Use of Combined Observational- and Model-Derived Photochemical Indicators to Assess the O$_3$-NOx-VOC System Sensitivity in Urban Areas

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Abstract: Tropospheric levels of O$_3$ have historically exceeded the official annual Mexican standards within the Monterrey Metropolitan Area (MMA) in NE Mexico. High-frequency and high-precision measurements of tropospheric O$_3$, NO$_y$, NO$_2$, NO, CO, SO$_2$, PM$_{10}$ and PM$_{2.5}$ were made at the Obispado monitoring site near the downtown MMA from September 2012 to August 2013. The seasonal cycles of O$_3$ and NO$_y$ are driven by changes in meteorology and to a lesser extent by variations in primary emissions. The NO$_y$ levels were positively correlated with O$_3$ precursors and inversely correlated with O$_3$ and wind speed. Recorded data were used to assess the O$_3$-Volatile Organic Compounds (VOC)-NO$_x$ system’s sensitivity through an observational-based approach. The photochemical indicator O$_3$/NO$_y$ was derived from measured data during the enhanced O$_3$ production period (12:00–18:00 Central Daylight Time (CDT), GMT-0500). The O$_3$/NO$_y$ ratios calculated for this time period showed that the O$_3$ production within the MMA is VOC sensitive. A box model simulation of production rates of HNO$_3$ ($P_{HNO3}$) and total peroxides ($P_{perox}$) carried out for O$_3$ episodes in fall and spring confirmed the VOC sensitivity within the MMA environment. No significant differences were observed in O$_3$/NO$_y$ from weekdays to weekends or for $P_{HNO3}$/P$_{perox}$ ratios, confirming the limiting role of VOCs in O$_3$ production within the MMA. The ratified photochemical regime observed may allow the environmental authorities to revise and verify the current policies for air quality control within the MMA.

Keywords: air quality; box model; NO$_y$; photochemistry; wind sector analysis

1. Introduction

Increased tropospheric levels of O$_3$ can be harmful for human health, vegetation and built infrastructure [1–3]. In the troposphere, O$_3$ is produced by photochemical reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO$_x$ = NO + NO$_2$) in a non-linear O$_3$-VOC-NO$_x$ system not fully unraveled yet [3]. Due to the non-linearity of the O$_3$-VOC-NO$_x$ system, O$_3$ production can be VOC sensitive when controlled by the input of VOCs and increase in response to increased VOC emissions, but constant NO$_x$ levels. Conversely, O$_3$ production can be NO$_x$-sensitive when NO$_x$ emissions govern the system, and O$_3$ mixing ratios increase in response to increased NO$_x$ emissions, but remain constant to variations of VOCs [4–6]. Typical VOC/NO$_x$ ratios for VOC-sensitive regimes are <4, while those for NO$_x$-sensitive regimes are >15 [5]. However, existing studies report changes in O$_3$ production during the daytime and from weekdays to weekends from VOC- to NO$_x$-sensitive regimes and vice versa within the same region as a result of changes in the emissions of precursors and meteorology [7–11]. Because the majority of existing policies to reduce the tropospheric levels of O$_3$ within urban areas focus on reducing the emissions of precursors, their success depends
strongly on untangling, with accuracy, the sensitivity of O₃ production. The sensitivity of the O₃ production system has been traditionally assessed using either photochemical box models or 3D chemistry/transport models to predict changes under different control scenarios of VOCs and NOₓ emissions or observational-based approaches (Table 1). Models are run frequently with recorded data for ambient air pollutants as input to infer the processes that govern the O₃ production. However, the accuracy of the results generated by emissions-driven models also depends on multiple assumptions in the input data (including the emission rates), which can be highly uncertain and could lead to contradictory results [5]. It has also been reported that different modeling systems applied to the same air basin can yield different results [12,13]. In addition, as exemplified in Table 1, modeling studies tend to cover short-term episodes, given the amount of resources needed to model large periods of time. Thus, an effort has to be made to choose modeling episodes that are representative of the phenomena being addressed.

| Reference | Location | Altitude (m a.s.l.) | Methodology | Chemical Species | Period | Photochemical Regime |
|-----------|----------|---------------------|-------------|------------------|--------|----------------------|
| [14]      | Baden-Württemberg and Berlin-Brandenburg, Germany; Po Valley, Italy | ~245; ~34 | Modeling | O₃, H₂O₂, HNO₃, NOₓ, VOC, and NOₓ | May 1998 | Berlin-Brandenburg and Po Valley: VOC-sensitive. Baden-Württemberg: NOₓ sensitive |
| [15]      | Seoul and Gyeonggi, Korea | 44 | Observations | NOₓ, NOᵧ, H₂O₂, O₃, CO, HCHO, and PAN * | 1 May–30 June 2004; 15 May–17 June 2004 | VOC sensitive |
| [16]      | Tokyo, Japan | 37 | Observations | NOₓ and NOᵧ and PM₁₀ | 24 July–13 August 2003; 1–15 October 2003 | NOₓ-sensitive regime during 12–14 August |
| [17]      | Beijing, China | 44 | Observations | NO, NOₓ, and NOᵧ | 1 August–9 September 2006 | VOC sensitive |
| [18]      | Pingtung, Chao-Chou, Kenting, Taiwan | ~17 | Modeling and observations | H₂O₂, HNO₃, and NOₓ | 5-day period by season during 2003–2004 | Pingtung, Chao-Chou: both regimes. Kenting: NOₓ-sensitive |
| [19]      | Monterrey, México | 540 | Modeling | O₃ and NOₓ | 22–27 August 2005 | VOC sensitive |

* Peroxyacetyl nitrate.

