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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Stable carbon isotope ratios of toluene in the boundary layer and the lower free troposphere" *by* J. Wintel et al.

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The paper by Wintel et al. presents carbon isotope ratio measurements for toluene in the lower troposphere. The authors use these measurements, combined with measurements of the mixing ratio of benzene and toluene, to gain insight into atmospheric mixing and photochemical processing of these compounds. Specifically, they use their measurements to differentiate between regimes where changes in VOC mixing ratios are dominated by mixing or photochemical removal. The use of isotope ratio measurements to gain insight into processes determining atmospheric variability of VOC is highly topical and has been emerging as promising tool during the last decade. Since there are very few published studies on this subject, the paper is a significant contribution to this area of research and merits publication in ACP. Using a small set of observations the authors demonstrate that fundamental concepts describing the impact of photochemical processing and atmospheric mixing processes can be used in a case study. Overall the quality of the measurements is impressive, although the number of measurements is relatively small. The basic concepts applied are sound and the authors present interesting examples for interpretation of VOC isotope ratio measurements in the atmosphere. My only criticism is that the paper does not fully describe limitations and uncertainties arising from the combination of very challenging measurements, the complex interaction of mixing and processing of VOC in the atmosphere, and a very small data set. I appreciate the overall concise and condensed presentation style. However, in several instances that the paper would benefit from more detailed presentation of the results and discussion. 1) The experiment description contains quite a few details about the Zepter-2 campaign which are not connected to the scientific content and interpretation of this paper. They should be deleted. Instead, the authors should provide a map giving the flight tracks, including altitude and time of the measurements, as well as some basic meteorology such as wind direction and speed. 2) Sample volume used for enrichment and sample mass: The authors provide information on sampling rate for GC-IRMS sample enrichment as well as mixing ratios for standards (test or calibration mixtures). However there is little information on sample volume enriched or total mass in the samples for calibrations, tests or ambient sample measurement. On page 11367 it is stated that the response function "can be used to calculate the toluene and benzene mixing ratios in samples of any given volume" (line 15-16) and "the peak size does not affect the isotope ratios". This is too far reaching. Clearly, these statements can only be valid for a certain range of volumes or peak sizes, respectively. These ranges need to be explicitly identified and information should be provided to which extent the volumes and peak areas for ambient samples fall into the range for which the assumptions have been verified experimentally. This is especially important for GC-IRMS isotope ratio measurements. For small sample masses not only the uncertainty of measurement increases (as shown in Figure 7), but often there also is systematic bias in isotope ratios for very small signals. The latter has the potential of creating an artificial relation between atmospheric mixing ratio and isotope ratio. More information and discussion should be provided. It also should be noted that the way the calibration functions are given (in ppt nAs-1) is only valid for a given (constant) volume. In order to be applicable to different volumes the calibration factor needs to be given in “mixing ratio x volume/signal” units. 3) 11364/26-11365/3: Humidity management is discussed later on, in a method description the statement is out of place. 4) 11366/10: “..comparison with an accurately known…”. What kind of sample was used, how was the comparison done and what is the origin of this V-PDB isotope ratio reference material? 5) Influence of humidity: I do not have access to the Hembeck Thesis describing the dynamic dilution system and therefore I am not able to evaluate if the mixing ratios given are based on dry air or humidified air volumes. The Iannone et al. measurement technique gives volumes measured for dry air since the volume is determined after humidity removal. The magnitude of the humidity dependence of the signal is in the right range to be due comparison of dry and humidified air volumes. Although, due to the very small correction, this has effectively no consequence for the ambient measurements, this is an interesting aspect the authors may want to look into. In any case, it is very impressive that the measurements have sufficient precision to identify such small systematic changes. 6) Precision (3.4.3): This subchapter should be combined with 3.4.1. and 3.4.4. The basic information on reproducibility, calibration, linearity, bias and accuracy can easily be presented in one combined subchapter. A plot of isotope ratio versus signal (or sample mass) including reproducibility for the mass (or signal) range studied would give the reader the necessary information on reproducibility and possible bias (see comment 2). Figure 7 shows the standard deviation for a signal range between 1 nAs and 6nAs, significantly further towards the lower end of signals than Figure 5. I am aware that standard A and B may (depending on how they were prepared) have in isotope ratios. However, this should not prevent combining the results for dependence of measured isotope ratio and standard deviation on signal height (or mass or mixing ratio) in one graph, for example by using different symbols for the two standards. It is typical for GC-IRMS that reproducibility and bias get worse towards lower signal intensity. However, this usually cannot be explained by simple counting statistics alone. For a signal of 1nAs (m/z= 44) the counting error for m/z=45, which is the lower signal, will be equivalent to around 0.12‰.This is only a small fraction of the experimentally observed standard deviation for a signal of 1nAs. Baseline signal and baseline isotope ratio, baseline drift, peak tailing, peak separation and details of peak integration will contribute to uncertainty and I am not sure to which extent (14) can be used to estimate precision below the signal range covered by tests. The authors also need to provide an evaluation to which extent possible bias for small signals may no longer be negligible compared to uncertainties estimated from (14). Later on in the discussion the authors mention that they excluded several data points due to being outside of the calibration range. The useful range of calibration, bias and reproducibility should be presented clearly in the method description. It should also be clarified if the data excluded from interpretation in 5.2 were excluded from all presentation and analysis of the data. I am not sure to which extent repeat measurements of ambient samples have been conducted. They may not even be possible due to the available limited sample volume. Nevertheless, there should be some information on results of repeat analysis of ambient samples, although not necessarily for the ZEPTER-2 mission. 7) 11370/15: It would be useful for the reader if a sample chromatogram is given. 8) 11371/5-7: As long as the assumption of a uniform isotope ratio of sources holds, dynamic processes only in combination with processing will result in changes of isotope ratios. 9) 11371/19-25: If the assumption of mixing aged air with fresh emissions is correct, this should be seen for all data measured in the boundary layer. It would also be very useful for the reader if the vertical profile for all flights would be shown, maybe relative to the height of the boundary layer. 10) 11372/21-1373/5: This data treatment is not entirely consistent with the two end point mixing assumption in 5.1. If I understand correctly, the data in Figure 12 include the data from within the boundary layer. If there is significant processing within the boundary layer, the source isotope ratio may be biased towards lower values. This maybe the reason that the source isotope ratio determined is lower than reported values in literature. An underestimated isotope ratio of emissions would also be more consistent with the findings presented in Figure 9, which shows that essentially all observed isotope ratios are heavier than -27 ‰.11) 11374/3-8 and Figure 13: The units for PCA should be clarified, they should be the product of units for OH radical concentration and units for time, such as molecules/cm3*s. Which type of regression procedure was used? Since both x and y values have substantial errors, a regression only considering possible errors for y-values may be biased. The observation of a slope close to unity for above boundary layer samples is intriguing. The problem of uncertainty in emission ratios and source isotope ratios may to some extent be eliminated by using the average boundary layer mixing ratios and isotope ratios as reference for calculating PCAs for above boundary layer air. Conceptually this would be equivalent to considering the boundary layer as source for above boundary layer VOC. 12) Summary and outlook: The paper contains a number of very interesting applications of VOC isotope ratio measurements to gain insight into atmospheric reactions and mixing processes. I think that this chapter does not do justice to the interesting findings and discussions in the paper. The summary part of this chapter is also very similar in content to the abstract. Conclusions should be added. 13) 11375/6-7: While it is intriguing that the slope of PCAs derived from different approaches is unity above the PBL, the values of the PCAs are not similar at all. The offset in PCA is larger than the highest PCAs derived from isotope ratios.

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