

We thank both referees for their assessment of our paper and the useful comments. We answered to the comments and questions point by point where it is appropriate.

Referee #1: Jocelyn Turnbull

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 focused 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 leave 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.

This sentence will be rephrased.

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

The same instrumentation (CRDS G1302, Picarro) was used for the MEGAPOLI campaign but not the same unit. The two instruments were compared in 2010 and the repeatability and the trueness of the 1 min averaged data are almost the same (listed in Lopez et al. (2013) for the MEGAPOLI campaign and in our study for the Multi-CO₂-campaign).

Lopez, M., Schmidt, M., Delmotte, M., Colomb, A., Gros, V., Janssen, C., Lehman, S. J., Mondelain, D., Perrussel, O., Ramonet, M., Xueref-Remy, I., and Bousquet, P.: CO, NO_x and ¹³CO₂ as tracers for fossil fuel CO₂: results from a pilot study in Paris during winter 2010, Atmos. Chem. Phys., 13, 7343–7358, doi:10.5194/acp-13-7343-2013, 2013.

Please clarify what is meant by “trueness”.

According to BIPM (2012), “measurement trueness” evaluates the “closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value”. This definition will be added in the text. “Measurement trueness” is different from “measurement accuracy” which evaluates “closeness of agreement between a measured quantity value and a true quantity value of a measurand”. We will add an explanation in the text.

BIPM : Vocabulaire international de métrologie - Concepts fondamentaux et généraux et termes associés (VIM, 3^e édition), Tech. Rep. JCGM 200:2012, available at <http://www.bipm.org/fr/publications/guides/vim.html> (last access: October 2015), 2012.

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?

A single example like the one of Fig. 1 appears enough to us for the main point of the paper. We prefer to keep the other figures in the supplement in order not to make the main text heavier.

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.

We will list the analysed VOCs in Section 2.2.3 and describe their urban sources and sinks as well as those of CO₂ and CO in the introduction.

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.

There is no difference in the results regarding the time of day that the meteorological events with low wind speed occurs. For example, during the Multi-CO₂ campaign, these events occurred during nights and days indifferently and the derived ratios are the same for all the different events.

We will point out the condition on the winds to be non-directional to support the assumption of “local” source. Figure 2 also illustrates this condition in the paper.

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?

We evaluated the 5th percentile for moving windows of three days. This running window allows accounting for the dependency of synoptic situations and finally the lowest values sample indifferently the different wind sectors. To illustrate this, we present here the averages we obtained on the background concentrations we determined doing a selection on wind directions. We obtained:

- For the continental sector (0-180°), average(CO₂, 5th percentile) = 410.2 ppm.
- For the oceanic sector (180-360°), average(CO₂, 5th percentile) = 402.4 ppm.

This definition of the background thus accounts for different wind sectors and does not correspond to a clean air sector only.

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.

A sentence will be added to explain that the two background definitions are compared 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.

We focused our analyses on specific situations with low wind speed. These events appear on the different time series thanks to significant peaks in the concentrations. Finally we focused on these peaks. Our method is worthy of interest because these peaks, in which the correlations are tight, are extracted “by themselves” in the asymptote. There is no need to extract the peaks by hand. Finally, the asymptotic value for the ratios shows that these peaks can be represented by a unique ratio and this one is calculated for well-correlated data only.

As a comparison, we also determined the ratio for each individual 30 min increment. This method is easier to set up for the calculation of the ratios but the instantaneous ratios we obtained show a larger variability. For example, the instantaneous $\Delta\text{CO}/\Delta\text{CO}_2$ ratio during the Multi- CO_2 campaign is 5.91 ± 2.61 whereas it is 5.55 ± 0.24 with our method, which confirms that our method allows a more precise determination of the ratios.

In figure 3, the asymptote appears to be ≈ 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.

The asymptotes are not equal to 0. This is a trick of the eye due to the scale of the y-axis. We will add the abscissa on the graphs.

Section 4.2. second paragraph. Temperature clearly correlates to the $\text{CO}:\text{CO}_2$ 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 $\text{CO}:\text{CO}_2$ 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.

We previously discussed the impact of the efficiency of the catalytic converter on CO emissions in Ammoura et al. (2014). CO emissions are more important when vehicles work at lower temperature than the optimal value. This optimal value is between 70 to 90°C and the time to reach this temperature is certainly longer in winter than in summer. And this excess of emissions may not be negligible in summer. To our best knowledge, no studies characterised the link between emissions and ambient temperature. Thus, we cannot rule out this possible explanation and we will add a sentence to mention this point.

Ammoura, L., Xueref-Remy, I., Gros, V., Baudic, A., Bonsang, B., Petit, J.-E., Perrussel, O., Bonnaire, N., Sciare, J., and Chevallier, F. : Atmospheric measurements of ratios between CO_2 and co-emitted species from traffic : a tunnel study in the Paris megacity, *Atmos. Chem. Phys.*, 14, 12 871–12 882, doi :10.5194/acp-14-12871-2014, 2014.

In interpreting these results, the authors should consider that Miller et al (2012) showed that using total CO_2 , the $\text{CO}:\text{CO}_2$ ratio can be much lower than the $\text{CO}:\text{CO}_{2\text{ff}}$ ratio, since even in winter there can be a significant biogenic CO_2 source. How would the seasonality in the biogenic CO_2 source/sink impact the $\text{CO}:\text{CO}_2$ ratio? Could this be important to the overall seasonal cycle observed?

Our ratios are evaluated thanks to the equation of the horizontal asymptote. The data points distributed around this asymptotic value were sampled during nighttime and

daytime indifferently. And for both of them, the ratio is unique (=equation of the asymptote). As night and day ratios fall into this line we may suppose that the impact of the biosphere is negligible.

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?

According to the 2010 Airparif inventory, the annual mean ratio between CO and CO₂ is 3.1 ppb/ppm. Analysing our measurements, we found an observed annual mean ratio which is equal to 4.9 ppb/ppm. We thus notice 37% of difference between the two ratios.

Airparif also provided us with CO and CO₂ total emissions for January and August. We estimated the monthly ratios for these two months:

- CO/CO₂)_{Jan} = 3.1 ppb/ppm
- CO/CO₂)_{Aug} = 3.6 ppb/ppm

It is difficult to draw a general conclusion with only two values but it seems that there is no pronounced seasonal variability in the Airparif inventory. We will add this short comparison in the paper.

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

Here as well we prefer not to make the main paper heavier.

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.

As mentioned previously, we will add a sentence in the text to allude to this possible influence.

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.

We thank the referee for the careful examination of the table of ratios. Our method determined an average ratio. If we use the $\langle \dots \rangle$ to represent an average, the ratios we determined correspond to $\langle \frac{\Delta species1}{\Delta species2} \rangle$ and not to $\frac{\langle \Delta species1 \rangle}{\langle \Delta species2 \rangle}$. If we focus on the ratio

between ΔCO and ΔCO_2 , the equation of the horizontal asymptote corresponds to $\langle \frac{\Delta\text{CO}}{\Delta\text{CO}_2} \rangle$ which is not equal, statistically speaking for two correlated variables, to $\frac{\langle \Delta\text{CO} \rangle}{\langle \Delta\text{CO}_2 \rangle}$. Finally, the usual simplification we can apply to derive other ratios does not work here and, for example : $\langle \frac{\Delta\text{CO}}{\Delta\text{CO}_2} \rangle \neq \langle \frac{\Delta\text{CO}}{\Delta\text{ethylene}} \rangle \times \langle \frac{\Delta\text{ethylene}}{\Delta\text{CO}_2} \rangle$. Therefore, it makes sense not to have this kind of mathematical links with the ratios we evaluated.

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:CO_{2ff} ratios.

We sum up in Tables 1 and 2 hereafter some comparisons with previous studies and with the latest available Airparif inventory. Table 1 presents a comparison of ratios to CO and acetylene for the Multi-CO₂ and CO₂-Megaparis/MEGAPOLI campaigns, and for five previous studies analyzing ratios in Paris (France), Mexico city (Mexico), New England (US) and London (United Kingdom). Estimates for the 2010 Airparif inventory are also listed in Table 1.

Table 2 exposes the comparison between the ratios we derived to ΔCO_2 and the ones referenced in previous studies to CO_{2ff}. The comparison with the Airparif inventory is also listed.

Examining the two tables carefully, we notice important differences between all proposed ratios. Each campaign occurred in specific conditions (seasonal ratios, annual ratios), using specific background signal (or no background signal at all) and calculating ratios with different methods (using a linear regression method, instantaneous ratios). These are as many different parameters which makes it the comparison really difficult to draw general conclusions to explain all the differences we can notice.

