

## ***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 presents for the first time vertical distributions of the isotopic composition of toluene in the boundary layer and the lower free troposphere. By combining isotope ratio measurements with mixing ratio data, the authors pick out a very promising tool to better identify and quantify sources of VOCs, as well as to gain insight in their physical and chemical processing in the atmosphere. Therefore the paper is suitable to be published in the journal. The paper contains yet some weak points which need to be corrected before publishing.

Specific comments

Section3:

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- The authors should consider reorganizing the subchapters in a sampling and a laboratory one. Subsection 3.4 refers only to the TD-GC-IRMS measurements, therefore it might be included in the laboratory subchapter.

- Page11362Line18- Page11363Line2: the authors should give in the ZEPTER2 campaign description only information relevant for the isotopic measurements and discussions. They should include on the other side data on humidity, wind and temperature (see recommendations for Section5.3).

- Page11364Lines26,27 and Page11365Lines1,2: remove the sentence 'Thorough characterization of the system showed that at this temperature water vapour can be removed sufficiently from the sample and most of the less volatile organic compounds pass through the trap without a significant loss' from the description of a measuring setup.

- Page11365Lines10,11: remove 'partial two dimensional gas chromatography'. Suggestion: 'The VOC are separated from each other and also from the ambient CO<sub>2</sub> by gas chromatography.'

- Page11365Line12: replace 'polar' by 'low polar'. As additional remarks: The DB-624 GC column with 6% Cyanopropyl-phenyl and 94% dimethylpolysiloxane is considered to be in the range of very low polar columns. It has a better selectivity for aromatics than the DB-5, but to increase the polarity, at least 17% Cyanopropyl-phenyl groups should be contained in the substrate. In that case, with some luck, the disturbing peak eluting with benzene (Page11370Line15) could have been better retained (in case it is a polar species) and separated from the compound of interest.

- Page11366Line19: consider revising 'These' with 'Two'

- Page11366Lines26,27: enumerate the five compounds which belong to standard B together with benzene and toluene, being used in the plots. Suggestion: 'Also a series of measurements of an eight-component working standard (hereafter referred to

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as “standard B”), containing ..., with known VOC mixing ratios was performed.’ The authors should moreover name these compounds in Figures 4 to 7, since in this form, comparison of the delta standard deviations in the peak area range around 6nAs presented in Figure 3 with those in Figure 7 is very confusing. Some details of standard preparation would be useful.

- Page11367Lines11to16: Information on the instrument linearity should be reformulated. Suggestion: ‘Within error ranges, the instrument was linear between ... and ... nA (corresponding to ... benzene and ... toluene)’. Preferably mass units should be used. Replace sentence ‘the derived parameters a ... can be used to calculate the toluene and benzene mixing ratios in samples of any given volume’ with ‘The majority of the measured samples fitted in the linearity range’.

- A better structure in describing systematic and statistical precision of data is needed (Subsubsections 3.4.1 to 3.4.4). For example, the authors start with linearity of IRMS and end with accuracy of the detection. In the middle, statistical treatment of data is discussed. Generally, the authors should consider concisely shortening this part (which has in this form the same length like the results and discussions together) and maybe renouncing to the sussubdivisions.

Instead, the discussions on the plentifulness of results should be more extensively exploited.

Page11371Lines5to7: Instead of using ‘and/or’ within ‘The distributions are strongly asymmetric, indicating that photochemical and/or dynamical processes took place in the air mass history’, better insert two sentences at the right place, describing which process is prevailing in the PBL and which in the free troposphere.

Page11371Lines19to22: consider reformulating ‘This may be due to fresh emissions from the ground, mixing into the boundary layer background air. If we assume this hypothesis to be true and neglect the influence of chemical processing, we can use the concept of two- endpoint-mixing to estimate the 13C source value of toluene (see

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Sect. 2)’ by starting with ‘the 13C source value of toluene can be estimated by making the assumption... Then we can use...’. Since the delta value is in the range of previous reports, the hypothesis made is correct.

Section5.2: The authors should consider further discussing the results presented in Figure 12. Firstly, are the 18 points consistent with the statements on Page11371Lines4,5 ‘21 in the free troposphere’ and on Page11372Lines15to19 ‘Four data points are excluded from the analysis... We excluded one more data point’? The authors don’t need to choose an initial concentration of 1ppb. They can calculate it. By assuming that in the PBL no chemical processing takes place (Section 5.1), one can reckon its ‘upper surface’ as the toluene emission source for the free troposphere, having a delta value of -28.2 per mil. The resulting concentration in that height (C0) would be then around 200ppt (see Equation 5), being at the lower end of the concentration range measured in the PBL, but consistent with Figure 10. Then, the statement in Page11372Line5 ‘constant with respect to toluene mixing ratios’ is not anymore true. There should be some dilution and still no chemistry.

Section5.3 would be the right place to discuss the temperature dependence of the kinetic isotope effect, which might be important since the sampled air was not underlying room temperatures. The trends of the data sets corresponding to PBL (fresh) and free troposphere (old) in Figure 13 are completely agreeing with the conclusions of Gensch et al. (JGR, 2011). Of course, the results on a single studied compound cannot be transferred to other species. Moreover, the magnitude of the discrepancy between  $\delta_{\text{toluene}}$  and  $\delta_{\text{toluene}}^{\text{vmr}}$  cannot be fully explained by this theory. Yet, the need of investigations on KIE temperature dependence to interpret the ambient measurements is now more than ever clear and therefore, it should be discussed at the latest here.

Other comments:

Figure 11: add the date in the caption: ‘... data of 25 October 2008’.

Figure 13: the units for photochemical age are molecules  $\text{m}^{-3} \text{s}$  (or corresponding

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non-SI units). Please revise.

Editorial revisions:

Page11360Line20 and Page11361Line15: revise 'provided that' with 'assuming that' or 'granted that'

Page11363Line21: use 'tubing' instead of 'hose'.

Page11364Line15: consider revising 'to transfer' with 'to focus and transfer'.

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