Atmos. Chem. Phys. Discuss., 13, 11357–11394, 2013 www.atmos-chem-phys-discuss.net/13/11357/2013/ doi:10.5194/acpd-13-11357-2013 © Author(s) 2013. CC Attribution 3.0 License.



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## Stable carbon isotope ratios of toluene in the boundary layer and the lower free troposphere

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Received: 25 March 2013 – Accepted: 18 April 2013 – Published: 26 April 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.



### Abstract

Measurements of stable carbon isotope ratios in VOC are a powerful tool to identify sources or to track both dynamical and chemical processes.

During the field campaign ZEPTER-2 in autumn 2008 whole air samples were collected on board a Zeppelin NT airship in the planetary boundary layer and the lower free troposphere over south-west Germany. These samples were analysed with respect to VOC mixing ratios and stable carbon isotope ratios using a gas chromatograph combustion isotope ratio mass spectrometer. In this study we present the results for toluene, one of the major anthropogenic pollutants.

<sup>10</sup> In the boundary layer we observed rather fresh emissions mixing into the background and derived a toluene source isotope ratio of  $\delta^{13}C = -28.2 \pm 0.5\%$ . Using the concept of the effective kinetic isotope effect, we were able to separate the effects of dilution processes and photochemical degradation in the free troposphere. We estimated the photochemical age of toluene in the atmosphere in two different ways (using isotope ratios and mixing ratios, respectively). The results differ strongly in the planetary bound-

ary layer, probably due to mixing processes, but are compatible with each other in the free troposphere.

#### 1 Introduction

Despite their low concentrations, volatile organic compounds (VOC) play an important

- <sup>20</sup> role in atmospheric (especially tropospheric) chemistry. The majority of anthropogenic VOC emissions stems from fossil fuel use and is emitted predominantly during road transport and oil production. The most abundant species being emitted in this context, are toluene and benzene (e.g. Williams and Koppmann, 2007; Reimann and Lewis, 2007).
- <sup>25</sup> Rudolph et al. (1997) presented a method to determine stable carbon isotope ratios in VOC at ambient concentration levels, using gas chromatography combustion



isotope ratio mass spectrometry (GC-C-IRMS). They proposed that measurements of the isotopic composition of VOC, beside measurements of their concentrations, would lead to valuable additional information on atmospheric processes, e.g. photochemical degradation. This initial methodology has been followed by a number of studies on this <sup>5</sup> subject (see e.g. the review of Goldstein and Shaw, 2003, and references therein).

Stable carbon isotope ratios in VOC were measured in various regions, affected by different amounts of air pollution (Tsunogai et al., 1999; Rudolph et al., 2002; Redeker et al., 2007; Nara et al., 2007; Saito et al., 2009; Spahn, 2009). Rudolph et al. (2002) measured isotope ratios in atmospheric VOC close to their anthropogenic sources. Several laboratory studies investigated the kinetic isotope effects for reactions between 10

VOC and different reactants (Anderson et al., 2003, 2004a,b; lannone et al., 2008, 2009; Farkas et al., 2003; Rudolph et al., 2000). By applying the concept of the hydrocarbon clock on VOC isotopologues, stable carbon isotope ratios have also been used to determine the photochemical age of VOC in the atmosphere (Rudolph and Czuba,

2000; Rudolph et al., 2003; Saito et al., 2002, 2009). 15

#### 2 Theoretical background for the interpretation of isotope ratios

All isotope ratios given in this paper are expressed in the  $\delta$ -notation, relative to the Vienna-Peedee Belemnite (V-PDB) standard for stable carbon isotope analysis. The  $\delta$ value is defined as the relative deviation from the standard's isotope ratio (Craig, 1957).

$${}_{20} \quad \delta^{13}C = \frac{\left({}^{13}C/{}^{12}C\right)_{sample} - \left({}^{13}C/{}^{12}C\right)_{V-PDB}}{\left({}^{13}C/{}^{12}C\right)_{V-PDB}} \times 1000\%$$
(1)  
$$\left({}^{13}C/{}^{12}C\right)_{V-PDB} = 0.0112372$$
(2)

A necessary requirement for the interpretation of isotope ratios is the knowledge of the kinetic isotope effect (KIE). The kinetic isotope effect  $\varepsilon$  describes, for a certain reaction,

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the relative difference between the rate coefficients k of two different isotopologues of the same compound. For example, the KIE (with respect to stable carbon isotopes) for the dominant reaction of toluene with OH is (Rudolph, 2007):

$$\varepsilon_{\rm OH} = \left(\frac{k_{\rm OH} \left({}^{12} {\rm C}_7 {\rm H}_8\right)}{k_{\rm OH} \left({}^{13} {\rm C} \,{}^{12} {\rm C}_6 {\rm H}_8\right)} - 1\right) \times 1000\% = 5.95 \pm 0.28\%$$
(3)

5

In many atmospheric situations an air parcel is affected not only by chemical reactions but also by dilution processes. The concept of the *effective kinetic isotope effect*  $\varepsilon_{eff}$ includes both: a chemical loss reaction (with OH in this case) with the kinetic isotope effect  $\varepsilon_{OH}$  and the time constant  $\tau_{OH}$ , as well as a dilution process (by mixing with "zero" background air) with the time constant  $\tau_{dil}$ , which does not result in isotopic fractionation.

