ATMOSPHERIC POLLUTANTS IN AND AROUND MANCHESTER, UNITED KINGDOM

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Abstract

Concentrations of nitrogen oxides (NO_x) and tropospheric ozone (O_3) at six locations in the Greater Manchester area were analysed over an eight year period. The various daily, weekly and seasonal trends were evaluated for each location. A correlation between NO_x and ozone concentrations was established - an increase in NO concentrations was found to cause a decrease in ozone concentrations. A period of extreme exceedance in NO_x was then identified, where hourly measurements of NO_x concentrations at Bury reach in excess of 2000µg/m^3. Its causes were investigated by examining the environmental conditions at the time, and comparing these to the conditions on the days with low NO_x concentration levels. It was revealed that extreme exceedance events occur for the most part in winter, when there is high pressure, little wind and a shallow and stable boundary layer. Periods of low NO_x concentrations are favoured by warm, windy conditions, with a deep and well-mixed boundary layer.

1. Introduction

One of the biggest environmental problems the human race has to face is that of air pollution. There is hardly a city in the world that is not affected and statistics show that in the developed world, air pollution causes more deaths than any other meteorological hazard. There is also a large economic impact, not only a result of reduced crop yields and building damage (with costs running into billions of pounds a year), but also from increased health care costs and lost work productivity due to the health problems air pollution can cause. It is estimated that in the United States of America alone these health problems create a bill that runs in billions of dollars per year **[1]**.

Legislation aimed at reducing pollution levels in our atmosphere has become common in the last 50 years. Pollution is not, however, a new problem. Smoke from burning coal and wood was a huge problem in Medieval England, so much so that King Edward I brought in the first recorded law aimed at reducing air pollution. It did not do much to alleviate the problem, however, and with the onset of the Industrial Revolution several centuries later, the quality of the air was inevitably going to get worse.

One of the main components of the smoke emitted was sulphur – which in large quantities can cause severe respiratory problems in humans. By the mid-nineteenth century dangerous and often fatal 'smoky fogs' were commonplace in Britain's industrial cities, particularly London. The word 'smog' was first used in the early twentieth century to describe this mixture of smoke and foggy air. It was difficult to bring in effective regulations because the owners of the factories held so much influence over governmental policies, and to reduce emissions would surely have a huge impact on their profits. It wasn't until 1952 that an event forced the UK parliament to make dramatic change in policy. Weather conditions in London created thick smog that lasted for no less than five straight days. Visibility in the city reduced to zero and almost 4000 people died as a direct result of breathing in the noxious fumes. The Clean Air Act was passed in 1956 making London and other industrial cities much cleaner with respect to this type of pollution.

Tackling air pollution remains a difficult task today. Whilst the so-called London-type smog may be a thing of the past in cities in developed nations, the increased use of private cars has created a whole new type of smog. This was first identified in Los Angeles in the 1950s and is thus often referred to as Los Angeles-type smog. This type of smog occurs when there are high levels of tropospheric ozone. Although it is vital for our well-being to have sufficient levels of ozone in the stratosphere to protect us from harmful UV-rays from the sun, ozone in the troposphere acts as a pollutant with significant negative health effects.

Two other pollutants which are still a huge problem in today's cities are nitrogen (nitric) oxide (NO) and nitrogen dioxide (NO_2), collectively known as nitrogen oxides (NO_x).

1.1 - Types of air pollutants

Air pollutants are defined as airborne substances that exist in the atmosphere in concentrations that are damaging to our health and to vegetation and buildings. They can come from natural sources such as volcanic eruptions or anthropogenic sources.

They can be separated into two main groups: **primary** air pollutants that are released into the atmosphere from a direct source such as a chimney or a car exhaust and **secondary** air pollutants which are created through chemical reactions in the atmosphere.

Nitrogen oxides are primary pollutants, the main anthropogenic sources being the burning of oil and coal in power plants and vehicles.
Inhaling high concentrations of NO_x is said to cause various heart and lung problems, along with increasing the chance of respiratory infection due to lowering resistance. There is also the possibility nitrogen oxides can assist the spread of cancer, but this theory is largely untested on humans.

Tropospheric ozone is a secondary pollutant. It can either be formed as part of the nitrogen cycle in the troposphere itself, or be transported down from the stratosphere. As the chemical reactions take place in the presence of sunlight, the Los Angeles-type smog is also known as photochemical smog.

Ozone can cause many health problems, ranging from the relatively minor such as eye irritations, to the more severe. Chronic illnesses such as asthma and bronchitis can be greatly aggravated by exposure to ozone. Even healthy people can be subject to problems such as reduced lung capacity when exposed to ozone for a period of a few hours.

It is this tropospheric ozone, and in particular its chemical precursor, nitrogen oxides, that will be studied in detail in this report. Daily, weekly and seasonal variations will be considered before looking at exceedance events in nitrogen oxides, and investigating any relationships which may exist between extreme exceedance events and the local atmospheric situation.

2. Background Information and Theory

Before examining the various trends of the concentration data, it is important to have an understanding of some of the processes involved in determining the formation and destruction of these particular air pollutants.

2.1 - Sources of Nitrogen Oxides

It has already been stated that nitrogen oxides are primary pollutants, the main sources being car exhaust fumes and power plant emissions. It is seemingly obvious to say that the concentration levels of NO_x will be directly linked to the levels of emissions. While this is undoubtedly true, there are several other factors. Firstly, the lifetime of nitrogen oxides vary depending on the conditions in the atmosphere; colder and wetter conditions lead to longer lifetimes. The second, and perhaps more important, factor relates to the atmospheric boundary layer and an understanding of this boundary layer, its properties and variations, is needed.

2.2 - Boundary Layer Physics

The Boundary Layer (also called the Atmospheric Boundary Layer, or the ABL) is the layer of atmosphere next to the surface of the earth, as shown in Figure 1. The air is very well mixed within this layer due to the amount of turbulence that exists. At the top of the boundary layer, however, there exists an inversion (i.e. a very stable layer) which effectively creates a barrier. There is very little mixing between the air in the boundary layer and the air in the free atmosphere above this stable layer, so air pollution that exists in the boundary layer is therefore trapped there.

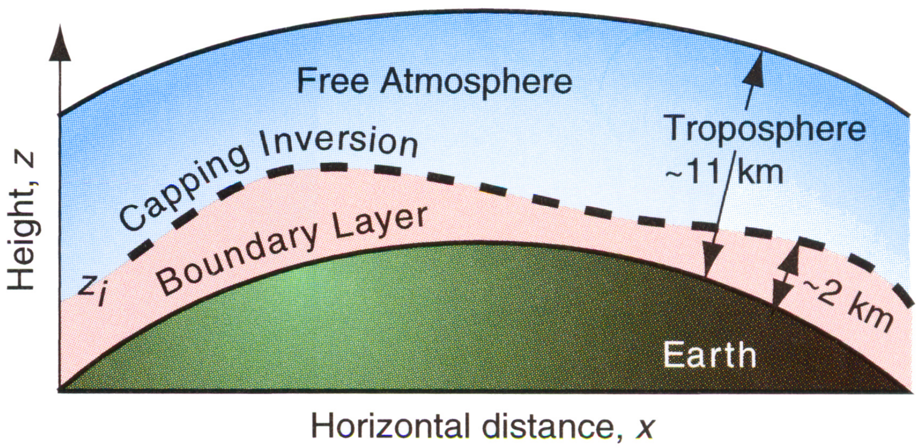


Figure 1 - A cross section of the troposphere showing the nature of the boundary layer. Ref:[2], p.376

The depth of the boundary layer is usually between 1 and 2 kilometres. It can vary considerably over even quite a short period of time. Clearly, the deeper the boundary layer, the more space the pollutants have to 'mix' in, therefore meaning lower pollution levels at ground. Exceedingly high concentrations are most probably caused by an extremely shallow boundary layer, causing all the pollutants to be trapped closer to the ground. It is this concept that will be explored in Section 5 of this report – Exceedance Events in NO_x.

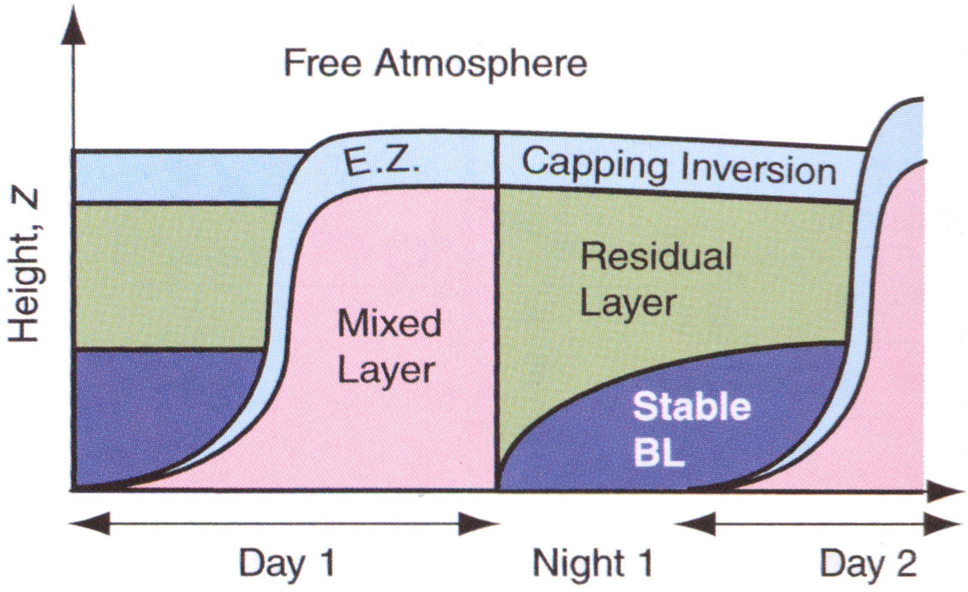


Figure 2 – A graph showing diurnal variation in the boundary layer. Ref:[2], p. 398

There is also quite a distinctive diurnal variation in the depth and properties of the boundary layer, as shown in Figure 2. Turbulence is mostly caused by surface heating by energy coming from the sun. Thus when this energy is 'turned off' at night time; this source of turbulence is taken away, and the boundary layer becomes very stable. Mixing of the atmosphere only really takes place very close to the surface during the night. After sunrise, the surface slowly heats up again, creating more and more turbulence. The mixed boundary layer grows in size, until the whole of the boundary layer consists of this mixed air at some point around midday.
In theory, this diurnal variation in the boundary layer should have an effect on the daily cycle of NO_x concentrations. This idea will be explored in Section 4 of this report – Variations and Trends in NOx and Ozone Data.

2.3 - <u>The Nitrogen Cycle</u>

Ozone is formed in the troposphere as part of the nitrogen cycle, which functions as follow:

1. The photolysis of nitrogen dioxide by ultraviolet radiation creates nitrogen oxide and a single oxygen atom.

$$NO_2 + hf \rightarrow NO + O$$

   where hf indicates the energy from ultraviolet radiation from the sun.

2. This single oxygen atom combines with an oxygen molecule to form ozone. This reaction must take place in the presence of a third molecule, M, which serves to absorb energy from the reaction as heat.

$$O_2 + O + M \rightarrow O_3 + M$$

3. The ozone then reacts with nitric oxide to form oxygen and nitrogen dioxide, thus completing the nitrogen cycle.

$$O_3 + NO \rightarrow NO_2 + O_2$$

The above cycle generally takes around three minutes to complete. The photolysis reaction in part 1 of the cycle is relatively slow when compared to reactions 2 and 3. It is clear, however, that in this cycle, all ozone that is created is also destroyed. Thus, a build up of ozone can only exist if the ratio of NO_2 to NO is sufficiently large enough. For this to happen, processes are required to convert NO to NO_2 without destroying any ozone.

2.4 - The VOC Oxidation Cycle

This chemical process is the main way the ratio of NO_2 to NO can reach the required levels for ozone build up.
Volatile organic compounds are another primary pollutant. They are primarily hydrocarbons, and the main anthropogenic source is once again the exhaust fumes of vehicles. These compounds are oxidised in the atmosphere by a series of reactions, from which carbon monoxide, carbon dioxide and water are produced. The processes are detailed below, where RH represents any hydrocarbon and R is the organic fragment of this hydrocarbon.

1. The extremely reactive hydroxyl radical (OH) attacks the hydrocarbon to form water and R:

$$RH + OH \rightarrow H_2O + R$$

2. R then reacts with an oxygen molecule in the presence of a third mass, M:

$$R + O_2 + M \rightarrow RO_2 + M$$

3. RO_2 then reacts with nitrogen oxide in the following manner:

$$RO_2 + NO \rightarrow NO_2 + RO$$

This third process is the key to allowing ozone build-up as it converts nitrogen oxide to nitrogen dioxide without causing the destruction of ozone.

2.5 - Build-up of ozone concentrations

The build up of ozone formation in the troposphere relies mostly on the presence of two sets of compounds: nitrogen oxides and VOCs. However, as nitrogen oxides are involved in both the formation and destruction of ozone, its involvement is slightly more complicated. Of course, if there were no nitrogen oxides whatsoever the ozone could not be created, and in some cases a reduction in NO_x emissions can help lead to a reduction in ozone concentration levels. In areas where there is a huge abundance of NO_x, the time scales of all the reactions involved mean that the high NO concentrations destroy ozone faster than NO_2 can create it.

These features mean that, in areas of high NO_x concentrations, a decrease in NO_x emissions can actually lead to an increase in ozone concentrations due to the reduction in ozone destroying NO. In these situations, a reduction in the amount of ozone in the atmosphere is more greatly achieved through the reduction of VOC emissions.

Local areas have been characterised as being either NO_x-limited, where a reduction in ozone levels is more likely through a decrease in nitrogen oxides, or VOC-limited, where the reduction of volatile organic compounds is more likely to decrease ozone concentrations. In general, rural areas are NO_x-limited, while urban areas tend to be VOC-limited.

2.6 - Sinks of Nitrogen Oxides

Nitrogen oxides can also be destroyed through reactions with other substances. The main example of this is the hydroxyl free radical molecule (OH). This is highly reactive and will react with almost any thing. It is generally formed through the following processes:

a) An ozone molecule is broken into a single oxygen atom and an oxygen molecule through photolysis by ultra-violet radiation.
b) The single oxygen atom formed can then react with water to form two hydroxyl radical molecules.

$$O + H_2O \rightarrow OH + OH$$

Concentrations of OH are likely to be highest at midday, and on a seasonal basis, in the summer, when there is more uv-radiation to photolyse ozone molecules and more ozone molecules to begin with.
OH will react with nitrogen dioxide in the presence of a third body, M to form nitric acid ($NO_2 + OH + M \rightarrow HNO_3 + M$) and in this way acts as a sink for NO_x.
As the hydroxyl level is also a main component of the VOC Oxidation Cycle, its presence also encourages the conversion of NO to NO_2 and thus encourages the build up of ozone.

