Air Pollution in Mexico City

Aodhan Sweeney

March 8th, 2021

1 Introduction

Within the past 50 years, Mexico City Metropolitan Area (MCMA) has seen its population double to over 21 million people. This increased population has lead to an inflated vehicle fleet with under regulated emission standards, as well as a large need for energy production culminating in Mexico City's designation by the UN as the worlds most polluted city in 1992 (Mage et al. (1996)). Since then efforts to reduce pollution have been relatively successful but in recent years have stagnated with due to improving standards of living and a continued population growth. One particular pollutant of concern is ozone (O_3), which after initially decreasing, concentrations has leveled off higher than recommended by the WHO (Velasco and Retama (2017)).

In the 1980s air pollution in the MCMA was identified as a major risk to public health and the environment. As a response to this, the Red Automática de Monitoreo Atmosférico (RAMA) (or the automatic atmospheric monitoring network) was established to collect data on major pollutants of concern in the MCMA. The implementation of RAMA uncovered high concentrations of all criteria pollutants: lead, carbon monoxide, nitrogen dioxide, sulphur dioxide, ozone and particulate matter. One of the highest concentrations of pollutants was ozone which exceeded air quality standards over 90% of days and had peaks over 300 ppb 40 days a year, ranking as some of the worst ozone pollution in the world (Molina et al. (2009)).

In order to address these high levels of pollutants the Mexican government restricted lead from gasoline, ordered the use of catalytic converters on newer fleets of cars, as well as more frequent vehicle inspections (Molina et al. (2009)). One of the most well known

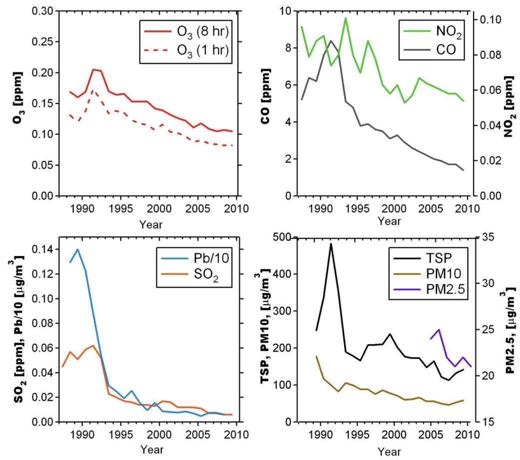

Figure 1: Air quality trends of the MCMA. Plots show the concentrations estimated as the average of the 5th annual maximum from RAMA stations with valid data for a given year for the following criteria pollutants: O3, NO2, CO, SO2, Pb (divided by 10), TSP (Total Suspended Particles), PM10 and PM2.5. From Molina et. al., 2010

rules is the "hoy no circula" rule, which prohibits personal vehicles from traveling in the state of Mexico on alternating days of the week based on licence plate numbers. Although regulations in recent decades have undoubtedly helped alleviate much of the air pollution in the MCMA region, these rules have also been met with criticism for unequally burdening Mexicans who cannot afford to buy a new car, while wealthier citizens have the option of buying a second car in order to get around the "hoy no circula" rule. Further, emissions testing has been shown to be vulnerable to corruption, with at least 80% of testing garages accepting bribes to pass emission tests according to evidence provided to the Mexican Supreme Court (Oliva (2015)).

Figure 1 shows the marked decrease of many pollutants after regulation. The sharp decrease in lead, carbon monoxide, and sulfur dioxide show progress as a result of the new government regulations. Of particular concern are those pollutants whose concentrations are still high, namely ozone (Molina et al. (2010)).

Mexico city's local meteorology worsens the air quality substantially. This is especially true in the winter and spring seasons with strong atmospheric inversions capping pollutants and proximity to the subtropical high inhibiting dispersion. On top of this, central Mexico has a latitude of about 19N and thus does not receive the synoptic forcing required to move pollutants out of the city (Molina et al. (2009)).

In this report, we will focus initially on Mexico City's photochemical pollution. We will then look at the influence of geography, local meteorology, and climate in creating the MCMA air pollution problem. Finally we will take a deep dive into ozone production provided by the RAMA station data.

