Atmospheric measurements of ratios between CO₂ and co-emitted species from traffic: a tunnel study in the Paris megacity

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Abstract

Measurements of CO₂, CO, NOₓ and selected Volatile Organic Compounds (VOCs) concentrations have been performed continuously during ten days in the Guy Môquet tunnel in Thiais, in a peri-urban area about 15 km south from the centre of Paris, between 28 September and 8 October 2012. This dataset is used here to identify the characteristics of traffic-emitted CO₂ by evaluating its ratios to co-emitted species, for the first time in the Paris region. High coefficients of determination (r² > 0.7) are observed between CO₂ and some compounds which are characteristic of the traffic source (CO, NOₓ, benzene, xylenes and acetylene). Weak correlations (r² < 0.2) are found with species such as propane, n-butane, i-butane, that are associated with fuel evaporation, an insignificant source for CO₂. To better characterize the traffic signal, we focus only on species that are well correlated with CO₂ and rush hour periods characterized by the highest traffic-related concentrations. To those concentrations, we remove the nighttime averaged weekday concentration obtained for each species that we infer to be the most appropriate background signal for our study. Then, we calculate observed ∆species/∆CO₂ ratios that we compare with the ones provided by the 2010 bottom-up high resolved regional emission inventory from Airparif, the association in charge of monitoring the air quality in Île-de-France, focusing on local emission data for the specific road of the tunnel. We find an excellent agreement (2 %) between the local inventory emission CO/CO₂ ratio with our observed ∆CO/∆CO₂ ratio. Former tunnel experiments carried out elsewhere in the world provided observed ∆CO/∆CO₂ ratios that differ from 49 % to 592 % to ours. This variability can be related to technological improvement of vehicles, differences in driving conditions and fleet compositions. We also find a satisfactory agreement with the Airparif inventory for n-propylbenzene, n-pentane and xylenes to CO₂ ratios. For most of the other species, the ratios obtained from the local emission inventory overestimate the observed ratios to CO₂, by 36 % to more than 300 %. However, the emission ratios of NOₓ, o-xylene and i-pentane are underestimated by 39 % to 79 %. One main cause of such high differences between
the inventory and our observations is likely the obsolete feature of the VOCs speciation matrix of the inventory that was not updated since 1998, although law regulations on some VOCs occurred since that time. Our study bears important consequences for the characterisation of the urban CO$_2$ plume and for atmospheric inverse modelling of urban CO$_2$ emissions that are discussed in the conclusion.

1 Introduction

In 2011, more than half of the world population was living in urban areas and this proportion is expected to reach 67% in 2050 (United Nations, 2012). Cities are therefore strategic places to address impacts and mitigation of climate change and, in particular, the reduction of greenhouse gas emissions. Here we focus on the Paris metropolitan area. Paris is part of the Île-France region which is inhabited by about twelve million people. Out of these, Paris and its suburbs concentrate eleven million inhabitants and constitute the third largest megacity in Europe. The most detailed description of its emissions is provided by the regional inventory developed by Airparif, the association in charge of monitoring the air quality in Île-de-France. According to the Airparif 2010 emission inventory, CO$_2$ emissions of Île-de-France represent about 13% of the total French anthropogenic CO$_2$ emissions, for a surface that extends only over 2% of the French territory (Airparif, 2013). Most of the regional CO$_2$ emissions are concentrated in the Paris metropolitan area. They are attributed essentially to the residential and tertiary sectors (43%) and to traffic (29%). As is quite common for emission inventories, there is no independent quantitative assessment of the Airparif database, and its uncertainties are poorly constrained. Moreover, Airparif emission estimates are based on activity proxies, calibrated from benchmark situations that may significantly differ from real ones. For instance, chassis dynamometer tests (Bosteels et al., 2006) characterized the vehicle emissions under controlled conditions and fuel composition, but cannot represent the diversity of real driving conditions well and fleet composition. Therefore independent evaluations of the inventory are needed and atmospheric...
measurement programs around the Paris megacity such as the CO$_2$-Megaparis project that sample the actual emission plume (Xueref-Remy et al., 2014) may provide new reference information to anchor the inventory. In the framework of the EU-FP7 Megapoli and CO$_2$-MegaParis projects, Lopez et al. (2013) measured the concentrations of CO$_2$ and of its carbon isotopes in winter 2010 in the centre of Paris and in the southwest peri-urban area. Using the $^{13}$CO$_2$ and radiocarbon ($^{14}$CO$_2$) signatures, 77% of the total CO$_2$ was attributed to anthropogenic sources and 23% to biospheric sources. The anthropogenic emissions were identified to originate for 30% from traffic and for 70% from gas heating. Measured emission ratios were compared to the Airparif emissions inventory, and showed good consistency with it. First encouraging estimates of the total CO$_2$ anthropogenic emissions of the Paris megacity by atmospheric inverse modelling have been obtained by Bréon et al. (2014) who compared their results to the Airparif inventory. In urban areas, Volatile Organic Compounds (VOCs) are also controlled by anthropogenic sources and thus represent potential tracers for inferring CO$_2$ urban emission sources. Gaimoz et al. (2011) set up such measurements in the centre of Paris in spring 2007 and identified major VOC sources. Traffic activities (exhaust and fuel evaporation) were found to be responsible for 65% of the total VOC emissions, industrial sources for 14%, natural gas and background for 8%, local sources for 4%, biogenic evaporation for 8% and wood burning for 1%.

