

Final Project Report:

**Characterization of Atmospheric Nitrogen Oxides over the Meadowlands**

To the Meadowlands Environmental Research Institute,

The New Jersey Meadowlands Commission

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## SUMMARY

This research project represents the first comprehensive *in-situ* measurement of atmospheric nitrogen over the Meadowland District. The original goal of this research was to determine the concentrations of atmospheric nitrogen oxides. During the project period and while measuring atmospheric nitrogen oxides, however, additional measurements were made for the ground-level ozone and aerosol nitrate in the spring for a better understanding of the mechanism of nitrogen in atmosphere. Therefore, this project has generated data beyond its original scope.

The results of atmospheric nitrogen oxides and ground-level ozone over the Meadowlands District are presented in 16 figures and 5 tables. Results of aerosol nitrate and its relationships with nitrogen oxides are also included in this report in the form of a manuscript, entitle “Relationships among the Springtime Ground-level  $\text{NO}_x$ ,  $\text{O}_3$  and  $\text{NO}_3$  in the Vicinity of Highways in the US East Coast” submitted previously to *Water, Air, and Soil Pollution*.

Atmospheric measurements of  $\text{NO}_x$  and  $\text{O}_3$  based at the Meadowlands have generated important results, including the following: The monthly average of  $\text{O}_3$  concentrations in the study area ranged from 11.1 to 36.2ppb with relatively higher values in summer than those in winter. No obvious seasonal variations were observed for  $\text{NO}_x$ , and the  $\text{NO}_x$  concentrations observed during the one-year period ranged from 17.0 to 29.0ppb, with the yearly average concentration being 22.6ppb. For the diurnal variations,  $\text{O}_3$  and  $\text{NO}_x$  showed different patterns. The peak of  $\text{O}_3$  concentrations (~33ppb) happened mainly around 2pm, while the peak of  $\text{NO}_x$  concentrations (38ppb) occurred around 7am. Obvious weekdays/weekends differences in the  $\text{NO}_x$  and  $\text{O}_3$  concentrations existed in this area, with the yearly average concentrations of  $\text{NO}_x$  in weekends much lower compared with those on weekdays. The negative correlation between the

hourly average  $\text{NO}_x$  and  $\text{O}_3$  concentrations found in the study area, suggests a potential VOC sensitive nature of the nitrogen cycle mechanism in atmosphere. Certain environmental factors, such as the ambient aerosol nitrate, temperature, humidity, and wind speed were found to affect  $\text{NO}_x$  and  $\text{O}_3$ , although the extent of the effects by each varied.

## **1. STATEMENT OF THE PROBLEMS**

Nitrogen oxides ( $\text{NO}_x$ ), highly reactive gases in the ambient air, such as NO and  $\text{NO}_2$ , are precursor molecules for the production of ground-level ozone ( $\text{O}_3$ ) (Finlayson-Pitts and Pitts, 1986). The  $\text{O}_3$  production rate strongly depends on the concentrations of NO and  $\text{NO}_2$ . High concentrations of  $\text{O}_3$  in the ambient air can trigger serious respiratory and other health-related problems. Therefore, an adequate knowledge of the characteristics of  $\text{NO}_x$  in the ambient air is crucial for the assessment of  $\text{O}_3$  pollution and air quality. According to EPA data, the major anthropogenic source of  $\text{NO}_x$  in ambient air in the United States is motor vehicle emissions, accounting for half of the total emissions. Additional sources of  $\text{NO}_x$  include electrical utilities and other industrial, commercial, and residential sources. Therefore, high concentrations of  $\text{NO}_x$  are often found in areas heavily impacted by traffic and power plants, although they can also come from natural sources and be transported over long distances by prevailing winds. Despite the critical role of  $\text{NO}_x$  in air quality, the concentration levels and temporal variations of NO,  $\text{NO}_2$ ,  $\text{NO}_x$  over the Meadowlands had not been monitored before the submission of this project proposal; this represents a serious data gap in air quality assessment in the district. With the heavy transportation and the existence of power plants and landfills in this region, the emissions of  $\text{NO}_x$  and production of  $\text{O}_3$  in the district could be substantial. Thus, the measurements of  $\text{NO}_x$  in the ambient air are critically needed.

## **2. ORIGINAL GOAL AND OBJECTIVES**

The research effort under this plan aims at generating new data of  $\text{NO}_x$  on ambient levels over the Meadowlands District, which will complement the on-going air quality monitoring research at the Meadowlands Environmental Research Institute (MERI). The ultimate goal of

this project is to contribute to the understanding and control of air pollution in the district, and maintaining the health of the Meadowlands. Within this context, the original objectives are:

- (1) To install a new NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer at MERI and to initiate atmospheric nitrogen monitoring at this location,
- (2) To measure the concentrations of atmospheric NO, NO<sub>2</sub>, and NO<sub>x</sub> in order to assess the current levels of NO<sub>x</sub> in the ambient air,
- (3) To generate temporal variations in particular seasonal trends of NO, NO<sub>2</sub> and NO<sub>x</sub> under ambient environmental conditions.

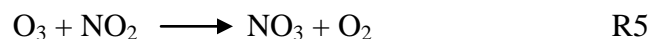
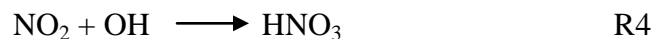
During the process of conducting this project and while measuring atmospheric NO<sub>x</sub>, the following additional measurements were made in order to better understand the characteristics of NO<sub>x</sub>: (1) the ground level ozone (O<sub>3</sub>), and (2) particulate-phase nitrogen (NO<sub>3</sub><sup>-</sup>) in the springtime. This report presents the data of NO<sub>x</sub> and O<sub>3</sub>; the results of NO<sub>3</sub><sup>-</sup> along with NO<sub>x</sub> and O<sub>3</sub> were in a manuscript submitted to *Soil, Air and Water Pollution* attached.

### 3. BACKGROUND

As two of the six principal NAAQS atmospheric pollutants, O<sub>3</sub> and NO<sub>x</sub> (NO + NO<sub>2</sub>) could induce serious adverse effects on human health and the ecological environment at high concentrations (Lee et al., 1996; WHO, 2000; Kampa et al, 2007). NO<sub>x</sub> also plays an important role in controlling O<sub>3</sub> concentrations via photochemical reactions in near ground atmosphere as shown below in reactions R1, R2 and R3 (Seinfeld and Pandis, 2006):



In addition, the photochemical reactions between NO<sub>x</sub> and O<sub>3</sub> could greatly influence nitrogen transfer from atmospheric to aquatic and terrestrial systems. During the daytime, HNO<sub>3</sub> could be directly produced via reaction R4, while at night, nitrate products (NO<sub>3</sub><sup>-</sup>, HNO<sub>3</sub>) could be produced via the mechanisms as shown in R5-R7:



Combustion processes, especially vehicle emissions, are the main sources of NO<sub>x</sub> in the air. They contributed more than a half of the total NO<sub>x</sub> emissions in the eastern US (Butler et al., 2005) and showed an increasing trend since 1990s (Parrish, 2006). Ground level O<sub>3</sub> mainly comes from two sources: regional background O<sub>3</sub> transported from the upper stratosphere via convection (Junge, 1962; Clapp and Jenkin, 2001) and local O<sub>3</sub> production mainly from photochemical reactions shown in R1-R3 (Seinfeld and Pandis, 2006). Therefore, it is important to conduct *in-situ* measurements of both NO<sub>x</sub> and O<sub>3</sub> and consequently investigate their characteristics.

#### 4. METHODOLOGY

The on-time monitoring of NO<sub>x</sub> and O<sub>3</sub> was conducted from June 1, 2007 to May 31, 2008 at the Meadowlands Environmental Research Institute (MERI) in Lyndhurst, New Jersey. Two new instruments 42i-D NO<sub>x</sub> Analyzer (Thermo Electron Corporation, Franklin, MA) and

49i O<sub>3</sub> analyzer (Thermo Electron Corporation, Franklin, MA) (Figure 1), were installed at MERI in the spring of 2007. Measurements of NO<sub>x</sub> and O<sub>3</sub> were made by pumping air into the two instruments via two separated plastic tubing lines with inlets installed on the roof of the MERI building. During the sampling period, the two analyzers were calibrated from time to time, and this interruption of the routine sampling resulted in certain gaps of data collection. NO<sub>x</sub> was determined on line by detecting the chemiluminescence in the range of 600 nm to 3,000 nm, and O<sub>3</sub> was measured by UV photometric method as O<sub>3</sub> molecules would absorb infrared radiation at a wavelength of 254nm. The relationship between absorbance of the UV-light and the ozone concentration follows the law of Lambert-Beer.

