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UNIVERSITY OF LONDON

Monitoring and Modelling of Nitrogen Dioxide in Urban Areas

by

Joanne O'Keeffe

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Abstract

Due mainly to the increase in road traffic, the quality of air in cities such as London is deteriorating and air quality standards are being exceeded. Two of the main secondary pollutants produced are nitrogen dioxide and ozone, which are of increasing concern due to their adverse effects on respiratory health. As a result, there is a need for the reduction and control of these pollutants.

With the introduction of the 1995 Environmental Act, the then Government delegated much responsibility for air quality management to local government. The aim of this thesis is to consider the need for monitoring and modelling, in order for Local Authorities to assess air quality and develop abatement strategies, especially with respect to pollution episodes. Firstly, the investigation focused on monitoring, in particular, the representativeness of monitoring stations and the usefulness of the data obtained. Experimental work has included both a survey of nitrogen dioxide diffusion tubes placed in and around the Imperial College campus (London) and the application of continuous monitoring equipment to investigate vertical profiles of nitrogen dioxide and ozone, within and above the urban canopy. This revealed marked profiles, resulting from the interaction of local sources and pollutants imported from upwind.

Following a review of available models, a new Lagrangian model called URBNOX was developed to investigate the role of physical and chemical processes in the dispersion of nitrogen dioxide and ozone in the lowest few hundred metres of the boundary layer. The model was applied to winter and summer nitrogen dioxide episodes. It was shown that different processes influenced the formation of each type of episode. Winter episodes are associated with inversion conditions and respond well to NO_x emission control. Summer episodes are more complex since they are influenced by ozone concentrations which accumulate upwind of an urban area. In this case, local control strategies for NO_x emissions need to be considered in conjunction with regional scale strategies for the control of ozone.

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'"Forty-two!" yelled Loonquawl. "Is that all you've got to show for seven and a half million years' work?"'

Douglas Adams, The Hitch-Hiker's Guide to the Galaxy

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Chapter 1- Introduction

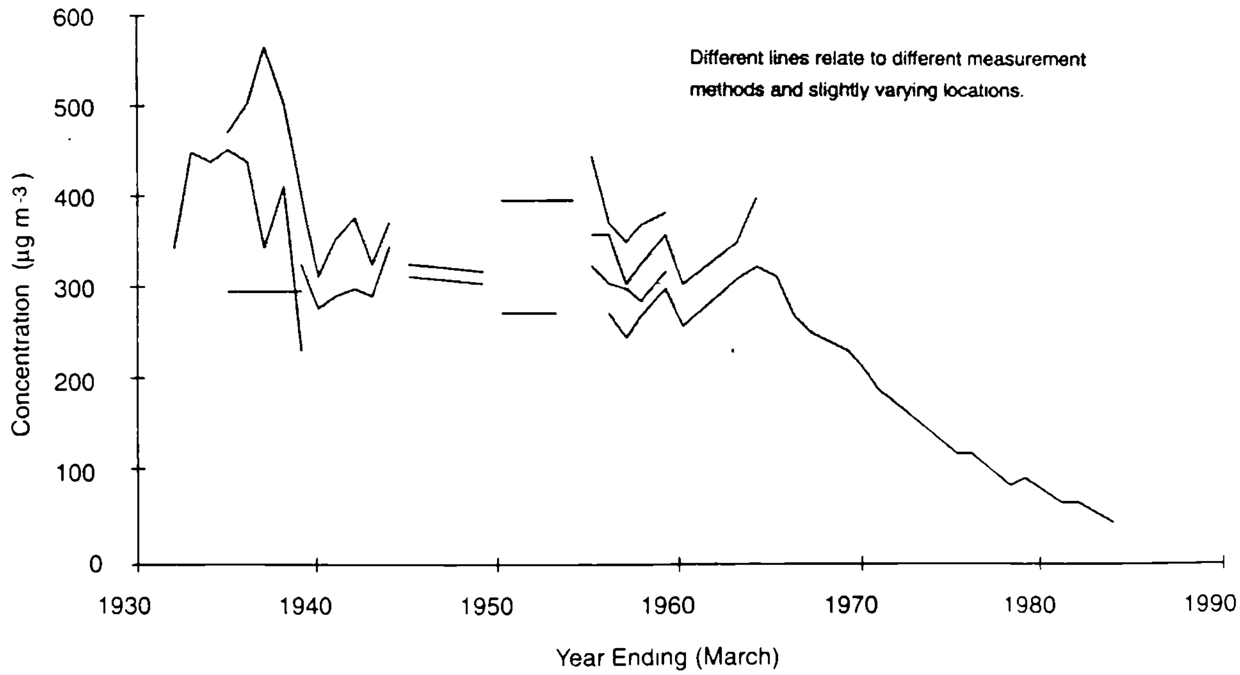
1.1 Urban Air Pollution- A General Background

Urban air pollution has been a problem for many centuries. However, the nature of the problem has changed over the twentieth century. The nineteenth century and the first half of the twentieth century were plagued by thick fogs and smoke. Sulphur dioxide and smoke were the main pollutants of concern. Some attempts had been made to reduce the problem and legislation such as the Alkali Acts 1863 and 1874 and the Public Health (Smoke Abatement) Act 1926 were introduced (NSCA, 1997). These had gone some way to improve air pollution from the industrial sector, but nothing had been done about pollution from domestic chimneys. Nonetheless, the great smog of 1952 was regarded as one of the worst air pollution episodes of the century and led to 4000 premature deaths (Brimblecombe, 1988; Bower *et al*, 1994). However, as a result of the Clean Air

Acts of 1956 and 1968, the urban areas of Great Britain are no longer subject to the thick smogs that caused so many fatalities in 1952. Long-term averages of sulphur dioxide and smoke have fallen over the decades, although they are still significant pollutants. For example, emissions of sulphur dioxide in the UK fell from 6.4 MT (megatonnes) in 1970 to 3.8 MT in 1990, while corresponding smoke emissions dropped from 1.0 MT to 0.5 MT (Bower *et al*, 1994; Gillham, 1992). This is further illustrated by Figure 1.1 below which shows the decline of sulphur dioxide in London, from the mid-1960s onwards.

Figure 1.1: Annual Mean Sulphur Dioxide (SO_2) Concentrations at County Hall, London (1931-1985)

(Source: UK QUARG I, 1993- taken from Laxen and Thompson, 1987)



However, the problem of urban air pollution is by no means solved. It has simply changed. The biggest threat to urban air quality now comes from the transport sector. The pollutants that are giving the most concern now are the oxides of nitrogen, ozone and particulates.

1.2 Oxides of Nitrogen- Their Formation and Chemistry

There is a group of nitrogen species that make up the oxides of nitrogen, including among others, nitrous oxide (N_2O), nitrates (NO_3) and dinitrogen pentoxide (N_2O_5). Nitric oxide (NO) and nitrogen dioxide (NO_2) are two of the best-known and widely distributed oxides and it is these that will be considered for the purposes of this study. Together, the sum of these two species are known as NO_x.

Nitric oxide occurs naturally, for example through lightning strikes, but the most important source is that of combustion. Power stations and the internal combustion engine are the most significant producers. This is illustrated by Table 1.1 which divides UK emissions of NO_x by source category.

Table 1.1: UK Emissions of NO_x (1995)

(Source: UKDoE 1997)

Source	Emissions (kilotonnes)*	Percentage of Total on 1995**
Power Stations	498	22
Domestic	66	3
Commercial/ Public Service	35	2
Refineries	47	2
Iron and Steel	48	2
Other Industrial Combustion	145	6
Non-Combustion Processes	2	<1
Extraction and Distribution of Fossil Fuels	112	5
Road Transport	1062	46
Railways	21	1
Civil Aircraft	16	1
Shipping	114	5
Military	41	2
Off-Road	81	4
Waste Treatment and Disposal	5	<1
Agriculture	2	<1
Total	**2293**	**100**

* Figures rounded to the nearest kilotonne

** Figures rounded to the nearest 1%

Nitrogen dioxide is formed from the oxidation of nitric oxide- again, combustion being the most important source. The majority of nitrogen dioxide comes from the transport sector- 76% of the nitrogen dioxide in London is attributed to road traffic (Chell *et al*, 1993). Nitric oxide is a primary pollutant, but nitrogen dioxide has the distinction of being both a primary and a secondary pollutant- the latter being more important. Nitrogen dioxide causes more concern as a pollutant since it is known to have adverse effects on respiratory health.

1.2.1 Health Effects of Nitrogen Dioxide

Much research has been carried out to determine what, if any, adverse effects nitrogen dioxide has on health. One of the best summaries is the study carried out by the UK Department of Health's Advisory Group on the Medical Aspects of Air Pollution Episodes (1993). This report states that nitrogen dioxide does not show a clear exposure-response relationship, especially with regard to asthmatics. In animal studies, nitrogen dioxide has been found to have severe effects on lung tissue and the immune-defence mechanisms of the respiratory tract at very high concentrations- far higher than those encountered in indoor or outdoor air in the UK. However, the lung tissue of healthy individuals shows very little response to both ambient levels and those during episodes. People with asthma nevertheless, show sensitivity at levels of 300 ppb (parts per billion) and it should be noted that the peak urban background level of nitrogen dioxide in London during the 1991 episode was 423 ppb. In addition, there is almost no evidence to suggest that the presence of nitrogen dioxide enhances allergenic responses in the respiratory tract, as there is with ozone.

Recently, there have been a number of studies investigating the health effects of mixtures of pollutants. These were defined as summer smog (the chief pollutants being ozone and nitrogen dioxide), vehicle smog (the chief pollutants being oxides of nitrogen and particles) and winter smog (the chief pollutants being sulphur dioxide and nitrogen dioxide). The best summary can be found in the Fourth

Report by the Advisory Group on the Medical Aspects of Air Pollution Episodes (1995). Much more research is required in this area, but there have been some preliminary findings. Amongst other results, it has been found that, during animal experiments, synergistic effects have been produced when gases are administered concurrently at high concentrations. Human exposure to gas mixtures, under controlled conditions, have produced an increased response to inhaled aeroallergens. The evidence suggests that all three main types of pollution episode may cause small mean reductions in lung function during episodes.

However, the lack of a concrete relationship between nitrogen dioxide and poor health does not mean that the subject should not be studied further and steps taken to reduce levels. More research is needed- especially into the effects of nitrogen dioxide upon asthmatics- since a tentative association has been found.

1.2.2 Formation of Nitrogen Dioxide

Although a small quantity of nitrogen dioxide is directly emitted as a primary pollutant, the majority of it is formed as a secondary pollutant from primary precursors. The most important of these is nitric oxide and one of the most important sources of this is from vehicle exhausts. Exhaust NO_x emissions are composed of between 90 and 95% nitric oxide and 10 and 5% nitrogen dioxide (UK QUARG I, 1993; Seinfeld, 1986). There are two major pathways from which nitric oxide is oxidised to form nitrogen dioxide. The first of these is the oxidation of nitric oxide by oxygen under combustion conditions. This reaction is responsible for the small amount of primary nitrogen dioxide formed in vehicle exhausts:

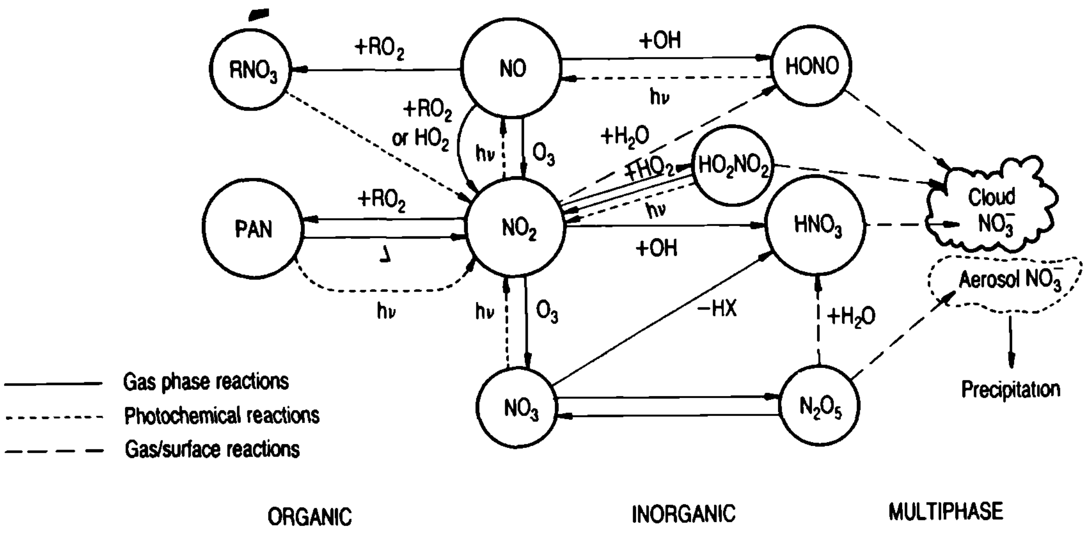
$$2NO + O_2 \rightarrow 2NO_2 \tag{1.1}$$

This reaction is second-order in nitric oxide, but can be defined as a three-body reaction as three molecules are involved (Bower *et al*, 1994). However, this is only thought to be significant when several ppm (parts per million) of nitric oxide exist and it cannot account for very much nitrogen dioxide in the vehicle wake, because of rapid dilution.

Once nitrogen dioxide is dispersed in the atmosphere, it becomes involved in many different reactions. Figure 1.2 summarises all the reactions between the different nitrogen species.

Figure 1.2: Summary of the Interplay Among the Various Nitrogen Species

(Source: UK PORG, 1990)



The other main pathway of nitrogen dioxide formation, especially in the atmosphere, is the reaction of nitric oxide with ozone. This explains why nitrogen dioxide is so closely associated with ozone:

$$NO + O_3 \Leftrightarrow NO_2 + O_2 \qquad (1.2)$$

This reaction forms nitrogen dioxide and oxygen and is reversible during the day. It can reach equilibrium in a matter of minutes. The reaction is reversible because nitrogen dioxide absorbs solar radiation and dissociates into nitric oxide and an oxygen atom as a result. The oxygen atom combines rapidly with atmospheric oxygen to regenerate ozone (UK PORG, 1987):

$$NO_2 + h\nu \rightarrow NO + O \quad (1.3)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (1.4)$$

(where M can be a molecule such as nitrogen or oxygen which dissipates the reaction energy and prevents the redissociation of the ozone formed) (UK QUARG I, 1993).

As a result of this, the lifespan of nitrogen dioxide is typically minutes during the day. When the reaction reaches equilibrium it is said to be in the photostationary state. The photostationary state defines the equilibrium between nitric oxide, nitrogen dioxide and ozone and it is shown in the equation below:

$$[O_3] = J\,[NO_2] / k_1\,[NO] \quad (1.5)$$

Where:

$[O_3]$ = concentration of ozone

$[NO_2]$ = concentration of nitrogen dioxide

$[NO]$ = concentration of nitric oxide

J = rate of dissociation of nitrogen dioxide

k_1 = rate of reaction of : $NO + O_3 \Leftrightarrow NO_2 + O_2$

It is important to note that although the photostationary state should be attained in theory, in practice it often is not. The state is perturbed in both clean and polluted air and it has been suggested that this is due to a more rapid conversion of nitric oxide to nitrogen dioxide by peroxy radicals from the interaction of insolation and hydrocarbons (UK PORG, 1990). Experimental results have shown that the deviations from the photostationary state can be very large- concentrations of ozone are often far larger than would be expected from the equilibrium. This is the result of a complex series of reactions involving a large number of hydrocarbons, reaction pathways and local meteorological conditions. The major effect of this is the conversion of nitric oxide to nitrogen dioxide by reactions OTHER than that with ozone, thus increasing the concentration of ozone (Calvert *et al*, 1991). Peroxy radicals from photochemical reactions perturb the photostationary state because they provide an alternative pathway for oxidising nitric oxide.

Nitrogen dioxide is very reactive and once formed it can be oxidised by reactions with free radicals. An important day-time sink involves its reaction with hydroxyl (OH) radicals to form nitric acid:

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (1.6)$$

For typical day-time hydroxyl radical concentrations which range between $1x10^6$ and $10x10^6$ molecules cm^{-3}, the rate of nitrogen dioxide oxidation can therefore range between 5 and 50% per hour.

As nitrogen dioxide is converted to nitric acid (in its gaseous form), it can then be easily removed from the atmosphere by wet or dry deposition. In addition, this process removes the active hydroxyl radicals. This reduces the oxidising capacity of the atmosphere. Therefore, it can be seen that these effects are important in determining the rate of photochemical ozone formation within the boundary layer (UK PORG, 1990).

However, it has been noted that, especially under conditions of elevated concentrations, that this series of reactions does not always satisfactorily explain levels of nitrogen dioxide observed. It has been suggested in a number of pieces of research (Harrison *et al*, 1996; Hov *et al*, 1984) that the oxidation of nitric oxide (Equation 1.1) could contribute more nitrogen dioxide than was previously realised, in terms of the atmospheric reactions. It was formerly thought to be only of importance in the formation of nitrogen dioxide at the tail pipe of vehicles but there is increasing evidence to suggest that it could be an important source of nitrogen dioxide, especially in episodes. Many studies have been carried out to determine the contribution of this reaction to levels in urban areas, especially under episode conditions (Bower *et al*, 1994; Derwent *et al*, 1995; Harrison *et al*, 1996; Hov *et al*, 1984). This thermal reaction has an inverse temperature dependence and the rate of formation of nitrogen dioxide is proportional to the square of the concentration of nitric oxide. As a result of this, it is normally considered to be too slow to make any significant contributions to nitrogen dioxide levels. However, if temperatures become suitably low and levels of nitric oxide become particularly high, then this reaction can become a significant nitrogen dioxide mechanism.

The question of how nitrogen dioxide is formed, especially during winter episodes is particularly important because it will have a bearing on whether a particular abatement strategy will be effective or not. One of the aims of the thesis will be to explore this area.

1.3 Ozone- Formation and Chemistry

Ozone is an important secondary pollutant which has come to prominence in the latter half of the twentieth century. It is being considered alongside nitrogen dioxide in this project because they have a very close association. This is especially important when taking into account urban areas. The distribution of ozone in urban areas is complex, mainly due to its interaction with nitrogen compounds.

The distribution and behaviour of ozone is mainly governed by photochemical reactions (as explained in Section 1.2.2). During the day-time the lifetimes of both ozone and nitrogen dioxide are often minutes in urban areas. Nitrogen dioxide will be photolysed to ozone and nitric oxide, and ozone will react with nitric oxide to form nitrogen dioxide. Then, during the night, nitrogen dioxide ceases to be photolysed and most of the ozone present will react with nitric oxide, thus increasing nitrogen dioxide levels and depleting ozone.

Ozone levels are generally higher in rural areas, upwind of an urban area. As this ozone-rich air moves over an urban area, it becomes mixed with nitric oxide which is emitted from the urban traffic. The evolution of the mixing layer during the day ensures that the ozone is mixed down from aloft where it reacts with the nitric oxide to form nitrogen dioxide. Over the centre of a major urban area, the rate of ozone being mixed down from aloft is overtaken by ozone consumption by nitric oxide being emitted from traffic. As a result ozone levels are severely depleted over urban areas. However, these ozone concentrations do increase with height, even reaching the rural concentrations far above the street canyon (UK QUARG I, 1993).

In addition, once formed, high levels of nitrogen dioxide suppress subsequent ozone formation, since it will react with hydroxyl (OH) radicals. These are then not available to attack volatile organic compounds (the precursors of ozone). Therefore, there are no peroxy (RO_2) radicals formed to break the cycle. This complex distribution and behaviour adds complications to trying to solve the problem of elevated nitrogen dioxide.

1.3.1 Health Effects of Ozone

Ozone has more noticeable effects on health than nitrogen dioxide and the link between ozone and adverse health effects has been easier to distinguish than with nitrogen dioxide. Again, many studies have been carried out to determine the effects of elevated ozone levels on health and a good summary can be found in The Advisory Group on Medical Aspects of Air Pollution Episode's report on ozone, published in 1991.

It has been found that at high concentrations of ozone, such as 1000 ppb upwards, over a time period of several hours, damage can be caused to the airways of the lungs. In addition to this, at lower levels of exposure (100-150 ppb), people with a predisposition to sensitive lungs, show an increased sensitivity to allergens and susceptibility to inflamed airways (UK EPAQS, 1994). The effect of a severe ozone episode on health was recorded in Los Angeles in 1979, when ten consecutive days were recorded with peak hourly ozone concentrations exceeding 0.35 ppm (this constitutes the second stage alert). A health survey was carried out during this time and 83% of the people surveyed reported health discomfort, 57% complained of eye irritation and 25% reported headaches, irritation in breathing, sore throats or stuffy noses. Hospitals reported increases of up to 50% in the number of patients being admitted with chronic lung disease (Elsom, 1992).

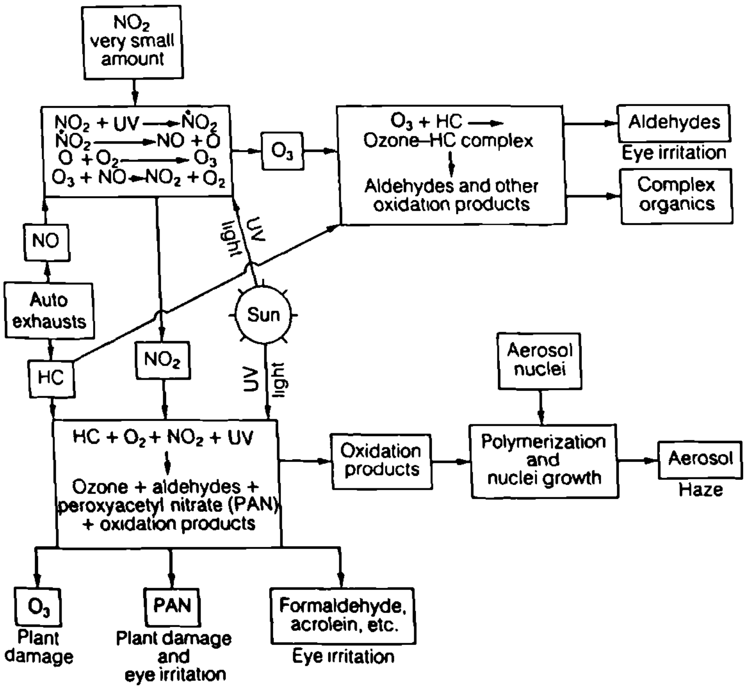
In conclusion, therefore, ozone can be said to increase the frequency of asthma attacks, cause eye and nose irritation, chest discomfort, headaches and nausea, worsen coughs, impair pulmonary function in healthy exercising individuals, reduce the resistance of lungs to disease and can scar the lungs over the long-term. It is suggested that 10% of the UK population is sensitive to ozone (UK PORG, 1993).

1.3.2 Formation of Ozone

As ozone is a secondary pollutant, there are no direct emissions of it into the atmosphere. Tropospheric ozone can be formed through a number of pathways. It is generated as a secondary pollutant, in the presence of strong insolation, from precursors such as volatile organic compounds (VOCs) and oxides of nitrogen, both of which are produced by industry and motor vehicles. This is known as photochemical smog. Figure 1.3 summarises the reactions which go to form photochemical smog.

Figure 1.3: Photochemical Smog Formation

(Source: Elsom, 1992)



The majority of ozone formed in the atmosphere was generated by the recombination of molecular and atomic ozone. Ozone is formed in both the stratosphere and the troposphere, but the majority of it is formed in the stratosphere. Atomic oxygen is produced here by the photodissociation of molecular oxygen with deep ultra-violet radiation:

$O_2 + h\nu\ (\lambda = <242nm) \rightarrow O + O$ (1.7)

$O + O_2 + M \rightarrow O_3 + M$ (1.8)

(where M can be a molecule such as nitrogen or oxygen which dissipates the reaction energy and prevents the redissociation of the ozone formed)

Some of this ozone is transported down to the troposphere under certain atmospheric conditions. However, in the troposphere, the only significant source of atomic oxygen comes from the dissociation of nitrogen dioxide. Ozone is then formed thus:

$NO_2 + h\nu\ (\lambda = 290\text{-}430nm) \rightarrow NO + O$ (1.9)

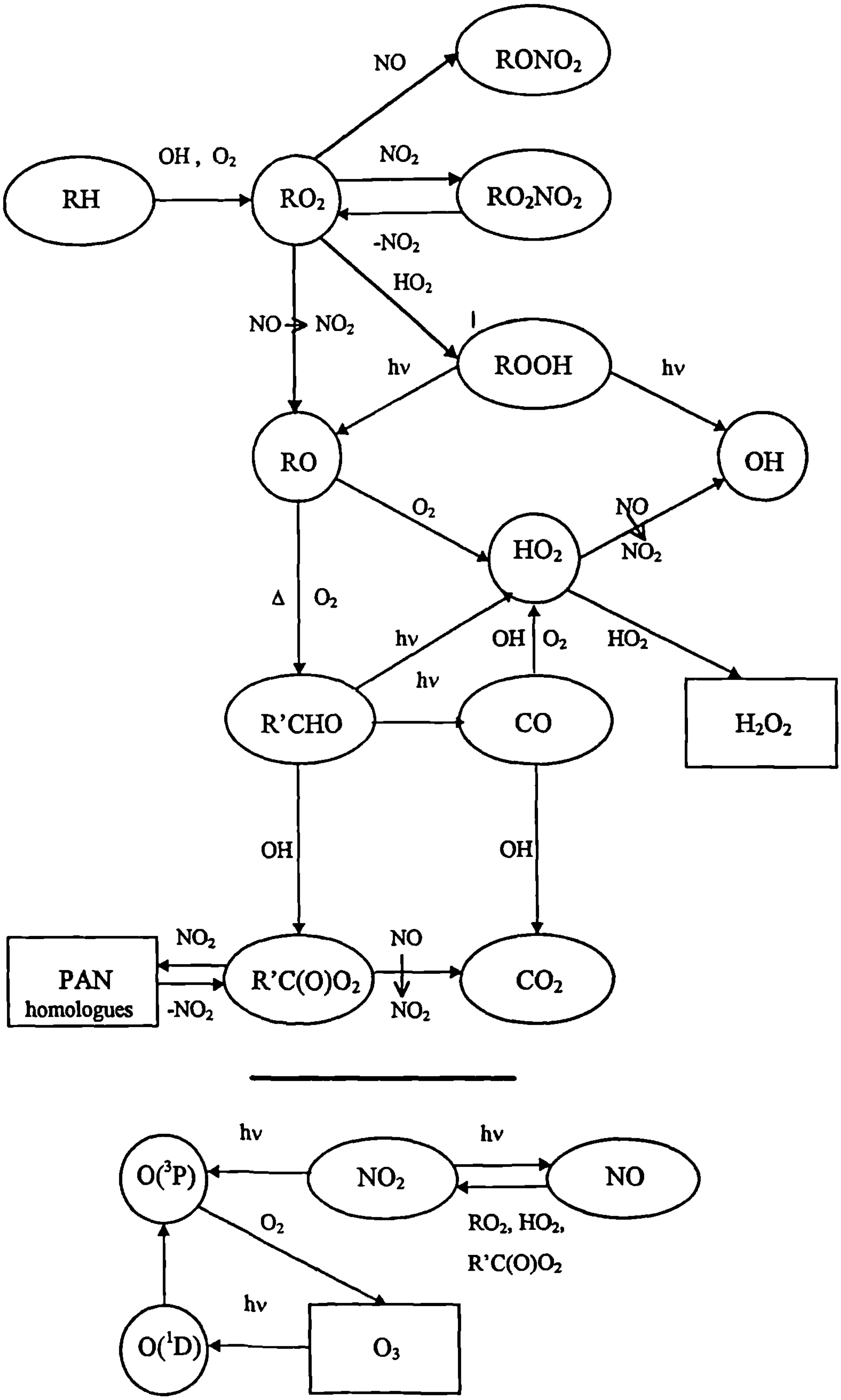
$O + O_2 + M \rightarrow O_3 + M$ (1.10)

The ozone produced usually goes on to react with nitric oxide to form nitrogen dioxide (Equation 1.2), as explained in detail in Section 1.2.2. As explained previously, ozone is an important component of the photostationary state (Equation 1.5).

If nitric oxide is oxidised to nitrogen dioxide by a species other than ozone, then this system is disturbed and excess ozone is produced. Peroxy radicals (RO_2) are produced by the photochemical decay of hydrocarbons, and react with nitric oxide. Therefore they are in competition with ozone to react with nitric oxide to form nitrogen dioxide. R can either represent a hydrogen atom or an organic radical and they can either occur naturally or be anthropogenic. Peroxy radicals are generated by the attack of hydroxyl radicals (OH) on a whole range of hydrocarbons. When the air is unpolluted, excess ozone production occurs by the oxidation of methane and carbon dioxide. However, in polluted air, the amount of ozone produced will depend on concentrations of organic radicals (from VOCs) and oxides of nitrogen (UK QUARG I, 1993; UK PORG, 1990; UK PORG, 1987). It should be noted that under conditions of high nitrogen dioxide, ozone formation will be suppressed, as described in Section 1.3. A summary of these reactions is shown in Figure 1.4:

Figure 1.4: Summary of Reactions Between Oxides of Nitrogen and Ozone

(Source: Dimitroulopoulou, 1997)



The ozone concentration in the boundary layer is a balance between input from downward transport and photochemical formation and output from chemical reactions and dry deposition. As shown previously in Section 1.2.2, ozone can be removed from the atmosphere by reacting with nitric oxide (Equation 1.2). It can also be removed by its reaction with nitrogen dioxide and unsaturated hydrocarbons:

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (1.11)$$

$$O_3 + RCH \rightarrow CH_2 \rightarrow RCHO + \text{Other Products} \qquad (1.12)$$

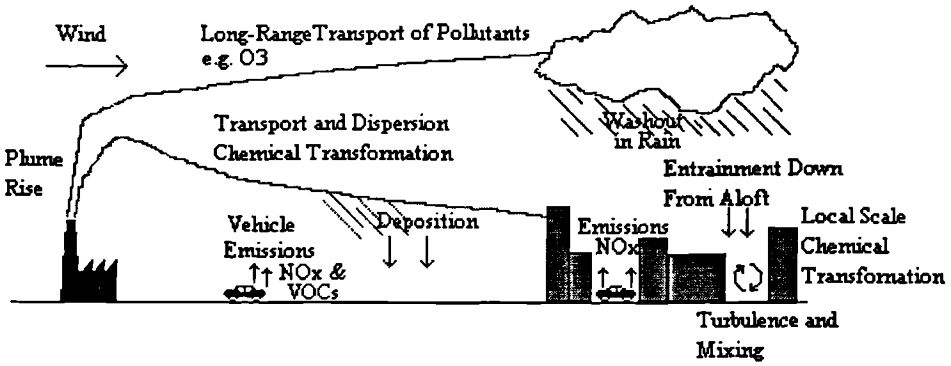
Reactions 1.2 and 1.11 are particularly important during the night because, due to the lack of insolation, photolysis of nitrogen dioxide and nitrogen trioxide does not occur and ozone is not regenerated.

Dry deposition is very important. This is where ozone is transported down through the boundary layer to the surface. The rate of downwards transport depends on the nature of the boundary layer (such as its wind speed) and its fate when it reaches the surface depends on the chemical reactivity of the surface with respect to ozone.

1.4 Pollutant Processes

Pollutant concentrations are influenced by both chemical and physical processes. Concentrations of nitrogen dioxide and ozone are determined by emissions, chemistry and meteorology. The chemical processes of nitrogen dioxide and ozone are discussed in detail in Sections 1.2.2 and 1.3.2. Atmospheric influences on the dispersion of nitrogen dioxide and ozone can take place over different scales. This is shown in Figure 1.5:

Figure 1.5: The Role of Physical Processes in Pollutant Dispersion



The majority of pollutants are dispersed in the boundary layer, which extends to approximately 1 km above the Earth's surface. The effect of the Earth's surface creates advection currents in the boundary layer, which will in turn affect the dispersion of pollutants. Local topography and surface roughness will also affect pollutant dispersion, due to increased levels of turbulence. For example, on the local scale, buildings lining the street canyon will affect air flow. On a larger scale, hills and mountains will alter air flow.

During transport and dispersion, pollutants will undergo chemical transformations. These can occur on scales ranging from a number of minutes to several hours. For example, nitrogen dioxide can be formed from nitric oxide and ozone within the street canyon in a matter of minutes. On the other hand, it can take many hours for ozone levels to build up in a plume over the city. As the formation of ozone is not instantaneous following emission, there is time for significant transport and mixing within the boundary layer. The formation of ozone can occur over a range of time scales. This is because each hydrocarbon that contributes to ozone formation degrades at a different rate and hence, produces different amounts of ozone.

1.5 Air Quality Standards

Air quality standards have been set for a number of different pollutants in order to aid the control of their adverse effects. The form of the standard will change depending on the nature of the pollutant and its effects. There are a number of different standards for both nitrogen dioxide and ozone. (Nitric oxide does not have any standards since it does not pose any health risks, although it could be said that the more nitric oxide there is, the more potential nitrogen dioxide could be formed). The standards range from those set by the EC to those set by the UK Government.

1.5.1 Nitrogen Dioxide

The Standards are summarised in Table 1.2 below:

Table 1.2: Summary of Air Quality Standards for Nitrogen Dioxide

Guideline Set By	Description	Criteria Based On	Value/ ppb ($\mu g\ m^{-3}$)
European Council		Calendar Year of Data;	
	Limit Value	98%ile of hourly means	104.6 (200)
	Guide Value	98%ile of hourly means	70.6 (135)
	Guide Value	50%ile of hourly means	26.2 (50)
World Health Organisation	Health Guideline	Hourly Mean	210 (400)
	Health Guideline	Daily Mean	80 (150)
	Vegetation Guideline	4- Hourly Mean	50 (95)
	Vegetation Guideline	Annual Mean	16 (30)
UK Department of the Environment	Very Good	Peak Hourly Mean Concentration in 24 Hours	<50 (96)
	Good		50-99 (96-190)
	Poor		100-299 (191-572)
	Very Poor		>=300 (573)
EPAQS	Health Guideline	Hourly Mean	150 (285)
United Nations Economic Commission for Europe (UNECE)	Vegetation Guideline* (critical level)	Annual Mean	15 (29)

* This Value now applies to NO_x and not NO_2

(Major Sources: WHO, 1987; UK PORG, 1993; UK QUARG I, 1993; UK EPAQS, 1996)

It should be noted however, that the WHO recommended in 1994 that changes should be made to their standards. These included the removal of the 24-hour guideline, the lowering of the hourly guideline and the addition of an annual average guideline (UK DoE, 1996). Recommendations have also been made to adjust four of the EC air quality standards, including nitrogen dioxide (ENDS, 1997). It should be noted that the standards contained in Table 1.2 and Table 1.3 will be used for comparisons throughout this thesis, despite any subsequent changes made by WHO or any other body responsible for setting standards.

1.5.2 Ozone

The Standards are summarised in Table 1.3 below:

Table 1.3: Summary of Air Quality Standards for Ozone

Guideline Set By	Description	Criteria Based On	Value/ ppb ($\mu g\ m^{-3}$)
European Council	Population Information Threshold	1-Hour Mean	90 (180)
	Population Warning Value	1-Hour Mean	180 (360)
	Health Protection Threshold	Fixed 8-Hour Means (Hours 1-8,9-16,17-0,13-20)	55 (110)
	Vegetation Protection Threshold	1-Hour Mean	100 (200)
	Vegetation Protection Threshold	24-Hour Means	32 (65)
World Health Organisation	Health Guideline	1-Hour Mean	76-100 (150-200)
	Health Guideline	Running 8-Hour Mean	50-60 (100-120)
	Vegetation Guideline	1-Hour Mean	100 (200)
	Vegetation Guideline	Daily Mean	33 (65)
	Vegetation Guideline	Growing Season Mean*	30 (65)
UK Department of the Environment	Very Good	Peak Hourly Mean Concentration in 24 Hours	<50 (100)
	Good		50-89 (100-179)
	Poor		90-179 (180-359)
	Very Poor		>=180 (360)
EPAQS	Health Guideline	Running 8-Hour Mean	50 (100)
United Nations Economic Commission for Europe (UNECE)	Vegetation Guideline	Growing Season Mean*	25 (50)
	Vegetation Guideline	1-Hour Mean	75 (150)
	Vegetation Guideline	Running 8-Hour Mean	30 (60)

*Growing season mean is defined as April-September for WHO, but is defined as Daytime (0900-1500 hours), April-September for UNECE

(Major Sources: WHO, 1987; UK PORG, 1993; UK QUARG I, 1993; UK EPAQS, 1994)

1.6 Pollution Episodes

Pollution episodes are periods of poor air quality. They can last up to a period of several days and extend over a large geographical area. In terms of nitrogen dioxide and ozone, they can be divided into two types, namely, winter and summer episodes. Winter episodes are characterised by high levels of nitrogen dioxide. The meteorological conditions usually include high pressure (anticyclonic) conditions which lead to atmospheric stability and inversions. Low mixing heights are also present. The stable conditions can trap nitrogen dioxide and other pollutants close to their sources and prevent dispersion. Low wind speeds are also a feature because they slow down the dispersion of the pollutants. Dense fogs can also occur if there are large concentrations of particles in the air at the same time.

On the other hand, summer episodes, although they are also characterised by high levels of nitrogen dioxide, often have substantial amounts of ozone present. Again, meteorological conditions have a very significant effect and certain conditions must exist before high concentrations of ozone develop. Firstly, the trajectory of the air mass must pass over areas of high emissions of precursors. There must be a high intensity of insolation, since this is one of the major driving forces behind the production of ozone. High temperatures (greater than 20 degrees Celsius) are also advantageous since these can influence the rate of chemical reactions and emissions of the precursors. Wind speeds are usually low- between 1 and 2 m/s, as they allow the precursors to build-up. Anticyclonic conditions are also major features. However, the pollutants in these types of episode are often capable of travelling long distances. As a result, ozone episodes in the UK quite often result from air masses, rich in ozone precursors, that originated in continental Europe.

The important thing to note from this is that there is essentially a difference between these two types of episode, although nitrogen dioxide plays a prominent role in both. This potentially has significant implications for abatement strategies -

i.e. it would appear that to consider one general abatement strategy to deal with both types of nitrogen dioxide episode would not be sufficient to actually deal with the problem.

1.7 New Legislation- The Environmental Act 1995 and the Creation of the National Air Quality Strategy

Over the last couple of years, a series of reports have been published outlining the Government's proposed strategy for tackling air quality. In the wake of the Rio Summit, the UK's strategy for sustainable development was published. This identified urban air quality and the control of photochemical pollution as key issues for environmental policy. Improving Air Quality was published in April 1994 and addressed for the first time the need for an overall framework for managing and improving air quality. This was followed by Air Quality- Meeting the Challenge which set out the conclusions that the Government reached about air quality policy. Three main areas were identified. These were:

- A new framework of national air quality standards and targets;
- New systems for local air quality management, based on the setting up of Air Quality Management Areas;
- Effective control of emissions, particularly from vehicles.

The emphasis is on integration between central government, local government, industry and the general public. The reports agreed that in general, air quality was improving but there were still problems with local air quality and episodes. As a result, proposals were put forward to give more powers to local authorities to enable them to take care of the air quality within their boundaries. Local authorities are already responsible for controlling air pollution from a range of industrial processes under the Environmental Protection Act 1990. However, there are no powers for local authorities to deal with pollution from motor vehicles. The control of pollution from motor vehicles comes under the provisions of the Road

Traffic Act 1972, the Road Vehicles (Construction and Use) Regulations 1986 and the Clean Air Act 1993.

It was proposed that legislation be put forward to provide a system requiring local authorities to periodically review air quality and establish areas to be targeted for air quality action. It was suggested that they be known as Air Quality Action Areas. Within these, a detailed assessment of local air quality and plans to improve it would be published. This is an excellent idea, but it should be asked whether local authorities will actually be able to control their air pollution. In other words, is the problem due to local emissions from vehicles and industry, or are the real problems due to larger scale pollution coming over from the European continent? Problems of scale need to be considered when dealing with pollution. Air pollutants interact over different scales, therefore it is important to differentiate between them in order to define the quantity of pollutants being emitted from a local 'hot-spot' and that coming in from beyond an urban area, for example, from the continent.

As mentioned above, local authorities became responsible for air pollution control under Part I of the Environmental Protection Act 1990 on 1 April 1991 (NSCA, 1997). Their responsibilities for managing air quality have been expanded by the Environment Act 1995. This new Act requires the Secretary of State to put together a national air quality strategy in consultation with the Environment Agencies, local authorities, industries and other relevant bodies.

The local authorities are obliged to review air quality within their boundaries, and assess whether air quality standards and objectives are being achieved or going to be when measured against the national air quality strategy. If any part of a local authority's area does not or will not meet the standards or objectives, then they are to designate these areas as 'air quality management areas'. Within these areas, the local authority should assess the air quality further, determining which standards are not being met and the reasons why. Within a year of such an area being designated, the local authority should draw up a plan of action for the area, setting out its methods (with target dates) in order to attain the standards (NSCA, 1997, UK DoE , 1996).

The final draft of the UK National Air Quality Strategy (NAQS) was published in March 1997 and was drawn up in response to the progress in understanding the problem of air pollution. As the level of understanding has increased, the need for a more comprehensive framework for the management of air quality has also increased (UK DoE, 1997). The aim of the strategy is to try and tackle the UK's outdoor air quality problems; indoor air quality and occupational exposure are not included and are tackled under separate projects supported by the Department of the Environment. The strategy is sharply focused on ambient air quality and therefore includes no provision to deal with related topics, such as water or noise pollution. It does not even consider very closely related subjects such as deposition. This may seem like a major oversight but the strategy has more chance of success if it is focused on one target as closely as possible. In addition, all these missing topics are being researched and dealt with under different projects. The aim of the strategy is reproduced below, taken from The United Kingdom National Air Quality Strategy, published in March 1997:

> *"The aim of NAQS is to set out, as far as is possible, the future of ambient air quality policy in the UK at least until the year 2005. A particular purpose is to ensure that all those who contribute to air pollution, or are affected by it, or have a part to play in its abatement, can identify both what is statutorily required from them and what further contribution they can voluntarily make in as efficient a manner as possible. Vital to this process is the notion that the Strategy must be evolutionary rather than a rigid structure determined by the conditions pertaining at the present time. The Act requires that the Secretary of State's polices on air quality are regularly reviewed, and it is the Government's intention to initiate the first review of this Strategy in 1999. Preparation for this first review will be assisted by the establishment of an Air Quality Forum, which will bring together representatives of all interests to ensure that the implementation of current policies is carefully monitored and reviewed, and that future priorities can be identified."*

Therefore, all local authorities will have to bear this strategy and its aims in mind when creating and implementing air quality management programmes in the future.

1.8 Thesis Aims

As a result, it is intended that the aim of this thesis is to focus on the following objectives:

- to consider the current state of monitoring and modelling, with respect to nitrogen dioxide. It will then be determined whether these are sufficient for a local authority to assess their air quality;

- to assess the different types of monitoring available by carrying out experimental work to analyse the spatial variability of nitrogen dioxide around the Imperial College campus in South Kensington;

- to investigate the distribution of nitrogen dioxide and ozone within and above the urban canopy;

- to review the different types of air quality model currently available for the study of urban air pollution;

- to develop a simple model which can be used to investigate the behaviour of nitrogen dioxide and ozone within an urban area;

- to investigate the conditions under which episodes occur and to determine the differences between the formation of winter and summer nitrogen dioxide episodes.

1.9 Thesis Structure

Chapter 2 contains all the work in this thesis associated with monitoring. It starts with a review of the current state of monitoring, especially with respect to local authorities. This chapter also includes the practical work. This consists of several local air quality surveys in order to investigate the spatial variability of nitrogen dioxide and to compare different monitoring techniques.

Chapter 3 is a review of the current state of urban air quality modelling. It categorises the models in terms of different urban scales, i.e. from single streets to city-wide and regional. It also highlights the existence of a gap in current modelling techniques.

Chapter 4 introduces URBNOX, which is an attempt to deal with the gap demonstrated in the modelling review. The development of URBNOX is described in detail, along with its parameters. The model is then used to investigate the formation of winter nitrogen dioxide episodes. This includes a series of sensitivity studies.

Chapter 5 details how URBNOX is used to explore the formation of summer episodes, by comparing the results to data recorded during an episode in May 1995. URBNOX is also compared to monitoring data gathered from the instruments set up in the Queen's Tower (as detailed in Chapter 2).

Chapter 6 discusses the overall findings of the investigation, along with recommendations and suggestions for further work.

Chapter 2 - Urban Air Quality Monitoring

2.1 Introduction

Under the new Environment Act, 1995, local authorities are expected to take responsibility for managing the air quality within their boundaries. In order to do this they will need to establish a framework in order to improve air quality and ensure that air quality standards are not exceeded. The ultimate aim of this framework will be to introduce various pollution abatement measures (both short and long term). However, abatement measures can be very costly, so before any local authority commits itself, a survey of the state of the air quality should be done first. Air quality monitoring is also a requirement under the EC Nitrogen Dioxide Directive (85/203) (Stevenson *et al*, 1997).

The aim of this chapter is to focus on air quality monitoring. It will explain the theory behind it and the objectives of a 'typical' monitoring survey. The chapter will focus on nitrogen dioxide followed by ozone. The different methods of monitoring both pollutants will be explored, along with the advantages and disadvantages of each. The practical section of this chapter is then introduced, the aims of which are to consider how spatial variability would affect monitoring strategies and to investigate the different options with which to monitor air quality.

2.2 Objectives of Monitoring

Monitoring is carried out to establish whether or not a particular area has an air quality problem. In order to do this to the fullest extent possible, there is a need to monitor as widely as possible, in other words, to carry it out over different time scales and in different locations. Monitoring, itself, only provides the raw measurements of ambient air quality – meaningful air quality data is produced by analysis and interpretation (McGinlay *et al*, 1996). The main objectives of monitoring can be summed up and are listed as follows:

- to assess whether or not air quality meets health-based standards or guidelines to assess the degree of health risk posed to the population by different pollutants in various parts of the city (in other words, to identify pollution hot spots);

- to identify any short-term periods during which health-based standards are exceeded so that the public can receive warnings and be offered advice about how they can minimise risks to their health and the authorities can justify the introduction of temporary emission-reduction measures (e.g. a pollution alert system);

- to measure changes in pollution concentrations to assess the effectiveness of short-term (e.g. temporary traffic bans) and/or long-term pollution control policies and measures (e.g. transport policies);

- to establish long-term trends in pollution concentrations with a view to assessing why those changes are occurring. The trends can also be monitored to ensure air pollution problems are not developing;

- to validate numerical prediction models and provide confidence in the accuracy of their results on which authorities may base their short-term and/or long-term pollution control actions;

- to check that licensed premises (e.g. industrial plants) comply with pollution regulations (e.g. emission limits);

- to provide data for the preparation of an environmental impact statement for a proposed large project (e.g. monitoring before and after development);

- to provide information to improve our understanding of the atmospheric processes transforming emissions to concentrations.

(Source: Elsom, 1996; UK NETCEN, 1997; McGinlay *et al*, 1996)

In addition, local authorities may have some extra reasons for carrying out monitoring surveys. These include integration with existing national networks, the planning of development and implementation, assessing impacts of local sources and answering specific local concerns about air quality (McGinlay *et al*, 1996).

However, it should be noted that the majority of air quality monitoring, especially that done by local authorities, is carried out to determine whether the air quality meets health standards and guidelines. Therefore the majority of monitoring equipment is set up very near ground level. More monitoring along a variety of scales, for example, vertical scales, is needed in order to investigate and understand the processes and dispersion of pollutants.

2.3 Examples of Monitoring Projects

Air quality monitoring is also carried out on a national scale, and there are several major projects, which are outlined further on in this section.

The general aims of the UK air quality monitoring project are as follows (as stated by UK NETCEN):

- To understand air quality problems in order that cost effective policies and solutions can be developed;

- To assess how far standards and targets are being achieved;

- To provide public information on current and forecast air quality;

- To assist the assessment of personal exposure to air pollution.

(Source: UK NETCEN 1997)

In 1993, levels of monitoring at both national and local scales were considered to be insufficient and uncoordinated (UK QUARG I, 1993, Beevers *et al*, 1994). When Urban Air Quality in the UK was published by UK QUARG in 1993, it contained the following recommendations:

- the expansion of air quality monitoring, in particular with monitoring sites in at least 24 of the UK's major towns and cities as part of the Enhanced Urban Network programme;

- the rationalisation and review (subject to the requirements of international legislation) of the UK Department of the Environment's total urban monitoring effort;

- the central co-ordination of all local monitoring programmes, in order to make the best use of both local and national resources;

- the enhancement of monitoring at both roadside and suburban locations, (which had very sparse coverage in comparison with central urban background and rural locations).

(Source: UK QUARG I, 1993)

There is substantial evidence from the literature that these recommendations have been acted upon. The United Kingdom Department of the Environment currently funds several national scale air quality monitoring programmes. They consist of :

- three automatic networks;
- six sampler based networks.

These monitoring networks measure a broad range of pollutants, including oxides of nitrogen, ozone, sulphur dioxide, particulate matter, carbon monoxide, hydrocarbons, lead, acid deposition and air toxins. They also employ a wide range of monitoring methods according to need. In 1996, it was recorded that there were over 60 automatic point monitoring stations and more than 1200 sampler measurement sites in the United Kingdom. Table 2.1 below summarises the United Kingdom national air quality monitoring networks:

Table 2.1: The United Kingdom Air Quality Monitoring Networks

(Source: McGinlay *et al*, 1996)

Network	**Urban**	**Hydro-carbons**	**Rural**	**Diffusion Tube**	**Smoke/ SO_2**	**Lead + Elements**	**Acid Deposition**	**Rural SO_2**	**TOMPs**
Pollutants	O_3 NO_x SO_2 CO PM_{10}	25 Species	O_3 NO_x SO_2	NO_2	Smoke SO_2	Lead Metals	Anions and Cations	SO_2	PAHs PCBs Dioxins
Site Numbers	46**	12***	16*	1190	222	25	32	29	4
Measurement Techniques	A	A	A	PS	AS	AS	AS, PS	AS	AS
Function	S	N	S	N	S	S	S	N	N

Where:

A = Automatic, AS = Active Sampler, PS = Passive Sampler,

S = Statutory, N = Non-statutory

* Includes one site operated by PowerGen

** Includes local authority affiliated sites

*** The hydrocarbon monitoring at Birmingham East, Middlesborough and Southampton Centre is co-located with the Urban site

In terms of this thesis, the monitoring networks that are of most interest are the Automatic Urban Network (AUN) and the Nitrogen Dioxide Diffusion Tube Network.

The Automatic Urban Network is, as its name suggests, a fully automatic network and was created from the merger of the former Enhanced Urban Network (EUN) and the Statutory Urban Network (SUN). The AUN imparts information on a wide range of pollutants and can be accessed through a public information service, which includes a free telephone service and the World Wide Web. The network also satisfies the requirements of the EC Directives on nitrogen dioxide, ozone and sulphur dioxide monitoring. The network is to be expanded with the affiliation of local authority monitoring sites.

The Nitrogen Dioxide Diffusion Tube Network was set up in 1993 to improve the spatial coverage of measurements and to monitor nitrogen dioxide levels over the period of introduction of catalytic converters on cars. Currently, 295 local authorities are taking part. They are required to operate four sites, two of which are background, one intermediate and one kerbside (as defined in Section 2.5). This ensures that a good overall picture of the air quality within a local authority is obtained and there is no bias towards only one type of site being investigated.

Other monitoring networks exist, other than those funded by the United Kingdom Department of the Environment. The London Air Quality Network was set up in February 1993. It is co-ordinated by the Association for London Government on behalf of the local authorities of London and is operated and managed by the South East Institute for Public Health. Its aim is to improve and co-ordinate air quality monitoring and provide data for informed action to reduce air pollution in London (Beevers *et al*, 1995). It was set up as a way in which London local authorities could work together on issues such as improving air quality.

By 1995, the Network had over 30 sites and all thirty three London local authorities contribute their monitoring data to the Network. In addition the local authorities surrounding London, for example, Kent, Essex and Hertfordshire, are starting to contribute data. It is now considered to be one of the most comprehensive and extensive monitoring networks in the United Kingdom.

The London Air Quality Network encompasses a range of sites which are shown Table 2.2:

Table 2.2: Classification and Number of Sites Operated by the London Air Quality Network

Site Classification	Number of Sites	CO	NO_2	O_3	SO_2	PM_{10}	TSP	Organics
Kerbside/ Roadside	10	x	x	x	x	x		
Urban Background	16	x	x	x	x	x		x
Suburban	6	x	x	x	x	x		
Rural	1		x	x	x	x		

2.4 Methods of Air Quality Monitoring

There are four main categories of air quality monitoring methods:

- Passive sampling;
- Active sampling;
- Automatic point monitoring;
- Long-path / remote monitoring.

Which method should be chosen depends on the aims of the monitoring survey, the type and resolution of data required, financial and personnel resources. There is a trade-off between instrument costs, complexity of use, reliability and performance. Generally, the more advanced the monitoring method, the higher the resolution and the quality of the data. However, they are usually more expensive, more difficult to operate, need more maintenance and have lower reliability than simpler monitoring methods.

Passive (or static) monitoring methods can be defined as those that do not have an active air moving component, such as a pump, in order to pull a sample to the collection medium (Boubel *et al*, 1994). Generally, they are a simple and inexpensive method of investigating air quality in an area to give a general picture of pollution levels. As it is cost-effective, it is possible to sample at many points over a wide area, therefore highlighting pollution 'hotspots', which then could be analysed in greater detail. These methods have been in use over the last hundred years. For example, lead peroxide candles were used to detect the presence of sulphur dioxide. There are two major principles in use, namely diffusion and permeation. Diffusion methods, usually in the form of diffusion tubes, are especially used for measuring concentrations of nitrogen dioxide. These are described in detail in Section 2.4.1.

Active (semi-automatic) sampling methods collect pollutant samples either by physical or chemical means for analysis in the laboratory. Typically, a known volume of air is pumped through a collector (for example, a filter or a chemical solution) for a known period of time. This is then removed for analysis. These methods are a good compromise between passive and automatic monitoring methods since samples can be taken daily (unlike passive samplers) but at a fraction of the cost of using an automatic sampler.

Automatic real-time point analyser methods produce high-resolution measurements (for example, minute readings) at a single point for both nitrogen dioxide and ozone and also sulphur dioxide, carbon monoxide and PM_{10}. These work by drawing air from one particular location into the analyser. In addition, there are gas chromatography analysers which can be used for measuring benzene, 1,3-butadiene and other hydrocarbon species. Usually, the concentrations are measured on-line and in real-time. This, however, is the most expensive and maintenance demanding method of the four.

Remote optical and long path analysers are the new generation of analysers. They use long-path spectroscopic techniques to make real-time measurements of pollutant concentrations integrated along a path between a light-source and a detector. One of the best-known examples is the OPSIS monitoring system.