3. Experimental/Method

This project did not involve the collection of any new raw data but instead made use of the UK National Air Quality Database **[4]**. This online database stores large quantities of high quality air pollutant concentration data from monitoring stations around the country.

There are over 1500 different sites across the United Kingdom that monitor air quality, mostly on an hourly basis. It was decided to focus on one particular region to analyse variations and search for a weekend effect. Different stations monitor different air pollutants, however, and so it was important to choose an area which has a sufficient number of stations that provide hourly readings in both nitrogen oxides and ozone.
Six locations around the Greater Manchester area were chosen as they represent several different types of backgrounds within a reasonably small area. Thus, we can make the tentative assumption that any local meteorological conditions will have the same effect on all the locations.

3.1 - Descriptions of monitoring station locations **[4]**

The sites chosen range from city centre to a completely rural setting. They are Bolton, Bury, Salford Eccles, Manchester Piccadilly, Manchester South (all in Greater Manchester) and Ladybower in the Peak District, approximately 25 miles east of Manchester.

Bolton – this monitoring station is in an urban location that is quite built up. There are three busy roads in the vicinity, with a combined traffic flow of 18,000-23,000 vehicles per day. The manifold inlet is approximately 9 metres above ground level.

Bury – this is a roadside location, 16 metres away from the very busy M62. This motorway has an annual average weekday flow of 169,000 vehicles. Also in the area (21 metres away) is a prominent roundabout with an average weekday flow of around 40,000 vehicles. Both the motorway and the roundabout are subject to congestion, especially during rush hour times. The monitoring station itself is in quite an open area, without any tall building obstructing its surroundings. One would expect the daily cycle and weekend effect to be very noticeable here.

Salford Eccles – this location is described as 'urban industrial'. Again, it is reasonably near (250m) to a busy road – the M602 which sees approximately 70,000 vehicles per day. It is also only 100m from Eccles town centre. The area is generally open but there are many suburban properties.

Manchester Piccadilly – this station is located in the corner of Piccadilly Gardens in the city centre. It exists in a pedestrianised zone surrounded by many several storey buildings.

Manchester South – this location is listed as 'suburban'. The general area is quite built up with suburban properties but the monitoring station itself is situated on the edge of a sports field. Thus the surrounding area is very open. The closest road is 85 metres away, and the closest motorway is 2 miles away.

Ladybower – this location is completely rural, the monitoring station being approximately 0.5 miles from Ladybower reservoir. There is a road nearby but it use is limited to access to the adjacent farm only. The surrounding area is mostly open moorland, with the closest trees being several hundred metres away.

3.2 – <u>A Brief Description of data handling and the statistics package</u>

Data was retrieved for an eight year period running from 1998-2005. The data was obtained in csv format which could then be read in by the statistical programming language, R. This is an open-source programming package which is based on S-plus and has many of the same characteristics. It is used widely within the field of environmental science and its main function in this project is to produce several time-series plots. It is possible to plot the mean of a particular hour for a given day. For example, it can calculate the mean of all the data that exists for a Monday at 9am throughout the time period.
It is also possible to sort the data for each location into descending order, and pick out the highest concentrations and when they occurred. This function was essential for identifying any extreme exceedance events. Examples of the main scripts used can be found in Appendix A.

4. Variations and Trends in NOx and Ozone Data

Results

The first thing R was used for was to obtain mean values of NOx and ozone concentrations in each location. These provide a general idea of what kind of values to expect for each location, and can be found in the table below.

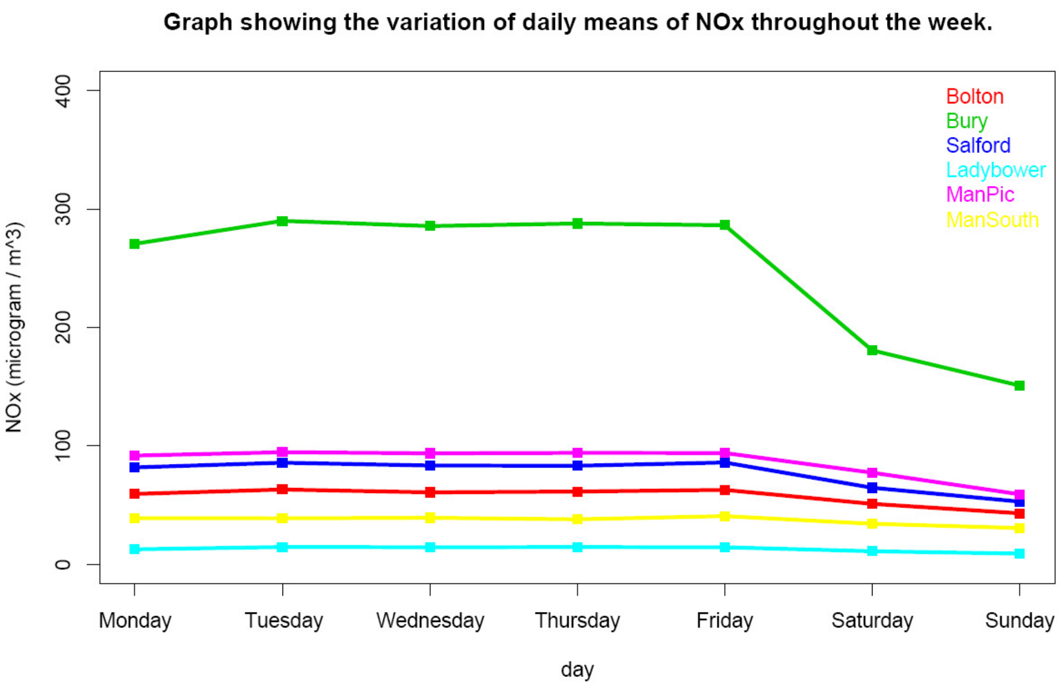
Location	Mean of NOx (µg/m^3)	Mean of Ozone (µg/m^3)
Bolton	57.4	41.0
Bury	250.1	19.0
Salford	76.8	33.2
Ladybower	12.9	53.9
Manchester Piccadilly	86.3	26.5
Manchester South	37.2	33.9

Table 1 - a table showing the mean hourly concentrations of nitrogen oxides and ozone at each location. All values are given to 1 decimal place.

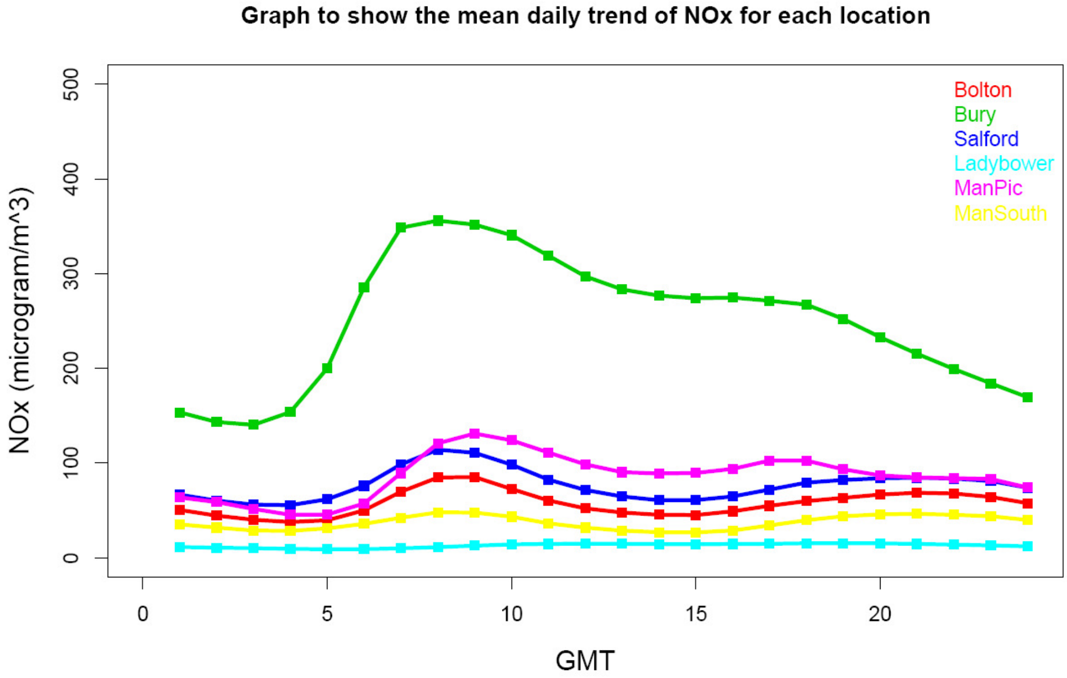
Scripts were then written to plot several graphs to show a range of different trends and variations. Each script was written to plot NOx data, and then altered slightly to create the same plots for ozone data.

NOx Plots

The first plots produced show how the means of the hourly data varies a) due to the day of the week (see Graphs 1) and b) due to the hour of the day (see Graph 2). The values shown relate to the mean of the relevant data throughout the 8 year period the datasets cover.



Graph 1 – a graph to illustrate how hourly measurements of nitrogen oxides vary with the day of the week at each location



Graph 2 – a graph to illustrate how hourly measurements of nitrogen oxides vary with the time of day at each location

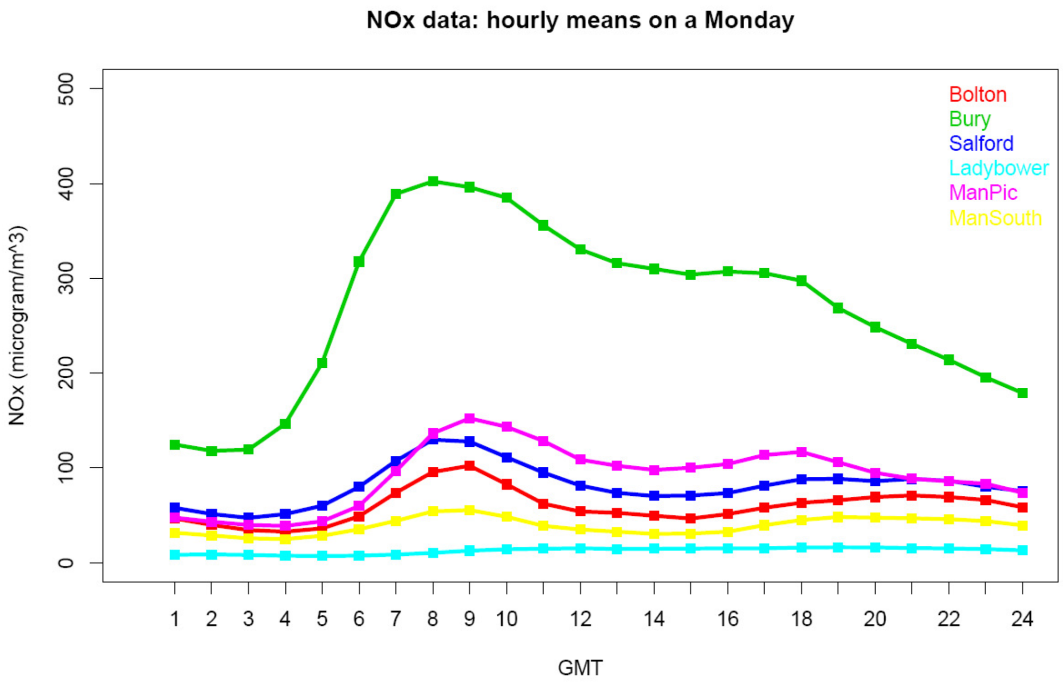
Graphs 1 and 2, together with the data given in Table 1, give important basic information about NOx concentrations with respect to location, weekly trends and daily cycles.

Firstly, the highest concentrations occur at the roadside location of Bury. Concentrations then decrease continually as the locations range from Manchester Piccadilly (city centre), Salford and Bolton (both urban locations), Manchester South (situated in suburbia). Finally, the lowest concentrations exist at Ladybower in a rural environment.

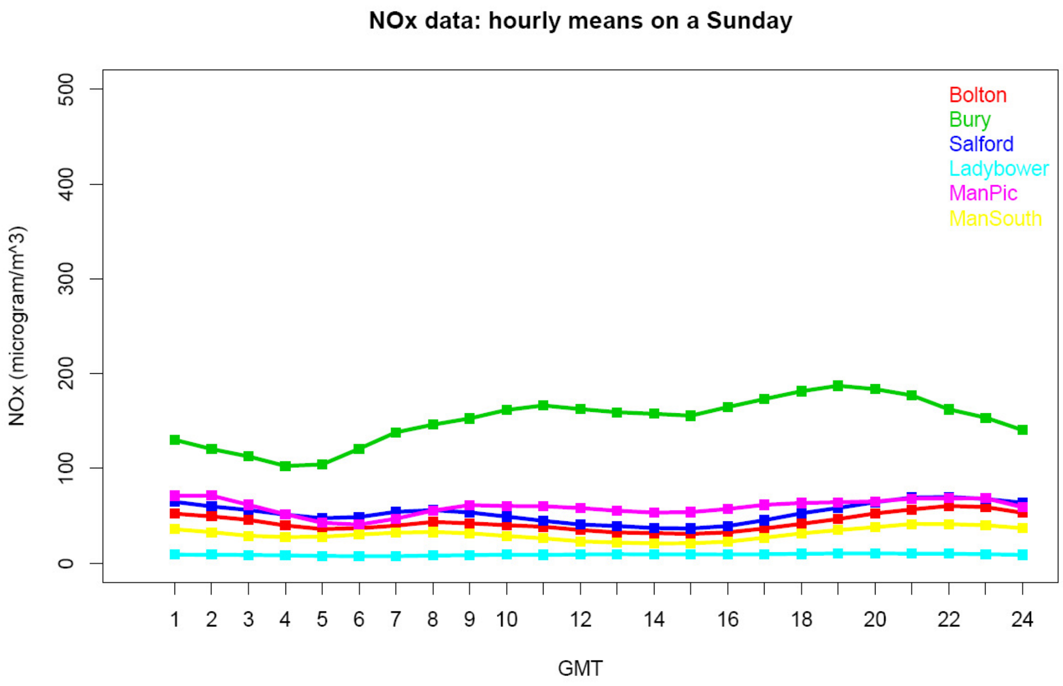
Secondly, the mean of hourly data remains fairly constant throughout the working week. At the monitoring stations in the roadside, urban and suburban locations, however, the mean drops at the weekend. This change is most substantial at Bury roadside, but still exists quite clearly in the other Greater Manchester locations. At Ladybower, however, there does not seem to be any variation at all throughout the week.

Thirdly, Graph 2 provides some information about the daily cycle of NOx concentrations. At Bury, the mean of hourly measurements varies quite considerably throughout the day. The highest concentrations occur in the morning, between 7 and 10am. The lowest concentrations are found at night time, particularly in the early hours of the morning. The daily cycles at the urban/suburban locations match that of Bury, although the gradients and peaks aren't as extreme. Again, the data from Ladybower shows little, if any, variation, throughout the day.

