Response to Reviewer 1

We thank the reviewer for taking the time to review our manuscript, and provide us with feedback. We have responded to the individual comments below, in italicized text. We have split the reviewer response into comments, which are denoted using bold text. We have provided a completely rewritten manuscript which has changed the entire scope of the paper, and our responses to some of the comments reflect this change. Additionally, since the paper has changed so drastically, we have only responded briefly here in response to the comments.

Anonymous Referee #1

Received and published: 13 August 2018

Vimont et al. present the analysis of previously published CO mole fraction and isotope measurements at three stations in Indianapolis. The evaluation of summer time indicates that photochemical production of CO from BVOCs is a significant source of CO in summer.

Comment 1

The scientific content of the paper is low.

Comment 1 Response: As stated in our previous response to the reviewer, we do not agree with this statement. Nonetheless, we have provided a rewritten paper which attempts to place constraints on the isotopic signatures of CO produced by oxidized VOCs.

Comment 2

At least 3 of the 5 figures (2, 3 and 5) were published previously; one other figure (Figure 1) simply shows three of the INFLUX stations of Figure 2 on a satellite image and has no additional scientific value.

Comment 2 Response: We have removed the original Figures 2 and 3. We have included a simple satellite image with only towers 1 and 2 (the two towers discussed in the paper). This figure shows the location of the two towers as well as the significant vegetative cover within the urban domain.

To address former figure 5, we do not agree that this figure is repetitive due to its previous publication. Without this figure, the readers have no visual representation of the actual isotopic data, and we believe it is inconvenient for the reader to have to look to a different publication to see the actual data. We have reduced the figure to only include towers 1 and 2, as the paper has changed focus we only discuss data from towers 1 and 2.

Comment 3

Also the entire dataset was already published previously, but then only the winter data were analyzed. The "new" part of the present manuscript is that the summer data were also analyzed, which in terms of the dataset means that simple Miller-Tans plots were produced in Figure 4.

It was not a good idea of the authors to split the analysis of one dataset into two papers that now are largely repetitive and both have little scientific value. The main result that there is isotope evidence for photochemical production of CO from BVOC in Indianapolis is valuable, but the paper as a hole has for me too little scientific substance to be published in ACP.

Response to Comment 3: We have rewritten the paper and included new data sets and analyses. Though we still use the summer data from Indianapolis, which was published previously, we now include 14CO2 derived fossil fuel CO2 data, as well as data from one year of CO isotopic analyses at a separate site in South Carolina. We analyze the summer isotopic signatures at Indianapolis by way of Miller Tans analysis, as before. We then use this in conjunction with previously published results and the fossil fuel CO2 data to calculate fossil fuel produced CO, and from there VOC produced CO. We then use mass balance to calculate estimates for the signatures of CO produced by oxidation of VOCs. We believe these additions provide significant scientific substance for publication in ACP.

Comment 4

The method description and data analysis is presented in a level of detail that is suitable for a thesis, but in my opinion not for a scientific publication. The analysis presented in Tables 2 in relation to the simplification of the CO budget was already performed in the previous publication by the authors, and is only shown in more detail here. The description of methods is very detailed and contains much material that should be considered general knowledge (e.g. the meaning of a correlation coefficient) or is repeated in too much detail from previous publications. The evaluation of the possible BVOC contribution resulting in table 4 is derived from a simple multiplication of an assumed OH level with rate constants and VOC abundances from the literature. It produces a result that is expected and the discussion then connects results from various previous studies.

Response to Comment 4: After carefully re-reading the paper, we agree with the reviewer in this comment. In the revision, we have moved the budget simplification section to a supplementary document. We feel that the simplification is important to the conclusions of the paper. Further, though subtle, we have changed the parameters in the calculations to represent highly polluted, hot conditions, which are different from previous publications.

We have removed discussion of correlation coefficients as well as all of the hydrocarbon calculations and table 4.

Response to Reviewer 2

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 #:". We have provided a fully rewritten manuscript (with supplement) to address the reviewer concerns. As such, this new manuscript has changed dramatically from the previously reviewed submission. Thus, we have responded to the comments here briefly to address the concerns of the reviewer.

Anonymous Referee #2

Received and published: 16 August 2018

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.

Nonetheless, though we still have included the previously published data shown in the previous version figure 5, we have followed the reviewer's suggestion and provided a rewritten manuscript focusing on the isotopic signatures of VOC produced CO. We have included new 14CO2 derived fossil fuel produced CO2 data, and 1 year of CO isotopic analyses from a site in South Carolina. We again use a Miller Tans analysis to determine the source signature of the Indianapolis urban enhancements. We then use the fossil fuel CO2 data and published values of the CO:CO2 ratio to determine fossil fuel CO. We then calculate VOC produced CO, and using mass balance and our isotopic measurements, we estimate the 13CO and C18O signatures of VOC produced CO. We then compare these results to our measurements at a remote, heavily *forested site in South Carolina which we believe has a large summertime contribution to its CO mole fraction measurements from oxidation of biogenic VOCs.*

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 have removed figures 2, and 3 in the revised manuscript and replace them with a single satellite image to avoid redundancy, showing both the tower locations and a modeled vegetative ground cover. We have limited the station numbers to the specific towers in the text, for clarity (towers 1 and 2).

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 have not made this change. Simple subtraction of isotopic values is not very informative without a proper isotope mass balance calculation, and we would prefer to leave it out. We have reduced the towers in the time series graph. We have provided this plot for the convenience of the reader, so they do not have to go searching for the data in another publication. It is meant to compliment the data table found in the supplementary information. The discussion of the paper has refocused on the isotopic signatures of the VOC source.

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 have added the requested changes to the plot.

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 have clarified the locations where the flasks are taken in the text:

"INFLUX has twelve instrumented towers within and around the urban boundary (Miles et al., 2017). The flask-sampling regime was described in detail by Vimont et al. (2017) and Turnbull et al. (2015). In brief, discrete hourly-integrated air samples are collected at six of the towers, although the integrated samplers (Turnbull et al., 2012) are moved between the twelve towers occasionally. Three of the towers have had continuous flask samples and were sampled for CO isotopes (towers 1-3, Turnbull et al., 2015; Miles et al., 2017; Turnbull et al., 2019) approximately six days per month, during the early afternoon when the strongest boundary layer mixing occurs (19:00 UTC, 14:00 local). Stable isotope measurements of CO were made on samples collected from July 2013 to July 2015. In this paper, we consider only the summer samples that were collected in July and August 2013, May-August 2014, and May – July 2015 (inclusive) from tower 1 (121 m above ground level (AGL), 39.5805° N, 86.4207° W), and tower 2 (136 m AGL, 39.7978° N, 86.0183° W) (figure 1)."

We have simplified the map figure (figure 1) to show only the two towers discussed in the text. We have referenced Miles et al., 2017, as the sampling at the towers is discussed in detail there.

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 was corrected

Comment 8: Page 6, Line 30 Please write a temperature of the second cryogenic trap.

Response to Comment 8: We have made this correction

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, and we have not made this change. We defer to the editor on this change.

Comment 10: Page 8, Line 13 – 16 Please cite the source of this explanation.

Response to Comment 10: We have added a reference to our table of reactions and contributed CO in this explanation. We also attempted to clarify that we are referring to the enhancements between the towers:

"One of the advantages to the INFLUX experiment is the ability to remove background signals from the urban measurements, and thereby derive the urban enhancement. This approach also allows the CO budget to be simplified. Both the oxidation of CH_4 to CO and the oxidation of CO to CO_2 via the OH radical are reactions that proceed slowly relative to the experimental scale of a few hours transit time. We can consider only this short time scale because we are only considering reactions that can occur when air masses are transiting between the background and urban sites (table S1). Because of this, we calculate

that these two processes have negligible impact on our urban CO enhancements, and can be disregarded given the short reaction time being considered (detailed below, table S1).”

This section has been moved to the supplementary information, for reference.

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 have added this result as requested. As in comment 10, this section has been moved to the supplementary material.

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 have added this formula as requested. As in comment 10 and 11, this section was moved to the supplement.

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 have made this change in the supplement:

“Using the same method and OH concentration as for CH_4 oxidation above, and a reaction rate for CO+OH of $1.44\text{x}10^{-13}$ cm^3 s^{-1} (Atkinson et al., 2006), we calculated the loss of CO during the transit of an air mass across the city:”

Comment 14: Page 10, Line 12 The same as Comment 11.

Response to Comment 14: We have reported this value as requested.

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 defer to the editor on making this 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: This section has been removed in the rewritten manuscript.

Comment 17: Reference Some of the references are not written in the proper form. Please correct them.

Response to Comment 17: We have completely redone the reference list due to the rewrite, and believe them to be correct.

Changes are highlighted in red text

Title:

An improved estimate for the $\delta^{13}C$ and $\delta^{18}O$ signatures of carbon monoxide produced from atmospheric oxidation of volatile organic compounds

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Abstract:

Atmospheric carbon monoxide (CO) is a key player in global atmospheric chemistry and a regulated pollutant in urban areas. Oxidation of volatile organic compounds (VOCs) is an important component of the global CO budget and has also been hypothesized to contribute substantially to the summertime urban CO budget. In principle, stable isotopic analysis of CO could constrain the magnitude of this source. However, the isotopic signature of VOC-produced CO has not been well quantified, especially for the oxygen isotopes. We performed measurements of CO stable isotopes on air samples from two sites around Indianapolis, USA over three summers to investigate the isotopic signature of VOC-produced CO. One of the sites is located upwind of the city, allowing us to quantitatively remove the background air signal and isolate the urban CO enhancements as well as the isotopic signature of these enhancements. In addition, we use measurements of $\Delta^{14}CO_2$ in combination with the CO:CO_2 emission ratio from fossil fuels to constrain the fossil fuel-derived CO and thereby isolate the VOC-derived component of the CO enhancement. Combining these measurements and analyses, we are able to determine the carbon and oxygen isotopic signatures of CO derived from VOC oxidation as -33.6‰ ± 1.0‰ and 1.3‰ ± 2.7‰, respectively. Additionally, we analyzed CO stable isotopes for one year at Beech Island, South Carolina, USA, a site thought to have large VOC-derived contributions to the summertime CO budget. The Beech Island results are consistent with isotopic signatures of VOC-derived CO determined from the Indianapolis data. This study represents the first direct determination of the isotopic signatures of VOC-derived CO and will allow for improved use of isotopes in constraining the global and regional CO budgets.

