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

**J. Wintel et al.**

wintel@uni-wuppertal.de

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Reply to the interactive comment by I. Gensch

We want to thank I. Gensch for her efforts and her numerous valuable and helpful comments. According to her suggestions, we made the following changes:

"- 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."

We rearranged the subchapters as suggested.

"- Page11362Line18- Page11363Line2: the authors should give in the ZEPTER2 cam-

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paign 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)."

We changed the formulation and included the desired metadata.

Before: The ZEPTER-2 campaign took place in the Lake Constance region in southwest Germany, a rural site with small townships and no large industries, in autumn 2008. The main objective of the campaign was to study the photochemical transformation of VOC and NOx due to free radicals (OH, HO2), the production of ozone as well as the formation and aging of secondary aerosol in the lower troposphere, i.e. the planetary boundary layer and the free troposphere directly above. A Zeppelin NT airship served as the measurement platform. It consists of a helium-filled envelope with a volume of about 8400 m3 covering an internal lightweight, rigid structure. Most of the scientific instruments were installed inside the cabin in the gondola beneath. Four propellers (three of them mounted pivoted) allow a full maneuverability at low speed or even stagnation. Depending on the environmental conditions, the Zeppelin can reach a maximum height of about 3000 m and a maximum speed of about 115 km/h. The maximum scientific payload is about 1 t (ZLT Zeppelin Luftschifftechnik GmbH & Co KG). Due to these features the Zeppelin NT is an excellent platform for atmospheric measurements in the lower troposphere. The Zeppelin was equipped, in different configurations, with instruments for the measurement of CO, NOx, O3, HONO, CH2O, particles, VOC, OH, column densities and photolysis frequencies of several trace gases. The instruments were operated by Jülich Research Centre, University of Heidelberg and University of Wuppertal. In addition, meteorological parameters were measured. The airborne measurements were supported by groundbased measurements using a mobile laboratory (a modified van, equipped with instruments for the measurement of particles, NOx, CO, O3 and VOC), which gave information about particle and trace gas sources on the ground. A chemical "weather forecast" as well as backward trajectories were provided by the Rhenish Institute for Environmental Research (RIU) at the University of Cologne with the European Air Pollution Dispersion (EURAD) model (for more information about ZEPTER-2 and the Zeppelin NT also see Haeseler2009,Urban2010).

After: The ZEPTER-2 campaign took place in the Lake Constance region in south-west Germany, a rural site with small townships and no large industries, in autumn 2008. A Zeppelin NT airship served as the measurement platform. ZEBIS was installed inside the cabin in the gondola. Depending on the environmental conditions, the Zeppelin can reach a maximum height of about 3000 m and a maximum speed of about 115 km/h. The maximum scientific payload is about 1 t (ZLT Zeppelin Luftschifftechnik GmbH & Co KG). The Zeppelin was equipped with various instruments in different configurations, amongst others a vacuum ultraviolet resonance flourescence instrument for the measurement of CO (for a description of the instrument see e.g. Gerbig(1999),Holloway(2000)). In addition, meteorological parameters were measured (for more information about ZEPTER-2 and the Zeppelin NT also see Haeseler2009). The airborne measurements were supported by ground-based measurements using a mobile laboratory (a modified van), equipped, amongst other things, with a whole air sampler. These air samples were analysed offline using a GC-FID system to determine VOC mixing ratios at ground level (Urban2010). In total, 25 flights were carried out on 14 days between 17 October 2008 and 8 November 2008 at different times of day (including the night), taking off from Friedrichshafen (47°39'N , 9°28'E). The ZEBIS whole air sampler was operated on board during 11 flights between 25 October 2008 and 7 November 2008. The individual flights passed over several regions of different land use, the Lake Constance, two forests (Altdorf forest and Tettnang forest), grassland and the city of Ravensburg. In this paper we present data of samples gathered during five flights (see Table 1). The corresponding flight tracks are shown in Figure 1 and the flight altitude above ground level (AGL) is shown in Figure 2. Air temperature, relative humidity, wind direction and wind angle are given in Table 2, as far as available.

