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Seasonal characteristics of ambient nitrogen oxides and ground–level ozone in metropolitan northeastern New Jersey

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ABSTRACT

Nitrogen oxides (NO_x) and ground–level ozone (O_3) were measured and meteorological parameters, wind speed, temperature, relative humidity and barometric pressure were monitored, to determine the seasonal variations of gas–phase pollutants in the Meadowlands. O_3 and NO_x were inversely related; the highest average NO_x concentration (29 ppb) occurred in winter while average O_3 concentrations peaked in summer up to 36.2 ppb. The seasonal variations of O_3 were more distinct than NO_x. In multiple linear and principal component regression analysis, ambient levels of NO_2 and O_3 were influenced primarily by wind speed. In time series and regression analysis, NO_2 and O_3 displayed an inverse relationship with wind speed but O_3 paradoxically increased with wind speed downwind.

The seasonality of O_3 was amplified mainly by wind speed and temperature, while NO_x displayed stronger dependence on diurnal source emissions. Concentrations of NO_x and O_3 were also influenced by differences in chemical processing through their complex emission–production and consumption mechanisms, making them interdependent. In intense solar radiation, O_3 was NO_x–dependent but as O_3 levels were inhibited by lower temperatures, NO_x concentrations increased. Higher O_3 on weekends indicated an apparent sensitivity to VOC precursors. This study provides a basis for improved air quality standards primarily in summer and during daily O_3 peaks. Additionally, plans for protection against health problems caused by O_3 and NO_X are feasible in this region.

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1. Introduction

Nitrogen oxides (NO_x) and ozone (O_3) are two of the six criteria pollutants assigned by the National Ambient Air Quality Standard (NAAQS), regulated by the United States Environmental Protection Agency (USEPA). NO_x comprise a mixture mainly of nitric oxide (NO) and nitrogen dioxide (NO_2), prominent in air quality studies (WHO, 2003; Brook et al., 2004). Although NO is a simple molecule, its production secondarily generates strong oxidizing agents and reactive nitrogen species notably NO_2, that may modulate the development of chronic inflammatory airway diseases (Ricciardolo et al., 2004). NO_2 has been generally kept at low levels through alert systems with published levels, next–day forecasts, real time air quality information and the Low Emission Vehicle program (Brook et al., 2004; NJDEP, 2006; USEPA, 2006). As a precursor pollutant of O_3, however, NO_2 poses a threat to public health (Ito et al., 2007; Berti et al., 2009; Lopez–Villarrubia et al., 2010; Linares et al., 2010; Kelly et al., 2011; Namdeo et al., 2011).

Produced from both natural and anthropogenic sources, NO_x is formed in the atmosphere by the action of lightning on molecular oxygen and other chemical reactions involving naturally occurring nitrogen and volatile organic compounds (VOCs) (Sillman, 1999; Godish, 2004; Brown et al., 2006). Previous studies have shown, however, that NO_x emissions from anthropogenic sources exceed natural sources (Godish, 2004). Increased combustion of fossil fuels and exhaust fumes may be extremely pervasive, causing serious environmental degradation, illnesses and deaths (Farrell et al., 1999; Godish, 2004; Ricciardolo et al., 2004; Gurjar et al., 2008). In the eastern United States, vehicular traffic contributed more than half of the total NO_x emissions with an increasing trend since the 1990s (Butler et al., 2005; Parrish, 2006). High temperature causes the oxidation of atmospheric N_2, first to NO and then to NO_2 (Sadanaga et al., 2008; Geddes et al., 2009), which plays a major role in the formation of ground–level O_3 (Farrell, 1999; Godish, 2004).

$$NO_2 + h\nu \rightarrow NO + O \quad \text{(R1)}$$
$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$
$$O_3 + NO + h\nu \rightarrow NO_2 + O_2 \quad \text{(R3)}$$
$$NO + RO_2 \rightarrow NO_2 + RO \quad \text{(R4)}$$

Although O_3 originates mainly from the upper stratosphere via convection movements, tropospheric O_3 production is largely dependent on the concentration of NO_x (Clapp and Jenkin, 2001) in photochemical reactions, as shown above (R1–R2). The complexity of these series of reactions results in both the production and destruction of O_3 (R3). The photolysis of NO_2 to NO and oxygen atoms, is the first in the reaction series. By oxidizing NO to NO_2, a reactive oxygen–containing molecule (RO_2) such as a VOC (R4), helps to promote O_3 production in the presence of bright sunlight or high energy radiation (Seinfeld and Pandis, 2006; Brown et al., 2006; Song et al., 2011). While many VOCs are short–lived or exist in trace amounts well below the detection limit of current sampling methods (Godish, 2004), NO_x and O_3 rapidly interconvert within minutes to hours via photochemical reactions (Seinfeld and Pandis, 2006; Wei et al., 2007; Sadanaga et al., 2008; Geddes et al., 2009), posing major risks to public health (Blanchard and

Tanenbaum, 2006; Torres–Jardon and Keener, 2006; Bigi and Harrison, 2010).

Over the past decade, there has been a steady decline in NO_x emissions but despite regulations, the national health–based O_3 standard has been repeatedly exceeded in many parts of the country (Sillman, 1999; Godish, 2004; USEPA, 2006; Sadanaga et al., 2008), including New Jersey (Madsen and Mottola, 2003; NJDEP, 2006). It is unclear how NO_x and O_3 interact with atmospheric conditions in northeastern New Jersey. The main objective of this study, therefore, is to assess the meteorological conditions on which ambient concentrations of NO_x and O_3 may strongly depend in this region. It attempts to characterize the seasonal patterns of NO_x and O_3 when concentrations are enhanced by local meteorology, and highlights the fundamental mechanisms that drive NO when altered under variable atmospheric conditions. These aspects of air quality research have not been fully studied particularly in the Meadowlands. An understanding of such mechanisms may lead to better regulation and provide a novel target in the reduction of air pollutants that cause respiratory and inflammatory diseases of the airways.

