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Volatile organic compounds in the atmosphere of Mexico City

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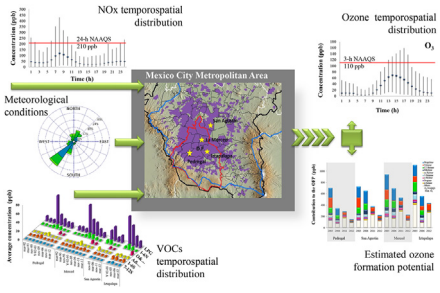
HIGHLIGHTS

- Atmospheric concentration of 64 VOCs were measured in Mexico City during 2011–2012.
- VOC compounds related to LPG leakages exhibited the highest concentrations.
- Correlation analysis among VOCs indicates that they also come from gasoline vehicles.
- Benzene is the toxic VOC that represent the highest risk to Mexicans.
- Toluene is the VOC with the highest ozone formation potential in Mexico City.

GRAPHICAL ABSTRACT



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ABSTRACT

The Mexico City Metropolitan Area (MCMA) is one of the most polluted megacities in North America. Therefore, it is an excellent benchmark city to understand atmospheric chemistry and to implement pilot countermeasures. Air quality in the MCMA is not within acceptable levels, mainly due to high ground levels of ozone (O_3). Tropospheric O_3 is a secondary pollutant formed from the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides and sunlight. To gain a better understanding of O_3 formation in megacities, evaluate the effectiveness of already-implemented countermeasures, and identify new cost-effective alternatives to reduce tropospheric O_3 concentrations, researchers and environmental authorities require updated concentrations for a broader range of VOCs. Moreover, in an effort to protect human health and the environment, it is important to understand which VOCs exceed reference safe values or most contribute to O_3 formation, as well as to identify the most probable emission sources of those VOCs. In this work, 64 VOCs, including 36 toxic VOCs, were measured at four sites in the MCMA during 2011–2012. VOCs related to liquefied petroleum gas leakages exhibited the highest concentrations. Toxic VOCs with the highest average concentrations were acetone and ethanol. The toxic VOC benzene represented the highest risk to Mexican citizens, and toluene

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contributed the most to O_3 formation. Correlation analysis indicated that the measured VOCs come from vehicular emissions and solvent-related industrial sources.

1. Introduction

The Mexico City Metropolitan Area (MCMA) is one of the largest cities in the world, with a population of 20.4 million inhabitants. Forty years ago, the MCMA included 8.8 million residents, a value that is expected to reach 25 million by 2025 (United Nations, 2011). This rapid growth has led to serious environmental and health problems. The MCMA is located inside an air basin at a latitude of 19.5°N and is surrounded by mountain ranges on three sides (to the west, south, and east), with a broad opening in the north and a gap in the southwest (Lei et al., 2007). The topography and meteorology of this air basin make wind circulation difficult, causing frequent thermal inversions and pollutant stagnation (De Foy et al., 2008).

In 2011, the Metropolitan Air Quality Index (IMECA) exceeded acceptable levels during 241 days (Secretaria de Medio Ambiente del Distrito Federal, 2012). High ground-level ozone (O_3) concentrations, along with elevated particulate matter (PM) concentrations, are mainly responsible for the pollution issue and make the MCMA of the most polluted cities in North America (Molina et al., 2007). Exposure to ground-level O_3 is harmful to human health and causes respiratory diseases, decreasing the capability of the lungs to perform normal functions. Tropospheric O_3, black carbon, and methane are short-lived pollutants that, after CO_2, are the most important contributors to the global warming effect, with multiple harmful impacts on human health, agriculture, and ecosystems (Institute for Governance & Sustainable Development, 2013). Tropospheric O_3 is a secondary pollutant formed from the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x) and sunlight. The rate of O_3 formation varies, depending on the amount of NO_x and VOCs in the atmosphere. Under some conditions, O_3 production increases with VOCs whereas, in others, it does not change or decreases with NO_x. To formulate effective environmental policies, the relationship between VOCs and NO_x must be studied for each location (Sillman, 1999).

