Non-parametric nature of ground-level ozone and its dependence on nitrogen oxides (NOx): a view point of vehicular emissions

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Abstract

Ground-level ozone has been studied extensively using classic parametric statistics (most commonly conventional linear regression). Very few researchers have considered ozone distributions and even those that do tend to apply parametric techniques. This study assesses ground-level ozone distributions at six locations in the UK and characterises the correlation of nitrogen oxides (NOx) and ozone at a roadside location. The distribution of ozone is investigated, applying Shapiro-Wilk test and graphical presentations. The histograms are right skewed and show maximum frequency at ozone mixing ratios from 0 to 5 ppb (particularly at urban centers and roadsides locations), which is probably caused by high levels of freshly produced NOx associated with road traffic. There is evidence that ground level ozone is not normally distributed (p-values < 0.05). NOx is a dominant sink for ozone at urban and roadside sites due to its ozone scavenging effects. Consistent with literature ozone is negatively correlated with NOx. The negative correlation is stronger at low NOx levels (up to approximately 80 ppb 24 hour mean, Spearman correlation coefficient R is '-0.72') and becomes weaker as NOx levels increase (over 80 ppb R value is '-0.53'). When NOx mixing ratios reach approximately 200 ppb or over the correlations become positive. This study investigates how the associations of ozone and NOx vary at different levels of their mixing ratios and suggests that due to the non-normal distribution of ozone, nonparametric statistics should be applied for ozone modelling.
Keywords: ground-level ozone, air pollution, nitrogen oxides, nitrogen oxides and ozone, ozone distribution, vehicular emissions and ozone.

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1 Introduction

Traditionally road traffic has been mainly linked with particulates (e.g. PM_{10} and $PM_{2.5}$), carbon monoxides (CO), and nitrogen oxides (NOx), whereas ozone has very rarely been studied in connection with traffic. This is because ozone is not directly emitted by traffic or any other combustion processes, rather, it is a secondary pollutant generated by atmospheric chemistry. Ozone is linked with traffic closely and ozone levels are affected by traffic in two main ways: (i) traffic is the main source of ozone precursors i.e. NOx and volatile organic compounds (VOCs) are emitted by traffic that react in sun light and produce ozone; (ii) freshly produced NO react with ozone and destroy it ($NO + O_3 \rightarrow NO_2 + O_2$) and that is the main reason that ozone concentrations are generally lower at roadsides and urban areas than in the surrounding rural areas [1].

Ozone is important at local levels, as well as at regional and intercontinental levels. At a given location ozone concentration is the sum of ozone produced by photochemical reactions, ozone brought in by regional transport and ozone descended from the stratosphere; minus ozone destroyed by NOx reactions and dry deposition [2]. Due to these sources and sinks ozone has a typical diurnal and seasonal cycle in the UK. The worrying factor regarding tropospheric ozone pollution is that in spite of the decreasing trends in its precursors, background ozone concentrations have been increasing in the UK, particularly in urban areas [3]. The Air Quality Expert Group (AQEG [3]) has expressed their concerns that ozone levels in urban areas are increasing at faster rates by comparison with surrounding rural areas, which in future may result in urban ozone levels as high as in the surrounding rural areas. If that happens it will increase ozone related health and environmental risks in these highly populated areas. Therefore it is vital to understand uncertainties in ozone predictions and quantify accurately the relationship of ozone with its sources and sinks.

Tropospheric ozone has been studied extensively throughout the World using classic parametric statistics (most commonly ordinary least square regression). Very few researchers have considered ozone distributions and even those that do tend to apply parametric techniques. The majority of classical statistical tests are based on the assumption that the data to which the tests are applied exhibit a normal distribution (i.e. bell shape, symmetrical and with a common mean and median). If the parametric tests are applied to non-normal data, they can result in biased or even erroneous results [4]. Therefore, before applying a classical test ,it is vital to check data distributions and if the data are non-normally distributed, robust and non-parametric methods should be applied that are not based on such assumptions.

This study intends to undertake a statistical analysis based investigation into ground-level ozone to determine whether ozone data are normally distributed or not. Ozone data distribution is compared spatially (6 monitoring sites) as well as temporally (different months and years). Variations in ozone concentrations are explained in terms of its correlation with NOx.

