

Interactive comment on “Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}\text{CO}_2$ ” by B. W. LaFranchi et al.

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In response to comments by Referee #1, in part, but also as a result of the evolution of thinking amongst the co-authors about this data set and what it reveals about emissions from the oil and gas industry in Weld County, Colorado, we no longer make estimates of emissions for methane (CH_4) and the other tracers related to the oil and gas operations located to the northeast of the tower. Referee #1 mentions at multiple points in his/her critique a concern over how representative the observations at BAO

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are of the emissions distribution in the surrounding regions – both to the north and east of the tower and to the south. For example, the referee states:

“However, this very complex situation also creates challenges and a key point in such studies is the question to which extent the composition of the available samples are a representative reflection of the emissions from the studied footprint regions.”

Therefore, in the revised manuscript, we have removed the absolute emissions estimates, and related discussion, of all the trace gases that show variability in emission ratio with wind direction. Instead, we present and discuss the tracer/ CO_2 ratios for these gases, and we have retained the absolute emission estimates of CO and C_2H_2 , for which the discussion now comes across as much more focused.

The section on “Spatial Considerations” (Sec. 3.3.1) now summarizes our reasoning for these changes:

“Thus, the top-down emissions estimates of the trace gases from oil and gas production will be sensitive to our assumptions about the geospatial scale of the observations: specifically, whether the observations are influenced by emission fluxes only in southwest Weld County or across a larger area that extends into the eastern part of Larimer County or other locations where CO_2 emissions are significant. Conversely, for CO and C_2H_2 , the consistency in the enhancement ratio between the two wind sectors supports the contention that the emissions estimates of these tracers are insensitive to presumptions about the precise area of emissions influencing the observations.

Because our analysis of trace gas emissions related to the oil and gas industry in the N/E wind sector is expected to be particularly sensitive to the uncertainty in the spatial footprint of observations, we refrain from estimating absolute emission rates for the trace gases related specifically to the oil and gas industry in Weld County (CH_4 , benzene, and the C3-C5 alkanes). Research is ongoing in trying to estimate emissions from this critically important emission sector, using a variety of observation platforms. Improved transport models that can accurately represent and account for the

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unique topography and meteorology of the Colorado Front Range will be required to reliably estimate emissions from the oil and gas sector in this region, whether using a tracer/tracer approach or inverse techniques. A more in depth study of the relationship between observed CO₂ff at BAO and trace gases linked to the oil and gas sector is planned for a future publication.”

These changes resulted in a fairly substantial reorganization of the manuscript and removal of many of the details describing the oil and gas industry bottom-up inventories, scaling factors, gridded emission inventories, and hypothetical footprints. These changes also address the concerns of both referees that the manuscript felt tedious, repetitive, and hard to follow. We feel the manuscript is much more tightly focused, as a result.

Additionally, a prominent theme in the critiques of both referees is the expressed desire to see figures showing the underlying dataset from which the median tracer/CO₂ff ratios are derived. Towards this end, we have added supplementary figures (S1-S10) that show a time series of wind direction and wind speed, as well as time series and histograms of the full data set from which the median tracer/CO₂ff ratios are derived. These figures also show the impact of the wind speed and low CO₂ff cut-off filters used. Additional details on these figures follow in response to more specific comments.

We thank the referees for their detailed and thoughtful critique of the manuscript. We have carefully considered each comment and incorporated nearly all of the suggested changes, where we feel appropriate, into a revised manuscript. Below, we provide a point-by-point response to the comments of both referees, with the referee comments in *italics*.

Referee 1:

The selected wind sectors are 135° (N/E) and 120° (S) wide. It is therefore by no means certain that within the sectors the air samples equally represent the whole sector. The large difference in tracer/CO₂ff ratios between the two studied wind sectors

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demonstrates that there is strong dependence on wind direction and it is possible that there is also significant dependence on wind direction within the selected sectors. The impact of uneven representation of different wind directions could be exacerbated by the use of medians and removal of samples with CO₂ff < 1.2 ppm (see below). The authors should provide information on frequency of observations as function of wind direction with a higher resolution, maybe 15°.

We have explored the variability of tracer/CO₂ff ratios with wind direction extensively. The defined wind sector boundaries were selected based on these analyses which determined that there is not a significant dependence on wind direction within the two wind sectors. To demonstrate this we have added three figures (Figs. 3a, 3b, and 3c) in the revised manuscript that show how the CO/CO₂ff and CH₄/CO₂ff ratios vary with wind direction, using two different sized wind direction bins. We have added the following text to the manuscript to describe these analyses:

“Figures 3a and 3b show the dependence of the CO/CO₂ff and CH₄/CO₂ff enhancement ratios on wind direction using two different size wind direction bins (40° and 135°), demonstrating a significant enhancement in CH₄ abundance (relative to CO₂ff) when winds are arriving from the north and east of the BAO tower. The CO/CO₂ff ratio, on the other hand, is relatively constant with wind direction, suggesting a consistent mix of CO and CO₂ff combustion sources throughout the region. The CH₄/CO₂ff variability with wind direction shows two distinct wind sectors within which the CH₄/CO₂ff ratio is relatively stable. A significant drop-off in the CH₄/CO₂ff ratio can be seen at around 115°-120°. This provides the basis for the definition of the N/E and S wind sector boundaries, which we use to examine differences in emissions for each trace gas considered in the analysis that follows.”

Combined with detailed information on the spatial distribution of emissions for key trace gases (CO₂, CH₄, CO, maybe one non-methane hydrocarbon) such as gridded emissions (similar to Figure 7, but for the complete study area and without weighting) this would allow the reader to form an own opinion on the representativeness of the top-

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down emission estimates.

This comment is less relevant now that we no longer derive emissions estimates for the trace gases that vary (with respect to CO₂ff) with wind direction. The lack of dependence of the CO/CO₂ff and C₂H₂/CO₂ff ratios with wind direction over a region that spans two very different source regions (urban/suburban and industrial/agricultural), suggests that this ratio is largely insensitive to the mix of emission source types in the region, and is therefore quite representative of the region as a whole.