2. Material and Methods

2.1. Study region

The Meadowlands District is located in northeastern New Jersey (41°N, 74°W) approximately four miles west of New York City. This heavily industrialized and densely populated region comprises residential developments and occupies 83 km^2 mostly at sea level (Figure 1). The prevailing winds blow from the southwest in summer and from the northwest in winter. On hot summer days, southwesterly winds are laden with air pollutants from the Washington, Baltimore and Philadelphia metropolitan areas that reach the Meadowlands and other areas in New Jersey (http://www.co.hunterdon.nj.us/mun/Holland/Climate.pdf). Air quality in the Meadowlands has been affected by surrounding major highways and transit systems, including the New Jersey Turnpike in the south.

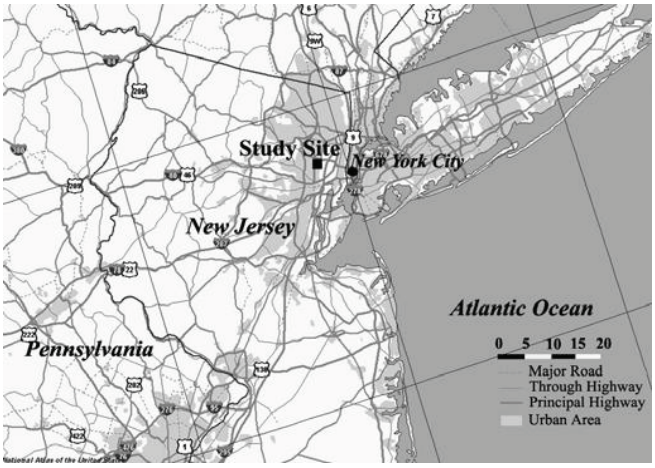

Figure 1. *Situation of study site/monitoring station in proximity to highways and pollutant source regions.*

2.2. Sampling methods

Measurements of NO_x and O_3 were obtained from June 1, 2007 to May 31, 2008 at the Meadowlands Environmental Research Institute (MERI) in Lyndhurst, New Jersey (41°N, 74°W), ~1 km away from major highways. A 42i–D NO_x analyzer (Thermo Electron Corporation, Franklin, MA) and 49i O_3 analyzer (Thermo Electron Corporation, Franklin, MA) were installed on the roof of the MERI building 8 m above the ground in spring 2007. Air was pumped into the instruments from inlets via two separate plastic tubes. To assure data reliability, reduce bias and associated errors, the sampling and monitoring instruments (analyzers) were calibrated bi–weekly (Munger et al., 1998). Inevitably, due to the large data set, there are minor gaps in the data collection resulting primarily from routine instrument calibrations.

Nitrogen oxides were determined on–line by detecting the chemiluminescence in a range of 600 nm to 3 000 nm, and O_3 was measured by the UV photometric method since O_3 molecules absorb infrared radiation at a wavelength of 254 nm. The relationship between absorbance of UV–light and O_3 concentration follows the law of Lambert–Beer. Hourly averaged data were derived from the original 5–minute interval data. Based on the Chauvenet's criterion, 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: 0.006%, 0.17% and 0.03%, for O_3, NO and NO_x respectively. In addition, consistent with EPA guidelines for NO_2 and O_3, 8–hour, daily and yearly averages were generated from the hourly averaged data. In this case, a valid day is defined as one with at least 75% of the possible 8–hour averages in the day. A day that is less than 75% complete is only considered valid if the daily maximum is greater than the standard (www.epa.gov).

For each day, the hourly averages were grouped into daytime (7:00 hrs to 19:00 hrs) and nighttime (19:01 hrs to 6:59 hrs) based on average solar radiation changes during a day in the spring time of N.J. (www.underground.com). Data collected for these two periods were distinguished mainly by the photochemical activity of O_3 and its precursors, similar to the approach used by Abdul–Wahab et al. (2005). Meteorological data obtained from MERI were supplemented with data from Weather Underground, a reliable and accurate web source containing specific localized weather conditions. The primary meteorological parameters were temperature, wind speed, relative humidity and atmospheric pressure.

2.3. Data analyses

Time series plotting techniques were used to visualize the seasonal, monthly, diurnal and weekday versus weekend patterns of NO, NO_2, NO_x and O_3 concentrations. Auto–correlations of the daily pollutant concentrations were conducted to estimate pollutant persistence, and cross–correlations between meteo–rological variables and pollutants were conducted to test the same day or lagged relationships between them. Multiple linear regression techniques are known to be effective in explaining significant relationships between weather parameters and seasonal characteristics (Ainslie and Steyn, 2007; Hatzianastassiou et al., 2007; Abe et al., 2009). This approach has also been central to the regulatory policy process and is useful in evaluating the risks of air pollution (Dominici et al., 2004; Ainslie and Steyn, 2007). In this study, therefore, the stepwise regression modeled the association between air pollutants and meteorological parameters, similar to the method used by Weisel et al. (1995) and Abdul–Wahab et al. (2005). The regression model was given as $y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \ldots + \beta_p x_p + \varepsilon$ where y is the dependent variable (O_3/NO_2), xi is the i^{th} independent variable, β_1 is the regression coefficient, β_0 is the intercept, p is the number of independent variables, and ε is the error with mean zero.

To overcome possible multicollinearity among the indepen–dent variables in the stepwise regression and to validate the relationship between air pollutants and meteorological variables, the principal component analysis (PCA) described by Liu et al. (2003) and Abdul–Wahab et al. (2005) was employed. The PCA, a special case of factor analysis, was conducted by transforming highly correlated independent variables, particularly O_3 precursors and wind speed, into principal components that are independent of each other (Liu et al., 2003; Abdul–Wahab et al., 2005; Gvozdic et al., 2011). Statistical analyses in this study were conducted with

Table 1. *Summary of monthly and yearly average concentrations and variations*

Month	Concentrations (ppb)	O_3	NO	NO_x	NO_2
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

Statistical Package for the Social Sciences (SPSS) version 18.0, Statistical Analysis System (SAS) 9.2, and MINITAB 16 software packages.

