We would like to thank both referees for their positive comments and the valuable suggestions for fixing some details, which will help us to prepare a revised manuscript meeting the high standards of ACP.

Both referees agree that isotope ratio measurements are potentially a very useful tool for investigating the atmospheric chemistry of volatile organic compounds (VOC), although referee 2 correctly points out that, unless additional information is available, there can be multiple solutions for explaining observed mixing ratios and carbon isotope ratios. (see below).

Referee 1
- Page8Line23-Page9Line2: reformulate. This information is not included in Fig. 2. Generally, the caption of Figure 2 must be more concrete. Is this for benzene, or for all VOC?
and
- Pages48-50: captions Fig. 3-5 in the main manuscript should contain the VOC of interest: 'Example plots ... VOC (benzene/toluene)...' (like in the supplement)

In our revised version the examples from paper and supplement are combined in the paper to assure that the information mentioned in the text is consistent with the figures presented in the paper itself.

- Page9Lines5-7: reformulate. 'There is a strong dependence between...' and what?
Done: "There is a strong dependence between carbon isotope ratios of ethylbenzene and o-xylene, ethylbenzene and p,m-xylene as well as o-xylene and p,m-xylene. The correlations between the carbon isotope ratio of toluene and the C_2-alkylbenzenes are only weak and no correlation between the carbon isotope ratios of benzene and any of the other aromatic VOC is found (Fig. 4, Table 9).

- Page44Lines33-34: Sentence 'The bars represent the mean concentration ratios normalized relative to the average of all available ratios' needs some more explanation, at least in text.
Changed: (now page 45)"The bars represent the ratio of the mean concentration ratios for the chosen interval of ∫[OH]dt over the average for all concentration ratios."

Generally, the axes of Fig.9-10 should be described.
Axis labels added

Editorial revisions:

- Page5Line17: replace second 'δ13A C' by 'δ13S C'
Done

- Page8Lines2and 22: replace 'Fig.2' by' Fig.3'
- Page8Line12: replace 'Figure 3' by' Figure 2'
- Page9Line14: replace 'Fig.3' by' Fig.2' and later in manuscript.
Figure 2 and 3 have been switched in order to be consistent with the text and to make sure that the first mentioning of the figures is consistent with their numbering.

- Page40Table11: in third row insert a 'but' before $<\delta13\text{Cglobal}$

Done

Referee 2:

General comments:

I am sure, one can generate a scenario where two air masses containing emissions from two nearby sources or from a nearby and a distant source are mixed before reaching the sampling site leading to exactly the same emission ratios and isotope ratios because of different transport times, different emission ratios and different isotope ratios at emission. In this case you need another independent information (such as backward trajectories) to interpret your data, which generally can be done.

Reply: Meaningful constraints for such underdetermined systems are typically derived by including additional information, in this work we use the carbon isotope ratio of emissions, the emission ratios, and wind direction. It has to be understood that in a complex urban environment even with such additional information, there always will be a range of possible solutions. However, in many cases the use of isotope ratios can help to substantially reduce the range of valid solutions. In this study the information on photochemical VOC processing derived from isotope ratios eliminates the possibility that the observed VOC concentration ratios can be explained by photochemical aging of VOC emissions from known sources. The referee mentions the possible use of back trajectories for identification of VOC sources. In this work we decided to only use wind directions for several reasons. Based on the photochemical age determined from the carbon isotope ratios it can be concluded that in many cases the observed VOC levels are dominate by local (nearby) emissions. In this case wind direction provides the necessary information for filtering data sets based on impact from different point sources. The measurements were made in the greater Toronto area, an urban region with about five million inhabitants, dense traffic and a number of industrial facilities emitting substantial amounts of aromatic VOC. While back trajectories may allow a more detailed interpretation of individual measurements, filtering data sets by wind direction allows clear and easy testing for statistically meaningful differences.

Here, the interpretation is based on measurement of samples with extremely long sampling times. How do these sampling times of 24 or even 64 hours affect the interpretation of the results? During these sampling times you may sample completely different air masses of different origin, transport times, emission ratios and source isotope ratios.

In the conclusion you state: ".. this does not allow differentiating between changes during sampling and mixing of air masses." I am not sure what you mean by "changes during sampling" (see below), changing emissions, changing wind directions? But nevertheless, don't you have to do this for your interpretation of the data?

Reply: Indeed, this is a general problem for the interpretation of all measurements averaging over time intervals long enough to allow changes in wind direction, vertical mixing, emission rates etc. This problem is pointed out in our paper. In other words the averages do (obviously) not allow identification of changes with time within the sampling period. In the absence of published detailed data sets with higher time resolution it is not possible to differentiate between mixing of air masses and sampling air masses with different photochemical ages during the sampling period. However, this problem should not be confused with the fact that the observations still represent the correct

average values for the measurement intervals and can be interpreted as such. We modified our conclusions to clarify this point:

(P21, L22- P22,L5) This is useful for determining meaningful averages from a limited set of measurements, However, this does not allow differentiating between changes of ∫[OH]dt with time during the sampling period and mixing VOC with different ∫[OH]dt in the atmosphere prior to sampling. Separating the impact of the two processes on the VOC isotope ratio would require VOC isotope ratio measurements in samples collected during very short time periods of only a few minutes or less. To our knowledge no such VOC isotope ratio measurements in an urban environment have been published.

Specific comments:
Title:
Change the title to "... ambient **aromatic** volatile organic compounds" because only these compounds are investigated (see first sentence of the abstract). 2
Done

P 4, L 5-6:
"... mixing ratios that are 3 to 5 orders of magnitude lower ... "
With respect to which reference value?
Clarified: "mixing ratios that are 3 to 5 orders of magnitude lower than for methane or carbon monoxide,
In the sentences before μmol mol-1 and nmol mol-1 are given. Maybe, giving mixing ratios here would be better.
nmol mol^{-1} etc. are IUPAC recommended units for mixing ratios

P 4, L 11:
Reference: Eckstaedt et al, 2012
Please correct reference (also in the References):
The author is Christiane Vitzthum-von Eckstaedt: Vitzthum-von Eckstaedt, C. .....
Done

P 4, equation 1 and P5, equation 2:
Skip "x 1000 ‰", see guidelines by Coplen 2011.
Literature is full of different ways to express delta values. In our opinion this is a matter of Journal style. The current form is based on a suggestion from the editor, if necessary we will make required changes in the final manuscript.
P 5, L 10 and L 17:
" ... is usually defined as the time integral of the OH concentration for an air mass ..."
In line 17 the "photochemical age" is mentioned. Using the isotope hydrocarbon clock approach, the photochemical age of the molecules of interest is determined. This is not necessarily the age of the air mass. Maybe, this should be mentioned here.
Reply: Indeed, it is one of the findings of this paper that different VOC have different PCAs and that it is therefore not correct to use the term PCA of an air mass. However, the "VOC ratio clock" assumes identical PCAs for different VOC, which in some literature is referred to as PCA of an air mass. We modified this part to avoid the impression of an inconsistency between introduction and discussion: "The term "photochemical age" is used for quantification of photochemical processing of a compound and it is usually defined as the time integral of the OH concentration (∫[OH]dt). Originally VOC concentration ratios were used to determine ∫[OH]dt, an approach that often is

referred to as hydrocarbon clock (Kornilova et al., 2015b; Stein and Rudolph, 2007; Kleinman et al., 2003; Rudolph et al., 2003; Thompson et al., 2003; Rudolph and Czuba, 2000; Jobson et al., 1999; Jobson et al., 1998). This concept implies that ∫[OH]dt is identical forthe VOC used for the calculation and sometimes the term photochemical history of an air masses is used (Parrish et al., 1992)."

P 5, L17:

The second "$\delta_A{}^{13}C$" must read "$\delta_S{}^{13}C$".

Done

P 7, 1. Paragraph

You used extremely long sampling times (24 h and even 64 h). Did you check the breakthrough volume of your sampling device? Can you comment on that?

Reply: In the cited paper by Kornilova et al. (which describes the measurement method) it is shown that (for the sampling conditions used) breakthrough does not occur for the studied VOC. We do not think that it is necessary to repeat details which are already published in a paper which describes and characterizes the used measurement method.

P 8, Chapter 3.1

In this chapter references to all Figures have to be carefully checked.

Figure 3 is obviously a reference to Figure 2. In the Figure Caption to Figure 2 you should change "VOC" to "benzene".

P 8, L 22:

Figure 3 does not show the change of isotope ratios with season. Should there a Figure be added? Figure 4 shows only benzene/toluene, Figure 5 shows only toluene, not all VOC

In our revised version the examples from paper and supplement are combined in the paper to assure that the information mentioned in the text is consistent with the figures presented in the paper itself. Figure 2 and 3 have been switched in order to be consistent with the text and to make sure that the first mentioning of the figures is consistent with their numbering.

P 8, L 5:

"... strong dependence between C$_2$-alkylbenzenes ..."

Strong dependence of C$_2$-alkylbenzenes of what? Please specify.

Changed: There is a strong dependence between carbon isotope ratios of ethylbenzene and o-xylene, ethylbenzene and p,m-xylene as well as o-xylene and p,m-xylene. The correlations between the carbon isotope ratio of toluene and the C$_2$-alkylbenzenes are only weak and no correlation between the carbon isotope ratios of benzene and any of the other aromatic VOC is found (Fig. 4, Table 9).

P 9, L 14:

Figure 3 does not show isotope ratios (see above).

Changed, see above

P 10, L 1:

Varying **the** extent of ...

Changed to: Variations in the extent of

P 10, L 6:

What do you mean by "steady state ☐-values"?

Clarified: Here $\delta^{13}C_{steady\ state}$ is the hypothetical average carbon isotope ratio of an atmospheric VOC in steady state between emissions and loss by reaction with the OH-radical.

P 10, L 19:
Again a wrong reference to Figure 3.
Fixed, see above

P 15, 2. Paragraph:
".. the observations are incompatible with the expected change of VOC concentration ratios"
What does that mean? Can that simply be explained by significantly different emission ratios? Is there any evidence for that?
Reply: Indeed, it is one of the conclusions drawn from the carbon isotope ratios that there must be sources with different emission ratios, which is discussed in more detail later in the paper.
P 16, 1. Paragraph:
What could be the large difference in the sources? All compounds are anthropogenic compounds emitted from similar sources with not too different emission ratios.
Reply: We are aware that there are quite a few publications, several of them cited in our paper, which base the interpretation of changes in VOC concentration ratios on this assumption. It is one of the conclusions drawn for the combination of isotope ratio and concentration ratio data that this assumption is (in our study) not justified. A more detailed look into sources with different emission ratios is presented later in the discussion.

P 17, L 15:
Here a reference to Figure 15 is given regarding nearby sources. What are these sources? Can they be specified?
Reply: Figure 12? The information is taken from the Canadian National Pollutant Release Inventory (as explained in the caption). This inventory is publicly available and cited. For the purpose of this paper the emission data are the relevant pieces of information. A presentation and discussion of the type of facilities and reasons for differences in emission ratios would not only add unnecessary length to our paper, but also distract from the main focus of the paper. Any reader interested in details can easily access the cited emission inventory and there are numerous publications discussing the factors that determine emission ratios.

P 21, L 15:
In the conclusion you state: ".. this does not allow differentiating between changes during sampling and mixing of air masses." What do you mean by "changes during sampling"?
Changed: "In this study sampling periods of at least several hours, in most cases of one day were used. This is useful for determining meaningful averages from a limited set of measurements, However, this does not allow differentiating between changes of ∫[OH]dt with time during the sampling period and mixing VOC with different ∫[OH]dt in the atmosphere prior to sampling. Separating the impact of the two processes on the VOC isotope ratio would require VOC isotope ratio measurements in samples collected during very short time periods of only a few minutes or less. To our knowledge no such VOC isotope ratio measurements in an urban environment have been published.

Table 3:
Some numbers are not consistent with Table 2.
In Table 2: Toluene 0.64 ± 0.44 - in Table 3: Toluene 0.63 ± 0.44
In Table 2: Ethylbenzene: 0.07 ± 0.05 - in Table 3: Ethylbenzene: 0.06 ± 0.17
Corrected

Table 4:

Is there any possible explanation for the huge difference in the concentration ratios for toluene/benzene and xylenes/benzene for the facilities Toronto? Is this due to differences between automobile exhaust and evaporation losses? Is it possible to specify this?

Reply: Table 14?: The Canadian National Pollutant Release Inventory provides emission data for (industrial) facilities, but no information on specific processes (or solvents and chemicals used). This information is rarely available (often proprietory). It can be speculated that for benzene, which is a known carcinogenic compound, emission controls in or close to densely populated areas are very tight. However, the important point is that our findings are consistent with the very low benzene emissions within the Toronto area. A discussion of processes and regulations behind emission data would be a paper with a very different focus.

References:
Please correct the reference to Niedojadlo et al.
The complete reference is:
... for NMVOCs, in: Simulation and Assessment of Chemical Processes in a Multiphase Environment, NATO Science for Peace and Security, Series C: Environmental Security, ed. by I. Barnes and M. M. Kharyatonov, Springer, the Netherlands, 2008.
Done

Figure 9 and 10:
Labeling of the y-axes are missing
Axis labels added

Stable carbon isotope ratios of ambient aromatic volatile organic compounds

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1   **Abstract.** Measurements of mixing ratios and stable carbon isotope ratios of aromatic volatile

2   organic compounds (VOC) in the atmosphere were made in Toronto (Canada) in 2009 and 2010.