In this paper, we use new atmospheric concentration data acquired in real conditions in Paris to evaluate the emission ratios of CO, NO$_x$ and VOCs relatively to CO$_2$ for the traffic sector in the Airparif inventory. These ratios carry the signature of the traffic emission plume because, during the combustion processes of fossil fuels, CO$_2$ is co-emitted with other species in ratios that are characteristic of each emission sector and fuel type. In order to focus on the traffic sector and be representative of the vehicle fleet, we have performed our atmospheric measurements in a road tunnel. Such an approach has been used before in several tunnels of the world, to study emission factors of VOCs (Ho et al., 2009) and trace gases (Chirico et al., 2011). In Western Europe, Popa et al. (2014) and Vollmer et al. (2007) provided CO/CO$_2$, N$_2$O/CO$_2$, and
CH$_4$/CO$_2$ ratios for vehicular emissions. In the Paris area, one study was conducted in a road tunnel in August 1996 (Touaty and Bonsang, 2000) to evaluate hydrocarbon vehicle emissions and to determine emission factors for non-methane hydrocarbons (NMHC) and CO.

Like the study of Touaty and Bonsang (2000), the present experiment was carried out in the Guy Môquet tunnel in Thiais, located about 15 km south of Paris centre. The campaign took place during 10 days from 28 September 2012 to 8 October 2012. CO$_2$, CO, VOCs and NO$_x$ concentrations were measured inside the tunnel in order to determine their ratios to atmospheric CO$_2$ for traffic in the Paris megacity. Our measurements enable us to update the results from the year 2000’s previous study. To our best knowledge, they also constitute the first study in a French tunnel involving CO$_2$, VOCs and NO$_x$ altogether and hence quantifying the ratios of these co-emitted species to CO$_2$ in Paris for the traffic sector.

This paper is structured as follows. The instrumental methods are described in Sect. 2, together with the Airparif inventory. Section 3 starts with a general description of the data (Sect. 3.1) and a discussion about the definition of background level concentrations (Sect. 3.2). In Sect. 3.3, we identify the co-emitted species due to road traffic by evaluating the correlations between these species and CO$_2$. Then, in Sect. 3.4, we quantify the emission ratios between these species and CO$_2$ for the present vehicle fleet. Finally (Sect. 4.1), we compare these measured ratios with the ones provided by previous experiments and by the most recent regional emission inventory of Airparif (2010) (Sect. 4.2). Section 4.3 refines the comparison with the latest European tunnel study.
2 Methods

2.1 Site description

The Guy Môquet tunnel (48°77′ N, 02°39′ E) is located in Thiais, about 15 km south from the centre of Paris. This tunnel was built on a highway and has been used since 1990. It is 600 m long, with a rectangle cross-sectional area of 64 m². It contains two separate tubes, one for each traffic direction. Each bore contains three lanes of traffic. The two tubes are not connected. The average traffic in each bore of the tunnel is about 60 000 vehicles per day. The speed limit is 90 km h⁻¹.

The tunnel is equipped with a longitudinal ventilation mode: a system of jet fans at two places on the tunnel ceiling. The aim of this ventilation system is to speed up the airflow towards the tunnel exit in case of fire emergency, pushing smoke outside. Under normal traffic conditions, the tunnel is self-ventilated, as traffic through the tunnel induces the airflow direction. We cannot be sure that the ventilation system has never been activated during the whole measurement campaign. However, we will mainly focus on traffic concentrations peaks during which the signal is strong enough not to undergo a significant effect of the ventilation/dilution on the concentration ratios between species (which is the heart of this study).

Vehicle speed and traffic counts were available every 6 min. All these data were provided by the Direction Régionale et Interdépartementale de l'Équipement et de l'Aménagement d'Île-de-France (DRIEA-IF). Vehicle speed and density are shown in Fig. 1d and h. During working days (from 1 October 2012 to 5 October 2012), around 61 000 vehicles crossed the tunnel daily, 58 000 on Saturday (on 6 October 2012) and 55 000 on Sunday (on 7 October 2012). Traffic density during the night (between 23:00 and 04:00 LT) was low with around 500 vehicles per hour, unlike traffic density during rush hours which was around 3100 vehicles per hour.
2.2 Air sampling and instruments

Air measurements were made at a single location within the tunnel, in the bore that leads to the city of Créteil, 550 m from the tunnel entrance and 50 m from its exit, from 28 September 2012 to 8 October 2012. Time is given as Local (Central European Summer) Time (UTC + 2 h).

Several instruments were operating during this study and the ones relevant to our study are presented here. A Cavity-Ring-Down Spectrometer (Picarro, model G2401) analysed continuous CO$_2$, CO and H$_2$O measurements with a time resolution of 1 s. This instrument was calibrated at the beginning of the campaign, using three 40 L gas tanks. These cylinders were calibrated for CO$_2$ and CO dry air mole fraction using a Gas Chromatograph against the NOAA-X2007 scale, with a precision better than 0.1 ppm. During the campaign, a fourth gas cylinder was analysed during 30 min every 8 h. It was used as a target to evaluate the repeatability of the data and the drift of the instrument. During the campaign, no significant drift was detected for CO$_2$ and CO measurements and the precision of the data (1 sigma) was estimated to be 0.04 ppm for CO$_2$ data and 16 ppb for CO data on 1 min averages. Thanks to the use of a sequencer, CO$_2$ and CO concentrations in the ambient air (outside the tunnel) were also measured with this analyser during 30 min every 4 h. To sum up, the sequence of CO and CO$_2$ measurements was: tunnel air for 4 h, ambient air for 30 min, tunnel air for 3 h 30, target gas cylinder for 30 min, ambient air for 30 min.

