Spatial and seasonal variability of measured anthropogenic non-methane hydrocarbons in urban atmospheres: Implication on emission ratios

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**HIGHLIGHTS**

- NMHC urban composition is consistent in French urban areas.
- NMHC urban composition is dominated by vehicle exhaust emissions.
- NMHC urban composition changes between summer and winter.
- Enhancement in combustion-derived products, light alkanes, alkenes, acetylene and benzene in winter.
- Twenty-one emission ratios of NMHC relative to acetylene are estimated on a seasonal basis.

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**ABSTRACT**

Continuous measurements of a wide range of non-methane hydrocarbons (NMHC) have been performed since 2001 in Paris megacity and three French medium-sized cities (Grenoble, Marseille, and Strasbourg). After a careful verification of the data measured, the ambient concentrations are used to analyze the spatial and seasonal variability of the anthropogenic NMHC and determine the present NMHC emission ratios relative to acetylene, a useful metric to evaluate and constraint emission inventories. We show that NMHC urban composition is consistent between all cities with no industrial influence and characteristic of the urban emission mixtures, which are mostly dominated by vehicle exhaust emissions. In winter, the urban NMHC composition generally shows an enhancement in combustion-derived products (alkenes, acetylene), C2–C3 alkanes and benzene, which presumes seasonal changes in emission ratio values. Present emission ratios of NMHC relative to acetylene are determined in Paris and Strasbourg both in summer and winter. They generally compare within a factor of two except for C7–C9 aromatics in Paris. On a seasonal basis, summertime emission ratios are three times higher than wintertime ones while they stay constant for combustion derived product (alkenes) and benzene. The unburned gasoline fraction (alkanes and C7–C9 aromatics) shows the maximum difference up to a factor of seven. These findings suggest that the emission ratios reflect seasonal changes in emissions and can be a useful metric to constraint temporally resolved emission inventories at different time of the year.

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1. Introduction

Volatile organic compounds (VOC) are important chemical constituents of urban air pollution, as precursors of tropospheric ozone (O₃) (Seinfeld, 1989) and secondary organic aerosols (SOA) (e.g. Odum et al., 1997; Kroll and Seinfeld, 2008). Several papers have shown the importance of VOC emissions on both ozone and SOA formation through air quality modeling studies (e.g. Zhang et al., 2004; Hodzic et al., 2009; Coll et al., 2010; Kim et al., 2011). Some VOC, such as benzene and 1,3-butadiene, are classified as toxic air pollutants and are subject to regulations (US EPA, 2008; Directive 98/70/CE).

Non-methane Hydrocarbons (NMHC), a subset of VOC, are emitted by both anthropogenic and biogenic sources. While on a global scale VOC emissions are dominated by biogenic sources (Guenther et al., 2006), in most urban areas the anthropogenic emissions are the principal contributor to NMHC sources. NMHC can be separated into several classes including alkanes associated with the incomplete combustion of tailpipe emissions and fuel evaporation from vehicles and gas stations (Watson et al., 2001); aromatics found as components of vehicle exhaust, fuel evaporation and solvent use; alkenes and alkynes mainly associated with combustion processes. Note that lighter alkanes (C₂–C₄) are components of natural gas and liquefied petroleum gas (LPG) (Harley et al., 1992; Blake and Rowland, 1995; Chen et al., 2001).

The development of emission inventories is a first step in regulating toxic air pollutants and developing strategies for controlling ozone and SOA pollution. They are essential for various applications such as determination of major air pollutant sources, establishment of emission trends over time with the implementation of emission reduction strategies, input for air quality modeling. However, high uncertainties persist with emission inventories due to the diversity and multiplicity of sources (e.g. Carmichael et al., 2003; Ma et al., 2006; Urbanski et al., 2011; Zhao and Wang, 2009; Zhao et al., 2011) and the evaluation of emission inventories still remains an important and critical task. In the last decade, numerous papers have evaluated emission inventories using satellite observations (e.g. Martin et al., 2003, 2006; Lin et al., 2010) or in-situ measurements (e.g. Vautard et al., 2003; Hodzic et al., 2005; Liouesse et al., 2010; Gaimoz et al., 2011). Recent studies have determined urban emission ratios (ER) of several NMHC versus inert species such as carbon monoxide or acetylene (C₂H₂) from ambient concentrations, and successfully used these ambient ratios to evaluate emission database (Baker et al., 2007; Warneke et al., 2007; Gentner et al., 2009; Coll et al., 2010; Russo et al., 2010; Borbon et al., 2013a). These studies point to strong disagreement between emission inventories and observations, especially regarding the dominating sources. Contrary to observations, emission inventories suggest that motor vehicle emissions is no longer the dominating source in northern mid-latitude urban areas (Borbon et al., 2013a; Gaimoz et al., 2011; Niedojadło et al., 2007) and solvent use related activities could be quite significant. Ambient concentrations used in these studies are typically collected during intensive field projects over short periods e.g. one month in summer, when photochemical pollution is maximum. One pending question is to what extent these ambient emission ratios reflect seasonal changes in emissions as suggested by temporally resolved inventories.

