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The Clean Air Act and Its Impact on Ground Level Ozone Pollution Levels in Los Angeles, California

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The Clean Air Act and Its Impact on Ground Level Ozone Pollution Levels in Los Angeles, California

By

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Marine Science

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Abstract

Ozone (O_3) occurs naturally as a protective, ultraviolet radiation-shielding “Ozone Layer” in the Stratosphere and as a photochemically produced pollutant in the Troposphere. The Clean Air Act (CAA) of 1970 regulates the emission and concentration of O_3 and five other atmospheric pollutants. Since the signing of the CAA, the ongoing question has been whether or not the National Ambient Air Quality Standards (NAAQS) and regulatory policies have had an effect on decreasing O_3 concentration. The Los Angeles metropolitan area is a prime example of how O_3 can be a public health hazard, and taint a city’s aesthetics and quality of life through photochemical smog. I chose LA for this study in attempt to contribute to the conversation regarding the effectiveness of the CAA. I explored daily maximum O_3 concentrations from 1980 to the present of three air quality monitoring stations in metropolitan LA from the AirData database of the U.S. Environmental Protection Agency. Various statistical metrics of this dataset were compared to the established NAAQS during this period. The NAAQS themselves were only exceeded twice at one station throughout the data available. While the average O_3 concentrations have been well below the NAAQS during this period, they have remained relatively constant. In contrast, variance about these averages have been steadily declining. It can be concluded that the CAA has had a positive impact on O_3 concentration from this more controlled, predictable range. Yet, the fight against air pollution will not be over until the concentration falls to natural levels.

Introduction

The US Clean Air Act

In 1955, United States president Dwight D. Eisenhower signed the Air Pollution Control Act. Due to the fact that smog-related deaths and illnesses were gaining more and more attention in the media at the time, the Eisenhower administration drafted and passed the Act as the first ever federal legislation to involve air pollution (Roewe, 2014). Yet, the Air Pollution Control Act only provided funds for federal research and was not effective in physically fixing the air pollution issue. The five million dollars in funds provided were, however, enough to turn the nation's attention to the growing pollution problem and eight years later, the Clean Air Act of 1963 was passed (Roewe, 2014).

The CAA of 1963 established a program within the U.S. Public Health Services and, unlike the previous piece of legislation, was able to establish and implement air pollution control regulations (Roewe, 2014). Funds were also available for research of the actual techniques involved in monitoring and controlling air pollution. Four years later, the federal government expanded their control by creating the Air Quality Act of 1967. This act allowed the federal government to regulate interstate air pollution transport by conducting tests and inspections on stationary sources. Three years later, the Clean Air Act of 1970 was signed by Richard Nixon and although this legislation was technically an amendment to the CAA of 1963, it set the ground work for the modern-day CAA (Legislation). Due to the fact that the legislation already in place was deemed inadequate, this new act allotted the federal government even more power in controlling and regulating emissions from industrial and mobile sources. The act created four major programs – the National Ambient Air Quality Standards (NAAQS), State Implementation Plans (SIPs), New Source Performance Standards (NSPS), and National Emission Standards for Hazardous Air Pollutants (NESHAPs) (Legal). At this time, the six criteria air pollutants were also established. These six pollutants are the most common nationally and they are particularly harmful to human health and the environment. These six pollutants are ground level ozone, nitrogen dioxide, particulate matter, lead, carbon monoxide, and sulfur dioxide. Since this new legislation called for more enforcement, the Environmental Protection Agency was established in the December of 1970 (Legal).

More work was done to the CAA in 1977 under Jimmy Carter's administration. In order to continue to encourage clean air after standards were met, a program titled Prevention of Significant Deterioration (PSD) that dealt with attainment areas was added to the act. Also, deadlines to initially meet the air quality standards set in the 1970 NAAQS were extended for non-attainment areas, or areas that did not meet one or more standards set in the legislation at that time. The next amendments were added in 1990 under George W. Bush, since the Reagan administration in the 80's did not look to pass any Clean Air legislation.

The growing national concern of acid rain and continued air pollution led to the 1990 amendments, and that legislation is what is still in place today. Again, the amendments increased government responsibility and authority and included legislation that focused on ozone protection and acid rain control. The 1977 NAAQS and NESHAPs were updated, as well (Legislation).

Ozone (O₃) as a pollutant

Overview

Ozone is a gas that can be found in both the Stratosphere and the Troposphere. Stratospheric ozone, or “good ozone”, occurs naturally and acts as a protective layer from the sun’s harmful UV rays. Although a single O₃ molecule has a short residency time in the atmosphere, new ozone molecules are constantly being created by the splitting of one atmospheric oxygen molecule by solar ultraviolet radiation that leads to a reaction with another complete atmospheric oxygen molecule ($3O_2 + UV \rightarrow 2O_3$). The maximum concentration of ozone in the Stratosphere is 12 ppm (Miller, 1998). Stratospheric ozone is referred to as a “shield” to the biosphere below because the formation of the ozone molecule itself is responsible for absorbing the sun’s harmful UV rays.

Tropospheric ozone is considered to be ground level ozone, or “bad ozone”. This gas is classified as one of the six criteria air pollutants covered in the Clean Air Act and it is the ozone that this research is going to focus on. This gas does occur naturally on the ground level in low concentrations, and but is mostly formed from the reaction of sunlight, volatile organic compounds (VOCs) and nitrogen oxides (NO_x).

Sources

The ozone that exists in the troposphere is a secondary pollutant. It is a product of the reaction that occurs between nitrogen oxides and Volatile Organic Compounds once they are in the presence of sunlight; in order to identify the sources of the O₃ pollutant, the sources of the precursors must be identified. Nitrogen oxide is a term that encompasses both nitric oxide and nitrogen dioxide. Fossil fuel combustion is responsible for more than half of the nitrogen oxides emitted globally, and in the United States (Hudman et. al., 2007). The gasses oxygen and nitrogen do not react with one another at normal temperatures. In conditions where the temperature is very high, the two are able to react. These conditions exists when coal is burned in an electric power plant, or when oil is burned as fuel in an automobile (LibreTexts, 2016). Nitrogen oxide can also occur naturally from a bolt of lightning due to the area of high temperature surrounding the lightning strike. When the initial nitrogen and oxygen react, for all three sources listed, the equation is this: $N_2 + O_2 = 2NO$. The nitric oxide formed then reacts with more atmospheric oxygen to form nitrogen dioxide ($NO + O_2 = NO_2$).

VOCs are identified as carbon containing compounds that readily vaporize to enter the atmosphere; they are gasses emitted from solids and/or liquids. Unlike most pollutants, the concentrations of VOCs are higher indoors than out. Household products, such as paints, cleaners, disinfectants, wood refinishers, etc. widely contain organic chemicals. When these products are used indoors, they release various kinds of VOCs when they dry. Outside the home, VOCs can be emitted from the incomplete combustion of fossil fuels. Pure gasoline is a liquid that emits VOCs. When gasoline is not used in the engine’s reaction, or drips from the gas pump, VOCs get released. Small amounts of stratospheric ozone can also migrate down to the Earth’s surface (Weingroff).

Impacts

The smog that results from ozone pollution has the ability to worsen asthma symptoms in adults and children with asthma by irritating a person's airways. It does this by causing the muscles in those airways to constrict, which blocks airflow in the lungs and traps it in the alveoli. This can trigger chest pain, cause coughing, throat irritation, airway inflammation, shortness of breath, wheezing, and cause chronic obstructive pulmonary disease (COPD) in anyone who is exposed to high levels of this pollutant.