The comparison with the latest Airparif inventory is also not completely satisfactory because we noted in Ammoura et al. (2014) that the VOC speciation matrix is out-dated and does not account for new regulations on fuel composition for example. Furthermore, the Airparif estimates are annual ratios which are difficult to compare with monthly ratios.

Ratios	Multi-CO ₂ (this study) – Paris – Autumn 2013	CO ₂ - Megaparis/MEGAPOLI (this study) – Paris – Winter 2010	Borbon et al. (2013) – Paris – Summer 2009	Boynard et al. (2014) – Paris – Winter 2010	Bon et al. (2011) - Mexico City – March 2006	Warneke et al. (2007) – New England (NYC, Boston) – Summer 2004	von Schneidermesser et al. (2010) – London - 2008	Airparif 2010
$\frac{\Delta Ethane}{\Delta Acetylene}$	0.75 (0.10)	0.53 (0.03)	4.94	3.75 (0.11)	-	3.097	-	1.32
$\frac{\Delta Propane}{\Delta Acetylene}$	0.48 (0.04)	0.35 (0.02)	1.90	0.32 (0.04)	-	2.187	-	0.77
$\frac{\Delta n - pentane}{\Delta Acetylene}$	0.17 (0.01)	0.11 (0.01)	0.65	0.18 (0.01)	-	0.463	-	2.31
$\frac{\Delta i - pentane}{\Delta Acetylene}$	0.28 (0.02)	0.34 (0.02)	2.27	0.40 (0.02)	-	1.192	-	4.89
$\frac{\Delta Ethylene}{\Delta Acetylene}$	1.09 (0.06)	0.84 (0.03)	0.61	2.30 (0.05)	-	1.343	-	2.61
$\frac{\Delta Propene}{\Delta Acetylene}$	0.21 (0.01)	0.17 (0.01)	0.44	0.38 (0.02)	-	0.408	-	1.67
$\frac{\Delta CO}{\Delta Acetylene}$	287.4 (12.4)	359.7 (32.3)	242	-	-	-	-	100.02
$\frac{\Delta Ethane}{\Delta CO}$	6.56 (0.59)	3.09 (0.24)	23.4	-	21.5 (10.8)	11.616	7.1	13.17
$\frac{\Delta Propane}{\Delta CO}$	3.19 (0.30)	2.27 (0.15)	9.02	-	61.7 (15.6)	7.733	2.7	7.73
$\frac{\Delta n - pentane}{\Delta CO}$	1.15 (0.11)	0.73 (0.06)	3.08	-	2.5 (0.2)	1.548	0.54	23.13
$\frac{\Delta i - pentane}{\Delta CO}$	2.18 (0.15)	2.04 (0.11)	10.8	-	3.3 (0.4)	3.991	1.6	48.92
$\frac{\Delta Acetylene}{\Delta CO}$	3.48 (0.28)	2.78 (0.25)	4.74	-	6.5 (0.3)	3.6	-	10.00

$\frac{\Delta Ethylene}{\Delta CO}$	5.47 (0.39)	5.13 (0.33)	7.64	-	7.0 (0.4)	4.564	2.4	26.06
$\frac{\Delta Propene}{\Delta CO}$	1.32 (0.08)	0.88 (0.09)	2.07	-	3.0 (0.2)	1.363	0.72	16.74

Table 1: Comparison between ratios to CO and actetylene presented in this study and the ones provided by previous studies or by the latest Airparif inventory.

Ratios	Multi-CO2	MEGAPOLI	Turnbull et al. (2011) – Sacramento – 2009 (/CO _{2ff})	LaFranchi et al. (2013) – Boulder – 2009/2010 (/CO _{2ff})	Miller et al. (2012) – Northeast U.S. aircraft – 2004/2009 (/CO _{2ff})	Airparif 2010
$\frac{\Delta Ethane}{\Delta CO2}$	49.81 (5.10)	31.70 (4.41)	-	-	-	36.57
$\frac{\Delta Propane}{\Delta CO2}$	32.07 (2.92)	20.28 (2.52)	64 (18)	N/E : 3265.1 (1714.4) S : 352.7 (186.3)	138 (25)	21.43
$\frac{\Delta n - pentane}{\Delta CO2}$	9.27 (0.97)	3.41 (0.60)	18 (2)	N/E : 480.6 (151.7) S : 54.4 (31.6)	14.0 (5.4)	64.29
$\frac{\Delta i - pentane}{\Delta CO2}$	13.57 (2.34)	11.47 (1.49)	64 (8)	N/E : 485.2 (181.3) S : 65.4 (35.3)	29.5 (8.3)	135.53
$\frac{\Delta Ethylene}{\Delta CO2}$	52.55 (3.87)	33.51 (6.24)	-	-	-	72.13
$\frac{\Delta Propene}{\Delta CO2}$	11.18 (2.51)	6.26 (0.96)	-	-	-	46.33
$\frac{\Delta Acetylene}{\Delta CO2}$	24.82 (2.13)	25.21 (4.85)	52 (7)	52.1 (15.5)	34.2 (5.6)	27.69

$\frac{\Delta CO}{\Delta CO_2}$	5.55 (0.24)	6.33 (0.24)	12 (3)	7.8 (1.5)	11.2 (2)	2.20
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Table 2 : Comparison between ratios to CO₂ and CO_{2ff} presented in this study and the ones provides by previous studies and by the latest Airparif inventory

Anonymous Referee #2

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.

We respond point by point to these concerns in the following.

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 $(.75 \times 385 + .25 \times 390) = 386.25$ and the CO measured value would be $(.75 \times 125 + .25 \times 100) = 118.75$. Our observed dCO/dCO₂ would then be $(118.75/386.25) = 3$ - 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.

We thank the reviewer for having detailed his hypothesis. However it does not fit the cases that we study. The reviewer highlights the impact of entrainment in the boundary layer. The entrainment zone is the region where the free troposphere air is mixed with the one present in the boundary layer. Even if some studies showed that this entrainment zone is thicker in urban areas, our measurements have most likely been acquired outside of this zone. For instance, Lidar measurements acquired in March 2011 in Paris (in Jussieu which is also our measurement site) showed that the boundary layer height during daytime (between 12h and 17h) was about 1135 m (Pal et al. 2012). The entrainment thickness was estimated in the same study and found to be around 400 m, meaning that more than 700 m (counted from the ground) were not influenced by the free troposphere. Our inlets were installed on the roof of a building, around 30 m above ground level and we may reasonably consider that our measurements were not influenced by the air in the free troposphere. Further, the calculation of the ratios in our method is based on the determination of the equation of a horizontal asymptote in which nighttime and daytime data points are mixed and used together for the analysis. The same ratio is thus found for nighttime and daytime data, supporting the fact that there is no influence of entrainment and free troposphere during the day in our analyses.

Pal, S., Xueref-Remy, I., Ammoura, L., Chazette, P., Gibert, F., Royer, P., Dieudonné, E., Dupont, J. C., Haeffelin, M., Lac, C., Lopez, M., Morille, Y., and Ravetta, F. : Spatio-temporal variability of the atmospheric boundary layer depth over the Paris agglomeration : An assessment of the impact of the urban heat island intensity, *Atmospheric Environment*, 63,

261–275, doi :10.1016/j.atmosenv.2012.09.046, 2012.

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).

The word “new” in the title does not refer to the use of the tracer-tracer method and to the determination of the ratios between the co-emitted species. It applies to the words “method for estimating emission ratios” and is therefore linked to our original approach to unambiguously compute the ratios with an asymptote.

Title: VOC’s are highlighted, but are essentially completely neglected in the manuscript.

We present a comparison of ratios between our study and previous ones or latest estimates from the Airparif inventory as an answer to the last comment of Referee #1 (see Tables 1 and 2 in this document).

The comparison with the latest Airparif inventory is not completely satisfactory because we noted in Ammoura et al. (2014) that the VOC speciation matrix is out-dated and does not account for new regulations on fuel composition for example. Furthermore, the Airparif estimates are annual ratios, which are difficult to compare with monthly ratios. Thus, we are not able to compare same quantities.

Regarding comparisons with previous studies, we notice important differences between all proposed ratios. Each campaign occurred in specific conditions (seasonal ratios, annual ratios), using specific background signal (or no background signal at all) and calculating ratios with different methods (using a linear regression method, instantaneous ratios). These are as many different parameters, which make the comparison really difficult to draw general conclusions to explain all the differences we can notice.