The hourly average data was derived from the original investigation at 5-minute intervals. The data point in each 1-hour range was treated as an outlier if it fell outside of the 3 times standard deviation from the mean, based on the Chauvenet's criterion. In this study, the percentages of the outliers for O<sub>3</sub>, NO and NO<sub>x</sub> were 0.006%, 0.17% and 0.03%, respectively. In addition, based on the EPA rules on the NO<sub>2</sub> and O<sub>3</sub> data, the 8-hour average, daily average and yearly average data were generated by the hourly average data (A valid day is defined as one with at least 75% of the possible 8-hour averages in the day. If a day is less than 75% complete, the day is counted valid if the daily maximum is greater than the level of the standard) ([www.epa.gov](http://www.epa.gov)). In each day, the hourly average data were divided into two parts in the study: daytime and nighttime. The time period from 7:00 to 19:00 was treated as daytime and the remaining hours were treated as nighttime, according to the average solar radiation changes during a day in the spring time of N.J. ([www.wunderground.com](http://www.wunderground.com)). The main processing and visualization of the data were carried out using Matlab and SigmaPlot.

## 5. RESULTS

### 5.1 NO<sub>x</sub> and O<sub>3</sub> Concentration Characteristics

#### 5.1.1 Summary of O<sub>3</sub> and NO<sub>x</sub> Concentrations

The monthly average O<sub>3</sub> concentrations in the study area ranged from 11.1ppb to 36.2ppb with relatively higher concentrations in summer and lower concentrations in winter, respectively (Table 1). Primarily, the time period from October 2007 to February 2008 was considered as the low ozone concentration season, while the March to September was treated as the high ozone concentration season. The yearly average concentration of ozone was 21.0ppb. The standard variations of ozone showed similar patterns in concentration with yearly average variations of ozone being 11.9ppb. As shown in Table 1, in June, July and August, both the concentrations and the variations of O<sub>3</sub> were high compared with other months.

For the monthly average NO<sub>x</sub> concentrations, no obvious seasonal variations were observed. In Table 1, the NO<sub>x</sub> concentrations ranged from 17.0 to 29.0ppb, and the yearly average concentration was 22.6ppb. Although the monthly concentrations of NO<sub>x</sub> were similar in different months, the summer season (June - August) showed relatively low NO<sub>x</sub> concentrations ranging from 17.0 to 19.6ppb. The standard variations of the NO<sub>x</sub> concentrations were relatively higher compared with ozone, even though their concentrations were at similar levels.

Similar to NO<sub>x</sub>, the NO and NO<sub>2</sub> concentrations did not show obvious seasonal variations, with yearly average concentrations being 6.51ppb and 16.1 ppb, respectively (Table 1). However, the daily standard variations of NO concentrations in each month were relatively higher to that of the NO<sub>2</sub>, probably due to the more reactive nature of NO. Compared with NO<sub>2</sub>, the concentrations of NO showed more significant seasonal variations. In winter (especially



December and January) the NO concentrations were higher than those in summer (especially in June and July).

### **5.1.2 Comparison with Results from Other Locations in the US East Coast**

Compared with other sites along the US East Coast (based on the EPA network), the 1<sup>st</sup> to 4<sup>th</sup> maximum concentrations of O<sub>3</sub> observed in the study area during the one-year measurement period were relatively high, with the values being 94.3, 94.0, 93.0 and 92.0 ppb, respectively (Table 2). In the observation period, the day when there was one 8-hour average O<sub>3</sub> concentration that exceeded the EPA standard (75ppb), was counted as the “Days > Std.”. In this study, there were 10 days when there was at least one 8-hour average O<sub>3</sub> concentration exceeding the EPA standard, and their concentrations were higher than those at other study sites as shown in Table 2.

The yearly average concentrations of NO<sub>2</sub> observed during this study period satisfied the EPA requirement (53ppb) well. In Table 3, the “# Exceed” was used to indicate the number of yearly average NO<sub>2</sub> concentrations exceeding the EPA standard. Even though the maximum concentrations of NO<sub>2</sub> were high, the average concentration of 16.1ppb was still within the EPA’s range of standard concentrations. The 1<sup>st</sup> and 2<sup>nd</sup> max concentrations and the mean concentration were comparable to other sites listed in Table 3.

## **5.2 Seasonal Concentration Variations of NO<sub>x</sub> and O<sub>3</sub>**

### **5.2.1 Daily-Based Patterns**

Temporal variations of the daily average NO<sub>x</sub> and O<sub>3</sub> concentrations during the one-year measurement period were shown in Figures 2 and 3, with different patterns for NO<sub>x</sub> and O<sub>3</sub>. The pattern of NO<sub>x</sub> was almost a flat line while the pattern of O<sub>3</sub> was a parabola line with its lowest point in December. The NO<sub>x</sub> concentrations were relatively higher in the winter and spring

period (from December to May), while the O<sub>3</sub> concentrations were relatively higher from April to August. Besides, both the daily average NO<sub>x</sub> and O<sub>3</sub> concentrations showed no continuous but rather, jumping characteristics, indicating significant variations among different days.

### **5.2.2 Monthly-Based Patterns**

Variations in monthly concentrations of NO<sub>x</sub> and O<sub>3</sub> during the one-year measurement period were presented in Figures 4 and 5, respectively. The distribution ranges for NO<sub>x</sub> were narrower in June to August and wider in December to May. While for O<sub>3</sub>, the wider distributions occurred in June to August, narrower variations were found in October, November and January. The opposite patterns in the concentration distributions of NO<sub>x</sub> and O<sub>3</sub> reflect different characteristics of these two species in the ambient air.

## **5.3 Diurnal Variations of NO<sub>x</sub> and O<sub>3</sub>**

### **5.3.1 Yearly-average Based Diurnal Variations**

Figure 6 showed the diurnal concentrations of O<sub>3</sub> and NO<sub>x</sub> with opposite patterns observed during the one-year study period at this location. The peak O<sub>3</sub> concentrations (~33ppb) occurred mainly around 2pm, and its lowest concentrations (~12ppb) occurred around 6am. During the daytime, the O<sub>3</sub> concentrations increased rapidly from 6am to 12pm, and from 12pm to 4pm the concentrations were maintained at very high levels with maximum concentrations around 2pm. However, after 4pm, the O<sub>3</sub> concentrations decreased rapidly until 8pm, and stayed at low levels from 8pm to 2am of the next day. The concentrations started to decrease rapidly again from 2am to 6am to reach the minimum concentration of the day.

The concentrations of NO<sub>x</sub> reached maximum (38ppb) around 7am in Figure 6. The NO<sub>x</sub> accumulation process mainly started from 4am and the concentration could be diluted rapidly from 7am to 10am, making NO<sub>x</sub> concentrations staying at the same level (~18ppb) before 4am

and after 10am. In addition, from 10am to the 4am of the next day, NO<sub>x</sub> concentrations changed little, except in cases where there was a slight increase of its concentration around 8pm. The pattern of diurnal variations of NO and NO<sub>2</sub> were primarily similar to that of the NO<sub>x</sub>, although some differences existed. NO<sub>2</sub> reached its highest concentrations earlier compared with NO<sub>x</sub>. Unlike NO<sub>x</sub>, there was no increase of concentration around 8pm for NO. Thus, the slight increase of NO<sub>x</sub> concentrations around 8pm could be mainly attributed to the presence of NO<sub>2</sub>.

### **5.3.2 Monthly Average Diurnal Variation Patterns**

To further investigate the pattern of seasonal and diurnal variations of NO<sub>x</sub> and O<sub>3</sub>, their monthly average diurnal variations were shown in Figure 7. In general, the diurnal variations of O<sub>3</sub> concentrations increased from January to June, and then decreased through December. The diurnal variations of O<sub>3</sub> concentrations from June to September were higher compared with other months, especially November to February. In addition, several O<sub>3</sub> concentration peaks were observed for each month, especially for months that showed relative lower diurnal variation levels. The less peaks observed in months with relatively higher diurnal variations might be the result of significant obscuration effect of higher peaks on the lower peaks. No obvious seasonal variations were found for the monthly average diurnal variations for the NO<sub>x</sub> concentrations. Comparatively, in April and May the diurnal variations of NO<sub>x</sub> concentrations were relatively higher, and in March and November such variations were relatively lower.

## **5.4 Weekdays/Weekends Differences of NO<sub>x</sub> and O<sub>3</sub> Characteristics**

### **5.4.1 Comparison of NO<sub>x</sub> and O<sub>3</sub> Concentrations Variations between Weekdays and Weekends**

Obvious weekdays/weekends differences in NO<sub>x</sub> and O<sub>3</sub> concentrations existed in this area. As shown in Table 4, the yearly average concentrations of NO<sub>x</sub> on weekends were much

lower compared with weekdays. This might result from the reduced traffic emissions on weekends. On the other hand, O<sub>3</sub> average concentrations on weekends were higher than that of the weekdays which indicates the possible negative influence of NO<sub>x</sub> on O<sub>3</sub>. Therefore, O<sub>3</sub> concentrations might be more sensitive to VOC (Volatile Organic Compound) than to NO<sub>x</sub>: the higher VOC concentrations lead to higher O<sub>3</sub> concentrations, while higher NO<sub>x</sub> concentrations lead to lower O<sub>3</sub> concentrations.

