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Non-methane hydrocarbons in the atmosphere of Mexico City: Results of the 2012 ozone-season campaign

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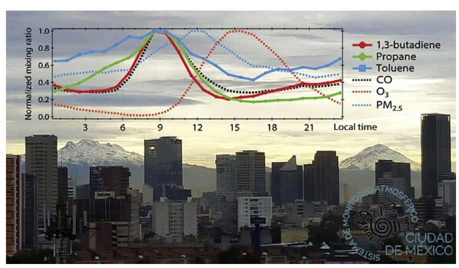
HIGHLIGHTS

- Accurate and continuous NMHC data are needed to evaluate control measures.
- Ambient concentrations of light alkanes and aromatic species have decreased.
- Correlations between species show vehicular traffic as the main source of NMHC.
- Olefins from a growing vehicular fleet have prevented an ozone reduction.
- By first time biogenic isoprene within the urban core was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

With the aim to strengthen the verification capabilities of the local air quality management, the air quality monitoring network of Mexico City has started the monitoring of selected non-methane hydrocarbons (NMHCs). Previous information on the NMHC characterization had been obtained through individual studies and comprehensive intensive field campaigns, in both cases restricted to sampling periods of short duration. This new initiative will address the NMHC pollution problem during longer monitoring periods and provide robust information to evaluate the effectiveness of new control measures. The article introduces the design of the monitoring network and presents results from the first campaign carried out during the first six months of 2012 covering the ozone-season (Mar-May). Using as reference data collected in 2003, results show reductions during the morning rush hour (6–9 h) in the mixing ratios of light alkanes associated with the consumption and distribution of liquefied petroleum gas and aromatic compounds related with the evaporation of fossil fuels and solvents, in contrast to olefins from vehicular traffic. The increase in mixing ratios of reactive olefins is of relevance to understand the moderate success in the ozone and fine aerosols abatement in recent years in comparison to other criteria pollutants. In the case of isoprene, the typical afternoon peak triggered by biogenic emissions was clearly observed for the first time within the city. The diurnal profiles of the monitored compounds are analyzed in terms of the energy balance throughout the day as a surrogate of the boundary layer evolution. Particular features of the diurnal profiles and correlation between individual NMHCs and carbon monoxide are used to investigate the influence of specific emission sources. The

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results discussed here highlight the importance of monitoring NMHCs to better understand the drivers and impacts of air pollution in large cities like Mexico City.

1. Introduction

Over the last two decades Mexico City has experienced a significant progress towards achieving cleaner air without compromising its economic growth. Its case has been used as an example for other cities of the world, especially in developing countries where rapid economic growth and environmental policies must evolve together (Parrish et al., 2011). This progress has been possible because of the concerted efforts of scientists, stakeholders and society. Mexico City has led the country in enforcing regulatory and control policies. Specific policies have included the requirement of catalytic converters in cars, distribution of cleaner unleaded fuels, substitution of natural gas for heavy oil in industry and power plants, reformulation of liquefied petroleum gas (LPG) for residential use, installation of vapor recovery systems in fuel service stations, implementation of inspection and maintenance programs for private vehicles, strengthening driving restrictions, improvement of the public transport by extending the subway infrastructure and implementing a bus rapid transport (BRT) system along confined lanes of main roads (SMA-GEM, 2012). These policies have responded to the integration of air quality information obtained by local authorities and scientific efforts to understand the physic and chemistry of the air pollution, as well as to evaluate the impact on human health, economic development, ecosystem sustainability and climate change. Special mention deserves the interdisciplinary studies based on intensive field campaigns that have provided a wealth of information on the emissions, dispersion and transformation of airborne pollutants within Mexico City and downwind regions (e.g., Doran et al., 1998; Molina et al., 2007, 2010).

