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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 (O_3) (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; Liousse 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 (C_2H_2) 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; Niedojadlo 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 (AASQA). 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 (AIRPARIF), 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 (Carbopack B and Carbosieve SIII) 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 ìm) for the C6–C9 range and the second one is a Plot Al_2O_3/Na_2SO_4 (50 m × 0.32 mm × 5 ìm) 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