

We thank the Editor Prof Jennifer Murphy and both referees for their comments and second review of our paper that further help us clarify the presentation and discussion of our results. We copy their remarks hereafter and insert our response in blue where appropriate.

Response to Co-Editor comments: Prof Jennifer G. Murphy

Comments to the Author:

The reviewers bring up several concerns that have not been addressed in the revised version of the manuscript. I encourage the authors to consider all of the comments brought forward by the reviewers, including the incorporation of some responses to the reviews of version 1 into the manuscript.

We have followed this recommendation, as we explain hereafter.

Below I highlight the specific aspects that I agree need to be addressed/improved in order for the manuscript to be acceptable for publication:

1) More emphasis is needed in the title that the 'new method' refers to the selection of low wind speed data rather than the tracer:tracer ratios. For example, "Exploiting stagnant conditions to derive robust emission ratio estimates for CO₂, CO, and VOC in an urban area". Because the authors are emphasizing the development of this 'method' they may want to provide some guidance in the conclusions section to others who seek to apply this in different urban areas.

We have changed the title according to the Editor's suggestion.

2) A more fully developed description of the VOC data is required.

We agree with the editor (and with the referees' comments) that too few information were given about VOCs. One of the reasons was that, in contrary to CO and CO₂ for which a complete year of measurement was available, VOC data were only available for specific campaigns and therefore the discussion was restricted to a few points. Nevertheless, in order to take the main points raised by the editor and the referees into account, additional information has been added as detailed below. Note that the discussion now refers to studies (Baudic et al., 2016; Waked et al., 2016) which were not published by the time of the first revision of this paper and which have helped improving the discussion on VOCs.

At a minimum, a list of each of the VOC that will be analyzed should be provided in the methods section.

We have added the list of measured VOCs in the methods section (2.2.1).

The VOCs analysed in our study were: acetylene, ethylene, propene, *i*-pentane, *n*-pentane, ethane, propane.

Furthermore, some information on the sources and sinks of the VOC is required to provide context for the results of the analysis. Are these VOC from similar sources to the CO and CO₂? Are they expected to have seasonal cycles in their emissions? How might their sinks/lifetimes change with season? I find that the language used on Line 371 and in Table 1 describing a 'satisfactory agreement' between the two campaigns is confusing. Given that you have found strong evidence for a seasonal cycle in the CO/CO₂ ratios, why is it expected that the VOC ratios would be consistent between campaigns? If you want to highlight ratios that remain consistent, I would recommend using that word, rather than 'satisfactory'. A further question about the VOC analyses – presumably the ratio of VOC₁/VOC₂ should be the inverse of VOC₂/VOC₁ – is that really true for your analyses? It would be good to confirm since it could highlight situations where the two tracers have sources that are not in common.

In order to give the requested information on VOCs but at the same time to keep the structure of the paper, we propose to include the VOC information (source, sinks, seasonal variations, ...) in a dedicated part of the discussion (4.3.2).

4.3.2 VOC emission ratios in Paris: Multi-CO₂ vs MEGAPOLI/CO₂-Megaparis

This section analyses the VOC emission ratios more specifically, as these compounds (which share common sources with CO and CO₂) were also measured during the two campaigns (Multi-CO₂ and MEGAPOLI/CO₂-Megaparis). In the presence of nitrogen oxides (NO_x), VOC oxidation lead to the formation of ozone and secondary organic aerosols, which impacts air quality and climate. Therefore characterizing VOC emissions in urban areas (which are always associated to high NO_x conditions) is of importance. VOCs include a large variety of compounds and information on their sources and sinks will be given here only for the compounds selected in this study. As already mentioned, among the various non-methane hydrocarbons measured during these campaigns, the selected compounds were the ones which presented a strong correlation with CO₂ and CO ($r^2 > 0.8$), allowing the use of our approach for the ratio determination. In urban areas, anthropogenic sources of VOCs are dominated by traffic, residential heating (including wood burning), solvent use and natural gas leakage, as was recently shown in Paris (Baudic et al., 2016) but also in other cities (Niedojadlo et al., 2007 in Wuppertal, Germany, Lanz et al., 2008, in Zurich, Switzerland, Morino et al., 2011, in Tokyo, Japan, McCarthy et al., 2013, in Edmonton, CA, USA). VOC levels, diurnal and seasonal variability and source contributions in Paris have been thoroughly described by Baudic et al. (2016). Therefore only minimal information is reported here. Ethane and propane are mainly associated with natural gas leakage sources (and to wood burning to a lesser extent), whereas acetylene, ethylene and propene predominantly come from combustion sources (which include wood burning and vehicle exhausts). Finally pentanes are associated with traffic emissions (vehicle exhaust and /or gasoline evaporation). None of them is a tracer of a specific source and therefore characterisation of sources are usually made by using either a ratio approach, often using CO or acetylene as tracer (see Borbon et al., 2013 and references therein) or an approach based on the determination of sources composition profiles (see Baudic et al., 2016 and references therein). The studied compounds usually show a seasonal cycle with a minimum in spring/summer and maximum in fall/winter. This typical seasonal cycle is due to the combination of several factors: emissions (the wood burning source has a pronounced maximum in winter), photochemistry (OH,

which presents higher values in summer, is the main sink of all the studied compounds) and finally dynamics (a shallower boundary layer in winter leads to more accumulation of the pollutants). We note that all compounds selected here have a lifetime (which ranges from a few hours for ethylene to almost 40 days for ethane) shorter than CO.