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

We have shown above that dilution effects may reasonably be neglected in our cases.

Line 23: This conclusion would rely on the observations being representative of more than a very local site, this is not discussed or established later is of high importance.

We will suppress the sentence.

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

The citation was added 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.

Our sentence refers to the interpretation of mole fraction ratios in terms of emission ratios. If atmospheric mixing merges plumes together this interpretation cannot work.

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.

This information is already given in Section 2.1. The measurements were made on the roof of two buildings, at 23 and 15 m above ground level, respectively.

During the events that we considered in our study, the wind speed was lower than 1 m/s. The emission area of influence can thus be estimated to a distance of about 3.5 km around the measurement sites. Therefore, we can suppose that these conditions with low wind speed are not representative of a very small area around the station (such as the respiration impact from students going in and out the university).

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.

Our selection accounts also for wind directions and actually there is no specific wind direction during the events that we considered (we spoke about “turning wind”). As the first reviewer advises it, we will rephrase the definition of the events we studied, adding the criterion about the wind direction.

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).

Our regression accounts for errors in both axes. We will add this clarification in the text.

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.

We choose to limit the error to 15% (which is the uncertainty on VOC data), keeping this way enough data points to define the asymptote and evaluate the ratio.

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?

We have shown that the low wind speed conditions in Paris sample the hours of the day and the days of the week rather evenly, so we do not expect noticeable biases. Furthermore, our results are supposed not to be sensitive to synoptic conditions because the used background level accounts for this synoptic scale (we defined it using a moving window oh three days).

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.

We agree that our sentence is too affirmative. Indeed, temperature certainly has an impact on the ratios but indirectly. We will rephrase the point adding the possible influence of sources such as vehicle or heating emissions, which are more important when the temperature is low.

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 here and there is no 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.

As we mentioned previously, during the events we considered in our study, the wind speed was lower than 1 m/s and the emission area of influence can thus be estimated to a distance of about 3.5 km around the measurement sites. This area almost matches the Paris area if we consider the site of Jussieu. Our ratios may be representative of this zone and not of a very local one.

Regarding the differences between our measurements and the inventory estimates, we revealed the possible influence of another source. Indeed, wood burning is a major part of CO emissions from the residential sector (around 90%) but is not taken into account in Airparif CO₂ emissions because it is referenced as biomass burning (and is thus not an anthropogenic component). The differences may be adjusted accounting for this source also for CO₂. However, we were not able to evaluate this point in our study but we will mention this point as outlooks of it.

List of changes

Changes in the text

P23588 L14-15: the end of the sentence from “although ...” was removed.

P23589 L5: “when considering” was replaced by “for”.

P23590 L2: “pollutants and greenhouse gases” was replaced by “CO₂”.

P23590 L3: “Airparif also estimated VOC emissions and their main origins are the same as those of CO₂ (such as traffic or residential heating)” was added at the end of this paragraph.

P23590 L7: “developed” was added between “itself” and “to estimate”.

P23592 L8: the definition of trueness “(closeness of agreement between the average of a huge number of replicated measured species concentrations and a reference concentration, BIPM (2012))” was added after “trueness”.

P23594 L15-17: the last sentence of this paragraph was rephrased.

P23595 L18: the sentence “Furthermore, it accounts for different wind sectors. We noticed a difference of 8 ppm between continental (0-180°) and oceanic (180-360°) sectors for the averaged CO₂ background derived from the 5th percentile calculation” was added after “measurements”.

P23595b L18: “It” was replaced by “This background definition”.

P23596 L8: the sentence “A comparison of the results obtained using the two background definitions successively is presented in Section 3.3.3.” was added at the end of the paragraph.

P23596 L15: “(type II model regression in which errors on both axes are accounted for)” was added after “slope”.

P23597 L17: “i.e” and “successively” were removed.

P23597 L18: “and” was replaced by “or”.

P23598 L1: “, which is lower than the 15% error imposed by the uncertainty on VOC data” was added after “10%”.

P23598 L15: “enough larger” replaced by “larger enough”.

P23600 L3-4: “drives the” was replaced by “is an important driver of”.

P23600 L16: “However, we cannot exclude the impact of other drivers such as traffic as several studies previously showed that CO emissions are more important when vehicles work at lower temperature than the optimal value (Ammoura et al., 2014; SETRA, 2009). However, to our best knowledge, no study characterised the link between vehicle emissions and ambient temperature.

The Airparif inventory does not seem to show a seasonal variability as there is almost no difference on CO/CO₂ ratios between winter and summer: 3.1 ppb/ppm in January against 3.6 ppb/ppm in August. The comparison between these estimates and our observations suggests the possible influence of another source. Indeed, wood burning is a major part of CO emissions from the residential sector (around 90%) but is not taken into account in Airparif CO₂ emissions because it is referenced as biomass burning (and is thus not an anthropogenic component). The differences may be adjusted accounting for this source also for CO₂ emissions and may explain that there is no seasonal variability in the Airparif inventory. However, we were not able to evaluate this point in our study.” was added at the end of the paragraph.

Changes in Acknowledgements:

P23603 L2: “as well as the Ville de Paris for funding the project entitled *Le CO₂ parisien* which” was added after “project”.

P23603 L2: “allowing” was replaced by “allowed”.

Changes in References:

P23603 L23: the reference “BIPM: Vocabulaire international de métrologie - Concepts fondamentaux et généraux et termes associés (VIM, 3^e édition), Tech. Rep. JCGM 200 :2012, available at <http://www.bipm.org/fr/publications/guides/vim.html> (last access: November 2015), 2012.” was added.

P23605 L8: the reference “SETRA: Emissions routières de polluants atmosphériques : courbes et facteurs d’influence, available at: <http://catalogue.setra.fr/documents/Cataloguesetra/0005/Dtrf-0005666/DT5666.pdf> (last access: September 2015), 2009.” was added.

Changes in Figures:

P23610 Figure 3: the zero lines were added on this plot.

A new method for estimating emission ratios in the urban atmosphere: examples of ratios to CO₂, CO and volatile organic compounds in Paris

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Abstract

We propose a new approach to estimate urban emission ratios that takes advantage of the enhanced local urban signal in the atmosphere at low wind speed. We apply it to estimate monthly ratios between CO₂, CO and some VOCs from several atmospheric concentration measurement datasets acquired in the centre of Paris between 2010 and 2014. We find that this approach is little sensitive to the regional background level definition and that, in the case of Paris, it samples all days (weekdays and weekends) and all hours of the day evenly. A large seasonal variability of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio in Paris is shown, with a difference of around 60% between the extreme values and a strong anti-correlation ($r^2=0.75$) with atmospheric temperature. The comparison of the ratios obtained for two short measurement campaigns conducted in two different districts and two different periods (fall and winter) shows differences ranging from -120% to +63%. A comparison with a highly resolved regional emission inventory suggests some spatial variations of the ratio within the city, although most of these differences seem to be rather driven by the seasonal variability.

1. Introduction

In response to changing air quality and climate, there is a growing interest in quantifying emissions of pollutants and greenhouse gases from urban areas (UNEP 2013, EEA 2014). Urban emissions are usually known through the combination of direct and indirect geospatial energy use statistics with emission factors for individual source sectors. The heterogeneity of the input data in space, time and type makes it difficult to monitor the uncertainties of these inventories. Such monitoring actually receives little incentive at the international level (e.g., Bellasse et al. 2015), but it has been an active topic for scientific research. Some studies have been based on measurement campaigns dedicated to specific sectors, for instance air-composition measurements in road tunnels for traffic emissions

(e.g., Touaty and Bonsang, 2000 ; Ammoura et al., 2014), or in ambient air for power plants (Zhanga and Schreifels, 2011), waste water treatment plants (Yoshida et al., 2014 ; Yver-Kwok et al. 2015) or for the overall city-scale emissions (Lopez et al., 2013; Turnbull et al., 2011, 2015). Measurements made in the ambient air are affected by dilution in the atmospheric boundary layer, but this effect cancels out **for** mole fraction ratios between the considered species. The mole fraction ratios estimated from ambient air can also be directly interpreted in terms of emission ratios provided that the measured molecules share the same origin. Ultimately emission ratios may be interpreted in terms of sectoral emissions. In practice, the mixing of air parcels of various origins and ages largely hampers the interpretation. To isolate the local urban signal, measurements for species with a significant life time in the atmosphere have to be corrected from background influence, usually based on other measurements made in the free troposphere or at a remote site (e.g., Lopez et al. 2013; Turnbull et al, 2015). Isotopic measurements, like those of $^{14}\text{CO}_2$, can also allow better focusing the analysis on anthropogenic activities (e.g., Levin and Karstens, 2007; Turnbull et al., 2011). Last, atmospheric transport models are used in a few studies to quantify the contributions of the different sources within an inverse modelling approach (e.g., Saide et al. 2011, Lauvaux et al., 2013; Bréon et al. 2015).

