Exploiting stagnant conditions to derive robust emission ratio estimates for CO$_2$, 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 CO$_2$, 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 not very 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 $\Delta$CO / $\Delta$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 (autumn 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 and Stephan, 2015), but it has been an active topic for scientific research. Some studies have been based on measurement campaigns dedicated to specific sectors, such as 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 (Zhang 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 is cancelled 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 lifetime 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 $^{13}$CO$_2$, can also allow the analysis to be more specifically focused on anthropogenic activities (e.g., Levin and Karstens, 2007; Turnbull et al., 2011). Finally, atmospheric transport models are used in a few studies to quantify the contributions of the different sources within an inverse modelling ap-
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 paper, we make the first attempt to fully exploit this well-understood behaviour. We use several measurement campaigns of CO\textsubscript{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 city in France. It comprises around 12 million people when including its suburbs. The population density is one of the highest in Europe, with 21,347 inhabitants per km\textsuperscript{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 the year 2010, emissions of CO\textsubscript{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\textsubscript{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 Sect. 3.3, including sensitivity tests (Sects. 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 ΔCO / ΔCO\textsubscript{2} ratio in Paris and Sect. 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; 23 m above ground level). A botanical garden of 28 ha, the Jardin des Plantes, lies about 500 m from the measurement site. The closest motorways are about 4 km to the south and 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 south-east of the Jussieu campus (48°49’ N, 2°21’ E; 15 m a.g.l.). 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 metres south of the site.

2.2 Instrumentation and air sampling

2.2.1 Joined MEGAPOLI/CO\textsubscript{2}-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 CO\textsubscript{2}-MegaParis project (https://co2-megaparis.lsc.ipl.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, \textit{i}-pentane, \textit{n}-pentane, ethane and propane were obtained with a time resolution of 30 min (air is sampled during the first 10 min and analysed during the next 20 min). More details can be found in Gros et al. (2011) and Dolgorouky et al. (2012).

A cavity ring-down spectrometer (CRDS, model G1302, Picarro Inc.) was also deployed to analyse CO\textsubscript{2}, CO and H\textsubscript{2}O mole fractions with a time resolution of 1 s (see Lopez et al., 2013, for more details).

2.2.2 Long-term continuous CO\textsubscript{2} and CO measurements

The CRDS performed continuous CO\textsubscript{2}, CO and H\textsubscript{2}O measurements in Jussieu from 4 February 2013 to 11 June 2014 with a time resolution of 1 s. This instrument was calibrated about every 2 months using three 40 L aluminium gas tanks. These cylinders were previously calibrated for CO\textsubscript{2} and CO dry air mole fractions against the NOAA-X2007 scale for CO\textsubscript{2} 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 min every 12 h between 4 February 2013 and
25 August 2013 and for 15 min 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 min averaged data to be, respectively, 0.05 and 0.03 ppm for CO2 and 6.8 and 3.7 ppb for CO. The instrument was compared to that of the MEGAPOLI/CO2-MegaParis used in 2010 and the repeatability and the trueness of the 1 min average 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 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 Sect. 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 synchronised. The chosen time interval was the one imposed by GC-FID measurements. Data from GC-FID were acquired for 10 min every 30 min, 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 min interval. Finally, in this study, all the data have the same time step of 30 min.

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 in the figure (Fig. 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 covary significantly despite the different lifetime of the species: CO2 and CO have typical lifetimes in the atmosphere (τ) that are 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 1 day so that VOCs with a τ longer than 2 days, like acetylene, can be almost considered as non-reactive species. For shorter-lived species, here only ethylene and propene (1 day > τ > 5 h), 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 (r2 > 0.70). These tight correlations between VOCs with different reactivity suggest a limited impact of the chemistry.

In Fig. 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 three periods were too short (they last around 2 h) 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, 07:00 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 Fig. 2a). 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 Fig. 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 CO$_2$ defined a continental clear-air background to correct the CO$_2$ 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 they 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. they increase local atmospheric mole fractions. We define background mole fractions as all measurements smaller than the 5th 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 3 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-CO$_2$ 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 min (black curves in Fig. 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$^\circ$) and oceanic (180–360$^\circ$) sectors for the averaged CO$_2$ 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 Sect. 3.1 that chemical sinks can be neglected for our measurements, but, in the case of CO$_2$ during the vegetation-uptake season (summer in particular), vegetation within Paris also contributes to populating the 5th percentile.

Our second option (for CO$_2$ only) defines the background from a publicly available analysis of the global atmospheric composition. We test it for CO$_2$, the species for which the first definition may be the least appropriate. The definition of the background level of CO$_2$ 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$^\circ$ × 1.9$^\circ$ (longitude–latitude) in space and of 3 h in time. It combines the information from 131 CO$_2$ stations over the globe and a transport model within a Bayesian framework and estimates the CO$_2$ surface fluxes over the globe together with the full 4-D CO$_2$ field.