A script was then written to separate the daily cycle of hourly means into the seven days of the week. Graph 3 shows the daily cycle of a typical working day (Monday), whereas the daily cycle at the weekend is represented in Graph 4, where the hourly means on a Sunday are plotted. The plots for the remaining days of the week can be found in Appendix B.



Graph 3 - a graph to show the daily cycle of nitrogen oxides at each location on a Monday

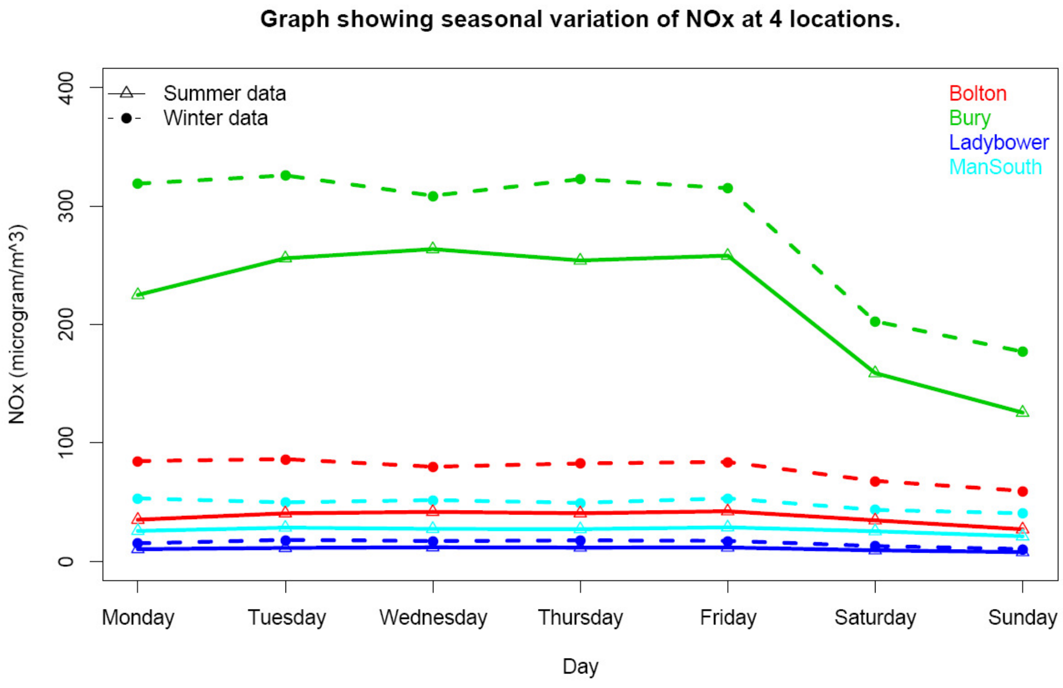


Graph 4 - a graph to show the daily cycle of nitrogen oxides at each location on a Sunday

These plots not only reiterate the results shown in the previous plots, but also reveal a difference in the daily trend on a working day and the daily trend at the weekend. Consider first the plot of Monday's data (Graph 3). The magnitudes of the concentrations are understandably smaller in the graph showing the average daily trend due to the concentrations being lower at the weekend than in the week (an effect seen most obviously at Bury, where the dip at the weekend is most substantial). Other than that, Monday's plots take roughly the same form as those in Graph 2.

On the other hand, the plot showing Sunday's data (Graph 4) takes on a completely different form. This time, the data does not vary nearly as much throughout the day. There is no peak in concentrations occurring between 7 and 10 am and in fact, the highest concentrations take place in the evening.
The results at Ladybower remain the same, with little variation seen.

The plot created by the final script written for showing variations in NOx data is shown in Graph 5. This graph shows the seasonal variation of the daily means of hourly data throughout the week at 4 of the 6 locations. The dashed lines with circular points show data from the winter months, whilst data from the summer months is represented by solid lines with triangular points.



Graph 5 – a graph showing the seasonal variation of nitrogen oxides at four of the six locations

Two main points can be deduced from this graph:

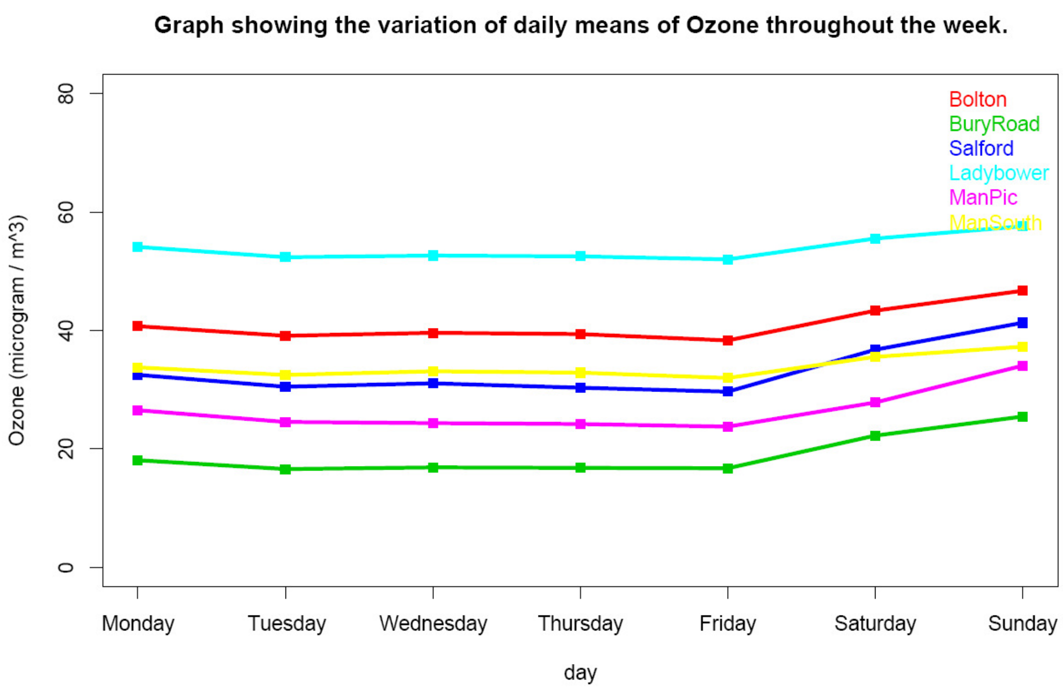
a) Concentrations of nitrogen oxides are higher in the winter months. This is true even at Ladybower.
b) The gradients of the lines connecting Friday and Saturday's points look to be unchanged between the summer and winter data. Thus, there is no obvious effect of seasonal variation on the weekend effect.

Ozone Plots

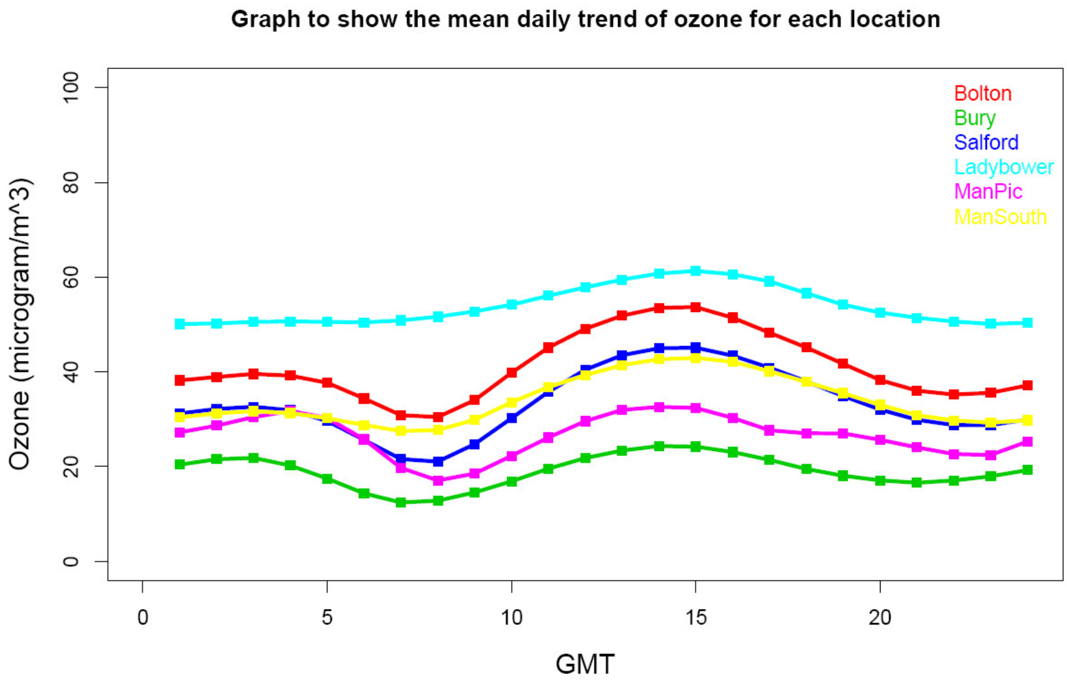
The plots created by the scripts adapted to show ozone data results can be seen in Graphs 6-10.

As with the NOx plots, the first two graphs (Graphs 6 and 7), together with Table 1, give the basic information about the variations in ozone due to location, weekly trends and daily cycles.

1) Conversely to NO_x, the highest ozone concentrations occur at Ladybower, with the lowest concentrations at Bury Roadside. Whilst NO_x concentrations at Ladybower show no variation in the daily or weekly cycle, this is not true for ozone concentrations.
2) Concentrations of ozone are generally higher at the weekend than during the week. This variation is most dramatic at Bury, but applies to all locations.
3) There is a variation in hourly readings throughout the day at all locations. The form of this daily cycle, however, differs at Ladybower to the other locations. The hourly values at Ladybower are all fairly constant, apart from an increase in magnitude during the afternoon. The daily cycles at the other locations have this peak in the afternoon, but a dip in concentrations is also evident at around 8/9am. This dip coincides with the peak of NO_x concentrations occurring each workday morning at the roadside, urban and suburban locations.



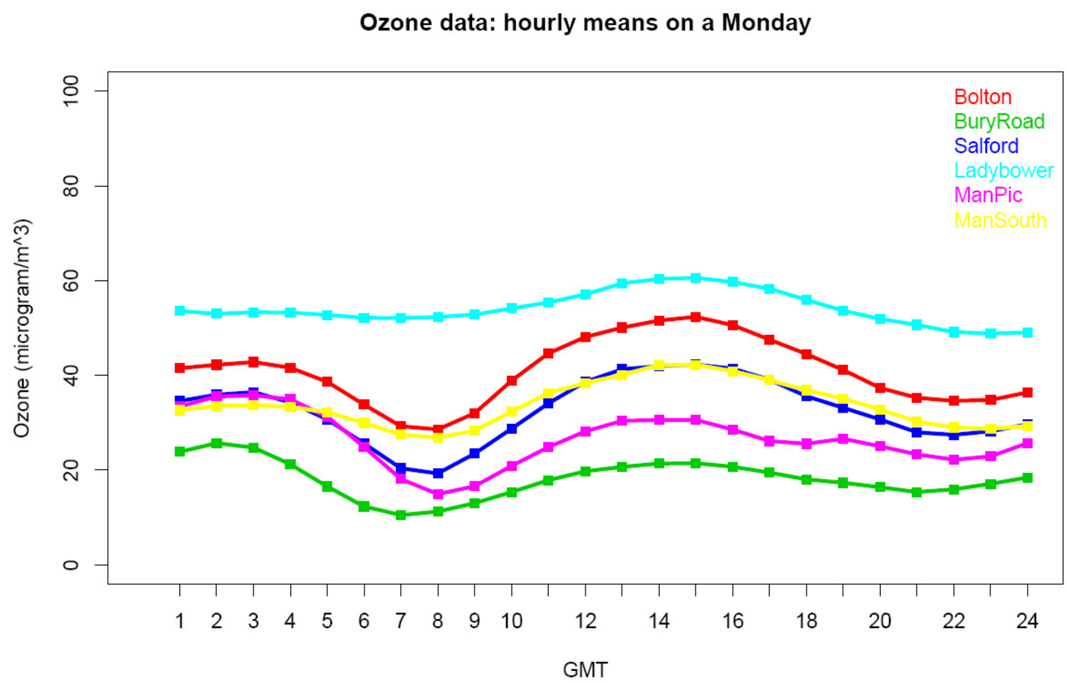
Graph 6 – a graph to illustrate how hourly measurements of ozone vary with the day of the week at each location



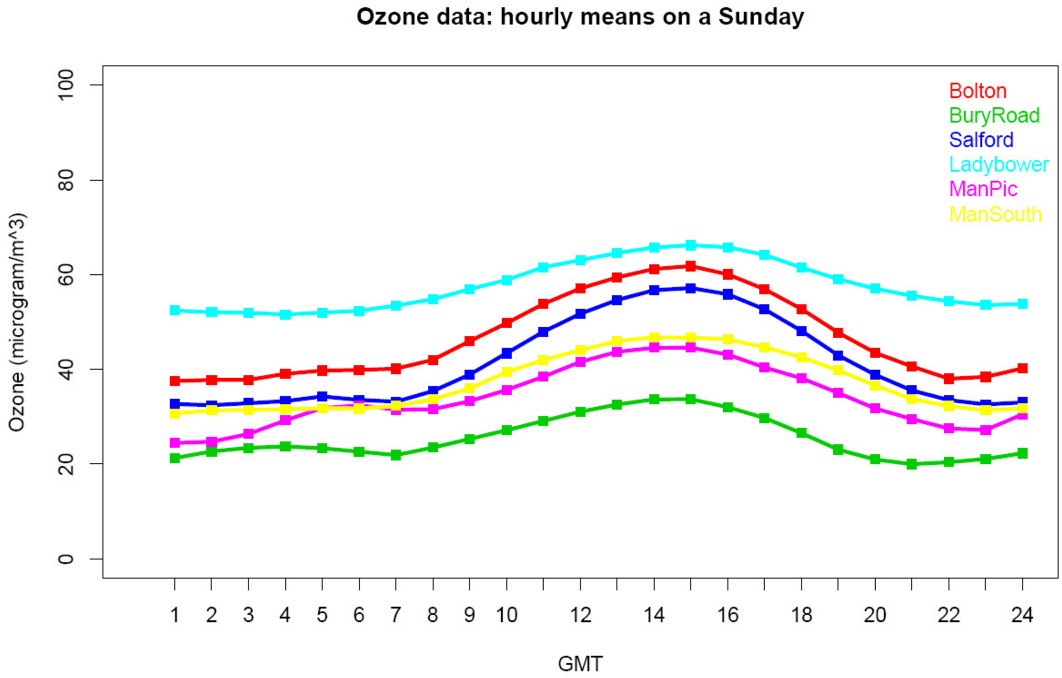
Graph 7 **– a graph to illustrate how hourly measurements of ozone vary with the time of day at each location**

The data was again separated into daily averages, and an average daily cycle at leach location for each day was plotted. Graphs 7 and 8 show the average daily cycles of ozone concentrations on a Monday and a Sunday respectively.