Ozone pollution affects ecosystems such as forests, wildlife refuges and areas, and other ecosystems that are home to trees and experience a heightened growing season. This is the case because, similar to the human lungs, O₃ enters the leaf area and impacts where photosynthesis occurs. Because of this, the plant has decreased levels of energy production and therefore slower growth and makes the entire plant susceptible to disease and more vulnerable to physical damage from insects and severe weather. When multiple plants in a high ozone area experience these same effects, animals in the area may experience habitat loss and food loss. Also, every plant that dies from ozone pollution lowers the ecosystem's species diversity. (Ecosystem, 2017)

The Impact of the Clean Air Act on Ozone Concentrations

Ozone Specific NAAQS Overview

The Clean Air Act's actual standards for the six different criteria air pollutant's concentrations are under the title of National Ambient Air Quality Standards. The process of evaluating, creating, and implementing these standards started in 1971 with the first Clean Air Act. There are both primary and secondary standards in this legislation. Primary standards deal with public health; these are said to be the standards that protect the human populations that are extra sensitive to the effects of air pollution. These groups include children, elderly, and asthmatics. Secondary standards, on the other hand, deal more with public welfare. These standards protect crops, animals, buildings, and other things (living and non-living) of that sort from damage caused by harmful air emissions. To determine these standards, the United States Environmental Protection Agency creates a plan that includes the reviews of scientific documents, which they then use to determine whether or not the current standards are set at an effective level. If they determine otherwise, a new standard is created.

The first NAAQS implemented for ozone pollution was not exclusive to O₃ molecules; the standards set in 1971 regulated the concentration totals of any photochemical oxidants. By definition, photochemical oxidants are secondary pollutants formed by reactions that take place in the presence of sunlight between nitrogen oxides and reactive hydrocarbons (PA. Gov., 2017). The legislation passed in 1971 referenced both primary and secondary standards; the values were to be measured by the hour, and the presence of total photochemical oxidants could not exceed 0.08 parts per million, or ppm. The goal of this legislation would be considered met if the concentrations did not exceed 0.08 parts per million more than one hour per year. If a goal, such as this one, is within CAA standards, that particular area is considered to be an "attainment" area; if the goal is not met in a particular area or city, it is labeled a non-attainment area.

In 1979, the photochemical oxidant legislation was changed to only pertain to the actual O₃ molecule; this was not a drastic change. Ground level ozone itself is a secondary pollutant. The measurements were still recorded every hour, but the maximum concentration levels changed to 0.12 ppm. Attainment for this amendment was defined as the number of days exceeding the maximum concentration was equal or less than one per year. When amendments for other criteria pollutants were added to the CAA in 1993, the EPA did not feel that the ozone standards had to change. It was not until 1997 when the EPA used the science available to determine that the standards in place were not effectively protecting both the public's health and welfare.

Thus, in 1997 new standards were passed and implemented. With the new legislation, the averaging time was every 8 hours and the maximum concentration went back down to 0.08 ppm. In order to reach attainment, an area had to have an annual fourth-highest daily maximum averaged over three years. The fourth day was picked due to the fact that it "more directly relates to ozone concentrations associated with health effects" (PA. Gov., 2017). Since it is over a longer span of time, the first three highest concentration days are considered outliers and probably exist under extreme circumstances. The three year averaging timespan along with the same regulations for attainment continued through the 2008 amendments, except the maximum concentration standard changed to 0.075 ppm for both the primary and secondary. The standards were again lowered in 2015 to 0.07 ppm.

Los Angeles Introduction

The metropolitan area of Los Angeles was chosen as the site of this study due to the reputation and ranking it has as being one of the worst cities globally for atmospheric pollution and the leading city in the United States for air pollution. The CAA's NAAQS are based on maximum values, and if there is anywhere maximum values could have the potential of being obtained, Los Angeles, California is that place. According to the Los Angeles Almanac, there were a total of 7,750,544 vehicles registered just in the city of LA in the year 2016 (Vehicle Registrations, 2017). As previously stated, automobiles are a major source of nitric oxides, which are a precursor to harmful ground level ozone. Another ingredient in the production of ozone is sunlight, and the city of Los Angeles has the coordinates 34.0522° N and 118.2437° W, indicating it is near the equatorial region and is subject to long days and strong sunlight year round.

Methods

Data

The AirData resource provided by the United States Environmental Protection agency was used to gather all of the daily data points from the year 1990 to the present. Three separate Air Quality Station's data were used for the daily average ozone concentration in parts per million. The stations included: West Los Angeles (sample site 06-037-0113), Downtown Los Angeles- North Main Street (sample site 06-037-1103), and Glendora (same site 06-037-0016). (Air Data, 2017) The daily maximum concentrations reported by the EPA were reported by following the CAA standards; the value was the highest eight hour average throughout the seventeen different eight hour averages collected over the course of a day. The average monthly concentrations over the twenty-seven year time span that were collected from all three sites were calculated in Microsoft Excel (2007). Microsoft Excel (2007) was also used to calculate annual averages from the monthly averages previously calculated, and the standard deviation between the yearly averages was also calculated. To normalize the standard deviations and minimize the effects from taking monthly averages to calculate annual, instead of daily, the coefficient of variance was also calculated:

$$CV^* = (\text{standard deviation}/\text{mean} \times 100) + 1.25$$

The concentrations were analyzed in their entirety to observe overall trends and compare the concentrations to the initial ozone standard of 0.12 ppm in the first CAA implemented, and the standards to follow.

Indicators

- Maximum monthly values over the entire 27 year time frame
- Minimum monthly values over the entire 27 year time frame
- Average monthly values for the entire 27 years compared to the NAAQS in place
- Average yearly values for each station
- Coefficient of variance between the monthly values for the entire 27 years

Results

Average Concentration Trends

Monthly

The average monthly O₃ concentrations, calculated by the daily concentration data, was plotted for site ID 06-037-1103 (Figure 1). The figure for the North Main Street site shows that the average monthly concentration never exceeded the corresponding NAAQS throughout the entire 26 year time series. When the running average was calculated by continuously averaging 12 average monthly O₃ concentration data points, it resulted in a horizontal line showing a constant running average (Figure 1). The particular amount of data points to calculate the running average was chosen to represent the 12 months in a year. Although the running average seems to represent a steady yearly average, there is a significance difference in the range of data points. In the year 1990 in Downtown Los Angeles, the range of concentration values was approximately 0.06 parts per million. In 2016, the range of concentration values was approximately 0.03 parts per million (Figure 1).

The average monthly O₃ concentrations, calculated by the daily concentration data, was plotted for site ID 06-037-0113 (Figure 2). The figure for West Los Angeles reveals that, like downtown, the NAAQS were never exceeded throughout the 26 years of this study. In 1990, the range of concentration values was not as great as it was in site ID 06-037-1103 (Figure 1); the range of concentration values in 1990 in West LA was approximately 0.04 ppm (Figure 2). The range of concentration values in 2016 was approximately 0.02 ppm (Figure 2). Although the difference was 0.01 ppm more downtown, there was still a decrease in the range of concentrations throughout the course of a single year from the year 1990 to 2016. From 2002 to 2003, there was a dramatic increase in value of the running average (Figure 2). This running average was calculated the same way it was in Figure 1 using the average of twelve data points on the plot to represent a yearly mean. Prior to the jump in 2002, the running average was a constant value at approximately 0.04 ppm until it dipped in 2001 to 0.03 ppm (Figure 2). After the jump, beginning in the year 2004, the running average was again a constant value, but that value was slightly higher, at approximately 0.045 ppm (Figure 2).

The plot of the average monthly O₃ concentration for site ID 06-037-0016 visually showed higher and more scattered monthly concentration values for the entire 26 years (Figure 3). The annual range of concentration values in the year 1990 was approximately 0.09 ppm, which was the highest range out of all three sample sites. In 2016, the last full year of the study, the range of concentration values was approximately 0.04 ppm (Figure 3). Although the initial range of average monthly concentration data points was the highest at this site, the difference in the range from 2016 to 1990 was also the largest; the difference in the ranges was 0.05 ppm. Glendora was the only station where concentration levels exceeded the standards. From 1997-1999, the average of the annual fourth daily maximum value was 0.12 ppm, when the standard was 0.08 ppm (Figure 3). From 2007-2009, the average of the annual fourth daily maximum value was 0.11 ppm, when the standard was 0.075 ppm (Figure 3). The running average at this site began with a steady decrease unlike the other stations. From 1990 to the year 2000, the value of

the running average decreased from 0.062 ppm to 0.038 ppm (Figure 3). After this initial decrease, the running average increased slightly and became steady at approximately 0.045 ppm.

