Characteristics and Causes of Peak Ozone Concentrations: A Case Study of the Large Maritime Urban Location of Auckland, New Zealand.

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Technical Report:
Peak ozone levels in the Auckland region

The University of Auckland, Auckland, New Zealand.

February, 2013.

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Summary

Tropospheric ozone (O_3) is a key component of photochemical smog and brown haze that has become a regular feature of the atmospheric environment of the greater Auckland urban area. Despite generally low surface concentrations, there is growing concern about the region's susceptibility to high ozone levels in the future. The origin of peak O_3 concentration is investigated using three years of data from a location on the east coast of Auckland urban area. The full O_3 dataset is compared with its two subsets, namely, low O_3 (1 to 10^{th} percentile) and peak O_3 (>90^{th} percentile) data. Variation in nitrogen oxides concentration and meteorological variables are examined in the three datasets. The highest frequency of peak O_3 concentrations occur in spring and winter during the afternoon hours under moderate temperature and moderate to high winds speeds. A large number of these peak O_3 events belong to offshore maritime winds coming from Hauraki Gulf. Three processes appear to be responsible for peak O_3 concentration, namely, photochemical reaction, advection via maritime winds, and down welling of O_3 from upper air. Peak O_3 concentration in any given season is the sum of O_3 introduced by one or more of these processes. The results suggest that regional background O_3 is mainly responsible for peak O_3 levels in winter and spring; the known 'same-day' and 'next-day' mechanism may also have some contribution to peak O_3 events especially in winter. Peak O_3 concentration events in autumn and summer are mainly attributed to local photochemical O_3 via same-day reaction while transport of regional background O_3 through horizontal and down welling from upper troposphere also contributed towards peak O_3 events. The very low incidence of peak O_3 in autumn and summer months is likely due to dry deposition of O_3 over aerosols particles and reduction of background O_3 levels by NO titration of O_3. The study demonstrates the complex nature of peak ozone events for an urban area in a maritime location. Despite generally low surface concentrations in the Auckland region currently, the results reveal the potential for and susceptibility to high ozone levels in the future.

Key words: Peak ozone events; Advection; Maritime location; New Zealand; Ozone sources

Introduction

Tropospheric ozone (O_3) is an important secondary pollutant because of its oxidative potential and reactive nature that play a central role in chemical processes in the atmosphere. Ozone is also the key component of photochemical smog and brown haze that has become a regular feature of the atmospheric environment of many cities the world over. The focus in the research reported here is on the Auckland urban area, the largest in New Zealand. Brown haze in Auckland generally occurs during cold, calm winter mornings (Senaratne, 2003; Senaratne & Shooter, 2004). Despite generally low surface concentrations, there is growing concern about the region's susceptibility to high ozone levels in the future. The city is almost surrounded by water, which makes it an interesting case study of pollution-causing processes in a mid-latitude maritime location.

Tropospheric O_3 can occur as local photochemical ozone and regional background O_3 (Husar & Renard, 1997). Local O_3 includes the human induced emission sources of O_3 precursor species. Regional or 'background' O_3 originates from a larger-scale process around or outside the small-scale process (Szepesi, 1987). This includes advection of O_3 from distant locations and downwelling from the upper troposphere. Photochemical O_3 is produced during the day from photochemical cycling of nitrogen oxides (NO_x = NO + NO_2) in the presence of volatile organic compounds (VOCs), whereas background O_3 is primarily a function of wind speed and wind direction (Husar & Renard, 1997). Certain atmospheric processes such as mixing layer depth, sea breezes (Adeeb & Shooter, 2003; McKendry, 1992), thunderstorm and lightening (Clarke & Griffing, 1985; Colbeck & MacKenzie, 1994; Sisterson & Kumar, 1986) also play an important role in determining background O_3 levels. The concentration of both categories of tropospheric O_3 varies with season (Khan, de Freitas, & Shooter, 2007). This seasonal variation depends on meteorological and anthropogenic forces. The aim of the current work is to examine the origin of peak seasonal O_3 concentration in the vicinity of the greater Auckland urban area, in particular the relative contributions of local photochemical versus regional sources in peak O_3 episodes.

Locally, photochemical production of O_3 is generally dominated by the following two reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + h\nu(+O_2) \rightarrow NO + O_3 \quad (2)$$

These two reactions constitute a cycle with no net chemistry; that is the overall effect of reaction-2 is the reverse of reaction-1 (Clapp & Jenkin, 2001). However, the reaction between NO and VOCs provides additional pathways for NO_2 formation without loss of O_3, which consequently increases O_3 concentration during the daytime. The O_3 production rate varies also depends on several other physical and meteorological factors, such as precursor's emissions, location, season, time of day and cloud cover (Jenkin & Clemitshaw, 2002). The night time chemistry of O_3 and NO_x is different from that during the day. At night, photolysis of NO_2 cannot occur; therefore, when reaction-1 occurs, NO_2 forms and both NO and O_3 are consumed. Thus, if sufficient amount of O_3 is available then concentration of NO_2 increases during the night (Brown, et al., 2006; Jenkin & Clemitshaw, 2002). Nitrogen dioxide (NO_2) also slowly reacts with O_3 and form NO_3. The principal reaction of NO_3 at night is often with NO_2 that forms N_2O_5. However, N_2O_5 is thermally unstable and decomposes to NO_2 and NO_3, thus building to an equilibrium (Jenkin & Clemitshaw, 2002; Riemer, et al., 2003)

$$NO_3 + NO_2 + (M) \leftrightarrow N_2O_5 + (M) \quad (3)$$

The nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5), are two important components of nocturnal atmospheric chemistry in the lower troposphere. Both of these gases have the potential to either remove the nitrogen oxide compounds from the atmosphere or to store it and re-release it when daylight returns. Dinitrogen pentoxide (N_2O_5) provides a significant pathway for the conversion of NO_x to HNO_3; this provides a major NO_3 and NO_x removal path at night via the heterogeneous hydrolysis (on the surface of aerosol particles) of N_2O_5 (Atkinson, Winer, & Pitts, 1986; Brown, et al., 2003; Cox, 1988).

There are also non-local sources of O_3 to consider. Variability of surface ozone concentrations due to advection and entrainment of regional 'background' O_3 in the Auckland area have been noted by (Adeeb, 2006; Adeeb & Shooter, 2004; Farkas, 1979). In studies elsewhere, (Austin & Midgley, 1994; Chan, et al., 2003; Davies & Schuepbach, 1994; Johnson & Viezee, 1981; Madronich, 1993; Monks, 2003; Sillman,

2005; Stohl, et al., 2003) have suggested that intrusion of stratospheric O_3 into the lower troposphere is an important mechanism for the build-up of non-photochemical O_3 in the boundary layer. Jain (2003) estimated that 50% of surface O_3 is produced from photolysis of NO_2, with the remainder being transported from the stratosphere. The average photochemical lifetime of O_3 in troposphere is two weeks (Cox, 1988), which allows O_3 to be transported long distances under favourable weather conditions. Concentrations of O_3 representative of the New Zealand region generally are measured near the geographic centre of New Zealand, at Baring Head near Wellington. Values of $70\mu gm^{-3}$ and $40\mu gm^{-3}$ for the winter and summer seasons, respectively, are considered typical background concentrations (Ministry for the Environment & National Institute of Water and Atmospheric Research, 2004).

Method

Air quality and meteorological data used in the study are from the Musick Point meteorological and air quality monitoring station run by the local regional government authority, the Auckland Council (Figure 1). The station was selected because of its unique location. There is open-ocean to the north and east of the station and built-up urban land to the south and west. Residential areas are located to the south, where approximately 30% of the houses have chimneys. The Otahuhu-Penrose light-industrial area is located approximately 11 km to the southwest. The Southern Motorway (State Highway 1) passes through the southwest sector. Thus, the site is exposed in the south and southwest to 'urban plume' emissions and to winds from the open-ocean in the north and east.

Based on the climate of the region and geographic location of the monitoring station, the data were allocated to two dominant wind sectors, namely, a 'marine winds sector' and an 'urban winds sector'. Marine winds are those from the north, north-east, east and south-eastern quadrants. Concentrations of NO_x and O_3 in this air would be indicative of regional background O_3 contribution free of any local influence. Urban winds are those from the south, southwest and northwest. Urban winds travel over the urban areas of Auckland before reaching the monitoring station and thus likely to be charged with pollutants.