In principle the authors' approach is based on the assumption that co-location of sources results, due to atmospheric mixing, in strong correlation between trace gas concentrations and CO₂ff. The main evidence they present are r² values in Table 1 and the correlation plots in Figure 3. Considering the importance of the validity of this assumption for all trace gases, the authors should present such plots for all trace gases investigated and use advanced regression tools (such as two-way regression allowing non-zero intercept) for an in depth study of this assumption.

The authors use the median of the ratio of tracer concentration over CO₂ff and its uncertainty for extrapolation to regional scale emission rates. I agree that the median will represent a value which is less sensitive to extreme values. However, this is not limited to situations with reduced atmospheric mixing. Another possibility may be less frequently occurring wind directions dominated by emissions different from those for the preferred wind directions (see above). This may have consequences for the footprint area that is represented by the median.

Presenting more detailed information about possible dependence between trace gas concentrations or emission ratios and meteorological conditions (wind direction, wind speed) would help the reader to understand the possible impact of using median values.

Both reviewers have suggested providing additional figures that would allow the reader to form an opinion on the representativeness of the calculated median ratios on the

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larger data set as a whole for all the trace gases studied. Referee #1 suggests providing the correlation plots for all the trace gases. In the original manuscript we have done this for CO and for CH₄ as two representative cases of a tracer that is constant and one that varies, respectively, with wind direction. We did, in fact, use a two way regression allowing a non-zero intercept to derive r² values in the Table 1. In the revised manuscript, we have also included the slopes for each tracer/CO₂ff relationship, equating to the geometric mean of X-Y and Y-X slopes, in a new version of Table 1. Referee #2 has suggested providing time series and histograms for each tracer/CO₂ff ratio, sorting the data by a number of variables (wind direction, speed, etc). In the interest of cohesion and space, we have provided these figures and a brief description as supplementary material (rather than embedded in the manuscript) to the revised manuscript. We chose, however, to represent the underlying data set not as correlation plots (except for CO and CH₄), but as time series and histograms.

A potential source of bias is the removal of observations with less than 1.2 ppm CO₂ff from the data set of trace gas concentration ratios. The way I understand the procedure for determining CO₂ff, the value of 1.2 ppm is not a detection limit, but simply the uncertainty of the result of a calculation using data with uncertainties. Consequently all results have validity within their uncertainty and there are well developed statistical methods to derive meaningful averages from data with known uncertainty, even if for a subset of data the uncertainty is of similar magnitude to the values. Simply removing these data is not the best way to deal with this problem and may introduce bias. I am aware that for small values of CO₂ff the uncertainty of emission ratios will be large and therefore potentially introduce very large uncertainty into the overall emission ratios. However, this does not mean that all high tracer/CO₂ff ratios are necessarily the result of error in CO₂ff. They may very well be real, reflecting the impact of sources with low CO₂ff emissions such as oil or gas wells, or cattle farms. Therefore eliminating these observations from the emission ratio estimates may cause bias by preferentially removing data that are primarily impacted by sources with low CO₂ff emissions (or not co-located with CO₂ff sources). I am wondering if the combination of using medians to

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reduce the impact of outliers combined with removing samples with CO₂ff < 1.2 ppm may not be a bit extreme in reducing the influence of exceptionally high tracer over CO₂ff ratios. How do the medians change if data with CO₂ff < 1.2 ppm are included?

In a strict sense, the 1.2 ppm value is the minimum detectable difference between two ¹⁴CO₂ measurements (observed and background). Thus, we do consider it a detection limit for the derived quantity, CO₂ff. The purpose of removing these low CO₂ff samples was to avoid “divide-by-zero” errors as CO₂ff approaches zero. Since values below 1.2 ppm are statistically equivalent to a concentration of zero, we selected this value as the cutoff for removing this uncertainty. Both reviewers have raised concerns about the use of this filter, so we re-examined the impact of using this filter on the tracer/CO₂ff ratios. We have added the following text to the manuscript to summarize this analysis:

“Samples are only used in the median ratio calculation when the estimated CO₂ff is above the 1.2 ppm 1σ detection limit to remove divide-by-zero errors, while no lower limit is used in the slope calculations. Removing this filter impacts the uncertainties of the median ratios (by up to 50%) due to divide-by-zero errors and instances of negative CO₂ff, but it has a smaller impact on the median ratios themselves, typically impacting the tracer/CO₂ff ratios by less than ±10%, except for the C₃-C₅ alkanes in the S wind sector which are impacted by between +15 and +30%. In general, the direction of the bias is positive in the S wind sector and negative in the N/E wind sector.

In the introduction the authors refer to measurements or use of “¹⁴CO₂” or “¹⁴C” in general. In many cases it would be useful to be more specific, for example to specify whether this refers to the concentration, total atmospheric (tropospheric) burden, ¹⁴C over total CO₂ ratio etc.

In our manuscript, the use of “¹⁴CO₂” and “¹⁴C” is always presented as a relative quantity to the total CO₂ or C abundance, as is typical for discussions of isotopic abundance. When referring to specific measurements or in quantitative terms, we use Δ¹⁴CO₂ (discussed in Sec. 2.4), which has a specific meaning according to Stuiver

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and Polach (1977). The definition of ‘¹⁴CO₂’ and ‘¹⁴C’ has been clarified in the first sentence of the introduction, which now reads:

“The relative abundance of radiocarbon (¹⁴C) in atmospheric CO₂ (¹⁴CO₂) is a powerful tracer. . .”

Page 1616, Line 4-11: “The primary advantageimproved” and “Further, ... source types” should be rephrased. It is my understanding that these are results of the study and conclusions derived from the study.