Ratios obtained during the Multi-CO₂ campaign are reported along with the results obtained for the MEGAPOLI/CO₂-Megaparis campaign in Table 1. For consistency, we note that the comparison is restricted to the MEGAPOLI/CO₂-Megaparis campaign. Indeed ratios presented in this table have been determined according to the method described previously in Section 3.3.1 which differs from the traditional ratio approach (where the ratio directly represents the slope of the scatter plot between two compounds). Ratios between the campaigns appear to agree within a twofold factor (except for $\Delta n\text{-pentane} / \Delta \text{CO}_2$) but present quite heterogeneous results. The previous section mentions the importance of the seasonal variability for the ratio $\Delta \text{CO} / \Delta \text{CO}_2$, as the Multi-CO₂ campaign occurred in fall, whereas the MEGAPOLI/CO₂-Megaparis campaign occurred in winter, associated with a higher residential heating contribution. If seasonality was the main driver of the ratio $\Delta \text{VOC} / \Delta \text{CO}_2$, we would observe higher ratios in winter as well (for compounds largely emitted by residential heating like acetylene and ethylene), which is not the case (ratio $\Delta \text{Acetylene} / \Delta \text{CO}_2$ is not significantly different between both campaigns and $\Delta \text{Ethylene} / \Delta \text{CO}_2$ is lower during MEGAPOLI/CO₂-Megaparis). Another possible driver of the $\Delta \text{VOC} / \Delta \text{CO}_2$ variability between the two campaigns is the inter-annual variation of VOCs (2010 for MEGAPOLI/CO₂-Megaparis, 2013 for Multi-CO₂). Indeed a recent study has shown significant trends of non-methane hydrocarbons in urban and background areas in France (Waked et al., 2016). These trends (from -3.2% to - 9.9 %) have been determined for acetylene and ethylene in Paris and are likely explained by efficient emission control regulation. Nevertheless, these trends would suggest lower ratios in 2013 than in 2010, which was not the case. As the temporal variability does not seem to be the main driver of the $\Delta \text{VOC} / \Delta \text{CO}_2$ difference, and given the complexity of VOC emission profiles, which differ within a same source (e.g., emissions from vehicle exhaust vary as a function of motor temperature and engine type, see Salameh et al., 2014 and references therein), we suggest that this difference arises from the heterogeneity of the VOC sources in the vicinity of the two measurements sites. For instance, remember that one, and only one, of the two sites is located close to an expressway. This would imply a low spatial representativeness of our VOC results obtained in very-low wind conditions.

	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	-	5.55/6.33 (0.24)	24.82/25.21 (2.13)	52.55/33.51 (3.87)	11.18/ 6.26 (2.51)	13.57/ 11.47 (2.34)	9.27/ 3.41 (0.97)	49.81/31.70 (5.10)	32.07/20.38 (2.92)
ΔCO		-	3.48/2.78 (0.28)	5.47/5.13 (0.39)	1.32/0.88 (0.08)	2.18/2.04 (0.15)	1.15/0.73 (0.11)	6.56/3.09 (0.59)	3.19/2.27 (0.30)
$\Delta\text{Acetylene}$			-	1.09/0.84 (0.06)	0.21/0.17 (0.01)	0.28/0.34 (0.02)	0.17/0.11 (0.01)	0.75/0.53 (0.10)	0.48/0.35 (0.04)

Table 1: Observed ratios between co-emitted species derived from our method for the Multi- CO_2 (in blue) and MEGAPOLI/ CO_2 -Megapolis (in red) campaigns. Numbers in brackets () correspond to 1 σ . 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.

1 3) Representativeness and footprint – given that the method emphasizes low wind speeds, it would
2 be valuable to have a sense of the scale of the region impacting the measurements at each site.
3 Especially given that a comparison is being made with the AirParif inventory, is it expected that the
4 citywide totals or average

5 **Our study focuses on low wind speed periods (less than 1 m.s^{-1} , i.e. less than 3.6 km.h^{-1}).**
6 **Considering this speed and a typical event length of about 3h, the extension of the influence zone**
7 **would be a circle with a radius of 11 km if the wind direction was constant. With a non-directional**
8 **wind, as in our case, the influence area is much smaller, likely spreading only a few hundred**
9 **meters around the site. Urban model simulations could confirm this point but this would involve**
10 **different resources and expertise than those of our study. We have added this information in**
11 **Section 4.1.**

Response to Referee #1:

I previously reviewed an earlier version of this paper, and this review addresses the revised draft.

As I said in my previous review, this is a nice study with a good dataset that has been carefully collected. The authors develop a clever data analysis method to determine emission ratios between trace gas species that biases the result towards periods of stagnant air when enhancements in trace gases are high. They thus avoid the problem of spurious emission ratios during periods of low signal-to-noise. The analysis shows a strong seasonal cycle in the CO:CO₂ ratio which is most likely (although not conclusively demonstrated to be) due to wood burning in winter.

General comments:

The revisions relative to the previous version are modest, mostly addressing the minor points of clarity. The largest revision was to further discuss the reasons for the seasonal cycle in the CO:CO₂ ratio and compare with the AirParif inventory – this is a very nice improvement to the paper. Many of my other comments have been very well addressed in the response to reviewers but have not been incorporated in the paper itself. To be clear, a question or comment in the review is meant to imply that it needs to be addressed in the paper itself unless the authors are able to justify why it should not be addressed. I've listed changes that still need to be added in my specific comments below.

As we explain later, we have included them all this time.

My main concern with the paper was and remains that the title and abstract imply a discussion of VOCs, but they are mentioned only briefly in the substance of the paper. In their response to reviewers, the authors make a case that there is insufficient data to make a useful comparison with other VOC emission ratio studies. Fair enough (although I disagree), but the authors need to make a choice here: either remove the VOC component from the paper altogether, or use the VOC data to draw some conclusions. The current state – with VOCs highlighted in the title but not really addressed at all – is not acceptable.