Here, we investigate the possibility of benefiting from an enhanced local urban signal at low wind speed for estimating emission ratios from atmospheric composition measurements. Indeed, when the atmosphere is not well ventilated, emission plumes get trapped in the atmospheric boundary layer close to their origin. The resulting large peaks in mole fractions time-series are easily visible compared to typical background variations. In this manuscript, we make the first attempt to fully exploit this well understood behaviour. We use several measurement campaigns of CO_2 , CO and Volatile Organic Compounds (VOCs) performed in Paris in 2010, 2013 and 2014 to validate the approach and to evaluate local emissions ratios. Paris is the third largest megacity in Europe and the largest one in France. It comprises around 12 million people when including its suburbs. The population density is one of the highest in Europe with 21347 inhabitants per km^2 (INSEE, 2014). According to the latest Paris inventory of Airparif (Association in charge of monitoring the air quality in the Paris region) provided for year 2010, emissions of CO_2 are mainly from the traffic (29%) and residential and service sectors (43%) (Airparif, 2013). **Airparif also estimated VOC emissions and their main origins are the same as those of CO_2 (such as traffic or residential heating).**

The paper is structured as follows. Section 2 presents the measurements and the data. Section 3 starts with a presentation of typical measurements and a discussion about the choice of the background level, presenting two different options. The analysis method itself **developed** to estimate urban emission ratios is described in Section 3.3 including sensitivity tests (Sections 3.3.2 and 3.3.3). Section 4 presents the results obtained for different periods of the year and different years. Section 4.1 gives the interpretation of the ratios determined with our method and discusses the representativeness of these ratios. Section 4.2 presents the seasonal variability of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio in Paris and Section 4.3

compares all ratios between co-emitted species obtained during two short campaigns in Paris.

2. Methods

2.1 Site description

All atmospheric composition measurements presented in this study have been made in the centre of Paris. The instruments were installed at two sites. The first one is located on the Jussieu campus of University Pierre et Marie Curie (UPMC) at the QualAir station (<http://qualair.aero.jussieu.fr>). This station stands on the roof of a building, on the left bank of the river Seine (48°50'N, 2°21'E and 23 m above ground level). A botanical garden of 28 hectares, the Jardin des Plantes, lies about 500 m from the measurement site. The closest motorways are about 4 km on the south and on the south-east, but the university is surrounded by many streets which are particularly congested during rush hours. The emission activities in the centre of Paris essentially originate from road traffic activities and from the residential and service sectors, since most industrial activities have been removed in the 1960s (AIRPARIF, 2013).

The second measurement site is the roof of Laboratoire d'Hygiène de la Ville de Paris (LHVP) located about 2 km from the Jussieu campus, south-east of it (48°49'N and 2°21'E and 15 m above ground level). It dominates a public garden of 4.3 hectares, the Parc de Choisy. Residential buildings and arterial roads also surround this site. The closest motorway is a few hundred meters south of the site.

2.2 Instrumentation and air sampling

2.2.1 Joined MEGAPOLI/CO₂-Megaparis winter campaign

Our first campaign was performed jointly within the MEGAPOLI European project (Megacities: Emissions, urban, regional and Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation project, <http://megapoli.info/>) and the CO₂-Megaparis project (<https://co2-megaparis.lsce.ipsl.fr>). This 'winter campaign' took place in Paris during January-February 2010 (Dolgorouky et al. 2012, Lopez et al. 2013).

Two instruments were deployed at the LHVP. A Gas Chromatograph equipped with a Flame Ionisation Detector (GC-FID, Chromatotec) sampled Non-Methane Hydrocarbons (NMHCs). Mole fractions of alkanes, alkenes, alkynes and aromatic compounds were obtained with a time resolution of 30 minutes (air is sampled during the first 10 minutes and analysed during the next 20 minutes). More details can be found in Gros et al. (2011) and Dolgorouky et al. (2012).

A Cavity Ring-Down Spectrometer (CRDS G1302, Picarro Inc) was also deployed to analyse CO₂, CO and H₂O mole fractions with a time resolution of 1 s (see Lopez et al., 2013, for more details).

2.2.2 Long-term continuous CO₂ and CO measurements

A Cavity ring-Down analyser (CRDS G1302, Picarro Inc.) performed continuous CO₂, CO and H₂O measurements in Jussieu continuously from 4 February 2013 to 11 June 2014 with a time resolution of 1 s. This instrument was calibrated about every two months using three 40 L aluminium gas tanks. These cylinders were previously calibrated for CO₂ and CO dry air mole fractions against the NOAA-X2007 scale for CO₂ and the NOAA-X2004 for CO. A fourth gas cylinder was used as a target to evaluate the repeatability of the data and the drift of the instrument. This target was analysed for 20 minutes every 12 h between 4 February 2013 and 25 August 2013 and for 15 minutes every 47 h since 26 August 2013. Using the target gas measurements, we estimate the repeatability and the trueness (closeness of agreement between the average of a huge number of replicated measured species concentrations and a reference concentration, BIPM (2012)) of the 1 minute averaged data to be, respectively, 0.05 ppm and 0.03 ppm for CO₂ and 6.8 ppb and 3.7 ppb for CO.

2.2.3 'Multi-CO₂' field-campaign

Several instruments were installed next to the CRDS analyser in Jussieu from 11 October 2013 until 22 November 2013 within the Multi-CO₂ project.

For the compounds of interest for this study (CO₂, CO and light VOCs), the same instruments that were used during the joined MEGAPOLI/CO₂-Megaparis campaign were deployed (see Section 2.2.1). VOC mole fractions were measured using a gas chromatograph (Chromatotec) calibrated against a reference standard (National Physics Laboratory, Teddington, UK). Some VOCs were selected for this study because they share the same origins (such as traffic or residential heating) than other VOCs, CO and CO₂: ethane, ethylene, acetylene, propane, propene, i-pentane and n-pentane. The total uncertainty of the data was estimated to be better than 15%.

Meteorological parameters (wind speed and direction, temperature) were also monitored (instrument WMR2000, OREGON Scientific).

2.3 Data processing

As the time resolution was different for both instruments (CRDS and GC-FID), the data have been synchronized. The chosen time interval was the one imposed by GC-FID measurements. Data from GC-FID were acquired for 10 minutes every 30 minutes, the given time stamp corresponding to the beginning of the measurement. Thus for each compound measured by the other instruments (CRDS and meteorological instruments), data have been averaged on the same 10 minutes interval. Finally, in this study, all the data have a same time step of 30 minutes.

3. Results

3.1 Typical time series and identification of specific meteorological events

Figure 1 shows an example of atmospheric gas dry air mole fractions time series collected during the Multi-CO₂ campaign in 2013, with a time step of 30 min. The wind speed during the same period is also represented on the figure (1e). Time series recorded during the joined MEGAPOLI/CO₂-Megaparis campaign in 2010, as well as the continuous measurements of CO₂ and CO in Jussieu are shown in the supplementary material.

Mole fractions of the different species appear to co-vary much, despite the different lifetime of the species: CO₂ and CO have typical life time in the atmosphere (τ) much longer than the observation period whereas acetylene has a τ of a 13 days and ethylene has a τ of a few hours. In comparison, the meteorological events in Paris during the campaign lasted from a few hours to one day so that VOCs with a τ longer than two days, like acetylene, can be almost considered as non-reactive species. For shorter-lived species, here only ethylene and propene (1 day $> \tau >$ 5 hours), we computed the correlations between these species and acetylene. When considering all the data of the Multi-CO₂ campaign (without any selection), coefficients of determination are high ($r^2 > 0.70$). These tight correlations between VOCs with different reactivity suggest a limited impact of the chemistry.

