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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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Reply to the interactive comment by J. Rudolph

We want to thank J. Rudolph for his efforts and his numerous valuable and helpful comments. According to his suggestions, we made the following changes:

"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." We reformulated subsection 3.1 and included the desired metadata.

Before: 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. 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.

“ 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.”

We reformulated the second and the third paragraph of subsection 3.4.1 and removed the benzene data from Figure3.

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.

“3) 11364/26-11365/3: Humidity management is discussed later on, in a method description the statement is out of place.”

We deleted this sentence.

“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?”

This sentence is misleading, we bought a certified reference standard gas. We deleted the part “determined through comparison…”.

“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.”

The mixing ratios prepared with the dynamic dilution system and the ones measured in the air samples are both based on dry air volumes, so the small humidity dependency must have another explanation.

“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."

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. A combination of the different data sets to determine the precision of the results seems to be a good idea, of course. But, unfortunately, we found the stability to be different during the campaign and afterwards. Therefore a combination is not appropriate; the standard A data gives the best impression of the precision of the ZEPTER-2 results. We agree, that precisions derived from the standard measurements should not be extrapolated towards smaller peak sizes. 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. Unfortunately, due to the limited sample volume, repeat analyses of the ambient samples were not possible.

"7) 11370/15: It would be useful for the reader if a sample chromatogram is given."

We included one.

"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."

We deleted "dynamic".

"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." We included vertical profiles of CO mixing ratios, toluene mixing ratios and toluene isotope ratios for all flights.

"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 ‰."

Actually, Fig. 12 showed data from the free troposphere, only. We changed the plot and included the PBL data to show the difference between the two data sets 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 the source isotope ratio in general might be biased due to processing in the PBL. We reformulated the last sentence of subsection 5.1.

Before: This value is in the range of previously reported source values, although it is close to the lower limit.

After: Since the 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.

“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.”

We corrected the units for the photochemical age. The regression method used takes into account both x- and y-errors. We agree, that upper PBL-like source values could be chosen for this plot, but due to the limited number of data points these source values are hard to determine and would therefore be arbitrary to a certain extent. Since the source values do not influence the slope of the regression lines at all, we would rather leave the plots as they are.

“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.”

We reformulated chapter 6:

Summary and conclusions

We collected whole air samples in the PBL and the lower free troposphere and afterwards analysed them in the laboratory with respect to toluene and benzene mixing ratios as well as toluene delta13C values. The GC-C-IRMS in use was carefully calibrated and characterised in order to identify possible problems and to determine the measurement errors. For sample volumes of 15 Ln (the typical sample size), the precision of the measured isotope ratios was well below 1‰ at toluene mixing ratios above 100 pptV, and below 0.5‰ at mixing ratios above 250 pptV. During a vertical profile flight over the Lake Constance we sampled air masses containing rather fresh emissions of toluene in the PBL. Using the concept of two-endpoint-mixing, we estimated a toluene source isotope ratio of delta0=-28.2+/-0.5 ‰Ẇe applied the concept of the effective KIE on the data obtained in the lower free troposphere and found the toluene mixing ratios in this layer to be affected much more by photochemical degradation than by dilution processes: Considering the error bars, we found no evidence for dilution in the free troposphere. Concerning the mixing ratio and isotope ratio characteristics, samples in the free troposphere differed strongly from those in the PBL, allowing the two regimes to be clearly distinguished. The photochemical ages of air masses were calculated in two different ways, based on toluene and benzene mixing ratios as well as toluene isotope ratios, and compared. The two methods yielded quite different results for the PBL, probably due to strong mixing in that regime. In the free troposphere the calculated photochemical ages correlated with a slope of 0.91+/-0.29, indicating again that the effect of mixing processes was rather weak in the free troposphere during the measurements. Although the number of measurements in the present study is rather small, our results show that stable carbon isotope ratios of VOC can be measured with sufficient precision in the PBL and the lower free troposphere to gain valuable information about photochemical and dynamical processes in the atmosphere. Our study thus is an important proof of concept and encourages further activities, which promise to considerably enhance our knowledge on VOC source characteristics, transport and exchange processes, as well as the photochemical state of air masses. “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.” We changed the formulation.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C5475/2013/acpd-13-C5475-2013-supplement.pdf