3. Results and Discussion

3.1. Seasonal patterns

The seasonal cycles of O_3 and NO_x were driven by their response to local meteorological conditions and resultant chain reactions among them. The average monthly/annual concen–trations and variations of O_3, NO_x, NO and NO_2 (Table 1), and time series graph show opposing trends in NO_x and O_3 concentrations (Figure 2), either amplified or diminished by a summer maximum and winter minimum. The monthly average diurnal variations of NO_x and O_3 display a gradual increase in O_3 variations from March to June, with pronounced variations until September, followed by a decrease through December. Such variations are apparently caused by photochemical differences across seasons. In months with relatively lower diurnal variations, the more prominent O_3 peaks were apparently obscured by lower peaks in months with relatively higher variations. Conversely, NO_x showed no pro–nounced diurnal variations except in April and May.

The annual average O_3 concentration was 21.9 ppb, with pronounced variations mainly in summer. Daily mean O_3 values displayed summer highs with a gradual decline into spring (March to August) and winter lows (December to February). The monthly NO_x concentrations ranged from 17.0 to 29.0 ppb and the annual average was 22.6 ppb with an increasing trend towards the winter. The seasonal variations in NO_x were common to several studies (Khoder, 2009; Smith et al., 2011; Guttikunda and Gurjar, 2011), attributed to the poor dependence of NO_x on meteorological conditions. Similar trends observed for NO and NO_2 consisted of a winter peak and summer minima (Khoder, 2009; Bigi and Harrison, 2010; Kan et al., 2010; Smith et al., 2011). This enhanced seasonality of NO_x levels in winter may be partly attributed to increased fossil fuels for domestic heating and driving. Therefore, anthropogenic sources seem to play a greater role in NO_x build–up than local meteorological conditions in winter; NO from traffic emissions is converted to NO_2 while the photochemical formation of O_3 is inhibited by the lack of intense solar radiation (Sadanaga et al., 2008; Geddes et al., 2009).

3.2. Monthly patterns

Figure 3 shows variations in monthly average NO_x and O_3 concentrations. Average O_3 ranged from 11.1 ppb to 36.2 ppb, with wide distribution ranges from June through August, and increased in the winter.

The distribution ranges displayed for NO_x were narrower in summer, June to August, than in winter and spring, December to May. Table 2 compares the average monthly concentrations of NO_x and O_3 with other locations in the US East Coast. Maximum O_3 values in the study area, 94.3, 94.0, 93.0 and 92.0 ppb,

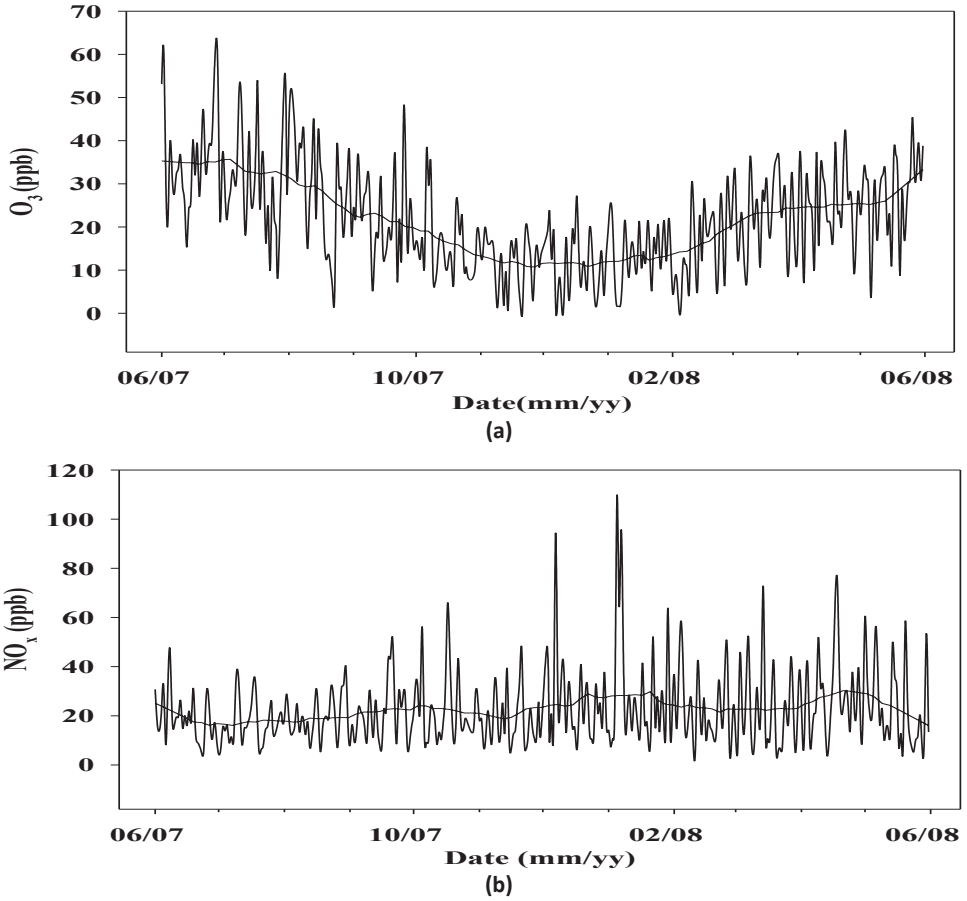

Figure 2. *Temporal variations of the daily average* ***(a)*** *O_3 and* ***(b)*** *NO_x concentrations during the one–year period (June 1, 2007 to May 31, 2008). Ozone displays summer maxima and winter minima with pronounced variations in the colder months; NO_x displays the opposite trend. Variations in NO_x are greater in the summer than in winter.*

Table 2. *Comparisons of O_3 concentrations with other nearby sites on US East Coast*

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

[1] Present study; [2–27] http://www.epa.gov

Table 3. *Comparisons of NO_2 concentrations with other nearby sites on US East Coast*

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

[1]Present study; [2–22] http://www.epa

respectively, were relatively higher than most sites within the EPA network. The 8–hour average O_3 concentrations calculated for 8 consecutive hours on a given day, denoted as "Days > Std", exceeded the EPA standard of 75 ppb on 10 days at the study site and were higher than levels at EPA sites. On the other hand, the annual average NO_2 concentration (53 ppb) satisfied the EPA requirement (Table 3). Despite high maximum NO_2 levels, the average concentration (16.1 ppb) was within the EPA standard and there were no exceedances ("# Exceed"). The 1st and 2nd maximum and mean concentrations were also comparable to other sites.