VOCs are emitted as gases from various daily emission sources, such as driving cars (Thornhill et al., 2010), painting buildings (Celebi and Vardar, 2008), and cooking. Some VOCs, such as isoprene and other monoterpenes, are naturally emitted into the atmosphere (Lindfors and Laurila, 2000). Other VOCs are considered to be toxic pollutants and have short- and long-term adverse effects on human health, including irritation of the mucous membranes, eyes, and throat, as well as mutagenic, carcinogenic, and teratogenic properties (Secretaría de Medio Ambiente del Distrito Federal, 2012). The formation of O_3 is influenced by the presence of NO_x in the atmosphere. By themselves, NO_x compounds are hazardous to human health, causing respiratory illnesses. NO_x ($NO + NO_2$) are emitted into the atmosphere from anthropogenic and natural sources, such as fossil fuel combustion and biomass burning (Zhang et al., 2003).

Various studies in the MCMA have found that air quality problems due to NO_x are caused by industrial sources, vehicles (Secretaria de Medio Ambiente y Recursos Naturales de México, 2010), and an inefficient public transportation system (Islas et al., 2011). In recent decades, the Mexican government has focused on reducing VOC and NO_x emissions, aiming to improve air quality in this region (Molina et al., 2007, 2009). To evaluate the effectiveness of these countermeasures, several measurement campaigns were carried out (Table 1) to determine the VOC concentrations in the MCMA over time.

Between March 1992 and March 1993, the Mexico City Air Quality Research Initiative campaign measured 25 VOCs (Streit and Guzman, 1996; Los Alamos National Laboratory, 1994). From 1992 to 2001, the MCMA campaign measured 9 VOCs during short periods of time (3–30 days) in March and November (Arriaga-Colina et al., 2004). This MCMA campaign was extended to include the measurements of 104 VOCs during February 2002 and April 2003. It also analyzed the interaction between emission patterns and meteorological parameters (Molina et al., 2007; Velasco et al., 2008). Two simultaneous campaigns were performed in March 2006: the MCMA 2006 campaign that included the analysis of 13 VOCs, and the Megacity Initiative: Local and Global Research Observations (MILAGRO) campaign that included the analysis of 50 VOCs at an urban site and 38 VOCs at a downwind site (De Foy et al., 2008; Molina et al., 2010). The MILAGRO campaign determined the sources, concentrations, and transformation processes of gases and fine particles emitted to the MCMA atmosphere by using a wide range of instruments at ground sites, on aircraft, and on satellites (Molina et al., 2010).

Since the last campaign of 2005–2006, the Mexican government has implemented several additional measures to reduce VOC emissions (Table 2). Efforts have been made to improve fuel quality, adopt cleaner technologies in automobiles, and implement programs for limiting the emission of pollutants from industries and vehicles (Molina et al., 2007, 2009). Assessment of the effectiveness of these new measures will require a new VOC measurement campaign to describe the temporospatial variations of VOCs in recent years. To assess the severity of the environmental problem, results obtained for toxic VOCs will need to be compared to reference concentrations. However, to date, VOCs have not been included in the Mexican Air Quality Standard, and a proper reference value for such comparisons has not been available. Finally, the database of VOC concentrations that is used for scientific purposes needs to be broadened and updated. A better understanding of O_3 formation in the MCMA could lead to the development of alternative approaches for reducing tropospheric O_3 concentrations and mitigating climate change due to these pollutants.

To address these needs, a new VOC measurement campaign in the MCMA was performed during 2011 and 2012. This campaign included 64 VOCs, 36 of which are toxic. This paper reports the results obtained during this campaign and estimates the O_3 formation potential (OFP) for each monitoring site. The results are compared with those of previous campaigns, with concentrations obtained for other megacities, and with reference values. Finally, probable emission sources for the measured VOCs are estimated. Conclusions reached in this work are relevant for the formulation of new, cost-effective strategies to control air pollution in megacities.

2. Materials and methods

2.1. Field campaign and sampling sites

Meteorological parameters of the MCMA are monitored by 12 automatic stations that constitute the Atmospheric Monitoring Network (REDMET). Fig. 1 shows the location of the four