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

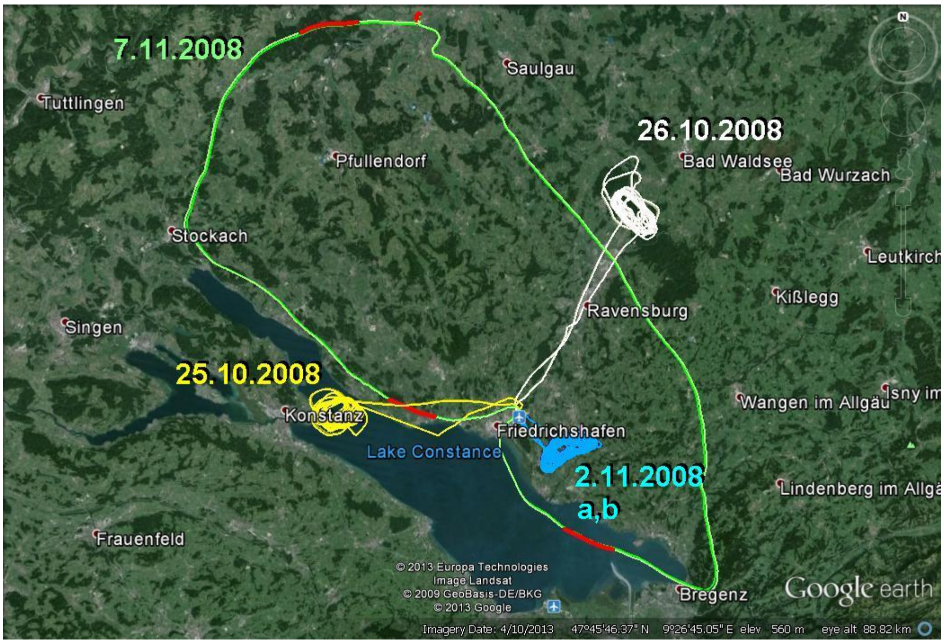

Fig. 1. Tracks of the five flights during which the whole air samples discussed in this paper were collected; in the flight track from 7 November 2008 the sampling times are marked in red.

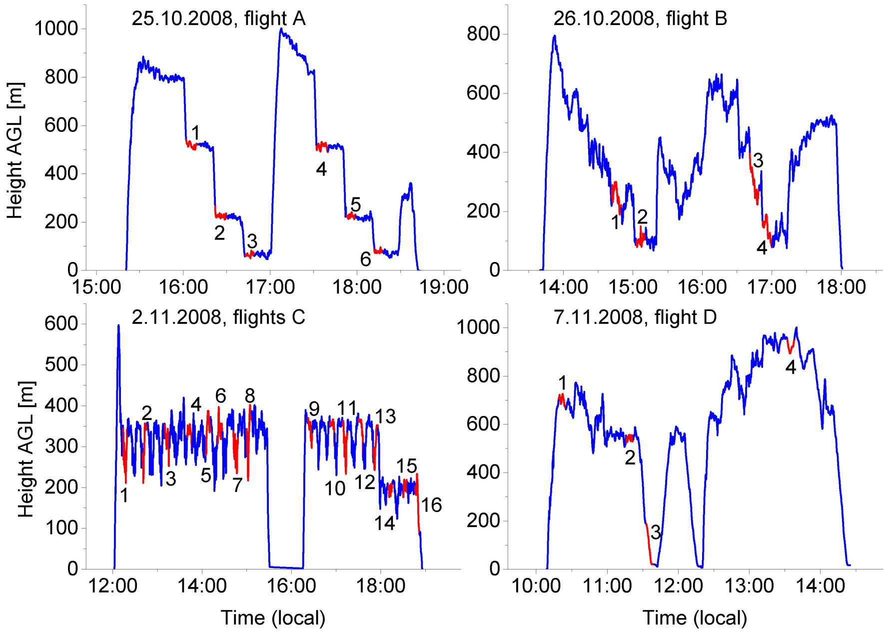

Fig. 2. Flight altitude above ground level versus local time; the sampling times are marked in red and enumerated in chronological order.