3.3. Diurnal variations of NO_x and O_3

Figure 4 presents the diurnal variations of NO_x and O_3. The major O_3 peak lasted from late morning until early afternoon. This photochemically active period was apparently accentuated by a preceding build–up of precursors and increased electrical loads for air conditioning particularly in the summer. This feature demonstrates O_3 dependence on both emissions and meteo–rological conditions. The lowest O_3 concentration (~12 ppb) occurred around 6:00 A.M. but it increased steadily to its highest peak (~33 ppb) around 2:00 P.M. High levels were maintained until 4:00 P.M. but decreased rapidly until 8:00 P.M., then gradually until 6:00 A.M. of the next day.

Conversely, NO_x displayed morning and late afternoon peaks which coincided with rush–hour traffic. The accumulation process

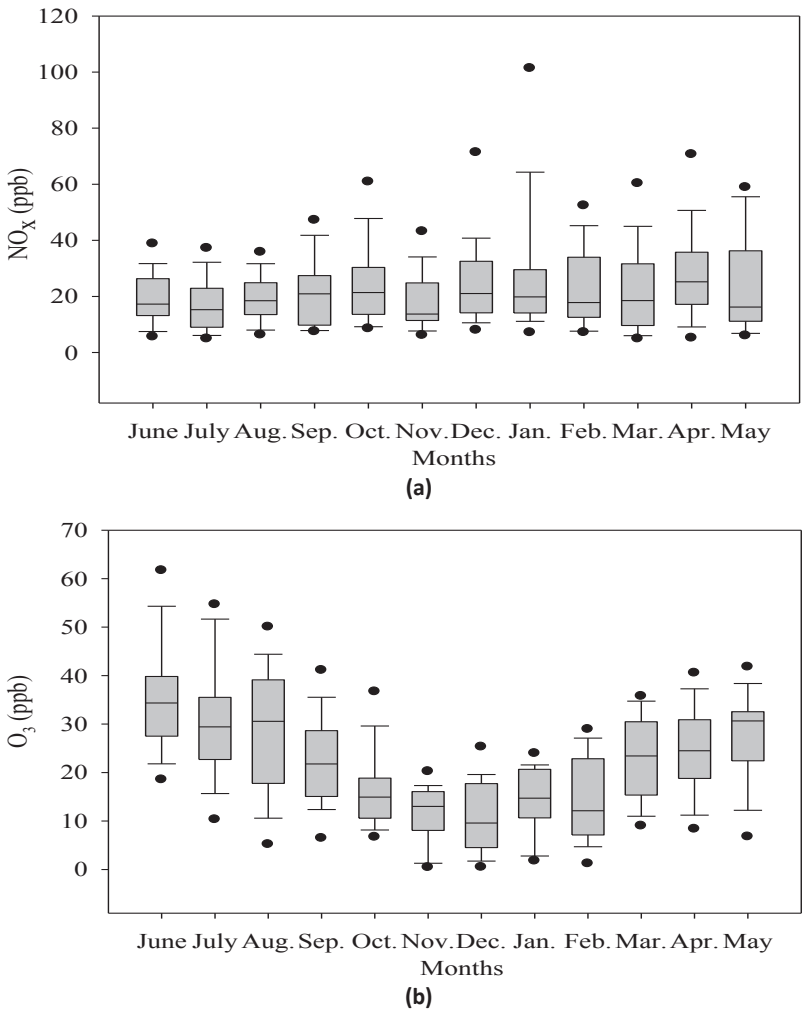

Figure 3. *Seasonal variations of monthly average NO_x and O_3 concentrations. Box plots show **(a)** NO_x and **(b)** O_3 concentrations from June 1, 2007 – May 31, 2008.*

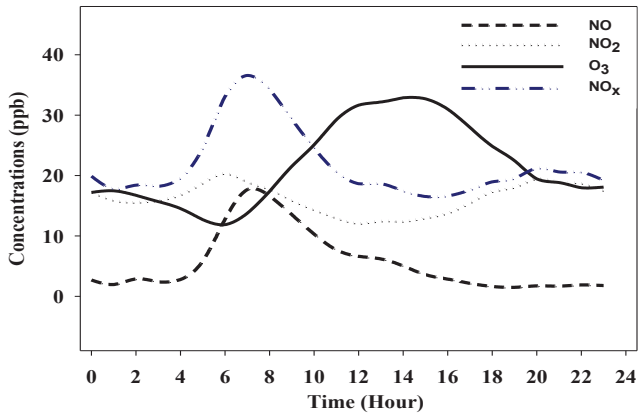

Figure 4. *Diurnal variations of NO, NO_2, NO_x and O_3 measured over 24–hour period. The morning NO, NO_2, NO_x peaks are followed by an O_3 photochemical peak later in the day.*

commenced from 4:00 A.M., reached a peak of 38 ppb around 7:00 A.M., then diluted rapidly until 10:00 A.M. to ~18 ppb; however, while NO_2 was also characterized by two daily peaks, NO was devoid of a second peak. The earlier NO_2 peak might be caused by nighttime balancing, where concentrations were higher than NO at night due to the oxidation of NO to NO_2 by O_3, in the absence of solar radiation (Song et al., 2011); these levels were maintained until early morning hours. The accumulation of NO_2 contributes to O_3 formation; however, O_3 is "scavenged" where there is an abundance of NO, resulting in lower O_3 concentrations in heavy traffic (Abdul–Wahab et al., 2005; Ainslie and Steyn, 2007; Sadanaga et al., 2008; Geddes et al., 2009).

