Atmos. Chem. Phys. Discuss., 15, C7967–C7970, 2015
www.atmos-chem-phys-discuss.net/15/C7967/2015/

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.

J. Turnbull (Referee)

j.turnbull@gns.cri.nz

Received and published: 13 October 2015

This paper describes a technique for determining emission ratios using periods of stagnant air, when mole fractions are high and therefore emission ratios can be determined more reliably than at other times. The authors show that during these periods, the choice of background is less critical than in other cases and therefore the emission ratios may be more reliable. The largest dataset is for the CO:CO2 ratio, and an interesting seasonal cycle in the ratio is demonstrated.

General comments: This paper develops a good dataset and the results are quite interesting. The title and content of the paper focuses on the "new" method for estimating emission ratios, using periods of stagnant air, yet it seems a bit of a stretch to call this an entirely new method. Perhaps previous authors have not explicitly stated that they are using stagnant events in determining emission ratios, but similar methods have certainly been used.

The paper would appeal to a wider audience if the authors reduced the emphasis on the "new method", and instead focussed on the more interesting aspect – the emission ratios that they determine. The seasonal cycle in the CO:CO2 ratio is discussed to some extent, but this can and should be fleshed out – how can this result be reconciled with the Airparif inventory? The VOC ratios are discussed only very very briefly and leaves the reader with all sorts of questions – they could be compared to the ratios expected from emission inventories and/or from studies for other urban areas.

For these reasons, I recommend major revisions to the paper. Note that the work presented appears sound, it simply doesn't go far enough to interpret and understand the results. With revisions, the paper will be entirely appropriate for ACP.

Specific comments:

Pg 23590 lines 6-8. This sentence is phrased awkwardly. Suggest revision for clarity.

Section 2.2.2. Is this the same Picarro unit as used for the MEGAPOLI campaign?

Please clarify what is meant by "trueness".

Section 3.1., first paragraph, and also in section 4.3. There is no page limit for ACP, so why not include these figures in the main paper, since they are important to the main point of the paper?

Section 3.1. Second paragraph. What VOC species were analysed? The only place they are listed is in table 1. A fleshed out discussion of the VOCs, their sources and sinks, etc should be added.

Section 3.1. third paragraph. In the short duration stagnant air events, no buildup of mole fractions is observed. But some build-up must have occurred, just not enough to be obvious. Does the time of day that the stagnation event occurs make a difference? I suggest that the definition of a stagnant event be one where the wind is so light that the wind direction meanders. The Nov 17/18 event would then by definition be excluded.

Section 3.2. The 5th percentile baseline method does not take into account changing wind direction. For example, the lowest values could be when the wind comes from a clean air sector. When the wind comes from a sector with significant sources upwind of the city, the urban background could be much higher. How might this impact the results?

Please add a sentence in the paragraph discussing the MACC CO2 product to tell the reader that you will compare the two background methods in a later section.

Section 3.3.1. How would the results differ if the ratio was determined for each individual 30 min increment (rather than determining the slope for each 4 hour window)? The 4 hour window method seems cumbersome to calculate, whereas calculating ratios for each increment would be much more straightforward.

In figure 3, the asymptote appears to be $\sim$0 in all cases, is this a trick of the eye, or am I missing something? If the former, zero lines should be added to the graphs.

Section 4.2. second paragraph. Temperature clearly correlates to the CO:CO2 ratio, but it is presumably not a direct driver, rather an indirect driver due to the possible explanations given, and - Another possible explanation for the seasonal cycle in CO:CO2 ratio is that the emission ratio from traffic increases in winter. Vehicle studies suggest that the largest CO emissions occur when the vehicle starts up, and that this startup burst of emissions is larger in cold conditions (before the catalytic convertor warms up). Presumably CO emissions from other source sectors might also be higher in winter due to the lower ambient temperature.

In interpreting these results, the authors should consider that Miller et al (2012) showed that using total CO2, the CO:CO2 ratio can be much lower than the CO:CO2ff ratio, since even in winter there can be a significant biogenic CO2 source. How would the seasonality in the biogenic CO2 source/sink impact the CO:CO2 ratio? Could this be important to the overall seasonal cycle observed?

The discussion of the Airparif inventory CO:CO2 ratios that is in the following section would fit better here. It appears that the observed annual mean ratio is substantially higher than the Airparif inventory. Why?

Section 4.3. First paragraph. As earlier, why not include these figures in the main paper?

As for CO:CO2, the difference in VOC:CO2 ratios with temperature might be due to less efficient vehicle combustion and/or less efficient catalytic convertors in cold temperatures.

Examining Table 1 in detail, there appear to be some inconsistencies in the ratios that should be discussed: The CO:CO2 and acetylene:CO2 ratios are consistent for both studies. The ethylene:CO2 ratio is higher in the Multi-CO2 campaign by 60%, yet ethylene:CO is very similar in both campaigns. Since CO:CO2 is the same in both campaigns, this doesn't make sense! A similar situation is seen for propene and n-pentane.

As I said in my general comments, this section is weak and would really benefit from a comparison of the observed VOC:CO2 ratios with inventories and/or studies from other urban areas. There are a number of urban and regional studies that have looked in detail at the ratios of VOCs:CO that would make useful comparisons, as well as several that have looked at VOC:CO2 or VOC:CO2ff ratios.

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