1. Introduction

The global carbon monoxide (CO) budget, along with regional and local CO budgets, remain uncertain (e.g. Holloway et al., 2000; Duncan et al., 2007; Granier et al., 2011; Zhou et al., 2017; Strode et al., 2018). CO stable isotope measurements can aid in the partitioning of the sources of CO, and hence improve global and regional budgets (e.g. Brenninkmeijer et al., 1999). Several studies have incorporated stable isotopes of CO to independently constrain the sources of CO (Manning et al., 1997; Bergamaschi et al., 2000; Park et al., 2015). On the global scale, mole fraction of carbon monoxide (CO) has four major sources which include biomass/biofuel burning, oxidation of methane (CH_4), the incomplete combustion of fossil fuels and the oxidation of volatile organic compounds (VOCs) (Logan et al., 1981; Duncan et al., 2007; Table 1). These sources are balanced by the oxidation of CO by the hydroxyl radical (OH) and a small soil sink, resulting in a residence time of CO in the atmosphere that is ≈2 months on average but varies by location and time of year (Logan et al., 1981; Duncan et al., 2007). Each CO source has a unique isotopic signature which is determined by the isotopic signature of the source material (e.g., CH_4) and the process(es) by which the CO is formed. The carbon isotopic signature of methane-derived CO is much more negative than that of the other sources, largely due to the depleted carbon isotopic signature of methane (Table 1, Brenninkmeijer et al., 1999). The oxygen isotopic signature can help distinguish between combustion (fossil fuel and biomass burning) and oxidation sources (methane and VOC-derived CO), with combustion sources having more positive isotopic values than oxidation sources (Table 1, Brenninkmeijer et al., 1999).

The isotopic signatures of CO from fossil fuel combustion and biomass burning have been relatively well quantified (Brenninkmeijer et al., 1999; Table 1). The ^{13}CO produced by oxidation of methane has also been well quantified, although the C^{18}O signature remains more uncertain (Brenninkmeijer et al., 1999). However the isotopic signatures of CO produced by the oxidation of volatile organic compounds (VOCs) remain poorly known (Brenninkmeijer and Röckmann (1997), Brenninkmeijer et al. (1999), and Gros et al. (2001). The carbon isotopic signature of CO produced by oxidation of VOCs has been estimated to around -32‰, from atmospheric measurements (Stevens and Wagner, 1989) and through analysis of the isotopic signature of isoprene, accounting for fractionation during the oxidation reaction (Sharkey et al., 1991; Conny and Currie, 1996, Conny et al., 1997).

Only two prior studies have tried to estimate the oxygen isotopic signature of VOC-derived CO, yielding very different values: 0‰ (Brenninkmeijer and Röckmann, 1997) or 15‰ (Stevens and Wagner, 1989), with a reported uncertainty of “greater than 3‰” (e.g. Gros et al., 2001; Table 1). As VOC oxidation is a major source of CO on global and regional scales (e.g. Logan et al., 1981; Guenther et al., 1995; Duncan et al., 2007), the large uncertainty in the associated isotopic signatures presents a major obstacle to using isotopes in investigations of the atmospheric CO budget.

Our study uses a new set of measurements to evaluate the carbon and oxygen isotopic signatures of CO produced from VOCs by analyzing the urban CO isotopic enhancements at Indianapolis, IN, USA. An urban setting for determining the isotopic signature of CO from oxidized VOCs may not seem like an obvious choice, because of the large CO enhancements from fossil fuel burning (EPA, 2014 , Mak and Kra, 1999; Popa et al., 2014; Turnbull et al., 2015; Vimont et al., 2017; Turnbull et al., 2018). However, previous literature suggests that during the summer months there may also be a large urban source of CO from the oxidation of VOCs, likely from biogenic sources (Guenther et al., 1993, 1995; Carter and

Atkinson, 1996; Kanakidou and Crutzen, 1999; Cheng et al., 2017, Turnbull et al. (2006) Miller et al. (2012))

Some of these studies aimed to quantify fossil fuel CO_2 enhancements (CO_{2FF}) by using CO enhancements as a proxy measurement but noted that the ratio of $CO:CO_{2FF}$ enhancements was higher in the summer than the winter at several sites in the eastern United States (Turnbull et al., 2006; Miller et al., 2012). A higher $CO:CO_{2FF}$ ratio is inconsistent with a stronger sink process such as an increase in OH during the summer months. Instead, a seasonal increase in a non-fossil fuel source provides the most likely explanation for the increase in the $CO:CO_{2FF}$ ratio. These studies hypothesized, but could not confirm, that oxidation of VOCs may be the source of this summertime increase in $CO:CO_{2FF}$ ratio.

Studies that model the effect of CO sources on the measured CO mole fraction have also indicated that oxidation of VOCs (particularly from biogenic sources) contributes significantly to the global and regional CO budget (e.g. Kanakidou and Crutzen, 1999). Isoprene and terpene emissions from broadleaf species have been shown to be a large source of VOCs (Guenther et al., 1995; Helmig et al., 1998; Harley et al., 1999), particularly in the southeastern United States (e.g. Chameides et al., 1988). Griffin et al. (2007) used the Caltech Atmospheric Chemistry Mechanism to investigate CO production by VOC oxidation at a regional scale in the United States. Their model determined that VOC oxidation could provide as much as 10-20% of the CO observed in parts of New England, but in a heavily polluted region such as the Los Angeles Basin, the percentage was much lower, on the order of 1% or less. Cheng et al. (2017) measured O_3 and CO mole fractions and then modeled CO production from the various sources using O_3-to-CO ratios. Their model suggested the oxidation of isoprene might equal or exceed the total anthropogenic production of CO within the urban region of Baltimore, USA.

This study focuses mainly on measurements from the Indianapolis FLUX project (INFLUX). INFLUX provides a sampling methodology that allows for quantitative removal of background air signals, which isolates the urban enhancement, and simplifies the source and sink budget analysis (Turnbull et al., 2015; Vimont et al., 2017; Turnbull et al., 2018). Measurements are made not only at tower sites within and downwind of the city, but also directly upwind of the city, so that the changes in CO mole fraction and isotopic values due to the urban influence can be isolated. The short transit time of air across the city means that removal of CO by OH (and the associated impact on the isotopic signature) can be ignored. Methane oxidation is similarly minimal in the short transit time, and biomass burning is known to be very small within the urban confines.

In addition to the CO mole fraction and stable isotopic measurements, $^{14}CO_2$ measurements were also performed on the INFLUX samples, allowing for accurate quantification of CO_{2FF} (Turnbull et al., 2015). This allowed us to partition the urban CO enhancement between fossil fuel and VOC-derived sources. We were then able to isolate the carbon and oxygen isotopic signatures of CO produced from VOC oxidation.

To further examine our estimates of the isotopic signatures of CO produced from oxidized VOCs, we analyzed bi-monthly samples from a site at Beech Island, South Carolina, USA. This site is heavily forested and the CO mole fraction at this site should be strongly influenced by isoprene oxidation during the summer. By analyzing the isotopic signatures at this site, we were able to compare the Beech Island isotopic signals to our estimates for VOC-derived CO.

2. Methods

2.1 Tower Sampling at Indianapolis

Indianapolis, Indiana is a metropolitan area of over one million people in the Mid-West region of the United States. It is surrounded by mostly agricultural land, interspersed with trees and foliage both inside and outside of its borders (figure 1). It has hot summers (25 to 30° C) and cold winters (-8 to 1° C) that result in a distinct growing season, with the winter being relatively devoid of biogenic fluxes of CO and CO_2 (Turnbull et al., 2015). INFLUX aims to develop and assess methods for determining urban greenhouse gas emissions. CO, though not a primary greenhouse gas, is measured and used as a tracer for fossil fuel CO_2 emissions and to provide information for source attribution.

INFLUX has twelve instrumented towers within and around the urban boundary (Miles et al., 2017). The flask-sampling regime was described in detail by Vimont et al. (2017) and Turnbull et al. (2015). In brief, discrete hourly-integrated air samples are collected at six of the towers, although the integrated samplers (Turnbull et al., 2012) are moved between the twelve towers occasionally. Three of the towers have had continuous flask samples and were sampled for CO isotopes (towers 1-3, Turnbull et al., 2015; Miles et al., 2017; Turnbull et al., 2019) approximately six days per month, during the early afternoon when the strongest boundary layer mixing occurs (19:00 UTC, 14:00 local). Stable isotope measurements of CO were made on samples collected from July 2013 to July 2015. In this paper, we consider only the summer samples that were collected in July and August 2013, May-August 2014, and May – July 2015 (inclusive) from tower 1 (121 m above ground level (AGL), 39.5805° N, 86.4207° W), and tower 2 (136 m AGL, 39.7978° N, 86.0183° W) (figure 1). The winter samples were examined in a previous study (Vimont et al., 2017) that determined in winter, CO enhancements in Indianapolis are primarily derived from fossil fuel combustion; the CO isotopic signature of the fossil fuel combustion source was also constrained. Though summer samples were also collected at tower 3 (39.7833° N, 86.1652° W), its proximity to Indianapolis' downtown district and its lower elevation above the ground (54 m AGL) meant that the signals there were strongly dominated by fossil fuel combustion sources, even in summer. Tower 2, located to the east of the urban region, was the ideal candidate for determining the isotopic signature of the oxidized VOC source of CO. Tower 2 "sees" a more mixed signal of urban and suburban sources including both fossil fuel sources and the influence of the substantial suburban vegetation (Turnbull et al., 2015; Turnbull et al., 2018).