In Figure 1, we identify some events when the mole fractions of all species were significantly higher than elsewhere over the campaign duration (1.25 to 6 times as high). These periods (30 and 31 October, 10 and 11 November) appear to be systematically linked to specific meteorological conditions when the wind speed was very low (less than 1 m.s⁻¹). The mole fractions obviously increased as the result of the stagnation of local emissions in the atmosphere. However, three periods with low wind speed do not correspond to significant peaks in mole fractions (on 5, 6 and 7 November 2013). These 3 periods were too short (they last around 2h) for the accumulation of emissions in the atmosphere to have taken place and did not result in high mole fractions. There is one more period that we can highlight and for which the wind speed was less than 1 m.s⁻¹, from 17 November 15:00 (UTC) to 18 November 7:00 (UTC). The mole fractions were higher than the common baseline due

to changes in synoptic conditions. However, no significant peaks are visible. We notice that during this period, even though the wind speed was low, wind came from one sector only (from 90 to 190°) whereas there is no specific wind direction associated to the large peaks of the other periods (turning wind, see Figure 2 (a)). In the case of a dominant wind direction, and despite low wind speeds, emissions did not seem to have accumulated in the atmosphere (there may have been slowly evacuated). The wind roses in the two different cases are represented in Figure 2. To summarise, **periods with low wind speed and non-directional winds are the focus of the present study because they show a distinct local emission signal in the mole fractions.**

3.2 Background levels

The previous data selection does not remove all influence of long-range transport (advection) and dispersion in the measurements and there is still a need to remove a background level, especially in the case of species with significant lifetime in the atmosphere like CO₂. Most of the previous studies whose main interest was CO₂ defined a continental clear-air background to correct the CO₂ data. For example, data from Mace Head in Ireland (Lopez et al., 2013) or from Jungfraujoch in Switzerland (Vogel et al., 2010) are often considered as background data for measurements in Europe, but strictly speaking they are too far from Paris to isolate the city signal. Measurements in the free troposphere have also been used as a baseline (Miller et al., 2012; Turnbull et al., 2011), but are particularly expensive to make and are not available for our study period. For short-lived species, the definition of the background is not as critical and the smallest measured value is often used.

Here, we investigate two options to define the urban background levels. The first option takes advantage of the fact that the urban emissions are positive fluxes, i.e. which increase local atmospheric mole fractions. We define background mole fractions as all measurements smaller than the fifth percentile of the species over a moving window. The moving window allows accounting for the dependence of the background on the synoptic situation or on the time of year, as the background changes seasonally for many gases. As the average characteristic time of synoptic changes is a few days, and in order to gather a significant amount of data, we define overlapping windows of three days that start every day at 00:00 (UTC), in increments of 1 day. Figure 1 displays the selected lowest 5% as black disks for some species measured during the Multi-CO₂ campaign. In order to avoid discontinuities, we linearly interpolate the selected data to obtain a background mole fraction time series with a time resolution of 30 minutes (black curves on Figure 1).

This background definition is simple to implement because it does not require additional measurements. **Furthermore, it accounts for different wind sectors. We noticed a difference of 8 ppm between continental (0-180°) and oceanic (180-360°) sectors for the averaged CO₂ background derived from the 5th percentile calculation. This background**

definition is expected to work well for all species that do not have local sinks in the atmosphere or at the surface. We saw in Section 3.1 that chemical sinks could be neglected for our measurements, but in the case of CO₂ during the vegetation-uptake season (summer in particular), vegetation within Paris also contributes to populating the fifth percentile.

Our second option (for CO₂ only) defines the background from a publicly available analysis of the global atmospheric composition. We test it for CO₂, the species for which the first definition may be the least appropriate. The definition of the background level of CO₂ relies on the global inversion product of the Monitoring Atmospheric Composition and Climate project (MACC v13.1, <http://www.copernicus-atmosphere.eu/>, Chevallier et al., 2010). This product has a resolution of $3.75^\circ \times 1.9^\circ$ (longitude-latitude) in space and of 3 h in time. It combines the information from 131 CO₂ stations over the globe and a transport model within a Bayesian framework and estimates the CO₂ surface fluxes over the globe together with the full 4D CO₂ field.

We extracted the 3-hourly time series of the CO₂ concentrations from the MACC database for the eight grid points that surround our two measurement sites, Jussieu and the LHVP. The CO₂ background mole fraction is estimated as the linear interpolation in time of the analysed CO₂ concentrations averaged over the eight grid points. In the following, we call $\Delta\text{species}$, the mole fractions excess from the background as defined by either method.

A comparison of the results obtained using the two background definitions successively is presented in Section 3.3.3.

3.3 Determination of the ratios between co-emitted species

3.3.1 Description of the method

We present next the method to evaluate ratios of excess mole fractions between 2 species ($\Delta\text{species}_1$ and $\Delta\text{species}_2$). We consider a moving window of 4 h in increments of 30 minutes (each period contains 8 points). On each period, we compute the coefficient of determination r^2 between $\Delta\text{species}_1$ and $\Delta\text{species}_2$ and use a linear regression to evaluate the slope (**type II model regression in which errors on both axes are accounted for**). This slope defines a ratio between the two considered $\Delta\text{species}$ over the 4h period. We also calculate the difference between maximum and minimum $\Delta\text{species}_1$, which is plotted on the x axis, over this period (we name it $\delta\Delta\text{species}_1$). The motivation for this amplitude computation will be developed in Section 4.1. These calculations are made if more than 5 points exist during the time period and if species excesses are linearly related (a p -value test relative to linear relationship of species excesses is conducted and $p\text{-value} < 0.001$ are selected). As an example, on a 4h period, we compute (i) the coefficient of determination r^2 between ΔCO and ΔCO_2 , (ii) the slope, which well fits the considered dataset (thus giving the $\Delta\text{CO} / \Delta\text{CO}_2$ ratio over this period) and (iii) $\delta\Delta\text{CO}_2$.

In Figure 3, we show some examples of ratios determined on each 4h period against the local corresponding species offset $\delta\Delta\text{CO}_2$. They have a simple structure with a horizontal asymptote when $\delta\Delta\text{CO}_2$ is high. The equation of the asymptote defines the average ratio. Interpretation and representativeness of this ratio are discussed in Section 4.1.

In order to unambiguously define the equation of this horizontal asymptote, and the related value of the ratio, we apply a filter on r^2 and on $\delta\Delta\text{species}_1$ that isolates the asymptote. We apply this criterion to measurements spread over a month. The sensitivity of the ratios to all tested criteria is presented in Section 3.3.2. The final choice of a criterion is a compromise between a cautious selection of points (derived from the criterion on r^2 and $\delta\Delta\text{species}_1$) to clearly extract the local-signal asymptote, and a selection of enough points to get a robust ratio. Finally, the equation of the horizontal asymptote is the ratio (we impose a slope of zero). The ratio uncertainty is computed at a confidence level of 68% ($1-\sigma$).

3.3.2 Sensitivity to the criterion on r^2 and $\delta\Delta\text{CO}_2$

We present here a sensitivity test for the criterion on r^2 and $\delta\Delta\text{CO}_2$ in the case of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio during the Multi- CO_2 campaign. We evaluate this ratio using the method described in Section 3.3.1 and vary the thresholds on r^2 (with values 0.6, 0.7, 0.8 and 0.9) and on $\delta\Delta\text{CO}_2$ (with values 15, 20, 25, 30, 35 and 40 ppm).

Considering a given r^2 (~~i.e.~~ $\delta\Delta\text{CO}_2$ can vary and be successively higher than 15, 20, 25, 30, 35 or 40 ppm), we find less than 10% difference between all the derived ratios. For the other case, considering a fixed $\delta\Delta\text{CO}_2$ offset and a varying r^2 , differences between all ratios were found to be less than 6%. However, tighter restrictions on the criterion result in fewer available data points that sample the emission conditions within the month less well. As an example, for the couple ($r^2 > 0.6$, $\delta\Delta\text{CO}_2 > 15\text{ppm}$), 211 points are selected in the asymptote whereas for the one ($r^2 > 0.9$, $\delta\Delta\text{CO}_2 > 30\text{ppm}$), only 39 points remain. We choose the criterion $r^2 > 0.8$ and $\delta\Delta\text{CO}_2 > 20\text{ppm}$ to determine the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio during the Multi- CO_2 campaign: it keeps more than a hundred points to define the asymptote. The same test was conducted on all studied ratios and differences between derived ratios do not exceed 10%, which is lower than the 15% error imposed by the uncertainty on VOC data. The data selection for several ratios, including $\Delta\text{CO}/\Delta\text{CO}_2$, is presented on Figure 3.