Each method has its advantages and disadvantages which are summarised in Table 2.3:

Table 2.3: Advantages and Disadvantages of Different Instrumented Air Monitoring Techniques

(Source: McGinlay *et al*, 1996)

Method	Advantages	Disadvantages	Capital Cost
Passive Samplers	Very low cost; Very simple; Useful for baseline and screening studies.	In general, only provide monthly or weekly averages.	£5 - £45 per sample
Active Samplers	Low cost; Easy to operate; Reliable operation and performance; Historical dataset.	Provides daily averages; Labour intensive; Laboratory analysis required.	£1000 - £2000 per sampler unit
Automatic Analysers	Proven high performance; Hourly data; On-line information and low direct costs.	Complex; Expensive; High skill required; High recurrent costs.	£6000 - £10 000 per analyser
Remote and Long-Path Sensors	Provide path or range-resolved data; Useful near sources and for vertical measurements in the atmosphere; Multi-component measurements.	Complex and expensive; Difficult to calibrate and validate; Not always comparable with conventional analysers.	> £50 000 per sensor

2.4.1 Diffusion Tubes- Description and Major Principles

One of the main ways in which to carry out an air quality monitoring survey is to use a passive sampling method. The most popular of these, especially with regard to nitrogen dioxide, are diffusion tubes.

Diffusion tubes were first introduced and used by Palmes *et al*, in 1976, for sampling nitrogen dioxide in the field of occupational hygiene. The tubes were initially used for indoor experiments- particularly for studying the effects of gas cooking (Campbell *et al*, 1992). Diffusion tubes were then applied to outdoor measurements of nitrogen dioxide after the evaluation by Atkins *et al* in 1986.

A nitrogen dioxide diffusion tube consists of an acrylic tube, approximately 7cm long with an internal diameter of 1cm. The ends of the tube are machined to take close fitting polythene caps. Disks, comprising a fine stainless steel mesh are coated with triethanolamine (TEA) and placed at one end of the tube where they are help in position be a polythene cap. The triethanolamine acts as an absorbent for nitrogen dioxide, by absorbing it as nitrite. This cap is usually coloured to aid identification, whereas the cap at the other end is a colourless polythene cap. This colourless cap is removed just before sampling which allows nitrogen dioxide to diffuse along the tube towards the absorbent (Atkins *et al*, 1986). There are several advantages of using TEA as an absorbent:

- it captures nitrogen dioxide efficiently;
- it has a high viscosity and a low vapour pressure, which makes it possible to coat solid materials to give stable sampling surfaces;
- the TEA-NO_2^- ion complex is quite stable which means the trapped nitrogen dioxide can be stored for considerable periods prior to analysis (Cox, 1994; Palmes *et al*, 1976).

A diagram of a diffusion tube can be seen in Figure 2.1. The basic principle on which the diffusion tube sampler operates is that of molecular diffusion, where gas molecules diffuse from a region of high concentration (i.e. the open end of the tube) to a region of low concentration (i.e. the end of the tube which contains the absorbent). The movement of molecules of the first gas through the second gas is described by Fick's Second Law. This states that the flux is proportional to the concentration gradient. This is illustrated in the equation below:

$$F_1 \quad = \quad - D_{12}\, dc_1 / dz \qquad (2.1)$$

Where:

F_1 = the flux of gas (1) through gas (2) in moles $cm^2 sec^{-1}$

D_{12} = the molecular diffusion coefficient for gas (1) in gas (2) in $cm^2 sec^{-1}$

c_1 = the concentration of gas (1) in gas (2) in mol cm^{-3}

z = the length of the diffusion path in cm

For a cylinder of length z and cross-sectional area πr^2 with a concentration gradient (c_1 - c_2) molecule cm^{-3} between its ends, the quantity, Q_1, of gas (1) transferred along the tube in t seconds is given by:

$$Q_1 \quad = F_1 \pi r^2 t \quad = \quad - \quad D_{12} (c_1 - c_2) \pi r^2 t \ / z \qquad (2.2)$$

If the concentration c_2 is maintained at zero by the removal of gas (1) by an efficient absorbent, then:

$$Q_1 \quad = \quad - \quad D_{12}\, c_1\, \pi r^2\, t / z \qquad (2.3)$$

The negative sign in the equation arises from the measurement of flux in the direction of decreasing concentration of gas (1).

It can be demonstrated from the kinetic theory of gases that the temperature coefficient of diffusion is small and therefore can be ignored. There is also no pressure dependence (Atkins *et al*, 1986). For the gas monitored, the diffusion coefficient must be determined, or obtained from the literature. The area and the length of the tube are determined by measurement (Atkins *et al*, 1986). A theoretical diffusion coefficient (i.e. D) of nitrogen dioxide in air is generally taken as 0.154 cm^2s^{-1} (Campbell, 1988).

Therefore:

$$Q = -0.154\,(c_1)\,(0.92)\,t\,/\,7.5\ \text{mol} \qquad (2.4)$$

Where:

πr^2 = $0.92 cm^2$

z = 7.5 cm

As a result, in one hour (3600 seconds), the diffusion tube absorbs $72c_1$ mol of nitrogen dioxide (Equation 2.5). The negative sign can be ignored as it just represents the direction of the gas flux from the high to low concentrations:

$$Q = 72 * c_1\ cm^3h^{-1} \qquad (2.5)$$

Hence, the atmospheric concentration of nitrogen dioxide (Y ppb) can be shown to be:

$$Y = 7.3099\ WX\,/\,t \qquad (2.6)$$

Where:

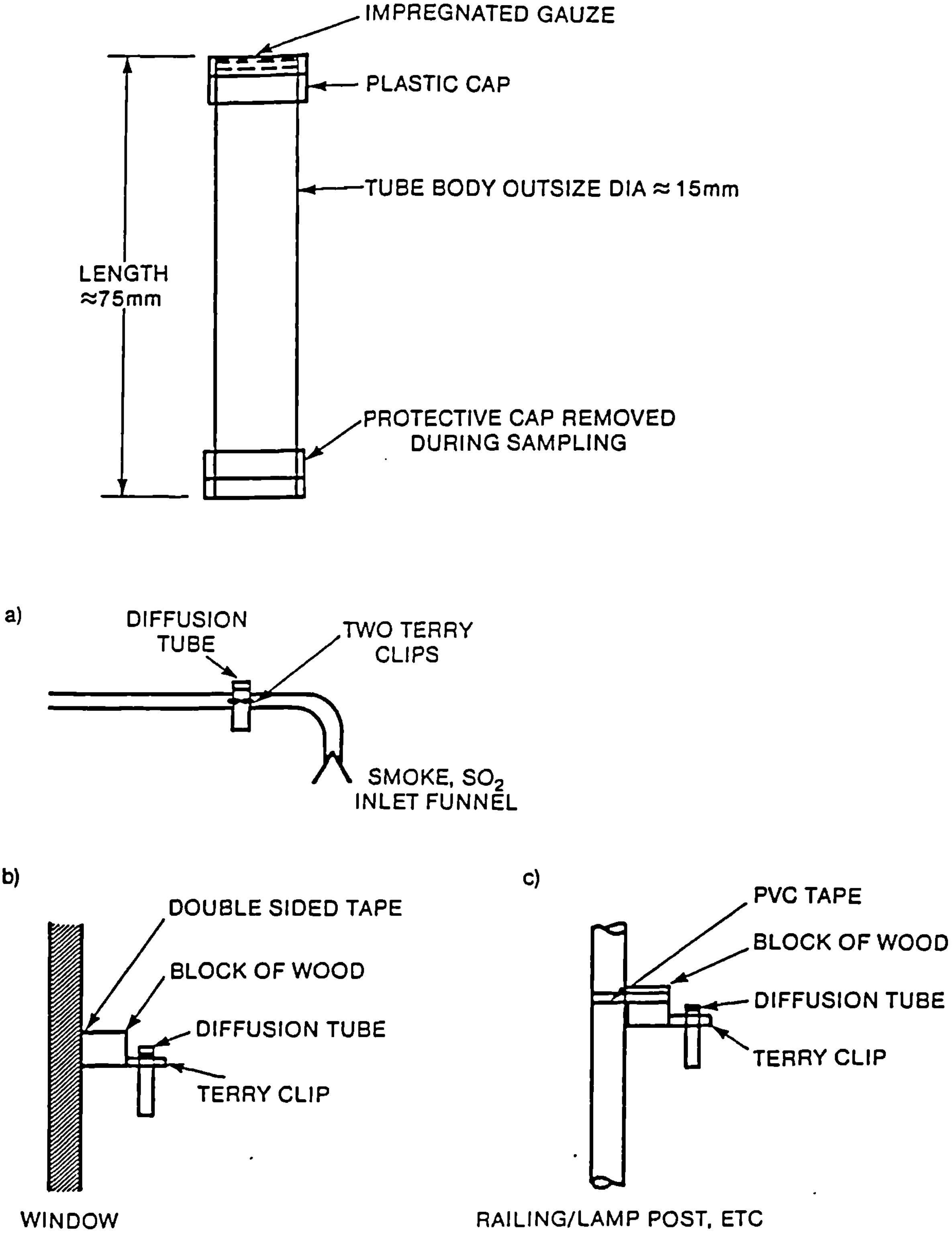
W = the volume of the solution used to dissolve the TEA (ml)

X = the concentration of NO^-_2 in the TEA (ppb)

t = the exposure time (h) (Gair *et al*, 1991)

Figure 2.1: Diagram of a Diffusion Tube

(Source: McGinlay *et al*, 1996)



2.4.2 Advantages and Disadvantages of Diffusion Tubes

There are several advantages to using diffusion tubes. Firstly, they are inexpensive to buy and use - especially in comparison with automatic monitors. Their principles are easy to understand and they are easy to use. They have great portability and are flexible in that they can be affixed to different types of sites, ranging from the sides of buildings, lamp-posts and even people (to assess personal exposure). In addition, they are very convenient to use in that they do not need a power supply or any protective housing.

However, that is not to say that they do not have any disadvantages. The main problem with diffusion tubes is that the only results that can be obtained from them are long-term averages, i.e. it is not possible to quantify any exposure less than a week in duration. As a result, it is not possible to construct diurnal profiles and any results obtained cannot be directly related to EC Air Quality Directives, since these require hourly measurements (UK QUARG I, 1993). They are less sensitive than continuous monitors. Diffusion tubes have a tendency to over-estimate levels of nitrogen dioxide because wind induced turbulence at the open end of the tube reduces the effective diffusion length (Harrison, 1996).

2.4.3 Continuous Monitoring Methods for Measuring Levels of Nitrogen Dioxide

Automatic analysers have been available for a couple of decades (Ashmore, pers. comm.). The most typical methods for determining concentrations of oxides of nitrogen are chemiluminescent monitors. The technique is specific to nitric oxide , but other nitrogen compounds can be measured if they can be converted to nitric oxide within the instrument. It is possible to measure nitrogen dioxide using this type of monitor, by first converting it to nitric oxide, thus producing a measurement of total NO_x. However, other nitrogen compounds (known as NO_y) can also be converted to nitric oxide within the monitor (albeit with varying degrees of efficiency, depending on the converter used). Nevertheless, interference from this is usually very low and so does not make the monitoring results too inaccurate. Chemiluminescent monitors have been adopted as the Reference Method of measurement of nitrogen dioxide in the Commission of the European Communities Directive on Air Quality Standards for Nitrogen Dioxide. They are also recommended for measuring nitrogen dioxide in the London Air Quality Network (Beevers, 1993).

The main principle behind chemiluminescent monitoring is specific to nitric oxide and is based on the detection of light emitted in the red part of the spectrum when nitric oxide reacts with ozone. When nitric oxide reacts with ozone, it gives an electronically excited nitrogen dioxide molecule (NO_2^*), which emits light in the 600-3000 nm region with a maximum intensity near 1200 nm:

$$\begin{array}{ll} NO + O_3 & (k_a) \rightarrow NO_2^* + O_2 \\ & (k_b) \rightarrow NO_2 + O_2 \\ NO_2^* & (k_c) \rightarrow NO_2 + h\nu \\ M + NO_2^* & (k_d) \rightarrow NO_2 + M \end{array} \qquad (2.7)$$

Where:

$M = (O_2 + N_2)$

k_a, k_b, k_c, k_d = reaction rates

In the presence of excess ozone (generated from within the instrument), the light emission varies linearly with the concentration of oxides of nitrogen from 1ppb to 10^4 ppb (Harrison, 1996). It can also be shown that the light intensity emitted from this reaction can be expressed in Equation 2.8:

$I = K\,[NO]\,[O_3]\,/\,[M]$ (2.8)

Where:

I = light intensity

$[NO]$ = concentration of nitric oxide in the instrument

$[O_3]$ = concentration of ozone in the instrument

$[M]$ = concentration of air inside in the instrument

K = rate constant

In order to maximise the light emission and therefore the response to nitric oxide, a high ozone concentration is employed and the instrument operates at low pressure. Commercial continuous monitors have a sensitivity from several ppt (parts per trillion) upwards.

As mentioned above, in order for nitrogen dioxide to be measured by the chemiluminscent technique, it must be converted to nitric oxide within the monitor. There are several methods with which to do this, outlined below:

- *Molybdenum at 300-400^{0}C*

  This is one of the most common converters to be found. These allow separate measurements of nitric oxide and nitrogen dioxide to be made, but there is a problem of NO_y conversion which, although occurs in small quantities, can interfere with the results.

- *The Photolytic Converter*

  This is where nitrogen dioxide is photolysed to give nitric oxide:

  $NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O$ (2.9)

  This has been shown to be a highly specific but not a quantitative way of measuring nitrogen dioxide after conversion to nitric oxide (UK PORG, 1990).

- *Ferrous Sulphate*

  A tube packed with crystals of ferrous sulphate will convert nitrogen dioxide to nitric oxide quantitatively, but again the problem of NO_y contamination exists- it has a particular affinity for converting peroxyacetyl nitrate (PAN). This is a problem at low nitrogen dioxide levels where the PAN concentration can be larger.

- *Gold at 300°C with Carbon Monoxide*

  A gold tube is heated to 300°C in the presence of carbon monoxide (0.3%) in the inlet air flow of the monitor. This will convert all NO_y compounds to nitric oxide (apart from ammonia and nitrous oxide). This method will therefore detect most reactive nitrogen compounds down to a few ppt. The main drawback with this method is that it is not specific, so other methods need to be employed in order to differentiate between the different species (UK PORG, 1990).

2.4.4 Calibration

Calibration is a very important part of the quality assurance and control (QA/QC) activities included in a monitoring programme. Quality assurance and control guarantees the quality of any data produced, ensuring it can be used with confidence. It is necessary to calibrate the volume or flow metering device and the sampling and analytical procedures. Before the instrument is calibrated, its conversion of nitrogen dioxide to nitric oxide should have a greater than 99 % efficiency. There are three main methods of NO_x monitor calibration and are collectively known as back-titration methods:

- *Standard Cylinders of Nitric Oxide*

This is the most common method of calibrating a NO_x monitor. Gas manufacturers, such as BOC, can supply cylinders containing a known concentration (usually between 100 and 1000 ppb) of nitric oxide. This is then introduced into the sampling system for a measured period of time. It is also possible to obtain standard cylinders of nitrogen dioxide for these purposes, but the nitrogen dioxide is not as stable as the nitric oxide.

- Permeation Tubes

These contain liquefied nitrogen dioxide which 'leaks' through a membrane at a constant rate when the tube is kept at a constant pressure and temperature. The rate of permeation is determined by weighing the tube at constant intervals. The nitrogen dioxide emitted is then mixed with a known flow of dilution air to produce a calibrated gas mixture.

- Gas Phase Titration

This is based on the reaction between nitric oxide and ozone. This is an effective technique which can be employed to relate ozone, nitric oxide and nitrogen dioxide primary standards. The nitrogen dioxide from the reaction can be measured on a calibrated nitrogen dioxide monitor or an end point for the titration can be detected by an ozone analyser (UK PORG, 1990).

2.4.5 Continuous Monitoring Methods for Measuring Levels of Ozone

The usual method for measuring levels of ozone is by ultra-violet (UV) absorption, and it is the method recommended by SEIPH for the London Air Quality Network. However, chemiluminescent monitors may be used as well. A description of the principles for each method can be found below:

- Chemiluminescent Monitoring

These types of monitors are based on the principle of the photometric detection of the chemiluminescence resulting from the gas-phase reaction of ethylene with ambient ozone:

$$C_2H_4 + O_3 \rightarrow \text{Products} + h\nu \qquad (2.10)$$

The ethylene for this reaction is usually provided from a gas cylinder and is mixed with air containing ambient ozone in a reaction chamber. The resultant photons are detected by a sensitive photomultiplier tube and converted into an analogue signal by electronic processing. Therefore, the resultant output is proportional to the light produced by the ozone-ethylene reaction. The degree of reaction is in turn proportional to the amount of ozone in the air sample. This technique is specific, has a rapid response and sufficient accuracy (i.e. greater than 99%) for ambient monitoring. This type of monitor must be calibrated against a known ozone concentration.

- Ultra Violet Absorption

These monitors make use of the intense ultra-violet absorption band of ozone. Ambient air and ozone-free reference air pass in sequence between an ultra violet light source and a sensitive detector. The instrument makes use of a mercury vapour lamp which determines the transmittance of ozone at 253.7 nm from the ratio of the intensity of light transmitted through the ambient air to that transmitted through reference air. The ozone concentration is determined using the Beer-Lambert absorption law, by using a microprocessor within the instrument.

The measurement is sensitive to temperature and pressure. To make the measurement as accurate as possible, temperature and pressure sensors can be placed within the instrument along with the microprocessor automatically adjusting for change in the value of the absorption coefficient.

This method of ozone monitoring is as specific and accurate as the chemiluminescent method, but it tends to have better specifications for zero and span drift. There is also no need for an ethylene gas cylinder.

2.4.6 Calibration

Ozone monitors are usually calibrated against an ozone source, whose concentration is determined by some absolute means. Often, an internal ozone generator is used as an instrument check between primary calibrations. There are two main methods:

- *Gas phase titration*

Gas phase titration makes use of the reaction between nitric oxide and ozone within a titration scheme. This can be done in two different ways. Either an end point for the titration is detected by an ozone monitor, or the nitrogen dioxide from the reaction is measured on a calibrated nitrogen dioxide monitor.

- *Ultra violet photometry*

Ultra violet photometry is based on the absorption of light by ozone at 253.7 nm. Some monitors are produced containing an ozone photometer. It is very important to know the photon flux from the lamp accurately and a stable power supply is required to ensure a continuous photon supply. It is difficult to determine the photon flux. A set of standard lamps is kept at a couple of laboratories in the United Kingdom (e.g. Harwell). This is one of the most accurate calibration methods for ozone monitors, but it is very difficult to carry out and so probably would not be the best method for a local authority to use.

2.4.7 Advantages and Disadvantages of Chemiluminescent and Ultra-Violet Absorption Monitors

The main advantage of these methods is that it is possible to measure peak concentrations, which is especially useful during an air pollution episode. It is also possible to measure diurnal concentrations and, as a result, construct profiles which can be useful for investigating the effects of meteorological factors and traffic flow on air quality. It is also easy to transfer the data to a central computer, ready for analysis, through a logger or telemetry.

However, there are also disadvantages associated with these methods. The monitors themselves are expensive to buy and maintain (see Table 2.3). They can be temperamental and breakdown easily, due to their delicate components. The places at which they can be sited are more limited than with passive monitoring methods since they require a power supply, air conditioning and security. They also need regular visits and calibration by trained personnel.

2.5 Types of Monitoring Site

Next to the monitoring method and equipment, the choice of monitoring site is one of the most important factors to consider when carrying out an air quality assessment. There are four main categories of site, which are described below:

a) Kerbside (also known as Roadside sites)

These sites generally give the highest pollutant concentrations (from vehicle emissions). Samples are usually taken between 1 and 3 metres from the roadside and 2 metres above ground level. Results from these sites show the typical pedestrian exposure and can highlight a specific problem. It must be clear that the site is representative of reasonable numbers of people, from pedestrians to cyclists, before the site is chosen.

b) Urban Background

This is a site where substantial numbers of people spend a considerable amount of time and where relatively high ambient pollutant concentrations exist. A typical example of this would be a site in a shopping precinct surrounded by busy roads (Beevers, 1993).

c) Suburban

These are categorised between urban background and rural sites. They represent residential sites on the edges of urban areas. They can be very useful to determine human exposure to air pollutants since large numbers of people live in these areas.

d) Rural

These should not be found within 100 metres of any pollutant source or anywhere near a building with a localised air circulation. They are also known as 'green field' sites and they are especially useful for monitoring ozone, especially from long-range transport. Ozone is a secondary pollutant known to occur at elevated concentrations in rural areas.
(Source: Beevers, 1993).

It is important to cover a range of different types of sites, especially if a monitoring network is being set-up. However, if due to financial or time limitations it is not possible to have every type of site represented, then, the type of site chosen should complement the objectives of the survey. Table 2.4 below shows the relationship between monitoring objectives and types of site:

Table 2.4: The Relationship Between Monitoring Objectives and 'Scales of Representativeness'

(Source: Beevers, 1993)

Monitoring Objective	**Appropriate Siting Scale**
Highest Concentration and Source Impact	Kerbside 0 – 100 metres Urban 100 – 500 metres Suburban 0.5 – 4 km
Greatest Population Exposure	Suburban, urban area conditions
General / Background	Suburban, rural 10 – 100 km

2.6 Air Quality Survey in South Kensington, London - Introduction and Aims

Over the last four years, many local authorities have set up their own air quality monitoring projects. This has even more importance now, with the introduction of the 1995 Environmental Act. This part of the chapter has a number of aims:

- to determine the spatial distribution of nitrogen dioxide, using diffusion tubes and to consider how spatial variability will affect monitoring strategies;

- to determine the temporal variation of nitrogen dioxide and ozone, along a vertical profile, using continuous monitoring equipment;

- to compare the two different monitoring methods used, in terms of such factors as ease of use.

2.7 Investigation of the Spatial Variability of Nitrogen Dioxide Around Imperial College Campus, South Kensington, London

2.7.1 Introduction

The aim of this part of the study was to carry out a simple investigation of the spatial variability of nitrogen dioxide around the Imperial College campus in South Kensington. This was done by selecting a wide variety of sites. Nitrogen dioxide diffusion tubes were chosen as the monitoring method. This is because it afforded the opportunity for the author to explore this methodology and understand the underlying principles behind an air quality survey. The other advantages of using diffusion tubes have been covered previously, in Section 2.4.2.

This part of the study was further sub-divided into two smaller projects:

- The Preliminary Experiment

This was carried out between October and December 1993. The aim of this was to become familiar with the technique of preparing and analysing diffusion tubes. The second aim was to investigate the reproducibility of the tubes.

- The Spatial Variability Experiment

Diffusion tubes were placed at a total of fifteen sites around the campus of Imperial College and surveyed over the winter and early spring of 1994. The aim of this experiment was to determine if there was any variation in levels of nitrogen dioxide along a series of transects.

2.7.2 Methodology

2.7.2.1 Site Location

- Preliminary Experiment

As the aim of this experiment was familiarisation with the monitoring technique, three sites were chosen. These were chosen with regard to the likelihood of there being different levels of nitrogen dioxide at each site. Care was taken to ensure that the sites were in a generally open area, thus avoiding any localised sources of nitrogen dioxide, or disturbances to the air flow.

The site are described as follows:

1. Intermediate Site (i)- Prince Consort Road:

Prince Consort Road is a single-lane, two-way street. The tubes were affixed at the top of the Biology Department Building (West Wing). The tubes were vertical. They were fixed to the roof, five stories up, on the side of the building facing towards Prince Consort Road. This is shown in the map in Figure 2.2:

Figure 2.2: Map of South Kensington, Indicating Diffusion Tube Sites

2. Intermediate Site (ii)- Prince's Gardens:

Prince's Gardens is a narrow, single-lane street which leads onto Exhibition Road. It is mainly used as a service road. The tubes were fixed (vertically) to a first floor balcony on the ICCET Building, on the side of the building facing towards Prince's Gardens.

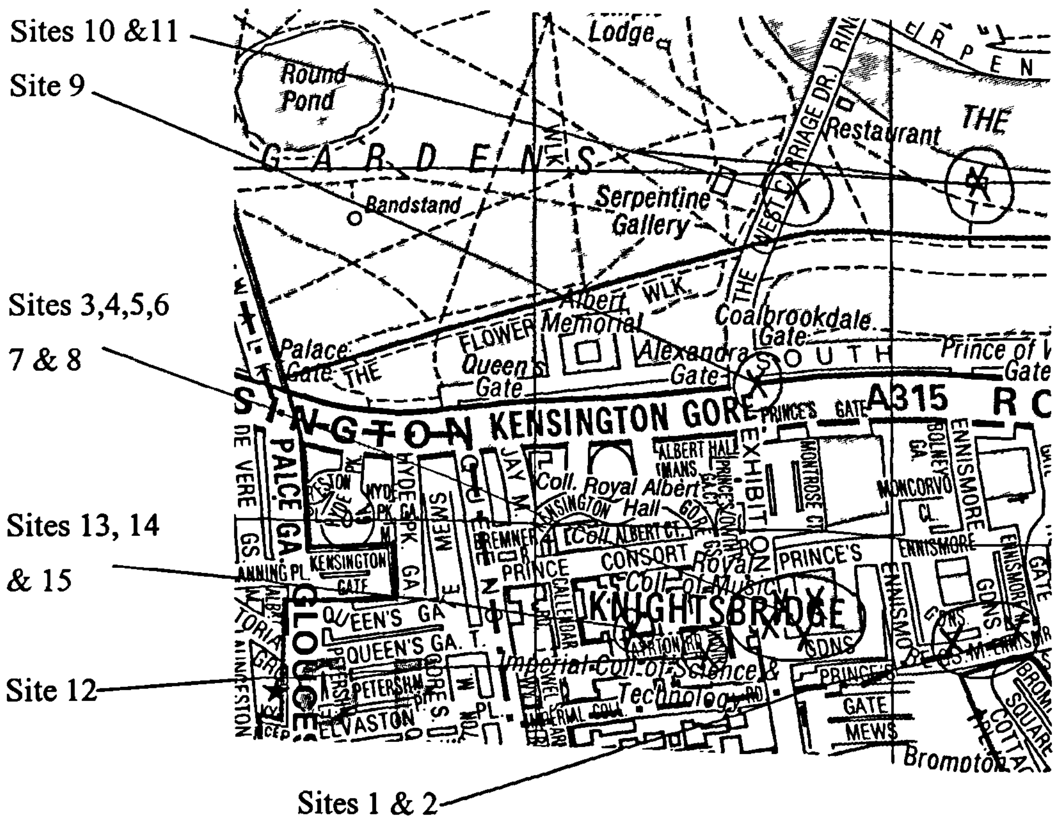
3. Roadside Site- Exhibition Road:

Exhibition Road is a busy, double-lane, two-way street. The tubes were fixed (vertically) to a first floor balcony, on the side of the building facing out into the street.

- The Spatial Variability Experiment

Three transects were set up. Two were along horizontal scales and one was along a vertical scale. The transects are shown in Figure 2.3:

Figure 2.3: Map Indicating Diffusion Tube Sites



Sites 10 &11

Site 9

Sites 3,4,5,6
7 & 8

Sites 13, 14
& 15

Site 12

Sites 1 & 2

There were fifteen sites in total. Descriptions of the sites are summarised in Table 2.5:

Table 2.5: Site Description and Summary

Site Number	Site Name	Site Category*	Site Description
1	Ennismore Arms (in Ennismore Mews)	Intermediate	Single lane mews, very little through traffic- quiet. Tube affixed to pub wall.
2	Brompton Mews	Intermediate	Single lane mews, very little through traffic- quiet. Tube affixed 2m up a signpost.
3	Prince's Gardens	Intermediate	Small green open space, off Exhibition Road. Tube affixed in the middle of Gardens.
4	Management School (i) (Exhibition Road)	Roadside	Exhibition Road is a busy, double-lane, two-way street. Tube affixed to a first floor balcony facing out into the street.
5	Management School (ii) (Prince's Gardens)	Intermediate	Small green open space, off Exhibition Road. Tube affixed to Management School Wall at ground level, facing into the Gardens.
6	Management School (iii) (Exhibition Road)	Roadside	Exhibition Road is a busy, double-lane, two-way street. Tube affixed to Management School wall at ground level, facing into the street.
7	ICCET (Prince's Gardens)	Intermediate	Prince's Gardens is a narrow, single-lane street, which leads onto Exhibition Road. No through traffic. Tube affixed to ICCET fence at ground level, facing into Prince's Gardens.
8	Exhibition Road	Roadside	Exhibition Road is a busy, double-lane, two-way street. Tube affixed approximately 2m up, on signpost on central island.
9	Hyde Park Traffic Lights	Roadside	Traffic lights situated at the junction of Kensington Road and West Carriage Drive. Both busy, double-lane, two-way streets. Tube affixed to traffic lights, approximately 2m up.
10	Serpentine Cafe (Hyde Park)	Background	Tube affixed approximately 2m up, on cafe wall. In green, open space, approximately 50m away from road or car park.
11	Hyde Park Road	Roadside	Hyde Park Road is a busy, double-lane, two-way street. Tube affixed approximately 2m up, on lamp-post at roadside.

Table 2.5 (continued)

Site Number	Site Name	Site Category*	Site Description
12	Imperial College, Parking Attendant's Hut	Roadside	Tube affixed at breathing height on parking attendant's hut at the entrance of Imperial College's car park (off Exhibition Road)
13	Queen's Tower (i)	Vertical	The Queen's Tower is a tall column situated in approximately the middle of the Imperial College. Tubes were affixed to the outside of the Tower about 20m up.
14	Queen's Tower (ii)	Vertical	The same as 13, except the tubes were affixed 65m up.
15	Queen's Tower (iii)	Vertical	The same as 13 and 14, except the tubes were affixed 70m up.

* Site categories based on those in Stevenson *et al*, (1997)

2.7.2.2 Diffusion Tube Preparation

As explained above in Section 2.4.1, diffusion tubes were chosen as the monitoring method for this set of experiments. They were supplied by Gradko International Ltd. The diffusion tubes were prepared based on the protocol outlined in Gair *et al*, 1991. However, a protocol is also outlined in Atkins *et al*, 1986.

The tubes were thoroughly cleaned before use. Each tube was separated into its component parts (i.e. the clear plastic tubes, meshes and caps) and thoroughly washed in two changes of distilled water and one change of Analar™ (highly purified) water. The tubes were subsequently handled at all times with forceps or gloved hands during the remainder of the preparation.

Each component was then dried in an oven, set at 40° C, for between one and two hours. Once dried, the meshes were placed carefully in the coloured caps (two meshes to one cap).

The absorbent, triethanolamine (TEA) solution, was made up by placing 5ml of TEA in a volumetric flask and making it up to 25ml with Analar™ water. Using a microsyringe, 250 μl of surfactant was added to the solution in the flask in order to prevent the solution drying out during tube exposure. The flask was then shaken vigorously to ensure the contents were well mixed. The meshes in the caps were then covered with 150 μl of the TEA solution (3 drops), again using the microsyringe. Once all the meshes were coated with solution, the tubes were assembled and tightly capped with the colourless cap. The tubes were then placed into plastic bags, which were then sealed and kept in a freezer until the tubes were to be used. This was done to avoid exposure of the tubes to contamination before they were used. It is estimated that, once prepared, the tubes have a life time of six weeks (Atkins *et al*, 1986). However, experience has shown that blank tubes can be kept in a freezer for several months without any detrimental effect on the tubes performance (Marsh, pers. comm.). It is advisable though, that the tubes are used as soon as possible after preparation.

2.7.2.3 Diffusion Tube Exposure

Two tubes were put up at each site, in order to test the reproducibility of the results. At some sites, three tubes were put up. The colourless cap was not removed from these third tubes because they were acting as controls. In theory, as these tubes were not exposed, they should ideally give a concentration of zero ppb.

At each site, the tubes were mounted vertically, with the coloured cap uppermost. They were attached to lamp-posts, the poles of road-signs, mesh fences and balcony balustrades. They were fixed as to ensure free air flow around the tube. The tubes were attached by means of terry clips. The tubes were always affixed between 2 and 3 metres high, for the horizontal transects. Ideally, they should have been fixed at breathing height, but vandalism becomes a problem when the tubes are placed at this height (Kirby, 1993).

Once the tubes were in place, the colourless cap was then removed in order to expose the tube to any nitrogen dioxide present. The exposure time was one week for the tubes in the Preliminary Experiment and the Spatial Variability experiment. The tubes were carefully labelled to aid identification and they were exchanged on the same day, noting down the exposure time.

2.7.2.4 Diffusion Tube Analysis

Once the tubes were collected they were placed in plastic bags, sealed and placed in a freezer to await analysis. This avoided any contamination of the tubes. It was advised that the tubes were analysed within 3 months of their exposure.

There are several tried and tested methods of analysing diffusion tubes. They include spectroscopy and chromatography. It was decided to use colorimetry which is a type of spectroscopy. The analysis is based on the Beer-Lambert Law:

$$\mathrm{Lg}\ I_0/I = elc \qquad (2.11)$$

Where:

I_0 = intensity of incident radiation

I = intensity of transmitted radiation

l = path length (m)

c = concentration (mol m^{-3})

e = molar absorption coefficient (m^2 mol^{-1})

This relates absorbance with concentration, thus enabling the concentration of a known species in solution to be determined. Colorimetry was chosen because it is more sensitive for nitrite than ion chromatography and is less complex to use. A description of the basic method can be found in Laxen *et al*,(1987). The reagent contained sulphanilamide as the diazotisable aromatic amine and N-(1-Naphthyl)-ethylenediamine dihydrochloride as the coupling reagent was used to determine the concentration of nitrite in each tube (Ames, pers. comm.). The colorimeter was calibrated using a series of standard solutions. The final concentrations were calculated by using the calculations outlined in Gair *et al*, 1991. These are reported in Section 2.4.1.

2.7.3 Results

The results for each set of experiments will be treated in turn.

-The Preliminary Experiment

The results are summarised in Table 2.6 below:

Table 2.6: Nitrogen Dioxide Levels Recorded at Three Different Sites Around the Imperial College Campus, South Kensington

Experiment No.	Site Name	NO_2 (ppb) Tube 1	NO_2 (ppb) Tube 2	NO_2 (ppb) Tube 3	NO_2 (ppb) Tube 4	NO_2 (ppb) Control
1	Prince Consort Road	40.4	47.1	43.2	35.7	10.9
	Prince's Gardens	37.2	42.2	36.7	43.7	3.5
	Exhibition Road	34.3	47.1	57.5	42.7	0
2	Prince Consort Road	46.6	39.7	35.7	44.6	0
	Prince's Gardens	37.7	44.2	42.2	45.1	0
	Exhibition Road	31.3	43.7	51.6	45.6	0

- The Spatial Variability Experiment

The results are summarised in Table 2.7 below:

Table 2.7: Average Nitrogen Dioxide Levels (ppb) Recorded at Fifteen Different Sites Around the Imperial College Campus, South Kensington

Site No.	**Site Category**	**Expt. 1** (Exposure-13th-20th January)	**Expt. 2** (Exposure-10th-17th February)	**Expt. 3** (Exposure-2nd-9th March)	**Expt. 4** (Exposure-16th-23rd March)	**Expt. 5** (Exposure-4th-11th April)
1	Intermediate	30.8	31.7	36.2	31.0	25.3
2	Intermediate	35.2	45.6	36.0	43.7	30.5
3	Intermediate	26.3	37.7	35.7	47.6	34.5
4	Roadside	TUBE LOST	46.8	49.1	37.5	32.0
5	Intermediate	34.2	42.9	38.2	30.8	24.8
6	Roadside	30.8	41.7	37.2	25.8	29.0
7	Intermediate	42.2	43.7	42.7	40.0	38.7
8	Roadside	63.2	60.0	62.0	50.0	49.1
9	Roadside	33.7	58.7	52.3	75.2	TUBE LOST
10	Background	31.2	54.5	37.3	33.2	29.5
11	Roadside	41.9	41.2	44.7	45.2	37.7
12	Roadside	46.6	40.4	59.7	43.9	30.8
13	Vertical	57.0	NO TUBE*	NO TUBE*	NO TUBE*	NO TUBE*
14	Vertical	43.9	NO TUBE*	NO TUBE*	NO TUBE*	NO TUBE*
15	Vertical	24.6	NO TUBE*	NO TUBE*	NO TUBE*	NO TUBE*

*** There is only one set of results for the Queen's Tower because access was denied for three months**

2.7.4 Discussion

- The Preliminary Experiment

One of the aims of this experiment was to see whether tubes placed at the same site would give readings within a couple of ppb of each other. However, it can be seen in Table 2.7 that the difference between the minimum and maximum readings in the first experiment for Prince Consort Road, Prince's Gardens and Exhibition Road are 11.4, 7.0 and 23.2 ppb respectively for the first experiment and 10.9, 7.4 and 20.3 for the second. Prince's Gardens has the best reproducibility and Exhibition Road has the worst.

There are several possible reasons for this. Although much care had been taken to ensure that each tube received the same dose of TEA, there could have been small differences which would contribute to the different levels observed. Differences may be due to variations in the microclimate which could affect the diffusion of nitrogen dioxide into the tube (UK QUARG I, 1993). It has already been established that when wind passes across the mouth of the tube, it reduces the path length down which the gas can diffuse, which may have some bearing on the results (Marsh, pers. comm.). In addition, particles can be deposited inside the tube which can influence the analysis. Sulphate and ammonium particles can be a problem for sulphur dioxide and ammonia but nitrate particles are not in general. The poor reproducibility may also have been due to imperfections in the colorimetric analysis system, which was still being developed at that time (Marsh, pers. comm.). It is possible to get air bubbles in the tubing which would give a higher signal than would be expected. However, the main reason was most likely to the short exposure time. It is usual to expose diffusion tubes from two weeks to a month. However, in this experiment, an exposure time of one week was tested. The disadvantage of using such a small exposure time is that a smaller signal is obtained from the tube during analysis. Therefore, a small error in the signal can be compounded to a large difference in concentration, if the signal itself is small.

Overall, these results would suggest that the reproducibility between tubes is not consistent and therefore this should be taken into consideration when analysing for nitrogen dioxide levels.

There was substantial contamination of the blank (control) tubes. This was rectified in the second experiment where no contamination was recorded. This was due to the use of a larger type of cap for the tube. However, this type of contamination has been found in another study (Gair *et al*, 1991), and concluded that this is insignificant in urban areas, where nitrogen dioxide levels are high, but could be significant in rural areas where nitrogen dioxide levels were low. This study also concluded that in order to minimise contamination, tubes should be stored in a freezer prior to analysis and analysed as soon as possible after exposure. This was carried out with all diffusion tube experiments within this project.

It is also interesting to note that there is little variation in nitrogen dioxide levels between the three different sites. Average concentrations in the first experiment for Prince Consort Road, Prince's Gardens and Exhibition Road are 41.6, 39.9 and 45.4 ppb respectively for the first experiment and 41.6, 42.3 and 43.0 for the second. There is not more than a 5 ppb difference between the sites although two of them are intermediate and one is a roadside site. The roadside site does show a slightly higher concentration of nitrogen dioxide than the intermediate sites which would be expected since that site is nearer to the source of nitric oxide, from which nitrogen dioxide is formed, than the other two sites.

There are a couple of possible reasons that there is so little variation between the levels of nitrogen dioxide recorded at the different sites. The first is that of the choice of monitoring sites. The three sites were spread over a very small scale (less than a quarter of a mile apart). Therefore it could be that the scale was too small to show any differences in nitrogen dioxide levels. The other reason is that nitrogen dioxide is primarily a secondary pollutant and therefore is more evenly distributed than primary pollutants, which have their highest concentrations closest to the point of emission. It is also impossible to determine any trend in nitrogen dioxide distribution on the basis of just two, week-long, experiments. However, this was not the aim of the experiment, as it was intended to be a familiarisation exercise.

- The Spatial Variability Experiment

In this section, broad trends from the data will be examined first and then some more specific points will be picked out. These will be observed empirically, rather than in a quantitative manner as the exposure period was too long to be able to identify any significant weather effects. This would be more appropriate to continuous monitoring data and has been explored in a number of surveys, such as the annual reports of the London Air Quality Network (Beevers *et al*, 1994, 1995; Barratt *et al*, 1996). This survey was carried out to observe the spatial variability of nitrogen dioxide and to determine the direction of the next stage of the project.

This experiment was carried out for a longer period of time and over a wider area than the previous experiment. There is more variation in levels between the different sites than in the previous experiment. If the roadside results are separated out from the intermediate results, as shown in Table 2.8 and Table 2.9, the following observations can be made:

Table 2.8: Average Nitrogen Dioxide Levels (ppb) Recorded at the Intermediate Sites Around the Imperial College Campus, South Kensington

Site No.	Site Category	Expt. 1 (Exposure-13th-20th January)	Expt. 2 (Exposure-10th-17th February)	Expt. 3 (Exposure-2nd-9th March)	Expt. 4 (Exposure-16th-23rd March)	Expt. 5 (Exposure-4th-11th April)	Mean NO_2 Level (ppb)
1	Intermediate	30.8	31.7	36.2	31.0	25.3	31.0
2	Intermediate	35.2	45.6	36.0	43.7	30.5	38.2
3	Intermediate	26.3	37.7	35.7	47.6	34.5	36.4
5	Intermediate	34.2	42.9	38.2	30.8	24.8	34.2
7	Intermediate	42.2	43.7	42.7	40.0	38.7	41.5
	Average	33.7	40.3	37.8	38.6	30.8	36.2

Table 2.9: Average Nitrogen Dioxide Levels Recorded at the Roadside Sites Around the Imperial College Campus, South Kensington

Site No.	Site Category	Expt. 1 (Exposure-13th-20th January)	Expt. 2 (Exposure-10th-17th February)	Expt. 3 (Exposure-2nd-9th March)	Expt. 4 (Exposure-16th-23rd March)	Expt. 5 (Exposure-4th-11th April)	Mean NO_2 Level (ppb)
4	Roadside	TUBE LOST	46.8	49.1	37.5	32.0	41.3
6	Roadside	30.8	41.7	37.2	25.8	29.0	32.9
8	Roadside	63.2	60.0	62.0	50.0	49.1	56.9
9	Roadside	33.7	58.7	52.3	75.2	TUBE LOST	55.0
11	Roadside	41.9	41.2	44.7	45.2	37.7	42.1
12	Roadside	46.6	40.4	59.7	43.9	30.8	44.2
	Average	43.2	48.1	50.8	46.3	35.7	45.2

It can be seen that on the whole, the roadside sites exhibit higher nitrogen dioxide concentrations than the intermediate sites. The overall average values for this set of experiments is 36.2 ppb of nitrogen dioxide for the intermediate sites and 45.2 ppb for the roadside sites. Again, this is due to the roadside sites being nearer the source of nitric oxide than the intermediate sites.

However, there is no obvious trend between the different months. Generally, it would be expected that concentrations of nitrogen dioxide are highest in the winter due to higher emissions of NO_x and meteorological conditions leading to a greater number of inversions. Although this experiment only ran for the first four months of the year, it would be expected that higher concentrations of nitrogen dioxide would be recorded in January and lower levels in March and April. Nevertheless, there is no trend observed. This could be due to the experiment only lasting four months, making it impossible to identify any trends with such a small data set. However, there is usually little seasonal change observed on nitrogen dioxide concentrations because although there are higher emissions in the winter, there is less ozone available to oxidise the nitric oxide to nitrogen dioxide (UK QUARG I, 1993). A study by Campbell (1988) demonstrated that nitrogen dioxide levels were subject to less variation in urban areas than in rural areas.

The busiest roads in this survey, such as Exhibition Road and the junction of Kensington Gore with Hyde Park show some of the highest levels of nitrogen dioxide, as shown in Table 2.9. In a traffic survey conducted in the Royal Borough of Kensington and Chelsea (1993), Exhibition Road was ranked as the 14th busiest, out of 59 roads surveyed (Royal Borough of Kensington and Chelsea, 1993). However, it should be noted that the levels in Hyde Park Road are lower than those in Exhibition Road. This is probably because Hyde Park Road is open, whereas Exhibition Road is lined by buildings, giving rise to street canyons and effects on dispersal. Therefore, nitrogen dioxide will be able to disperse easily away from Hyde Park Road, whereas it will be trapped in the Exhibition Road canyon.

One of the most interesting features of the survey was the vertical variation of the nitrogen dioxide concentration as measured at differing heights up the Queen's Tower. The results in Table 2.7 show that nitrogen dioxide concentrations decrease significantly with height. This is most likely to be because as the vertical height increases, the distance away from the emissions of nitrogen dioxide precursors increases. However, there was still nitrogen dioxide present 70 metres above the road and therefore it was decided to explore this area in more detail. The work done to explore this area can be found later on in Chapter 2 and in Chapter 5.

It is not possible to determine directly whether any of the sites exceeded the EC Nitrogen Dioxide Directive since a year's worth of data is required in order to carry out the analysis. The Directive is based upon the 98th percentiles of annual average concentrations and therefore a year's data is needed. It is also not possible to compare the data with any of the other standards because these require hourly and daily means, which are not possible to obtain from diffusion tube data. This is a limitation of using diffusion tubes because a year's worth of data is needed to determine whether a site is exceeding a nitrogen dioxide standard or not. However, there is a way of indirectly comparing less than a year's worth of diffusion data with the EC Nitrogen Dioxide Standard. It has been shown that a factor of approximately 2.5 exists between the annual average concentrations and the 98th percentile value (Campbell *et al,* 1992). However, it should be realised that the actual factor is site specific and may lie between 2 and 3. The factor of 2.5 can be applied to the nitrogen dioxide concentration obtained from the diffusion tube data in order to calculate the 98th percentile. This can then be directly compared with the Directive.

In order to make a comparison with this adjusted value for the annual average and hence make an estimate of whether any of the sites exceed the EC Directive, the concentrations for each site over the period of monitoring were averaged and the results are shown in Table 2.10:

Table 2.10: Comparison of Diffusion Tube Results With the EC Directive for Nitrogen Dioxide

Site Number	Site Category	Average NO_2 Concentration (ppb)	2.5 * NO_2 Concentration (ppb)	Exceedence of EC Directive (based on adjusted annual average)
1	Intermediate	31	77.5	no
2	Intermediate	38	95	no
3	Intermediate	36	90	no
4	Roadside	41	102.5	no
5	Intermediate	34	85	no
6	Roadside	32	80	no
7	Intermediate	41	102.5	no
8	Roadside	57	142.5	yes
9	Roadside	54	135	yes
10	Background	37	92.5	no
11	Roadside	42	105	yes
12	Roadside	44	110	yes

It can be seen from using this factor of 2.5 therefore, that four of the sites would exceed the EC Directive Limit Value of 104.6 ppb. This is not definite as a year's data is needed to make a proper comparison, but it does serve as a very useful indication. It should also be noted that these results were mainly collected during the winter when levels of nitrogen dioxide are higher. This may have lead to a slight overestimation of the adjusted annual average. It is interesting to note that all the sites that would exceed the value are roadside sites. This is because these sites are closest to the sources of nitric oxide emissions and hence, nitrogen dioxide formation, and therefore have the greatest exposure.

2.7.5 Conclusions

This survey went some way to illustrate the differences in nitrogen dioxide levels at different sites. Firstly, levels of nitrogen dioxide differed with proximity to busy roads, with the highest levels being recorded at the roadside sites. However, levels of nitrogen dioxide did not differ as much as expected. There was a relatively uniform distribution within the area surveyed, compared with a primary pollutant such as nitric oxide which has elevated concentrations near a source of emission such as a power station or a roadside (UK QUARG I, 1993).

On the whole it was difficult to identify any trends with such a short-term experiment. It has been estimated that a dataset encompassing at least three years is needed to identify any long-term changes in the state of the air quality. This is especially important if diffusion tubes are exposed monthly, therefore only giving twelve readings for the year. A one year survey is adequate if monthly changes are to be observed and to obtain a general picture of the air quality, but these should really be compared with the air quality in other years.

The observation of most interest was the vertical distribution of nitrogen dioxide. On examining the literature, it was found that there have been very few studies in this area. Examples are Laxen *et al*, (1987) and the two studies reviewed in the first (interim) UK PORG report (1987). Therefore it was decided to expand this area of the project and investigate in some detail the vertical distribution of nitrogen dioxide. This is explored and reported in detail in Section 2.8. In order to be able to study episodes, it is important that the pollution processes are understood. Therefore it is important to investigate pollutant behaviour on the vertical as well as the horizontal scale.

2.8 Investigation of the Vertical Distribution of Nitrogen Dioxide and Ozone

2.8.1 Introduction

The aim of this part of the study was to carry out an investigation of the vertical distribution of nitrogen dioxide. It was also decided to include ozone monitoring in the survey. Although the investigation is primarily involved with nitrogen dioxide, ozone is very closely associated with it, as explained in Chapter 1. The distribution of ozone in urban areas is complex. Levels are generally lower over urban areas than rural areas. This is because the greater concentrations of nitric oxide present in urban areas react with the ozone to form nitrogen dioxide, thus depleting ozone levels over cities.

In addition, there have been very few studies of the vertical distribution of ozone above urban areas. There have been two which are documented in the first PORG report (1987). These showed that, during the day, there was a well-mixed atmosphere with no gradient, but at night-time there was ozone depletion below inversions at about 200 m (UK QUARG I, 1993). It was hoped that this survey would provide some more insight into the vertical distribution of ozone, where the results from the previous studies would be backed up, or to determine the existence of an ozone gradient during the day. It was decided to try and run the experiment over as many months as possible, firstly in order to investigate any seasonal variations on both ozone and nitrogen dioxide and secondly, to try and capture data from any pollution episodes that might develop.

A continuous monitoring method was chosen for this survey. The instruments were lent by the Atmospheric Chemistry Research Unit at Silwood Park, Berkshire. This was done, again, for the opportunity to explore another air quality monitoring method and become familiar with it. Diffusion tubes were also found, in the previous experiment, to have their limitations. It was not possible, for example, to compare any of the results with air quality standards and data such as hourly averages and diurnal profiles were not available. As a result, it was not possible to get as much out of the results as was desirable.

The main advantage of using continuous instruments is that it is possible to obtain very detailed datasets in 'real time', which enable a clear picture of the air quality to be built up. There is also no chemical analysis needed after monitoring to determine the results, therefore the results can be obtained almost immediately.

Due to the limitations imposed by availability of equipment and suitable sites, one site was initially chosen and another was added during the course of the survey. The survey is described in detail in the subsequent sections.

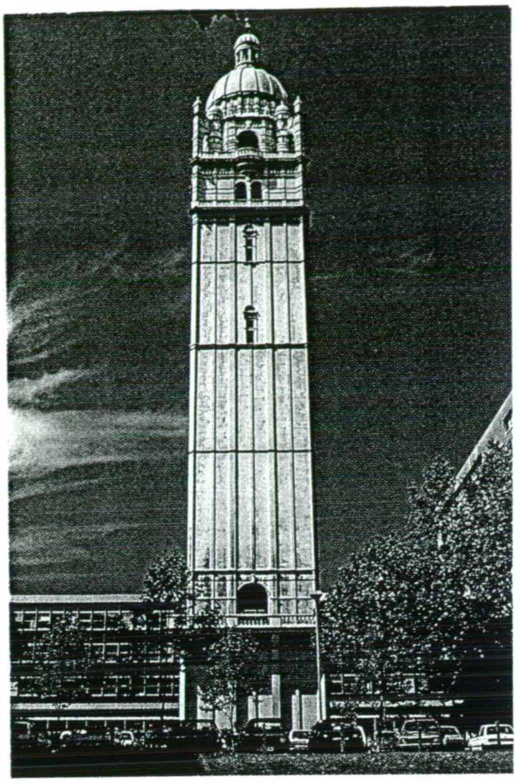
2.8.2 Methodology

2.8.2.1 Site Location

The aim of this experiment was to investigate air quality along a vertical scale. It was decided to use the same site as was used in the diffusion tube survey and set the instruments up in the Queen's Tower. In order to make the most of the survey, it would have been advantageous to find other sites suitable to determine vertical distribution in a number of areas. However, due to instrument availability, financial constraints and difficulties of obtaining permission, it was decided to confine the survey to the one site.

The Queen's Tower is a tall column situated approximately in the centre of the Imperial College campus, South Kensington, in the west of London. It is situated between Exhibition Road and Queen's Gate. A picture of the Tower is shown in Figure 2.4.

Figure 2.4: The Queen's Tower, Imperial College, South Kensington



Prior to the setting up of the instruments, the Tower was examined thoroughly in order to find suitable sites. Originally, it would have been ideal to set up a site on every floor of the Tower to get as detailed a profile as possible. However, this proved to be impractical for a number of reasons. A power supply is needed to run continuous instruments and while the Tower has an electricity supply, it does not have power sockets on every floor. Therefore, an instrument could only be set up on the floors with power sockets. As a result, there were only two floors that were suitable. These were at the heights of 20 metres and 65 metres above street level. In addition, both these floors have windows through which a sample inlet can be threaded through to sample the air outside. Both floors were enclosed within the Tower with the advantage that the instruments would not be exposed to the weather outside.

The main disadvantage of the site was that access was limited. Access could only be obtained between the hours of 10am and 5pm, Monday to Friday. It was also not possible to go up the Tower alone, for safety reasons. Access was denied completely on few occasions due to maintenance work.

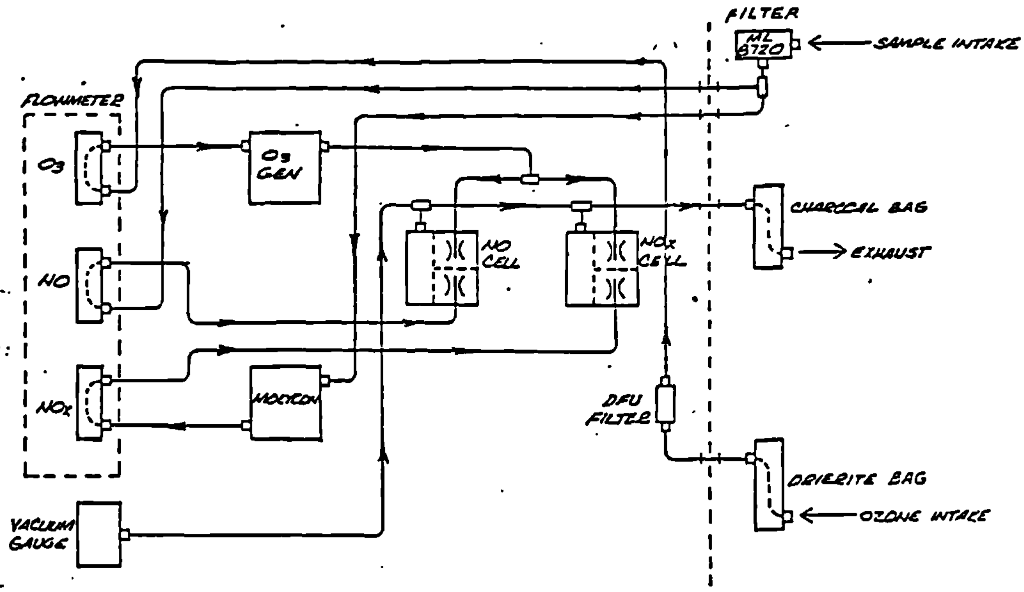
2.8.2.2 Instrumentation

As explained earlier, it was decided to use automatic continuous instruments for this monitoring survey. They were supplied by the Atmospheric Chemistry Research Group at Silwood Park. Several types of instrument were used throughout the survey and they are described in turn, below:

- Oxides of Nitrogen Monitoring Instruments

A Nitrogen Oxides Analyser (Model 8840), supplied by Monitor Labs was used to measure levels of nitric oxide, nitrogen dioxide and total NO_x at both the upper and lower Queen's Tower sites. A simplified block diagram of the instrument can be seen in Figure 2.5. It is a gas-phase chemiluminescence-detection device which performs a continuous gas analysis of total NO_x, nitric oxide and nitrogen dioxide. Its operation is based on the chemiluminescence of an activated nitrogen dioxide species, produced by the chemical reaction between ozone and nitrogen dioxide, as explained in detail in Section 2.4.3. A photomultiplier tube measures the chemiluminescent emission intensity. All the readings are produced in real time.

