Mobile mini-DOAS measurements of the outflow of nitrogen dioxide from the Toluca Valley Metropolitan Area, Mexico

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Abstract: NO₂ outflow fluxes were calculated from the City of Toluca, Mexico during January-February 2017 using a mobile zenith viewing mini-DOAS instrument. Measurements were performed in a cross-section of the outflow plume from the Toluca Valley Metropolitan Area with an instrument operating in the visible wavelength region (356 to 510 nm). NO₂ retrievals were conducted in the 405 to 465 nm wavelength range. From these measurements, differential vertical columns of NO₂ along the measurement route were derived. Using mass-averaged wind speed and wind direction from the Weather Research & Forecasting model, with a 1 km resolution, outflow fluxes of NO₂ were calculated from each of the transect measurements. The average NO₂ outflow flux for the entire campaign was 1.81 kg/s (156.24 ton/day). To our knowledge, this is the first time that mobile mini-DOAS measurements have been conducted around the City of Toluca and therefore the first time that NO₂ outflow fluxes have been reported for this metropolitan area. Comparing our results with emissions inventories we found large variabilities of NO₂ emissions reported in emissions inventories and between emissions inventories and our measurements. From these discrepancies we infer that emissions inventories underestimate NO₂ emissions from the TVMA. This study contributes to our understanding of outflow fluxes from metropolitan areas and their possible exchange, being the Toluca Valley Metropolitan Area a few kilometers away from the Mexico City Metropolitan Area, one of the largest megacities of the world.

Keywords: nitrogen dioxide; Toluca; DOAS; emissions; atmosphere.

Introduction

The Toluca Valley Metropolitan Area (TVMA) is considered the second most important of the 56 metropolitan areas in Mexico. Despite its significance, very little research has been conducted regarding emissions and pollution in this region. Previous studies conducted at the TVMA are mainly based on studying particulate matter in the atmosphere, encompassing chemical characterizations of airborne particulate matter (Romero-Guzmán et al., 2018), the concentration of elemental carbon in suspended particles with aerodynamic diameter equal to or less than 2.5 μm (Martínez-Medina et al., 2020) and the level of contamination by heavy metals (Cu, Pb, Zn, Fe, and Mn) in urban dust (Aguilera et al., 2022). Analyses have also been conducted regarding the characterization of atmospheric and surface urban heat islands and their seasonality (Rivera et al., 2017). Studies have also explored the possibility of emission and transport of pollutants from the TVMA to the Mexico City Metropolitan Area (MCMA), specifically regarding precursors that would lead to ozone formation in the MCMA (García-Reynoso et al., 2009). In addition, Maldonado-Pacheco et al. (2021) conducted a carbon monoxide emissions inventory assessment of the TVMA using satellite and modeling data, while Borsdorff et al. (2020) studied carbon monoxide emissions of Toluca using TROPOMI observations.

Because of the lack of more detailed studies and the importance the TVMA has gained during the last decades due to its close vicinity with the MCMA, population growth, increased industrial activities and hosting an international airport with considerable cargo air transport; a field campaign was conducted during January, February and March 2017. Several research groups from the National Autonomous University of Mexico (UNAM), conducted research activities with the aim of intensively characterizing the atmospheric composition of the TVMA using different measurement strategies such as ground-based gas measurements (CO, NOₓ, O₃, SOₓ and non-methane hydrocarbons), black carbon and particulate matter (mass and chemical composition -elemental carbon, organics, ions and polycyclic aromatic hydrocarbons-), meteorological variables (solar radiation, temperature, relative humidity, wind direction and magnitude) as well as mobile-based measurements (Peralta, 2018).

In this research paper results from mobile mini-DOAS measurements of NO₂ of the outflow of the TVMA, conducted during January and February 2017, are presented. Our results were additionally compared with emissions inventories...
with the objective of validation. Mobile mini-DOAS measurements have been successfully conducted at different urban areas such as St. Petersburg (Ionov et al., 2022), Beijing (Huang et al., 2020), Montevideo (Osorio et al., 2018), and Tijuana (Rivera et al., 2015). To our knowledge, we are reporting the first mobile mini-DOAS measurements conducted in the TVMA.

Materials and Methods

Study Area

Toluca de Lerdo (19.29 N, 99.65 W, 2680 m.a.s.l.) is the capital city of the State of Mexico, with a population of approximately 820,000 inhabitants. It forms part of the TVMA, which accounts for almost two million inhabitants. The TVMA is divided into 14 municipalities: Almoloya de Juárez, Calimaya, Chapultepec, Lerma, Metepec, Mexicaltzingo, Otzolotepec, Ocoyoacac, Rayón, San Antonio la Isla, San Mateo Atenco, Toluca, Xonacatlán and Zinacantepec (Jiménez-Sánchez et al., 2016).

