

Review on:

Stable carbon isotope ratios of ambient volatile organic compounds
by Kornilova et al.

The authors present measurements of mixing ratios and stable carbon isotope ratios of aromatic compounds obtained in Toronto, Canada. They determined $\int [OH] dt$ to investigate the photochemical processing of the different VOC. Based on their results that $\int [OH] dt$ shows a dependence on VOC reactivity they arrive at the conclusion that mixing of air masses dominates the $\int [OH] dt$ values. Comparing the mixing ratios and isotope ratios of different pairs of VOC they conclude that sources with different emission ratios have a larger impact on the VOC composition than photochemical processing.

This study is yet another proof of the strength of isotope ratios for the investigation of atmospheric VOC. Although an interpretation maybe difficult (see my general comment), the attempt to disentangle transport and mixing from photochemical processes is an important approach to understand the organic composition of air masses and to identify sources and fate of these compounds.

The paper is the first investigating the relation between VOC concentrations and isotope ratios in an urban and more or less polluted environment. Therefore, it contributes to the progress of isotope ratios as a tool for the investigation of atmospheric processes that are not possible with concentration measurements alone. The paper should therefore be published in ACP after minor revision.

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.

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?

Specific comments:

Title:

Change the title to “... ambient **aromatic** volatile organic compounds” because only these compounds are investigated (see first sentence of the abstract).

P 4, L 5-6:

“... mixing ratios that are 3 to 5 orders of magnitude lower ... “

With respect to which reference value? In the sentences before $\mu\text{mol mol}^{-1}$ and nmol mol^{-1} are given. Maybe, giving mixing ratios here would be better.

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.

P 4, equation 1 and P5, equation 2:

Skip “x 1000 ‰”, see guidelines by Coplen 2011.

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.

P 5, L17:

The second “ $\delta_A^{13}\text{C}$ ” must read “ $\delta_S^{13}\text{C}$ ”.

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?

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

P 8, L 5:

“... strong dependence between C_2 -alkylbenzenes ...“

Strong dependence of C_2 -alkylbenzenes of what? Please specify.

P 9, L 14:

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

P 10, L 1:

Varying **the** extent of ...

P 10, L 6:

What do you mean by “steady state δ -values”?

P 10, L 19:

Again a wrong reference to Figure 3.

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?

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.

P 17, L 15:

Here a reference to Figure 15 is given regarding nearby sources. What are these sources? Can they be specified?

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”?

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

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?

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.

Figure 9 and 10:

Labeling of the y-axes are missing