For variations of NO<sub>x</sub> and O<sub>3</sub> concentrations on weekdays and weekends, obvious differences were also found, as shown in Figure 8, Figure 9 and Table 4. Both NO<sub>x</sub> and O<sub>3</sub> showed smaller variations during weekends compared with weekdays. For the two components of NO<sub>x</sub>, NO<sub>2</sub> showed less concentration variations compared with NO. Such difference in variations was also found between Sunday and Saturday. Although the concentrations of NO<sub>x</sub> and O<sub>3</sub> were similar on Saturday and Sunday, their variations were both higher on Saturday compared with Sunday.

#### **5.4.2 Diurnal Variations of NO<sub>x</sub> and O<sub>3</sub> in Weekdays/Weekends**

The average major patterns of diurnal variations of NO<sub>x</sub> and O<sub>3</sub> on weekdays and weekends were shown in Figure 10. Diurnal variations of O<sub>3</sub> concentrations in weekdays and weekends were similar, both showing one peak in the early afternoon hours. While for NO and NO<sub>2</sub>, two peaks were observed both on weekdays and weekends: the first peak for both NO and NO<sub>2</sub> was much smaller on weekends compared with weekdays, and there was no significant difference between weekdays and weekends on the second peak. In addition, for weekdays, the first peak of NO and NO<sub>2</sub> was much more significant than the second one, especially for NO concentrations.

#### **5.5 NO<sub>x</sub>-O<sub>3</sub> Correlations**

### **5.5.1 Overall Correlation**

The correlation between hourly average  $\text{NO}_x$  and  $\text{O}_3$  concentrations in the study area showed mainly negative correlations. This may suggest the potential VOC sensitive nature of the study area, which means that higher  $\text{NO}_x$  concentrations would lead to lower concentrations of  $\text{O}_3$ . As shown in Figure 11, the maximum concentrations of  $\text{O}_3$  decreased with the increase of  $\text{NO}_x$ .

### **5.5.2 Weekdays/Weekends and Daytime/Nighttime Differences of the Correlation**

Even though the major correlation between  $\text{NO}_x$  and  $\text{O}_3$  concentration were similar, regardless of weekdays or weekends, daytime or nighttime, some differences existed between these time periods (Figures 12 and 13). Compared with weekdays, on weekends, the  $\text{O}_3$  could range much smaller for specific concentrations of  $\text{NO}_x$ , even though the  $\text{NO}_x$  concentrations were relatively lower, while  $\text{O}_3$  concentrations were relatively higher. This may indicate that on weekends, the inhibition ability of the  $\text{NO}_x$  to  $\text{O}_3$  concentrations was more significant.

A similar situation accounted for the difference between weekends and weekdays. As shown in Figure 13, for specific  $\text{NO}_x$  concentration, the maximum concentration that  $\text{O}_3$  could reach was much lower in the daytime compared with nighttime. This also indicates that  $\text{NO}_x$  concentrations could inhibit the  $\text{O}_3$  concentration more significantly in daytime than nighttime and might be attributed to the fact that the main inhibition effects were via photochemical reactions, which would occur mainly at night.

## **5.6 Effects of Environmental Factors**

### **5.6.1 Effects of Ambient $\text{NO}_3^-$ on $\text{O}_3$ and $\text{NO}_x$ Variations**

To explore the effects of particulate nitrate and nitric acid (jointly defined as  $\text{NO}_3^-$ ) on the variations of  $\text{O}_3$  and  $\text{NO}_x$  in the ambient air, a case study was carried out during the spring of

2007 with daily  $\text{NO}_3^-$  sampling at the same location for gas-phase  $\text{NO}_x$  and  $\text{O}_3$  sampling in this study. The results show that  $\text{NO}_3^-$  was involved in the  $\text{O}_3$  variations, and a higher  $\text{NO}_3^-$  level was primarily associated with a lower  $\text{O}_3$  level. As shown in Table 5, the daily average concentrations of  $\text{NO}_3^-$  showed a significantly negative correlation with those of  $\text{O}_3$ , while no correlations between  $\text{HNO}_3$  and  $\text{O}_3$  were found. Strong positive correlations between  $\text{NO}_3^-$  and  $\text{NO}_x$  were also observed; these can be explained by the reaction equations R5-R7.

### **5.6.2 Effects of Meteorological Parameters on $\text{O}_3$ and $\text{NO}_x$ Variations**

Meteorological parameters, ambient temperature, humidity, and wind speed, influenced the atmospheric  $\text{O}_3$  and  $\text{NO}_x$  concentrations, as shown in Figures 14 to 16. Primarily, the concentrations of  $\text{O}_3$  were influenced by temperature on both daily and hourly scales as seen in Figure 14. The daily average  $\text{O}_3$  concentrations increased exponentially to the increase of temperature as indicated in Figure 14a. The hourly average  $\text{O}_3$  concentrations increased with a narrower range when the temperature reached  $\sim 80\text{F}$ . On the other hand, the temperature did not show much influence on  $\text{NO}_x$  concentrations, suggesting that the  $\text{NO}_x$  might not vary as a function of ambient temperature.

The ambient humidity showed some influence on both  $\text{O}_3$  and  $\text{NO}_x$ . Higher humidity corresponded to the lower  $\text{O}_3$  concentrations but with higher  $\text{NO}_x$  concentrations. The daily average  $\text{O}_3$  concentrations mainly decreased linearly with the increase of humidity while the cvdaily average  $\text{NO}_x$  did not show obvious correlations (Figures 15a and 15c). However, on an hourly averaged scale, their correlations with humidity are much more obvious. As shown in Figure 15b, with the increase of humidity, while the upper boundary of  $\text{O}_3$  did not change much, the lower boundary of  $\text{O}_3$  decreased obviously. For  $\text{NO}_x$ , both the upper and lower boundaries obviously increased with the increase of humidity.

The daily average wind speed did not have an obvious influence on O<sub>3</sub> and NO<sub>x</sub> concentrations. However, their hourly average values could exert an effect on the O<sub>3</sub> and NO<sub>x</sub> concentrations, as indicated in Figure 16. Higher hourly average wind speed could increase O<sub>3</sub> concentrations (Figure 16b), while it would reduce the higher boundary and increase the lower boundary of NO<sub>x</sub> profiles (Figure 16d). Detailed mechanisms of these patterns need to be further explored.

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## Reference

- Butler, J. T., Likens, E. G., Vermeylen, M. F., Stunder, J.B. B., 2005. The impact of changing nitrogen oxide emissions on wet and dry nitrogen deposition in the northeastern USA. *Atmospheric Environment* 39, 4851-4862.
- Clapp, L.J., and Jenkin, M.E., 2001. Analysis of relationship between ambient levels of O<sub>3</sub>, NO<sub>2</sub> and NO as a function of NO<sub>x</sub> in the UK. *Atmospheric Environment* 35, 6391-6405.
- Junge, E.C., 1962. Global ozone budget and exchange between stratosphere and troposphere. *Tellus* 14, 363–377.
- Kampa, M., Castanas, E., 2007. Human health effects of air pollution. *Environmental Pollution* 151, 362-367.
- Lee, D.S., Holland, M.K., Falla, N., 1996. The potential impact of ozone on materials in the UK. *Atmospheric Environment* 30, 1053–1065.
- Parrish, D.D., 2006. Critical evaluation of US on-road vehicle emission inventories. *Atmospheric Environment* 40, 2288–2300.
- Seinfeld H. J., Pandis N. S., 2006. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley-Interscience, 2<sup>nd</sup> edition (August 11, 2006).
- WHO, 2000. *Guidelines for Air Quality*. World Health Organization, Geneva, 190.



## Figure Captions:

Figure 1. Instrumentation for NO<sub>x</sub> and O<sub>3</sub> measurements.

Figure 2. Temporal variation of the daily averaged NO<sub>x</sub> concentrations during the one-year period from June 1<sup>st</sup> 2007 to May 31<sup>st</sup> 2008.

Figure 3. Temporal variation of the daily averaged O<sub>3</sub> concentrations (06/01/2007- 05/31/ 2008).

Figure 4. Seasonal variations of monthly averaged NO<sub>x</sub> concentrations.

Figure 5. Seasonal variations of monthly averaged O<sub>3</sub> concentrations.

Figure 6. Diurnal variations of NO<sub>x</sub> and O<sub>3</sub> observed in the one-year period.

Figure 7. Monthly variation of the diurnal variations of NO<sub>x</sub> and O<sub>3</sub>.

Figure 8. Concentration variations of yearly averaged NO<sub>x</sub> concentrations for weekdays and weekends.

Figure 9. Concentration variations of yearly averaged O<sub>3</sub> concentrations for weekdays and weekends.

