**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$" *by* B. W. LaFranchi et al.

Anonymous Referee #2

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The authors applied the unique tool of atmospheric $^{14}CO_2$ to derive fossil fuel origin CO2 (CO2ff) in the Colorado Front Range, which by far is the most accurate approach to obtain this component (to a detection limit of $\sim$ 1.2 ppm). Then using the observed tracer/CO2ff enhancement factors and the relatively well-known emissions of CO2ff from inventory they estimated emissions of the other tracer gases, such as CO, CH4 and a suite of hydrocarbons in the region, assuming the tracer/CO2ff enhancement factors are proportional to the E_tracer/E_CO2ff emission ratios. The authors then compare these top-down emission estimates with the bottom-up inventory-derived es-

timates. One clear advantage of this approach is its ability to estimate emissions for a suite of tracer gases that normally would be difficult to obtain from bottom-up inventories and often with large uncertainties. The other advantage is its simplicity because the use of tracer/CO2ff ratios greatly minimizes variations that could have come from transport and boundary layer high (BLH) change. However, this approach is not new. For example, it has been applied successfully in the northeast U.S. aircraft samples by Miller at al. (2012). But, the location investigated and sampling method used (from a tall tower) in this paper are very different from the aircraft samples above the ocean investigated by Miller at al. (2012), and thus it's interesting to see how well this tracer/CO2ff approach is applied here. Since this method could potentially be very useful in estimating emissions for many other co-emitted and co-located tracer gases, I believe this work is of great interests to the atmospheric science community and thus suitable for publication in ACP.

The paper is mostly well written and concise. However, several points require clarification before it can be published.

Major comments

One main assumption for this tracer/CO2ff approach is the relatively constant spatial and temporal distributions of tracer/CO2ff ratios in the divided sectors. The effect (and uncertainties) of potential spatial variation on tracer/CO2ff ratios has been thoroughly discussed in the paper. However, much less has been said about temporal variations, except for one sentence stating that "there is no apparent seasonality to any of the considered tracer/CO2ff enhancement ratios". Here I would like to raise a few questions regarding temporal variations.

1. Temporal variation and sampling frequency: One of my concerns is how representative the medians of the measured tracer/CO2ff 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 CO2ff time series (Fig.2).

Each sample here only represents a short time event of $\sim$ 2 mins. I would suggest adding a figure of time series of all tracer/CO2ff ratios determined for individual samples and histograms of ratios (similar to Fig.7 in Miller at el, 2012), but with 5 categories: 3 wind sectors (N/E, S and W), wind speed <2m/s, and CO2ff<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/CO2ff ratios; 4) how the ratios with CO2ff<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.

Can the authors elaborate on possible diurnal variation of tracer/CO2ff ? If a tracer gas is not co-emitted with CO2ff and has a different diurnal variation pattern than CO2ff, then tracer/CO2ff ratio would likely vary with the collection time in a day. For example, CO2ff 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/CO2ff 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 CO2ff variation from S wind sector been investigated? If there is a diurnal variation for CO2ff then it would likely result in a lower midday tracer/CO2ff 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 CO2ff (within one wind sector) is observable at the sampling elevation of 300 m, then it would not introduce variations/uncertainties to the tracer/CO2ff enhancement ratios.

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 1σ 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

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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 supper 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.

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.

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 CO2ff and for individual tracer gases. But I think a large portion of the scaling up and details about uncertainties

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can also go to the Appendix.

Minor comments (and technical corrections)

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

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 Δ14C 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?

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?

P1620, line2: "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?

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

P1622, line 1: ". . .(Δ14ff = -1000 ‰ or can be measured." What value was actually used in your calculation? For gasoline, Δ14C can be less dead ($\sim$950-960‰ Djuricin et al., 2010) due to the addition of modern C source ethanol. The error from this may

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be small (probably would increase CO2ff by $\sim$0.3 ppm) but it should still be discussed.

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?

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

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.

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

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?

P 1628, Line 7: "…from a distribution of 500 estimates of the median from a random-

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ized re-sampling of the data (boot-strapping with replacement)." How is the number 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?

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.

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.

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

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

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

P1653, Line 16: "CO is underestimated in the NEI08 inventory in both Weld/Larimer counties and the Denver metro counties by a factor of $\sim$2, consistent with prior evaluations of earlier NEI inventories in the US over larger scales." In this sentence, "underestimated" should be changed to "overestimated".

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."

Figures and tables:

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.

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.

Fig.2: It would be good to add the mean wind direction and mean wind speed (of individual sample) plots, parallel to the $\Delta14C$ and CO2ff time series.

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

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

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

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

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