The observational methods to assess the O₃ production sensitivity based on datasets of robust measurements for involved species in the O₃-VOC-NOₓ system represent a feasible alternative to the traditional modeling approach. One advantage of this approach over pure modeling studies is that larger time frames (several months or more worth of data) can be used (Table 1). Some of the typical photochemical indicators used in the observational approach are hydrogen peroxide (H₂O₂) [5,18,20], nitric acid (HNO₃) [5,18,20], total odd nitrogen (NOᵧ = NO + NO₂ + peroxyacetyl nitrate (PAN) + HNO₃ + other inorganic and organic nitrates) [12,21,22] and the O₃/NOᵧ ratio [23–25]. For example, from a numerical assessment conducted for six polluted regions in the U.S., O₃/NOₓ ratios ≤ 6 and ≥8 were determined for VOC- and NOx-sensitive regimes, respectively, when mixing ratios of O₃ are >100 ppb; and O₃/NOₓ ratios ≤ 11 and ≥15 in VOC- and NOₓ-sensitive conditions, respectively, in environments of O₃ mixing ratios < 80 ppb [25]. In Southern Taiwan, two VOC-sensitive urban areas with O₃/NOₓ ratios < 6 and one NOₓ-sensitive area with O₃/NOₓ ratios > 7 were observed during 2003–2004 [18]. O₃/NOₓ average ratios of 5.1 ± 3.2 and 13.6 ± 4.7 for VOC- and partially NOₓ-sensitive O₃ production, respectively, at two sites in Valencia, Spain, were observed during 2010–2011 [26]. The observed variations in the O₃/NOₓ ratios both for VOC- and NOₓ-sensitive regimes arise from different behaviors of the indicator relative to the environmental conditions (clean, moderately polluted or highly polluted environments) [25].
The photochemical indicators that have been used arise from the analysis of the main reaction pathways of the O$_3$-VOC-NO$_x$ system. In a simplified manner, the initial steps of the oxidation of VOCs in the atmosphere can be represented by the following reactions [25]:

\[
\text{VOC} + \text{HO}^* \rightarrow \text{RO}_2^* \tag{1}
\]

(where R is a general hydrocarbons chain)

\[
\text{RO}_2^* + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2^* + \text{R}' \tag{2}
\]

(where R’ is an intermediate VOC)

\[
\text{HO}_2^* + \text{NO} \rightarrow \text{HO}^* + \text{NO}_2 \tag{3}
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3 \tag{4}
\]

\[
\text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 \tag{5}
\]

\[
\text{HO}_2^* + \text{RO}_2^* \rightarrow \text{ROOH} \tag{6}
\]

\[
\text{HO}^* + \text{NO}_2 \rightarrow \text{HNO}_3 \tag{7}
\]

O$_3$ accumulates in the atmosphere as NO is transformed to NO$_2$ (through Reaction 2) without destroying O$_3$; i.e., as the NO + O$_3$ → NO$_2$ + O$_2$ reaction becomes less relevant because of the presence of VOCs that provide a source of odd hydrogen radicals that foster other reactions. Thus, the prevalence of a given photochemical regime is driven by the chemistry of hydrogen radicals. For example, it has been shown that the chain terminating steps that involve the formation of peroxides (Reactions 5 and 6) and nitric acid (Reaction 7) compete as radical sinks, and if peroxides dominate, then a NO$_x$-sensitive condition will occur [5,25]. Similar theoretical arguments are provided to justify the use of NO$_y$ as a photochemical indicator: the split between regimes can be established from the strength of odd nitrogen sources against odd hydrogen sources. Further details can be found elsewhere [5,25].

In Mexico City, a VOC-sensitive regime was determined for most of the urban area using the O$_3$/NO$_y$, O$_3$/NO$_z$ and NO$_y$ indicators derived from tropospheric measurements made at three monitoring sites within the city [12]. In addition, a numerical simulation carried out by a 3D photochemistry/transport model was used to estimate the transition values of the indicators between regimes for a two-week period in April 2004; the transition value was ~8.1, and the average O$_3$/NO$_y$ at the studied site was 2.6. Besides Mexico City, other large metropolitan areas in the country also experience frequent O$_3$ episodes, although they have received relatively little attention. For instance, the Monterrey Metropolitan Area (MMA; Figure 1), which is the third-largest metropolitan area in Mexico, has historically experienced high levels of O$_3$, PM$_{10}$ and PM$_{2.5}$. Official reports show that within the MMA, breaches of the 1 h 110 ppb and running 8 h 80 ppb O$_3$ official Mexican standards (Norma Oficial Mexicana or NOM, in Spanish) were frequent during 2000–2013 [27].

At the Obispado monitoring site (OBI) located near the downtown area of Monterrey (Figure 1), the O$_3$ 1 h NOM was exceeded annually between two and 17 times during 2000–2013, whereas the O$_3$ running 8 h NOM was breached between four and 38 times during the same period. Furthermore, an increase in the frequency of breaches of both the O$_3$ 1 h average and the O$_3$ running 8 h average is expected due to the introduction of lower standard values of 95 and 70 ppb, respectively, applicable since October 2014. This highlights the importance of untangling the O$_3$ production sensitivity system to introduce effective emission controls, which can lead to an improvement in the air quality within the MMA. To date, only one study has recently assessed the O$_3$ production sensitivity system within the MMA [19]; a VOC-sensitive regime was observed based on numerical simulations performed with the Community Multi-scale Air Quality (CMAQ) model. However, those results come from a six-day
O3 episode during summer 2005, which may not be representative of the environmental conditions prevailing the rest of the year [19].