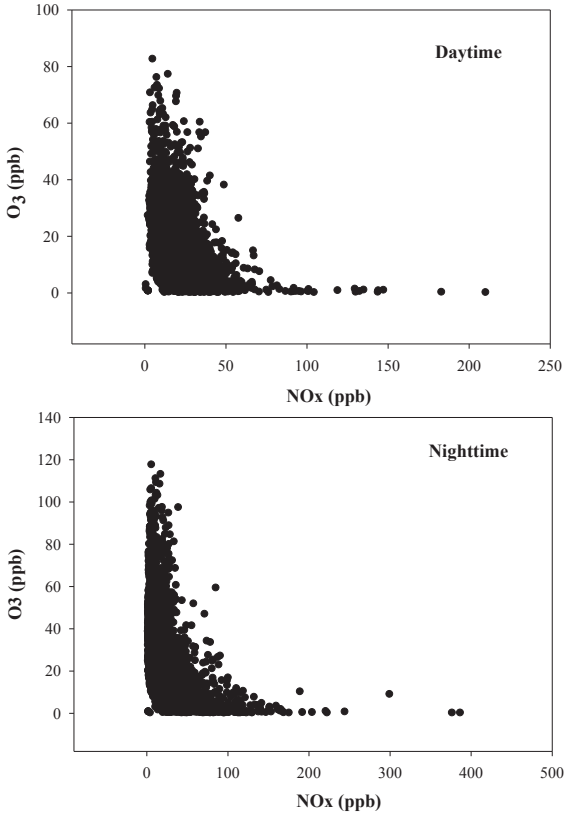

Figure 5. *Daytime/nighttime comparison of the correlations between NO_x and O_3. Maximum O_3 concentrations are enhanced by NO_x precursors in the day but are inhibited at night.*

The effect of NO_x on O_3 is further demonstrated when compared to specific NO_x concentrations. Maximum O_3 levels during the day were at times much lower than in the nighttime (Figure 5), indicating that NO_x could inhibit O_3 concentrations more significantly in the daytime than at night. Hence, photochemical reactions greatly inhibited at night, were apparently the primary factor responsible for these differences. Abdul–Wahab et al. (2005) found in their stepwise multiple regression analysis, that solar levels contributed significantly to high daytime O_3 concentrations with NO as the principal precursor, while at night, NO_2 was the primary influence. Temperature inversions, a feature that is common in urban areas, may also contribute to this process (Hussein et al., 2006). These are caused when high daytime surface temperatures generate convective winds within the urban boundary layer, while at night a reversal of daytime atmospheric mixing occurs with the absence of solar heating (Hussein et al., 2006). Atmospheric convection decreases with increasing stabilization in the urban boundary layer and the development of an inversion layer. Atmospheric stability restricts vertical motions and increases pollution concentrations near the surface, particularly when accompanied by radiation induced inversions during early morning hours, thus enhancing NO_x concentrations (Ainslie and Steyn, 2007; Guttikunda and Gurjar, 2011).

3.4. Weekday/weekend comparisons

In Figure 6, both NO_x and O_3 displayed smaller variations on weekends than on weekdays. NO_x and O_3 levels were similar on Saturday and Sunday and their variations were higher on Saturday than on Sunday. Of the two components of NO_x, however, NO_2 showed less pronounced weekday variations than NO (Figure 7). The contrast between NO_x and O_3 concentrations on weekdays and weekends were further demonstrated by their diurnal variations, often influenced by cyclical patterns of local meteorological factors. While O_3 concentrations on weekdays and weekends displayed a unimodal peak in the early afternoon hours, bi–modal peaks were observed for NO_x and NO_2; there was a single NO peak. The first NO_x peak was more significant than the second, particularly for weekday concentrations.

The average NO_x concentrations were much lower on weekends than on weekdays, reflecting reduced levels of vehicular emissions on weekends. Conversely, average O_3 concentrations on weekends were higher than on weekdays. The negative correlation in hourly average NO_x and O_3 concentrations suggested that VOC rather than NO_x, contributed to elevated O_3 concentrations, by the so–called "weekend effect". Lower NO levels and VOC emissions on weekend mornings consume less O_3 which accumulates later by photochemical reactions (Pudasainee et al., 2006). While a direct relationship existed between NO_x emissions and ambient concentrations on weekdays, the reduction of NO_x did not automatically lead to a proportional decrease in O_3 levels on weekends. In fact, several studies have shown that O_3 levels in the ambient air paradoxically increased when emissions of NO_x decreased (Heuss et al., 2003; Bernstein et al., 2004; Sadanaga et al., 2008). Similar observations were made in a potential nonattainment area of Cincinnati, Ohio where a reduction in NO emissions contributed to an increase in local O_3 (Torres–Jardon and Keener, 2006). Khoder (2009) also found many sites with elevated O_3 on weekends when traffic and O_3 precursor levels were substantially reduced, although motor vehicle emissions near busy streets are known to contribute to high local NO_x concentrations.