2 Mexico City Air Pollution

Air pollution is one of the leading causes of death for Mexicans in the MCMA Murray (2020). Over the past thirty years, primary pollutants like Carbon Monoxide (CO) and sulfur dioxide (SO_2) have largely decreased from enhanced regulation and restrictions on driving (Vallejo M (2003)). Nitric Oxide and Nitrogen Dioxide (NO and NO_2 respectively) are directly emitted to the atmosphere during the early morning and late afternoon rush hours from vehicle exhaust. These NOx compounds are then exposed to high amounts of ultraviolet radiation and undergo a series of chemical reactions with hydrocarbons to produce photochemical smog, a combination of ozone (O_3), nitric acid, aldehydes, peroxyacl nitrates (PAN) and other secondary pollutants (G. Tyler Miller and Hackett (2011)). This smog is also associated with high amounts of atmospheric aerosols which efficiently scatter light producing a blanket of reduced visibility over the MCMA. In figure 2 we see an example of this smog over the MCMA region on March 3rd, 2021. In this figure, the angle of solar incidence allows for greater scattering of sunlight off of the smog at 9am. When the sun is setting, we can see volcanos that were completely shrouded during the day time because of the smog (7pm).

One of these secondary pollutants is 0_3 which over the past decade have remained relatively constant (as shown in figure 1) despite efforts to reduce its production (Velasco and Retama (2017)). Tropospheric O_3 is harmful to both plants and animals because it can oxide organic tissue JACOB (1999). Because of tropospheric ozone's presence as a pollutant in the MCMA region and because of its difficulty in reduction, we pay close attention to tropospheric ozone formation in the MCMA region.

Tropospheric ozone is created in the MCMA as a product of reactions involving various reactive hydrocarbons and NO_2 following figure 3. In the creation of tropospheric

Figure 2: Smog over MCMA region looking west at 7pm and 9pm local time.

ozone, organic peroxy and oxy radicals (RO_2 and RO) propagate the reaction and are thus considered part of the HOx family.

The chain is initiated by the production of OH from photolysis of an initial ozone molecule and then reaction of the produced $O(^1D)$ with H_2O to produce $2OH$. Propagation of the cycle is now carried by the reactions between OH and the hydrocarbons following equation 1.

$$\mathrm{RH} + \mathrm{OH} \xrightarrow{\mathrm{O_2}} \mathrm{RO_2} + \mathrm{H_2O} \tag{1}$$

This RO_2 then reacts with NO to form NO_2 and oxy radical RO. The NO_2 now can photolyze and produce O_3. Another production pathway for O_3 comes from the RO radical. One typical pathway for its production of NO_2 is through equations 2, and 3.

$$\mathrm{RO} + \mathrm{O_2} \longrightarrow \mathrm{RCHO} + \mathrm{HO_2} \tag{2}$$

$$\mathrm{HO_2} + \mathrm{NO} \longrightarrow \mathrm{OH} + \mathrm{NO_2} \tag{3}$$

The net reaction for equations 1 through 3 is then equation 4. We see that the initiation

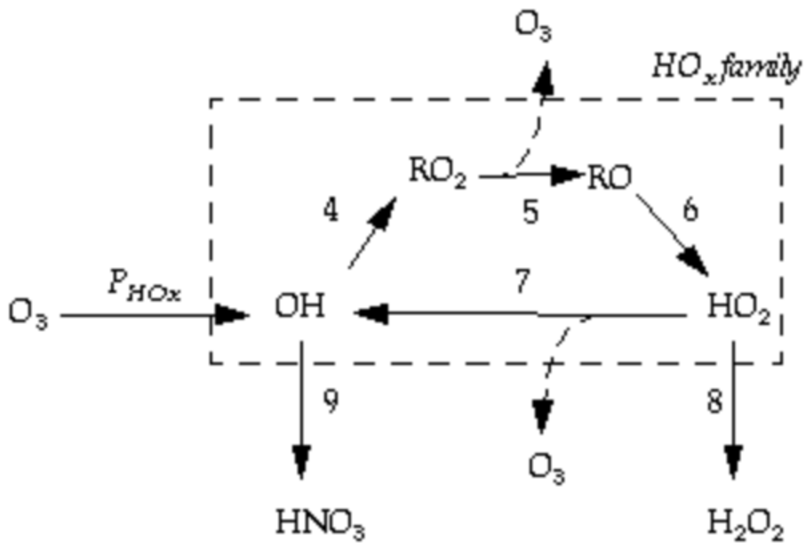

Figure 3: HO_x family cycling of O_3 contributing to tropospheric ozone production.