2 Methodology

The study is based on the statistical analysis of ozone and NOx data measured at several air quality monitoring sites in the UK. The sites include a roadside (Kirkstall Road Leeds), a kerbside (Marylebone Road London), 2 urban centres (Nottingham and Leeds centre), 1rural (Harwell) and 1 remote (Strath Vaich) air quality monitoring sites. All the sites, except Kirkstall are part of the UK Automatic Urban and Rural Network (AURN). The Kirkstall site is part of facilities available at Institute for Transport Studies (ITS) University of Leeds for the monitoring of air pollution, traffic and meteorological variables. The Kirkstall site [53°48'31.38"N and 1°35'21.40"W] is located on Kirkstall Road (A65), Leeds. Kirkstall Road runs North-West to South-East through the city of Leeds. At all these sites ozone is measured by ultraviolet absorption analyser and NOx by Chemiluminescent analyser, which are the standard methods for measurement of ozone and NOx in the Europe and UK. The details of AURN sites can be found at reference [5].

Ozone data distributions have been studied using simple graphical methods and statistics tests. The graphical methods used in this study include histograms, scatter diagrams and time variation plots. In addition to graphical presentation, the Shapiro-Wilk test has also been applied to estimate ozone normality. Spearman Rank correlation, which is a non-parametric or distribution free approach, has been applied to estimate the degree of co-variance between ozone and NOx. The statistical language R and the associated 'openair package' have been used for performing statistical analysis and making diagrams; see [6] for more details of these software.

3 Results and discussions

3.1 Ozone data distribution

Firstly ozone data from the Kirkstall site have been analysed in details and then compared with data from AURN sites. The Kirkstall data analysed are for a 2 years periods (Nov. 2007 to Oct. 2009). Figure 1 shows a histogram of hourly ozone mixing ratios collected at Kirkstall site and shows that ozone data are not normally distributed (p-value for Shapiro-Wilk test is less than 0.01). The histogram shows very high frequency (nearly 2500) at ozone levels 0 to 5 ppb (first column). The frequency when ozone mixing ratio is 40 or over is relatively low. The histogram is skewed towards right. The first bar of the histogram needs investigations to prove that it comes from genuine measurements and is not due to an error or artefact.

3.1.1 Ozone distribution when ozone is less than 5ppb

This section explains whether the first bar of the histogram (in Figure 1) is a result of genuine ozone measurements or not. Ozone (ppb) hourly average data from Kirkstall site had 16194 data points (excluding missing values). Out of the total 2462 data points have ozone mixing ratios less than 5ppb and 20 data points

have ozone concentrations even less than 1 ppb. Firstly, the lower detection limit of the monitor (photometric ozone analyser, model 400E) is checked, which is < 0.6 ppb and hence it is low enough to give an accurate ozone measurements for any mixing ratios higher than 0.6 ppb. Secondly whether these data points are distributed over all 12 months or condensed only in 1 or 2 months. Thirdly to find out if these 2462 data points lie where ozone mixing ratios are expected to be low (e.g. winter months, night hours) or not. If these data points mostly lie in winter months (day or night) or in summer night time then we can say that they are genuine, otherwise they will be considered due to an artefact and discarded.

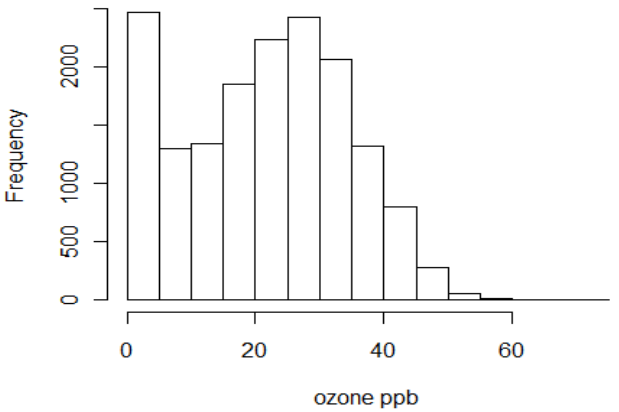

Figure 1: Histogram of mean hourly ozone ppb from Kirkstall site Nov. 2007 to Oct. 2009 indicates that the data are not normally distributed (p-value < 0.010 for Shapiro-Wilk test).