"- Page11364Lines26,27 and Page11365Lines1,2: remove the sentence ' Thorough characterization of the system showed that at this temperature water vapour can be

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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."

We deleted that sentence.

"- Page11365Lines10,11: remove 'partial two dimensional gas chromatography'. Suggestion: 'The VOC are separated from each other and also from the ambient CO2 by gas chromatography.'"

We changed that.

"- 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."

We changed that.

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

We would rather leave 'These' but replace "working standards" with "dilutions".

"- 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 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."

There seems to be a misunderstanding. Fig. 6 and 7 refer to measurements of standard A, the other figures refer to measurements of standard B. From the standard B measurements only benzene and toluene results were used. We added the names of the standards to the captions of Fig. 4-7 to clear up the picture a little bit and also enumerated the compounds in Fig. 6 and 7.

“- 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’.”

We reformulated the second and the third paragraph of subsection 3.4.1 and removed the benzene data from Figure3. We would rather keep the units we used, because to us they seem to be more appropriate for the discussion of atmospheric measurements.

Before: We found response curves of the type y(x) = ax (Pearson R > 0.999) for both compounds (see Fig. 2). The sample volume was 25Ln for all standard measurements. Since the detector signal at a given mixing ratio is proportional to the sample volume, the derived parameters a (benzene: a = 75.2±0.7pptnAs−1; toluene: a = 73.0±1.2pptnAs−1) can be used to calculate the toluene and benzene mixing ratios in samples of any given volume. It was also checked whether the delta13C values depend on the peak size. Figure 3 shows the averaged isotope ratios of benzene and toluene versus the averaged major ion (m/z 44) peak areas for the three dilution steps, the error bars represent the corresponding standard deviations. A constant fit y(x) = c was applied to the data. All delta13C values of toluene agree well with each other within the range of their standard deviations. For benzene this is not the case, but all delta13C values agree with each other in the range of 1.3sigma. Since the standard deviations were calculated from maximum six values and therefore have an uncertainty of 30% themselves, we assume in the following that for both substances the peak size does not affect the isotope ratios.

After: The sample volume was 25 Ln for all standard measurements. We found response curves of the type y(x)=ax (Pearson R>0.999) for both compounds (see Fig. 2) for peak areas ranging from 7.9 nAs (4.3 nAs) to 30.5 nAs (18.1 nAs) in the case of benzene (toluene). Since the response curves show neither curvature nor offset over these ranges of peak areas, we extrapolate the response curves down to 0 nAs. Then, the corresponding mixing ratios can be calculated for all benzene (toluene) peak areas, less than 30.5 nAs (18.1 nAs) via: X=a*peak area*25Ln/sample volume with a=75.2 +/- 0.7 ppt/nAs (a=73.0 +/- 1.2 ppt/nAs). All ZEPTER-2 peak areas are well below these upper limits. Also, it was checked whether the delta values depend on the peak size. Figure 3 shows the averaged isotope ratios of toluene versus the averaged major ion (m/z 44) peak areas for the three dilution steps, the error bars represent the corresponding standard deviations, the peak areas range from 4.3 nAs to 18.1 nAs. A constant fit y(x) = c was applied to the data. All delta values agree well with each other within the range of their standard deviations. To fill the gap below 4.3 nAs, we use data from calibration measurements, that were carried out during the VERDRILLT field campaign in 2010 on the same laboratory system as the ZEPTER-2 measurements. Between the two campaigns, the GC columns were changed and an additional MS for compound identification was integrated, but these changes should not affect the isotope ratios of well separated peaks like the toluene peak. We found no systematic increase or decrease for 41 dilutions of a stable VOC mixture with toluene peak areas ranging from 0.5 nAs to 6 nAs (a linear fit applied to the data yields a slope of 0.19 +/- 1.04 ‰nAs). Therefore we may assume, that the isotope ratios do not depend on the peak size for toluene peak areas between 0.5 nAs and 18.1 nAs.

