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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A new method for estimating emission ratios in the urban atmosphere: examples of ratios to CO_2, CO and volatile organic compounds in Paris" *by* L. Ammoura et al.

Anonymous Referee #2

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Overview: Ammoura et al. present a manuscript showing measurements of CO2, CO and VOC's made in Paris as part of two intensive campaigns as well as longer-term observations. They analyze data in low wind conditions in what they term a new method to derive dCO/dCO2 ratios with the interest of learning about emissions characteristics in the Paris region. This manuscript is well placed in ACPD. Much of the data appears sound, and the analysis pursued by the authors is worthwhile. However, I find there to be a couple key conceptual issues the authors have failed to address adequately that I will outline in detail below. Most importantly, there is a fundamental flaw in the

interpretation of observed ratios as representative of emission ratios assuming dilution effects cancel between species. I outline this below, and this is a fundamental flaw that must be address. There are also some key considerations about the representativeness of observations that need more details. Finally, the authors indicate in the title and abstract that they will consider VOC's as well, but this data is largely neglected and not analyzed or discussed. Once these concerns outlined in detail below have been addressed, and VOC data have either been added into the analysis and discussion (what I would encourage), I would reconsider the manuscript for publication in ACP.

Conceptual Issue:

Dilution-mentioned in line 38-40 "Measurements made in the ambient air are affected by dilution in the atmospheric boundary layer, but this effect cancels out when considering mole fraction ratios between the considered species." This actually is a common misconception that is not true in the cases discussed in this manuscript. This actually potentially significantly impacts the interpretation of all the analysis and requires closer examination and discussion. I can illustrate this with a simple thought experiment. Let us assume we are considering observations in Paris. Let the emissions source impacting our observation have a dCO/dCO2 ratio of 5 ppb/ppm (in the normal range reported in the study here). Now the important part-let us imagine a scenario where the background CO2 concentration is 380 ppm, while the free troposphere is at 390 ppm. This is just putting some simple numbers down, but this is a realistic scenario where extra-urban vegetation has drawn the boundary layer value down below the free troposphere before entering the city. Let us assume CO has 100 ppb in both the background and free troposphere. If our source emits enough CO2 to raise the boundary layer by 5 ppm, then in the absence of any entrainment/dilution the observed CO2 would be 385 ppm and the observed CO would be 125 ppb, and the dCO/CO2 observed would match the emissions ratio of 5. Now if there is some dilution of say 25%, then the CO2 measured value would be (.75*385 + .25*390) = 386.25 and the CO measured value would be (.75*125 + .25*100) = 118.75. Our observed dCO/dCO2

would then be (18.75/6.25) = 3 - significantly different than the emissions ratio (25/5) = 5, the value we are interested in which this manuscript is attempting to measure. This is just a simple thought experiment, but clearly illustrates that dilution can change the perceived emission ratio. This is true when the background and free troposphere value are different-a situation that happens often for CO2, but also can happen frequently for CO. If the CO2 background value matched the free troposphere in the above example, we would see the dilution effects cancel. This is a critically important point that is neglected entirely in the manuscript as it is asserted in lines 38-40 that dilution effects all cancel. This is an issue the authors need to consider and include in their analysis-particularly as it might have a large seasonal influence that would exactly match the seasonality reported-where the dCO/dCO2 ratio drops during spring/summer. One might argue this becomes embedded in a discussion of what background value is used in the analysis, and filtering for larger delta signals lessens the impact of this concern. This would perhaps be a key place to explore this issue. Also is a place where more analysis of the VOC data could be used for further tests of this impact as for some VOC's the background value and free troposphere value will be very similar much of the time. Relatedly, using the lower 5% values may seem like a reasonable empirical choice-it almost certainly will not produce a background value that equals the free troposphere value for any of these urban sites, so could produce a bias that varies seasonally.

Detailed Issues: Title and beyond: Calling this a 'new method' is a bit misleading, as people have studied tracer-tracer ratios extensively for decades. The tracer-tracer method has also been used in urban regions in a variety of ways; see say Wunch et al., GRL 2009 or Newman et al., ACP, 2013. There are new details in the reported approach, but it is overstating to call it a whole new method and is not needed. Generally this could be better represented in the introduction with more citations (23 references in total is a bit light and doesn't do justice to the prior tracer-tracer work done).

Title: VOC's are highlighted, but are essentially completed neglected in the manuscript.

Line 15: the assessment of sensitivity to background concentration may change when dilution effects are considered.

Line 23: This conclusion would rely on the observations being representative of more than a very local siteâĂŤthis is note discussed or established later is of high importance.

Line 32: This citation is not actually in the references.

Line 40-42: ".. molecules share the same origin" This is again a slight misconception that is common. The source either needs to be the same, or their needs to be sufficient atmospheric mixing between multiple sources before the observation. Subtle but important distinction.

Section 2.1: What height are the inlets? Where are the inlets related to surroundings? On a tower above the urban canopy? On a building? This is really important when considering the representativeness of the observations. Even more so than usual as looking at low wind conditions means stagnant air might only be representative of a very small area in the direct vicinity of the observations.

Line 175/Figure 1: The assertion that no significant peaks are visible is not true. I can clearly see a rather substantial CO2 and CO feature at this low wind event. The signal is more modest than on the days of greater focus, but there is clearly very detectable enhancement there and this should be accurately represented in the text.

Line 178-179: this statement needs reassessment in light of the above comment.

Line 235: What type of linear regression is performed? Variance in both the x and y axis will be comparable so it is important to perform a regression that accounts for error in both axes (such as a Type II model regression).

Line 285-286: This statement makes a case that perhaps the dCO2 threshold choice should be defined in a way to limit the error to a certain %. If you know the ppm error, then you could define this.

Possible Biased sampling: In addition to a need to discuss the representativeness of the observations, we must also consider possible bias to the sampling. Notably, the analysis is only performed during stagnant conditions (the opposite actually of many biased samplings that only occur during sunny/well mixed conditions). What bias might this introduce?

Line 324-325: It is reasonable to assess if temperature could be used as a predictor for emission ratios, but is not reasonable to consider it the driver of changing emissions ratios without establishing a physical mechanism that would explain it.

Line 329-336: This is a very important paragraph, but I haven't been convinced that the analysis is actually robust to establish this paradoxical conclusion. dCO/dCO2 from emissions are expected to show the opposite seasonality reported hereâĂŤand there is not reason to think our notion of CO/CO2 emissions ratios from say vehicles is so grossly in error. I find it much more likely that errors in the analysis method/interpretation are better explanations for this discrepancy. Examples include: Dilution as discussed above could produce exactly the signal seen here and this is not addressed in the method. If the sampling (let's say in the Park) happens to see very strong respiration signal in spring/summer this would lower the CO/CO2. This relates to a question of representativeness-what are the sites really representative of and what sources are in that domain? Considering only stagnant conditions are studied this may be a very small region. The authors need to establish what the size of this region may be. Representativeness needs to be addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23587, 2015.