of the chain with one O_3 yields $2\,O_3$ after each cycle JACOB (1999).

$$RH + 4\,O_2 \longrightarrow RCHO + 2\,O_3 + H_2O \tag{4}$$

The chain is terminated through the loss of HOx radicals. In a situation with little NOx the peroxy radicals may react with themselves instead of with NO to produce peroxides and other oxygenated compounds (as depicted by reaction 8 in figure 3) JACOB (1999). In the case of high NOx concetrations, the primary HOx sink is the oxidation of NO2 by OH (shown as reaction 9 in figure 3).

Various studies have looked into the production of ozone in the MCMA region, attempting to uncover why tropospheric ozone levels have not fallen off as sharply as other pollutants (Molina et al. (2010)) (Velasco and Retama (2017)). Ozone formation is non-linear and therefore characterizing its control is difficult (Velasco and Retama (2017)), (Ryerson et al. (2001)). Studies have found that the city is largely a VOC limited regime (meaning production of ozone is determined by the amount of VOCs present) where as the surrounding metropolitan area is more of a NOx limited regime. This means that policies attempting to limit ozone production would be more effective if they focused on VOC emissions as opposed to reducing NOx (Velasco and Retama (2017)).

Sources of VOCs can be either anthropogenic or natural. In the MCMA, anthropogenic sources of VOCs are more important to the production of ozone. Garzon et. al. 2015 showed that the most important VOC for ozone production in the Mexico City region was Toluene, even compared to other VOCs with higher concentrations like propane (Garzón et al. (2015)). Toulene can be produced from industrial emissions, car exhaust, and paint products (Garzón et al. (2015)).

In the next section we will look at the meteorological conditions that contribute to Mexico City's air pollution.

3 Meteorology of Mexico City

Mexico city has a temperate subtropical climate with three distinct seasons: the cold dry season (Oct - Feb), the warm dry season (Mar - May), and the wet season (Jun - Sep) (Molina et al. (2009)). Diurnal variations in temperature are largest in the warm dry season where little cloud cover and low humidity allow for efficient radiative cooling at night. The wet season has large convective storms which work to cleanse the air and rids the lower atmosphere of pollution through precipitation and high winds. This leads to the worst air pollution of the MCMA in the hot dry season.

Mexico city is a high altitude city with mean height of 2240m above sea level. It is surrounded by mountains to the east, west, and south with a small gap in topography to the north figure 4. This high elevation and reduced oxygen levels constrict proper burning of fuel in cars and industry and as a result emit more hydrocarbons and Carbon Monoxide EPA (1978).

One of the most problematic characteristics of the meteorology of the MCMA is the frequent thermal inversions (Molina et al. (2009)). These inversions frequently form in the cold dry/warm dry seasons. These thermal inversions occur frequently at night and are thought to be a result of a combination of the efficient radiative cooling the low levels, and mountain valley winds (Molina et al. (2009)).

During the dry seasons when air pollutants are worst, the diurnal cycle of flow can be characterized as in figure 5. This flow can be described in three ways following (Edgerton

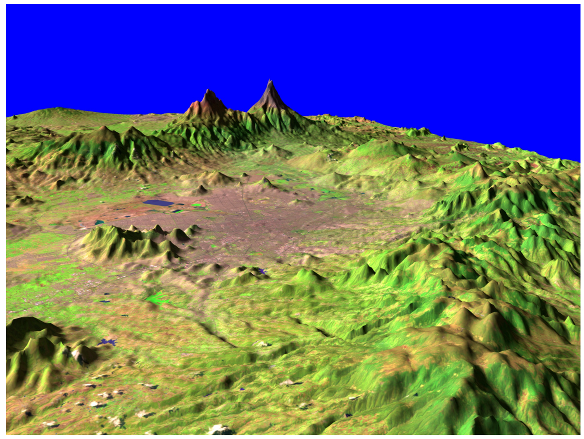

Figure 4: Exaggerated topographic map of the MCMA provided by NASA. The largest mountains (situated to the south/south east are the same as seen in 2. A small gap for flow is situated to the north of the city.

et al. (1999)): Early Morning: Cooled air masses air sink along the slopes of the mountain chains and slide underneath the cold polluted air in MCMA. The boundary layer is low. Noon: The boundary layer grows from insolation. The height of the now mixed boundary layer sucks fresh air from the northern boundary into the MCMA. Late Afternoon: Synoptic flow of the upper troposphere is capable of sweeping out some air. This air is moving northward from tropics. This happens as the heated lower level air mixes vertically, helping to flush out the heavily polluted low levels (Edgerton et al. (1999)). If a strong thermal inversion exists throughout the day much of this mixing is prohibited (Edgerton et al. (1999)).