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{OH}}/\tau_{\text{OH}}}{1/\tau_{\text{OH}} + 1/\tau_{\text{dil}}} \tag{4}$$

For a substance emitted at time t = 0, the following equation can be derived, which relates the changes in the VOC mixing ratio c to the changes in the isotope ratio  $\delta$ (Rudolph, 2007).

$$\delta(t) = \delta(0) - \varepsilon_{\text{eff}} \ln\left(\frac{c(t)}{c(0)}\right)$$
(5)

If air masses are mixed, which contain "fresher" and "older" amounts of the same substance, respectively, Eq. (5) is invalid. In these cases, provided that chemical processing can be neglected, the concept of *two-endpoint mixing* can be applied. We consider two mixing air masses, #1 and #2. If one air mass contains much larger VOC concentrations than the other ( $c_1 \gg c_2$ ) and at the same time has a much smaller volume



 $(V_1 \ll V_2)$ , the resulting isotope ratio  $\delta$  and the VOC concentration *c* are linked to each other by the following equation (Rudolph, 2007):

$$\delta = \delta_1 + \frac{(\delta_2 - \delta_1)c_2}{c}$$

<sup>5</sup> The *photochemical age* (see Parrish et al., 1992) of a certain compound in an air mass is a measure for the degree of photochemical processing this compound has experienced since it has been released to the atmosphere. It is defined as

$$[OH]_{avg}t = \int_{0}^{t} [OH]dt'$$

25

and can be derived from isotopic measurements (Rudolph and Czuba, 2000) via:

$$[OH]_{avg} t = \frac{\delta(t) - \delta(0)}{\varepsilon_{OH} k_{OH}}$$

Even in cases when air masses mix, which contain different "ages" of the same compound, Eq. (8) can be applied and gives a concentration-weighted mean photochemical age, provided that  $\delta(0)$  is the same for both air masses (Rudolph and Czuba, 2000).

Also, if two compounds (*a* and *b*) with different reaction constants ( $k_{OHa}$  and  $k_{OHb}$ ) are emitted from the same source in a certain known ratio ( $c_a(0)/c_b(0)$ ), their photochemical age can be calculated from their concentrations ( $c_a(t)$  and  $c_b(t)$ ) at a given time *t*. This is the "conventional" way to calculate the photochemical age (see Roberts et al., 1984; Rudolph and Johnen, 1990; Parrish et al., 1992).

$$[OH]_{avg}t = \frac{1}{k_{OHb} - k_{OHa}} \left( \ln\left(\frac{c_a(t)}{c_b(t)}\right) - \ln\left(\frac{c_a(0)}{c_b(0)}\right) \right)$$
(9)

It should be mentioned, that photochemical ages derived from Eq. (9), may be strongly biased if air masses of different ages mix (see e.g. Rudolph and Johnen, 1990; McKeen et al., 1990, 1996; Rudolph and Czuba, 2000; Saito et al., 2009).

(6)

(7)

(8)

#### 3 Experiment

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### 3.1 Measurement campaign

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 NO<sub>x</sub> due to free radicals (OH, HO<sub>2</sub>), 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 m<sup>3</sup> covering an internal lightweight, rigid structure. Most of the scientific instruments were installed inside the cabin in the gon dola beneath. Four propellers (three of them mounted pivoted) allow a full maneuver ability at low speed or even stagnation. Depending on the environmental conditions, the
 Zeppelin can reach a maximum height of about 3000m and a maximum speed of about
 115 km h<sup>-1</sup>. The maximum scientific payload is about 1t (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, NO<sub>x</sub>, O<sub>3</sub>, HONO, CH<sub>2</sub>O, particles, VOC, OH, column densities and <sup>20</sup> 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,  $NO_x$ , CO,  $O_3$  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



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the European Air Pollution Dispersion (EURAD) model (for more information about ZEPTER-2 and the Zeppelin NT also see Häseler et al., 2009; Urban, 2010).

#### 3.2 Whole air sampler

Ambient whole air samples were collected using the ZEBIS (ZEppelin Based Isotope Sampler) instrument and afterwards analysed in the laboratory using a GC-C-IRMS system. ZEBIS consists of a swing piston compressor (NPK09 DC, KNF Neuberger), a custom-made electrical control unit and two canister modules, each containing four evacuated SilcoCan<sup>TM</sup> canisters (Restek GmbH, Bad Homburg, Germany) with a volume of 6L (see Fig. 1).