3   Consistent with the kinetic isotope effect for reactions of aromatic VOC with the OH-radical the

4   observed stable carbon isotope ratios are on average significantly heavier than the isotope ratios

5   of their emissions. The change of carbon isotope ratio between emission and observation is used

6   to determine the extent of photochemical processing (photochemical age, $\int[OH]dt$) of the

7   different VOC. It is found that $\int[OH]dt$ of different VOC depends strongly on the VOC

8   reactivity. This demonstrates that for this set of observations the assumption of a uniform

9    $\int[OH]dt$ for VOC with different reactivity is not justified and that the observed values for

10   $\int[OH]dt$ are the result of mixing of VOC from air masses with different values for $\int[OH]dt$.

11   Based on comparison between carbon isotope ratios and VOC concentration ratios it is also

12   found that varying influence of sources with different VOC emission ratios has a larger impact

13   on VOC concentration ratios than photochemical processing. It is concluded that for this data set

14   the use of VOC concentration ratios to determine $\int[OH]dt$ would result in values for $\int[OH]dt$

15   inconsistent with carbon isotope ratios and that the concept of a uniform $\int[OH]dt$ for an air mass

16   has to be replaced by the concept of individual values of an average $\int[OH]dt$ for VOC with

17   different reactivity.

18

19   **1. Introduction**

20   Anthropogenic volatile organic compounds (VOC) are important pollutants that play key

21   roles in the production of ozone, aerosol formation and significantly affect regional air quality in

22   general. Their total annual global emission is estimated at 150 TgC per year (Niedojadlo et al.,

23   2008; Piccot et al., 1992). On a global scale, about 60 to 80% of anthropogenic emissions are

2

1 associated with fossil fuel production, its distribution, use and storage, and up to 20 to 30% with

2 biomass burning (Reimann and Lewis, 2007; Rudolph et al., 2002). Since anthropogenic VOC

3 are rather diverse, classification of their emission sources is quite challenging, thus frequently

4 these emissions are grouped according to the commodities or activities with which they are

5 associated (Niedojadlo et al., 2008; Sawyer et al., 2000; Piccot et al., 1992; Watson et al., 1991),

6 for instance, vehicular exhaust, evaporated fuel, solvent use, etc. Aromatic VOC are an important

7 part of anthropogenic emissions (up to 44%), with benzene, toluene, ethylbenzene and xylenes as

8 major components (up to 75%) (Jang and Kamens, 2001).

9   In the atmosphere many VOC undergo chemical transformation via gas-phase reactions

10 with hydroxyl radicals (OH), nitrate radicals (NO_3), chlorine radicals (Cl) and ozone (O_3), with

11 OH contributing the most to these oxidation processes. This oxidative processing is especially

12 important for aromatic VOC and heavy alkanes, since it may result in the formation of

13 oxygenated and nitrated products that may contribute to the formation of secondary organic

14 matter (Saccon et al., 2015; Irei et al., 2006; Forstener et al., 1997).

15   It has been shown by many studies that the use of stable carbon isotope ratios is

16 beneficial in providing insights into photochemical transformation and physical processing of

17 ambient volatile organic compounds (Gensch et al., 2014; Rudolph, 2007; Stein and Rudolph,

18 2007; Ghosh and Brand, 2003; Goldstein and Shaw, 2003; Rudolph et al., 2003; Rudolph et al.,

19 2002; Meier-Augenstein, 1999). McKinney et al. (1950) introduced one of the first mass

20 spectrometers that were able to differentiate carbon and oxygen isotopologues in carbon dioxide

21 and oxygen molecules (Richet et al., 1977; McKinney et al., 1950). This development was

22 followed by extensive studies of the stable carbon isotope composition of carbon monoxide,

23 carbon dioxide and methane in ambient samples (Brenninkmeijer et al., 1995; Lowe et al., 1994;

3

1   Stevens et al., 1972) and theoretical modelling and interpretations began to be presented

2   (Brenninkmeijer et al., 1995; Kaye, 1987; Richet et al., 1977; Craig, 1953).

3   While some trace gases, such as methane, carbon monoxide, or carbon dioxide are

4   present in the atmosphere at μmol mol^{-1} or high nmol mol^{-1} levels and are easy to measure with

5   state of the art isotope ratio mass spectrometry, most VOC are present at mixing ratios that are 3

6   to 5 orders of magnitude lower than for methane or carbon monoxide, thus making the

7   measurement of their isotopic composition challenging. In 1997 a method which allowed the

8   determination of stable carbon isotope composition for ambient compounds present at low

9   mixing ratios was introduced (Rudolph et al., 1997). It was followed by isotope ratio

10   measurements of various VOC, where it was applied and expanded (Kornilova et al., 2015a;

11   Kornilova et al., 2015b; Kawashima and Murakami, 2014; Wintel et al., 2013; Vitzthum-von

12   Eckstaedt et al., 2012; Giebel et al., 2010; Redeker et al., 2007; Nara et al., 2006; Turner et al.,

13   2006; Komatsu et al., 2005; Czapiewski et al., 2002; Rudolph et al., 2002; Saito et al., 2002).

14   Still, the number of publications containing measurements of isotope ratios of ambient VOC and

15   their sources is very limited (Kornilova et al., 2015b; Gensch et al., 2014; Elsner et al., 2012).

16   The stable carbon isotope ratio is determined by the ratio of ^{13}C to ^{12}C atoms in the

17   sample and is usually expressed in delta notation (δ^{13}C) relative to a reference value (Vienna

18   Peedee Belemnite, VPDB) with ^{13}C/^{12}C = 0.0112372 (Craig, 1953)). Since changes in ^{13}C/^{12}C

19   are small, δ^{13}C is expressed in parts per thousand (‰) (Eq. 1).

20

$$\delta^{13}C = \frac{R_{sample}(^{13}C / {}^{12}C) - R_{VPDB}(^{13}C / {}^{12}C)}{R_{VPDB}(^{13}C / {}^{12}C)} \times 1000‰$$

Eq. 1

21

4

1

The presence of ^{13}C isotopes slightly affects the reaction rate of the molecule, as ^{13}C containing

isotopologues react slower than ^{12}C-only isotopologues. The relative difference between these

rate constants (^{12}k and ^{13}k), known as kinetic isotope effect (KIE), is expressed in epsilon

notation (ε) in parts per thousand (‰) (Eq. 2).

$$\varepsilon_{OH} = \frac{^{12}k - ^{13}k}{^{13}k} \times 1000‰ \qquad \text{Eq. 2}$$

6

Since ^{12}C is more reactive, the sample gets enriched in ^{13}C with time and the magnitude of this

depends on the extent of processing as well as the KIE.

The term "photochemical age" is used for quantification of photochemical processing of

a compound and it is usually defined as the time integral of the OH concentration for an air mass

($\int[OH]dt$). Originally VOC concentration ratios were used to determine $\int[OH]dt$, an approach

that often is referred to as hydrocarbon clock (Kornilova et al., 2015b; Stein and Rudolph, 2007;

Kleinman et al., 2003; Rudolph et al., 2003; Thompson et al., 2003; Rudolph and Czuba, 2000;

Jobson et al., 1999; Jobson et al., 1998). This concept implies that $\int[OH]dt$ is identical for the

VOC used for the calculation and sometimes the term photochemical history of an air masses is

used (Parrish et al., 1992). The isotope hydrocarbon clock approach is similar, but uses stable

carbon isotope ratios (Rudolph and Czuba, 2000) (Eq. 3):

$$\int[OH]dt = \frac{\delta_A\,^{13}C - \delta_S\,^{13}C}{k_{OH}\varepsilon_{OH}} \qquad \text{Eq. 3}$$

18

1 where $\int[OH]dt$ is the average photochemical age, $\delta_A{}^{13}C$ and ~~$\delta_A{}^{13}C$~~ $\delta_S{}^{13}C$ are the stable carbon

2 isotope compositions of ambient and freshly emitted VOC respectively, k_{OH} is the rate constant

3 for the reaction of VOC and OH, and ε_{OH} is the KIE (Eq.2). <u>Since this approach only uses one</u>

4 <u>compound for calculating $\int[OH]dt$ it is possible to determine an average value of $\int[OH]dt$ for</u>

5 <u>individual VOC.</u>

6   In this paper we present stable carbon isotope ratios of ambient aromatic VOC measured

7 at a suburban area in 2009 and 2010. The results will be used to determine $\int[OH]dt$ for VOC with

8 different reactivity and to determine the impact of photochemical processing on the change in

9 VOC concentration ratios.

10

11 **2. Materials and method**

12   Selective VOC sampling from ambient air was done using cartridges (13 to 15 cm long,

13 1/4" OD) filled with Carboxene 569, a mass flow controller and a diaphragm pump with a

14 sampling flow rate set between 10 and 50 mL min^{-1} as described in detail by Kornilova et al.

15 (2015a). VOC were quantitatively extracted from cartridges using a thermal desorption unit with

16 helium as a carrier gas (60 to 80 mL min^{-1}) at 553 K for 40 min. Desorbed VOC were focused

17 using a two stage preconcentration system. Compounds were then separated using a HP5890

18 Series II gas chromatograph equipped with a DB-1 column (100 m, 0.25 mm ID, 0.5μm film

19 thickness). Separated compounds were directed to a combustion interface (1/4" OD, 0.5 mm ID,

20 44 cm long ceramic tube with copper, nickel and platinum wires inside) where they were

21 converted to H_2O and CO_2. H_2O was removed by Nafion tubing, while CO_2 was directed into an

22 Isotope Ratio Mass Spectrometer (IRMS) where m/z 44, 45 and 46 were analysed. Performance

23 characteristics of the sampling and analysis procedures discussed by Kornilova et al. (2015a) are

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1 summarized in Table 1. The accuracy of $\delta^{13}C$ measurements was 0.5 ‰ for sample masses

2 exceeding 3 ng of the target compound. For a typical 24h sample this mass corresponds to an

3 atmospheric mixing ratio of 20 to 30 pmol mol^{-1}.- $\delta^{13}C$ results are not reported here for sample

4 masses that were lower than this.

5 Ambient VOC were collected at a site located in the Northern part of the Greater Toronto

6 Area (GTA) on the premises of the Downsview location of Environment Canada (43°46′N,

7 79°28′W) from 2009 to 2010 (Fig. 1). Samples were collected from Monday to Thursday over 24

8 h time periods (7 to 7 AM), Friday sampling lasted 6 to8 h (7 AM to 4 PM) and Friday to Sunday

9 samples were collected over 64 h (4 PM on Friday to 7 AM on Monday). Most samples were

10 collected between Fall 2009 and Winter 2010 (October 2009 to February 2010), with some

11 additional samples collected in March 2010, and from August 2010 to September 2010. The

12 average sampling flow rate was 24 to 25 mL min^{-1}. In total, 74 samples were analysed for VOC

13 concentrations and carbon isotope ratios, although in several of those samples carbon isotope

14 ratios could only be determined for some of the target compounds.

15

16 **3. Results and discussion**

17 **3.1 Overview**

18 Averages and some basic statistics for concentrations of ambient aromatic VOC collected

19 in Toronto (2009 to 2010) are summarized in Table 2. Mixing ratios determined for the targeted

20 VOC are in the low to mid pmol mol^{-1} range and are similar to mixing ratios reported by

21 Canada's National Air Pollution Surveillance Program (NAPS, 2009-2010) for downtown

22 Toronto and two suburban locations in Toronto (Table 3). The observed mixing ratios are also

23 within the range of values reported in several measurement series at various locations in North

7

1 America (Kornilova et al., 2015b; Jobson et al., 2004; Pankow et al., 2003; Riemer et al., 1998;

2 Hagerman et al., 1997; Roberts et al., 1984).

3   Except for benzene, the VOC mixing ratios are linearly correlated with each other with y-

4 axis intercepts close to zero. Except for the linear correlation between the mixing ratios of

5 ethylbenzene and o-xylene, the y-axis intercept is statistically not different from zero (95%

6 confidence interval) (Table 4, Fig. 2). The VOC concentration ratios observed are within or close

7 to the range of values reported in literature. Exceptions are the toluene over benzene ratio and the

8 p,m-xylene over o-xylene ratio, which are higher than previously reported ratios (Table 5) but

9 similar to the ratios that can be derived from the NAPS data reported for other locations in

10 Toronto in Table 3.

11   Averages and basic statistics for measured carbon isotope ratios are summarized in Table

12 6. The majority of the determined $\delta^{13}C$ values are comparable with those observed in other

13 ambient studies (Table 7). The only exception is the value reported by Redeker et al. (2007) for

14 benzene, which is about 3 ‰ lighter than the average for our measurements, and close to the 10th

15 percentile of our observations.

16   Figure 3 shows the frequency distribution for the measured carbon isotope ratios. The

17 lower end of the distribution is close to the carbon isotope ratios reported in literature for their

18 emissions (Table 8). The only exception are the benzene and toluene carbon isotope ratios

19 reported by Turner et al. (2006) for industrial stack emissions which are about 3 to 5 ‰ heavier

20 than the lower end of our observations. Turner et al. (2006) reported no details of the type of

21 industrial emissions studied and therefore the possible impact of such heavier industrial

22 emissions on ambient carbon isotope ratios cannot be evaluated. Only 13 of our 275 measured

23 carbon isotope ratios are significantly below the carbon isotope ratios reported by Rudolph et al.

8

1 (2002) for emissions in Toronto, whereas 186 observations are significantly heavier (95 %

2 confidence limit determined from the uncertainty of the emission ratios and measurement errors).

3   Overall, there is little systematic change of the carbon isotope ratios with season (Fig. 3).

4 The only significant exceptions are the carbon isotope ratios of the C_2-alkylbenzenes, which are

5 approximately 2 ‰ lighter in spring and fall compared to summer and winter (T-test, 99.9%

6 probability).

