetic isotope effects used are listed in Table 1.

6

7 3.2. PCA from detailed mechanistic concepts

8 ~~The presently known~~The reaction sequence resulting in the formation of nitrophenols from
9 oxidation of toluene proposed by Forstner et al. (1997) is shown in Fig. 1. It does not include
10 details of the various branching reactions and alternate pathways resulting in other products or
11 isotope fractionation due to loss reactions of secondary POM. While in many cases branching
12 ratios are known, there is little direct knowledge on isotope fractionation resulting from branching
13 reactions. Nevertheless, isotope effects for specific pathways can be estimated from the type of
14 reaction and known principles of isotope fractionation. For example, after formation of the cresol
15 ~~intermediate~~first generation product (Fig. 1), the probability that an OH radical is added to the
16 ring is 92 % ~~of the time~~ (Atkinson et al., 1980) while reaction at the phenolic OH group, which is
17 expected to result in formation of nitrophenols, occurs ~~with for~~ 8% probability of all reactions. The
18 reaction of the phenolic OH group is expected to result in negligible carbon isotope fraction since
19 it is a secondary isotope effect, while the OH radical addition will have a carbon isotope effect
20 similar to that of other OH addition reactions to aromatic rings. Similarly, the main gas phase loss
21 process of nitrophenols is expected to be through reaction with the OH radical, occurring through
22 an OH addition to the ring greater than 80 % of the time (Bejan et al., 2007). Since an OH radical

1 is added to the ring, fractionation typical for reaction at the 6 carbon atoms of aromatic ring is
2 expected to occur for 80% of the loss reactions. Similarly, the main gas phase loss process of
3 nitrophenols is expected to be through reaction with the OH radical, occurring through an OH
4 addition to the ring greater than 80 % of the time (Bejan et al., 2007) and since an OH radical is
5 being added to the ring, fractionation typical for reaction at the aromatic ring is expected to occur
6 for 80% of the loss reactions. Reaction at the alkyl group or the phenolic OH results in a much
7 lower KIE than for addition to the aromatic ring and therefore their contribution to the KIE is
8 negligible.

9 Another complication is the distribution between gas phase and PM. It ~~was~~is assumed that
10 there are no chemical losses when the nitrophenols partition into PM, and that there is equilibrium
11 between the gas and particle phases. Since phase distribution processes typically have very small
12 isotope effects, partitioning between gas phase and PM is expected to have only a marginal impact
13 on the carbon isotope ratio. This is consistent with the findings of Saccon et al. (2015). However,
14 partitioning will influence the loss rate for SVOC since it is assumed that there is little to no
15 chemical loss in the PM phase. It has been reported that phenols can be oxidized in aqueous
16 solutions under conditions somewhat similar to atmospheric conditions in fog or cloud water (Yu
17 et al., 2016). However, these reactions are very slow compared to the reaction of nitrophenols with
18 OH-radicals in the gas phase (details see Part 1 of the Supplement). Furthermore, uncertainty in
19 phase partitioning will only result in minor uncertainties of the photochemical nitrophenol loss
20 rate since it has been reported that only approximately 20 % of the nitrophenols partition into the
21 particle phase (Saccon et al., 2013, 2015). There is no information available that would allow
22 estimating the rate of exchange of nitrophenols between gas phase and PM. It was assumed that
23 phase partitioning is fast compared to gas phase reactions. There are indications that in some cases

1 exchange between gas phase and PM is slower than formation or loss reactions of SVOC in the
2 gas phase (Saccon et al., 2015), but the reported average of the difference in carbon isotope ratios
3 between gas phase and PM is negligible (0.3 ± 0.5) ‰.

4 Reaction rate constants for which no laboratory measurements are available are estimated
5 on the following principles.~~There are also some reaction rate constants which for which no~~
6 ~~laboratory measurements are available.~~ The rate constant for 3-methyl-4-nitrophenol ~~was is~~
7 estimated based on the position of its substituents on the aromatic ring relative to other isomers
8 that have known rate constants, such as 3-methyl-2-nitrophenol and 4-methyl-2-nitrophenol. For
9 2,6-dimethyl-4-nitrophenol it ~~was is~~ assumed that loss reactions due to addition of the OH radical
10 to the aromatic ring are negligible since the nitro and hydroxyl substituents both direct reactions
11 to positions that already are occupied by other substituents and that reaction at positions 3 or 5 is
12 unlikely to occur. It should be noted that reaction at the phenolic OH-group of 2,6-dimethyl-4-
13 nitrophenol will not directly impact the carbon isotope ratio since this secondary carbon isotope
14 effect will be negligible, independent of the rate of this reaction. ~~There is no information available~~
15 ~~that would allow estimating the rate of exchange of nitrophenols between gas phase and PM. It~~
16 ~~was assumed that phase partitioning is fast compared to gas phase reactions. There are indications~~
17 ~~that in some cases exchange between gas phase and PM is slower than formation or loss reactions~~
18 ~~of SVOC in the gas phase (Saccon et al., 2015), but the reported average of the difference in carbon~~
19 ~~isotope ratios between gas phase and PM is negligible (0.3 ± 0.5) ‰.~~

20 Using these assumptions, a set of differential equations ~~was is~~ derived that describe the
21 change in concentration of the isotopologues of the ~~reactant precursor~~, the ~~intermediate first~~
22 generation product (phenols), and the ~~observed second generation~~ product, nitrophenols (Eq. 6 to
23 98). Here, $^{12}\text{C}_{\text{prod/int/pre}}$ and $^{13}\text{C}_{\text{prod/int/pre}}$ are the concentrations of each of the ^{12}C and ^{13}C

1 isotopologues of the ~~product~~second generation nitrophenol, first generation intermediate phenolic
 2 compound and aromatic precursor, respectively. ${}_{int}^{12}Y$ and ${}_{int}^{13}Y$ are the yields of the ~~intermediate~~
 3 first generation product from reaction of the precursor and ${}_{prod}^{12}Y$ and
 4 ${}_{prod}^{13}Y$ the yields of nitrophenols from reaction of the ~~intermediate~~ phenols. ~~For the sake of~~
 5 ~~convenience, the reference carbon isotope ratio for the calculations was set to unity and Eq. (9) is~~
 6 ~~then used to derive δ values from the concentrations of the isotopologues. These carbon isotope~~
 7 ~~ratios represent the difference between the carbon isotope ratios of precursor emissions and~~
 8 ~~reaction products.~~ The rate constants k^{12} and k^{13} for different isotopologues ~~can~~are calculated
 9 from rate constants and the KIE.

10

$$d^{12}C_{prod} = -^{12}C_{prod}k_{prod}^{12}[OH]dt + {}_{prod}^{12}Y^{12}C_{int}k_{int}^{12}[OH]dt \quad \text{Eq. 6a}$$

$$d^{13}C_{prod} = -^{13}C_{prod}k_{prod}^{13}[OH]dt + {}_{prod}^{13}Y^{13}C_{int}k_{int}^{13}[OH]dt \quad \text{Eq. 6b}$$

$$d^{12}C_{int} = -^{12}C_{int}k_{int}^{12}[OH]dt + {}_{int}^{12}Y^{12}C_{pre}k_{pre}^{12}[OH]dt \quad \text{Eq. 7a}$$

$$d^{13}C_{int} = -^{13}C_{int}k_{int}^{13}[OH]dt + {}_{int}^{13}Y^{13}C_{pre}k_{pre}^{13}[OH]dt \quad \text{Eq. 7b}$$

$$d^{12}C_{pre} = -^{12}C_{pre}k_{pre}^{12}[OH]dt \quad \text{Eq. 8a}$$

$$d^{13}C_{pre} = -^{13}C_{pre}k_{pre}^{13}[OH]dt \quad \text{Eq. 8b}$$

$$\delta^{13}C_{prod} = \left(\frac{{}_{prod}^{13}C_{prod}}{{}_{prod}^{12}C_{prod}} - 1 \right) \times 1000 \text{‰} \quad \text{Eq. 9}$$

11 Details of the numerical integration of these coupled differential equations are described
 12 in Part 2 of the supplement. The largest uncertainty arises from the possible isotope dependence
 13 of the yields in Eq. 6 and 7, but uncertainty in kinetic isotope effects also will contribute to
 14 uncertainty in the calculated carbon isotope ratio. Eq. 6 to ~~9-8~~ only describe the fractionation
 15 relative to the carbon isotope ratio of the precursor emissions. In order to determine carbon isotope

1 ratios that can be compared with observations we use the carbon isotope ratios for emissions
2 reported by Rudolph et al. (2002). To obtain insight into the possible impact of ~~these~~ uncertainties
3 in model parameters we use different scenarios.

4 Since the yields of nitrophenols from the reaction of light aromatic VOC are small, the
5 feedback of differences in yields for isotopologues of the product on the carbon isotope ratio of
6 the ~~intermediate first generation product~~ is very small, ~~and it~~ cannot be distinguished if the isotope
7 fractionation occurs during formation of the ~~intermediate first~~ or the ~~final second generation~~
8 product. The consequence is that at low values for the PCA the reaction channel specific isotope
9 fractionation for the formation of nitrophenols is determined by the following equation.

$$10 \quad KIE_{For} = \frac{{}^{13}Y_{prod} k_{int}^{13} {}^{13}Y_{int} k_{pre}^{13}}{{}^{12}Y_{prod} k_{int}^{12} {}^{12}Y_{int} k_{pre}^{12}} \quad \text{Eq. 10}$$

11 KIE_{For} represents the total isotope fractionation during formation of nitrophenols following
12 the initial reaction of the precursor with the OH-radical (for details see Part 3 of the Supplement).