- <sup>10</sup> The compressor is operated continuously during a flight. At times when no canister is being pressurized, the exhaust valve at the end of the sample line is opened and the compressor provides a flow of ~8Lnmin<sup>-1</sup>, thus flushing the system. Each canister is locked by a normally closed solenoid valve (Clippard Europe, S.A., Louvain-la-Neuve, Belgium), which can be switched both manually or automatically. To fill a certain can-
- ister, the corresponding solenoid valve is opened and the exhaust valve at the end of the sample line is closed simultaneously. When a pressure of 4 bar is reached, both valves are switched again, thereby closing the canister and allowing the sample line to be flushed. During ZEPTER-2 it took ~3–5 min to fill one canister, depending on the flight level.
- The samples were taken from the meteorology mast in front of the Zeppelin NT gondola using a 10m inlet line (1/4" FEP hose, 3mm ID, Bohlender GmbH, Grünsfeld, Germany). Particles, OH, ozone, H<sub>2</sub>O and CO<sub>2</sub> might corrupt the measurements of carbon isotopes in VOC. The inlet was equipped with a particle filter (Bohlender GmbH) that removes particles larger than 10 μm. OH radicals are destroyed by col-
- lision with the line wall. A special ozone-removing device did not seem to be necessary, since the reactions between the aromatic hydrocarbons of interest and ozone are negligible: the reaction constant for the reaction between ozone and toluene is  $(1.5\pm0.8) \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and for the reaction between ozone and benzene



 $(7 \pm 4) \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Lloyd, 1984). H<sub>2</sub>O is removed in the laboratory system prior to analysis, CO<sub>2</sub> is separated chromatographically from the VOC sample (see Sect. 3.3).

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 landuse, 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).

#### 3.3 Laboratory system

The air samples were analysed using a commercial gas chromatograph combustion isotope ratio mass spectrometer (GC-C-IRMS), consisting of: (i) a thermal desorption system (TDS) with water traps for sample preparation, combined with a cold injection
<sup>15</sup> system (CIS) to transfer the sample to the gas chromatograph, (ii) a gas chromatograph (GC), equipped with a cold trapping system (CTS) to cryo-focus the sample at the beginning of the column, (iii) a combustion furnace to oxidize the VOC to CO<sub>2</sub> and H<sub>2</sub>O, followed by a water trap to remove the produced H<sub>2</sub>O, and (iv) an isotope ratio mass spectrometer (IRMS) to determine the <sup>13</sup>C/<sup>12</sup>C ratios of the individual VOC. The GC-IRMS used in this study is very similar to the system described by lannone et al. (2007). Therefore, the individual parts of the system are described only briefly here.

The TDS (TDSG Large, Gerstel GmbH&Co. KG, Mühlheim a.d. Ruhr, Germany) is used to cryogenically extract the VOC from the whole air sample, to remove the sample humidity and to determine the sample volume. The flow rate during preconcentration was set to 1 Ln min<sup>-1</sup>. The water traps are Silcosteel treated (Restek GmbH, Bad Hom-

<sup>25</sup> Was set to 1 Lnmin . The water traps are Silcosteel treated (Restek GmbH, Bad Homburg, Germany) stainless steel tubes operated at a temperature of –20°C. 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. The preconcentration trap is packed with glass beads (mesh 60/80) and is operated at -150 °C. For desorption the trap is heated to 230 °C at a rate of 40 °C min<sup>-1</sup>. Following the desorption the VOC sample is dried in two additional water traps, which are also approximated at a temperature of -20 °C.

dried in two additional water traps, which are also operated at a temperature of -20°C.
 Finally, the VOC are cryo-focussed again in the CIS at a temperature of -150°C.

The CIS (KAS 4, Gerstel GmbH&Co. KG) is a glass tube packed with glass beads (mesh 80/100). For desorption of the sample the CIS is heated to  $250^{\circ}$ C at a rate of  $12^{\circ}$ C s<sup>-1</sup>.

- The VOC are separated from each other and also from CO<sub>2</sub> using a partial twodimensional gas chromatography technique. VOC separated on a non-polar J&W DB-5 ms column (30 m × 0.5 µm film × 0.32 mm ID) are transferred to a polar J&W DB-624 column (30 m × 1.8 µm film × 0.32 mm ID) for additional separation during a single measurement. Prior to compound separation, the VOC sample is cryo-focussed once again
   in the CTS (Gerstel GmbH&Co. KG). During focussing the CTS is kept at -150 °C, dur
  - ing desorption the CTS is heated to  $250^{\circ}$ C at a rate of  $12^{\circ}$ Cs<sup>-1</sup>.

20

The GC temperature programme starts with a 4min isothermal phase at  $-20^{\circ}$ C followed by a temperature ramp of  $4^{\circ}$ Cmin<sup>-1</sup> to  $200^{\circ}$ C, followed by a ramp of  $10^{\circ}$ Cmin<sup>-1</sup> to  $250^{\circ}$ C, and is helt isothermal for 10min. The average flow velocity of the He carrier gas is set to  $40 \text{ cm s}^{-1}$ .

