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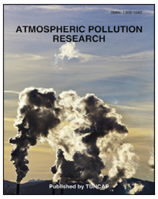

Original article

Diurnal and seasonal variation of volatile organic compounds in the atmosphere of Monterrey, Mexico

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ABSTRACT

Volatile organic compounds (VOCs) were characterized in Monterrey, the third largest city in Mexico. In total, 53 VOCs were characterized, of which 29 were analyzed. Three sampling campaigns were performed during the spring of 2011 and the spring and the fall of 2012, using 4-h time intervals from 6:00 am to 10:00 pm. Measurements were performed on the premises of a monitoring station located in downtown Monterrey. The highest concentrations were found in the fall; the two spring measurements exhibited no statistically significant differences. VOC concentrations exhibited a marked diurnal behavior with higher concentrations during the morning intervals. Solar radiation peaked during the noon interval, allowing for greater secondary pollutant production. VOCs reached their lowest levels in the 14:00–18:00 time interval. Correlation analysis found evidence of mobile sources, fugitive fuel emissions, and the use of solvents as possible sources of the majority of the compounds. Additionally, the VOC–O_3–NO_x relationship was studied. The results indicate that the atmosphere in Monterrey, Mexico is sensitive to the concentration of VOCs.

1. Introduction

The presence of volatile organic compounds (VOCs) in the environment has been studied due to their high concentration in urban areas. Anthropogenic activities emit large quantities of VOCs into the atmosphere (Carter, 1994; Atkinson, 2000; Mugica et al., 2002, 2003; Mendoza et al., 2009). For example, the use of vehicles and fuel transportation generate emissions of benzene, toluene, and other gasoline components (Franco and Pacheco, 2015); solvent use emits toluene, hexane, octane, and nonane, among others (Friedrich and Obermeier, 1999; Na et al., 2003; Mugica et al., 2003; Wöhrnschimmel et al., 2006; Mendoza et al., 2009); food production generates ethene, propene, butane, and acetylene, among others (Wöhrnschimmel et al., 2006). Trees and other small plants are also sources of VOCs. Isoprene, emitted primarily by biogenic sources (Fuentes et al., 2000), and monoterpenes are the most reactive natural VOCs in the lower atmosphere (Fuentes et al., 2000; Guenther et al., 2000).

VOCs have adverse effects on human health (WHO, 2000). For example, exposure to benzene has been linked to different types of leukemia (Lynge et al., 1997). Prolonged exposure to toluene, xylenes, trimethylbenzene, and styrenes can cause irritability, loss of appetite, nausea, and migraines (Sitting, 1991). High concentrations of VOCs cause depression of the central nervous system (Maroni et al., 1995) and inflammation of the respiratory system when inhaled (Mølhave, 1991).

The atmospheric chemistry of VOCs is complex. Their oxidation reactions are dependent on the presence of sunlight. During the day, VOCs interact with hydroxyl radicals ($^{\bullet}OH$) (Finalyson-Pitts and Pitts, 2000). At night the primary oxidizing agents are nitrogen oxides ($NO_x = NO + NO_2$). Ozone (O_3) reacts with VOCs with or without solar radiation (Finalyson-Pitts and Pitts, 2000; Albaladejo et al., 2003). During their residence time in the atmosphere, VOCs produce nitrogenized organic compounds, such as PAN (peroxyacetyl nitrate), and are precursors of oxygenated VOCs (aldehydes and ketones) (Possanzini et al., 2002). Furthermore, their oxidation

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and chain breaking aids in secondary organic aerosol formation (Watson et al., 2001; Na et al., 2003) and plays an important role in the production of atmospheric O_3 (Wöhrnschimmel et al., 2006). VOC evolution in the atmosphere depends on reactivity, reaction mechanisms, as well as the presence of solar energy and the availability of other reagents (Carter, 1994; Atkinson, 2000; Derwent et al., 2010). VOCs reactivity is referenced to the amount of O_3 produced in the atmosphere during the VOCs residence time. Alkenes and substituted aromatic compounds are the most reactive, followed by aldehydes (Derwent et al., 2010).

In Mexico, the study of VOCs in the atmosphere has been limited (Mugica et al., 2003). However, some research was conducted in Mexico City (Mugica et al., 2001, 2003; Velasco et al., 2007; Bon et al., 2011) and in the north of the country in the city of Mexicali (Mendoza et al., 2009). The Monterrey Metropolitan Area (MMA), the third most populated city in Mexico, has a wide variety of industrial complexes and a 1.89 vehicular fleet. Thus, atmospheric pollution is a serious problem; for example, the high O_3 concentrations exceeded the 0.11 ppm set by the Mexican Standard NOM-020-SSA-1993 for 31 days between January and October 2014 (SIMA, 2015). Additionally, Gonzalez-Santiago et al. (2011) identified concentration levels of $PM_{2.5}$ that were consistently higher than the 50 $\mu g/m^3$ established in the standard NOM-025-SSA1-1993, with average concentrations of up to 124 $\mu g/m^3$ in the Santa Catarina area, one of the municipalities conforming the MMA. However, no studies have been performed in Monterrey, although personnel with the Integral Environmental Monitoring System (SIMA) have planned to begin the quantification of benzene, toluene, and xylenes in the near future. Characterization and analysis of VOC concentrations is important to design and regulate strategies to reduce emissions and secondary pollutants production in the city. In addition, a decrease in VOCs will reduce the levels of particulate matter less than 2.5 μm in diameter ($PM_{2.5}$), because an important component of some particles is secondary organic carbon (Amador-Muñoz et al., 2011).