This work analyzes the spatial and seasonal variability of the urban NMHC composition by using observations collected by the French air quality networks between 2001 and 2010 in four French urban areas (Paris megacity, Grenoble, Marseille and Strasbourg). The objective is to (1) compare the NMHC composition between French urban areas, (2) to show how this composition changes with season and (3) how this seasonal change affects the emission ratios. The timescale of interest is the season. Analysis of multi-year trends of NMHC emission ratios which is not the purpose of this paper is described in a companion paper (Borbon et al., 2013b). First, we test the consistency of the urban composition for a wide range of NMHC as suggested by Parrish et al. (1998). In particular, these tests detect the potential influence of nearby sources that could locally affect the NMHC distribution but are not representative of the regional urban NMHC emission mixture. Second, we show the implication of the seasonality of NMHC urban composition on the values of urban emission ratios. Datasets are described in Section 2. In Section 3, the quality of the data is assessed which is a first prerequisite when using routine NMHC observations. Section 4 examines the spatial and seasonal composition of urban NMHC regarding source signature for the four cities investigated. In Section 5, emission ratios are derived from present ambient data. Conclusions are given in Section 6.

2. Data set

In France, a long-term monitoring program for NMHC, launched by ADEME (Agence de la Maîtrise de l’Energie et de l’Environnement) and the French Ministry of the Environment started in 2001 and was operated by four local French Air Quality Monitoring Network (AAQA), Usually, 38 compounds belonging to the European ozone precursor priority list (Kotzias et al., 1995) are measured: 15 alkanes, 11 alkenes, 11 aromatics and acetylene. In this paper, we analyze hourly measurements of 31 NMHC performed by four urban air quality networks located in Paris (AIR-PARIF), Strasbourg (ASPA), Grenoble (ATMO-RH) and Marseille (ATMO-PACA) and equipped with an on-line thermodesorption/GC–FID analyzer (Gas Chromatograph coupled to Flame Ionization Detection) as described by Veillerot et al. (1998) and Badol et al. (2004). Briefly, air collected at a constant flow rate is first dried through a permeable Nafion membrane, then preconcentrated on a cool multi-sorbent trap (Carpack B and Carbosieve SII) maintained at −30 °C by a Peltier cooling system. Then the trap is quickly heated up to 300 °C (40 °C s⁻¹) and compounds are desorbed and injected into the Perkin Elmer Auto-System for separation and analysis with the FID detector. Separation is performed using a dual capillary column system equipped with a switching facility: the first column is a CP Sil 5CB (50 m × 0.25 mm × 1.0 μm) for the C6–C9 range and the second one is a Plot Al2O3/Na2SO4 (50 m × 0.32 mm × 5 μm) for the C2–C5 range.

The location of the sites is reported in Fig. 1. The Prado station in Marseille (South-Eastern France) is an urban station largely influenced by the traffic (43°27’N, 5°13’E) located in the Southern part of the city near one of the busiest roads of the city (27,000 vehicles a day). For Strasbourg (Eastern France), NMHC monitoring is performed in Schiltigheim (48°21’N, 7°25’E), which is a town of about 31,000 inhabitants located in the Northwestern suburb of Strasbourg. This suburban station is located in a residential zone surrounded within a 10-km range by a few industries (i.e. refineries, printing factories and other solvent use related activities) and Strasbourg harbor. In Grenoble (South Eastern France), NMHC measurements are carried out at the station of Champagnier (45°06’N, 5°43’E), which is a suburban site along a North-West/ South-East axis where several chemical industries are implemented. In Paris, NMHC are measured at the station of Les Halles (48°51’N, 2°20’E), representing an urban site.