The plots showing the daily cycles of ozone on the remaining days can be found in Appendix C.



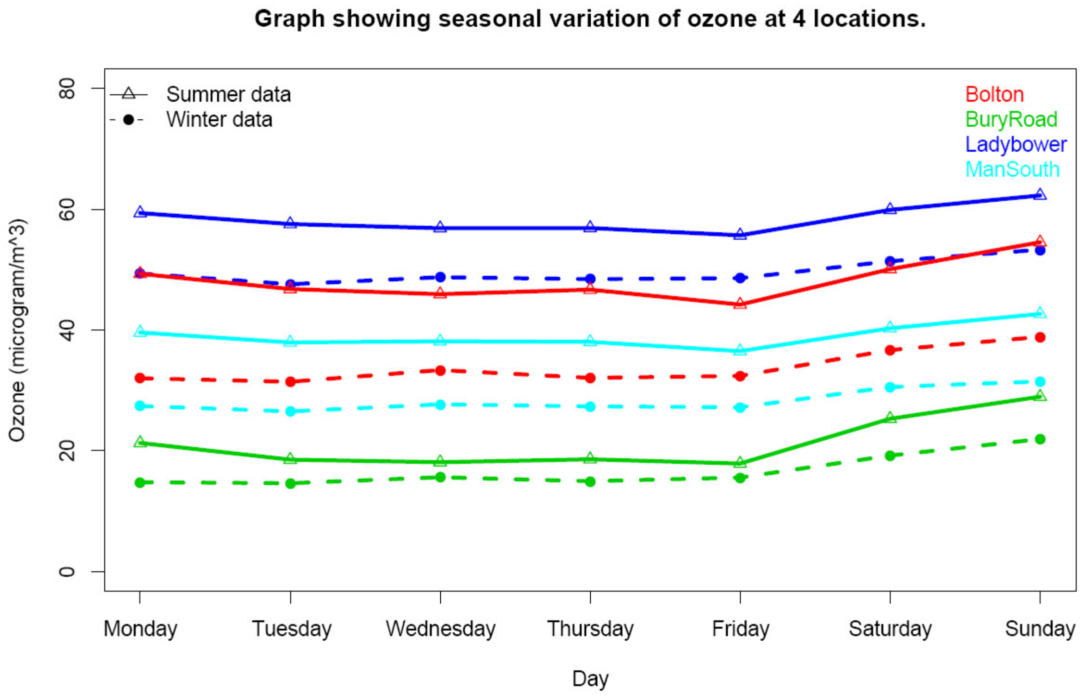
Graph 8 - a graph to show the daily cycle of ozone at each location on a Monday



Graph 9 - a graph to show the daily cycle of ozone at each location on a Sunday

Once again, the example of a daily cycle on a working day (in this case, on an average Monday) differs greatly from the daily cycle at the weekend. The cycles at Ladybower remain unchanged, but this cannot be said for the other locations. The graph showing Monday's daily cycle is practically identical to the graph showing the average of all day in the week. The dip in concentrations occurring in the morning on Monday's plot, however, does not exist on the Sunday. On this day, the daily cycles at all locations match that of Ladybower, with concentrations increasing throughout the day, reaching a peak in the late afternoon, before declining again at night time.

Graph 10 is the final ozone variation plot and shows the seasonal variation of ozone concentrations at the same 4 locations as were chosen to show seasonal variations in NO_x concentrations.

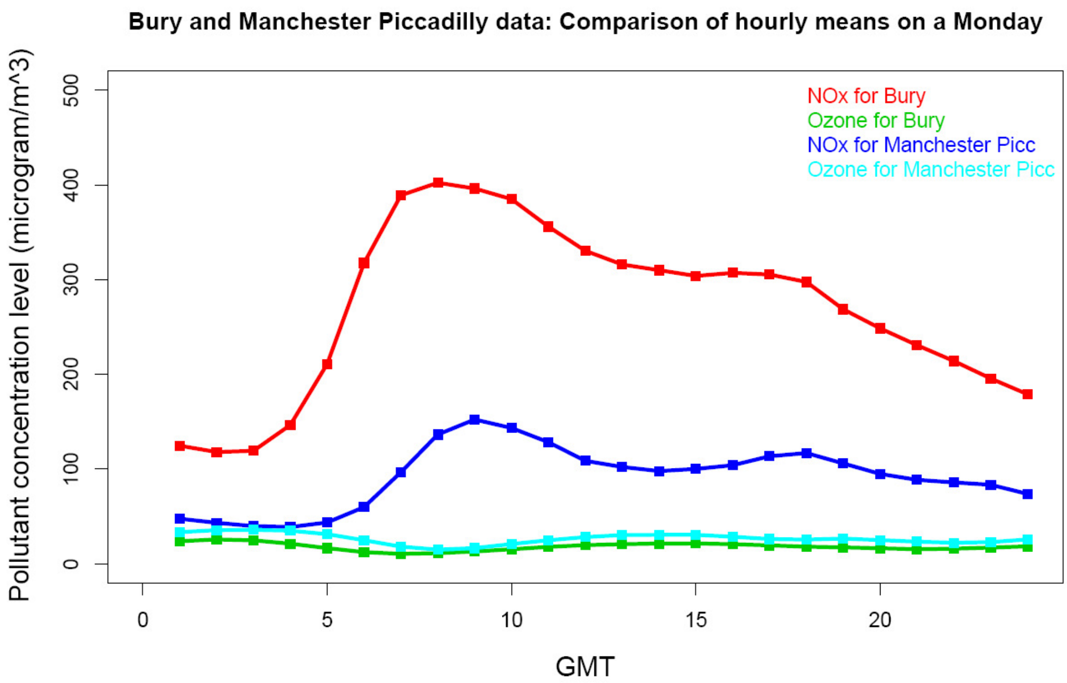


Graph 10 – a graph showing the seasonal variation of ozone at four of the six locations

This graph clearly shows that ozone levels are higher in the summer months. There is also a difference in the importance of the weekend effect - the gradients of the lines connecting Friday and Saturday's points look to be steeper in the summer than in the winter. Thus, with respect to ozone, seasonal variation affects not only the levels of concentrations, but also the extent to which the weekend effect is important.

Direct Comparison Plots

A script was written to create plots showing how concentrations of ozone compare to concentrations of NO_x. As the daily and weekly variations of concentrations were most evident at Bury and Manchester Piccadilly, these two locations were chosen to show this direct comparison. The comparison of hourly means on a Monday can be found in Graph 11. The plots showing comparisons on the remaining days of the week are in Appendix D.



Graph 11 – a graph showing a direct comparison of ozone and NOx measurements on a Monday and Bury and Manchester Piccadilly

Graph 11 shows that as NO_x concentrations rise, ozone levels fall. The rate of change of concentrations is a lot higher in NO_x, however. That is, a large increase in NO_x levels corresponds to a very small decrease in ozone levels.

Discussion

4.1 – Variation of NO_x concentrations due to location

Location clearly has a big impact on NO_x concentrations. By far the highest concentrations exist by the roadside at Bury, with the lowest coming from the rural location of Ladybower, as can be seen in Graph 1. This is hardly surprising given that one of the main sources of nitrogen oxides is from car exhausts.
As expected, as the location environment changes from city centre to suburban to rural NO_x concentrations decrease. The location does not only have an impact on the general magnitude of NO_x concentrations, but also on the daily trend of the data. The hourly readings vary a huge amount by the roadside, and there is also a significant variation at the other urban and suburban locations. This daily cycle looks to be non-existent at Ladybower.

4.2 – Daily trend of NO_x concentration data

As mentioned earlier, the daily variation in hourly data is most greatly pronounced at Bury. If further proof was needed that vehicles were to blame for a large proportion of NO_x emissions here it is – the daily cycle matches almost perfectly the common usage of the car.

Consider the daily cycle of a typical work day, for example a Monday (as shown in Graph 3). Despite the fact that one of the main chemical reactions causing the destruction of nitrogen oxides is favoured during daylight hours (when there is more OH due to photolysis), NO_x concentrations are highest during the working day when vehicles are most in use. There is a large surge in concentrations at around 8am, during the peak of the morning rush hour.

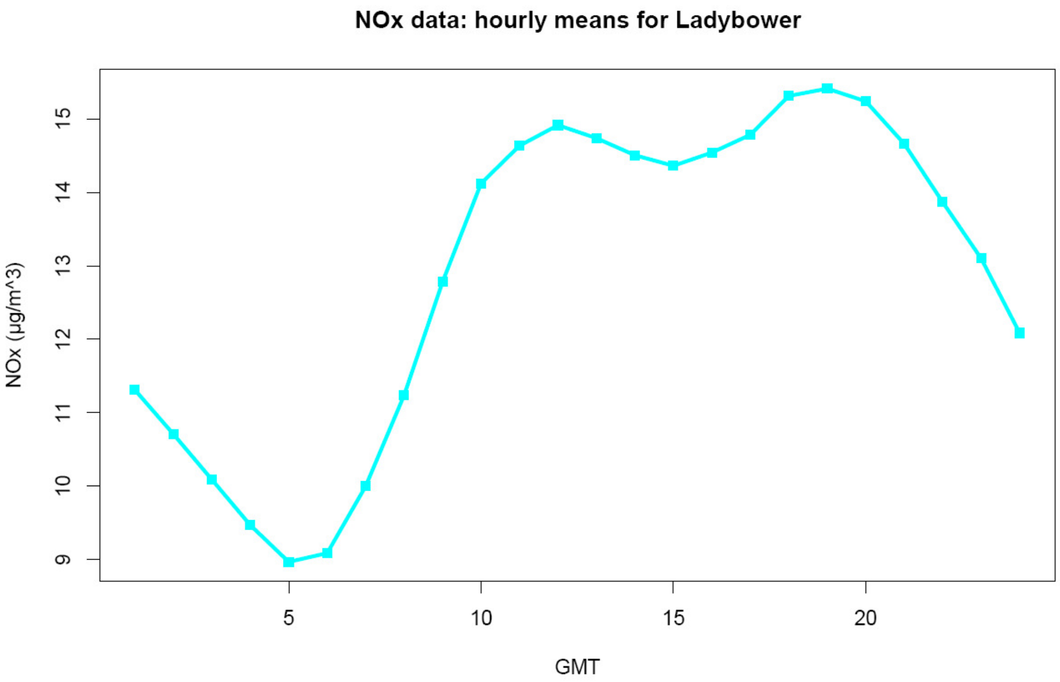
After this peak, NOx levels start to decrease steadily, with another increase in concentrations at around the time of the afternoon rush hour. This increase is a lot more subtle and is spread out over a longer period of time. There are a few reasons why this peak is a lot less dramatic that of the morning rush hour, where at Bury concentration levels rise by almost four times.

The biggest factor is probably the nature of the boundary layer, and how its depth varies throughout the day. During the morning rush hour, the depth of the mixed layer still pretty small, meaning that pollutants being emitted into the atmosphere will be trapped at a lower level. By mid-afternoon, the mixed layer will have reached the full height of the boundary layer. Therefore, assuming that the boundary layer itself is not too shallow, the pollutants will have more room to dissipate into, and so concentrations will be lower.

It is also worth noting that in the afternoon the rush hour itself is spread out over a longer period of time. For instance, whilst both workers and school children tend to have to reach their respective destinations for 9am, schools tend to finish considerably earlier than most jobs. Thus, the school run will occur earlier in the late afternoon whilst the evening commute for the workers takes place in the early evening.

Another possible factor relates again to the chemical reactions involving OH. As stated earlier, this is one of the main sinks of nitrogen oxides. As OH is formed through photolysis, and so its build up is directly related to the amount of sunlight present. Therefore, the highest concentrations of OH in the atmosphere are likely to be highest in the afternoon, thus causing the levels of NO_x to be considerably lower than they otherwise would be. This is likely to be more of a factor on a seasonal rather than a daily scale.

At Ladybower the daily variation of NO_x concentrations looks practically non-existent. There is the possibility that this is due to the scale of the y-axis on the plot. As the concentrations at Ladybower are so small anyway, any variation may well not show up. A graph showing solely Ladybower data will determine whether or not this is the case.



Graph 12 – a graph presenting the daily cycle of nitrogen oxides at Ladybower on a more suitable scale

Graph 12 does indeed show that the lack of a daily cycle was due to the scale of the graph. The scale on this graph is so small, however, and difference between the highest and lowest concentrations is so little, that it is difficult to say whether this variation is trivial or not. Of course, the diurnal variation of the depth of the boundary layer is expected to have an effect on the daily variation of pollutant concentration levels. The daily cycle at Ladybower does not seem to match this diurnal variation, however. We would expect the highest concentrations to exist at night time, when the boundary layer has the least mixing. The dataset used shows the exact opposite, with the highest levels occurring in the daytime.

It can be deduced from this that, although the variation in the boundary layer depth is indeed a factor, when there are a lot fewer sources of NO_x in the area anyway, the diurnal variation of the ABL does not have a direct effect on concentration levels.

In conclusion, with respect to the daily cycle of NO_x concentrations, the diurnal variation of the ABL and the rate of emissions are of equal importance.

4.3 – Variation of NO_x concentration data through the week

Throughout the working week, the average hourly readings and daily trends remain fairly constant. When examining the data from the weekend, however, we can see substantial differences. From Graph 2 we can see that the average magnitude drops sharply on the Saturday and is lower still on the Sunday. Likewise, from the individual daily graphs for the weekend data, shown in Graphs 3 and 4, it is clear that the daily cycle so prominent during the working week is completely different on the Sunday.

Once again, the differences between a working day and the weekend can be explained by the pattern of vehicle usage. At the location which is barely affected by emissions from exhausts (Ladybower) there is no real variation in hourly readings to speak of, either a variation throughout the day or throughout the week.