Apparently, temporal changes, proximity to emission source and meteorological factors, particularly temperature differences play a smaller role in weekend O_3 behavior; however, they do not necessarily explain the weekend effect but may modify it (Munger et al., 1998). Weekday/weekend differences in O_3 are intricately related to interactions with its chemical precursors: NO_x and VOC, respectively (Sadanaga et al., 2008). Compared to weekdays,

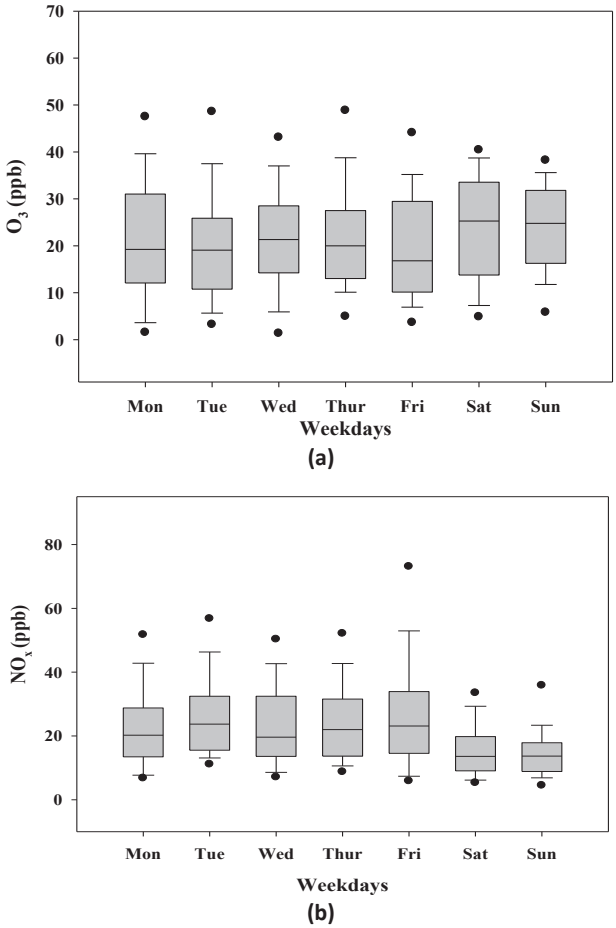

Figure 6. *Variations in yearly average NO_x and O_3 concentrations on weekdays. There are smaller variations on weekends (Saturday and Sunday) than on weekdays especially for NO_x.*

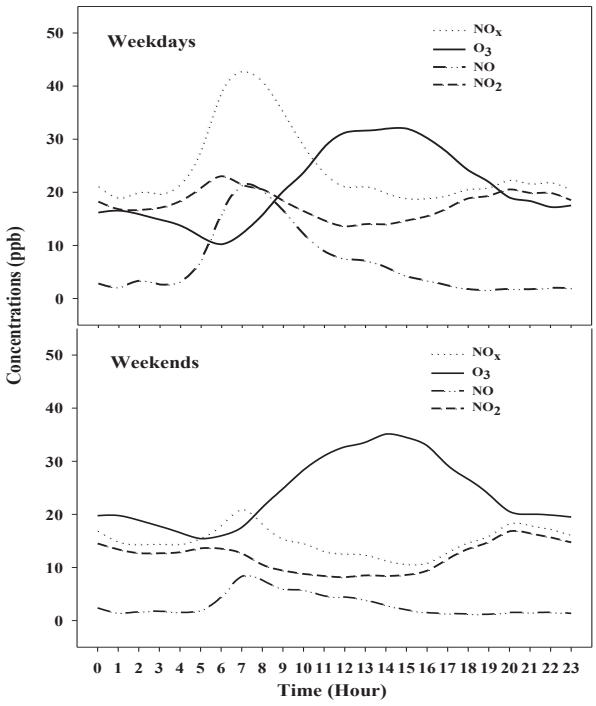

Figure 7. *Diurnal variations of NO_x and O_3 on weekdays and weekends. While the O_3 peak is similar for both weekdays and weekends, NO, NO_2 and NO_x display much smaller morning peaks on weekends than on weekdays.*

however, O_3 could range much smaller for specific concentrations of NO_x on the weekends, even though NO_x concentrations were relatively lower than O_3 concentrations (Figure 8). This might be an indication that on weekends, the inhibition effect of NO_x on O_3 concentrations was more significant.

4. Meteorological Influences

When examined by individual series with lagged observation to test for autocorrelations, the most significant correlation was at 24 hour lags. Except for O_3 and temperature which showed a consistent pattern of positive autocorrelations, there were slight variations among the other variables after 24 hour lags. On the other hand, in the test of cross–variability O_3 showed a negative correlation with all meteorological variables except temperature. While O_3 demonstrated a negative correlation with NO, there was a positive correlation with NO_2 up to 48 hour lags.

Table 4 presents a summary of the variables associated with O_3 and NO_2 concentrations in the stepwise regression model. The analysis showed that with one unit increase in temperature and wind speed, mean O_3 concentrations increased by 0.4 and 0.6 units respectively, when the other weather variables were kept constant. The high numerical value of the coefficient corresponding to barometric pressure (–7.349), demonstrated the sensitivity of O_3 concentrations to a single unit change; the maximum, minimum and average values were 30.74 in Hg, 28.90 in Hg and 30.02 in Hg, respectively. Variability in O_3 with the meteorological parameters increased slightly, from 51% to 52% after NO and NO_2 were included in the regression model, and the log of O_3 showed greater variability (54%); variations in the log of

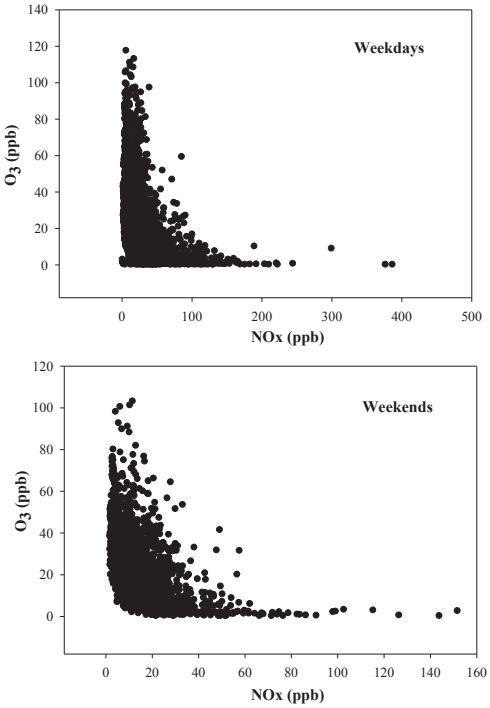

Figure 8. *Weekday/weekend comparison of the correlations between NO_x and O_3.*

NO_2 were similar (>53%), although NO_2 was apparently less dependent on meteorological variables. With one unit increase in wind speed, NO_2 concentrations decreased by 0.4 units.