We have included a discussion about VOC results in the new section 4.3.2.

My second general issue was that the paper highlights the “new method” rather than the results. I appreciate the authors comments in response to the second reviewer that their “new method” refers to the data analysis technique to derive the emission ratios, rather than that the tracer:tracer method is new, but the title and abstract remain misleading. Some rewording to make this distinction is needed.

We have changed the title to “ Exploiting stagnant conditions to derive robust emission ratio estimates for CO₂, CO and Volatile Organic Compounds in Paris “. We have also removed the word “new” from the abstract (it does not appear elsewhere).

Overall, this paper is a nice contribution and is suitable for publication in ACP, but still needs some significant revisions to address the concerns previously raised as well as some additional more minor comments.

We have addressed all comments in the revised version of the paper.

Specific comments from previous review that require follow-up:

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

This was answered in the response to reviewers, but needs to be added in the paper text.

We have added the information ("The instrument was compared to the MEGAPOLI/CO₂-Megapolis one in 2010 and the repeatability and the trueness of the 1 min averaged data were found to be almost the same.") in the section.

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.

The authors say in the response to reviewers that they will add this information, but I don't see it in the paper text.

We have added this information in Section 2.2.1.

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 had not explained where we made the modification of the text and apologize for this, but we had inserted "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" in the section.

In the revised version, we have further improved it to "It samples different wind sectors and not just clean air ones. For instance, 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"

I am not convinced of the argument presented in the response to reviewers (and in any case, it should be addressed in the paper itself). You say that wind from the continental sector gives a background of 410.2 ppm whereas from the oceanic sector background is 402.4 ppm. So if the wind varies between these two sectors over the three day moving window, wouldn't the background be too low for the times during that window when the wind was from the continental sector?

The reviewer is correct about the impact on the background estimate, but our method for the ratio estimation is not that sensitive to the background definition (see our discussion in Section 3.3.3).

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:CO_{2ff} 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 explanation in the response to reviewers is a reasonable justification – put it in the paper!

We have added “ The impact of the biosphere in this seasonality seems to be negligible because night-time and day-time measurements yield the same ratios (i.e. the same asymptotes with our method)” in the first paragraph of Section 4.2.

As I said in my general comments, this section 4.3 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 VOC:CO that would make useful comparisons, as well as several that have looked at VOC:CO₂ or VOC:CO_{2ff} ratios.

See my general comment in this review. This section remains very weak and needs to be expanded to give meaningful interpretation of the VOC ratios OR the VOC component should be removed altogether.

We have included discussions about VOC results in the new section 4.3.2.

New specific comments:

Lines 44-47. See also Turnbull et al 2015 for discussion of how choice of background can strongly influence the calculated emission ratios.

We refer now to this paper again in what was line 45 after “ measurements for species with a significant 44 life time in the atmosphere have to be corrected from background influence”.

Lines 62-66. Does AirParif account for biogenic and/or natural sources? Surely they must be important at least for some species.

In the Airparif inventory, natural/biogenic emissions are not taken into account for CO₂. They are taken into account for VOCs (biosphere and soils – apart cultivated ones). To clarify this point in the paper, we have added the following sentences in section 4.2:

“The Airparif inventory does not include biogenic and/or natural sources of CO₂ for two reasons: 1/ Airparif respects the definitions given by the UNFCCC; and 2/ the carbon cycle of the biomass lifetime is estimated too short to take into account this emission sector. However, our study shows that CO₂ emissions from biomass burning might represent a non negligible part of the Paris CO₂ budget.”

Section 2.1. Please add something about the footprint of the sampling sites.

In Section 2.1, we have added: “The footprint of the sites depends on wind direction and speed. As we will explain in Section 3.1, we will restrict the analysis to low turning winds, which restricts the measurement footprint to a few hundred meters around each site.

Line 115. Remove word “continuously”.

We have removed the word.

Lines 135-137. Please provide references to justify that the VOC sources are shared with CO and CO₂.

124 Lines 160-169. Please provide references for justification of the lifetimes of the various species.

125 **We have included references in the section we have added to discuss VOC results (4.3.2).**

126

127 Section 3.2. Please also see Turnbull et al 2015 for discussion of background choice and how it
128 influences emission ratios. They show that measurements from sites far afield and/or from the free
129 troposphere can give misleading emission ratios since they implicitly incorporate emissions from a
130 large area rather than just the urban area of interest.

131 **We added " Further, continental and free-tropospheric measurements may be misleading for the**
132 **interpretation of local emissions (Turnbull et al. 2015)".**

133 Section 3.2. I'm still not convinced about the CO₂ background choice, particularly in summer. In
134 summer, drawdown will result in low CO₂ values during the afternoon, whereas at night, the effective
135 background might be expected to be higher, but the 3 day moving window doesn't account for this.
136 Presumably the MACC background with its 3 hourly data addresses this issue, but I don't see any
137 mention of it in the paper.

138 **We have added " [These results show that the definition of the background does not significantly**
139 **affect the derived ratios, even during the summer months] when MACC and its 3-hourly resolution**
140 **explicitly account for the daily cycle of vegetation activity, while the 3-day moving window does**
141 **not" in Section 3.3.3.**

142 Section 3.3.1. r^2 is not really a good way to evaluate goodness of fit in this case when there are errors
143 in both species. Please justify the use of r^2 vs chi-squared or other statistic.

144 **We were more familiar with r^2 and have therefore developed the method with it. We consistently**
145 **present the method evaluation in this configuration, like the sensitivity to the criterion on r^2 in**
146 **3.3.2.**

147 Section 4.1. As is clearly pointed out in the paper, the method of calculating ratios biases the results
148 to periods of stagnant air. How might the footprint of the sampling site vary between stagnant air
149 and periods of strong mixing, and would it change the interpretation?