4.4 – Variations in ozone data and correlation between NO_x and ozone concentrations

Ozone concentrations also vary with location, with the lowest concentrations occurring at the places with the highest NO_x concentrations and vice versa.
There is a daily variation in ozone levels at all locations, although its form differs depending on location and the day of the week. The highest concentrations of ozone in all cases occur in the late afternoon.
There are two reasons for this. Firstly, reaction 1 of the Nitrogen Cycle is much more likely to take place in the afternoon and at midday, when the uv-rays from the sun are at their strongest.
The second factor stems from the NO_2 to NO ratio. As mentioned earlier, this ratio needs to be relatively high (approximately 10:1) if there is to be a noticeable increase in ozone levels. At night time, the main component of NO_x is NO, and so ozone levels remain low. At sunrise, however, the free radicals needed to convert this NO to NO_2 through the VOC-cycle are formed through photolysis of various VOC compounds. Over a few hours of this cycle taking place, NO_2 gradually becomes the main component of NO_x, thus allowing ozone build up to take place. Eventually, NO_2 levels decrease, partly through the sink reaction involving OH, and partly through dilution due to the boundary layer expanding. As night time draws near, uv-radiation also decreases and reaction 1 of the Nitrogen Cycle takes place a lot less frequently. Ozone can no longer be formed, and much of the existing ozone is destroyed in reactions with NO. Thus, ozone levels diminish in the evening, leading into the night.
The above reasons explain the daily cycles at Ladybower, as well as all the other locations at the weekend. During the working week, however, the daily cycle of ozone concentration levels at the urban/suburban/roadside locations

has an added feature – a dip in concentration levels in the morning. This dramatic decrease in concentrations coincides with the peak of NO_x concentrations occurring during the morning rush hour. The time scales of all the reactions involved provide a reason for this. The sudden increase in car exhaust fumes creates a huge surge in NO, NO_2 and VOC concentrations. The reaction with NO that destroys ozone is quite fast, whereas the reactions which create the single oxygen atom and increase the NO_2 to NO ratio are comparatively slow. The sudden increase in NO in particular means that ozone is destroyed a lot faster than it can be created, meaning that concentrations are even lower at this time of day than during the night when no ozone can be created due to the lack of uv-radiation. Once this peak in NO_x concentrations subsides, ozone formation resumes as normal.
The lack of a morning peak in NO_x concentrations at the weekend due to the reduced use of cars means that this dip in ozone concentrations does not occur at the weekend. Thus, ozone concentration levels are generally higher at the weekend than during the working week.

Ozone concentration levels do indeed appear to be very dependent on NO_x concentration levels. This is further emphasised in Graph 11, where the concentrations of both pollutants are plotted on the same axis. From this we can conclude that the area is VOC-limited, that is a reduction in ozone levels is much more likely through the reduction of VOC emissions as opposed to NO_x emissions.

4.5 – Variation throughout the seasons

NO_x concentrations are highest in the winter months. This could be related to the fact that emissions will be so much higher in the colder, winter months - people are more likely to use their cars than to walk, and power stations will be required to create more electricity to cope with the extra demand due to people using their heaters more.

The main reason, however, is probably due to the fact that the lifetime of NO_x is longer in the winter, when the presence of its main sink, OH is severely diminished.

Ozone concentrations are understandably higher during the summer months, when uv-rays coming from the sun are at their most abundant and the strongest. The fact that NO_x concentrations are lower in the summer months will also cause a rise in ozone concentration levels.

The weekend effect in ozone is also stronger in the summer, when the increase in ozone concentrations at the weekend is bigger. As the lifetime of NO_x is shorter in the summer, this means that nitrogen oxides emitted on the Friday are less likely to survive into the weekend, which explains this further increase in ozone build-up.

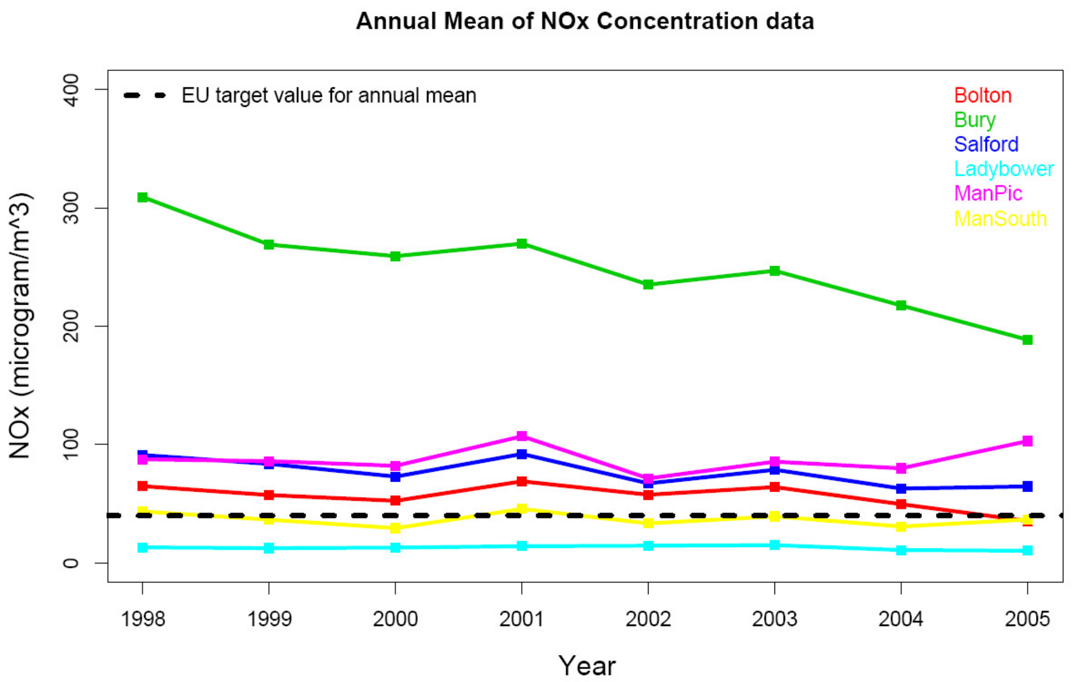
5. Exceedance events in NOx

Results

For the first part of this section of the project, scripts were written to create plots to show:

a) the annual mean of NOx concentrations for each location for the 8 year period the dataset covers, and how this compares to the EU guidelines for NO_2 (Graph13).
b) the number of times the hourly measurement exceeds 200µg/m^3 in a calendar year, and, again, how this compares to the EU guideline that concentrations of NO_2 should not exceed this hourly measurement more than 18 times in a calendar year. (Graph 14).

It should be clarified at this point that the EU guidelines refer solely to nitrogen dioxide concentrations, whilst the data sourced from the UK National Air Quality Archive consists of both nitrogen oxide and nitrogen dioxide, i.e. NO_x. The lifetime of NO, however, is quite short (about 10 minutes), and so it can be assumed that the majority of the NO_x is in fact nitrogen dioxide. For the purpose of this experiment, therefore, NO_2 and NO_x will be considered to take the same value.

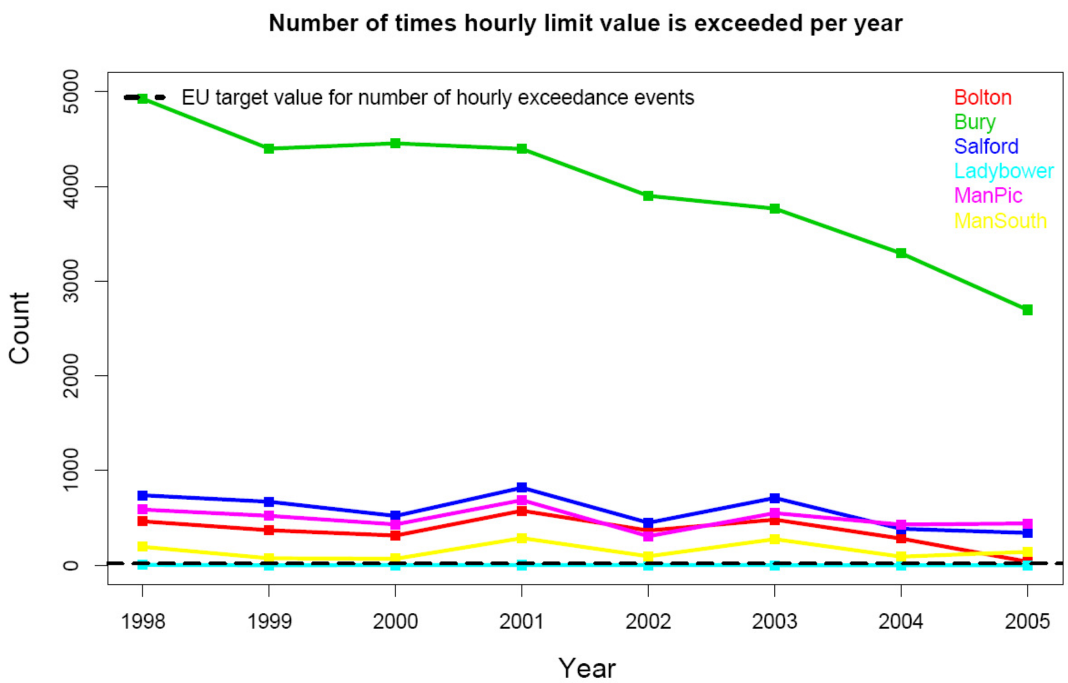


Graph 13 – a graph showing the nitrogen oxides annual means at each location

EU guidelines have set a target that annual means of NO_2 should not exceed 40µg/m^3 in any given location. The overall trend observed in Graph 13 shows that EU guidelines are being grossly violated. All the locations studied in Greater Manchester have failed to meet the EU target in the last 8 years, and only the suburban location of Manchester South has managed to meet the target at all in this period. The monitoring stations in Manchester Piccadilly and Salford regularly hit annual means of about double that of the EU

guidelines, whilst the worst offender, Bury, has annual means of between 4 to 6 times that of the EU guidelines.
On a more positive note, annual means have been generally decreasing over the 8 year period. The graph shows that, in Bury, the annual mean of NO_x concentration has decreased by over 100µg/m^3 between 1998 and 2005.
There is no problem at Ladybower, where the annual means are consistently below the target level.

The second EU guideline relates to the number of times the hourly measurements of NO_2 concentrations exceed 200µg/m^3 in a calendar year. There was initially some confusion whether this meant the total number of hours which exceeded this amount in a year, or whether it referred to 'exceedance episodes', for example the number of days in a year which had hourly measurements that exceeded the given limit. A report on Nitrogen Dioxide in the UK found on the DEFRA website by the Air Quality Expert Group **[3]**, helped to clarify this issue: a list in the appendix of this article states an example of a site exceeding this limit more than 800 times in a year. Therefore, the guideline was taken to refer to the total number of hours in a year where the hourly limit of 200µg/m^3 was surpassed.



Graph 14 – a graph illustrating the number of times at each location the EU recommendation for how often an hourly limit should be surpassed

Graph 14 shows the number of hours in a calendar year in which the recommended limit was exceeded. Once again, with the exception of Ladybower, this guideline is repeatedly broken. Bury is once more the worst offender, with almost 5000 hours in 1998 exceeding the hourly limit. This graph is consistent with Graph 13, and shows the situation as improving in recent years.

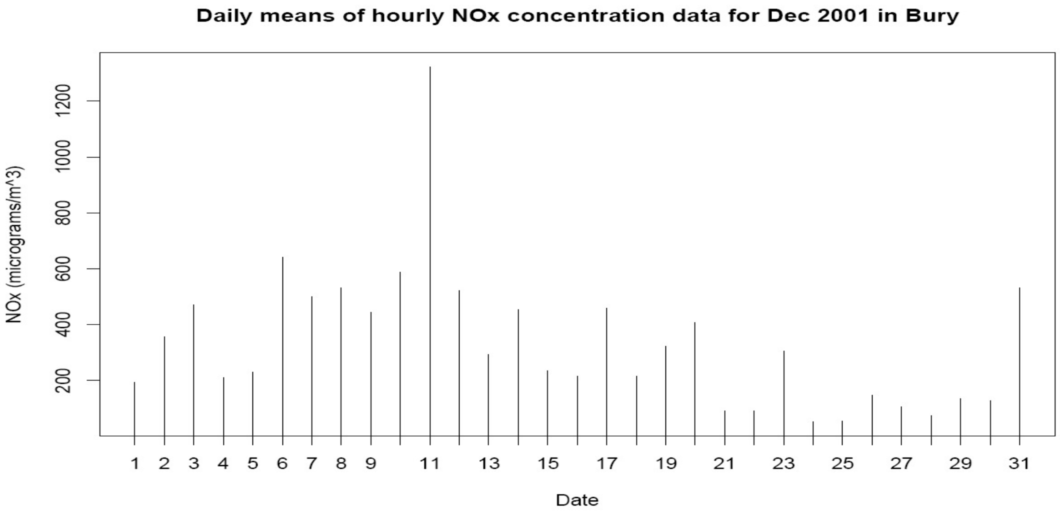
A short script was then written that picked out the top 50 values of NO_x concentrations for each location. These were examined, and it was noted that dates which came up time and time again were those of the 11^{th} and 12^{th} of December 2001. It was therefore decided to examine the data from this month and then investigate the meteorological environment of the time.

A script was written to plot several graphs showing how NO_x concentrations varied throughout December 2001 at Bury, Bolton, Manchester South and Ladybower. These four locations were so chosen because they represent four different types of environments – roadside, urban, suburban and rural. They are also the best sites to choose with respect to where the monitoring stations are themselves situated – these four sites are least affected by tall buildings and vegetation. The quality of data should thus be superior here.

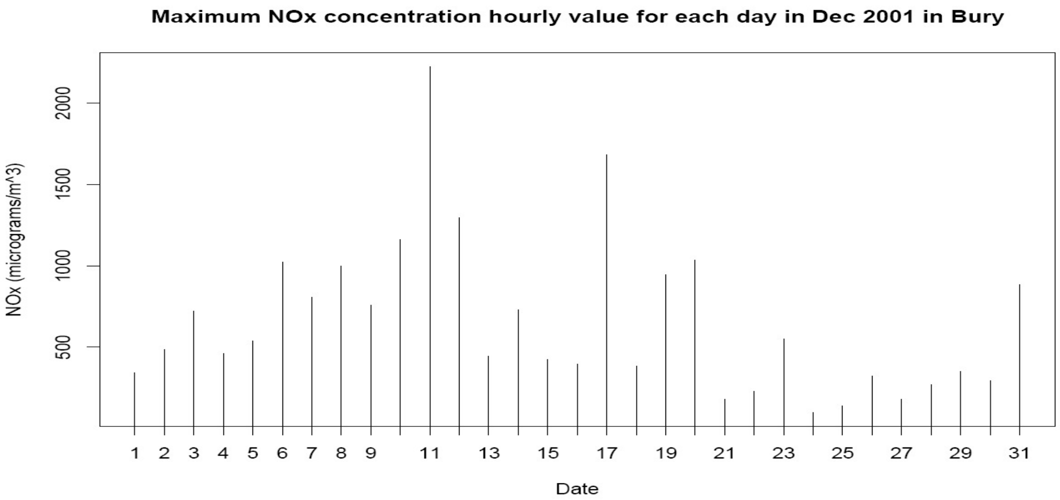
For each of the four locations two histograms were initially plotted: the first shows the mean value of hourly measurements for each day and the second shows the maximum hourly measurement on each day. The plots generated for Bury can be found in Graphs 15-16, Bolton's graphs are shown in Graphs 18-19, whilst the monthly trends at Manchester South and Ladybower can be found in Graphs 21-22 and 24-25 respectively.