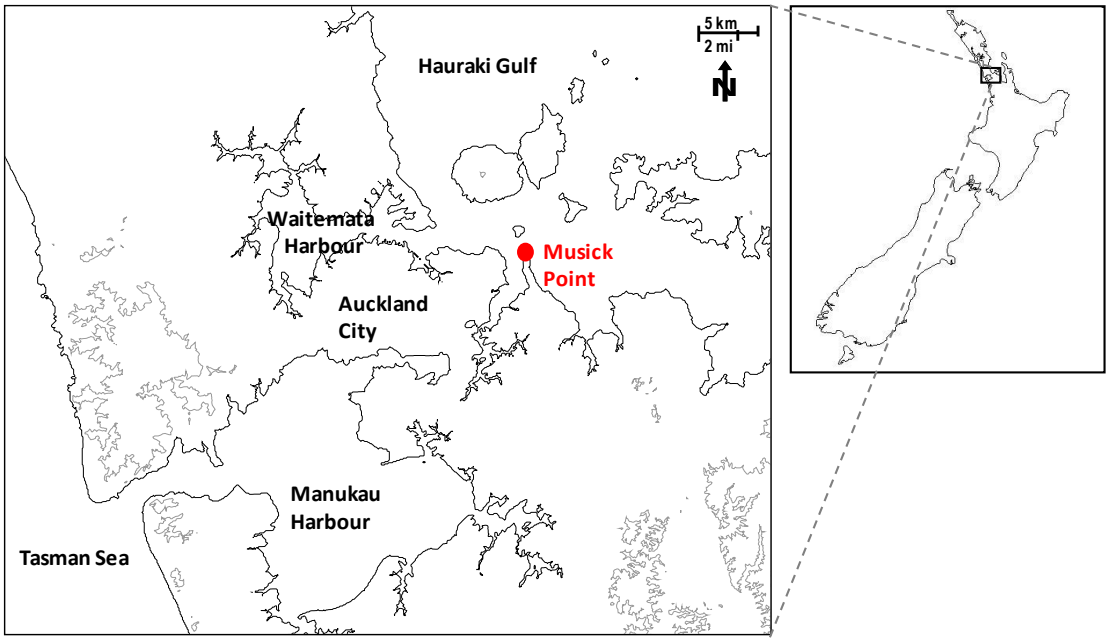

Figure 1: Map of the Auckland Region

The continuous data that comprised the three-year dataset (hereinafter referred to as $O_{3(F)}$ data) were allocated to one of two data subsets. The first subset comprised of data from 1st to 10th percentile O_3 cases (hereinafter referred to as low $O_{3(L)}$ data) and represents O_3 cases with low concentrations. The second subset comprised of data greater than 90th percentile O_3 cases (hereinafter referred to as $O_{3(H)}$ data). The evolution of O_3 was examined in the three datasets by analysing changes in meteorological variables and NO_x concentration. Data were sorted according to season. Wind speed and near surface air temperature data were also allocated to one of 'low', 'moderate' and 'high' categories (Table 1). Next, the data were processed according to time of day. The high and low O_3 concentrations primarily depend on the local diurnal meteorological and emission patterns of NO_x. They were allocated to four time segments. The first comprised of the six hours from 01:00 to 06:00 h, which represents the time when the NO_x emissions are lowest. The second is the period 07:00 to 11:00 h when NO_x emissions are highest, corresponding to the first ('rush-hour') period at the beginning of the working day. The third time segment is the 12:00 to 17:00 h period when NO_x was reduced either by increased ventilation due to strong day time convection or by chemical reaction with O_3 and other chemical species present in the air. The fourth period is 18:00 hour to 24:00 h, and represents a second diurnal peak of NO_x due to evening rush hour road traffic.

Table 1: Descriptors for 'low', 'moderate' and 'high' categories of air temperature and wind speed.

Category	Air temperature (°C)		Wind speed (m s^{-1})	
	Code	Range	Code	Range
Low	$T_{a(L)}$	0 – 25th Percentile 2.9 – 12.3°C	$WS_{(L)}$	0 – 25th Percentile 0 – 3 m s^{-1}
Moderate	$T_{a(M)}$	26th - 75th Percentile 12.4 – 17.6°C	$WS_{(M)}$	26th - 75th Percentile 3.1 – 8.0 m s^{-1}
High	$T_{a(H)}$	76th – 100th Percentile 17.7 – 25.3°C	$WS_{(H)}$	76th – 100th Percentile 8.1 – 21.0 m s^{-1}

Analysis of data proceeded in three steps. First, monthly and diurnal trends were obtained to identify seasonal variations in each season in three years long full dataset. Next, seasonal means for O_3, NO_x and meteorological variables were obtained from the full dataset, and low and high O_3 datasets. Changes in meteorological variables and NO_x concentration were examined as O_3 increased from $O_{3(F)}$ and $O_{3(L)}$ to $O_{3(H)}$ levels. To estimate the magnitude of the peak O_3 events, frequency tables for high O3 dataset were also examined in conjunction with seasonal means of meteorological variables and NO_x concentration. The chi-squared test statistic was used to test the in(dependence) of O_3 from meteorological variables followed by Pearson's residuals analysis which is used as a measure of discrepancy between O_3 and meteorological variables.

Weekday and weekend analyses were conducted to further assess the impact of NO_x on O_3. A Quantile-Quantile plot method was used for this purpose. The Q-Q plots enable comparison of the entire range of distributions across the full range of concentration values from the smallest to the largest (Cleveland & McRae, 1978). The procedure makes it possible to compare the general tendency between the two entire distributions. Ozone distribution from full dataset for Sunday, Tuesday and Friday were compared, Sunday being the lowest NO_x emission day and Tuesday and Friday being the highest NO_x emission day. The *p*th percentile (Quantile) of a set of data is a value such that *p* percent of the data is less than or equal to the value. Percentiles of one set of data are plotted against the corresponding percentiles of the other set of data. If both distributions are nearly the same, the points plotted will be close to the line $Y=X$. One-way ANOVA analysis was also used to determine statistical significance.

Results

Seasonal and diurnal variations

Seasonal patterns in O_3 can result from any or all of the following: the seasonality of the tropospheric background O_3; systematic seasonal shifts in prevailing wind; the seasonality of photochemical oxidation and removal processes; and the temporal pattern of man-made precursor emissions (Husar & Renard, 1997). Here the important seasonal features of tropospheric ozone are examined through daily maximum ozone averaged over each month of three years study period (Figure 2). The mean monthly NO_x of daily maxima is also plotted for comparison with O_3 levels. The three-year O_3 dataset shows seasonal patterns of tropospheric ozone at Musick Point. Figue 2 shows a clear signal of peak O_3 levels from late winter to spring (i.e. August to November) and early summer.

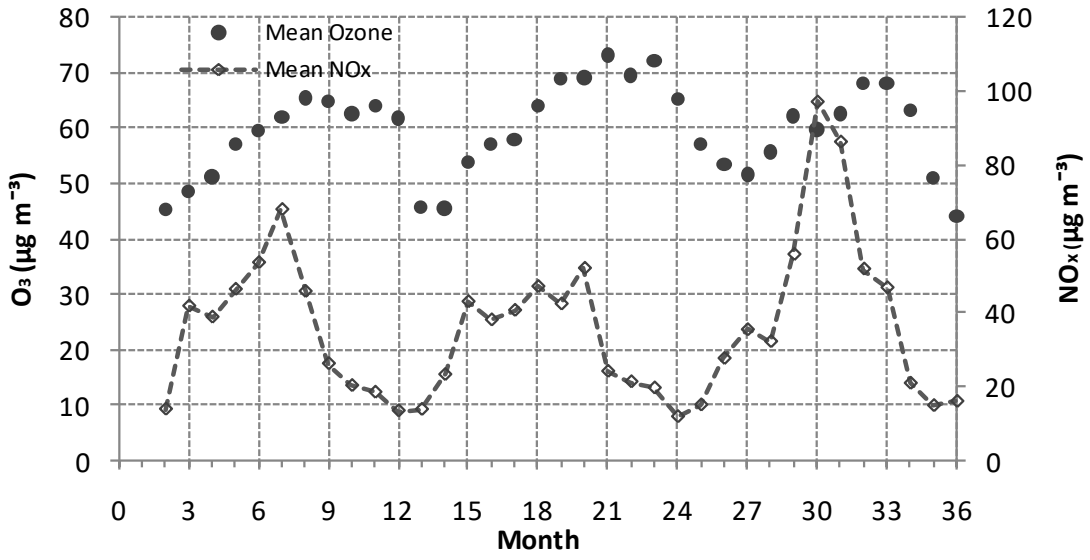

Figure 2: Daily maximum O_3 and NO_x concentrations averaged over each month of the three-year study period from 2004 to 2006.

A consistent dip in O_3 concentration during mid-to-late summer and early autumn is also evident. The mean NO_x concentration was low in summer months when near surface temperature was high, which resulted in a deeper mixed layer and increased ventilation over the region. In autumn and winter, however, low near surface temperature and reduced mixing height favor the accumulation of NO_x, the concentration of which was highest in the winter months. Another feature is the consistent seasonal lag between O_3 and NO_x concentration. The peak NO_x levels in winter are followed by the peak O_3 in spring while low NO_x levels in spring and early

summer are followed by very low O_3 concentrations in late summer. The O_3 concentration recorded at Baring Head in New Zealand is considered to represent regional background O_3 levels for area. The monitor facility at Baring Head is aligned in such a way that it captures the photochemical pollutant from the air flow that is coming from the ocean and is free from anthropogenic influences. The average monthly O_3 concentration from Baring head for the year 2004 and 2006 were compared with O_3 concentration at the urban air quality monitoring site at Musick Point Auckland (Figure 3). The mean O_3 concentration here is higher than at Baring Head; however, both stations show similar seasonal patterns of surface O_3 concentration, with high correlation coefficients, > 0.85 for both years. The mean difference in O_3 concentration between Baring Head and Musick point stations is least during winter, spring and early summer and highest in the summer and autumn months.