![Figure 1](image)

**Figure 1.** The Monterrey Metropolitan Area (MMA) in the national context in northeast Mexico and the location of the Obispado (OBI) site within the MMA. The shadowed white square surrounding the OBI site represents the 4 km × 4 km domain used for modeling purposes.

This study presents the assessment of the O3 photochemical production regime within the MMA over a one-year period carried out by combining box-modeling and observational approaches to analyze the behavior of two photochemical indicators. The photochemical indicator O3/NOy was derived from recorded data within the MMA for tropospheric air pollutants from September 2012 to August 2013, which was used to analyze the O3 production system. Ratios of the HNO3 and total peroxide production rates (P_{HNO3}/P_{perox}) were computed using a box-model and were subsequently employed to evaluate the results derived from the recorded ambient data. Additionally, the existence of a weekend effect in the O3 production within the MMA was evaluated using the O3/NOy and P_{HNO3}/P_{perox} ratios.

2. Methods

2.1. Study Site Description and Air Pollutant Monitoring

The MMA is located in northeast Mexico, some 230 km S of the United States border, and lies at an average altitude of 550 m a.s.l. (Figure 1). It is the third-most populous urban area in the country with around 5.12 million inhabitants and the second-largest industrial region [28]. The MMA also has the highest vehicle motorization index in Mexico of around 0.5 vehicles per inhabitant. Continuous measurements of typical criteria air pollutants (O3, NO, NO2, CO, SO2 and PM10) and meteorological parameters (wind speed (WS), wind direction (WD), relative humidity (RH), pressure, solar radiation (SR) and temperature) have been made since November 1992 at five monitoring sites that form part of the Integral Environmental Monitoring System (SIMA) of the Nuevo Leon Government. PM2.5 measurements began in 2003.

Additionally, NOy measurements were conducted at the OBI site from July 2012 to August 2013 using a Thermo Scientific chemiluminescence analyzer 42i-Y, in accordance with the United States Environmental Protection Agency (EPA), RFNA-1289-074. The OBI site location near the MMA...
downtown (25°40′33″ N, 100°20′18″ W; Figure 1) is ideal to record emissions from the industrial, domestic and mobile sources depending on air masses’ trajectories. Table 2 shows the instrumentation used to measure air pollutants and meteorological parameters at OBI. Calibration and maintenance procedures were carried out according to official protocols established in the Mexican standards NOM-036-SEMARNAT-1993 and NOM-156-SEMARNAT-2012.

Table 2. Instrumentation used to measure air pollutants and meteorological parameters during July 2012–August 2013 at the Obispado (OBI) site. WS, wind speed; WD, wind direction; SR, solar radiation.

| Parameter | Instrument Model | Detector | EPA Equivalent Method Number | Stated Precision (±) |
|-----------|------------------|----------|-------------------------------|-----------------------|
| O₃        | Thermo Environmental 49C | UV photometry | EQOA-0880-047 | 1 ppb |
| NO–NO₂–NOₓ | Thermo Environmental 42C | Chemiluminescence | RFNA-1289-074 | 0.4 ppb |
| NO–DIF–NOᵧ | Thermo Environmental 42 NOy | Chemiluminescence | RFNA-1289-074 | 30 ppb |
| PM₁₀      | Met One BAM 1020 | Beta attenuation | EQPM-0798-122 | 5 µg·m⁻³ |
| CO        | Thermo Environmental 48C | Non-dispersive IR | RFCA-0981-054 | 1 ppm |
| SO₂       | Thermo Environmental 43C | Fluorescence | EQSA-0486-060 | 1 ppb |
| WS        | Met One 010C | Anemometer | n.a. | 1% |
| WD        | Met One 020C | Potentiometer | n.a. | 3° |
| Temperature | Met One 060A | Multi-stage thermistor | n.a. | 0.5 °C |
| Pressure  | Met One 090D | Barometric sensor | n.a. | 1.35 mbar |
| RH        | Met One 083E | Capacitance sensor | n.a. | 2% |
| SR        | Met One 095 | Pyranometer | n.a. | 1% |

n.a.: not applicable.

2.2. Capture Rate and Seasonal and Wind Sector Analyses

Figure 2 shows the data capture of validated 1 h averages of air pollutants and meteorological data recorded at OBI from September 2012 to August 2013. Data capture for air pollutants and meteorological parameters ranged from 84.6% (SO₂) to 96.0% (CO) and from 96.0% (RH) to 98.8% (pressure), respectively. To perform seasonal analyses, 4 seasons were defined according to temperature records in the northern hemisphere: fall (September–November 2012), winter (December 2012–February 2013), spring (March–May 2013) and summer (June–August 2013). Wind-sector analyses were carried out by diving the dataset into 8 wind sectors of 45° starting from 0° ± 22.5°. The lower bound of wind each sector was established by adding 0.5° to avoid the duplication of data.

![Figure 2](image-url)

Figure 2. Data capture of 1 h averages for air pollutants and meteorological parameters recorded at the OBI site from September 2012 to August 2013.

2.3. Meteorology at the MMA

The climate at the MMA is semi-arid, with an annual average temperature of around 23 °C. Figure 3a shows that at OBI, the monthly temperature averages in summer are higher than 25 °C,
whereas temperatures in winter are typically below 20 °C. Similarly, the SR exhibits the highest monthly averages in summer and the lowest ones by late fall-early winter. The RH varies drastically during the year, with the lowest and highest averages typically observed in spring and fall, respectively. The rainfall within the MMA is frequent by late summer-early fall and scarce in the winter [29].