13 This greatly reduces the number of scenarios that need to be considered.

14 The basic parameters used for solving these differential equations are listed in Table 2. The
15 rate constants are for 298 K for consistency with published literature data available for comparison.
16 Rate constants for this temperature are used in the determination of PCA from carbon isotope ratios
17 of light aromatic VOC (Kornilova et al., 2016). The laboratory studies of formation of
18 methylnitrophenols (Irei et al., 2015) from toluene were conducted at room temperature. In order
19 to determine the dependence of the calculated isotope ratio on the KIE different scenarios are used.
20 To understand uncertainties arising from the assumptions made to estimate KIEs which have not
21 been determined experimentally different scenarios are used. In the first scenario (Scenario 1) it is

1 assumed that formation of nitrophenols is entirely via abstraction of a hydrogen atom from the
2 phenolic OH group and that, since it is a secondary KIE, there is no isotope fractionation from this
3 reaction step. It is also assumed that there is no reaction channel specific isotope fractionation for
4 the formation of the phenolic intermediate from the precursor, This is equivalent to the assumption
5 that $\frac{^{12}Y}{int} = \frac{^{13}Y}{int}$ and $^{12}Y k_{int}^{12} = ^{13}Y k_{int}^{13}$ and $\frac{^{12}Y}{int} = \frac{^{13}Y}{int}$.

6 Another scenario (Scenario 2) is based on the assumption that the isotope fractionation for
7 formation of nitrophenols from the intermediate is identical to the fractionation for all reactions of
8 the intermediate and that there is no reaction channel specific isotope fractionation. It should be
9 noted that for the formation of nitrophenol from the reaction of benzene, the two scenarios will be
10 identical since the reaction of phenol with the OH-radical occurs predominantly via abstraction
11 from the OH group (Atkinson et al., 1992) and it is assumed that this secondary carbon isotope
12 effect is negligible ($k_{int}^{12} = k_{int}^{13}$). For the reactions of toluene and xylene these two scenarios
13 represent an estimate for the upper and lower limit of carbon isotope fractionation resulting from
14 reactions of ~~intermediates~~the first generation product.

15 The third scenario (Scenario 3) is based on laboratory studies of the formation of
16 nitrophenols from gas phase reactions of toluene in the presence of NO₂ (Irei et al. 2011; Irei et
17 al., 2015) and the lower end of atmospheric observations of nitrophenol carbon isotope ratios
18 reported by Saccon et al. (2015). Details of how these observations can be used to constrain the
19 isotope fractionation during formation of nitrophenols from aromatic VOC and the uncertainties
20 of these constraints are given in Part 4 of the Supplement. In these experiments it was found that
21 the $\delta^{13}C$ value of the formed methyl nitrophenols is on average 3 ‰ lower than predicted by a
22 mechanistic model assuming that the formation of nitrophenols from cresols is entirely via
23 abstraction of the phenolic hydrogen atom and that this pathway results in no further isotope

1 ~~fractionation between cresols and formed methylnitrophenols.~~ Scenario 3 ~~therefore~~ uses an overall
2 isotope fractionation 3 ‰ greater than in Scenario 1. It should be noted that this does not
3 necessarily imply a specific process for the formation of methylnitrophenols from ~~cresols~~phenols.
4 ~~This 3 ‰ carbon isotope fractionation could be the result of delocalization of the phenolic radical~~
5 ~~over the aromatic ring structure, which could result in a secondary carbon isotope effect larger~~
6 ~~than typical secondary isotope effects, an isotope effect for the formation of nitrophenols from the~~
7 ~~phenoxy radical or a reaction channel specific fractionation during the formation of the phenolic~~
8 ~~intermediate from the precursor.~~

9 The results of the numerical integration are plotted in Fig. 2 for 2,6-dimethyl-4-nitrophenol,
10 4-nitrophenol, and 2-methyl-4-nitrophenol together with predictions from mass balance. For
11 comparison the median, 10 and 90 percentiles as well as the lowest and highest carbon isotope
12 ratios reported by Saccon et al. (2015) are also shown. For 2-methyl-4-nitrophenol the results of
13 laboratory studies reported by Irei et al. (2015) are included.

14 The predictions by the mechanistic models are very similar for the methylnitrophenol
15 isomers (see example in Fig. S1) and for a wide range of PCAs the difference in predicted carbon
16 isotope ratios between the isomers is less than the estimated accuracy of 0.5 ‰ for carbon isotope
17 ratio measurements of methylnitrophenols (Saccon et al. 2013).

18 For ~~the~~ methylnitrophenols and 2,6-dimethyl-4-nitrophenol in all three scenarios the shape
19 of the functions describing the dependence between carbon isotope ratio and $\int[\text{OH}]dt$ is very
20 similar and the difference in the intercept with the y-axis is determined by the isotope fractionation
21 specific for the reaction channel resulting in formation of nitrophenols and the kinetic isotope
22 effect for the reaction of the precursor as well as the carbon isotope ratio of precursor emissions.

1 The steep increase in $\delta^{13}\text{C}$ at low values of $\int[\text{OH}]\text{dt}$ is the result of the high reactivity of
2 the phenolic ~~intermediate-first generation product~~ and the resulting rapid increase in ~~the-its~~ carbon
3 isotope ratio ~~of the intermediate~~ (Fig. 3). The exception is Scenario 1 for nitrophenol which
4 assumes that the kinetic isotope effect for reaction of phenol with the OH-radical is negligible.

5 At high PCA the dependence between carbon isotope ratio and PCA is nearly linear,
6 representing conditions where the ~~intermediate-first generation~~ phenol is in quasi steady state
7 between formation from the precursor and loss reactions (Fig. 3). The PCA ($\int[\text{OH}]\text{dt}$) for transition
8 between the initial steep increase and the nearly linear range depends primarily on the reaction rate
9 constants of the phenolic intermediates. At high values for $\int[\text{OH}]\text{dt}$ the slope of the dependence
10 between $\delta^{13}\text{C}$ and $\int[\text{OH}]\text{dt}$ is mainly determined by the rate constant and kinetic isotope effect for
11 the reaction of the nitrophenol with the OH-radical since most of the aromatic precursor has been
12 consumed (Fig. 3). Nevertheless, due to the continuing formation of nitrophenols from the
13 precursor and the increase in $\delta^{13}\text{C}$ of the precursor this slope is slightly steeper than predicted by
14 the rate constant and kinetic isotope effect for the reaction of the nitrophenol alone. It should be
15 noted that the carbon isotope ratios of the precursor predicted by our mechanistic models are ~~fully~~
16 consistent with the range of carbon isotope ratios of aromatic VOC in the atmosphere reported by
17 Kornilova et al. (2016) (Fig. 3).

18 ~~At high values for $\int[\text{OH}]\text{dt}$ the rate constants or kinetic isotope effects for the loss reaction~~
19 ~~of nitrophenols have a substantial impact on the dependence between $\delta^{13}\text{C}$ and $\int[\text{OH}]\text{dt}$ (see~~
20 ~~example in Fig.S2). However, as can be seen in Fig. 2 and S2, for the methyl nitrophenols and 2,6-~~
21 ~~dimethyl 4 nitrophenol this range is well outside of the range of the carbon isotope ratios in~~
22 ~~ambient air reported by Saccon et al. (2015).~~

1 ~~Rate constants for reaction of the precursor and intermediate with the OH radical as well~~
2 ~~as the kinetic isotope effect for reaction of the precursor with the OH radical have been measured~~
3 ~~in laboratory studies (see Table 2). Nevertheless, they have some uncertainties that will impact the~~
4 ~~dependence between carbon isotope ratio and $\int[\text{OH}]dt$. However, for the range of carbon isotope~~
5 ~~ratios reported by Saecon et al. (2015) the uncertainty of predicted carbon isotope ratios for~~
6 ~~reasonable errors of measured rate constants and isotope effects is less than 0.5 ‰ (see example~~
7 ~~in Fig. S3).~~

8 ~~It is not surprising that the largest uncertainty in the prediction of the dependence between~~
9 ~~carbon isotope ratio results from the limited knowledge of isotope fractionation effects specific for~~
10 ~~the reaction channels leading to formation of nitrophenols. For the range of carbon isotope ratios~~
11 ~~observed in ambient studies uncertainties of the rate constants and kinetic isotope effects known~~
12 ~~from laboratory studies result in uncertainty of nitrophenol carbon isotope ratios typically less than~~
13 ~~± 0.5 ‰, which is similar to or below the estimated accuracy of ambient measurements of~~
14 ~~nitrophenol carbon isotope ratios (Saecon et al., 2013; Saecon et al., 2015).~~

16 **3.3. Comparison of predicted carbon isotope ratios with laboratory and ambient** 17 **measurements**

18
19 For 2,6 dimethyl-4-nitrophenol and methylnitrophenols, the lower end of mass balance
20 predictions is substantially heavier than the lower end of ambient observations, but for
21 methylnitrophenols mass balance predicts carbon isotope ratios well within the range of the
22 laboratory results reported by Irei et al. (2015). The lower end of carbon isotope ratios predicted
23 by Scenario 1 for 2,6 dimethyl-4-nitrophenol and methylnitrophenols is 3 ‰ to 4 ‰ heavier than

1 the lower end of ambient observations reported by Saccon et al. (2015). Furthermore, six out of
2 the seven carbon isotope ratios of methylnitrophenols observed in laboratory studies by Irei et al.
3 (2015) are more than 2 ‰ lighter than predictions based on Scenario 1.