The concentrations of all criteria pollutants in Mexico City have substantially decreased during the last 25 years, and some of them, such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), total suspended particulate matter (SPT) and lead (Pb) are in compliance with the Mexican Air Quality Standards (M-AQS) for health protection; however, the concentrations of ozone (O_3) and particles with aerodynamic diameter $\leq$ 10 and 2.5 μm (PM_{10} and $PM_{2.5}$, respectively) still exceed the standard threshold concentrations. In 2012–2014 the 1-h O_3 concentration exceeded the M-AQS of 110 ppb on 118–126 days of each year with a maximum concentration of 185 ppb on 9 May 2014, while the 8-h O_3 moving average concentration exceeded the M-AQS of 80 ppb on 108–120 days. For comparison, 343 and 341 days exceeded the 1-h and 8-h O_3 standards in 1991, when the city recorded the highest O_3 concentrations. With respect to particles, the annual PM_{10} concentration has never met the M-AQS of 50 $\mu g\ m^{-3}$ since the outset of the air quality monitoring in the city in 1986, while the 24-h M-AQS of 120 $\mu g\ m^{-3}$ was only recently met in 2013. The $PM_{2.5}$ concentration meets the 24-h M-AQS of 65 $\mu g\ m^{-3}$, but does not meet the annual standard of 15 $\mu g\ m^{-3}$; during the last three years it ranged from 26 to 28 $\mu g\ m^{-3}$ (SMA-GDF, 2015).

The high levels of particles and O_3 are still a public health threat in Mexico City. In a recent study Riojas-Rodríguez et al. (2014) found that reductions of PM_{10} to 20 $\mu g\ m^{-3}$ and O_3 to 50 ppb would prevent 2300 and 400 premature annual deaths (13 and 2 deaths per 100,000 inhabitants) using population and air quality data from 2005. In a similar study based on $PM_{2.5}$ data from 2010 López-Villegas and Pérez-Rivas (2014) estimated the prevention of 753 and 1421 premature annual deaths (4 and 7 deaths per 100,000 inhabitants) with associated costs of over 1.3 and 4 million US dollars if the annual $PM_{2.5}$ average concentration would meet the M-AQS and the World Health Organization (WHO) guideline of 10 $\mu g\ m^{-3}$, respectively. Note that these studies have estimated the premature deaths and economic benefits considering each pollutant separately. The savings on health-related costs would be much larger if other pollutants were included and their synergic impact considered.

The topography, meteorology, great population density (>20 million inhabitants over 3540 km^2) and magnitude of the economic activities and associated emissions enhance the photochemical formation of secondary pollutants, such as O_3, organic aerosols, carbonyls, peroxides, formaldehyde, glyoxal, nitric acid, etc. The formation of secondary aerosols contributes up to 75% of the afternoon $PM_{2.5}$ budget (Paredes-Miranda et al., 2009). The control of such pollutants depends on the accurate characterization of the ambient concentrations and emissions (biogenic and anthropogenic) of their precursor species: volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The reactions involved in the photochemical transformations are non-linear and therefore difficult to evaluate. However, the intensive field campaigns mentioned above have provided detailed information to suggest that the formation of secondary pollutants in Mexico City, in particular of O_3, has shifted in recent years to a regime where VOC reductions would be more effective. Modeling studies and analysis of measurements indicate that O_3 production is generally VOC limited within the city (e.g., Tie et al., 2007; Lei et al., 2008; Zhang and Dubey, 2009; Song et al., 2010). This has been supported by studies of radical budgets showing significant chain termination by NO_x chemistry (Wood et al., 2009; Volkamer et al., 2010; Sheehy et al., 2010), and by the weekend effect showing large reduction in NO_x and CO but not in O_3 compared to weekday concentrations (Stephens et al., 2008).

Similar to the photochemistry, many studies have documented the distribution, diurnal pattern, magnitude, and reactivity of VOCs within and downwind of Mexico City since the nineties (e.g., Blake and Rowland, 1995; Arriaga-Colina et al., 2004; Velasco et al., 2007, 2008; de Gouw et al., 2009; Bon et al., 2011). These studies have provided valuable information, but their duration has been restricted to a few weeks since the majority have been part of intensive field campaigns. With the aim of addressing the VOC pollution problem during longer monitoring periods and evaluating O_3 and $PM_{2.5}$ reductions according to new control measures, the environmental authorities of Mexico City through its Air Quality Monitoring Network (MC-AQMN) have developed a program to monitor continuously over 50 non-methane hydrocarbons (NMHCs) every hour in existing air quality monitoring stations inside and outside the urban area. The program started in 2012 and considers campaigns during the following 4 years in a first stage.

It is important indicate that VOCs containing oxygen, chlorine, or other elements besides carbon and hydrogen, such as aldehydes, ethers, alcohols, ketones, esters, chlorinated alkanes and alkenes, among others have not been included in this study, and therefore it is more appropriate to use the term NMHCs. The term of NMHCs is usually used for hydrocarbon of relevance in the O_3 formation with less than 12 carbons.