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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stable isotope measurements confirm volatile organic compound oxidation as a major urban summertime source of carbon monoxide in Indianapolis, USA" *by* Isaac J. Vimont et al.

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We thank the reviewer for taking the time to review this paper and provide us with detailed feedback. We have responded to the individual comments below. Each comment is denoted by "Comment #:".

Anonymous Referee #2

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Discussion paper

General Comments:

This manuscript by Vimont et al. presents CO stable isotopes on air samples collected during the summers of 2013 – 2015 at three tower sites (one background site and two urban sites) in and around Indianapolis, USA. They collected the background air samples from the windward site of the city to remove the background CO signal from the urban measurements and detect the urban CO enhancement to characterize the stable isotopic compositions of the summer time urban CO source. Their isotope results pointed out that the BVOC oxidation could be an important urban source in the summertime.

General Comment 1:

If their CO data have not been published elsewhere, it could be worth publication in ACP. Since the data have already been reported in the previous paper (Vimont et al. 2017), it is hard to recommend this manuscript for publication in the current state. They should work hard to add some new experimental data to support or improve their summertime analysis; e.g. try to determine stable isotopic compositions (especially for oxygen isotope) of photochemically produced CO from BVOC because their isotope analysis depends heavily on it.

Response to General Comment 1:

While it is true that the full Indianapolis data set (Figure 5) was included in a previous publication, it was only included at the request of a reviewer for that manuscript. We made no attempt to analyze the summer data from Indianapolis in that earlier paper, and to date, no one else has either. It is not uncommon for previously published data to be analyzed or re-analyzed in subsequent publications.

The focus of the two papers is substantially different. The wintertime data was analyzed with the goal of providing an estimate of the isotopic composition of fossil fuel produced CO. The winter time data showed significant deviation from previous fossil

fuel isotopic estimates, which was explained by differing emissions regulation. This manuscript attempts to quantify the BVOC fraction of CO in an urban region, using published values for the isotopic signatures. While the importance of BVOC-produced CO as an urban CO source has been previously suggested by modeling studies and inferred indirectly from other types of observations (e.g. Kanakidou and Crutzen, 1999, Turnbull et al., 2006, and Cheng et al., 2017, referenced in the manuscript), to our knowledge, our study presents the most direct and conclusive evidence of this source. As emission regulations have succeeded in lowering urban CO from traffic, the BVOC-produced CO has become increasingly important. We felt this result was important enough and removed enough from the wintertime conclusions to warrant a separate paper.

Nonetheless, we have accepted the reviewer's recommendations and plan to submit a revised manuscript with additional data that help to constrain the isotopic signature of VOC-produced CO. Please see the comment titled "Proposed Revisions to Manuscript" for details (posted as an additional comment in the discussion section of this paper).

Specific Comments:

Comment 1:

Figures 1, 2, 3 It will be a lot better to draw the maps in same range (latitude and longitude) and plot the same stations; the readers could easily compare the figures 1, 2, 3. Also, it is better to limit the number of the stations to six stations that you mentioned in Page5 line 17 of the text (perhaps stations 1, 2, 3, 5, 6, 9 ?).

Response to Comment 1:

We will remove figures 1,2, and 3 in the revised manuscript and replace them with a single map to avoid redundancy, showing both the tower locations and a modeled vegetative ground cover/usage overlay. We will limit the station numbers to the specific towers in the text, for clarity.

Comment 2:

Figure 2 The readers want to see more useful information in the map such as land use and cover classification than just showing the road map.

Response to Comment 2:

See response to Comment 1

Comment 3:

Figure 3 The figure seems exactly the same as Figure 1 in Turnbull et al. 2015. The authors should make the original version of the figure or just refer Turnbull et al. 2015.

Response to Comment 3:

See response to Comment 1

Comment 4:

Figure 5 Add graphs showing the time series of the deference between the data (CO mole-fraction, carbon-13, and oxygen-18) from the urban site (Towers 2 and 3) and those from the background site (Tower 1) to Figure 5, because the discussion in this paper is focused on the deference between the urban site and the background site

Response to Comment 4:

We will add traces that show this difference for CO mole fraction. Simple subtraction of isotopic values is not very informative without a proper isotope mass balance calculation, and we would prefer to leave it out.

Comment 5:

Figure 5 (horizontal axis) Please show the months in horizontal axis. Furthermore, could you please draw two-way arrow below the horizontal axis to show the period you used in the manuscript for discussing the summertime source of CO.

Response to Comment 5:

We will make these changes to the revised manuscript.

Comment 6:

Page 5, Line 17 Please add the name of the six stations. (perhaps Towers 1, 2, 3, 5, 6, 9 ?).

Response to Comment 6:

We will add the tower numbers to the map figure as well as in this location, but are going to limit the map figure to the three towers used in this study.

Comment 7:

Page 6, Line 25 The temperature of the cryogenic trap (-60 oC) is different from that in Vimont et al. 2017 (-70 oC).

Response to Comment 7:

This is a typographical error and will be corrected in the revised manuscript

Comment 8:

Page 6, Line 30 Please write a temperature of the second cryogenic trap.

Response to Comment 8:

We will add this temperature to the text

Comment 9:

Page 7, Formula (1) Remove 103 and permil from the formula.

Response to Comment 9:

This was included at the request of the editor prior to posting in ACPD. We will seek the editor's recommendation before making this change

Comment 10:

Page 8, Line 13 – 16 Please cite the source of this explanation.

Response to Comment 10:

We will add a reference to our table of reactions and contributed CO in this explanation. We will also clarify that we are referring to the enhancements between the towers. The rate of reaction of CH4 with OH and CO with OH over 2-3 hours produces relatively little CO and thus changes the isotopic signature of the enhancement negligibly (shown in the table). Any overall contribution from the CH4+OH source and CO+OH sink in the atmosphere is removed with the background subtraction in this experiment.

Comment 11:

Page 9, Line 16 The reader wants to know the result of the calculation (1.4 nmol:mol CO), before moving on to the next explanation (the change in stable isotopic compositions).

Response to Comment 11:

We will add this into the revised manuscript as requested.

Comment 12:

Page 10, Line 10 Even though the formula is simple, I think it is better to show the formula (e.g.ΔXCO = (XCO,i) e-kt) in the text.

Response to Comment 12:

We will add this formula to the text in the revised manuscript as requested.

Comment 13:

Page 10, Line 12 I think the word “net loss” is used as the meaning of “total loss” in the text. The word “net loss”, however, might be confused with the same word meaning the opposite of “gross loss” for some readers and may think that the authors have mistaken

“net loss” as “gross loss”. Can you use the other apposite word?

Response to Comment 13:

We will make this change as requested

Comment 14:

Page 10, Line 12 The same as Comment 11.

Response to Comment 14:

We will report the calculated value as requested in the revised manuscript.

Comment 15:

Page 10, Formula (5) Remove 103 and permil from the formula.

Response to Comment 15:

Similar to the response to comment 9, this was included at the request of the editor. We will consult the editor on this request for change.

Comment 16:

Page 18, Line 30 - Page 19, Line 1 This sentence explains about the “short” lifetimes of monoterpenes in the atmosphere. Why are there no explanations about the lifetimes of monoterpenes that react with OH ?

Response to Comment 16:

We will better explain this in the revised manuscript and explicitly discuss the reactions with OH

Comment 17:

Reference Some of the references are not written in the proper form. Please correct them.

Response to Comment 17:

We will correct the references in the revised manuscript.

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