4 Scenario 3 predicts for 4-nitrophenol at small values of the precursor's PCA ($\int[\text{OH}]dt \leq 10^{11}$
5 s molecules cm^{-3}) that the carbon isotope ratios are lower than the lower limit of ambient
6 observations in an urban area of Toronto (Saccon et al. 2015). Similarly, the methylnitrophenol
7 carbon isotope ratios predicted by Scenario 2 for a $\int[\text{OH}]dt$ of less than 3×10^{10} s molecules cm^{-3}
8 are lighter than the lowest ambient observations (Saccon et al., 2015). Kornilova et al. (2016)
9 reports that 25 % of PCA derived from carbon isotope ratio measurements of benzene and toluene
10 are below 1.1×10^{11} s molecules cm^{-3} and 1.6×10^{10} s molecules cm^{-3} , respectively. However, it has
11 to be considered that for mixing air masses of different PCA, the PCA derived from carbon isotope
12 ratios of the precursor and the reaction product based PCA are not necessarily identical (see 3.5).

13 For high PCA mass balance predicts a substantially lower slope for the dependence
14 between PCA and carbon isotope ratios than all three scenarios based on a mechanistic model.
15 This is due to the conceptual limitation of the mass balance, which does not include the change in
16 carbon isotope ratio resulting from atmospheric reaction of nitrophenols and consequently it
17 cannot be expected that a mass balance can correctly predict carbon isotope ratios at high PCA.

18 Most of the observed nitrophenol carbon isotope ratios correspond to PCA at the lower end
19 of PCA predicted by Scenario 3 (Figure 2). For this range a linear approximation can be used (Part
20 5, Supplement). There is a substantial range of PCA where $\delta^{13}\text{C}$ can be predicted by a linear
21 approximation. Table 3 shows the regression parameters for Scenarios 2 and 3 for a linear
22 approximation in a range where the difference between exact solution and linear approximation is
23 within the typical measurement accuracy of 0.5 ‰ (Saccon et al., 2013). Except for 4 nitrophenol

1 ~~essentially all of the measurements reported by Saccon et al. (2015) are within the linear range of~~
2 ~~Scenario 3. Furthermore, for methylnitrophenols and 2,6 dimethyl 4 nitrophenol the slopes of the~~
3 ~~linear range for different scenarios are, within their uncertainty, identical. This allows determining~~
4 ~~differences in PCA independent of the scenarios, although the absolute PCA values will be highly~~
5 ~~dependent on the assumption made for the different scenarios. The estimated accuracy of the~~
6 ~~nitrophenol carbon isotope ratio measurements published by Saccon et al. (2015) is 0.5 %. This~~
7 ~~corresponds to uncertainty~~ Based on the estimated accuracy of 0.5 % for nitrophenol carbon
8 ~~isotope ratio measurements, differences in $\int[\text{OH}]dt$ in the range of 6×10^9 s molecules cm^{-3} and~~
9 ~~9×10^9 s molecules cm^{-3} can be determined from carbon isotope ratio measurements of~~
10 ~~alkylnitrophenols. This is similar to the sensitivity of $\int[\text{OH}]dt$ derived from measurement of carbon~~
11 ~~isotope ratios of toluene (Kornilova et al., 2016). However, for PCA derived from nitrophenol~~
12 ~~carbon isotope ratios uncertainty of model predictions will also contribute to the overall~~
13 ~~uncertainty. The overall uncertainty can be described an uncertainty independent of PCA and a~~
14 ~~contribution proportional to the PCA. Detailed estimates of uncertainty are given in Part 6 of the~~
15 ~~Supplement.~~

18 **3.4. PCA determined from carbon isotope ratios of nitrophenols**

19 Based on the dependence between PCA and carbon isotope ratio of VOC reaction products
20 (Fig. 3) $\int[\text{OH}]dt$ can be determined from measured carbon isotope ratios of ambient nitrophenols
21 under the assumption of a uniform PCA of the observed nitrophenols. The average PCA
22 determined from product carbon isotope ratios are compared in Table 3 with $\int[\text{OH}]dt$ values
23 calculated directly from precursor isotope ratios, which have been published by Kornilova (2012)

1 and Kornilova et al. (2016). The ~~product-nitrophenol~~ derived PCA is based on Scenario 3. ~~Scenario~~
2 ~~3 was chosen since the predicted carbon isotope ratios agree with results from laboratory studies~~
3 ~~(Fig. 3) and are consistent with the results of available ambient carbon isotope measurements.~~ It
4 should be noted that, although collected at locations only 3 km apart, precursor and product
5 samples were in most cases not collected simultaneously, and in some cases even in different years.
6 Nevertheless, the substantial number of samples in most of the data sets and the low uncertainty
7 of the mean PCA justify a comparison of ~~the averages and distribution of~~ precursor derived PCA
8 with $-\int[\text{OH}]dt$ values calculated from ~~second generation~~ product carbon isotope ratios.

9 Similar to precursor ~~carbon~~ isotope ratio based PCA the product isotope ratio derived PCA
10 increase substantially with decreasing precursor reactivity. This has been explained by Kornilova
11 et al. (2016) by mixing of air masses with different PCA, which results in a lower weight for VOC
12 with high reactivity in aged air due to faster photochemical removal. However, the weighting of
13 contributions from different air masses differs between precursor isotope ratio derived PCA and
14 product isotope ratio derived PCA. Details will be discussed in Section 3.5.

15 All precursor ~~carbon~~ isotope ratio derived PCA differ significantly from the PCA
16 determined from nitrophenol carbon isotope ratios. Toluene and xylene precursor derived PCA are
17 lower than ~~reactant-second generation product~~ derived PCA by approximately 4×10^{10} s molecules
18 cm^{-3} and 3×10^{10} s molecules cm^{-3} , respectively. The average PCA derived from 4-nitrophenol
19 carbon isotope ratios is approximately 50 % higher than the average PCA calculated from benzene
20 carbon isotope ratios.

21 Uncertainty of the calculated average PCA can result from uncertainty of parameters used
22 to calculate PCA from carbon isotope ratios. The 10 percentiles and the 90 percentiles of ~~the~~

1 ~~nitrophenol-second generation product carbon~~ isotope ratios range from approximately -36 ‰ to -
2 31 ‰. For this range errors of rate constants and kinetic isotope effects for reactions of the
3 precursors or the ~~nitrophenols-second generation product~~ only have a small impact on the
4 dependence between PCA and carbon isotope ratio (Fig. S2 and S3) and therefore cannot explain
5 the difference in average PCA. However, Changes uncertainties in the carbon isotope ratios of
6 VOC emissions as well as the isotope fractionation for reactions or branching of the intermediates
7 in the reaction sequence resulting in nitrophenol formation can have a significant impact on PCA
8 calculated from nitrophenol carbon isotope ratios (Table ~~S6~~S5, S6).

9 However, PCA derived from precursor's carbon isotope ratio measurements also strongly
10 depend on the carbon isotope ratios of the emissions (Kornilova et al., 2016). For a decrease in
11 emission isotope ratios of 1 ‰ the PCA derived from carbon isotope ratios of benzene, toluene
12 and m-xylene increase by 0.9×10^{11} s molecules cm^{-3} , 0.3×10^{11} s molecules cm^{-3} , and 0.09×10^{11} s
13 molecules cm^{-3} , respectively. Consequently, a decrease in the carbon isotope ratio of emission by
14 1 ‰ would reduce the difference between precursor and product derived PCA for benzene, toluene
15 and xylene by approximately 0.7×10^{11} s molecules cm^{-3} , 0.15×10^{11} s molecules cm^{-3} , and less than
16 0.01×10^{11} s molecules cm^{-3} , respectively. An approximately 3 ‰ decrease in the carbon isotope
17 ratio of toluene emissions would be able to explain the difference in PCA derived from toluene
18 carbon isotope ratios and methylnitrophenol carbon isotope ratios. Similarly, an increase in the
19 carbon isotope ratio of benzene emissions by 2.5 ‰ would eliminate the difference between
20 benzene and 4-nitrophenol derived PCA. However, a 2-3 ‰ error in the carbon isotope ratio of
21 emissions is substantially larger than the uncertainty derived from VOC emission studies (Rudolph
22 et al., 2002; Rudolph, 2007; Kornilova et al., 2016). Moreover, a carbon isotope ratio of benzene
23 emissions heavier by 2.5 ‰ than the value used in our calculations (Table 2) would not be

1 compatible with the lower end of ambient benzene carbon isotope ratios reported by Kornilova et
2 al. (2016). The discrepancies between the m,p-xylene and 2,6-dimethyl-4-nitrophenol derived
3 PCA cannot be explained by uncertainty of the carbon isotope ratios of xylene emissions.
4 However, it should be noted that the precursor based PCA is derived from ambient observations
5 of the combined isotope ratios of p-xylene and m-xylene, whereas only m-xylene is precursor of
6 2,6-dimethyl-4-nitrophenol.

7 An increase in the carbon isotope fractionation specific for the formation of nitrophenols
8 from the intermediate phenol of approximately 3 ‰ would result in very good agreement between
9 precursor and second generation product derived PCA for toluene and xylene. However, for the
10 conditions of the laboratory studies reported by Irei et al. (2015) a model with such an additional
11 isotope fractionation for the formation of nitrophenols from reaction of the intermediate would
12 predict carbon isotope ratios on average by 2.5 ‰ lighter than the measured values. However, for
13 the conditions of the laboratory studies reported by Irei et al. (2015) a model with such an
14 additional isotope fractionation for the formation of nitrophenols from reaction of the intermediate
15 would predict methyl nitrophenol isotope ratios for the 7 laboratory measurements reported by Irei
16 et al. (2015), which are on average by 2.5 ‰ lighter than the measured values. Based on the
17 reported average experimental uncertainty of less than 1 ‰ this difference is significant at a higher
18 than 99.9 % confidence level.

19 For the formation of 2,6-dimethyl-4-nitrophenol from m-xylene no laboratory results are
20 available, which would allow constraining carbon isotope fractionation for reactions of the

1 intermediate phenol. However, it is unlikely that carbon isotope fractionation for reactions of the
2 intermediate dimethyl phenol are substantially larger than for the cresol intermediates.