After separation, the VOC eluting from the GC flow through a commercially available combustion interface (Model GC5-MK1, GV Instruments Ltd., Manchester, UK), where they are oxidised quantitatively to  $CO_2$  and  $H_2O$ . The combustion interface consists of a quartz tube partially situated in a heated zone of 350°C and, further downstreams,

within a furnace kept at 850°C. The part of the quartz tube within the combustion furnace, where the oxidation takes place, is packed with CuO pellets (size 0.1–0.5 mm), which provide the oxygen necessary for the reaction.



The gas flow then passes through a cold trap where water generated during the combustion process is removed. The cold trap consists of a coiled capillary, kept at -100 °C, as suggested by Leckrone and Hayes (1998).

The CO<sub>2</sub> is transferred to the source of an Isoprime IRMS (GV Instruments Ltd., <sup>5</sup> Manchester, UK) through an open split. The three ion beams comprising m/z 44, 45 and 46 are detected by Faraday cup collectors.

At the beginning and the end of each measurement run, pulses of a certified CO<sub>2</sub> reference standard gas (Air Liquide Deutschland GmbH, Düsseldorf, Germany) are introduced as a calibration gas. The  $\delta^{13}$ C value of the standard gas is –25.80±0.2‰, determined through comparison with an accurately known  $\delta^{13}$ C V-PDB value.

Data processing (e.g. peak integration, calibration, correction according to Santrock et al., 1985) is accomplished using the *Continuous Flow Data Processing* software (GV Instruments Ltd.).

### 3.4 Calibration/characterisation

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<sup>15</sup> A custom-made dynamic gas dilution system (for details see Hembeck, 2008) was used to dilute VOC gas standards at ppm levels with dry or humidified N<sub>2</sub> to produce working standards with different VOC volume mixing ratios at typical ambient levels (ranging from ~100ppt to some ppb in the case of toluene and benzene) and with different humidities. These working standards were used to calibrate and characterise the GC-C-IRMS system.

A stable mixture of VOC in air (hereafter referred to as "standard A"), diluted down to typical atmospheric mixing ratios (0.7 ppb of benzene and 0.2 ppb of toluene), was measured every day during the canister measurements to determine the reproducibility of the measurements (major ion peak areas, isotope ratios) and to identify possible drifts.

Also a series of measurements of an eight-component working standard (hereafter referred to as "standard B") with known VOC mixing ratios was performed after the campaign under various conditions (concerning dilution and humidity) to check the



linearity of the system, to investigate the impact of sample humidity on both major ion (m/z 44) peak areas and isotope ratios, and to calibrate the detector's response (major ion peak areas) on VOC mixing ratios.

#### 3.4.1 Detector response and linearity

15

Since the present study focusses on toluene and benzene, only the calibration of these compounds will be presented here. Standard B contains a toluene mixing ratio of  $184 \pm 5$  ppb and a benzene mixing ratio of  $335 \pm 4$  ppb. 16 measurements of the diluted standard B at three different levels of VOC mixing ratios (0.3-1.3 ppb of toluene and 0.6-2.4 ppb of benzene) and at a constant relative humidity of ~50% were taken into account for the calibration. 10

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:  $a = 75.2 \pm 0.7$  ppt nAs<sup>-1</sup>; toluene:  $a = 73.0 \pm 1.2$  pptnAs<sup>-1</sup>) can be used to calculate the toluene and benzene mixing ratios in samples of any given volume.

It was also checked whether the  $\delta^{13}$ C 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 <sup>20</sup> corresponding standard deviations. A constant fit y(x) = c was applied to the data. All  $\delta^{13}$ C values of toluene agree well with each other within the range of their standard deviations. For benzene this is not the case, but all  $\delta^{13}$ C values agree with each other in the range of  $1.3\sigma$ . 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. 25



#### 3.4.2 Influence of sample humidity

If water is not removed from the sample prior to the GC-C-IRMS measurements, it is known to cause a number of problems. It may influence the cryo-enrichment of VOC and thereby the peak areas. It may disturb the gas chromatography which results in unstable retention times. Additionally, if water molecules reach the IRMS, they may form  ${}^{1}\text{H}^{12}\text{C}^{16}\text{O}_{2}^{+}$  ions which have the same mass as  ${}^{13}\text{C}^{16}\text{O}_{2}^{+}$  ions and therefore corrupt the isotope ratio measurements (see Leckrone and Hayes, 1998).

To determine the effectivity of the water traps in use and to estimate the impact of the residual water in the sample, 23 measurements of humidified dilutions of standard B were carried out. The VOC mixing ratios were kept constant (2.9ppb of benzene and 1.6ppb of toluene), the relative humidity (RH) level was varied in five steps between 16% and 80%. The sample humidity is hard to control with the gas dilution system and changes during sample enrichment, we estimate the error of the sample humidity to be ~5% RH.