The first sentence (“The primary advantage. . .”) is not stating a result from this study, but rather an assumption we make about the confidence limits that we expect from this approach. The second statement (“Further, . . . source types”) does state a result and has been removed from the introduction.

Page 1619, line 8: It is more conventional to use GC-MS than GC/MS.

Manuscript revised to use the more conventional ‘GC-MS’.

Page 1619, lines 11-22: The description of measurement uncertainty for hydrocarbons requires some clarifications: - “...with lower relative uncertainties estimated for samples with lower mole fractions”. This is the only published technique for atmospheric NMHC analysis I can remember where the relative measurement error increases with sample concentration. Is this correct? - The stated relative uncertainty for C₃H₈, C₂H₂ and n-C₄H₁₀ below 1 ppb is 15%, for 20-50 ppb a factor of three larger. This implies that for 20-50 ppb the relative measurement uncertainty is around 45%. If this is correct, this needs some explanation/discussion. Unless there is some specific reason I would not put much trust into a NMHC measurement technique that has a relative uncertainty of 45% at 20-50 ppb. - The relative repeatability is stated to be <2%. What are the reasons for the much larger uncertainties? Calibration uncertainties, non-linear calibrations or other sources of non-random error (bias)? - The repeatability for C₂H₂ and C₃H₈ is given as -25% and +12%. Repeatability usually has no sign. - Some of

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my problems in understanding the description of measurement error in this paragraph maybe due to terminology. It would be better to use standard terminology for analytical chemistry such as reproducibility and accuracy. If this for some reason is not possible, a definition should be provided.

Work on the GC-MS nonlinearity determination, which was underway during the submission period of the manuscript, lead us to originally attribute higher uncertainties to higher mole fractions, following the increased nonlinearity error we observed with increasing mole fractions. We now treat nonlinearity as a bias (of +5 to +12%) rather than include it with other known causes of uncertainty, and discuss its potential impact on our conclusions in the revised manuscript. In short, the 5-12% bias for all NMHCs except for propane translates directly to a 5-12% overestimate of the tracer/CO₂ff ratios and the emission rate for C₂H₂.

The asymmetric reproducibilities (synonymous with repeatabilities) are attributed to the different impact that a temperature instability during sample preconcentration has on quantitation, depending on whether the anomalous temperature occurs during a BAO sample analysis (negative bias) or during analysis of the reference gas (positive bias). Since two sequential reference gas measurements are averaged to determine the detector sensitivity, there is a positive bias of half that of the negative bias, or 12%. As this temperature instability is a random, sporadic occurrence, we conservatively allow for large negative uncertainties and smaller positive uncertainties in all analyses.

We have replaced the description of the NMHC measurements with the following:

“The non-methane hydrocarbons (C₂H₂, benzene, and C₃–C₅ alkanes) are measured using a gas chromatography-mass spectrometric (GC-MS) technique, with cryogenic pre-concentration (Montzka et al., 1993; Miller et al., 2012). Measurement uncertainties for the hydrocarbons considered in this study vary by compound, and include known issues regarding (1) absolute calibration standard preparation errors, (2) the transfer of the absolute scale to the dry compressed whole air reference gases used in

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routine analyses, (3) uncertainty in assumed detector sensitivity due to analyte losses during random and sporadic temperature anomalies during the pre-concentration step, and (4) chromatographic baseline interferences (propane only). Storage tests have shown negligible drift in the hydrocarbon mole fractions of reference gases. Therefore, assigned total uncertainties (1σ) are 5% for n-C₄H₁₀, i-C₅H₁₂, n-C₅H₁₂, and C₆H₆, and 15% for C₃H₈ due to chromatographic baseline interferences, and 15% for C₂H₂ due to primarily to absolute calibration scale uncertainties. Measurement reproducibility (1σ) is generally < 2% for compounds present at mole fractions > 10 ppt. For C₂H₂ and C₃H₈, the most volatile of these compounds, reproducibility was somewhat poorer during these flask analyses due to the instability of the temperature of the cryogenic pre-concentrator (approximately –25% and +12%). The asymmetric reproducibility is attributed to the different impact that the temperature instability has on quantitation, depending on whether the anomalous temperature occurs during a BAO sample analysis or during analysis of the reference gas. This is primarily a problem only for the higher volatility species, C₂H₂ and C₃H₈. As this temperature instability is a random, sporadic occurrence, we conservatively allow for large negative uncertainties and smaller positive uncertainties in all analyses. An additional bias arising from non-linearity in the GC-MS response to varying analyte concentrations (except for propane, which is marginally linear) is estimated to result in an overestimate in the reported concentrations on the order of 5% to 12%. We do not include this bias implicitly in our emission calculations, but we discuss its (minor) impact on our results and conclusions below.”

Page 1620, lines 3-5: Instead of stating the intent the authors should simply provide the specific criteria used for the selection.

The intent, actually, is relevant. The flasks selected for radiocarbon analysis were “cherry-picked” in order to increase the dynamic range of the observations for developing the tracer/CO₂ff correlations. There were no specific criteria for selecting which flask samples to analyze. Each flask package contained 6 simultaneously collected flask pairs. The continuous CO and CO₂ data was visually inspected during the times

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when each flask was sampled and, in general, of the three flask pairs selected in each package, two had relatively high CO and CO₂ and one had relatively low CO and CO₂. We have clarified this in the revised manuscript.

Page 1622, Line28- page 1623, line 1: Since the background $\Delta 14C$ is based on smoothing and filtering, short term variability in stratospheric or oceanic impact on individual samples may not be completely eliminated. Short term variability of background $\Delta 14C$ may be used to obtain an estimate of the possible magnitude of this.

This is perhaps best quantified as the residuals from the smoothing algorithm, or the standard deviation of the differences between all of the individual samples and the smoothing fit. We have calculated this value to be 1.7‰ which is on par with our analytical uncertainty. This is mentioned in Sec 2.5 of the revised manuscript.