Two gas chromatographs, equipped with a flame ionization detector (GC-FID), were installed to measure Non-Methane Hydrocarbons (NMHCs). Both instruments are described in details in Gros et al. (2011). Measurements were provided with a time resolution of 30 min. Air was sampled during the first 10 min of each 30 min segment and analysed during the next 20 min. Previous measurements and tests have shown a good stability of the detector over several weeks (Gros et al., 2011). Therefore only one calibration has been performed during the campaign (1 October) and consisted in the direct injection (repeated 3 times) of a 4 ppb calibration gas mixture (National Physics...
Laboratory, Teddington, UK). Mean response factors of these three injections were used to calibrate NMHC during the campaign. NMHC concentrations in ambient air were estimated on 2 October 2012 between 13:50 and 16:30 LT. The total uncertainty on the data was estimated better than 15 %.

A chemiluminescent analyser (API TELEDYNE, model T200UP) continuously measured Nitrogen Oxides (NO and NO$_2$) concentrations with a time resolution of 1 min. Calibration of the instrument is regularly checked at the laboratory by injecting 30 ppb from a 10 ppm NO calibration gas mixture (Air Liquide, France). In order to check the calibration parameters within the range of values expected in the tunnel, 500 ppb of NO from the Air Liquide standard were injected in the instrument prior to the campaign. The response of the instrument was found very good ($506.5 \pm 4.5$ ppb, variability coefficient $< 1 \%$, $n = 35$) and therefore the instrument was operated with the same parameters during the campaign. NO$_x$ concentrations in ambient air were also measured on 2 October 2012 between 13:51 and 16:39 LT. For NO concentrations over 2300 ppb, the instrument showed saturation and was no more quantitative.

### 2.3 Data processing

As the temporal sampling was different for each instrument, a common averaged time was defined a posteriori to get all datasets on a similar temporal resolution. The chosen time interval was the one imposed by GC-FID measurements. Data from GC-FID were acquired during 10 min every 30 min, the reported time corresponding to the beginning of the measurement. Thus for each compound measured by the other instruments, data were averaged on the same 10 min interval. Doing so, all the final data have a time step of 30 min with a resolution of 10 min.

NO and NO$_2$ data were screened because of the characteristics of the analyser. Since the instrument saturated when NO concentrations reach 2300 ppb, a filter was applied to remove the NO and NO$_2$ data when the NO concentration exceeds 2200 ppb.
2.4 Airparif inventory

Airparif (http://www.airparif.asso.fr/en/index/index) has been developing an inventory of emissions for greenhouse gases and air pollutants with a spatial resolution of 1 km × 1 km and a temporal resolution of one hour for Île-de-France. The emissions are quantified by sectors: energy, industry, road transport, agriculture, solvent uses, waste treatment, etc. Emissions (in tons) are assessed for five typical months (January, April, July, August and October) and three typical days (weekday, Saturday and Sunday) to account for seasonal and weekly cycles. A speciation matrix is used to extract emissions for each specific VOC from the total VOCs emissions in the inventory. This speciation matrix is provided by the Institute for Energy Economics and The Rational Use of Energy (IER). The extraction is possible for each specific VOC and by SNAP (activity).

Thanks to in-situ vehicle counters, Airparif also provides emission estimates specific to some roads. Such information was available for this study in the Thiais tunnel.

The latest version of the inventory, whose results are used in this study, was made for the year 2010, but the speciation matrix for VOCs was established in 1998 and has not been updated yet.

3 Results

3.1 Data overview

The temporal evolution of the concentrations for the whole campaign and with a time step of 30 min is shown in Fig. 1. The average speed and density of vehicles in our tunnel section are also represented in this figure.

During working days, rush hours are easily identifiable for all studied species with one peak in the morning, between 06:00 and 09:00 LT, and another one in the afternoon between 16:00 and 19:00 LT. Almost 4050 vehicles cross the tunnel per hour at the
beginning of the rush periods, but the vehicle density and speed then decrease along with the congestion in the tunnel. The average speed of vehicles during rush hours is lower than 20 km h\(^{-1}\), whereas out of these periods it is faster than 60 km h\(^{-1}\). These peaks are linked to the commutation of Paris active inhabitants going back and forth to their working place. For comparison purpose, the average vehicle speed in Paris city has been determined to be 15.9 km h\(^{-1}\) from a recent study performed the Paris city local administration.

Concentrations were significantly higher during traffic peaks than during nighttime or at other times of the day. Compared to traffic peaks, we notice a decrease in concentrations during nighttime by 40% for CO\(_2\) and propane, and by 80% to 94% for the other compounds. For periods during daytime out of traffic peaks, the decrease, compared to traffic peaks periods, was about 15% for propane, 30% for CO\(_2\) and between 65% and 90% for the others. Since the traffic signal in terms of gas concentrations is so much stronger during rush hours, we will focus on these periods in the following. Indeed, in order to evaluate concentration ratios, enough concentration variability is required (gradients can thus be calculated) and these strong signals were encountered only during traffic peaks periods.

3.2 Background levels

The long lifetime of some of the studied species, like CO\(_2\), induces a large variety of emission origins and potentially elevated background levels in the measured concentrations. Since we aim at characterizing the ratios of the studied species relatively to CO\(_2\) for tunnel traffic activity only, the concentrations have to be corrected from other influences, like the nearby biogenic contribution, or the baseline level.