3 The formation of 4-nitrophenol from atmospheric oxidation of benzene proceeds via
4 phenol, which reacts with OH-radicals, in contrast to methyl substituted phenols, primarily by H-
5 abstraction from the phenol group. Consequently, a reaction channel specific carbon isotope
6 fractionation substantially different from that for reactions of ~~methyl-substituted~~methyl-substituted
7 phenols cannot be ruled out. However, a model scenario that would result in good agreement
8 between precursor and second generation product derived average PCA for benzene would also
9 predict that the lowest carbon isotope ratio for 4-nitrophenol ~~exceeds significantly higher than~~
10 approximately 30 % of the measured ambient carbon isotope ratios reported by Saccon et al.
11 (2015) ~~—~~ by more than the measurement uncertainty.

12 In addition to the formation of nitrophenols via OH-radical initiated oxidation, reaction of
13 the intermediate cresol with NO₃ also has to be considered a possible reaction pathway for the
14 formation of the methylnitrophenols (Carter et al., 1981). Here, it was proposed that at NO_x levels
15 greater than 20 ppb and ozone levels much larger than NO levels, the reaction with NO₃ would
16 dominate over the proposed reaction with OH-radicals. However, since [OH] and [NO₃] each
17 exhibit very pronounced diurnal cycles, with [OH] peaking during the day and [NO₃] peaking at
18 night due to its fast photolysis during daytime, reactions with NO₃ during the day can be ignored.
19 The proposed reaction pathway of the cresol + NO₃ reaction is through an addition reaction,
20 resulting in a similar estimated KIE as the addition of the OH group. Consequently, the carbon
21 isotope ratio of nitrophenols formed via this reaction pathway will not depend significantly on the
22 formation pathway. However, due to the possible nighttime processing of the phenolic
23 intermediate in the presence of NO₃ this may create a difference between the true value for $\int[\text{OH}]dt$

1 and the PCA derived from the carbon isotope ratio of the nitrophenol. To determine this possible
2 bias Scenario 3 was modified. At a value for $\int[\text{OH}]\text{dt}$ corresponding to the average carbon isotope
3 ratios reported by Saccon et al. (2015) the OH radical concentration was set to zero and replaced
4 by a mechanism representing reaction of the intermediate at 1 pmol mol^{-1} of NO_3 until the phenolic
5 intermediate was nearly completely depleted. The resulting average bias in $\int[\text{OH}]\text{dt}$ ~~is corresponds~~
6 ~~to less than 0.2 ‰ in carbon isotope ratio~~ for all of the methylnitrophenol isomers when compared
7 to the unmodified Scenario 3.

8 The reactions of cresols with OH-radicals is substantially faster than the formation of
9 cresols from reaction of toluene with OH-radicals. This does not allow the build-up of high
10 concentrations of cresols during the day. This limits the possible role of the NO_3 reaction pathway.
11 For the same reason it is unlikely that the NO_3 reaction pathway plays a substantial role for the
12 formation of 4-nitrophenol or 2,6-dimethyl-4-nitrophenol.

13 ~~The sensitivity estimates above are based on the range of nitrophenol carbon isotope ratios~~
14 ~~reported by Saccon et al. (2015). For isotope ratios outside of this range, errors in PCA caused by~~
15 ~~uncertainty of the parameters used for calculating $\int[\text{OH}]\text{dt}$ may differ. While there is an effectively~~
16 ~~linear dependence between PCA and carbon isotope ratio for a range of approximately 5 to 8 ‰~~
17 ~~for the mechanistic models (Fig. 3, Table 2), eventually the slope of the dependence of carbon~~
18 ~~isotope ratio on PCA begins to decrease substantially (Fig. 3). In this region, a change in carbon~~
19 ~~isotope ratio or one of the model parameters could result in a larger change in PCA than for low~~
20 ~~carbon isotope ratios. However, the region of decreasing sensitivity depends strongly on precursor~~
21 ~~reactivity. For Scenario 3 this occurs at approximately 5×10^{10} s molecules cm^{-3} in the case of 2,6-~~
22 ~~dimethyl 4 nitrophenol and 3×10^{11} s molecules cm^{-3} in the case of 4 nitrophenol.~~

1 Figure 4 shows the frequency distributions for PCA determined from the carbon isotope
2 ratios of 4-nitrophenol (Fig. 4a) and methylnitrophenols (Fig. 4b) using Scenario 3. For
3 comparison percentiles for PCA derived from carbon isotope ratios of benzene (Fig. 4a) and
4 toluene (Fig. 4b) reported by Kornilova et al. (2016) are also shown. Consistent with the difference
5 in average PCA (Table 3), PCA derived from 4-nitrophenol carbon isotope ratios are shifted
6 approximately 2×10^{11} s molecules cm^{-3} towards higher values than PCA derived from benzene
7 carbon isotope ratios, but the width of the two PCA distributions are very similar (Fig.4a). The
8 PCA independent uncertainty for 4-nitrophenol carbon isotope ratio derived PCA is only 7×10^{11}
9 s molecules cm^{-3} (Table S5), which cannot explain the difference in average PCA. The PCA
10 dependent relative uncertainty is 32 % (Table S5). Combined with the PCA independent
11 uncertainty this could just explain the difference in the average PCA. However, such a scenario
12 also predicts a more than 30 % narrower distribution for 4-nitrophenol derived PCA than the best
13 estimate. Such a distribution would be substantially narrower than the distribution of PCA derived
14 from benzene carbon isotope ratios.

15 ~~In contrast to this~~ The PCA distribution derived for methylnitrophenols is, compared to
16 the toluene derived distribution, not only shifted to lower values, but also much narrower (Fig. 4b).
17 This discrepancy cannot be explained by the uncertainty of PCA derived from methylnitrophenol
18 carbon isotope ratios. While uncertainty of the assumptions made to determine the dependence
19 between PCA and carbon isotope ratios of nitrophenols can to some extent explain the difference
20 in average PCA it cannot explain a substantial difference in the width of the distributions since
21 nearly all observed carbon isotope ratios are within or close to the linear range of dependencies
22 between nitrophenol carbon isotope ratio and PCA (Fig. 2, Table 3).

1 3.5. Average PCA and mixing of air masses

2

3 Based on measurement of carbon isotope ratios of several aromatic VOC Kornilova et al.
4 (2016) concluded that mixing ratios and average PCA of aromatic VOC in Toronto typically are
5 determined by mixing of air masses with VOC of different origin and different PCA. While
6 $\int[\text{OH}]dt$ determined from the carbon isotope ratios of aromatic VOC represent for all practical
7 purposes the correct concentration weighted average PCA for the studied VOC (Rudolph and
8 Czuba, 2000; Kornilova et al., 2016), the situation is different for PCA derived from carbon isotope
9 ratios of VOC reaction products such as nitrophenols. In case of atmospheric mixing of VOC and
10 VOC reaction products the PCA derived from product carbon isotope ratios can differ from
11 $\int[\text{OH}]dt$ calculated for VOC isotope ratios for several reasons.

12 For nitrophenols with different PCA the decrease in sensitivity of the PCA-carbon isotope
13 ratio dependence outside of the linear range (~~Fig. 3, Table 3~~) will reduce the apparent PCA derived
14 from nitrophenols compared to the VOC derived PCA. On the other hand, with increasing PCA
15 the VOC precursor concentrations will not only decrease due to atmospheric dilution, but also due
16 to chemical reactions, which reduces their weight for average PCA. In contrast to this nitrophenols
17 are formed as result of precursor reactions, which will counteract the effect of atmospheric dilution.
18 However, in contrast to light aromatic hydrocarbons the polar nitrophenols are ~~water soluble~~water-
19 soluble and ~~can be~~ found both in the particle and gas phase (Saccon et al., 2013). Consequently,
20 they will be removed not only by chemical reactions, but also by wet and dry deposition. Carbon
21 isotope fractionation resulting from physical removal processes is much smaller than isotope
22 fractionation during chemical reactions and therefore will have little direct impact on the carbon
23 isotope ratio of nitrophenols. ~~but~~ However, physical removal processes will reduce the

1 ~~concentration contribution to~~ nitrophenol concentrations ~~s from~~ aged air masses and therefore
2 reduce the weight of aged air in samples representing air masses with different PCA. Combined,
3 these effects ~~can have the potential to~~ create a complex situation with ~~sometimes~~ substantial
4 differences in PCA derived from precursor carbon isotope ratios compared to nitrophenol derived
5 PCA.

6 Consequently, mixing of aged air with fresh emissions of light aromatic VOC can result in
7 discrepancies between precursor carbon isotope ratio derived PCA and benzene carbon isotope
8 ratio derived PCA. Lower values for precursor derived PCA can be expected if fresh emissions
9 are mixed with aged air masses under conditions which allow accumulation of reaction products.
10 ~~Nevertheless, a simple general consequence of the mixing of aged air with fresh emissions of light~~
11 ~~aromatic VOC is the absence of very low values for 4 nitrophenol derived PCA whereas in the~~
12 ~~case of dominant fresh emissions values close to zero can be expected for precursor derived PCA~~
13 ~~(Fig. S4aS7a). This is the consequence of the delay in formation of nitrophenols following~~
14 ~~precursor emissions although details on how PCA are impacted by the influence of aged air masses~~
15 ~~depends on details of mixing as well as the possible removal of nitrophenols by deposition (Fig.~~
16 ~~S4b). The accumulation of polar low volatility reaction products is not only limited by gas phase~~
17 ~~reactions, but also by deposition (An example . The 4 nitrophenol depositional loss rates used for~~
18 ~~the calculations are relative to the removal of 4 nitrophenol by reaction with the OH radical,~~
19 ~~although it must be considered that loss by deposition will be independent of the OH radical~~
20 ~~concentration. However, the actual~~The principle of the impact of deposition on the PCA will only
21 ~~depend on the relative contribution of deposition to the overall 4 nitrophenol loss since this will~~
22 ~~influence the weight an air mass with a given PCA will have on the average PCA. For an average~~
23 ~~OH radical concentration of 10^6 molecules cm^{-3} a deposition loss equal to the photochemical 4-~~

~~1 nitrophenol loss rate corresponds to a deposition lifetime of approximately 6 weeks and a total
2 lifetime of 3 weeks. For depositional loss 10 times faster than chemical removal the 4-nitrophenol
3 lifetime is approximately 4 days is explained in Part 7 of the Supplement.~~

4 While conceptually mixing of two air masses with different PCA explains the difference
5 in the frequency of observations of ~~very low PCA~~ between precursor and product derived PCA, it
6 can be expected that for urban sites a range of PCA will be a more realistic situation. For the
7 average precursor derived PCA the distribution for individual PCA observations is known
8 (Kornilova et al., 2016). ~~For comparison of the average PCA w~~We use these distributions to
9 calculate the PCA distribution for 4-nitrophenol and understand the source of differences in the
10 average PCA.