Yearly

The average yearly O₃ concentration for all three sample sites were calculated by averaging the monthly average concentration values for each year (Figure 4). The difference between the yearly average and the running average is the fact that the running average is continuously calculating an average with an overlapping twelve data points, whereas the yearly average is a set calculation for each year, using the twelve monthly average concentration values previously calculated. The trends between the yearly and running averages are very similar. Site ID 06-037-0016, or Glendora, still shows a significant decrease in its yearly average (Figure 4). This yearly average decline is much more dramatic than the running average decline, and it drops from 0.07 ppm to 0.04 ppm. The yearly average for all three sites does not show a steady average value like the running average does. The peak in the West LA concentration values (sample site 06-037-0113) still exists between 2002 and 2003 (Figure 4). After the year 2002, the trends between all three sample sites show peaks and falls on the same years. All three sample sites have a relative maximum in 2003, 2006, and 2015 (Figure 4). Prior to the year 2002, sample site 06-037-1103 and 06-037-0113 both had a relative minimum yearly concentration value in the year 1993 (Figure 4).

The standard deviations of the yearly averages (Figure 4) reaffirm the results of the diminishing range in average monthly O₃ concentration values over the course of a single year (Figure 5) that can be seen at each sample site (Figure 1; Figure 2; Figure 3). Standard deviation is a unit-less measure of how far a data set varies from the calculated average. In this case, the same 12 months used in the average of the yearly O₃ concentration calculation used in Figure 4 were used to calculate each standard deviation. From 1990 to 1998, all three sample sites have a higher, more variable standard deviation value; site 06-037-0016 has the largest drop (from 0.035 to 0.02) during this time frame (Figure 5). Site 06-037-0113 has the lowest standard deviation values overall and most steady throughout the entire 27 years. Site 06-037-1103 has an absolute maximum standard deviation value in the year 1994, which corresponds with relative maximums of the other two stations (Figure 5).

Trends in Data Variance

Coefficient of Variance

In order to better account for the risk measure calculated by the standard deviation of each yearly average O₃ concentration (Figure 5), the coefficient of variance was calculated. This value was calculated by using the standard deviations for each year and dividing each by the average O₃ concentration value for that year, then multiplying the product by 1.25 which is a standard corrector for this equation (Figure 6). Coefficient of variance is a more reliable measurement of variance than standard deviation due to the fact that it adjusts for the size of the data set which adds realistic context to the value. For sample site 06-037-1103, the CV highlighted the standard deviation absolute maximum of 1994 (Figure 5). The CV in 1994 at site 06-037-1103 reached 63.3% (Figure 6); this percentage indicates that 63.3% of the values used

to calculate the average O₃ concentration in the year 1994 strayed from the average value. Up to the year 2000, all three sample sites experienced fluxes of CV values (Figure 6).

Sample site 06-037-0113 had its maximum CV value in the year 1992 with a value of 42.8%. The CV for this site then dropped to 24.8% by the year 1995, and rose again to 39% in 2000 (Figure 6). After this rise and fall and rise again pattern, the CV steadily decreased to 13% in 2016 (Figure 6). Sample site 06-037-0016 only reached a 30.5% CV in the year 2016; sample site 06-037-0016 experienced the lowest decrease in CV over the course of the study (Figure 6). The decrease in site 06-037-0016 was even less than sample site 06-037-1103, which ended up with a 22.5% CV despite the fact that this was the site with the highest CV overall (Figure 6). The highest CV overall is referring to the 63.3% variance in 1994 that was previously mentioned.

Monthly Maximum Values

In order to observe where the overall decreasing trend of CV came from, both the monthly maximum O₃ concentration values and the monthly minimum O₃ concentration values were plotted from the daily data retrieved from the AirData database. Sample site 06-037-1103 showed not only an overall decrease in the highest maximum monthly O₃ concentration values, but an overall decrease in a range of these values over the years (Figure 7). The lowest monthly concentration in the year 1990 was right at 0.02 ppm, and it increased slightly in the later years to approximately 0.03 ppm (Figure 7). The highest maximum O₃ concentration in the year 1990 was 0.135 ppm, but ended up being halved and becoming relatively steady beginning in the year 2010 (Figure 7). Sample site 06-037-0113 showed the same trend in monthly maximum O₃ concentration values (Figure 8). Site 06-037-0113 did not experience increase in the lowest monthly maximum O₃ value that site 06-037-1103 did. In 1990, the lowest data point was at 0.04 ppm, and it stayed constant at that value besides outliers in the years 1993, 2000, and 2001 (Figure 8). Both sites have a very visual decrease in range of monthly maximum O₃ data points over the 27 years.

Sample site 06-037-0016 did not seem to follow the distinct pattern on a decreasing range in monthly maximum O₃ concentration values (Figure 9). The lowest monthly maximum O₃ concentration value did remain at around 0.03 throughout the 27 years, which was also the case in the other two sample sites (Figure 9). Although, the highest maximum monthly O₃ concentration values did not dramatically decrease like they did in sample site 06-037-1103 (Figure 7) and site 06-037-0113 (Figure 8). In 1990, the highest data point was at 0.143 ppm, and in 2017 the highest monthly maximum O₃ concentration was 0.10 ppm (Figure 9). For the entirety of the study, the maximum monthly O₃ concentrations for sample site 06-037-0016 only had a slight decrease (approximately 0.033 ppm) in range and the data points still had a visually sporadic pattern that the other two sites did not experience after the year 2010 (Figure 9).

Monthly Minimum Values

The monthly minimum O₃ concentrations for each sample site did not show the same trends that the monthly maximum concentration plots did. Sample site 06-037-1103, or Downtown LA, with the exception of three outlier data points that reached values of up to 0.06

ppm, had monthly minimum values that kept the same range in data throughout the study (Figure 10). Although, in 1990, the lowest monthly minimum O₃ value was 0.001 ppm, and reached 0.0 ppm in 1991. The lowest values began to increase from these minimal values in the year 2002, and by 2017 the lowest monthly minimum value was up to 0.012 ppm (Figure 10). Although the annual range of about 0.03 ppm stayed constant over the course of the study, all of the actual concentration values of the monthly minimum increased as the years went on at sample site 06-037-1103 (Figure 10).

Sample site 06-037-0113 followed the same increasing trend but not as closely as sample site 06-037-1103 did (Figure 11). In 1991, site 06-037-0113 also had a minimum monthly minimum O₃ concentration value at 0.0 ppm. Unlike sample site 06-037-1103, sample site 06-037-0113 also experienced a value of 0.0 ppm in the year 2012 (Figure 11). In 2017, the lowest value was higher than 0.01 ppm. These values experience the same overall increase in the year 2002 that the running average for this site also showed (Figure 2). The last site, site 06-037-0016, showed a major decrease in the range of the monthly minimum O₃ concentration values per year from the beginning to the end of the study. From 1991-1996, there were monthly minimum values that reached 0.06 ppm (Figure 12). Those data points were the highest out of all of the minimum monthly values recorded. The overall lowest monthly minimum O₃ concentration data points did experience an increase like the other two stations overall, yet there were still five instances after the year 2006 where the concentration value was under 0.006 ppm (Figure 12).

Seasonal Trends

The monthly averages for all twelve months of the year 1990 were plotted to see the trends of O₃ concentrations seasonally (Figure 13). The year 1990 was chosen since it was the first year of the study and, theoretically, should have experienced the highest O₃ concentrations out of the entire study. There is an obvious peak in concentrations during the summer months, beginning in May and decreasing again in October (Figure 13). The range between the highest summer concentration (July) and the lowest winter month (January) is 0.073 ppm. There was a difference of 0.072 ppm between July and December (Figure 13).

The same plot was generated for the year 2016 at the same sample site (06-037-1103) since 2016 was the last full year of the study (Figure 14). The trend of this plot is much more subtle than the 1990 graph (Figure 13). The highest points are still in the summer months, but there is no peak; the shape of the figure resembles a rolling hill rather than a mountain. The highest average monthly O₃ concentration in 2016 was in August, and the difference between the August concentration and the January concentration was 0.05 ppm, which is 0.023 ppm lower than the difference in 1990 (Figure 13, Figure 14). The difference between August and December was also 0.05 ppm in 2016.