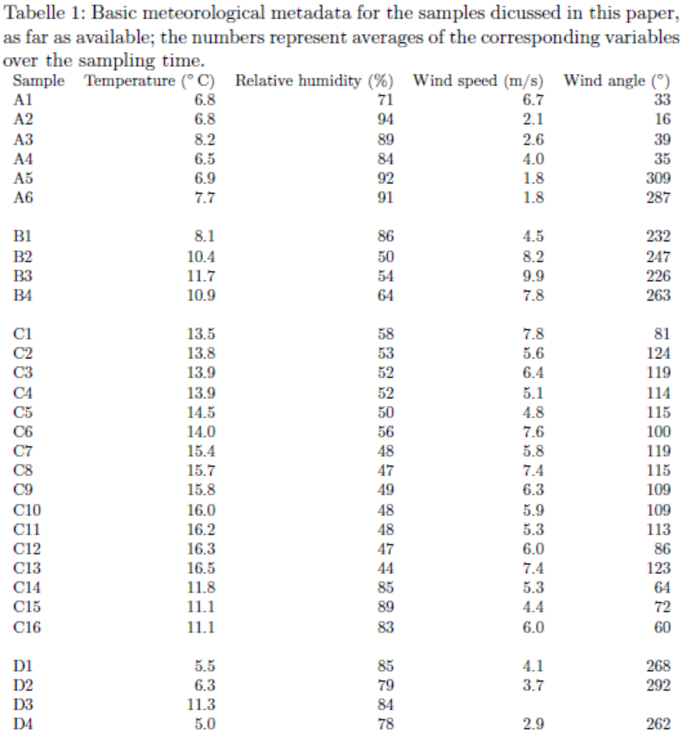

Tabelle 1: Basic meteorological metadata for the samples dicussed in this paper, as far as available; the numbers represent averages of the corresponding variables over the sampling time.

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

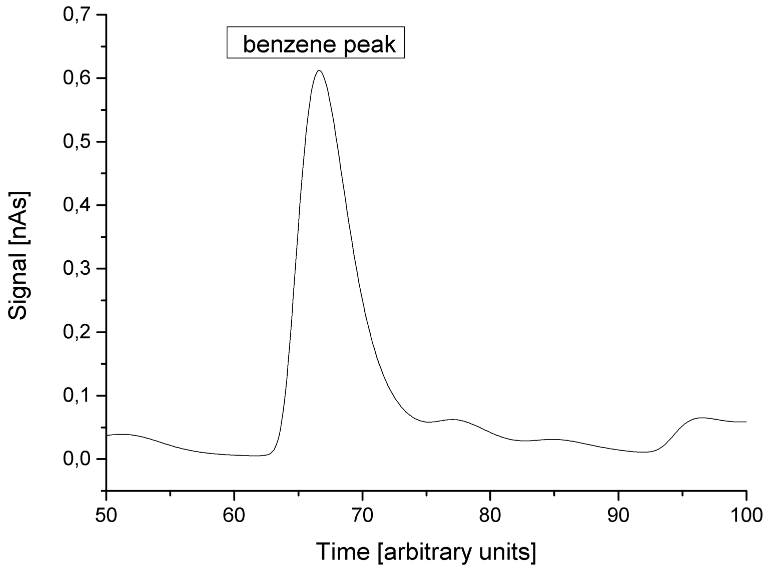

Fig. 4. Part of sample chromatogramm, showing the peak overlap between benzene and another so far unidentified compound