“- 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

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(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."

We would rather leave the subchapters as they are, because they base on quite different measurements: to determine the reproducibility of the results we measured the same dilution of standard A every day over the course of the campaign measurements. Later on, after the campaign, we measured dilutions of standard B with different mixing ratios but constant humidity, to check the detector response and linearity, and we measured dilutions of standard B with constant mixing ratios and varying humidity to determine the influence of humidity. We feel that the use of subsubchapters contributes to the clarity of the text. We would rather not shorten the calibration part because we feel that the calibration is a very important component for a proof-of-concept study like this one.

"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."

According to this comment and the one of J.Rudolph, we deleted "and/or dynamical".

"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 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."

We reformulated that part, as suggested:

Before: 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 delta13C source value of toluene (see Sect. 2). Figure 11 shows the delta13C values versus the inverse volume mixing ratios. A linear fit yields a toluene delta13C source value of delta0 = $-28.2\pm0.5‰\dot{T}$his value is in the range of previously reported source values, although it is close to the lower limit (see Sect. 4).

After: The delta13C source value of toluene can be estimated by making the assumption that in this case we observed fresh emissions from the ground, mixing into the boundary layer background air without undergoing significant photochemical processing. Then we can use the concept of two-endpoint-mixing. Figure 11 shows the delta13C values versus the inverse volume mixing ratios. A linear fit yields a toluene delta13C source value of delta0 = $-28.2\pm0.5‰\dot{S}$ince this delta source value is in the range of previous reports, the hypothesis made is correct in the first approximation. Nevertheless, the value might be slightly biased due to photochemical processing, which might be the reason, why it is close to the lower limit of the previously reported values.

“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.”

We filtered the data once again and excluded every data point with a peak area smaller than 0.8 nAs from the discussion. The total number of samples is now 30: 14 from the PBL, 16 from the free troposphere. The results do not change significantly. We changed Fig.12 and included the PBL data to show the difference between the two data sets (PBL and lower free troposphere) and to support the assumption, that one certain data point from the free troposphere can be excluded from the analysis because it shows a more boundary-layer-like signature. We agree, that an upper-PBL-like concentration could be chosen for Fig.12, but due to the limited number of data points this value would be arbitrary to a certain extent, anyway. Since the initial concentration does not influence the calculation of the effective KIE at all, we would rather keep the value we used. We changed the sentence “(i) the PBL is well-mixed and therefore quite homogeneous and constant with respect to toluene mixing ratios and isotope ratios” to “(i) the PBL is well-mixed and therefore at least its “upper surface” is quite homogeneous and constant with respect to toluene mixing ratios and isotope ratios”.

“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 tavdelta and tavvmr 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.”

We added the following remarks to chapter 2:

Lately, Gensch et al. (2011) pointed out the relevance of the temperature dependence of the KIE for the interpretation of atmospheric measurements. To check, whether this effect has to be taken into account in the discussion of the results presented in this study, we used laboratory measurements of KIE values for the reaction of toluene and OH at different temperatures presented by Anderson (2005) and extrapolated these down to 0°C (a conservative lower boundary for air temperatures during ZEPTER-2). We found that the epsilon value at 0°C differs from the value at room temperature by about 0.3 ‰ similar to the error of the epsilon value. Therefore we conclude, that the temperature dependence of the KIE, although generally important, plays no role for the data discussed 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 m-3 s (or corresponding 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'."

We improved that, as suggested.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 11357, 2013.