Page 1625, lines 23-27: Did the scaling of emission increase “by total dollar amount” include corrections for changes in energy prices? If not, how much error might this introduce?

This comment is no longer relevant given the removal of top-down estimates of gases related to the oil and gas industry.

Page 1627, Line 15-17 and later discussion: Co-location is not the only condition necessary for reducing sensitivity of tracer/tracer ratios to variations in boundary layer height. Due to the variability of boundary layer height temporal (such as diurnal) variability of emissions may also play an important role. Furthermore, the authors discuss boundary layer height as source for CO₂ff variability, potential inversion layers and their height may also be important and may exhibit more variability than boundary layer height. Some information about distribution of samples as function of time of day or vertical stability may help the reader to understand the possible impact of vertical mixing on measured tracer/CO₂ff ratios.

While emissions of two trace gases from co-located sources will roughly experience

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the same mixing, dilution, and transport dynamics, the reviewer accurately points out that having temporally co-varying sources is also an important condition for this to be true. We have modified the language in this section to reflect this. The larger point here is that, in general, tracer/tracer ratios generally experience less variability (at least short-term variability) than individual tracer mole fractions because the ratios are less sensitive to short-term atmospheric dynamics.

Instead of boundary layer, perhaps “mixing layer” is a more general and relevant term.

All samples are collected at the same time of day – roughly 12:30 local time (Page 1618, lines 6-8). The implications of this are discussed in more detail in our response to Referee #2.

Page 1629, line 3-5: “. . .no apparent seasonality. . .”. Depending on variability of the ratios, seasonal variability may still be substantial. Only a low upper limit of seasonal variability (constrained by the observations) can justify conclusions based on absence of seasonal variability.

Yes, this is not to say that there is absolutely no seasonality to the ratios, rather that the median ratios between different seasons are not statistically different (in part due to the large within-season variability, as the reviewer suggests). On the other hand, there are rather large and obvious seasonal differences in the mole fractions. We have clarified this statement to read: “. . .no apparent (statistically significant). . .”.

Page 1629, line 21: Without any prejudice about the environmental awareness Sky Truth tries to create, I think Sky Truth is not the equivalent of a scientifically reviewed source. Furthermore, when I tried to find the specific information cited here using the URL provided, I could not do so within 10 min.

In the revised manuscript, the Colorado Oil and Gas Information System (COGCC) is cited instead, on Page 1629 and also in Figure 1.

Page 1630, line 9-11: What kind of regression method was used? Where the regres-

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sion curves forced through the zero point? Since both variables have uncertainties, a “two-way” regression using uncertainties of the data points without forcing the regression line through the zero point would be a better way to get results unbiased by assumptions about the data set (as long as the error estimates are reasonable).

For estimating r^2 values (and slopes in the revised manuscript), a “two-way” regression was, in fact used. We use a “Model II” regression analysis (<http://www.mbari.org/staff/etp3/regress/history.htm>), where the geometric mean of an X-Y and Y-X regression is determined. The line is not forced through a zero point.

Page 1631, line 21-24: I agree that the data demonstrate strong wind direction dependence. However, the selected wind sectors are quite wide and there is no evidence presented that the methane/CO₂ff ratios are independent of wind direction within the chosen sectors.

See prior discussion and Figure 3 (a and b) in revised manuscript.

Page 1633, line 6-14: Electrical power plants using fossil fuels are major sources of CO₂. Large scale, state of the art power plants are strong CO₂ sources, but are low in emissions of CO or acetylene. Contribution from this type of source can have a major impact on the C₂H₂/CO₂ff ratio. I think the potential use of CO or C₂H₂ as proxy for CO₂ff will always be highly dependent on the specific situation investigated.

Yes, this is true, and we are not advocating that one could use an existing dataset of CO or C₂H₂ and infer CO₂ff without doing a thorough analysis for each particular location and situation. We only suggest that the more consistency found between tracer/CO₂ff ratios in different locations the more promising that particular tracer will be for further evaluation as a proxy for CO₂ff.

Page 1634, line 22-26: I am not sure that after filtering for wind sector, wind velocity, and CO₂ff > 1.2 ppm the number of data points for a given season is necessarily proportional to the length of observation periods.

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After taking a closer look, the reviewer is correct. When we apply our wind and low CO₂ff cutoff, there are, in fact, more samples during the months of November to April than there are between May and October. We’ve modified the text to reflect this.

Subchapter 3.3.1 in general: This discussion of “spatial considerations” would benefit from a presentation of wind direction (and maybe wind velocity) dependence of trace gas concentrations and tracer/CO₂ff ratios. Instead of the detailed narrative (“for example there are...”) maps giving gridded emission rates covering the complete potential footprint area should be presented. This would allow shortening the text part and at the same time provide the reader with a more comprehensive overview than examples.

The wind direction analysis presented in Figure 3 and associated discussion has been covered above. The “narrative” presented in Sec 3.3.1 is not based on an analysis of gridded emissions inventories, but rather from a consideration of where the population centers and major highways are located with respect to where the oil and gas fields are located. This information can be gleaned simply from the map presented in Figure 1. We then use county level statistics from the Vulcan CO₂ data product and from the COGCC to back up these assumptions. Further, given the decreased emphasis on emission estimates for the spatially varying tracers, the emissions grids would likely distract from the ideas we want to present in this manuscript.

Page 1636, line 25- page 1637, line 9: Differences between top-down emission estimates from emission ratios and bottom-up emissions may generally be caused by error in emission ratio or error of emission rates. It is interesting to have an example backed-up by some numbers. However, these are straightforward calculations and most of this lengthy discussion could be replaced by a small table (maybe even presenting more than one example without lengthening the text).

This section of the text has been deleted.