We found the peak areas to increase with increasing sample humidity (see Fig. 4). For toluene, the peak area changes by less than 7% over the whole humidity range, for benzene the effect is even smaller. Since the mixing ratio calibration (see Sect. 3.4.1) was carried out with standard B dilutions containing 50% RH, we estimate 3.5% to be the upper limit for the humidity-induced error of the measured peak areas. This
 worst-case estimation is also valid for the ZEPTER-2 samples.

Figure 5 shows averaged  $\delta^{13}$ C values for the five different sample RH levels mentioned above and also for dry samples. No systematic drift can be seen in the data, also the values for dry samples agree well with all the other values. We therefore conclude, that the isotope ratio measurements are not corrupted by the sample humidity.

#### 25 3.4.3 Precision of the results

Eleven measurements of standard A were used to determine the precision of the peak areas and the  $\delta^{13}$ C values. Since the precisions are generally expected to depend on



the peak size, we selected five well-separated peaks of different sizes (including the benzene and toluene peaks), calculated the standard deviations of the  $\delta^{13}$ C values  $\sigma_{\delta}$  and the peak areas  $\sigma_{A}$  and plotted these standard deviations versus the mean peak areas *A*. We estimated the uncertainties of the standard deviations via

$$5 \quad \Delta\sigma = \frac{\sigma}{\sqrt{2n}} \tag{10}$$

where n is the number of measurements.

Figure 6 shows  $\sigma_A$  plotted versus *A*, both given in nAs. We applied a linear fit (Pearson *R* = 0.81) to the data and derived the following function

10  $\sigma_A = 0.06 \,\text{nAs} + 1.3 \,\% \times A$ 

which was later used to estimate the precision of the ZEPTER-2 peak areas.

The precision  $\sigma_{\delta}$  of the measured isotope ratios  $\delta$  naturally depends on the amount of carbon available for the isotope analysis, i.e. the peak size. Based on counting statistics, one would expect a dependency of the following form (see Brand, 2004, and the references therein):

$$\sigma_{\delta} \propto \frac{1}{\sqrt{A}} \tag{12}$$

Figure 7 shows  $\sigma_{\delta}$  (in ‰) plotted versus A (in nAs). Fitting a function of the form

20  $y(x) = ax^b$ 

to the data yields an exponent of  $b = -0.6 \pm 0.2$ , which is in agreement with the theory, i.e. Eq. (12). Therefore we fixed the exponent *b* to the theoretical value of b = -0.5 and derived the following function to estimate the precision of the ZEPTER-2 isotope ratios:

$$_{25} \quad \sigma_{\delta} = \frac{0.65\%}{\sqrt{A/1\,\mathrm{nAs}}}$$

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(11)

(13)

(14)

#### 3.4.4 Accuracy of the isotope ratios

The IRMS is calibrated during every run with ten peaks of a certified CO<sub>2</sub> reference gas (see Sect. 3.3). The error of the mean of the measured isotope ratios for these ten reference gas peaks (expressed as a  $\delta^{13}$ C value) was always smaller than 0.1‰, the uncertainty of the reference gas  $\delta^{13}$ C value is specified to be 0.2‰. Combining these two errors, we estimate the accuracy of the IRMS  $\delta^{13}$ C measurements to be 0.22‰.

It is important to mention, that this is only the accuracy of the last step of the analysis, the isotope ratio measurement of the  $CO_2$  gas that reaches the IRMS. During other steps of the analysis, for example during the sample enrichment, some isotopic fractionation may occur. To estimate the accuracy of the measurement process in whole, a VOC standard gas with known VOC  $\delta^{13}$ C values would be required. Such a standard gas was not available during the measurements reported in this paper, therefore there might be an additional error in the absolute  $\delta^{13}$ C values.

#### 4 Results

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<sup>15</sup> Unfortunately, we found the benzene peak to overlap with a much smaller peak of a so far unidentified substance in the ZEPTER-2 chromatograms. It turned out, that this peak overlap corrupts the measured  $\delta^{13}$ C values of benzene, so we do not use them in the discussion. However, the effect on the benzene mixing ratios is small. A very conservative estimation, based on the maximum peak size of the small peak, yields <sup>20</sup> a maximum error induced on the benzene peak areas of 0.2 nAs).

For every flight presented, we determined the height of the planetary boundary layer (PBL) based on in-situ CO measurements with a time resolution of 1 s. As an example, Fig. 8 shows the vertical profile of CO, measured on 25 October 2008. Below 500 m height a.g.l. the CO mixing ratio ranges from 200 to 250 ppb, this height regime is interpreted as the well mixed PBL. Between 500 and 750 m a very sharp decrease from 200 to 100 ppb can be seen, marking the transition from the PBL to the free troposphere.



Above 750m a relatively constant CO mixing ratio of 100ppb characterises the free troposphere.