7   ~~There is no clear dependence between mixing ratios and carbon isotope ratios (Fig. 5),~~

8 ~~although in some cases the mixing ratios on average differed for different ranges of carbon~~

9 ~~isotope ratios (see below).~~ There is a strong dependence between carbon isotope ratios of ~~the C_2~~

10 ethylbenzene and o-xylene, ethylbenzene and p,m-xylene as well as o-xylene and p,m-xylene.

11 The ~~alkylbenzenes and some weak~~ correlations between the carbon isotope ratio of toluene and

12 the C_2-alkylbenzenes are only weak and ~~. N~~no correlation between the carbon isotope ratios of

13 benzene and any of the other aromatic VOC is found (Fig. 4, Table 9). None of the y-axis

14 intercepts of the linear regressions are significantly different from zero (95 % confidence

15 interval), which is consistent with the finding that the carbon isotope ratios of emissions for

16 different aromatic VOC are similar (Rudolph et al., 2002). There is no clear dependence

17 between mixing ratios and carbon isotope ratios (Fig. 5), although in some cases the mixing

18 ratios on average differed for different ranges of carbon isotope ratios (see below).

19

20 **3.2 Ambient carbon isotope ratios and atmospheric VOC processing**

21   The observed carbon isotope ratios cover a range of more than 8 ‰ (Fig. 3), which

22 cannot be explained by measurement errors (Table 1) or uncertainty of the carbon isotope ratios

23 of known VOC sources (Table 8). Although the existence of unidentified sources of VOC with

9

1   very heavy carbon isotope ratios cannot be completely ruled out, it is unlikely that this could

2   explain the observed variability of measured carbon isotope ratios since such an unidentified

3   source would have to be of approximately the same magnitude as the known sources to explain

4   the absence of a systematic dependence between VOC carbon isotope ratio and VOC mixing

5   ratios (Fig. 5).

6   Anderson et al. (2004) reported that the reaction of aromatic VOC with the OH-radical,

7   which is the dominant loss process for light aromatic VOC in the atmosphere, results in

8   enrichment of ^{13}C in the residual VOC. Variations in the rying extent of reaction with OH-

9   radicals can therefore explain the observed variability of carbon isotope ratios as well as the

10 absence of a significant number of δ^{13}C values lower than the δ^{13}C values of emissions (Table

11 8). Table 10 summarizes the rate constants and KIEs for the reaction of the studied compounds

12 with the OH-radical as well as the δ^{13}C values reported for their emissions in Toronto by

13 Rudolph et al. (2002). Included in Table 10 are also the δ^{13}C values calculated from $\delta^{13}C_{steady}$

14 $_{state}$= $\delta^{13}C_{emissions}$ +ε_{OH}. Here $\delta^{13}C_{steady\ state}$ is the hypothetical average carbon isotope ratio of an

15 atmospheric VOC for in steady state between emissions and loss by reaction with the OH-

16 radical. For comparison the average of measured δ^{13}C values is also given in Table 11.

17   The averages of the measured δ^{13}C values are consistently lighter than the predictions for

18 steady state. However, only for toluene and benzene, the least reactive of the light aromatic

19 VOC, this difference is statistically significant at the 99% confidence level. Since the

20 measurements were made at a location impacted by substantial emissions within a less than 10

21 km radius it is not surprising that for VOC with a short atmospheric residence time the average

22 carbon isotope ratio is closer to a steady state between emission and removal reaction than for

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10

1   less reactive VOC. Indeed, the Pearson product moment correlation coefficient for the difference

2   between steady state and average measured isotope ratios and atmospheric residence time is

3   0.863 and the R^2 for a linear correlation is 0.745. However, this is only based on data for 5

4   different compounds and the average of the carbon isotope ratios is the result of isotope ratio

5   measurements covering a wide range of $\delta^{13}C$ values (Fig. 3).

6   Table 11 shows a breakdown of measured $\delta^{13}C$ values into different ranges by

7   compound. The number of observations with $\delta^{13}C$ values heavier than steady state between

8   emission and removal is in the range of 25 % for the C_2-alkylbenzenes whereas for ~~benzene and~~

9   toluene less than 10 % of the observations fall into this range. For benzene, the by far least

10   reactive of the studied VOC, the percentage of data points close to steady state $\delta^{13}C$ values is

11   even smaller. There is no systematic dependence between the percentages of $\delta^{13}C$ values close to

12   the source isotope ratios and VOC reactivity. This is compatible with the concept that

13   photochemical aging is an important process resulting in changes in the carbon isotope ratios of

14   ambient VOC as well as the predicted dependence between carbon isotope ratio and the rate

15   constant for the atmospheric VOC removal reactions (Equation 3).

16   In principle these findings are similar to the change in VOC concentration ratios as result

17   of photochemical processing, which has been used to study and quantify photochemical VOC

18   processing in the atmosphere (Kleinman et al., 2003; Jobson et al., 1999; Jobson et al., 1998;

19   Parrish et al., 1992; Rudolph and Johnen, 1990). It has been shown that the ∫[OH]dt determined

20   from $\delta^{13}C$ values of VOC is a valid approximation for the age of the studied VOC even in the

21   case of mixing air masses with different values for ∫[OH]*dt* (Rudolph and Czuba, 2000), whereas

22   the use of VOC concentration ratios to quantify VOC processing requires an identical ∫[OH]*dt*

1   for VOC with different reactivity (Rudolph and Johnen, 1990), a condition that often is referred

2   to as photochemical age of the air mass (Parrish et al., 1992). The validity of the assumption of

3   an identical $\int[OH]dt$ for VOC of different reactivity can be tested by a comparison of carbon

4   isotope ratios predicted by Equation 3 for identical $\int[OH]dt$:

5

6 $$\frac{\delta_A^{A\,13}C - \delta_s^{A\,13}C}{\delta_A^{B\,13}C - \delta_s^{B\,13}C} = \frac{k_{OH}^A \varepsilon_{OH}^A}{k_{OH}^B \varepsilon_{OH}^B} \qquad\qquad \text{Eq. 4}$$

7   In Table 12 the slopes calculated for identical values for the average $\int[OH]dt$ of different

8   VOC are compared with the slopes determined from linear regression of measured carbon

9   isotope ratios. With the exception of the dependence between toluene and ethylbenzene, which

10   have similar reactivity towards the OH-radical, the calculated slopes differ substantially from the

11   observed slopes demonstrating that the assumption of an identical $\int[OH]dt$ for VOC with

12   different reactivity is not valid. This strongly points towards mixing air masses containing VOC

13   with different values for $\int[OH]dt$. This is consistent with the location of the sampling site at the

14   outskirts of a major city and a sampling duration that lasted at least several hours, in most cases

15   about one day.

16

17   **3.3 Photochemical age and mixing of air masses**

18   Carbon isotope ratios of VOC allow calculation of the average $\int[OH]dt$ of the individual

19   volatile organic compound without the requirement of a uniform $\int[OH]dt$ and therefore our

20   observations can be used to determine the $\int[OH]dt$ of VOC with different atmospheric life time

21   independent of assumptions about atmospheric mixing. Table 13 lists basic statistics for the

12

1   values of $\int[OH]dt$ determined from our $\delta^{13}C$ measurements based on Equation 3 using the kinetic

2   data and carbon isotope ratios of VOC emissions listed in Table 10.

3   Due to the uncertainty of the carbon isotope ratios of emissions and measurement errors

4   low values of $\int[OH]dt$ have large relative uncertainty. The consequence is a substantial number

5   of negative $\int[OH]dt$ values. Nevertheless, out of the 275 $\int[OH]dt$ values only 13 are below zero

6   at a 95 % confidence limit determined from the uncertainty of the $\int[OH]dt$ whereas 166 of the

7    $\int[OH]dt$ values are significantly larger than zero (95% confidence limit).

8   The values for average $\int[OH]dt$ of the different VOC differ substantially. The highest

9   average $\int[OH]dt$ of $3.1x10^{11}$ s molecules cm^{-3} is found for benzene, whereas the average $\int[OH]dt$

10   for the most reactive VOCs is only $3.4 x10^{10}$ s molecules cm^{-3} (Table 13). There is strong

11   evidence for a systematic dependence between atmospheric residence time and average $\int[OH]dt$

12   (Fig. 6). The Pearson product moment correlation coefficient for the dependence between

13   $\int[OH]dt$ and atmospheric residence time is 0.981 and R^2 for a linear fit is 0.963. The correlation

14   is strongly influenced by the data point for the benzene. When excluding this data point the

15   Pearson product moment correlation coefficient is 0.760 and R^2 for a linear fit is 0.578. The

16   finding of differences in $\int[OH]dt$ for VOC with different reactivity is similar to the results of a

17   comparison of the ages of ethane and n-butane derived from carbon isotope ratios reported by

18   Saito et al. (2002) for the western North Pacific. They report that the age of ethane in most cases

19   is approximately an order of magnitude larger than the age of n-butane, which is similar to the

20   $\int[OH]dt$ -reactivity dependence in Figure 6, although the range of VOC reactivity covered in this

21   paper does not include the low reactivity of ethane.

22   The dependence of the $\int[OH]dt$ on VOC reactivity is also seen for individual samples. In

23   Figure 7 the $\int[OH]dt$ of different VOC are compared with $\int[OH]dt$ determined for p,m-xylene,

13

1   the most reactive VOC. Since the $\int[OH]dt$ is a linear function of the carbon isotope ratios

2   (Equation 3) it is not surprising that the comparison showed strong correlations between the

3   values for $\int[OH]dt$ of the C_2-alkylbenzenes and no significant linear correlation between the

4     $\int[OH]dt$ of benzene and $\int[OH]dt$ of p,m-xylene. With the exception of 4 data points for $\int[OH]dt$

5   of toluene the values for $\int[OH]dt$ of less reactive VOC were consistently higher than those for

6   p,m-xylene, the most reactive of the studied VOC.

7   The systematic dependence of $\int[OH]dt$ on VOC reactivity can be explained by mixing of

8   air masses that have been subject to different extents of photochemical processing. During

9   photochemical aging VOC of high reactivity will be removed at a faster rate than VOC of low

10   reactivity. Consequently the relative contribution to VOC of low reactivity compared to VOC of

11   high reactivity increases with increased photochemical processing and mixing of air masses that

12   have been subject to different degrees of photochemical processing will result in average $\int[OH]dt$

13   values that decrease with increasing VOC reactivity.

14

15   **3.4 Photochemical age and VOC concentration ratios**

16   For VOC with identical $\int[OH]dt$ the change in concentration ratios can be predicted from

17     $\int[OH]dt$ (Kleinman et al., 2003; Parrish et al., 1992; Rudolph and Johnen, 1990) as long as their

18   emission ratios are similar. In case of mixing of air masses with different $\int[OH]dt$, the change in

19   VOC concentration ratios depends on the relative contributions from the different air masses and

20   therefore is difficult to predict. The possibility to derive $\int[OH]dt$ for VOC from their carbon

21   isotope ratios allows studying the dependence between VOC ratios and $\int[OH]dt$ of the individual

22   compound. The only condition for this is a narrow range of carbon isotope ratios for the

23   emissions of the studied VOC.

14

1   Figure 8 shows some examples for the dependence between VOC concentration ratios

2   and $\int[OH]dt$ of o-xylene and toluene. The ratios exhibit substantial scatter, especially for ratios

3   relative to benzene or toluene. Overall there is no clear dependence between $\int[OH]dt$ and VOC

4   ratios. For many VOC pairs the ratios show substantial deviations from the dependence between

5     $\int[OH]dt$ and concentration ratios predicted for identical values for average $\int[OH]dt$. However, for

6   VOC pairs with similar reactivity or low reactivity for both VOC prediction and observation

7   agree. This suggests that, similar to the dependence between VOC concentrations and carbon

8   isotope ratios (Fig. 5) mixing of air masses with different VOC concentration ratios plays a

9   major role in determining VOC ratios.

10   A change in VOC concentration ratios may be caused by varying impact from emission

11   sources with different emission ratios or different $\int[OH]dt$. With increasing photochemical age

12   the concentrations of a more reactive VOC will decrease faster than the concentration of a less

13   reactive VOC. In case of mixing air masses containing VOC with different $\int[OH]dt$ the relation

14   predicted by the hydrocarbon clock concept is no longer applicable, but qualitatively the ratios

15   for concentrations of more reactive VOC over those of less reactive VOC will still decrease with

16   increasing $\int[OH]dt$.

17   Figure 9 shows the relative change in the ratios for the concentration of different VOC

18   over the concentration of benzene averaged for 4 intervals of $\int[OH]dt$ derived from the p,m-

19   xylene carbon isotope ratio. Also shown is the relative change in $\int[OH]dt$ of benzene for the

20   same intervals. Although the averages have substantial uncertainties, there is evidence for a

21   systematic dependence. For the C_2 alkyl benzenes the difference between the lowest and highest

22   ratios is significant at the 90% confidence level (T-test). Furthermore, it is unlikely that the

23   observation of similar trends for all ratios is a coincidence. Most importantly, the observations

15

1   are incompatible with the expected change of VOC concentration ratios with increasing $\int[OH]dt$.

2   Benzene is the by far least reactive of these VOC; consequently photochemical processing is

3   expected to decrease the alkylbenzene over benzene concentration ratios, which is not observed.