Discussion

Overall Trends

O₃ Concentration Trends

The purpose of this research was to contribute to the overall conversation regarding the effectiveness of the CAA, a unique piece of legislation that the U.S. has been enforcing for the last 47 years. Specifically, this study was interested in O₃ levels in Los Angeles, California. In order to be able to understand the impacts of the CAA on this certain kind of air pollution molecule, there must be a general understanding of how O₃, a secondary pollutant, behaves generally in the atmosphere. Theoretically, O₃ should not exist in the Troposphere except for at extremely low (almost an absolute zero) concentration. As previously mentioned, O₃ is a product of the reaction that takes place between nitrous oxides and VOCs (Hudman et al., 2007). In order to decrease the concentration of O₃ in the atmosphere, the concentrations of the two reactants must first decrease. Along with creating NAAQS for O₃ pollution, the CAA also continuously strengthened their NAAQS regarding nitrous oxides, which are mainly emitted through automobile emissions, during the time of this study. By 1994, congress stated that NO₂ levels had to be 90% of what they were in 1990 (Lee et al., 2007).

Changing standards regarding nitrogen dioxide, though, have to be paired with new technologies that decrease the amount of incomplete combustion that takes place in an automobile's engine. An example of this would be the catalytic converter that was invented in 1970, and is since then being constantly improved. Since new technology is required, new cars (relative to the time the technology was invented) are the only ones on the road driving with decreased emissions. Decreasing NO_x emissions take time; the yearly averages of the data in this study were not significantly decreased until the year 1999 (Figure 4). This decrease could in part be due to the increasing amount of cars on the road with less NO_x emissions. 1999 was only 2 years after the decrease in NAAQS from 0.12 ppm to 0.08 ppm, which would be a more direct factor influencing the decrease in the yearly average concentration of O₃ at that time.

Besides the initial decrease (1990-1999), the monthly concentrations of O₃ did not seem to vary for the worse or better. When the NAAQS went from 0.08 ppm to 0.075 ppm, it had no observable effect on the monthly concentrations.

Regional Trends

Sampling site 06-037-1103 was located directly in Downtown LA on North Main Street. It was expected that this sampling site would be the site with the highest O₃ concentrations overall, even with the CAA being enforced. This prediction was based on the fact that the precursors for the O₃ pollutant are major byproducts of automobiles and Downtown LA was by far the most populated sample site. Yet, that was not the case. The sampling site with the highest, least regulatory O₃ concentration throughout the study was sampling site 06-037-0016. This sampling site was located in the mountainous county of Glendora.

According to an LA Times article titled *Pollution Burdens* (2015), Glendora was in the 83.95 percentile for O₃ and the 84.22 percentile for “toxic releases” (as of 2014). Downtown LA, however, was only in the 40 percentile for O₃ but was in the 77.51 percentile for “toxic releases”. The rankings regarding O₃ were nearly halved from Glendora to Downtown LA. Yet, the actual emissions coming from both areas were less than 10% away from one another. The “toxic releases” category does cover every pollutant, along with pesticide usage, so these numbers are not directly correlated with O₃ concentrations. However, the similar magnitudes of physical emissions when compared to the drastic differences of the O₃ concentrations can be used as an indicator that the O₃ molecules present in Glendora were most likely formed elsewhere.

The annual wind pattern in LA follows a WSW pattern, or it blows from the west-southwest. The coordinates for the county of Glendora are 34.1361° N, 117.8653° W, whereas the coordinates for LA are 34.0522° N, 118.2437° W. Glendora is located more east and more north than Downtown LA, which means that a wind gust blowing from the south west would transport air and the pollutants it contains from the urban area of LA to the region of Glendora, naturally. When the many vehicles and households emit the nitrous oxides and VOCs in the city, they are reacted but then transported and deposited in Glendora. In addition to the wind patterns, the topography of Glendora aids in trapping the O₃ molecules. The altitude of Glendora is 774’ above sea level, whereas the altitude of Downtown LA is 285’ above sea level. It is because of this that the O₃ molecules are able to build up and continuously increase in concentration (Fehsenfeld et al., 1983).

Another O₃ concentration trend that can be classified as a regional trend is the jump experienced by sample site 06-037-0113 in the year 2002 (Figure 2). Immediately prior to the peak, there was a sharp decrease in the running average of O₃ concentration and after the jump, the running average went right back to the stable concentration it had in the years leading up to 2002. This sample site was the site chosen to resemble a coastal area, being that it is located in West LA and more towards the Pacific Ocean. With that in mind, the driving force behind this behavior could be the 1997-1998 El Niño event that occurred. According to Ziemke et al. (2003), this particular weather event had the largest detected increases in tropospheric O₃ between the years 1979-2000. An El Niño begins in the west Pacific, over the countries like Indonesia, and then makes its way eastward towards the west coast of the U.S., and the changes in the air pressure that result from the shift have the ability to have effects that last far longer than a year (Ziemke et al., 2003).

During this weather phenomenon, the warm temperatures of the Pacific’s surface waters shift from west of the Dateline to the east (Ziemke et al., 2003). When this shift occurs, the air convection over the east Pacific Ocean is enhanced, resulting in a higher pressure system. High air pressure is then associated with tropospheric divergence, which increases O₃ concentrations by suppressing upwelling (Ziemke et al., 2003). The reason sample site 06-037-0113, or the sample site located in West LA, sees the effect of this weather pattern and no other site does is that it is the closest to the Pacific ocean, and El Niño events do not actually take place directly over land in California.

Impact of the CAA

Trends in Variance

From the results of this study, it can be concluded that the impact of the CAA on controlling O₃ pollution has its major success in decreasing the variability of every daily O₃ concentrations (Figure 5). A coefficient of variance calculation is designed to show the percent of data points that vary from the average value, and the plot of all three stations CV do show that they all decrease over the time period that this study covers. Although, it was found that this decrease in variance comes from a decrease in the highest monthly maximum O₃ concentration values and a decrease in the lowest monthly maximum concentration values. The effect of the CAA on the monthly minimum O₃ concentrations were not as dramatic; some monthly minimum values reached lows of 0.0 ppm, therefore there was not a lot of decreasing potential.

This decrease in maximum concentration values occurs when the NAAQS decrease from 0.12 ppm to 0.08 ppm. With the strengthening of the NAAQS, the state of California also had to reevaluate and create more intense SIPs. According to the California Air Resources Board (2017), the SIPs beginning in 1997 have State SIP measures which include regulatory and incentive programs regarding consumer products, fuels, and mobile sources which are designed to meet the NAAQS. Each SIP has a 15 year scope, so it can be predicted that the variability of O₃ is only going to decrease as time goes on.

Seasonal Variance

O₃ is produced photochemically, meaning where there is sunlight O₃ is being produced (Hudman et al., 2007). When there is more sunlight, more O₃ is produced. In the northern hemisphere, there is more sunlight in the summer months (late May – early October). The seasonal plot of 1990, the first year of the study, had a far greater slope between the winter and summer months than 2016, the last full year of the study, had. The decrease in coefficient of variance can ultimately be considered a result of this decrease in seasonality. Since the coefficient of variance was calculated per year, and the mean and standard deviation used to calculate it were of the twelve months, it only makes sense that both would decrease. Again, this decrease in seasonality is a result of the strengthened SIPs that California has been continuously updating with every NAAQS. Thus, this is where the CAA has had most of its success regarding controlling the O₃ concentration.

Potential Error

The farthest this study dates back is 1980, and that data was only available for one station; the North Main Street station in Downtown LA (sample site 06-037-1103) was the only site that had data from 1980, the other two had data available from 1990 on. That being said, the CAA was passed in 1970. There were 10 years of the daily maximum O₃ concentration values that were not recorded when the CAA was initially passed. The absent data could show that there was a significant decrease in overall O₃ concentration in this time period, which would support that the CAA was very impactful in LA. Yet, since the 27 year period of which this study observed, there were 4 different NAAQS that were passed, each being lower than the last.

Along with the missing 10 years, there were also years during the study that did not have data available for every day. However, there was never an instance where a full month did not have data. By using the averages of monthly O₃ concentrations, it was a goal to diminish the impacts of the missing daily data.

The extent and the amount of data used to draw conclusions from this study were more than enough to produce valid results and a valid discussion. With other studies of this kind, the CAA and other environmental legislation in the U.S. and world-wide have the potential to be created and enforced in the most efficient, effective way possible.