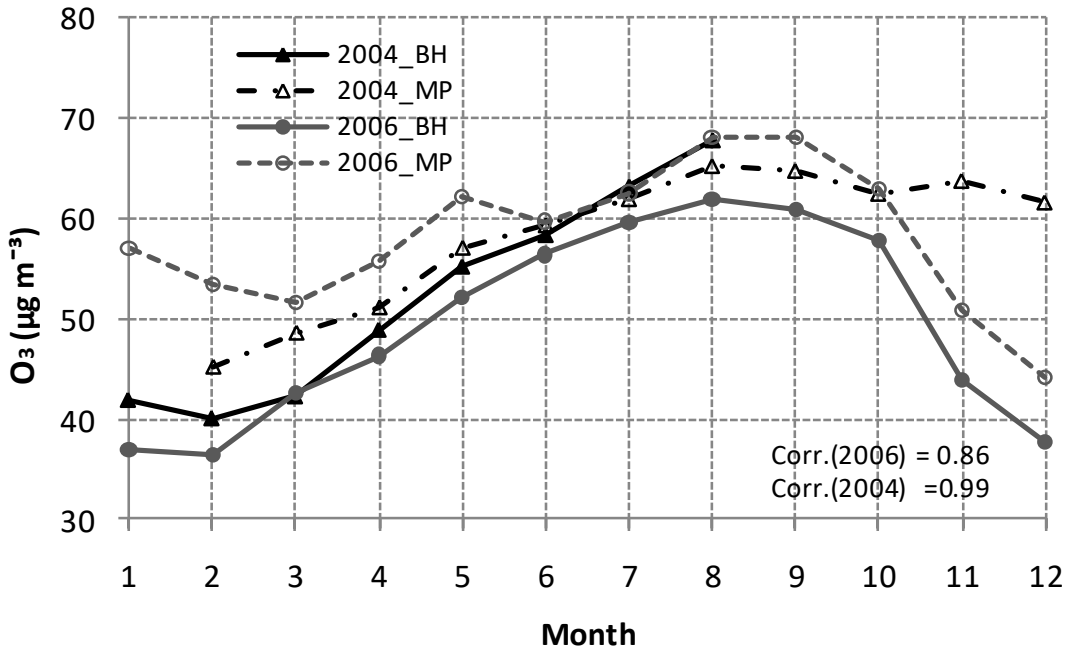

Figure 3: Mean monthly O_3 concentration at Baring Head and Musick Point monitoring stations for 2004 and 2006.

The O_3 full ($O_{3(F)}$) and O_3 low ($O_{3(L)}$) datasets were compared with the peak O_3 dataset to isolate meteorological and seasonal phenomenon responsible for peak O_3 levels (Table 2). The results show marked variations in the mean meteorological variables (wind speed, wind direction and air temperature) in the $O_{3(F)}$, $O_{3(L)}$ and $O_{3(H)}$. A positive correlation between O_3 concentrations, wind speed and temperature suggest low O_3 levels during weak winds and cold temperatures and peak O_3 under relatively strong

winds and warmer temperatures. The average wind speed in $O_{3(L)}$ is almost half the average wind speed of the $O_{3(F)}$, whereas it is almost one third of wind speed in $O_{3(H)}$. The air temperature in $O_{3(L)}$ was also about 1.4 °C lower than air temperature in $O_{3(F)}$, while the difference in mean air temperatures between $O_{3(L)}$ and $O_{3(H)}$ was about 1.94 °C. The wind direction ratio (marine wind frequency/urban wind frequency) W_D was much lower than unity (W_D <1.0) in $O_{3(F)}$ and $O_{3(L)}$ (except for summer $O_{3(L)}$), but increased significantly in $O_{3(H)}$, implying larger contribution of marine winds during periods of peak O_3. There was a small difference in the mean NO_x concentrations in $O_{3(L)}$ and $O_{3(F)}$, but the NO_x levels in $O_{3(H)}$ dataset were negligible. The highest mean NO_x levels were observed in winter (66 µg m^{-3}) under cold and calm condition when mean O_3 levels were the lowest. The negative correlation between O_3 and NO_x is normal in urban conditions and reflects a combined effect of photochemical reaction, pollutant dispersion and local meteorology on the two chemical species.

Table 2: Seasonal means of wind speed, air temperature, O_3 and NO_x for the full O_3 dataset, low O_3 dataset and high O_3 dataset, where W_S is mean wind speed, W_D is wind direction ratio of marine to urban wind frequency and T is air temperature.

Meteorological variables									
	Full dataset			Low Ozone			High Ozone		
Season	W_S (ms^{-1})	T (°C)	W_D ratio	W_S (ms^{-1})	T (°C)	W_D ratio	W_S (ms^{-1})	T (°C)	W_D ratio
Autumn	3.91	16.62	0.62	2.4	15.5	0.23	6.4	15.9	5.0
Winter	4.02	11.33	0.44	2.6	8.9	0.23	6.6	12.8	2.9
Spring	4.45	13.93	0.47	1.9	12.0	0.21	5.3	14.4	1.9
Summer	4.43	17.92	0.48	2.1	17.6	1.19	4.8	18.7	1.4
Average	4.20	14.95		2.23	13.51		5.80	15.45	
Pollutant species									
Season	O_3 µg m^{-3}	NOx µg m^{-3}		O_3 µg m^{-3}	NOx µg m^{-3}		O_3 µg m^{-3}	NOx µg m^{-3}	
Autumn	40.3	12.0		12.0	43.3		67.5	4.2	
Winter	46.0	18.6		9.4	65.9		68.1	3.5	
Spring	52.5	8.0		13.4	42.7		69.5	4.1	
Summer	39.3	5.7		16.5	14.7		71.3	4.5	
Average	44.5	11.1		12.8	41.6		69.1	4.1	

Although mean wind speed in $O_{3(H)}$ dataset was significantly higher than $O_{3(F)}$ and $O_{3(L)}$ datasets, it was not the marine winds but southwesterly urban winds that show peaks during the daytime, particularly in the afternoon hours (Figure 4). For rest of the day (late evening, night and early morning), the urban wind speed remained lower than that

for the marine winds. Since most of the peak O_3 levels occurred during afternoon hours (42% of high O_3 dataset), when mean wind speed in the high O_3 dataset rose to 5.80 m s^{-1}. This is to be expected given the mid-latitudinal position of New Zealand, where both the frequency and magnitude of southwesterly prevailing winds is higher than northeasterly and easterly wind flow. In the same way, lower mean air temperature in $O_{3(L)}$ is due to the fact that most of the low O_3 events occurred in the morning or evening time of the day.

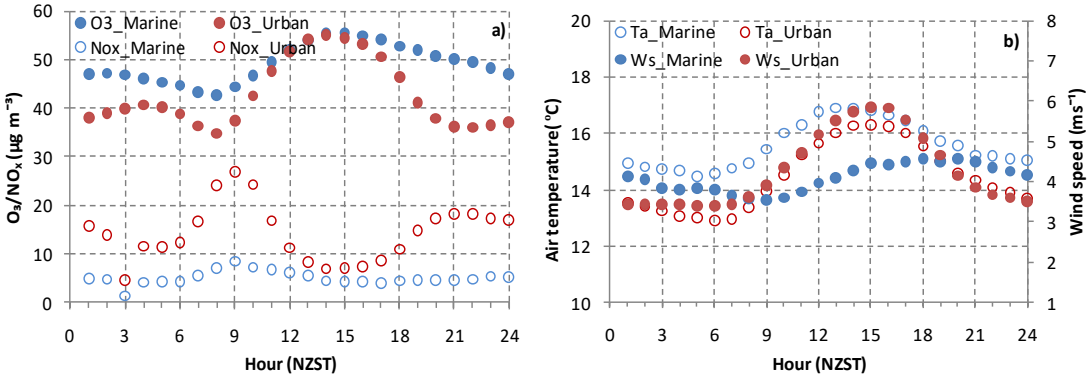

Figure 4: Plots of mean hourly a) concentrations of O_3 and NO_x (left panel) and b) wind speed and air temperature (right panel) for the three years from 2004 to 2006.

The seasonal and diurnal trends of three years of data suggest a strong periodicity in the O_3 concentration. Chi-Squared test static of independence with Pearson's residual analysis is used to examine the possible association of seasonal and diurnal variations in O_3 concentrations with meteorological variables (Figure 5). The Chi-square value is the sum of the squared Pearson's residual and defined as $\chi^2 = \text{sum} \sum(r_{ij}^2)$, whereas Pearson's residual is the $r_{ij} = (O_{ij} - E_{ij})/(E_{ij})^{1/2}$, where O_{ij} is the observed and E_{ij} is the expected frequency of the respective cells of the contingency table. To assess the independence of the variables, two-way contingency tables were constructed and Pearson's residuals which are a measure of discrepancy between the observed and expected frequencies were then calculated. 'Association Plots' are used to present the resulting Pearson's residuals. Each cell is represented by a rectangle that has signed height proportional to the corresponding Pearson's residual and width proportional to the square root of expected frequencies (Zeileis, Meyer, & Hornik, 2007). Thus, the total area of each rectangle is proportional to the raw residual $(O_{ij} - E_{ij})$. The rectangles in each row are positioned relative to a dotted baseline which indicates independence or expected frequency (Meyer 2003). The more a rectangle deviates from the base-line

of expected frequency, the stronger the relationship between the two variables in each category. The colour shading in rectangles is used to represent the sign and pattern of deviation from independence; although the main purpose of the residual shading is not to visualize significance, but the pattern of deviation from independence (Friendly, 2001). Rectangles corresponding to small residuals ($|r_{ij}| <2$) are shaded gray indicating no significant dependence; rectangles with medium residuals ($2=< |r_{ij}| <=4$) are shaded with light blue and light red colour for positive and negative residuals respectively with $p < 0.1$. Rectangles with large residuals ($|r_{ij}| >4$) are shaded with solid blue or red colour indicating highly significant dependence ($p< 0.01$). The colour key to the right of the plots defines the (in) dependence pattern. Only low and high O_3 data were used for Pearson's residual analysis.