For the samples in this study, collection was done when the wind was approximately from the west, so that Tower 1 provides a clean-air background for the towers further to the east (Turnbull et al., 2012). Tower 2 is east of the city, with only a small residential influence and one major highway nearby, with significant foliage within its influence footprint

(Turnbull et al., 2015). The distance between towers 1 and 2 is 51 km, and the average wind speed during the period sampled for this study was 4.4 m s^{-1}, which results in an average transit time of air from tower 1 to tower 2 of 3.2 hours.

The air samples were collected in Portable Flask Packages (PFP's) provided by the National Oceanic and Atmospheric Administration Global Reference Network (NOAA GRN)(https://www.esrl.noaa.gov/gmd/ccgg/aircraft/sampling.html). One-hour integrated samples were collected; this sampling regime allows for smoothing of very short-term variability that may be difficult to interpret (Turnbull et al., 2012). NOAA's Earth System Research Laboratory (ESRL) provides the infrastructure and logistical support for these PFP's, and the CO mole fraction measurements used in this study (Novelli et al., 2003). $^{14}CO_2$ measurements were performed at GNS Science with support from University of Colorado INSTAAR (Turnbull et al., 2015b).

2.2 Tower Sampling at Beech Island, South Carolina

Beech Island, South Carolina, USA (33.4057 °N, 81.8334°W) is a tall tower (305m AGL) site in the NOAA Global Greenhouse Gas Reference Network (GGGRN). Samples for CO stable isotopes were collected approximately bi-monthly for one year from this site. This site uses "grab sampling" rather than the integrating sampling used at the INFLUX towers. Flasks are flushed and then filled and pressurized over about a two minute period. Flasks are measured by the same methods as the INFLUX samples. However, although $^{14}CO_2$ measurements are made on some flasks from this site, limitations on the available air in each flask mean that the CO stable isotopes were measured on different flasks (collected on different dates) than the $^{14}CO_2$ measurements.

2.3 Stable Isotope Analysis

The stable isotopic measurement procedure is described in detail in Vimont et al. (2017). Briefly, the air is extracted from the PFP by vacuum transfer through a cold loop trap at -70° C that removes water vapor. Next, a mass flow controller is used to regulate the flow of the sample through a second cryogenic trap at -196° C that removes CO_2, N_2O, and any other condensable species. The remaining air is passed through acidified I_2O_5 suspended on a silica gel matrix (Schutze's reagent, (Schutze, 1944)) that quantitatively oxidizes CO to CO_2, adding an oxygen with a consistent isotopic signature. The sample passes through a second cold loop trap (-70° C) to remove any traces of sulfuric acid that has evolved from the reagent and finally the CO-derived CO_2 is trapped on a third cryogenic trap (-196° C) while the remaining gasses are pumped away. The CO-derived CO_2 is then transferred to a cryogenic focusing trap and finally released through a GC column (PoraBond Q) to the isotope ratio mass spectrometer (GV Instruments IsoPrime 5KeV).

Following convention, we use delta notation to report our isotopic results:

$$\delta^{13}C_{VPDB} = \left(\frac{R_s}{R_{VPDB}} - 1\right) * 10^3‰ \qquad (1)$$

where R_s is the ratio of 13-carbon to 12-carbon in the sample and R_{VPDB} is the ratio of 13-carbon to 12-carbon in the international standard Vienna Pee Dee Belemnite. The same notation describes $\delta^{18}O$ except the international standard of reference is Vienna Standard Mean Ocean Water (VSMOW). Because we are oxidizing CO to CO_2 in this analysis, we correct our CO_2 $\delta^{18}O$ data to account for the added oxygen, as described in Mak and Yang (1998):

$$\delta^{18}O_{CO}=2\delta^{18}O_{CO_2}-\left(2\delta^{18}O_{CO_2std}-\delta^{18}O_{COstd}\right) \qquad (2)$$

where the subscript CO indicates the original $\delta^{18}O$ signature of the sample, CO_2 indicates the $\delta^{18}O$ of the CO_2 measured in the mass spectrometer, CO_2std indicates the $\delta^{18}O$ of the CO_2 measured on the standard gas and CO_{std} indicates the calibrated $\delta^{18}O$ of the CO in the same standard gas (standard gas procedure was described in Vimont et al. (2017)). Once the samples have been analyzed in the mass spectrometer, a correction for the ^{17}O contribution to the $\delta^{13}CO$ measurement is applied to the data based on the recommendations of Brand et al. (2009) (Vimont et al., 2017). This correction is required because ^{13}CO and $C^{17}O$ are indistinguishable in our mass spectrometer. The 1σ repeatability over two years for our analysis system is 0.23‰ for $\delta^{13}C$ and 0.46‰ for $\delta^{18}O$. For a more complete description of system performance, see Vimont et al. (2017).

We note that a significant deviation from the standard CO_2 ^{17}O correction has been observed and quantified for CO, particularly in the high northern latitudes (Röckmann and Brenninkmeijer, 1998; Röckmann et al., 1998). This so called "^{17}O excess", or $\Delta^{17}O$, is a result of mass-independent fractionation (MIF) that arises in OH photolytic formation, which in turn affects CO during removal by OH (Röckmann et al., 1998; Huff and Thiemens, 1998). This effect can introduce error of up to 0.35‰ in the corrected $\delta^{13}C$ values and is only quantifiable by measuring $\delta^{17}O$ (Röckmann and Brenninkmeijer, 1998). However, though we do not measure $\delta^{17}O$ for our samples, our data analysis approach (section 2.5) eliminates the need for this correction because both background and urban samples will see similar $\Delta^{17}O$ effects.

2.4 Radiocarbon CO_2 Analysis

Each of the INFLUX samples analyzed for the stable isotopes of CO was also analyzed for $^{14}CO_2$. $^{14}CO_2$ is the best tracer for fossil fuel produced CO_2 because fossil fuels contain no ^{14}C (Levin et al., 2003; Turnbull et al., 2006). $^{14}CO_2$ measurements were made by extracting CO_2 from whole air in each flask at INSTAAR, University of Colorado, followed by graphitization and AMS ^{14}C measurement at GNS Science, New Zealand (Turnbull et al., 2015b). CO_2ff was determined for each sample using Tower 1 as background, and the $^{14}CO_2$ results for these and other INFLUX flask samples were reported in detail by Turnbull et al (2015) and Turnbull et al (2018). The measurement precision of ~1.8‰ results in uncertainties in CO_{2FF} of better than 1 μmol:mol CO_{2FF} for these samples.

2.5 Regression Plot Analysis

At Indianapolis, the CO measured at tower 2 is typically 20 nmol:mol higher than the background CO of ~150 nmol:mol at tower 1. It is necessary to remove the background signal from the polluted tower to accurately constrain the urban CO signals. Using the method described by Miller and Tans (2003), we calculate the isotopic signature of the urban source:

$$\delta_s = \frac{\left(\delta_{meas} X_{CO_{meas}} - \delta_{bkg} X_{CO_{bkg}}\right)}{\left(X_{CO_{meas}} - X_{CO_{bkg}}\right)} \qquad (3)$$

where δ_S is the $\delta^{13}C$ or $\delta^{18}O$ of the urban source (figure 2), X indicates the mole fraction and the subscript "meas" indicates the $\delta^{13}C$ (or $\delta^{18}O$) and CO mole fraction measured at tower 2. The subscript "bkg" indicates the $\delta^{13}C$ (or $\delta^{18}O$) and CO mole fraction measured at tower 1. In order to obtain a best-fit solution using (3) for all the data, we regressed the numerator against the denominator using an ordinary least squares (model 1) Y|X approach (Isobe et al.,1990; Zobitz et al., 2006), which assumes mole-fraction to be independent.

To account for uncertainty in our measurements, we used a Monte Carlo technique. Using the propagated measurement uncertainties, we assigned an error distribution to each point. We assumed a normally distributed error curve based on QQ plot analysis of our data against a synthetic normally distributed data set (not shown). This analysis allows us to assess if two data sets have the same distribution. 10,000 regressions were run, randomly selecting values for each data point from that point's error distribution. The reported slopes are the median values from the 10,000 regressions. The reported errors on the slope are 1σ for the slopes of each simulation.

At the Beech Island measurement site, no local background measurement site with CO isotope measurements exists, and the Miller Tans plots cannot be used. Therefore, we instead performed a Keeling plot analysis, in which the isotopic measurements are plotted against the reciprocal of the mole fraction (Keeling, 1958). This method uses the relationship:

$$\delta^{18}O_{obs} = I_{\delta 18O} + M(X_{CO}^{-1}) \qquad (4)$$

where $\delta^{18}O_{obs}$ is the observed $\delta^{18}O$ at the measurement site, M is the slope determined from a regression of the data, and X_{CO} is the observed CO mole fraction. $I_{\delta 18O}$ is the intercept determined from a regression of the data. The intercept represents the isotopic signature of the sources influencing the measurement site (Keeling, 1958). The Keeling plot assumes that the background concentration and isotopic values are constant over the period of analysis, which is a reasonable but imperfect assumption for this dataset measured over the summer season. The benefits and limitations of this approach are discussed more fully in section 3.3.

To assess the uncertainty of our Keeling plot analysis, we perform a standard Monte Carlo analysis and additionally use a sampling with replacement Monte Carlo method (often referred to as a bootstrap Monte Carlo). Briefly, the boot strap Monte Carlo consist of calculating a linear regression for 1000 randomly chosen sample sets. These sets are chosen from the original data, at random, such that the number of data points is always constant (n=7 for both summer and winter at Beech Island). However, in some sample sets, points may be selected more than once, or not at all. In this way, any disproportionately large influence on the model by outlier points can be assessed, and the distribution of the model parameter of interest (in our case, the intercept) is representative of data as a whole. We report the mean of the 1000 intercepts, and both the 1σ standard deviation as well as the standard error of the mean are reported for the error on that value. The bootstrap Monte Carlo distributions are shown in the supplementary material (section S2).