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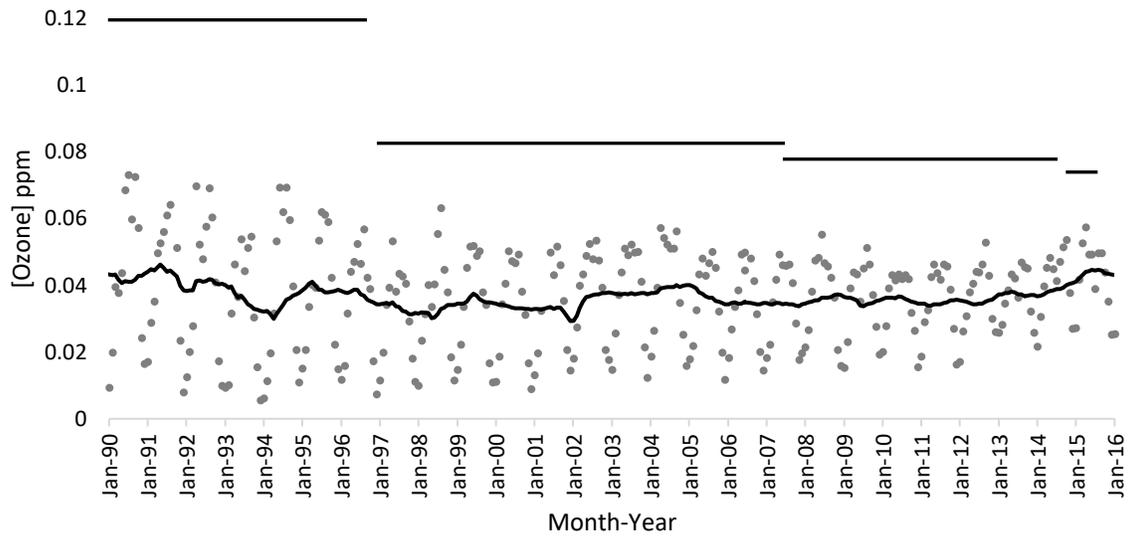


Figure 1: The plot of the monthly average O₃ concentration recorded by site ID 06-037-1103 from 1990 to the present, along with the running average of twelve data points.

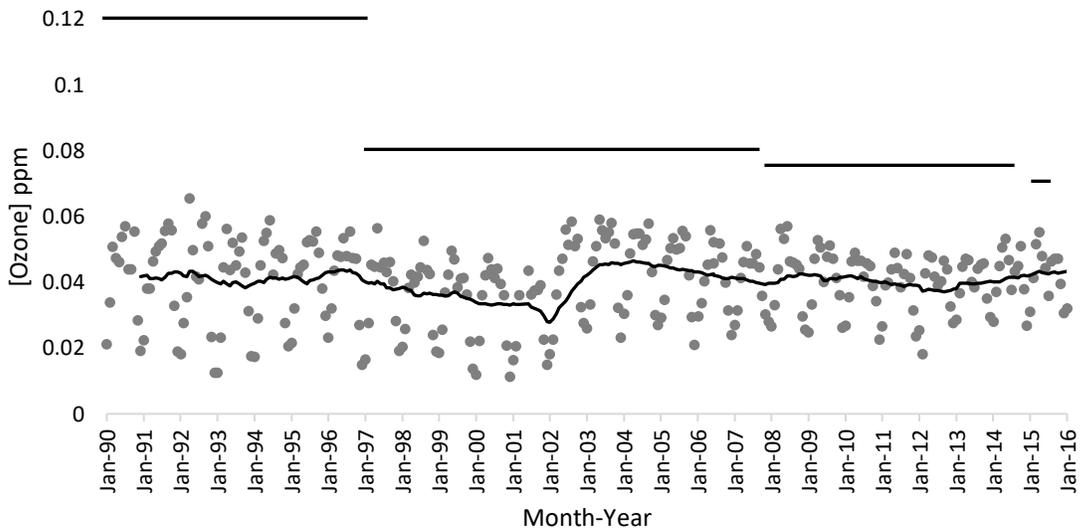


Figure 2: The plot of the monthly average O₃ concentration recorded by site ID 06-037-0113 from 1990 to the present, along with the running average of twelve data points.

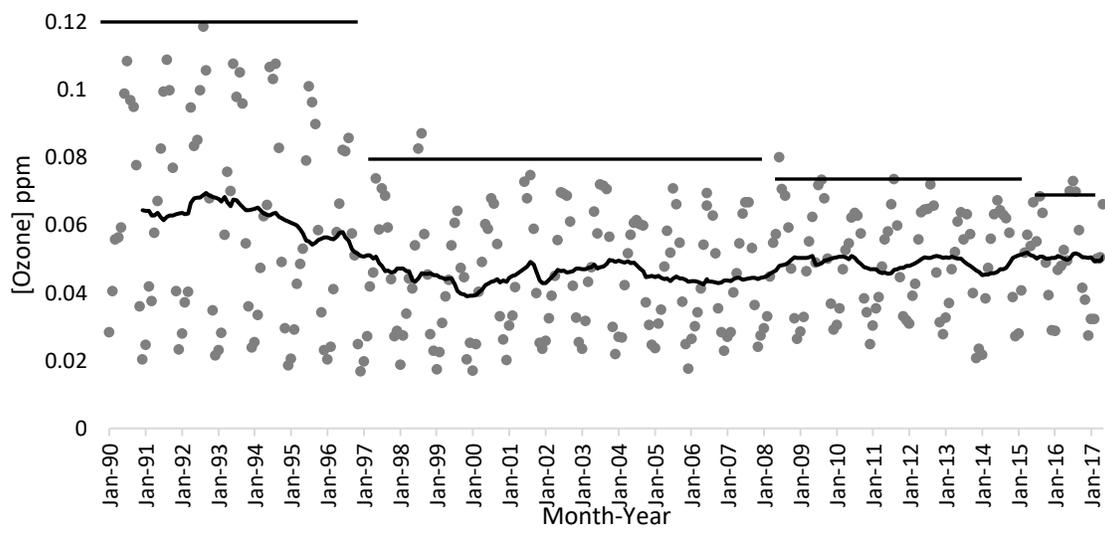


Figure 3: The plot of the monthly average O₃ concentration recorded by site ID 06-037-0016 from 1990 to the present, along with the running average of twelve data points.

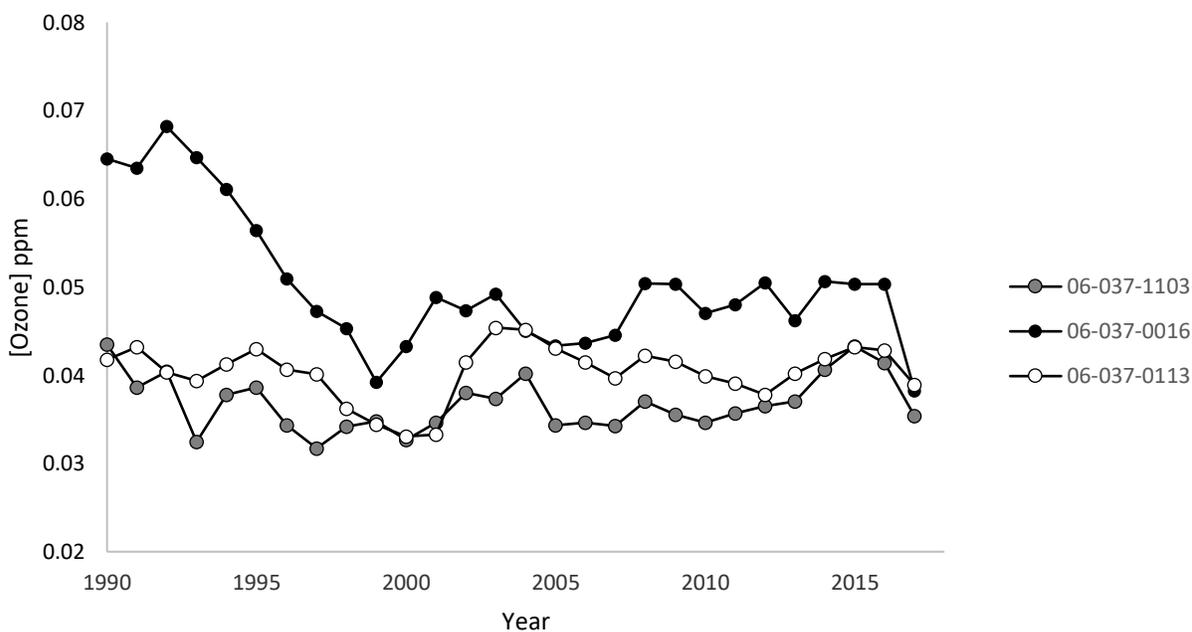


Figure 4: The yearly averages of all three sample sites starting at 1990 and ending in 2016, calculated from the monthly averages calculated from daily data.