4 Invesitgation of Ozone in Mexico City with RAMA Data

As a result of high pollution levels in the late 20th century, the mexican government established a air quality monitoring network throughout Mexcio City and the subsequent region. This network, called the Red Automática de Monitoreo Atmosférico (Automatic Atmospheric Monitoring Network) aka RAMA, has taken hourly data at 32 different locations throughout the MCMA. Data is available here: `http://www.aire.cdmx.gob.mx/`.

Armed with the record from RAMA, we pay special attention to Ozone pollution in

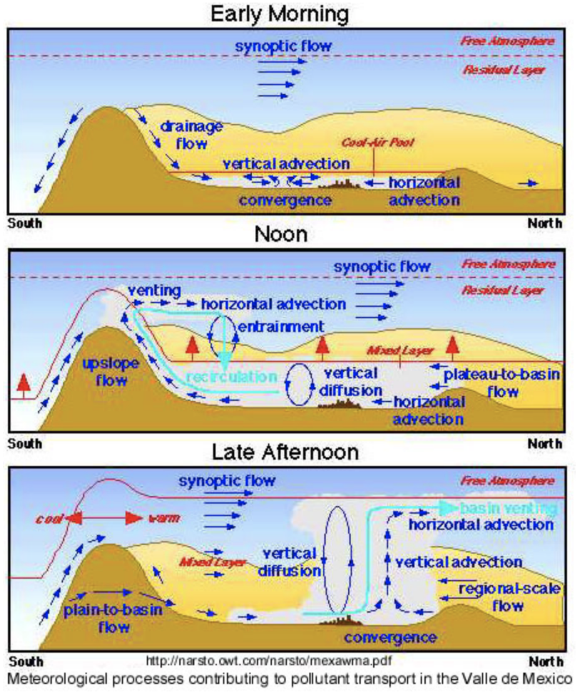

Figure 5:

Mexico City and develop four science questions to test using the RAMA network data:

- Can we reproduce the diurnal and annual cycles of O_3 in the MCMA using RAMA?
- Can we reproduce the long term trend of ozone production in literature using RAMA?
- Has the COVID-19 lockdown affected O_3 production in the MCMA?
- What controls interannual variability of ozone production in the MCMA?

4.1 Diurnal and Annual Cycles of O_3 in the MCMA

O_3 concentrations are dependent on sunlight, precipitation, and presence of precursor gases (VOCs and NO_2). Because of this, there is good reason to believe assume that O_3 has a distinct diurnal and seasonal cycle, and are frequently referenced in the literature (Velasco and Retama (2017)). Here we use RAMA data from 2019, averaged by local time hour over each season, to reproduce these cycles and provide insight into the unique peaks of both O_3 production and one of its precursors NO_2 figure 6.

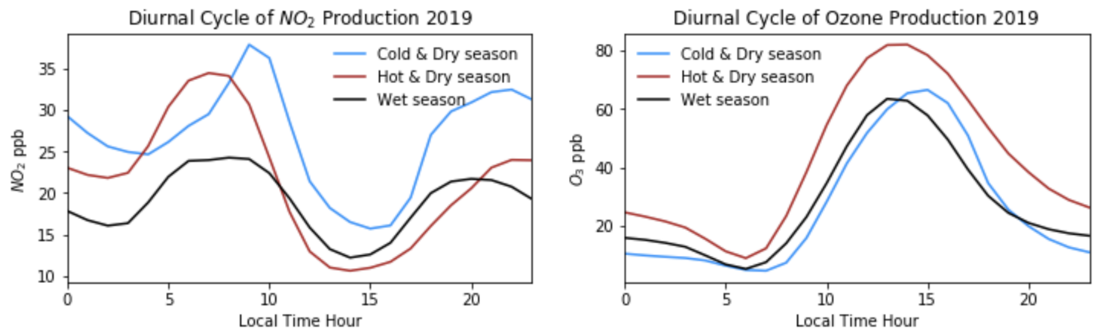

Figure 6: Diurnal cycles from each season of 2019 for both NO_2 (left) and O_3 (right).