Autumn: The large positive residual rectangle for $O_{3(L)}$ indicates that the frequency of $O_{3(L)}$ cases was considerably higher during autumn months. Most of the time, relatively weak winds ($0 >= WS = <3.1$) blew from urban sector and the near surface air temperature remained moderate to high ($12.4>= T <=25.3$). The $O_{3(L)}$ events occurred during morning hours of the day, which is probably due to excessive titration of O_3 by NO_x emitted from morning traffic. The Pearsons's residual is also positive for early morning and evening hours but less significant ($p < 0.1$) suggesting that although morning time was the most important, but low O_3 may also have higher frequency in the early morning and evening hours.

Spring: Pearson's residual analysis of three years long O_3 data suggest that spring is the most important time with respect to peak O_3 events. The large positive Pearson's residual for $O_{3(H)}$ implied that most of the peak O_3 events occurred in spring whereas NO_x levels remained considerably low at this time of the year. The peak O_3 events mostly occurred under marine wind conditions with moderate to high wind speed ($3.1 >= WS <=21.0$) and moderate air temperature ($12.4 >= T <=17.6$) in the afternoon hours of the day.

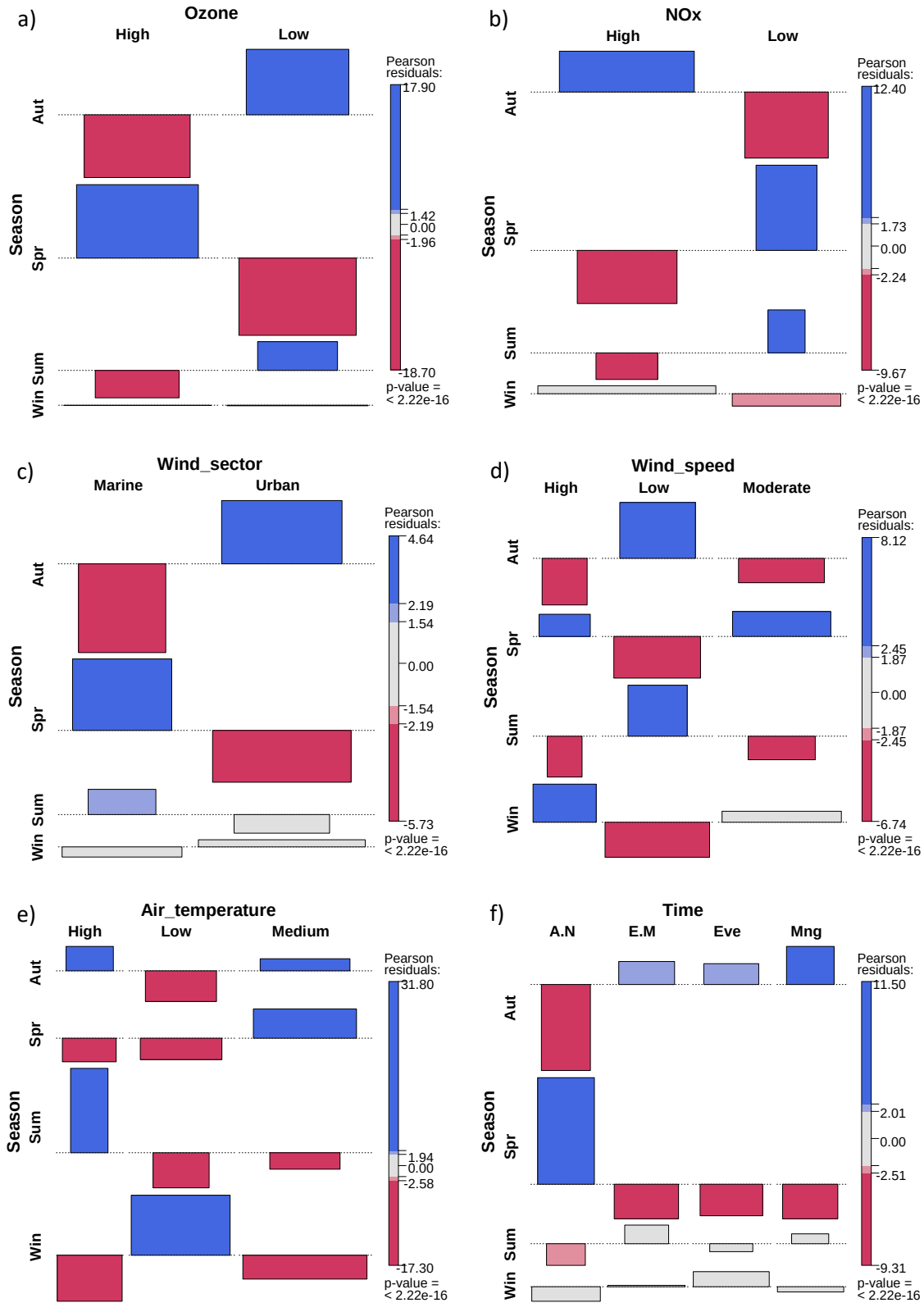

Figure 5: Association plots of dependence for season and meteorological, pollutants and temporal variables for the low($O_{3(L)}$) and high $O_{3(H)}$) ozone dataset.

Summer: Some of the highest O_3 concentrations occur during the summer, but a positive variance at $p < 0.01$ for $O_{3(L)}$ reflects higher frequency of low O_3 and low NO_x conditions in the warmer summer months. The meteorological conditions during summer show a dominance of marine winds at $p<0.1$ (weak significance) with rather small positive residual, low wind speed ($0 \leq Ws \leq 3.1$) and higher air temperature ($17.7 \geq Ta \leq 15.3$). There was no significant dependence of these low O_3 incidences on time of the day; however, a weak statistical significance of negative variance at $p< 0.1$ for afternoon time segment suggests that it is unlikely to experience low O_3 during the afternoon hours.

Winter: The Chi-squared test statistic and Pearson's residual was not significant ($p>0.1$) for O_3, wind sectors and time segments (Figures 5 and 6). The relative size of rectangles (Pearson's residuals) of these variables is insufficient to assess the 'strength' of association between the variables. The main reason for the independence of the variables is the symmetrical contribution of $O_{3(H)}$ and $O_{3(L)}$ cases (40% each) in winter (see Table 3). The same is true for NO_x, which also reflects equal contribution of NO_x cases in low and high O_3 dataset. In other words, that there is a similar contribution of low and high O_3 and NO_x cases in winter months and there is no plausible statistical dependence of O_3 on meteorological and diurnal variables during winter months.

Diurnal variations in O_3 levels

The Chi-squared test statistic and Pearson's residual analysis was employed to assess the effect of meteorological variables on the diurnal cycle of O_3 (Figure 6). The Pearson residual for the afternoon time segment (12:00 to 17:00 hours) was highly significant ($p< 0.01$) for wind direction, wind speed and air temperature for $O_{3(H)}$. The large positive residual suggests that there was a high frequency of peak O_3 cases in the afternoon hours under marine wind conditions, moderate to high wind speeds and moderate air temperature. In the morning hours, $O_{3(L)}$ is dependent (significantly) on weak urban (southwesterly) wind flow conditions, and low air temperature. In the evening and during night time, the frequency of $O_{3(H)}$ is low under weak winds and low temperatures, while wind direction appeared not to be important ($p_{(wind\_sector)} >0.1$) at these times. This implies that, in the evening and at night, O_3 concentrations remain low in both marine and urban air masses; in effect, an O_3 reduction by NO_x due to reaction (1) that eventually increased NO_x concentration in the late evening and at night.