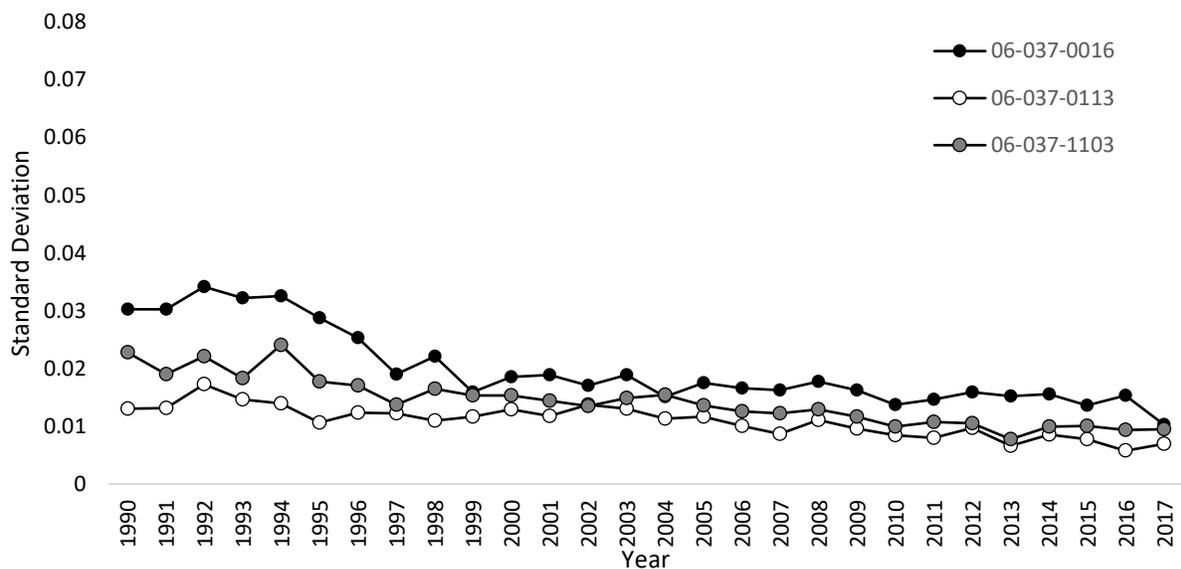


Figure 5: The standard deviation for the yearly averages graphed in Figure 4. These data points were calculated from the average monthly O₃ concentration values used to calculate each yearly average in Figure 4.

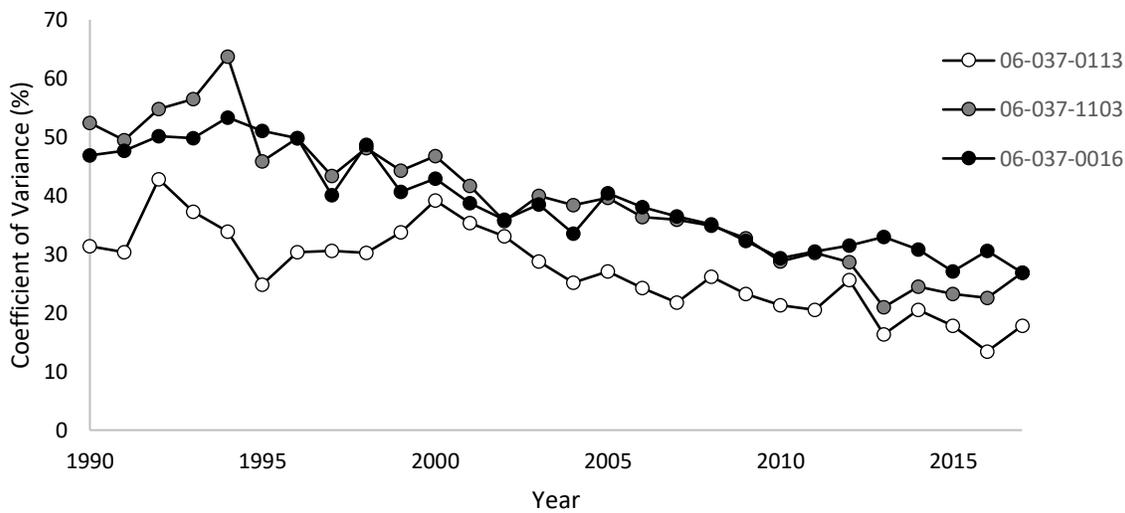


Figure 6: This is the plot of the annual coefficient of variance, recorded in a percentage value, for all three stations over the 27 year time span of the study.

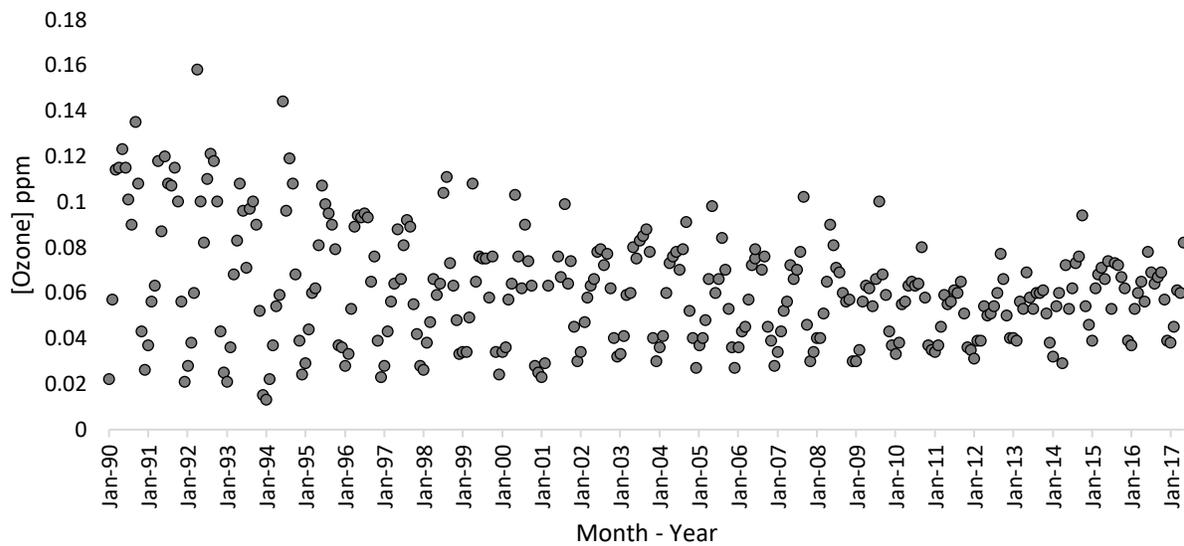


Figure 7: This is a plot of the maximum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-1103, which is the station located on North Main Street, Downtown LA.