In figure 6 we see a wave 2 structure in NO_2 production in all seasons. This wave 2 structure likely comes from an early morning and mid/late afternoon peak in vehicle emissions which is the primary source of NO_2 in the MCMA. Ozone, whose creation is dependent on sunlight (as well as NO_2 and VOCs) has a mid day peak associated with high amounts of solar radiation.

Seasonality is split into the wet season (Jun-Sep), cold dry season (Oct-Feb), and warm dry season (Mar-May). The wet season has the lowest peak amounts of both O_3 and NO_2. This is probably due to efficient cleansing of air by precipitation and strong winds associated with it. Ozone sees its largest concentrations in the Hot & Dry season due to low amounts of precipitation and sufficient solar radiation, compared with the Cold & Dry season which has less insolation. The high production of O_3 in the Hot & Dry season is associated with lower amounts of NO_2 due to NO_2s destruction as a result of O_3 production.

4.2 Long Term Trend of O_3

Long term trends of O_3 in the MCMA are closely monitored in order to evaluate the effectiveness in policy, and to evaluate health risks. Timeseries of O_3 in the MCMA are saturated in the literature and provided in figure 1. Here we try and recreate this timeseries using an adapted definition of ozone concentration with the RAMA data. Here, we find monthly average diurnal cycles in O_3 averaged over all RAMA stations from 1986 to 2019. We then show the long term trend in both the max and mean of the monthly averaged diurnal cycles 7.

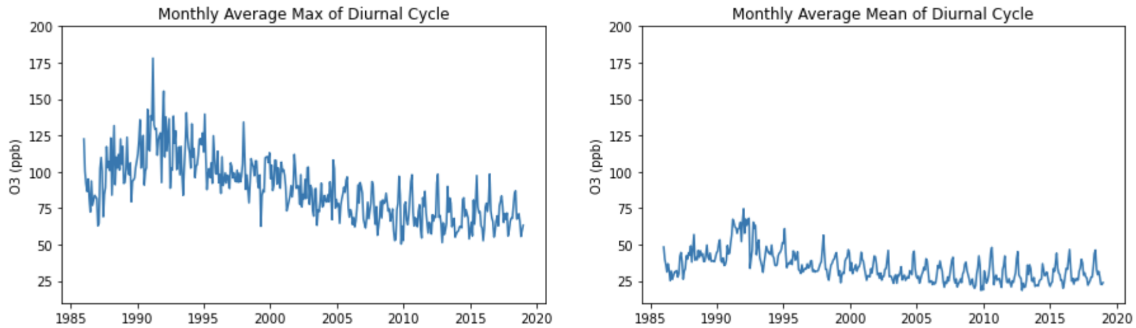

Figure 7: Long term trend of both max and mean of monthly averaged diurnal cycles of O_3.

Figure 7 shows a peak in both max and mean monthly averaged diurnal cycles over the MCMA in the early 1990s. This largely confirms data presented in 1. Diurnal maxes are significantly larger than diurnal means pointing to the importance of the diurnal cycle in explaining O_3 variability in the MCMA. Concentrations steeply increase and reach their peak before policy engagements discussed in the introduction, we then see the concentration trend stagnate in the 21st century.

4.3 Effects of COVID-19 Lockdowns O_3 in the MCMA

Here we show a comparison of the average diurnal cycles over the Hot & Dry seasons (Mar-May) of 2019 and 2020. Lockdowns in Mexico City were initiated at nearly the same time as those in the USA (march/april). We presume that lockdowns discouraged travel and vehicle emissions would be lower, thus meaning lower NO_2 and O_3 concentrations. Results are plotted in figure 8.

NO_2 shows a marked reduction in peak diurnal emissions from 2019 to 2020 as expected due to less vehicle usage. Unfortunately, this decrease is not observed in O_3 production whatsoever. This is likely due to the fact that some authors have found that the MCMA is a VOC limited regime for O_3 production (Velasco and Retama (2017)). Essentially, even though MCMA saw large reductions in NO_2 emissions during the lockdown, O_3 production matched its pre-lockdown levels because there were still sufficient VOCs in the MCMA region.