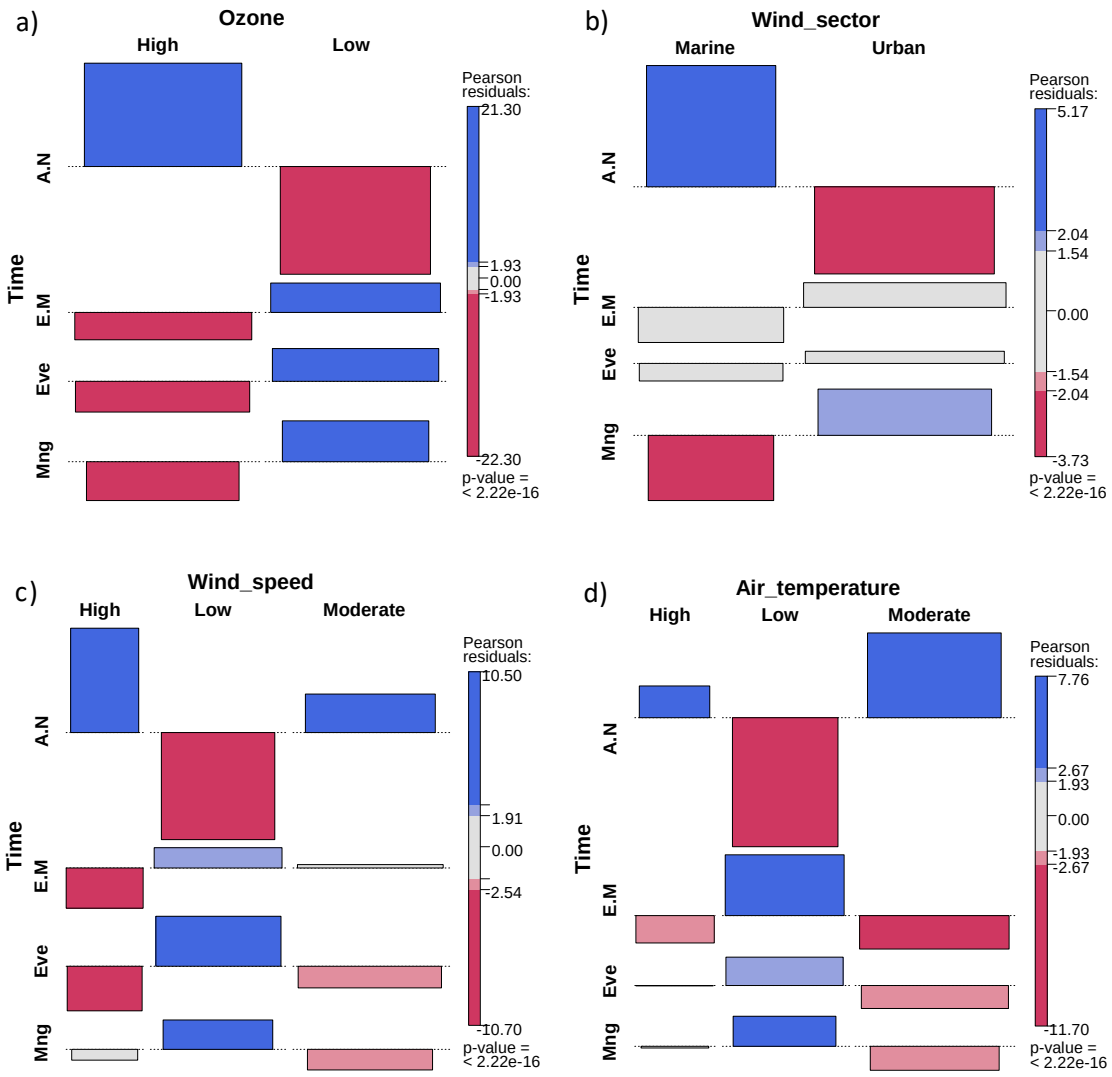

Figure 6: Association plots of time segments and meteorological pollutant variables for $O_{3(L)}$ and $O_{3(H)}$.

Peak O_3 concentration as a function of wind direction and wind speed

The Chi-squared test and Pearson's residual of O_3 was highly significant ($p < 0.01$) for the three meteorological variables, namely, wind direction, wind speed and air temperature (Figure 7). The association plots show clear departure from independence and a strong relationship between O_3 and the three meteorological variables. A positive Pearson's residual at $p < 0.01$ indicates that, relative to urban wind sector, the contribution of the peak O_3 events is much higher under marine wind conditions, moderate to high wind speeds and moderate air temperature. The O_3 concentration remained low under weak urban wind conditions and either low or high air temperature. The association plot of wind sector and NO_x paints an inverse picture and indicates a strong dependency of peak NO_x levels on urban winds.

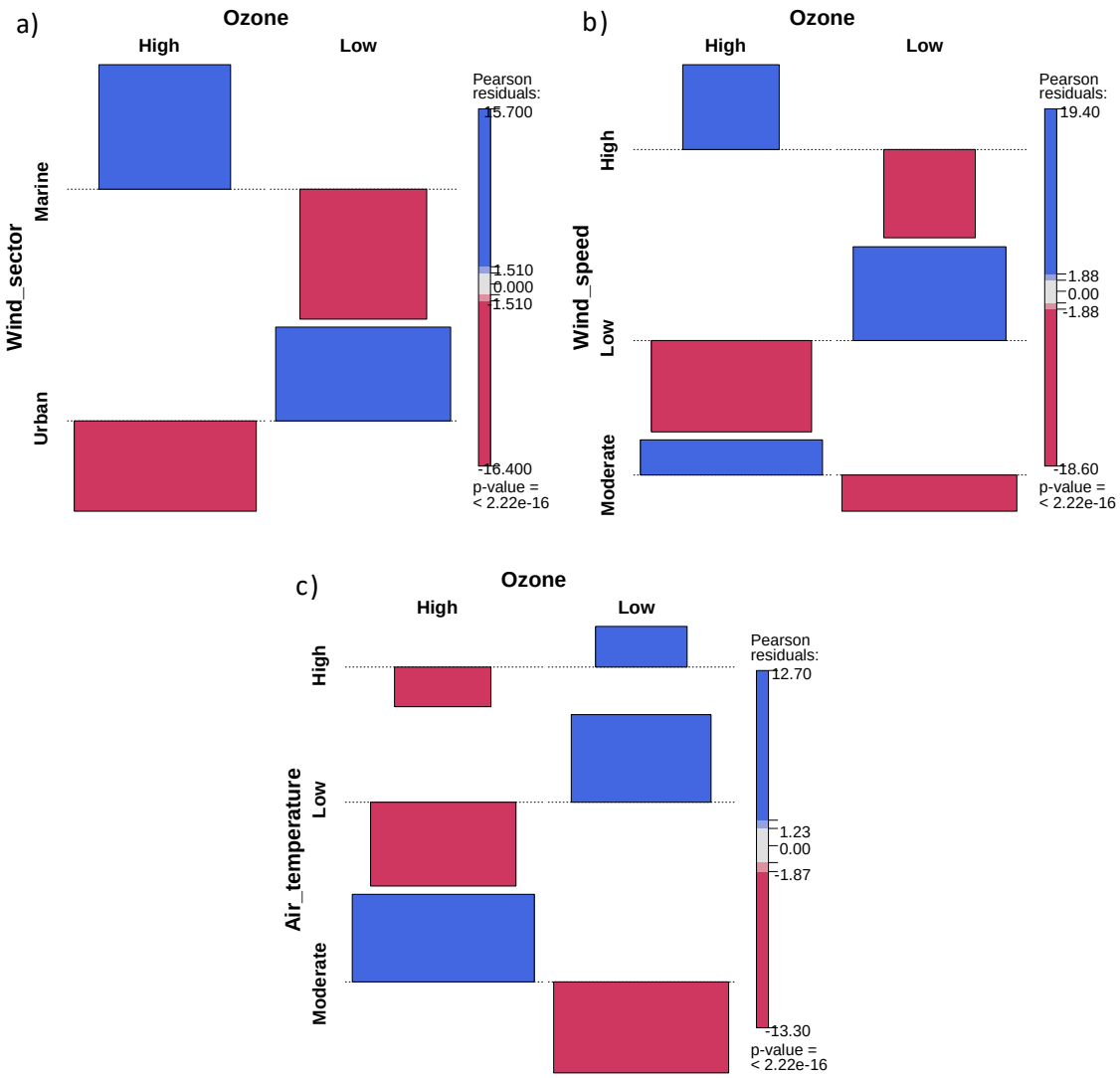

Figure 7: Association plots of ozone and meteorological variables for $O_{3(L)}$ and $O_{3(H)}$.

To examine meteorological controls and relative magnitude and source contribution of peak O_3, it is important to identify the seasonal and temporal distribution of low and high O_3 cases. A frequency table of $O_{3(F)}$, $O_{3(L)}$ and $O_{3(H)}$) cases were calculated for four seasons, four-time segments, two wind sectors, as well as three categories (low, moderate, high) of wind speed and near surface air temperature. A summary of results is presented in Table 3 as percent frequencies. Although the data were almost equally distributed in the four seasons in $O_{3(F)}$, there are marked differences in meteorological conditions in low and high O_3 data. The frequency of $O_{3(L)}$ cases was quite high in autumn and winter. These seasons account for almost 75% of low O_3 (<=10 percentile) cases. In contrast, spring has a loading of only 7% of $O_{3(L)}$ data. On the other hand, almost 85% data in the $O_{3(H)}$ dataset belongs to only spring and winter whereas autumn and summer together makes only 15% of peak O_3 cases. An important feature of the

seasonal percentage is equal contribution (40% each) of both $O_{3(L)}$ and $O_{3(H)}$ cases in winter. Figure 5a shows that, as a consequence of this, the relationship between O_3 and the winter season is not significant ($p>0.1$). The frequency of peak O_3 events was the lowest in both autumn and summer.

Table 3: Percent allocation of season, time segment (see text), wind direction, wind speed and air temperature to ozone concentration in the 'full', 'low' and 'high' O_3 datasets.

Season	Percent allocation in the 'full' dataset	Percent allocation in the 'low' O_3 dataset	Percent allocation in the 'high' O_3 dataset
Autumn	27	35	7
Winter	26	40	40
Spring	26	7	45
Summer	21	18	8
Time Segment			
Early morning (1:00-6:00 hrs)	25	35	23
Morning (7:00-11:00 hrs)	21	29	14
Afternoon (12:00-17:00 hrs)	25	1	42
Evening (18:00-24:00 hrs)	29	35	21
Wind Sector			
Marine winds	33	15	52
Urban winds	67	85	48
Air temperature (ºC)			
Low	25.0	47.8	19.7
Moderate	51.2	33.2	70.0
High	23.8	19.0	10.3
Wind speed (m s^{-1})			
Low	35.2	61.4	15.7
Moderate	53.2	38.5	58.5
High	11.6	0.1	25.8

The diurnal variations in O_3 distribution indicate a specific pattern with very small (1%) contribution of low O_3 concentrations to $O_{3(L)}$ and a large contribution (42%) of peak O_3 concentrations to the $O_{3(H)}$ in the afternoon hours. Except for the afternoon, the low O_3 data ($O_{3(L)}$) is almost equally distributed in the remaining three-time segments, that is early morning, late morning and evening. The large percent frequencies (70%) in $O_{3(L)}$ in the early morning and evening indicate that O_3 tends to be low in the evening and at night. This is generally the time when photochemical reaction is not possible due to reduction or absence of sunlight. In contrast, during the morning hours (7:00 to

11:00), O_3 concentrations are generally low because of titration by morning emissions of NO_x and VOCs (Figure 8). Both time segments (evening and early morning) also accounted for 44% of peak O_3 cases. This is complemented by a very large (42%) data allocation to $O_{3(H)}$ in the same afternoon time segment. The frequency of peak O_3 in the afternoon hours is twice as high as evening or early-morning morning hours. The photochemical production of O_3 is not possible in the absence of sunlight and only O_3 loss processes are active. The large proportion of peak O_3 cases in the evening and early morning hours could therefore be a sum of both photochemical production of O_3 during day time and regional and background transport of O_3 over the diurnal cycle.