4   Figure 10 shows the relative difference between the averages for all VOC concentration

5   ratios and the average concentration ratios for VOC without significant depletion of ^{13}C relative

6   to the isotope ratio of emissions. The separation between these two groups is based on the 95%

7   confidence limit calculated from measurement error and uncertainty of $\delta^{13}C$ of emissions (Table

8   10). For comparison the change in ratios predicted from the average $\int[OH]dt$ of the VOC in

9   Table 13 is included in Figure 10. For C_2-alkylbenzenes the predicted and observed changes in

10   concentration ratios agree within their uncertainties, although for the o-xylene over ethylbenzene

11   concentration ratio the high uncertainty does not allow a meaningful comparison. However,

12   VOC concentration ratios relative to benzene or toluene show a substantial difference between

13   prediction and observation. Moreover, for concentration ratios relative to benzene the samples

14   with negligible photochemical processing have ratios lower than the average, which can only be

15   explained by impact of sources with different VOC emission ratios. Specifically, it can be

16   concluded that sources directly impacting the sampling location on average have lower emission

17   ratios relative to benzene than emissions from sources located at a distance allowing for

18   photochemical aging of the VOC. This demonstrates that in this case the differences in emission

19   ratios are larger than the impact of photochemical aging.

20   Based on the location of the sampling site, traffic related emissions are expected to have a

21   major impact on VOC concentrations. Other potentially important sources are emissions from

22   industrial facilities. In Table 14 VOC emission ratios for transportation related emissions from

23   literature and industrial facilities in Ontario and the Toronto region reported by the National

16

1   Pollutant Release Inventory (NPRI) are compared with the average ratios for our measurements.

2   Although VOC concentration ratios in vehicular emissions cover a range of nearly a factor of 2,

3   the observed average ratios relative to benzene are consistently at the upper end or above this

4   range but close to emission ratios for industrial facilities in Ontario. Since emission ratios

5   relative to benzene for industrial facilities in the Toronto area are much higher than the average

6   for Ontario (Table 14) differences in emission ratios from industrial facilities between Toronto

7   and the rest of Ontario can be ruled out as explanation for the lower concentration ratios relative

8   to benzene for samples with little photochemical processing. In contrast to the concentration

9   ratios relative to benzene, due to the similarity in emission ratios for industrial facilities and

10   traffic (Table 14) and the possible change of these ratios due to photochemical processing, it is

11   difficult to extract information about contributions from these two source types from

12   concentration ratios for alkyl benzenes without additional information.

13   Most of the major sources of light aromatic VOC in Ontario are located Southwest and

14   West of the sampling site (Fig. 11). Therefore insight into the impact of emissions from

15   industrial facilities on concentration ratios and carbon isotope ratios can be gained by filtering

16   the samples based on predominant wind direction during sampling. In Table 15 the average VOC

17   carbon isotope ratios for the two wind sectors are compared. With the exception of toluene the

18   average carbon isotope ratios for samples collected under the influence of airflow from North or

19   East is are heavier than in samples with wind from the South or West sectors. For benzene this

20   difference is statistically significant at the 98% level (T-test) and for the C2-benzenes at a >90%

21   level. This is consistent with the existence of larger sources of aromatic VOC in the S+W sector

22   compared to the N+E sector (Fig. 11). The absence of a statistically significant difference in

17

1   isotope ratios for toluene is most likely due to the existence of a nearby major industrial source

2   of toluene east of the sampling site (Fig. 12).

3   Based on the difference in carbon isotope ratios between samples for the two wind

4   sectors it is expected that there also will be differences in concentration ratios. In Table 15

5   average VOC concentration ratios for samples dominated by southerly or westerly airflow are

6   compared with ratios for samples with winds from either North or East. For ratios relative to

7   benzene substantial differences between the two wind sectors are found. For the C_2-

8   alkylbenzenes the difference is statistically significant at >95 % (T-test), for toluene at the 89 %

9   level. However, for concentration ratios between alkylbenzenes no statistically significant

10   differences can be seen. The lower concentration ratios relative to benzene in the N+E samples

11   can therefore be explained either by impact of aged air which is, relative to benzene, depleted in

12   the more reactive alkyl benzenes due to photochemical processing or lower emissions of

13   alkylbenzenes from industrial facilities in the N+E sector.

14   VOC carbon isotope ratios can be used to test which of these two factors dominates.

15   Using the carbon isotope ratio of p,m-xylene the N+E sector samples are separated into two

16   groups of samples with different values for $\int[OH]dt$. The separation into two groups is based on

17    $\int[OH]dt$ of p,m-xylene being larger than zero at the 99% confidence limit. The confidence limit

18   was calculated from the uncertainty of the isotope ratio of emissions, the measurement

19   uncertainty and the uncertainty of the KIE. This $\int[OH]dt$ is 3×10^{10} OH-radicals cm^{-3} s, which

20   corresponds to approximately 8 h for an average OH radical concentration of 10^6 cm^{-3}. The

21   average concentration ratios for these two groups are included in Table 15. The average $\int[OH]dt$

22   of p,m-xylene for samples dominated by recent emissions of p,m-xylene is 2.3×10^9 OH-radicals

23   cm^{-3} s corresponding to 0.6 hours for an average OH radical concentration of 10^6 cm^{-3}. However,

18

1   it should be noted that, due to the uncertainty in the isotope ratio of p,m-xylene emissions this

2   average value has an uncertainty of approximately 1.3×10^{10} OH-radicals cm^{-3} s corresponding to

3   nearly 4 hours for an average OH radical concentration of 10^6 cm^{-3}. For samples dominated by

4   aged p,m-xylene the average $\int[OH]dt$ is 7.4×10^{10} OH-radicals cm^{-3} s corresponding to 21 h for an

5   average OH radical concentration of 10^6 cm^{-3}.

6   In contrast to the expected decrease in the concentration ratios for more reactive VOC

7   over less reactive VOC with increasing $\int[OH]dt$, the average ratios are always higher for the aged

8   samples. Although the difference is statistically significant at a > 90 % level for only 6 of the

9   concentration ratios, this finding rules out photochemical processing as main reason for the

10   observed changes in VOC concentration ratios. For this set of observations differences in

11   $\int[OH]dt$ derived from carbon isotope ratios most likely reflect differences in the footprint area

12   that impacts VOC concentration ratios. Samples with low values for $\int[OH]dt$ represent the

13   impact of nearby sources, most likely traffic related emissions, consistent with concentration

14   ratios that are close to the typical traffic dominated VOC ratios (Table 14).

15   The concentration ratio of p,m-xylene over ethylbenzene has been used as an indicator of

16   photochemical processing (Miller et al., 2012; Monod, 2001). It has been reported that the ratio

17   of p,m-xylene to ethylbenzene emissions is nearly constant for different sources (i.e. exhaust,

18   petrochemical activities, solvent use, etc.) and varies from 3.5 to 4.0 (Nelson and Quigley, 1983).

19   Since photochemical removal is approximately 3 times faster for p,m-xylene than for

20   ethylbenzene (Table 6), it has been suggested that any value of this ratio lower than 3.5 is a good

21   indicator of photochemical ageing (Nelson and Quigley, 1983; Miller et al., 2012; Monod, 2001;

22   Civan et al., 2015). This is in contrast to the higher concentration ratio of p,m-xylene to

23   ethylbenzene observed in samples with photo-chemically aged p,m-xylene for the N+E sector

19

1   compared to samples dominated by recent emission of p,m-xylene (Table 15). Although the

2   observed relative increase in concentration ratios of 50% has an uncertainty of 40% and is

3   statistically not significant (T-test), it is inconsistent with the decrease by approximately 60%

4   which ~~would~~ is expected from the difference in the average $\int[OH]dt$ for these two data sets. This

5   can be explained by the difference in xylene over ethylbenzene emission ratios between traffic

6   related emissions and industrial facility emissions (Table 14). Samples with low values for the

7   average $\int[OH]dt$ for p,m-xylene will be dominated by emissions from nearby sources, most

8   likely traffic, while for samples with higher $\int[OH]dt$ for p,m-xylene the footprint area will be

9   much larger and industrial emissions will play a more significant role.

10

11   **4. Conclusions**

12   Measurement of carbon isotope ratios of ambient VOC can be used to obtain detailed

13   insight into origin and sources of VOC. This is especially important in cases where different

14   source types impact ambient VOC levels and the source location alone does not allow identifying

15   the dominant source type. In such cases the use of VOC concentration ratios can result in

16   incorrect estimates of photochemical processing. Moreover, the comparison of $\int[OH]dt$ derived

17   from carbon isotope ratios of VOC demonstrates that in the case of mixing of air masses with

18   differences in $\int[OH]dt$ the average $\int[OH]dt$ for VOC with different reactivity differ. Typically

19   $\int[OH]dt$ for more reactive VOC will be lower than $\int[OH]dt$ for less reactive VOC. It can

20   therefore be concluded that in this study the assumption of a uniform $\int[OH]dt$ for different VOC

21   is not justified and consequently the use of VOC concentration ratios to determine $\int[OH]dt$

22   would give incorrect results.

20

1   The use of carbon isotope ratios or $\int[OH]dt$ derived from carbon isotope ratios allows

2 differentiation between samples impacted by emissions from different footprint areas. The

3 comparison of carbon isotope ratios and VOC concentration ratios demonstrates that in this study

4 differences in the emission ratios for different types of VOC sources have a larger impact on

5 ambient VOC concentration ratios than photochemical aging.

6   For the VOC studied here reaction with the OH-radical is the only relevant loss process

7 in the atmosphere. Although the OH-radical concentration exhibits significant seasonal, diurnal

8 and spatial variability, $\int[OH]dt$ derived from isotope ratios also depends on the time between

9 emission of the VOC and observation. Consequently these $\int[OH]dt$ also contains information on

10 the footprint area which impacts the observation sites. VOC have widely different photochemical

11 reactivity; the reactivity of VOC used in our study cover a range of a factor of nearly 20. Values

12 for average $\int[OH]dt$ derived from carbon isotope ratios cover the range from effectively zero to

13 approximately 8×10^{11} OH-radicals cm^{-3} s corresponding to 9 days for an average OH radical

14 concentration of 10^6 cm^{-3}. The lower end of useful values for $\int[OH]dt$ that can be determined

15 from VOC carbon isotope ratios strongly depends on the uncertainty of the carbon isotope ratio

16 of emissions. Due to the limited number of studies of carbon isotope ratios of VOC emissions,

17 this substantially contributes to uncertainty in isotope ratio derived $\int[OH]dt$. For the most

18 reactive VOC used in this study the uncertainty in $\int[OH]dt$ resulting from uncertainty in the

19 carbon isotope ratio of emissions corresponds to 4 h at an average OH radical concentration of

20 10^6 cm^{-3}. The uncertainty in $\int[OH]dt$ of p,m-xylene due to carbon isotope ratio measurement

21 errors corresponds to less than 1.5 h. Therefore more detailed understanding of the carbon

22 isotope ratio of VOC emissions will reduce the lower end of meaningful values for $\int[OH]dt$ that

23 can be determined from carbon isotope ratios of atmospheric VOC.

21

In this study sampling periods of at least several hours, in most cases of one day were used. ~~While t~~This is useful for determining meaningful averages from a limited set of measurements, However, this does not allow differentiating between changes of $\int[OH]dt$ with time during the sampling period ~~sampling~~ and mixing of ~~air masses~~VOC with different $\int[OH]dt$ in the atmosphere prior to sampling. Separating the impact of the two processes on the VOC isotope ratio would require VOC isotope ratio measurements in samples collected during short time periods of only a few minutes or less. To our knowledge no such VOC isotope ratio measurements in an urban environment have been published.

The finding of a dependence between average $\int[OH]dt$ and VOC reactivity is similar to the finding of a substantial difference in $\int[OH]dt$ between ethane and n-butane in a marine environment (Saito et al., 2002) as well as global modelling studies (Thompson et al., 2003; Stein and Rudolph, 2007). However, to our knowledge, apart from this study no data that would allow systematic study of the relation between VOC concentration ratios and carbon isotope ratios in urban areas have been published. It can therefore not be decided to which extent the observed discrepancy between $\int[OH]dt$ derived from carbon isotope ratios and changes in VOC concentration ratios is a general problem for determining $\int[OH]dt$ from VOC concentration ratios or limited to conditions specific for this or similar data sets.

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Table 1. Performance of the system for analysis of volatile organic compounds in ambient air.

Compound	Detection Limit[a] (ng)	Relative precision in concentration measurement[b] (%)	Precision in $\delta^{13}C$ measurement[c] (‰)
Benzene	1.5	4	0.3
Toluene	0.4	4	0.2
Ethylbenzene	0.6	6	0.2
o-Xylene	0.4	8	0.3
p,m-Xylene	0.5	9	0.3

[a] Detection limit calculated using 3σ, where σ is the standard deviation of blank values determined from 3-4 repeat measurements.
[b] Precision calculated as relative standard deviation (%) of peak area for >10 repeat measurements.
[c] Precision calculated as standard deviation of $\delta^{13}C$ values for >10 repeat measurements.

Table 2. Mixing ratios (nmol mol^{-1}) determined for volatile organic compounds collected in Toronto (2009-2010).

Compound	N[a]	Mean	s[b]	Median	Minimum	Maximum	90th percentile	10th percentile
Benzene	65	0.13	0.12	0.11	0.02	0.74	0.28	0.03
Toluene	73	0.64	0.44	0.56	0.05	2.11	1.39	0.16
Ethylbenzene	69	0.07	0.05	0.05	0.01	0.26	0.14	0.02
o-Xylene	66	0.05	0.03	0.04	0.01	0.17	0.10	0.01
p,m-Xylene	68	0.17	0.13	0.14	0.01	0.74	0.36	0.04

[a] Number of measurements.
[b] Sample standard deviation.

Table 3. Average mixing ratios (nmol mol^{-1}) calculated from data reported by the National Air Pollution Surveillance Program (NAPS) for three locations in Toronto during the time periods covered in this work.