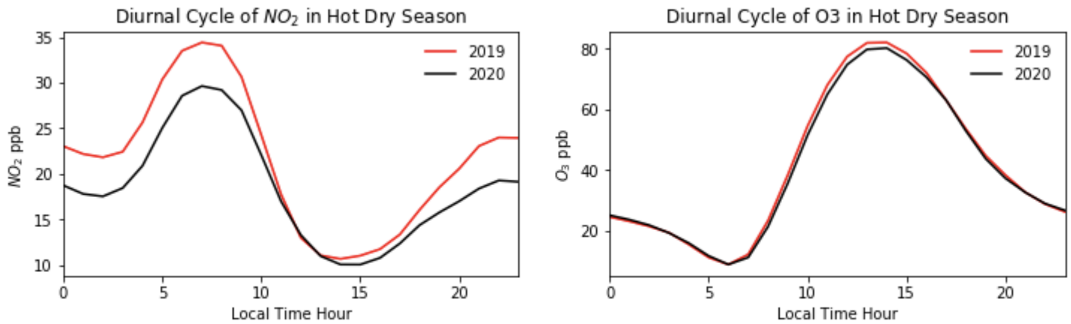

Figure 8: Diurnal cycles of O_3 and NO_2 measured by RAMA in 2019 vs 2020.

4.4 Interannual Variability of O_3 in the MCMA

Given the opportunity to investigate Ozone levels in the MCMA region back to 1986, we are equipped to ask questions about the interannual variability of ozone in the MCMA. As previously stated, tropospheric ozone in the MCMA is a product of reactions involving NO_2 and VOCs in the presence of sunlight. Thus, we expect the largest causes of interannual variability to be those that limit these necessary ingredients. It is no surprise that the largest control on interannual variability in the MCMA is policy, evident in figure 7 and by other authors in figure 1.

Higher order effects may effect the amount of sunlight or local meteorology of the MCMA. Sunlight can be moderated by cloud cover, and local meteorological changes could manifest themselves as changes in precipitation and associated winds. Other authors have found impacts of the El Nino teleconnections over the MCMA region in precipitation and solar intensity as a result of decreased cloud cover (Velasco and Retama (2017)), (Bravo Cabrera (2018)).

Here, we compare a 1-month time lagged ENSO 3.4 index to the detrended diurnal maxima, and diurnal mean ozone levels in the MCMA region from 1999-2019. Trend removal is done by using a harmonic decomposition of the 1986-2019 timeseries and removing the first two harmonics, analogous to a high pass filter. Because of the large signal resulting from policy changes in the late 1980s and 1990s, we only use detrended data from 1999-2019. We then remove the seasonal cycle in order to compare anomalies to the ENSO 3.4 timeseries. Results are plotted in figure 9 and 10.

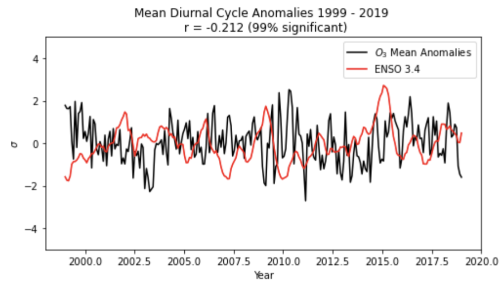

Figure 9: ENSO 3.4 and mean of O_3 diurnal cycle anomalies from 1999-2019.

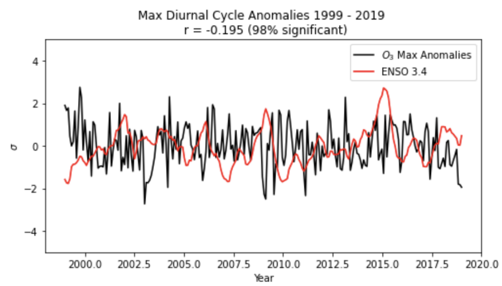

Figure 10: ENSO 3.4 and max of O_3 diurnal cycle anomalies from 1999-2019.

We see that the correlations are almost negligibly small between ENSO and O_3, although results are significant above the 95%.