In $O_{3(F)}$ dataset, the percent frequency of urban winds is higher than marine winds by a factor of 2; however, most of the low O_3 events occurred under urban wind conditions that increased urban wind sector contribution towards low O_3 to 85% and further reduced contribution of marine winds to only 15%. In contrast, the percent frequency of marine and urban winds to $O_{3(H)}$ are comparable with marine winds having slightly higher (52%) frequency towards peak only cases than urban winds. The results for air temperature and wind speed show the clear relationship of only with meteorological conditions that are specific to peak only incidences (Table 3). Table 3 indicates that in most of the cases, peak only occurs under moderate near surface air temperature and wind speeds. In more than 84% peak only cases the wind speed was moderate to high and air temperature was moderate for up to 70% peak O_3 cases; whereas in most of the low only cases, both wind speed and air temperature were low.

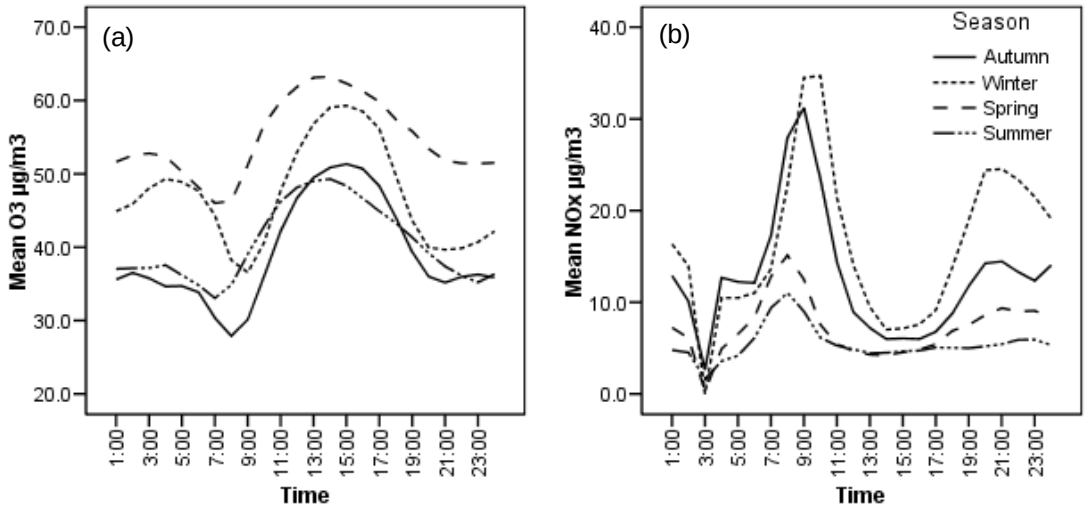

Figure 8: Mean hourly concentrations of O_3 (a) and (b) NO_x over summer, autumn, winter and spring seasons for the three years period 2004-2006.

The time series plot of the hourly mean only and NO_x concentration suggest a bi-model for almost all the four seasons over the diurnal cycle (Figure 8). The mean only concentrations are the highest in spring and winter, with two peaks one in the afternoon and second at night-time between 3:00 to 5:00 hours (Figure 8a). Summer and autumn show the same diurnal cycle; however, the only concentrations are much lower than spring and winter. Highest mean concentration of NO_x is observed in winter and autumn in morning hours of the day (08:00 – 11:00 hours), with the second peak in evening (19:00 – 21:00 hours) hours of the day (Figure 8b). Although spring and summer have the same diurnal pattern, the magnitude of the mean NO_x concentration is much lower than winter and autumn. The diurnal variations in only concentration is the sum of both photochemical and background contribution to the surface only budget whereas peaks in the NO_x concentrations are predominantly a function of morning and evening traffic emissions from the Auckland urban domain.

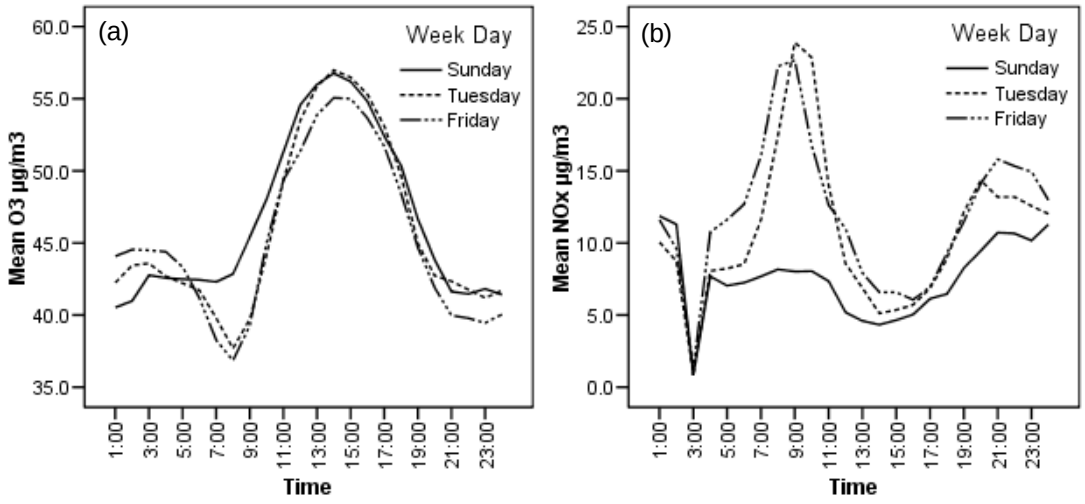

Figure 9: Mean hourly concentrations of (a) O_3 and (b) NO_x on weekends (Sundays) and weekdays (Tuedays and Fridays) over the three years period 2004 to 2006.

Weekday-weekend differences

Use of motor vehicles varies between days of the week as do emissions of NO_x. A preliminary analysis of the data shows that NO_x emissions were the highest on Tuesdays and Fridays and lowest on Sundays. These days were examined to explore the effect of low and high NO_x on O_3 concentration data. Figure 9b shows that the highest NO_x concentrations occur on Tuesdays and Fridays during the morning and evening traffic rush hours. A dip in the O_3 concentration in the morning (Figure 9a) indicates titration

of the available O_3 by NO; the resultant NO_2 species is then photolysed and produces O_3 again in the late morning to afternoon. However, despite the significant difference in NO_x levels on weekdays and weekends, the difference in O_3 concentration in the afternoon is negligible (Figure 9a). One-way ANOVA for O_3 on three days suggests no significant difference in O_3 concentrations in the afternoon hours. In general, NO_x concentrations are lowest on weekends (Sundays); however, in the afternoon between 13:00 to 16:00 hours, NO_x concentration on Sunday is comparable to NO_x concentration on Tuesday and Friday. NO_x levels are low in the afternoon, which is likely be the result of dispersion and mixing in the day time convective environment and photo-oxidation of NO_2. One of the important sources of NO_x at night time during winter months is the emissions from domestic home heating. A weak correlation between O_3 and NO_x under maritime wind conditions indicates that peak O_3 levels in the maritime winds especially from Hauraki Gulf are independent of variations in NO_x.

The Quantile-Quantile plot (Figure 10) shows the extent of variation between weekday and weekend distributions of O_3 and NO_x. Figures 10a and 10c show a linear relationship between weekdays and weekends. Most of the variations in O_3 concentration take place in the first 40% of the data. The departure of data points from reference line Y=X indicates higher O_3 concentration on Sundays than on Fridays and Tuesdays. The deviation from the reference line Y=X was significantly higher on Friday-Sunday than Tuesday-Sunday. This implies that the difference in O_3 concentration between Friday-Sunday was higher than Tuesday-Sunday. The tendency for higher O_3 values to occur on weekends appears to be due to less NO_x emissions and therefore less titration of O_3.

The one -way ANOVA with Post-Hoc Test for mean differences in O_3 concentration between Sundays, Tuesdays and Fridays suggests no statistically significant difference at $\alpha = 0.05$, in the afternoon hours. The Q-Q plots of NO_x distributions show significant differences in NO_x concentrations between weekdays and weekends (Figures 10b and 10d). The departure of NO_x data points from the reference line Y=X is quite evident. The higher the percentile, the greater is the departure from the reference line. This implies that in low concentrations the difference in NO_x on weekdays and weekends was also low, but the higher NO_x levels predominantly occurred on weekday. That NO_x levels were quite high on weekdays compared to Sundays is what would be expected.