Location	Etobicoke West[a]		Downtown Toronto[b]		Etobicoke South[c]		This work	
Compound	mean	s[d]	mean	s[d]	mean	s[d]	mean	s[d]
Benzene	0.18	0.07	0.23	0.10	0.20	0.10	0.13	0.12
Toluene	0.49	0.31	0.62	0.55	0.68	0.65	0.~~63~~64	0.44
Ethylbenzene	0.06	0.04	0.07	0.04	0.09	0.06	0.~~06~~07	0.~~17~~05
o-Xylene	0.05	0.04	0.07	0.04	0.07	0.05	0.05	0.03
p,m-Xylene	0.18	0.13	0.23	0.13	0.27	0.21	0.17	0.13

[a] Elmcrest Road, Toronto, ON, Canada.
[b] 223 College S., Toronto, ON, Canada.
[c] 461 Kipling Ave., Toronto, ON, Canada.
[d] Sample standard deviation.

Table 4. Linear regression analysis of mixing ratio correlations. Values above the diagonal are R^2 and below are the intercepts[a].

	Benzene[b]	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Benzene[b]		<0.3	<0.3	<0.3	<0.3
Toluene	NA		0.495	0.586	0.488
Ethylbenzene	NA	0.011 (0.008)		0.825	0.964
o-Xylene	NA	0.003 (0.006)	0.008 (0.003)		0.877
p,m-Xylene	NA	0.020 (0.023)	-0.007 (0.005)	-0.014 (0.011)	

[a] Standard error of intercept (nmol mol^{-1}) in parenthesis. The values are for linear fits of the mixing ratio of the more reactive VOC versus the mixing ratio of the less reactive VOC.
[b] No significant correlation was found for linear regressions of the mixing ratios of any of the VOC versus the mixing ratios of benzene.

Table 5. Ratios of VOC mixing ratios. Values below the diagonal are the ratios for the measurements presented in this work[a], values above the diagonal give the range of ratios observed in literature[b].

	Benzene	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Benzene		1.5-3.7	0.11-1.2	0.23-3.2	0.46-0.3.8
Toluene	6.6 (0.6)		0.07-0.35	0.14-0.86	0.27-1.1
Ethylbenzene	0.69 (0.08)	0.080 (0.01)		0.6-2.1	1.2-4.3
o-Xylene	0.52 (0.07)	0.069 (0.007)	0.64 (0.04)		1.7-2.9
p,m-Xylene	1.8 (0.2)	0.22 (0.003)	2.7 (0.07)	3.7 (0.2)	

[a] Standard error of ratios in parenthesis. The ratios are for the mixing ratio of the more reactive VOC over the mixing ratio of the less reactive VOC. For compounds with correlated mixing ratios the slope of the linear regressions and standard errors of the slopes is given, in the absence of correlation the average of the ratios and standard error of average ratios is given.
[b] Range of observations in urban, residential and commercial areas reported by Hoque et al., (2008), Karl et al. (2009), Miller et al. (2011), Alghamdi et al. (2014), de Gennaro et al. (2015) and Rad et al. (2014).

Table 6. Stable carbon isotope composition ($\delta^{13}C$, ‰) of ambient VOC collected in Toronto (2009-2010).

Compound	N[a]	Mean	s[b]	Median	Range	10th percentile	90th percentile
Benzene	44	-25.0	3.4	-26.0	-39.4 to -13.6	-28.4	-20.9
Toluene	73	-24.8	3.2	-25.7	-28.5 to -7.7	-27.4	-20.5
Ethylbenzene	58	-24.0	4.0	-23.4	-34.8 to -17.4	-28.5	-18.8
o-Xylene	44	-23.3	3.5	-23.3	-30 to -16.5	-28.0	-18.4
p,m-Xylene	56	-24.0	4.1	-23.8	-34.6 to -16.4	-28.4	-18.9

[a] Number of measurements.
[b] Sample standard deviation.

1   **Table 7.** Average and standard deviation of reported stable carbon isotope composition measurements (δ^{13}C, ‰) of ambient light
2   aromatic VOC[a].

Location	Benzene	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Toronto[b]	-24.6 (2.3)	-25.0 (1.1)	-25.3 (2.7)	-24.9 (1.5)	-25.6 (1.0)
Belfast[c]	-23.8 (2.5)	-26.9 (0.9)	-26.5 (1.4)	-26.3 (1.3)	-27.4 (1.7)
Crossgar and Hillsborough[d]	-28.3 (1.7)				
South-west Germany[e]		-27 to -23			
Egbert[f]	-25.3 (2.6)	-24.8 (1.7)	-23.7 (3.6)	-23.4 (2.6)	-23.8 (3.0)
Yurihonjo[g] (Japan)			-29.6 to -23.5		

3   [a] Sample standard deviation is given in parenthesis.
4   [b] Urban Canada (Rudolph et al., 2002).
5   [c] Urban Northern Ireland (Redeker et al., 2007).
6   [d] Rural Northern Ireland (Redeker et al., 2007).
7   [e] Vertical profile over rural area, only range of data available (Wintel et al, 2013).
8   [f] Rural Canada (Kornilova et al., 2015b).
9   g Urban Japan, only range of data available (Kawashima and Murakami, 2014).
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Table 8. Average stable carbon isotope ratios ($\delta^{13}C$, ‰) of major sources of ambient VOC. The sample standard deviation is given in parenthesis.

Source	Benzene	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Gasoline[a]	-27.0 (-24.5 to-29.9) [b]	-26.0,-28.1[b]	-27.4 (2.8)	-26.5 (1.9)	-27.9 (1.2)
Tunnel[c]	-26.5 (1.0)	-27.5 (1.0)	-27.4 (0.9)	-27.3 (0.4)	-26.9 (2.0)
Gas Station[c]	-29.1 (0.3)	-27.4 (0.6)	-28.2 (0.4)	-27.1 (0.6)	-27.7 (0.5)
Gas Station[d]	-27.35 (1.6)	-27.08 (0.7)	-26.48 (1.6)		-27.4 (0.8)
Underground garage[c]	-27.7 (0.7)	-27.1 (0.7)	-27.5 (1.1)	-27.2 (1.1)	-27.7 (1.0)
Biomass burning[e]	-26.0 (0.1)	-26.5 (0.9)	-25.7 (0.5)		
Biomass burning[f]	-27.6 (1.6)	-27.1 (1.3)			
Fossil fuel combustion[f]	-26.9 (0.3)	-27.5 (0.6)			
Industrial stack[g]	-23.5 (0.11)	-25.4 (0.48)			

[a] Averages and standard deviations were calculated from the results of analysis of 4 individual gasoline samples reported by Smallwood et al. (2002).
[b] For benzene only average and range are available, for toluene only two individual values were reported.
[c] (Rudolph et al., 2002).
[d] (Kawashima and Murakami, 2014).
[e] (Czapiewski et al., 2003).
[f] (Giebel et al., 2010).
[g] (Turner et al., 2006).

Table 9. Regression analysis of delta values. Values above diagonal are R^2, and below are the intercepts.

	Benzene[b]	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Benzene[b]		<0.3	<0.3	<0.3	<0.3
Toluene	NA		0.361	0.356	0.335
Ethylbenzene	NA	-0.04 (4.31)[a]		0.820	0.963
o-Xylene	NA	-2.58 (4.31)	-2.54 (1.56)		0.825
p,m-Xylene	NA	-0.49 (4.57)	-0.19 (0.64)	-1.64 (1.63)	

[a] Standard error of intercept (‰) in parenthesis. The values are for linear fits of the mixing ratio of the more reactive VOC versus the mixing ratio of the less reactive VOC.
[b] No significant correlation was found for linear regressions of the mixing ratios of any of the VOC versus the mixing ratios of benzene.

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Table 10. Summary of kinetic data, carbon isotope ratio of emissions, carbon isotope ratio calculated for steady state between emission and loss, and average measured carbon isotope ratio for light aromatic VOC[a].

Compound	k_{OH}[b] (10^{-12} cm^3 molec^{-1} s^{-1})	ε_{OH} (‰)[c]	$\delta^{13}C$ source (‰)[d]	$\delta^{13}C$ steady state (‰)	Average of $\delta^{13}C$ measured (‰)
Benzene	1.22	7.83 (0.42)[e]	-28.0 (0.2)	-20.1 (0.5)	-25.0 (0.5)
Toluene	5.63	5.59 (0.28)	-27.6 (0.5)	-21.7 (0.5)	-24.8 (0.4)
Ethylbenzene	7.0	4.34 (0.28)	-27.7 (0.2)	-23.4 (0.4)	-24.0 (0.5)
o-Xylene	13.6	4.27 (0.05)	-27.2 (0.2)	-22.9 (0.2)	-23.3 (0.5)
p,m-Xylene	20.5[f]	4.83 (0.05)[g]	-27.4 (0.4)	-22.6 (0.4)	-24.0 (0.6)

[a] Values in parenthesis are the standard error of the mean.
[b] Rate constants for 298 K (Atkinson and Arey, 2003;Finlayson-Pitts and Pitts, 2000).
[c] Carbon kinetic isotope effects for reaction with OH radicals (Anderson et al., 2004a;Anderson et al., 2004b;Rudolph et al., 2002).
[d] Isotopic composition of traffic related VOC emissions in Toronto (Rudolph et al., 2002).
[e] Average ε calculated from 8.13 (0.8) (Anderson et al., 2004b) and 7.53 (0.5) (Rudolph et al., 2002).
[f] Average of $k_{OHp-xylene}=1.43\times10^{-11}$ cm^3 molec^{-1} s^{-1} and $k_{OHm-xylene}=2.36\times10^{-11}$ cm^3 molec^{-1} s^{-1}.
[g] ε_{OH} (‰) is for p-xylene, no value is available for m-xylene.

Table 11. Overview of the number of observations within different ranges of carbon isotope ratios[a].

Range for $\delta^{13}C$	Benzene	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
$<\delta^{13}C_{source}$[b]	1 (2%)	0	4 (7%)	4 (9%)	4 (7%)
$\approx \delta^{13}C_{source}$[c]	10 (23%)	32 (44%)	14 (24%)	5 (11%)	15 (27%)
$> \delta^{13}C_{source}$ **but** $<-\delta^{13}C_{global}$[d]	28 (64%)	15 (21%)	4 (7%)	6 (14%)	4 (7%)
$\approx\delta^{13}C_{steady state}$[e]	2 (4 %)	23 (31%)	19 (33%)	17 (39%)	21 (38%)
$> \delta^{13}C_{steady state}$[f]	3 (7%)	3 (4 %)	17 (29%)	12 (27%)	12 (21%)
Total	44	73	58	44	56

[a] The value in parenthesis gives the percentage of observation. The confidence intervals used to determine the $\delta^{13}C$ ranges were calculated from measurement error, uncertainty of $\delta^{13}C$ of emissions, and uncertainty of ε_{OH}.
[b] Number of $\delta^{13}C$ measurements below the 95% confidence limit of $\delta^{13}C$ of emissions.
[c] Number of $\delta^{13}C$ measurements within the 95% confidence limit of $\delta^{13}C$ of emissions.
[d] Number of $\delta^{13}C$ measurements above the 95% confidence limit of $\delta^{13}C$ of emissions but below the 95% confidence limit of $\delta^{13}C$ calculated for steady state between emissions and loss.
[e] Number of $\delta^{13}C$ measurements within the 95% confidence limits of $\delta^{13}C$ calculated for steady state between emissions and loss.
[f] Number of $\delta^{13}C$ measurements above the 95% confidence limit of $\delta^{13}C$ calculated for steady state between emissions and loss.

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1 **Table 12.** Comparison of slopes calculated from Eq. 4 based on the assumption that different
2 VOC have identical $\int[OH]dt$ (above diagonal) with slopes determined from linear regression of
3 the observations (below diagonal).

	Benzene	Toluene	Ethylbenzene	o-Xylene	p,m-Xylene
Benzene		3.29	3.18	6.07	6.08
Toluene	NA[a]		0.97	3.15	1.85
Ethylbenzene	NA	0.96 (0.17)[b]		3.26	1.91
o-Xylene	NA	0.85 (0.18)[b]	0.89 (0.07)[b]		0.59
p,m-Xylene	NA	0.95 (0.18)[b]	1.0 (0.03)[b]	0.93 (0.07)[b]	

4 [a] Not available, no correlation found.
5 [b] Standard error in parenthesis.
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7
8 **Table 13.** Overview of $\int[OH]dt$ [a] of light aromatic VOC calculated from their stable carbon
9 isotope ratios.

Compound	Mean[b]	Median[c]	90th percentile	75th percentile	25th percentile	10th percentile
Benzene	31 (5)	21(14)	76	49	11	-4.1
Toluene	8.5 (1.1)	5.7 (8)	21	12	1.6	0.61
Ethylbenzene	12.1 (1.7)	14 (5.7)	29	20	2.3	-2.8
o-Xylene	6.8 (0.9)	6.8 (2.6)	15	10	1.9	-1.5
p,m-Xylene	3.4 (0.6)	3.6 (2.4)	8.7	6.5	0.5	-1.0

10 [a] $\int[OH]dt$ in 10^{10} s molecules cm^{-3}.
11 [b] Standard error of mean in parenthesis.
12 [c] 95% confidence interval in parenthesis.

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Table 14. Comparison of observed VOC concentration ratios (mol/mol) with VOC emission ratios for industrial facilities and mobile transportation.

VOC concentration ratios	Facilities Ontario[a]	Facilities Toronto[a]	Gasoline engines[b]	Traffic Sarnia[c]	Traffic 8 European cities[d]	Average all observations
Toluene/Benzene	6.2	120	2.6±1.9	3.6	2.0±0.4	6.6±0.56
Ethylbenzene/Benzene	0.68	13	0.20±0.19	0.57	0.38±0.08	0.69±0.083
∑ Xylenes/Benzene	5.3	114	0.65±0.50	2.3	1.6±0.4	2.3±0.17
∑ Xylenes/Toluene	0.86	0.96	0.34±0.28	0.63	0.81±0.2	0.35±0.019
∑ Xylenes/Ethylenzene	7.9	8.6	4.0±1.3	4.1	4.1±0.5	3.5±0.096

[a] Calculated from emissions reported by the National Pollution Release Inventory (NPRI) for 2009 and 2010.