Figure 10. Variations of the diurnal variations of NO<sub>x</sub> and O<sub>3</sub> for weekdays and weekends.

Figure 11. The overall correlations between NO<sub>x</sub> and O<sub>3</sub>.

Figure 12. The weekdays/weekends comparison of the correlations between NO<sub>x</sub> and O<sub>3</sub>.

Figure 13. The daytime/nighttime comparison of the correlations between NO<sub>x</sub> and O<sub>3</sub>.

Figure 14. The Correlations between Temperature and O<sub>3</sub>, NO<sub>x</sub> concentrations in daily averaged scale (a, c) and hourly averaged scale (b, d) respectively.

Figure 15. The Correlations between Humidity and O<sub>3</sub>, NO<sub>x</sub> concentrations in daily averaged scale (a, c) and hourly averaged scale (b, d) respectively.

Figure 16. The Correlations between Wind Speed and O<sub>3</sub>, NO<sub>x</sub> concentrations in daily averaged scale (a, c) and hourly averaged scale (b, d) respectively.

Table 1. Summary of Monthly and Yearly Averaged Concentrations and Variations

Month	Concentrations (ppb)	O <sub>3</sub>	NO	NO <sub>x</sub>	NO <sub>2</sub>
1	Average± StdEv	14.1±6.3	12.1±19	29.0±24.7	16.9±7.1
	Minimum	1.6	0.9	7.0	6.0
	Maximum	24.9	79.6	109.9	30.3
2	Average± StdEv	15.2±8.8	7.3±7.3	23.2±13.8	15.9±7.2
	Minimum	1.1	1.1	7.0	5.5
	Maximum	29.4	30.0	58.0	29.0
3	Average± StdEv	23.2±8.4	6.4±8.0	22.7±16.3	16.3±9.1
	Minimum	7.2	0.6	4.6	4.0
	Maximum	36.2	38.0	72.8	34.7
4	Average± StdEv	25.0±8.8	7.5±6.7	27.7±16.3	20.2±10.8
	Minimum	7.3	0.8	4.3	3.4
	Maximum	41.7	26.0	73.9	53.5
5	Average± StdEv	27.4±9.3	6.3±7.8	24.0±17.1	17.7±10.4
	Minimum	3.8	0.6	5.2	4.7
	Maximum	45.4	31.7	60.1	37.4
6	Average± StdEv	36.2±11.6	3.7±4.0	19.3±9.5	15.5±6.2
	Minimum	15.3	0.5	4.6	4.1
	Maximum	63.0	15.7	46.9	33.3
7	Average± StdEv	30.5±11.9	2.7±2.3	17.0±9.3	14.3±7.6
	Minimum	9.9	0.2	4.4	4.1
	Maximum	55.6	9.6	38.4	34.0
8	Average± StdEv	29.0±12.9	5.0±3.4	19.6±8.2	14.6±5.9
	Minimum	5.2	0.3	5.4	3.3
	Maximum	52.0	13.7	39.9	28.6
9	Average± StdEv	22.5±9.4	5.0±5.0	20.6±11.5	15.5±7.0
	Minimum	5.5	0.6	7.2	5.8
	Maximum	46.6	17.8	52.1	34.3
10	Average± StdEv	16.3±8.0	7.4±7.9	23.8±14.3	16.4±6.7
	Minimum	6.7	0.5	8.2	7.2
	Maximum	38.1	32.4	65.5	33.1
11	Average± StdEv	11.5±6.0	5.4±6.5	18.2±10.3	12.9±4.9
	Minimum	0.2	0.8	6.0	5.1
	Maximum	20.7	31.0	47.7	24.8
12	Average± StdEv	11.1±7.2	9.1±12.3	25.8±17.1	16.7±8.0
	Minimum	0.3	0.7	6.1	5.4
	Maximum	27.2	64.0	94.4	46.5
Yearly	Average± StdEv	21.9±11.9	6.5±8.9	22.6±15.0	16.1±7.9
	Minimum	0.2	0.2	4.3	3.3
	Maximum	63.0	79.6	109.9	53.5

Table 2. Comparisons of O<sub>3</sub> concentrations with other nearby sites along the US East Coast

Sites	8-Hour Mean (ppb)					
	1 <sup>st</sup> Max	2 <sup>nd</sup> Max	3 <sup>rd</sup> Max	4 <sup>th</sup> Max	Days > Std	# Days
Lyndhurst, NJ (The Study)	94.3	94.1	92.7	92.1	10	282
EPA Standard	75 (8-hour average)					
Oceanville, NJ	76	72	72	72	1	173
Leonia, NJ	89	89	85	82	6	172
Bayonne, NJ	90	86	81	81	7	175
East Brunswick, NJ	94	89	86	83	13	183
West Long Branch, NJ	89	86	86	83	10	183
Chester, NJ	86	84	82	81	9	162
Jackson, NJ	100	90	85	85	15	182
Albany, NY	88	84	78	77	5	195
New York, NY	84	81	78	77	5	203
New York, NY	90	87	82	82	6	207
East Farmingdale, NY	94	93	85	83	8	202
White Plains, NY	101	91	86	82	10	186
Greenwich, CT	105	102	90	88	14	172
Middletown, CT	91	83	83	82	8	182
Hagerstown, MD	84	80	78	75	3	212
Baltimore, MD	82	65	62	62	1	212
Lynn, MA	86	81	79	78	5	182
Boston, MA	83	73	72	72	1	178
Cooleemee, NC	89	84	82	81	6	214
Greensboro, NC	88	83	83	81	5	195
Pittsburgh, PA	84	79	79	79	7	214
State College, PA	81	77	74	74	2	209
East Providence, RI	88	86	85	77	4	175
Mclean, VA	102	90	81	80	6	213
Hampton, VA	88	82	79	79	4	179

Table 3. Comparisons of NO<sub>2</sub> concentrations with other nearby sites in the US East Coast

Sites	1-Hour Mean (ppb)			Annual Mean
	1 <sup>st</sup> Max	2 <sup>nd</sup> Max	Mean	# Exceed
Lyndhurst, NJ (The Study)	77.4	72.7	16.1	0
EPA Standard	-	-	53	-
Leonia, NJ	84	83	19	0
East Orange, NJ	79	76	21	0
Bayonne, NJ	82	80	18	0
East Brunswick, NJ	56	53	11	0
Chester, NJ	49	48	6	0
Elizabeth, NJ	93	89	27	0
New York, NY	89	87	25	0
New York, NY	97	90	36	0
Lynn, MA	61	61	8	0
Boston, MA	54	50	7	0
Pittsburgh, PA	113	94	14	0
State College, PA	42	41	6	0
East Providence	31	31	6	0
Mclean, VA	72	68	13	0
Westport, CT	62	60	12	0
New Haven, CT	64	62	15	0
Beltsville, MD	49	49	9	0
Baltimore, MD	78	73	18	0
Winston-Salem, NC	61	61	11	0
Charlotte, NC	59	58	11	0

Table 4. Weekdays/weekends Variations of NO<sub>x</sub> and O<sub>3</sub> concentrations

Weekdays		<u>Average Concentration (ppb)</u>			
		O <sub>3</sub>	NO	NO <sub>2</sub>	NO <sub>x</sub>
Monday	Average± StdEv	21.8±13.3	6.68±10.2	16.5±8.0	23.2±18.2
	Minimum	0.3	0.5	3.3	6.1
	Maximum	55.6	66.0	46.5	95.7
Tuesday	Average± StdEv	20.0±12.0	8.4±8.2	18.4±6.6	26.8±14.7
	Minimum	1.4	0.8	8.5	9.9
	Maximum	53.6	39.9	37.4	63.8
Wednesday	Average± StdEv	21.8±12.2	6.9±7.4	16.8±7.8	23.7±15.2
	Minimum	0.2	0.7	5.0	6.0
	Maximum	63.0	32.4	35.7	65.5
Thursday	Average± StdEv	22.1±11.9	7.03±6.2	17.4±7.5	24.4±13.7
	Minimum	3.3	0.5	6.5	7.5
	Maximum	54.4	26.3	42.0	68.1
Friday	Average± StdEv	19.6±12.1	8.23±10.6	19.1±10.0	27.3±20.6
	Minimum	0.6	0.3	4.3	5.1
	Maximum	53.1	64.0	53.5	94.4
Saturday	Average± StdEv	24.0±12.3	4.5±11.3	12.3±5.9	16.8±17.1
	Minimum	2.2	0.5	4.1	4.6
	Maximum	60.6	79.6	30.3	109.9
Sunday	Average± StdEv	24.0±10.0	3.58±6.2	11.6±4.9	15.2±11.1
	Minimum	1.6	0.2	3.4	4.3
	Maximum	50.3	39.2	25.3	64.4

Table 5. Pearson correlations among  $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{NO}_x$ ,  $\text{O}_3$ .