11 Figure 5 shows the resulting PCA distributions calculated for different depositional loss
12 rates of 4-nitrophenol. With increasing loss by deposition, the centers of the distributions shift
13 towards lower PCA and become narrower, which is the consequence of decreasing contributions
14 of air-masses with high PCA. The center of the distribution resulting from a depositional loss rate
15 five times faster than loss due to reaction with the OH-radical has its maximum at a value for
16 $[OH]dt$ of approximately 5×10^{11} s molecules cm^{-3} , which is close to the average of PCA derived
17 from observed 4-nitrophenol carbon isotope ratios (Table 3).

18 A comparison of calculated distributions with the carbon isotope ratio derived PCA
19 distributions shows that not only the averages but also the widths of the distributions agree for
20 depositional loss rates of 4-nitrophenol between three and seven times faster than reaction with the
21 OH-radical (Fig. 6) within the statistical errors of the observations. Based on an average OH-
22 radical concentration of 10^6 radicals cm^{-3} the 4-nitrophenol loss by deposition corresponds to a life

1 time in the range of 6 days to 2 weeks. This is at the lower end of the atmospheric residence time
2 of PM. However, only a small fraction of atmospheric 4-nitrophenol is found in the particle phase
3 (Saccon et al., 2013), which explains that the atmospheric residence time of 4-nitrophenol exceeds
4 the average residence time of particulate matter in the lower troposphere. Isotopic evidence does
5 not allow differentiation between different processes unless the isotope fractionation resulting
6 from these processes differ. Consequently the total atmospheric with no or very small isotope
7 fractionation effects. To our knowledge there are no published values for wet or dry deposition
8 rates of 4-nitrophenol. Consequently, we cannot identify the contribution of specific types of
9 physical deposition processes. Based on current knowledge chemical reactions in the condensed
10 phase are too slow to contribute to atmospheric loss of 4-nitrophenol (see detailed estimate in Part
11 1 of the Supplement). - but the relatively low deposition rates are consistent with the observation
12 that only a small fraction of atmospheric 4 nitrophenol is found in the particle phase (Saccon et
13 al., 2013).

14 The contribution of an air mass with a given PCA derived from 4-nitrophenol carbon
15 isotope ratios depends on the deposition rate relative to the rate of reaction of 4-nitrophenol and
16 the benzene precursor with the OH-radical (Part 7, Supplement). However, there is no direct
17 connection between deposition rates and the reaction rate with OH-radicals and therefore for
18 individual observations the ratio of depositional loss rate over the impact of OH-radical chemistry
19 can vary substantially. For example, during rain events it can be expected that deposition will be
20 faster than on average whereas removal as well as formation of 4-nitrophenol due to reaction with
21 OH-radicals will be slower.

22 Indeed, rain has a substantial impact on the atmospheric concentrations of nitrophenols in
23 the particle phase as well as in the gas phase. Substantial precipitation during sampling or on the

1 day before sampling, reduces the nitrophenol concentrations by a factor between 3 and 6 (Fig. 7a).
2 In contrast, precipitation has no significant impact on PCA (Fig. 7b). Changes in PCA are within
3 the uncertainty of the averages for different precipitation conditions and, except for 4-methyl-2-
4 nitrophenol below 25%. ~~Precipitation during or immediately before sampling reduces~~
5 ~~contributions from air masses with different PCA independent of the PCA of the air masses. This~~
6 ~~reduces the the atmospheric concentrations, but does not significantly impact the average PCA.~~
7 ~~This is consistent with the assumption that deposition is an important loss process for atmospheric~~
8 ~~nitrophenols, and that deposition does not result in significant carbon isotope fractionation of~~
9 ~~nitrophenols.~~

10 For the precursor of methylnitrophenols, toluene, the PCA distribution is very different
11 from the distribution observed for benzene, the precursor of 4-nitrophenol (Kornilova et al., 2016).
12 The average PCA for toluene is approximately only one third of the benzene PCA and the
13 distribution peaks at PCA close to zero, indicating a strong influence from very recent toluene
14 emissions. The different behavior of benzene and toluene ~~has been~~ explained by the difference
15 in reactivity and the different geographical distribution of emission sources (Kornilova et al.,
16 2016). There are substantial sources of toluene within the area of Metropolitan Toronto, whereas
17 most major sources of benzene are located in the surrounding regions.

18 The low average PCA derived from methylnitrophenol carbon isotope ratios is consistent
19 with a dominant role of local emissions of toluene and demonstrates that air masses containing
20 methylnitrophenols with high PCA are only of limited importance in determining the
21 methylnitrophenol derived PCA. This is supported by the dependence of methylnitrophenol
22 concentrations, carbon isotope ratios and PCA on wind speed shown in Fig. 8 and 9.

1 Figure 8 indicates that when the maximum wind speed over the sampling time-period is
2 lowest, concentrations for 2-methyl-4-nitrophenol are highest and the corresponding carbon
3 isotope ratios are lowest, indicating that methylnitrophenols may be dominantly produced from
4 local emissions with limited mixing. This is consistent with the observed PCA (Fig. 9), which is
5 lowest when wind speed is lowest and increases with increasing wind speed. This can be explained
6 by a decrease of the impact of local emissions resulting in a larger relative contribution of aged 2-
7 methyl-4-nitrophenol originating from further away. A similar trend is observed for 3-methyl-4-
8 nitrophenol. 4-methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol were not considered due to
9 the small number of samples. 4-nitrophenol did not show any systematic trend. This is consistent,
10 with the, compared to toluene, lower reactivity of benzene, the 4-nitrophenol precursor and the
11 lower local emission rates for benzene (Kornilova et al., 2016). Both factors will greatly diminish
12 the role of local emission and local photochemistry on the average PCA derived from 4-
13 nitrophenol carbon isotope ratios.

14 **4 Summary and Conclusions**

15 Similar to primary emissions of VOC for secondary pollutants PCAs derived from carbon
16 isotope ratios decreases with increasing reactivity of the precursor. However, for the nitrophenols
17 studied here the reactivity of the secondary pollutant is highly correlated to the reactivity of the
18 primary pollutant. Consequently, the available experimental evidence does not allow distinction
19 between the impacts of reactivity of primary or secondary pollutant. –This allows probing
20 atmospheric processing of pollutants at different timescales and consequently differentiating
21 between impact from local emission and long-range transport. In principle carbon isotope ratios of
22 secondary organic pollutants provide better insight into the formation of secondary products than
23 carbon isotope ratios of precursors. However, currently the use of carbon isotope ratios of

1 secondary organic pollutants is limited by uncertainties and gaps in understanding of the formation
2 mechanism and the carbon isotope fractionation during the reaction sequence.

3 ~~Using available p~~Available published ambient observations of precursor and ~~reactant second~~
4 ~~generation products carbon~~ isotope ratios ~~as well as results of a published laboratory study of~~
5 ~~isotope ratios of the photochemical oxidation products of toluene provide constraints for the~~
6 ~~parameters and their uncertainty in a mechanistic model describing the dependence between~~
7 ~~carbon isotope ratio and PCA of second generation products formed by photo oxidation of light~~
8 ~~aromatic VOC. Predictions by this mechanistic model are consistent with results of laboratory~~
9 ~~experiments studying the formation of methylnitrophenols from photo oxidation of toluene. it was~~
10 ~~possible to identify the most plausible scenario for a mechanistic model describing the dependence~~
11 ~~between carbon isotope ratios of atmospheric nitrophenols, and atmospheric processing of their~~
12 ~~precursors, light aromatic VOC.~~

13 Mixing of air masses with nitrophenols of different values for $\int[\text{OH}]dt$ plays an important
14 role in determining their carbon isotope ratios and needs to be considered in the interpretation of
15 carbon isotope ratios of secondary organic pollutants and the relation between concentrations and
16 carbon isotope ratios. ~~Loss processes such as physical processes based on diffusion, solubility or~~
17 ~~chemical reactions such as secondary isotope effects that cause only very small isotope~~
18 ~~fractionation can still have a strong indirect impact on the carbon isotope ratio of nitrophenols if~~
19 ~~they play a major role in determining their atmospheric residence time. Although deposition will~~
20 ~~not have a substantial direct impact on the carbon isotope ratios of nitrophenols, deposition of~~
21 ~~nitrophenols plays a major role in determining the atmospheric residence time of nitrophenols in~~
22 ~~the atmosphere.~~ Consequently, the dependence between atmospheric residence time and carbon
23 isotope ratios of nitrophenols results in a strong dependence between average nitrophenol PCA

1 and deposition rate. The dependence of deposition rate on factors only weakly related to
2 photochemical reactivity of the atmosphere can explain the absence of a significant dependence
3 between the concentration of nitrophenols and their carbon isotope ratios. Similarly, dispersion in
4 the atmosphere has an indirect, but visible impact not only on the concentration of nitrophenols,
5 but also on their carbon isotope ratios. ~~It should be noted that t~~These results are based on
6 observations in a major urban area with substantial local and regional nitrophenol precursor
7 emissions. Due to the increasing uncertainty of the predictions of the mechanistic model with
8 increasing PCA and the non-linearity of the dependence between nitrophenol carbon isotope ratios
9 and PCA any extrapolation of these results are not necessarily correct forto regions without
10 substantial emission sources for the light aromatic compounds. ~~—~~ may be highly uncertain.