Figure 2.5: Block Diagram of the Nitrogen Oxides Analyser



A sampling inlet, in the form of tubing, was connected to the instrument in order to convey ambient air for sampling into the machine. It is very important that the tubing is made of some inert material that does not interfere with the air being drawn in, thereby affecting the measurements. Teflon tubing (approximately a quarter of an inch in diameter) was considered to be suitable. It was also important to ensure that the tubing was kept clean, again to prevent interference with the air sample and that the joints attaching it to the instrument were as tight as possible to prevent leaks.

- Ozone Monitoring Instruments

A range of different types of ozone analyser were used throughout the duration of the survey. They are described below:

A Bendix Model 8002 Ozone Analyser was used at the lower Queen's Tower Site.

It uses the principle of photometric detection of the chemiluminescence resulting from the gas phase reaction of ethylene with ozone, as explained in Section 2.4.5. A simplified block diagram of the instrument can be seen in Figure 2.6.

An Ultra-Violet Photometric Ozone Analyser (AAL Model 427) manufactured by Analysis Automation Limited was used at the upper Queen's Tower site. Again, the principle of its operation is described in Section 2.4.5. A flow diagram of the instrument can be seen in Figure 2.7.

Figure 2.6: Block Diagram of the Bendix Ozone Analyser

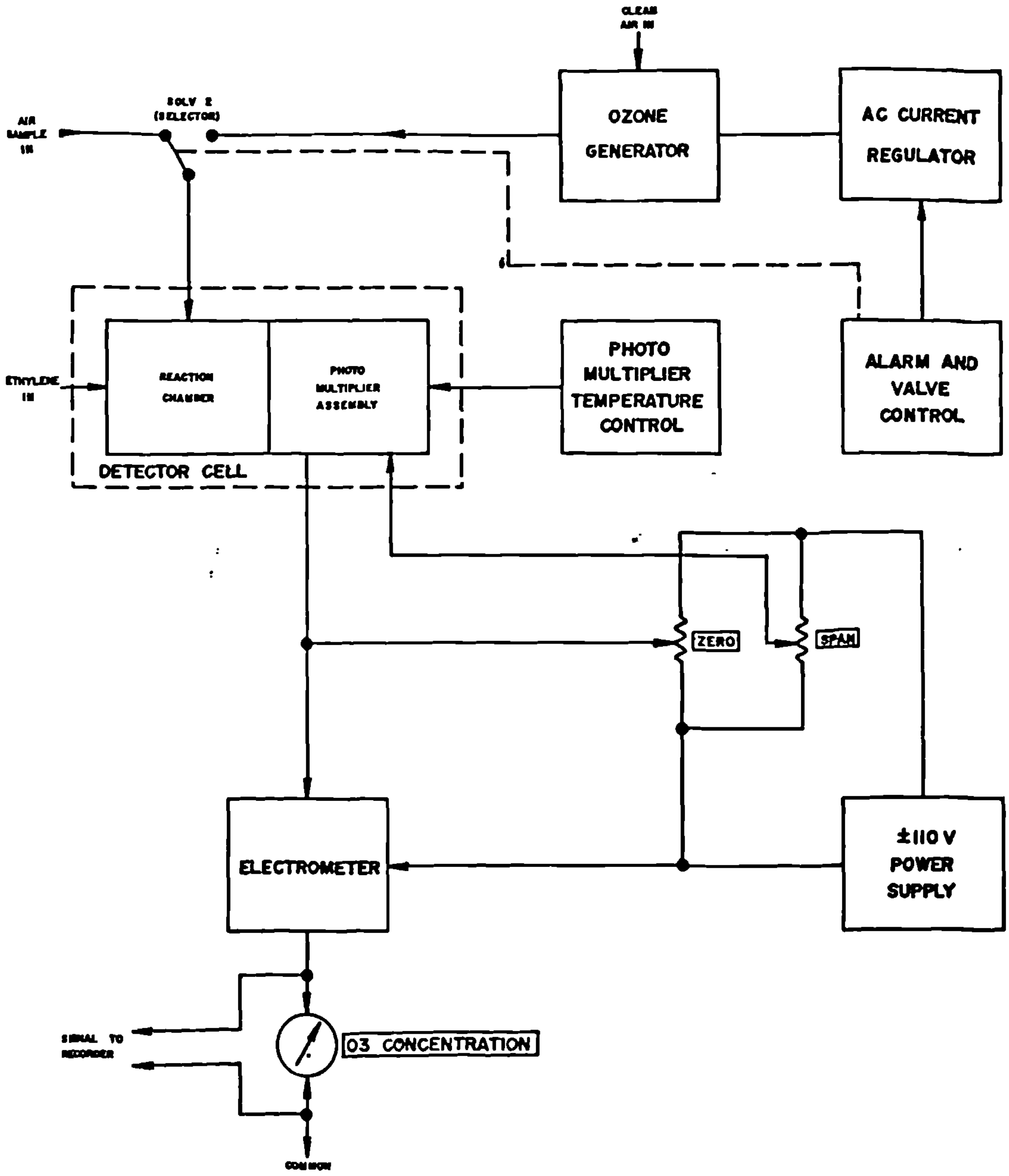
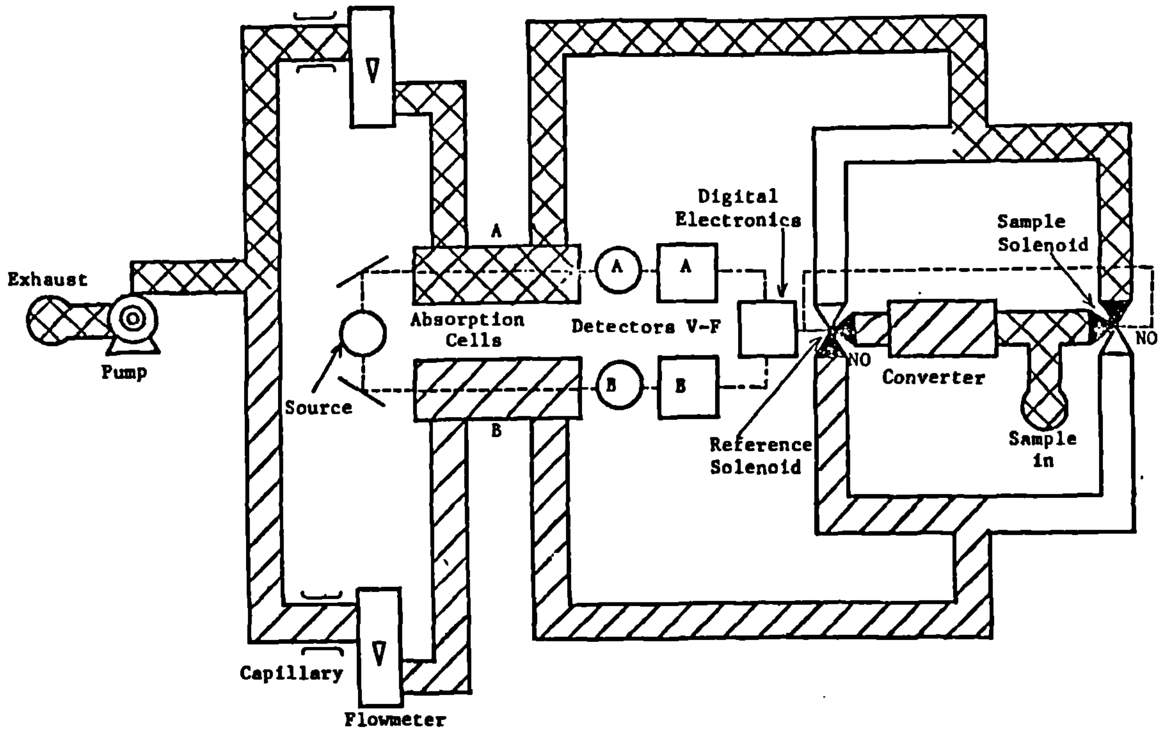


Figure 2.7: Block Diagram of the Ultra-Violet Photometric Ozone Analyser



2.8.2.3 Calibration

The instruments were calibrated using both lamp actinometry and back titration. A description of both of these methods can be found in Sections 2.4.4. and 2.4.6.

2.8.2.4 Experimental Set-Up and Duration

The survey ran from September 1994 to July 1995, with several breaks for maintenance and re-evaluation. The aim was to obtain examples of concentrations in both winter and summer months in order to try and investigate seasonal variation of both nitrogen dioxide and ozone along the vertical scale.

The first part of the survey was initiated in September 1994. Due to limited instrument availability, only one nitrogen oxides analyser was available. To utilise this in the most efficient manner possible, it was decided to set the instrument up on the higher level, in order to ascertain concentrations above street level, since there were already plenty of other monitoring surveys being carried out by other organisations to determine concentrations at ground level. If necessary, measurements such as these could be obtained and analysed in order to extrapolate some type of vertical profile. However, it is important to be aware that the greater the distance of such a site from the Tower, the lower the accuracy of the profile due to the time discrepancy.

An ozone analyser was made available in January 1995 and this was set up on the upper level, again for the reasons mentioned above. The survey was then interrupted in March 1995 in order to re-evaluate and to have the instruments maintained. It was decided to run the survey intensively over a one-month period, during the summer, in order to obtain some profiles with which to compare the results of URBNOX. URBNOX is a Lagrangian dispersion model which is described and investigated in Chapters 4 and 5. Instruments were made available to be able to place one ozone monitor and one oxides of nitrogen monitor on each level. This part of the survey was run during July 1995.

2.8.2.5 Data Collection and Processing

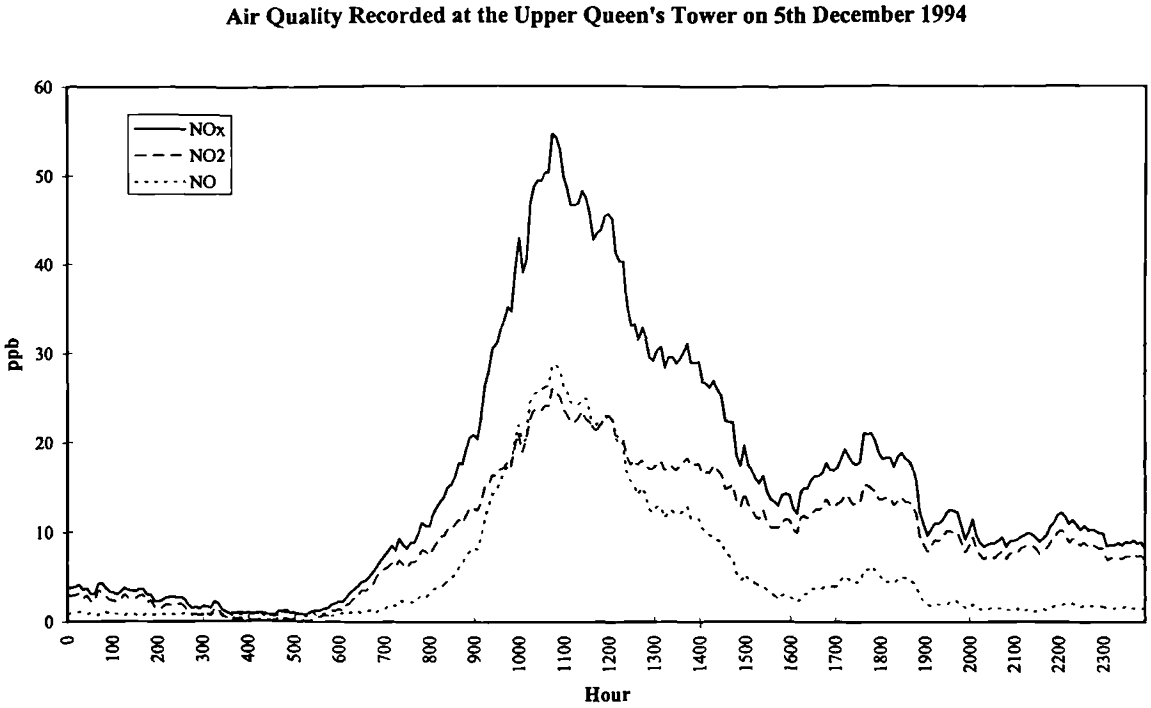
Output from the instruments were linked to a data logger. This was an 8-channel A/D converter connected to a PC via the serial port. The outputs from the data logger were then stored in data files set up by a custom ACRU logging program on the hard disk. The files were then downloaded onto a floppy disk from the PCs once a week and then processed using a second custom ACRU program and Microsoft Excel™.

2.8.3 Results

Data capture from this part of the air quality survey was less than 100%. The low rate of data capture was due to factors such as a number of components of the instruments failing, permission to access the tower being erratic and several power failures due to the ancient wiring within the tower. The environment within the tower was found to be rather unsuitable for running air monitoring instruments. A lack of air conditioning within the tower made the interior extremely warm and may have affected the performance of the instruments.

The lack of data capture made it impossible to carry out an in-depth analysis of the vertical distribution of nitrogen dioxide and ozone in an urban area. However, some examples of suitable data were selected in order to give a preliminary idea of the behaviour of ozone and nitrogen dioxide around the Queen's Tower. Figure 2.8 shows a time-plot of a day in December.

Figure 2.8: Graph to Show the Diurnal Profile of Oxides of Nitrogen, December 1994.



Firstly, it can be seen immediately that the levels of nitrogen dioxide recorded on the 5th of December 1994, did not exceed the WHO Health Guideline of 210 ppb (hourly mean) and would be placed in the Department of the Environment's VERY GOOD band (a peak hourly mean in 24 hours, of less than 50 ppb).

It can be seen from the graph that levels of nitric oxide, nitrogen dioxide and total NO_x are extremely low during the night and the early hours of the morning. This is due to reduced levels of traffic during the night and hence, reduced emissions of oxides of nitrogen. It also may be due to poor atmospheric mixing, preventing the oxides of nitrogen from diffusing out of the street canyon.

Concentrations then start to rise from about 6am onwards. This is most likely due to the early morning increase in traffic. A peak in concentrations would usually be expected between 8 and 9am, coinciding with the 'rush-hour' peak (Royal Borough of Kensington and Chelsea, pers. comm.). However, the peak in this case occurred at 11am. There are two possible reasons why this should be so. It could be because the peak in traffic occurred at 11am on that day. Alternatively, as these concentrations were measured at 65 metres above ground level, there could have been a time-lag between the increased emissions of NO_x at street level and it diffusing upwards through the street canyon to be recorded at the upper tower site. This could depend on the wind speed dropping.

Once the concentrations peak, a decline in concentration is observed. This is followed by another small peak exhibited between 4 and 7pm, which corresponds to the evening rush-hour. Levels fall further between 7 and 8pm and then stabilise at approximately 10 ppb for NO_x, 8 ppb for nitrogen dioxide and 2 ppb for nitric oxide.

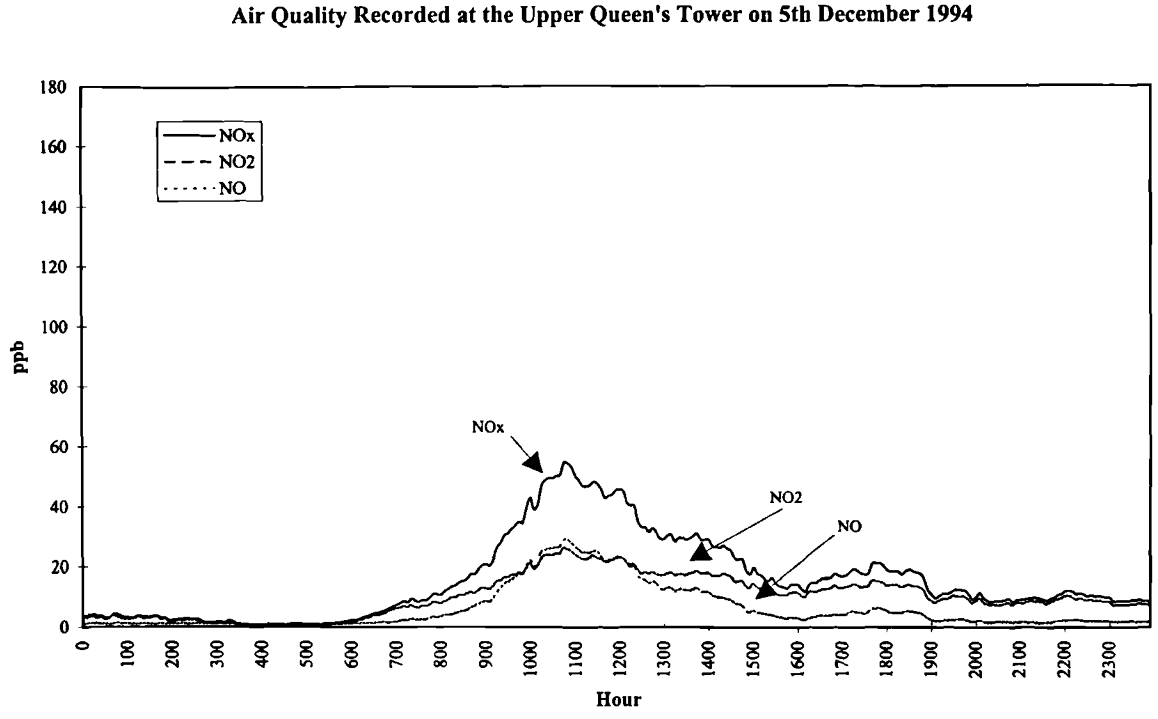
For the majority of the twenty four hours, concentrations of nitrogen dioxide are greater than those of nitric oxide. This is most probably because there are sufficient oxidants present (for example, ozone or hydroxyl radicals) to oxidise the majority of nitric oxide being emitted. However, during the rush hour peak, emissions of nitric oxide from traffic outstrip the availability of these oxidants and hence, more nitric oxide is recorded. It must also be noted that that the variability in the second half of the twenty four hours is far less for nitrogen dioxide, the secondary pollutant, than it is for the primary pollutant, nitric oxide.

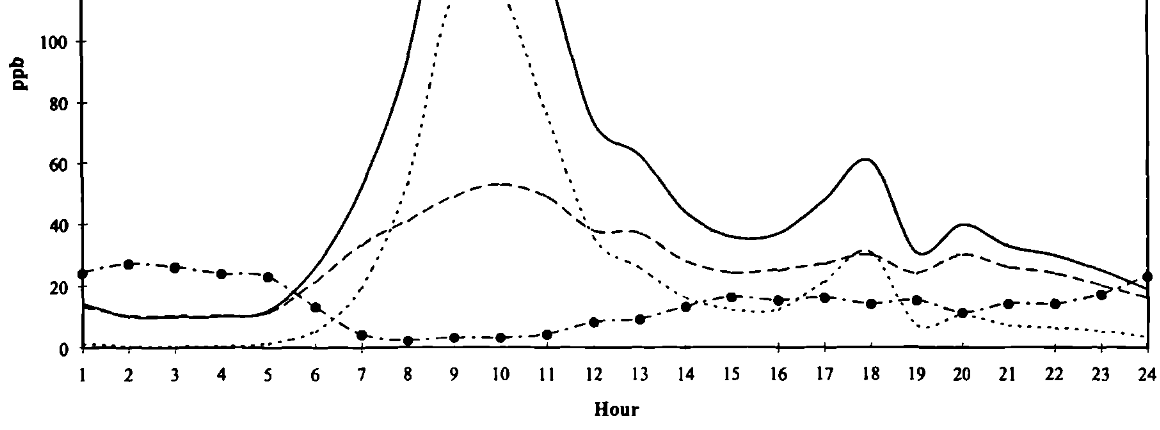
It is not possible to make any comment about the photostationary state, since it was not feasible to record any ozone on that day due to instrument failure.

This data was then compared with data from the Department of the Environment's automatic monitoring network. The site chosen was Bridge Place which is situated on the second storey on a building in Victoria (approximately 3 miles from South Kensington). Although it is situated higher than ground level, it is still within the street canyon (albeit a back street) and closer to NO_x emissions than the Queen's Tower site. It is an urban background site. It is not possible to make a direct comparison between the sites, since they are not in the same place, but due to a lack of data from the lower Tower site, this is the nearest site (with data) available for comparison. The two sets of data can be seen in Figure 2.9:

Figure 2.9: Comparison of the Queen's Tower Data with Bridge Place Data for 5th December 1994

(Source: NETCEN Archive)





It can be immediately be seen that although the two sites have similar distribution, the concentrations are very different indeed. It should also be noted that the peak concentrations occur at different times. This is most likely to be due to the rush hour occurring at different times as the sites are in two different places. The peak NO_x concentration at Bridge Place was nearly 180 ppb, compared with the 60 ppb at the upper Queen's Tower. On the basis of the this result alone, it would suggest that there is a definite gradient of oxides of nitrogen, where concentrations decrease with height, as distance away from the source of emission increases. However, much more monitoring and data collection is required to investigate this further and produce a definite result.

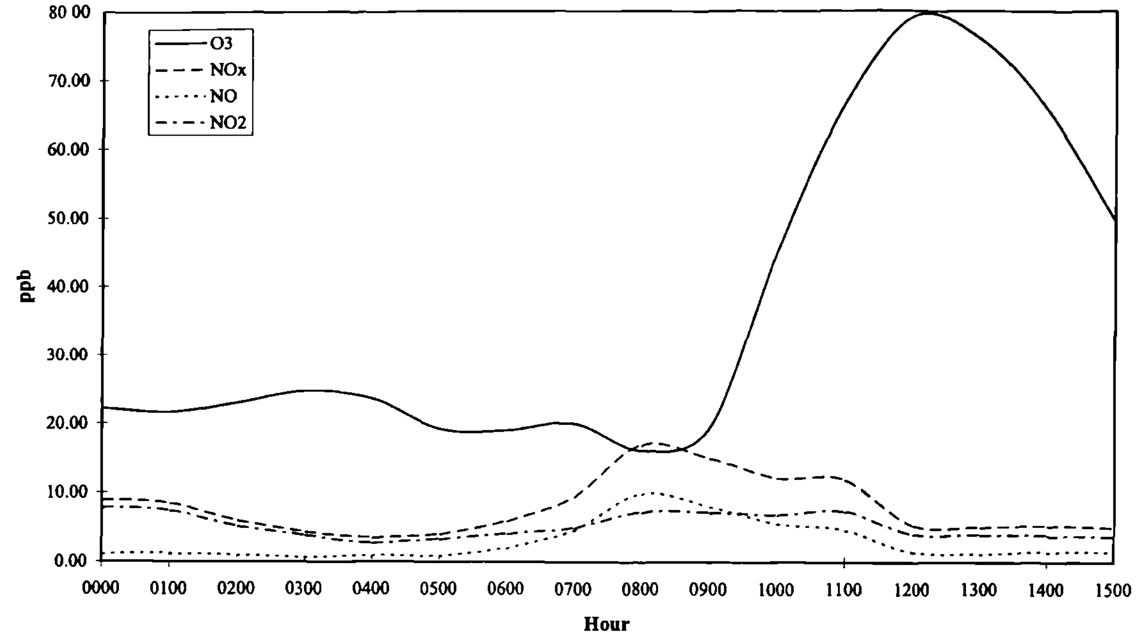
This result is partially backed up when the concentrations of nitrogen dioxide and nitric oxide are compared at both sites. During the peak at Bridge Place, the nitric oxide concentration is greater than the nitrogen dioxide concentration. This does not happen at the top of the Tower, where nitric oxide barely exceeds nitrogen dioxide. This is because as the nitric oxide diffuses aloft, it becomes diluted. The greater concentration of ozone aloft will therefore convert all the nitric oxide to nitrogen dioxide. It can be seen that there is more variation in nitric oxide concentrations with height, than there are with nitrogen dioxide. Caution should be exercised here though because these differences could be due to other factors (such as traffic density) as the sites are different. This requires further investigation. However, even with this uncertain premise, it is still an interesting point to consider. The variation in nitric oxide is greater probably because it is a primary pollutant and so the greater the distance above ground level, the lower the concentrations recorded. Nitrogen dioxide, the secondary pollutant, exhibits less variation with height, although it does become lower with increasing height. It would therefore be very interesting to record nitrogen dioxide concentrations at heights above the street canyon during an air pollution episode to see if air quality standards are still breached higher up.

Although ozone was not recorded at the Queen's Tower site, it was recorded at Bridge Place. Ozone levels were typically low (for the winter). There was a background of approximately 20 ppb during the night, since there was little nitric oxide present to react with it. Levels were lower during the day due to increased emissions of nitric oxide from traffic, even though there would be more insolation to promote formation. It was interesting to note that all the Queen's Tower readings of NO_x that were less than 20 ppb were completely made up of nitrogen dioxide. This is consistent with the night time ozone concentration of 20 ppb.

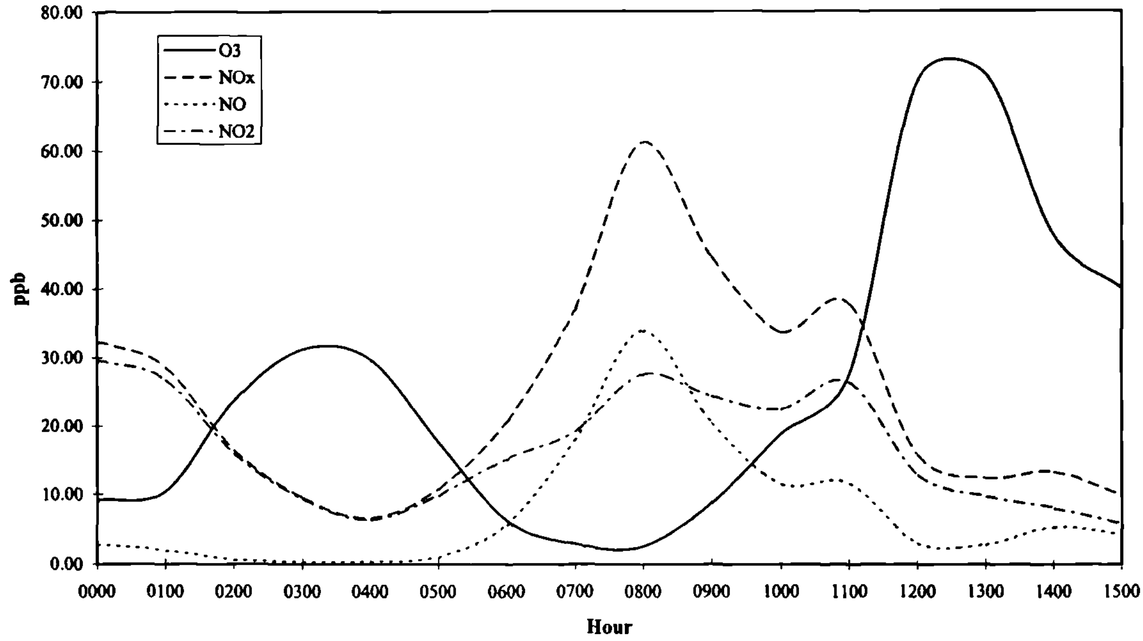
The second set of results to be analysed in this chapter was captured on Friday 28th of July 1995. Data is shown from both the upper and lower sites and it gives a good example of the air quality during a typical day in summer. The diurnal profiles are shown in Figure 2.10:

Figure 2.10: Time Plots of the Air Quality Recorded at the Queen's Tower

Air Quality Recorded at the Upper Queen's Tower Site on Friday 28th July 1995



Air Quality Recorded at the Lower Queen's Tower Site on Friday 28th July 1995



Firstly, it can be seen from this set of results, that neither of the sites exceed any of the air quality standards for nitrogen dioxide and would be classified as VERY GOOD in the Department of the Environment's air quality bandings. Ozone would also be classified as VERY GOOD (peak hourly mean concentration in 24 hours of less than 50 ppb), slipping back to GOOD (peak hourly mean concentration in 24 hours of between 50 and 80 ppb) around midday. The EPAQS standard (a running 8-hour mean of 50 ppb) was exceeded at both sites. In addition, the WHO Health Guideline (a 1-hour mean of between 76 and 100 ppb) was exceeded briefly at both sites.

The graphs show that vertical profiles do exist for the species measured. Similar distribution patterns exist as discussed previously. Again, levels of nitrogen dioxide, nitric oxide and therefore, total NO_x are higher at the lower Tower site than at the upper Tower site. A very prominent peak of nitric oxide and NO_x can be observed during the rush-hour at approximately 8am. This peak is also recorded at the upper Tower, although it is a lot flatter. It is interesting to note that the rush-hour peak in emissions is sufficient that it can be recorded above the street canyon. This shows that atmospheric mixing is sufficient to allow the increased emissions to diffuse upwards out of the street canyon.

At both sites nitric oxide is greater than nitrogen dioxide during the peak. At the lower site, which is closer to the sources of nitric oxide, there is a larger quantity of nitric oxide, which depletes the majority of the ozone, thus limiting conversion to nitrogen dioxide. At the upper site, there is more ozone and as the nitric oxide diffuses upwards, it becomes diluted. As a result, it would be expected that all the nitric oxide would be converted to nitrogen dioxide. As this has not happened, it is most likely that the photostationary state has been achieved.

At the upper Tower site, there is very little variation in the levels of all the oxides of nitrogen, unlike at the lower Tower site. Again this is due to proximity to emissions. The ozone concentrations can be divided into two sections, those during the night and those during the day. During the day, there is a difference in ozone levels between the two sites, especially during the rush hour. As would be expected, levels of ozone are lower at the lower Tower site. This is due to nitric oxide from traffic reacting with the ozone. The small peak of nitric oxide recorded at the upper Tower site causes concentrations of ozone there to dip. Once the rush hour is past and nitric oxide levels fall, ozone levels begin to rise until they peak at around 1pm. Ozone is about 10 ppb higher at the upper site than at the lower site.

Levels of ozone were lower during the night. The upper site recorded a general background level of approximately 20 ppb, with little variation. However, at the lower site, the peak ozone concentration was 30 ppb, at 3am. It then steadily decreased to reach a low at 8 am. Therefore, the most nitrogen dioxide that could be obtained is 30 ppb. It can be seen that the peak nitrogen dioxide recorded at the lower site was 25 ppb at 8am.

It would have been advantageous to compare these results to concentrations measured by the London Air Quality Network site in Kensington (the nearest site to the Queen's Tower). However, this site was off-line and no results were recorded for that day, making a comparison impossible.

These results did not show much evidence of a plume, containing high concentrations of ozone, being transported across London, although it is possible that ozone was being entrained down from above into the canyon. Evidence from the Sibton and Lullington Heath sites also did not show any evidence of an ozone plume (NETCEN Archive). It would be interesting to set up a vertical monitoring survey on the south-eastern edge of London to try and identify ozone plumes as they are transported in from the continent, before they are depleted by nitric oxide emissions. It would also be useful to try and monitor the vertical distribution of a summer photochemical episode in order to analyse its behaviour more thoroughly.

2.8.4 Conclusions

It was shown that concentrations of nitric oxide, nitrogen dioxide and ozone differed with height. Nitric oxide showed the most variation since it is a primary pollutant and exhibits highest concentrations near the source of emissions, in this case, traffic at street level. Nitrogen dioxide and ozone showed less variation as they are both secondary pollutants. Ozone concentrations tend to increase with height as levels of nitric oxide (which deplete ozone) decrease. However, atmospheric mixing will more evenly distribute ozone and make the gradient less marked. Nitrogen dioxide tends to decrease with height, with more of it being present near the source of its precursor, nitric oxide. To take this study further, a model is needed to make quantitative comparisons with measured data. This is discussed later, mainly in Chapters 4 and 5, where a Lagrangian dispersion model called URBNOX has been developed to investigate the behaviour of nitrogen dioxide and ozone in urban areas.

Despite few datasets, it was still possible to make some observations about the vertical distribution of nitrogen dioxide and ozone in an urban environment. However, as the results were few, it is advised that these observations should be investigated further and more monitoring results collected.

2.9 Discussion and Conclusions

The aim of this chapter was to explore the area of urban air quality monitoring. It started off by putting forward the different reasons why air quality monitoring was important and where it fitted into an air quality management programme. The different methods of monitoring air quality were then described and discussed in turn, outlining their strengths and weaknesses. The chapter then moved onto the practical section where two small-scale air quality monitoring surveys were carried out. The first used passive sampling methods to determine the local distribution of nitrogen dioxide around the Imperial College campus in South Kensington. The second used continuous, automatic methods of monitoring to investigate the vertical distribution of nitrogen dioxide and ozone in South Kensington.

Air quality monitoring is a very important part of an air quality management strategy. Monitoring is a way of determining the state of the air quality in a given area and establishing the existence of a problem. If a problem is found, action can be taken to alleviate it. This is more cost-effective than just implementing pollution control over a wide area. Monitoring can then be used to chart the progress and effectiveness of a particular pollution control policy.

There are many methods available for monitoring air quality. They all have their strengths and weaknesses. Two types of method for monitoring nitrogen dioxide were focused on and used in the two surveys.

Diffusion tubes were the first method to be used. The major points in their favour are that they were found to be cheap and very simple to use, enabling a large number to be deployed without incurring a huge expense. They were easy to prepare and analyse and the components were not overly expensive to replace. They were very versatile in that they can be sited in a wide variety of places, ranging from a lamp post at a roadside, to the top of a Tower. The experiment itself did not require a lot of maintenance in that once the tubes were put out, they could be left for the required exposure time and then analysed in one block. It was also a simple process to repeat an experiment.

However, a few disadvantages were found. Using the tubes was a very good way of obtaining a general picture of the distribution of nitrogen dioxide in an area, but it was not a good method to investigate the behaviour of a pollutant in detail. It was also difficult to determine if there had been any exceedences of air quality standards. The best way this could be done was to collect a year's worth of data and then compare it to the EC Nitrogen Dioxide Directive. The risk with this is that it is only possible to determine the existence of an air quality problem after running the experiment for a long period of time. However, it is feasible that an air quality problem can be determined if the tubes exhibit consistently high results. It is also very difficult to investigate the behaviour of a pollutant since it is not possible to construct diurnal profiles using the tubes. Finally, as the tubes are so small, there is sometimes the problem of tube theft.

In contrast, using continuous monitoring instruments was found to have a different set of advantages and disadvantages. The problem of identifying pollutant behaviour was rectified in that it was possible to obtain hourly data and diurnal profiles. Air pollution behaviour and distribution can then be analysed in depth. It was also easier to compare the data to a range of air quality standards.

However, there was found to be a trade-off between the quality and detail of data obtained and the ease of use of the instruments. Continuous monitors are very expensive to buy and have on-going running costs. The National Environmental Technology Centre have estimated the capital costs to average at £27, 100 (McGinlay *et al*, 1996). This will include in addition to the instrument, the calibration system, the data logger and recording system, the modem for downloading the data, the enclosure, any gas cylinders required, site installation and a computer upon which to process the data. This includes just one analyser and it should be expected that approximately another £8000 should be added to the above cost for every extra instrument bought. The running costs need to be added on top of this to include routine site operation and calibration, regular service and maintenance (including component replacement), audits, training and site utilities. These will vary considerably, but can be expected to be in the order of £5 000 to £10 000 per year. Therefore the setting up of a continuous monitoring site needs to be considered very carefully before implementation and should be embarked on as a long-term project (on a scale of years) in order to make it as cost-effective as possible.

Once logged, downloading the data and subsequently analysing it was found to be fairly straightforward, since it was all carried out on a computer. However, it was also found that the instruments themselves required a large time commitment to ensure they were working correctly. The large number of parts of the system and the delicate nature of some of the components meant that there was frequent instrument failure and subsequent poor data capture. Continuous monitors are less versatile than diffusion tubes in that they need a large, secure site and hence there are fewer places where they can be put. The Tower was found to be very secure but the instruments often require a stable environment at which to work efficiently. This often requires an air-conditioned site. The Tower was not air conditioned, nor could the financial budget (or the electrical supply in the Tower) stretch to installing an air conditioning unit. This is likely to have affected the data capture.

In conclusion therefore, it is recommended that, when embarking on an air quality monitoring survey, a preliminary survey is carried out using diffusion tubes. A large area can be surveyed at a relatively low cost, therefore making it possible to identify problem areas. Once any problem areas or areas of interest have been identified, continuous instruments can be set up to monitor the problem further and in greater detail. This would seem to be a cost-effective way of monitoring air quality as efficiently as possible.

The two air quality monitoring surveys around Imperial College found that nitrogen dioxide does not exhibit very much spatial or temporal variability on a local level. This is due to it being a secondary pollutant and not being directly emitted from a source such as traffic. Its precursor, nitric oxide however, is a primary pollutant and is directly emitted from vehicles and is found in higher concentrations when traffic density is higher, such as at rush-hour. As levels of nitric oxide become higher, however, levels of nitrogen dioxide subsequently rise but not in such a marked manner.

Preliminary findings also showed that both nitrogen dioxide and ozone varied with height. Ozone concentrations tend to increase with height, since as height increases there is less nitric oxide present to react with and deplete the ozone. However, a marked ozone gradient is tempered by a well-mixed atmosphere, which will distribute the ozone more evenly. Nitrogen dioxide will decrease with height, as does nitric oxide. Nitric oxide shows a very marked gradient, since as height increases so does the distance away from the emission sources. As a result there is less nitric oxide to be oxidised to nitrogen dioxide and hence levels will decrease. The survey was limited by poor data capture and only one site. A very interesting extension to this survey would be to create a small network of sites along vertical gradients at different points across London (or any other urban area) to investigate the differences in the composition of vertical profiles across the city.

The vertical distribution of nitrogen dioxide and ozone, especially the evolution of profiles as an urban area is traversed, will be investigated further in this thesis. A simple, two-dimensional, Lagrangian diffusion model called URBNOX has been developed in order to investigate the situations under which exceedences of air quality standards for nitrogen dioxide occur and the distribution of ozone, nitrogen dioxide and nitric oxide within an air column as it crosses an urban area.

Chapter 3 - Modelling Review

3.1 Introduction

The previous chapter investigated air quality monitoring, one of the principle components of an air quality management strategy. The aim of this chapter is to provide the introduction to another important component - air quality modelling. This chapter consists of a review of the development of air quality modelling. It will describe the major types of models in existence, their uses and their strengths and weaknesses. The aim of this review is to form an introduction to URBNOX, the model developed for this project. The review will highlight some of the gaps in current modelling practice and show how URBNOX will go some way towards filling some of these gaps.

There are several reasons for air quality modelling. At the most simple level, models can be used to test our understanding about the behaviour of air pollutants, by comparison with air quality measurements. However, as models can also be developed to predict levels of air pollution under certain sets of conditions, they can be used for more applied purposes in investigating different methods of pollution abatement. Regional and city scale models can aid identification of the major sources contributing to air quality problems and therefore allow targeted control strategies to be developed (UK QUARG I, 1993). In addition they can help in the design of monitoring networks by indicating locations with poor air quality.

3.2 Basic Components of an Air Quality Model

An air quality model can be defined as follows:

> *"An urban air quality simulation model is a numerical technique or methodology, based upon physical principles, for estimating pollutant concentrations in space and time as a function of the emissions distribution and the attendant meteorological and geophysical conditions. They thus serve as tools to provide objective answers to the many 'what if...?' questions that are regularly faced by decision makers in the fields of air pollution control, transportation planning and land-use planning."* (Source: Johnson *et al*, 1976).

At the most basic level, a model requires two types of data input:

-information on the source or sources, including the pollutant emission rate;

-meteorological data, such as wind speed (Boubel *et al*, 1994).

However, although this will give some idea about the amount of pollution present and their general dispersion patterns, this makes no provision for any of the chemical reactions that might occur, especially when secondary air pollutants such as nitrogen dioxide are concerned. Therefore a comprehensive air quality model will include a scheme to model chemical behaviour. However, this is not as vital if an inert pollutant is being investigated, such as carbon monoxide.

Emissions form the pollution input to the model and it is important to get these as accurate as possible. There are several types of emissions sources and they can be categorised as either stationary or mobile. Stationary sources include chimney stacks, while mobile sources include motor vehicles, aircraft and ships. Sources can be represented spatially and temporally within a model. Spatially, a source can be classified as a point, an area or a line. A point source is a discrete emissions point, such as a stack or an exhaust pipe. A line source is one where a point source moves at a rate far greater than the lateral dispersion from an imaginary line drawn form that emission, such as a busy road. A line source can also be a row of point sources, such as a line of traffic. If there is a large group of stationary sources within one area and the emissions come together to form one large source, then this known as an area source. The classification of this will depend on the scale used (Gould, 1996).

When considering emissions in a temporal form, a source will either be continuous or form discrete puffs. However, it should be noted that continuous sources can vary in their emissions rates, while puffs can give rise to high concentrations of emissions over short periods of time. On the other hand, mobile sources can be described as continuous but they can give rise to high concentrations over short periods of time, for example, in rush hours.

While single sources can be easily modelled, many areas to be modelled comprise many different sources, varying over space and time. Emissions will therefore be entered as an emissions database or emissions inventory. Emissions inventories can be constructed over different resolutions, for example, the National Atmospheric Emissions Inventory is on a 10 x 10 km^2 grid and the London Emissions Inventory is on a 1 x 1 km^2. Obviously, the finer the resolution, the greater the potential accuracy of representation.

Meteorological data and behaviour are also major components. These often ‘drive’ the model and have very important effects on the distribution and transport of pollutants. In order to model the atmospheric processes properly, examples of meteorological parameters that should be included are wind speeds, wind direction, temperature, atmospheric diffusion, atmospheric stability, turbulence, strength of insolation (incorporating cloud cover) and boundary layer height.

Most pollutants are dispersed in the boundary layer, which extends to approximately 1 km above the Earth's surface, (although it can fluctuate depending on a number of conditions). Therefore, understanding the characteristics of the boundary layer and representing them accurately in a model is extremely important. The boundary layer is affected by the Earth's surface, which creates advection currents in the boundary layer and hence affects the dispersion of pollutants.

Other factors that affect the dispersion of pollutants and should be taken into account when modelling are local topography and surface roughness. For example, buildings, hills, mountains, vegetation and bodies of water will all affect air flow and therefore pollution dispersion.

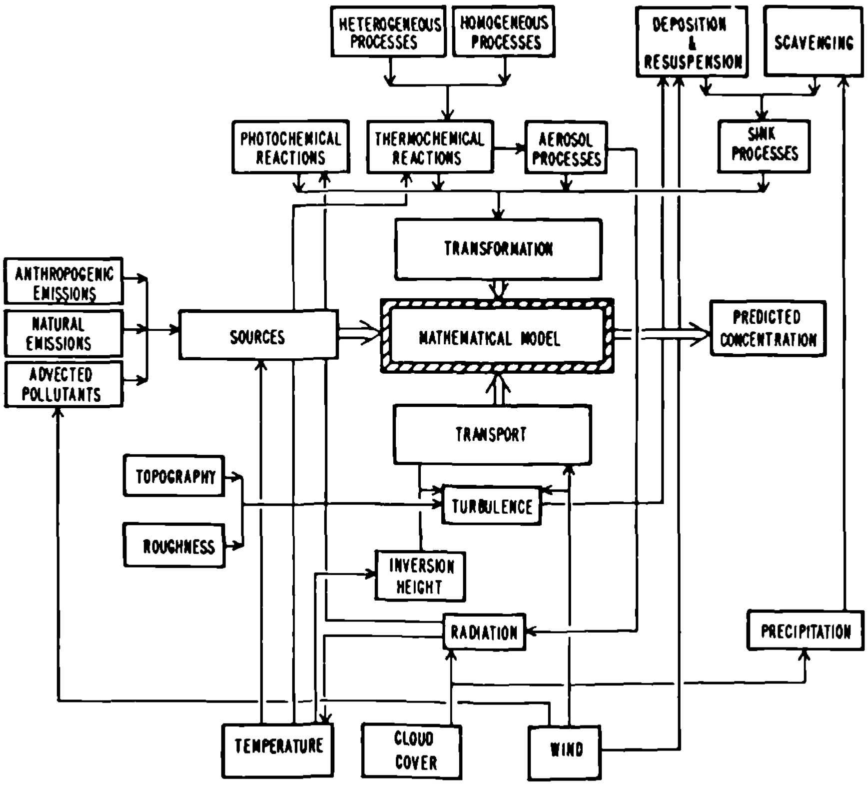
As well as being subject to transport and dispersion, pollutants will undergo chemical transformations. Primary pollutants will often combine to form secondary pollutants. Therefore, a chemical scheme will often be incorporated into a model. These can include reactions with other species or a rate of deposition, as a pollutant can be lost to the Earth's surface. Chemical schemes can range from being very simple to extremely complicated. They can be made up of one or two reactions, or they can consist of elaborate schemes which incorporate in excess of 300 reactions. Sometimes, however, the chemistry can be left out of a model if the dispersion of a fairly inert species, such as carbon monoxide, is being investigated in isolation.

Finally, air quality models can operate on a local basis, where the effects of a pollutant release and episodes can be studied, or they can operate on a long-range basis, such as modelling ozone over the continental scale.

The general structure of a good air quality model is shown in Figure 3.1:

Figure 3.1: Diagram Showing the Basic Components of an Air Quality Model

(Source: Seinfeld, 1986)



3.3 Urban Air Quality Modelling

Urban air quality modelling has progressed substantially over the last couple of decades. Many different types of model can and have been developed- examples of these will be discussed further on in the next section. However, it should be noted that there are several features of the urban environment that should be taken into account when developing an air quality model. These are discussed below:

3.3.1 Special Features of the Urban Environment

Urban environments have a number of special features that need to be taken into consideration when modelling air quality, since they tend to have profound effects on pollution dispersion.

One of the most important features of an urban area is that there are generally large numbers of buildings lining both sides of the street giving rise to street canyons. As a result, these canyons will have a substantial effect on wind flow patterns. On average, urban wind speeds are lower than those in rural areas, due to the sheltering and drag effect of the buildings. However, there are some differences in wind speed due to the time of day. During the day, urban wind speeds are sometimes considerably less than those in rural areas. However, during the night there may be greater mechanical turbulence over an urban area so that the higher wind speeds aloft are transferred to the air at lower levels as a result of turbulent mixing (Barry *et al*, 1992).

The large number of buildings present will also have a substantial effect on general air flow, due to increased surface roughness. As a result of this there is greater turbulence than there would be in a rural area. In addition, the street canyons can cause air to be channelled down them. This will add complexity to representing air flow within an urban air quality model.

The temperature in urban areas is very different from that in rural areas. Urban temperatures are known to potentially be several degrees higher than those in rural areas. This phenomenon is known as the urban heat island. The reasons for this are summarised, as taken from Barry *et al*, (1992):

- Changes in the radiation balance due to atmospheric composition;

- Changes in the radiation balance due to the albedo and thermal capacity of urban surface materials, and to canyon geometry;

- The production of heat by buildings, traffic and industry;

- The reduction of heat diffusion due to changes in airflow patterns as the result of urban surface roughness;

- The reduction in thermal energy required for evaporation and evapotranspiration due to the surface character, rapid drainage and generally lower wind speeds of urban areas.
  (Source: Barry *et al*, 1992).

Rivers and open spaces such as parks have the potential to affect air quality if they are large enough. Open spaces often have some type of vegetation cover, resulting differing albedos, heat budgets, deposition rates and air flow. This also applies to bodies of water. As a result, pollution distribution could be substantially different over these areas, compared with the rest of the urban area and it may be advantageous to consider these when developing a model, especially if it is of a particular city.

3.4 Examples and Review of Existing Urban Air Quality Models

The purpose of this section is to describe and examine different air quality models as applied to different urban scales. The different types of model can be categorised under two main scales, namely:

- Roads and Junctions (Local 'Hot-Spots')

The models in this category can be further sub-divided into 4 groups:

- Gaussian models, as applied to roads, such as CALINE;
- Simple, empirical models such as the U.K. Department of Transport's Design Manual for Roads and Bridges (Volume 11) and CAR;
- Canyon models such as the Canyon Plume Box Model;
- Computational Fluid Dynamics, which is a new approach to air quality modelling.

- Urban Area and Regional (Urban Background)

The models that fall into this category can be further sub-divided as follows:

- Chemical models, which detail the chemical interactions of species in order to investigate their behaviour;
- Urban Box Models, such as the Urban Airshed Model.

There are also some 'New Generation' models which have developed from the Gaussian models, such as UK-ADMS, which make an attempt to cover all scales.

3.4.1 Modelling Roads and Junctions

This is one of the smallest scales on which to model within the urban area and is generally known as the microscale. This is where pollutants such as nitric oxide are emitted. Dispersion will occur over tens to hundreds of metres, over a time scale of minutes. These types of models are generally used to model local 'hot-spots', such as a congested junction. Different types of modelling at this scale include Gaussian models adapted for roads, simple empirical models, and canyon modelling. Each category will be discussed in turn.

3.4.1.1 Gaussian Models

These are some of the most widely used models because they are fairly simple to use and deal with a good number of parameters. Pollutant dispersion is described by the Gaussian equation. It makes the assumption that the expanding plume of pollutants has a 'normal', i.e. Gaussian, distribution of concentration in both the vertical and lateral directions. Roads are treated as line sources and the basic equation can be modified to take into account factors such as plumes in the wake of buildings.

One of the most important and well-known models in this category is the CALINE series of models. The first version was published in 1972 by Beaton, (Benson, 1992). CALINE 1 was very simple and consisted of a series of tables and nomagrams which allowed the user to predict carbon monoxide levels near roadways (in a manner similar to the Design Manual for Roads and Bridges). The calculations were based on estimated meteorology and traffic densities. The dispersion was calculated from a modified version of the Gaussian Diffusion model.

Since then it has had several major redevelopments, the current version being CALINE 4. CALINE 2 replaced the first version in 1975 (Benson, 1992). It was slightly more complex and comprised a couple of additions- namely, the ability to calculate carbon monoxide concentrations for dips in the terrain and for winds parallel to the roadside. However, there were problems with over-prediction in stable, parallel wind scenarios. The model was also found to be unable to handle multiple line sources and modify its dispersion parameters for surface roughness. Therefore, an improved version was developed.

The third generation CALINE model was developed in 1979 by Benson in order to overcome the problems of the second version (Benson, 1992). It still has the basic Gaussian dispersion but it uses new horizontal and vertical dispersion to take into account surface roughness, averaging time and turbulence induced by traffic. A finite point source with multiple links was added and this significantly reduced the overpredictions. It also has an algorithm for deposition and settling velocity, enabling particulates to be modelled (Szepesi, 1989).

As a result of this, in 1980 the U.S. Environmental Agency authorised CALINE 3 for use in estimating concentrations of non reactive pollutants near highways. The main problem with this version of the model was its limited capacity. CALINE 3 can only assess the impact from 20 links and calculate concentrations at 20 receptors. However, the majority of urban intersection schemes require between 70 to 100 links to fully characterise traffic behaviour (Bull, 1995). However, CALINE has been modified by other consultancies and modellers in order to improve this. The other main disadvantage is that it is able to predict fairly inert, primary pollutants such as carbon monoxide, but it runs into difficulties when other pollutants need to be assessed, such as nitrogen dioxide, as the model has no chemical scheme incorporated. The input requirements consist mainly of meteorological parameters. These consist of such factors as wind speed, wind direction, stability class and mixing height.

The fourth and most recent version of CALINE was developed in 1984 and is a 'refined and extended' version of CALINE3 (Benson, 1992). It is able to predict nitrogen dioxide levels in addition to carbon monoxide. It has also been extended in order to model intersections. This version also has the original Gaussian dispersion but with an added lateral plume and more provision for vehicle turbulence. CALINE4 is able to model nitrogen dioxide concentrations because it has a computational scheme which models the dispersion of the reacting chemical species separately from the plume chemistry. The nitrogen dioxide formation is driven by a simple set of reactions. The final concentration of nitrogen dioxide is governed by the initial concentrations entered into the model and the time of travel from the element to the receptor. This scheme was found to work adequately, after validation, but was advised not to be used under certain wind conditions, such as winds parallel to the road (Benson, 1992).

As a result of much testing and validation, it has been found to be suitable for modelling highway and line sources, urban and rural areas, simple terrain, transport distances of less than 50 km and for 1 to 24 hours averaging time (Szepesi, 1989). The CALINE series of models are some of the most widely used models. This is because it is readily available in the form of a user- friendly package. The concept of the model is easy to understand and it has been substantially validated and modified in order to keep it up to date. As it has been so widely used, it enables the intercomparison of results from different studies. It is relatively cheap to buy, along with a back-up system or it can be downloaded for free from the World Wide Web.

There are a couple of disadvantages however. The model does have its limitations, but these are to be expected in any model. The lack of chemistry is its biggest drawback, especially with the current interest of modelling secondary pollutants. The simple nitrogen dioxide scheme gives good results (Benson, 1992) but it is not recommended for use under certain wind conditions. It is also based on United States measurements and therefore not compatible with UK pollution characteristics.

3.4.1.2 Empirical Models

The first air quality models were very simple and empirical, when the requirements for air quality modelling and computer facilities were very moderate. At first, during the 1960s, only relatively inert, primary pollutants were being modelled and levels of other pollutants were extrapolated from these.

A well known example of one of these types of model is the Department of Transport's Design Manual for Roads and Bridges, (particularly Volume 11). Although it is a simple, empirical model, this has proved very useful in air quality modelling in the UK. It introduced new requirements for the content of a detailed air quality report, for the planning of new road systems, to include the modelling of concentrations of nitrogen dioxide, particulates and benzene.

The model itself consists of a step by step guide to calculating likely changes in local pollution levels if a proposed road were to be built. The guide is based on a series of graphs which can be used to calculate concentrations of carbon monoxide, nitrogen oxides, hydrocarbons and particulate matter. It is an estimation technique and requires the derivation of effective traffic flows, which are calculated from a knowledge of vehicle type and flow and associated emission rates. These are updated every so often in response to new research. These are then combined with receptor position to determine ground level pollutant concentration. Certain assumptions have been made in relation to these factors, which are discussed in detail within the Manual. They also state clearly the effects these assumptions will have on the results and areas of possible over or under-estimation.

The main purpose of the model is to determine whether a proposed road scheme needs a more detailed air quality analysis. Air quality levels are estimated at selected locations near a road network, in order for comparison with chosen air quality standards. This is done by estimating the average concentrations at specified locations for high growth peak hour traffic flow. These average air quality results are then compared with air quality standards. Some difficulties with the direct comparison of the average concentrations with the air quality standards have been acknowledged, especially with regard to oxides of nitrogen.

However, a scheme has been devised to convert these average concentrations to an appropriate value which can be directly compared with the air quality standard. In terms of the oxides of nitrogen, the difficulties occur because the majority of traffic emissions are in the form of nitric oxide and the air quality standard (the EC Directive) is specific to nitrogen dioxide. Another problem is added in that the dispersion model used for the Manual makes the assumption that there is no chemical transformations of the pollutants that will modify their concentrations. This is untrue for the oxides of nitrogen, where nitric oxide is oxidised to nitrogen dioxide. In order to be able to make a comparison, an assumption is made where one molecule of nitric oxide is capable of forming one molecule of nitrogen dioxide, hence the entire NO_x concentration is taken as nitrogen dioxide.