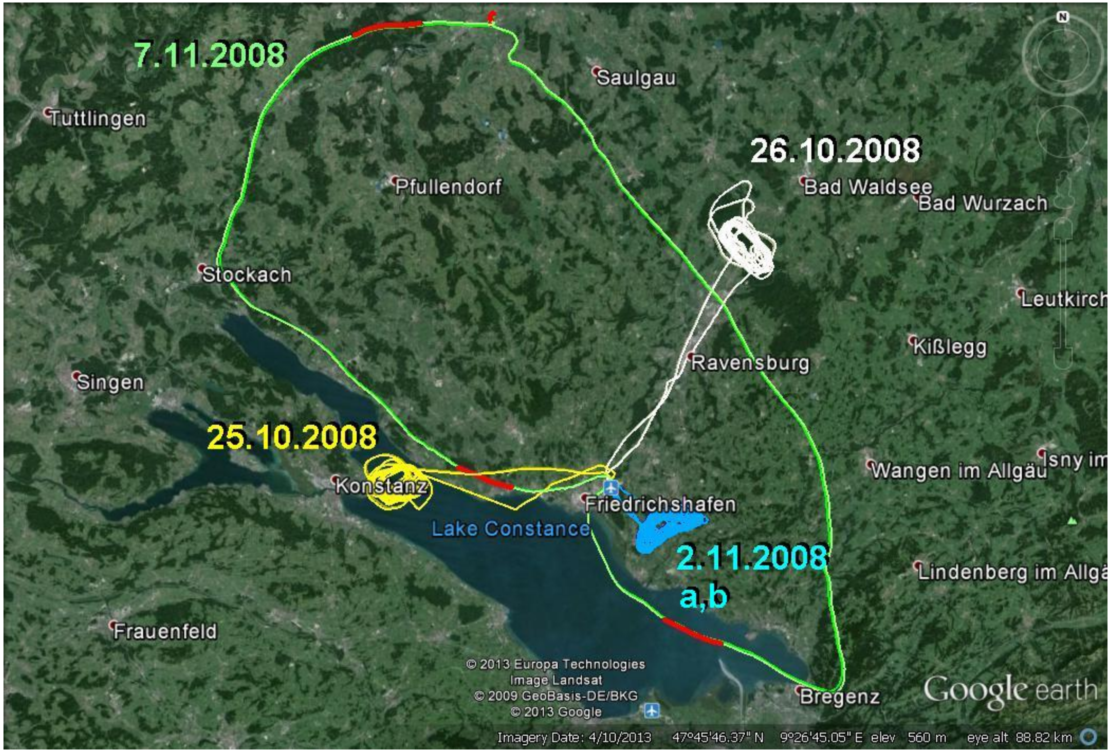

**Fig. 1.** Tracks of the five flights during which the whole air samples discussed in this paper were collected; in the flight track from 7 November 2008 the sampling times are marked in red.