3.3.3 Sensitivity to the background choice

In this section, we test the influence of the chosen background definition on the obtained $\Delta\text{CO}/\Delta\text{CO}_2$ ratio using the methods described in Section 3.3.1. We compare $\Delta\text{CO}/\Delta\text{CO}_2$ ratios for 2013 using the 5th percentile or MACC simulations as background levels (MACC simulations for 2014 were not available when this study was conducted). The evolution of the ratios for both options is presented in Figure 4. We evaluate the relative difference between the ratios derived from the two options (in % of the ratio obtained with

the fifth percentile as background). Differences vary from -17% in August 2013 to +11% in September 2013. The highest differences are found for the summer months (11% on average), and the lowest ones for the winter months (3.2% on average). These results show that the definition of the background does not significantly affect the derived ratios, even during the summer months. This comes from the fact that urban mole fractions during low wind speed periods are usually **larger enough** than the background mole fractions (from around 1.25 to 6 times more).

After these analyses, we finally choose to define background levels using the fifth percentile on a running window of 3 days as described in Section 3.2.1. However, tests were conducted using the tenth percentile (and a running window of 3 days) or changing the length of the running window between 1 and 5 days (but still considering the fifth percentile). No significant difference was found using the tenth percentile (less than 2% difference between the two derived $\Delta\text{CO}/\Delta\text{CO}_2$ ratios). Comparing $\Delta\text{CO}/\Delta\text{CO}_2$ ratios obtained with different lengths of the running window, ratios differ by less than 6% from one case to another, thus consolidating our choice for background levels.

4. Discussion

We apply the method presented in Section 3.3.1 to assess ratios between co-emitted species in Paris. In this section, we first discuss the interpretation and the representativeness of the ratios determined using the method previously presented. Then, we divide the analysis in two parts. First we focus on the seasonal variability of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio using continuous measurements acquired from February 2013 to June 2014. Then we compare the ratios between co-emitted species and CO_2 obtained for the two short campaigns (in Section 4.3).

4.1 Interpretation and representativeness of the ratios determined with the asymptotic method

The x axis in Fig. 3 ($\delta\Delta\text{species}_1$) represents the variability of the species excess over a 4h-period. Large values correspond to a strong increase or decrease in the species local emissions, and highlight the concentration peaks that occur at low wind speed. The presence of an asymptotic value in the monthly ratio plots like that of Fig. 3 suggests that the ratios do not vary much within the month. This stability is also confirmed by the regular spread of the selected events throughout the month. For instance, applying our method to the continuous CO and CO_2 measurements acquired in 2013/2014 in Paris, we notice that all days (weekdays and weekends) and all hours of the day were sampled equally: no period type is systematically missing (see Figure 4). This feature allows our method to yield a robust average ratio per month in Paris.

4.2 Seasonal variability of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio in Paris

The evolution of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratios in Jussieu between March 2013 and May 2014 is presented in Figure 5. It shows a large seasonal variability with a maximum value in winter and a minimum value in summer. There is a difference of around 60% between these extreme values (minimum value: 3.01 ppb/ppm, maximum value: 6.80 ppb/ppm).

Given the large seasonal cycle observed, we hypothesise that temperature is an important driver of the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio. The monthly atmospheric temperature measured during the low wind speed periods is also shown in Figure 5. The two curves are much anti-correlated ($r^2=0.75$): when the temperature is high, the ratio is low - and reciprocally. This is likely the consequence of higher emissions when temperatures are low because residential heating is important whereas in summer, when temperatures are high, emissions mainly come from traffic, residential cooking and service sectors which all together seem to correspond to a lower $\Delta\text{CO}/\Delta\text{CO}_2$ ratio. The difference in emissions between the two extreme seasons relies on the importance of residential heating use. The differences in the ratios may indicate that higher ratios are observed for residential heating than for other sources. This is not in agreement with data from the Airparif inventory: the annual CO/CO_2 for residential heating and for the other sectors are respectively 2.7 ppb/ppm and 7.1 ppb/ppm. This is in accordance with spatialised European emission inventories (Vogel et al., 2013). However, we cannot exclude the impact of other drivers such as traffic as several studies previously showed that CO emissions are more important when vehicles work at lower temperature than the optimal value (Ammoura et al., 2014; SETRA, 2009). However, to our best knowledge, no study characterised the link between vehicle emissions and ambient temperature.

The Airparif inventory does not seem to show a seasonal variability as there is almost no difference on CO/CO_2 ratios between winter and summer: 3.1 ppb/ppm in January against 3.6 ppb/ppm in August. The comparison between these estimates and our observations suggests the possible influence of another source. Indeed, wood burning is a major part of CO emissions from the residential sector (around 90%) but is not taken into account in Airparif CO_2 emissions because it is referenced as biomass burning (and is thus not an anthropogenic component). The differences may be adjusted accounting for this source also for CO_2 emissions and may explain that there is no seasonal variability in the Airparif inventory. However, we were not able to evaluate this point in our study.

4.3 Emission ratios in Paris: Multi-CO₂ vs MEGAPOLI/CO₂-Megaparis

The ratios between the co-emitted species for the Multi-CO₂ campaign, derived from our method, are presented in Table 1. The ones for the MEGAPOLI/CO₂-Megaparis campaign are reported in the supplementary material.

Generally, ratios are different between the two campaigns. We notice differences from -120% to +63%. A satisfactory agreement is found between the two campaigns for the ratios that are reported in bold in Table 1 (less than 15% of difference). Several explanations can be given for these differences. First, measurements were not carried out in the same year: 2010 for the joined MEGAPOLI-CO₂-Megaparis campaign and 2013 for the Multi-CO₂ one. The differences in the ratios may illustrate some evolution in the emission structure (as an example, some technological improvements can occur for vehicles or heating systems). Secondly, these differences may highlight the importance of the seasonal variability of the ratios, which was shown in Section 4.2. Indeed, measurements were performed in autumn (October-November) for the Multi-CO₂ campaign and in winter (January-February) for the MEGAPOLI/CO₂-Megaparis one. The $\Delta\text{CO} / \Delta\text{CO}_2$ ratio from the latter campaign is also reported in Figure 5 for the corresponding month of the year: it aligns well on the seasonal variability observed in Jussieu, even though this campaign was made four years before. Furthermore, average temperatures during the low wind speed periods were not the same: 10°C during the Multi-CO₂ campaign, 3°C during the MEGAPOLI/CO₂-Megaparis one. This is in agreement with the argument developed in Section 4.2: residential heating is more important in the heart of winter and its emissions make the $\Delta\text{CO} / \Delta\text{CO}_2$ ratio higher. Finally the instruments were not installed at the same location in the centre of Paris (there are 2 km between the two locations). Thus the emission area of influence could be different because the local activities are not exactly the same around the two sites. As an example, highways, where the vehicle speed is limited to 80 km.h⁻¹ and the vehicle flow is high, are closer to the LHVP (MEGAPOLI/CO₂-Megaparis measurements), leading this site to be more influenced by large traffic emissions. This spatial variability of the ratios in Paris is confirmed by the latest Paris emission inventory Airparif 2010. Airparif provides annual CO and CO₂ emissions by districts in Paris. Jussieu is in the 5th district and the LHVP in the 13th. According to the latest Airparif inventory, the annual CO/CO₂ ratios are respectively 2.43 ppb/ppm and 3.74 ppb/ppm for the 5th and the 13th districts. However, the good agreement between the ratio from the MEGAPOLI/CO₂-Megaparis campaign (measurements in 2010) and the one derived in Jussieu (measurements in 2014) indicates that the seasonal variability is the main driver for the evolution of the ratios.

5. Conclusion

We have investigated the possibility to characterise local urban emissions through atmospheric mole fraction measurements collected during low wind speed periods. In the

case of Paris, we have shown that this approach significantly reduces the sensitivity of the results to the species background level definition, even in the case of CO₂. Thanks to long-term continuous measurements, we have also shown that the low wind speed conditions in the centre of Paris (especially in Jussieu) sample the hours of the day and the days of the week rather evenly, so that the method characterises an average urban atmosphere.

The comparison of ratios obtained for the two measurement campaigns, Multi-CO₂ and MEGAPOLI/CO₂-Megaparis, shows differences from -120% to +63% for 9 atmospheric species. Such differences may reveal spatial and seasonal variability in the ratios because the two campaigns took place at different sites, during different years and seasons. However, the evolution of the ratios seems to be mainly influenced by the seasonal changes. This seasonal variability was assessed for the CO to CO₂ ratios for the period from February 2013 to June 2014, showing a strong anti-correlation with monthly atmospheric temperature, likely linked to seasonal changes in emissions sources (for example, domestic heating is predominant in winter and non-existent in summer). We provide evidence on the importance of residential heating in the total $\Delta\text{CO}/\Delta\text{CO}_2$ ratio. This ratio is higher than the ones for other sectors which is in contradiction to current estimates from the Airparif inventory.