11

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1 **Tables**

2 **Table 1.** Parameters, including the rate constant of the precursor with the OH radical (k_{OH}), KIE
 3 and the **carbon** isotope ratio of emissions ($\delta^{13}C_0$) used for the determination of the PCA by Eq. (5).
 4 The uncertainty of the parameter is given in parenthesis.

	Precursor		Product	Product Abbreviation
Benzene	k_{OH}^a ($cm^3 \text{ molec}^{-1} s^{-1}$)	1.39×10^{-12}	4-nitrophenol	4-NP
	ϵ^b (‰)	7.83 (0.42)		
	$\delta^{13}C_0^c$ (‰)	-28.0 (0.2)		
Toluene	k_{OH}^a ($cm^3 \text{ molec}^{-1} s^{-1}$)	5.63×10^{-12}	4-methyl-2-nitrophenol	4-me-2-NP
	ϵ^b (‰)	5.95 (0.28)	3-methyl-4-nitrophenol	3-me-4-NP
	$\delta^{13}C_0^c$ (‰)	-27.6 (0.5)	2-methyl-4-nitrophenol	2-me-4-NP
m-Xylene	k_{OH}^a ($cm^3 \text{ molec}^{-1} s^{-1}$)	2.31×10^{-11}	2,6-dimethyl-4-nitrophenol	2,6-dime-4-NP
	ϵ^b (‰)	4.83 (0.05)		
	$\delta^{13}C_0^c$ (‰)	-27.4 (0.4)		

5 ^a Calvert et al., 2002, uncertainty not included since the uncertainty resulting from error in the rate constants
 6 is small compared to uncertainties derived from error in the **carbon** isotope ratio and KIE. ^b Anderson et al.
 7 (2004). ^c Rudolph et al. (2002); for m-xylene the value reported for p+m-xylene is given.
 8

Table 2. Parameters used to determine the PCA for individual products. Units of k (rate constant) are in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. Since 80 % of the phenols are in the gas phase (Saccon et al., 2013), the rate constant for the product loss was adjusted to 80 % of the gas phase rate constant. If available, the uncertainty of the parameter is given in parenthesis.

Precursor			Intermediate			Product (Gas + PM)		
Benzene	k^a	1.39×10^{-12}	Phenol	k^a	2.70×10^{-11}	4-NP	k^e	3.40×10^{-13}
	ϵ_{OH}^b (‰)	7.83 (0.42)		ϵ_{OH}^d (‰)	0		ϵ_{OH}^f (‰)	5.36
	$\delta^{13}\text{C}_0^c$ (‰)	-28.0 (0.2)						
Toluene	k^a	5.63×10^{-12}	4-me-phenol	k^a	5.0×10^{-11}	4-me-2-NP	k^h	2.87×10^{-12}
	ϵ_{OH}^b (‰)	5.95 (0.28)		ϵ_{OH}^g (‰)	5.47		ϵ_{OH}^i (‰)	5.95
	$\delta^{13}\text{C}_0^c$ (‰)	-27.6 (0.5)						
Toluene	k^a	5.63×10^{-12}	3-me-phenol	k^a	6.8×10^{-11}	3-me-4-NP	k^j	2.92×10^{-12}
	ϵ_{OH}^b (‰)	5.95 (0.28)		ϵ_{OH}^g (‰)	5.47		ϵ_{OH}^i (‰)	5.95
	$\delta^{13}\text{C}_0^c$ (‰)	-27.6 (0.5)						
Toluene	k^a	5.63×10^{-12}	2-me-phenol	k^a	4.1×10^{-11}	2-me-4-NP	k^k	2.87×10^{-12}
	ϵ_{OH}^b (‰)	5.95 (0.28)		ϵ_{OH}^g (‰)	5.47		ϵ_{OH}^i (‰)	5.95
	$\delta^{13}\text{C}_0^c$ (‰)	-27.6 (0.5)						
m-xylene	k^a	2.31×10^{-11}	2,6-dime-phenol	k^l	6.59×10^{-11}	2,6-dime-4-NP	k^m	0
	ϵ_{OH}^b (‰)	4.83 (0.05)		ϵ_{OH}^g (‰)	4.83		ϵ_{OH}^m (‰)	0
	$\delta^{13}\text{C}_0^c$ (‰)	-27.4 (0.4)						

^a Reaction rate constant taken from Calvert et al., 2002. ^b Kinetic isotope effects taken from Anderson et al., 2004. ^c Carbon isotope ratio of emissions taken from Rudolph et al. (2002) and Kornilova et al. (2016); for m-xylene the value reported for p+m-xylene is given. ^d Reaction occurs via OH abstraction (Atkinson et al., 1992) and the secondary carbon isotope effect is assumed to be negligible. ^e Rate constant from Grosjean (1991). ^f Estimated based on loss reaction proceeding mostly by addition to the aromatic ring (Grosjean, 1991) and the carbon kinetic isotope effects reported by Anderson et al. (2004). ^g 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). Estimated on the assumption that reaction proceeds through primarily through addition pathway (Atkinson et al., 1980) and the kinetic isotope effect for reactions of aromatic VOC reported by Anderson et al. (2004). ^h Rate constant from Bejan et al. (2007). ⁱ Estimate based on the carbon kinetic isotope effects for reactions of aromatic VOC reported by Anderson et al. (2004). ^j Rate constant assumed to be the average of the rate constants for 3-me-2-NP ($3.69 \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) and 4-me-2-NP reported by Bejan et al. (2007). ^k Rate constant estimated to be identical to the rate constant reported for 4-me-2-NP by Bejan et al. (2007). ^l Reaction rate constant from Atkinson and Aschmann (1990). ^m Assumed to have no loss reaction that results in carbon isotope fractionation, see text.

Table 3. Linear approximation for dependence of carbon isotope ratios and PCA for nitrophenols formed by the photochemical oxidation of aromatic VOC.

	R ²	Slope ^a (10 ⁻¹² ‰ cm ³ s ⁻¹ molecules ⁻¹)	Intercept ^a (‰)	Limit δ ¹³ C ^b (‰)	Initial δ ¹³ C ^c (‰)
4-NP					
Scenario 2	0.993	4.28 (0.001)	-35.1 (0.002)	-28.1	-35.5
Scenario 3	0.967	14.4 (0.04)	-37.9 (0.005)	-34.8	-38.4
4-me-2-NP					
Scenario 2	0.985	64.7 (0.1)	-38.1 (0.004)	-32.5	-38.6
Scenario 3	0.985	64.7 (0.1)	-35.7 (0.005)	-30.1	-36.2
3-me-4-NP					
Scenario 2	0.982	80.7 (0.1)	-38.1 (0.005)	-33.1	-38.6
Scenario 3	0.982	80.9 (1.0)	-35.7 (0.006)	-30.7	-36.2
2-me-4-NP					
Scenario 2	0.988	56.4 (0.1)	-38.1 (0.003)	-32.0	-38.6
Scenario 3	0.988	56.6 (0.1)	-35.7 (0.004)	-29.6	-36.2
2,6-dime-4-NP					
Scenario 2	0.985	89.2 (0.1)	-36.2 (0.004)	-30.3	-37.4
Scenario 3	0.985	89.4 (0.1)	-34.5 (0.07)	-28.5	-35.0

^aFrom linear regression for a range with <0.5 % deviation from exact calculation; value in parenthesis is statistical error of linear regression. ^bUpper end of linear range where exact calculations deviate more than 0.5 % from the linear approximation. ^cFrom exact calculations

Table 3. Averages and uncertainty of the mean PCA for nitrophenols in both PM and in the gas phase and PM calculated for Scenario 3. Also shown are the average carbon isotope ratios. The number of data points used is shown in brackets. For comparison PCA calculated from the carbon isotope ratios of the precursor VOC reported by Kornilova et al. (2016) for Toronto are included.

Precursor	Average PCA ^a (10 ¹¹ s molec cm ⁻³)	Product	Average δ ¹³ C (‰)	Average PCA (10 ¹¹ s molec cm ⁻³)
Benzene	3.1 ± 0.5 (43)	4-NP	-33.5 ± 0.3	4.7 ± 0.3 (58)
Toluene	0.85 ± 0.11 (73)	Methyl- nitrophenols	-33.1 ± 0.1	0.42 ± 0.02 (120)
p,m- Xylene	0.34 ± 0.06 (56)	2,6-dime-4-NP	-33.4 ± 0.5	0.11 ± 0.04 (19)

^a Average carbon isotope ratio and PCA determined by Kornilova (2012) and Kornilova et al., (2016)

Table 5. Change of average PCA derived from carbon isotope ratios of nitrophenols resulting from changes in carbon isotope ratios of emissions and isotope fractionation for reactions of intermediates. The calculations were based on in Scenario 3.

Change	4-NP	4-me-2-NP	3-me-4-NP	2-me-4-NP	2,6-dime-4-NP
Δ PCA (10^{11} -s molecules cm^{-3}) for decrease in source signature ($\delta^{13}\text{C}_0$) of 1‰	1.6	0.14	0.14	0.18	0.09
Resulting relative change (%)	34	35	28	36	45
Δ PCA (10^{11} -s molecules cm^{-3}) for increase in fractionation for reaction of intermediates by 1‰	0.13	0.16	0.15	0.18	0.08
Resulting relative change (%)	3	25	36	32	52

Figure Captions

Figure 1. Proposed formation mechanism of 2-methyl-4-nitrophenol from toluene oxidation (adapted from Forstner et al., 1997).