Then, from the average peak hour concentration, an empirical estimate is made of the 98th percentile of 1-hour concentrations of NO_x, enabling it to be compared with the EC Directive. This empirical relationship is based on a study of the distribution of concentrations at the roadside. It has been admitted in the Manual, that this was done some years ago and may not be representative of the current situation. Once this value has been established, then another estimate is made of the contribution of the background level to these concentrations. These are derived from the analysis of concentrations recorded at the Department of the Environment's monitoring network. However, it is not stated from which year this was done and therefore, again may not be a true indication of the current situation (UK DoT, 1995).

There are both advantages and disadvantages to this type of model. It is advantageous because it is very simple to use and does not require sophisticated computing power. As stated in the previous paragraph, it is only meant to be a preliminary air quality test in order to determine whether a more detailed, sophisticated test should be carried out. Therefore, this is a good way of saving both time and money. However, with the quantity of empirical estimation in the final comparison with the air quality standards and the lack of chemistry, especially when investigating secondary pollutants such as nitrogen dioxide, there is a danger of over-simplified results. It is also important that the concentrations from monitoring networks used are as up to date as possible.

Finally, it should be noted that the current version of the model uses a mixture of air quality standards, based on the Air Quality Standards Regulations 1989. This uses EC Limit Values for nitrogen dioxide, sulphur dioxide, particulate matter and lead, although sulphur dioxide and lead are not assessed in road assessments. There are no statutory requirements for carbon monoxide or hydrocarbons, so the DMRB uses the US standard for carbon monoxide and the EPAQS standard for benzene. It is not known at this time, whether modifications are going to be made to adopt the standards recommended in the National Air Quality Strategy instead.

Other types of empirical model include CAR (Calculation of Air pollution from Road traffic) (den Boeft *et al*, 1996). The CAR model was designed to be a simpler version of the TNO Traffic Model (a Gaussian line source model). Its parameters consist of emissions, dilution and background concentration. The model can calculate concentrations of benzene, nitrogen dioxide and carbon monoxide. The calculations are performed over five stages, namely:

- The city background level; (this has to be derived from measurements or estimated);
- The local street emission;
- The street specific contribution to average concentrations;
- The annual average concentration and percentiles;
- The traffic contribution to the nitrogen dioxide concentration.

(Source: den Boeft *et al*, 1996).

The most interesting feature of this model is its provision for the effects of street architecture. A series of wind tunnel experiments was carried out prior to the development of CAR. These studies came up with the following conclusions:

-The most obvious effect of buildings was the change of direction of the local street level wind in the wake of, and between buildings;

- The contribution of pollutant that reaches the receptor point after recirculation in the lee of, or between buildings was on the whole, found to be much smaller than the direct contribution of the plume blowing directly onto the receptor point;

- Rows of trees were found to have a variable effect on the concentration pattern, varying from slightly negative to very positive.

(Source: Eerens *et al*, 1993)

These findings were originally used to aid the development of the TNO Traffic Model, which is a rather complex street dispersion model. CAR evolved from this as a less complex means of getting a general picture of air quality. As a result, CAR incorporates variables which take into consideration the effect of trees on dispersion and the shape of the street (for example, whether it is a wide open road, or a narrow one enclosed by buildings).

There is little information about its chemistry to calculate nitrogen dioxide concentrations, but it is stated that the module for the calculation of the nitrogen dioxide concentration is derived from the TNO model (den Boeft *et al*, 1996). This is stated as follows:

> *' A semi-empirical relation is used to determine the nitrogen dioxide concentrations from the calculated local traffic contribution of* NO_x *and the estimated background ozone concentrations.'* (Source: den Boeft *et al*, 1996).

The lack of detailed chemistry, especially for a secondary pollutant such as nitrogen dioxide could lead to errors of estimation of final concentrations by the model.

This would be a good model for a local authority to use because although its manual gives caveats concerning it use for making important financial decisions concerning air quality management, it is a very quick and simple way of obtaining an indication of the air quality in a street and the likely effects of implementing a policy measure. It does not require excessive computer power and is easy to use. Again, as this model is capable of calculating percentiles, it would probably be a very good model for local authorities to use under the new National Air Quality Strategy.

3.4.1.3 Canyon Modelling

This type of modelling investigates pollutant dispersion within the street canyon, i.e. a single road surrounded by buildings. Generally, this is where the highest pollution concentrations can be found, due mainly to high levels of traffic and low ventilation in the canyon. The models are usually concerned with short range dispersion at ground level (Gould, 1996). Simulations are made of the dispersion from traffic along the road of interest, although it should be noted that other roads may contribute to pollutant levels in the road of interest. According to a number of papers on the subject (dePaul *et al*, 1985; Yamartino *et al*, 1986; Nakamura *et al*, 1988; Dabberdt *et al*, 1991), the geometry and shape of the street canyon is one of the most important parameters in this area of modelling. This is because the geometry of the canyon modifies wind flow and turbulence to such an extent that it significantly affects dispersion.

As a result, it is very difficult to model street canyon geometry and the resulting pollutant dispersion. However, many canyon models have been developed over the last 20 years, one of the earliest being the STREET model which investigates the dispersion of carbon monoxide (Johnson *et al*, 1973). DePaul *et al*, (1985), built on this model to develop a simple semi-empirical model to predict street level pollutant concentrations from ambient meteorological and pollution conditions. This was done by measuring the rate of pollutant exchange between the street canyon and the upper air for a typical uniform canyon shape under ambient wind conditions. The model was then developed from these results, using an estimation of concentration at the roof level of the canyon to extrapolate to the street level.

Simple modelling studies by Nakamura *et al*, (1988), determined several relationships between meteorological parameters above and within the canyon. It was found that the wind direction above the canyon was related to that within, and there was a linear relationship between wind speed above and within the canyon. Meanwhile, Yamartino *et al*, (1986) developed the Canyon Plume Box Model which comprised a series of sub-models to describe vehicle induced dispersion, plume transport, advective and turbulent exchanges at the top of the canyon and impacts from upwind intersections. It also attempted to model a secondary pollutant, nitrogen dioxide, by incorporating a very simple chemical scheme. A similar, more recent model to this is the OSPM model (Berkowicz *et al*, 1994).

3.4.1.4 Computational Fluid Dynamics Modelling

The use of computational fluid dynamics packages for dispersion modelling is one of the latest developments. This is beginning to prove very useful when modelling on the microscale in urban areas, for example, at the street canyon level. A recent example of some work in this area is by Scaperdas (1996) and Sca perdas *et al*, (1997), where computational fluid dynamics is used to model the small scale variation of carbon monoxide at an urban canyon junction. This work was an attempt to develop a method to analyse the significance of monitoring data by modelling micro-scale flow and dispersion patterns around real urban building configurations. It was found that wind direction significantly influenced monitored concentrations. However, one of the main drawbacks of this method is that it requires a lot of computing power and specialist expertise, which may not be available to a local authority.

3.4.2 Modelling Urban and Regional Areas

The above models are very local scale and generally do not include the urban background. In this category, pollutant dispersion occurs over a larger scale of tens of kilometres as air moves within the boundary layer (which extends approximately 1 km up into the atmosphere, from ground level). The time scale is hours rather than minutes. Different types of modelling at this scale include detailed chemical models and box models. These are discussed in subsequent sections.

3.4.2.1 Chemical Models (Lagrangian)

The models in the previous sections have dealt mainly with dispersion. The majority of them do not have any provision for any chemical reactions that may occur between the pollutants. This is a reasonable assumption if the species are inert, primary pollutants such as black smoke and carbon monoxide. However, pollutants such as ozone and nitrogen dioxide, which are currently of concern, are secondary and have a detailed and complex chemistry associated with them. Including a complex chemical scheme, along with a detailed dispersion mechanism can make a model very complex and difficult to use. It may also require an impractical amount of computing power.

In addition to dispersion modelling, models can also be used to model chemical behaviour. The majority of models developed to study air pollution chemistry do include a dispersion scheme since the two are so closely interlinked. Several models have been developed to investigate the production of oxides of nitrogen in urban areas- for example studies have been carried out to determine the contribution of the 'quadratic' nitrogen reaction to levels of nitrogen dioxide in the street canyon (Hov *et al*, 1984) . A simple model was developed to investigate the simultaneous effect of chemical conversion of nitric oxide to nitrogen dioxide and the turbulent dilution of the vehicle exhaust plume. From this model, the following factors were thought to influence nitrogen dioxide formation:

- the reaction rate of the reaction: $NO + NO + O_2 \rightarrow NO_2 + NO_2$;
- the initial oxygen deficit in the exhaust gas;
- the degree of dilution and intensity of mixing with time;
- the background concentrations of ozone, nitrogen dioxide and nitric oxide;
- the ratio of NO_2 / NO_x in the exhaust emissions;
- the initial concentration of NO;
- the characteristic reaction time of the exhaust gases;
- the air temperature.

Overall, the model showed that the quadratic nitrogen dioxide reaction contributed somewhat to measured nitrogen dioxide levels, but only under extreme conditions with respect to the initial mixing of the exhaust gas plume would the contribution be substantial.

When modelling nitrogen dioxide, existing models, such as CALINE, are modified with a simple chemical scheme to calculate nitrogen dioxide concentrations or a simple box model is created in response to a set of measurements such as the December 1991 episode (Derwent *et al*, 1995).

The majority of chemical and box models are either Lagrangian or Eulerian in form. Lagrangian models consider how the air parcel is affected by emissions along its path. The Lagrangian model consists of following the history of air along trajectories, often over changing meteorological and topographical conditions. This is particularly useful for modelling the long range transport of pollution and can be used to trace back to the source of pollution. This includes all models where plumes can be broken up into elements such as particles and puffs (Zannetti, 1992). Lagrangian models are popular because, like the Gaussian models, they are simple in concept and application. They can handle detailed chemistry and meteorology and can quickly evaluate the effect of input parameters.

Lagrangian models can be divided into two major types:

- Source models (forwards);
- Receptor models (backwards).

Source models start an air parcel along its trajectory from the source point of the emissions and subsequent concentrations are modelled from that point, going forwards in time. In contrast, receptor models involve the air parcel following a trajectory backwards in time from a specified end point. This means that the history of a trajectory that led to that particular end point can be traced.

The majority of Lagrangian models are box models are where the air mass over a region is treated as a box (either in the form of a parcel or column of air) into which pollutants are emitted and undergo chemical reactions. Also taken into account by the model is transport in and out of the box by meteorological processes.

One of the largest and most well known Lagrangian models is the EMEP Acid Deposition Model. This is a receptor-oriented, one layer trajectory model. The formulation of the model is based on budget equations for the chemical development within air parcels following the atmospheric motions. These are expressed as ordinary first order differential equations and are integrated in time along the two dimensional trajectories of the air parcels. During transport, emissions from the underlying grid of a 150 km resolution, chemical processes in the air, and wet and dry deposition to the ground are taken into account. The trajectories are calculated from the wind field at a level representing the transport within the atmospheric boundary layer. The purpose of the model was to quantify the atmospheric deposition of acidifying species to Europe and to determine the source of the supply. One of the main advantages of using a Lagrangian instead of a Eulerian approach for this task is that it is fairly modest in its computer requirements, as it carries out its calculations in sequence. The Lagrangian approach also makes it possible to calculate separately the contributions of different sources and to scale results with respect to changes in emissions. This is particularly useful for aiding policy making decisions (Williams, 1996).

However, it should be noted that there are a couple of disadvantages associated with them. The main one being that any errors in trajectory determination tends to grow exponentially in time and trajectories can be advected out of the area of calculation (Pasquill, 1983). They are also incapable of treating variation of the wind with increasing height and it is impossible to model three-dimensional wind fields. The vertical variation of the wind speed is taken into account either by using a vertical average wind speed over the height of the air parcel, or by using wind speed data at a representative height for the whole of the model. In addition, it should also be noted that concentration outputs are the average concentrations over the volume of the air parcel or box.

One of the most interesting Lagrangian models to deal with chemical interactions over an urban area is the London Plume Model (Hough, 1986; Hough *et al*, 1987). This is a two layer box model which represents a moving part of the boundary layer. It has an extensive chemical scheme comprising 180 chemical species and 339 chemical reactions (Dimitroulopoulou, 1997). It has mainly been used to investigate three case studies, two with a moving box and one with a stationary box. The first two case studies investigated the influence of the London air plume over rural areas in Southern England and the effects of emission abatement strategies downwind of London. The third case study with fixed box investigated photochemical behaviour in London itself. A more detailed description of this and other detailed photochemical models, such as the UK Photochemical Trajectory Model is given in Dimitroulopoulou, (1997). The complicated chemical scheme in the London Plume Model is handled by a numerical integration package called FACSIMILE, which was developed at AEA Technology, UK. This is a fairly specialised package and would not be very convenient for a local authority to use.

Although these models are very good at describing the detailed chemistry that occurs within an air parcel, they tend not to characterise the urban area itself in any great detail, especially at street level. They characterise the events that happen in the air mass well above the urban area very well, but do not characterise the urban background itself.

3.4.2.2 Urban Box Models (Eulerian)

This is where the air mass over an urban area is treated as a box, either in the form of a parcel or a column of air into which pollutants are emitted and undergo chemical reactions. Meteorological processes that affect transport in and out of the box are also considered. Under the Eulerian approach, the atmosphere over a region is divided into a grid. The concentration of pollutants at a particular geographical point is calculated, as the air moves through the framework and chemical transformations occur within each cell. In the simplest form of the model, the change in concentration in a box over time is calculated from the net flow of pollutant through the sides, plus the emissions into the box, divided by the box volume.

The main advantage of using this modelling technique is that they can deal with complex, three-dimensional wind fields. In principle, they can take the vertical variation of wind speed with height into account more easily than the Lagrangian models. As a result, most weather prediction models have a Eulerian format. Eulerian models can model in three-dimensions which enables the production of pollution maps, which is advantageous for studying pollution episodes. However, the models can become very complex and as the calculations are carried out simultaneously, can require a phenomenal amount of meteorological information and computing power. In addition, there is often a very coarse resolution which leads to the bottom one hundred metres being treated as one uniform entity. However, the last one hundred metres is often of great interest. Therefore it would be useful to have a model that characterised this area in order to investigate pollutant dispersion just above the canyon.

The London Plume Model, as described in the previous section, is an example of a Lagrangian urban box model. Eulerian urban box models tend to be used widely in the United States, for example, in the urban airshed models. A particular example is the Urban Airshed Model (UAM) developed by Scheffe *et al*, (1993). This is a three dimensional photochemical grid model, designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations. It is based on the diffusion equation, which is solved in the model along the x, y and vertical directions. It also contains a detailed photochemical scheme and is widely used by many organisations. This type of model is especially good at modelling air quality in a city with complex windfields, such as Athens. This is less important for a city such as London, which has less complex wind patterns, although it could be argued that the London heat island and coastal effects are strong enough to influence the wind.

3.4.3 The New Dispersion Models

There have been substantial advances in our understanding of the structure and formation of the boundary layer and dispersion. As a result, modelling theory has evolved further and consequently a new approach to modelling is being developed. A prime example of one of these types of model is the UK Atmospheric Dispersion Modelling System (UK-ADMS). This was developed in 1994 by Carruthers *et al.* Their aim was to produce a model with more reliable and accurate results since air quality standards are becoming more stringent and finely tuned. It was also an attempt to investigate pollutant dispersion on several scales.

The central theme of the model is that it presents a new, advanced approach to the modelling of the boundary layer. It uses the theory that vertical profiles of mean velocity, temperature and turbulence in the boundary layer depend on the values of the height above ground, the height of the boundary layer and the Monin-Obukhov length. This is a length scale determined by the friction velocity, the heat flux and the air temperature at the surface. As this theory is universal, it means that this model can be used at any location (both rural and urban) (Carruthers *et al*, 1994; Smith, pers. comm.).

There are several reasons why ADMS has a number of advantages over existing dispersion models. Firstly, the structure of the model is divided up into a number of modules. Each of these modules deals with one aspect of the model, either a part of the dispersion process, the data input or the data output. A control programme interlinks and sequences all the modules during model runs. The main advantage of this system is that each module can be modified independently of the rest of the model, which allows the model to be kept scientifically up to date.

The model can take into account many factors that influence dispersion, including plume rise, wet and dry deposition, radioactive decay, hilly and other terrain of variable roughness, coastal regions and large buildings. This makes the model applicable to many different situations and very versatile. It is also capable of calculating percentiles which is very useful for comparison with air quality standards and should give it the potential to make it a valuable tool for using in conjunction with the National Air Quality Strategy.

As yet, there is no chemical scheme incorporated in the model. This is currently being developed by the team at Cambridge Environmental Research Consultants. However, it will prove a difficult task, since incorporating a chemical scheme within a Gaussian framework is very complicated.

Finally, it is very user-friendly. It has been designed so it can operate through Microsoft Windows™. Therefore, it could easily be used by a local authority.

While ADMS seems to be a real advance in dispersion modelling and has the potential to become a major tool for air quality modelling, there are still a few disadvantages and factors requiring further development. It has been found that when the complex terrain and building modules are used, run times (using a

Pentium personal computer) can take several days. This is also true for multiple source assessments (Bull, 1997).

On a final note, it has been found from a recent study commissioned by Her Majesty's Inspectorate of Pollution (1996) to compare R91 and ADMS predictions against archived measurements for five large combustion plants. It was found that ADMS gave more reliable predictions than R91 (Carruthers *et al*, 1996). This gives some indication that ADMS may well be in a position to become one of the most heavily used models. The newly created Environment Agency is planning to investigate this further.

3.5 Conclusions

It can therefore be seen from this chapter that dispersion modelling is extremely varied and can range from the very simple to the vastly complex. It was intended that the previous sections should illustrate a few examples of the types of models available to investigate the dispersion of pollutants, particularly in urban areas. Although the list of examples discussed here is not exhaustive, the major types of model have been illustrated.

All the models discussed above have their advantages and disadvantages, but it should always be remembered that it is an impossible task to model accurately and include every parameter of the environment that will affect pollutant dispersion and behaviour. In addition, it is not just the model itself that determines modelled pollutant concentrations, the input data plays a major role. This will include various meteorological factors and emission factors and these datasets are subject to their own limitations.

However, it can be seen from the discussion in this chapter that the local and large scale models do not mesh together easily. The large scale models do not really give the background air quality just above the street canopies. This is important because pollutants above the canopy can be entrained down into the canyon and affect air quality there. They also do not adequately cover the marked concentration profiles over the lowest 100 to 200 metres. This is the gap that the work in this thesis tries to address.

In relation to the National Air Quality Strategy, guidelines have not yet been issued in regard to modelling. The Department of the Environment is currently investigating this area. It is more difficult for national guidelines on modelling to be issued since the Department of the Environment is not easily able to recommend one model over another because of commercial complications.

To continue this study of the behaviour of nitrogen dioxide in urban areas, a simple Lagrangian model, URBNOX has been developed. It is an attempt to bridge the gap in modelling demonstrated above. A chemical scheme to describe a secondary pollutant formation will be coupled with vertical dispersion to describe pollutant behaviour at both the street level and some distance above that. In the next few chapters, it will be used in a number of studies to investigate the vertical distribution of pollutants in urban areas. It will also be attempted to determine the factors under which elevated nitrogen dioxide levels occur. In addition, URBNOX will be used to investigate the role of scale in urban modelling studies. Finally, a preliminary investigation into nitrogen dioxide abatement will be made to round off the study.

Chapter 4 - URBNOX: Model Development and Winter Episodes

4.1 Introduction

The previous chapter was a review to illustrate the development of urban air quality modelling. It showed the major types of model available and was intended to demonstrate some of the gaps in current air quality modelling. It also introduced URBNOX, a simple air quality model which was developed to investigate the behaviour of nitrogen dioxide and forms a major part of the work presented in this thesis.

The aim of this chapter is two-fold. It will start by describing the structure and the basic parameters of URBNOX. The second part of the chapter will then present preliminary runs to investigate the formation of winter episodes, including some basic sensitivity studies.

The model was originally tested by running a conceptual base case to illustrate the events of a typical winter episode. There were two main reasons for this. Firstly, to investigate the behaviour of the chemistry and secondly to illustrate some of the problems encountered in modelling. As mentioned in the previous chapter and explained in detail in this one, URBNOX is a simple Lagrangian diffusion model. It comprises a simple chemistry in order to study the downwind distribution of nitrogen dioxide, nitric oxide and ozone in urban situations.

4.1.1 Introduction to Winter Episode Modelling

Under winter conditions, Bower *et al* (1994) showed, amongst others, using a very simple model, that the quadratic equation ($2NO + O_2 \rightarrow 2NO_2$) has an important role to play in the formation of nitrogen dioxide episodes. It is a slow reaction which normally does not contribute significantly to nitrogen dioxide formation under ambient levels of nitric oxide. However, Bower showed that under episode conditions and high levels of nitric oxide, this mechanism contributed significantly to the high levels of nitrogen dioxide being formed. In the same study, a simple box model was used to explain the hourly rate of change of episode peak concentration. It was shown, using the parameters explained in the paper, that there was an hourly increase in NO_x of 46 ppb.

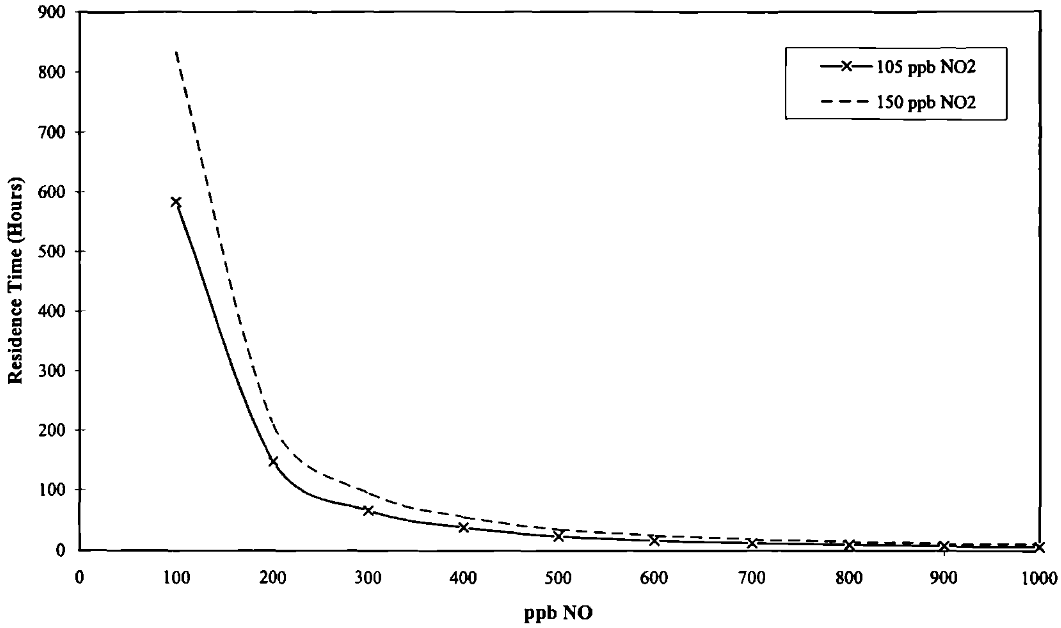
A similar approach to the above was taken to investigate how long it would take for levels of nitrogen dioxide formed from the quadratic equation to exceed the EC Directive of 105 ppb and the EPAQS Standard of 150 ppb, under differing concentrations of nitric oxide. The reaction rate was taken as $(1200*EXP(530/Temperature))*2*(8.31*10^{-3})$ s^{-1} per mol / dm^3 (Smyth, 1993), as used in URBNOX. The results are summarised in Table 4.1. The results are also shown in a graph in Figure 4.1.

Table 4.1: Number of Hours Taken for Concentrations of Nitrogen Dioxide to Exceed Air Quality Standards Under Differing Concentrations of Nitric Oxide

Nitric Oxide Concentration (ppb)	Amount of NO_2 Produced per Hour Using the Quadratic Equation (ppb)	Number of Hours Taken to Reach 105 ppb of Nitrogen Dioxide	Number of Hours Taken to Reach 150 ppb of Nitrogen Dioxide
100	0.2	583	833
200	0.7	148	211
300	1.6	66	94
400	2.8	38	54
500	4.5	23	33
600	6.4	16	23
700	8.7	12	17
800	11.4	9	13
900	14.4	7	10
1000	17.0	6	9

It can be seen that under ambient conditions of nitric oxide, it takes hundreds of hours for levels of nitrogen dioxide to exceed the air quality standards, from the quadratic equation. However, as levels of nitric oxide reach very high concentrations, it takes less than a day for nitrogen dioxide levels to build up to levels greater than 100 ppb.

Figure 4.1: Graph to Show the Number of Hours Taken For Concentrations of Nitrogen Dioxide to Exceed Air Quality Standards Under Differing Concentrations of Nitric Oxide



Therefore, it can be seen that this simple calculation goes some way towards predicting the conditions under which high levels of nitrogen dioxide are built up. However, it does not make any provision to consider the meteorological conditions that occur during episodes which can have a significant effect on the dispersion and build up of nitrogen dioxide.

URBNOX has been developed in order to investigate both winter and summer episodes. It contains both meteorological and chemical parameters in order to investigate how they affect the formation and dispersion of nitrogen dioxide under episode conditions.

4.2 Introduction to URBNOX

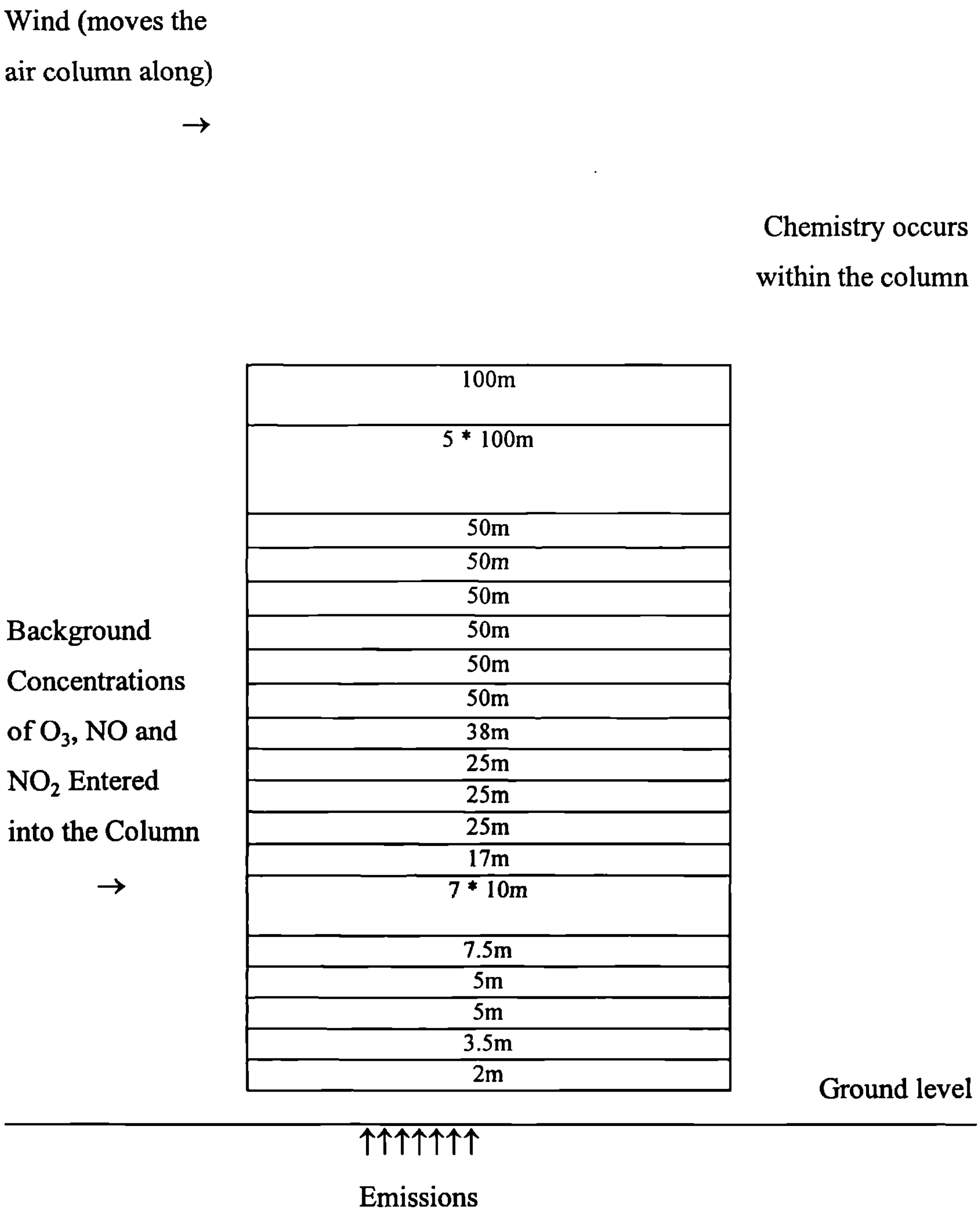
The aim of this section is to provide an introduction to the development of the model and explain why it has been developed. As explained in the previous chapter, the problems associated with urban air quality modelling can be summarised thus:

- incorporating chemistry and keeping it simple;
- difficulties of dealing with dispersion and chemistry within the same model;
- reflecting horizontal and vertical scales.

The aim of URBNOX is to make an attempt to overcome these problems. URBNOX is a simple Lagrangian diffusion model, simulating a column of air moving across an urban area. A Lagrangian model was chosen because it is easier to simulate chemical behaviour within a Lagrangian framework than a Gaussian one. A Eulerian framework was not chosen due to constraints on computing power. In addition, one of the keys aims of this thesis is to investigate the vertical variation of nitrogen dioxide and ozone distribution. Therefore, any model used or developed to investigate this will require very good vertical resolution, especially near the ground. It has been acknowledged in ApSimon *et al* (1994) that a Lagrangian model will offer a better resolution than any of the current Eulerian models. It is a source model in that the air column will start off at the source point of the emissions and concentrations will be modelled forward in space from that point.

The column is divided into graduated layers (typically 30), with thinner layers of a few metres thickness close to the surface and deeper layers aloft). Starting off with background concentrations upwind of the city, emissions are introduced at the bottom of the column. It comprises a simple chemistry in order to study the vertical and downwind distribution of nitrogen dioxide, nitric oxide and ozone in urban situations. Vertical mixing is dependent on a turbulence profile, as a function of height (K_z). A simple diagram of the model's structure is shown in Figure 4.2.

Figure 4.2: Diagram of Structure of URBNOX



URBNOX is intended to be a very simple model. It will be used to investigate the vertical distribution of nitrogen dioxide and ozone. An investigation will also be made to try and determine the conditions under which high levels of nitrogen dioxide are formed. In addition to this, the model was utilised to study the formation of summer episodes. The studies will take place in this chapter and over the next chapter.

This investigation will commence by outlining the structure of the model and describing some of its parameters. The model will then be used in the illustrative study contained in this chapter where a winter episode will be modelled. It will be based on the December 1991 episode. Sensitivity studies will be carried out on a number of the parameters. These will be covered in this chapter. A preliminary validation of URBNOX will then be carried out, using the data recorded at the Queen's Tower (as reported in Chapter 2). It is hoped this will also provide some insight into the vertical distribution of nitrogen dioxide and ozone.

A case study is then presented, using data recorded from a photochemical episode in May 1995, supplied by the South East Institute of Public Health (SEIPH). This will be used to try and validate URBNOX and to investigate the factors under which summer episodes of ozone and nitrogen dioxide are formed. This, and the Queen's Tower validation, can be found in Chapter 5.

4.3 The URBNOX Model and its Parameters

URBNOX has a number of variable parameters contained within its structure and for ease, the major ones are summarised over:

- The Chemical Scheme;
- Diffusion Profile and K-value (diffusivity);
- Emissions;
- Wind Speed;
- Insolation;
- Mixing Height;
- Background Concentrations of ozone, nitrogen dioxide and nitric oxide;
- Fraction of NO_x Emission taken as NO and NO_2.

Each of these parameters will then be taken in turn and discussed in detail in the following sections.

4.3.1 Chemistry in the Model

The chemical scheme contained within URBNOX is very simple and comprises the following three reactions, along with the following reaction rates:

$NO_2 + h\nu \rightarrow NO + O$ RJNO2 $= 0.01\ s^{-1}$ in strong sunshine (4.1)

$NO + O_3 \rightarrow NO_2 + O_2$ RK2 $= 1.0 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (4.2)

$2NO + O_2 \rightarrow 2NO_2$ RK1 =

(1200*EXP(530/Temperature))*2*(8.31*10^{-3}) $dm^3 mol^{-1} s^{-1}$ (4.3)

i.e. (118)

(Source of RK1 and RK2: Campbell, 1986);

(Source of RK1: Smyth, 1993).

The role of these chemical reactions within urban nitrogen chemistry is discussed in depth in Chapter 1. One of the aims of developing URBNOX was to find out if the above chemistry, along with certain assumptions about meteorological conditions and atmospheric stability, could be used to explain high NO_2 concentrations measured in urban areas.

4.3.2 Diffusion in the Model and Diffusivity

Some models, such as the EMEP model, treat vertical mixing by assuming instantaneous vertical mixing of the chemical species, which results in a uniform vertical concentration profile. This can result in the underestimation of concentrations near the ground. A correction factor for this was determined by Metcalfe *et al* (1989), which was applied to the concentrations.

Vertical mixing in URBNOX (and hence the distribution of pollutant concentrations) is determined by the diffusion equation:

$$\partial C / \partial t = \partial / \partial z \, (K_Z \, \partial C / \partial z) \qquad (4.4)$$

where:

C = concentration

t = time

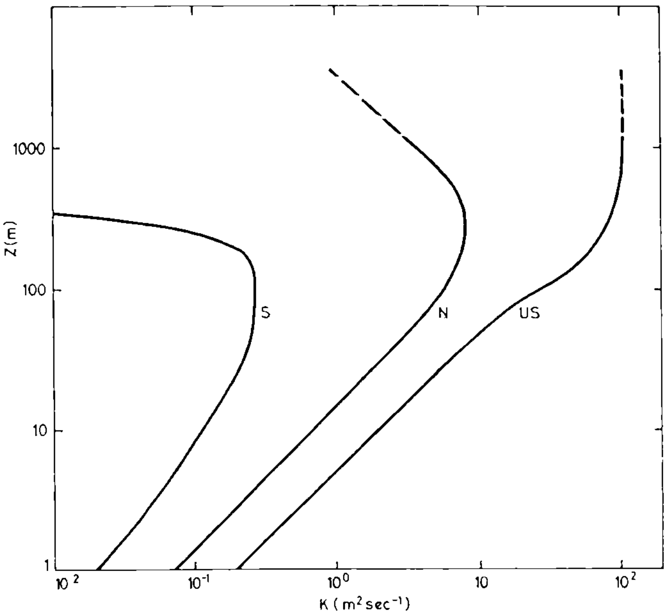
z = height

K_z = vertical diffusivity

K_z is the vertical diffusivity, which is a function of height for different stability conditions. Near the surface it is very small, varying approximately linearly with height near the ground. It then departs significantly from this form at heights which increase with increasing stability. It rises with height to values close to the maximum value over most of the mixing layer. K_Z then starts to fall with height above approximately 100 metres in stable conditions and 500 metres in unstable conditions (Pasquill, 1974). This is illustrated in Figure 4.3.

Figure 4.3: Profiles to Show Variation of K-Value With Height

(Source: Pasquill, 1974)



In a similar manner to the work done with the TERN model (ApSimon *et al*, 1994), K_z can be simplified and is taken here to increase in proportion to height to a maximum value (K_{max}) at height Z_0. K_z then remains constant at this value over the rest of the mixing layer. Above the mixing height, K_z is assumed to be negligible.

This is a very simple approach and was used, instead of a more complex profile, in order to keep the model simple and uncomplicated. The values of Z_0 and K_{max} can be varied to represent different stability conditions, as explained in Box 4.1. This is taken from ApSimon *et al* (1994). The TERN model describes diffusion profiles in rural areas. These would not necessarily apply over urban areas since the internal boundary layer modifies the bottom of the profile. As a result, urban K_Z values will not be as small as those in rural areas. A large range of K_Z values are investigated in the modelling studies presented here.

Box 4.1

At night

Pasquill stability Category F conditions are assumed when geostrophic winds, G, are less than $6ms^{-1}$ and cloud cover is < 3/8. In this case surface inversions are likely to form, extending over the lowest 100m or so. Z_o is taken as 75m, and $Kmax$= 0.09 G, with $Hmix = max$ (G*25,100).

Category E conditions are assumed when G is $< 6ms^{-1}$ and cloud cover > 3/8, or

$6 < G < 10$ and cloud cover < 3/8. Z_o is taken as 100m and $Kmax = 0.4G$, with $Hmix = max$ (50*G, 200).

Category D conditions are assumed when $G > 10ms^{-1}$, or $6 < G < 10$ and cloud cover > 3/8. Z_o is taken as 150 m, and $Kmax$ as 0.16 G^2, the quadratic dependence on G reflecting the depth of $Hmix$ varying linearly with wind speed.

During the Day

The diffusivity will depend on a combination of mechanical mixing due to high wind speeds and convective thermals. The diffusivity adopted is hence chosen according to the dominant effect, taking the maximum of the values A and B prescribed below (subject to a maximum value of 100 m^2s^{-1}), with Z_o taken as 200m. $Hmix$ is determined by the daytime mixing layer depth model as indicated in the paper.

(i) $A = 0.55\ 10^{-3}.\ H^{1/3}\ Hmix^{4/3}$ corresponding to convective mixing , where H is the upward heat flux into the atmosphere determined from the incoming insolation, J, as a function of zenith angle, multiplied by a factor Cf which depends on cloud cover;

$$H = 0.4(J-100) * Cf.$$

where:

Cloud Cover (oktas)	0	1	2	3	4	5	6	7	8
Cf	1.00	0.89	0.81	0.76	0.72	0.67	0.59	0.45	0.23

(ii) $B = 0.16\ G^2$ corresponding to mechanical mixing in stronger wind-neutral conditions. Over the sea, $Kmax$ is taken as proportional to the square of the depth of the mixing layer, this being proportional to geostrophic wind speed but corresponding to a reduced surface roughness, and adjusted for stability effects when the sea is cold relative to the overlying air mass (ApSimon *et al.*, 1983).

(Source: ApSimon *et al*, 1994)

A fourth- order Runge-Kutta method is used to integrate the diffusion equation in the model- using a time step of 1 second. It was used because it is flexible, simple and gives sufficient accuracy with low K_Z values.

4.3.3 Emissions

Emissions of NO_x are adjusted at the bottom of the air column every 10 km as it crosses the urban area. The urban area itself was taken to be 40 km across (approximately the size of London). The emission factor is derived from one of the many emissions inventories available. In total, four emissions inventories were examined. These were:

- National Atmospheric Emissions Inventory (NAEI) 1991;
- London Plume Model Inventory (LPM) 1991- this uses a 'per capita' approach;
- NAEI 1994;
- London Emissions Inventory.

The National Atmospheric Emissions Inventory is compiled by AEA Technology at the National Environmental Technology Centre on a 10 x 10 km^2 Ordnance Survey Grid. The inventory is put together from different categories of sources, namely area, such as vehicle classes, and point sources, such as power stations. Contributions from these different sources are totalled for each grid square, usually in tonnes per annum (NETCEN Archive).

The London Emissions Inventory was compiled by the London Research Centre (Chell *et al*, 1993). It covered an area of 1940 square kilometres, including the whole of Greater London. It is based on the Ordnance Survey 1 x 1 km^2 national grid, which gives it a finer resolution than that of the NAEI. The different categories of sources include line sources (such as roads and railways), area sources (such as from agricultural land) and point sources (such as from industrial plants) (Hutchinson, 1996).

The emission factor using the London Plume Model was calculated by taking the total NO_x emissions for the UK (NAEI 1991) and dividing it by the total population in order to obtain a per capita figure. This was then adjusted with respect to the population density of London to obtain an average emission (Hough *et al*, 1987).

The inventories were used in two major ways throughout the modelling studies:

1. The emissions for all the grid squares over London were totalled and averaged. This average figure was used to represent the emissions which were introduced into the bottom of the column every 10 km, over 40 km. This is done for all the runs in Chapter 4.

2. The emissions for the grid squares 5117 to 5417 were used as a 40km strip of emissions. This was then repeated with the grid squares 5118 to 5418. This is explored in Chapter 5.

4.3.4 Wind speed

Wind speeds are approximately logarithmic (or written as a power law), as shown in Equation 4.5:

$$u(z) = u_{10} (z / 10)^n \qquad (4.5)$$

where:

$u(z)$ = wind speed at height (z)
z = height
u_{10} = wind speed at a reference height of 10m
n = function of surface roughness
(Source: Clarke *et al*, 1979)
or, alternatively:

$u(z) = u^* / \kappa \ln (z - z_o / z_o)$ (4.6)

where:

$u(z)$ = wind speed at height (z)

z = height

u^* = the frictional velocity

κ = Von Karman Constant

z_o = roughness height (i.e. a measure of the surface roughness over which the wind blows)

The wind speed profile usually increases with increasing height because the drag effect decreases with height as it passes over the ground. The wind patterns over a city are difficult to model, therefore the wind speed for the model is taken as an average over the mixing layer depth, and the drag effect is not included. The wind speed is the parameter in the model that drives the column of air forward over the urban area.

4.3.5 Insolation

Insolation plays an important role in urban air chemistry for the following reasons:

- solar radiation initiates the formation of free radicals;
- it is very important for the dissociation of nitrogen dioxide.

Insolation initiates the dissociation of nitrogen dioxide, as shown in the equation below:

$NO_2 + hv \rightarrow NO + O$ (4.7)

The rate of this reaction can be expressed as :

$$R_p = J_{NO2} * [NO_2] \quad (4.8)$$

where:

R_p = rate of the photodissociation

J_{NO2} = photodissociation rate coefficient

$[NO_2]$ = concentration of NO_2

(Source: Campbell, 1986).

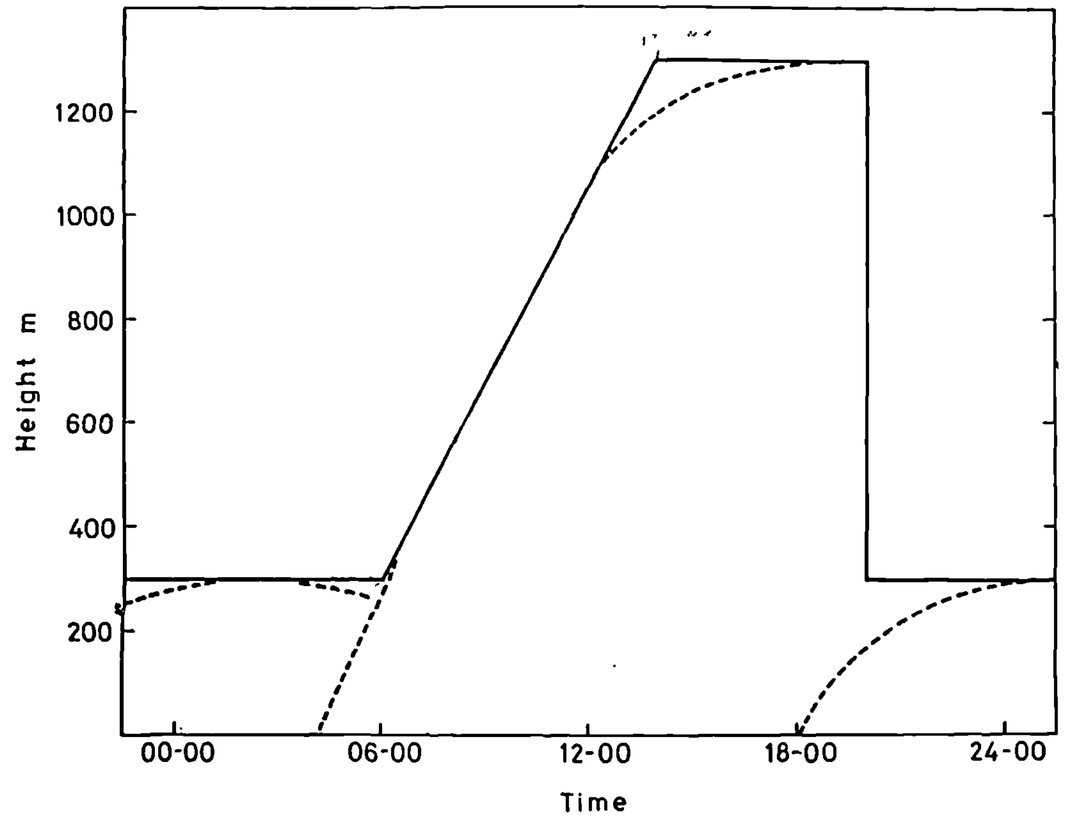
J_{NO2} is dependent on the solar angle, surface albedo, altitude and cloud cover.

4.3.6 Mixing Height

This can also be referred to as the boundary layer. This is not a static entity but evolves and changes over the course of the day. Many models, such as the TERN model, have incorporated a changing mixing layer. This is particularly important for models that run on a temporal basis. This approach was not used in URBNOX, since it is primarily a simple, spatial-scale model. It is sufficient to assign a value for the mixing layer that would be appropriate for the conditions that were being modelled. The diurnal changes in the mixing layer are illustrated by Figure 4.4 on the next page:

Figure 4.4: The Variation of the Mixing Height Throughout the Diurnal Cycle (Source: Hough, 1986)

Where: the solid line represents the mixing height for the model representation, and the broken lines are an approximation to the real situation.



4.3.7 Background Concentrations of Nitrogen Dioxide, Nitric Oxide and Ozone

These were included in URBNOX to represent the concentrations in the air upwind of the city and hence, to see what effect these would have on subsequent concentrations within the city.

4.3.8 Fraction of NO_x Emission taken as NO and NO_2

Although a small quantity of nitrogen dioxide is directly emitted as a primary pollutant, the majority of it is formed as a secondary pollutant from nitric oxide. One of the most important sources of this is from vehicle exhausts. Exhaust NO_x emissions are composed of between 90 and 95% nitric oxide and 10 and 5% nitrogen dioxide (UK QUARG I, 1993; Seinfeld, 1986; Hov *et al*, 1984). The nitric oxide is oxidised by oxygen under combustion conditions. This reaction is responsible for the small amount of primary nitrogen dioxide formed in vehicle exhausts:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (4.9)$$

This reaction is second-order in nitric oxide, but can be defined as a three-body reaction as three molecules are involved (Bower *et al*, 1994). However, this is only thought to be significant when several ppm (parts per million) of nitric oxide exist and it cannot account for very much nitrogen dioxide in the vehicle wake, because of rapid dilution.

There is some debate about the percentage of nitrogen dioxide formed from vehicle exhausts. Therefore, it was decided to assume, for the purposes of using URBNOX, that 95% of the total emissions were nitric oxide and 5% nitrogen dioxide. This will be explored in the sensitivity studies.

4.4 URBNOX Base Case

In this chapter, as explained in Section 4.1, a winter episode was simulated by the model. Summer episodes will be thoroughly explored in Chapter 5. As stated previously, these simulations are based on an air column moving across London, using representative emission histories. The emission factor used in URBNOX for these illustrative studies was taken from the National Atmospheric Emissions Inventory (NAEI) for 1991. This year was chosen in order to base the illustrative winter episode as closely as possible on the one that occurred in December 1991. The emissions for all the grid squares over London were totalled and averaged. This average figure was used to represent the emissions which were introduced into the bottom of the column every 10 km, over 40 km. Of this total NO_x emission, 95% of it was assumed to be NO and 5% NO_2 (Seinfeld, 1986).

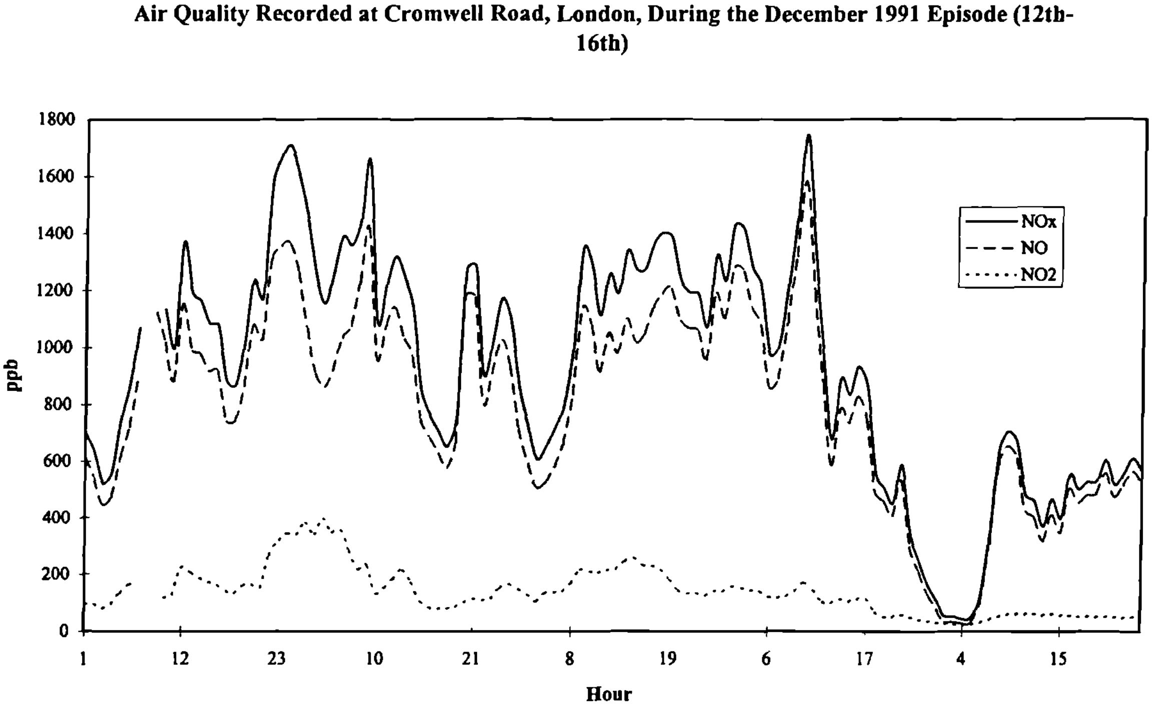
4.4.1 Winter Episode

This aim of this base case was to simulate an nitrogen dioxide episode similar to the one that occurred in December 1991. While not as severe as the sulphur dioxide smogs of the 1950s, it was nonetheless the most severe episode of its kind, and indeed since monitoring began in 1971 (UK QUARG 1, 1993). The episode began on the 12th of December and began to disperse on the 15th of December. It was remarkable because of the very high levels of nitrogen dioxide that were produced. It was characterised by classical winter stagnation conditions. In the few days leading up to the episode, the weather had been unusually sunny with north-easterly winds. Nitrogen dioxide build-up started on the 12th, and for the next few days meteorological conditions were characterised by low temperatures, low wind speeds (between 0 and 3 ms^{-1}) and a low boundary layer height (Smyth, 1993). Overall, conditions were very stable and typically anticyclonic from an anticyclone that was centred over the Alps and affecting south-east England (UK QUARG 1, 1993). Levels of nitric oxide soared, peaking at 1580 ppb at Cromwell Road towards the end of the episode on the 15th of December. Nitrogen dioxide exceeded the EC Directive Limit Value of 200 ug/m^3

(approximately 105 ppb) for the 98th percentile of hourly values in a calendar year (UK PORG, 1990) to reach levels over 400 ppb. The WHO Guideline of 210 ppb (hourly mean) was also exceeded. A time plot of nitrogen dioxide and nitric oxide levels for the duration of the episode can be seen in Figure 4.5 and Figure 4.6.

Figure 4.5: Time Plots of the Air Quality Recorded During the December 1991 Episode

(Source: NETCEN Archive)



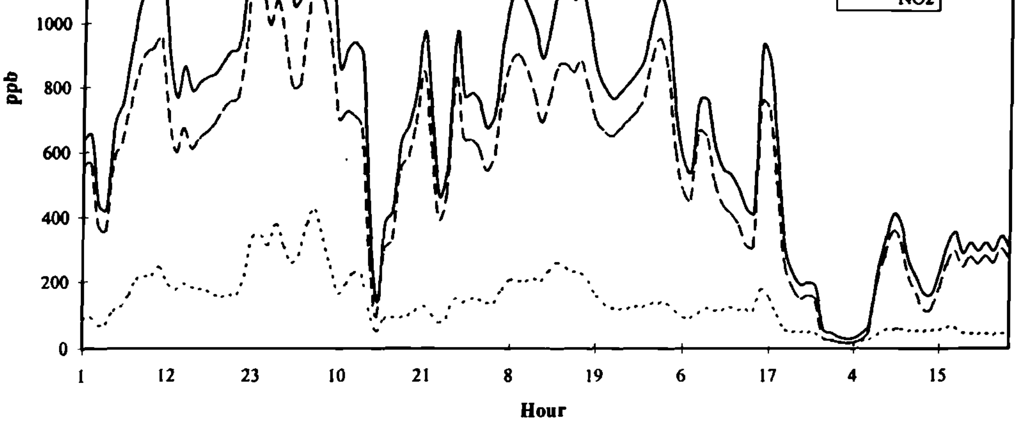
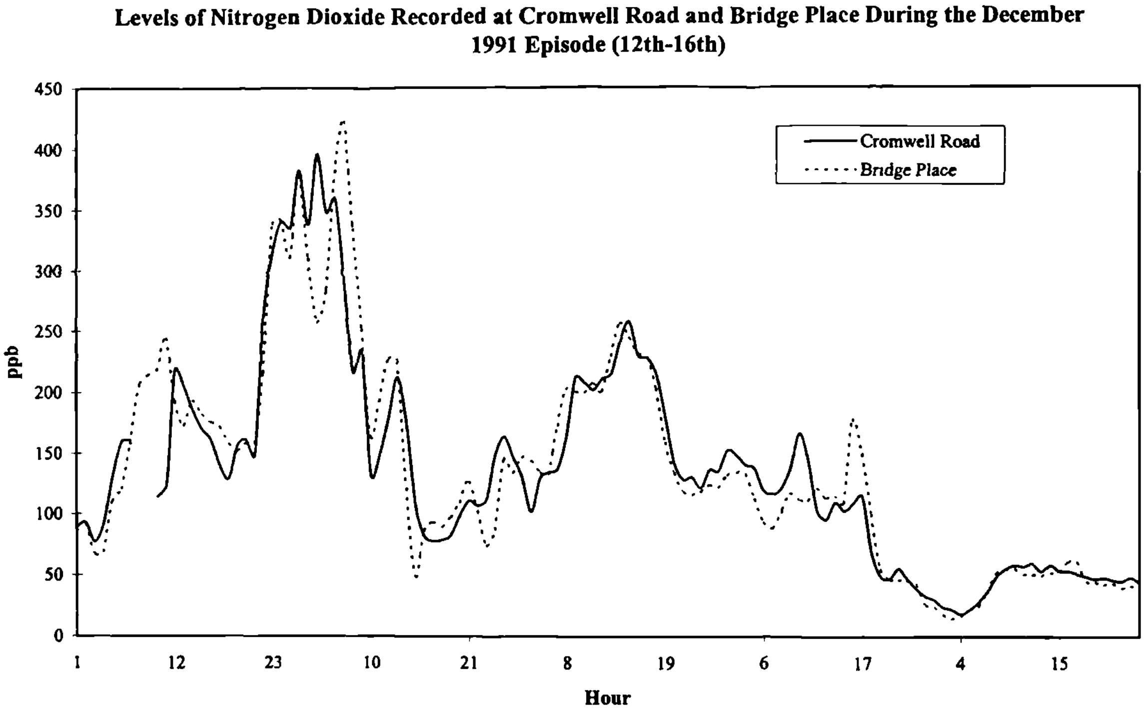


Figure 4.6: Time Plots of Nitrogen Dioxide Recorded at Two Sites During the December 1991 Episode

(Source: NETCEN Archive)



The model was therefore run using parameters as close to the above conditions as possible. Ambient winter background levels of ozone, nitrogen dioxide and nitric oxide to be entered into the model were taken as 9, 21, and 48 ppb respectively, as taken from Smyth (1993) (based on data from Warren Spring Laboratory, now NETCEN). Typical inversion conditions were chosen, which included a low mixing height of 150m. This was taken from Bower *et al* (1994), and was derived from Crawley ascent data during the December 1991 episode. The model run was initiated during the evening, since this is generally the time when NO_2 levels build up. Therefore, the dissociation rate of nitrogen dioxide was taken to zero in order to simulate the absence of any insolation. A low wind speed of 2 m/s was chosen as a representative wind speed for the episode. Vertical diffusivity (K_Z) was given the low value of 0.18 m^2s^{-1}. This was calculated using the scheme in ApSimon *et al*, (1994), and summarised in Section 4.3.2. As stated in Section 4.4, the emissions for this illustrative study were derived from the NAEI 1991. The emissions for the Greater London area were totalled and averaged to give a figure over every 10 km. The full range of parameters is summarised in Table 4.2:

Table 4.2: Summary of the Parameters Used in the Winter Episode Base Case

Parameter	**Value**
Wind Speed	2 m/s
Mixing Height	150 m
Diffusivity	0.18 m^2s^{-1}
Z_o	75 m
Dissociation Rate	0.0 s^{-1} to simulate the absence of sunlight
Emission Factor	8.55 x 10^{-8} mol/s/m^2
Fraction of NO_x Emission Factor as NO	95 %
Distance Travelled by the Air Column	40 km
Background Ozone	9 ppb
Background Nitrogen Dioxide	21 ppb
Background Nitric Oxide	48 ppb

The results are shown in Figure 4.7 and Figure 4.8 over the next two pages. Ozone was not plotted since it was rapidly depleted to negligible levels.