	$\text{HNO}_3$	$\text{NO}$	$\text{NO}_2$	$\text{O}_3$
$\text{HNO}_3$		0.111	0.114	0.106
$\text{NO}_3^-$	0.321**	0.448***	0.588***	-0.513***

\*\*  $p < 0.01$ , \*\*\*  $p < 0.001$



Figure 1

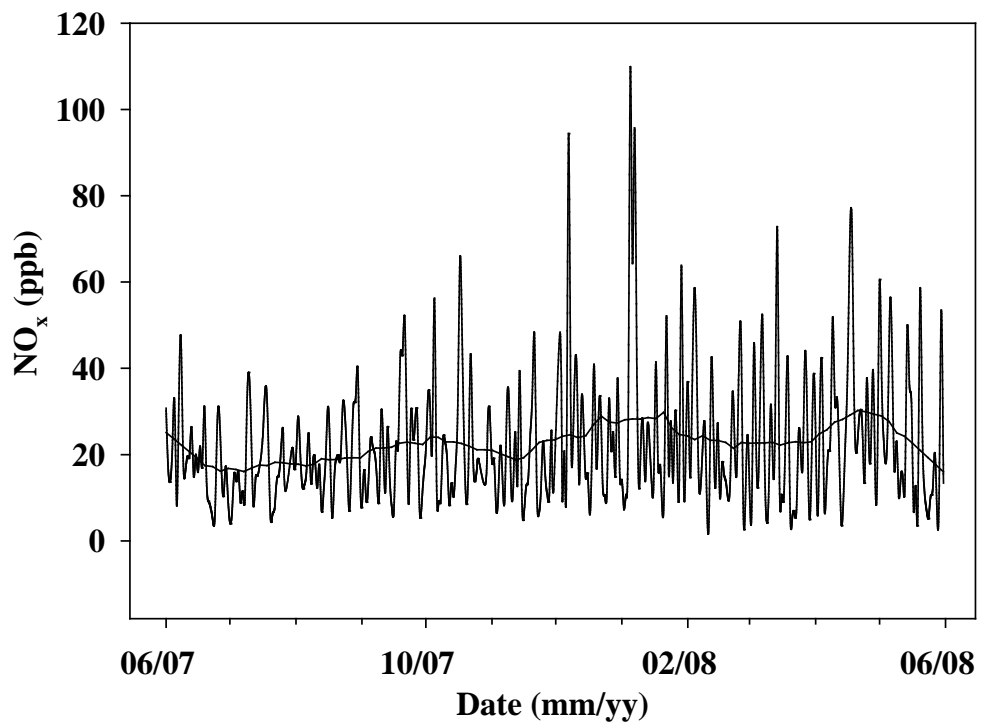


Figure 2



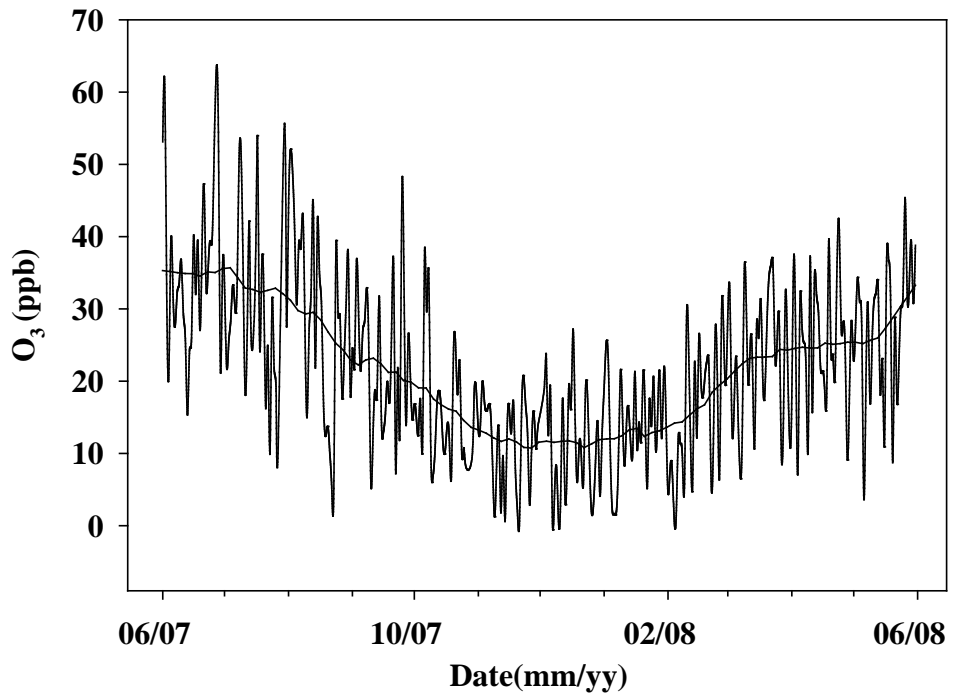