Figure 3b shows the frequency of the counts of WD occurrence at OBI by season from September 2012 to August 2013. Overall, the predominant WD is NE with frequencies of 34%–38% in spring and summer, respectively, although in winter, the greatest frequency of around 26% is observed for the E sector. Calm conditions (1 h averages) with a WS of less than 0.36 km·h$^{-1}$ occurred <1% of the time. A high WS (>15 km·h$^{-1}$) is typically observed in spring and summer for the E sector with frequencies > 2% of the time. By contrast, a WS < 3 km·h$^{-1}$ shows the highest frequency in winter, mostly for the W and SW sectors.

Figure 3. (a) Annual profile of the temperature, solar radiation (SR) and relative humidity (RH); (b) frequency of the counts of recorded wind direction occurrences at the OBI site during September 2012–August 2013. The horizontal black line shows monthly medians, and the red dots show monthly averages.

2.4. Statistical Analyses

To have a better understanding of the O$_3$/NO$_y$ photochemical indicator data obtained here, statistical tests were performed to analyze and interpret the observed pollutants’ dynamics. Descriptive statistics and seasonal profiles of data recorded at OBI from September 2012 to August 2013 were calculated using the openair package [30] for R software [31]. Correlations among air pollutants and meteorological data recorded were tested using a multiple linear regression analysis. A principal component analysis (PCA) was carried out to isolate the variables that govern the O$_3$ production within the MMA. The variables identified as drivers of the O$_3$ production were subject to a cluster analysis (CA) to select daytime periods of enhanced photochemical activity. O$_3$/NO$_y$ ratios calculated for the selected photochemical periods were analyzed by season, and a wind sector analysis was carried out to identify spatial variations in the photochemical processing of air masses arriving at OBI during September 2012–August 2013. Finally, the presence of a weekend effect in the diurnal production of O$_3$ was tested using an ANOVA analysis for O$_3$/NO$_y$ ratios during the enhanced photochemical activity period. Data correlations, PCA, CA and ANOVA were carried out using IBM SPSS Statistics software v.19.0 (IBM, Armonk, NY, USA) for Windows.

2.5. Box Model Description and Simulations

Ratios of the HNO$_3$ and total peroxide production rates ($P_{\text{HNOK}}/P_{\text{perox}}$) during high photochemical activity periods can be used to assess the O$_3$ production regime [25]. For example, typical VOC-sensitive
regimes exhibit $P_{HNO_3}/P_{perox}$ ratios > 2. For periods of enhanced photochemical activity within the MMA from September 2012 to August 2013, $P_{HNO_3}$ and $P_{perox}$ were calculated using the California/Carnegie Institute of Technology (CIT) 3D air quality model [32–34] in a box-model configuration [35]. Hourly-average $P_{HNO_3}/P_{perox}$ ratios were calculated from the reaction rates constants estimated by the CIT model (i.e., the SAPRC90 photochemical mechanism [36]):

$$P_x = \sum_i k_i [A_i][B_i] - \sum_j k_j [C_j][x]$$

(8)

where $P_x$ is the rate of the production of pollutant $x$ and $k_i$ and $k_j$ are the reaction rate constants for the corresponding production and consumption reactions, respectively. Thus, $\sum_i k_i [A_i][B_i]$ accounts for the production of chemical species $x$ from all relevant reactions ($[A_i]$ and $[B_i]$ are the concentrations of the corresponding reactants in the $i$-th reaction). Similarly, $\sum_j k_j [C_j][x]$ accounts for the consumption of species $x$ ($[C_j]$ is the concentration of the species that reacts with $x$ in the $j$-th reaction, and $[x]$ is the concentration of $x$).

The model domain comprised a box of 16 km$^2$, centered at the OBI site (Figure 1). The model vertical structure is analogous to that used by Young et al. [35] to account for the evolution of the mixing layer, setting the top of the domain at 3100 m a.g.l. Emissions data were obtained from the National Emissions Inventory of Mexico 2005 (NEI) [37]. Emission rates for CO, NO$_x$, VOCs, SO$_x$ and NH$_3$ were derived following the methodology reported by Mendoza and García [38] to obtain temporally-distributed and chemically-speciated emission rates. The chemical speciation profiles for NOx and VOC emissions were obtained from the U.S. EPA SPECIATE database for sources of emissions included in the NEI [39]. Meteorology inputs (temperature, humidity, WS and WD, SR and mixing layer height) were derived from 1-h average data recorded at the OBI site. SIMA 1-h averages of CO, NO, NO$_2$, O$_3$ and SO$_2$, together with 4-h average diurnal data for reactive hydrocarbons (RHCs), ketone, formaldehyde, acetaldehyde and isoprene data were used to constrain the model. The average RHC and individual VOC species data were obtained during sampling campaigns carried out within the MMA in the spring and fall of 2011 and 2012 [40,41]. Additionally, the CIT model was modified to include speciated NO$_z$ (NO$_y$–NO$_x$) data in the initial conditions, which was calculated from NO$_y$ and NO$_z$ measurements made at the OBI site. NO$_z$ was speciated using the average contributions of the 3 main species that typically form most of the NO$_z$ produced in urban centers: 55% HNO$_3$, 40% PAN and 5% nitrous acid (HONO) [42,43].

Table 3 shows the modeled periods, which were chosen because the O$_3$ levels breached the 110 ppb 1 h NOM applicable during 2012–2013. The modeled periods include weekends and weekdays in the fall and spring, when O$_3$ typically exceeds the official air quality standards.