The histogram in Fig. 9 gives an overview of the toluene isotope ratios measured during ZEPTER-2. The total number of samples is 38, 17 taken in the PBL and 21 in
the free troposphere. The mean error of the δ<sup>13</sup>C values is 0.6‰. The distributions are strongly asymmetric, indicating that photochemical and/or dynamical processes took place in the air mass history. The most frequent δ<sup>13</sup>C values of the distributions (between -27‰ and -26‰) are in the vicinity of source values reported in the literature, e.g.: -26.5‰ (v. Czapiewski et al., 2002), between -28.4‰ and -27.1‰ (Rudolph et al., 2002), -26.1‰ and -27.2‰ (Thompson, 2003). As expected, we find higher δ<sup>13</sup>C values in the free troposphere than in the PBL, since more positive δ<sup>13</sup>C values correspond to "older" air masses.

The observed volume mixing ratios range from 17 to 690 ppt in the case of toluene and from 96 to 730 ppt in the case of benzene.

#### 15 **5** Discussion

### 5.1 $\delta^{13}$ C source value

In the data gathered on 25 October 2008, both volume mixing ratios (VMR) and  $\delta^{13}$ C values of toluene show a pronounced vertical profile in the planetary boundary layer (see Fig. 10). 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  $\delta^{13}$ C source value of toluene (see Sect. 2). Figure 11 shows the  $\delta^{13}$ C values versus the inverse volume mixing ratios. A linear fit yields a toluene  $\delta^{13}$ C source value of  $\delta_0 = -28.2 \pm 0.5\%$ . This value is in the range of previously reported source values, although it is close to the lower limit (see Sect. 4).



# 5.2 Effective KIE: dilution and photochemical degradation in the free troposphere

For the interpretation of data collected in the free troposphere we assume the following, simplified situation: (i) the PBL is well-mixed and therefore quite homogeneous and constant with respect to toluene mixing ratios and isotope ratios; (ii) the toluene background concentration in the free troposphere is zero. In other words, all air parcels in the free troposphere, containing toluene in significant amounts, stem from the same source (the PBL) and undergo only dilution and photochemical processing (reactions with the OH radical). Assuming this, we can use Eq. (5) to calculate the effective KIE  $\varepsilon_{eff}$ , which contains information about the time constants of dilution and photochemical

 $\varepsilon_{\rm eff}$ , which contains information about the time constants of dilution and photochemical degradation.

To do so, we plot the toluene  $\delta^{13}$ C values measured in the free troposphere versus the logarithm of the corresponding toluene VMR (see Fig. 12). Since we do not know the value of c(0), characterising the "source", and since this value does not influence the calculation of  $\varepsilon_{\text{eff}}$ , we just set c(0) = 1 ppb to get rid of the units. Four data points

<sup>15</sup> the calculation of  $\varepsilon_{\text{eff}}$ , we just set c(0) = 1 ppb to get rid of the units. Four data points are excluded from the analysis, because the amounts of toluene in the samples are lower than the lowest values in the calibration and therefore our error estimates are not reliable. We excluded one more data point from the analysis which we regard as an outlier (its  $\delta$  value is about 3‰ higher than those of the neighbouring data points from the same flight, although the mixing ratios are almost the same).

We apply two linear fits, one to the whole data set and one only to the data points from 2 November 2008, the day on which most of the free tropospheric samples were taken. Both fits yield a high correlation coefficient (Pearson R = -0.90 and -0.94, respectively), indicating that the data follow the theory nicely and the assumptions above are justified. For the whole data set we find  $\varepsilon_{\text{eff}} = 5.10 \pm 0.76\%$  and for the data

from 2 November 2008  $\varepsilon_{\text{eff}} = 4.1 \pm 1.1 \%$ . These values match within their  $\sigma$ -intervals, therefore we conclude that the dynamical and photochemical situation at least did not

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change much over the time period from 26 October 2008 to 7 November 2008 and that the results we gain by using the whole data set are quite representative for this period.

If we consider the error bars,  $\varepsilon_{\text{eff}} = 5.10 \pm 0.76\%$  equals  $\varepsilon_{\text{OH}} = 5.95 \pm 0.28\%$  (see Sect. 2). In other words, our results show no significant influence of dilution in the lower

<sup>5</sup> free troposphere during the time period we span with our measurements. Decreases of the toluene concentration may be caused only by reactions with OH. Since the free troposphere is much less turbulent than the boundary layer and photochemistry generally plays a dominant role there, our findings seem to be plausible.

#### 5.3 Photochemical age

<sup>10</sup> As described in Sect. 2 there are two ways to estimate the photochemical age  $[OH]_{avg} t$ of the studied compounds in an air mass: on the one hand, based on the VMR ratio of two compounds with different lifetimes and a known emission ratio; on the other hand, based on the isotope ratio  $\delta$  of a single compound with a known source isotope ratio  $\delta_0$ . To distinguish between the two methods we want to refer to the results based on volume mixing ratios as  $([OH]_{avg} t)_{VMR}$  and to the results based on isotope ratios as  $([OH]_{avg} t)_{\delta}$ . In the further discussion we assume that toluene and benzene share the same sources (e.g. traffic), so we may use these two compounds to calculate  $([OH]_{avg} t)_{VMR}$  and compare the results to  $([OH]_{avg} t)_{\delta}$  derived from toluene  $\delta$  values.