Page 1641, line 19 – page 1645, line 3: The discussion of the influence of footprint area on emission ratios is based on “hypothetical footprints that are not intended to

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accurately represent atmospheric transport". I do not see how these hypothetical footprints are connected to the specifics of the observational data set such average and preferred wind direction or wind speed. Moreover, the focus is solely on methane and, given the very different emission patterns in the studied area, it is not clear to me how this can be extrapolated to other trace gases investigated. Therefore this discussion provides limited insight into the key question of how well the observations represent the footprint area chosen for comparison of top-down and bottom-up inventories. It should be significantly shortened or maybe even deleted in order to make room for more detailed presentation of the underlying observational data.

Given the removal of any top-down estimates of CH₄ emissions, we have deleted this section in the revised manuscript.

Subchapters 3.3.2-3.3.6: This about 9 pages (1638-1648) long discussion primarily presents comparison with published emission estimates and emission ratios. This part should be shortened by presenting the comparison in the form of tables. It would also make it much easier for the reader to obtain a good overview how the results from this study compare with that of other studies. Some of the data are already presented in the form of graphs.

Table 1 in the original manuscript (and Table 3 in the revised manuscript) presents the bottom-up and top-down estimates of emissions for CO and C₂H₂, along with the relevant bottom-up information on CO₂ff. Given the shifted focus in the revised manuscript towards providing emission estimates only for CO and C₂H₂, this section should be much more manageable for the reader. All of the comparisons of top-down to bottom-up emissions are provided in Table 3 and Figures 7a and 7b. Comparison of the CO/CO₂ff ratio between this and other studies is provided in Fig. 5. The comparison of C₂H₂/CO₂ff ratios between this study and one other study is not, however, in table or graph form. This seemed appropriate given that there was only one prior evaluation of this ratio for comparison, in contrast to the CO/CO₂ff ratio for which there have been several examples published.

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Chapter 4 in general: This chapter is in principle a summary and conclusion section focusing on methane and carbon monoxide. It should be shortened and combined with the conclusions. It also contains another comparison with literature and therefore this part of the chapter would better be presented in combination with chapter 3 in tables or graphs.

This section has been paired down to focus solely on the implications for the carbon monoxide emission inventory. We feel that it should stand alone from the analysis in Chapter 3 because it touches primarily on dissecting and discussing the bottom-up inventory for CO and offering recommendations for improving the mobile source model used to construct the NEI CO inventory. The discussion in this section is presented as "implications" for the results discussed in the previous section, and thus seems an appropriate final section to the paper.

We have added a figure to summarize the comparison between the NEI/Vulcan CO/CO₂ ratios for the on-road sector and the tailpipe emissions observations of Bishop and Stedman (2008).

Conclusions: The conclusions mainly consist of comparison with emission estimates from literature and emission inventories, which to some extent is redundant with comparisons in other chapters. This part can be shortened. What I miss is some summarizing evaluation to which extent the observed emission ratios are representative for the area chosen for comparison.

The "representativeness" of the tower observations is evaluated in the most straightforward way possible. The strong correlations of CO and C₂H₂ with CO₂ff across all wind sectors provides strong evidence that these gases are closely associated with fossil fuel combustion throughout the region. This is true despite there being a clear difference in the overall mix of sources between the Denver metro region and the oil and gas –heavy regions to the northeast. Still, it is an open question, in particular for CH₄ and the alkanes. We have paraphrased this in the conclusion.

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Figure 1: This figure should be replaced by figures including gridded emission data. Furthermore, some information about the scale (for those readers not familiar with the Denver area) would be useful.

We feel that including emissions grids would not add any significant information to this discussion, for reasons we have discussed above. The map provides the basic geographic distribution of oil and gas and urban/suburban sources that is needed to interpret the results.

Figures 4-6 and 9 and Table 1 present emission estimates and emission ratio comparisons, which to some extent are redundant. All these comparisons should be combined into one chapter, which would allow more compact presentation of these comparisons.

Figure 9 has been removed. We believe that the remaining figures are not redundant and quite necessary for visualizing the various aspects of our analysis: a comparison of CO/CO₂ ratios with bottom-up values and literature examples, a comparison of tracer/CO₂ ratios for each gas species, a comparison of top-down and bottom-up emissions of CO and C₂H₂, and a deconstruction of the CO and CO₂ inventories to show the on-road sector differences in the CO/CO₂ ratio. Table 1 (now Table 3 in the revised manuscript) has some redundant information to some of the figures, but there is added information in Table 3 related to the bottom-up emissions estimates that is critical. Further, it is often useful to have numbers in both table and graph form.

As mentioned previously, we feel that Section 4 should stand alone and not be included with the other top-down vs bottom-up comparisons.

Referee 2:

1. Temporal variation and sampling frequency: One of my concerns is how representative the medians of the measured tracer/CO₂ enhancement factors are. In other words, is the sampling frequency high enough to capture the true average while the temporal variations seem large from the individual sample CO₂ time series (Fig.2).

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Each sample here only represents a short time event of 2 mins. I would suggest adding a figure of time series of all tracer/CO₂ ratios determined for individual samples and histograms of ratios (similar to Fig.7 in Miller et al, 2012), but with 5 categories: 3 wind sectors (N/E, S and W), wind speed <2m/s, and CO₂<1.2 ppm. The figure will show 1) if there is a difference between different wind sectors; 2) if there is seasonal variation; 3) distribution of the tracer/CO₂ ratios; 4) how the ratios with CO₂<1.2 ppm compare with the rest, besides they carrying larger errors (and to see if taking them out would bias the medians). Most importantly, the figure would allow readers to evaluate the data set themselves.

As detailed above, we have added figures as supplementary material (Figs. S3-S10) showing the time series and histograms of tracer/CO₂ ratios, showing the N/E and S wind sector differences and illustrating the impact of the wind speed and low CO₂ cut-off filters on the data used to derive emission ratios. For the purposes of conserving space, we ignore the W wind sector since we don't use this data in our analysis, but, in general the ratios in the W wind sector, when they show the influence of recent emissions, resemble those in the S wind sector.