We extracted the 3-hourly time series of the CO$_2$ concentrations from the MACC database for the eight grid points that surround our two measurement sites, Jussieu and the LHVP. The CO$_2$ background mole fraction is estimated as the linear interpolation in time of the analysed CO$_2$ 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 Sect. 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 two species ($\Delta \text{species}_1$ and $\Delta \text{species}_2$). We consider a moving window of 4 h in increments of 30 min (each period contains eight points). In 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 4 h 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 $\delta \text{species}_1$). The motivation for this amplitude computation will be developed in Sect. 4.1. These calculations are made when more than five points exist during the time period and when 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 4 h period, we compute (i) the coefficient of determination $r^2$ between $\Delta \text{CO}$ and $\Delta \text{CO}_2$, (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 Fig. 3, we show some examples of ratios determined on each 4 h 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 Sect. 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 $\delta \text{species}_1$ 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 Sect. 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 $\delta \text{species}_1$) 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 0). 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 Sect. 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, which sample the emission conditions within the month less well. As an example, for the couple ($r^2 > 0.6$, $\delta \Delta \text{CO}_2 > 15$ ppm), 211 points are selected in the asymptote, whereas for the one ($r^2 > 0.9$, $\delta \Delta \text{CO}_2 > 30$ ppm), only 39 points remain. We choose the criterion $r^2 > 0.8$ and $\delta \Delta \text{CO}_2 > 20$ ppm to determine the $\Delta \text{CO} / \Delta \text{CO}_2$ ratio during the Multi-CO$_2$ campaign: it keeps more than 100 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
Figure 3. Selected ratios to $\Delta$CO$_2$ plotted vs. the local CO$_2$ offset ($\Delta$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 Sect. 3.3.2 (the used criteria depend on the considered species).

15% error imposed by the uncertainty on VOC data. The data selection for several ratios, including $\Delta$CO / $\Delta$CO$_2$, is presented in Fig. 3.

3.3.3 Sensitivity to the background choice

In this section, we test the influence of the chosen background definition on the obtained $\Delta$CO / $\Delta$CO$_2$ ratio using the methods described in Sect. 3.3.1. We compare $\Delta$CO / $\Delta$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 Fig. 5. We evaluate the relative difference between the ratios derived from the two options (in percent of the ratio obtained with the 5th 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 5th percentile on a running window of 3 days as described in Sect. 3.2.1. However, tests were conducted using the 10th 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 5th percentile). No significant difference was found using the 10th percentile (less than 2% difference between the two derived $\Delta$CO / $\Delta$CO$_2$ ratios). Comparing $\Delta$CO / $\Delta$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 Sect. 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 $\Delta$CO / $\Delta$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 Sect. 4.3).

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

The x axis in Fig. 3 ($\Delta$species$_1$) represents the variability of the species excess over a 4 h 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 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 Fig. 4). This feature allows our method to yield a robust average ratio per month in Paris despite, for example, 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 3 h, 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 metres 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 \(\Delta CO / \Delta CO_2\) ratio in Paris

The evolution of the \(\Delta CO / \Delta CO_2\) ratios in Jussieu between March 2013 and May 2014 is presented in Fig. 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\(^{-1}\); maximum value: 6.80 ppb ppm\(^{-1}\)). The impact of the biosphere in this seasonality seems to be negligible because night-time and daytime 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 \(\Delta CO / \Delta CO_2\) ratio. The monthly atmospheric temperature measured during the low wind speed periods is also shown in Fig. 5. The two curves are much anti-correlated (\(r^2 = 0.75\)): when the temperature is high, the ratio is low – and vice versa. 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 \(\Delta CO / \Delta CO_2\) 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 / CO\(_2\) for residential heating and for the other sectors is respectively 2.7 and 7.1 ppb ppm\(^{-1}\). 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 / CO\(_2\) ratios between winter and summer: 3.1 ppb ppm\(^{-1}\) in January against 3.6 ppb ppm\(^{-1}\) 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 CO\(_2\) 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 CO\(_2\) emissions from biomass burning might represent a non-negligible part of the Paris CO\(_2\) budget, but we could not confirm it. The differences may be adjusted to account for this source.