Figure 2 (bottom right) shows that the 2462 data points when ozone < 5 ppb is distributed in all 12 months regardless of winter or summer season. However the majority of these hours come from winter months (Nov. to Feb.). Data from summer months (not shown here) indicate that ozone mixing ratios less than 5 ppb mostly occur during night time hours. Figure 2 (bottom left) shows high frequency over night hours (including early morning and evening) and low during day time (especially 10:00 to 16:00). Figure 2 (top right) shows similar frequencies for most days except Sunday.

Ozone levels in the UK are generally higher during the summer and lower during the winter, a trend demonstrated for the Kirkstall dataset later in section 3.2.2. Likewise ozone levels are generally observed to be lower at night and higher in the daytime. The reason for low levels of ozone during the winter and at night is most probably the lack (or reduced level) of solar radiation and lower temperatures which are responsible for reduce photochemical ozone production rates. In addition, dry deposition of ozone during the night can further reduce

ozone levels. Ozone levels are also linked to traffic activity by the NOx scavenging effect, which are generally low on Sunday, therefore Figure 2 (top right) shows low frequency of low ozone on Sunday as compared to other days.

The above explanations clearly indicate that the 2462 data points are genuine measurements. This will become clearer in section 3.1.3, where the distributions of ozone data from different monitoring stations at which different instruments are used are compared.

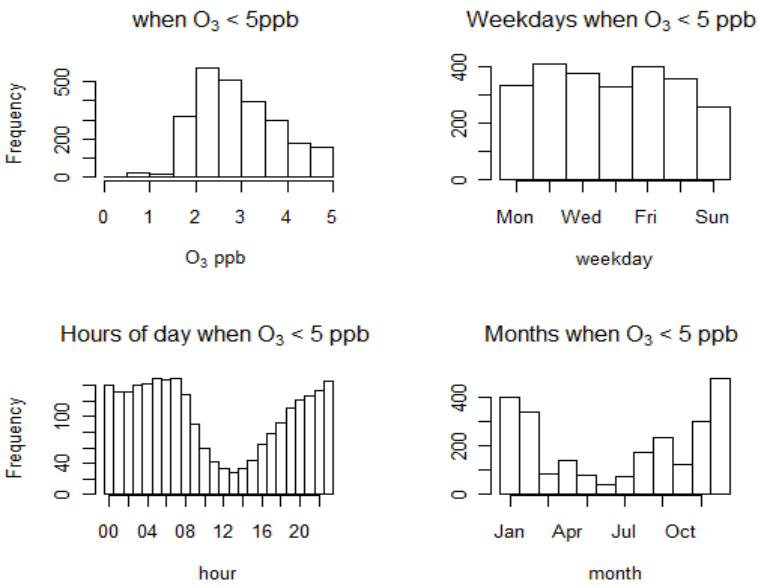

Figure 2: Histograms showing the frequency of months, hours and weekdays when ozone (O_3) < 5 ppb.

3.1.2 Ozone distribution for different months

Shapiro-Wilk test of normality gives p-values less than 0.01 for each month of the year 2008, which reveals that hourly ozone data do not follow a normal distribution in any month of the year at Kirkstall site. Histograms of ozone for each month January to December 2008 are shown in Figure 3, showing how ozone distributions vary in different months.

There are 2 main categories of histograms in Figure 3 winter and summer months. In winter months (January, February, September, October, November, December) the highest frequency of ozone is found when the mixing ratios of ozone are 0 to 5 ppb, whereas in the rest of the months (March to Aug) the highest frequency can be observed when ozone mixing ratios are approximately 30 ppb. The winter months can be again subdivided into 2 groups i.e. September, October, November when the distribution is somewhat bimodal (highest frequency of ozone can be observed at 0 to 5 ppb and also at around 30 ppb) and

January, February, December where the highest frequency of ozone is mainly at 0 to 5 ppb.

Although the ozone distribution during the summer months seems closer to normal distribution, statistically it still appears to be non-normal (p values < 0.05). The reason for the difference in ozone distributions during summer and winter months is most probably the difference in the amount of solar radiation and temperature. Solar radiation and temperature are the 2 main meteorological factors responsible for photochemical ozone production and that is why the amount of ozone is mostly lower in winter months. In contrast, during the summer months photochemical ozone production is high which results in high ozone mixing ratios as shown in Figure 3.