[b] Average and standard deviation calculated from 16 measurements of the composition of exhaust from of gasoline engines using ethanol free or low ethanol fuel reported by the United States Environmental Protection Agency, Speciate Data Base.

[c] Calculated from average ratios reported by Miller et al. (2011) for ambient observations dominated by traffic related emissions in Sarnia (Southern Ontario, Canada).

[d] Calculated from mixing ratios reported by Monod et al. (2001) for observations dominated by traffic related emissions in 8 major cities in Europe.

Table 15. Comparison of observed VOC concentration ratios (mol/mol) for different dominant wind directions and different $\int[OH]dt$.

VOC concentration ratios	S+W[a]	N+E[b]	N+E Recent[c]	N+E Aged[c]
Toluene/Benzene	8.2±1.5	6.1±0.90	4.9±2.2	7.7±1.6
Ethylbenzene/Benzene	1.0±0.2	0.61±0.10	0.37±0.11	0.82±0.16
o-Xylene/Benzene	0.76±0.17	0.44±0.09	0.24±0.06	0.68±0.15
p,m-Xylene/Benzene	2.8±0.67	1.5±0.27	0.81±0.22	2.2±0.44
Ethylbenzene/Toluene	0.11±0.01	0.13±0.04	0.074±0.012	0.17±0.074
o-Xylene/Toluene	0.084±0.012	0.069±0.008	0.048±0.012	0.084±0.014
p,m-Xylene/Toluene	0.29±0.039	0.029±0.078	0.16±0.03	0.42±0.16
o-Xylene/Ethylbenzene	0.93±0.24	0.94±0.23	0.66±0.07	1.2±0.51
p,m-Xylene/Ethylbenzene	2.5±0.14	2.7±0.37	2.2±0.15	3.3±0.80
p,m-Xylene/o-Xylene	3.6±0.27	3.3±0.23	3.4±0.20	3.1±0.28
∑ Xylenes/Benzene	3.3±0.81	1.8±0.34	1.0±0.29	2.7±0.55
∑ Xylenes/Toluene	0.35±0.051	0.34±0.076	0.21±0.042	0.49±0.15
∑ Xylenes/Ethylenzene	3.3±0.17	3.5±0.34	2.8±0.21	4.1±1.1

[a] Average ratio for data with winds dominantly from southern or western sectors. Only data points for which at least during 80% of the sampling time the wind direction was within ± 45° of the dominant wind direction are included. The number of data points is between 14 and 20. The uncertainty stated is the standard error of the mean.

[b] Average ratio for data with winds dominantly from northern or eastern sectors are included. Only data points for which at least during 80% of the sampling time the wind direction was within ± 45° of the dominant wind direction are included. The number of data points is between 15 and 20. The uncertainty stated is the standard error of the mean.

[c] Data for the N+E sector filtered based on $\int[OH]dt$ determined from the p,m- xylene carbon isotope ratio. Aged refers to samples with $\int[OH]dt > 0$ at the 99% confidence limit. The confidence limit was calculated from the uncertainty of the isotope ratio of emissions, the measurement uncertainty and the uncertainty of the KIE. Recent represents samples with $\int[OH]dt$ below this limit. The values given are the average ratios and the standard error of the mean. The number of data points for Recent is 5, for Aged there are between 7 and 9 values.

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1   **Figure Captions**

2   **Figure 1**. Location of sampling site in Toronto (S). Also shown are the locations for VOC
3   sampling by the National Air Pollution Surveillance Program (NAPS) in Toronto (A: Elmcrest
4   Road, Toronto, ON, Canada, B: 223 College St., Toronto, ON, Canada, C: 461 Kipling Ave.,
5   Toronto, ON, Canada. The map was produced using ©Google Earth, 2015.

6
7   **Figure 2.** ~~Frequency distribution for VOC carbon isotope ratios measured in Toronto in 2009~~
8   ~~and 2010. Observations for different seasons are identified as follows: Fall- dotted, winter- black,~~
9   ~~and spring and summer- hatched. The solid vertical lines are the isotope composition of traffic~~
10 ~~related emissions (Rudolph et al., 2002).~~ Example plots for the dependence between mixing
11 ratios for different VOC pairs.

12
13 **Figure 3**. Frequency distribution for VOC carbon isotope ratios measured in Toronto in 2009
14 and 2010. Observations for different seasons are identified as follows: Fall- dotted, winter- black,
15 and spring and summer- hatched. The solid vertical lines are the isotope composition of traffic
16 related emissions (Rudolph et al., 2002). ~~Example plots for the dependence between mixing~~
17 ~~ratios for different VOC pairs.~~

18
19 **Figure 4**. Example plots for the dependence between carbon isotope ratios for different VOC
20 pairs.

21
22 **Figure 5**.Example plots of VOC mixing ratios versus carbon isotope ratios.

23
24 **Figure 6**. Dependence between average $\int[OH]dt$ (photochemical age, PCA) and photochemical
25 life time for light aromatic VOC. The average tropospheric life time was calculated using the rate
26 constants given in Table 10 and an average tropospheric concentration of 1.16×10^6 OH-radicals
27 cm^{-3} (Spivakovsky et al., 2000). Vertical error bars are the standard error of the mean.

28
29 **Figure 7.** Dependence between the $\int[OH]dt$ (PCA) of different VOC and the $\int[OH]dt$ (PCA) of
30 p,m-xylene. Only data with $\int[OH]dt$ larger than zero at a 95 % confidence limit are shown.

31
32 **Figure 8.** Plot of VOC concentration ratios versus $\int[OH]dt$ (PCA) determined from carbon
33 isotope ratios. The lines show the change in carbon isotope ratios predicted for identical $\int[OH]dt$
34 of the different VOC.

35
36 **Figure 9.** Relative change of VOC concentration ratios and $\int[OH]dt$ (PCA) of benzene for
37 different ranges of $\int[OH]dt$ (in units of 10^{10} s molecules cm^{-3}) derived from the carbon isotope
38 ratio of p,m-xylene. The bars represent the ratio of the mean concentration ratios for the chosen
39 interval of $\int[OH]dt$ over ~~normalized relative to~~ the average ~~of~~ for all ~~available~~ concentration
40 ratios. The error bars are the relative standard errors of the mean. The range of $\int[OH]dt$ for the
41 lowest $\int[OH]dt$ bin was chosen to include all $\int[OH]dt$ which are not significantly larger than ~~0~~

zero. (95 % confidence limit). The other ranges were chosen to include between 8 and 12 data points in each bin.

Figure 10. Relative difference between the average of all VOC concentration ratios (mol/mol) and the average VOC concentration ratios for VOC with carbon isotope ratios that are not higher than the carbon isotope ratios of emissions (95 % confidence limit) (squares). The circles show the relative change expected for a uniform $\int[OH]dt$ calculated from the average $\int[OH]dt$ of all observations (Table 13). The error bars show the standard error calculated from error propagation. For data points with error bars smaller that the size of the data point no error bars are show.

Figure 11. Location of facilities in southern Ontario with significant emissions of xylenes. The numbers represent the annual emissions in tons year^{-1}. Emission data were taken from the National Pollutant Release Inventory (NPRI). Only sources contributing at least 5% to the total emissions are shown. Also shown is the location of the sampling site. The map was produced using ©Google Earth, 2015

Figure 12. Location of facilities in Toronto with significant emissions of toluene. The numbers represent the annual emissions in ton year^{-1}. Emission data were taken from the National Pollutant Release Inventory (NPRI). Only sources contributing at least 5 % to the total emissions are shown. Also shown is the location of the sampling site. The map was produced using ©Google Earth, 2015.

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5   Figure 1

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2   Figure 2

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51

Benzene

Toluene

Number of occurances (y-axis): 0, 5, 10, 15, 20, 25, 30, 35

$\delta^{13}C$ (‰) (x-axis): <-28, -27, -25, -23, -21, <-20

1

2

Ethylbenzene

Number of occurances

14
12
10
8
6
4
2
0

<-28   -27   -25   -23   -21   <-20

$\delta^{13}C$ (‰)

1

2

o-Xylene
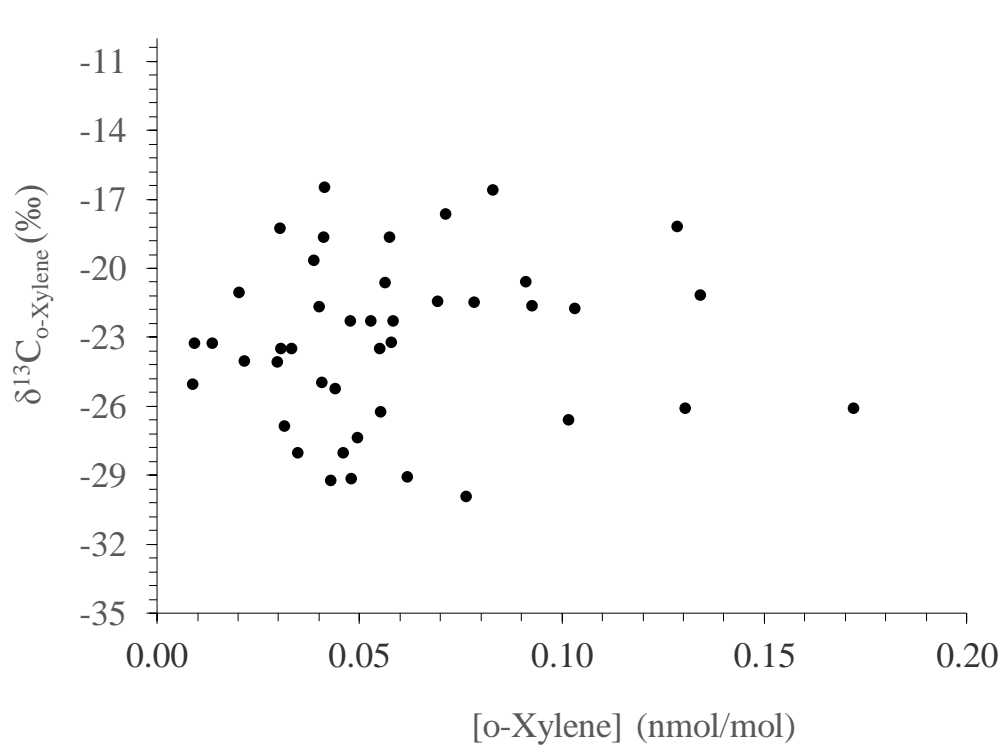
p,m-Xylene

Number of occurances

$\delta^{13}C$ (‰)