150 **In the presence of strong mixing, the footprint would be much larger, the signal would be smaller**
151 **and the background definition would become critical. This is why we choose to avoid those**
152 **situations (see Section 3.1).**

153 In the text, references to figures point to the wrong figure numbers in several cases.

154 **We have checked all references and found only one case (former line 292). We have corrected it.**

155

Response to Referee #2:

Overall, I am rather disappointed by the revisions made in response to feedback from myself and the other reviewer. The author's made interesting, valid measurements, and have conducted interesting analyses, but there remain issues that need to be addressed (some larger than smaller) in order for me to recommend publication. Concerns raised by myself and the other reviewer need to be rigorously addressed—given the substantial feedback raised the modification of a couple sentences and addition of 2 paragraphs really isn't sufficient.

The new revision addresses all points.

"new method" issues. Both of the reviewers raised the point that the 'selling' of the manuscript in the title, abstract, and body as a new method was not accurate and misleading—and this has not been addressed by the authors. The authors may feel they are presenting a new method, but this needs to be accurately conveyed by the manuscripts language, and as both reviewers have taken issue it would seem the current language is inappropriate.

We have removed "new" from the while text, including the title.

Relatedly, the number of references is still light, in part because prior with CO/CO₂ emission ratios is still not very well cited.

We have added a reference to Turnbull et al. (2006) for the CO/CO₂ ratio measurement and will be happy to add more, provided they enrich the text.

VOC's: there has been some small addition of VOC results, but still far from sufficient. There needs to be discussion in the analysis and conclusion of these results! Are these results consistent with the hypothesis put forward regarding seasonality of CO/CO₂? Do these ratios show the impact of wood burning as theorized for CO/CO₂? As stated before, if VOC's are to be included, then they need to be fully incorporated in the analysis. It isn't even clear if Table 1 and Table 2 listed in the response to reviewer 1 made it into the paper.

We have included discussions about VOC results in the section we have added 4.3.2.

Representativeness of sampling: The author's has not expanded or explained the representativeness of sampling to my satisfaction. The authors assert in the comments to reviewers, wind speed was < 1m/s and they estimate the area of influence to be ~3.5 km. First—how is this estimated?

Our study focuses on low wind speed periods (less than 1 m.s⁻¹, i.e. less than 3.6 km.h⁻¹). Considering this speed and a typical event length of about 3h, the extension of the influence zone would be a circle with a of radius 11 km if the wind direction was constant. With a non-directional wind, as in our case, the influence area is much smaller, likely spreading only a few hundred meters around the site. Our previous estimate of 3.5 km made in our review was likely much too large. Urban model simulations could confirm this point but this would involve different resources and expertise than those of our study. We have added this information in Section 4.1.

Second—this would be considered by many to be a rather local signal, and not necessarily of the representative of the entire Paris urban domain. Could this region of influence be different seasonally and explain the seasonal signal seen?

The reviewer is correct and this interpretation is discussed in Section 4.3 when analysing the difference between the Jussieu and LHVP results.

Background selection/importance of dilution: The author's assert that they need not worry about dilution since their sampling sites are at 30m or closer to the ground, and the entrainment layer does not extend this low (not this discussion is only in response to reviewer and not in the main text). This is not an accurate conclusion. Every urban observation of CO₂ shows a strong diurnal cycle, with minimum value seen in the middle of the day and maximum value in early morning, completely due to boundary layer dilution/mixing dynamics, even though emissions peak during the day. See for example Figure 1 in McKain et al., PNAS. 2012. Emissions in the night accumulate in the shallow mixed layer, and are diluted as the mixing layer develops throughout the day. The fact that the observations in Salt Lake City were near the surface and not in the direct entrainment zone does not remove them from being impacted by this dilution—air mixes within the mixed layer. So, the author's assertion that they do not need to consider this dynamic needs re-assessment. As I indicated before, the author's may be able to pursue an argument that these issues may not matter because the size of the signal they are working with is very large... I am not partial to how the argument is made, but the author's must explicitly address this issue in the manuscript and explain why their background approach is robust to these errors. The also must address to what level their approach might be in error—a 10% bias may be significant.

Our mole fraction measurements are obviously affected by boundary layer dynamics, but the inferred monthly ratios are not since daytime and night-time measurements appear to share the same asymptote. We have added "[throughout the month] and even throughout the day" and "despite, e.g, boundary layer dynamics during the day." in Section 4.1 when highlighting the robustness of the inferred ratios.

Exploiting stagnant conditions to derive robust emission ratio estimates for CO₂, CO and Volatile Organic Compounds in Paris

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Abstract

We propose an 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.

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., Bellassem 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, Xueref-Remy et al., 2016). 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 (e.g., Turnbull et al., 2006). 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 (Turnbull et al., 2015), 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 anthropogenic 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 **expressway** 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 **acetylene, ethylene, propene, *i*-pentane, *n*-pentane, ethane and propane** 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 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. The instrument was compared to the MEGAPOLI/CO₂-Megapolis one used in 2010 and the repeatability and the trueness of the 1 min averages data were found to be almost the same.

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-Megapolis 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. **Furthermore, continental and free-tropospheric measurements may be misleading for the interpretation of local emissions (Turnbull et al., 2015).** 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. It samples different wind sectors and not just clean air ones. For instance, 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 can 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° × 1.9° (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 $\Delta species$, 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 ($\Delta species_1$ and $\Delta species_2$). 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 $\Delta species_1$ and $\Delta species_2$ 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 $\Delta species$ over the 4h period. We also calculate the difference between maximum and minimum $\Delta species_1$, which is plotted on the x axis, over this period (we name it $\delta \Delta species_1$). 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 -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- σ).