Figure 2. Dependence between carbon isotope ratio and PCA ($\int[\text{OH}]dt$) for several nitrophenols calculated for different scenarios using a mechanistic model and mass balance. Also shown are the median, 10 and 90 percentiles as well as the lowest and highest carbon isotope ratios measured by Saccon et al. (2015) in an urban area. The triangles and squares represent the carbon isotope ratios of 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, respectively, reported by Irei et al. (2015) for laboratory studies.

Figure 3. Dependence between carbon isotope ratio and PCA ($\int[\text{OH}]dt$) for 2-methyl-4-nitrophenol, its precursor (toluene) and the phenolic intermediate calculated for Scenario 3. Also shown are the median, 10 and 90 percentiles as well as the lowest and highest carbon isotope ratios for toluene reported by Kornilova et al. (2016) for an urban area in Toronto (Canada).

Figure 4. Frequency distribution of PCA determined from the carbon isotope ratios of 4-nitrophenol (a) and methyl-nitrophenols (b) using Scenario 3. For comparison the median (dotted line), 75 and 25 percentiles (dashed line) and 10 and 90 percentiles (solid line) determined by Kornilova et al. (2016) from carbon isotope ratios of benzene (a) and toluene (b) are included.

Figure 5. PCA distributions calculated for different depositional loss rates of 4-nitrophenol. The depositional loss rates are given as multiples of the chemical loss rate of 4-nitrophenol due to reaction with OH-radicals. For comparison, the PCA distribution determined from the precursor carbon isotope ratio distribution (Kornilova et al., 2016) is also shown (solid line).

Figure 6. Comparison of PCA distributions calculated for different depositional loss rates of 4-nitrophenol. The depositional loss rates are given as multiples of the chemical loss rate of 4-nitrophenol due to reaction with OH-radicals. For comparison, the PCA distribution determined from the 4-nitrophenol carbon isotope ratios reported by Saccon et al. (2015) are also shown. The error bars represent the statistical uncertainty resulting from the limited number of observations.

Figure 7. Average nitrophenol concentrations (a) and PCA (b) determined from carbon isotope ratios reported by Saccon et al. (2015) using Scenario 3 for different precipitation conditions during and before sampling. No rain: In total less than 1 mm on the day of sampling and the day before; light rain: between 1 mm and 10 mm precipitation on the day of sampling or a total of >4 mm on the day of sampling and the day before; heavy rain: > 20 mm precipitation on the day of sampling or > 10 mm on the day of sampling and > 20 mm on the day before. Precipitation data were taken from Environment Canada: Historical Data, Toronto North York site.

Figure 8. Plot of concentrations (black diamonds, left axis) and carbon isotope ratios (open diamonds, right axis) of 2-methyl-4-nitrophenol as a function of the maximum wind speed during sampling (Environment Canada: Historical Weather Data, Toronto North York Site). Points were sorted in order of increasing wind speed and each point is an average of 10 filter samples; samples collected while there was precipitation were excluded. Error bars are the errors of the mean.

Figure 9. The PCA of 2-methyl-4-nitrophenol as a function of the maximum wind speed during sampling (Environment Canada: Historical Data, Toronto North York site). Points were sorted in

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order of increasing wind speed and each point is an average of 10 filter samples; samples collected while there was precipitation were excluded. Error bars are the errors of the mean.

Figures

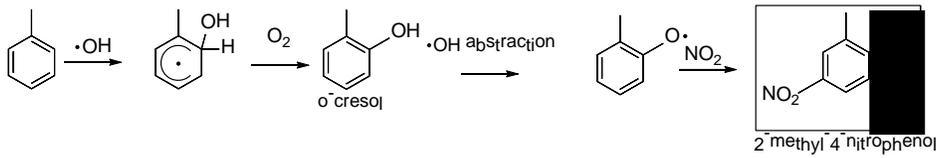
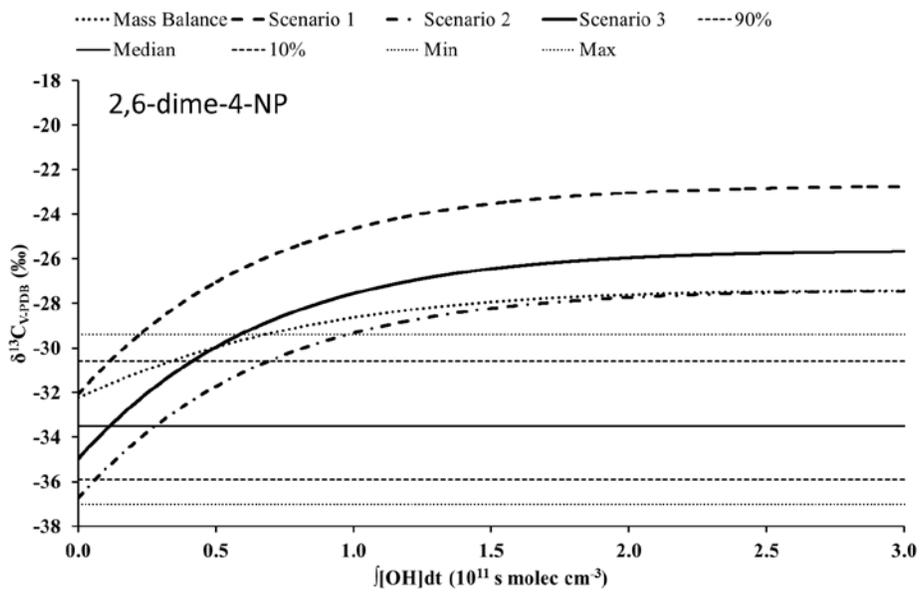


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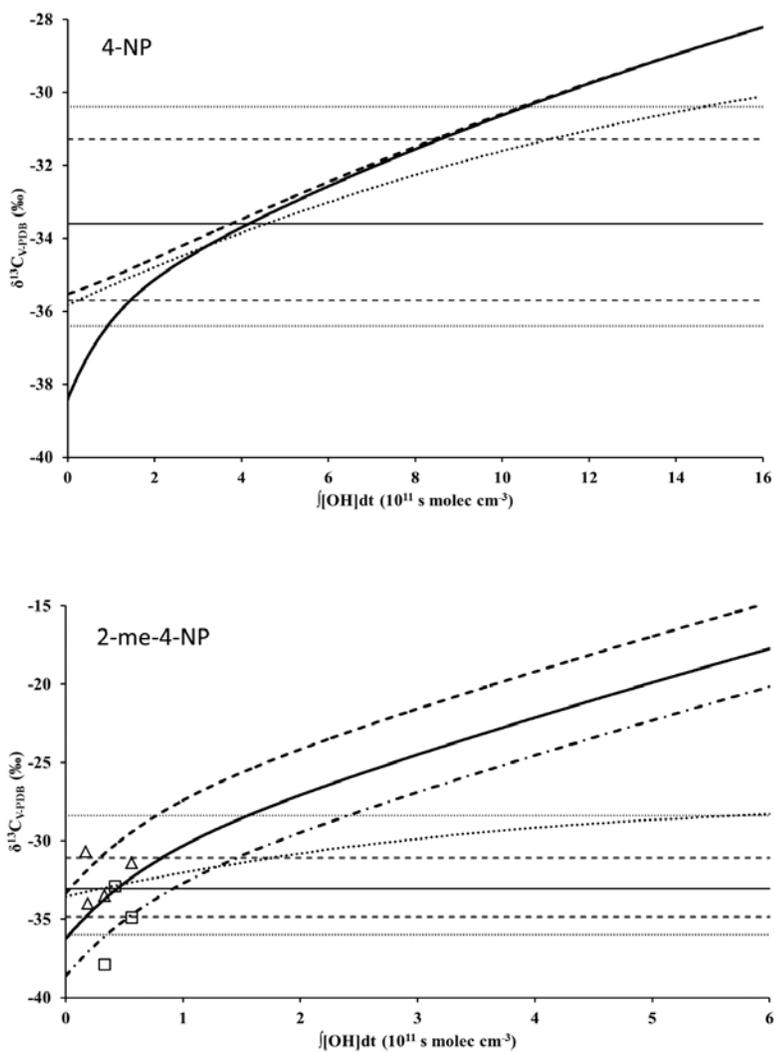


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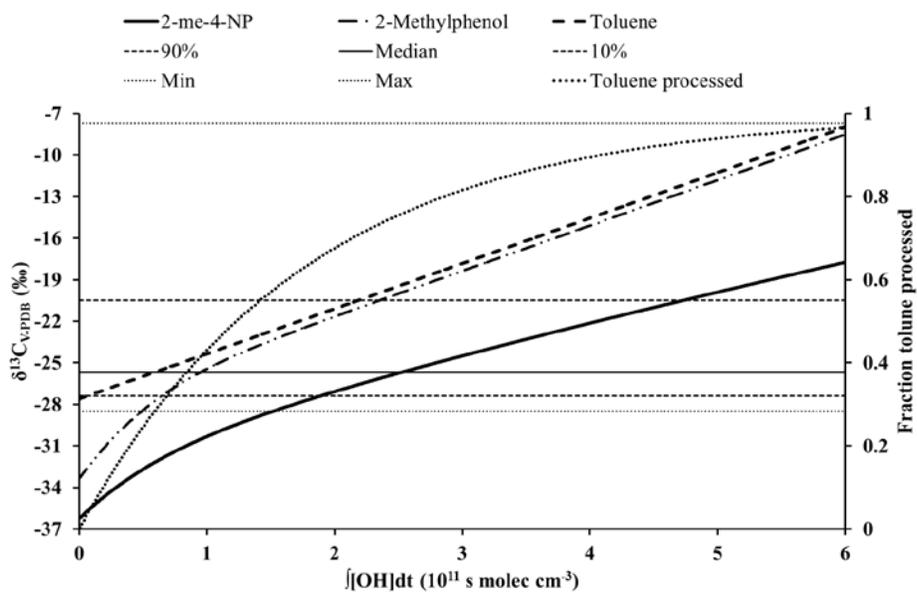