Figure 3

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3   Figure 4

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59
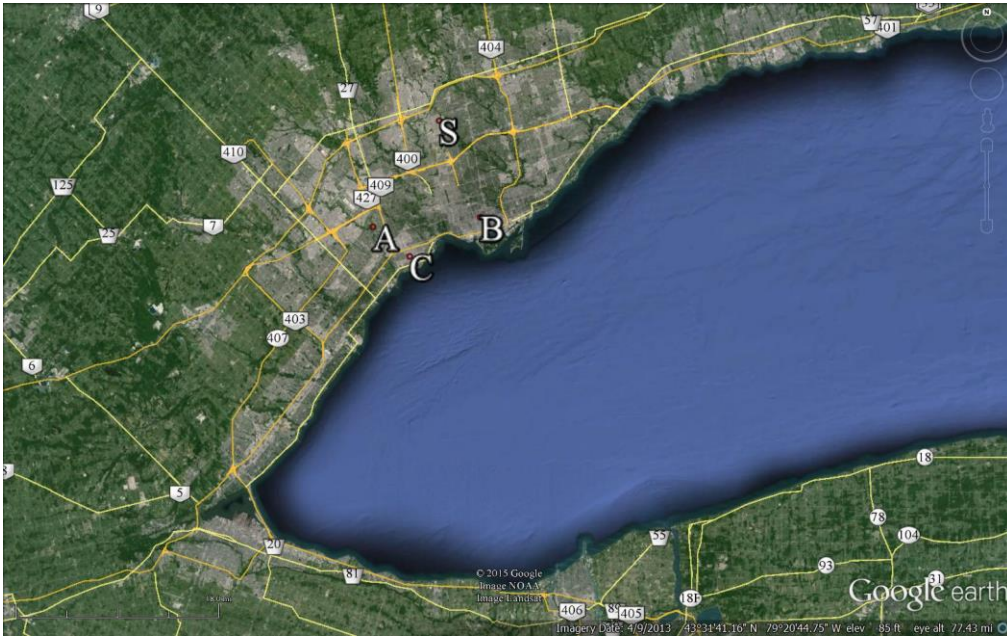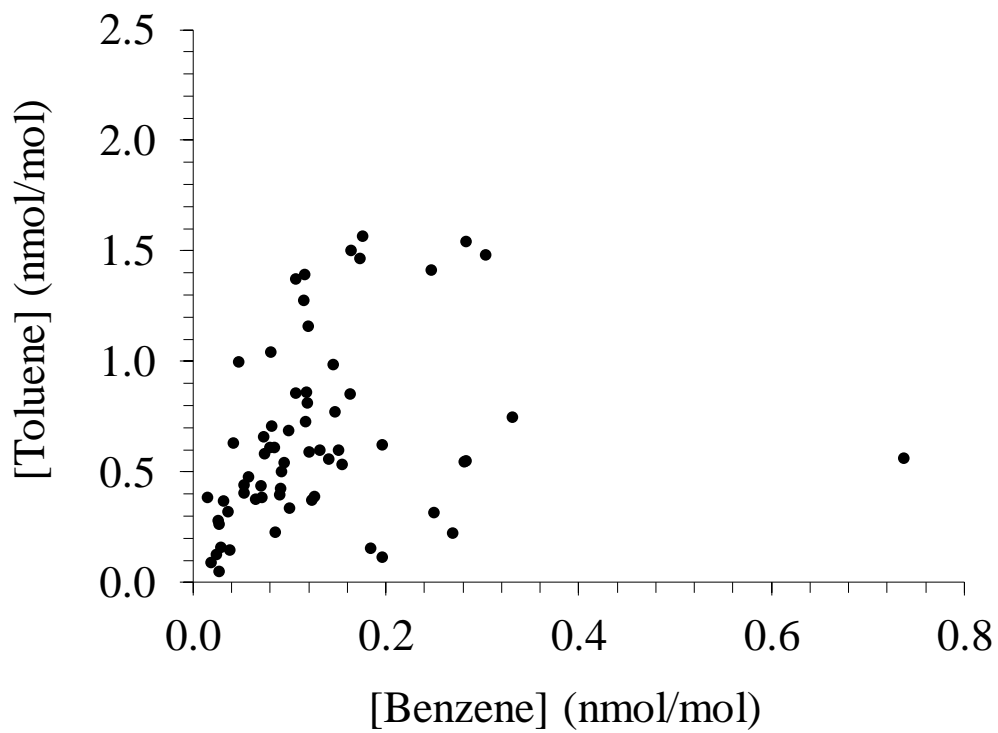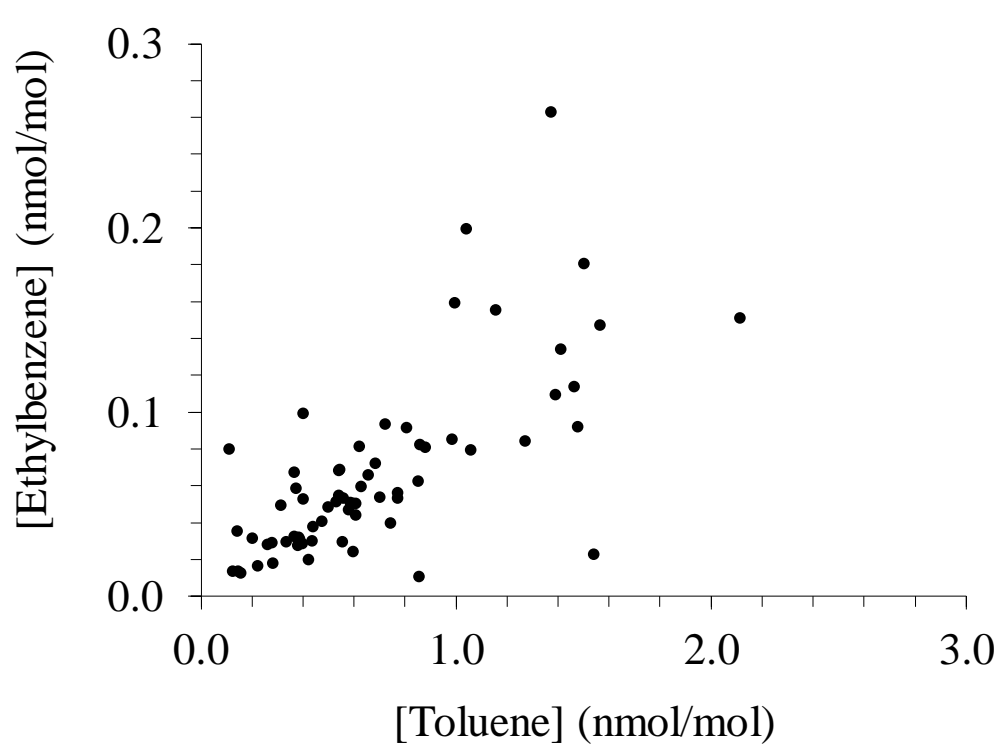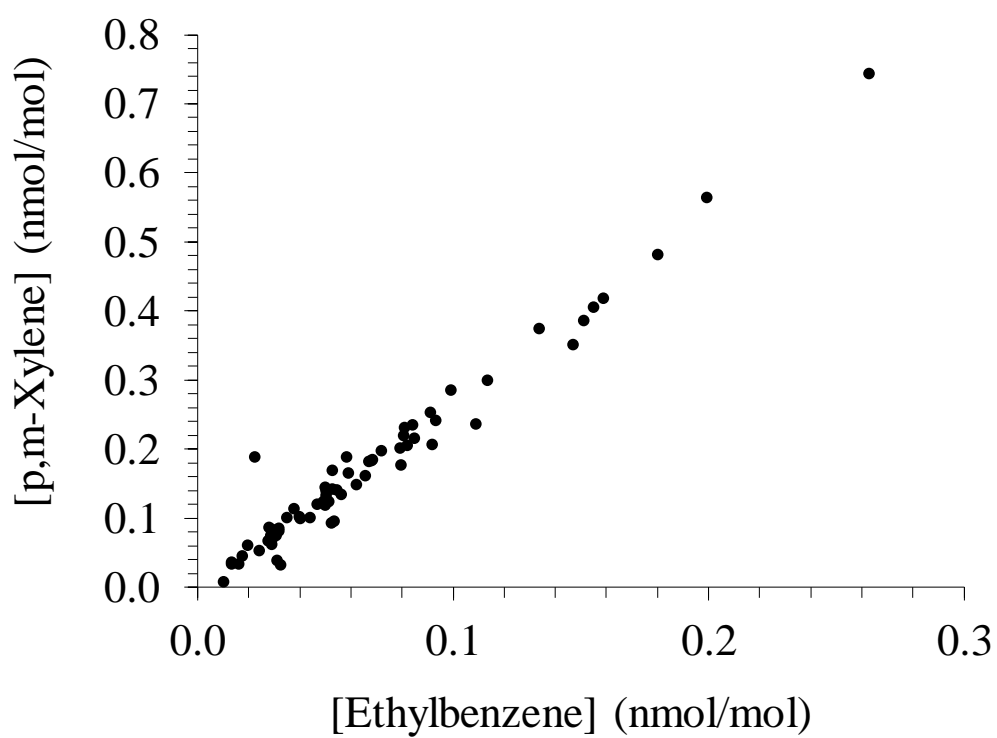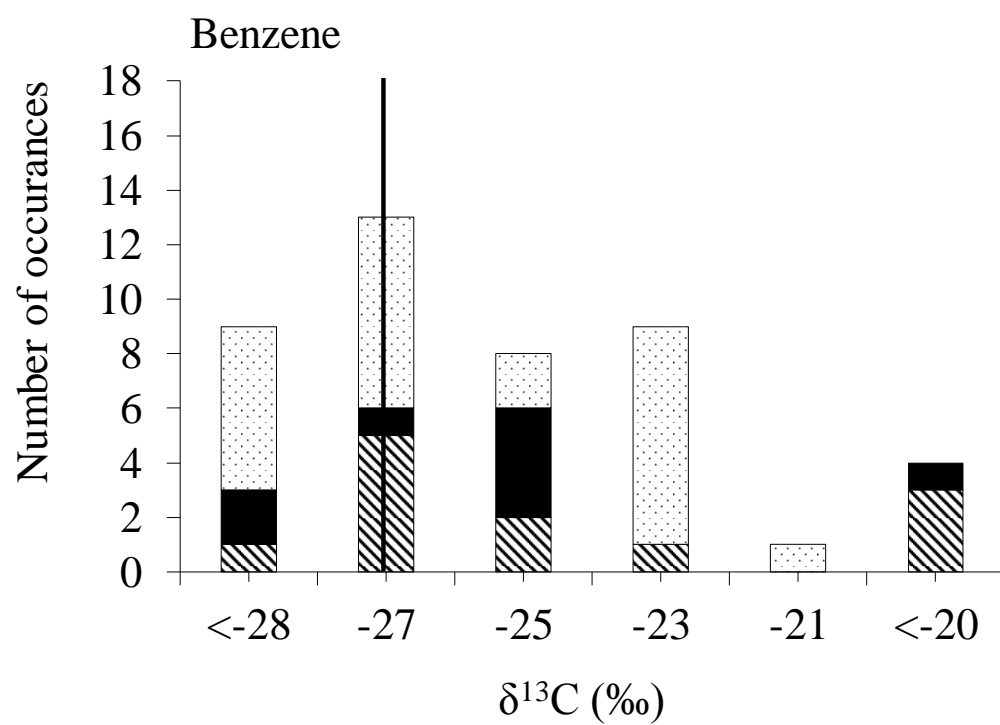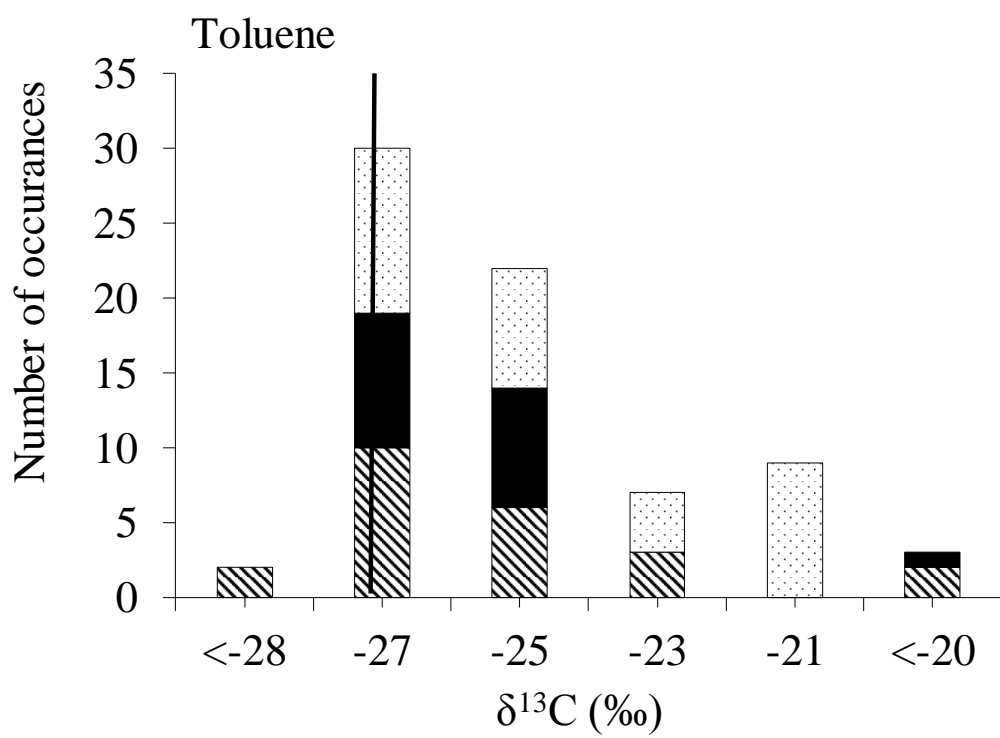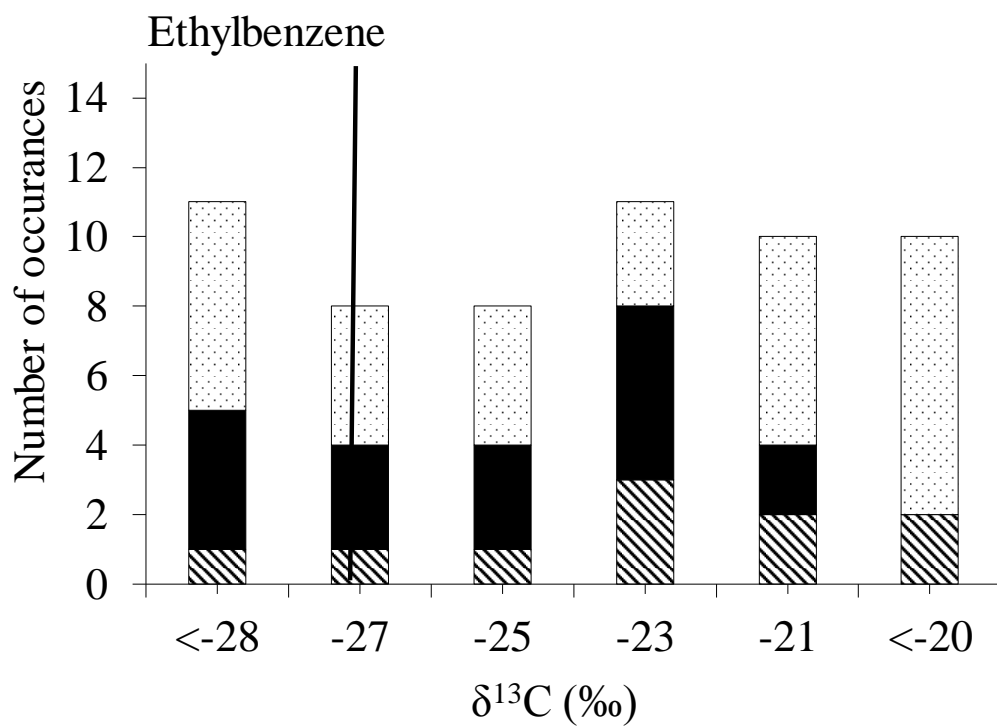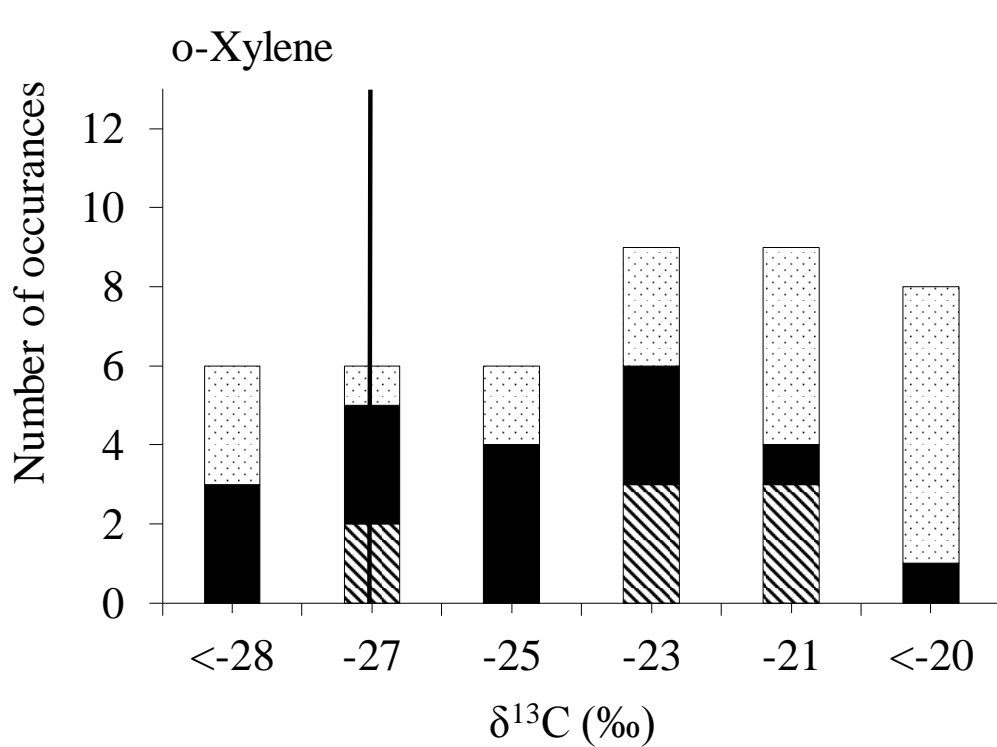