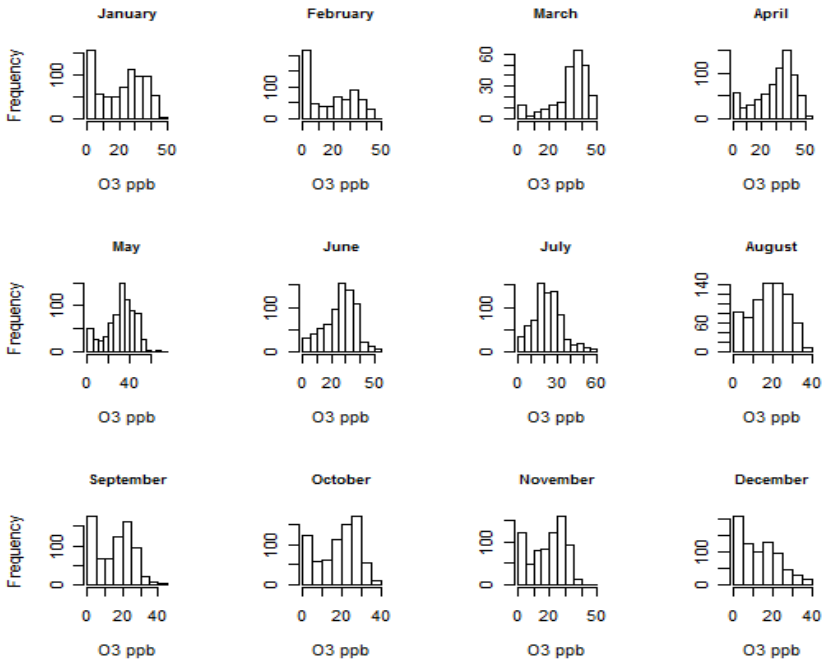

Figure 3: The distribution of ozone during different months of the year, hourly mean ozone data from Kirkstall site.

3.1.3 Ozone distribution at different sites

Ozone distributions vary spatially from place to place in the UK depending on the nature of the monitoring site. Roadside and urban centre monitoring sites are generally characterized by high levels of fresh NOx that react with ozone and keep ozone levels low at these sites. In contrast, rural and remote monitoring sites have generally low levels of NOx and high levels of ozone.

Figure 4 shows ozone distributions at 6 different monitoring sites. Ozone distributions at kerbside and roadside monitoring sites (Marylebone and Kirkstall) show high frequencies for low ozone mixing ratios i.e. the first column of the histogram is taller than the rest of the columns, which shows that low ozone mixing ratios occur more frequently than higher ozone mixing ratios. Particularly at the Marylebone site the frequency of higher ozone mixing ratios is very low; the reason probably is that Marylebone site is situated in London at the kerb of very busy road where road traffic exhausts produce a huge amount of fresh NOx [7]. Although the Kirkstall site is a roadside monitoring site, the traffic levels on this road in Leeds is not as high as at Marylebone Road and hence the difference in ozone mixing ratio is clear. In contrast, the Harwell and Strath Vaich monitoring sites have totally different ozone distributions; the histograms almost look like a bell shaped symmetric diagram (statistically it is still non-normal, as p-values < 0.05). The higher frequencies of ozone at rural and remote sites occur at about 30 ppb (60µg.m^{-3}). The reason is probably that these sites are far away from busy roads and receive very low fresh NOx inputs. The other two sites Leeds and Nottingham centre (urban centre sites) are intermediate between rural and roadside monitoring sites. These sites although are urban, receive reasonable high levels of fresh NOx which could reduce ozone mixing ratios but still the frequency of high ozone concentrations are higher than the roadside monitoring sites.

