

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 #3

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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

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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.

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:

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

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dependence of carbon isotope ratio on PCA begins to decrease substantially (Fig. 3).'
Also Table 2 should be Table 3 (?)

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.

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

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

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

Page9Lines17-19 and Page10Lines3-4: Reformulate. Instead of '% of the time' use 'probability for the reaction channel'

Page10Lines2-6: Reformulate, maybe split in more sentences.

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

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.'

Page11Lines17-18: It should be 'The rate constants k13 for different isotopologues can be calculated from rate constants and the KIE.'

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.

Page12Line13: This is no equation

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

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...'

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.

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.' ...?

Page23Line10: Replace 'Figure 7' by 'Figure 4'.

Page24Line23: Replace 'nitrophenols but physical' by 'nitrophenols. Physical '

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

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.'

Page35Table2: Reformulate footnote g. The expression makes no sense.

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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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