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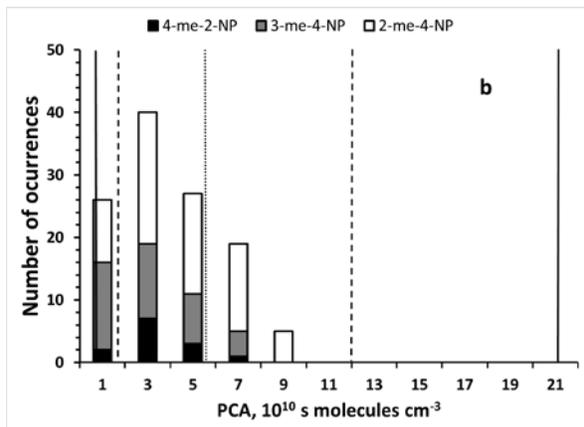
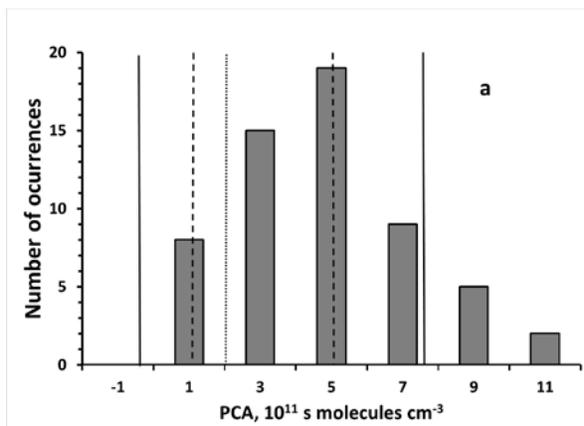


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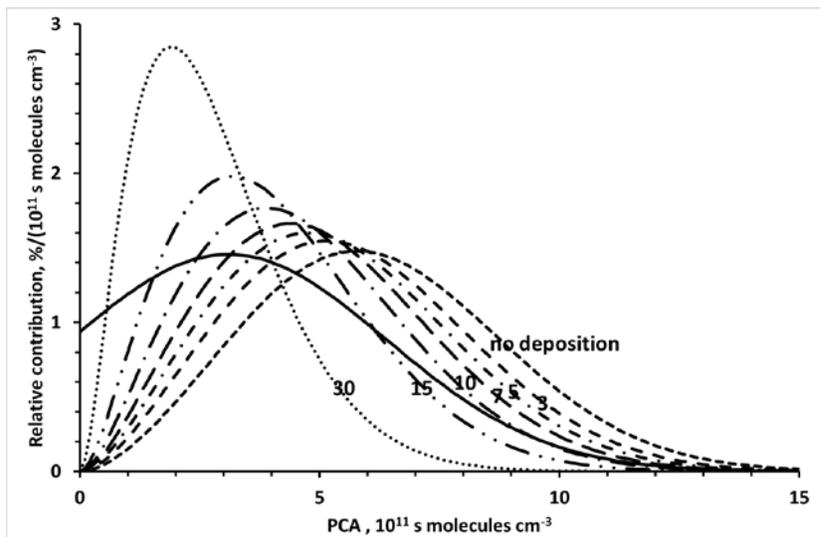


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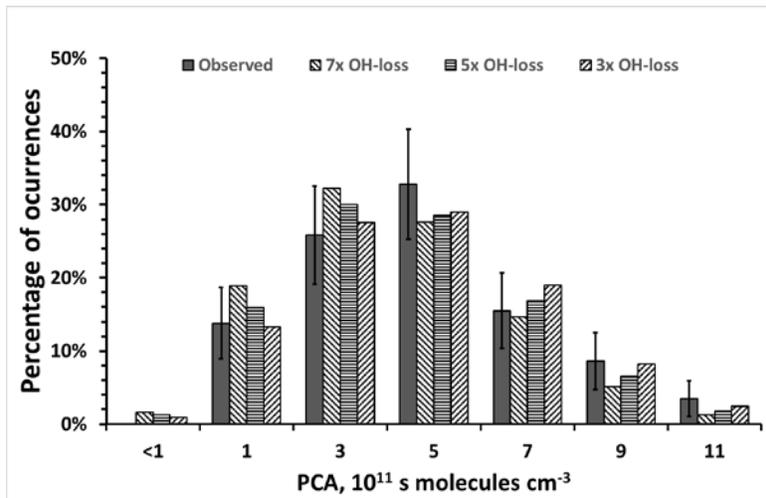


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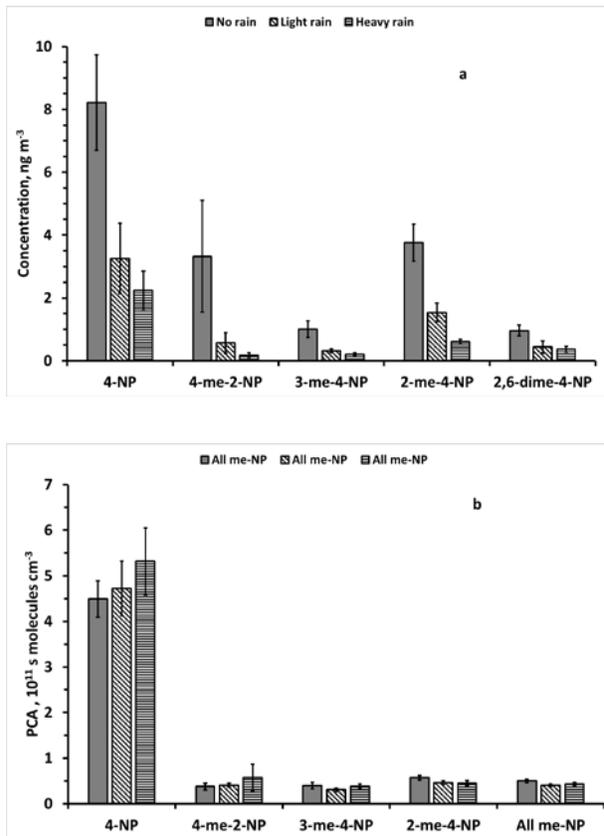


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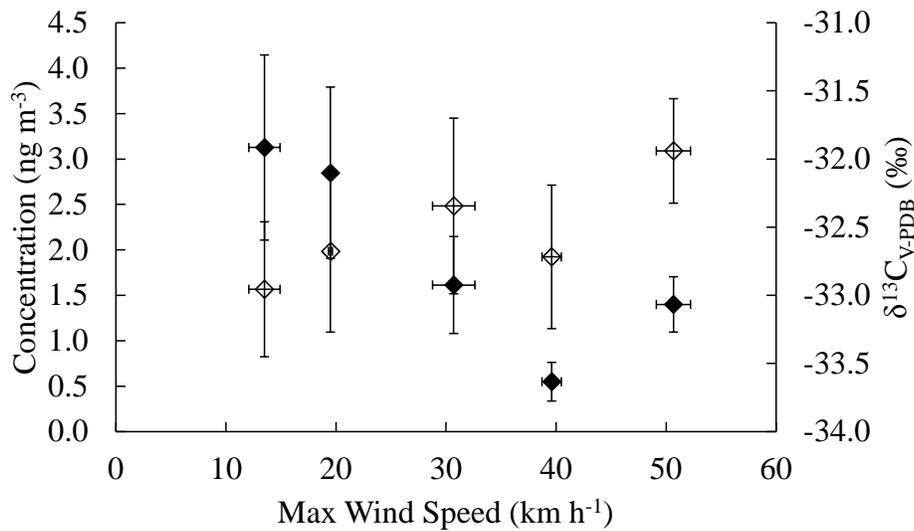


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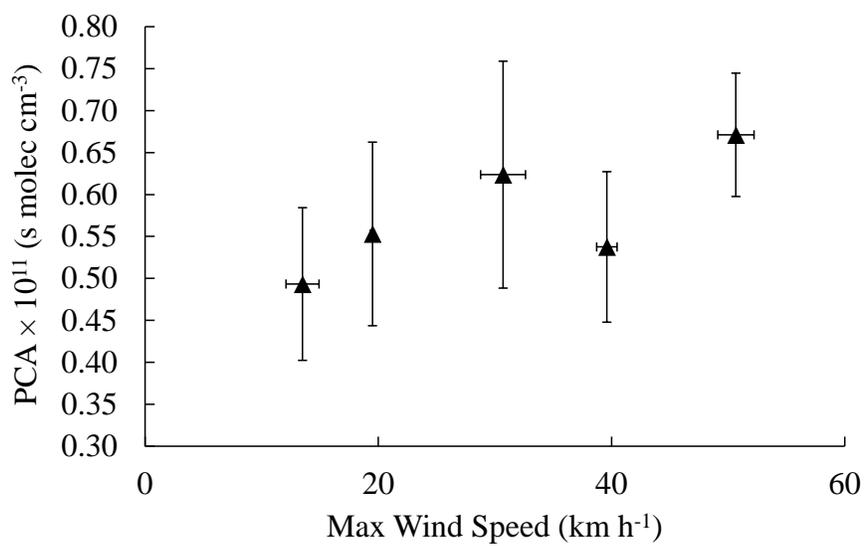


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