Figure 3

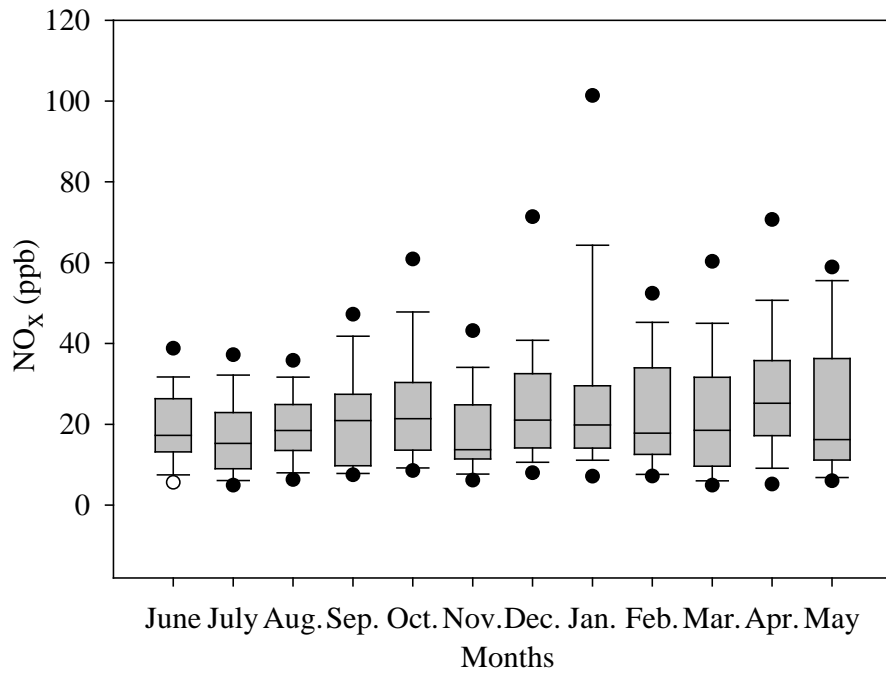


Figure 4

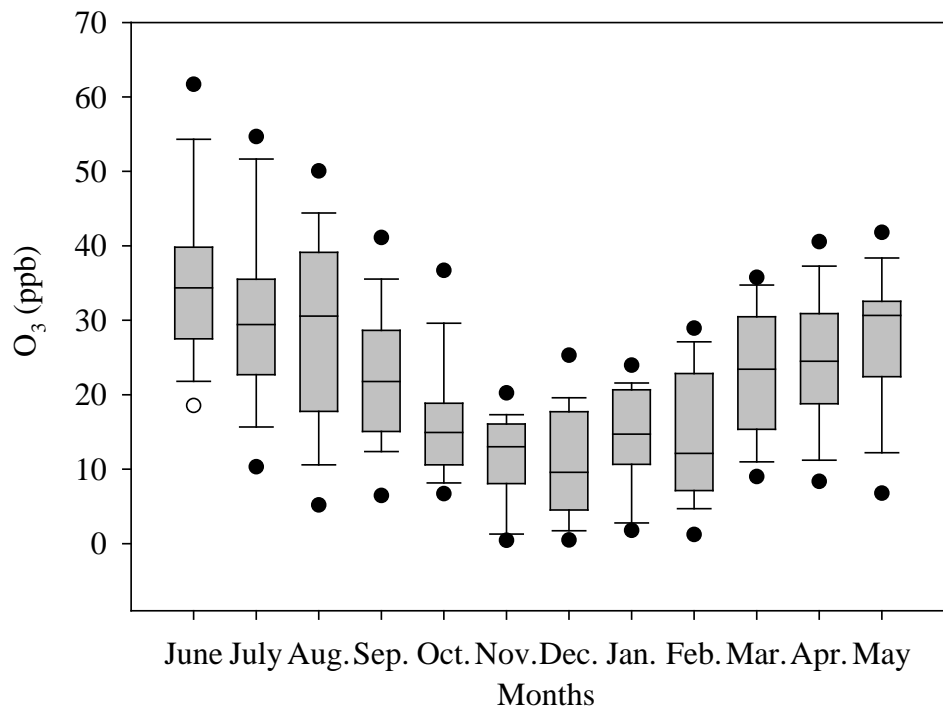


Figure 5

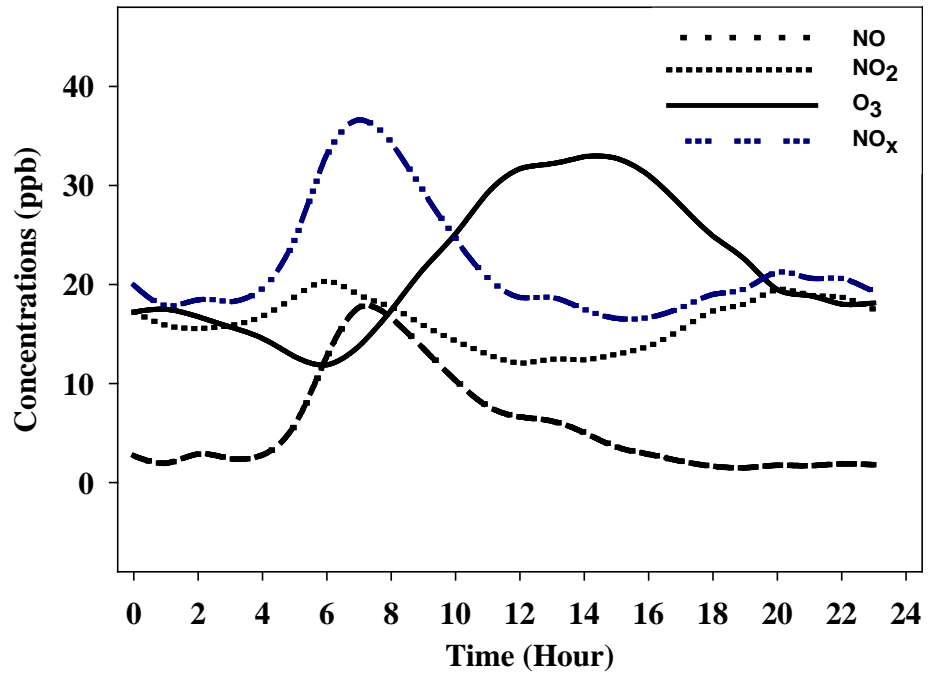


Figure 6

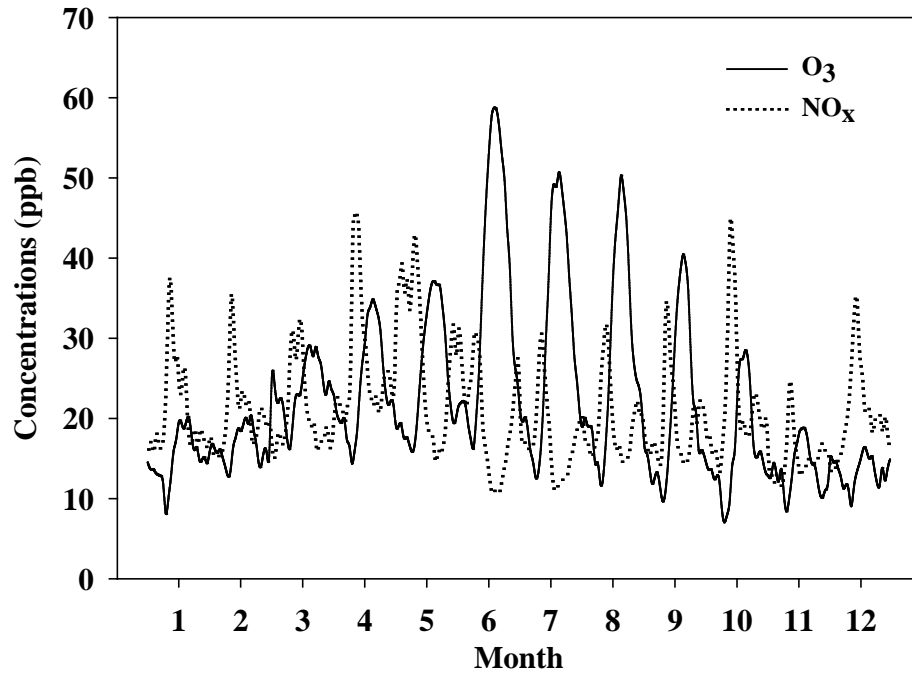


Figure 7

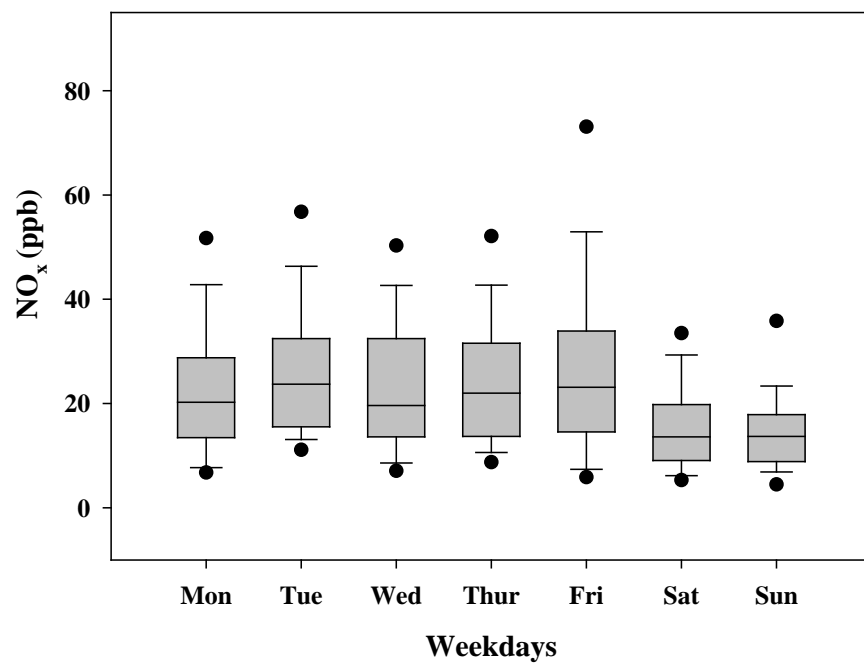