In previous tunnel studies (Popa et al., 2014; Touaty and Bonsang, 2000; Vollmer et al., 2007; Ho et al., 2009; Araizaga et al., 2013), two sampling sites were installed, one near the entrance of the tunnel, representing the background concentrations, and another one near the exit. The difference of concentrations between these two samples represented vehicle emissions in the tunnel. The current configuration of the Thiais tunnel...
tunnel did not enable us to install two sampling sites, and background levels had to be defined differently. Apart from CO$_2$ and CO, it was not possible to use the few measurements made outside the tunnel (Sect. 2.2), because they do not include all species and are not performed on regular basis, while, according to previous measurements, ambient VOCs concentrations vary significantly during the day and from one day to another (Gros et al., 2011).

Given the available information, background concentrations can be approximated (i) by nighttime concentrations (as performed by Chirico et al., 2001) or (ii) by daily concentrations out of the traffic peaks. In our case, nighttime concentrations were the lowest measured concentrations of the whole campaign. Vehicle density was quite low, around 500 vehicles h$^{-1}$, and averaged vehicle speed was relatively high, more than 70 km h$^{-1}$. For (ii), the daytime concentrations outside rush hours were higher than nighttime ones by 10% (CO$_2$) to 60% (propene). Vehicle density during these periods was high as well, around 3500 vehicles h$^{-1}$. For our study, we choose option (i) because it corresponds to the lowest density of vehicles. We focused on four nights during weekdays and evaluated averaged concentrations between 23:00 and 04:00. However, tests with option (ii) and even using the sparse measurements made outside the tunnel are presented in the Supplement: they show that the definition of the background does not affect the estimated ratios to CO$_2$ showed in the following. This comes very likely from the fact that the traffic signal during rush hours inside the tunnel is much larger than the concentrations measured during all other periods of time, inside or outside of the tunnel (from twice to around ten times more).

### 3.3 Correlations between co-emitted species and CO$_2$

Gros et al. (2011) and Gaimoz et al. (2011) characterized the VOC sources in Paris and identified the main traffic-related VOCs. Based on their results, we select benzene, toluene, xylenes, ethylbenzene, n-propylbenzene, m&p-ethyltoluene, propene, acetylene, ethylene, i-pentane, n-pentane, i-butane, n-butane and propane for the correlation study to CO$_2$. We also consider CO, NO, NO$_2$ and NO$_x$, as done by Chirico et al. (2011).
For background concentrations, we use the averaged values during the night (cf. Sect. 3.2). We focus on working days (five days between Monday, 1 October and Friday, 5 October 2012) only. For each species, we calculate $\Delta$Species as the differences between each concentration point measured in the tunnel during traffic peaks and the average concentration calculated for the nights of working days only. We compute the coefficient of determination $r^2$ for all corrected concentrations $\Delta$Species and $\Delta$CO$_2$ using the scatterplot between the two (Fig. 2). Generally, tight correlations are found between the selected compounds and CO$_2$ ($r^2 = 0.58$–0.89). In all cases, a $p$ value value test was performed, resulting in each $p$ value lower than 0.001. However, correlations were poor for propane, i-butane and n-butane with respectively a coefficient of determination $r^2 = 0.15$, $r^2 = 0.22$ and $r^2 = 0.031$. All coefficients of determination are listed in Table 2.

Inside the Thiais tunnel, CO is exclusively emitted by traffic activities. The strong correlation between $\Delta$CO and $\Delta$CO$_2$, $r^2 = 0.89$, supports that the emitted CO$_2$ in the tunnel has the same origin as CO, i.e. traffic. Strong correlations are also found between CO$_2$ and benzene, toluene, xylenes, ethylene, acetylene and propene ($r^2 = 0.60$–0.81) because these compounds dominate in vehicle exhaust (e.g., Gaimoz et al., 2011; Chirico et al., 2011). This is also consistent with the high coefficient of determination ($r^2 = 0.85$) seen between CO$_2$ and NO$_x$, which are also traffic tracers.

Propane is one of the main compounds emitted by fuel evaporation. Fuel evaporation does not emit CO$_2$ and this can explain the poor correlation between $\Delta$propane and $\Delta$CO$_2$ ($r^2 = 0.15$). Coefficients of determination for i-butane and n-butane, which also come from fuel evaporation, were also low (respectively $r^2 = 0.22$ and $r^2 = 0.031$). Therefore, these compounds (propane, i-butane and n-butane) will not be further considered in this study.
3.4 Ratios of co-emitted species to CO$_2$ in traffic peaks

In the following, we assess the ratios between co-emitted compounds and CO$_2$ in the traffic peaks. We define the ratio as the slope of the scatterplot between $\Delta$Species and $\Delta$CO$_2$, using a linear regression fit (Bradley et al., 2000; Popa et al., 2014). For each co-emitted species, the error on the ratio was computed using a confidence interval at 68% (1-$\sigma$). This method seems more robust than the calculation of instantaneous ratios. Indeed, this method constrains the ratio to be unique. The uncertainty is thus lower (instantaneous ratios show a larger variability, which leads to large uncertainty). The ratios of the selected co-emitted species to CO$_2$ are presented in Table 1. We notice that the outliers do not influence the linear regression within a 1-$\sigma$ uncertainty.

$\Delta$VOCs to $\Delta$CO$_2$ ratios are shown in decreasing order of magnitude. The higher the ratio is, the more the corresponding species is emitted. In the tunnel, i-pentane and toluene were the most emitted VOCs. This result is in good agreement with the vehicle exhaust source profile published in Gaimoz et al. (2011) and with the VOCs profile determined for the traffic sector from this tunnel campaign (Gros et al., 2014).