2.6 Calculation of the VOC oxidation isotopic signatures using mass balance

The CH_4 oxidation source, the biomass-burning source, and the OH oxidation sink have negligible impacts for the Indianapolis CO budget (detailed calculations can be found in the supplementary material, section S1). In order to constrain the remaining two sources (fossil fuel combustion and VOC oxidation), we use a simple isotope mass balance approach. We assume that the δ_s calculated at each polluted tower (section 2.5, equation (3)) can be represented by:

$$\delta_s = f_{VOC}\delta_{VOC} + f_{FF}\delta_{FF} \qquad (5a)$$

$$f_{VOC} = \frac{X_{CO\text{-}VOC}}{X_{CO\text{-}ENH}} \qquad (5b)$$

$$f_{FF} = \frac{X_{CO\text{-}FF}}{X_{CO\text{-}ENH}} \qquad (5c)$$

where f_{VOC} and δ_{VOC} are the fraction (as compared to total urban CO enhancement) and isotopic signature of CO added from VOC oxidation, and f_{FF} and δ_{FF} are the fraction and isotopic signature of CO added from fossil fuel combustion. $X_{CO\text{-}VOC}$, $X_{CO\text{-}FF}$, and $X_{CO\text{-}ENH}$ are the mole fractions for VOC-produced CO, the fossil fuel-produced CO, and the total urban CO enhancement, respectively. The isotopic signatures of fossil fuel combustion at Indianapolis were previously determined from wintertime measurements when fossil fuel combustion is the only significant CO source in Indianapolis and are -27.7 ± 0.5‰ and 17.7± 1.1‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively (Vimont et al., 2017). That study found that the isotopic signature in the winter did not vary significantly with temperature, and that the primary source within the city was emissions from transportation (Vimont et al., 2017). Therefore, we use these values as the fossil fuel produced CO isotopic signatures for Indianapolis. Because we have only two sources (supplementary material, Section S1), we can derive $X_{CO\text{-}VOC}$ as:

$$X_{CO\text{-}VOC}=X_{CO\text{-}ENH}-X_{CO\text{-}FF} \qquad (6)$$

In order to determine $X_{CO\text{-}VOC}$ we need to determine $X_{CO\text{-}FF}$. This is done using the fossil fuel CO to CO_2 ratio:

$$X_{CO\text{-}FF}=R_{COFF:CO2FF}{}^{*}\,X_{CO2\text{-}FF} \qquad (7)$$

where $X_{CO2\text{-}FF}$ is the fossil fuel produced enhancement in the CO_2 mole fraction, determined by $^{14}CO_2$ measurements (section 2.4). $R_{COFF:CO2FF}$ is the ratio of CO_{FF} to CO_{2FF} and was determined to be 7 ± 1 nmol:µmol for Indianapolis in the winter, when nearly all CO produced is from fossil fuel combustion, primarily vehicles (Turnbull et al., 2018). We assume that this ratio holds across all seasons. We then solve equations (7), (6) and (5a) to determine δ_{VOC}. We report the mean and standard error of the mean for our set of samples as our estimate of the isotopic value and uncertainty of δ_{VOC}.

Simple filtering is applied to these data. Any samples with calculated $X_{CO\text{-}VOC}$ values that were near zero, negative, or exceeded the total urban enhancement were removed. $X_{CO\text{-}VOC}$ values that are negative or exceed the total enhancement are obviously non-physical. Positive values of $X_{CO\text{-}VOC}$ that are extremely low (less than 5% of the total enhancement), while physical, create extreme outliers when $\delta^{13}C_{VOC}$ or $\delta^{18}O_{VOC}$ are calculated. Large overestimates of $X_{CO\text{-}VOC}$ arise because the ratio method can produce unrealistically low calculated $X_{CO\text{-}FF}$ values if the $X_{CO2\text{-}FF}$ enhancements are not significantly different from zero. It is unclear from our data why the $X_{CO2\text{-}FF}$ enhancements are occasionally near or below zero. Conversely, the ratio method can overestimate $X_{CO\text{-}FF}$ thereby underestimate $X_{CO\text{-}VOC}$ when $X_{CO2\text{-}FF}$ is highly elevated, without a corresponding elevation in $X_{CO\text{-}ENH}$. One example of how this can occur is if the local power plant (the Harding Street Power Plant) plume is sampled by the polluted tower. In the period of this study, the Harding Street Power Plant contributed about 28% of Indianapolis' CO_{2FF} emissions and, while this source is often dispersed, the plume from this source is occasionally observed at tower 2. This source has a $CO{:}CO_{2FF}$ ratio of <0.1 nmol:μmol, due to CO emissions controls fitted to the exhaust stack. Because we use a constant value for $R_{CO:CO2FF}$, any day where tower 2 samples contain power plant emissions will produce low or negative $X_{CO\text{-}VOC}$ values. We do not attempt to identify the power plant plume, but as stated above, simply filter extremely low $X_{CO\text{-}VOC}$ values as outliers.

3. Results and Discussion

3.1 Determination of the urban enhancement CO isotopic signatures

The full time series from Indianapolis was published in Vimont et al. (2017). However, we have reproduced the data from towers 1 and 2 (figure 3) here to highlight the summertime data (not discussed in Vimont et al., 2017). The summertime mole fraction and isotopic data can be seen in table S2 in the supplementary material. One of the more salient features of the summer Indianapolis data as compared to the winter data is that, while tower 2 CO mole fraction remains enhanced over tower 1 throughout the year, the $\delta^{18}O$ values at tower 2 tend to be much closer to those of tower 1 during the summer, yet are more positive during the winter. This is consistent with the hypothesis that the wintertime urban enhancement is dominated by a fossil source, while the summertime enhancement is a mixed source. Further, this mixed source must be more depleted in ^{18}O than fossil fuel produced CO. The $\delta^{13}C$ results are more difficult to interpret from the time series alone, which underscores the need for the Miller Tans method at Indianapolis.

The Miller Tans Monte Carlo regression analysis produced isotopic results of -29.6 ± 1.0‰ for $\delta^{13}C$ and 12.5 ± 2.1‰ for $\delta^{18}O$ of the overall urban summertime CO source (figure 2). The $\delta^{13}C$ source signature is very similar to that determined in winter (-27.7±0.5‰, Vimont et al., 2017). In contrast, the $\delta^{18}O$ signature is substantially lower in summer than in winter (17.7±1.0‰ in winter, Vimont et al., 2017). These results are consistent with our hypothesized mixing of two sources of CO with different isotopic signatures contributing to the summertime CO enhancement. The determined $\delta^{13}C$ of the urban CO source stays relatively consistent between winter and summer, suggesting that the VOC oxidation source must have a $\delta^{13}C$ signature that is only slightly more negative than the fossil fuel source. In contrast, $\delta^{18}O$ of the urban source changes substantially from summer to winter, indicating a VOC $\delta^{18}O$ signature that is more negative than the fossil fuel source. The increased scatter in the $\delta^{18}O$ regression relative to $\delta^{13}C$ is also consistent with this interpretation: variability in the relative contributions of fossil fuel and VOC CO sources for different samples will impart more variability in $\delta^{18}O$ than $\delta^{13}C$.

Day to day variability in the VOC oxidation source is expected and supports the hypothesis that secondary production of CO by VOCs is strongly contributing to the urban enhancement. For example, isoprene has a short atmospheric lifetime in urban regions and rapidly forms CO (Atkinson and Arey, 2003). Isoprene oxidation is highly variable because isoprene emissions depend exponentially on the ambient temperature, and the rate at which isoprene is oxidized will increase as NO_x increases (Guenther et al., 1995; Carter and Atkinson, 1996). Additionally, boundary layer mixing will vary day to day, affecting the magnitude and transport of all sources within the tower domain.

3.2 Determination of the VOC-produced CO $\delta^{18}O$ isotope signature

To determine the VOC-produced CO isotopic signature, we first determined the fossil fuel-produced CO_2 source (section 2.4). The $^{14}CO_2$, the derived CO_{2FF} mole fractions, and the calculated CO_{FF} and CO_{VOC} mole fractions are presented in table 2. The uncertainties reported are 1σ for CO_{2FF} and $\Delta^{14}CO_2$, while the uncertainties on the calculated CO_{FF} and CO_{VOC} values are the propagated errors for equations (6) and (7).

Using the mass balance approach described in section 2.6 we use the isotopic source signatures determined in section 3.1 to calculate the mean isotopic signatures of VOC oxidation derived CO: -33.6‰ ± 1.0‰ for $\delta^{13}C$ and 1.3‰ ± 2.7‰ for $\delta^{18}O$.

The $\delta^{13}C$ results compare well to the later of previously published estimates of the VOC oxidation signature: -32 ± 2 ‰ (e.g. Brenninkmeijer et al., 1999). As stated above, this value is reasonable given the expected carbon isotopic ratio of isoprene and the fractionation processes associated with the isoprene oxidation reaction (e.g. Sharkey et al., 1991). Our $\delta^{18}O$ result compares well with the previously published results from Brenninkmeijer and Röckmann (1997) (~0‰) but contradicts Stevens and Wagner (1989) (~15‰). We re-examine the methods and uncertainties of the previous studies to understand what might cause this discrepancy.

Stevens and Wagner (1989) performed a Keeling plot analysis of samples collected in rural Illinois. They assumed a constant background, with VOC oxidation as the only added CO source, and performed a Keeling plot analysis. Their results indicated -32.2‰ for $\delta^{13}C$ and 15‰ for $\delta^{18}O$ of the added CO source. They also measured four samples from a coastal site in Australia and obtained an average $\delta^{18}O$ of 5‰ for the atmospheric $C^{18}O$ signature. They did not perform a Keeling analysis on the Australian data. They reasoned that the effect of oxidation by OH on the Australia samples would reduce the $\delta^{18}O$ by 10‰, which meant the source (assumed to be dominated by VOC and methane oxidation) must have been 15‰, in agreement with their rural Illinois samples.