Figure 8

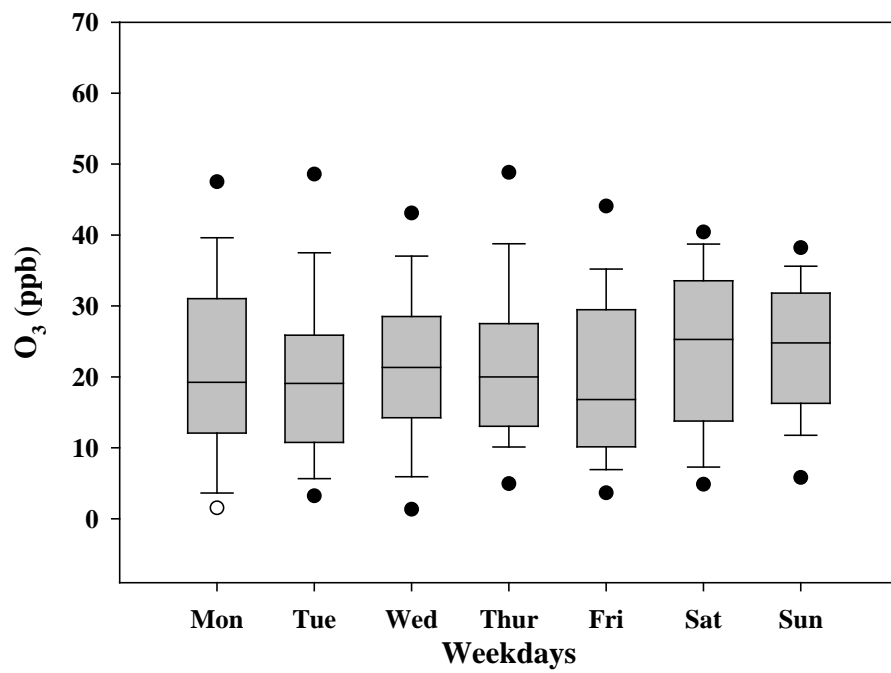


Figure 9

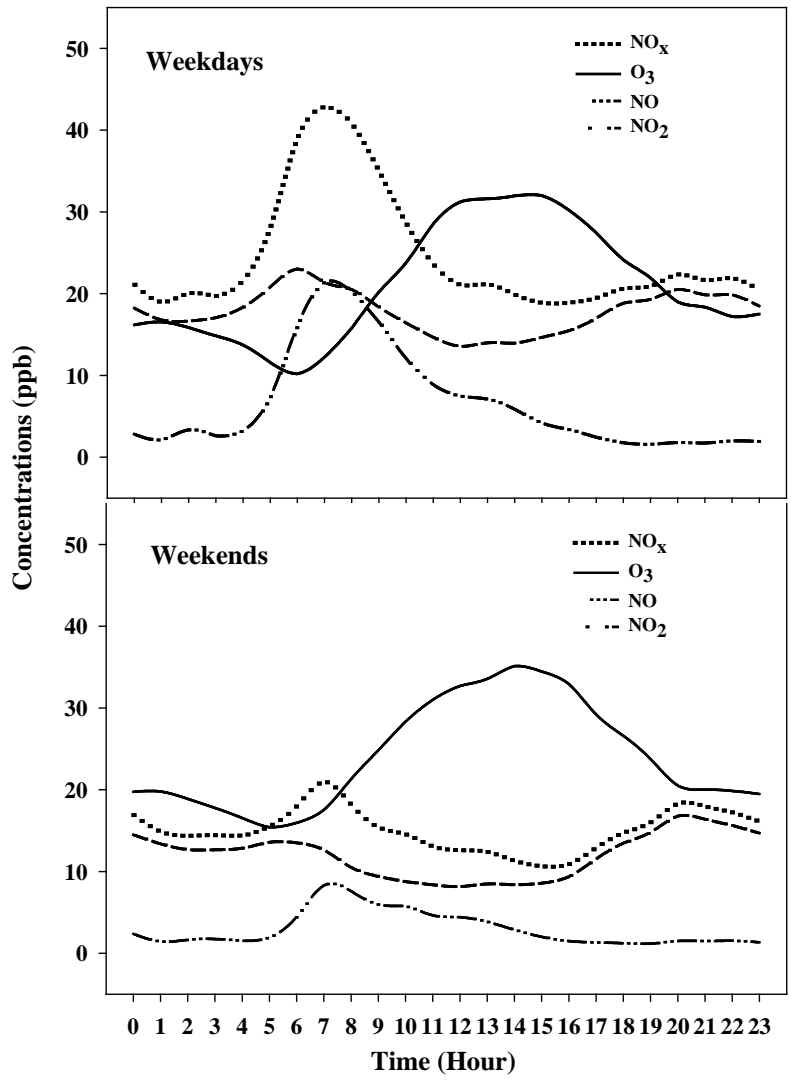


Figure 10



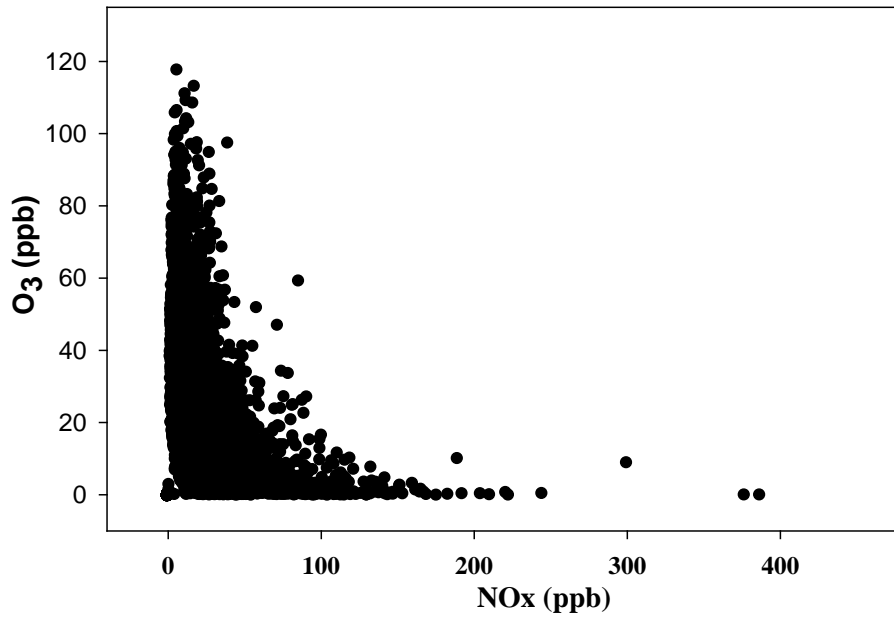


Figure 11

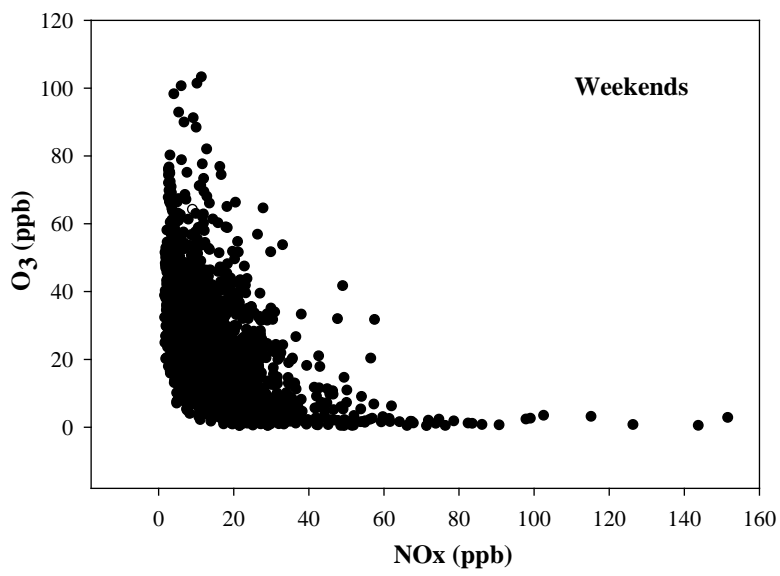
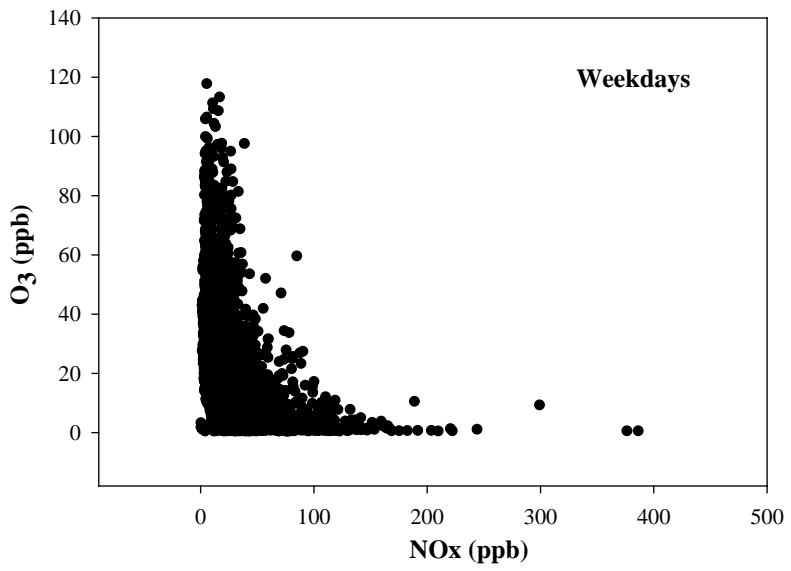