4 Discussion

4.1 Comparison with previous campaigns

Of the studies that focused on traffic emissions, few have evaluated concentration ratios to $\Delta$CO$_2$. To our best knowledge, none of previous tunnel studies reported $\Delta$VOC to $\Delta$CO$_2$ ratios. Table 2 lists $\Delta$CO to $\Delta$CO$_2$ ratios for vehicle emissions from previous studies. Generally, their ratios are higher than ours, except for the latest Swiss study (Popa et al., 2014). The comparison with the oldest studies shows indeed a significant difference in $\Delta$CO to $\Delta$CO$_2$ ratios: the ratio from the study of Bradley et al. (2000) is almost 500% higher than ours. For more recent studies, the ratios reported by Bishop and Stedman (2008) and Vollmer et al. (2007) were respectively 11 to 120% and 9% higher.
than ours. There were fifteen years between the campaign of Bradley et al. (2000) and ours, during which vehicles benefited from significant technological improvement, especially catalytic converters that reduce vehicle CO emissions. Furthermore, fuel use is not the same in France, in the USA and in Switzerland. American vehicles have been mostly using gasoline for decades (diesel vehicles only reached 3% in 2012) whereas in France and particularly in the Île-de-France region, diesel is the most used fuel (according to Airparif, 78% of vehicles use diesel). Switzerland is in between, with 22% of the fleet using diesel (2010). Furthermore, gasoline vehicles are known to emit much more CO than diesel vehicles. Thus, European emission policies set higher thresholds for CO emissions from gasoline consumption (about a factor 3 in 2000 and a factor 2 since 2005 compared to diesel) while their CO$_2$ emissions are only of a few percents higher (ADEME, 2013). This results in a much higher CO/CO$_2$ emission ratio for gasoline vehicles than for diesel ones. The large differences in the fuel partition of each national fleet is thus likely one main reason why the $\Delta$CO/$\Delta$CO$_2$ ratios measured in the United States are effectively higher than the ones observed in Switzerland – and even more in France. However, this point cannot be more detailed because we did not have further information on the fleet composition evolutions between 1997 and 2012.

Finally, the ratio from the latest study (Popa et al., 2014, in Switzerland) is half the value of the one measured during our campaign. Measurement years were almost the same (2011 for Popa et al. and 2012 for our study), and no significant evolution occurs in the fleet composition during this year. Furthermore, the mean age of the Swiss fleet and the French one is also nearly the same, around 8 years. The comparison with this study will be further analysed in Sect. 4.3.

### 4.2 Comparison of the measured ratios with the Airparif inventory

In this section, we compare the emission ratios derived from our observations in the tunnel during our campaign with those given by the Airparif 2010 inventory.

As Airparif provides emission estimates in tons for each compound, we convert our measured concentrations ratios (in ppb ppm$^{-1}$ or ppt ppm$^{-1}$) into mass ratios (t kt$^{-1}$).
or kg kt$^{-1}$). Our measurements were made in September and October and we notice that these months were typical months as regards annual average traffic emissions. Thus, we use annual emissions from the Airparif inventory to evaluate the ratios. The comparison is summarized in Table 3 and Fig. 3.

The Airparif inventory is sufficiently detailed (Sect. 2.4) to provide emissions estimates related to the specific area of this tunnel road, where our experiment was conducted. These ratios are shown in the second column in Table 3 and in green bars in Fig. 4. We notice a good agreement for the $\Delta CO$ to $\Delta CO_2$ ratio: the difference between the ratio inferred from our observations and the one from the Airparif inventory is less than 2%. The agreement is also satisfactory for the n-pentane to CO$_2$ and n-propylbenzene to CO$_2$ for which we notice a difference with the observed ratios lower than 15%. Airparif overestimates most of the other ratios by 36% or more (up to about 320% for ethylene). NO$_x$ to CO$_2$, o-xylene to CO$_2$ and i-pentane to CO$_2$ ratios are underestimated by 39% to 79%. The case of xylenes can be distinguished. Indeed, if we consider the separation between m&p-xylenes on the one side and o-xylene on the other side, we note significant differences between the specific Airparif ratios and the observed ones. However, if we evaluate the ratio considering total xylenes, we obtain a better agreement with only 7% of difference between the two (observed $\Delta$xylenes to $\Delta CO_2$: 24.4 kg kt$^{-1}$, Airparif xylenes to CO$_2$: 26.1 kg kt$^{-1}$). A problem in the speciation of xylenes may be responsible for this change.

Airparif accounts for the specific fleet composition in the tunnel which is different on this highway than in the Paris centre, for instance. Heavy goods vehicles do not run in the centre of Paris whereas the two-wheelers represent 16% of the total of vehicles. In the tunnel, heavy vehicles are allowed (5% of the fleet composition) whereas motorized scooters constitute less than 2% of the total vehicles. To assess the impact of this specificity on our study, we also compare our results to the traffic ratios obtained from the whole regional emission inventory. The Airparif regional ratios are given in the first column in Table 6 and in blue bars in Fig. 3. These results indicate a significant spatial variability in the whole Airparif inventory, which makes it important to select...
inventory data from the specific tunnel road for proper comparison. Doing otherwise systematically increases the misfits (except for i-pentane and o-xylene), that increase up to about 1200 %. The Thiais tunnel is a highway tunnel, where motorized scooters are not allowed while they constitute an important source of traffic emissions around Paris, particularly of CO emissions. Almost half of traffic-emitted CO is due to scooters and motorbikes: 57 210 t year$^{-1}$ on a total of 117 170 t year$^{-1}$ for the whole traffic sector (Airparif, 2013). We can notice the same trend as regards total VOC emissions: 6990 t year$^{-1}$ are emitted by two-wheeler vehicles over a total of 14 850 t year$^{-1}$ for traffic.