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 ($\delta\Delta\text{CO}_2$ can vary and be 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 5. 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 **when MACC and its 3-hourly resolution explicitly account for the daily cycle of vegetation activity, while the 3-day moving window does not**. 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 **and even throughout the day**. For instance, applying our method to the continuous CO and CO₂ 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 **despite, e.g, boundary layer dynamics during the day**.

Our study focuses on low wind speed periods (less than 1 m.s⁻¹, i.e. less than 3.6 km.h⁻¹). Considering this speed and a typical event length of about 3h, the extension of the influence zone would be a circle with a radius of 11 km if the wind direction was constant. With a non-directional wind, as in our case, the influence area is much smaller, likely spreading only a few hundred meters around the site. Urban model simulations could confirm this point but this would involve different resources and expertise than those of our study.

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). **The impact of the biosphere in this seasonality seems to be negligible because night-time and day-time measurements yield the same ratios (i.e. the same asymptotes with our method).**

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 (2010): the annual CO/CO₂ for residential heating and for the other sectors are respectively 2.7 ppb/ppm and 7.1 ppb/ppm. 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 so far. The Airparif inventory does not 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%) the Airparif inventory does not include biogenic and/or natural sources of CO₂ for two reasons (Airparif, 2013): 1/ Airparif respects the definitions given by the UNFCCC; and 2/ the carbon cycle of the biomass lifetime is estimated too short to account for this emission sector. However, our study shows that CO₂ emissions from biomass burning might represent a non-negligible part of the Paris CO₂ budget, but we could not confirm it. 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.

4.3 Comparison between Multi-CO₂ and MEGAPOLI/CO₂-Megaparis campaigns

4.3.1 CO to CO₂ emission ratios in Paris

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

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, **expressways**, 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 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.

4.3.2 VOCs emission ratios in Paris: Multi-CO₂ vs MEGAPOLI/CO₂-Megaparis

This section analyses the VOC emission ratios more specifically, as these compounds (which share common sources with CO and CO₂) were also measured during the two campaigns (Multi-CO₂ and MEGAPOLI/CO₂-Megaparis). In the presence of nitrogen oxides (NO_x), VOC oxidation lead to the formation of ozone and secondary organic aerosols, which impacts air quality and climate. Therefore characterizing VOC emissions in urban areas (which are always associated to high NO_x conditions) is of importance. VOCs include a large variety of compounds and information on their sources and sinks will be given here only for the compounds selected in this study. As already mentioned, among the various non-methane hydrocarbons measured during these campaigns, the selected compounds were the ones which presented a strong correlation with CO₂ and CO ($r^2 > 0.8$), allowing the use of our approach for the ratio determination. In urban areas, anthropogenic sources of VOCs are dominated by traffic, residential heating (including wood burning), solvent use and natural gas leakage, as was recently shown in Paris (Baudic et al., 2016) but also in other cities (Niedojadlo et al., 2007 in Wuppertal, Germany, Lanz et al., 2008, in Zurich, Switzerland, Morino et al., 2011, in Tokyo, Japan, McCarthy et al., 2013, in Edmonton, CA, USA). VOC levels, diurnal and seasonal variability and source contributions in Paris have been thoroughly described by Baudic et al. (2016). Therefore only minimal information is reported here. Ethane and propane are mainly associated with natural gas leakage sources (and to wood burning to a lesser extent), whereas acetylene, ethylene and propene predominantly come from combustion sources (which include wood burning and vehicle exhausts). Finally pentanes are associated with traffic emissions (vehicle exhaust and /or gasoline

evaporation). None of them is a tracer of a specific source and therefore characterisation of sources are usually made by using either a ratio approach, often using CO or acetylene as tracer (see Borbon et al., 2013 and references therein) or an approach based on the determination of sources composition profiles (see Baudic et al., 2016 and references therein). The studied compounds usually show a seasonal cycle with a minimum in spring/summer and maximum in fall/winter. This typical seasonal cycle is due to the combination of several factors: emissions (the wood burning source has a pronounced maximum in winter), photochemistry (OH, which presents higher values in summer, is the main sink of all the studied compounds) and finally dynamics (a shallower boundary layer in winter leads to more accumulation of the pollutants). We note that all compounds selected here have a lifetime (which ranges from a few hours for ethylene to almost 40 days for ethane) shorter than CO.