Can the authors elaborate on possible diurnal variation of tracer/CO₂? If a tracer gas is not co-emitted with CO₂ and has a different diurnal variation pattern than CO₂, then tracer/CO₂ ratio would likely vary with the collection time in a day. For example, CO₂ would be related to traffic and may have higher concentration in middle of the day, while CH₄ and other tracers that come from oil and gas systems would not. Then the midday tracer/CO₂ ratios would likely be lower than in other times, especially in the S wind sector (Denver metro counties where traffic is heavier). Has the diurnal CO₂ variation from S wind sector been investigated? If there is a diurnal variation for CO₂ then it would likely result in a lower midday tracer/CO₂ ratio for C₃-C₅ alkanes, which in turn may be partially responsible for the lower top-down estimates for these tracers (Fig 6b), in addition to the other possible cause by chemical sinks for these short life tracers. Of course, if no diurnal variation of CO₂ (within one wind

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sector) is observable at the sampling elevation of 300 m, then it would not introduce variations/uncertainties to the tracer/CO₂ff enhancement ratios.

All of the samples used in this analysis were collected at the same time of day (give or take 30 minutes): 12:30 local time, when the boundary layer is expected to be well mixed. Thus it is not possible to evaluate the diurnal variability of CO₂ff or the tracer/CO₂ff ratios. Continuous observations of CO and CO₂ are available at the BAO tower, however, any analysis of these data are confounded by the potential biogenic contribution to the CO₂ signal, which would lead to an over-estimate of the CO/CO₂ff ratio during the daytime when photosynthesis draws down CO₂ and an under-estimate of the CO/CO₂ff ratio at night when respiration may contribute to the total CO₂ signal. Thus, we have qualified our analysis (with a statement in Sec. 3.3) with the caveat that our annual estimates of emissions are biased towards the emission sources that are most active during the daytime hours.

2. Negative CO₂ff values: As the authors indicated “there are instances of negative CO₂ff values (14% of all samples), which is not physically realistic”. Although 3% lie within the 1 σ envelope around zero the relatively large number of negative CO₂ff values reported here may indicate there was a larger than expected heterotrophic respiration component (CO₂het) at the collection site. These events mostly happened from September to January when CO₂het contribution is expected to be high. The authors may want to look into this more closely, such as how they are related to wind direction, wind speed, total CO₂, or CO₂ex (CO₂ex = CO₂total – CO₂bg)? Or try to determine it from a transport model (Stohl et al., 2005). Although the top-down estimates may not be super sensitive to this CO₂het correction, which has been demonstrated by the double and 0 CO₂het sensitivity tests, knowledge about the size and seasonal variation of this CO₂het correction term is important for an accurate estimate of CO₂ff.

The heterotrophic respiration term is an important parameter for accurately estimating CO₂ff, and if one were to use the CO₂ff observations to try to derive absolute fluxes of fossil fuel combustion (e.g. using an inverse modeling scheme), it would be

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important to attempt to more critically evaluate the correction on a sample-by-sample basis, rather than using seasonal averages. Miller et al. (2012) uses one such strategy, for example, where a transport model is combined with a terrestrial ecosystem model. For the purposes of this study, we have quantified the potential bias resulting from not knowing the heterotrophic respiration correction exactly and determined that the impact is small. The reviewer suggests some useful recommendations for future evaluations of the negative CO₂ff samples, which we feel are beyond the scope of the present study, but are certainly worth further analysis.

3. Sampling strategies: Besides 14% of all samples have negative CO₂ff values, more than 52% of the samples had <1.2 ppm CO₂ff, lower than the detection limit, and thus not included in the median determination. This is understandable because uncertainty on the tracer/CO₂ff ratios would become much larger when CO₂ff gets smaller. Low CO₂ff in sample indicates the sampling site is not seeing a strong anthropogenic signal due the collection elevation at 300 m. The advantage of collecting sample at a higher elevation is that the air would be well mixed and thus represents a large area. However, samples at a lower elevation would have a higher signal, and thus lower uncertainty in the tracer/CO₂ff ratio. How do you balance the two? What are the criteria in determining this sampling elevation? Also why use the mean wind direction over 30 min immediately prior to sampling to calculate wind direction. How do you decide data with <2m/s wind speed are removed. I know samples with low wind speed would be too local, but how certain cutting points are decided? Also how does BLH change diurnally? What is the average wind speed? It would be good to plot the mean wind direction and mean wind speed (of individual sample) along with the CO₂ff time series in Fig.2.

In fact, only 29% of all the CO₂ff values are below 1.2 ppm, and only 24% of the post wind-speed-filter N/E and S wind sector samples are below 1.2 ppm. The sampling strategy was not optimized for this particular study, but rather, was designed to meet the larger goals for the NOAA tall tower network program (<http://www.esrl.noaa.gov/gmd/ccgg/towers/>) to provide adequate spatial coverage for

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continental scale inverse modeling efforts (e.g. Carbon Tracker). In general, a higher sampling altitude is thought to be sensitive to emissions representative of a larger area. The tower is equipped with an in situ sensor for CO₂ and CO that switched between sample inlets at three heights (22m , 100m and 300 m above ground level). Observed vertical gradients between the lowest and highest sampling levels are very small (< 1 ppm for CO₂) during well-mixed midafternoon conditions representative of most flask samples (Andrews et al., 2013). The ¹⁴CO₂ sampling strategy is bound to the sampling strategy for the larger program, although the strategy for choosing flasks for ¹⁴CO₂ analysis is designed to expand the dynamic range of CO₂ observations as much as possible.

We chose a 30 minute averaging time for the wind observations in order to ensure that the determined wind direction and speed was representative of the sampled air mass, thus avoiding a situation where the wind direction or speed encountered during the 1 minute sampling period was not representative of the larger scale wind patterns responsible for air mass transport. The wind speed filter of 2 m/s was chosen as a middle ground where the filter is set as high as possible, but low enough so that too many samples are not removed from the analysis for adequate statistics. We have added two figures as supplementary material (S1 and S2) that show the mean wind direction (S1) and speed (S2) for each flask sample used in this analysis.