Even if we use the inventory data from the relevant geographical area, our calculated ratios mostly do not well agree with the ones from the inventory, especially for VOCs to CO$_2$ ratios. This may be caused by some out-dated features of the speciation matrix that was made in 1998 (see Sect. 2.4). For instance, the regulation of benzene in fuel became stricter in year 2000: benzene has been limited to 1 % in the fuel composition since then instead of 5 % before. The fuel composition was also regulated in aromatic compounds content, becoming limited to 35 % since January 2005 instead of 42 % before. The impact of these changes on the benzene and aromatics emissions is not yet taken into account in the speciation matrix of the inventory and may explain that the related ratios to CO$_2$ are overestimated for the emission inventory.

4.3 Additional investigation in the comparison with the latest Swiss study

The comparison with the Airparif inventory in Sect. 4.2 suggests some refinement to our comparison in Sect. 4.1 to the recent tunnel measurements made in Switzerland by Popa et al. (2014). The Swiss fleet composition and the French one are very different, in particular in diesel use (Sect. 4.1). In order to assess the impact of this difference on the emission ratios, we separately compute CO to CO$_2$ ratios for gasoline and diesel fuel in Île-de-France and in Switzerland, based respectively on the emission inventories delivered by Airparif and by the Swiss Department of Environment, transports and
Energy (OFEV, 2010). Using the distribution diesel vehicles/gasoline vehicles in each region, we can then get the total CO to CO\textsubscript{2} ratio. Results are compiled in Table 4. The gasoline emission ratio is almost 3 times higher in France than in Switzerland and reflects the impact of two-wheelers emissions. Indeed, motorcycles in Île-de-France, around 8% of the total fleet, only use gasoline fuel and as we said previously, they emit almost half of the CO emissions. In Switzerland, less than 4% of vehicles are motorcycles and they emit around 20% of the total traffic-emitted CO. The gasoline ratios are lower than the gasoline ratios in both cases. The total ratios, which are the product of CO/CO\textsubscript{2} and of the relative percentage of diesel and gasoline vehicles in each case, are almost the same in Switzerland and in the Paris region, even if Swiss and French fleet compositions are different. Therefore the difference in diesel and gasoline vehicles in the two fleet compositions does not seem to explain the difference between the \(\Delta\text{CO} / \Delta\text{CO}_2\) ratio from Popa et al. (2014) and ours.

Then, we note that the two campaigns have been made in different traffic conditions. On the one hand, Popa et al.’s ratio is representative of fluent highway traffic: driving conditions stayed constant while vehicles crossed the tunnel, and the averaged vehicle speed was higher than 80 km h\(^{-1}\). On the other hand, in our study we have focused on traffic jam period, with some frequent stops and low speed (less than 20 km h\(^{-1}\)) during which the combustion and the catalytic converter are less efficient. According to SETRA (SETRA, 2009), a branch of the French Department of Energy and Environment, vehicles emit twice as much CO when they work at a temperature which is 40% of the optimal value whereas CO\textsubscript{2} emissions remain almost the same (CO emissions are multiplied by 3 if vehicles are completely cold). Based on these results, \(\Delta\text{CO} / \Delta\text{CO}_2\) ratios are therefore expected to be 2 or 3 times higher in the case of less effective combustion. To complete the analysis of Sect. 4.1, the quality of the combustion could therefore not explain the difference with the previous studies (excepted Popa et al., 2014).
To assess the influence of the vehicle speed on $\Delta CO$ to $\Delta CO_2$ ratio, we evaluate this ratio in the tunnel when the speed was higher. We use daily data, between 12:00 and 16:00 LT, for working days only, when the speed was higher than 50 km h$^{-1}$ and vehicle density was still important (around 3800 vehicles h$^{-1}$). We use the method presented in Sects. 3.3 and 3.4 to evaluate the ratio. The comparison between the two periods is shown in Table 5.

Vehicle speed appears to affect the $\Delta CO$ to $\Delta CO_2$ ratio: it decreases when the averaged speed is increasing but the standard deviation shows a larger variability. However, a dilution effect with the ambient air should also be considered. Indeed, in the Swiss study, air flow in the tunnel is well-known and the two sampling sites allow isolating vehicle emissions from the tunnel. In our study, it may be possible that, when average speed is high and the tunnel is not congested, some ambient air is brought in the tunnel and mixed with the tunnel air thanks to a piston effect, changing the ratios compared to rush hours. This dilution effect, combined with a random use of the ventilation may explain the weak correlations between co-emitted species and $CO_2$ found out of traffic peaks and justifies the focus on the rush periods.