Ratios obtained during the Multi-CO₂ campaign are reported along with the results obtained for the MEGAPOLI/CO₂-Megaparis campaign in Table 1. For consistency, we note that the comparison is restricted to the MEGAPOLI/CO₂-Megaparis campaign. Indeed ratios presented in this table have been determined according to the method described previously in Section 3.3.1, which differs from the traditional ratio approach (where the ratio directly represents the slope of the scatter plot between two compounds). Ratios between the campaigns appear to agree within a twofold factor (except for $\Delta n\text{-pentane}/\Delta\text{CO}_2$) but present quite heterogeneous results. The previous section mentions the importance of the seasonal variability for the ratio $\Delta\text{CO}/\Delta\text{CO}_2$, as the Multi-CO₂ campaign occurred in fall, whereas the MEGAPOLI/CO₂-Megaparis campaign occurred in winter, associated with a higher residential heating contribution. If seasonality was the main driver of the ratio $\Delta\text{VOC}/\Delta\text{CO}_2$, we would observe higher ratios in winter as well (for compounds largely emitted by residential heating like acetylene and ethylene), which is not the case (ratio $\Delta\text{Acetylene}/\Delta\text{CO}_2$ is not significantly different between both campaigns and $\Delta\text{Ethylene}/\Delta\text{CO}_2$ is lower during MEGAPOLI/CO₂-Megaparis). Another possible driver of the $\Delta\text{VOC}/\Delta\text{CO}_2$ variability between the two campaigns is the inter-annual variation of VOCs (2010 for MEGAPOLI/CO₂-Megaparis, 2013 for Multi-CO₂). Indeed a recent study has shown significant trends of non-methane hydrocarbons in urban and background areas in France (Waked et al., 2016). These trends (from -3.2% to -9.9 %) have been determined for acetylene and ethylene in Paris and are likely explained by efficient emission control regulation. Nevertheless, these trends would suggest lower ratios in 2013 than in 2010, which was not the case. As the temporal variability does not seem to be the main driver of the $\Delta\text{VOC}/\Delta\text{CO}_2$ difference, and given the complexity of VOC emission profiles, which differ within a same source (e.g., emissions from vehicle exhaust vary as a function of motor temperature and engine type, see Salameh et al., 2014 and references therein), we suggest that this difference arises from the heterogeneity of the VOC sources in the vicinity of the two measurements sites. For instance, remember

that one, and only one, of the two sites is located close to an expressway. This would imply a low spatial representativeness of our VOC results obtained in very-low wind conditions.

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. Due to the heterogeneity of VOC sources, ratios that include VOCs are more difficult to interpret in terms of representativeness in low wind speed conditions.

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	$\Delta\text{Acetylene}$	$\Delta\text{Ethylene}$	$\Delta\text{Propene}$	$\Delta i\text{-pentane}$	$\Delta n\text{-pentane}$	ΔEthane	$\Delta\text{Propane}$
ΔCO_2	-	5.55/6.33 (0.24)	24.82/25.21 (2.13)	52.55/33.51 (3.87)	11.18/ 6.26 (2.51)	13.57/11.47 (2.34)	9.27/3.41 (0.97)	49.81/31.70 (5.10)	32.07/20.38 (2.92)
ΔCO		-	3.48/2.78 (0.28)	5.47/5.13 (0.39)	1.32/0.88 (0.08)	2.18/2.04 (0.15)	1.15/0.73 (0.11)	6.56/3.09 (0.59)	3.19/2.27 (0.30)
$\Delta\text{Acetylene}$			-	1.09/0.84 (0.06)	0.21/0.17 (0.01)	0.28/0.34 (0.02)	0.17/0.11 (0.01)	0.75/0.53 (0.10)	0.48/0.35 (0.04)

880

881 **Table 1:** Observed ratios between co-emitted species derived from our method for the Multi-CO₂ (in blue) and MEGAPOLI/CO₂-Megaparis (in
882 red) campaigns. Numbers in brackets () correspond to 1 σ . The mole fraction ratio is reported in ppb/ppm for $\Delta\text{CO}/\Delta\text{CO}_2$, all others to ΔCO_2 are
883 reported in ppt/ppm. Those that do not include ΔCO_2 are reported in ppb/ppb. Ratios in bold mean that there is a satisfactory agreement
884 between the two campaigns (less than 15% of difference).

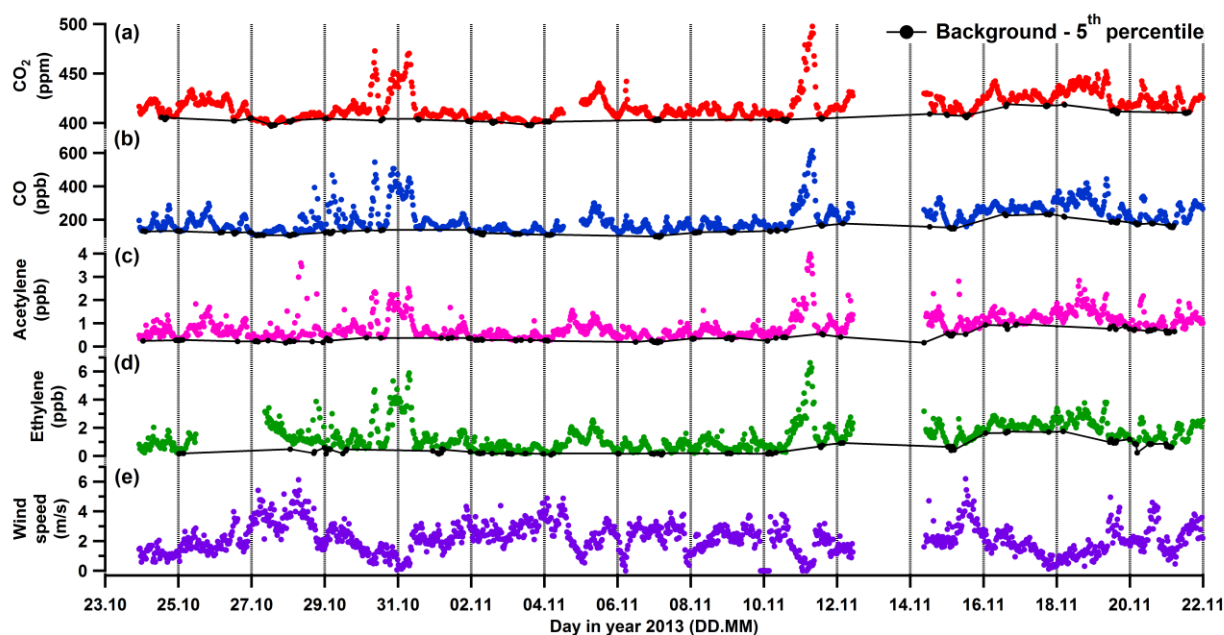


Fig.1: (a-d) Temporal variation of the mole fraction of selected compounds monitored during the Multi-CO₂ campaign (30 minutes time step). The black lines represent the background levels defined with the calculation of the 5th percentile (black disks). **(e)** Wind speed during the campaign. Time is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