Site characteristics, operating rates and duration of the monitoring program are reported in Table 1 for each station. The duration of the monitoring period is variable depending on the network. In Paris and Strasbourg, the monitoring covers almost one decade of measurements whereas in Marseille the monitoring stopped after two years of operation. The operating rate in Strasbourg, Grenoble
and Paris sites is good and equal to 93%, 70% and 68%, respectively. In Marseille, the operating rate falls to 38% since its implementation in June 2001. These values were calculated for the entire period of available measurements.

Meteorological data (wind direction, wind speed and temperature) were also available at each sites either provided by Meteo-France or by the network, directly. These data will be useful for applying the consistency test in the following section.

3. Consistency tests

In order to insure the quality of AASQA data, the measuring system integrates a systematic quality assurance (QA) and quality control (QC) procedure as described in Badol et al. (2004). This procedure mostly consists of regular checks (every two weeks) of NMHC response coefficients based on the use of certified calibration standards and control charts based on chromatographic retention time.

However, the effort required to perform data quality procedure throughout the duration of the monitoring is highly time-consuming and this is one of the reasons why the monitoring program stopped after two years in Marseille (Table 1). Experimental errors cannot be excluded (Fortin et al., 2005). It is therefore crucial to control a posteriori the quality of the data in order to test their veracity for the purpose of our study. In this context, consistency tests have been implemented and adapted from Parrish et al. (1998). Parrish and co-workers first showed the good correlation between NMHC pairs and/or isomers with same sources and atmospheric lifetime regardless of the urban atmosphere. Any deviation from the main distribution of points could arise from instrumental problems or contamination of the sampling site by local sources that are not regionally representative. Examples of consistency tests for three representative hydrocarbon pairs at the four French sites are displayed in Fig. 2. Fig. 2a–c show the good correlations between NMHC pairs (for most of the cases $0.72 < r < 0.95$) above a threshold. This threshold usually marks low concentrations close to detection limits (DL) for which the correlation can be degraded as illustrated by the trimethylbenzene and pentane pairs (Fig. 2a and b). Fig. 2a–c also highlight that the distributions of NMHC pairs are relatively well superimposed at all the urban sites. Nevertheless, above the threshold, data pairs can diverge from the main distribution as illustrated by some points of the pentane pairs in Paris (Fig. 2b). This could be due to errors in peak integration due to retention time shifting for instance and thus these data should be filtered. The distribution can be bidirectional as illustrated by ethylbenzene vs. toluene in Strasbourg (Fig. 2c). Color-coding this distribution according to wind direction (Fig. 2d) shows an enrichment in toluene in the Southern sector where a petrochemical refinery and Strasbourg Harbor (storage and transport of petrochemical products) are located within a 10 km radius. This local contamination is not regionally representative and thus corresponding data have been isolated. Finally, the consistency test procedure from Parrish et al. (1998) was extended by adding:

- a concentration threshold. This threshold was defined as 3 times the DL value, which corresponds to the limit of quantification (Badol et al., 2004) and appeared as a good compromise in Fig. 2.
- a meteorological filter by using wind direction in order to depict any influence of nearby local sources. Such filter is crucial when industrial activities with sporadic emissions are implemented within the urban area under investigation.

All data diverging from the uniform hydrocarbon pair pattern, below 3xDL or related to industrial emission have been left out from the data set. After applying the different filters, 68%, 59%, 49% and 36% of the VOC measurements can be analyzed in Strasbourg, Paris, Grenoble and Marseille, respectively.

Table 1
Status of the hourly monitoring of NMHC in France since 2001.

| City      | Location       | Type  | Operating network | Operating rate (%)* |
|-----------|----------------|-------|-------------------|---------------------|
| Paris     | Les Halles     | Urban | AIRPARIF          | 70.55               |
| Grenoble  | Champagnier    | Urban | ATMO-RH           | 70.15               |
| Marseille | Prado Avenue   | Urban | ATMO-PACA         | 37.60               |
| Strasbourg| Strasbourg Ouest| Urban| ASPA              | 92.66               |

*The operating rate is calculated from the duration of the monitoring which is variable from one network to another.
Note that the application of consistency tests also reveals the uniform pattern of all NMHC at all sites except the ones impacted by industrial activities. These commonalities will be further discussed in the next section.