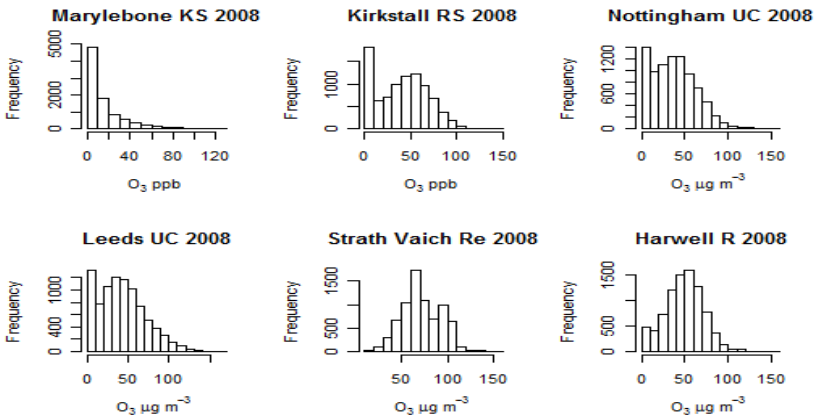

Figure 4: Ozone mean hourly data distribution at different monitoring sites in the UK, where KS, RS, UC, Re and R define the type of monitoring site and stand for kerbside, roadside, urban centre, remote and rural respectively.

After the comparison of different monitoring sites and studying ozone distributions during different months, it can be concluded that ozone data in the UK do not follow a normal distribution and hence non-parametric statistics should be used for its analysis.

3.2 Ozone and NOx correlation

The scatter plot of 24 h average NOx and ozone data from the Kirkstall site Leeds is shown in Figure 5, and exhibits a clear negative correlation between NOx and ozone and as NOx mixing ratios increase ozone mixing ratios decrease. Most probably the negative correlation is due to NO reactions with ozone which destroys ozone molecules and produces NO_2: ($NO + O_3 \rightarrow NO_2 + O_2$).

In Figure 5 along the x-axis 3 main segments can be observed. In the first segment (NOx ppb < 80, left circle - solid line) the negative correlation between ozone and NOx seems very strong (Spearman correlation coefficient (R) value is '-0.72') and ozone mixing ratios decrease linearly with increases in NOx mixing ratios. In this area the data points are dense, as on this monitoring site most data points lie in this segment. In the next segment (middle circle - dashed line, 80 < NOx ppb < 220) the negative correlation is still there but not linear. In this section data points are relatively sparse and the negative correlation is weaker (R value '-0.53'). In the last segment (right circle – dotted line, NOx ppb > 220) the negative correlation between ozone and NOx disappears and the curve becomes almost totally horizontal. The negative correlation turns into positive correlation (R value '+0.30'). The positive correlation between ozone and NOx at atypically high NOx concentrations is most probably due to NO_2 oxidation which gives rise to ozone formation. As this correlation is based on 24 h mean ozone and NOx data, the correlation will be further investigated in section 3.2.1 using 1 minute and hourly data from the Kirkstall monitoring site.

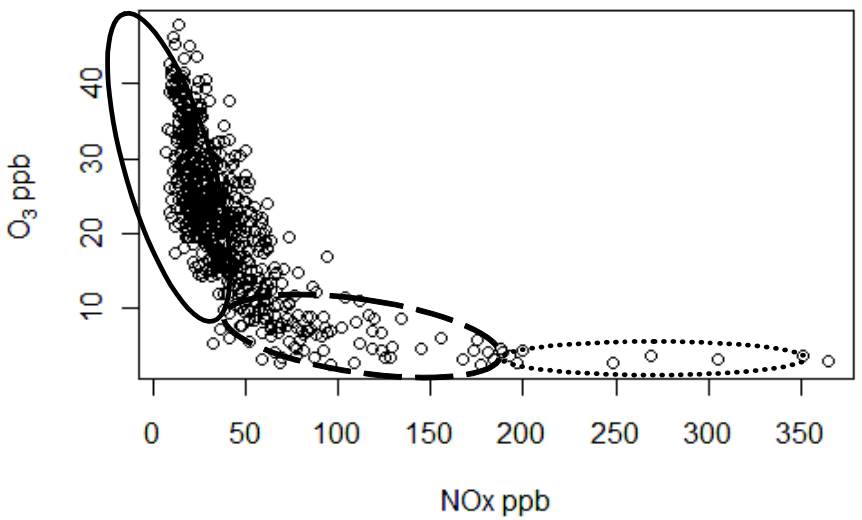

Figure 5: Scatter plot between 24 h mean ozone and NOx data from KS site (01/11/2007 to 31/10/ 2009).