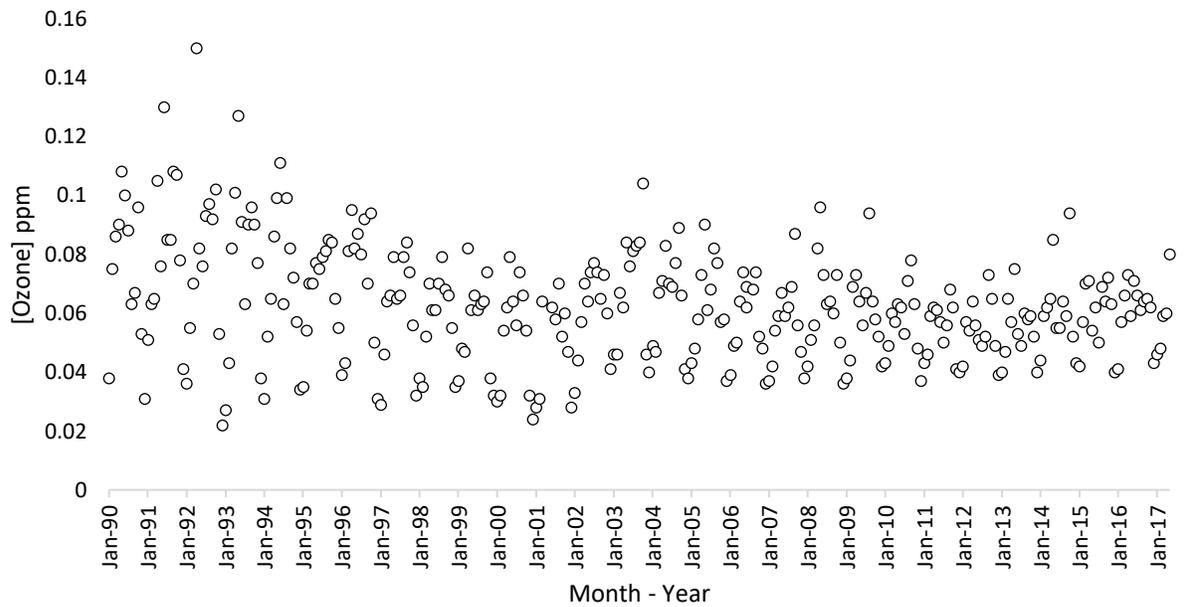


Figure 8: This is a plot of the maximum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-0113, which is the station located in West LA.

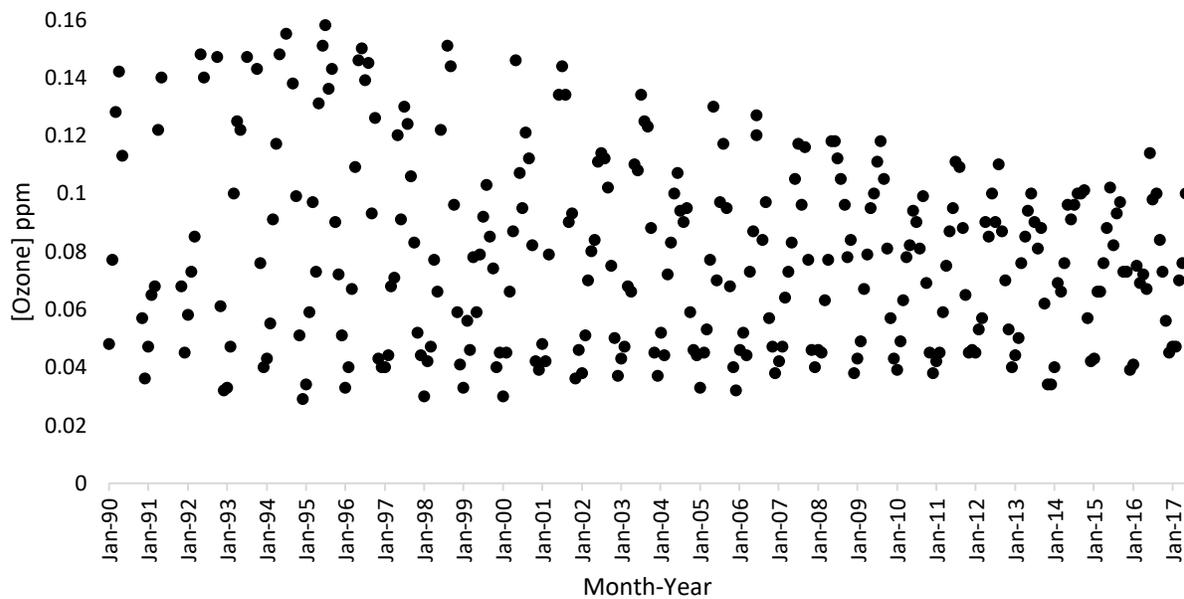


Figure 9: This is a plot of the maximum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-0016, which is the station located in Glendora.

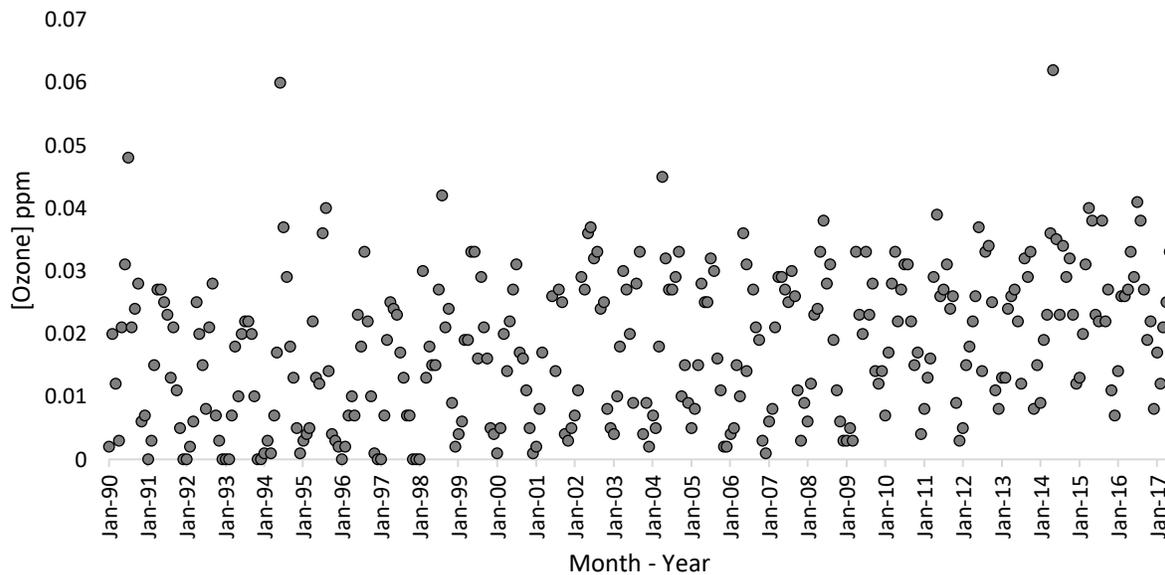


Figure 10: This is a plot of the minimum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-1103, which is the station located on North Main Street, Downtown LA.

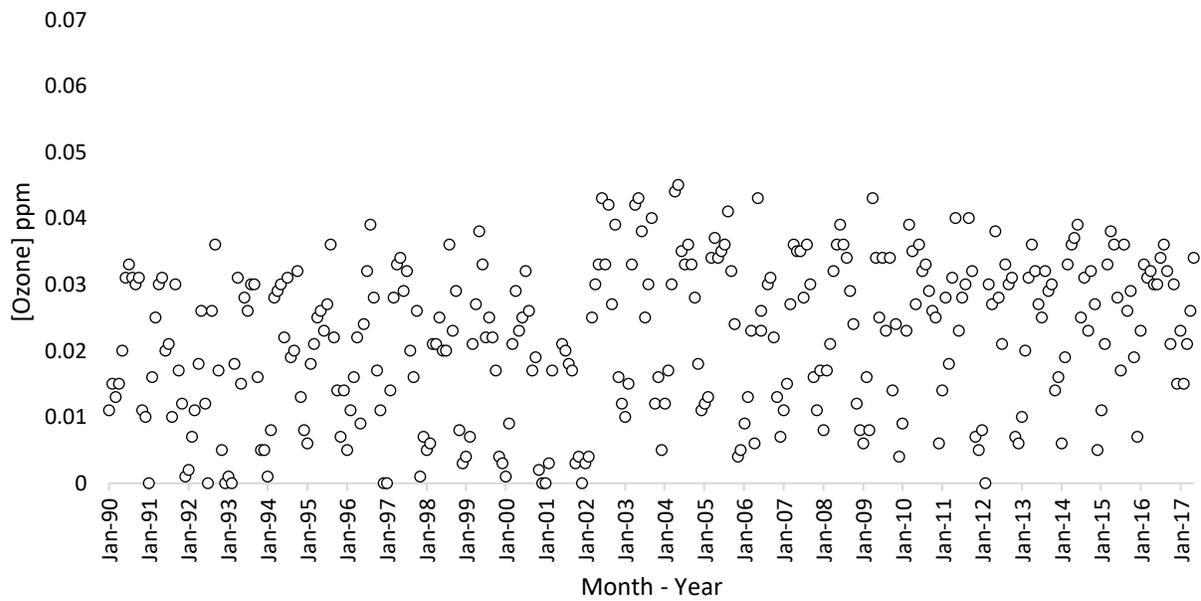


Figure 11: This is a plot of the minimum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-0113, which is the station located in West LA.