The determination of these average ratios may be useful to assess the estimates provided by emission inventories. Indeed, city-scale emission inventories mainly focus on air quality, and the link with greenhouse gases, especially with CO₂, is not well made. The combination of the well-known total pollutant emissions with the ratios estimated by our experimental approach should allow a better quantification of total CO₂ emissions.

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	ΔCO_2	ΔCO	$\Delta\text{Acetylene}$	$\Delta\text{Ethylene}$	$\Delta\text{Propene}$	$\Delta\text{i-pentane}$	$\Delta\text{n-pentane}$	ΔEthane	$\Delta\text{Propane}$
ΔCO_2	-	5.55 (0.24)	24.82 (2.13)	52.55 (3.87)	11.18 (2.51)	13.57 (2.34)	9.27 (0.97)	49.81 (5.10)	32.07 (2.92)
ΔCO		-	3.48 (0.28)	5.47 (0.39)	1.32 (0.08)	2.18 (0.15)	1.15 (0.11)	6.56 (0.59)	3.19 (0.30)
$\Delta\text{Acetylene}$			-	1.09 (0.06)	0.21 (0.01)	0.28 (0.02)	0.17 (0.01)	0.75 (0.10)	0.48 (0.04)
$\Delta\text{Ethylene}$				-	0.11 (0.01)	0.19 (0.01)	0.10 (0.01)	0.57 (0.04)	0.35 (0.02)
$\Delta\text{Propene}$					-	0.72 (0.04)	0.36 (0.03)	1.87 (0.20)	1.13 (0.09)
$\Delta\text{i-pentane}$						-	0.44 (0.01)	1.73 (0.11)	0.89 (0.06)
$\Delta\text{n-pentane}$							-	2.66 (0.21)	1.14 (0.08)
ΔEthane								-	0.20 (0.01)
$\Delta\text{Propane}$									-

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Table 1: Observed ratios between co-emitted species derived from our method for the Multi- CO_2 campaign. Numbers in brackets () correspond to 1σ . The mole fraction ratio is reported in ppb/ppm for $\Delta\text{CO}/\Delta\text{CO}_2$, all others to ΔCO_2 are reported in ppt/ppm. Those that do not include ΔCO_2 are reported in ppb/ppb. For readability, the diagonal (unity ratios) has been replaced by dashes (-). Ratios in bold mean that they are in a satisfactory agreement with the ones from the MEGAPOLI/ CO_2 -Megapolis campaign (less than 15% of difference).

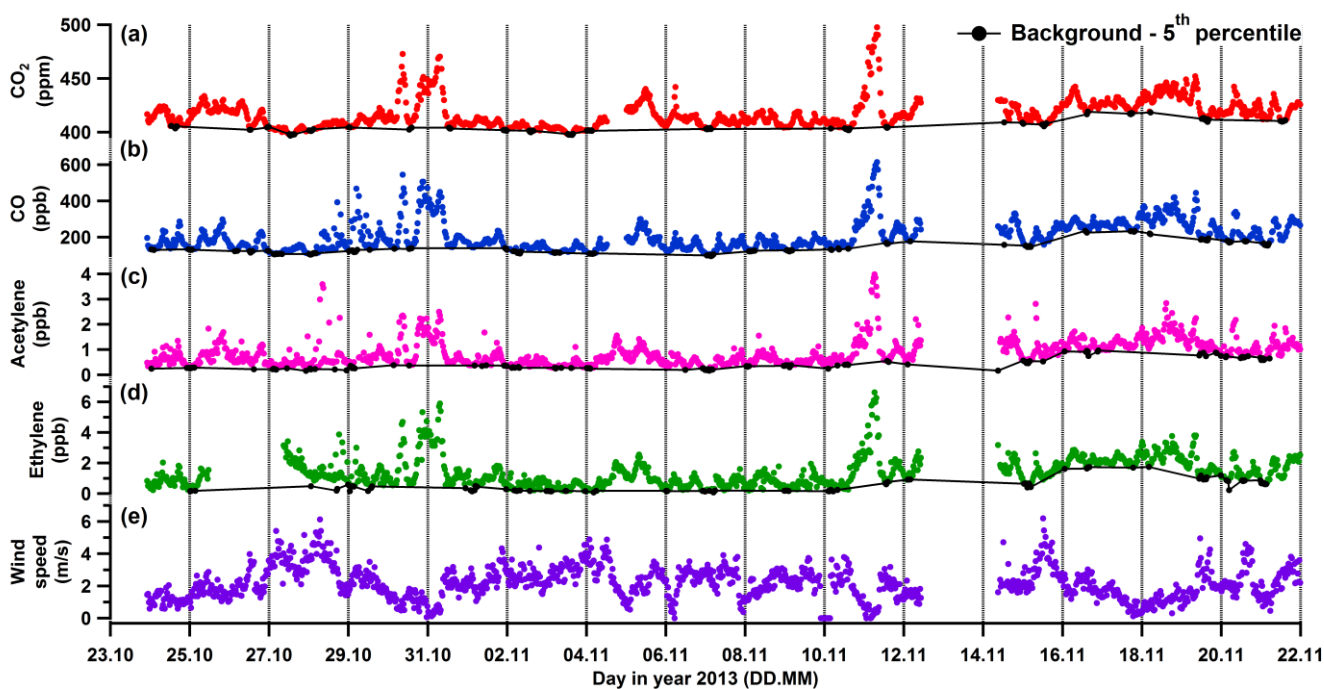


Fig.1: (a-d) Temporal variation of the mole fraction of selected compounds monitored during the Multi-CO₂ campaign (30 minutes time step). The black lines represent the background levels defined with the calculation of the 5th percentile (black disks). **(e)** Wind speed during the campaign. Time is given in UTC.

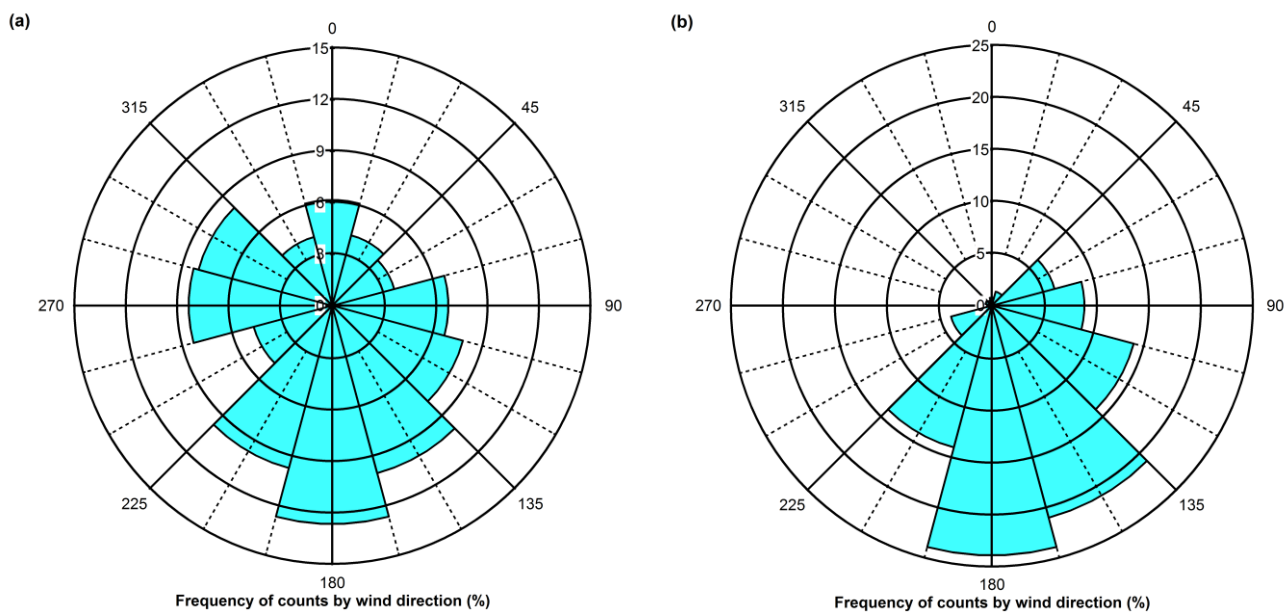


Fig. 2: Wind roses for two low wind speed situations. **(a)** Wind rose for 10-11 November 2013 (significant peak in mole fractions). **(b)** Wind rose for 18 November 2013 (no significant peak in mole fractions). The percent scale is not the same for the two wind plots.