Figure 4.7: Modelled Vertical Profiles of Nitrogen Dioxide Across the Urban Area During Typical Winter Episode Conditions

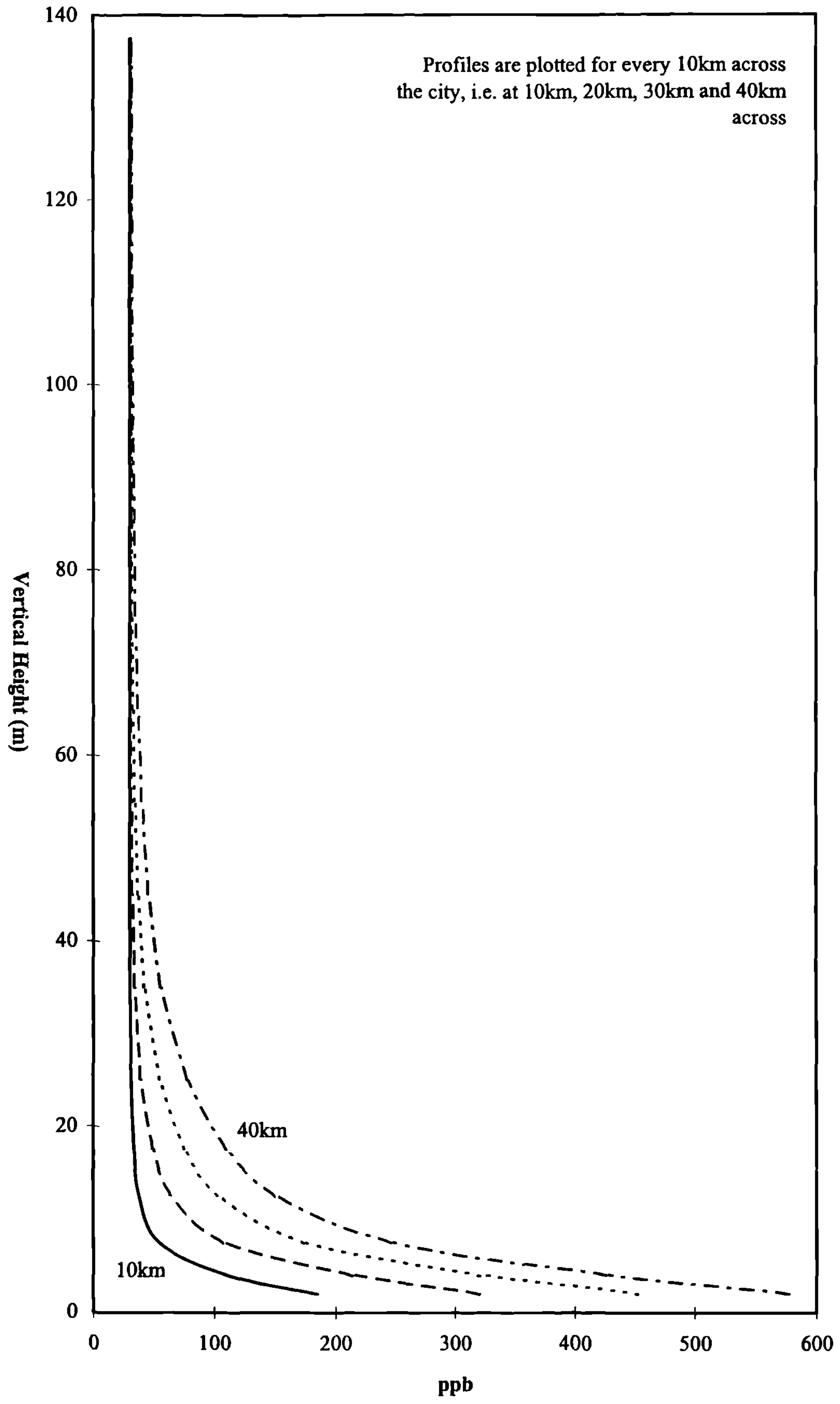
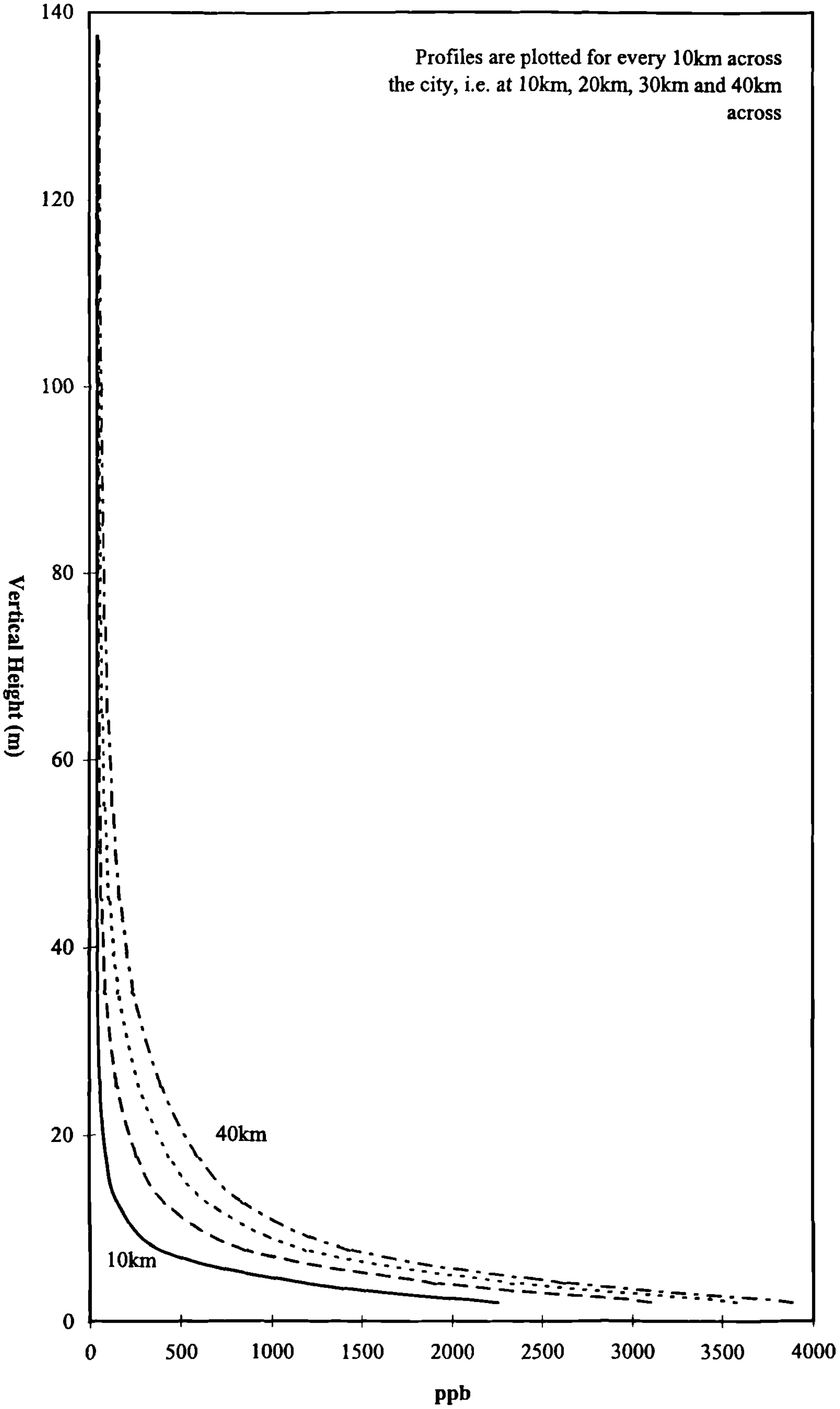


Figure 4.8: Modelled Vertical Profiles of Nitric Oxide Across the Urban Area During Typical Winter Episode Conditions



It is immediately apparent from the graphs that levels of nitric oxide become very high, particularly near the ground. Initially, these high levels are being formed by the emissions introduced into the model. As the diffusivity is low, along with stable atmospheric conditions, these remain trapped near the ground causing levels to decrease with height, as they would in a typical inversion. As the air column travels across the city and emissions are being fed into the base of the column, concentrations of nitric oxide and nitrogen dioxide increase, to reach a maximum at the downwind edge of the urban area. This would suggest that the emissions generated within the urban area (i.e. local effects) do play a very significant role in episode creation, and hence could be controlled accordingly.

The ozone is rapidly depleted to a negligible level by the high concentrations of nitric oxide present, forming oxygen and nitrogen dioxide (McKendry, 1993). This means there is little ozone to be dispersed downwind of the urban area and this is explored further in Chapter 5. The chemistry of this process is explained in detail in Chapter 1.

Once the nitrogen dioxide is formed, it is usually dissociated back to nitric oxide in presence of sunlight. However, as the model was run under night time conditions, this reaction does not occur. As a result, levels of nitrogen dioxide build up. Under the conditions in the model, levels of nitrogen dioxide accumulated in excess of 500 ppb. The maximum nitrogen dioxide level recorded during the December 1991 episode was 423 ppb at Victoria between 6 and 7 am on the 13th (Smyth, 1993). Therefore, URBNOX is slightly overpredicting but this may be due to its simplified chemical scheme which does not take any of the night-time chemical reactions. A full discussion about night-time chemistry can be found in Dimitroulopoulou (1997). However, the NO_2 : NO_x ratio for the base is 0.1. This is very low and compares well with measured NO_2 : NO_x ratios of 0.15 (Cromwell Road) and 0.2 (Bridge Place) (Bower *et al*, 1994).

4.4.1.1 Sensitivity Studies - Chemistry and Emissions

- Chemistry

A set of sensitivity studies was then carried out to determine the relative contribution, and hence importance, of the two reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (4.10)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (4.11)$$

The list of runs is shown in Table 4.3:

Table 4.3: List of Scenarios

Scenario
(1) Emissions with the $2NO + O_2 \rightarrow 2NO_2$ reaction switched off
(2) Emissions with the $NO + O_3 \rightarrow NO_2 + O_2$ reaction switched off
(3) Emissions with both reactions switched off
(4) No emissions with both reactions switched on
(5) No emissions with the $2NO + O_2 \rightarrow 2NO_2$ reaction switched off
(6) No emissions with the $NO + O_3 \rightarrow NO_2 + O_2$ off

It should be noted that all the other parameters were kept the same as for the previous run and a full summary can be seen in Table 4.2.

The results are summarised in Table 4.4:

Table 4.4: Results of Sensitivity Scenarios

Scenario	NO_2 Concentration in Lowest Layer at the Downwind Edge of the Urban Area (ppb)	NO Concentration in Lowest Layer at the Downwind Edge of the Urban Area (ppb)	O_3 Concentration in Lowest Layer at the Downwind Edge of the Urban Area (ppb)
Winter Base Case	577.5	3887.1	0.0
(1)	250.5	4213.0	0.0
(2)	570.4	3894.2	9.0
(3)	241.5	4222.0	9.0
(4)	30.2	38.8	0.0
(5)	30.0	39.0	0.0
(6)	21.2	47.8	9.0

It is clear from these results that the emissions being fed into the air column have the biggest influence over the quantities of nitric oxide and nitrogen dioxide present. When there are no emissions present, levels of nitric oxide and nitrogen dioxide fluctuate around the background levels fed into the column, as would be expected. When emissions are present, under the conditions in the model, levels of nitrogen dioxide still exceed air quality standards.

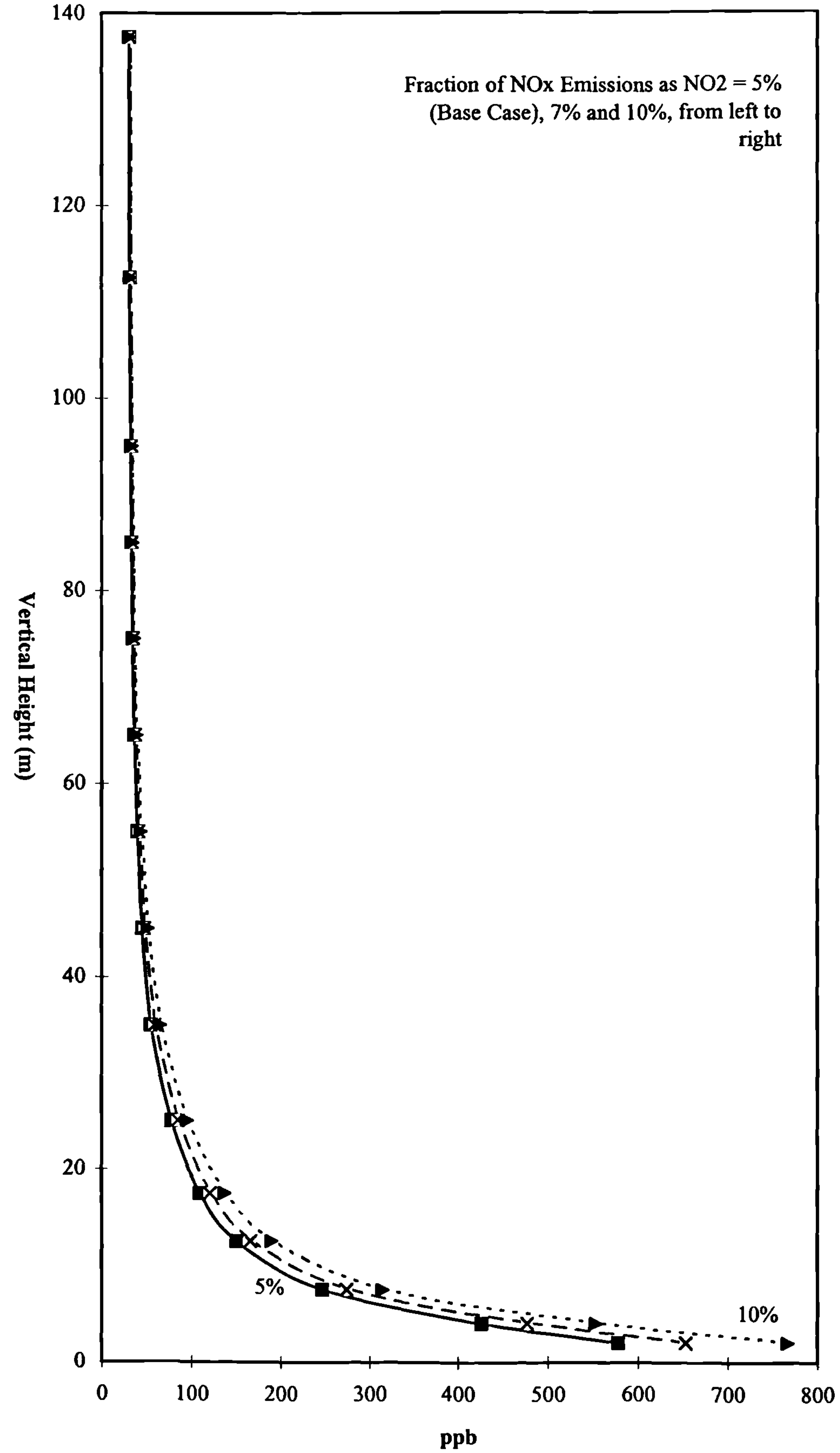
The reactions have a secondary influence, especially when there are no emissions. Both reactions have a different effect under different circumstances. For instance, when emissions are present, Reaction 4.11 contributes to produce 570.4 ppb of nitrogen dioxide. This is compared with 250.5 ppb produced with Reaction 4.10. However, when there are no emissions present, Reaction 4.10 contributes to produce more nitrogen dioxide than Reaction 4.11. The reason why less nitrogen dioxide is present in Scenario 6 is because it is limited by the ozone.

Therefore it can be seen from these model scenarios that Reaction 4.11 makes a significant contribution to high levels of nitrogen dioxide. However, there is some controversy over the significance of this reaction. In most atmospheric situations, the formation of nitrogen dioxide from primary emissions of NO_x is usually controlled by the reaction of nitric oxide with ozone. However, this reaction is unable to account for the high levels of nitrogen dioxide formed in the winter, since concentrations of ozone are so much lower at that time (Finlayson-Pitts *et al*, 1986). It is not yet clear exactly how nitric oxide is oxidised to nitrogen dioxide. The quadratic thermal oxidation reaction is the generally accepted mechanism, but there are still some doubts concerning it. This is mainly because the reaction rate is second order in nitric oxide, i.e. the speed of oxidation increases as the square of the nitric oxide concentration. Therefore under 'normal' conditions, when nitric oxide levels are low, the rate of oxidation drops to a very low rate, so reducing the importance of the reaction. However, under typical winter episode conditions with lower temperatures, with an accumulation of nitric oxide, oxidation speeds up and the reaction becomes significant. A consensus was reached by a Department of the Environment Discussion Group (1993) that the quadratic thermal reaction was indeed responsible for the high nitrogen dioxide levels observed in 1991. It is thought that Reaction (4.11) is enhanced in the presence of other vehicle exhaust constituents (Harrison *et al*, 1996).

- Fraction of NO_x Emissions as Nitrogen Dioxide

A sensitivity study was then carried out to determine the effect of the nitrogen dioxide fraction of the NO_x emissions on the concentrations of nitrogen dioxide subsequently produced. Studies by NETCEN (formerly Warren Spring Laboratory) have indicated between 5 and 10% nitrogen dioxide in total NO_x emissions from vehicles. However, it should be noted that these are for average driving cycles and not for idling engines (Smyth, 1993). This area is currently being investigated by Cox (1996). The winter base case was therefore repeated using 7% and 10% nitrogen dioxide and the results are shown in Figure 4.9.

Figure 4.9: Modelled Vertical Profiles of Nitrogen Dioxide at the Downwind Edge of the Urban Area Under Different Fractions of NO_x Emissions



The difference in fraction has more effect on nitrogen dioxide concentrations at the bottom of the column than at the top. This may be due to the small diffusivity value used. As would be expected, the greater the fraction of nitrogen dioxide in the emissions, the greater the concentration of nitrogen dioxide produced. When the nitrogen dioxide fraction is doubled from 5 to 10%, there is an approximately 200 ppb increase in nitrogen dioxide concentrations at ground level, at the downwind edge of the urban area.

- Emissions Inventories

Emissions inventories are a very important component of air quality management systems and have a wide range of applications in both air quality modelling and the formulation of control policies. It is therefore important that they are as accurate as possible (Hutchinson, 1996; Seika *et al*, 1996). There are many different emissions inventories available, as explained in Section 4.3.3. The aim of this sensitivity study is to investigate how the results from URBNOX are affected by using different emissions inventories. A summary of the different inventories used is shown in Section 4.3.3. Figure 4.10 below shows the difference between the average values for nitrogen oxides emissions between each inventory, over the Greater London area. URBNOX was run using the same parameters for the winter base case, using a different inventory for each run. The results are presented in Table 4.5, Table 4.6 and Figure 4.11.

Figure 4.10: Graph to Illustrate the Differences Between Four Different Emissions Inventories

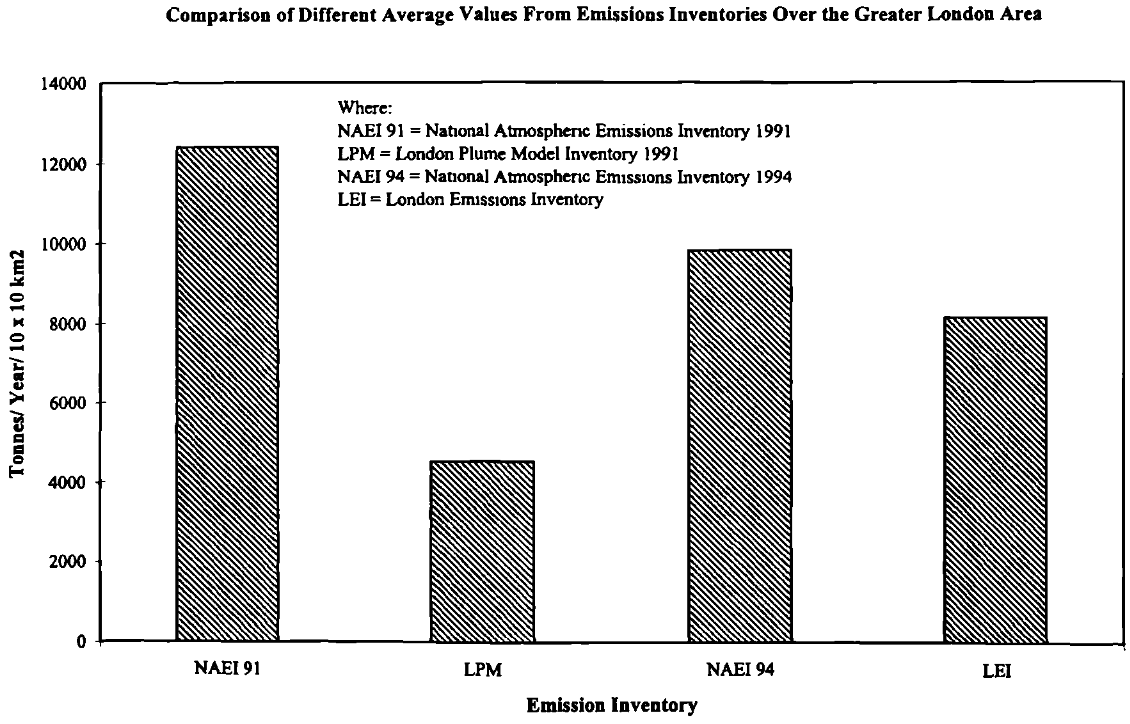


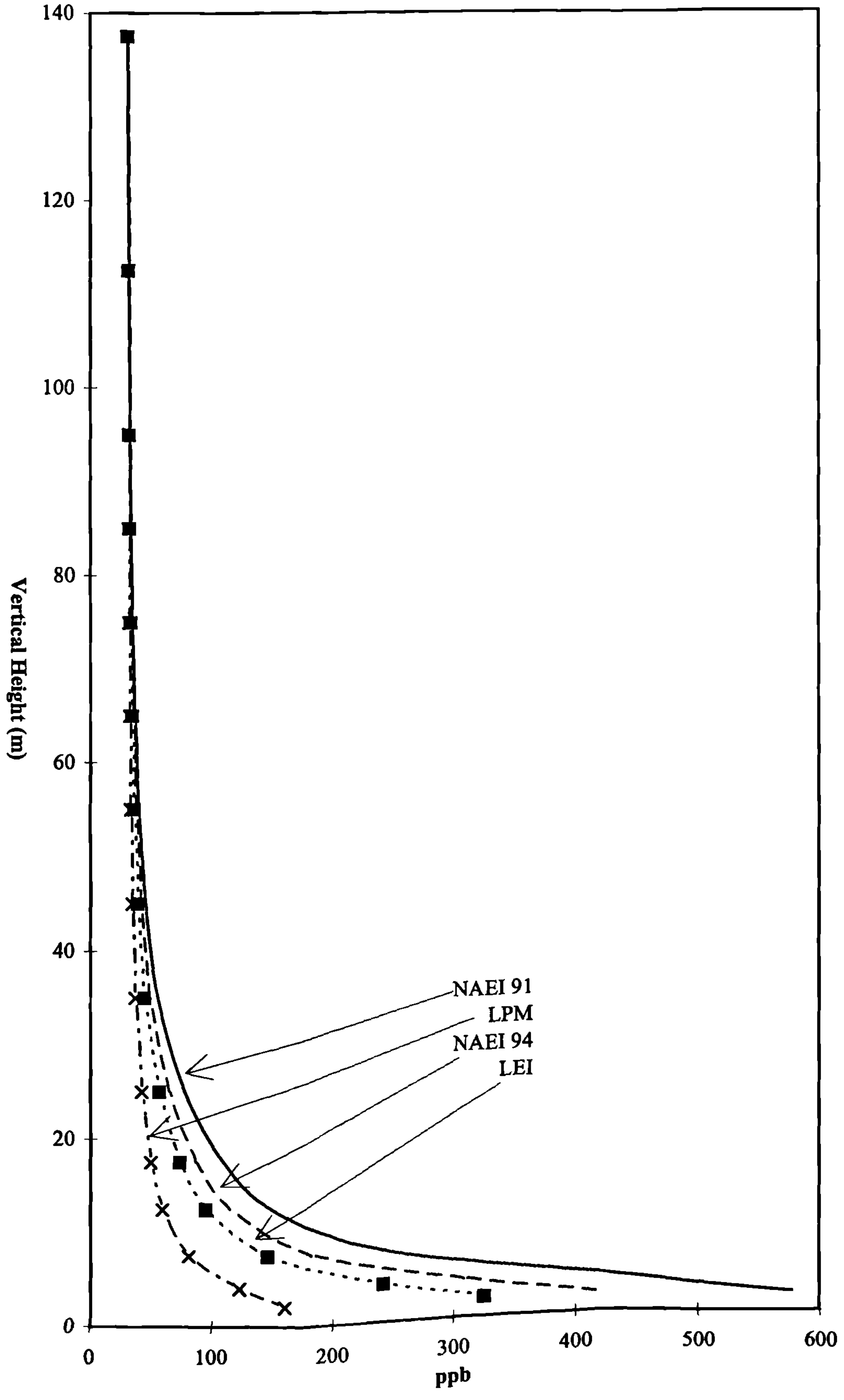
Table 4.5: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Using Different Emissions Inventories

Vertical Height (m)	**Emission Inventory**			
	NAEI 1991 (Base Case)	**LPM 1991**	**NAEI 1994**	**LEI**
137.5	30.7	30.4	30.6	30.5
112.5	31.3	30.5	31.0	30.8
95.0	32.2	30.8	31.7	31.4
85.0	33.0	31.0	32.3	31.8
75.0	34.2	31.3	33.1	32.5
65.0	36.2	31.8	34.5	33.6
55.0	39.4	32.6	36.8	35.3
45.0	44.9	33.9	40.7	38.3
35.0	55.0	36.4	47.9	43.8
25.0	77.5	41.7	63.8	55.9
17.5	109.5	49.1	86.3	73.0
12.5	150.1	58.4	114.7	94.5
7.5	246.4	80.3	182.2	145.5
4.0	426.2	122.0	308.7	241.6
2.0	577.5	159.8	417.0	325.0

Table 4.6: Modelled Nitric Oxide Concentrations (ppb) at the Downwind Edge of the Urban Area Using Different Emissions Inventories

Vertical Height (m)	**Emission Inventory**			
	NAEI 1991 (Base Case)	**LPM 1991**	**NAEI 1994**	**LEI**
137.5	45.0	41.1	43.8	42.9
112.5	50.2	43.1	47.9	46.4
95.0	59.4	46.5	55.2	52.5
85.0	66.6	49.2	61.0	57.4
75.0	77.0	53.1	69.3	64.3
65.0	93.1	59.2	82.3	75.1
55.0	118.8	69.0	102.9	92.4
45.0	160.9	85.0	136.7	120.7
35.0	234.8	113.2	196.2	170.6
25.0	387.7	171.8	319.4	274.0
17.5	591.7	250.5	484.0	412.3
12.5	842.9	347.7	686.9	582.9
7.5	1433.3	576.4	1163.9	984.0
4.0	2628.3	1036.2	2127.3	1793.1
2.0	3887.1	1512.9	3137.0	2638.3

Figure 4.11: Modelled Vertical Profiles of Nitrogen Dioxide at the Downwind Edge of the Urban Area Using Different Emissions Inventories



It can be seen from the graph that the four emissions inventories do differ markedly from each other and this does have an effect on the levels of nitrogen dioxide subsequently produced by the model. The effect is more noticeable at ground level. It is interesting to note that even using the NAEI inventory for 1994 which demonstrates a fall in emissions, URBNOX still produces levels of nitrogen dioxide well in excess of the EC Limit Value of 105 ppb, although levels are significantly lower. Therefore, from these results, it is shown that emissions do have a substantial effect on levels of nitrogen dioxide produced under episode conditions. This set of URBNOX runs indicates that reducing emissions will bring levels of nitrogen dioxide down to more acceptable concentrations. However, the results show that levels are still very high, which is most probably due to the meteorological factors. This will be examined in the next set of sensitivity studies.

On a final note, the fact that different results can be achieved using different emissions inventories for the same year (the London Plume Model inventory is based on data for 1991), should be taken into account when modelling.

4.4.1.2 Sensitivity Studies - Meteorological Factors

The next set of sensitivity studies investigates the sensitivity of the model to the meteorological parameters. It is important to establish the importance of meteorological factors in influencing high concentrations of nitrogen dioxide. This will have implications for episode control, since it is easier to control emissions than meteorological factors.

- Wind Speed

URBNOX was run using the same parameters summarised in Table 4.2, except that the wind speed was changed for each run. The concentrations of nitrogen dioxide produced for this set of runs is shown in Table 4.7. Vertical profiles are shown in Figure 4.12. Nitric oxide concentrations are summarised in Table 4.8.

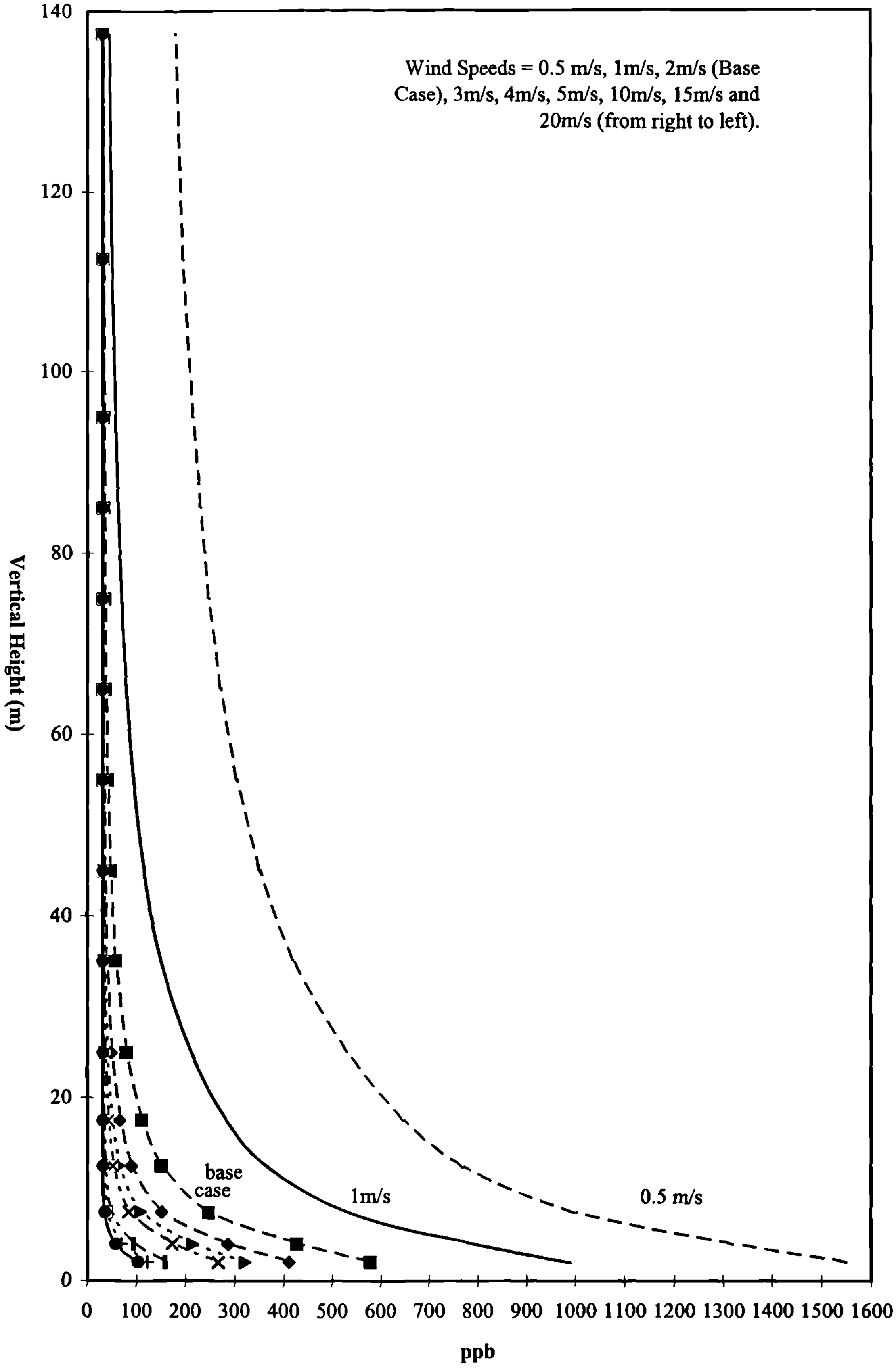
Table 4.7: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Under Differing Wind Speeds

Vertical Height (m)	**Wind Speed (m/s)**								
	0.5	**1**	**2 (Base Case)**	**3**	**4**	**5**	**10**	**15**	**20**
137.5	177.0	44.8	30.7	30.2	30.1	30.1	30.1	30.1	30.0
112.5	191.8	49.6	31.3	30.3	30.1	30.1	30.1	30.1	30.0
95.0	212.7	56.8	32.2	30.5	30.2	30.1	30.1	30.1	30.0
85.0	227.0	62.0	33.0	30.6	30.2	30.1	30.1	30.1	30.0
75.0	245.1	69.0	34.2	30.9	30.3	30.2	30.1	30.1	30.0
65.0	269.4	78.9	36.2	31.4	30.5	30.2	30.1	30.1	30.0
55.0	302.8	93.3	39.4	32.4	30.8	30.4	30.1	30.1	30.0
45.0	349.1	114.8	44.9	34.3	31.6	30.7	30.1	30.1	30.0
35.0	416.6	148.9	55.0	38.2	33.4	31.6	30.2	30.1	30.1
25.0	529.8	211.7	77.5	48.1	38.5	34.5	30.5	30.1	30.1
17.5	645.5	284.1	109.5	65.0	48.4	40.9	31.8	30.5	30.2
12.5	766.7	365.3	150.1	88.4	63.5	51.2	34.5	31.6	30.7
7.5	997.8	533.0	246.4	150.6	107.0	83.6	46.1	37.4	34.1
4.0	1320.3	792.8	426.2	285.4	214.1	172.0	92.7	68.3	56.5
2.0	1550.6	989.3	577.5	409.7	320.8	266.5	157.5	120.7	101.7

Table 4.8: Modelled Nitric Oxide Concentrations (ppb) at the Downwind Edge of the Urban Area Under Differing Wind Speeds

Vertical Height (m)	**Wind Speed (m/s)**								
	0.5	**1**	**2 (Base Case)**	**3**	**4**	**5**	**10**	**15**	**20**
137.5	419.0	123.2	45.0	39.6	39.0	38.9	39.0	39.0	39.0
112.5	447.9	144.5	50.2	40.6	39.3	39.0	39.0	39.0	39.0
95.0	488.8	175.7	59.4	43.1	39.9	39.2	39.0	39.0	39.0
85.0	517.0	197.7	66.6	45.2	40.6	39.4	39.0	39.0	39.0
75.0	552.4	226.1	77.0	48.7	41.9	39.9	39.0	39.0	39.0
65.0	600.5	265.7	93.1	54.8	44.3	40.9	39.0	39.0	39.0
55.0	666.8	321.9	118.8	65.8	49.1	43.2	39.1	39.0	39.0
45.0	759.8	403.4	160.9	86.2	59.1	48.3	39.4	39.0	39.0
35.0	898.1	529.0	234.8	126.9	81.9	61.3	40.7	39.2	39.0
25.0	1138.8	755.2	387.7	223.8	143.4	101.0	46.6	40.6	39.5
17.5	1405.5	1015.1	591.7	374.7	254.1	182.6	67.5	47.4	42.2
12.5	1706.1	1312.8	842.9	575.9	413.5	309.1	112.2	66.6	51.6
7.5	2355.7	1964.2	1433.3	1088.3	852.8	685.2	295.6	167.0	111.9
4.0	3577.2	3197.0	2628.3	2217.8	1910.5	1672.3	997.4	683.1	504.5
2.0	4841.7	4470.1	3887.1	3446.2	3103.0	2827.9	1991.2	1558.7	1290.8

Figure 4.12: Modelled Vertical Profiles of Nitrogen Dioxide at the Downwind Edge of the Urban Area Under Varying Wind Speeds



It can be seen from the results that concentrations of nitrogen dioxide increase with a decrease in wind speed, especially nearer the ground. This is to be expected since a lower wind speed will limit the dispersion of pollutants. Also, the lower the wind speed becomes, the greater the ground level concentration of nitrogen dioxide.

It can also be seen that under the conditions used in the model, the downwind nitrogen dioxide concentration at ground level does not dip below the EC Directive Limit Value of 104.6 ppb until the wind speed reaches a high 20 m/s. This suggests that the wind speed is not the major factor controlling nitrogen dioxide concentrations in the model, although it clearly has some effect.

It is a point of interest to consider this study in terms of the air column's residence time over the urban area. The wind speed can be converted into the number of hours the column of air spends over the urban area. Therefore, 0.5 m/s is equivalent to 22 hours, 1 m/s to 11 hours, 2 m/s to 5.5 hours, 3 m/s to 4 hours, 4 m/s to 3 hours, 5 m/s to 2 hours, 10 m/s to 1 hour and 20 m/s to half an hour. As a result, it can be seen that an episode will still occur with just 1 hour's residence time over the urban area.

- Diffusivity (K_Z Value)

The diffusivity in the model was then explored since it is another important meteorological factor which influences the dispersion of pollutants. This was investigated by running URBNOX with varying K_Z values and the same parameters as before. The results for nitrogen dioxide are shown in Table 4.9 and vertical profiles are shown in Figure 4.13. Nitric oxide concentrations are covered in Table 4.10.

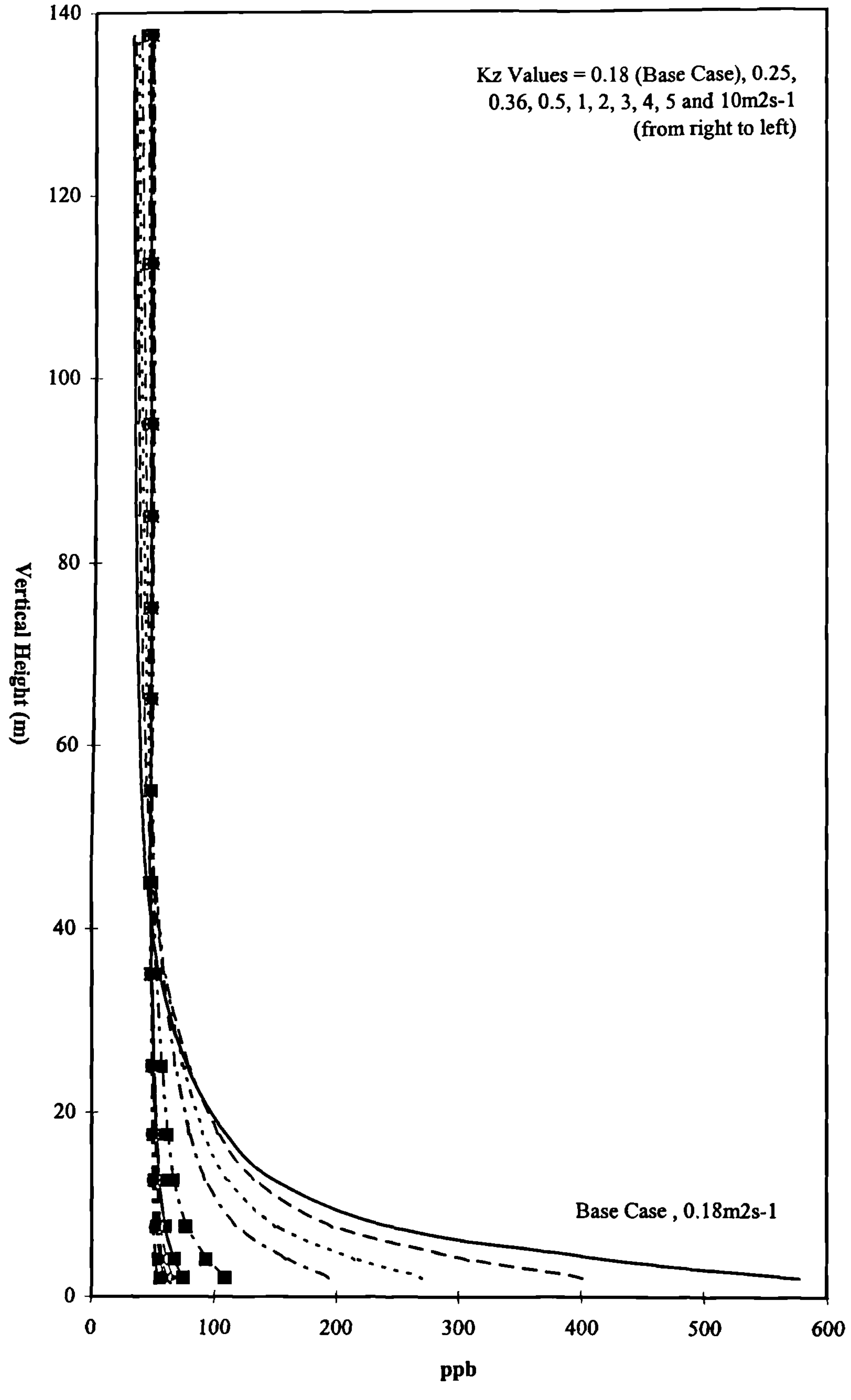
Table 4.9: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Under Differing Diffusivity (K_Z) Values

Vertical Height (m)	**K_Z (m^2s^{-1})**									
	0.18 (Base Case)	**0.25**	**0.36**	**0.5**	**1**	**2**	**3**	**4**	**5**	**10**
137.5	30.7	31.8	34.1	36.8	42.0	44.7	45.5	45.9	46.2	46.7
112.5	31.3	32.8	35.3	37.9	42.6	44.9	45.7	46.0	46.3	46.7
95.0	32.2	34.3	37.0	39.5	43.4	45.3	45.9	46.2	46.4	46.8
85.0	33.0	35.4	38.3	40.7	44.0	45.5	46.1	46.3	46.5	46.8
75.0	34.2	37.0	40.0	42.1	44.7	45.9	46.3	46.5	46.6	46.9
65.0	36.2	39.3	42.3	44.1	45.7	46.3	46.5	46.7	46.8	47.0
55.0	39.4	43.0	45.8	46.9	47.0	46.9	46.9	46.9	47.0	47.1
45.0	44.9	48.7	50.8	50.9	48.9	47.6	47.4	47.3	47.2	47.2
35.0	55.0	58.5	58.8	56.9	51.6	48.8	48.1	47.8	47.7	47.4
25.0	77.5	77.9	73.4	67.3	56.1	50.7	49.3	48.7	48.4	47.7
17.5	109.5	102.5	90.3	78.8	60.8	52.8	50.6	49.6	49.1	48.1
12.5	150.1	131.7	109.3	91.3	65.9	55.0	52.0	50.7	49.9	48.5
7.5	246.4	196.4	149.3	116.8	76.1	59.4	54.9	52.8	51.6	49.3
4.0	426.2	308.3	215.0	158.0	92.7	66.9	59.7	56.4	54.5	50.7
2.0	577.5	401.6	270.4	193.5	107.9	74.0	64.3	59.8	57.2	52.1

Table 4.10: Modelled Nitric Oxide Concentrations (ppb) at the Downwind Edge of the Urban Area Under Differing Diffusivity (K_Z) Values

Vertical Height (m)	**K_Z (m^2s^{-1})**									
	0.18 (Base Case)	**0.25**	**0.36**	**0.5**	**1**	**2**	**3**	**4**	**5**	**10**
137.5	45.0	57.5	84.4	118.8	195.4	245.6	262.9	271.5	276.7	287.0
112.5	50.2	66.5	96.2	130.8	203.2	249.7	265.6	273.5	278.3	287.8
95.0	59.4	80.8	113.7	147.8	214.1	255.3	269.4	276.4	280.6	288.9
85.0	66.6	91.3	126.0	159.7	221.7	259.2	272.0	278.3	282.1	289.7
75.0	77.0	105.5	142.0	174.8	231.1	264.1	275.2	280.8	284.1	290.7
65.0	93.1	126.2	164.4	195.5	243.8	270.6	279.6	284.1	286.7	292.0
55.0	118.8	157.2	196.3	224.3	261.2	279.6	285.6	288.6	290.3	293.8
45.0	160.9	204.5	242.7	265.1	285.5	292.0	293.9	294.8	295.3	296.3
35.0	234.8	281.7	314.5	326.4	321.2	310.3	306.2	304.0	302.7	300.0
25.0	387.7	429.8	444.4	433.8	382.1	341.4	327.0	319.6	315.2	306.3
17.5	591.7	611.4	593.6	552.8	447.6	374.7	349.2	336.4	328.6	313.0
12.5	842.9	825.6	763.9	685.9	519.6	411.3	373.7	354.7	343.3	320.4
7.5	1433.3	1307.3	1133.4	968.5	669.5	487.2	424.4	392.8	373.8	335.6
4.0	2628.3	2232.5	1813.8	1475.6	931.9	619.5	512.7	459.1	426.8	362.2
2.0	3887.1	3178.2	2492.7	1974.2	1186.0	746.9	597.6	522.6	477.6	387.3

Figure 4.13: Modelled Vertical Profiles of Nitrogen Dioxide at the Downwind Edge of the Urban Area Under Different K_Z Values



Diffusivity can be used as an indication of atmospheric stability. The lower the K_Z value, the more stable the atmospheric conditions. The results from this sensitivity study show that the K_Z value has a great effect on the concentration of nitrogen dioxide produced in URBNOX and hence, whether it exceeds the EC Directive Value or not. Above a diffusivity of 2 m^2s^{-1}, which is still indicative of stable atmospheric conditions, it can be seen that levels of nitrogen dioxide have fallen well below the EC Limit Value of 104.6 ppb. It can also be seen that mixing is greater with high diffusivity, as would be expected. Levels are lower and nowhere near episode concentrations under a value of 10 m^2s^{-1}, which is indicative of neutral conditions. It should also be noted that an inverse relationship is shown between the diffusivity and the nitrogen concentration, i.e. when the K_Z value is doubled from 0.18 to 0.36, then the corresponding nitrogen dioxide concentration is approximately halved at ground level.

Although the diffusivity clearly has an effect on the concentration of nitrogen dioxide, the same cannot be said to be true of the ozone present. The ozone is still depleted to negligible levels for every diffusivity sensitivity scenario. This is due to the large amounts of nitric oxide present which immediately scavenge any of the ozone present. Nitric oxide follows the same pattern as nitrogen dioxide where it becomes increasingly well mixed with greater diffusivity.

It should be noted that the K_Z value of 0.18 m^2s^{-1} used for the base case is very extreme and there is some uncertainty whether it would be this low in an urban area, due to its characteristic meteorological conditions. However, it does show how nitrogen dioxide levels do build up substantially under stable atmospheric conditions.

- Diffusion Profile and Z_0

Consideration should be given to whether the vertical profiles in URBNOX are ending in the correct place. In the original base case, the profile extends right down to ground level and the same chemical behaviour is being assumed all the way through the air column. This is not strictly accurate since the last few metres of the air column, down to ground level, could be considered as part of the street canyon, and as a result the chemistry and parameters would be different. A simple way to investigate this is to take the last 14 metres of the air column and forming them into one, very well mixed layer. This would go some way to simulate the turbulence present in the street canyon. The base case was repeated using the same parameters as before, using this modified diffusion profile with a deeper, well mixed, bottom layer. The sensitivity to the diffusion profile was then investigated by running the base case under a profile with a Z_0 of 200 m. This was done with the original profile and the new profile with the well mixed bottom layer. These runs were then repeated using K_Z values of 1, 5, 10 and 20. The results for the base case K_Z value of 0.18 m^2s^{-1} are presented in Figure 4.14 and Figure 4.15. The nitrogen dioxide results for the runs using the other K_Z values are presented in Table 4.11 and Table 4.12.