4. Urban NMHC composition

In this section, we examine the spatial and temporal composition of urban NMHC at the four monitoring sites on filtered datasets. Only data between 2002 and 2004 when all stations were still operational (Table 1) are used for this initial comparison. First, the variability of NMHC urban composition is compared between the different sites. Second, the seasonal variability of NMHC urban composition between the summer and winter seasons is discussed.

Fig. 3 depicts the percentage (in volume) composition for each NMHC family of the four cities during summer 2003 and winter 2004 when measurements were time coincident. Note that a different period is analyzed for Marseille (2002–2003), as there is no available data in winter 2004.

4.1. Spatial variability in composition

As already suggested in the previous section by correlation plots, the urban composition of selected NMHC is highly consistent between all cities regardless of the season. The contribution of alkanes to total NMHC is greater for all cities both in summer and winter (40–53%) followed by aromatics including benzene (27–47%), alkynes (8–22%) and acetylene (less than 5%). This implies that sources, transport and photochemical removal that affect the NMHC distribution in French urban environments are most likely of same relative importance. Given the short source-receptor transport time at the Marseille site (less than one hour) and no clear evidence of photochemistry effect in the Paris background urban area (Borbon et al., 2013a,b), it can be concluded that the ambient NMHC distribution in all cities is dominated primarily by an urban source mixture with similar composition throughout the different cities. As already reported in European urban areas and worldwide (Borbon et al., 2001, 2003a, 2013b; Derwent et al., 2000; Parrish et al., 2009; von Schneidenmesser et al., 2010), primary sources of NMHC mostly include gasoline exhaust tailpipe emissions for >C3-NMHC (Borbon et al., 2013a), the use of natural gas for C2–C3 alkanes and evaporation for the unburned fraction of gasoline (C4–C9). The use of solvent is also often pointed out (Gaimoz et al., 2011).

4.2. Seasonal variability in composition

The composition of NMHC urban air clearly changes between summer and winter in all cities as seen in Fig. 3. These trends are confirmed for the following years for Paris and Strasbourg (not shown here). In winter, an enrichment in the fraction of combustion products (alkynes and acetylene) relative to summer of 5%, 4%
and 13% is observed for Paris, Strasbourg and Grenoble, respectively. Same trend is observed for the C2–C3 alkane fraction related to the use of natural gas (ethane and propane) up to a 30% increase and for benzene in all cities up to a 4% increase. Conversely, in summer, an enrichment in the unburned gasoline related fraction is observed for C4–C8 alkanes and >C7-aromatics. These seasonal changes are either due to changes in source types or source composition. Given the nature of the compounds affected by seasonality, the additional contribution of combustion sources in winter and of evaporative losses in summer is suspected and will be further discussed in the next section. The NMHC composition observed in Marseille is poorly affected by the seasonality of emissions except for benzene and C2–C3 alkanes. This trend cannot be confirmed for the following years because the monitoring stopped.

4.3. Changes in source signature by comparing NMHC urban composition to emission profiles from previous studies

Here we qualitatively examine the composition of the potential sources that affect the distribution of NMHC and their seasonal variability in French urban atmospheres by compiling relevant emission profiles either found in the literature or collected during field campaigns. The various emission source profiles discussed above are displayed in Fig. 4 for summer and winter and for different classes of hydrocarbons.

4.3.1. Vehicle exhaust emissions

Emission factors at vehicle exhaust pipes (Dynamometer profile) have been determined by Fontaine (2000) and reported by Borbon et al. (2003b) through a dynamometer study for the running French fleet in the year 2000. The emission profiles combine emission factors of catalyst, non-catalyst gasoline passenger cars and non-catalyst diesel passenger cars weighted by their percentage in the urban running fleet in France in 2000. In the updated emission profile reported here, diesel vehicles represent 70% of the running passenger car fleet while they only represented 16% in the study by Borbon et al. (2003b). In winter, the vehicle exhaust emission profile distinguishes between cold start and hot emissions by considering results from the European driving cycle (ECE) and the ECE-cold and ECE-warm phases in Fontaine (2000).

4.3.2. Evaporative losses

Evaporation from gasoline usually refers to vehicle emissions (diurnal losses, hot soak losses, and running losses) and gasoline storage facilities emissions. Here, we use NMHC concentrations
determined in a tunnel in Marseille during the ESCOMPTE 2001 campaign (Cros et al., 2004) with ten 2 L-stainless steel canister sampling performed by the University of California, Irvine and analyzed by GC–FID and GC–MS techniques (detail about the analytical system can be found in Barletta et al. (2011)). The resulting profile is a composite of tailpipe exhaust and running evaporative losses. In addition, the composition of the headspace vapors of fuels distributed in MidWestern United States in summer (Headspace-summer profile) and winter (Headspace-winter profile) by Lough et al. (2005) is reported. While this profile may not be representative of the composition of fuels distributed in France at molecular level, it provides at least a relevant fingerprint of major chemical families.