Table 3. Selected time periods to assess the O$_3$ production sensitivity using the California/Carnegie Institute of Technology (CIT) photochemical box model.

| Period | Date             | Season |
|--------|------------------|--------|
| 1      | 1–8 September 2012 | Fall   |
| 2      | 22–29 September 2012 | Fall   |
| 3      | 6–13 March 2013   | Spring |
| 4      | 12–19 March 2013  | Spring |

3. Results and Discussion

3.1. Air Pollutants Annual Profiles

The recorded air pollutants exhibit an annual profile as a result of changes in precursor emissions and meteorology. Figure 4 shows the annual profile for O$_3$, NO$_y$, NO, NO$_2$ and CO recorded at the OBI site from September 2012 to August 2013. The O$_3$ exhibits the highest mixing ratios in spring 2013 as result of high photochemistry between NO$_x$ and VOCs and the lowest ones in winter 2012 in antiphase
with NO\textsubscript{2} as a result of the reduced SR and low temperatures (Figure 3a). A downward spike in the O\textsubscript{3} mixing ratios is observed by mid-summer 2013, which is likely caused by a high WS typical of early summer. The decrease in O\textsubscript{3} during summer causes another peak in the annual cycle, which is observed by early fall. However, frequent rainfall leads to lower monthly averages of O\textsubscript{3} during fall than those in spring. The highest mixing ratios of NO\textsubscript{y} are observed during winter as a result of the low SR and low temperature, which increase the NO\textsubscript{2} and NO build-up [23]. In contrast, the lowest mixing ratios of NO\textsubscript{y} are observed during summer due to enhanced dispersion, large mixing height depths and high photochemical activity of O\textsubscript{3} precursors.

**Figure 4.** Annual profile of air pollutants recorded at the OBI site during September 2012 to August 2013. The horizontal black line shows monthly medians, and the red dots show monthly averages.

Table 4 shows the results of linear correlation analyses between NO\textsubscript{y} and NO\textsubscript{2}, NO, O\textsubscript{3}, CO, SR, temperature and WS. A strong correlation between NO\textsubscript{2} and NO\textsubscript{y} ($R = 0.819$) is observed in winter as a result of the low photolysis rates of NO\textsubscript{2}, which suggests that NO\textsubscript{2} is the main component of NO\textsubscript{y}. Figure 5 shows the annual profiles of the NO\textsubscript{y} − NO difference and the NO\textsubscript{x}/NO\textsubscript{y} ratio. The NO\textsubscript{y} − NO difference exhibits the maxima and minima in winter and summer, respectively, which are in antiphase with the observed mixing ratios of O\textsubscript{3} from September 2012 to August 2013. In contrast, the NO\textsubscript{x}/NO\textsubscript{y} ratio exhibits the maxima by late fall-early winter and minima in early spring. The high values in the NO\textsubscript{x}/NO\textsubscript{y} ratio observed during winter confirm a build-up of NO\textsubscript{2} and NO, which implies that...
NO₂ is a low fraction of the total NOₓ due to low photochemical processing [22]. During spring, low NOₓ/NOᵧ ratios indicate an enhancement of the photochemical processing of the air masses, which could confirm the high O₃ mixing ratios observed in the season (Figure 4). The presumed high contribution of NO₂ to NOᵧ during spring could also explain the weak correlation between NOᵧ and NO₂ (R² < 0.411) and between NOᵧ and NO (R² < 0.275) (Table 4). Finally, very weak correlations between NOᵧ and O₃ (R² < 0.151) are seen during the whole year due to their antiphase annual cycle, this is underlined during spring and summer when the photo-dissociation of NO₂ to produce O₃ is enhanced [44].

Table 4. Correlation coefficients (R²) between NOᵧ and air pollutants and meteorological parameters recorded at the OBI site from September 2012 to August 2013.

| Parameter          | Fall 2012 | Winter 2012 | Spring 2013 | Summer 2013 |
|--------------------|-----------|-------------|-------------|-------------|
| O₃ (ppb)           | 0.106     | 0.151       | 0.065       | 0.070       |
| NO₂ (ppb)          | 0.676     | 0.819       | 0.411       | 0.783       |
| NO (ppb)           | 0.610     | 0.661       | 0.275       | 0.615       |
| CO (ppm)           | 0.420     | 0.664       | 0.227       | 0.712       |
| Solar radiation (kW m⁻²) | 0.001 *  | 0.004       | 0.001 *     | 0.009       |
| Temperature (°C)   | 0.024     | 0.022       | 0.005       | 0.063       |
| Wind speed (km h⁻¹) | 0.247     | 0.203       | 0.112       | 0.225       |

* No significant correlation, p > 0.05.

Figure 5. (a) Annual profile of the difference NOᵧ–NO for data recorded at the OBI site from September 2012–August 2013; (b) NOₓ/NOᵧ ratios during the same period. The horizontal black line shows monthly medians, and the red dots show monthly averages.

3.2. Wind Sector Analysis

Figure 6a shows pollution roses of the O₃ mixing ratios at OBI by WS. Overall, the mixing ratios of O₃ > 50 ppb are frequent in air masses arriving from the NE and E sectors at a WS > 5 km h⁻¹ and
an increase in frequency at a WS > 10 km·h$^{-1}$, likely due to the local transport of O$_3$ and precursors from the upwind dense industrial area [40,45]. Similar to the MMA, an increase in the O$_3$ mixing ratios caused by upwind precursor emissions was observed at the Shangdianzi site near Beijing, China [22]. In that site, it was observed that large emissions of VOCs enhance the production of O$_3$ linked with an increase in the NO$_y$ levels. Such an increase in NO$_y$ levels (>50 ppb) is also observed at OBI when the WS ranged from 1–5 km·h$^{-1}$ for all wind sectors (Figure 6b), and for a WS > 5 km·h$^{-1}$ in air masses from the N-NE-E sectors, the location of major industrial sources of NO$_x$ and VOC emissions.