The value of 0‰ suggested by Brenninkmeijer and Röckmann (1997) was based on a model-driven interpretation of CO isotope measurements in the southern hemisphere. Using mass balance, they were able to determine the oxidation of methane and VOCs should produce CO with an oxygen isotopic value near to 0‰, while the value of 15‰

suggested by Stevens and Wagner (1989) could not be consistent with the measurements. Bergamaschi et al. (2000) used an atmospheric inversion combined with CO mole fraction and isotopic measurements in an attempt to determine the isotopic signatures of CO sources at the global scale. However, their study resulted in wide ranges for $\delta^{13}C$ (-17‰ to -31‰) and $\delta^{18}O$ (-30‰ to +23‰) isotopic values, dependent on the input parameters of their model. Later studies using $\delta^{18}O$ to partition the global budget generally use the 0‰ value for $\delta^{18}O$ despite the lack of consensus (e.g., Park et al., 2015). By leveraging the INFLUX measurements, we are able to place a constraint on the VOC-produced CO isotopic signatures without relying on the uncertain assumptions of a constant background / VOCs as the only source, or on the use of a model to derive the CO mass balance.

3.3 Beech Island South Carolina Isotopic Data

The Beech Island results are shown in figure 4, while the data can be found in the supplementary information (table S3). The most striking feature of this data is that while the $\delta^{13}C$ and $\delta^{18}O$ both decrease from spring into summer and then increase into the fall and winter, the mole fraction values do not exhibit much seasonality. While any true seasonal cycles or trends are impossible to determine with only a single year of data, this nonetheless is consistent with a strong summer source of oxidized VOC produced CO.

The CO source isotopic signatures at Beech Island, South Carolina are shown in figure 5. During the summer months (June-July-August-September), the Keeling plot analysis (section 2.5) produces a $\delta^{13}C$ signature of -31.2‰ ± 0.2‰ and a $\delta^{18}O$ signature of 5.8‰ ± 0.7‰ using a standard Monte Carlo simulation and a $\delta^{13}C$ signature of -30.9‰ ± 0.2‰ (5.7‰ 1σ), and a $\delta^{18}O$ signature of 5.6‰ ± 0.1‰ (2.4‰ 1σ) using the bootstrap Monte Carlo method. During the winter months (December-January-February-March), we obtain a $\delta^{13}C$ signature of -27.3‰ ± 0.2‰ and a $\delta^{18}O$ signature of 21.1‰ ± 0.3‰ using the standard Monte Carlo method. Using the bootstrap Monte Carlo, we obtain a $\delta^{13}C$ of -26.8‰ ± 0.1‰ (3.7‰ 1σ) and a $\delta^{18}O$ of 20.4‰ ± 0.2‰ (5.0‰ 1σ).

The wintertime source signatures derived at Beech Island are consistent with prior estimates of fossil fuel combustion sources (δ^{13}C: ~-27.5‰, δ^{18}O: ~23.5‰, Brenninkmeijer et al., 1999). The Beech Island δ^{13}C value is consistent with the wintertime value found at Indianapolis (-27.7‰ ± 0.5‰, Vimont et al., 2017), while the δ^{18}O value differs slightly from the value found at Indianapolis during the winter (17.7‰ ± 1‰, Vimont et al., 2017). At Indianapolis, the winter CO urban enhancement was found to be primarily fossil fuel in origin, but it was noted that the oxygen isotopic signature was significantly different from prior estimates of fossil fuel combustion, possibly due to Indianapolis' emission regulation (Vimont et al., 2017). Nonetheless, this suggests that the main driver of CO variability during the winter at Beech Island is likewise fossil fuel combustion. In contrast, the summer CO source isotopic signatures at Beech Island (δ^{13}C ~-31‰, δ^{18}O~ 6‰) are lighter than for Indianapolis (δ^{13}C: -29.6‰, δ^{18}O: 12.5‰), and both summertime signatures are lighter than the winter CO source isotopic signatures at either site. As stated above, the more or less constant CO mole fraction time series at Beech Island (figure 4) is likely due to the large influence from CO produced by oxidation of VOCs during the summer, which offsets the expected summertime CO mole fraction minimum, such as is seen at Indianapolis (figure 3). The much higher contribution of CO produced by oxidized VOCs Beech Island relative to Indianapolis is reasonable, given the more concentrated fossil fuel source in the Indianapolis urban area and the higher concentrations of biogenic VOCs expected at the densely forested and warmer Beech Island site.

The Keeling approach implicitly assumes constant background CO mole fraction and isotopic composition, which is unlikely to be correct for Beech Island for the entire duration of the summer. However, this approach is still useful for an approximate estimation of the CO source isotopic composition. This is particularly true for δ^{18}O, where the difference between the inferred source isotopic signature and the measured δ^{18}O values is larger than the scatter in the measured values.

We also assess the effect of the OH seasonal cycle on our results. An increase in OH would increase the oxidation of CH_4 as well as CO. CH_4 oxidation would produce CO with lighter (more negative) $\delta^{13}C$, while OH oxidation of CO favors ^{12}C and would leave the remaining CO heavier (more positive) (Brenninkmeijer et al., 1999). For $\delta^{18}O$, OH oxidation of CO has an inverse isotope effect, favoring the heavier ^{18}O, meaning both CO removal via OH and CO production via VOC oxidation by OH would drive the oxygen isotopic signature more negative (Stevens et al., 1980; Brenninkmeijer et al., 1999). It may be possible that the competing effects of OH oxidation on $\delta^{13}C$ and complementary effects on $\delta^{18}O$ could produce the source signatures seen in our Beech Island analysis. However, as stated above, the Keeling plot analysis describes the isotopic signature of the primary driver of mole fraction fluctuations within the measurement scope. The strength of the OH concentration at surface rural sites is largely driven by solar zenith angle, and therefore depends on the latitude of the site as well as the season (e.g. Daniel and Solomon, 1998; Duncan et al., 2007). By splitting the data between winter and summer, we assume that the OH concentration (Duncan et al., 2007), on average, is unlikely to be significantly different from day to day within a given season. Therefore, we conclude that to first order, the contribution of OH oxidation of CO to the seasonal background CO mole fraction and isotopic composition is constant at Beech Island.

Biomass burning could also contribute to the changes in the seasonal isotopic and mole fraction differences, both on a global scale as well as regional or local scales. However, biomass burning would produce a shift in $\delta^{13}C$ towards more positive values (biomass burning $\delta^{13}C \sim -24‰$, table 1; Brenninkmeijer et al., 1999; Saurer et al., 2009) which is inconsistent with our results. We would expect the oxygen isotopic values to decrease, but only by 1 or 2‰ relative to the winter values (biomass burning $\delta^{18}O \sim 17‰$, table 1; Brenninkmeijer et al., 1999; Saurer et al; 2009). Therefore, we dismiss biomass burning as a major summer source of CO variability at Beech Island and assume our summer Keeling plot results describe a mixture of CO produced by oxidation of VOCs and fossil fuel combustion.

While the small dataset from Beech Island does not allow for a direct estimate of the isotopic signatures of VOC-produced CO, it is consistent with the values we obtained from Indianapolis and with Brenninkmeijer and Röckmann (1997). Further, they help us to rule out the 15‰ value for $\delta^{18}O$ suggested by the prior Stevens and Wagner (1989) study. The Beech Island data suggest the main driver of local CO wintertime variability is fossil fuel combustion, with a $\delta^{18}O$ isotopic signature of approximately 20‰. During the summer months, the addition of VOC-produced CO shifts the overall source $\delta^{18}O$ to approximately 6‰. If the oxygen isotopic signature of CO produced by oxidation of VOCs was 15‰, as suggested by Stevens and Wagner (1989), this result would be impossible.

4. Conclusions

We analyzed carbon monoxide stable isotopes and $\Delta^{14}CO_2$ during three summers at Indianapolis and determined the isotopic signature of the urban CO enhancement during the summer. Additionally, we analyzed stable isotopes approximately bi-monthly for one year at Beech Island, South Carolina. Using the $\Delta^{14}CO_2$ data and the ratio of $CO:CO_{2FF}$, we calculated the fossil fuel component of the CO mole fraction enhancement. We then used isotope mass balance and the Indianapolis CO_{FF} isotopic signatures from prior work to calculate the isotopic signature of CO produced from oxidized VOCs: -33.6‰ ± 1.0‰ for $\delta^{13}C$ and 1.3‰ ± 2.7‰ for $\delta^{18}O$. A separate set of CO isotopic measurements from a forest site strongly influenced by VOC-derived CO (Beech Island, SC) is consistent with these results. Our estimate for the carbon isotopic signature of VOC-produced CO agrees well with and confirms prior estimates. Our oxygen isotopic result agrees well with estimates made by Brenninkmeijer and Röckmann (1997) using isotope mass balance within a model based on atmospheric observations but does not support prior work by Stevens and Wagner (1989).

This result is an important step to improving the constraints on global and regional CO budgets. Additional studies that quantify the isotopic signature of VOC-produced CO could confirm whether our result is valid regionally and globally, as well as help to further improve the associated uncertainty bounds.

Author contributions:

IJV performed the measurements, data analysis, and wrote the article. JCT assisted in data analysis and provided multiple coauthor revisions. VVP provided assistance with measurement issues, data analysis, and multiple coauthor revisions. PFP assisted in several of the measurements. CS provided several coauthor revisions. NM and SR provided logistical support for sample collection for the measurements. BHV and JWCW provided laboratory and equipment support.

Competing Financial Interests:

There are no competing financial interests for any of the authors.

Funding Sources:

This research was generously funded by the National Institute of Standards and Technology (grant 60NANB10D023) and the National Oceanic and Atmospheric Administration Climate Program Office's AC4 program (award NA13OAR4310074). The lead author and the analysis system development were supported through funding in conjunction with the INSTAAR contract for isotopic analysis (RA-133R-15-CQ-0044) with The National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) Global Greenhouse Gas Reference Network (GGGRN).

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Data Availability:

Data for this experiment is available in table 2 in the manuscript, and the supplemental material.