The TVMA has undergone important industrial and demographic growth during the last four decades, in part because it is strategically geographically located, only 60 km away from the MCMA (Castellazzi et al., 2017). Industries established at the TVMA focus on manufacturing automobiles and their components, production and distribution of beverages, food, textiles, electronics, chemicals, and pharmaceuticals. The TVMA hosts an international airport as well, located 10 km approximately from the city center to which considerable cargo air transport has been transferred from the MCMA.

Mobile-DOAS measurements

Mobile mini-DOAS instruments, described by Galle et al. (2003) are well known devices based on the Differential Optical Absorption Spectroscopy measurement technique (Platt and Stutz, 2008). Mini-DOAS instruments are typically integrated by a lightweight spectrometer coupled to a telescope that collects zenith scattered light which is led through an optical quartz fiber into the spectrometer. A Global Positioning System (GPS) receiver and the spectrometer are controlled by the Mobile-DOAS software (Zhang and Johansson, 2004) which stores the time, position as well as each measured spectrum and performs a real time preliminary evaluation of the amount of the trace gas of interest present in each measured spectrum.

Collected spectra were reevaluated using the QDOAS software (Danckaert et al., 2013). The retrieval was conducted in the 405-465 nm region and the NO (Vandaele et al., 1996), O (Bogumil et al., 2003), O(Hermans et al., 1999) and H2O (Rothman et al., 2010) cross sections were included into the fit, as well as a Ring spectrum (Chance and Spurr, 1997). An example of the DOAS fit is shown in Figure 1.

Figure 1. Example of a DOAS fit of NO2 in the wavelength region of 405-465 nm where the black line represents the measured differential optical density, and the orange line represents the result of the DOAS fit for NO2. A NO2 column density of 4.21 x1016 molecules/cm2 was obtained from this measured spectrum. The spectrum was taken on January 19th, 2017, at 13:07 Local Time.
NO$_2$ fluxes were calculated using the Mobile-DOAS software (Zhang and Johansson, 2004), according to Equation 1.

$$ F = DC \times MFC \times \left[ d \times \left( \cos \left( \text{travel angle} - \text{wind direction angle} + \frac{3\pi}{2} \right) \right) \right] \times WS \tag{1} $$

Where DC corresponds to the differential slant column density quantified from each measured spectrum, MFC is a mass conversion factor defined depending on the molecular weight of the species of interest, $d$ is the distance traveled between two measured spectra and WS is the wind speed. Wind speed and wind direction were obtained from modelling exercises conducted using the Weather Research Forecasting model (next subsection of the Materials and Methods section).

The measurement strategy for each traverse consisted of taking a dark spectrum (a spectrum without light entering the detector of the spectrometer) as well as a reference spectrum at zenith position, ideally outside of the pollutants plume originating from the urban area, followed by the measurement of several spectra, at zenith position, along the measurement path. With this strategy it is possible to quantify the outflow of the urban area (following Equation 1) when the wind direction is suitable. Each traverse took 1 to 1.5 hours approximately. Figure 2 shows an example of a traveled route along with the retrieved NO$_2$ columns at each measurement position.

![Traveled route for a measurement conducted on January 19th 2017. NO$_2$ columns are color coded, where red represents the higher and blue the lowest values (see as a reference the values presented in Figure 4).](image)

**Weather Research Forecasting Model**

Wind profiles were obtained from numerical simulations using the Advanced Research Core (ARW) of the Weather Research and Forecasting (WRF) v3.8.1 model (Skamarock et al., 2008). The simulated period corresponds to the same dates of the measurements. The configuration considers a double nested domain comprising the Toluca Valley, with a resolution of 9 km for the parent domain, 3 km for the intermediate domain and 1 km for the innermost domain with 60 vertical levels (Figure 3). The initial conditions for the WRF model were obtained from the 0.25 degrees Global Forecasting System (GFS) simulations. The sub-grid turbulence was parametrized using the MYNN2 PBL scheme (Nakanishi and Niino, 2006); radiation was calculated for all wavelengths using the RRTMG scheme (Iacono et al., 2008). Kain-Fritsch cumulus scheme was used for the big domain (Kain, 2004), with no cumulus scheme used for the nested domain. Finally, all domains use a WSM6 Microphysics scheme (Hong and J. Lim, 2006).
Emissions inventories

The basic methodology for developing emissions inventories in Mexico was developed by the National Institute of Ecology (now the National Institute of Ecology and Climate Change) and includes technical manuals that have made it possible to standardize the criteria and methods for estimating emissions. Emission inventories are composed of estimates of all pollutant emissions generated in a given area (EPA, 2001). These can come from fixed sources (such as industries), mobile sources (such as motor vehicles), and from natural sources (such as soil and vegetation).