Figure 4.14: Vertical Profiles of Nitrogen Dioxide for Diffusion Profile Sensitivity Study

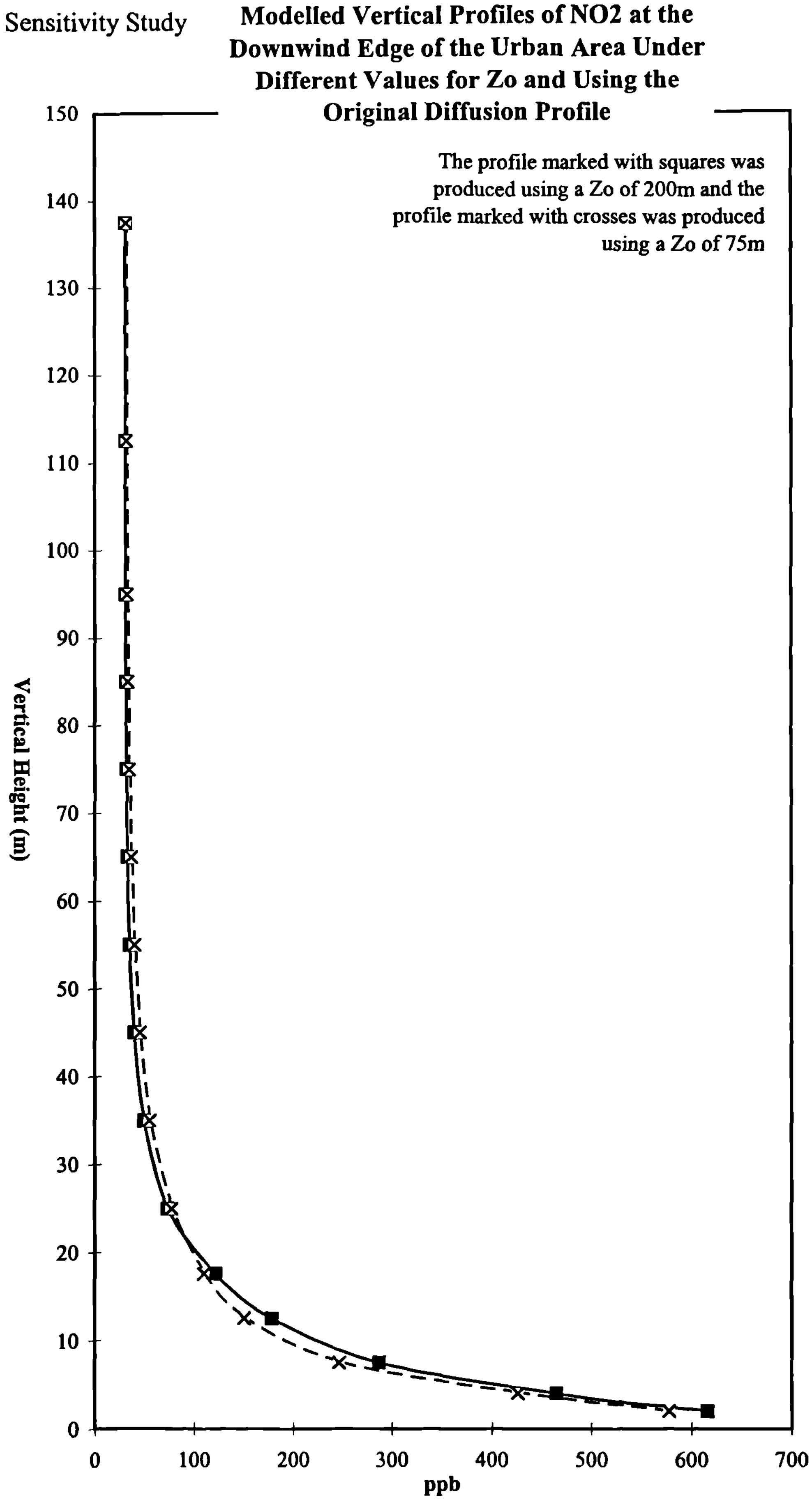
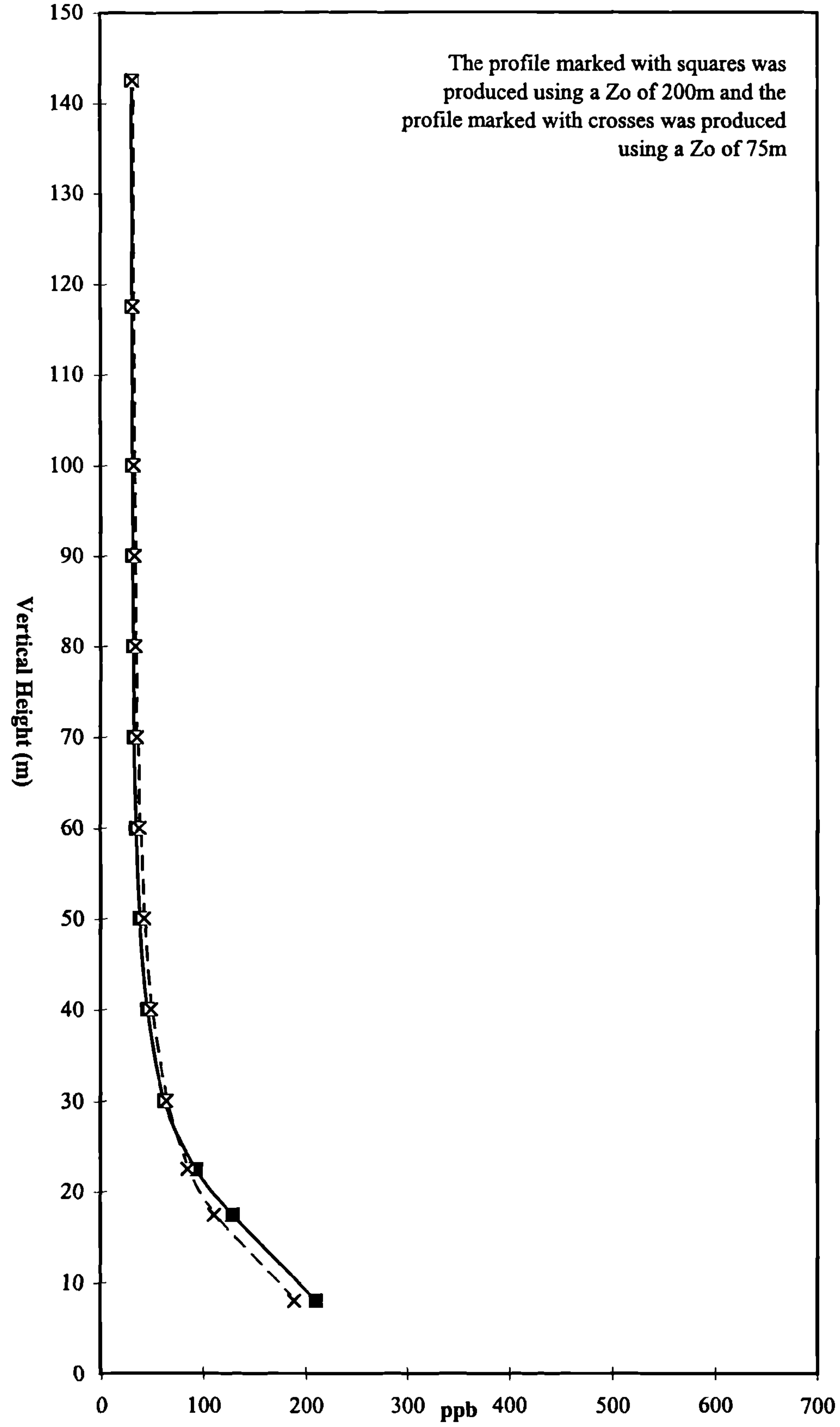


Figure 4.14 (ctd.) **Modelled Vertical Profiles of NO2 at the Downwind Edge of the Urban Area Under Different Values for Zo and Using the Diffusion Profile With a Well Mixed Bottom Layer**



The profile marked with squares was produced using a Zo of 200m and the profile marked with crosses was produced using a Zo of 75m

Figure 4.15: Vertical Profiles of Nitric Oxide for Diffusion Profile Sensitivity Study

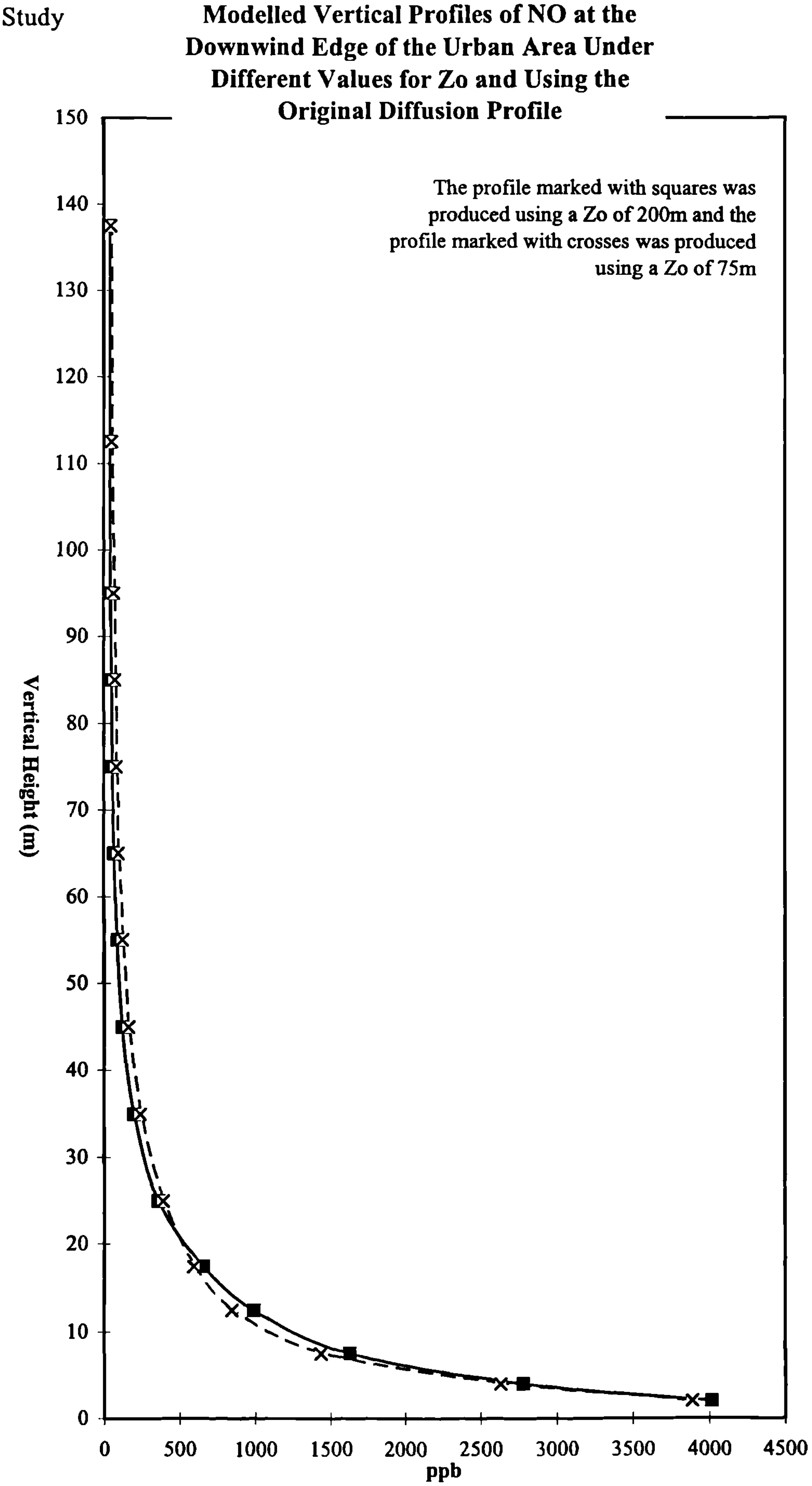


Figure 4.15 (ctd.) **Modelled Vertical Profiles of NO at the Downwind Edge of the Urban Area Under Different Values for Zo and Using the Diffusion Profile With a Well Mixed Bottom Layer**

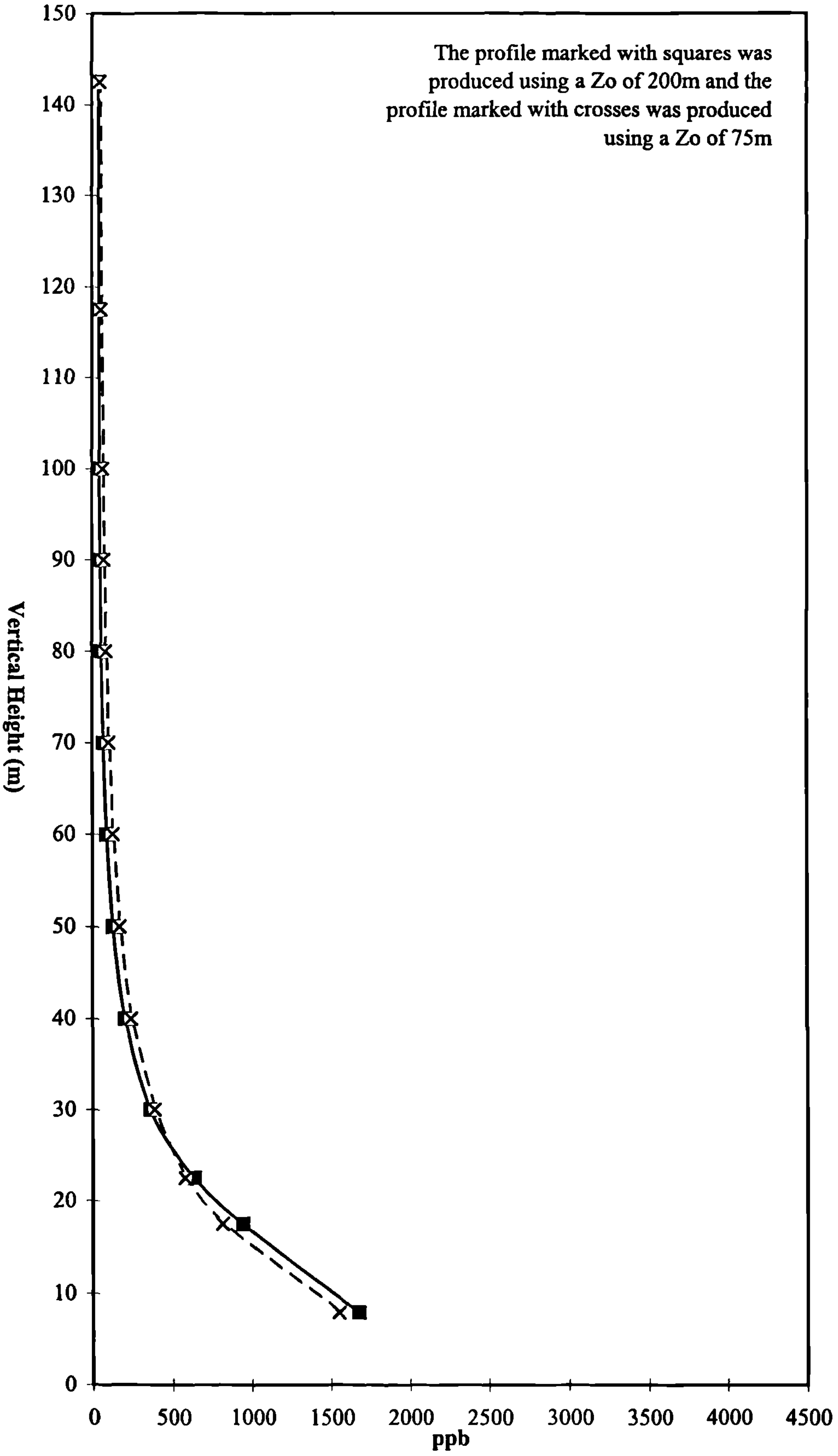


Table 4.11: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Using the Original Diffusion Profile

Vertical Height (m)	$K_Z = 0.18$ (Base Case)		$K_Z = 1$		$K_Z = 5$		$K_Z = 10$		$K_Z = 20$	
	$Z_e =$ 200 m	$Z_e =$ 75m	$Z_e =$ 200 m	$Z_e =$ 75m	$Z_e =$ 200 m	$Z_e =$ 75m	$Z_e =$ 200 m	$Z_e =$ 75m	$Z_e =$ 200 m	$Z_e =$ 75m
137.5	30.2	30.7	37.5	42.0	45.3	46.2	46.3	46.7	46.7	46.9
112.5	30.3	31.3	38.4	42.6	45.5	46.3	46.3	46.7	46.8	47.0
95	30.6	32.2	39.9	43.4	45.7	46.4	46.5	46.8	46.8	47.0
85	30.9	33.0	41.1	44.0	46.0	46.5	46.6	46.8	46.9	47.0
75	31.5	34.2	42.7	44.7	46.2	46.6	46.7	46.9	46.9	47.1
65	32.6	36.2	44.9	45.7	46.6	46.8	46.9	47.0	47.0	47.1
55	34.8	39.4	47.7	47.0	47.1	47.0	47.1	47.1	47.1	47.1
45	39.5	44.9	51.5	48.9	47.7	47.2	47.4	47.2	47.3	47.2
35	49.7	55.0	56.9	51.6	48.5	47.7	47.8	47.4	47.5	47.3
25	73.7	77.5	64.7	56.1	49.7	48.4	48.4	47.7	47.8	47.5
17.5	121.4	109.5	74.3	60.8	51.2	49.1	49.1	48.1	48.1	47.6
12.5	177.8	150.1	82.9	65.9	52.4	49.9	49.7	48.5	48.4	47.8
7.5	287.0	246.4	95.8	76.1	54.6	51.6	50.7	49.3	48.9	48.3
4	464.8	426.2	113.1	92.7	57.4	54.5	52.1	50.7	49.6	49.0
2	615.7	577.5	128.6	107.9	60.2	57.2	53.4	52.1	50.3	49.6

Table 4.12: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Using the New Diffusion Profile With the Well Mixed Lowest Layer

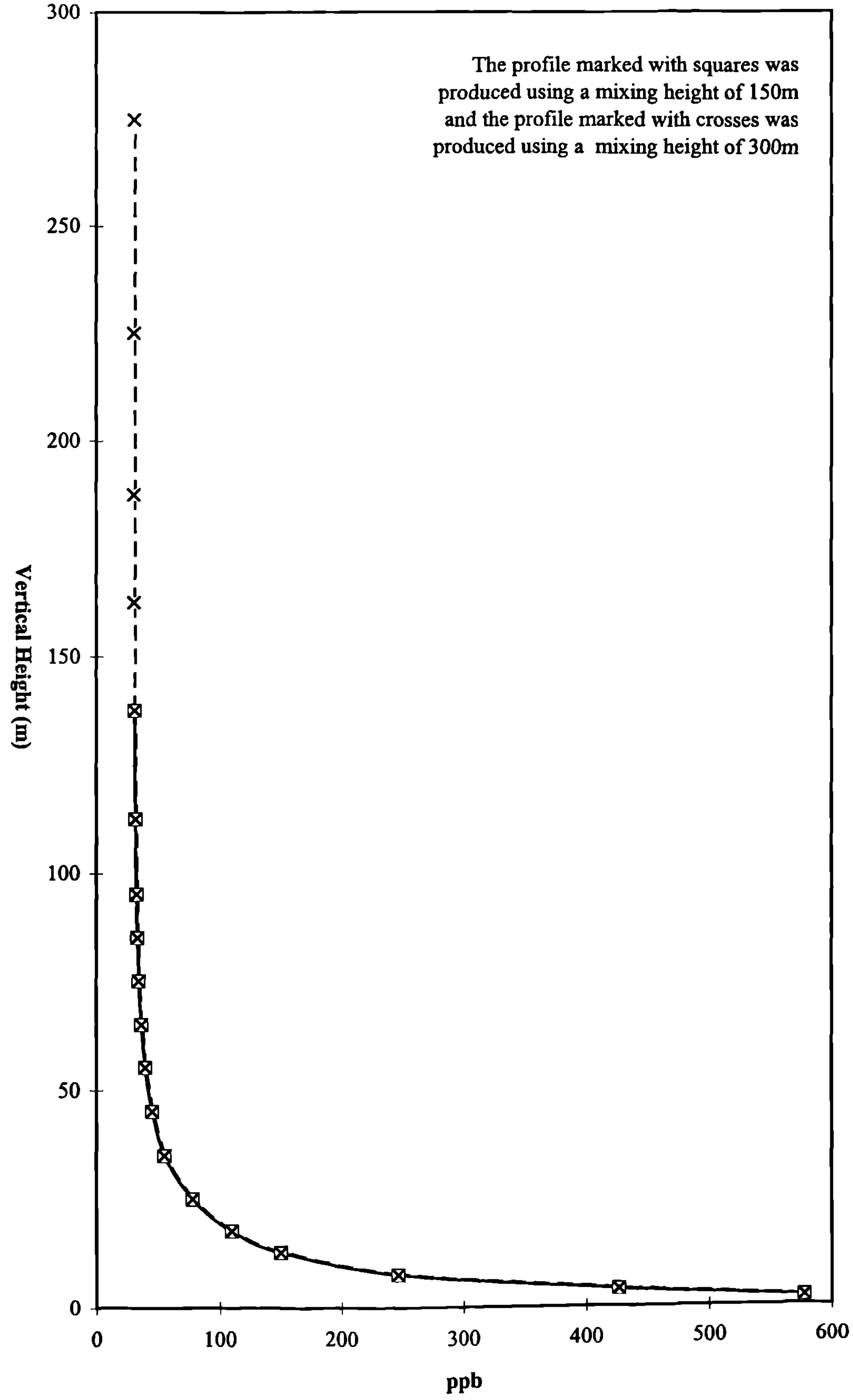
Vertical Height (m)	$K_Z = 0.18$ (Base Case)		$K_Z = 1$		$K_Z = 5$		$K_Z = 10$		$K_Z = 20$	
	$Z_0 =$ 200 m	$Z_0 =$ 75m	$Z_0 =$ 200 m	$Z_0 =$ 75m	$Z_0 =$ 200 m	$Z_0 =$ 75m	$Z_0 =$ 200 m	$Z_0 =$ 75m	$Z_0 =$ 200 m	$Z_0 =$ 75m
142.5	30.2	30.8	36.5	40.7	44.6	45.5	45.6	46.0	46.1	46.3
117.5	30.3	31.2	37.3	41.3	44.7	45.6	45.7	46.1	46.1	46.3
100	30.6	32.0	38.6	42.1	45.0	45.7	45.8	46.1	46.2	46.4
90	30.9	32.7	39.7	42.6	45.2	45.8	45.9	46.2	46.2	46.4
80	31.4	33.6	41.1	43.3	45.4	45.9	46.0	46.2	46.3	46.4
70	32.3	35.1	43.0	44.2	45.8	46.0	46.2	46.3	46.4	46.4
60	34.1	37.5	45.4	45.4	46.2	46.2	46.4	46.4	46.5	46.5
50	37.7	41.5	48.8	47.1	46.9	46.5	46.7	46.5	46.6	46.6
40	45.2	48.6	53.6	49.6	47.7	46.9	47.1	46.7	46.8	46.7
30	61.9	63.9	60.6	53.8	48.9	47.6	47.6	47.1	47.1	46.8
22.5	93.1	84.7	69.2	58.2	50.3	48.3	48.3	47.4	47.4	47.0
17.5	128.6	110.3	77.0	62.9	51.6	49.1	48.9	47.8	47.7	47.2
8	210.0	188.5	92.0	75.7	54.1	51.3	50.1	48.9	48.3	47.7

The results for both nitrogen dioxide and nitric oxide show that the output of URBNOX is far more sensitive to the alteration in the profile than the value of Z_0 used. The results are also increasingly sensitive with decreasing K_Z value. Having a deeper, well mixed bottom layer has approximately just over halved concentrations of both nitrogen dioxide and nitric oxide in the bottom layer. It could be inferred therefore, that turbulence has a significant role to play in dispersion of pollutants. This has already been recognised and investigated in great detail in a number of street canyon models, for example, dePaul *et al* (1985), Yamartino *et al* (1986), Dabberdt *et al* (1991) and Berkowicz (1994). It is a very complex subject and in order to keep URBNOX as simple as possible, it will not be taken any further in this study. The modification of the diffusion profile used is adequate for the purposes of this study. However, there are a number of options available to explore this area in future studies. The effects of turbulence can be investigated by using URBNOX to model dispersion over the street canyon and then use a canyon model in tandem to investigate subsequent dispersion and behaviour within the canyon. Alternatively, the k-profile can be modified in greater detail to take into account conditions in the street canyon.

- Mixing Height

A run was carried out with a mixing height of 300m, as an example of a typical low, evening mixing height (Hough, 1986). The profile for nitrogen dioxide is shown in Figure 4.16.

Figure 4.16: Modelled Vertical Profiles of Nitrogen Dioxide at the Downwind Edge of the Urban Area Using Different Mixing Heights



It is clear from the profiles that the mixing height has no effect on the concentrations of nitrogen dioxide produced. This is also true for nitric oxide, although the results have not been plotted here.

- Insolation

The sensitivity of URBNOX to the dissociation rate of nitrogen dioxide, which is also taken to represent the amount of insolation present, is examined next. Although the winter base case was run with no dissociation rate to simulate the absence of insolation, several runs were carried out with varying dissociation rates. This was done to determine whether there would be any effect on the extreme levels of nitrogen dioxide present in the base case. The results are shown in Table 4.13.

Table 4.13: Modelled Nitrogen Dioxide Concentrations (ppb) at the Downwind Edge of the Urban Area Under Differing Dissociation Rates

Vertical Height (m)	**Dissociation Rate (s^{-1})**				
	0.0 (Base Case)	**0.003**	**0.005**	**0.007**	**0.01 (Strong Dissociation)**
137.5	30.7	27.4	24.9	23.0	21.4
112.5	31.3	28.1	25.8	23.9	22.3
95.0	32.2	29.4	27.2	25.4	23.9
85.0	33.0	30.4	28.3	26.6	25.1
75.0	34.2	31.9	29.9	28.2	26.7
65.0	36.2	34.1	32.2	30.7	29.2
55.0	39.4	37.5	35.9	34.4	33.1
45.0	44.9	43.3	41.9	40.5	39.3
35.0	55.0	53.7	52.5	51.3	50.2
25.0	77.5	76.4	75.3	74.2	73.2
17.5	109.5	108.5	107.5	106.5	105.5
12.5	150.1	149.1	148.2	147.2	146.3
7.5	246.4	245.5	244.6	243.7	242.8
4.0	426.2	425.4	424.6	423.8	423.0
2.0	577.5	576.7	576.0	575.3	574.6

It can be seen that as the dissociation rate increases, the concentration of nitrogen dioxide decreases. However, the effect is not very significant and only reduces the concentration of nitrogen dioxide present by 3 ppb at the most. Therefore, it can be said that the nitrogen dioxide dissociation rate does not have a significant effect on determining the concentrations present and whether an episode is formed or not. This will be explored further in the next chapter, where summer episodes are considered and dissociation rates are more significant.

4.5 Discussion

As stated at the very beginning, the aim of this chapter was to illustrate, using several examples, how the URBNOX model operates and to investigate the behaviour of ozone, nitric oxide and nitrogen dioxide. From the winter base case, it can be seen that URBNOX mimics the behaviour of ozone, nitric oxide and nitrogen dioxide quite acceptably, although there is some over-prediction of concentrations. Sensitivity studies have been carried out on both the chemical and meteorological parameters. These show that the emissions, wind speed and diffusivity have the greatest effect on the output from URBNOX. This shows that it simply is not sufficient to only consider emissions when modelling episodes. Meteorological factors should also be included. This has some implications for episode control, in that it is possible to reduce and control emissions but not the meteorological factors. This could be overcome, in part, by taking heed of weather forecasts and planning public information accordingly. For example, if the correct weather was predicted for a pollution episode, then steps could be taken to try and control emissions such as by encouraging the public to leave their cars at home.

The modelling studies in this chapter show that winter episodes are mainly formed by emissions (under certain meteorological conditions) within the urban area. This would suggest that control methods for this type of episode can be aimed at reducing emissions within the urban area and can be dealt with by the relevant authorities within that area.

The next chapter will on to investigate the formation of summer episodes in some detail, along with a validation study of the model. The aim of this is to see if summer episodes are subject to the same factors as winter episodes and hence whether they are also mainly formed from local emissions or from precursors entering the urban area from upwind.

URBNOX is currently running on a spatial scale and while this is very useful for comparing concentrations of the pollutants both upwind and downwind of an urban area, it does not give any information on the build-up of pollutants over time. URBNOX has been developed further in order to run on a temporal scale and this is explored further in the next chapters.

It is important to realise that, although modelling can be useful in examining different scenarios and discovering the potential effectiveness of an air quality control measure before it is implemented, models are, at best, only an approximation of a situation. Care should be taken when acting on the predictions of a model, since when developing a model, many assumptions have to be made and every effective parameter may not have been taken into consideration. However, the simplicity of a model carries equal importance in order to make it easy to run and accessible to a large range of people.

Chapter 5: Summer Episodes

5.1 Introduction

The previous chapter was intended to show the development of URBNOX and to use it to explore the behaviour of winter episodes, by comparing it to the December 1991 episode. The intention of this chapter, is to take this work one stage further and use URBNOX to investigate the vertical distribution of nitrogen dioxide on an average summer's day, by comparing it to data recorded at the Queen's Tower on the Imperial College campus in South Kensington, London. In addition the effects of upwind ozone concentrations on subsequent nitrogen dioxide formation within an urban area will be investigated.

To expand the scope of the study further and to explore the formation of summer episodes in detail, URBNOX was compared with data recorded and supplied by the South East Institute of Public Health during a summer air pollution episode which occurred at the beginning of May 1995. Summer episodes have very different chemistry and behaviour from winter episodes.

5.2 Introduction to Summer Photochemistry

The formation of nitrogen dioxide and ozone is covered in some detail in Chapter 1 (Sections 1.2.2 and 1.3.2). It is also shown that these three species exist in an equilibrium called the photostationary state, unless perturbed by peroxy radical reactions associated with ozone formation. It can be argued that the amount of nitrogen dioxide formed in an urban area will depend in part, on the quantity of ozone present upwind of the urban area.

The relationship between ozone and total NO_x in order to form nitrogen dioxide can be investigated through a series of simple equations which are shown below.

The total oxidant conserved can be represented thus (disregarding additional ozone production):

$$O_{3b} = O_3 + NO_2 \qquad (5.1)$$

and the total NO_x as:

$$NO_x = NO + NO_2 \qquad (5.2)$$

At equilibrium (i.e. the photostationary state):

$$k_1 [O_3] * [NO] = J [NO_2] \qquad (5.3)$$

Hence:

$$[NO] = J [NO_2] / k_1 [O_3] \qquad (5.4)$$

This can be simplified to:

$$[NO] = B * [NO_2] / [O_3] \qquad (5.5)$$

Where: $B = J / k_1$

This will be a changing ratio because while k_1 is a constant, J is the dissociation rate which is subject to change, i.e.:

$k_1 = 1*10^7\ dm^3 mol^{-1} s^{-1}$ (Campbell, 1986)

If $k_1\ [O_3] * [NO] = J\ [NO_2]$, this can be rewritten in terms of ppb units, i.e.:

$$k_1\ [O_3] * [NO] * (0.04166 * 10^{-9})^2 = J\ [NO_2] * (0.04166 * 10^{-9}) \qquad (5.6)$$

Therefore:

$$k_1^* = k_1 * (0.04166 * 10^{-9}) = 4.166 * 10^{-4} \qquad (5.7)$$

If: $J = 0.01\ s^{-1}$ to represent strong insolation (Campbell, 1986),

then, using ppb units:

$$B = +/- \quad 0.01 / 4.166*10^{-4} = 24 \text{ (for strong insolation)} \qquad (5.8)$$

Similarly, if:

$J = 0.0067$ then $B = 16$;

$J = 0.0033$ then $B = 8$.

If Equations (5.1) and (5.5) are substituted into Equation (5.2), then the total NO_x can be represented by:

$$NO_x = (B^* NO_2 / (O_{3b} - NO_2)) + NO_2 \qquad (5.9)$$

or

$$(O_{3b} * NO_x) - (NO_x * NO_2) = B\ NO_2 + (O_{3b} * NO_2) - NO_2{}^2 \qquad (5.10)$$

This can be solved quadratically as follows:

$$NO_2{}^2 - NO_2\ (NO_x + O_{3b} + B) + O_{3b} * NO_x = 0 \qquad (5.11)$$

Let: $q = (NO_x + O_{3b} + B) / 2$ and $r = O_{3b} * NO_x$ (5.12)

Therefore:

$$NO_2 = + q\ (+/-) \sqrt{}\, q^2 - r \qquad (5.13)$$

This equation can then be used to indicate approximately how much nitrogen dioxide will be formed from certain concentrations of ozone and total NO_x. This is useful to discover how much ozone needs to present in order to exceed the EC Directive for nitrogen dioxide of 104 ppb. Therefore, Table 5.1 shows concentrations of nitrogen dioxide formed under different conditions of ozone and total NO_x.

Table 5.1: Levels of Nitrogen Dioxide Formed Under Varying Concentrations of Ozone and Total NO_x

O_{3b}	NO_x	NO_2 Formed		
		B = 24	B = 16	B = 8
150	10	9	9	10
	50	41	43	47
	100	76	81	89
	150	101	108	119
	200	116	124	134
	300	131	137	143
	500	140	144	147
100	10	8	9	9
	50	36	40	44
	100	62	67	75
	150	76	81	88
	200	83	88	93
	300	90	93	96
	500	94	96	98
50	10	7	7	8
	50	25	29	34
	100	36	40	44
	150	41	44	46
	200	43	45	48
	300	46	47	49
	500	48	48	50

The results from using this simple equation show that there needs to be high concentrations of both ozone and total NO_x in order for high levels of nitrogen dioxide to be produced. The EC Directive for nitrogen dioxide is not breached unless there are at least 150 ppb of ozone present. At the same time there also needs to be at least 150 ppb of NO_x present. This suggests that an ozone episode will cause a nitrogen dioxide episode, which could have important implications for abatement. The results also show that the dissociation rate (related to the amount of insolation) has an effect on the amount of nitrogen dioxide formed. When there are 150 ppb of both ozone and nitrogen dioxide present, an episode is formed when B is 16 and 8 (i.e. lower levels of insolation) but not when it is 24. This once again, highlights the importance of meteorological factors in the formation of episodes.

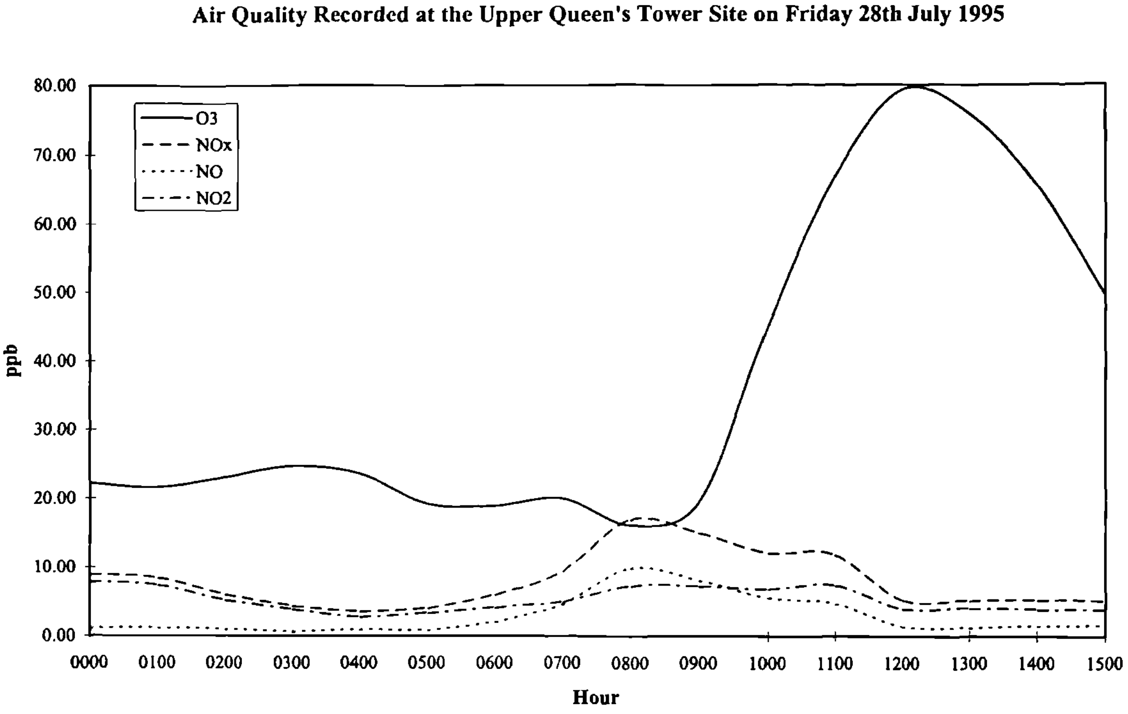
The above is useful as a simple guide to the amount of nitrogen dioxide produced from varying concentrations of ozone. However, it does not take into account the potential effects various meteorological parameters could have on episode formation, which are important. Therefore, it is preferable to use a model which incorporates both meteorological factors and chemistry in order to obtain a clear picture of nitrogen dioxide and ozone behaviour in episodes. URBNOX will be used to investigate how factors such as diffusivity and background ozone concentration affect episode behaviour and will be compared with the results given above.

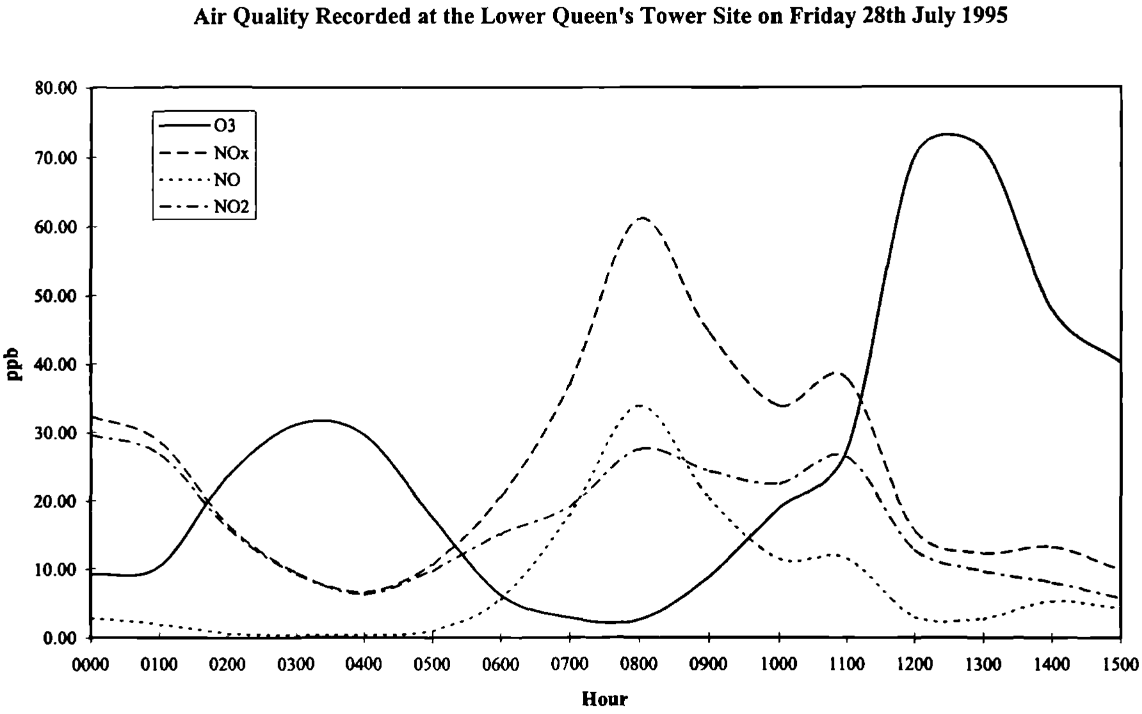
5.3 Comparison of URBNOX to Measurements Made From the Queen's Tower, Imperial College Campus on Friday 28th July, 1995

The Queen's Tower is a tall column situated in approximately the middle of the Imperial College Campus to the west of Central London. Measuring sites were set up at two heights within the Tower. These were 20 and 65 metres above street level. A more detailed description of the method of the monitoring survey can be found in Chapter 2.

The monitoring survey was carried out for the whole of the month of July 1995. Measurements for Friday 28th July were chosen for comparison with URBNOX, as an example of a typical day during the summer. The air quality for both the Upper and Lower Tower sites are shown in Figure 5.1:

Figure 5.1: Air Quality Recorded at the Queen's Tower on Friday 28th July 1995





It can be seen from the graphs that levels of nitrogen dioxide start off very low during the night at both heights- approximately 10 ppb at 65 metres and 20 ppb at 20 metres. These start to rise during the early morning to peak at around 8:30am, corresponding to the rush hour and increased emissions of oxides of nitrogen. At this point, the rush hour peak of oxides of nitrogen is very conspicuous at 20 metres, but is only slightly enhanced at 65 metres. Correspondingly, ozone is almost depleted at the lower height, whereas at the upper level there is a decrease of only a few ppb, matching the rise in NO_x concentrations. As the mixing layer evolves throughout the morning, ozone is mixed down from aloft. This contributes to the rising ozone levels recorded at 20 metres during the morning. Levels of nitrogen dioxide, nitric oxide and NO_x start to fall again once the rush hour is over. In parallel, insolation levels start to increase, dissociating the nitrogen dioxide. The decline in NO_x also contributes to the rising levels of ozone around midday as there is less nitric oxide to scavenge on it.

Meteorological conditions for the 28th of July were nothing particularly unusual. Atmospheric stability was neutral and the sky was slightly overcast with temperatures averaging at 16.4 degrees centigrade. Wind speed averaged at 6.1 m/s and came from a southerly direction (London Weather Centre, 1995). These conditions would not encourage levels of pollution to build up, which would explain why levels of nitrogen dioxide and nitric oxide did not accumulate but ebbed and flowed with diurnal emission levels. The southerly wind direction may go some way to explaining why levels of ozone were slightly higher than average, especially higher up the Tower. A southerly wind could bring continental ozone in over London.

5.3.1 Comparison With URBNOX

URBNOX was then used to model concentrations at 8am and 11am. The parameters are summarised in Table 5.2. A detailed description of the model can be found in Chapter 4, Section 4.3. Once again, in the base runs included here, the simple NO_x chemistry is incorporated. However, several factors have not been included in the chemical scheme. These are photochemical production of ozone and the conversion of nitrogen dioxide to nitrate. Ozone losses by deposition are also ignored. These are discussed in a subsequent section.

Table 5.2: Summary of parameters used for URBNOX runs in comparison with data recorded from the Queen's Tower

Parameter	**Values for 8am Run**	**Values for 11am Run**
Wind Speed	6 m/s	6 m/s
Mixing Height	500 m	1200 m
Z_o	200 m	200 m
Diffusivity	20 m^2s^{-1}	50 m^2s^{-1}
Dissociation Rate	0.005 s^{-1}	0.006 s^{-1}
Emissions	London Emissions Inventory	London Emissions Inventory
Wind Direction	Southerly	Southerly
Fraction of NO_x Emission Factor as NO	95 %	95 %
Distance Travelled by the Air Column	40 km	40km
Background O_3	20 ppb	65 ppb
Background NO_2	4 ppb	4 ppb
Background NO	2 ppb	2 ppb

Due to constraints of time and budget, it was not possible to record meteorological data during the Queen's Tower Survey. Therefore, it was decided to use data recorded by the London Weather Centre (LWC), assuming that the meteorological conditions near the Queen's Tower would be very similar to those at the LWC site. The LWC's meteorological site is situated on top of the MI5 Building, by the River Thames, opposite the Tate Gallery.

The wind speed was taken as the average wind speed recorded for that day by the London Weather Centre. The wind direction was approximately southerly during the morning. The London Emissions Inventory was used since it was the most recent inventory and has the greatest resolution, although it has been modified for use in the model. The wind direction determines which grid squares are used. The diffusivities (K_Z values) were selected as examples of typical values for neutral to unstable conditions. The modified diffusion profile (as discussed in Chapter 4) which assumes a very well mixed, lowest layer of 14 metres was used as it gives a better representation of the situation in an urban area. The dissociation rates were also selected as typical examples for those times of day (Campbell, 1986). The background concentrations of ozone, nitrogen dioxide and nitric oxide were taken from the first QUARG report (1993) as examples of concentrations upwind of an urban area. The resulting profiles are shown in Figure 5.2 and Figure 5.3.

Figure 5.2: URBNOX- Modelled Vertical Profiles for Conditions Observed at 8am on Friday 28th July 1995

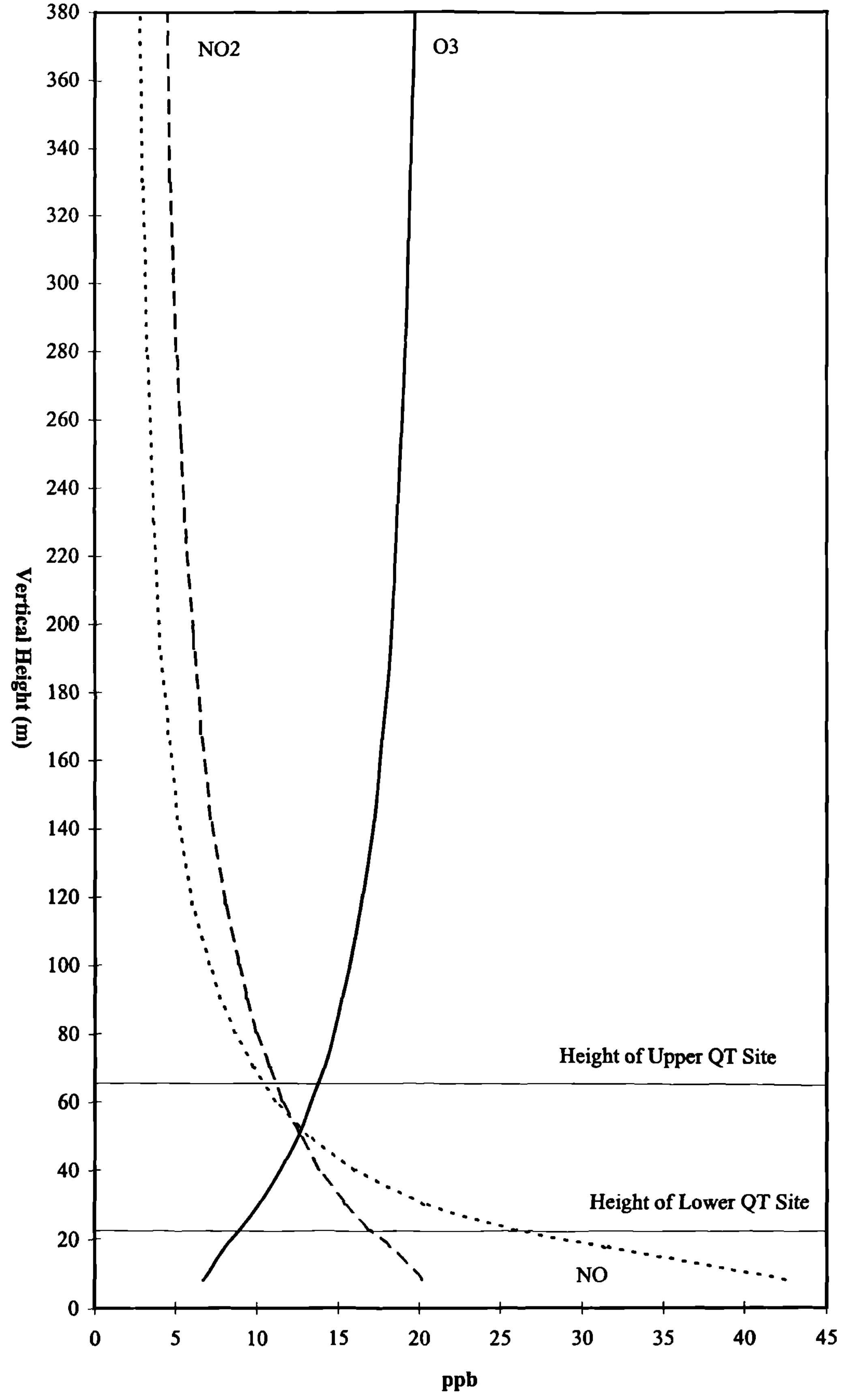
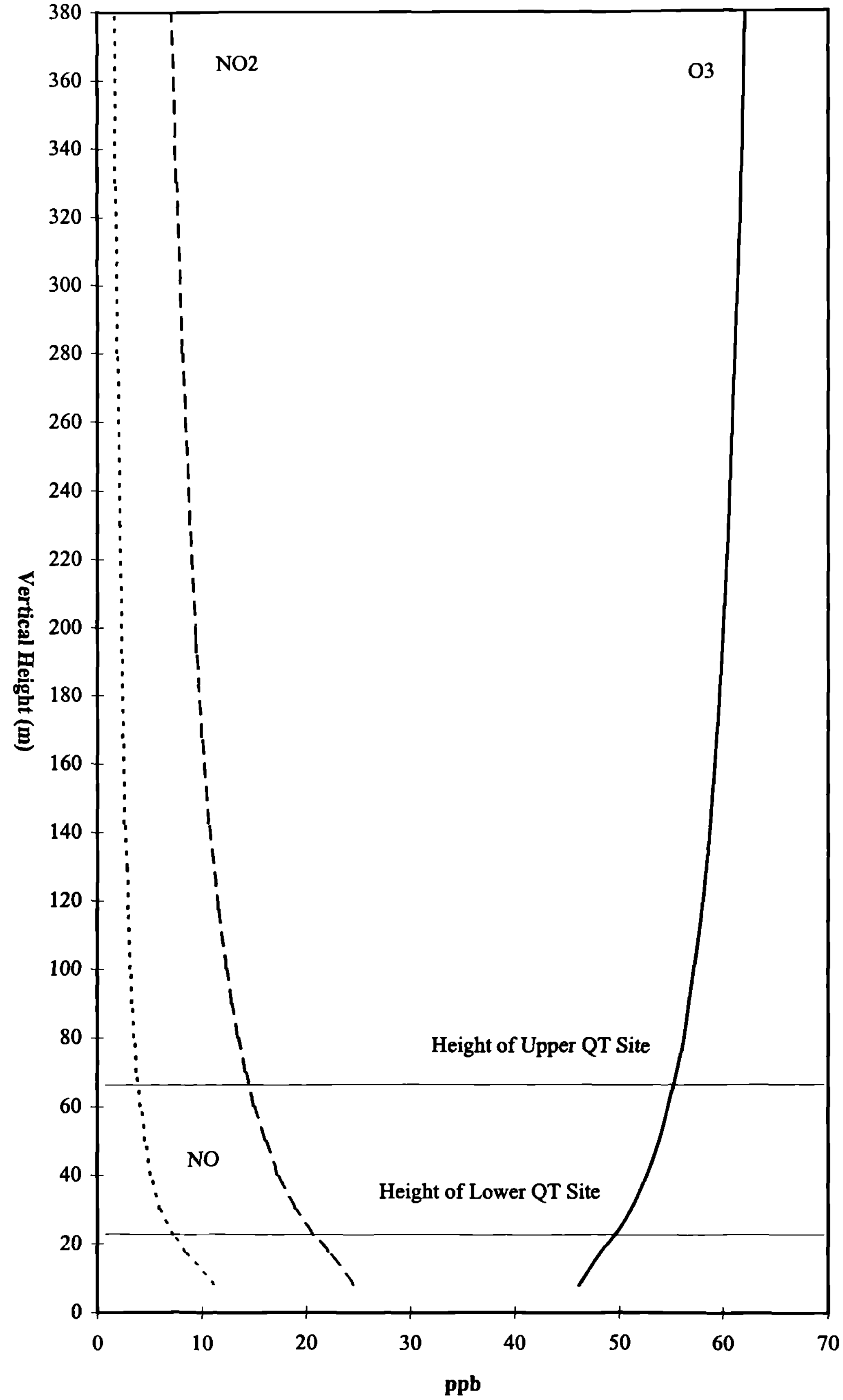


Figure 5.3: URBNOX- Modelled Vertical Profiles for Conditions Observed at 11am on Friday 28th July 1995



It can be seen from the profiles that the model results fit the recorded data well at the bottom of the tower, but less so at the top. The 8 am profile fits the data more closely than the 11 am profile. This is shown in Table 5.3.

Table 5.3: Comparison of Modelled and Measured Data for the 28th of July 1995

	Measured Data (ppb)			URBNOX Concentration (ppb)		
	O_3	NO_2	NO	O_3	NO_2	NO
Upper Tower (8am)	16	7	10	14	11	10
Lower Tower (8am)	3	27	34	8	17	27
Upper Tower (11am)	67	7	5	55	14	4
Lower Tower (11am)	27	26	11	49	21	7

Firstly, it can be seen that the model produces a good fit to the pattern of distribution observed in the measured data. Ozone levels can be seen to be higher with height and both nitrogen dioxide and nitric oxide are lower. This is to be expected since there will be more nitric oxide present close to the source of emissions at ground level. As a result there is more nitric oxide to scavenge on any ozone present, thus reducing ozone concentrations and increasing nitrogen dioxide levels.

The profiles for the measured data are more marked than those shown for the modelled data. This is may be because one average wind speed is used throughout the profile in the model, whereas the wind speed actually varies with height and so may make a difference to the levels of pollutants present. For the 8 am study, it can be seen that the modelled ozone concentration fits closely for the Upper Tower, but overpredicts for the Lower Tower. URBNOX was found to reproduce nitric oxide levels closely, albeit with a slight under-prediction for the Lower Tower. However, the 11 am run shows a slightly poorer fit all round. Generally, the Upper Tower shows a better fit than the Lower Tower. This may be because the measurements from the Lower Tower exhibit sensitivity to local conditions, i.e. the Tower is situated near the Exhibition Road. The model results may be more indicative of pollutant behaviour slightly above the canopy.

The reason for this disparity in results may be due to the diffusivity in the model. The model incorporates a simple diffusion profile with a k-value to represent the atmospheric stability. The measured data was collected within an urban area. It is possible that a more complex diffusion profile is needed especially to take into account the effect of street canyons.

Also, the measured data shows increased nitric oxide concentrations at 8 am as a result of rush-hour traffic. Correspondingly, at 11 am when traffic levels decrease, the measured nitric oxide levels decrease. The modelled data does show this pattern. However, the emissions currently have no adjustment to take into account peaks (especially those that correlate with traffic flows) and troughs in nitric oxide emissions. This is because the model currently runs on a spatial scale and not a temporal scale. This will be addressed later in the chapter.

The model is structured to follow the evolution of nitrogen dioxide, nitric oxide and ozone concentrations inside a column of air as it crosses an urban area. The data from the Tower is measuring the levels of ozone, nitrogen dioxide and nitric oxide on a very local scale. This makes the two slightly incompatible for a true validation. A better validation exercise would be to compare URBNOX with a series of results from several different monitoring stations. This is carried out in the next part of this chapter.

5.3.1.1 Sensitivity Studies

A series of sensitivity studies was then carried out in order to investigate the sensitivity of the results to the diffusivity, the background concentration of ozone and the dissociation rate. These factors were investigated to determine their importance in influencing concentrations of nitrogen dioxide (and ozone) under summer conditions.

- Diffusivity (K_Z Value)

The runs for 8am and 11am were repeated using different K_Z values. The other parameters were kept the same and are summarised in Table 5.2. For the 8am run, the K_Z value was halved from 20 m^2s^{-1} to 10 m^2s^{-1} in order to investigate nitrogen dioxide and ozone behaviour under more stable atmospheric conditions. Similarly, the K_Z value for the 11am case was reduced from 50 m^2s^{-1} to 20 m^2s^{-1}, i.e., neutral conditions. The results are shown in Table 5.4 and the profiles are shown in Figure 5.4 and Figure 5.5.

