

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.

Isaac J. Vimont et al.

isaac.vimont@colorado.edu

Received and published: 27 October 2018

We have included this response in a separate comment as it applies to both reviews and seemed appropriate to include a separate comment.

We have carefully considered the reviewer remarks and have decided to provide a manuscript with major revisions, including two additional data sets. This will expand the scope of the paper. The revised manuscript will still begin with the same Miller-Tans analysis of the summertime data. We then will include radiocarbon measurements of

C1

CO₂ that have been analyzed to infer the fossil fuel CO₂ mole fraction. We will then use best estimates of the fossil fuel CO:CO₂ emission ratios at Indianapolis to estimate the fossil fuel CO component of the CO budget.

With the assumption that fossil fuel combustion and BVOC oxidation are the only two CO sources between the towers, we will subtract the fossil fuel CO enhancement from the total CO enhancement to estimate the COVOC enhancement. Once we have these estimates, we will use our results, combined with the previously published wintertime fossil fuel derived CO isotopic signatures in a simple mass balance calculation to provide estimates of the VOC-derived CO isotope signatures. Only 3 studies have previously attempted to quantify the BVOC isotopic signatures (Stevens and Wagner, 1989; Brenninkmeijer, 1993; Brenninkmeijer and Rockmann, 1997). Gros et al. (2002, Table 1) show the values of the VOC oxidized CO isotopic signatures from these studies, as well as their estimated uncertainties. Of particular note, the oxygen isotopic value is estimated at “greater than 3‰”. However, Stevens and Wagner (1989) provide a value of 15‰ while Brenninkmeijer (1993) and Brenninkmeijer and Rockmann (1997) estimate the value around 0‰. We will discuss the details of each of these studies, but broadly speaking, these studies determined these values by either assuming a constant background (Stevens and Wagner, 1989) or estimating the values by removing the combustion sources (through mass balance) and then evaluating the methane and VOC oxidation sources (Brenninkmeijer, 1993; Brenninkmeijer and Rockmann, 1997).

Our analysis simplifies the enhancement budget to VOC oxidation and fossil fuel combustion. This provides a simple mass balance calculation, wherein we calculate the VOC isotopic signature explicitly. We then present the mean and standard error of all of our samples, which provides an improved estimate of the isotopic signatures, with quantified uncertainty, particularly for the oxygen isotopes.

We do note that our Indianapolis sample set is limited to around 20 data points (we are still finalizing the data set and determining which data to include, which is why we do not have an exact number). Further, our mass balance calculations of the VOC oxidation

C2

signature yield a large spread in the data. We filter the calculated VOC signatures at 3σ . We believe the mean values we obtain are reasonable as they are consistent with the previous estimates of the isotopic signatures, with improved uncertainty.

We will then introduce a second CO isotope dataset from a NOAA GMD network site in Beech Grove, South Carolina, USA. This may have elevated BVOC-produced CO in the summertime based on its remote location and time series of CO mole fraction data produced by NOAA GMD (which we will also include). We will use this site for an independent estimate of isotopic signatures of BVOC-produced CO. The estimates obtained from Beech Grove and from Indianapolis compare well with each other.

For the South Carolina data, we have only a single year of analyses with 0-2 samples per month. Further, we do not have a “background” site, so we rely on comparing several methods of isotopic source determination (Keeling Plots, modified miller tans plots, and using INX Tower 1 as a background in a traditional miller-tans plot). These methods work well for analysis of CO₂ isotopes, but for a short-lived gas like CO, there is significantly more uncertainty in the interpretation of the results. Nonetheless, the various approaches yield results that are consistent with each other and with VOC isotopic signatures derived from INX data.

References

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C3

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-506>, 2018.

C4