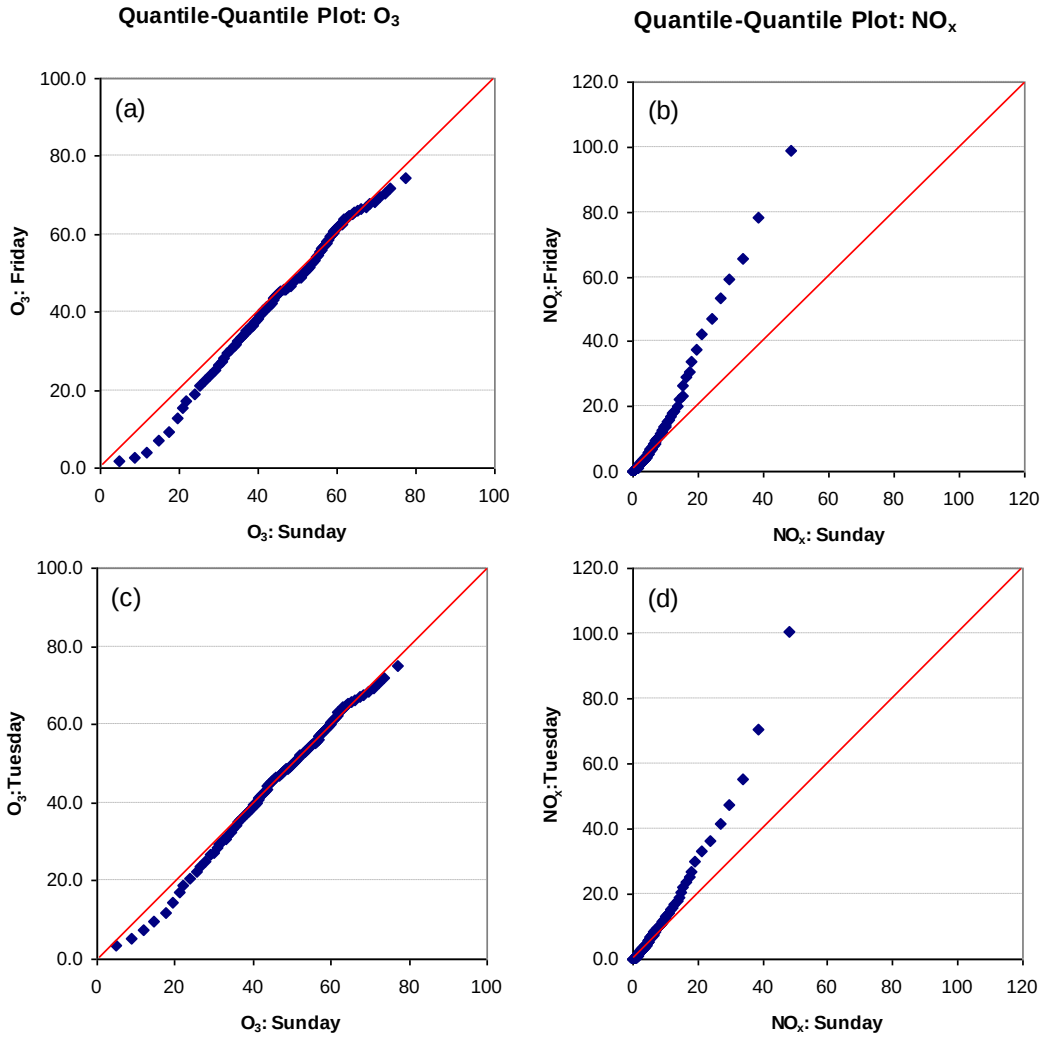

Figure 10: Quantile-Quantile plots of mean hourly O_3 and NO_x for weekdays and weekends over the three years period 2004 to 2006: a) Friday against Sunday O_3 percentiles, b) Friday against Sunday NO_x percentiles, c) Tuesday against Sunday O_3 percentiles, and d) Tuesday and Friday NO_x percentiles. Straight black line Y=X.

Discussion

The concentration of O_3 in the lower atmosphere is a function of thermodynamic structure (vertical stability) of the atmosphere, horizontal air transport, and photochemical formation and destruction of O_3. The photochemistry of surface O_3 and its precursor species (NO_x, VOCs and OH radicals etc.) is a complex non-linear process in which formation and destruction of O_3 occur simultaneously. The equilibrium is continually shifted either towards the production or loss and based on factors such as solar irradiance, air temperature, composition of atmospheric gases and intensity of dry deposition of O_3 on the aerosol particles and the land surface. Our analysis suggests

that basic meteorological variables such as solar irradiance, air temperature, wind speed and wind direction play a crucial role in determining the photochemical and background O_3 levels at a given point in time and space. Given the maritime environment and predominant westerly and easterly air flow, air masses from almost all directions moving over Auckland contain a large maritime component of ozone. The location of Musick Point is such that urban winds carries emissions from industries, traffic, businesses and households from the urban district before reaching the station, while marine winds arrive from Haurki Gulf and do not have any direct source of pollutant emissions. The O_3 concentrations in urban winds are considered to be the result of both chemical reaction between NO_x, O_3 and VOC and background O_3, whereas O_3 concentrations found in marine winds are considered to be background O_3, free from human influence.

Analysis of O_3 and local meteorological conditions suggest that most of the peak O_3 concentrations are to be found in the clean air mass from the Hauraki Gulf in the afternoon hours of the day under relatively stronger winds and warmer temperatures. More than 85% of the peak O_3 concentrations (>64 $\mu g\ m^{-3}$) events are observed to occur from late winter to spring months, and the lowest are found in summer and autumn months reflecting the known seasonal cycle (maximum in spring and minimum in summer) of tropospheric background O_3 concentrations observed at most of the places in northern hemisphere (Solberg, Danielen & Mohnen 1977, Lam et al 1996, Chan 1998, Chan et al 2003, Lal et al 2000) and mid-latitudes of the Southern Hemisphere (Fabian & Pruchniewicz, 1977; McKendry, 1996) , Natural variability of O_3 concentration has been widely reported in the research literature. According to the US National Research Council (1991) “much of the variation in ozone comes from natural fluctuations in the weather and not from year-to-year changes in emissions (pages 50 to 65)". Low O_3 concentrations in winter and spring high and summer low is also consistent with the other work conducted in New Zealand (Adeeb & Shooter, 2004; Farkas, 1979) .

Research shows that photochemical O_3 production takes place downwind of major sources of O_3 precursors species in conditions with relatively low NO_x, high temperature and solar radiation (Chen, Ho, Lai, Tsai, & Chen, 2004; McKendry, 1996; Sillman, 1995; Wakamatsu, Uno, Ohara, & Schere, 1997). Enhanced photolysis rates

are observed in air temperatures above 25^{o}C (Olszyna, Luria, & Meagher (1997) and Walcek (1997); while in low temperatures, the photolysis of NO_2 slows down, although same amount of O_3 may be produced but at further distances downwind of the sources. The statistics from three years data show that the average air temperature in summer was 18^{o}C. There were less than 10 cases where temperature exceeded 25^{o}C; therefore, in general, O_3 tends to form at some distance downwind of urban areas over the ocean. This means that the same O_3 might have returned with the local land-sea air circulation cell. Recirculation of pollutants with sea and land breezes is well documented. Hurley et al (1993) in work in Perth, Australia and Bell and Fisher (1995) in their work over Auckland discussed this phenomenon in terms of 'same-day' and 'next-day' circulation of pollutants. In the 'same-day' mechanism, light land breezes from the south, southwest and western quadrants advect the precursor species towards the coast and possibly offshore. Light synoptic southwesterlies may have the same effect. In either case the primary pollutants are advected away offshore and photochemical reactions may proceed to raise O_3 concentration. The polluted air mass then may be advected back towards the east coast by the mature sea breeze or easterly prevailing winds in the afternoon. In the 'next day' case, prevailing winds push elevated concentrations of O_3 precursors offshore, where O_3 forms; however, the photochemical pollutant traps above nocturnal boundary layer in the residual layer. On the next day, when inversion breaks down, the same O_3 returns to the land mass in the afternoon, and increases O_3 concentration. Bell and Fisher (1995) suggest that, due to complexity of 'next day' events, frequency of such mechanism would be far less than 'same day' mechanism.

Spring: The highest frequency of peak O_3 events was observed in spring months. A large number of peak O_3 events occurred under marine winds from Hauraki Gulf, moderate air temperatures (>=12.4 Ta <=17.6 ^{o}C) and wind speed (3.1>=Ws<=8 ms^{-1}). In contrast, NO_x levels remained very low during spring and peaks to only 15 $\mu g\ m^{-3}$ in the morning hours (7:00 – 9:00) of the day. Comparison of the seasonal cycle of O_3 at Baring Head and the coastal location of Musick Point suggest that the mean peak O_3 concentrations in spring at Musick Point are up to 9% higher than the background O_3 levels observed at Baring Head. High levels of O_3 are usually formed in the sunny afternoon and under warmer temperatures (Land & Chand, EPA, Zvygintsev 2007). Ozone has a longer lifetime in the maritime environment and free atmosphere and can travel hundreds of kilometres without chemical transformation (Chand and Lal. 2003).

In the Auckland case, peak O_3 levels in the afternoon hours may have significant amount of photochemical O_3 that is formed over ocean due to downwind transport of O_3 precursor species from Auckland urban areas in the morning hours. This is transported back to Auckland with the onshore winds that contributes to peak O_3 concentrations particularly in the afternoon hours of the day ('same day' mechanism). However, the more important contributor to the O_3 budget is background O_3 that contributes to peak O_3 levels through horizontal advection and downward transfer of O_3 from the free atmosphere. Several researchers have attributed the increase in O_3 concentration from winter to spring to downward flux of O_3 from the upper troposphere (for example, Danielson & Mohnen,1977). Our analysis shows a strong positive correlation of O_3 with wind speed and air temperature. According to Husar and Renard (1997), if O_3 increases with the increasing wind speed, the source of O_3 is regional transport rather than local photochemical sources. Considering the seasonal and diurnal variations and the effect of local meteorological variables on O_3, the dominant process responsible for peak O_3 concentrations over the Auckland area is the horizontal advection and down-welling of O_3 from the upper troposphere. The photochemical ozone also contributes to the total O_3 budget by 'same-day' mechanism, however, photochemical part is much smaller in spring months.