5 Summary and conclusion

This study pioneered the measurement of CO to $CO_2$ and VOCs to $CO_2$ ratios for traffic emissions in the Paris area. Fifteen co-emitted species, characteristic of traffic emissions, were found to strongly correlate with $CO_2$. VOCs to $CO_2$ ratios enabled to identify the most emitted species: here, i-pentane and toluene were the most emitted VOCs. We compared our results with other studies made in the United States and in Switzerland. Previous tunnel studies only reported CO to $CO_2$ ratios and differences from 9 % to more than 500 % were found with the ratio inferred from our observations. Such differences may be explained by the significant technological improvements of vehicles (such as the development of catalytic converters) but also by the large differences in fleet composition (diesel/gasoline use) and driving conditions (traffic jams/fluent traffic,
high/low speed regimes). A comparison with the latest Paris regional inventory was done focusing on the specific road of the Thiais tunnel. In most cases, it indicated that the inventory overestimates the ratios to CO$_2$, even though satisfactory agreement is found for the CO to CO$_2$, n-pentane to CO$_2$, n-propylbenzene to CO$_2$ and xylenes to CO$_2$ ratios. VOC emissions for the traffic sector are the most overestimated, suggesting that the VOCs speciation matrix should be updated in the inventory, in order to account for the latest regulations about fuel composition. The evaluation of the mean ratios for the whole regional inventory indicated significant spatial variability in the inventory data. The fact that the best fit to our measurements is seen when the inventory data for the tunnel road is isolated, suggests some skill in this inventory variability. The satisfactory agreement found for several ratios to CO$_2$ suggests that data from the inventory are representative of low speed regimes. Our data suggests a $\Delta$CO/$\Delta$CO$_2$ ratio smaller by about one third in high-speed regime, but with much higher uncertainty. This point also confirms the limited representativeness of specific campaigns, like the previous ones or ours. In our case, more measurements are needed within the Paris megacity to draw a general picture of the emission ratios around Paris for the traffic sector, which is characterized by a large spatial (highways vs. small streets) and temporal (weekday vs. weekend) variability. The varying ratios of co-emitted species to CO$_2$ also imply that traffic does not have a unique imprint in the urban plume, but rather leaves various signatures. Depending on whether these signatures overlap with those of the other emission sectors like domestic heating, the ratios may or not allow identifying the emission composition of the urban plume. Finally, this variability of the ratios bears important consequences for atmospheric inverse modelling. Indeed it has been suggested that measurements of CO, and of possibly other co-emitted species, could help constraining the estimation of fossil fuel CO$_2$ emissions (Levin and Karstens, 2007; Kort et al., 2013; Lopez et al., 2013; Rayner et al., 2014). Our study shows that this is possible only through a good quantitative knowledge of the large variations of the emission ratios in space and time, which somehow moves the difficulty without necessarily reducing it. In this respect, isotopic measurements of CO$_2$ are a tool of choice.
for bringing information about fossil fuel vs. natural CO$_2$ emissions that is easier to extract (e.g., Levin et al., 2003; Lopez et al., 2013), even though such measurements are expensive and much more difficult to make.

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References


Atmospheric measurements of ratios between CO$_2$ and co-emitted species from traffic

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Table 1. Observed emission ratios to \( \Delta \text{CO}_2 \) and coefficient of determination \((r^2)\). Numbers after ± signs correspond to 1 sigma. Concentration ratios for \( \Delta \text{CO} \) and \( \Delta \text{NO}_x \) are reported in ppb ppm\(^{-1}\), all others are reported in ppt ppm\(^{-1}\).

<table>
<thead>
<tr>
<th>Species</th>
<th>Observed ratios to ( \Delta \text{CO}_2 )</th>
<th>Coefficient of determination ((r^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \text{CO} )</td>
<td>8.44 ± 0.45</td>
<td>0.89</td>
</tr>
<tr>
<td>( \Delta \text{NO} )</td>
<td>3.32 ± 0.23</td>
<td>0.85</td>
</tr>
<tr>
<td>( \Delta \text{NO}_2 )</td>
<td>1.10 ± 0.09</td>
<td>0.82</td>
</tr>
<tr>
<td>( \Delta \text{i-pentane} )</td>
<td>35.22 ± 4.43</td>
<td>0.60</td>
</tr>
<tr>
<td>( \Delta \text{Toluene} )</td>
<td>24.26 ± 2.91</td>
<td>0.63</td>
</tr>
<tr>
<td>( \Delta \text{Acetylene} )</td>
<td>20.14 ± 1.67</td>
<td>0.79</td>
</tr>
<tr>
<td>( \Delta \text{Ethylene} )</td>
<td>14.01 ± 1.91</td>
<td>0.60</td>
</tr>
<tr>
<td>( \Delta \text{Propene} )</td>
<td>13.17 ± 1.37</td>
<td>0.69</td>
</tr>
<tr>
<td>( \Delta \text{n-pentane} )</td>
<td>12.93 ± 1.45</td>
<td>0.66</td>
</tr>
<tr>
<td>( \Delta \text{Benzen}e )</td>
<td>8.84 ± 0.67</td>
<td>0.81</td>
</tr>
<tr>
<td>( \Delta \text{m- and p-xylenes} )</td>
<td>6.06 ± 0.63</td>
<td>0.70</td>
</tr>
<tr>
<td>( \Delta \text{o-xylene} )</td>
<td>4.38 ± 0.43</td>
<td>0.72</td>
</tr>
<tr>
<td>( \Delta \text{Ethylbenzene} )</td>
<td>3.32 ± 0.36</td>
<td>0.67</td>
</tr>
<tr>
<td>( \Delta \text{n-propylbenzene} )</td>
<td>3.12 ± 0.41</td>
<td>0.58</td>
</tr>
<tr>
<td>( \Delta \text{m- and p-ethyltoluene} )</td>
<td>1.75 ± 0.18</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Table 2. ∆CO to ∆CO$_2$ ratios for traffic emissions, comparison with previous studies (continued from Popa et al., 2014). Results of this study are shown in bold.