The plots show a surge in concentration levels at all locations on the 11^{th} December 2001, with the exceptions of Ladybower and Manchester South. In the case of Ladybower, the values before the 11^{th} of the month are missing, and so the high values on that day cannot strictly speaking be referred to as a surge. The values on the 11^{th} are around six times those during the rest of the month, as well as the maximum value being over 25 times greater than the mean value of NO_x concentrations at Ladybower. It can therefore be assumed that the extreme exceedance event occurring at the other stations is also taking place at Ladybower. As this location is rural with practically no vehicle use in the near vicinity, it can also be deduced that the factors that are causing this sudden increase in concentration levels are most likely to be environmental as opposed to a practical factor such as a sudden massive increase in vehicles in the area.

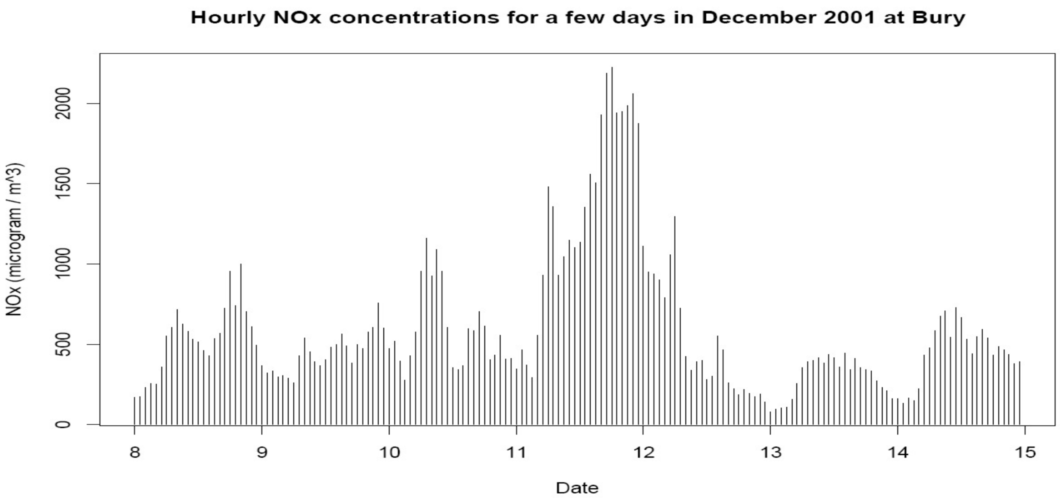
At Manchester South, the highest concentrations occur on the 12^{th} of the month as opposed to the 11^{th}. It is possible that this extreme event is taking place over the night between the 11^{th} and the 12^{th}, thus creating this anomaly. To investigate this notion, further graphs were plotted showing the individual hourly values for the days surrounding these two dates. These plots can be found in Graphs 17, 20, 23 and 26.