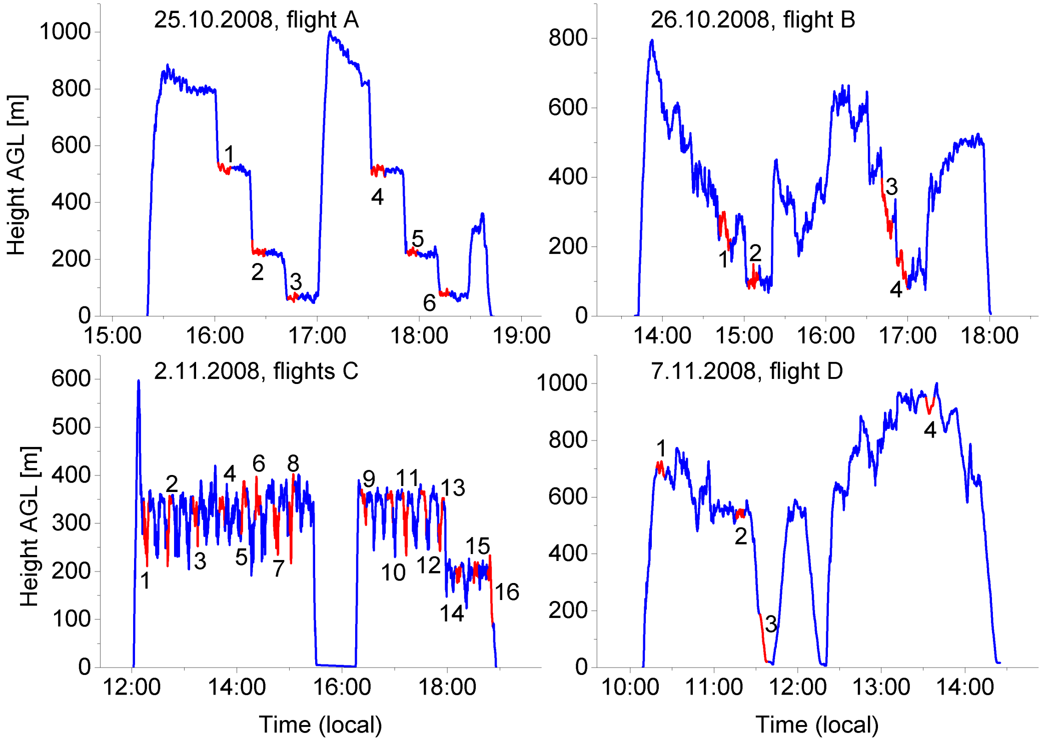

**Fig. 2.** Flight altitude above ground level versus local time; the sampling times are marked in red and enumerated in chronological order.

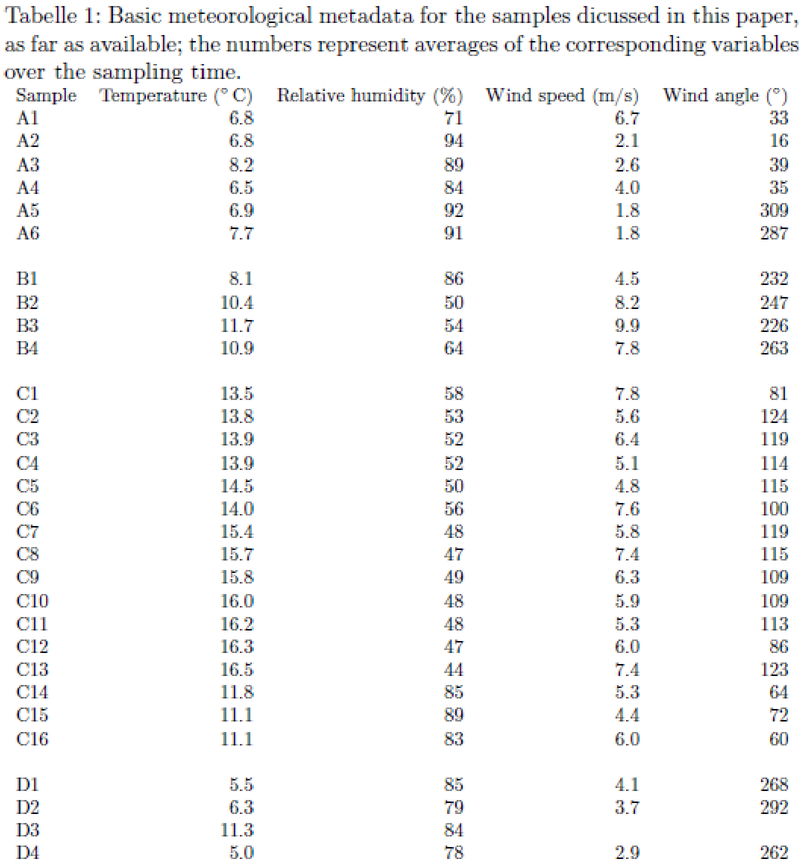

Tabelle 1: Basic meteorological metadata for the samples dicussed in this paper, as far as available; the numbers represent averages of the corresponding variables over the sampling time.