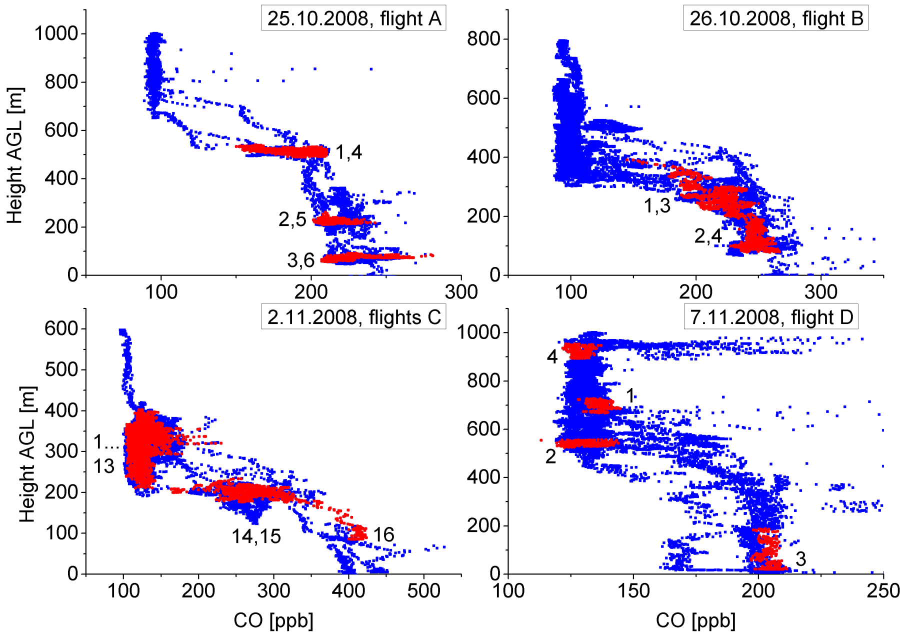

Fig. 5. Vertical profiles of CO mixing ratios for all flights, visualizing the height of the PBL; the sampling times are marked in red.