The VMR emission ratios  $c_0(\text{toluene})/c_0(\text{benzene})$  reported in the literature range from about two to about four (e.g. Roberts et al., 1984; Gelencsér et al., 1997; Kourtidis et al., 2002; de Gouw et al., 2005; Warneke et al., 2007). During ZEPTER-2 groundbased measurements yielded a ratio of 1.8 in the city of Ravensburg (Urban, 2010). Therefore we estimate the emission ratio to be  $c_0(\text{toluene})/c_0(\text{benzene}) \approx 1.8$ ; the source  $\delta$  value of toluene is estimated to be  $\delta_0 = -28.2\%$  (see Sect. 5.1).

Figure 13 shows the photochemical ages, based on these source values, for all data obtained during the campaign. Obviously, the absolute values of  $([OH]_{avg} t)_{VMR}$  and  $([OH]_{avg} t)_{\delta}$  differ strongly. This is not surprising, since the source values used are



just rough estimates and therefore may produce an offset between ([OH]<sub>avg</sub> t)<sub>VMR</sub> and ([OH]<sub>avg</sub> t)<sub> $\delta$ </sub>.

Two separate linear fits are applied, to the PBL data and to the free troposphere data, which give slopes of  $2.55 \pm 0.58$  and  $0.91 \pm 0.29$ , respectively. A slope unequal to one cannot be explained by inappropriate source values, since these do not influence the slope. As already mentioned (see Sect. 2), we would expect the two methods to give different results, if air masses of different ages have mixed. Obviously, in this case, heavy mixing in the PBL distorted ([OH]<sub>avg</sub> *t*)<sub>VMR</sub>.

The slope of the free troposphere data does not deviate significantly from one. This result supports the assumption we made in Sect. 5.2, i.e. that the PBL acts as a more or less uniform VOC emission source for the free troposphere above, and it agrees well with the finding, that mixing plays a minor role in the free troposphere.

The strong scatter of the data is not surprising, either. Air mass exchanges between the PBL and the free troposphere mainly occur in the form of single, localised events,

e.g. due to rising thermals. The PBL can therefore only on average be regarded as a homogenious VOC emission source (reflected by the "correct" slope of the fit line).

### 6 Summary and outlook

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During ZEPTER-2 whole air samples were collected in the PBL and the lower free troposphere using the whole air sampler ZEBIS on board the Zeppelin NT and were afterwards analysed in the laboratory. The GC-C-IRMS in use was carefully calibrated and characterised in order to identify possible problems and to estimate the measurement errors.

During one flight (25 October 2008) we sampled rather fresh emissions of toluene in the PBL. Using the concept of two-endpoint-mixing, we derived a toluene source isotope ratio of  $\delta_0 = -28.2 \pm 0.5\%$ .

We applied the concept of the effective KIE on the data obtained in the lower free troposphere and found, that the toluene mixing ratios in this layer were influenced much





more by chemical degradation than by dilution processes. In the free troposphere we found no evidence for dilution.

Furthermore, we calculated the photochemical age of air masses in two different ways (based on toluene and benzene mixing ratios and toluene isotope ratios, respec-

<sup>5</sup> tively) and compared the results. As expected, the two methods yielded quite different results in the PBL, probably due to strong mixing, but similar results in the free troposphere.

Our results show, that it is possible to measure VOC mixing ratios and isotope ratios in the PBL and the free troposphere with sufficient precision to gain meaningful infor-<sup>10</sup> mation about the state of the atmosphere. Therefore, our study is an important proof of concept for further activities. As an outlook, we want to mention that ZEBIS was modified and took part in another campaign (VERDRILLT) in spain aboard a CASA 212 AR aircraft (Linke, 2012). A new whole air sampler (MIRAH) for deployment on the German research aircraft HALO has been developed and successfully tested during the <sup>15</sup> aircraft campaigns TECHNO and TACTS. The laboratory system has been improved (e.g. better chromatographic separation, additional mass spectrometer for compound identification).

Acknowledgements. We gratefully thank M. Gallus and the Atmospheric Chemistry Group at the University of Wuppertal for measuring VOC mixing ratios in standard B and F. Rohrer,
 Institute for Energy and Climate Research (IEK-8, Troposphere), Research Centre Jülich, for providing the CO data. Special thanks go to F. Bühler, H.-P. Heuser, P. Knieling, C. Linke, and H. Spahn for their support during ZEPTER-2 and to C. Linke and D. Offermann for many helpful discussions during the preparation of this paper. The ZEPTER-2 project was financially supported by the German Federal Ministry of Education and Research under grant number 01LP0803A.