5 Conclusion

Mexico City is currently the second largest city in the Americas. Its rapid industrialization has lead to dangerous amounts of ambient pollutants, and poses severe health risks to the population. Both explosions in population and in the vehicle fleet of the MCMA have exhasterbated the problem, which is further worsened because of the high altitude, semi-arid climate. Of particular concern is O_3 which has seen a stagnation of pollutant levels in the past 20 years. Using station data from the MCMA provided by the mexican government, we saw the impacts of NO_2 production on O_3 and investigated the seasonal and diurnal cycle of O_3 in the region. The impact of the COVID-19 lock down was found to be negligible in the region despite large reductions in NO_2, corroborating previous studies claims that the MCMA is a VOC limited regime. A final investigation of the interannual variability of O_3

in the MCMA found that ENSO has a very small but robust correlation with the amount of O_3 in the region. The correlation is potentially a result of changes in cloud cover and precipitation associated with ENSO found by other authors, but specifics were not looked into in this study.

References

Bravo Cabrera, J., A. R. E. R. G. F. . R. L. O. (2018). Los efectos del enos sobre la precipitación en la ciudad de méxico. *Investigaciones Geográficas*, 97.

Edgerton, S., X. Bian, J. Doran, J. Fast, J. Hubbe, E. Malone, W. Shaw, C. Whiteman, S. Zhong, J. Arriaga, E. Ortiz, M. Ruiz, G. Sosa Iglesias, E. Vega, T. Limon, F. Guzman, J. Archuleta, J. Bossert, S. Elliot, and R. Petty (1999, 10). Particulate air pollution in mexico city: A collaborative research project. *Journal of the Air Waste Management Association 49*, 1221–1229.

EPA, U. E. P. A. (1978). U.s. epa. altitude as a factor in air pollution. *EPA 600*, 9–78.

G. Tyler Miller, J. and D. Hackett (2011). *Living in the Environment, 2nd ed.* Nelson.

Garzón, J. P., J. I. Huertas, M. Magaña, M. E. Huertas, B. Cárdenas, T. Watanabe, T. Maeda, S. Wakamatsu, and S. Blanco (2015). Volatile organic compounds in the atmosphere of mexico city. *Atmospheric Environment 119*, 415–429.

JACOB, D. J. (1999). *Introduction to Atmospheric Chemistry.* Princeton University Press.

Mage, D., G. Ozolins, P. Peterson, A. Webster, R. Orthofer, V. Vandeweerd, and M. Gwynne (1996). Urban air pollution in megacities of the world. *Atmospheric Environment 30*(5), 681–686. Supercities: Environment Quality and Sustainable Development.

Molina, L., B. de Foy, O. Vazquez-Martinez, and V.-H. Páramo (2009, 01). Air quality, weather and climate in mexico city. *58*, 48–53.

Molina, L. T., S. Madronich, J. S. Gaffney, E. Apel, B. de Foy, J. Fast, R. Ferrare, S. Herndon, J. L. Jimenez, B. Lamb, A. R. Osornio-Vargas, P. Russell, J. J. Schauer, P. S. Stevens, R. Volkamer, and M. Zavala (2010). An overview of the milagro 2006 campaign: Mexico city emissions and their transport and transformation. *Atmospheric Chemistry and Physics 10*(18), 8697–8760.

Murray, C. J. L. e. a. (2020). Global burden of 87 risk factors in 204 countries and territories, 1990–2019: a systematic analysis for the global burden of disease study 2019. *The Lancet 396*(10258), 1223 – 1249.

Oliva, P. (2015). Environmental regulations and corruption: Automobile emissions in mexico city. *Journal of Political Economy 123*(3), 686–724.

Ryerson, T. B., M. Trainer, J. S. Holloway, D. D. Parrish, L. G. Huey, D. T. Sueper, G. J. Frost, S. G. Donnelly, S. Schauffler, E. L. Atlas, W. C. Kuster, P. D. Goldan, G. Hübler, J. F. Meagher, and F. C. Fehsenfeld (2001). Observations of ozone formation in power plant plumes and implications for ozone control strategies. *Science 292*(5517), 719–723.

Vallejo M, Jáuregui-Renaud K, H. A. e. a. (2003). Efectos de la contaminación atmosférica en la salud y su importancia en la ciudad de méxico. *Gac Med Mex 139*, 57–63.

Velasco, E. and A. Retama (2017). Ozone's threat hits back mexico city. *Sustainable Cities and Society 31*, 260–263.