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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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Reviewer apologises for the delay (partly caused by the struggle with reviewing this manuscript).

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, (2) adding a sufficient analysis of uncertainties, and (3) refraining from using largely oversimplified model approach / evaluation framework.

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).

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.

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?

– What is the point of using rate coefficients for 298K only (see the comment to P9L8)?

– 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?

– What are the grounds for comparing precursor and products from samples collected in different years/seasons?

Since the environmental data on observational conditions (e.g. temperature, back-trajectory analysis) are available, you should compare the samples arriving from the same catchment areas, on the days with similar temperatures, precipitation rate, etc. Model calculations should account for these parameters, too. Without such clustering of the data, no consistent evaluation of your results is possible!

I encourage the authors to address all the points raised (as opposed to the initial review where some of my comments were neglected) and wish good luck with improvements.

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).

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.”?

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 ε (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.

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.

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 $^{13}C/^{12}C$ ratio – and retrieving final δ-value from molecular ratios. You could use starting composition (or emission) of 0‰ for Cpre 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 Cpre initialised in the model, also using $^{13}C/^{12}C$ 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 ^{13}C-substituted isotopologue transfers one ^{13}C and six ^{12}C atoms to the products, which in turn define molecule concentrations used to calculate further reaction steps. If in Eqs. 6-9 you use Rst=1 for defining Cpre, then you react ^{13}C-isotopologues several times faster (whilst ^{12}k/^{13}k 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.

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.

P15L14-17: In what terms do you measure the consistency and imply that it full? The model uses toluene emission δ^{13}C typical for its major source; sink fractionation will expectedly enrich leftover "ambient" toluene in ^{13}C. Statistically speaking, the maximum δ^{13}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 δ^{13}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.

P18L17-P19L2: Causation does not imply correlation. 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.

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).

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 mass-dependent diffusion effects for larger molecules like toluene are small). Wet deposition includes aqueous/heterogeneous chemistry, where, e.g., equilibrium/solubility IEs may play role.

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.

Specific comments

P2L5: “... oxidation of aromatic VOCs **by OH radicals**”.

P2L10-11: “included knowledge of KIEs...” -> “takes into account the KIEs” (or reformulate)

P2L12: “these values” -> “model parameters” (or reformulate the sentence)

P2L15: Remove “normal” (or explicate why only the KIEs with ε>1 should be used?)

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”.

P3-8: The introduction and description of the methods in Sects. 1-3 are sloppy and are hard to follow, also due to poor usage of terminology (well-established in cited literature however). May references are doubled or vague, e.g. “precursor” and “reactant” on P11L10 may (or may not) refer to the same entity, use of “secondary” (e.g. on P3, P6, P8) is not clear to me. “Product” is used often without specifying “of what”, which flaws the line of argumentation for a process involving multiple conversion steps. These sections require to be improved, e.g. usage of “precursor VOC”, “product SOA”, clear relationship between the two is required, otherwise the Reader will be lost (I am dealing isotope kinetics and acquainted with works of Rudolph’s lab, however you got me lost in Sects. 1-3). I suggest adding a conceptual graphic (a flow-chart, e.g. a rework of Fig. 1 fused with Table 2) for all steps involving the interconversions of C from emission of VOCs to formation of POM, including typical δ^{13}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.

P3L14-16: **Stable carbon** isotope ratios; also P5 and further: you may like to state in

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the beginning of the manuscript that you are communicating on the stable isotope C ratios only.

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

P3L22-23: Isotope ratios cannot be depleted; species can be depleted in ^{13}C.

P4L11: Do you mean **singly substituted** ^{13}C-containing species?

P4L12-13: Please be precise about the reservoirs you imply (also further), i.e. leftover atmospheric burden becomes enriched.

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.

P6L8-10: Unclear, please reformulate or provide how “minimum contribution” is quantified.

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

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).

P9L11: It is not “presently proposed” however not “known” (cf. caption to Fig. 1, where it is correct).

P9L19: “... occurs in remaining 8% of the time/cases” (should comply with P9L18).

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)?

P10L17-18: Reformulate, e.g. “There are also some reactions for which no laboratory measurements of rate constants are available”.

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 ...”

P11L9: I suggest numbering (or recapping) the assumptions referred to here (in contrast to all assumptions mentioned heretofore).

P11L10: Are “reactant” and “precursor” (3 and 4 lines below) the references to the same entity?

P12L12: You imply isotope fraction**ation**?

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?

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).

P13L2: Which KIE is implied?

P14L14: Define the “mechanistic models” (or name the corresponding scenarios). You refer to only one model earlier (P13L21).

P14L19: Consider reformulation (“shape of dependence”?)

P15L6: Define “quasi steady state”. If you mean that production is equilibrated with loss, specify the interval.

P16L 1-7: This paragraph is not scientific. Which and how large are “some” uncertainties? What “reasonalble errors” are you referring to?

P19L19-22: You do show in this study (also in Table 5 referred) anything about the effect of branching of intermediates.

P21L17-19: Reformulate "lowest ... ratio is significantly higher than 30% of ..." or specify how you set significance levels.

P22L14-15: Bias in PCA is expressed in per mil (wrong units, not PCA?)

P23L 2: Which carbon isotope ratio is implied?

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.

P25L23: Do you mean "a range of derived PCA will be more realistic"?

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).

P28L21: "increasing reactivity" of what?

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.

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.

Technical comments

P2L17: effect**s** (not one unknown IE was tested?)

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

P4 Eqs.1&2: Using “x 1000‰” is redundant (you have indicated above that δ and ε are expressed in per mil). Avoid using “x” instead of correct multiplication sign (e.g. bullet).

P7L3: Remove “approximately”

P7L9: “... based on nitrophenols formation and removal in the atmosphere ...”

P10L22: Consider reformulation (use of “direct reaction to position” is vague and uncommon).

P16L11: Reformulate “ambient studies”.

P25L7: Reformulate (“dominant fresh emissions”)

P20L3 | P21L6,8 | P23L12,20 | P24L18 | P25L7,9,17 | P28L15,20: Add or correct the use of commas.

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.

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