In the case of the TVMA inventories report emissions from particulate matter ($PM_{10}$ and $PM_{2.5}$), sulfur dioxide, carbon monoxide, volatile organic compounds, ammonia and nitrogen oxides. The main nitrogen oxides reported sources correspond to mobile sources (private cars, busses -public transportation-, taxis, motorcycles and in general vehicles with a load capacity less than 3.8 tons -which also include vehicles used for transportation of goods-), point sources (such as glass production; automotive, chemical, pulp and paper, food and beverages, textile, electronic and metallic industries), domestic combustion (gas or wood), farms, railroad and airport equipment, agricultural burning as well as biogenic sources (SEMARNAT, 2016).

Results and Discussion

Mobile-DOAS NO$_2$ calculations

Mobile-DOAS measurements were conducted between January 16$^{th}$ and February 24$^{th}$, 2017. Of all measurements conducted (19 in total), 16 were considered for the analysis because of their completeness and other quality parameters such as appropriate wind direction for the TVMA NO$_2$ outflow flux measurement. Fluxes were calculated following Equation 1 and using the output from the WRF model. Wind speed and wind direction were interpolated for each measurement point (latitude and longitude) and the average wind speed and wind direction, up to the Planetary Boundary Layer (PBL) was used for flux calculation. PBL information was extracted from the WRF model results. In Table 1 all the measurements conducted during the field experiment are presented along with more details such as date, measurement interval (Local Time), PBL altitude (meters above ground level -magl-) and NO$_2$ flux in kg/s.

The average NO$_2$ flux for the entire measurement campaign was 1.81 kg/s (156.24 ton/day). An example of a measurement conducted on January 19$^{th}$, 2017, between 12:40 and 13:28 local time is shown in Figure 4. Figure 5 shows the daily calculated NO$_2$ average fluxes for all measurement days during the field campaign.
Table 1. Summary of all measurements conducted during the field experiment.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time (LT)</th>
<th>Altitude PBL (magl)</th>
<th>NO$_2$ flux (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16/01/17</td>
<td>12:32 – 13:56</td>
<td>1150</td>
<td>1.363</td>
</tr>
<tr>
<td>17/01/17</td>
<td>11:25 – 12:33</td>
<td>750</td>
<td>3.104</td>
</tr>
<tr>
<td>18/01/17</td>
<td>12:38 – 13:40</td>
<td>1000</td>
<td>2.206</td>
</tr>
<tr>
<td>18/01/17</td>
<td>13:53 – 14:32</td>
<td>1250</td>
<td>1.110</td>
</tr>
<tr>
<td>19/01/17</td>
<td>12:40 – 13:28</td>
<td>1100</td>
<td>1.850</td>
</tr>
<tr>
<td>20/01/17</td>
<td>11:45 – 12:44</td>
<td>850</td>
<td>1.277</td>
</tr>
<tr>
<td>24/01/17</td>
<td>10:25 – 11:24</td>
<td>350</td>
<td>1.670</td>
</tr>
<tr>
<td>24/01/17</td>
<td>11:25 – 12:23</td>
<td>600</td>
<td>3.088</td>
</tr>
<tr>
<td>24/01/17</td>
<td>12:25 – 13:22</td>
<td>850</td>
<td>2.106</td>
</tr>
<tr>
<td>24/01/17</td>
<td>13:34 – 14:14</td>
<td>1100</td>
<td>1.411</td>
</tr>
<tr>
<td>24/01/17</td>
<td>14:16 – 15:05</td>
<td>1200</td>
<td>1.064</td>
</tr>
<tr>
<td>17/02/17</td>
<td>8:28 – 9:25</td>
<td>450</td>
<td>1.660</td>
</tr>
<tr>
<td>17/02/17</td>
<td>9:32 – 10:04</td>
<td>800</td>
<td>1.404</td>
</tr>
<tr>
<td>23/02/17</td>
<td>11:20 – 12:03</td>
<td>950</td>
<td>1.728</td>
</tr>
<tr>
<td>23/02/17</td>
<td>12:05 – 12:59</td>
<td>1200</td>
<td>1.852</td>
</tr>
<tr>
<td>23/02/17</td>
<td>13:06 – 13:43</td>
<td>1500</td>
<td>2.041</td>
</tr>
<tr>
<td>16/01/17</td>
<td>12:32 – 13:56</td>
<td>1150</td>
<td>1.363</td>
</tr>
<tr>
<td>17/01/17</td>
<td>11:25 – 12:33</td>
<td>750</td>
<td>3.104</td>
</tr>
<tr>
<td>18/01/17</td>
<td>12:38 – 13:40</td>
<td>1000</td>
<td>2.206</td>
</tr>
</tbody>
</table>

Figure 4. Example of a NO$_2$ column measurement conducted on January 19th, 2017, between 12:40 and 13:28 local time. NO$_2$ columns (circles) along with their error (bars) are presented.