In contrast, mixing ratios of O$_3$ < 25 ppb at OBI are typical during winter and show the highest frequency at a WS < 1 km·h$^{-1}$ and a reduced frequency at a WS < 5 km·h$^{-1}$ for all wind sectors, except for NE and E sectors. Similar to O$_3$, the NO$_x$ exhibits low mixing ratios (<25 ppb) at a WS > 10 km·h$^{-1}$; however, at a low WS, mixing ratios of NO$_x$ > 50 ppb are common for the SW and E sectors, which is likely due to the photochemical processing of NO$_x$ emissions from mobile sources under stagnant conditions.

![Figure 6. (a) Pollution roses of 1-h O$_3$ averages and (b) pollution roses of NO$_x$ by wind speed (WS) recorded at the OBI site from September 2012–September 2013.](image)

### 3.3. The Enhanced Photochemical Period

Photochemical indicators around the period of maximum photochemical activity for the chemical species involved in the O$_3$ production system may reflect daytime variations in photochemistry within the planetary boundary layer, and therefore, such indicators can be used to assess the photochemical regime of O$_3$ production [5,26]. For example, O$_3$/NO$_y$ ratios were estimated from data recorded in the period of 13:00–17:00 Central Daylight Time (CDT, GMT-0500) during April 2004 at a downwind receptor site of photo-chemically-aged air masses within Mexico City [12]. Likewise, O$_3$/NO$_y$ ratios from measurements made during 13:00–16:00 CET at two sampling sites in Valencia, Spain, during August 2010–May 2011 and May–October 2011 were calculated [26]. In the current study, the variables that govern the O$_3$ production within the MMA were isolated using a PCA for NO$_y$, NO$_2$, NO, O$_3$, CO, SO$_2$, PM$_{10}$, PM$_{2.5}$ and temperature, WS, WD and SR data recorded from September 2012 to August 2013.

Table 5 shows that three components designated as PC1-3 are significant, which accounted for 67.2% of the total variability. The PC1 revealed a positive correlation among the precursors of O$_3$; NO$_y$, NO$_2$, NO, CO, SO$_2$, PM$_{10}$, PM$_{2.5}$ and temperature, WS, WD and SR data recorded from September 2012 to August 2013.
NO, NO₂ and CO. The PC2 correlates positively with O₃ and SR, which is explained by the photolysis of NO₂ during the daytime. The PC3 correlates positively with WD and temperature, which comprise the effect of the air mass origin and planetary boundary layer height that influences the dispersion of O₃. Dendrograms for the O₃ and SR data recorded within the MMA (PC2) were constructed to identify the hours of enhanced photochemistry, the period of maximum O₃ production. Figure 7 shows the annual average period of enhanced O₃ production from 12:00 to 18:00 CDT and O₃ depletion from 19:00 to 11:00, respectively.

**Table 5.** Results of the PCA performed using observations for air pollutants and meteorological data recorded at the OBI site from September 2012 to August 2013.

| Component | PC1   | PC2   | PC3   |
|-----------|-------|-------|-------|
| NO₂       | 0.481 | 0.055 | −0.009|
| NO        | 0.387 | 0.067 | −0.123|
| NO₂       | 0.375 | 0.029 | 0.151 |
| O₃        | −0.226| 0.447 | 0.075 |
| CO        | 0.400 | 0.110 | 0.081 |
| SO₂       | 0.206 | 0.339 | −0.348|
| PM₁₀      | 0.230 | 0.354 | −0.062|
| PM₂₅      | 0.261 | 0.234 | 0.129 |
| SR        | −0.090| 0.497 | 0.031 |
| Temperature| −0.197| 0.370 | 0.411 |
| WS        | −0.288| 0.276 | 0.084 |
| WD        | 0.175 | 0.339 | 0.794 |
| Cumulative variance (%) | 39.5 | 59.5 | 67.2 |

**Figure 7.** Dendrogram derived from the cluster analysis (CA) performed for 1-h averages of O₃ and SR data recorded at the OBI site from September 2012 to August 2013. The red cluster shows the period of enhanced photochemical activity.

3.4. **Use of the O₃/NOy Photochemical Indicator**

The photochemical indicator O₃/NOy was derived from measurements made during the period of 12:00–18:00 CDT at OBI during September 2012–August 2013. Figure 8 shows a box plot by season for O₃/NOy ratios at OBI. Overall, the O₃/NOy ratio ranged from 0.1 in fall 2012 to 4.8 in summer 2013, while medians and averages in O₃/NOy ranged from 0.8 and from 0.9 in winter 2012 to 2.2 and to 2.3 in summer, respectively. The low O₃/NOy ratios calculated at OBI during winter result from low O₃ levels and high NOy levels, whereas the high O₃/NOy ratios during summer derive from moderate O₃ levels, but low NOy levels. The O₃/NOy ratios observed in all seasons suggest that the O₃ production within the MMA is VOC sensitive throughout the entire year. This is in good agreement with prior results of O₃ production being VOC sensitive within the MMA based on
numerically-modeled $O_3$/NO$_y$ ratios that ranged between 2.9 and when the highest 3.5 for the OBI site [19] and that are within the range of those calculated in the current study. The differences observed between the current and the referred prior results may arise from the fact that their modeled ratios were provided exclusively for 13:00 CDT and limited to a pollution episode in summer 2005.