4. Structure of the paper: The manuscript is quite long. Large portions are about scaling up emissions and comparison of the top-down estimates with the bottom-up estimates from inventories. Although the comparisons are important a lot of the details could go to an Appendix(?) I like how careful the authors are in allowing reasonably large uncertainties for tracer/CO₂ ratio, inventory scaling up for CO₂ and for individual tracer gases. But I think a large portion of the scaling up and details about uncertainties can also go to the Appendix.

With the removal of large sections of text describing the emissions estimates for the gas and oil related tracers, we think the reviewer will be satisfied with how the manuscript

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reads. Many of the tedious details in scaling up emissions stemmed from the need for different approaches to scale up the combustion vs oil and gas tracer emissions. Much of this has been removed from the revised manuscript.

P1612, line 22: "... has been influenced primarily by the equilibration of atmospheric ¹⁴CO₂ with the oceanic and terrestrial carbon reservoirs." Replace "equilibration" by "exchange".

Replaced.

P1618, line1: 'Prior to deployment, each flask in the PFP unit is flushed with clean dry air and then pressurized to 140kPa with synthetic air containing 330ppmCO₂.' I am wondering what is the purpose of pressurizing the flasks to 140kPa with synthetic air containing 330ppmCO₂? What is the $\Delta^{14}C$ for the CO₂ in this synthetic air? Often CO₂ in commercially available synthetic air is close to ¹⁴C free, and would likely to contaminate your air samples. Unless this is a compressed clean air with modern ¹⁴C signature?

The reason for prepping the PFP flasks by pressurizing with a 330 ppm CO₂ "fill gas" is to "condition" the flask surface with some amount of CO₂ (which has been found to undergo negligible exchange with sampled air) so that the CO₂ in the sampled air has less interaction with the flask surfaces. The reason for using a concentration of 330 ppm, specifically, is so that the fill gas has sufficiently different concentration from ambient and it is obvious when a failure occurs that causes insufficient flushing of the flask or failure to collect a sample.

P1619, line16: "Only C₃H₈ was observed at mole fractions greater than 50 ppb during the study period; these 2 samples were removed from this analysis." Which "2 samples"? Do you mean C₃H₈ samples greater than 50 ppb were removed?

With our updated work on the nonlinearity of the GC-MS measurements we have concluded that C₃H₈ does not suffer from the nonlinearity bias that other gases suffer from

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and have recalculated the C3H8/CO2ff ratios with those points included. For those trace gases that are impacted, we treat this error as a bias of +5-12% and discuss the implications for this bias on our analysis.

P1620, line 2: "The selection is based on an analysis of continuous CO and CO2 observations with the intent of selecting a combination of both locally-impacted and background samples." For this study shouldn't you be focused on locally-impacted samples rather than background samples at this site, because of the CO2ff detection limit of 1.2 ppm?

In hindsight, for the purposes of this study, a better strategy might have been to try to capture as many high CO2ff samples as possible. The problem with this strategy, however, is that if one were to try to derive absolute fluxes of CO2ff from these data, the emissions estimate would be biased high. Selecting both high CO2ff and low CO2ff samples hopefully provides a more representative data set.

P1620, line 25: "For the observations described in this study, the (1σ) repeatability (standard deviation) of NWT3 and NWT4 samples was $\pm 2.2\%$." Please indicate $n=?$ Standard deviation is statically meaningless if n is small.

Evaluation of the NWT3 and NWT4 repeatability is ongoing. As of April 2012, 140 NWT3 and NWT4 samples had been analyzed, when the repeatability was determined to be 2.2%. The NWT3 and NWT4 samples analyzed concurrently with the data in this analysis ($n = 40$) showed a repeatability of 1.4% and 2.0% respectively.

P1622, line 1: "...($\Delta 14ff = -1000\%$ or can be measured." What value was actually used in your calculation? For gasoline, $\Delta 14C$ can be less dead (-950-960% Djuricin et al., 2010) due to the addition of modern C source ethanol. The error from this may be small (probably would increase CO2ff by 0.3 ppm) but it should still be discussed.

By definition, CO2ff has a $\Delta 14C$ of -1000%. If the fuel use in the region is a fuel/biofuel blend, the CO2ff detected would represent only the fossil portion of CO2 from those

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combustion sources, rather than the total CO2 emitted from anthropogenic combustion sources. The Vulcan data product for the mobile sector (which is the sector where a fuel/biofuel mix is expected) is derived from activity statistics, and thus would estimate total CO2 emissions from both the fossil and modern components of gasoline. Therefore, the presence of ethanol in gasoline would lead to a slight overestimate of the tracer/CO2ff ratios and, subsequently, the tracer emission rates. If the average $\Delta 14C$ of "fossil" fuel is -950% instead of -1000%, the emission rates (and tracer/CO2ff ratios) estimated in this study would be biased high by 5%. We have added the following text to Sec. 3.3:

"It should be noted that the Vulcan estimates may include emissions of modern (non-fossil) CO2 from the on-road sector in locations where biofuels are used, including Colorado, which would lead to a positive bias in ECO2ff, and therefore, Ex. This bias would scale directly with the fraction of total CO2ff (all sectors) in the Vulcan estimate that is from biofuels. For some perspective, a fleet-wide 15% biofuel blend in the on-road sector (33% of the total CO2ff emissions in the region; see Table 2) would result in a +5% bias in our estimates of Ex. This would be roughly equivalent to assigning a value of -950% (rather than -1000% for $\Delta 14ff$ in our derived CO2ff estimate."

P1623, line 7: How was the unusually high (15 ppm) "CO2bio mole fraction" estimated? By subtracting CO2ff from the total CO2 enhancement, I guess? If CO, and a large number of other anthropogenic tracers were elevated in this particular sample, which is not consistent with a higher 14C value, then is it possible that this particular sample got contaminated during sample prep?