While in the stepwise regression the diagnostic tests for regular normality assumption of the residuals for NO_x and O_3 confirmed independent normal distribution (Figure 9), significant correlation among certain independent variables, notably NO, NO_2 and wind speed, was expected. Therefore, these variables were transformed into principal components, making them independent of each other, to improve the estimate of variability among them. From principal component regression equations, partial regression coefficients and constants were computed. The transformation of the standardized to general linear regression for $\log(O_3)$ and $\log(NO_2)$ was computed, with temperature (Temp), wind speed (Wind), relative humidity (Hum) and atmospheric pressure (Press); the final general partial regression model given as:

$$\log(O_3) = 2.085584 + 0.007906\,\text{Temp} - 0.009584\,\text{Hum} - 0.01629\,\text{Press} + 0.022426\,\text{Wind} - 0.025547\,\text{NO} - 0.011489\,NO_2 \quad (1)$$

$$\log(NO_2) = 0.55519229 + 0.00098969\,\text{Temp} + 0.006073206\,\text{Hum} + 0.009186\,\text{Press} - 0.03839\,\text{Wind} + 0.02248296\,\text{NO} \quad (2)$$

Consistent with the linear regression analysis, PCA demonstrated similar relationships between the log of O_3 and meteorological variables. There was a positive association with temperature and wind speed, whereas the coefficients of relative humidity and barometric pressure were negative. Similarly, there were positive associations between the log of NO_2 and all variables except with wind speed, comparable to the coefficients in the linear regression model. In both time series and regression models, wind speed accounted for the greatest variability in the concentrations of O_3 and NO_2 than any other meteorological variable. The overall trend was an inverse relationship between wind speed and O_3 concentrations (Figure 10). The dispersal of pollutants by strong winds through vertical mixing and forced convection apparently contributed to lower O_3 and NO_2 concentrations. Ito et al. (2007) found that NO_2 exhibited a very strong negative correlation with wind speed; however, while pollutant concentrations are generally inversely proportional to wind speed, concentrations may increase downwind even at high wind speeds (Kim et al., 2004; Ainslie and Steyn, 2007). The monitoring site was downwind of constant traffic on the New Jersey Turnpike and other heavily traveled roadways. While NO_2 concentrations decreased with wind speed, the increase in O_3 concentrations could be due to prevailing southwesterly winds from east coast urban areas, the direction associated with transport of precursor pollutants over hundreds of miles downwind from their original emission sources before being transformed into O_3 (Farrell et al., 1999; Ainslie and Steyn, 2007).

While high O_3 concentrations are generally associated with conditions that suppress vertical mixing, such as relatively light winds and thermal inversions in the atmosphere (Sillman, 1999; Godish, 2004), previous studies have shown a non–linearity between concentrations of gas–phase pollutants and wind speed (Bigi and Harrison, 2010). In a two–stage model, Kim et al. (2004) found that downwind direction was an important determinant of increased exposure to traffic pollutants. Abdul–Wahab et al. (2005) reported that O_3 was weakly correlated with wind speed but was positively correlated with wind direction. Similar observations were made by Ainslie and Steyn (2007) of higher O_3 concentrations downwind in a multiple linear regression model.

Table 4. *Model summary of variables associated with pollution concentrations*

Independent Variables	**Dependent Variables**				
Coefficients (Cumulative R^2)	**O_3**	**O_3**	**log O_3**	**NO_2**	**log NO_2**
Temperature	0.412 [c]	0.388 [c]	0.009 [c]	0.029	0.000
	(0.260)	(0.260)	(0.169)	(0.005)	(0.006)
Relative humidity	–0.375 [c]	–0.361 [c]	–0.011 [c]	0.070 [b]	0.004 [c]
	(0.456)	(0.456)	(0.411)	(0.109)	(0.156)
Barometric pressure	–7.349 [c]	–0.736 [c]	–0.172 [b]	1.729	0.090 [a]
	(0.499)	(0.494)	(0.448)	(0.165)	(0.235)
Wind speed	0.598 [c]	0.422 [a]	0.015 [b]	–0.449 [c]	–0.019 [c]
	(0.514)	(0.514)	(0.489)	(0.333)	(0.419)
NO		–0.253 [a]	–0.018 [c]	0.657 [c]	0.015 [c]
		(0.522)	(0.527)	(0.537)	(0.537)
NO_2		0.059	0.009 [c]		
		(0.523)	(0.544)		