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Figures and Tables

Table 1: The four main CO sources and the OH sink listed with their isotopic signatures and uncertainties, with values as in (Brenninkmeijer et al., 1999)

Isotopic Sources and Sinks				
Source/Sink	**$\delta^{13}C$ (VPDB)**	**Uncertainty**	**$\delta^{18}O$ (VSMOW)**	**Uncertainty**
Global Sources				
Fossil Fuel Combustion	-27.5‰	≤1‰	23.5‰	≤1‰
Biomass Burning	-22.9‰	1-3‰	17.15‰	1-3‰
CH_4 Oxidation	-52.6‰	1-3‰	0‰	>3‰
VOC Oxidation	-32‰	1-3‰	0‰	>3‰
CO Oxidation by OH Fractionation Factors	5‰	unknown	-10‰	unknown

Table 2: VOC signature calculation table. $\Delta^{14}CO_2$ and $X_{CO2\text{-}FF}$ values reported from Turnbull et al. (2015,2018). $X_{CO\text{-}ENH}$ 1σ uncertainty is ± 0.7 nmol:mol, $\Delta^{14}CO_2$ 1σ uncertainty is ~±1.8‰ (Turnbull et al., 2015,2018), and $X_{CO2\text{-}FF}$ 1σ uncertainty is ±1 µmol:mol (Turnbull et al., 2015,2018).

Date	$X_{CO\text{-}ENH}$ (nmol:mol)	$\Delta^{14}CO_2$ (‰)	$X_{CO2\text{-}FF}$ (µmol:mol)	$X_{CO\text{-}FF}$ (nmol:mol)	$X_{CO\text{-}VOC}$ (nmol:mol)	$\delta^{13}C_{VOC}$ (‰)	$\delta^{18}O_{VOC}$ (‰)
5/5/15	11.1	10.6	0.7	5.1	6.0	-31.2	8.0
5/12/14	9.5	17.4	0.6	4.0	5.5	-31.0	8.6
5/28/14	12.5	14.6	0.8	5.9	6.6	-31.2	7.8
5/16/14	20.3	6.7	2.6	17.9	2.4	-43.7	-26.8
6/8/15	38.7	9.4	3.2	22.2	16.6	-32.1	5.5
6/30/15	12.7	12.5	1.3	8.9	3.8	-34.0	0.1
6/3/14	13.2	18.0	1.4	9.6	3.7	-34.5	-1.1
7/29/13	27.5	23.9	0.5	3.5	23.9	-29.8	11.7
7/27/13	19.9	22.7	1.9	13.1	6.8	-33.2	2.4
8/1/13	12.3	26.1	1.3	9.4	2.9	-35.6	-4.4
8/22/14	46.2	5.2	5.7	39.8	6.4	-41.1	-19.7
8/20/14	9.8	16.1	0.8	5.3	4.5	-31.8	6.3
8/12/14	25.0	17.7	2.6	18.1	6.9	-34.5	-1.3
8/21/14	27.1	9.6	2.6	17.9	9.2	-33.2	2.4
9/1/14	9.2	19.4	0.0	0.1	9.1	-29.6	12.4
9/2/14	25.6	12.6	1.4	9.9	15.7	-30.8	9.2

Figure 1: Satellite Image of INFLUX tower locations. Arrow indicates predominant wind direction during sampling. Samples from this study were taken from towers 1 and 2 (shown). Also note the vegetation cover between the two towers.

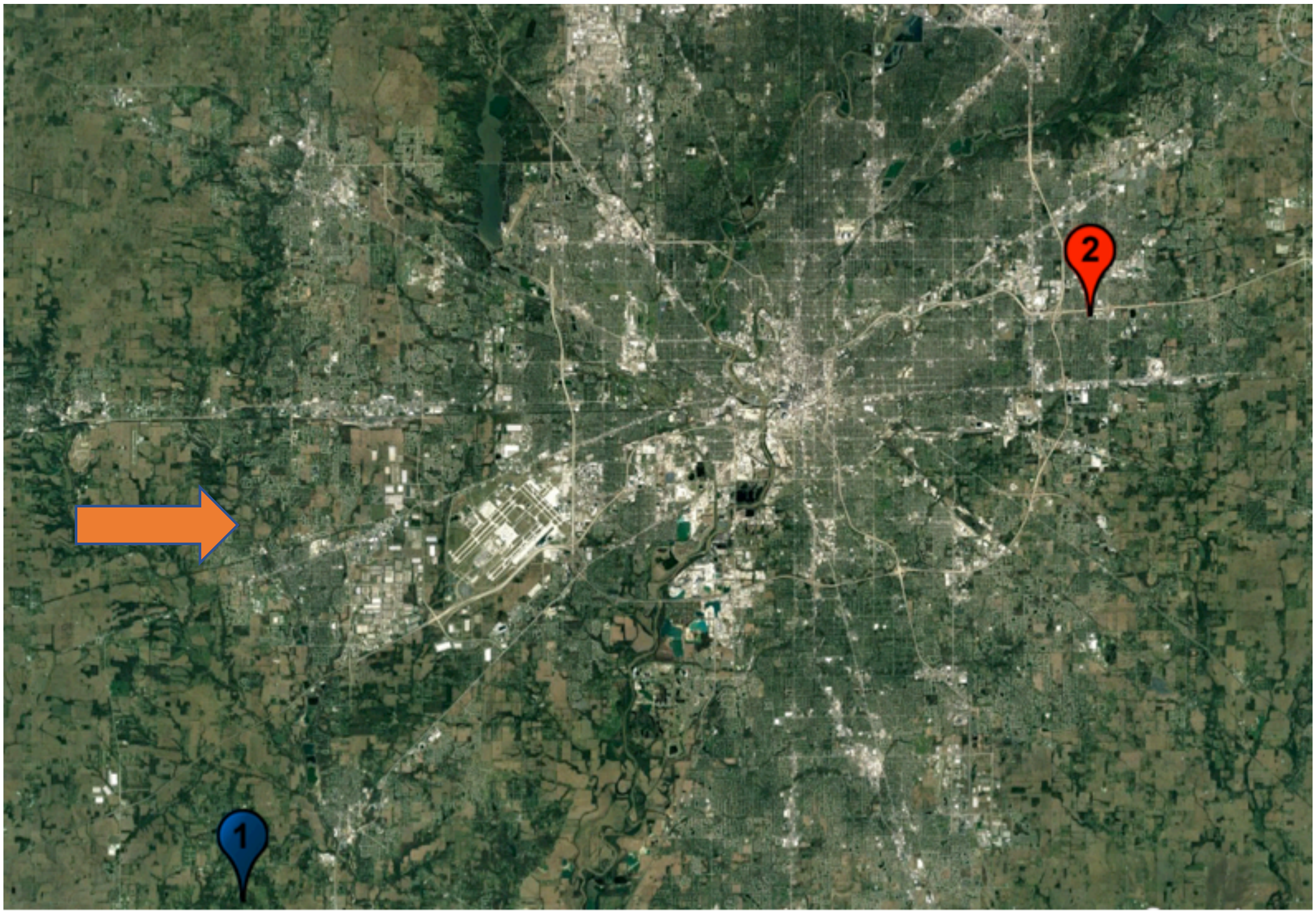
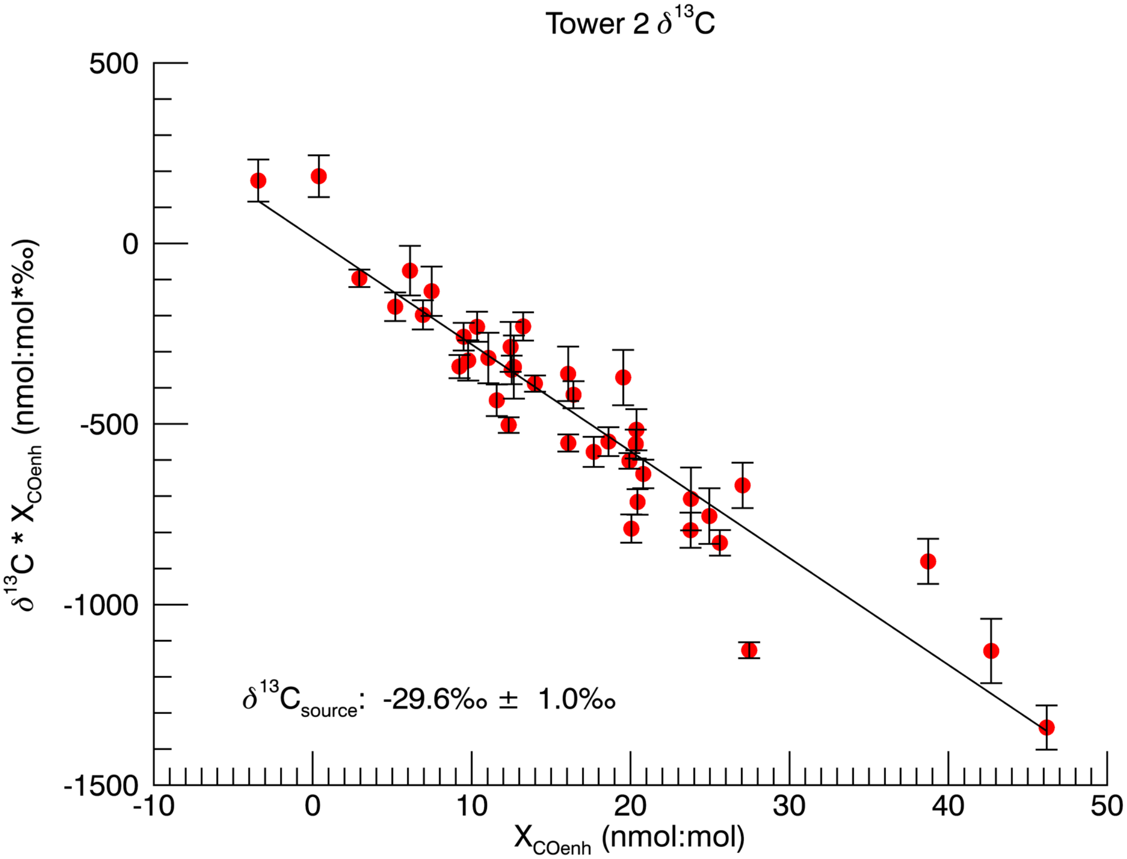


Figure 2: Indianapolis Miller Tans plots for late spring through summer (May, June, July, August, September). The error bars represent the propagated error for the calculation of the enhancements (see text for details).