<table>
<thead>
<tr>
<th>Reference</th>
<th>∆CO/∆CO$_2$ (ppb ppm$^{-1}$)</th>
<th>Location</th>
<th>Measurement year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bradley et al. (2000)</td>
<td>50 ± 4</td>
<td>Denver, CO, USA</td>
<td>1997</td>
</tr>
<tr>
<td>Vollmer et al. (2007)</td>
<td>9.19 ± 3.74</td>
<td>Gubrist tunnel, Switzerland</td>
<td>2004</td>
</tr>
<tr>
<td>Bishop and Stedman (2008)</td>
<td>9.3 . . . 18.4</td>
<td>Chicago (IL), Denver (CO), Los Angeles (CA), Phoenix (AZ), USA</td>
<td>2005–2007</td>
</tr>
<tr>
<td>Popa et al. (2014)</td>
<td>4.15 ± 0.34</td>
<td>Islisberg tunnel, Switzerland</td>
<td>2011</td>
</tr>
<tr>
<td><strong>This study</strong></td>
<td><strong>8.44 ± 0.45</strong></td>
<td><strong>Paris, France</strong></td>
<td><strong>2012</strong></td>
</tr>
</tbody>
</table>
Table 3. Comparison between mass observed ratios to CO$_2$ and mass emission ratios provided by the 2010 Airparif inventory, only for the traffic source. The first column shows ratios from the Airparif inventory for the whole Île-de-France region, the second one shows the specific Airparif ratios for the tunnel road. Observed ratios are in bold. The last column reports the relative differences between the specific Airparif ratios for the tunnel road and observed mass ratios. Emission ratios for CO and NO$_x$ are reported in t kt$^{-1}$, all others are reported in kg kt$^{-1}$.

<table>
<thead>
<tr>
<th>Compound $i$</th>
<th>$i$/CO$_2$ (Airparif (2010) mean in Île-de-France region)</th>
<th>$i$/CO$_2$ (Airparif (2010) in the tunnel road)</th>
<th>Observed mass ratios 2012</th>
<th>Relative difference between inventory ratios in the tunnel area and observed mass ratios (in % of the observed mass ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>9.7</td>
<td>5.3</td>
<td>5.2</td>
<td>+2</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>4.4</td>
<td>4.6</td>
<td>7.6</td>
<td>-39</td>
</tr>
<tr>
<td>i-pentane</td>
<td>64.3</td>
<td>21.6</td>
<td>55.2</td>
<td>-61</td>
</tr>
<tr>
<td>Toluene</td>
<td>176.9</td>
<td>68.3</td>
<td>50.2</td>
<td>+36</td>
</tr>
<tr>
<td>Acetylene</td>
<td>44.6</td>
<td>16.5</td>
<td>11.9</td>
<td>+39</td>
</tr>
<tr>
<td>Ethylene</td>
<td>94.2</td>
<td>37.2</td>
<td>8.9</td>
<td>+318</td>
</tr>
<tr>
<td>Propene</td>
<td>52.5</td>
<td>20.6</td>
<td>12.5</td>
<td>+65</td>
</tr>
<tr>
<td>n-pentane</td>
<td>34.9</td>
<td>18.0</td>
<td>20.7</td>
<td>-13</td>
</tr>
<tr>
<td>Benzene</td>
<td>74.1</td>
<td>33.7</td>
<td>15.5</td>
<td>+117</td>
</tr>
<tr>
<td>m- and p-xylene</td>
<td>67.6</td>
<td>24.0</td>
<td>14.2</td>
<td>+69</td>
</tr>
<tr>
<td>o-xylene</td>
<td>2.6</td>
<td>2.1</td>
<td>10.2</td>
<td>-79</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>32.8</td>
<td>12.4</td>
<td>7.8</td>
<td>+59</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>22.8</td>
<td>7.7</td>
<td>8.9</td>
<td>-13</td>
</tr>
</tbody>
</table>
Table 4. CO to CO\textsubscript{2} ratios (ppb ppm\textsuperscript{−1}) for gasoline and diesel contribution in Switzerland and the Île-de-France region, using annual emission inventories.

<table>
<thead>
<tr>
<th></th>
<th>CO/CO\textsubscript{2} \textsubscript{gasoline}</th>
<th>CO/CO\textsubscript{2} \textsubscript{diesel}</th>
<th>CO/CO\textsubscript{2} \textsubscript{total}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switzerland (2010)</td>
<td>13.52</td>
<td>1.32</td>
<td>10.84</td>
</tr>
<tr>
<td>Île-de-France (2010)</td>
<td>37.44</td>
<td>1.41</td>
<td>9.34</td>
</tr>
</tbody>
</table>
Table 5. $\Delta$CO to $\Delta$CO$_2$ ratios in the Thiais tunnel depending on vehicle averaged speed.

<table>
<thead>
<tr>
<th></th>
<th>Low speed period ($&lt; 20$ km h$^{-1}$)</th>
<th>High speed period ($&gt; 50$ km h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$CO/$\Delta$CO$_2$ (ppb ppm$^{-1}$)</td>
<td>Coefficient of determination $r^2$</td>
<td>$\Delta$CO/$\Delta$CO$_2$ (ppb ppm$^{-1}$)</td>
</tr>
<tr>
<td>8.44 ± 0.45</td>
<td>0.89</td>
<td>5.68 ± 2.43</td>
</tr>
</tbody>
</table>
Figure 1. (a–c) and (e–g) Temporal variation of the concentration of the selected compound during the whole tunnel campaign. (d) Averaged speed. (h) Vehicle density. Time is given in local (UTC + 2 h).
Figure 2. Correlations between ΔCO₂ and selected co-emitted species. The red line represents the linear regression fit between ΔCO₂ and the considered species. The linear regression does not intercept the (0, 0) point because of the uncertainty on the background level.
Figure 3. Comparison between observed ratios to CO$_2$ and emission ratios provided by the 2010 Airparif inventory, only for the traffic source. In blue, ratios from the Airparif inventory for the whole Île-de-France region, in green ratios from the Airparif inventory using emissions only in the tunnel area, in red, ratios from our study. Ratios for CO and NO$_x$ are reported in t kt$^{-1}$, all others are reported in kg kt$^{-1}$. 