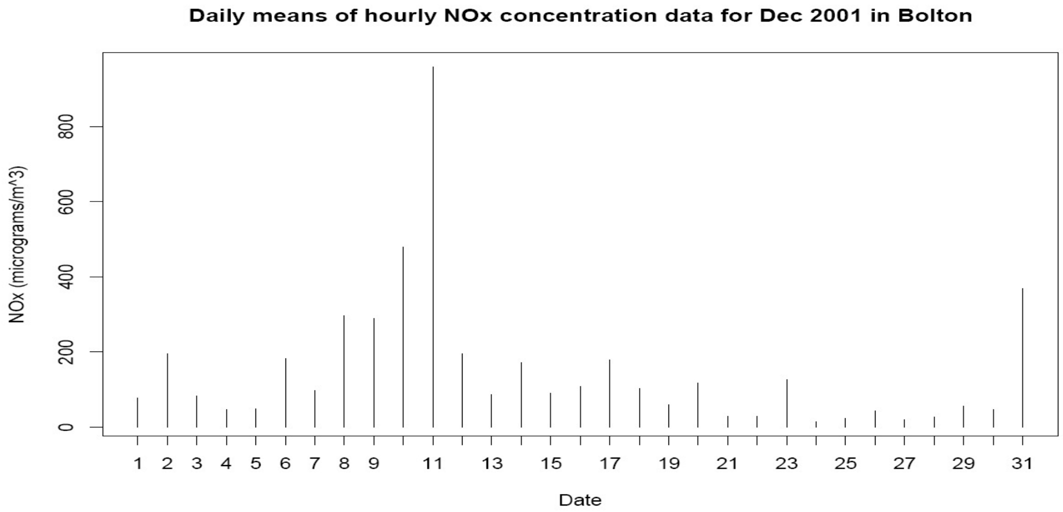
Graph 15



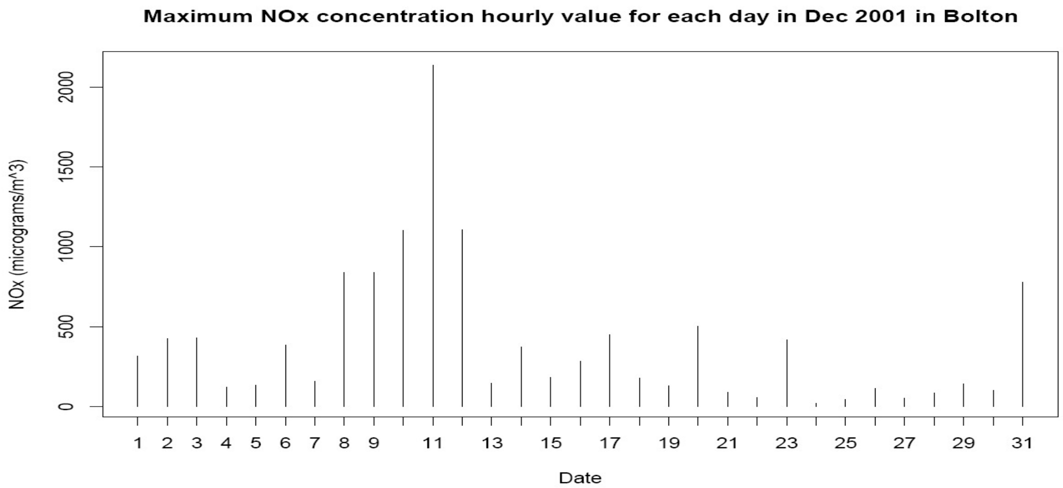
Graph 16



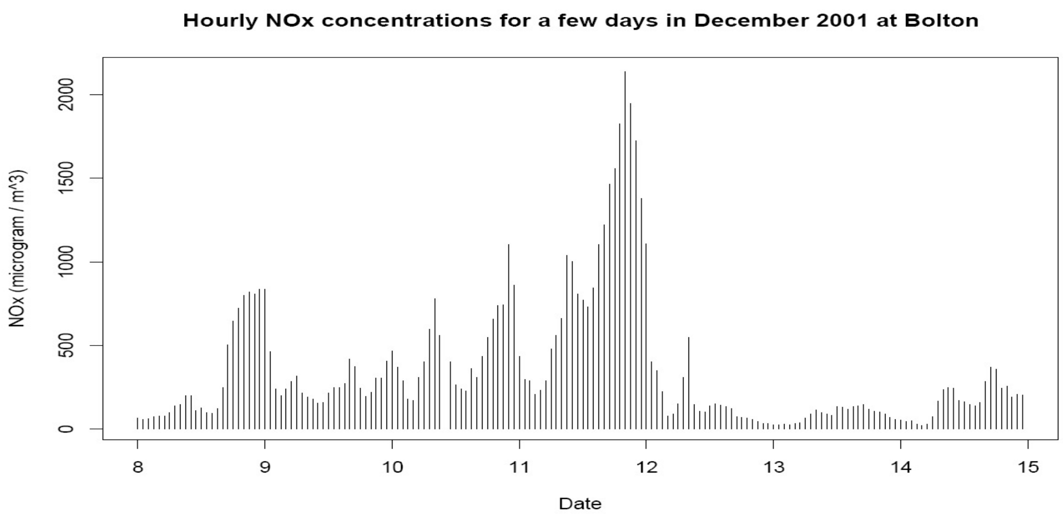
Graph 17



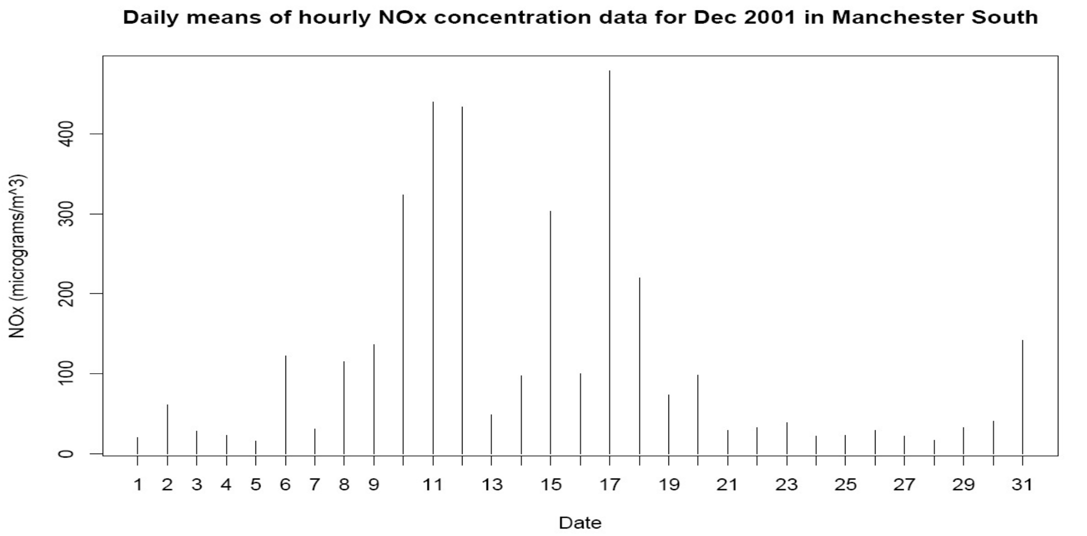
Graph 18



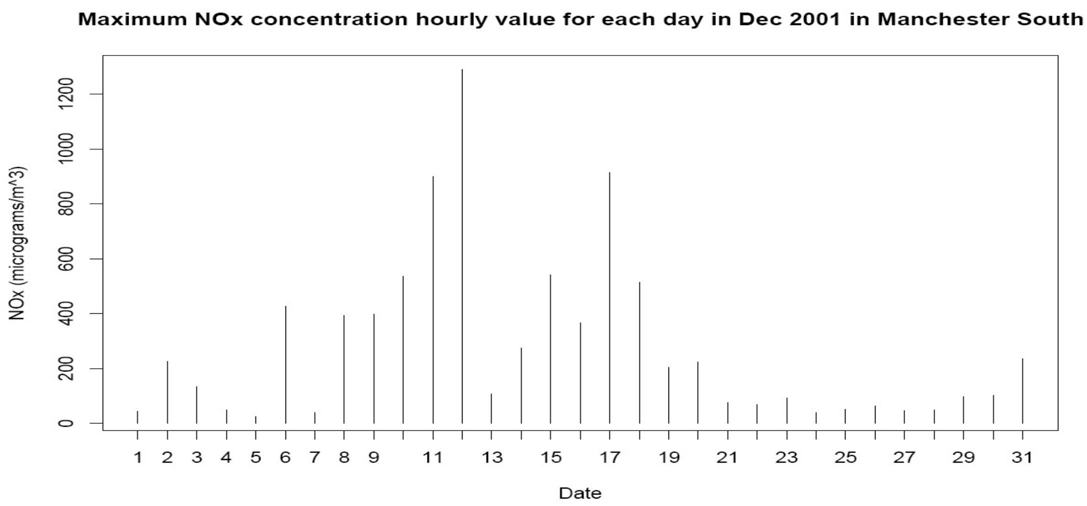
Graph 19



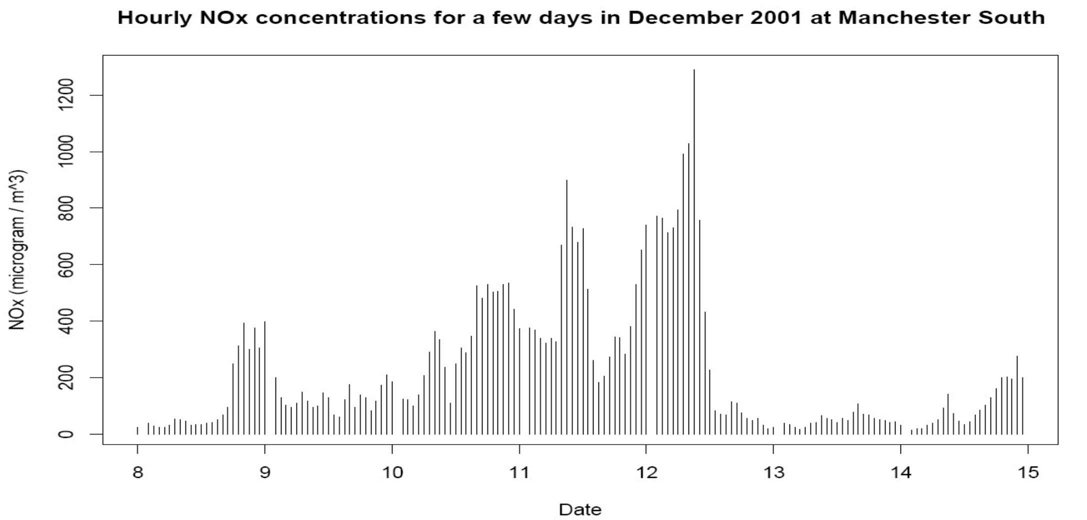
Graph 20



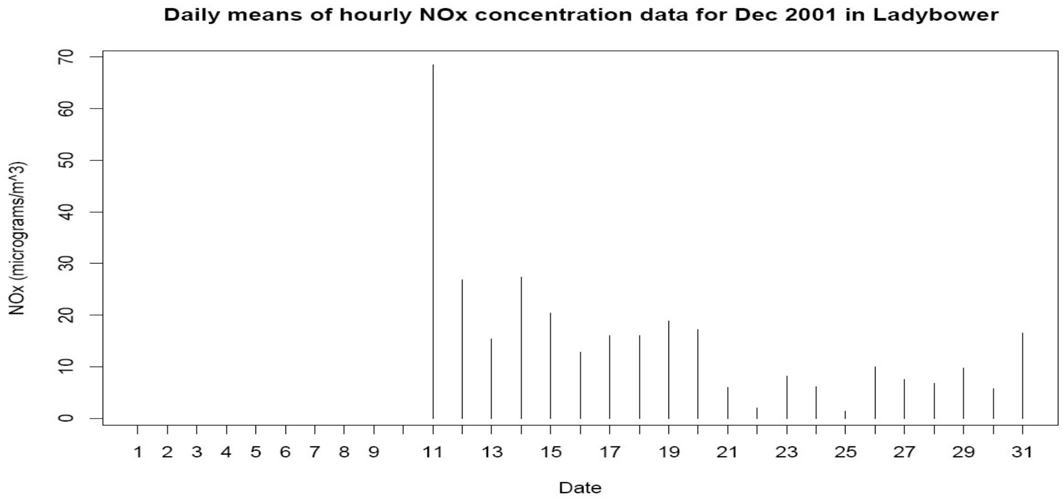
Graph 21



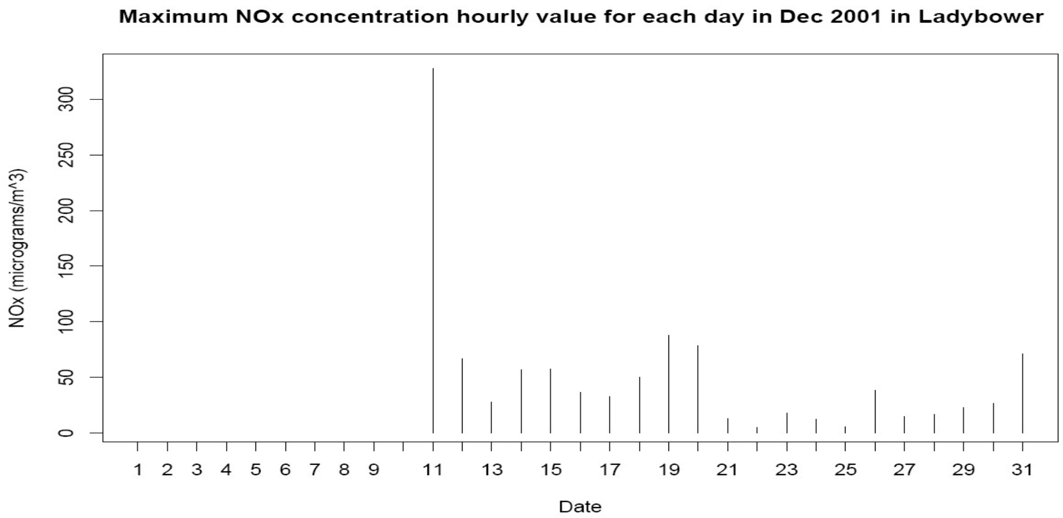
Graph 22



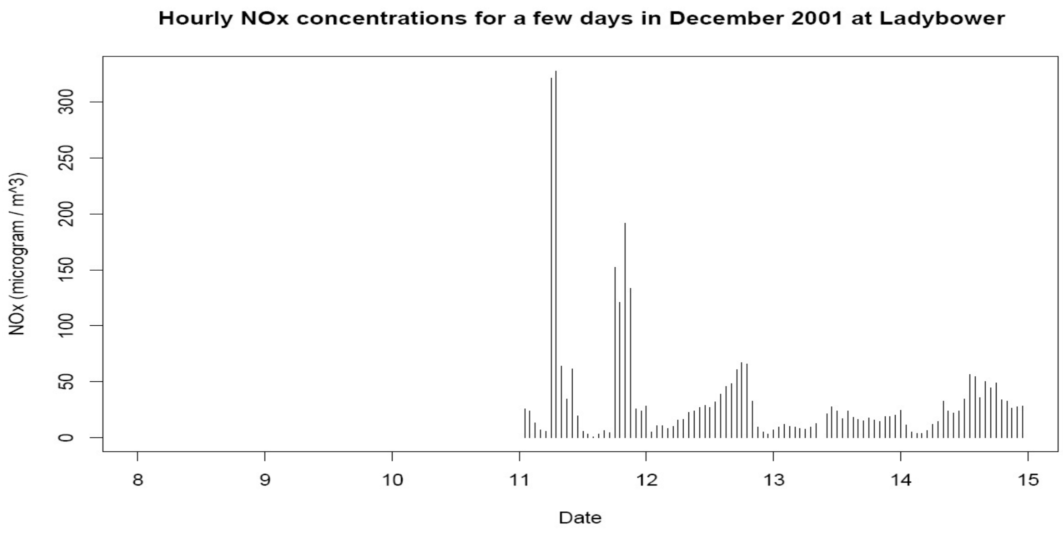
Graph 23



Graph 24



Graph 25



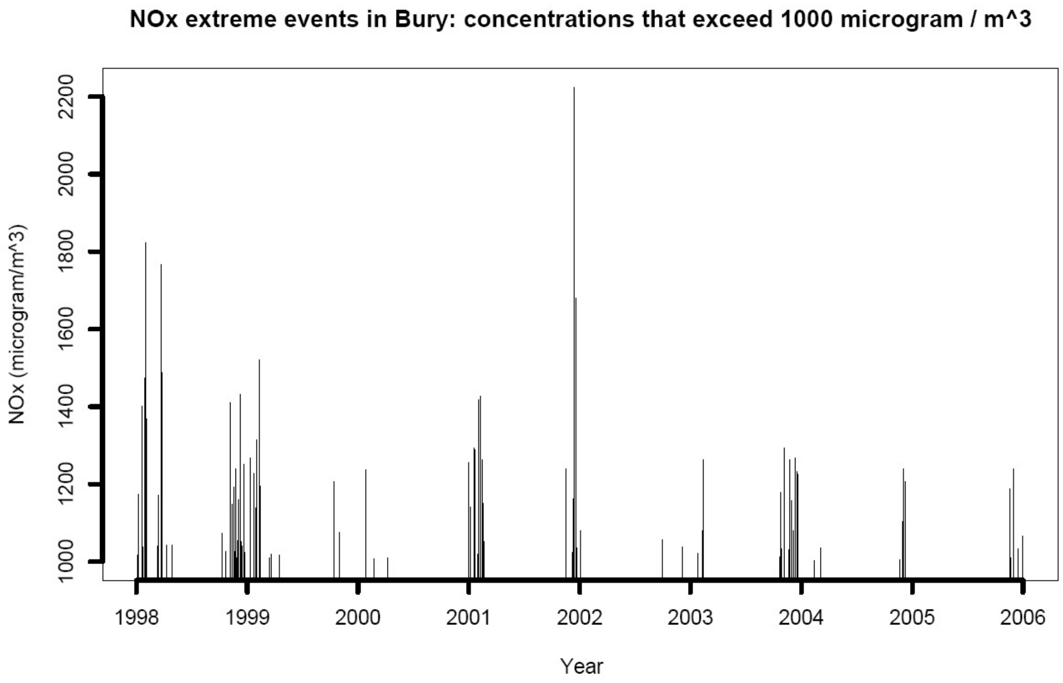
Graph 26

Discussion

5.1 – EU guidelines and how well they are adhered to

The only location where NO_x concentrations are consistently below the recommended EU limits is at Ladybower. Given the rural setting of this site, this is hardly surprising.

The location with the worst record is Bury, although graphs 13 and 14 show that conditions at Bury are improving.



Graph 27

Graph 27 shows the hourly measurements of NO_x at Bury that exceed 1000µg/m^3. It is clear that even these extremely high concentrations occur on a regular basis. The improvement in conditions is apparent in this plot, as the extreme events in the latter years are not only smaller in magnitude, but also more spaced out. This would imply that the extreme events are becoming less frequent over time.
The seasonal variation in NO_x is also quite evident here, as these extreme events only occur during the winter.

Thus we can conclude that conditions at Bury are improving but are still far from being acceptable, with around 3000 hourly exceedance events in 2005. It is debatable whether one can really expect any better at a roadside location by such a busy motorway.

5.2 – An extreme exceedance event that occurred in December 2001

The graphs plotted of NO_x concentrations during the month of December 2001 show that there is indeed an extreme exceedance event that occurs mostly on the 11th December, although some of its effects are also seen on the 12th.
Of course, an increase in pollution levels can be due to an increase in emissions. However, an increase of this kind and magnitude is much more likely to be caused by environmental and meteorological factors, such as the depth of the boundary layer.
In order to confirm this, the atmospheric conditions of the period were investigated. Vertical profiles of the local area were looked at, as well as pressure charts of the United Kingdom.

Using the month of December 2001 to investigate the links between pollutant concentration levels and the concurrent nature of the boundary layer has the added bonus that the month consists of days with particularly low levels of pollution as well as the extreme event. These low events occur around the 24th and 25th of the month. However, the 25th of December is obviously Christmas Day, thus being a public holiday and so emissions of nitrogen oxides are likely to be reduced in the first place, due to fewer vehicles on the roads. The analysis of this low event will therefore concentrate solely on December 24th.

The depth of the boundary layer was determined using Skew-T profiles, retrieved from an archive on the University of Wyoming's website **[6]**. The nearest place for which these profiles are measured is at Nottingham, approximately sixty miles south-east of Manchester. When considering this on a large scale, however, this distance is negligible, and there is not expected to be much difference between the features of the boundary layer at the two places. Skew-T profiles are created four times a day in 6-hour intervals: at 00Z, 06Z, 12Z and 18Z.

Figure 3 shows a profile representing 18Z on December 11th 2001. The line on the left represents the dew point sounding and the line on the right is the temperature sounding. This analysis will focus mostly on the temperature sounding. When the temperature increases with height, this indicates a very stable layer.

As the profile in Figure 3 shows, the air temperature close to the surface does indeed increase with height and therefore there is very little mixing in the atmosphere at this level. Further Skew-T profiles taken from this day, as well as the 12th, can be found in Appendix E**.** The temperature soundings from this period show that the boundary layer is generally very stable and compressed, thus not allowing the air pollutants emitted or formed close to the surface to 'escape' to higher in the atmosphere. This is one of the causes of the especially high concentrations of nitrogen oxides over this period.

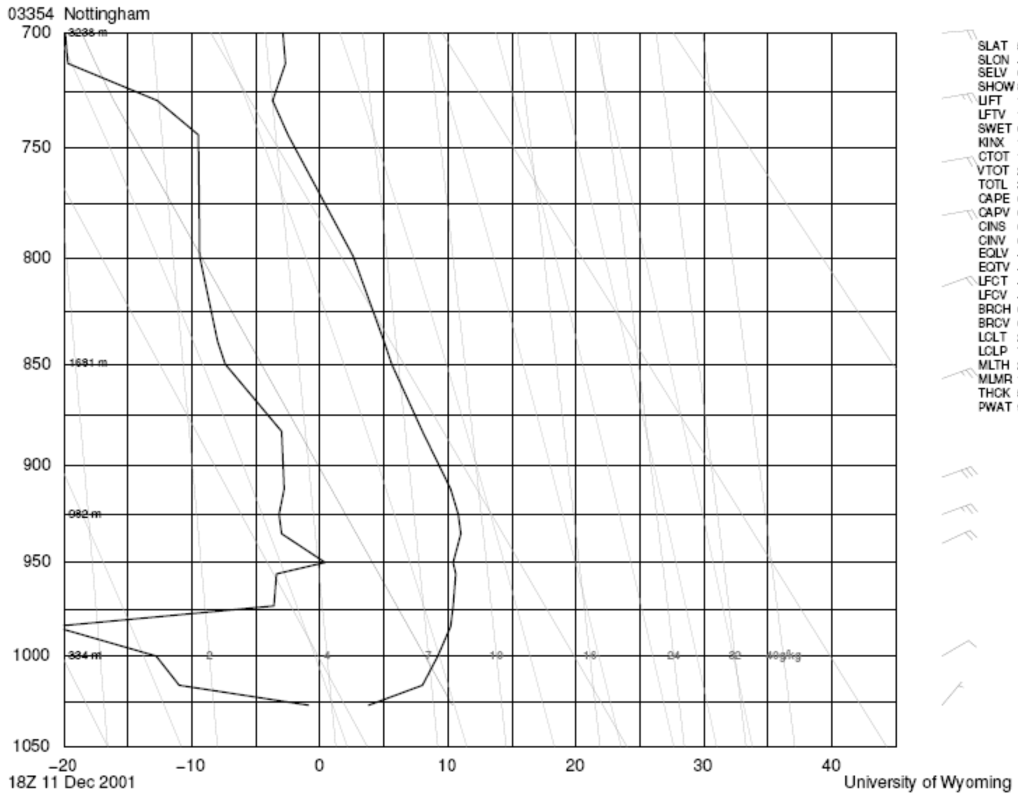


Figure 3 – a skew-T vertical profile at 18 Z on 11 Dec 2001, Nottingham. Ref:[6]

Figure 4 is a pressure map of the North-Eastern Atlantic and Western Europe for December 11th 2001, taken from a paper archive **[5]**. This pressure map clearly shows that on the day of the extreme exceedance in NOx event, there was a large area of high pressure sitting over the United Kingdom. The area of Greater Manchester sits towards the centre of this high, some way from the closest isobar.

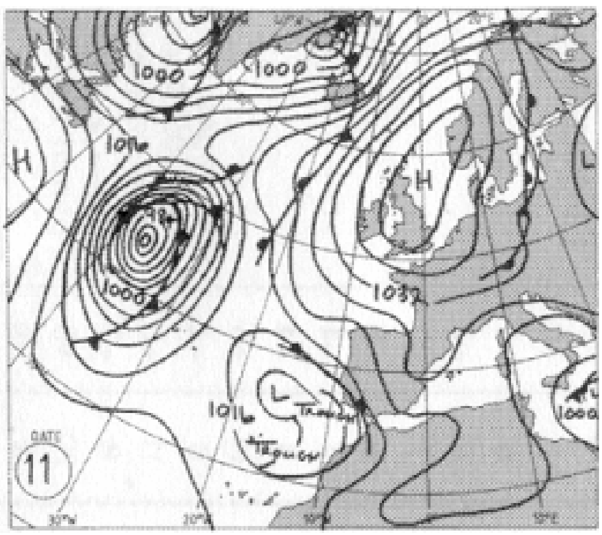
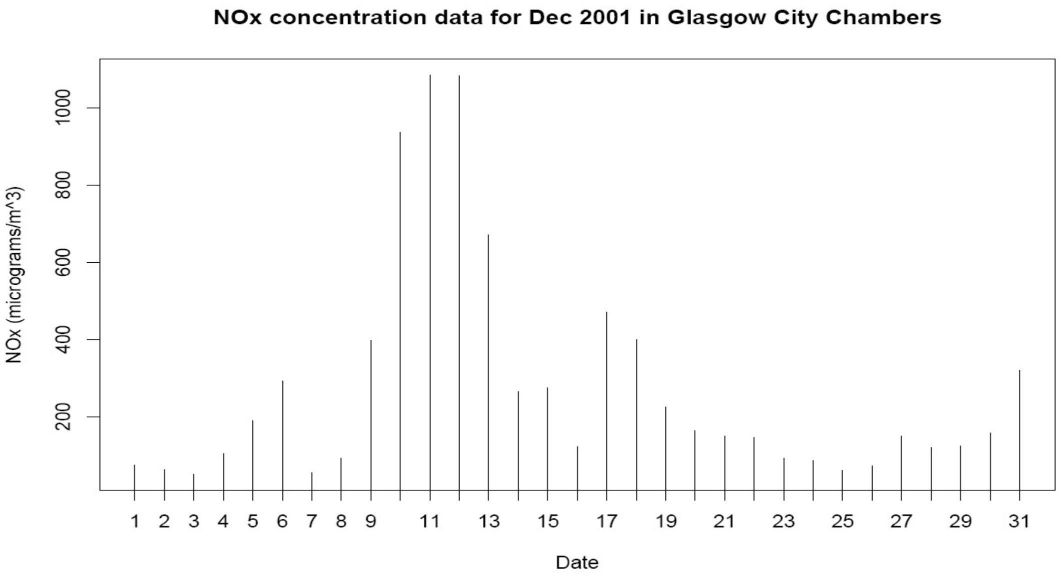


Figure 4 – A Pressure chart covering the UK on 11/12/2001. Ref:[5]

These features have two consequences. First of all, the high pressure sitting over the area will actually serve to 'squash' the boundary layer down by limiting the amount of upwelling in the air. Secondly, the lack of isobars close to the area means that the pressure gradient is very small, meaning that there will be little wind. Undoubtedly, this will also encourage high concentrations of NO_x to accumulate as there is little wind to disperse the pollutants.