Figure 5.4: Sensitivity to Diffusivity- URBNOX-Modelled Vertical Profiles of Nitrogen Dioxide and Ozone for the Queen's Tower 8am Run

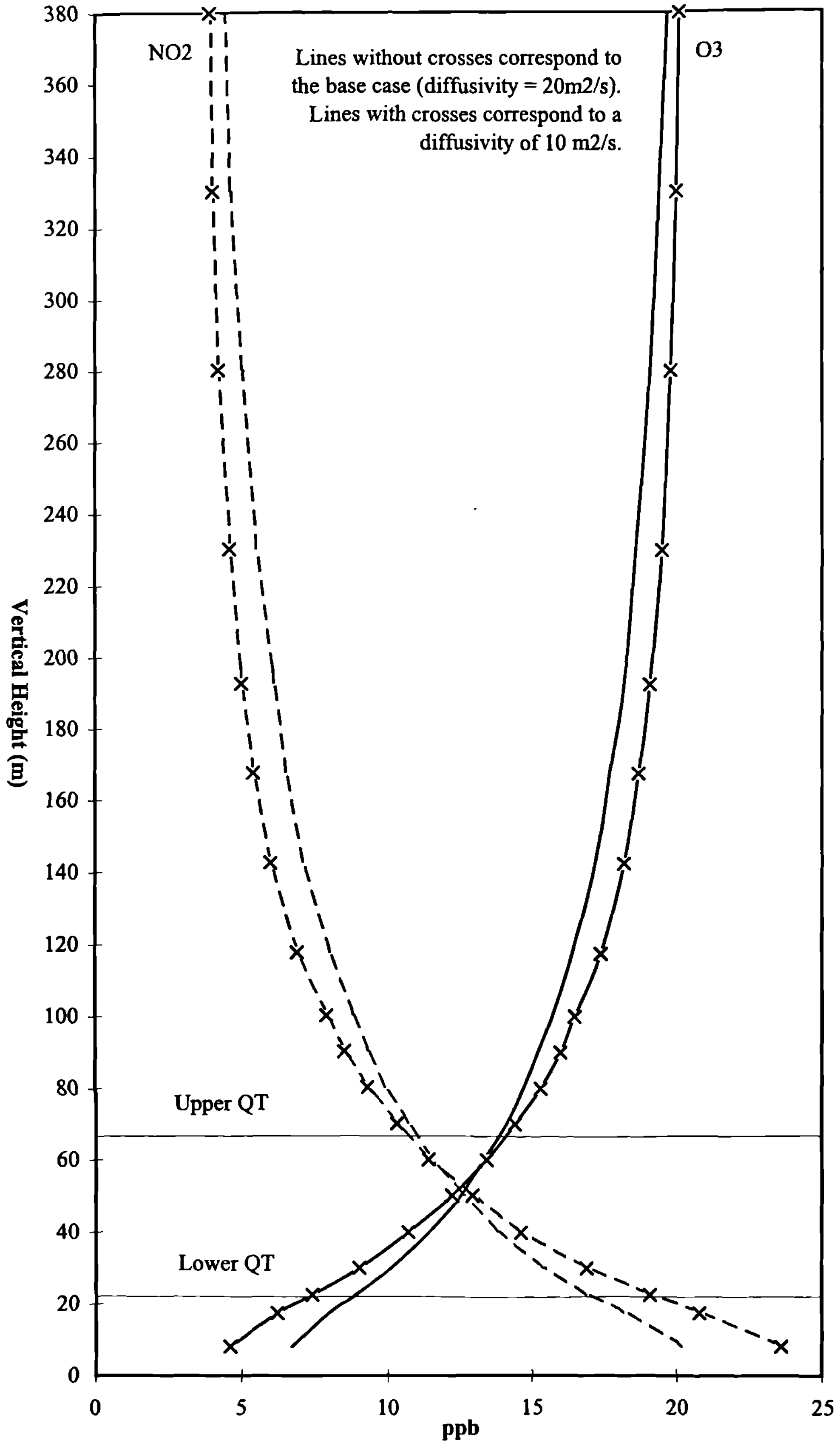


Figure 5.5: Sensitivity to Diffusivity- URBNOX-Modelled Vertical Profiles of Nitrogen Dioxide and Ozone for the Queen's Tower 11am Run

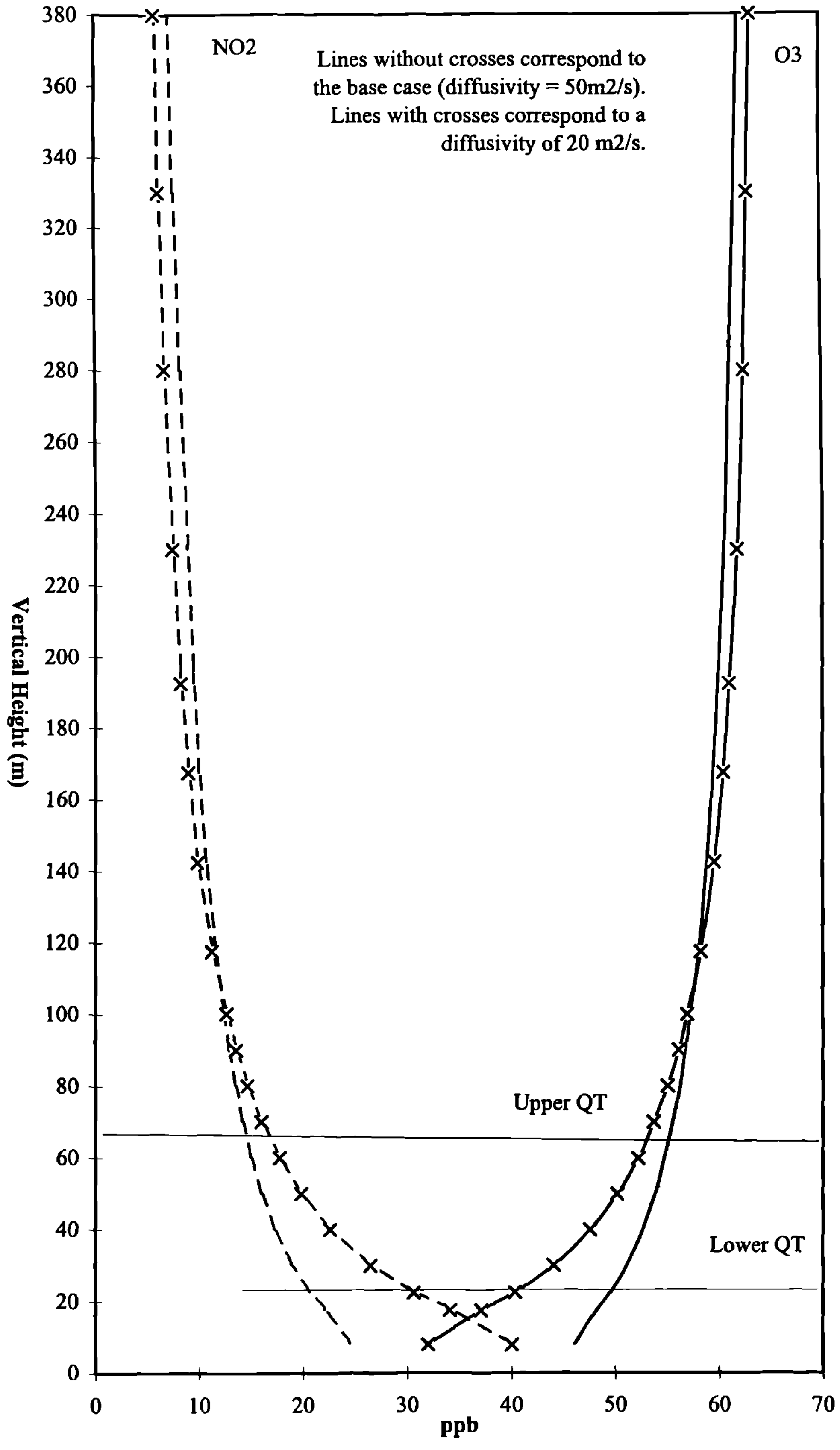


Table 5.4: Comparison of Results from Diffusivity (K_Z Value) Sensitivity Study

	K_Z 20 m^2s^{-1} (Base case)		K_Z 10 m^2s^{-1}		K_Z 50 m^2s^{-1} (Base case)		K_Z 20 m^2s^{-1}	
	Lower Tower (8am)	**Upper Tower (8am)**	**Lower Tower (8am)**	**Upper Tower (8am)**	**Lower Tower (11am)**	**Upper Tower (11am)**	**Lower Tower (11am)**	**Upper Tower (11am)**
O_3 (ppb)	8	14	7	14	49	55	40	52
NO_2 (ppb)	17	11	20	11	21	14	32	14
NO (ppb)	27	10	39	10	7	4	13	5

The results from this sensitivity study show that the results are sensitive to the K_Z value only in terms of the Lower Tower site and not at the Upper Tower site. The pattern of distribution also remains the same. There is a greater difference between the results of the 11am run than the 8am run. For example at the Lower Tower site, the reduction of the K_Z value from 50 to 20 m^2s^{-1} in the 11am run, causes a 10 ppb increase in the concentration of nitrogen dioxide. However, during the 8am run, when the K_Z value is reduced from 20 to 10 m^2s^{-1} nitrogen dioxide only increases by 3 ppb.

- Background Concentration of Ozone

So far in this investigation using URBNOX, very little consideration has been given to the effect of upwind ozone (designated as the 'background concentration' in URBNOX) on subsequent concentrations of nitrogen dioxide in the urban area. A description of behaviour is covered in Section 1.3 and a simple investigation has been carried out in Section 5.2, but this effect has not been considered in any of the URBNOX modelling studies.

To investigate this, both the 8am and 11am runs were repeated using the same parameters as before, (summarised in Table 5.2), apart from a substantial increase in the background concentration of ozone to 120 ppb. This was done to see what effect an ozone episode upwind would have on nitrogen dioxide formation in the downwind urban area. The results for the Upper and Lower Tower sites are summarised in Table 5.5 and the profiles are shown in Figure 5.6 and Figure 5.7.

Figure 5.6: Sensitivity to Background Ozone Concentration- URBNOX-Modelled Vertical Profiles of Nitrogen Dioxide and Ozone for the Queen's Tower Study (8am)

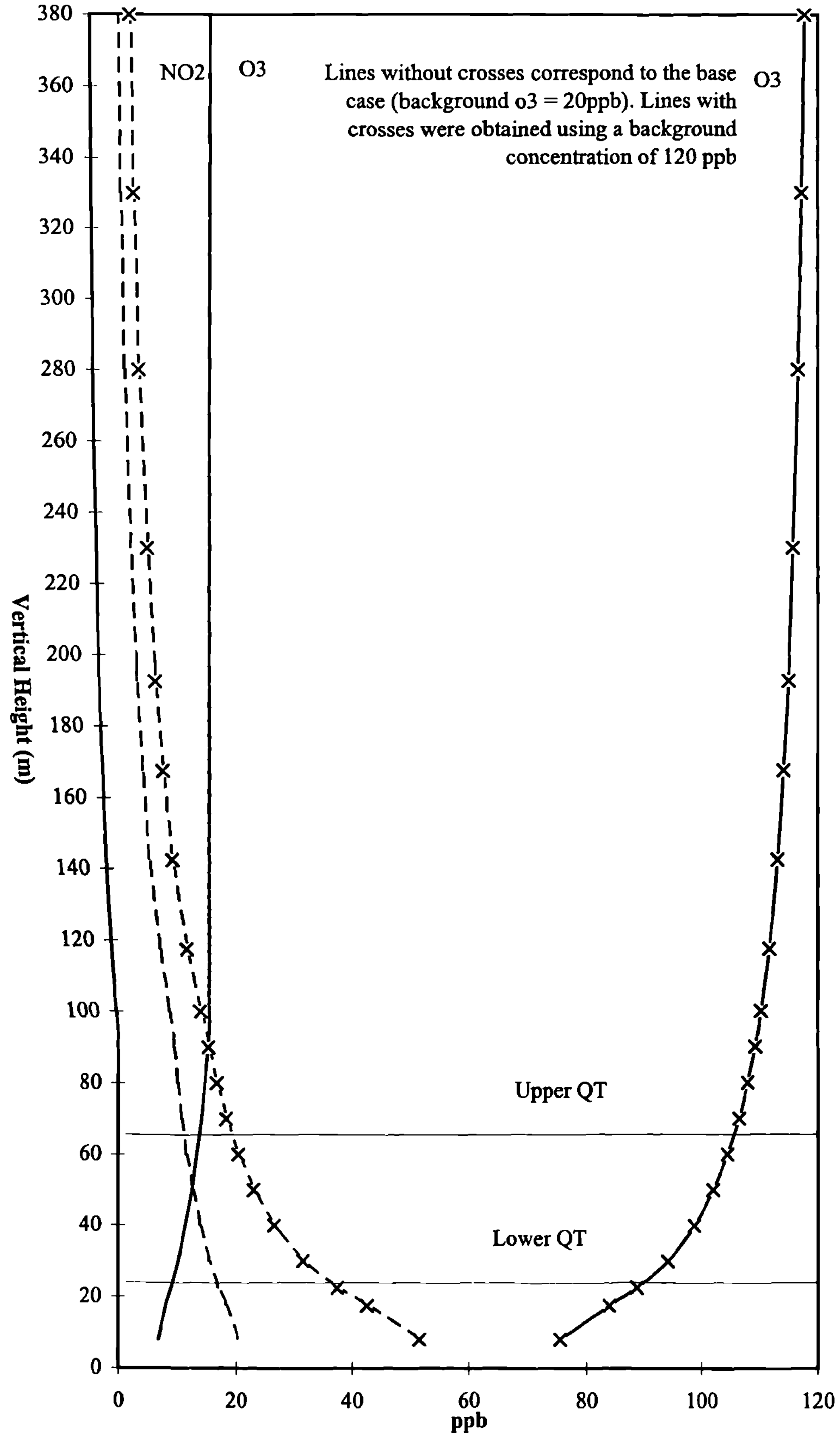


Figure 5.7: Sensitivity to Background Ozone Concentration- URBNOX-Modelled Vertical Profiles of Nitrogen Dioxide and Ozone for the Queen's Tower Study (11am)

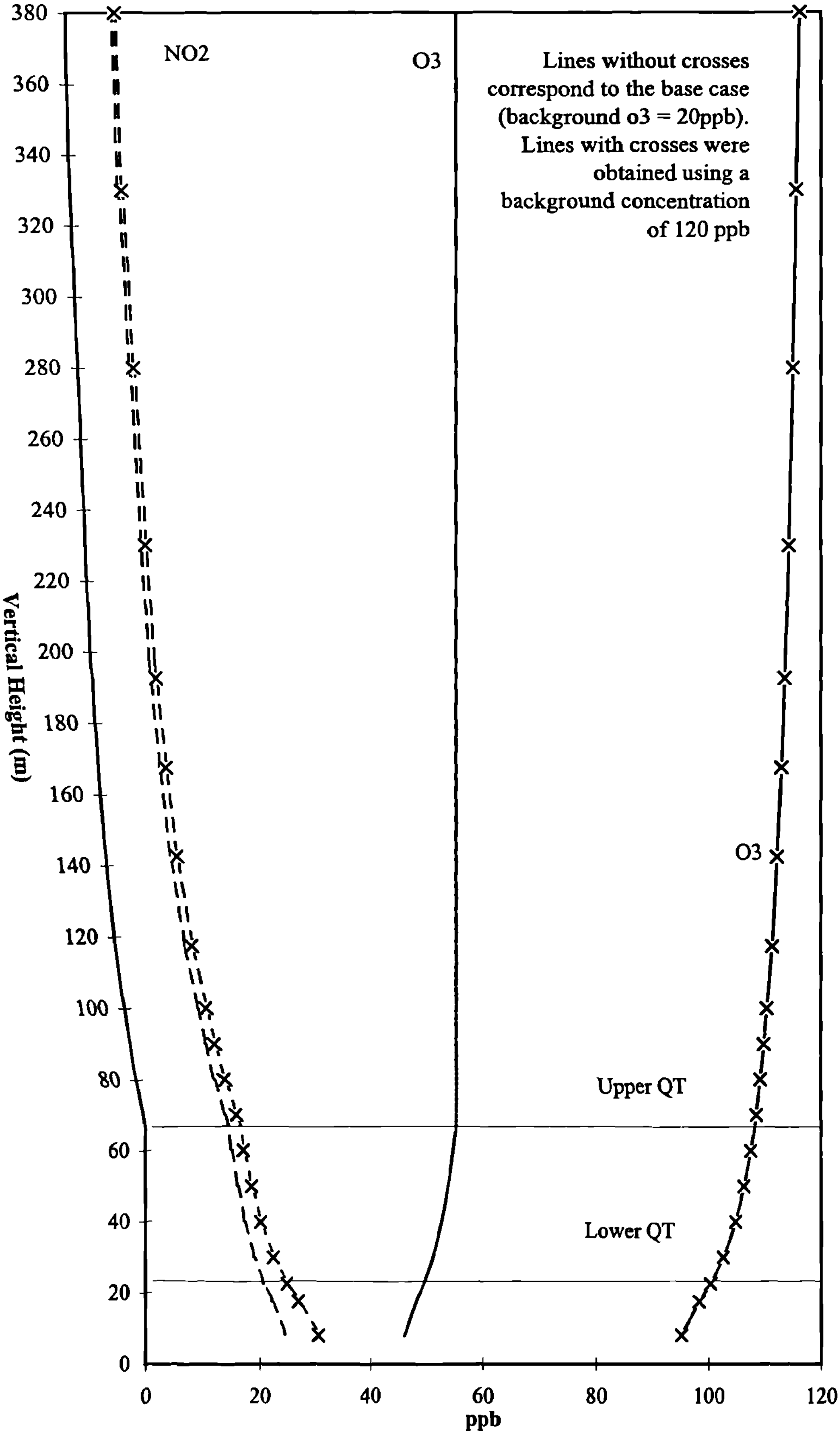


Table 5.5: Comparison of Results from Upwind Ozone Sensitivity Study

	Upwind O_3- 20ppb (Base case)		Upwind O_3- 120ppb		Upwind O_3- 65ppb (Base case)		Upwind O_3- 120ppb	
	Lower Tower (8am)	Upper Tower (8am)	Lower Tower (8am)	Upper Tower (8am)	Lower Tower (11am)	Upper Tower (11am)	Lower Tower (11am)	Upper Tower (11am)
O_3 (ppb)	8	14	85	103	49	55	99	108
NO_2 (ppb)	17	11	40	19	21	14	26	17
NO (ppb)	27	10	6	2	7	4	4	2

The results from this sensitivity study show that the model is indeed sensitive to the background ozone, whilst being limited by the nitric oxide present. As the ozone enters the urban area it is depleted by the nitric oxide present to form nitrogen dioxide. The greater amount of ozone present increases the nitrogen dioxide concentrations (and hence, depletes the nitric oxide present). It can be observed that there are greater concentrations of nitrogen dioxide present with the increased background of ozone. This is most noticeable at the Lower Tower site during the 8am run. However, the increase in background ozone alone is not sufficient to raise nitrogen dioxide levels to episodic proportions. The process is limited by the nitric oxide. These results indicate that an increase in the background concentration of ozone alone is not sufficient to cause an episode of nitrogen dioxide- there also needs to be adequate nitric oxide and the 'correct' meteorological factors. This could have important implications for summer episode abatement strategies. On comparison with the results shown in Table 5.1, it can be seen that there some difference between the two sets of results, suggesting that physical processes should be taken into account as well as chemical ones.

- Dissociation Rate

The sensitivity of URBNOX to the dissociation rate of nitrogen dioxide (which is also taken to represent the amount of insolation present) was then examined. Both runs were repeated with differing dissociation rates to investigate the effect they would have on the amount of nitrogen dioxide present. The results are summarised in Figure 5.8 and Figure 5.9.

It can be seen that although the increase in dissociation rate causes a decrease in nitrogen dioxide concentration, the difference between levels is not large (10ppb at the most). However, it does have a greater effect than in the winter runs. This is shown in Section 4.4.1.2. Therefore from these results, it can be determined that the dissociation rate does not greatly influence the amount of nitrogen dioxide present in an urban area. This is backed up by the results in Table 5.1.

Figure 5.8: Sensitivity to the Dissociation Rate- URBNOX Modelled Vertical Profiles of Nitrogen Dioxide for the Queen's Tower Study (8am)

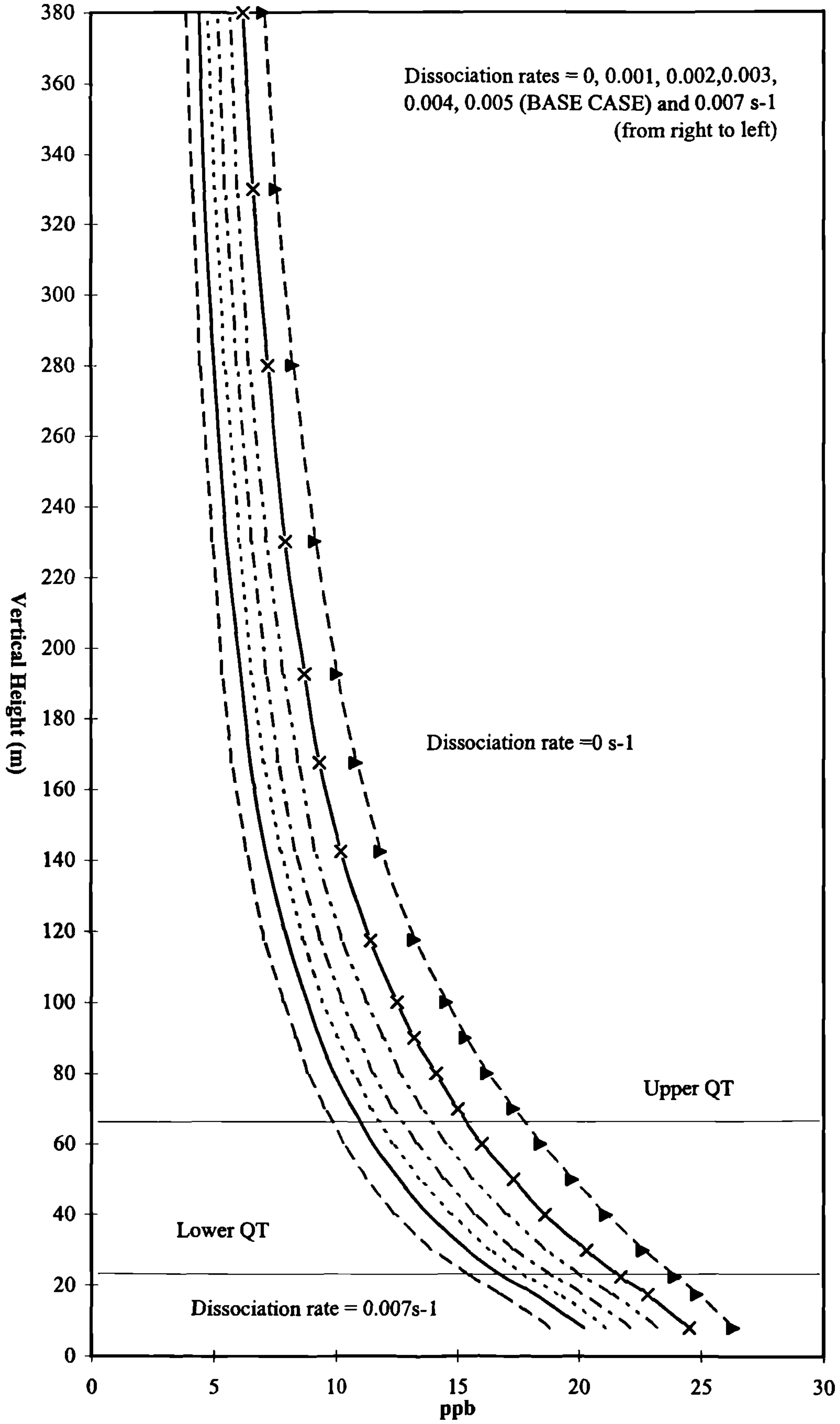
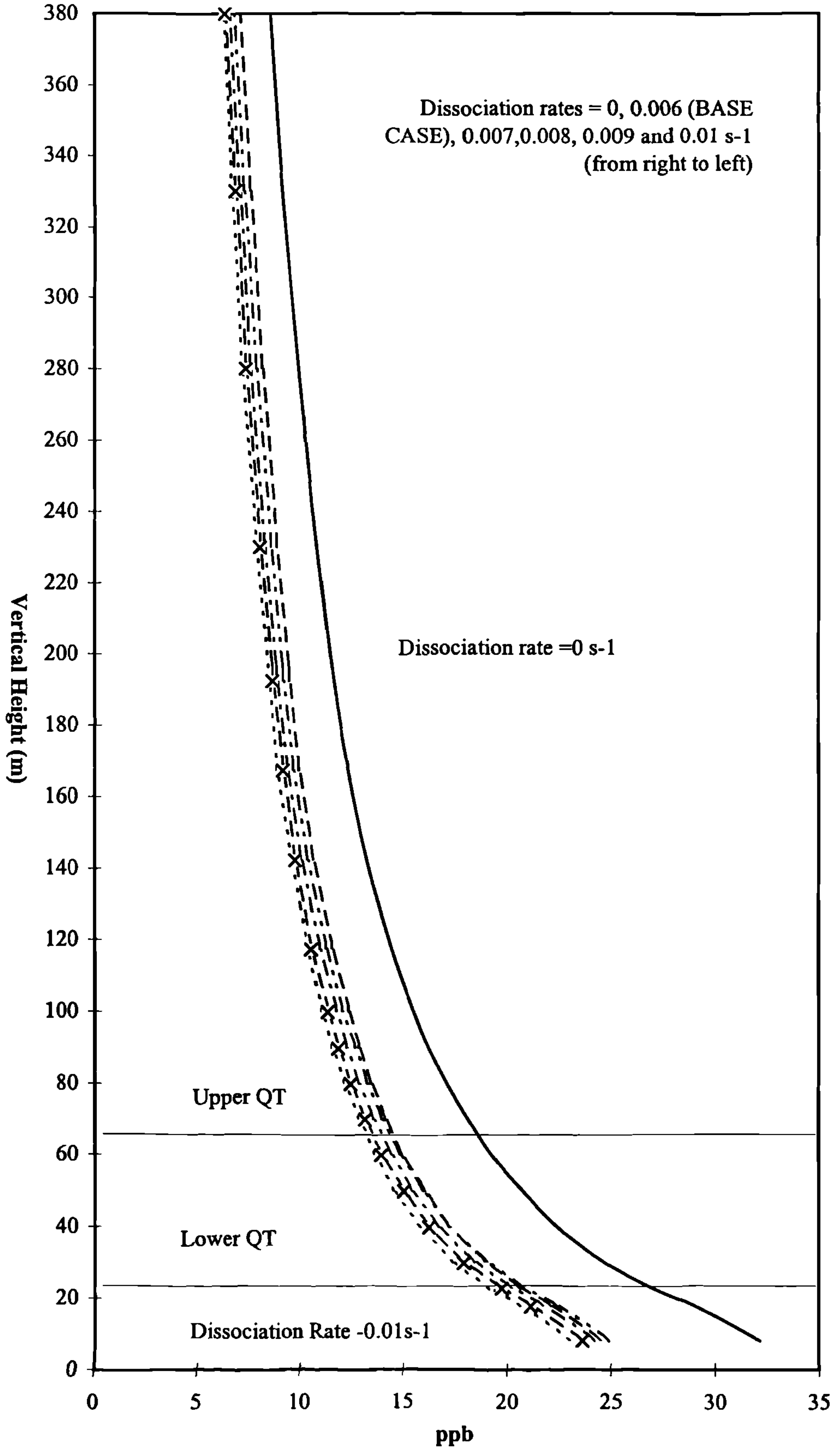


Figure 5.9: Sensitivity to the Dissociation Rate- URBNOX Modelled Vertical Profiles of Nitrogen Dioxide for the Queen's Tower Study (11am)



5.3.2 Discussion

URBNOX reproduces the characteristics of concentrations observed along the vertical scale. Both modelled and measured data illustrate that there is a difference in pollutant levels along the vertical scale thus highlighting the need for local authorities to consider this when investigating air quality and formulating their management strategies. It has also been illustrated that the upwind concentration of ozone can influence the nitrogen dioxide levels within the urban area, an aspect which also should be taken into account when planning an abatement strategy.

The model reproduces the characteristics of an average summer's day. This was done using the London Emissions Inventory (1993). However, there are several different inventories available, such as the National Atmospheric Emissions Inventory and using these may give different results. A comparison of a selection of different inventories can be found in Chapter 4 (Section 4.4.1.2). This is also discussed further in the next section.

It has also been shown that the diffusion profile used in URBNOX although simplistic, is suitable and gives a good representation of the pattern of distribution. It would be possible however, to construct a more complex diffusion profile, with a separately evolving boundary layer within the urban area.

Due to the many problems encountered during the running of the Queen's Tower monitoring experiment, it was resolved that a more detailed analysis of monitoring data and comparison with URBNOX was needed. As a result of both time and financial limitations, it was decided to request data from the South East Institute of Public Health (SEIPH). This was also done in order to investigate a summer episode in detail. However, vertical data was not available for this part of the investigation. Therefore, it was decided to analyse the horizontal distribution of nitrogen dioxide and ozone during an episode.

5.4 SEIPH Data Analysis - Summer Episodes

5.4.1 Introduction and Aims

The South East Institute of Public Health (SEIPH) is responsible for operating and managing the London Air Quality Network. This is a network of over 30 monitoring sites situated within the Greater London area, which is described in detail in Section 2.3 (Chapter 2). A description of the different classifications of sites can be found in Section 2.5. SEIPH kindly agreed to supply air quality data from a summer episode to be analysed in this project.

Firstly, the data is presented and the major points of the episode will be picked out and described. However, the main aim of this piece of work is to examine in detail the formation of summer episodes using URBNOX. The results from URBNOX will be compared with the measured data. As stated in the previous section, the horizontal distribution of nitrogen dioxide and ozone will be investigated as there was no vertical data available.

5.4.2 Description of Sites Used in the Data Analysis

After careful consideration data from five sites were chosen for the analysis. The sites were selected so that they formed an approximate transect running from east to west across the centre of London. The sites are described in Table 5.6. Data were supplied from a photochemical episode that occurred between the 1st and the 7th of May, 1995.

Table 5.6: Description of Chosen Sites

Site Name	Address	Classification	Start Date	Pollutants Measured
Bexley	Iris Avenue, Bexley DA8 2DH (Co-ords: 548400 174400)	Suburban	1993	CO NO_2^* O_3 SO_2 PM_{10}
Tower Hamlets (1)	Holy Family School, Shirbutt Street, E14 0DE (Co-ords: 537500 180900)	Urban Background	January 1994	CO NO_2^* O_3 SO_2 PM_{10}
Tower Hamlets (2)	Queen Mary Westfield College, Engineering Dept., Corner of Bancroft & Mile End Roads (Co-ords: 535900 182300)	Roadside	March 1994	CO NO_2^*
Kensington and Chelsea	Sion Manning School, St. Charles Square, North Kensington, W10 (Co-ords: 524000 1817000)	Urban Background	March 1995	CO NO_2^* O_3 SO_2 PM_{10}
Ealing	Ealing Town Hall, Uxbridge Road, W5 2HL (Co-ords: 512600 180700)	Urban Background	March 1995	CO NO_2^* O_3 SO_2

*Levels of NO_x and NO are also included

5.5 Validation of URBNOX Against an Episode of Poor Air Quality on 6th May 1995

5.5.1 Introduction

There were several notable pollution episodes throughout 1995. One of these occurred during the first week of May. This episode was particularly notable because the highest sustained levels of ozone, nitrogen dioxide, sulphur dioxide and PM_{10} were recorded for 1995.

The data collected for this episode is analysed in depth in the Third Report of the London Air Quality Network (Barratt *et al*, 1996). The aim of this section is to take SEIPH's analysis one step further and compare their data to the results modelled by URBNOX. In addition, the model will be used to investigate the behaviour of a typical summer episode. The second aim of this section is to analyse the episode in terms of the five sites chosen (as summarised in Table 5.6)

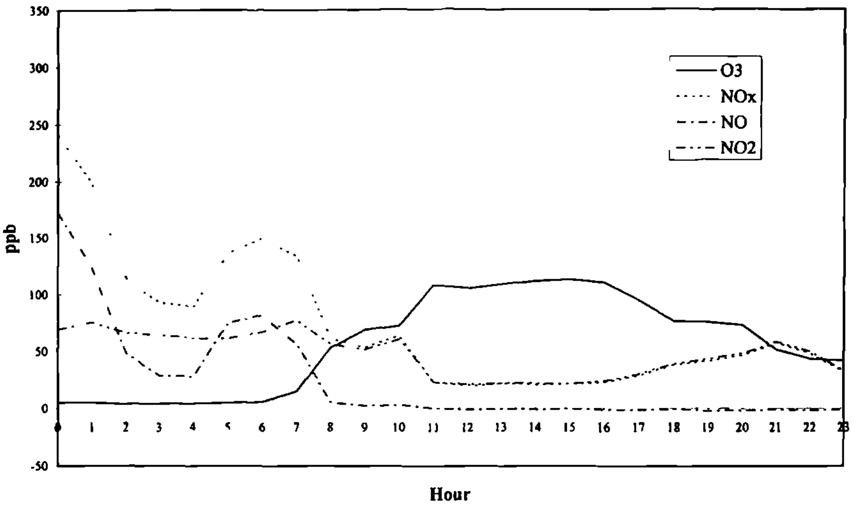
5.5.2 Analysis of an Episode of Poor Air Quality on the 6th May 1995

The episode began on the 1st of May and dispersed on the 7th of May. The main feature of the meteorological conditions was a system of high pressure which resulted in the anticyclonic conditions invariably associated with high pollution levels. The London-wide analysis of this episode has already been carried out by the Air Quality Team at SEIPH and the results of this can be found in the Third Annual Report of the London Air Quality Network (Barratt *et al*, 1996).

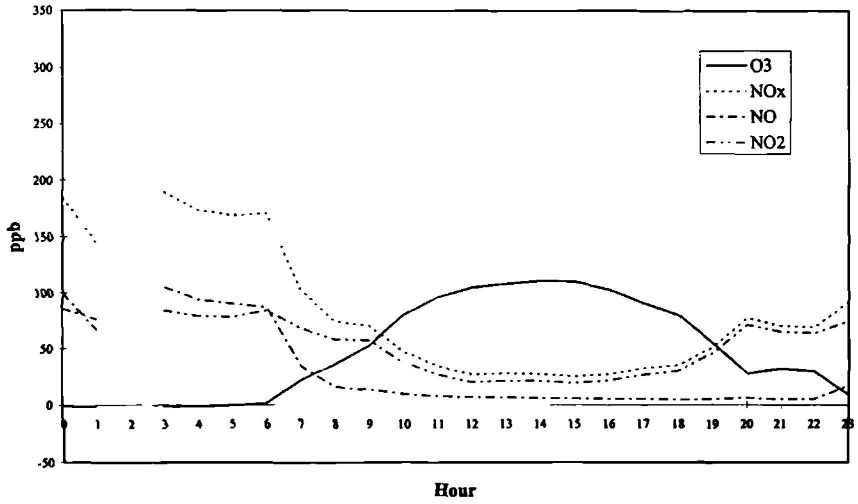
The air quality for the worst day of the episode, 6th May , was plotted for the five chosen sites and can be seen in Figure 5.10.

Figure 5.10: Air Quality Recorded at Selected Sites Across London During An Air Pollution Episode Recorded on May 6th 1995 (Source of Data: LAQN)

Bexley (Suburban)



Tower Hamlets (Urban Background)



Tower Hamlets (Roadside)

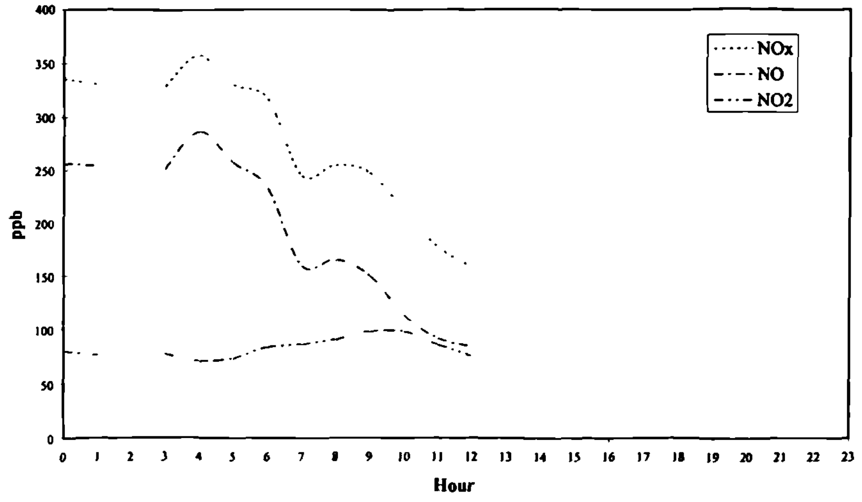
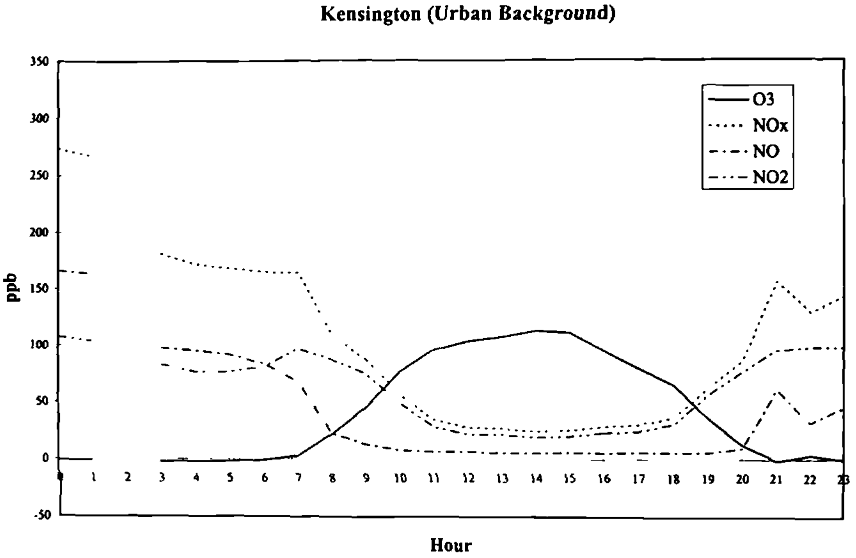
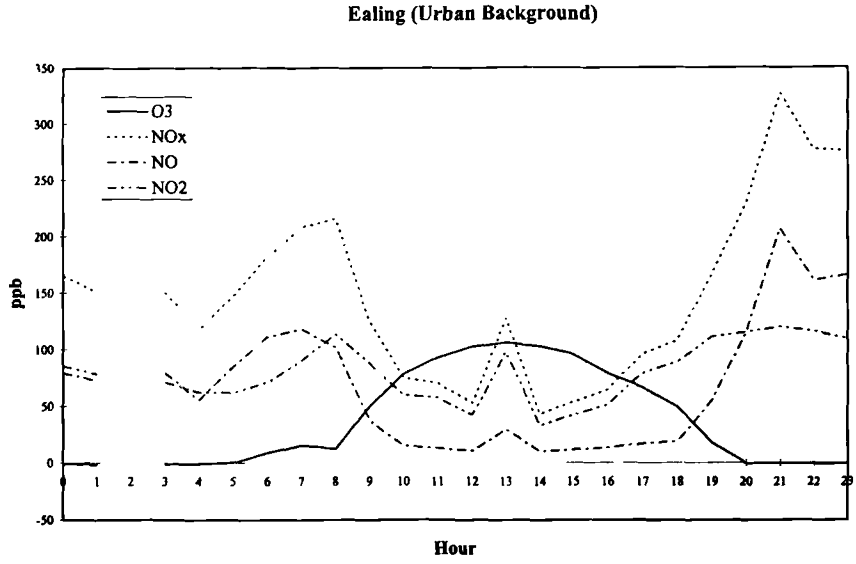


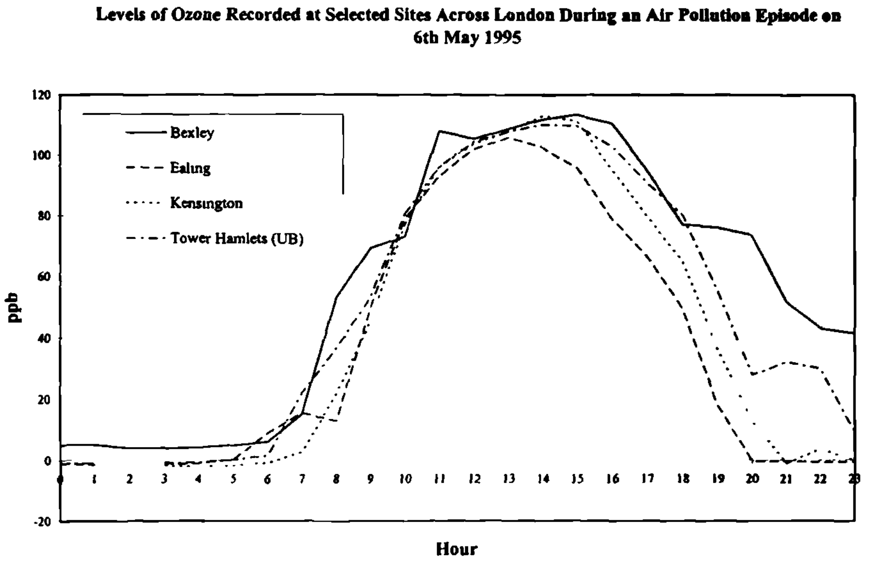
Figure 5.10 (continued)



Kensington (Urban Background)



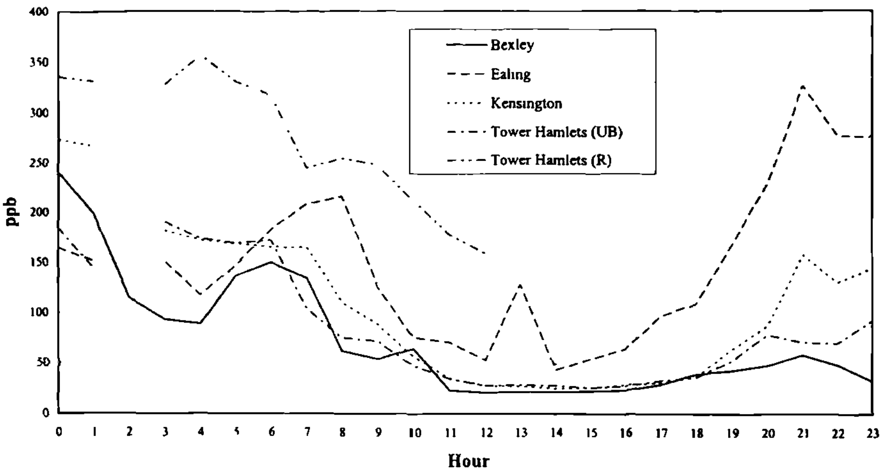
Ealing (Urban Background)



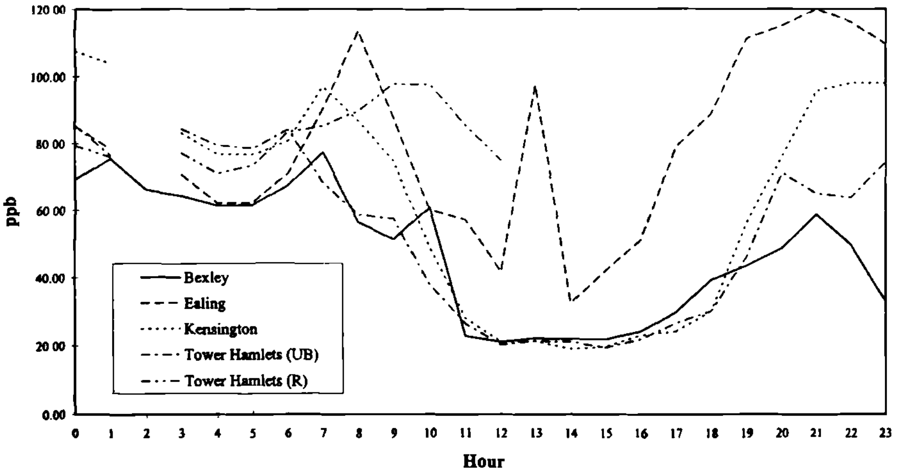
Levels of Ozone Recorded at Selected Sites Across London During an Air Pollution Episode on 6th May 1995

Figure 5.10 (continued)

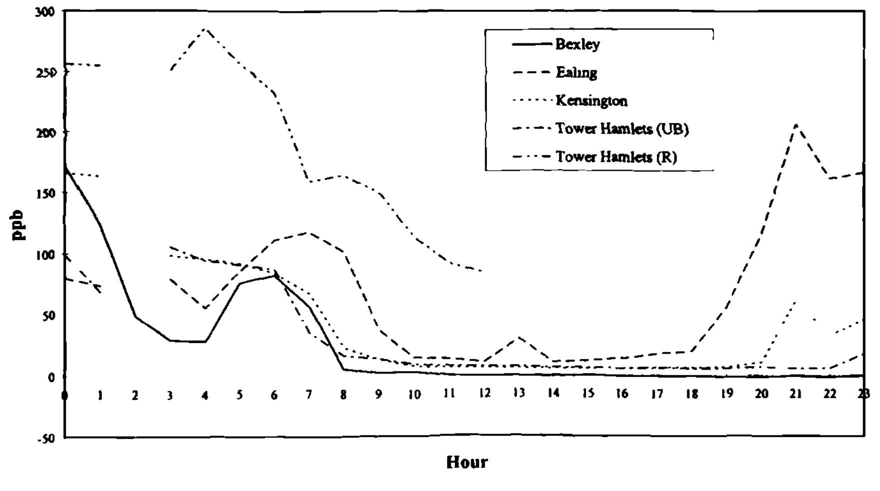
Levels of NOx Recorded at Selected Sites Across London During an Air Pollution Episode on 6th May 1995



Levels of Nitrogen Dioxide Recorded at Selected Sites Across London During an Air Pollution Episode on May 6th 1995



Levels of Nitric Oxide Recorded at Selected Sites Across London During an Air Pollution Episode on May 6th 1995



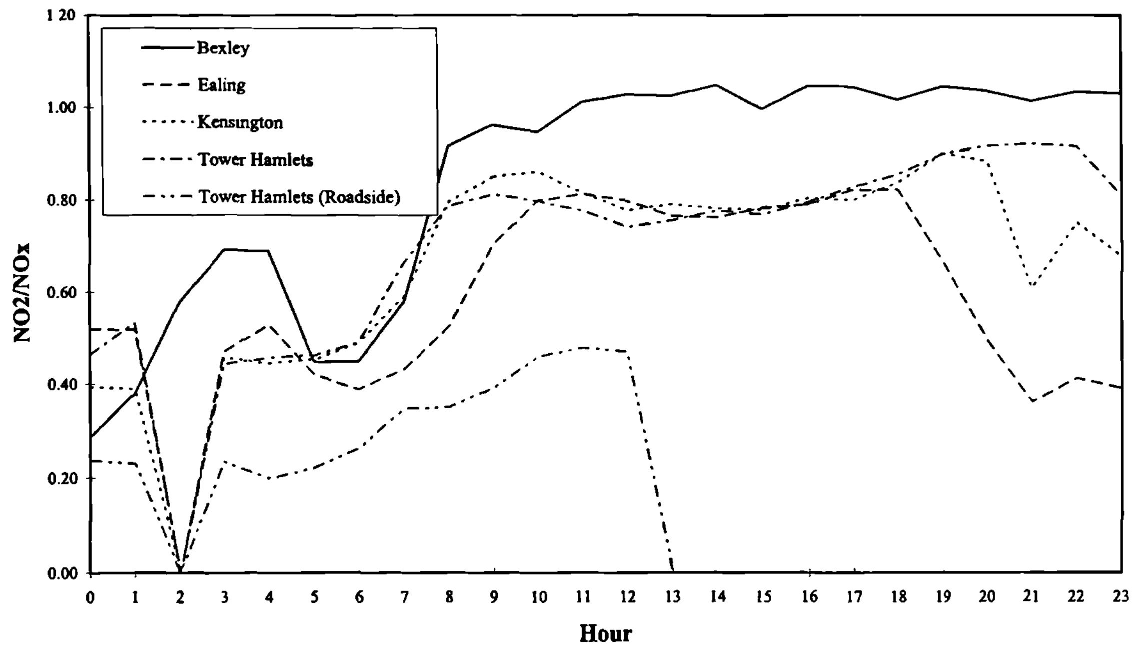
It can be seen from the graphs that all the sites suffer exceedences of air quality standards. The EPAQS Standard for Ozone (the one chosen for the National Air Quality Strategy) was exceeded at all four sites. In addition, the WHO Health Guidelines and the EC Population Information Threshold were exceeded. The air quality had a Department of the Environment rating of POOR. Fewer standards were exceeded for nitrogen dioxide (levels did not even come close to exceeding the new EPAQS Standard), but levels recorded at the Ealing site put the air quality firmly in the POOR band. The Ealing site exhibited the poorest air quality for nitrogen dioxide, but the other sites (with the exception of the Tower Hamlets Roadside site, as there were no measurements available after 1200 hours on that day) did not exceed any standards, although concentrations were higher than average.

On examination of the graphs, it can be seen that there are some substantial differences in concentrations between the five different sites. Bexley had higher concentrations of ozone than any of the other four chosen sites and Ealing had the lowest. In contrast, Bexley had the lowest concentrations of nitrogen dioxide and the Tower Hamlets roadside site had the highest. However, out of the three urban background sites Ealing had the highest concentrations of nitrogen dioxide. These findings can be explained by reason of Bexley being a suburban site. These sites are more rural in character than the urban background sites which explains why the ozone levels are higher. It also should be noted that the Bexley site is situated at the edge of London so any ozone coming in from a south-easterly direction would not yet have gone over London and been depleted.

During the episode, conditions were mainly stable during the night and unstable during the day. The stable conditions may have aided the progressive build-up of pollutants that was observed over several days. Neutral conditions started to occur on the 7th of May, when the episode began to disperse.

The NO_2/NO_x ratios are fairly typical for an episode of elevated nitrogen dioxide levels. Figure 5.11 shows the change in ratios throughout the day on 6th May.

Figure 5.11: Graph to Show NO_2/NO_x Ratios at Selected Sites Across London on May 6th 1995



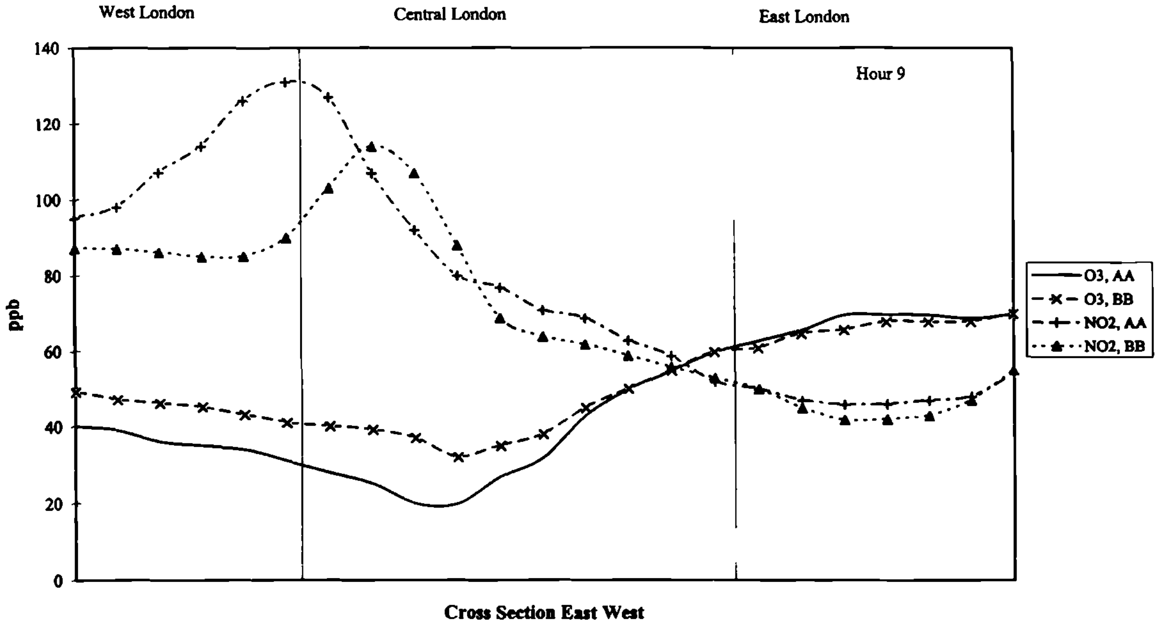
It can be seen from the graph that the ratios fall into three distinct categories, according to the type of site. The roadside site in Tower Hamlets exhibits the lowest ratio of all the sites- only reaching a peak of 0.4, consistent with typical summer ratios near roadside emissions. This is because the site is near to a continuous source of nitric oxide which has very quickly depleted all the available ozone, thus allowing only a limited amount of nitrogen dioxide to be produced. At the other extreme, the Bexley suburban site showed the highest ratio of 1.0. This is due to ozone concentrations being higher and the nitric oxide concentrations being lower than at the other site categories. As a result, there is more ozone available to oxidise the nitric oxide to nitrogen dioxide. The ratios for the urban background sites fall in between these two extreme categories as the sites are not so close to sources of nitric oxide so as to deplete all the ozone. These results back up the findings in the first QUARG report (1993) that the ratio of NO_2:NO_x is seen to increase the further from the NO_x source a measurement is taken as more of the nitric oxide is oxidised to nitrogen dioxide by ozone.

5.6 Modelling Air Quality on May 6th 1995 Using URBNOX

URBNOX was run with the aim of modelling nitrogen dioxide and ozone levels recorded on the 6th May and comparing them to the recorded data. The ozone and nitrogen dioxide monitoring sites from the London Air Quality Network were used by SEIPH to statistically produce contour plots of concentrations on the 6th of May, one of the worst days of the episode. Cross-sections (designated AA and BB) were then derived from the contoured data, with hourly data plotted to show the development of ozone and nitrogen dioxide over the 24 hours (Barratt *et al*, 1996). An example of one of these plots is reproduced in Figure 5.12, by courtesy of SEIPH:

Figure 5.12: Nitrogen Dioxide and Ozone Plots From Transects Across London for May 6th 1995

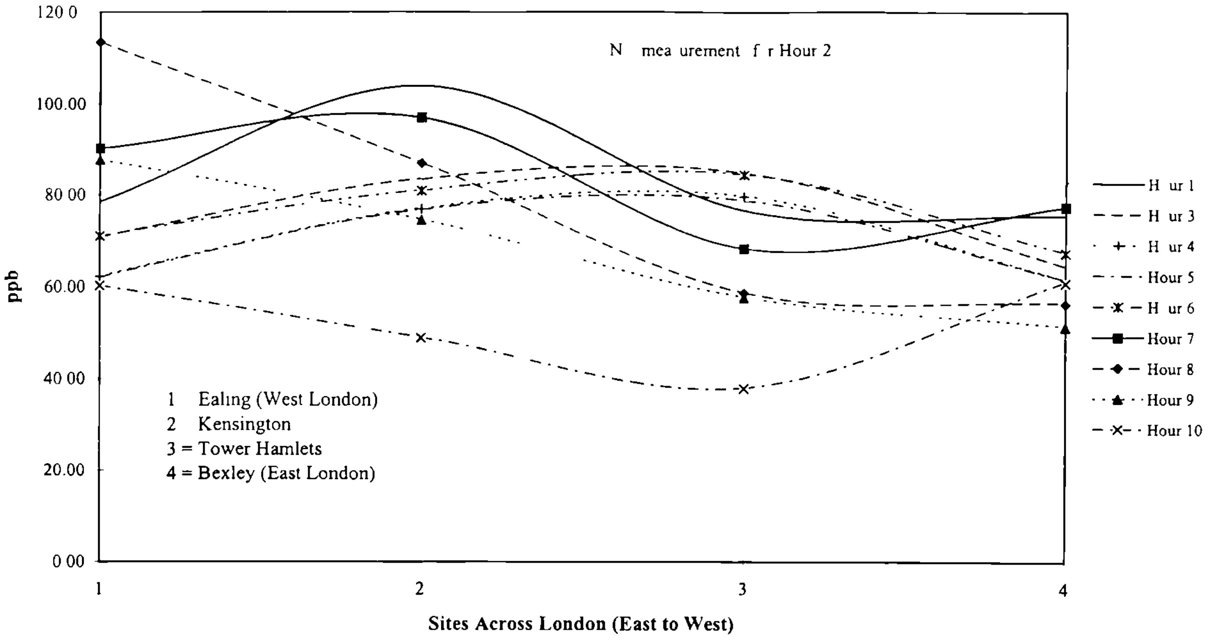
Source: LAQN Database (SEIPH)



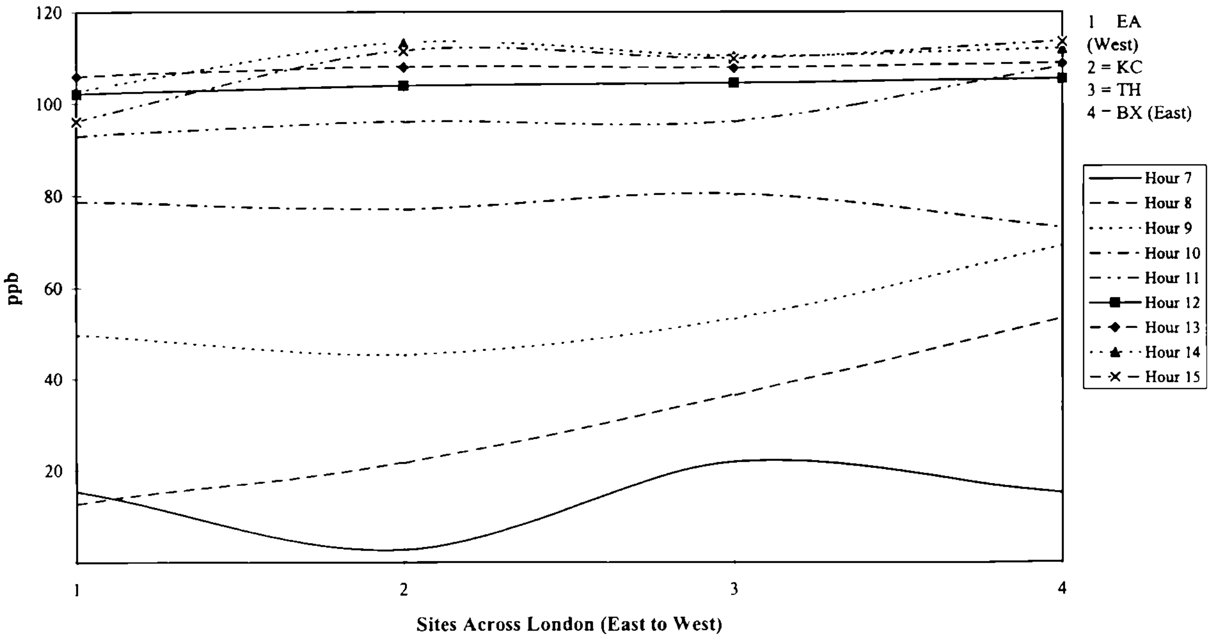
This type of plot was then applied on a simple scale, to the data collected for the four sites. An example for both nitrogen dioxide and ozone is illustrated in Figure 5.13.

Figure 5.13: Plots to Show the Development of Ozone and Nitrogen Dioxide For Selected Sites Across London on May 6th 1995.