Figure 12

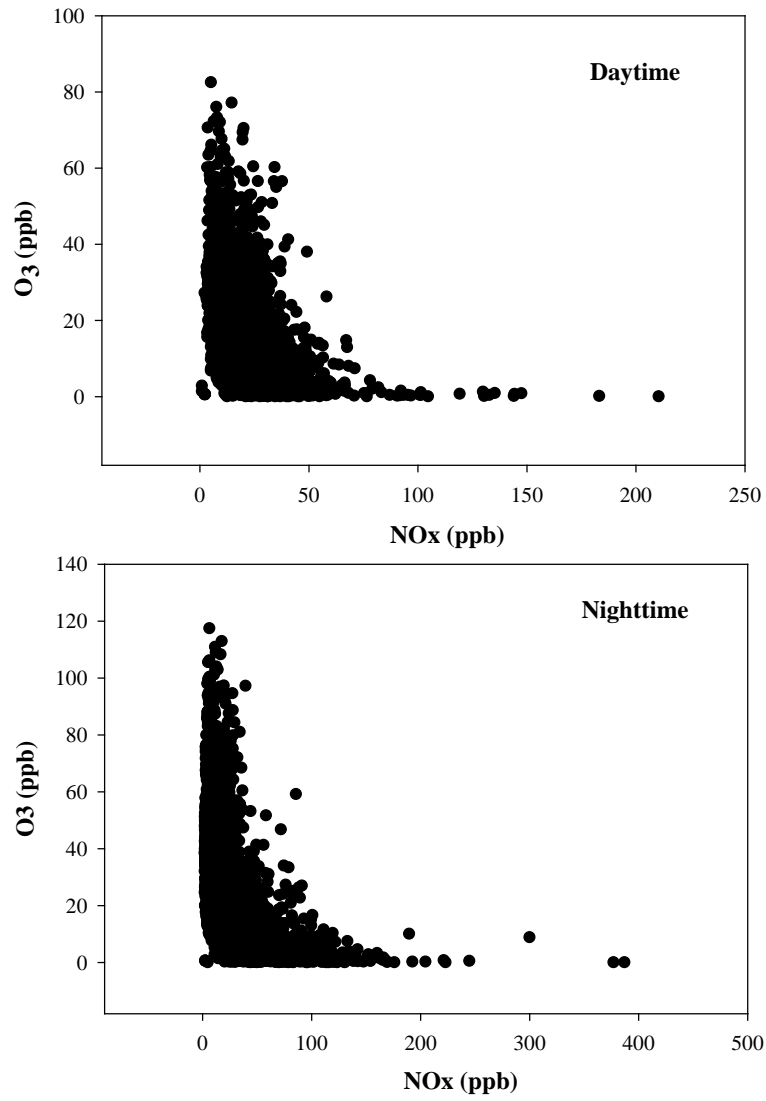


Figure 13

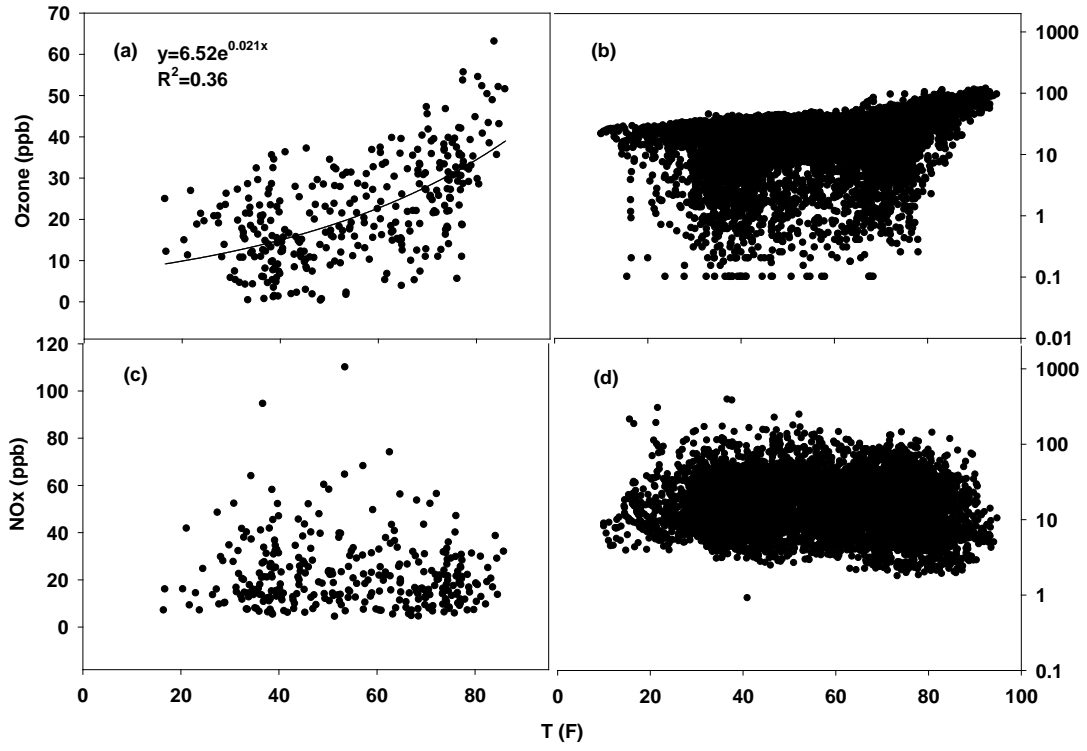


Figure 14

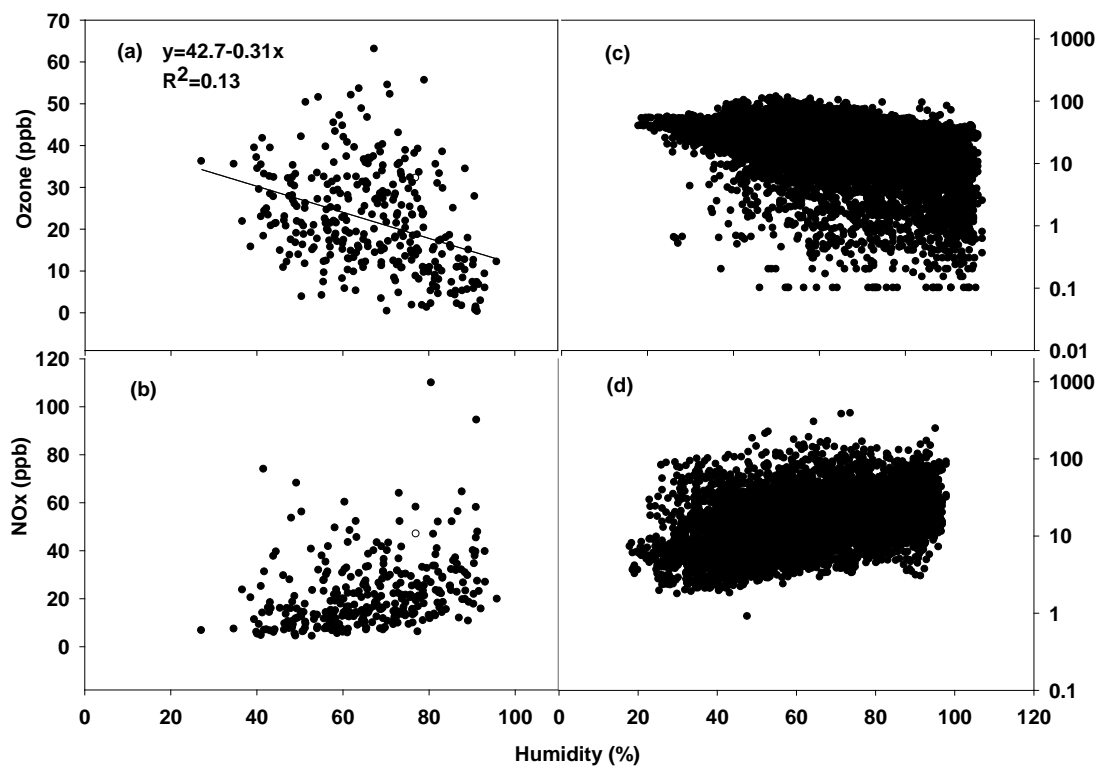


Figure 15

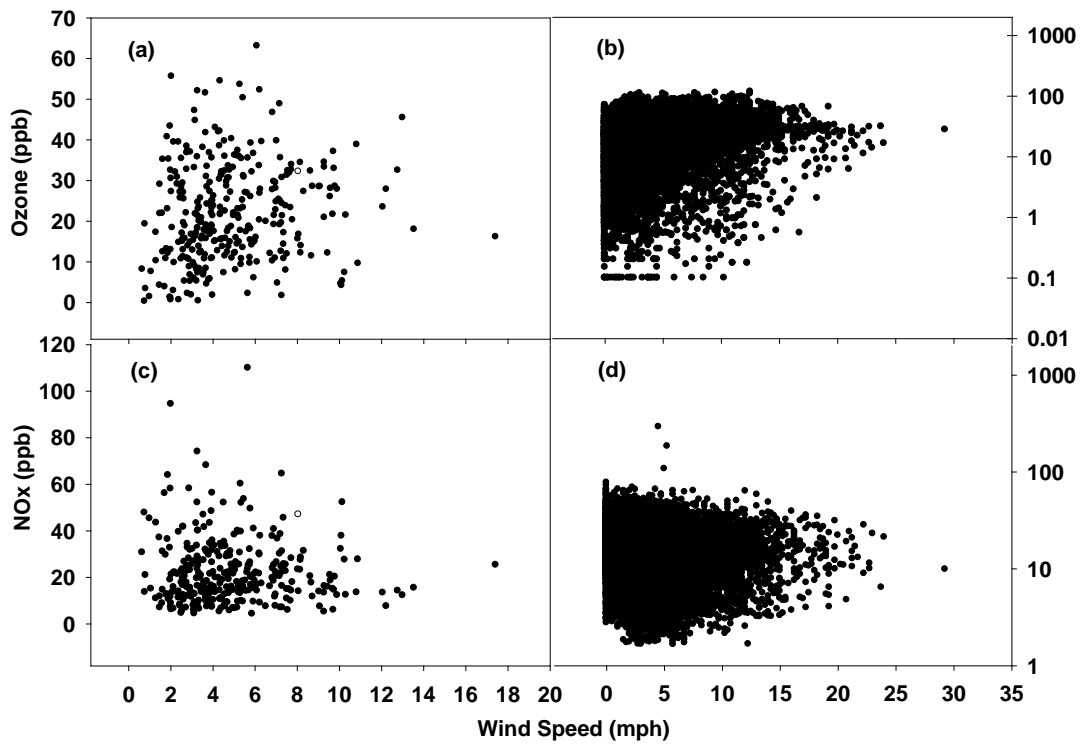


Figure 16