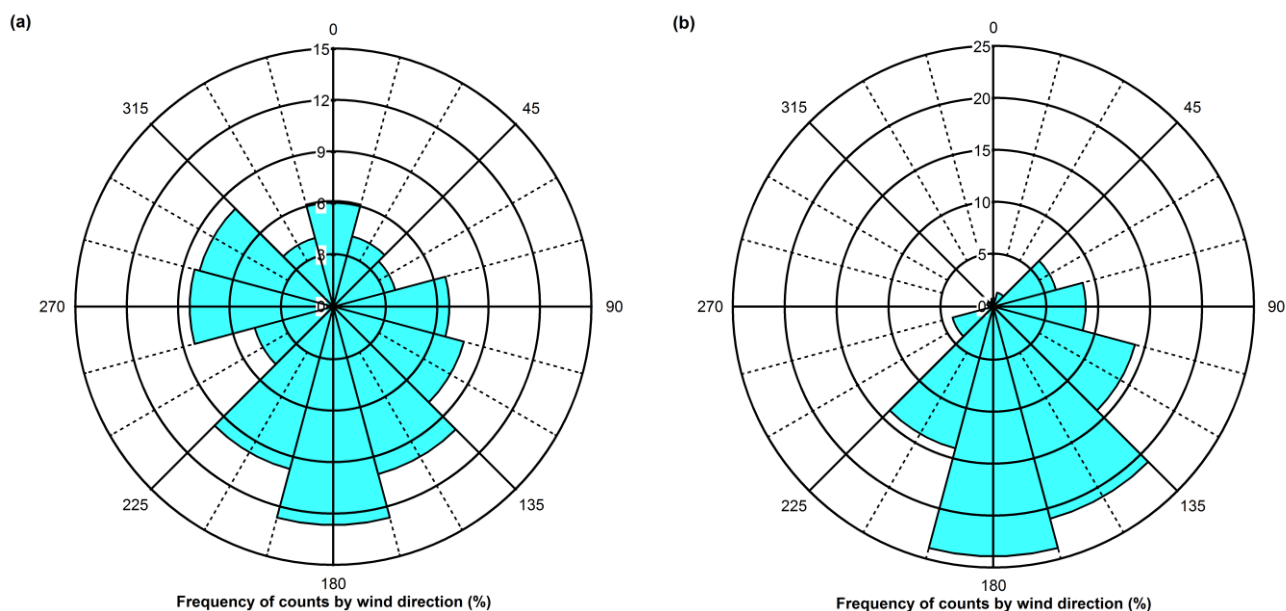


Fig. 2: Wind roses for two low wind speed situations. **(a)** Wind rose for 10-11 November 2013 (significant peak in mole fractions). **(b)** Wind rose for 18 November 2013 (no significant peak in mole fractions). The percent scale is not the same for the two wind plots.

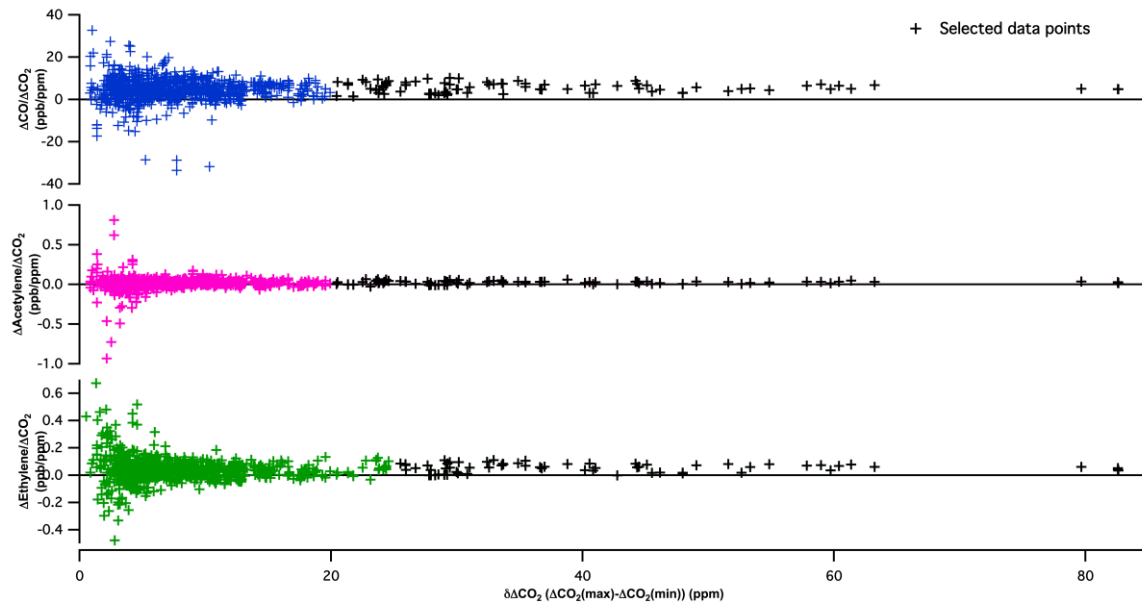


Fig. 3: Selected ratios to ΔCO_2 plotted versus the local CO_2 offset ($\delta\Delta\text{CO}_2$) from the measurements acquired during the Multi- CO_2 campaign. Black data points were selected to determine the equation of the horizontal asymptote using the criteria described in Section 3.3.2 (the used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