| Sample | Temperature (° C) | Relative humidity (%) | Wind speed (m/s) | Wind angle (°) |
|---|---|---|---|---|
| A1 | 6.8 | 71 | 6.7 | 33 |
| A2 | 6.8 | 94 | 2.1 | 16 |
| A3 | 8.2 | 89 | 2.6 | 39 |
| A4 | 6.5 | 84 | 4.0 | 35 |
| A5 | 6.9 | 92 | 1.8 | 309 |
| A6 | 7.7 | 91 | 1.8 | 287 |
| B1 | 8.1 | 86 | 4.5 | 232 |
| B2 | 10.4 | 50 | 8.2 | 247 |
| B3 | 11.7 | 54 | 9.9 | 226 |
| B4 | 10.9 | 64 | 7.8 | 263 |
| C1 | 13.5 | 58 | 7.8 | 81 |
| C2 | 13.8 | 53 | 5.6 | 124 |
| C3 | 13.9 | 52 | 6.4 | 119 |
| C4 | 13.9 | 52 | 5.1 | 114 |
| C5 | 14.5 | 50 | 4.8 | 115 |
| C6 | 14.0 | 56 | 7.6 | 100 |
| C7 | 15.4 | 48 | 5.8 | 119 |
| C8 | 15.7 | 47 | 7.4 | 115 |
| C9 | 15.8 | 49 | 6.3 | 109 |
| C10 | 16.0 | 48 | 5.9 | 109 |
| C11 | 16.2 | 48 | 5.3 | 113 |
| C12 | 16.3 | 47 | 6.0 | 86 |
| C13 | 16.5 | 44 | 7.4 | 123 |
| C14 | 11.8 | 85 | 5.3 | 64 |
| C15 | 11.1 | 89 | 4.4 | 72 |
| C16 | 11.1 | 83 | 6.0 | 60 |
| D1 | 5.5 | 85 | 4.1 | 268 |
| D2 | 6.3 | 79 | 3.7 | 292 |
| D3 | 11.3 | 84 | | |
| D4 | 5.0 | 78 | 2.9 | 262 |

**Fig. 3.** Basic meteorological metadata

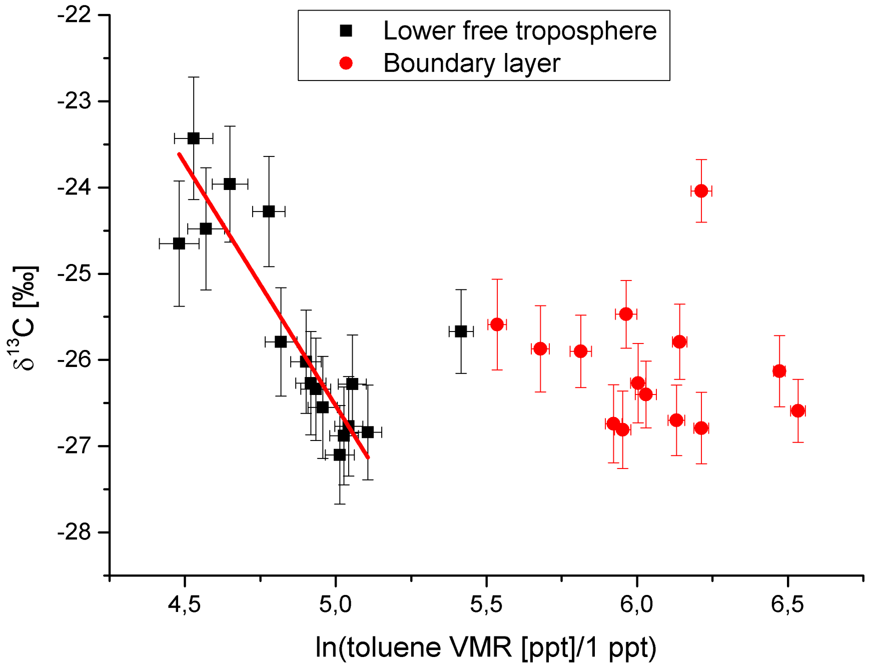

**Fig. 4.** Toluene delta values versus the logarithm of toluene volume mixing ratios, divided by 1ppt (see text for details); the two regimes (boundary layer, lower free troposphere) are clearly distinguishable