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 Table 1. Overview of the analysed flights.

Date	MEZ	Flight area		Flight profile
25 Oct 2008	14:25–17:40	Lake Constance	47°40′ N 9°11′ E	vertical profile
26 Oct 2008	12:45–16:45	Altdorf forest	47°51′ N 9°41′ E	vertical profile
2 Nov 2008	12:00-15:30	Tettnang forest	47°38′ N 9°34′ E	constant altitude
2 Nov 2008	16:10–19:00	Tettnang forest	47°38′ N 9°34′ E	constant altitude
7 Nov 2008	10:05–14:25	Large-scale	48°3′ N–47°29′ N; 9°1′ E–9°48′ E	constant altitude
	Date 25 Oct 2008 26 Oct 2008 2 Nov 2008 2 Nov 2008 7 Nov 2008	Date         MEZ           25 Oct 2008         14:25–17:40           26 Oct 2008         12:45–16:45           2 Nov 2008         12:00–15:30           2 Nov 2008         16:10–19:00           7 Nov 2008         10:05–14:25	Date         MEZ         Flight area           25 Oct 2008         14:25–17:40         Lake Constance           26 Oct 2008         12:45–16:45         Altdorf forest           2 Nov 2008         12:00–15:30         Tettnang forest           2 Nov 2008         16:10–19:00         Tettnang forest           7 Nov 2008         10:05–14:25         Large-scale	Date         MEZ         Flight area           25 Oct 2008         14:25–17:40         Lake Constance         47°40′ N 9°11′ E           26 Oct 2008         12:45–16:45         Altdorf forest         47°51′ N 9°41′ E           2 Nov 2008         12:00–15:30         Tettnang forest         47°38′ N 9°34′ E           2 Nov 2008         16:10–19:00         Tettnang forest         47°38′ N 9°34′ E           7 Nov 2008         10:05–14:25         Large-scale         48°3′ N–47°29′ N; 9°1′ E–9°48′ E



Fig. 1. Gas flow system of the whole air sampler ZEBIS; one canister is shown as an example, the total number of canisters is eight.





**Fig. 2.** VOC mixing ratios versus detector response for three dilution steps of standard B; each data point is the average of four to six measurements. The error bars of the mixing ratios reflect the uncertainty of standard B's composition as well as the uncertainty of the dilution process, the error bars of the average peak areas represent the standard errors. Most error bars are smaller than the symbol size.





**Fig. 3.** Isotope ratios of benzene and toluene versus major ion peak areas for three dilution steps of standard B; each data point is an average of four to six measurements. The error bars of the isotope ratios represent the standard deviations. Error bars of the peak area are not shown, since they are not relevant for the constant fit.





**Fig. 4.** Averaged major ion peak areas of benzene and toluene for different sample humidities; the error bars represent the standard deviations of the peak areas. The uncertainty of the humidity values is roughly 5% RH (see text). We find a small but nevertheless significant systematic increase of the peak areas with increasing humidity.











**Fig. 6.** Standard deviations of the peak area versus the mean peak area for five peaks of different sizes; the error bars represent the uncertainties of the standard deviation (see text). A linear fit (red line) is applied to the data.





**Fig. 7.** Standard deviations of the  $\delta^{13}$ C values versus the mean peak areas for five peaks of different sizes; the error bars represent the uncertainties of the standard deviations (see text). Two power function-fits are applied to the data: with a free exponent (blue line) and with an exponent fixed to -0.5 (red line, for details see text).





**Fig. 8.** CO mixing ratios, measured on 25 October 2008; the time resolution is 1 s. Data points from time periods during which canisters were filled, are coloured red. Blue lines mark the estimated height of the different atmospheric layers.





**Fig. 9.** Histogram of all toluene  $\delta^{13}$ C values measured during ZEPTER-2; the mean error is 0.6‰, i.e. roughly half the bin width.





**Fig. 10.** Vertical profiles (height a.g.l.) of toluene volume mixing ratios and  $\delta^{13}$ C values in the planetary boundary layer, measured on 25 October 2008.





**Fig. 11.**  $\delta^{13}$ C values of toluene versus the inverse volume mixing ratio; a linear fit (Pearson R = 0.87) is applied to the data.











**Fig. 13.** Comparison of photochemical ages:  $([OH]_{avg}t)_{VMR}$  (derived from toluene/benzene ratios) versus  $([OH]_{avg}t)_{\delta}$  (derived from toluene  $\delta^{13}$ C values); the source values were estimated rather roughly (see text) and their uncertainties are not included in the error bars. Data from the PBL are represented by blue squares, data from the free troposphere by black dots. Two linear fits are applied (green: to PBL data, slope  $2.55 \pm 0.58$ ; red: to free troposphere data, slope  $0.91 \pm 0.29$ ). A line y = x (purple) is shown for comparison.