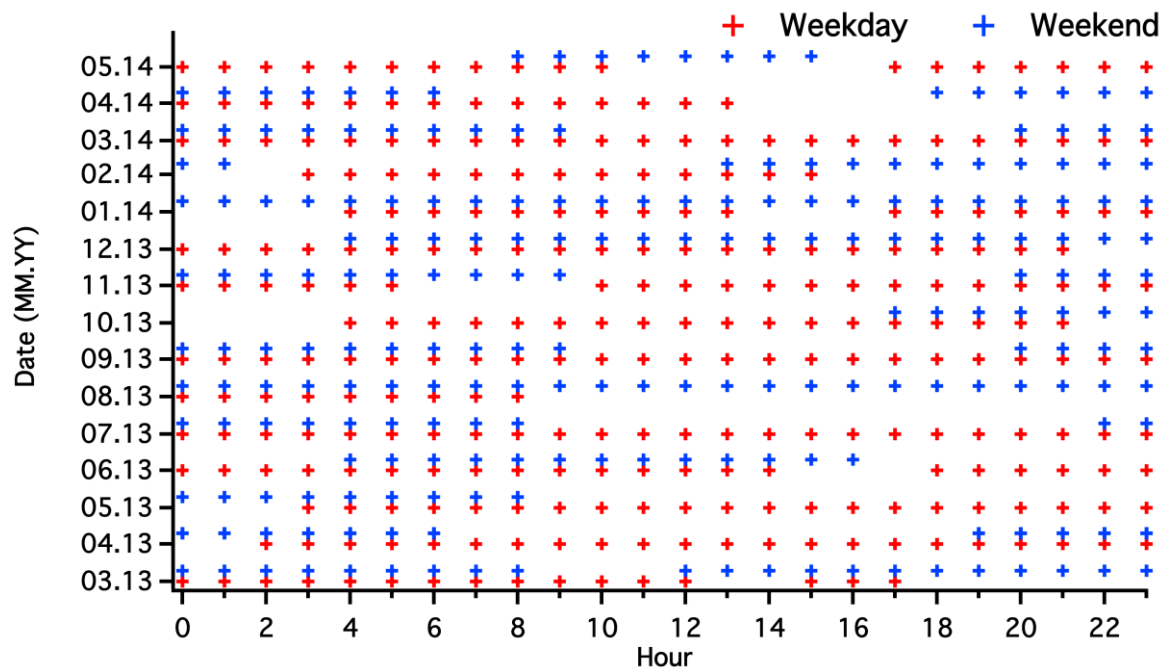


Fig.4: Days (weekdays in red crosses and weekends in blue crosses) and hour sampled per month with our method.

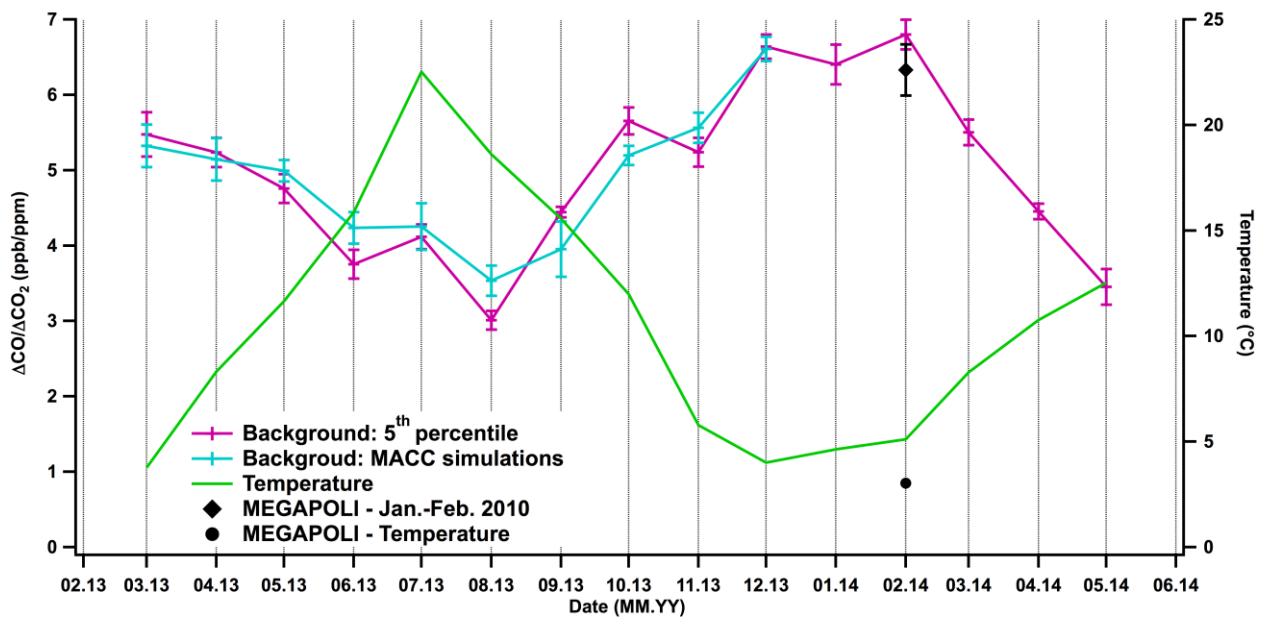


Fig.5: Monthly ΔCO to ΔCO_2 ratios in Paris. Results using background levels defined with the 5th percentile are given in violet. The ones using the MACC simulations are in blue. Error bars on the ratios correspond to 1σ . The ratio from the MEGAPOLI- CO_2 -Megaparis campaign and the corresponding average 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.