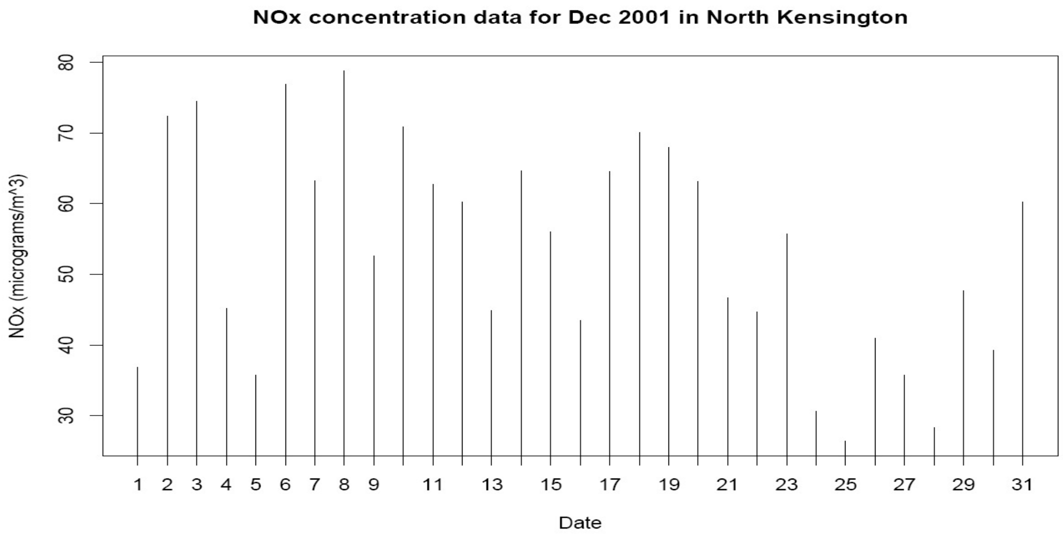
From this pressure map, high concentrations would be expected throughout the north and midland areas of England, as well as much of Scotland. An isobar crosses the south of England, however, so it is very possible that enough winds were generated to disperse much of the pollutants.

Further data was retrieved from the UK Air Quality Database that gave NO_x concentrations for a range of locations in Scotland and London in December 2001. Graphs 28 and 29 show one example from Scotland and one example from the London area. Other plots created for these locations can be found in Appendices F and G. Each value on the plots represents the mean of all the hourly measurements on that particular day.



Graph 28

The example plot from Scotland, Graph 28, shows the monthly trend at Glasgow City Chambers. As expected, there is a great surge in concentration levels around the 11th and 12th of the month, which then recedes again in the following days. All the plots created using data from locations in Scotland show the same kind of trend, as can be seen in Appendix F.



Graph 29

Graph 29, showing the monthly trend at North Kensington in London, is reasonably indicative of all the plots created using data from the London area (see Appendix G). There is no surge in concentrations around the 11th, in fact the values on and around this date are not even the maximum values over the month. A vertical profile for Herstmonceux, East Sussex (Figure 5) shows that the atmosphere at the surface here is not as stable as it is further north and the first capping inversion layer, although still quite low, implies a much deeper boundary layer than at Nottingham. The lack of high concentrations of NO_x in London is therefore due to an increased depth and instability to the boundary layer and light winds in the London area dispersing the pollutants, as indicated on the pressure chart.

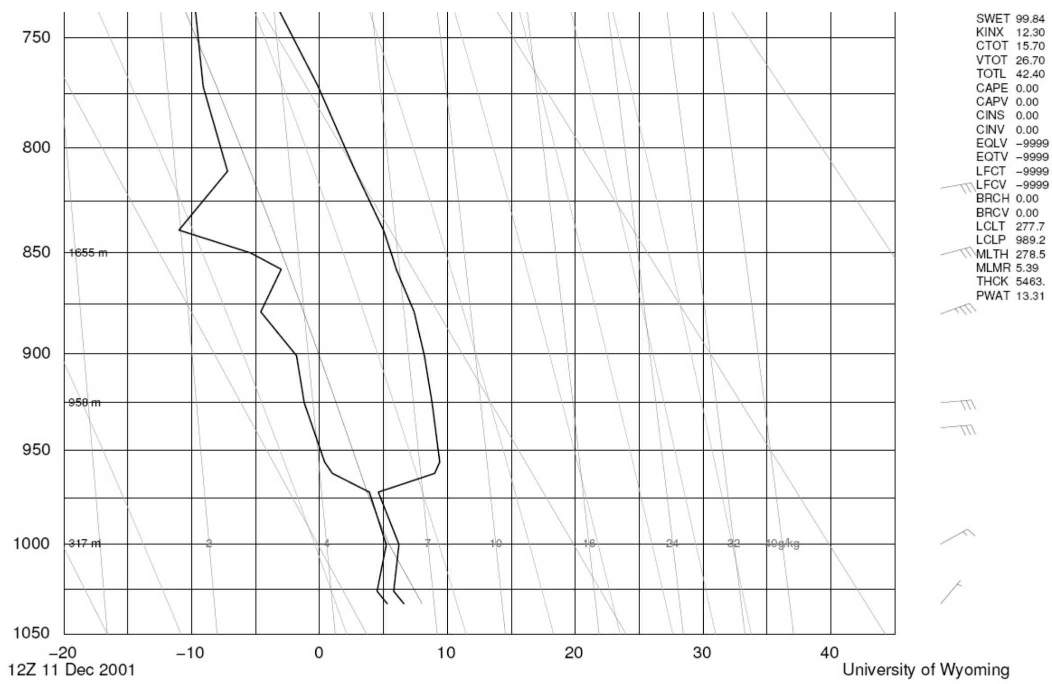


Figure 5 - a skew-T vertical profile at 12 Z on 11 Dec 2001, Herstmonceux, Sussex. Ref:[6]

This can all be compared to a day where the concentrations of NO_x are especially low. Figure 6 shows the Skew-T profile of Nottingham on the 24th December 2001, whilst Figure 7 shows the pressure chart of the same date.

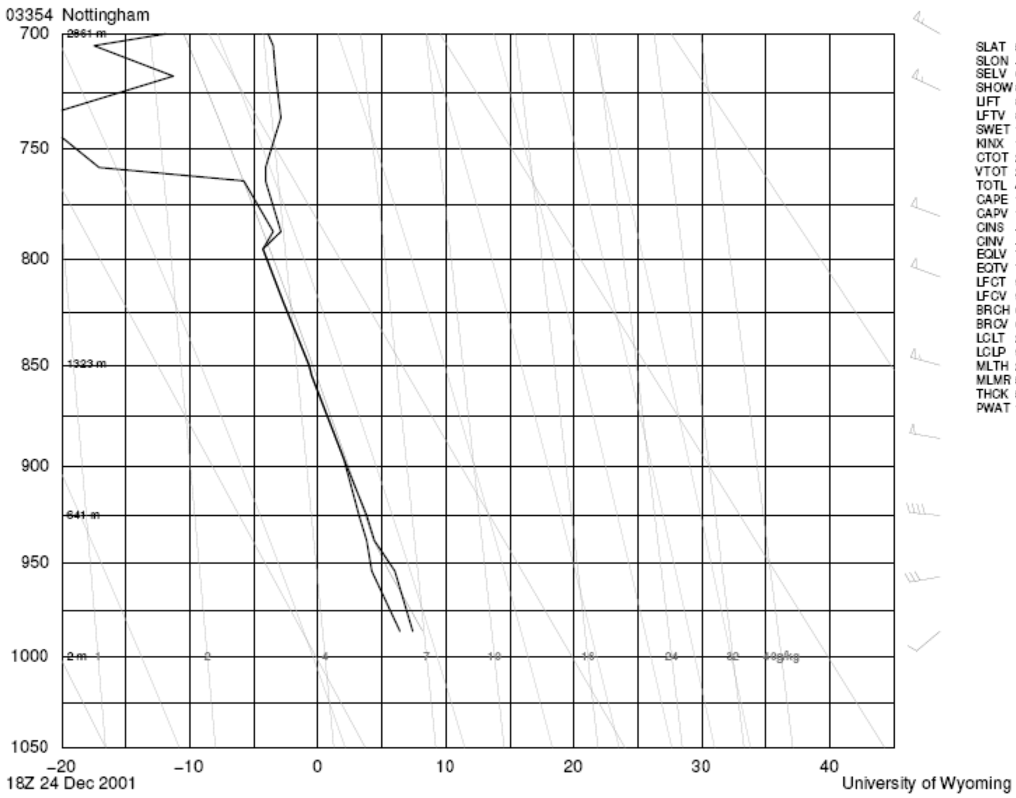


Figure 6 - a skew-T vertical profile at 18 Z on 24 Dec 2001, Nottingham. Ref:[6]

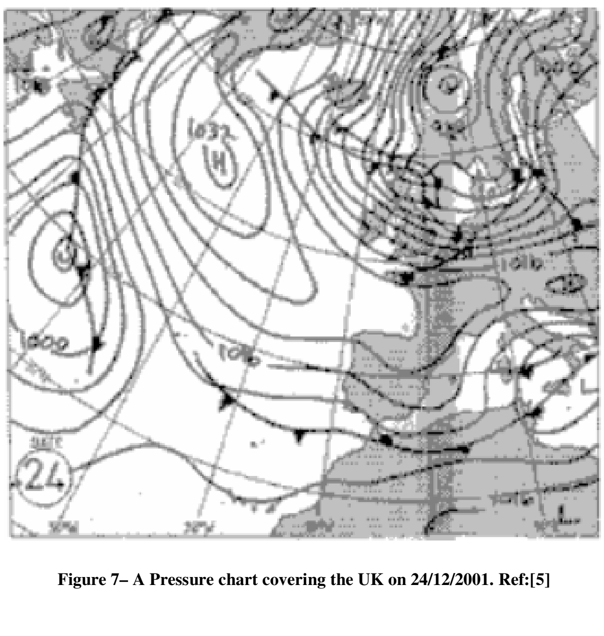


Figure 7– A Pressure chart covering the UK on 24/12/2001. Ref:[5]

The atmospheric conditions on this day were very different to the conditions on the 11th December. Figure 7 shows many isobars covering the United Kingdom, therefore this particular day will have been accompanied by high winds. These high winds would do a lot to disperse any pollutants in the atmosphere, thus producing low concentration levels at monitoring stations. This is corroborated by the fact that concentration levels are low at all the locations examined, including those in Scotland and London.

Figure 6 also shows ideal conditions for a low pollution day. The first inversion in temperature does not occur until well over 1 kilometre high, and the atmosphere below this level looks to be very unstable and thus well mixed.

Therefore, it can be assumed that areas of high pressure and a stable boundary layer will lead to high pollution concentration levels, whereas high winds and a deep, well mixed boundary layer leads to low concentrations of pollutants.

6. Errors and Uncertainties

Due to the nature of this project, and the fact that no raw data has been collected, it is not possible to perform quantitative data analysis itself. This section will instead discuss some of the possible sources of uncertainty.

A main source of uncertainty is the equipment used to collect the data. All scientific measurements include an error of some variety and this is no exception. The measurements are collected automatically many times in a day. As there is no one there in person to monitor the collection, there are plenty of chances for errors to go unnoticed.

The biggest uncertainty is that due to location. Take for example, the case of Manchester Piccadilly. The monitoring station is located in the centre of a city centre square, surrounded by reasonably tall buildings. These buildings can cause the wind around the monitoring station to channel, severely tampering with the quality of the data collected.
Ideally, the monitoring stations should sit in open spaces with no obvious immediate obstructions. The best example of this is at Manchester South.

It should also be noted that in the data there are a lot of missing values, which could also affect the quality of the results, especially those where averages are taken. There is also the fact that the data spans over 8 years. In terms of technology, this is a very long time and the equipment used to measure concentrations towards the end of the period may be much more sophisticated and accurate than earlier equipment. This could cause problems when looking at how the trends varying over the years. The same point applies to looking how trends vary due to location – the type and quality of equipment may differ from place to place.

Last but not least, the very nature of the way concentrations of nitrogen oxides are measured creates a level of uncertainty when discussing exceedance events in NO_2. As it is difficult to distinguish between nitrogen oxide and nitrogen dioxide at detection, the concentrations measured are combined NO_x, and thus comparisons between the concentrations measured and EU guidelines can draw problems. It is still possible to compare the to due to the short life time of NO, but this is a source of uncertainty nonetheless.

7. Conclusions

Analysis of the data presents various daily, weekly and seasonal trends of NO_x and ozone concentrations which vary with the location and setting of the monitoring stations. Clearly, a strong relationship exists between high NO_x concentrations and increased emissions from vehicles, as well as a correlation between NO_x and ozone concentrations.

In the area investigated, a reduction in NO_x concentrations generally leads to an increase in ozone concentrations, resulting in the so-called 'Weekend Effect', that is when ozone levels at the weekend are higher than during the working week. The Greater Manchester area and its surroundings can therefore be said to be VOC-limited.

Furthermore, a study of periods of both high and low concentrations in NO_x reveals a link between concentration levels and the behaviour of the atmospheric boundary layer. High concentration levels are encouraged by a shallow, stable boundary layer and high pressure, and days with low concentration levels are likely to be accompanied by winds and a deep boundary layer.

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[3] Air Quality Expert Group (2003): Report on Nitrogen Dioxide in the United Kingdom, *http://www.defra.gov.uk/corporate/consult/aqeg-no2/*

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