Figure 5. Daily averaged NO$_2$ fluxes calculated from all measurements conducted during the field campaign (see Table 1). Standard deviations of daily measurements are shown as vertical lines.

Comparison between Mobile-DOAS measurements and emissions inventories

Most of the emissions of pollutants released to the atmosphere in the State of Mexico come from anthropogenic sources, mainly from mobile sources (INECC, 2014). According to the Secretariat of the Environment of the State of Mexico, 81.27% of NOx emissions come from mobile sources (mainly from private cars and pick-ups), 9.99% are
released by point sources, 6.01% come from vegetation and 2.73% come from area sources (SMAEM, 2007). In Table 2 and Figure 6, we present a comparison of NOx emissions extracted from published emissions inventories as well as the results obtained in this field campaign.

Table 2. Comparison of emissions inventories and results from the field campaign conducted in the TVMA.

<table>
<thead>
<tr>
<th>Year</th>
<th>NOx emissions (tons/year)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>16949</td>
<td>SEGEM, 2005</td>
</tr>
<tr>
<td>2004</td>
<td>39983</td>
<td>GEM, 2007</td>
</tr>
<tr>
<td>2005</td>
<td>78012</td>
<td>INECC, 2005</td>
</tr>
<tr>
<td>2008</td>
<td>72768</td>
<td>INECC, 2008</td>
</tr>
<tr>
<td>2010</td>
<td>39776</td>
<td>IEECCGEM, 2014</td>
</tr>
<tr>
<td>2013</td>
<td>30576</td>
<td>INECC, 2013</td>
</tr>
<tr>
<td>2016</td>
<td>26352</td>
<td>INECC, 2016</td>
</tr>
<tr>
<td>2017</td>
<td>57028</td>
<td>This study*</td>
</tr>
</tbody>
</table>

* Reported as NO2.

There is large variability between NOx reported in emissions inventories over the years. The years when the highest emissions were reported are 2005 and 2008, while 2000 and 2016 are the years when the lowest emissions were disclosed. Comparing our measurements with emissions inventories, we deduce that emissions inventories underestimate NOx emissions.

Conclusions

To our knowledge, the work presented in this paper presents the first NO2 outflow estimate of the TVMA and contributes to our understanding of the abundance of NO2 in the atmosphere and possible transport trajectories from the TVMA to the MCMA. With our results, a comparison with current emission inventories was conducted with the objective of validation. We found large variabilities of NOx emissions reported in emissions inventories and between emissions inventories and our measurements. From these discrepancies we infer that emissions inventories underestimate NOx emissions from the TVMA. We attribute the differences found between emissions inventories and our measurements to possible gaps in reporting and some large differences within sectors. In most cases the differences can be traced down to the use of different emission factors or the employment of different methodologies.
applied to generate emissions inventories (Van Amstel et al., 1999). Differences can also be attributed to a combination of local influencing factors at the street level and different aspects introducing inaccuracies to the used emission inventories, including deficient emission factors (Macdonald et al., 2021).

Following the results obtained from this first field campaign, additional field experiments are planned in the TVMA with the objective to further contribute to this valuable information that was first obtained during this initial assessment.

Comparing NO2 emissions from the TVMA (1.81 kg/s) with other metropolitan areas in Mexico, they were found to be smaller than emissions from the MCMA (3.66-4.40 kg/s, Johansson et al., 2009), and much higher than the Tijuana metropolitan area (0.33 kg/s, Rivera et al., 2013). Relating NO2 emissions from the TVMA with other metropolitan foreign areas, they were found to be larger than Sarnia, Canada (0.44 kg/s, Davis et al., 2019) and the Mannheim/Ludwigshafen area, Germany (0.57 kg/s, Ibrahim et al., 2010). However, they were found to be smaller than Beijing, China (2.01- 2.19 kg/s, Johansson et al., 2008) and St. Petersburg, Rusia (2.44 kg/s, Ionov et al., 2022).

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Author contributions: C.I.R.-C.: writing, analysis and interpretation of data, conceptualization, provide materials, design, data collection, editing, project administration, funding acquisition; O.E.J.: writing, analysis and interpretation of data, design, data collection, editing; A.R.-A.: writing, analysis and interpretation of data, provide materials, design, data collection, editing, supervision; and J.A.: writing, analysis and interpretation of data, data collection, editing.

References