3.2.1 Correlation between NOx and ozone for 1 minute and hourly data

When NOx mixing ratios reach about 200 ppb the correlation between ozone and NOx becomes positive as demonstrated in section 3.2. In this section those 6 days (12–15 December 2007; 11–12 February 2008) when NOx mixing ratios were 365, 304, 250, 198, 271 and 354 ppb, respectively, are further investigated. Figure 6 shows the scatter plot along with their R values for 1 minute data for the 6 days. Over these days ozone and NOx have positive correlation coefficients, except on 13/12/2007 where the correlation is negative despite the fact that NOx mixing ratio is as high as 304 ppb. Figure 6 (top row, middle column) shows that the scatter plot for 13/12/2007 looks somewhat different from the other scatter plots. The main difference is that for some reason there are some higher ozone mixing ratios at the start of the scatter plot. Hourly mean NOx and ozone mixing ratios show more clearly those high ozone mixing ratios points (not shown here).

To find out an explanation for these data points, the author investigated the meteorological variables to see if there was some explanation, as only NOx and ozone correlation cannot provide an answer. It was found from the observations of meteorological variable that on 13 December 2007 the sun came out about 09.00 am and was shining until 12.00. The solar radiation triggered photochemical ozone formation and the ozone mixing ratios reached the highest level of the day (7 to 8 ppb); the average ozone on the day was about 3ppb. As a high level of NOx (304 ppb) was present on the day, probably NOx reacted with photochemically formed ozone and brought the ozone level down, explaining the negative correlation on 13 December.

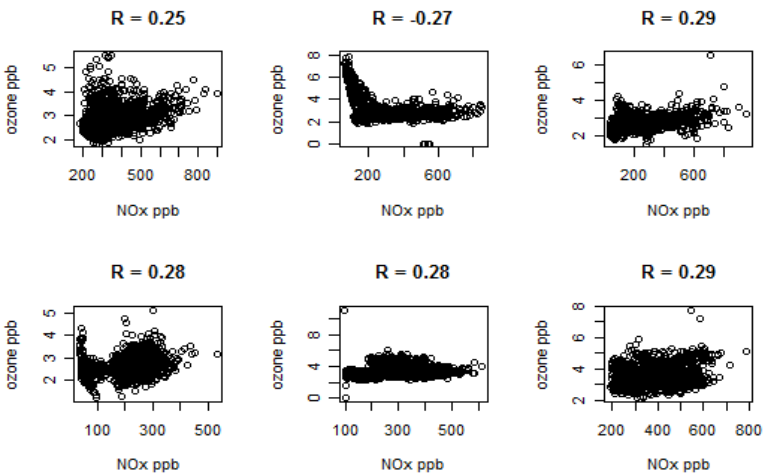

Figure 6: Scatter plot of ozone vs. NOx for the six days when NOx mixing ratios were nearly as high as 200 ppb or over and NOx is mostly positively correlated with ozone; R stands for Spearman correlation coefficients.

3.2.2 Temporal variations in NOx and ozone mixing ratios

In this section the correlation between ozone and NOx has been investigated using time variation charts (Figure 7). These diagrams depict the association of ozone and NOx showing how their mixing ratios change on average during different hours of the days, days of the week or months of the year.

Figure 7 reveals that ozone mixing ratios are normally higher during spring and summer (March, April, May and June) and lower during winter months (January, February, November and December), where as NOx mixing ratios are higher in winter (January, February, November and December) and lower during summer months (May, June, July and August). In winter the high NOx ratios are probably resulted by slow chemical reactions and slower pollutant dilution due to stagnant atmospheric conditions; the opposite happens in summer (better chemistry and dilution). On the other hand ozone is a secondary pollutant and is mostly produced in the atmosphere by photochemical reactions of NOx and VOCs driven by solar radiation (Ultraviolet radiation – UV). Therefore in winter because of low UV radiation and temperature ozone production is minimal (if any at all); and whatever ozone is present is consumed by freshly produced NO (remember UV radiations are required for ozone production but not for its destruction). But in summer high UV radiation and temperature are responsible for the relatively higher levels of ozone.