2. Methodology

2.1. Sampling site

Sampling was conducted in the city of Monterrey, Mexico, between May 2011 and April 2012. Monterrey is the capital of the state of Nuevo Leon and is located in the northeast section of the country. The MMA (Fig. 1), which includes nine municipalities, has a total surface area of 5346.80 km^2, and a population of 3.93 million people. The city center has an average altitude of 540 meters (m), and mountains, which act as natural barriers, surround the city. The MMA has a variety of industrial complexes including production of glass, steel, cement, paper, among others. Due to the large demographic explosion, there are 1.89 million vehicles.

All of the samples were collected in the central station of SIMA. The station is located in the southeastern area of the first block of Monterrey at an altitude of 556 m above sea level. Information on how the station was selected is described elsewhere (Menchaca et al., 2015).

2.2. Sampling

Samples were taken at a single point in agreement with the supersites PM monitoring system of the U. S. EPA (1999). All samples were collected at the Obispado station (center) of the SIMA of the state government in Nuevo León (Fig. 1). The station is located in the southeast section of downtown Monterrey at an altitude of 556 m above sea level with the geographical coordinates: 25° 40′ 32″ N, 100° 20′ 18″ W. Three sampling campaigns were performed; each consisted of seven non-consecutive days during a two-week period, on the following dates: May 28 to June 9, 2011; June 6–18 and October 13–25, 2012. Sampling was done in 4-h intervals from 6:00–22:00 h. In total, 28 samples were collected in each campaign.

Samples were collected using Entech (USA) SUMMA® electropolished stainless steel containers (6 L) following the United States Environmental Protection Agency (US EPA) Analytical Method TO-14 (US EPA, 1999). The air intake into the container was controlled with a Restek (USA) Veriflo® SC423XL flow regulator with an approximate flow rate of 25 ml/min.

The sampling train, consisting of a steel container and a flow controller, was assembled prior to each collection event. Leak tests were performed prior to sample collection. Once the sampling was completed, the container valves were shut and a stainless steel lid was placed on the container to prevent further intake or output. Samples were stored at ambient temperature prior to being sent to the laboratory for analysis. The containers as well as the calibrated flow regulators were provided by TestAmerica Inc. (Austin, TX, USA), and were prepared by the manufacturer following the procedures required by the TO-14 methodology (US EPA, 1999).

Meteorological data and criteria pollutant (PM_{10}, $PM_{2.5}$, O_3, NO_x, etc) for the sampling campaigns were obtained from the SIMA data records for the Obispado Station.

2.3. Analytical method

After collection, the samples were sent to the laboratory at TestAmerica, Inc. in Austin, Texas for analysis. The procedure established in the US EPA TO-14 method was followed. Prior to starting the analysis, the sample was preconcentrated using two Tenax traps that removed CO_2 and moisture. After the second trap, the sample was passed to a cryofocalizer where it was heated to 60 °C to desorb the analytes into the gas chromatograph/mass spectrometer (GC/MS) for separation and quantification. The Agilent GC/MS system (USA) is equipped a split/splitless injector with electronic pressure control to ensure gas flow through the temperature program (rises to 150 °C at 8 °C/min). The process uses software from Entech (USA). The separation was conducted in a single capillary column, 60 m long RTX-1, with an internal diameter of 0.32 mm, 1 m film thickness. Once the sample was separated, it passed into the MS for identification and quantitation. Calibration was done in accordance to the US EPA TO-14 method prior to every analysis, and calibration checks were done for each batch. The analytic laboratory reported quality assurance/quality control for every analyzed batch. The overall uncertainty of the method was 6%, and the method detection limit (mdl) was less than or equal to 0.2 ppbv for all pollutants, except for TNMOC that had a mdl of 2.6 $\mu g/m^3$.

2.4. Statistical analysis

Concentrations greater than the method detection limits were classified by season (spring and fall), by campaign (in chronological order: 1, 2, 3) and by time interval (6:00–10:00, 10:00–14:00, 14:00–18:00 and 18:00–22:00). Addinsoft XL-Stat 2013© software was used to calculate the mean, variance, and standard deviation. Additionally, a discriminant analysis was performed, using the same software, to observe differences between groups ($\alpha = 0.05$) at a tolerance of 0.0001. No validation or prediction models were used, and observations with missing data were eliminated. The dependent variable (y) was defined as the classification group, i.e., time interval, while the independent variables (x) were the data observed for each compound. The p-value of the Fisher's square distance was used to accept significant differences among the groups.