CO2bio = CO2tot - CO2bkg - CO2ff. There is no evidence to suggest that this sample was contaminated, but it cannot be ruled out.

P1625, Line 10: ".....are estimated from population statistics or additional factors." What are the additional factors? Please specify.

This section of text has been removed as a result of the scaled back analysis of oil and

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gas emissions.

P1625, Line 13: "For these species, uncertainty limits for the scaled emissions are assigned as the base year estimates (i.e. no change in emissions) on the low end..." But in table 1, the min scaled emissions (bottom-up) are lower than base year estimates for CH₄ (N/E) and C₃–C₅ alkanes (N/E) though the scaling factor listed =0 (?) On the other hand, for CH₄, the max scaled emission (99.8) is higher than the values obtained by max scale factor X base emission (64.3 x 1.3 = 83.6). In text, the authors did mention some extra uncertainties for CH₄, then why not just change the min/max scaling factors to account for the extra uncertainty? It may be helpful to the readers if the authors add a table to show the bases/assumptions for how the scaling factors (and scaling uncertainties) were calculated for all the tracer gases.

This section of text has been removed as a result of the scaled back analysis of oil and gas emissions.

P 1626, Line 23: "... were included their top-down emission calculations." Add "in" after "included".

Added.

P1628, line 3: "Samples are only used in the ratio calculation when estimated CO₂ff is above the 1.2 ppm detection limit." As for discarding data with <1.2 ppm CO₂ff, maybe you could also state what uncertainty for the ratio would be when CO₂ff is <1.2 ppm. Is it better to filter the ratios by removing relative uncertainty, say greater than 100% at the 1-sigma level, as what is done in Miller et al. 2012?

This would be roughly equivalent to removing samples less than 1.2 ppm, which is the point at which the relative uncertainty is 100%. An additional 13 samples could potentially be included in the analysis, but the results would not change significantly.

P 1628, Line 7: "...from a distribution of 500 estimates of the median from a randomized re-sampling of the data (boot-strapping with replacement)." How is the number

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of boot-strapping 500 chosen? How does this boot-strapping number affect the 95% confidence intervals. In other words, how different it is from a 1000 boot-strapping?

Theoretically, one could be 40% more certain of the 95% confidence intervals by using 1000 iterations rather than 500 iterations ($1000^{-2}/500^{-2}$). For CO and C₂H₂ (for which we derive emission estimates), there is a negligible difference between confidence intervals derived from 500 and 1000 iterations.

P 1629, Line 4: "While variability in the absolute mole fractions of the tracers and CO₂ff has a strong seasonal dependence (e.g. Fig. 2b)," Take out "tracers" because Fig.2b is only CO₂ff. However, it would be interesting to see the plots of other tracers.

Changes made.

P1634: for eq. 4, I suggest to change "α" to "αCO₂", also define it more clearly in text so that readers would not confuse it with other scaling factors listed in Table 1. Other α factors are for scaling up the bottom-up emissions for comparisons.

Changes made.

P1638, Line 27: "The observations off of the eastern seaboard of the United States..." take out "off".

Changes made.

P1640, Line 24: "and found relative agreement (within 6 %)" change to "relatively good agreement..."

Changes made.

P1652, line 23: "in air masses arriving passing over Weld and Larimer counties..." change to "in air masses traveling from Weld and Larimer counties.

Changes made.

P1653, Line 16: "CO is underestimated in the NEI08 inventory in both Weld/Larimer

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counties and the Denver metro counties by a factor of 2, consistent with prior evaluations of earlier NEI inventories in the US over larger scales." In this sentence, "underestimated" should be changed to "overestimated".

Changes made.

P1661, Line 6: "however, and given the limited evaluation of C2H2 emission sources in the literature, to date, further studies are recommended." Change to "however, given the limited evaluation of C2H2 emission sources in the literature as of today, further studies are recommended."

Changes made.

Fig.1: Add scale, latitude and longitude to this map. Also it looks like you should be able to label the background site NWR on the map too. There is definitely an advantage of using a relatively nearby background site – seasonal cycles may be minimized for the tracer gases, which favors the use of year-around R.

Changes made. The CAR aircraft site has also been labeled.

Fig. 2, 3, 6: use "upper panel" and "lower panel" for "above panel" and "below panel". And label them "a" and "b", respectively, since that's how they were referred in the text.

Changes made.

Fig.2: It would be good to add the mean wind direction and mean wind speed (of individual sample) plots, parallel to the $\Delta 14C$ and $CO2ff$ time series.

Supplementary figures added (S1 and S2)

Fig.3 Caption: "Data are separated into one of three wind sectors", take out "one of".

Changes made.

Fig 4: Use $CO/CO2ff$ directly as the axis label, instead of R.

Changes made.

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Table 1: For CO, combined # should be 69 (N/E=44 and S=25), instead of "68" as listed(?).

Corrected.

Table 2: Add lifetime of CO2 and major sources for CO2ff in this table as well.

The lifetime of CO2 is not well-defined by a single number; further, it is not relevant to this analysis because the only CO2 loss process that influences CO2ff is dilution with background air. We have added the fractional contribution of the major Vulcan CO2 emission sectors for the region (Denver Metro plus Weld/Larimer counties) to Table 2.

References

Andrews, A. E., Kofler, J. D., Trudeau, M. E., Williams, J. C., Neff, D. H., Masure, K. A., Chao, D. Y., Kitzis, D. R., Novelli, P. C., Zhao, C. L., Dlugokencky, E. J., Lang, P. M., Crotwell, M. J., Fischer, M. L., Parker, M. J., Lee, J. T., Baumann, D. D., Desai, A. R., Stanier, C. O., de Wekker, S. F. J., Wolfe, D. E., Munger, J. W., and Tans, P. P.: Atmos. Meas. Technol. Discuss., 6, 1461-1553, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 1609, 2013.

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