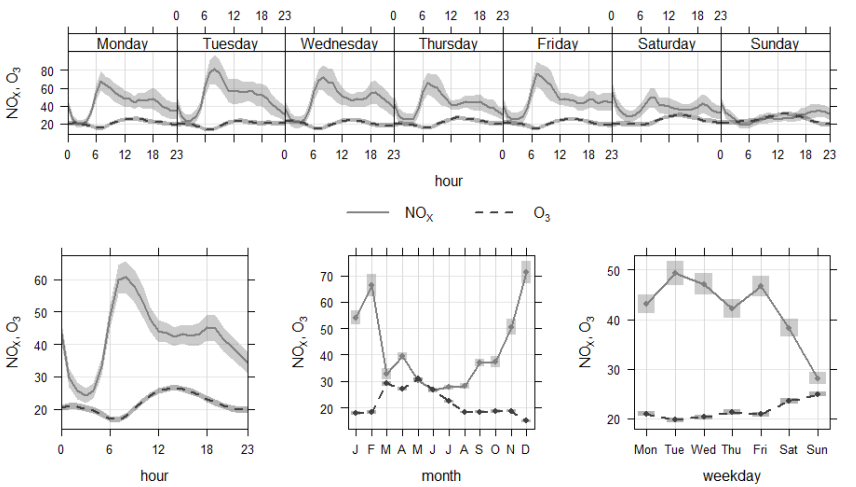

Figure 7: Time variation plot of ozone and NOx mixing ratios (ppb) hourly mean data from Kirkstall site Nov 2007 to Oct 2009.

On a weekly basis traffic volume seems to be the dominant factor for controlling NOx and ozone mixing ratios. On Kirkstall Road the volume of road traffic is higher during weekdays and lower during the weekend; as many companies and institutes do not operate at the weekend. Figure 7 clearly shows the lowest NOx and highest ozone levels on Sunday, followed by Saturday. As

on Sunday low traffic volumes produce less NOx which result in less ozone destruction and hence ozone levels are higher. Higher ozone levels at the weekend are called the ozone weekend effect (OWE) and is studied by several authors (e.g. 8, 9, 10, and 11). The diurnal changes in NOx and ozone levels seem to be linked with both traffic volume and meteorology. Although NOx and ozone are strongly correlated and both of them are strongly linked with the volume of road traffic, the diurnal average trend of ozone seems to be dominated by solar radiation. The highest ozone mixing ratios were observed at 13.00 to 15.00 hour when UV radiation is often at a maximum; and lowest ozone levels at 06.00 to 07.00 hour in the morning due to the overnight dry deposition and NOx scavenging effect. NOx levels are strongly linked with traffic volume and reached a maximum level at 08.00 to 09.00 am when roads traffic activity is at peak. After that NOx levels come down but rise again at about 17.00 to 18.00 hours in the evening, probably due to late afternoon traffic peak hours.

It was observed that correlation between NOx and ozone is stronger during winter (R for January was '-0.80') and weaker during summer (R for May '-0.40'). NOx is probably the dominant controlling factor for ozone levels in winter when there is not much photochemical ozone production and as solar radiation and temperature increase they weaken the correlation between NOx and ozone. Therefore for ozone prediction in addition to NOx it is essential to quantify the role of meteorology and traffic flow in controlling ozone levels, which is part of our future plan.

4 Conclusion

This study investigates ozone distribution and its association with NOx at a roadside monitoring site, where most of the NOx is believed to be emitted by road traffic. The study demonstrates that ozone distribution is not a fixed phenomenon and rather it varies both spatially and temporally. Our data show that ground-level ozone is not normally distributed and hence should be studied by using non-parametric or distribution free statistics. The study also shows that generally ozone is negatively correlated with NOx, although the strength and nature of correlation may vary as NOx level changes. The negative correlation is strongest at NOx levels up to 80 ppb and becomes weaker afterward. The correlation changes to positive when NOx levels go as high as 200 ppb or over. Moreover, the correlation is stronger in winter months and night times; and weaker in summer months and daytimes probably due to solar radiation. On-going investigations are intended to explore the associations between ozone and traffic flow using traffic volume, speed and fleet composition characteristics for better understanding the relationship of ozone with road traffic, which may be helpful in accurate ozone prediction. Accurate prediction of ozone episodes may help to pre-warn the public of the potential high levels of ozone and aid policy makers the development of effective mitigation strategies.

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