Winter: Although both the mean concentrations and frequencies of peak O_3 events in winter were similar to spring season; however, unlike spring months, the magnitude of low O_3 events was also equal to the number of peak O_3 events in winter months. Almost all peak NO_x events occurred in pollutant laden urban winds from southeast to northwest, whereas most of the peak O_3 events occurred under marine winds conditions. During morning and evening traffic rush hour time, the meteorological condition were ideal for increased NO_x levels, which is primarily due to strong inversions and very low mixing height that inhibit pollutant dispersion. The atmospheric chemistry in the morning hours reflects NO_x saturated regime (Sillman -2004), in which O_3 concentration decreases with increasing NO_x concentration. As a result, the O_3 levels reduced to very low concentrations. As the day progressed, the increase in surface temperature resulted in the breakdown of inversion conditions and a rapid increase in mixed layer height. The NO_x levels start declining in the late morning due to photo-oxidation. Relatively stronger winds move the polluted air mass away from their immediate sources towards the coast. Meteorological conditions at this time are

favourable for both photochemical formation of O_3 and introduction of background O_3 in to the Auckland land mass. Comparison of mean O_3 concentrations at Musick Point with Baring Head indicate a nominal (4%) difference in O_3 levels between the two sites, which suggests that contribution of photochemical O_3 in winter is even smaller than spring. This is reasonable considering low temperatures and solar radiation in winter months that inhibit effective photochemical production of O_3. In the evening hours, a second NO_x peak is observed, which is due to evening traffic emission. Owing to the absence of sunlight, only reaction-1 was possible at this time that resulted in O_3 loss and low O_3 concentrations.

Summer: Higher temperatures and solar radiation increase photochemical activity in the summer months. The mean concentrations of both O_3 and its precursor species (NO_x) in summer are the lowest of all seasons, which is consistent with surface O_3 research in other parts of the world (for example Solberg, 1996). The frequency of peak O_3 events during summer months was also one of the lowest (only 8%), implying that, for most of the time during warmer summer months, O_3 concentrations remained either low or moderate. Majority of these peaks occurred during afternoon hours, while mean O_3 concentration of the 8% peak O_3 cases was of the order of 71.3 $\mu g\ m^{-3}$. Ozone concentrations remained significantly low in the evening and at night time, which reflects low background O_3 levels in summer months. Wind speed under urban wind sector are slightly higher than marine winds throughout the diurnal cycle. This wind speed pattern is different from rest of the three seasons, which exhibit stronger wind flow in the urban wind sector only during daylight hours. Comparison of mean O_3 levels at Musick point with Baring Head shows significant differences in O_3 concentration between the two stations. In the summer months of January and February, the O_3 concentrations at Musick Point were up to 20 $\mu g\ m^{-3}$ higher than Baring Head. As discussed earlier, high O_3 levels may form on warm sunny afternoons tens of kilometres downwind of the O_3 precursor's sources. The meteorological conditions that are favourable for photochemical reaction are also ideal for the development of sea breezes that occur frequently over the region from November to March. Considering the typical nature of the O_3 photochemistry, it is possible that on cloud free, warm summer days, emission from Auckland urban areas are advected offshore with the morning land breeze where photochemical reaction took place that resulted in high levels of O_3 over the ocean. In the afternoon hours, the same O_3 returned to the land mass with the

onshore sea breeze inflow, resulting in peak O_3 levels over Auckland (same-day mechanism). However, Bell and Fisher (1995) argue that this is unlikely in Auckland case. The reason given is that the wind direction in the morning is dependent on the synoptic flow or the elementary sea breezes from the three harbours, which in turn are dependent on the small-scale coast line shape. Wind direction in the afternoon is dependent on the mature sea breeze flow, which in turn is affected by large scale shape of the coast line and modifies by the synoptic flow. In addition, mature, large-scale sea breeze flow is affected by the Coriolis force, which deflects the mature east coast sea breeze to the south, and the mature west coast sea breeze to the north (Bell & Fisher, 1995). During the afternoon hours, onshore sea breeze is generally normal to the coast. Thus, the same-day mechanism can provide an important pathway for increased O_3 concentrations. Horizontal and vertical advection of background O_3 also make a significant contribution to concentrations in the surface layer. However, compared to spring and winter, the contribution of background O_3 from horizontal and vertical advection is much smaller in summer months, which can be attributed to dry deposition and more importantly photochemical loss of O_3 in the remote troposphere (Solberg-1996). Thus, unlike spring and winter, photochemistry appears to be the most important process that controls O_3 concentrations in summer.

Autumn: The O_3 precursor concentration during autumn months is not much different from winter, especially from night time hours to afternoon hours of the day. In the same way, frequency of low O_3 cases are also close to winter frequencies of $O_{3(L)}$ events. However, unlike winter, contribution of peak O_3 cases in autumn months is the lowest of all the four seasons (7%). Analysis of meteorological conditions during autumn months suggests that, while mean wind speed in autumn is comparable to winter months, air temperature and sunshine hours during autumn are much higher than winter. In the same way, the relative wind direction ratio of 0.62 for $O_{3(F)}$, suggests that in the full dataset, the contribution of marine winds was much higher in autumn than rest of the three seasons. These conditions appear to be quite favourable for high incidence of peak O_3, yet the overall contribution of peak O_3 in autumn was the lowest. Comparison of mean O_3 concentration at Musick Point and Baring Head suggest that similar to summer time, the mean O_3 levels at Musick Point were significantly higher than the background O_3 levels at baring head. While photochemical production of O_3 appears to be the dominant process in autumn, dry deposition and loss of background O_3 via

reaction-1 ($NO + O_3 \rightarrow NO_2 + O_2$) at remote maritime environment is probably the main reason behind low incidence of peak O_3 in autumn (Solberg 1997).

The weekday-weekend analysis was carried out to estimate the effect of photochemical O_3 on peak O_3 concentration events. The results show that in the first 40% of data, O_3 was slightly higher on weekend which is consistent with research overseas (for example (Bronnimann & Neu, 1997; Qin, Tonnesen, & Wang, 2004). In the remaining 60% of data, there is no noticeable variation between weekdays and weekend; whereas Q-Q plots for NO_x showed significantly higher NO_x levels on weekdays compared to weekends. On week days, O_3 reduces to its lowest levels in the morning hours reflecting extensive titration by NO. In the afternoon, however, O_3 concentrations on both weekdays and weekends were almost same. The results clearly indicate that photochemical reaction is not the controlling but a contributing factor in the diurnal variations of O_3 concentrations while background O_3 is critical in determining O_3 concentration over the region.

Summary and conclusion

In this work the origin of seasonal peak O_3 concentration is examined using three years data from a location on the east coast of Auckland urban area. The full O_3 dataset is compared with its two subsets, namely, low O_3 (1 to 10^{th} percentile) and peak O_3 (>90^{th} percentile) data. The seasonal variations in O_3 depend on several factors including changes in emissions, synoptic and local meteorology and seasonality of background O_3. Although peak O_3 events occurred in all the four seasons, 85% of the total peak O_3 events occurred in spring and winter only. Most of the time during the summer and autumn months, O_3 concentrations remained low, and almost 75% of the total low O_3 events belong to these two seasons only. Most of the peak O_3 levels in spring and winter seasons occurred in the afternoon hours and at night time. Horizontal advection and down-welling of O_3 from the upper troposphere (background O_3) appears to be the dominant processes responsible for peak O_3 concentration over the Auckland area in the two seasons. Photochemical ozone also contributes to the total O_3 budget by 'same-day' mechanism; however, because of relatively cold conditions in winter and spring, there is little local photochemical O_3 to add to peak concentrations. In summer and autumn, O_3 levels remained low for most of the time and both seasons have minimum

number of peak O_3 events. Photochemistry in both seasons appears to be the most important process that controls O_3 concentrations in these two seasons. Low background O_3 levels in the two seasons can be attributed to dry deposition and photochemical loss of O_3 in the remote troposphere.

Peak O_3 levels are observed in both marine and urban wind condition. However, contribution of marine winds is slightly more (52%) than urban winds (48%), while low O_3 events predominantly occurred in urban wind conditions (85%). Ozone has positive correlation with wind speed and air temperature. The concentration of O_3 remained significantly low in the morning hours of the day under colder temperatures (Ta<=12.3 ºC) and calm winds(Ws<=3.1 m s^{-1}) from urban wind sector while peak O_3 occurred under moderate air temperature (12.4=<Ta <=17.6 ºC) and moderate to high wind speeds (Ws >3.1 m s^{-1}).

Ozone has a diurnal pattern of low morning and evening concentration and peak afternoon O_3 levels. The second O_3 peak is observed at late night/early morning hours. This diurnal trend is also driven by NO_x - O_3 chemistry, local meteorological conditions and regional background O_3 inflow. In the morning and evening rush hour traffic, O_3 is increasingly titrated by NO. This diurnal trend of O_3 is consistent in all seasons. The peak O_3 between 0100 to 0600 h, particularly under marine wind conditions, is a function of regional background O_3. In all seasons, large number (42%) of peak O_3 concentrations occurred in the afternoon (13:00 -17:00 hours), while early morning (during the night) and evening together accounted for 44% of the peak O_3 events. Both same-day and next-day mechanism are contributing factors for increase in O_3 concentration. However, considering the specific local and synoptic meteorology of the region, next-day mechanism is unlikely especially in the warmer seasons of summer and autumn.

Overall, the study demonstrates the complex nature of peak ozone events for an urban area in a maritime location. Despite generally low surface concentrations in the Auckland region currently, the results reveal the potential for and susceptibility to high ozone levels in the future.

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