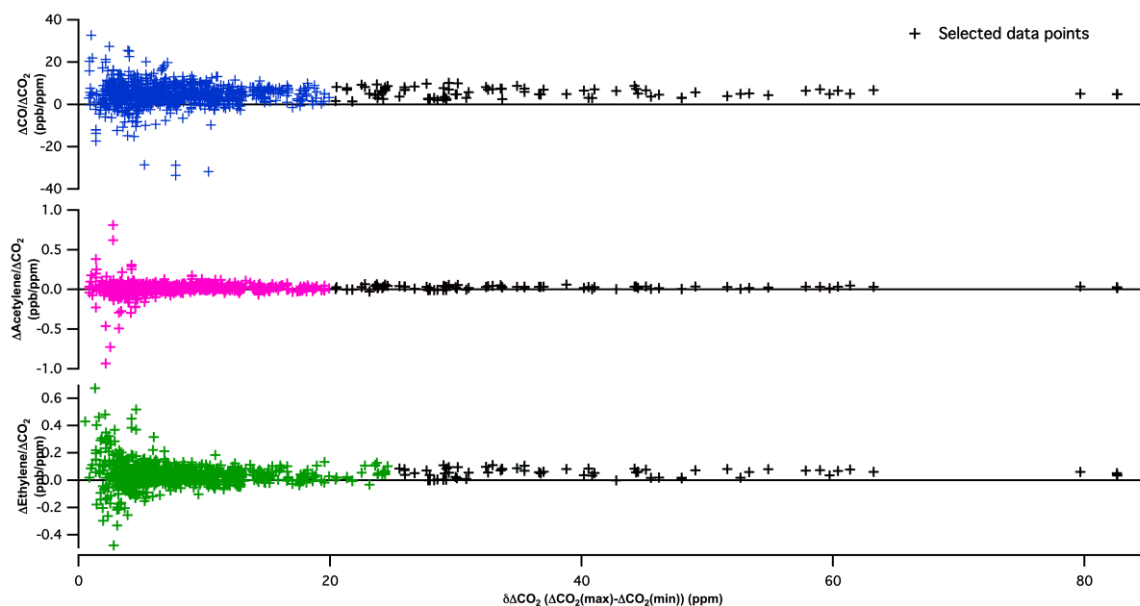


Fig. 3: Selected ratios to ΔCO_2 plotted versus the local CO_2 offset ($\delta\Delta\text{CO}_2$) from the measurements acquired during the Multi- CO_2 campaign. Black data points were selected to determine the equation of the horizontal asymptote using the criteria described in Section 3.3.2 (the used criteria depend on the considered species).

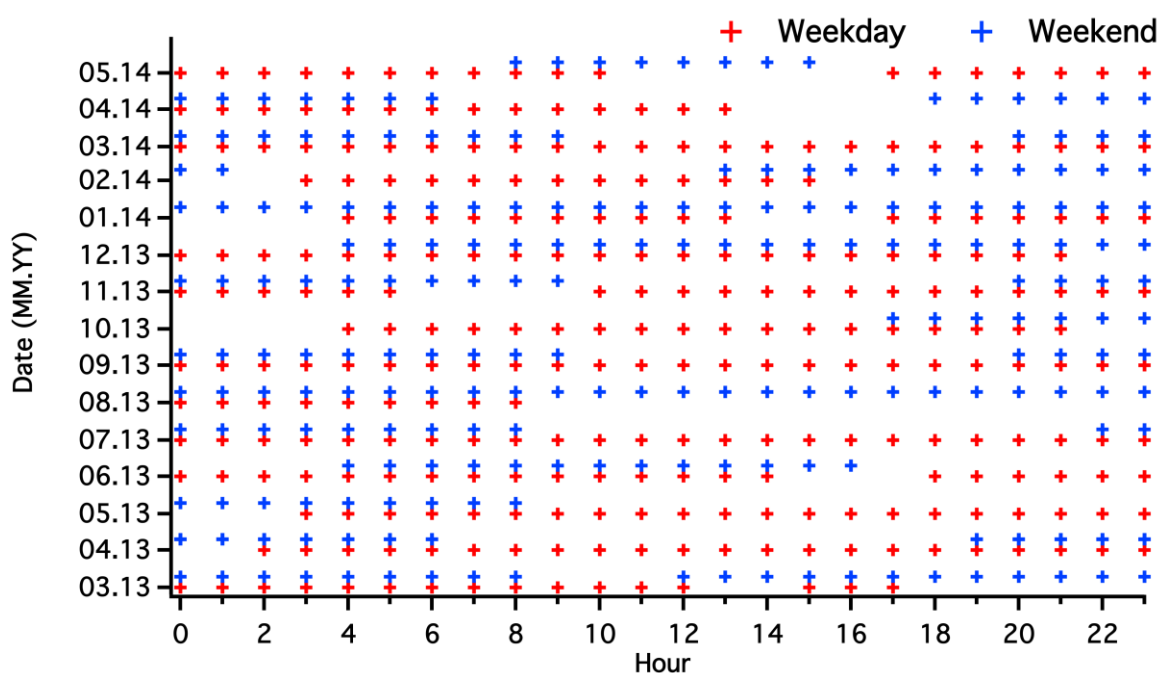


Fig.4: Days (weekdays in red crosses and weekends in blue crosses) and hour sampled per month with our method.

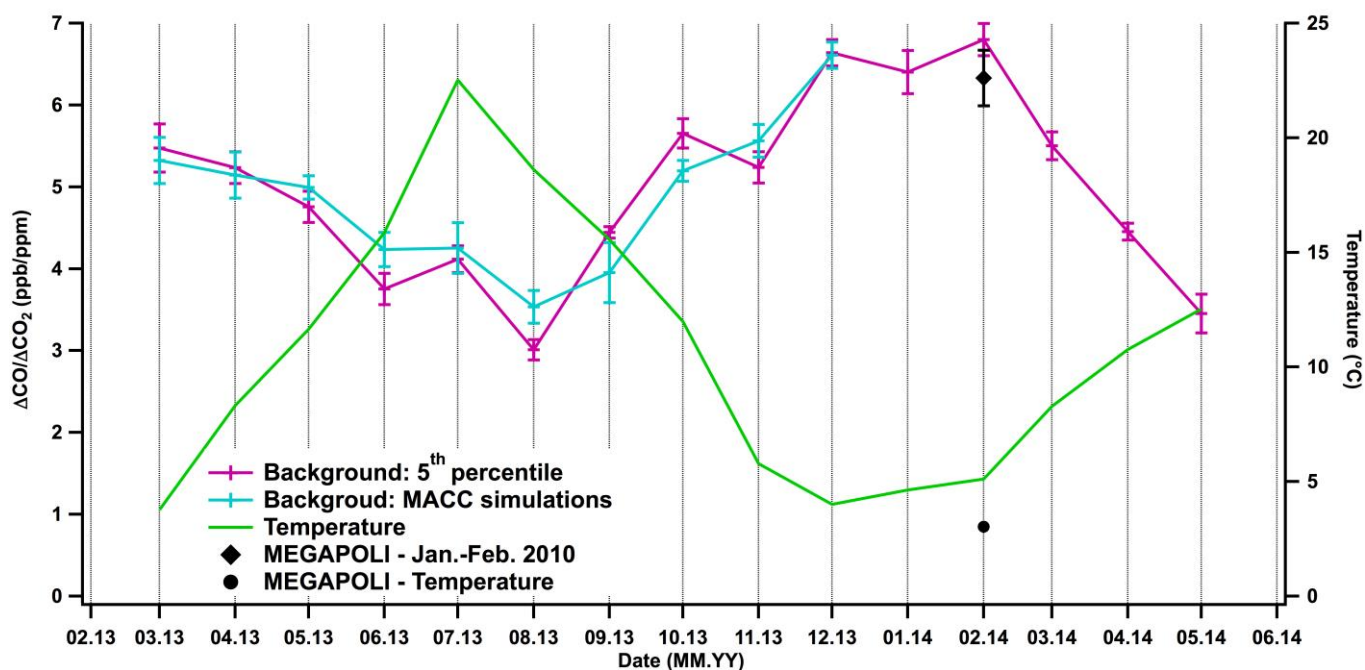


Fig.5: Monthly ΔCO to ΔCO_2 ratios in Paris. Results using background levels defined with the 5th percentile are given in violet. The ones using the MACC simulations are in blue. Error bars on the ratios correspond to 1σ . The ratio from the MEGAPOLI- CO_2 -Megaparis campaign and the corresponding average temperature are represented by a black disk. Temperature corresponding to the selected data for the ratio calculation averaged by month is represented in green as a proxy for season.