The $O_3$/NO$_y$ ratios calculated from 12:00 to 18:00 CDT at OBI were used to construct pollution roses by WS, which are shown in Figure 9. Overall, $O_3$/NO$_y$ ratios < 2 are predominant at a WS < 5 km·h$^{-1}$ for all wind sectors and increased proportionally to WS, at a WS > 5 km·h$^{-1}$, although, this is only seen for the NE, E and SE sectors. The highest $O_3$/NO$_y$ ratios observed (>4) were recorded in air masses arriving from the easterly sectors, NE-E-SE at a WS > 5 km·h$^{-1}$, and exhibit the highest frequency in line with the highest WS observed. Low $O_3$/NO$_y$ ratios are typical in winter as result of low temperatures and low WS occurrence. A low WS may influence the formation and local transport of $O_3$ by limiting the horizontal and vertical mixing and the reactions of $O_3$ precursor emissions, which can also occur during other seasons. Moreover, at a low WS, the observed high values of NO$_x$/NO$_y$ in Figure 5 suggest a low contribution of NO$_x$ to NO$_y$, which is typical of low photochemical processing commonly seen in VOC-sensitive regimes [46]. By contrast, a high WS may enhance the photochemical processing of $O_3$ precursors and the transport of air masses travelling over rural areas located east of the MMA that typically have NO$_x$-sensitive regimes.

Figure 8. $O_3$/NO$_y$ ratios by season derived from observations made at the OBI site during September 2012–August 2013. Ratios below six are typical of VOC-sensitive regimes.

Figure 9. Pollution roses by WS of 1 h $O_3$/NO$_y$ ratios calculated between 12:00 and 18:00 Central Daylight Time (CDT, GMT-0500) at the OBI site from September 2012 to August 2013.
No weekend effect (significant differences, $p > 0.05$) was observed in the $O_3$ mixing ratios and $O_3/NO_y$ ratios between weekdays and weekends of all seasons (Table 6; Figure 10), despite the lower average $O_3/NO_y$ ratios during weekdays. This lack of a weekend effect in the $O_3$ mixing ratios and the average $O_3/NO_y$ ratios arise from the limiting role of VOCs in the weekday $O_3$ production, while reduced vehicular NOx emissions during weekends increase the VOC/NOy emission during weekends [47,48]. This decrease has counteracting effects on the $O_3$ production leading to similar $O_3$ mixing ratios ($\pm 5\%$) during weekdays and weekends, which was also reported for Mexico City between 1986 and 2007 [49]. By contrast, a weekend effect in $O_3$ levels was observed between 2007 and 2009 within the urban areas of Oporto and Lisbon in Portugal and London, which was ascribed to changes in meteorology [9]. Within the MMA, the lowest difference between weekdays and weekends in the $O_3/NO_y$ ratios is seen in winter, when the lowest $O_3/NO_y$ is also observed and contrasts with the largest difference seen in summer when the highest $O_3/NO_y$ was calculated. The higher $O_3/NO_y$ ratios observed during summer are likely due to a combination of low NOx emissions and meteorological conditions that foster the fast dispersion of air pollutants, limiting the presence of photochemically-processed air masses in the MMA [47].

![Average daily cycles for $O_3$ and NOx mixing ratios and $O_3/NOy$ ratios during weekdays and weekends from September 2012 to August 2013. The shading represents the 95% confidence intervals estimated through the bootstrap resampling.](image)

**Figure 10.** Average daily cycles for $O_3$ and NOx mixing ratios and $O_3/NOy$ ratios during weekdays and weekends from September 2012 to August 2013. The shading represents the 95% confidence intervals estimated through the bootstrap resampling.

**Table 6.** Results of the ANOVA carried out for the average $O_3/NOy$ ratios calculated between 12:00 and 18:00 CDT at the OBI site during weekdays and weekends from September 2012 to August 2013.

| Season    | Weekdays  | Weekends  |
|-----------|-----------|-----------|
| Fall 2012 | 1.31 ± 1.07 | 1.81 ± 1.45 |
| Winter 2012 | 1.17 ± 0.67 | 1.29 ± 0.85 |
| Spring 2013 | 1.41 ± 1.25 | 1.77 ± 1.08 |
| Summer 2013 | 2.13 ± 1.16 | 2.85 ± 1.65 |

*Significance level $\alpha = 0.05$.

3.5. Box Modeling

The $P_{perox}$ was calculated by summing the production rates of H$_2$O$_2$ ($P_{H2O2}$), hydroperoxides and other peroxides, although $P_{H2O2}$ represents by far the largest contribution to $P_{perox}$. The $P_{HNO3}$ was estimated from the reaction rate of the HO$^+$ + NO$_2$ → HNO$_3$ reaction. Figure 11a shows the distribution of the hourly average $P_{HNO3}/P_{perox}$ ratios calculated between 12:00 and 18:00 CDT for
each modeled period. The modeled $P_{\text{HNO}_3}/P_{\text{perox}}$ ratios are consistently $>2$ for all selected periods, which correspond to a VOC-sensitive regime and are in good agreement with the results derived from the observational approach described here. Negative values of $P_{\text{HNO}_3}/P_{\text{perox}}$ ratios account for 5.6% of the total data and are observed mostly between 12:00 and 13:00 CDT due to peroxide consumption at the beginning of the period of enhanced $O_3$ production. Figure 11b shows that the $O_3/NO_y$ ratios calculated for the whole modelling period were consistently $<6$, which confirms the VOC-sensitive regime in $O_3$ production within the MMA suggested by the $P_{\text{HNO}_3}/P_{\text{perox}}$ results.

![Figure 11](image.png)

**Figure 11.** (a) $P_{\text{HNO}_3}/P_{\text{perox}}$ ratios derived from box modeling for periods of $O_3$ mixing ratios exceeding the 110 ppb 1 h official Mexican standard in early-fall 2012 and spring 2013. Ratios greater than two, indicated by the horizontal dotted line, are typical of VOC-sensitive regimes; (b) $O_3/NO_y$ ratios derived from observations made at the OBI site during the same periods. $O_3/NO_y$ ratios lower than six are typically observed in VOC-sensitive regimes.

