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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 #1

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The paper presents a comparison between bottom-up (emission inventory based) and top-down (atmospheric observation based) emissions for Denver (Colorado) and adjacent counties. The authors determine emissions by using trace gas measurements (CO2, CO, 14-CO2, methane and non-methane hydrocarbons) in air samples collected during a time period slightly exceeding one year. The use of 14-C measurement to determine carbon dioxide from fossil fuel use (CO2ff) eliminates some of the possible interferences from exchange of atmospheric carbon dioxide with the biosphere. Emission rates then are calculated by scaling emission ratios relative to CO2ff to regional

scales by using CO2 emissions from bottom-up emission inventories. Since validation or correction of emission inventories is a very important problem in Atmospheric Chemistry, the subject of the paper is relevant for ACP. Overall the paper presents an interesting data analysis and valuable insight into the use and value of top-down emission inventories. I find the paper especially interesting since it presents an analysis of a very complex situation characterized by the presence of strong trace gas sources with widely varying emission ratios. 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. Apart from several details that should be addressed, my main concern is that for such a complex situation the authors do not present enough details of the data set underlying their top-down analysis. Therefore, in spite of the substantial length of the paper, the presented information is insufficient to allow the reader an own opinion about assumptions made to derive emission rates. 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 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 acerbated 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 °. 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-down emission estimates. 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.

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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. 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

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not co-located with CO2ff sources). I am wondering if the combination of using medians to 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? I am aware that this potentially adds additional length to an already quite lengthy paper. However, adding graphs and tables presenting more detailed information on trace gas concentrations and CO2ff may also allow shortening the text part of the discussion in Chapter 3. Specifically, the paper contains very repetitive discussion and comparison of emission ratios and emission rate estimates, which can be condensed. Similarly several of the figures contain redundant information adding unnecessary length.

Following are some specific suggestions and details the authors may want to consider for revising their manuscript. In the introduction the authors refer to measurements or use of "14 CO2" or "14-C" 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, 14-C over total CO2 ratio etc. Page 1616, Line 4-11: "The primary advantage ....improved" and "Further, ... source types" should be rephrased. It is my understanding that these are results of the study and conclusions derived from the study. Page 1619, line 8: It is more conventional to use GC-MS than 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 cal-

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ibrations 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 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. Page 1620, lines 3-5: Instead of stating the intent the authors should simply provide the specific criteria used for the selection. Page 1622, Line28- page 1623, line 1: Since the background Δ14C 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 Δ14C may be used to obtain an estimate of the possible magnitude of this. 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? 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. 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. 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. Page 1630, line 9-11: What kind of regression method was used? Where the

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regression 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). 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. 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. 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. 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. 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). 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 accurately represent atmospheric transport”. I do not see how

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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. 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. 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. 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. 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. 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.

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