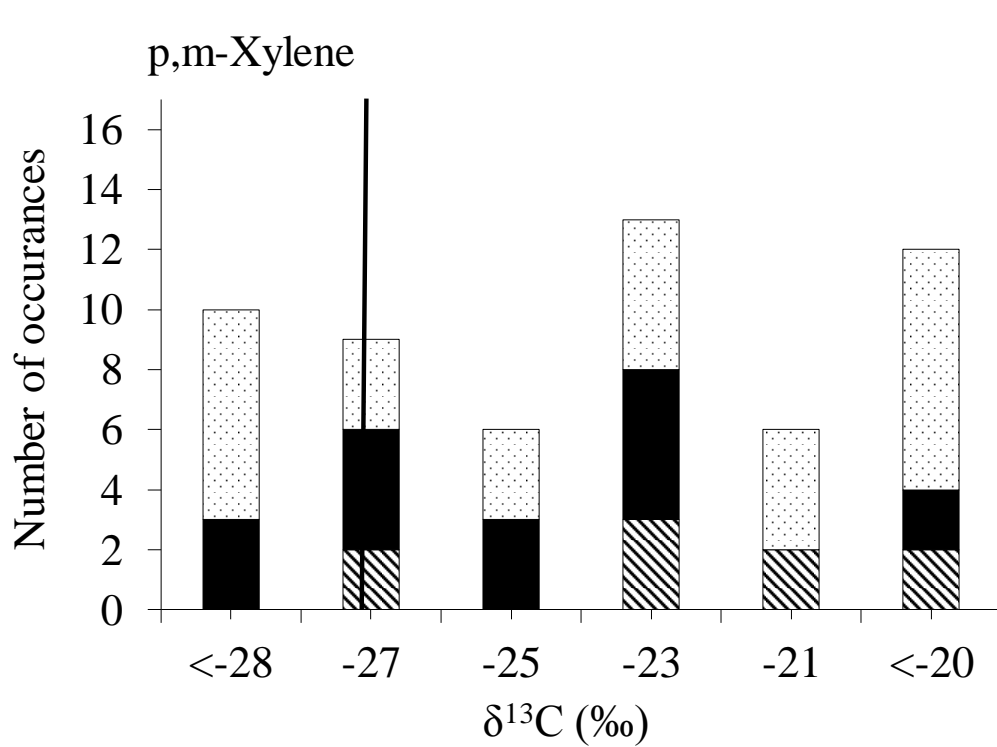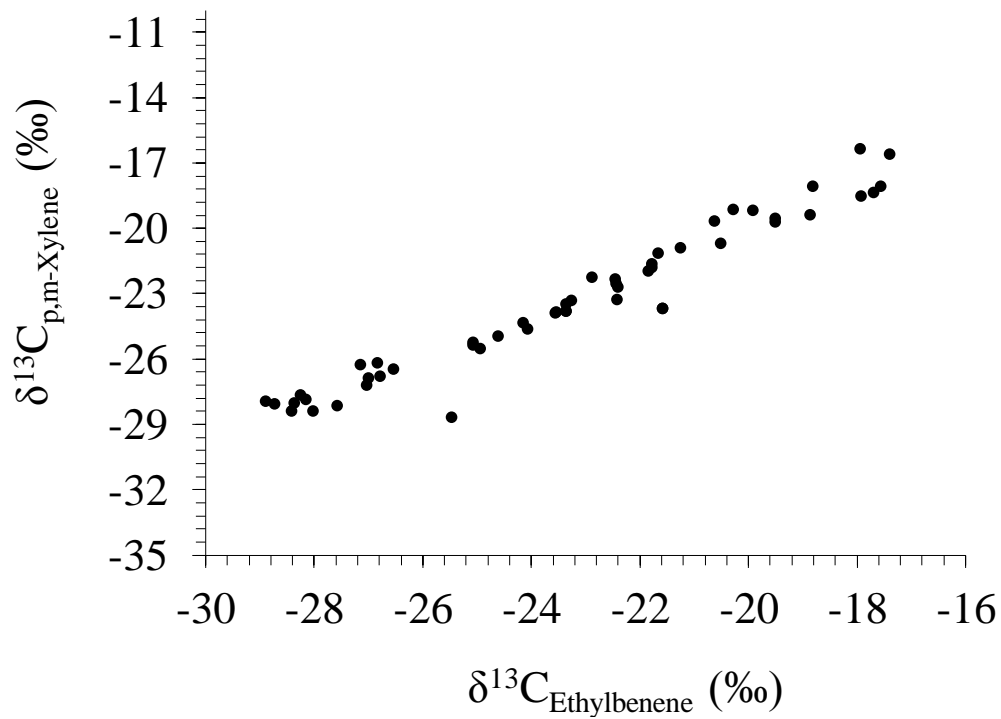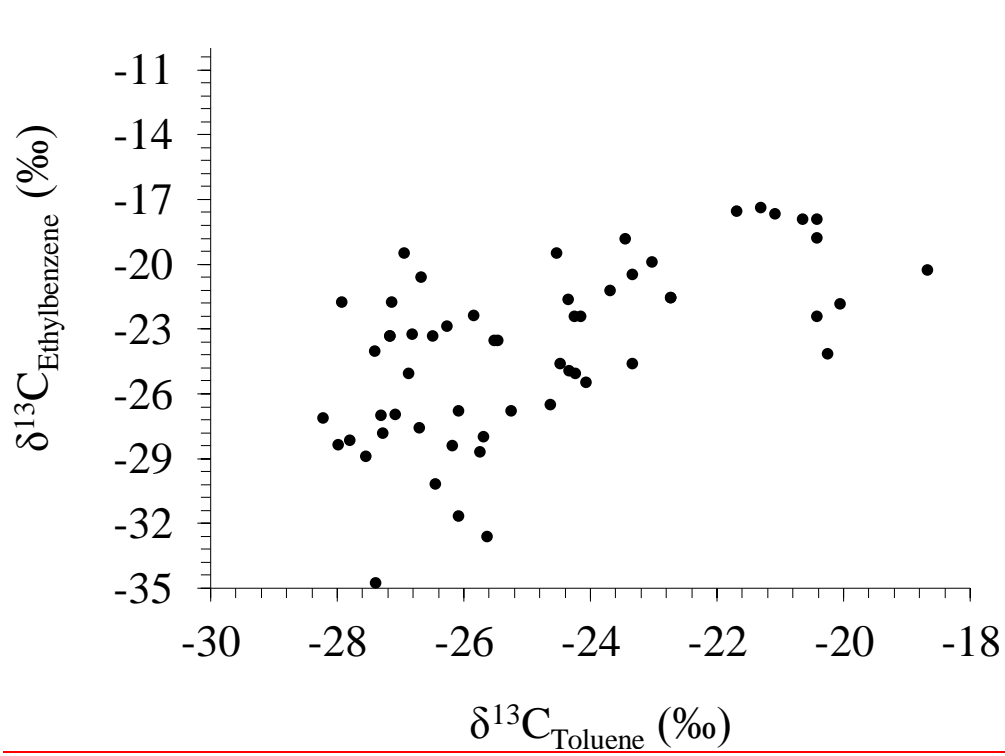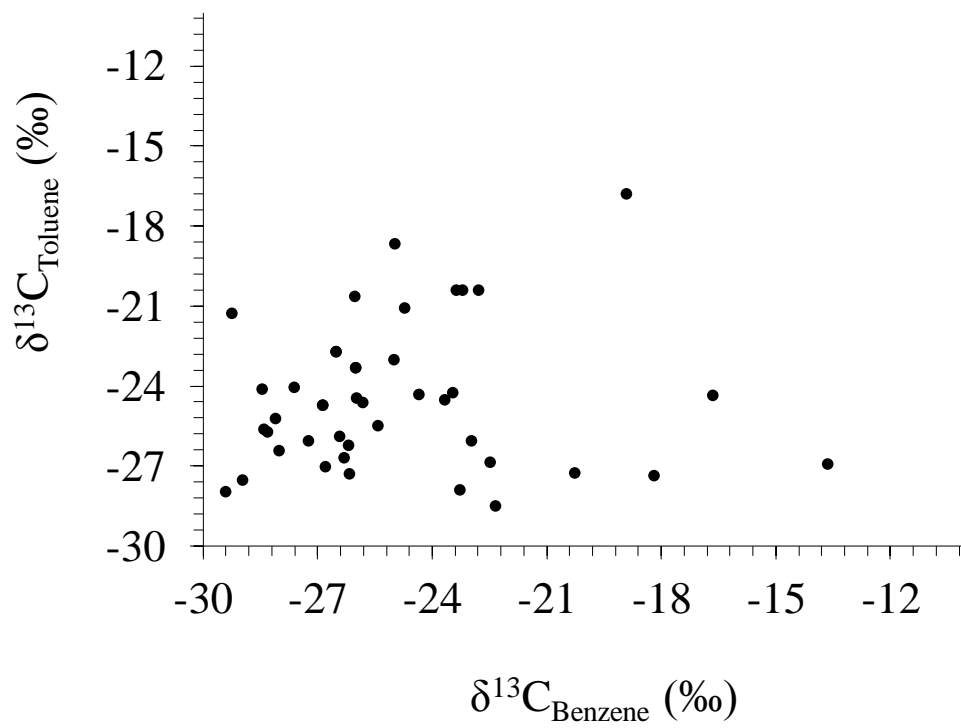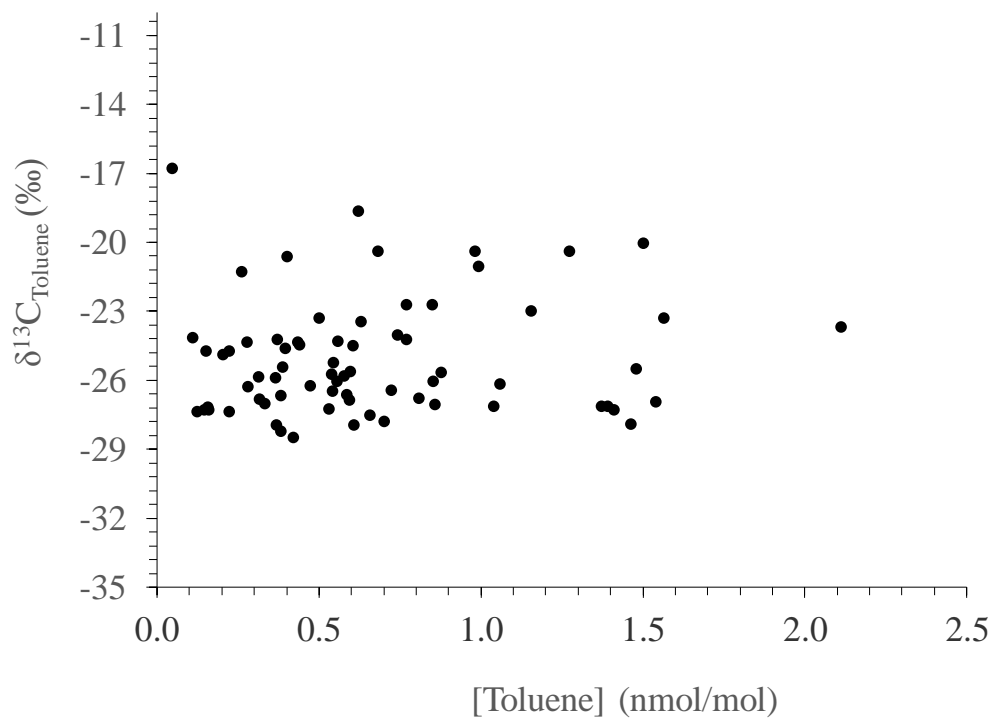
Figure 5

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2   Figure 6

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2 Figure 7

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a

b

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