4.3.3. Combustion sources other than traffic

An influence of additional combustion sources is suspected in wintertime. The existing literature only reports on the emission profiles of biomass burning emissions. Here we report the emission profile of fireplace wood combustion representative of residential wood burning in temperate regions (Akagi et al., 2011). Even if this profile is not representative of all type of domestic combustion, it provides a sense of the composition of combustion sources other than fossil fuel combustion emissions.

In Fig. 4a, the Dynamometer, Tunnel and Headspace-summer profiles are reported. They show the progressive enrichment of traffic emissions (Tunnel) and gasoline vapors in the gasoline unburned fraction (>C4-alkanes and >C7-aromatics) compared to traffic emissions at tailpipe exhaust (Dynamometer). The enrichment is consistent with the observed changes in the summertime NMHC composition of French urban atmospheres depicted in Fig. 3.

In Fig. 4b, the Headspace-winter, ECE-warm, cold and combustion profiles are reported. They point to the enrichment of vehicle cold-start emissions and domestic combustion in acetylene, alkenes and C2–C3 alkanes compared to vehicle hot-start emissions. These results are consistent with the observed changes in the wintertime NMHC composition of French urban atmospheres depicted in Fig. 3 except for alkenes in Marseille.

Despite the observed seasonal changes, the overall NMHC composition in French urban atmospheres shows the clear signature of traffic exhaust emissions regardless of the season at least for >C3 NMHC.

5. NMHC urban emission ratios

The objective of this section is to show the effect of the seasonality of NMHC urban composition on the values of emission ratios. For that purpose, we analyzed emission ratios in both Paris and Strasbourg for the most recent measurement periods: summer 2009 and winter 2010. Note that the composition of NMHC urban emissions is still consistent between Strasbourg and Paris in 2009 and 2010 and shows same seasonal changes as the ones discussed in section 3 and 4. Given the consistency of the composition of NMHC urban emissions between the four French urban areas for the period 2002–2004, same features are expected for Grenoble and Marseille.

5.1. Methodology

A commonly used method to determine emission ratios is to utilize an orthogonal regression fit to calculate the slope of the scatterplot between two compounds, here a particular VOC vs. acetylene. As shown by Warneke et al. (2007) followed by Borbon et al. (2013a,b), the distribution of points within the scatterplot can be affected by photochemistry, especially during summer. We compared nighttime and daytime datasets in Paris and Strasbourg for both summer and winter (results not shown here). The comparisons show that the daytime and nighttime scatterplots agree pretty well for both seasons, which indicates that emission ratios are not affected by photochemistry. We also compared the relative differences between daytime and nighttime datasets and the reaction rate coefficients with the radical hydroxyl (OH) reported in Atkinson and Arey (2003). The comparison indicates that the difference is not dependent on atmospheric lifetime of the species towards OH rate coefficients and thus, daytime and nighttime data can be used together to determine emission ratios.

Scatterplots of selected NMHC versus acetylene in Paris and Strasbourg for summer 2009 and winter 2010 are illustrated in Fig. 5. The orthogonal fit through the data is given by the solid lines. As expected from previous sections, the scatterplots suggest that the emission ratios are affected by the seasonality of the emissions but not equally. The plots are usually more scattered in winter suggesting the effect of a more complex mixture of emission sources compared to summer. These values will be discussed in the next section. Fig. 5d (iso-pentane versus acetylene in Strasbourg) shows an example of bidirectional scatterplots, especially in summer as also seen for all alkanes, ethylene, propene, toluene and (m + p)-xylene. Data points that do not lie within the main distribution of points refer to extremely high levels of iso-pentane. By applying the orthogonal regression, VOC and acetylene are assumed to be interdependent, which is not true for compounds with different origin as illustrated for iso-pentane. Therefore we decided to fit the data with simple linear regression, which
minimizes the effects of extremely high levels. The resulting slope of the fitting curve gives an emission ratio value typical of the urban emission mixing. In the following, the emission ratios are obtained by calculating the linear regression for bidirectional scatter plots.