[a] *p–value < 0.05*
[b] *p–value <0.01*
[c] *p–value <0.001*

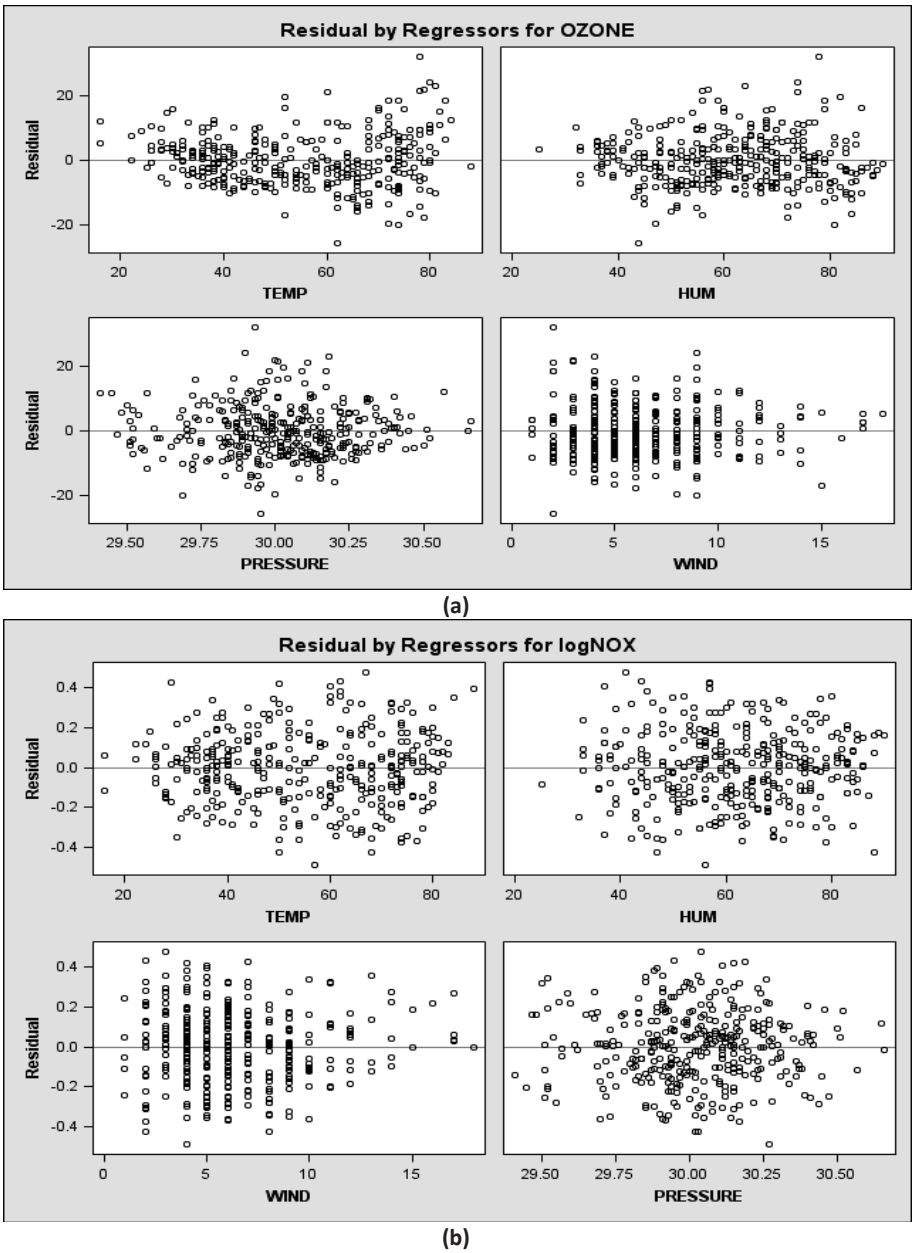

Figure 9. *Residual plots of regression model for* ***(a)*** *O_3 and* ***(b)*** *NO_x. Residuals show symmetry and are along a straight line with no specific pattern against meteorological variables around zero.*

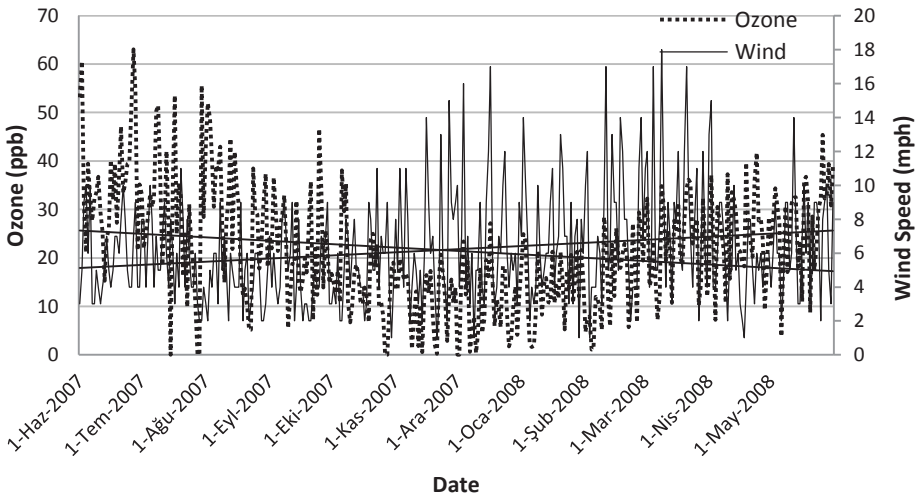

Figure 10. *Inverse relationship between O_3 and wind speed. Ozone concentrations decrease as wind speeds increase.*

5. Conclusions

In this study, the temporal variability of NO_x and O_3 concentrations was governed by the seasonality of atmospheric processes which acted interdependently. Although adjustments were made to reduce bias caused by such factors, the methods used in this study could not authenticate the level of uncertainty pertaining to the role of these factors. Despite this limitation, the evidence is adequately consistent and plausible to draw reasonable conclusions. Based on the analysis, the seasonal patterns of NO_x and O_3 are altered under variable atmospheric conditions and chemical mechanisms that are inextricably related. Elevated O_3 concentrations are primarily influenced by wind, solar energy and temperature as well as chemical inter–conversions with NO_x. These chemical characteristics exist on short timescales in concert with emission sources, particularly the mechanisms that drive NO either to destroy or enhance ambient O_3 levels.

If these results can be replicated at other locations, it may be possible to reduce future exposure to pollutants by developing a health and weather risk–warning system, based on the patterns of high pollutant concentrations. From the perspective of abatement, this approach presents additional challenge to the attainment of in–state controls. It can increase the benefits of improved ambient air quality that have not been completely achieved. The health implications of O_3 exposure in the summer and on weekends when its association with atmospheric conditions and chemical processing are the strongest, should be explored in future studies.

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