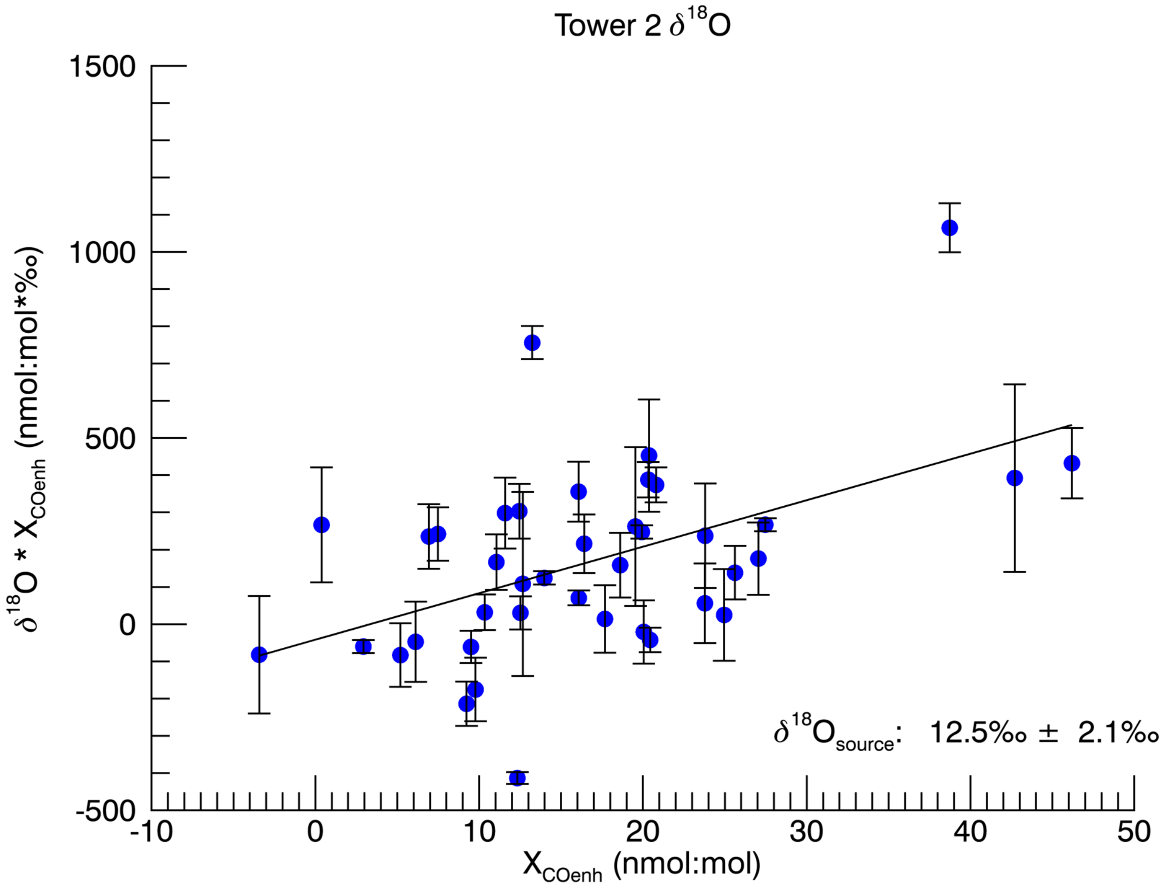

Tower 2 δ^{18}O
1500
1000
500
0
-500
δ^{18}O * X_{COenh} (nmol:mol*‰)
-10
0
10
20
30
40
50
X_{COenh} (nmol:mol)
$\delta^{18}O_{source}$: 12.5‰ ± 2.1‰

Figure 3: Time series of towers 1 and 2 at Indianapolis. These data were previously shown in Vimont et al. (2017), but are reproduced here for the convenience of the reader. The curves shown are for sighting purposes only. They are a simple single harmonic polynomial smoothing and are meant to aid the reader in viewing the seasonal variability. The error bars represent 1σ uncertainty. CO mole fraction 1σ uncertainty is ± 0.5 nmol:mol. The red arrows indicate the time periods used in this study, and these data, along with $\delta^{13}C$ and $\delta^{18}O$ 1σ uncertainty is listed in the supplementary material (table S2).

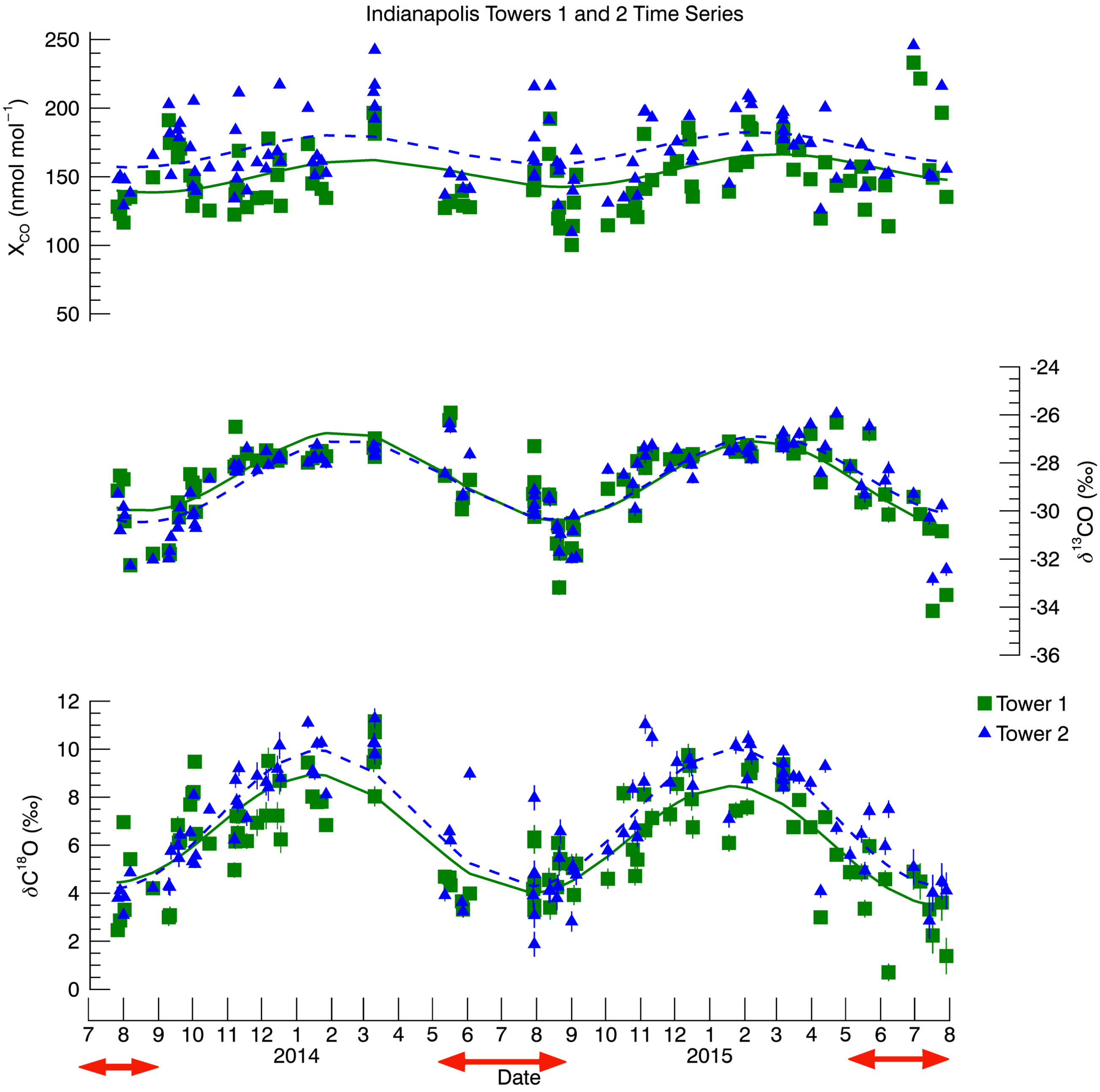


Figure 4: Time series for Beech Island, South Carolina. No curves were fit to the data due to the short time frame for the measurements. The error bars represent 1σ uncertainty. CO mole fraction 1σ uncertainty is ±0.5 nmol:mol. Uncertainty for $\delta^{13}C$ and $\delta^{18}O$ is listed in the supplementary material (table S3). The CO mole fraction data is taken from the NOAA GGGRN dataset (Andrews et al., 2009).