Additionally, to confirm the lack of a weekend effect in $O_3$ production within the MMA determined from the observational approach, an ANOVA analysis was performed to compare the modeled $P_{\text{HNO}_3}/P_{\text{perox}}$ and $O_3/NO_y$ ratios for weekdays and weekends of the modeled periods. Table 7 shows that no significant differences ($p > 0.05$) are observed between the average $P_{\text{HNO}_3}/P_{\text{perox}}$ ratios during weekdays and weekends and between the average $O_3/NO_y$ ratios during weekdays and weekends as shown in Table 6, which confirms the limiting role of VOC in production within the MMA.

**Table 7.** Results of the ANOVA performed for the averages of modeled $P_{\text{HNO}_3}/P_{\text{perox}}$ ratios and $O_3/NO_y$ ratios between 12:00 and 18:00 CDT at the OBI site during the weekdays and weekends of September 2012 and March 2013.

| Period   | $P_{\text{HNO}_3}/P_{\text{perox}}$ * | $O_3/NO_y$ * |
|----------|-------------------------------------|--------------|
| Weekdays | $13.14 \pm 21.59$                   | $1.33 \pm 0.78$ |
| Weekends | $14.38 \pm 19.52$                   | $2.01 \pm 0.95$ |

* Significance level $\alpha = 0.05$. 

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The $O_3$ sensitivity results presented here are relevant in the context of new energy-oriented projects that are under development in the northeast of Mexico, some of them located east of the MMA. Such projects include new natural gas combined-cycle power plants that are projected to start operations by late 2016, which could have an accumulated installed capacity of up to +1.3 GW. Currently, electric utilities already installed east of the MMA add up to a total capacity of +2.1 GW, all of those being natural gas combined-cycle plants. The new facilities are projected to be supplied with natural gas imported from Texas and with shale gas expected to be exploited from the Cuenca de Burgos Basin that is also located east of the MMA. The Burgos Basin represents around two-thirds of the estimated 550 trillion cubic feet of shale gas recoverable in Mexico, which is the sixth largest reservoir in the world [50]. The introduction of shale gas extraction and energy production will likely increase the regional emissions of VOCs and NO$_x$, impacting the photochemistry of the MMA airshed during events of enhanced regional transport [51]. Increasing NO$_x$ levels upwind of the MMA could foster higher $O_3$ levels.

Finally, from the perspective of control strategies that could be put into place to help alleviate the air pollution problem that the MMA faces, it is relevant to match the results obtained here with the local emissions inventory. According to the latest comprehensive official inventory published for the MMA [37], 47% of the VOC emissions come from mobile sources and 43% from area sources; only 8% come from point sources. In contrast, the contribution of NO$_x$ emissions is led by mobile (48%) and point (33%) sources. From a mass-basis perspective, one could argue that control strategies should target VOC emissions from mobile sources, in particular light-duty vehicles, which account for more than 70% of these emissions, and area sources. For the latter, the main contributions are from domestic use of solvents (34%), surface cleaning (13%), liquefied petroleum gas (LPG) leaks (16%), building painting activities (9%), industrial painting processes (9%) and fugitive emissions from gasoline distribution and handling in service stations (9%). However, it has to be recognize that the composition of these VOC mixtures changes from source to source, making their ozone-forming potential different. Further studies are needed to compare the reactivity of these mixtures to establish the real benefits of reducing the emissions of one source or another. If NO$_x$ emission control strategies are explored, these should be accompanied with VOC control strategies to ensure $O_3$ reductions [19].

4. Conclusions

Continuous measurements of tropospheric $O_3$ and NO$_y$ were made at the OBI site near the downtown MMA and used to assess the sensitivity of the $O_3$ production system from September 2012 to August 2013. Within the MMA, $O_3$ exhibits maxima in spring in response to the enhanced photolysis of NO$_2$, whereas the minima are observed in winter due to the reduced SR. The highest mixing ratios of $O_3$ were observed in easterly air masses at a WS of 5–10 km·h$^{-1}$, and the lowest ones were recorded in calm winds throughout the entire year. The NO$_y$ peaks during winter and decreases during summer, which suggests that during summer, the photochemical production is oriented to $O_3$ rather than to NO$_y$. During winter, the recorded data revealed that NO and NO$_2$ are the major components of NO$_y$. The $O_3$ production is enhanced between 12:00 and 18:00 CDT in line with the period of maximum SR. $O_3$/NO$_y$ ratios $<$ 6 were observed during the year studied, suggesting that $O_3$ production within the MMA is VOC sensitive. Modeled $P_{HNO_3}/P_{perox}$ ratios $>$ 2 for periods of $O_3$ episodes in fall and spring confirm the VOC-sensitive environment within the MMA derived from the observational analysis performed. The non-significant differences observed in $O_3$/NO$_y$ and in $P_{HNO_3}/P_{perox}$ between weekdays and weekends suggest the lack of a weekend effect in $O_3$ production. The lack of an $O_3$ weekend effect within the MMA confirms the limiting role of VOCs in $O_3$ production during weekdays. This study demonstrates the usefulness of high-precision measurements of $O_3$ and NO$_y$ to assess the $O_3$-VOC-NO$_x$ system’s sensitivity and to independently test the accuracy of box chemical models. The results presented here allow the wholly independent validation of current air quality policies directed to reduce tropospheric $O_3$ levels and, if required, the design and implementation of new ones.
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