5.2. Comparison of NMHC urban emission ratios

The urban emission ratios relative to acetylene of major NMHC in summer 2009 and winter 2010 are reported in Table 2 for Paris and Strasbourg, and are quantitatively compared in Fig. 6 for France. The ratios of the emission ratios between the different data sets have been calculated for each NMHC group, and their geometric means are reported in Fig. 6.

5.2.1. Comparison on a spatial basis

In Fig. 6a, the urban emission ratios calculated from the Paris data set are compared to the ones determined by Borbon et al. (2013a) from a time coincident data set collected at another urban site in Paris in the framework of the MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation) campaign. The emission ratios between Paris and Paris-MEGAPOLI all agree within a factor of 1.5 for most of the NMHC. Given the uncertainty expected from NMHC measurements using different techniques and operated by different groups, the emission ratios determined here are representative of the mixing of urban emissions in the Paris region.

In Fig. 6b and c, the emission ratios determined in Paris are compared to those determined in Strasbourg for summer and winter, respectively. The urban emission ratios between Paris and Strasbourg generally agree within a factor of 2, with the exception of C7–C9 aromatic compounds regardless of the season. Given the factor of 1.5 in the NMHC urban composition in Paris (Fig. 6a), the relative composition of NMHC is fairly similar between both cities for alkenes, alkanes and benzene. This Paris feature already depicted and discussed by Borbon et al. (2013a,b) could be either due to the greater abundance of aromatics in the gasoline distributed in the Paris region or the higher proportion of powered-two-wheeler vehicles.
Table 2
Urban emission ratios (ppbv ppbv⁻¹) of NMHC relative to acetylene in Paris and Strasbourg obtained by calculating an orthogonal regression fit of summer and winter data. The standard deviation is indicated in brackets.

| NMHC          | Paris (AIRPARIF) | Winter 2010 | Strasbourg (ASPA) | Winter 2010 |
|---------------|------------------|-------------|-------------------|-------------|
|               | Summers 2008/2009|             |                   |             |
| Ethane        | 7.16 (0.35)      | 3.75 (0.11) | 1.74 (0.33)⁺      | 1.12 (0.07)⁺|
| Propane       | 2.95 (0.13)      | 0.32 (0.04) | 1.67 (0.17)⁺      | 0.81 (0.06)⁺|
| n-Butane      | 2.67 (0.21)      | 0.82 (0.04) | 2.03 (0.17)⁺      | 0.57 (0.04)⁺|
| i-Butane      | 1.58 (0.11)      | 0.41 (0.02) | 0.87 (0.09)⁺      | 0.32 (0.02)⁺|
| n-Pentane     | 0.76 (0.06)      | 0.18 (0.01) | 0.98 (0.09)⁺      | 0.24 (0.02)⁺|
| i-Pentane     | 3.00 (0.28)      | 0.40 (0.02) | 1.77 (0.17)⁺      | 0.34 (0.03)⁺|
| n-Hexane      | 0.32 (0.02)      | 0.08 (0.01) | 0.22 (0.03)⁺      | 0.05 (0.01)⁺|
| n-Heptane     | 0.17 (0.01)      | 0.062 (0.004)| 0.07 (0.02)⁺     | 0.023 (0.003)⁺|
| n-Octane      | 0.033 (0.003)    | 0.011 (0.003)| nd                | nd          |
| i-Octane      | 0.18 (0.01)      | 0.07 (0.01) | 0.07 (0.01)      | 0.016 (0.002)⁺|
| Ethylene      | 2.78 (0.11)      | 2.30 (0.05) | 1.65 (0.12)⁺      | 2.01 (0.06)⁺|
| Propene       | 0.60 (0.03)      | 0.38 (0.02) | 0.70 (0.07)⁺      | 0.29 (0.02)⁺|
| 1-Butene      | 0.06 (0.01)      | 0.04 (0.003)| 0.06 (0.01)      | 0.04 (0.01)⁺|
| Benzene       | 0.26 (0.02)      | 0.20 (0.01) | 0.17 (0.04)      | 0.23 (0.02)⁺|
| Toluene       | 2.52 (0.25)      | 0.78 (0.04) | 0.69 (0.04)⁺      | 0.17 (0.01)⁺|
| (m + p)-Xylenes| 0.88 (0.09)    | 0.31 (0.01) | 0.28 (0.03)⁺      | 0.06 (0.01)⁺|
| o-Xylene      | 0.24 (0.01)      | 0.10 (0.01) | 0.07 (0.01)      | 0.021 (0.003)⁺|
| Ethylbenzene  | 0.17 (0.01)      | 0.09 (0.01) | 0.04 (0.01)      | 0.020 (0.003)⁺|
| 1,2,3-Trimethylbenzene | 0.12 (0.01) | 0.05 (0.01) | nd                | nd          |
| 1,2,4-Trimethylbenzene | 0.17 (0.01) | 0.05 (0.004)| nd                | nd          |
| 1,3,5-Trimethylbenzene | 0.062 (0.003) | 0.023 (0.002) | nd                | nd          |