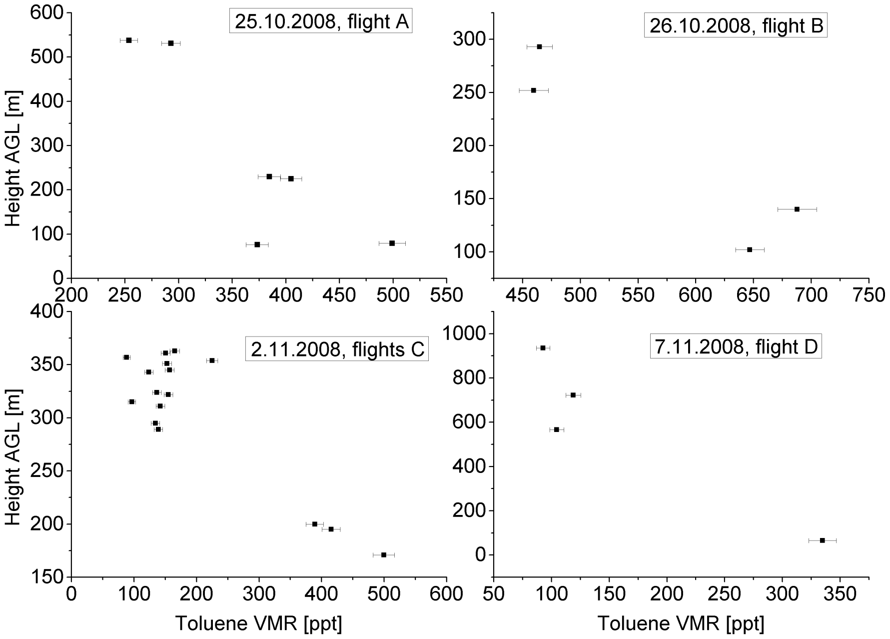

Fig. 6. Vertical profiles of toluene volume mixing ratios for all flights

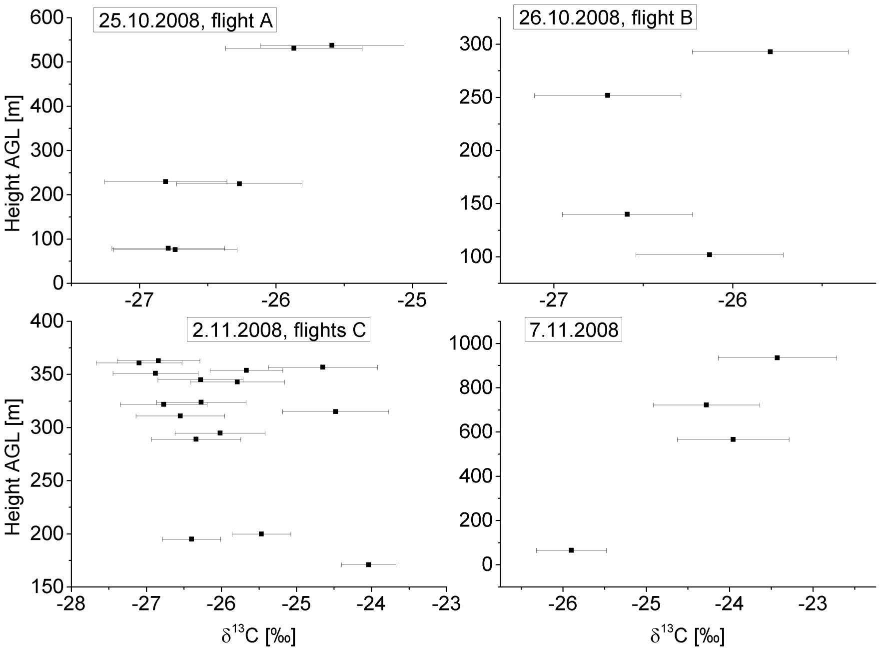

Fig. 7. Vertical profiles of toluene delta values for all flights

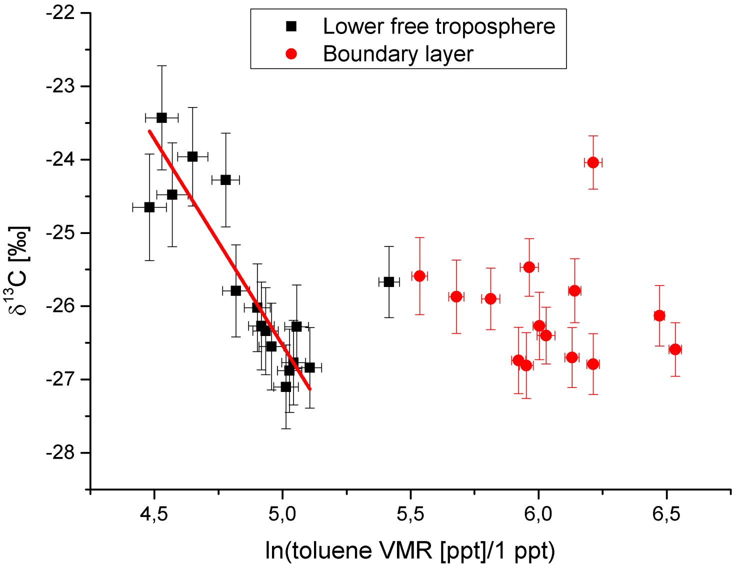

Fig. 8. Toluene delta values versus the logarithm of toluene volume mixing ratios, divided by 1ppt (see text for details); the two regimes (boundary layer, lower free troposphere) are clearly distinguishable