Figure 4. Days (weekdays in red crosses and weekends in blue crosses) and hour sampled per month with our method.
for CO$_2$ emissions as well and may explain why 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-CO$_2$ and MEGAPOLI/CO$_2$-MegaParis campaigns

4.3.1 CO to CO$_2$ emission ratios in Paris

The ratios between the co-emitted species for the Multi-CO$_2$ and MEGAPOLI/CO$_2$-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/CO$_2$-MegaParis campaign and 2013 for the Multi-CO$_2$ 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 Sect. 4.2. Indeed, measurements were performed in autumn (October–November) for the Multi-CO$_2$ campaign and in winter (January–February) for the MEGAPOLI/CO$_2$-MegaParis one. The $\Delta$CO / $\Delta$CO$_2$ ratio from the latter campaign is also reported in Fig. 5 for the corresponding month of the year: it aligns well on the seasonal variability observed in Jussieu, even though this campaign was made 4 years before. Furthermore, average temperatures during the low wind speed periods were not the same: 10°C during the Multi-CO$_2$ campaign and 3°C during the MEGAPOLI/CO$_2$-MegaParis one. This is in agreement with the argument developed in Sect. 4.2: residential heating is more important in the heart of winter and its emissions make the $\Delta$CO / $\Delta$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/CO$_2$-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 CO$_2$ 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 / CO$_2$ ratios are respectively 2.43 and 3.74 ppb ppm$^{-1}$ for the 5th and the 13th districts. However, the good agreement between the ratio from the MEGAPOLI/CO$_2$-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-CO$_2$ vs. MEGAPOLI/CO$_2$-MegaParis

This section analyses the VOC emission ratios more specifically, as these compounds (which share common sources with CO and CO$_2$) were also measured during the two campaigns (Multi-CO$_2$ and MEGAPOLI/CO$_2$-MegaParis). In the presence of nitrogen oxides (NO$_x$), VOC oxidation leads to the formation of ozone and secondary organic aerosols, which impacts air quality and climate. Therefore character-
Table 1. Observed ratios between co-emitted species derived from our method for the Multi-CO$_2$ and MEGAPOLI/CO$_2$-MegaParis campaigns. Numbers in parentheses correspond to 1σ. The mole fraction ratio is reported in ppb ppm$^{-1}$ for 1CO$_2$/1CO; all other ratios to 1CO$_2$ are reported in ppt ppm$^{-1}$. Those that do not include 1CO$_2$ are reported in ppb ppb$^{-1}$. Ratios in bold mean that there is a satisfactory agreement between the two campaigns (less than 15% of difference).

<table>
<thead>
<tr>
<th>Species</th>
<th>Multi-CO$_2$</th>
<th>MEGAPOLI/CO$_2$-MegaParis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1CO$_2$/1CO</td>
<td>1CO$_2$/1n-pentane</td>
</tr>
<tr>
<td>Ethane</td>
<td>24.82/25.21 (2.13)</td>
<td>24.84/25.23 (2.12)</td>
</tr>
<tr>
<td>Propene</td>
<td>3.48/3.78 (0.25)</td>
<td>3.47/3.79 (0.25)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>5.56/5.83 (0.24)</td>
<td>5.55/5.83 (0.24)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>11.18/11.57 (0.39)</td>
<td>11.18/11.57 (0.39)</td>
</tr>
<tr>
<td>Propene</td>
<td>1.32/0.88 (0.08)</td>
<td>1.32/0.88 (0.08)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>5.97/5.13 (0.39)</td>
<td>5.97/5.13 (0.39)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.28/0.33 (0.02)</td>
<td>0.28/0.33 (0.02)</td>
</tr>
<tr>
<td>Propene</td>
<td>0.17/0.16 (0.01)</td>
<td>0.17/0.16 (0.01)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.68/0.64 (0.06)</td>
<td>0.68/0.64 (0.06)</td>
</tr>
</tbody>
</table>

isising VOC emissions in urban areas (which are always associated to high NOx 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 CO$_2$ 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) as well as in other cities (Niedojado et al., 2007, in Wuppertal, Germany; Lanz et al., 2008, in Zurich, Switzerland; Morino et al., 2011, in Tokyo, Japan). 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 are tracers of a specific source and therefore characterisation of sources is 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 autumn/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-CO$_2$ campaign are reported along with the results obtained for the MEGAPOLI/CO$_2$-MegaParis campaign in Table 1. For consistency, we note that the comparison is restricted to the MEGAPOLI/CO$_2$-MegaParis campaign. Indeed ratios presented in this table have been determined according to the method described previously in Sect. 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 2-fold factor (except for Δn-pentane / ΔCO$_2$) but present quite heterogeneous results. The previous section mentions the importance of the seasonal variability for the ratio ΔCO / ΔCO$_2$, as the Multi-CO$_2$ campaign occurred...
in autumn, 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 interannual variation of VOCs (2010 for MEGAPOLI/CO2-MegaParis, 2013 for Multi-\text{CO}_2).

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., 2015, 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 Conclusions

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 \( \text{CO}_2 \). Thanks to continuous long-term 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-\text{CO}_2 and MEGAPOLI/\text{CO}_2-MegaParis, shows differences from \( -120 \) to \( +63 \% \) for nine 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \), 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 \( \text{CO}_2 \) emissions.

6 Data availability

All the data presented in this paper are available upon request. Please contact Lamia Ammoura (lammoura.lsce@gmail.com) for further information.

The Supplement related to this article is available online at doi:10.5194/acp-16-15653-2016-supplement.

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