nd: non determined.
⁺ The emission ratio is obtained by calculating a linear regression fit (see Section 5.1 for explanation).

Fig. 6. (a): Comparison of the emission ratios relative to acetylene measured in Paris to the ones measured during the 2009 summer MEGAPOLI campaign (Paris-MEGAPOLI); (b) and (c): Comparison of the emission ratios relative to acetylene measured in Paris and Strasbourg for summer 2009 and winter 2010, respectively. The values of the ratio are given by the geometric mean of the ratios between Paris and Paris-MEGAPOLI and Paris and Strasbourg for each VOC group.
5.2.2. Comparison on a seasonal basis

The emission ratios reported in Table 2 are slightly affected by the seasonality of emissions for benzene and alkenes indicating their common emission sources related to fossil fuel combustion regardless of the season. In contrast, emission ratios of other NMHC are, on average, 3 times higher in summer than in winter. This is probably a combined effect of enhanced emissions of acetylene in winter and of other NMHC in summer. Note that the emission ratio of ethane and propane is also higher in summer suggesting that the emission ratios are rather controlled by seasonal changes in acetylene emissions and higher natural gas leakage source for these two VOC in summer. For C4-alkanes and C7–C9 aromatics which show the maximum seasonal differences (3–7 times higher), the additional contribution of gasoline evaporation in summer can be suspected as already suggested in Fig. 4. The additional contribution of diffuse emissions from solvent cannot be excluded for aromatics. These last results show that emission ratios determined on a seasonal basis reflect the seasonal changes in source emissions and can be a useful metric to evaluate and better constraint temporally resolved emission inventories.

Our results strengthen and extend the ones reported by Borbon et al. (2013a,b). So far urban emission ratios have been always determined for one season, usually summer, while our study point to strong seasonal changes in urban emission ratio values.

6. Conclusions

In France, a long-term monitoring program, launched by ADEME and the French Ministry of the Environment and operated by the local French Air Quality Monitoring Network, has been performing measurements of 31 NMHC since 2001. NMHC were collected in four French cities: Paris, Grenoble, Marseille and Strasbourg. We analyzed the spatial and seasonal variability of the composition of anthropogenic NMHC emissions in the four cities and we determined the most recent emission ratios relative to acetylene in summer and winter for Paris and Strasbourg. Conclusions of this work can be summarized as follows.

1. We tested the consistency of the urban composition for a wide range of NMHC. Results showed that overall all NMHC follow the same pattern when they are not impacted by local industrial emissions.

2. We examined the spatial and seasonal composition of urban NMHC ambient concentrations for years of time coincident measurements and compared it to emission source profiles. The urban composition is highly consistent between all cities with a dominant contribution to total NMHC of alkanes, and is characterized by the signature of vehicle exhaust emission. Emission composition changes seasonally in accordance with changes expected from emission source profiles. Indeed, NMHC source fingerprint showed an enhancement in combustion products (C2–C3 alkanes, alkenes, benzene and acetylene) in winter and in gasoline related products in summer. This indicates a seasonality in NMHC source signature in urban atmospheres, which implies modifications of emission ratios between winter and summer.

3. We determined emission ratios in Paris and Strasbourg for both summer 2009 and winter 2010. The emission ratios of NMHC between datasets collected in Paris and Strasbourg generally compare within a factor of 2 for both seasons except for C7–C9 aromatics.

4. We showed that emission ratios change up to a factor of seven between summer and winter for a wide range of species, especially for C4-alkanes and C6-aromatics characterizing the unburned gasoline fraction. This shows that emission ratios reflect the seasonal changes in anthropogenic emissions and they can be a useful metric to constraint temporally resolved emission inventory when determined at different periods of the year.

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