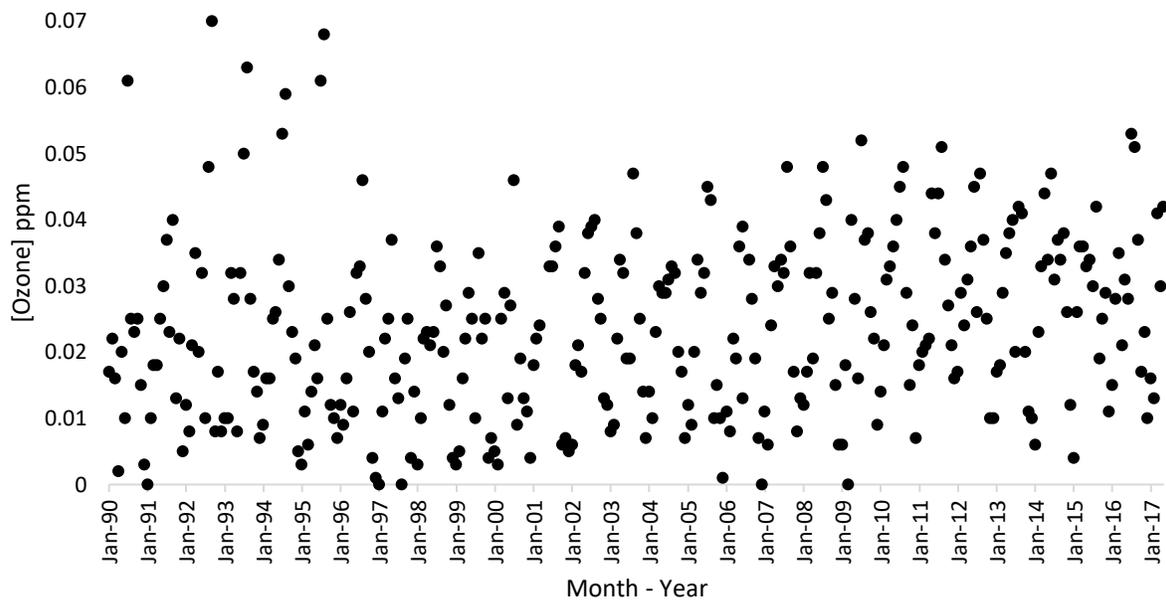


Figure 12: This is a plot of the minimum O₃ concentration for each month taken from the raw daily concentration values for sample site 06-037-0016, which is the station located in Glendora.

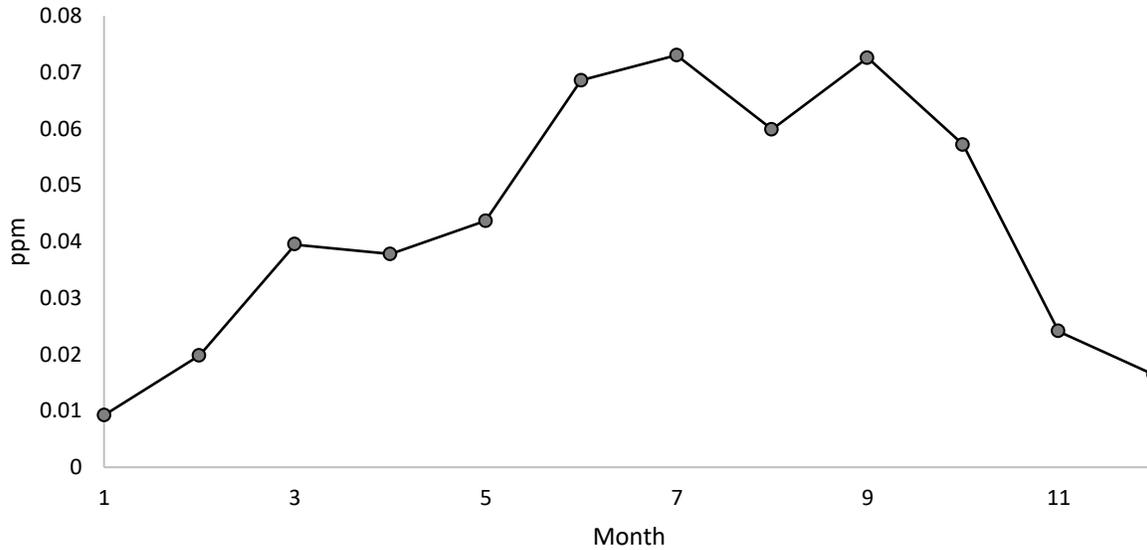


Figure 13: The plot of the monthly average values for the year 1990, with the months along the x-axis. The data is taken from sample site 06-037-1103. January is month 1, February is month 2, March is month 3, April is month 4, May is month 5, June is month 6, July is month 7, August is month 8, September is month 9, October is month 10, November is month 11, and December is month 12.

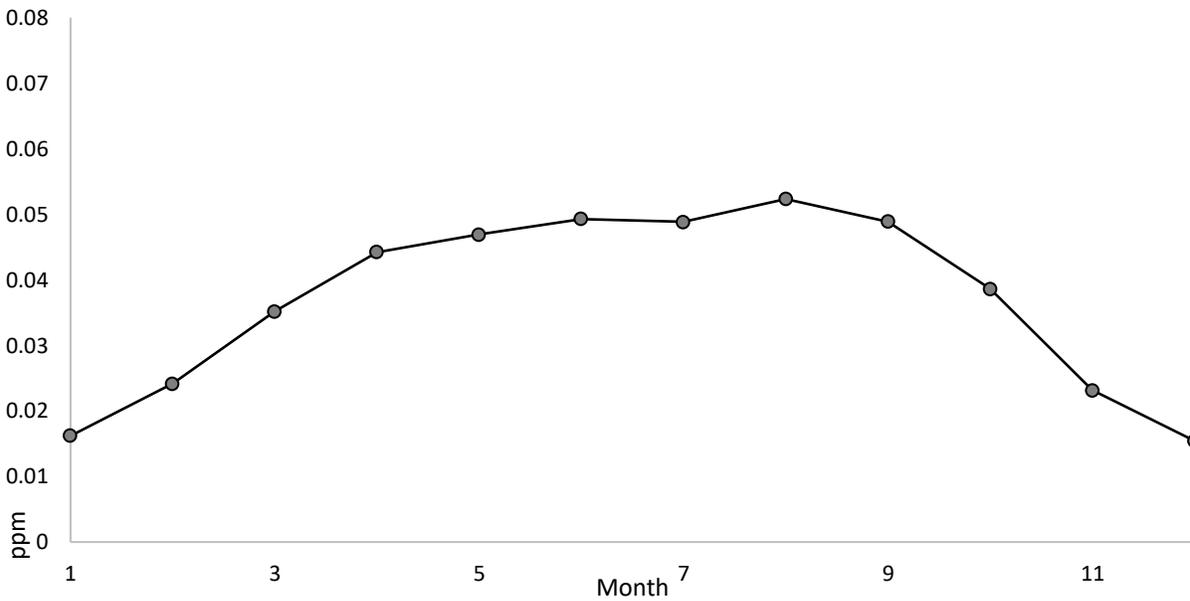


Figure 14: The plot of the monthly average values for the year 2016, the last full year in the study, with the months along the x-axis. The data is taken from sample site 06-037-1103. January is month 1, February is month 2, March is month 3, April is month 4, May is month 5, June is month 6, July is month 7, August is month 8, September is month 9, October is month 10, November is month 11, and December is month 12.