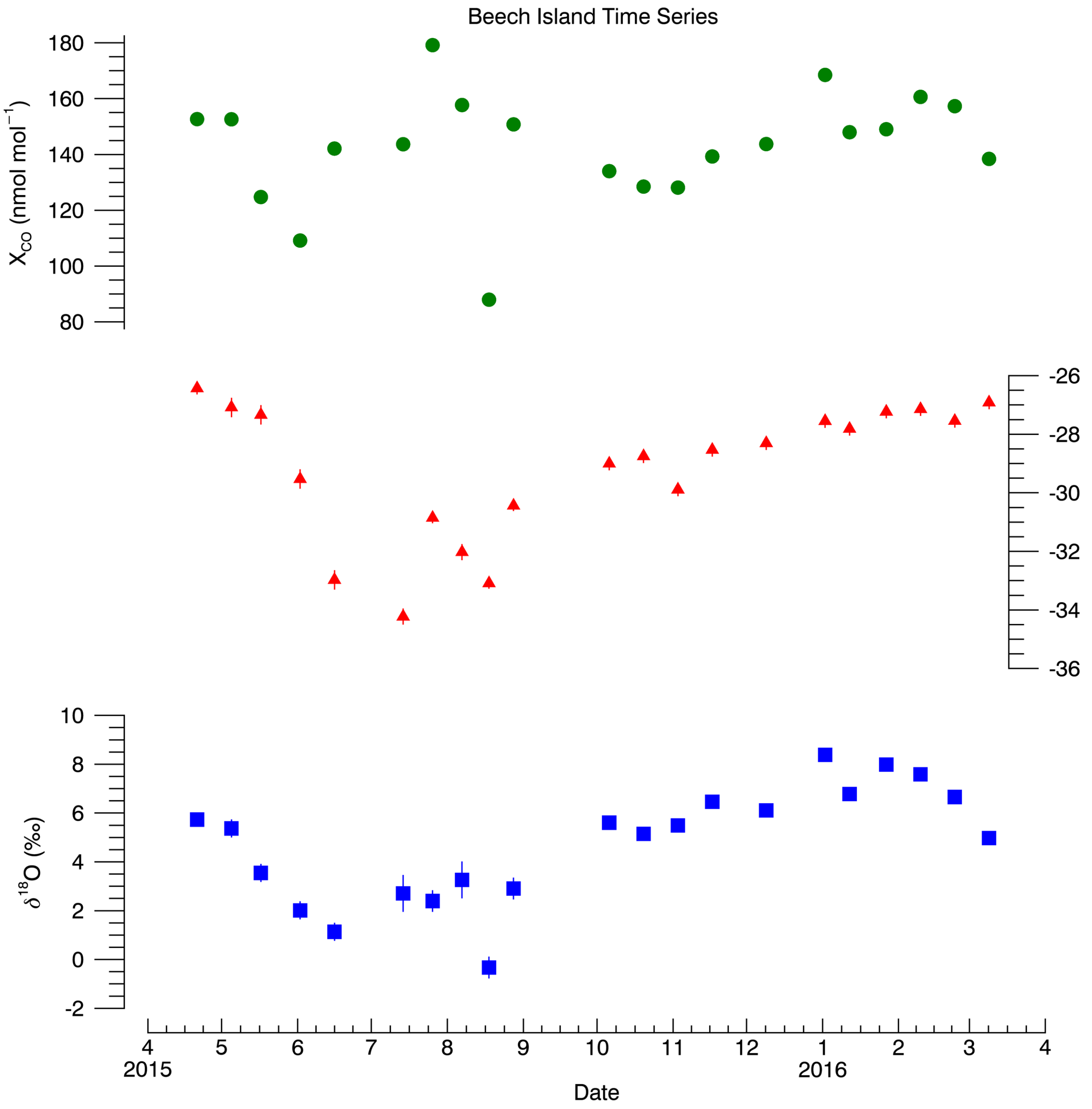
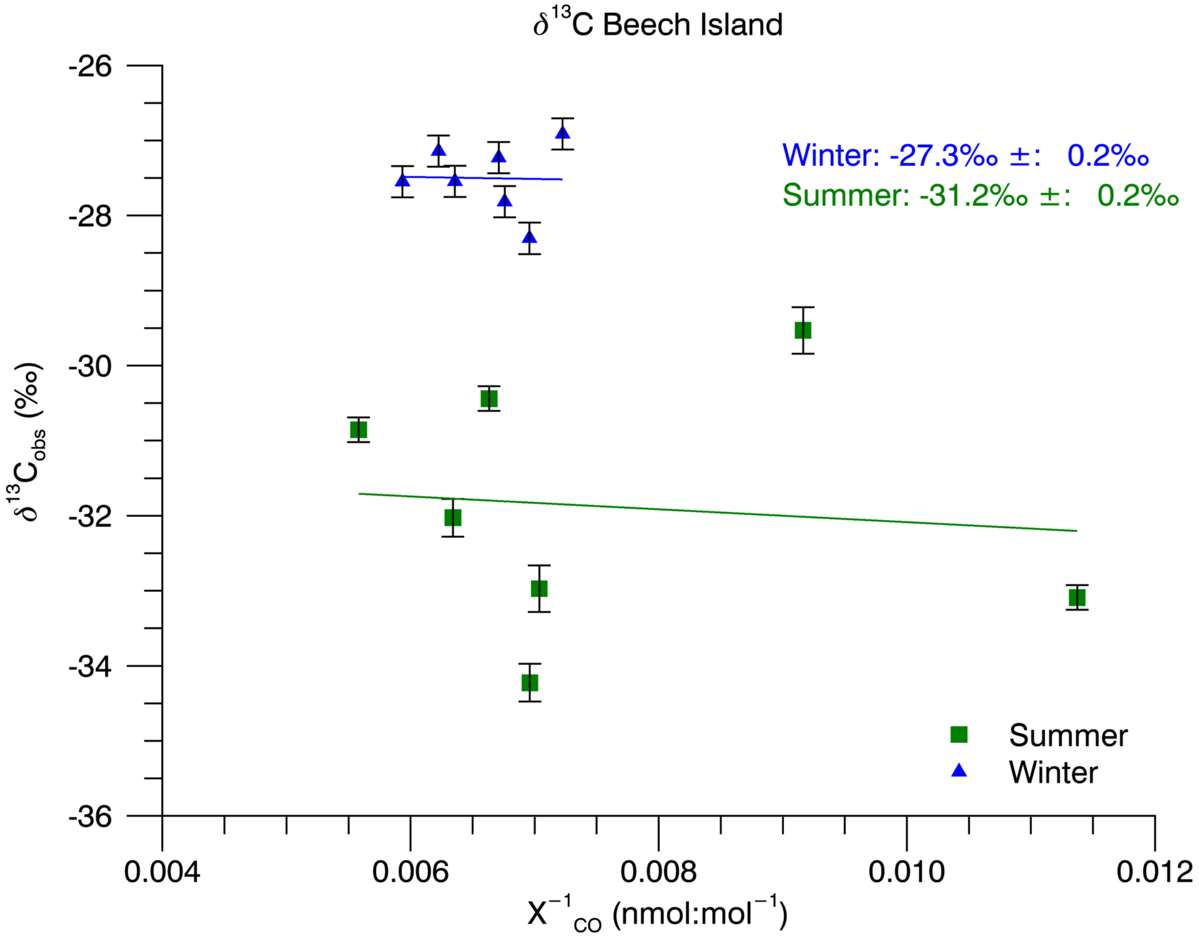
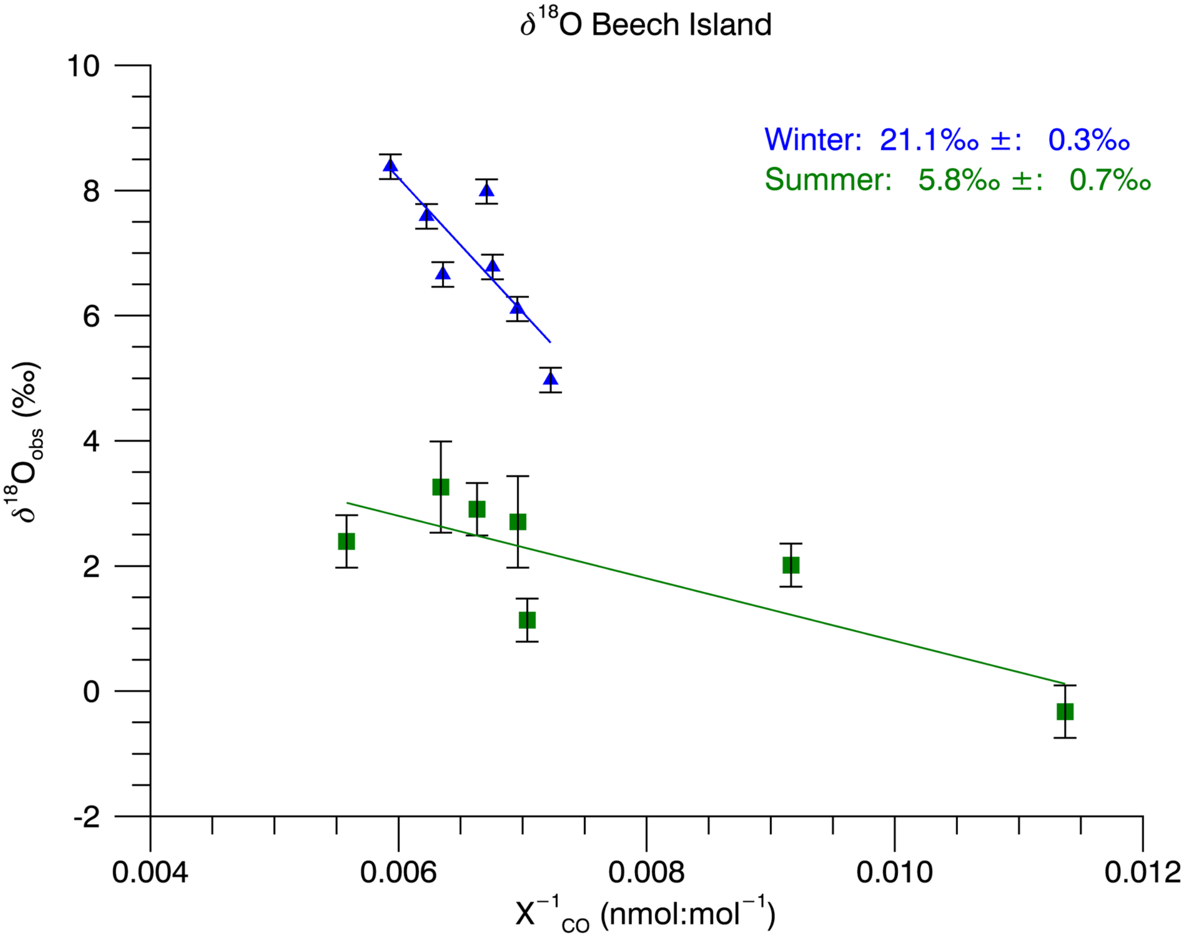


Figure 5: Beech Island Keeling plots. The reported intercepts and uncertainties are the standard Monte Carlo simulation results. We also performed a bootstrap Monte Carlo. Those results are reported in the text.




δ18O Beech Island
Winter: 21.1‰ ±: 0.3‰
Summer: 5.8‰ ±: 0.7‰
δ18Oobs (‰)
10
8
6
4
2
0
-2
0.004
0.006
0.008
0.010
0.012
X−1CO (nmol:mol−1)