Nitrogen Dioxide Development During the Morning (May 6th 1995)



Ozone Development During the Day (May 6th 1995)



URBNOX was then used to try and recreate this data. In this case, there were more data available to study the episode, than in the previous one. However, it is all surface data as no vertical data were available. Therefore the aim was to discover if this surface background data were compatible with the model. The original form of URBNOX was again used, but during the course of this particular investigation, it was discovered that there was a need to incorporate temporal factors into the model. A temporal version of URBNOX is subsequently introduced in a later section.

The base run chosen was Hour 9, since it can be seen from the SEIPH transect that it exhibited some of the highest concentrations shown on May 6th. The model was run using parameters as close as possible to the conditions recorded. The parameters are summarised in Table 5.7.

Table 5.7: Summary of parameters used for URBNOX runs in comparison with SEIPH Data (6th May 1995)

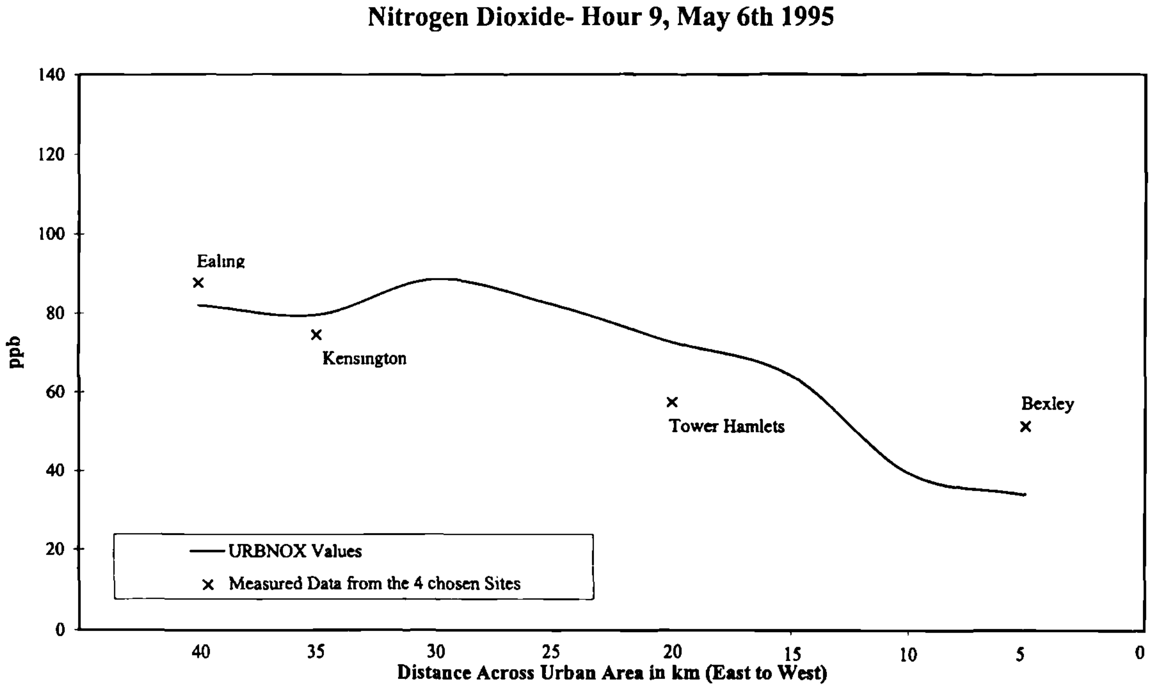
Parameter	Values
Wind Speed	2 m/s
Mixing Height	500 m
Diffusivity	30 m^2s^{-1}
Z_o	200m
Dissociation Rate	0.005 s^{-1}
Emissions	London Emissions Inventory
Wind Direction	Easterly
Fraction of NO_x Emission Factor as NO	95 %
Distance Travelled by the Air Column	40 km
Background O_3	103 ppb
Background NO_2	12.7 ppb
Background NO	0.4 ppb

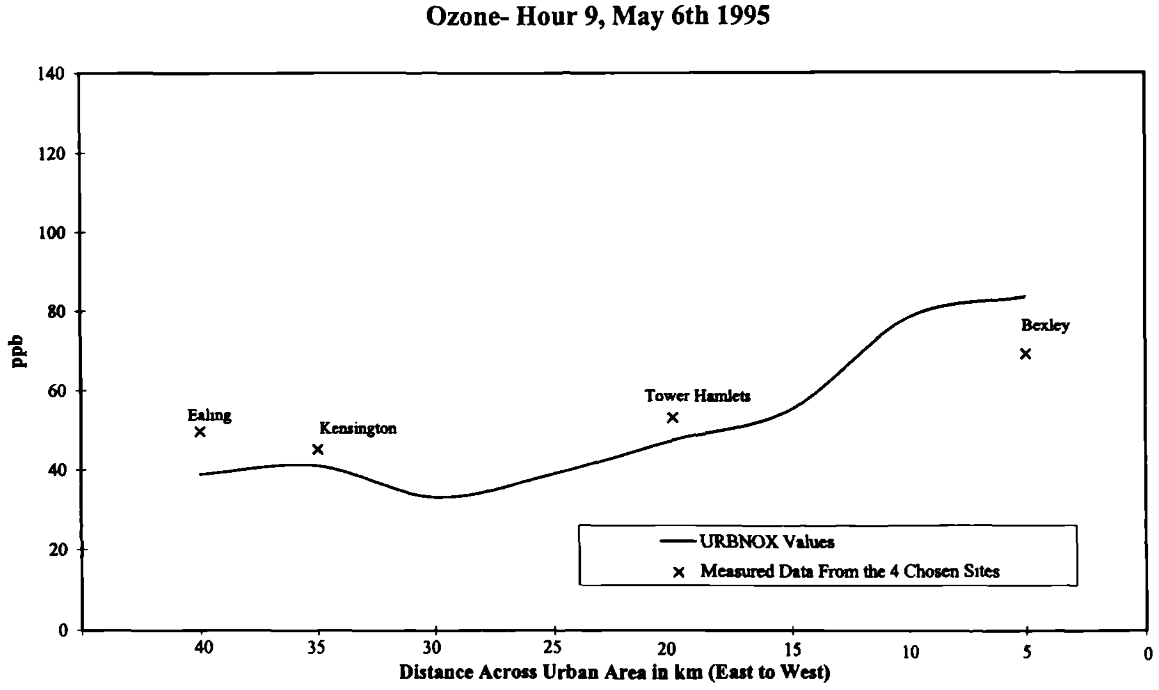
As with the URBNOX runs for the Queen's Tower, it was decided to use data recorded by the London Weather Centre (LWC). The details of the site are described in Section 5.2.1. SEIPH uses London Weather Centre data for their analyses.

The wind speed was taken as the average wind speed recorded for that day by the London Weather Centre. The wind direction was approximately easterly during the time period of interest (LWC, 1995; Barratt *et al*, 1996). The London Emissions Inventory was used since it is one of the most recent inventories and has the greatest resolution being on a 1 x 1 km^2 grid (although it has been used on a 10 x 10 km^2 in this case). The wind direction determines which grid squares are used. The grid squares chosen were the ones that had one of the four measuring sites contained within their boundaries. They were grid squares, 5417 (Bexley), 5318 (Tower Hamlets), 5218 (Kensington) and 5118 (Ealing). The diffusivity (K_Z value) was selected as an example of a typical value for neutral to unstable conditions. The modified diffusion profile (as discussed in Chapter 4) which assumes a very well mixed, lowest layer was used as it gives a better representation of the situation in an urban area. The dissociation rate was also selected as a typical example for that time of day (Campbell, 1986). The background concentrations of ozone, nitrogen dioxide and nitric oxide used were the average concentrations recorded at the Lullington Heath on the 6th May (NETCEN Archive). These were to represent the type of concentrations that would be entering London.

The results are summarised and compared with the data from the four chosen sites across London in Figure 5.14. In order to compare them with SEIPH's data more easily, they have been plotted to show the evolution of both nitrogen dioxide and ozone going across the urban area, rather than as vertical profiles.

Figure 5.14: Plots of Nitrogen Dioxide and Ozone from URBNOX Compared with SEIPH Data From Selected Sites Across London



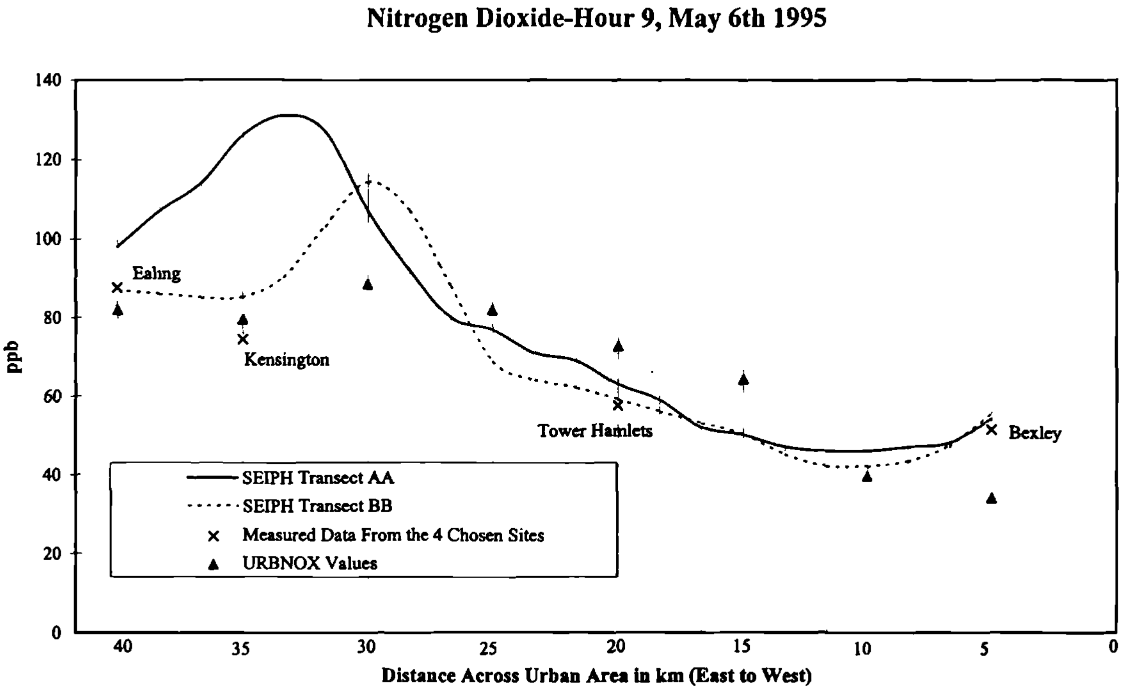


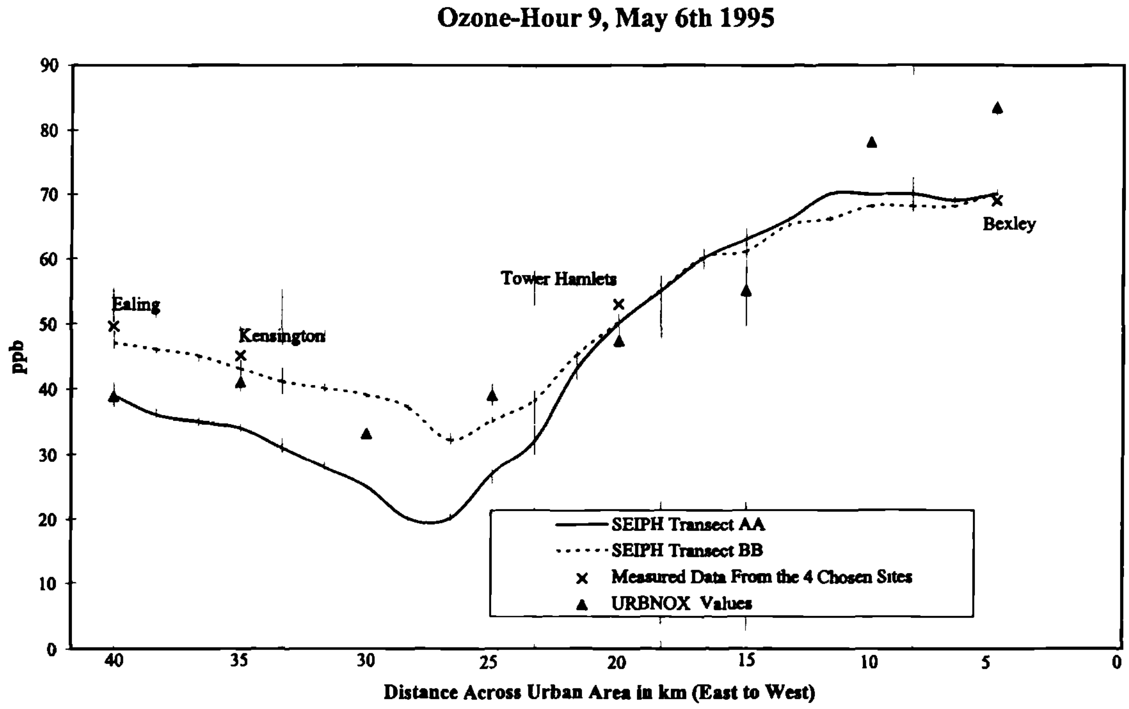
The results from URBNOX show that as the column of air crosses the urban area, nitrogen dioxide levels increase, finally peaking at 30 km, falling around 35 km and then slightly rising again at the end. Ozone can be seen to fall and rise in tandem with the nitrogen dioxide. Both the modelled nitrogen dioxide and ozone illustrate very well their pattern of behaviour as they cross the urban area. The ozone concentration falls with increasing distance across the urban area as it comes into contact with the emissions of nitric oxide. As a result of this levels of nitrogen dioxide can be seen to increase. It can also be seen that the large background concentration of ozone entered into the model causes an increase in nitrogen dioxide levels. The extent of its influence will be investigated in the subsequent sensitivity studies. This pattern of behaviour however, is not so clearly illustrated by the measurements from the four SEIPH sites. This may be due to the small number of sites being analysed. It is illustrated more clearly in the SEIPH transects.

It can be seen from the graphs that the results from URBNOX show a reasonable fit to the recorded measurements. Generally in this case, URBNOX slightly underpredicts for ozone and slightly overpredicts for nitrogen dioxide. The horizontal pattern of distribution has a better fit for ozone than it does for nitrogen dioxide. However, within the uncertainties connected with the emissions and representativeness of the sites, the agreement is encouraging.

The previous comparison concentrated on selected background sites. A further comparison is given in Figure 5.15, where the results from URBNOX are compared with the transects taken from contoured data, based on the overall London Air Quality Network (Barratt *et al*, 1996).

Figure 5.15: URBNOX Results For Hour 9 Compared With SEIPH Transects





Again, it can be seen that the results from URBNOX have a reasonable fit to the transects. The model does not exhibit the extreme peak the transects show. This is most probably due to the way in which the transects were constructed. The transects were also slightly to the north of the four measuring stations used.

5.6.1 Sensitivity Studies

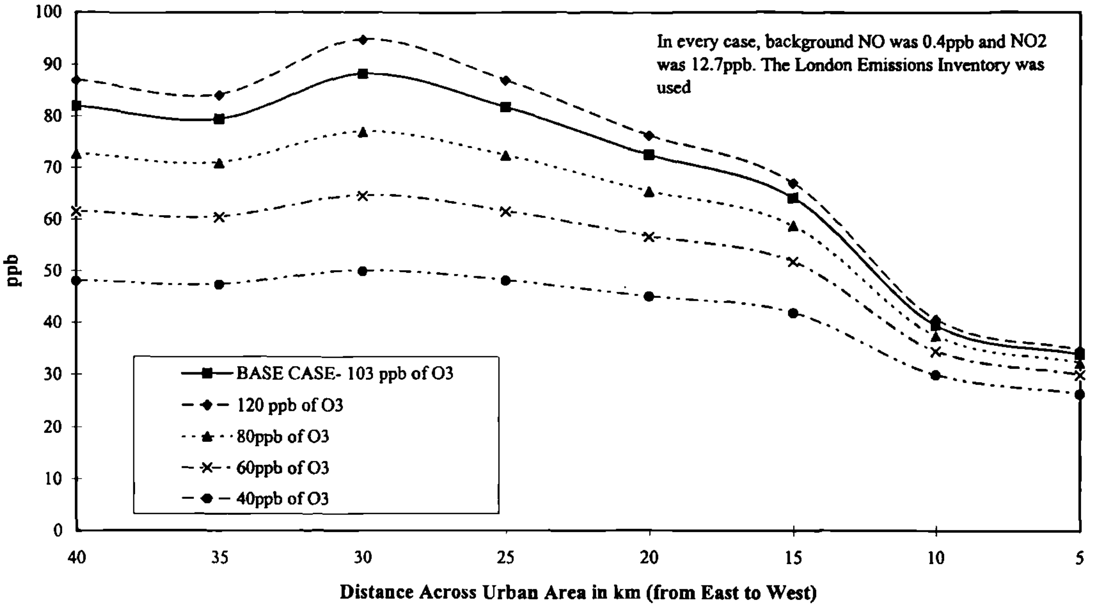
Sensitivity studies were then carried out. These were done to investigate the effect that background ozone could have on potential nitrogen dioxide formation in the urban area. Additionally, the effect of cutting emissions on nitrogen dioxide concentrations was also analysed. Sensitivity studies to investigate the individual parameters and structure of the model have been covered earlier in the thesis, particularly in Chapter 4.

- Background Concentration of Ozone

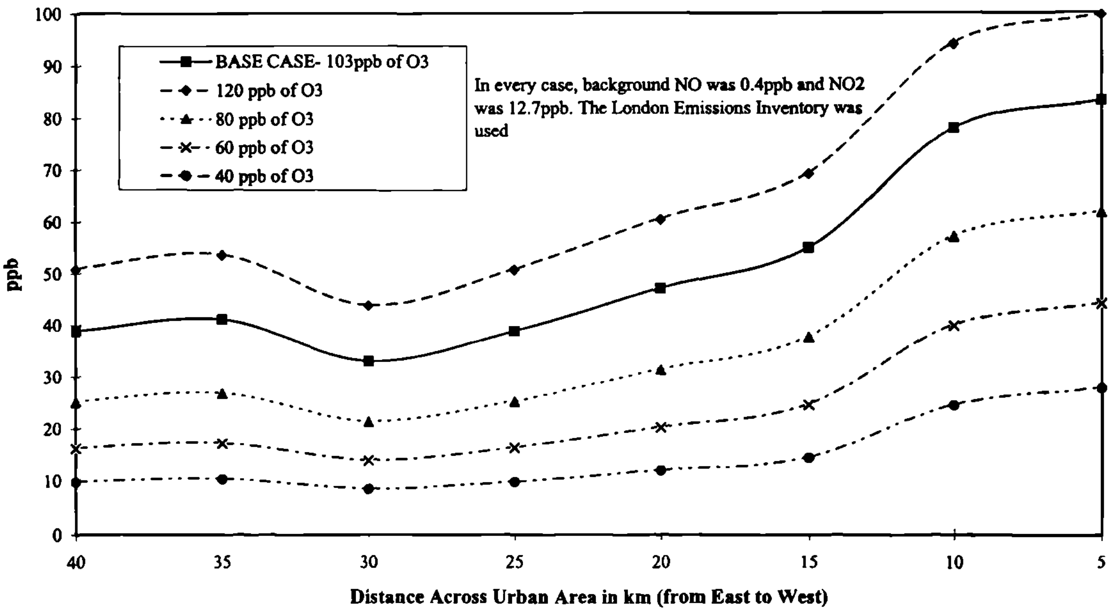
It is known that an ozone plume coming over from the continent can cause an increase in the levels of nitrogen dioxide formed within an urban area downwind of the plume (Barratt *et al*, 1996). This sensitivity study was designed to investigate the effect that ozone upwind of an urban area has on nitrogen dioxide formation within. The model was run using the same parameters as summarised in Table 5.7. Differing background ozone concentrations were used, ranging from 40 to 120 ppb. The results are presented in the graphs shown in Figure 5.16.

Figure 5.16: Results of Upwind Ozone Sensitivity Studies

URBNOX-Modelled Concentrations of Nitrogen Dioxide Across an Urban Area Using Varying Background Concentrations of Ozone



URBNOX-Modelled Concentrations of Ozone Across an Urban Area Using Varying Background Concentrations of Ozone



It can be seen that as the background concentration of ozone increases, the level of nitrogen dioxide increases in the urban area. There is approximately a 10 ppb increase in nitrogen dioxide at the downwind edge of the urban area for every 20ppb increase in ozone. There is no overall change in the pattern of distribution. It should also be noted that the maximum peak of nitrogen dioxide becomes more prominent as the background ozone increases.

It can also be seen that the increased background level of ozone leads to greater overall concentrations of ozone within the urban area itself. However, the nitric oxide emitted from the urban area still causes the ozone concentrations to dip. The graph shows that the ozone is not completely depleted over the urban area which suggests that the nitrogen dioxide formation is limited by the nitric oxide. This was tested further by re-running the model with the same parameters as before, but using a background ozone concentration of 120 ppb and doubling the background nitric oxide concentration to 0.8 ppb. The peak nitrogen dioxide in the lowest layer was found to be 95 ppb, which suggests that the background nitric oxide does contribute. However, when this run was repeated but with a higher nitric oxide background of 5 ppb, the peak nitrogen dioxide was 97 ppb, thus showing that the situation is not wholly limited by the nitric oxide. It was found that if both the background nitric oxide and nitrogen dioxide were doubled to 0.8 and 25.4 ppb respectively, the peak nitrogen dioxide produced was 106 ppb. These results therefore, can be seen to agree in principle with the simple equation shown in Section 5.2. In order for a nitrogen dioxide episode to occur, high levels of both ozone and total NO_x are required.

It is interesting to note that if the K_Z value is reduced to 20 m^2s^{-1} (i.e. making the atmospheric conditions more stable) and the original 120 ppb ozone run is repeated, then the peak nitrogen dioxide is 106 ppb. This analysis suggests that upwind ozone concentrations can significantly affect the formation of nitrogen dioxide in downwind urban areas. This includes influencing the formation of nitrogen dioxide episodes. Local authorities should be aware of this when considering any nitrogen dioxide abatement strategy. However, it should also be noted that episodes are significantly affected by meteorological factors.

- Emissions

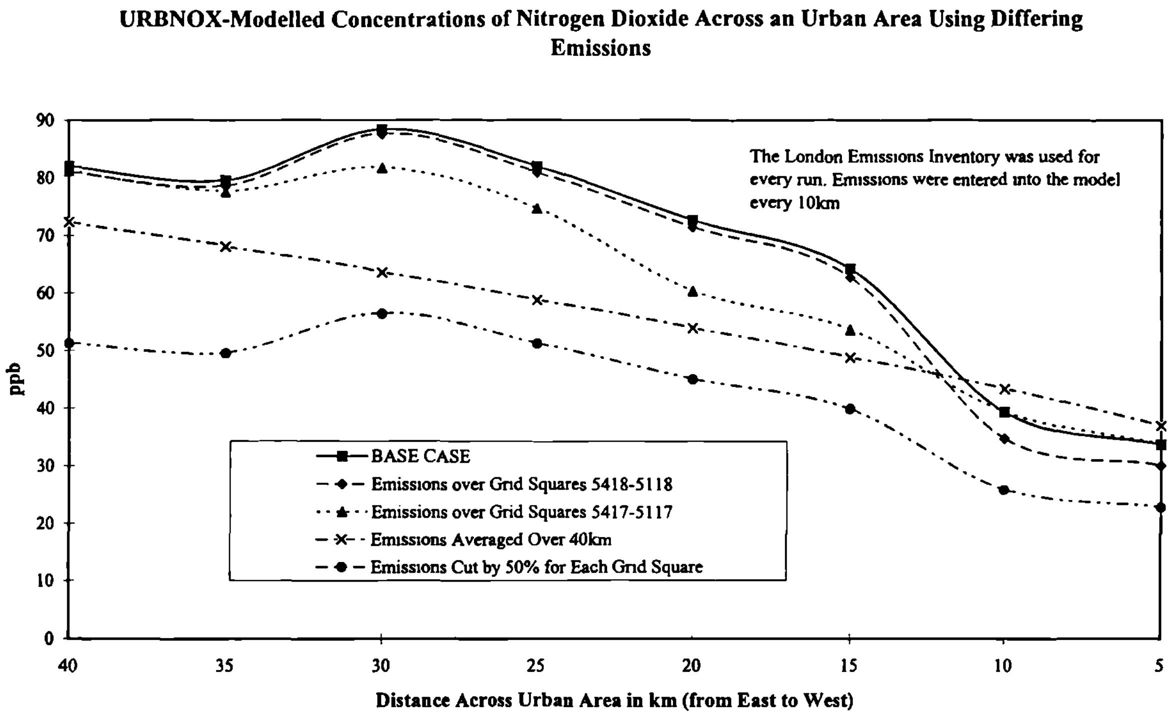
The aim of this sensitivity study is to investigate the contribution of emissions to nitrogen dioxide formation under summer conditions. An emissions sensitivity study has already been carried out for winter conditions in Chapter 4. However, this study takes a different approach from the previous one. The study in Chapter 4 investigated the differences between a range of different inventories. The purpose of this one is to examine one inventory in detail and to look at the different ways it can be used. Several runs will also be carried out to determine the effects that emissions reductions will have on nitrogen dioxide formation.

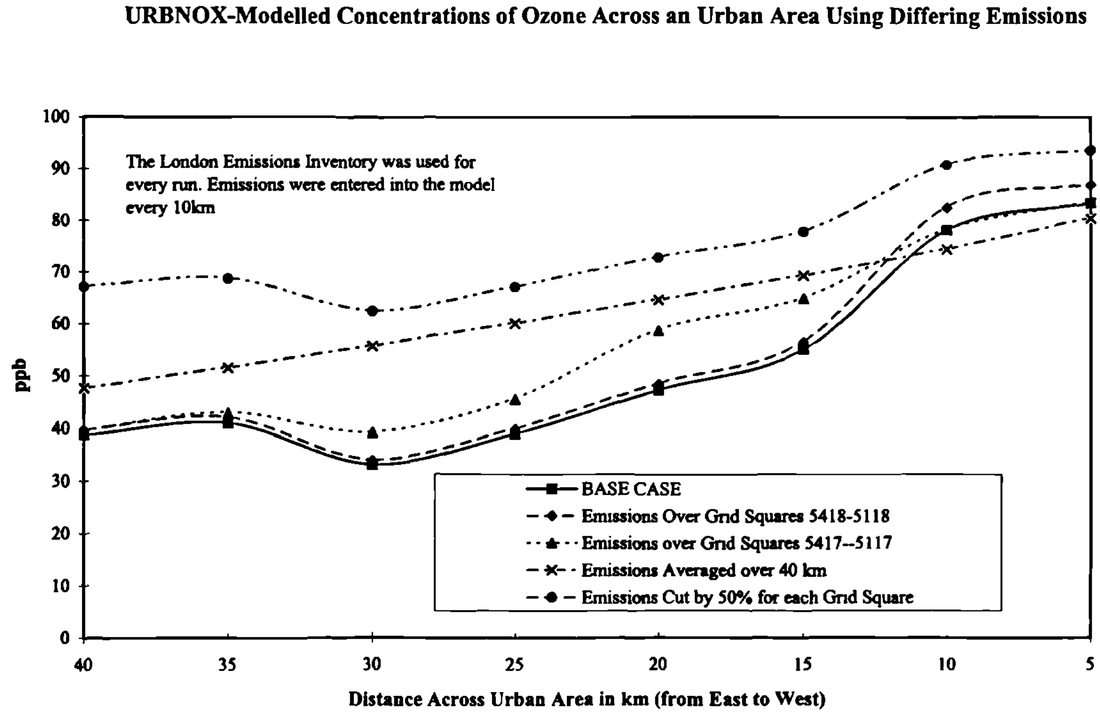
All the parameters were kept the same as for the original base run and can be seen in Table 5.7. Only the emissions were changed each time. The first four runs were as follows:

- Emissions used from grid squares 5418-5118;
- Emissions used from grid squares 5417-5117;
- Average emissions per grid square over the Greater London area used;
- Emissions cut by 50% per grid square.

The results are summarised in the graphs presented in Figure 5.17.

Figure 5.17: Summary of Results from Emissions Sensitivity Study



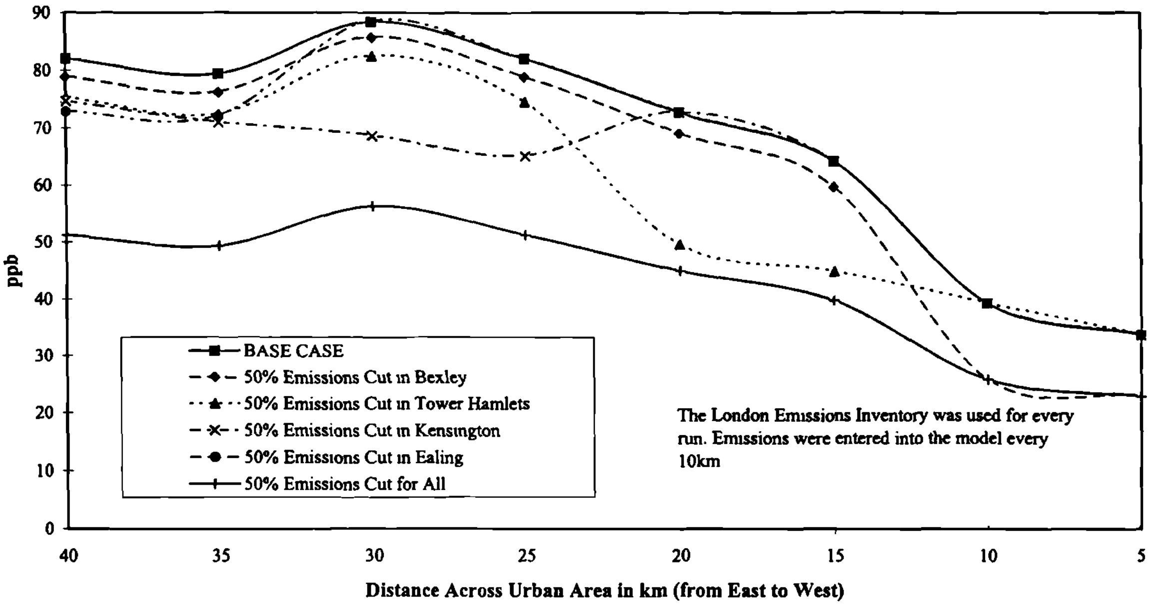


It is shown that the different ways an emission inventory can be used gives rise to different concentrations of nitrogen dioxide. This could have important implications in the modelling of episodes. It is important to ensure that the emissions inventory is used as accurately as possible.

It is interesting to note that if the emissions were cut by 50% for each grid square, then the subsequent levels of nitrogen dioxide formed are well below any of the air quality standards. In order to explore this further, the model was re-run as before but instead of cutting the emissions by 50% in all the squares at once, they were cut sequentially, a square at a time. The results are summarised in the graphs presented in Figure 5.18.

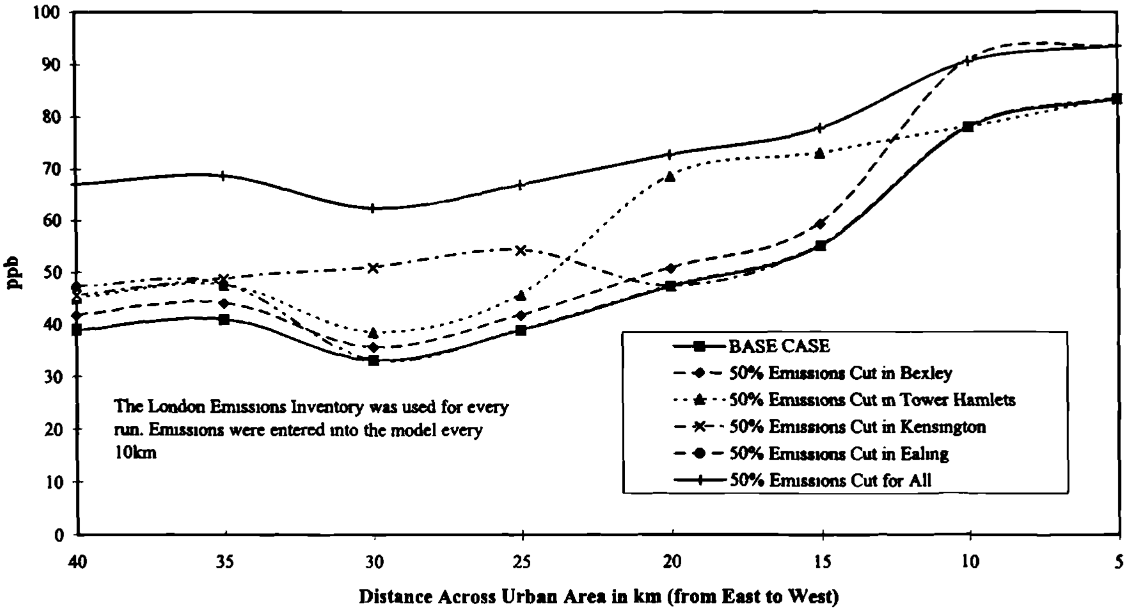
It can be seen that if emissions are reduced in one square, then as would be expected, the subsequent fall in nitrogen dioxide concentrations is greatest in that square. However, the reduction also causes a fall in nitrogen dioxide levels downwind of that grid square, but no more than 10 ppb. This can be looked at in another way. Assuming one grid square to be equivalent of the area of a local authority shows a cut in emissions by one local authority will cause nitrogen dioxide levels to fall within its boundaries and will cause only a slight reduction in the levels measured in neighbouring authorities, especially those downwind. This indicates that for any significant fall in nitrogen dioxide levels to occur, a synchronised effort to cut emissions should be made by all the authorities.

Figure 5.18: URBNOX Results from a 50% Emissions Reduction Per Grid Square



URBNOX-Modelled Concentrations of Nitrogen Dioxide Across an Urban Area With a 50% Reduction in Emissions Per Grid Square

The London Emissions Inventory was used for every run. Emissions were entered into the model every 10km



URBNOX-Modelled Concentrations of Ozone Across an Urban Area With a 50% Reduction in Emissions Per Grid Square

The London Emissions Inventory was used for every run. Emissions were entered into the model every 10km

5.6.2 Discussion

From the above study, it can be seen that URBNOX reasonably reproduces the characteristics of a summer episode and has a good fit to the recorded data. It has a slightly less successful fit to the SEIPH transects. The most noticeable thing missing from the URBNOX results was a high peak of nitrogen dioxide, exceeding the EC Directive Limit Value of 104.6 ppb, as was demonstrated in the recorded data. This may be due to the model's simplicity, for example, the diffusion profile and K_Z value were kept uniform throughout the model runs which may not have been the case in London on May 6th, 1995.

The sensitivity studies highlighted some interesting results. It was shown that the ozone concentration upwind of an urban area can affect the subsequent nitrogen dioxide formation downwind. It can have a significant influence on the formation of episodes, providing the meteorological conditions are right.

The emissions sensitivity studies showed the potential effect an emissions reduction could have on nitrogen dioxide levels. It was shown that only a city-wide cut would have any significant effect on lowering levels. This was only a preliminary study however, and needs more investigation.

The main limitation of this part of the study was that a true comparison could not be made between the model and the data since the data was recorded on a temporal basis and URBNOX runs on a spatial scale. This leads to problems in that the emissions and meteorological factors, such as the mixing height are not represented diurnally. Therefore, it was decided to round the study off by adapting URBNOX into a time based version and carrying out a number of preliminary runs.

5.7 Further Development of URBNOX

As stated at the end of the previous section, URBNOX was adapted to run on a temporal scale (URBNOX-T) in order to investigate whether or not this would make any difference to the fit with the measurements. In the original version of URBNOX, a fundamental assumption is made in order to keep the model simple, i.e. all the parameters are kept constant for each model run. The development of URBNOX-T was an attempt to remove this simplification in order to make the model more realistic. This involved changing the parameters so that they varied diurnally, i.e. the dissociation rate of nitrogen dioxide, the mixing height, the K_Z value, the Z_0 value and the emissions. A series of diurnal variation factors was added to adjust the emissions to correspond with the time of day. This was taken from Dimitroulopoulou (1997), and is shown in Table 5.8.

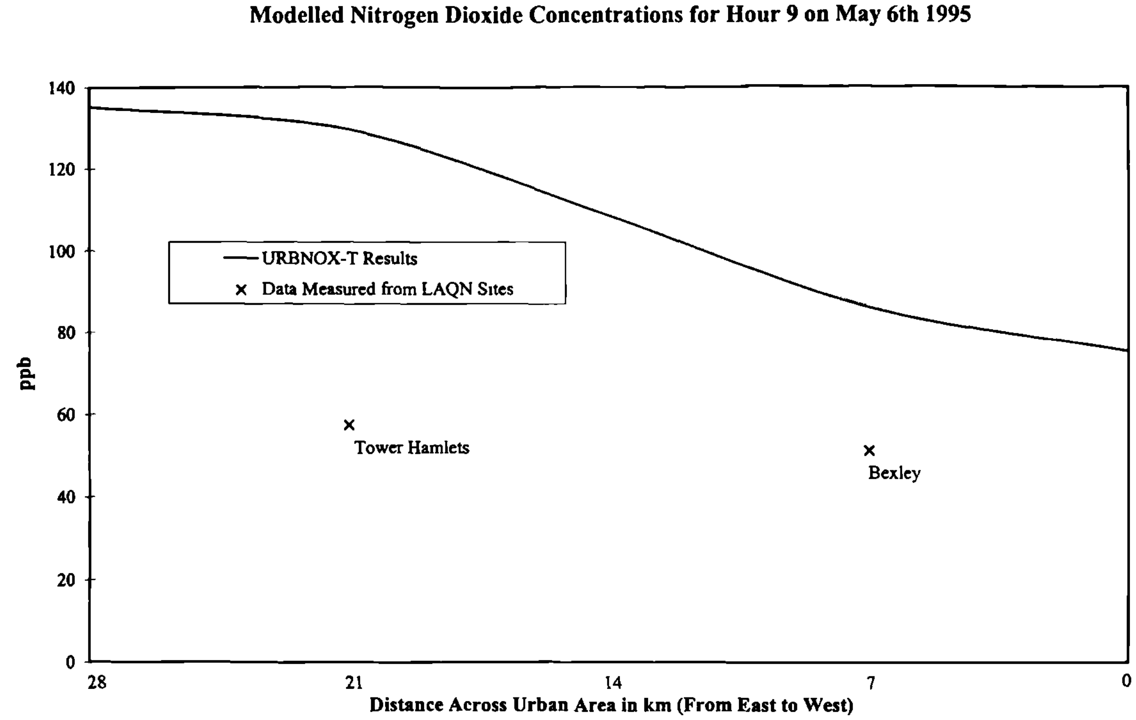
Table 5.8: Diurnal Variation Factor as Used in URBNOX-T

(Source: Dimitroulopoulou, 1997)

Time (Hours)	Diurnal Variation Factor
00:00 - 06:00	0.275
06:00 - 09:00	1.667
09:00 - 15:00	1.227
15:00 - 18:00	1.684
18:00 - 00:00	0.931

URBNOX-T was run to try and recreate the levels of nitrogen dioxide, nitric oxide and ozone observed during Hour 9 on May 6th 1995. A description can be found in Section 5.5. The same parameters were used as far as possible in order to keep the two studies, for both time and distance, fairly compatible. For example, the London Emissions Inventory was used for this run. The results are summarised in the graph presented in Figure 5.19.

Figure 5.19: Modelled Nitrogen Dioxide Concentrations for 6th May 1995, Using URBNOX-T



The model was run several times in order to obtain results for hour 9 at increasing distances across the urban area. The results were compared with data from Bexley and Tower Hamlets. The measured data for Bexley and Tower Hamlets shows an approximately 10% difference in levels of nitrogen dioxide between the two sites. The results from the run using the original version of URBNOX showed a 55% difference. This may be due to the emissions in the model not increasing as they would in a 'rush-hour' situation. In the modified version of URBNOX, the difference in levels between the two sites is reduced to 35%. However, the magnitude of the nitrogen dioxide concentrations has increased, showing substantial over-prediction by the model. In order to investigate these results, a thorough verification of the code is needed as was carried out for the original version of the model. Sensitivity studies are also needed, including ones to investigate the background concentrations of ozone, nitrogen dioxide and nitric oxide, the starting time of the trajectory and the meteorological parameters.

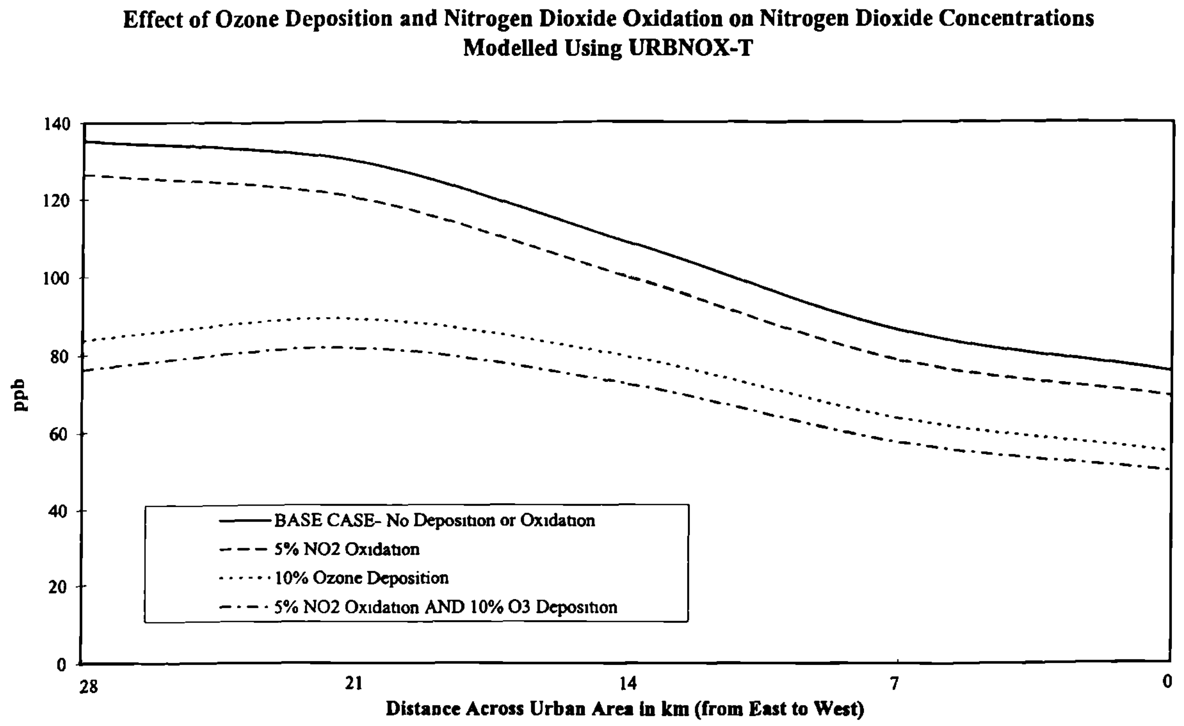
In developing URBNOX further, there are some processes that should be considered. Some nitrogen dioxide will be lost from further oxidation and this has not been considered within the model. Ozone is modelled in terms of its reaction with nitric oxide but there is no provision made for its production or its depletion. In the boundary layer, ozone may be lost by deposition or produced by photochemical reactions. Ozone production is unlikely to be very great in the lowest one hundred metres, where depletion is usually greater as a result of scavenging by nitric oxide. However, more ozone is produced in the upper boundary layer, where it is entrained downwards. In order to illustrate this, URBNOX-T was slightly modified to incorporate simple factors for ozone deposition and nitrogen dioxide depletion. A factor of 5% per hour was incorporated into the model to represent nitrogen dioxide oxidation. Ozone deposition is a complex subject in its own right and so it was decided to incorporate a simple factor as with the nitrogen dioxide oxidation factor. Based on data from Wesley (1989), an average percentage deposition of 10% per hour was calculated. The model was run using the same parameters as for the URBNOX-T base run. The runs carried out were as follows:

- incorporating a nitrogen dioxide depletion factor of 5 %;
- incorporating an ozone depletion factor of 10 %;
- incorporating both the nitrogen dioxide and ozone depletion factors.

The results are summarised in the graphs shown in Figure 5.20. It should be noted that ozone production was not included, although it is an important process. However, this cannot be done adequately without incorporating a complex chemical scheme and so it was decided not to include it within the scope of this study. This could be solved by coupling this model with a model that includes a full photochemical scheme, such as the London Plume Model.

It can be seen from the graph that the pattern of distribution is still the same. It is interesting to note that ozone deposition has more effect on levels of nitrogen dioxide than nitrogen dioxide oxidation. The results show that both nitrogen dioxide oxidation and ozone deposition do have some effect on the results from the model. Therefore, it may be advantageous to include these permanently in the model. The main problem with the ozone deposition is that are no clear deposition velocities for urban areas and so existing velocities for vegetation and soil have to be adapted. These may not be entirely accurate for urban areas.

Figure 5.20: Results of Ozone Deposition and Nitrogen Dioxide Oxidation Incorporation into URBNOX-T



5.8 Discussion

The aim of this chapter was to use URBNOX to investigate the behaviour of nitrogen dioxide, nitric oxide and ozone within an urban area, under summertime conditions. Both average and episodic conditions were investigated. Several points of interest were analysed. These included the vertical distribution of nitrogen dioxide, ozone and nitric oxide, and the contribution of upwind ozone to nitrogen dioxide formation in urban areas. The structure of URBNOX was also examined to see if it could reproduce levels as seen in various sets of measurements.

It was found that URBNOX is able to reasonably model the typical patterns of pollutant distribution and behaviour of both average summer days and summer episodes. There is however, some over and under prediction of actual numbers. A number of sensitivity studies were carried out, with particular emphasis on the role of background ozone in nitrogen dioxide formation. It has been shown that the upwind ozone does have a significant effect on subsequent levels of nitrogen dioxide produced. An ozone episode occurring upwind of the urban area can cause levels of nitrogen dioxide to peak upwards of 100 ppb, thus causing two breaches of air quality standards. However, meteorological conditions also have an important role in episode formation.

Emissions were also found to contribute to the formation of summer nitrogen dioxide episodes, as with winter episodes. Sensitivity studies also showed that for the risk of nitrogen dioxide episodes to be diminished significantly, emissions need to be reduced across the whole of the urban area, not just in selected areas.

The structure of URBNOX was also examined and it was adapted to run on a temporal, rather than a spatial scale. However, it was discovered that in order for it to run on its new scale, many of the parameters needed to be modified, thus requiring more detail in the input data, such as a diurnal emissions factor. It is recommended that URBNOX-T be adapted further, incorporating suitable diurnal emissions and diffusivities. The chemical behaviour should also be modified to include such important parameters as nitrogen dioxide and ozone deposition. These have not been carried out to date due to time constraints.

Overall, it can be seen that URBNOX provides a useful insight into the behaviour of episodes (both winter and summer). The incorporation of a diffusion profile demonstrates the vertical distribution of pollutants and how pollutants aloft can affect concentrations at ground level. This is an area that needs to be developed in order to understand pollutant processes enabling good long-term abatement strategies to be formed. URBNOX is a very simplistic model and has a tendency to over and underpredict some pollutant levels, but there is a lot of scope for development.

Chapter 6 - Conclusions and Recommendations For Further Research

6.1 Introduction

From the work carried out in this investigation of nitrogen dioxide in urban areas, a number of general conclusions can be drawn. Recommendations for further research are also made in this chapter. This thesis has addressed nitrogen dioxide concentrations in urban areas and the formation of episodes, leading to the exceedence of environmental standards. Nitrogen dioxide differs from other pollutants such as carbon monoxide and sulphur dioxide because it is mainly a secondary pollutant, formed by chemical reactions in the atmosphere. This can complicate abatement strategies, since the response to emissions reductions is not always straightforward.

At the time this study was undertaken, revision of air quality standards was being carried out. The National Air Quality Strategy was introduced in the United Kingdom, as explained in Chapter 1. However, no matter what standards are set, there is a requirement to comply with them. Compliance with these can be checked by carrying out air quality monitoring.

During the course of this investigation, conventional monitoring strategies consisted of using cheap and simple techniques, namely, diffusion tubes and more sophisticated continuous monitoring at a limited network of hot-spots and background sites. There are several national monitoring networks currently in existence which measure a broad range of pollutants. This study has benefited from the use of data from the London Air Quality Network (courtesy of SEIPH) and the NETCEN Archive (from the World Wide Web).

However, the requirements of the National Air Quality Strategy now make it necessary for local authorities to extend air quality management further, i.e. areas of poor air quality must be declared and a long-term abatement strategies developed. Modelling is often used to explore the effectiveness of potential abatement strategies.

This investigation also reviewed the current techniques for modelling and explored some new ideas to extend current ideas on dispersion and chemistry. In particular, the latter part of this study addressed the formation of nitrogen dioxide episodes. It is important to distinguish between the contributions of emissions over different distance scales.

6.2 General Conclusions

Two of the main components of air quality management are monitoring and modelling. The introduction of the National Air Quality Strategy has made it necessary for local authorities to carry out both in order to determine whether they have a problem with their air quality. It is therefore important for a local authority, working under a set budget, to get as accurate results as possible from any monitoring and modelling they carry out in order to create the most efficient abatement strategy possible.

This study concentrated on three main topics of investigation. These are discussed and concluded as follows.

6.2.1 Monitoring

Monitoring networks are usually set up with regard to investigating compliance with air quality standards. As a result, monitoring stations are usually set up at background sites and at 'hot spots' such as busy junctions. A common technique for analysing spatial variability is the use of diffusion tubes. These are cheap and simple to use, enabling large numbers to be deployed in a variety of places. However, it is not possible to use them to investigate episodes. Early on in the study this technique was used in a very dense manner. Tubes were set up at fifteen sites within the confines of the Imperial College campus in South Kensington. This demonstrated a fairly uniform concentration of nitrogen dioxide. Average concentrations at both roadside and intermediate sites were found to be no greater than 46 ppb. The amount of nitrogen dioxide formed is limited by the amount of ozone available to react with emissions of nitric oxide.

This, however, does not necessarily give a full picture about human exposure, since people spend different amounts of time in different places, especially indoors and inside vehicles. Fixed point monitoring will also give limited information about the effect of abatement strategies, since it does not distinguish between the contributions and interactions of different sources and pollutants. In addition, most monitoring networks only give information on pollutant levels at street level. A thorough understanding of the situation is needed to give confidence in planning an effective long-term strategy.

Other types of monitoring can be useful to aid the analysis of urban pollutant behaviour in more depth. Continuous monitoring allows the investigation of the diurnal behaviour of pollutants. It is also possible to chart the evolution of an episode using this method. However, this is an expensive and labour intensive method to use, so it is usual to choose a smaller number of sites. These tend to be more selective as a result. An idea explored in this thesis was to try and build a three-dimensional picture of nitrogen dioxide concentration. As an extension of what the local authorities are doing to monitor air quality, a recommendation is made to look at the air mass above the city. In this study, measurements were made along the vertical scale in order to examine the role of different physical and chemical processes and their influence on the interaction between air within the urban canopy and that just above it, i.e. the interaction between fresh emissions and imported air.

Continuous monitors were set up at 20 metres and 65 metres in the Queen's Tower on the Imperial College campus, in order to illustrate how this could characterise nitrogen dioxide and ozone above the canopy as well as within it. The results clearly showed substantial differences in concentrations of nitric oxide, nitrogen dioxide and ozone between the different heights. They also provided examples of how these differences arise because ozone is scavenged by nitric oxide from vehicle emissions. Conversely, nitric oxide levels are higher nearer ground level since this is close to the source of emission. Levels then decline with height and thus, distance away from the source. Nitrogen dioxide tends to decrease with height, with more of it being present near the source of its precursor, nitric oxide. However, the gradient is less marked as nitrogen dioxide is a secondary pollutant and there are added complexities due to photochemical dissociation. The distribution is also more complex because it is a consequence of both chemical formation and destruction, with a small contribution from primary emissions. This was explored subsequently in the modelling studies.

This part of the study was very labour intensive. As a result of this and the hostile environment within the Tower, it was only possible to obtain a limited amount of data. It was not possible to capture an episode which would have been useful for analysis. Data from a summer nitrogen dioxide episode in May 1995 was supplied by SEIPH in order for comparison with the modelling study. However, all this data was recorded at street level and it would have been useful to obtain some vertical data in order to get a picture of the air mass over the city.

6.2.2 Modelling

Modelling is an extremely useful way of predicting air quality levels and standard exceedences, in response to different abatement strategies. A review was undertaken to examine the different types of model available, ranging over different scales. These include models to investigate pollutant behaviour at the local scale in street canyons and at 'hot-spots' such as road junctions and large scale urban airshed models and box models which investigate air quality over a whole city or a region. It was recognised that neither category of model sufficiently examined the chemical and physical processes affecting pollutant concentration profiles in the lowest 100 to 200 metres of the boundary layer, which characterises the general interactions in the air directly over the city, just above the street canyon. As demonstrated by the Queen's Tower measurements, these concentration profiles can be complex when dealing with species that have a non-linear chemistry.

URBNOX was developed in an attempt to fill this gap and to examine episode conditions over an urban area such as London. It is a simple Lagrangian model, simulating a column of air moving across an urban area. The column of air extends several hundred metres upwards and so represents the distribution of pollutants in the lowest few hundred metres of the boundary layer. The model was also developed to try to incorporate both a dispersion scheme along with a simple chemical scheme to model nitrogen dioxide. The intention was to gain a better conceptual insight into nitrogen dioxide episode conditions, both in winter and summer. It was assumed that the air parcel was advecting across London. Both regional and London inventories were used, which highlighted some interesting differences between the two. URBNOX was mainly used for investigating the formation of nitrogen dioxide episodes, under both winter and summer conditions. These conclusions are discussed in the next section.

6.2.3 Winter and Summer Episodes

Winter episodes coincide with inversion conditions, i.e. with low diffusivities and wind speeds. The model confirmed previous simpler studies with box models, indicating the importance of the quadratic thermal oxidation reaction ($2NO + O_2 \rightarrow 2NO_2$), as concentrations of NO_x build up. In practice, the significant amount of nitrogen dioxide produced depends on concentrations of NO_x emitted, around the order of 1000 ppb. This can only occur when vertical diffusion is very restricted. It is also evident, due to the quadratic nature of the reaction, that a relatively modest reduction in NO_x emissions can have a significant effect in reducing exceedences of air quality standards. Hence, abatement strategies could centre on the reduction of emissions to reduce accumulation. This could take the form of encouraging people to leave their cars at home and use alternative forms of heating.

Summer episodes, on the other hand, were found to be more complex and linked to regional ozone. Although, meteorological conditions such as low wind speed encourage the formation of high levels of nitrogen dioxide, due to poor dispersion, summer episodes do not simply result from an accumulation of emissions. Sensitivity studies showed that the quantity of ozone upwind of an urban area had influences over the amount of nitrogen dioxide formed. URBNOX was also used to demonstrate how an ozone episode, formed by emissions upwind of London, could cause a nitrogen dioxide episode within the city. However, it was also shown that the diurnal behaviour of nitrogen dioxide may cause its pattern of distribution to differ from that of ozone. As a result of photodissociation, concentrations of nitrogen dioxide may peak earlier in the day. URBNOX proved to be a useful tool in exploring such factors affecting peak nitrogen dioxide concentrations.

The non-linear chemistry and interactions with other pollutants makes devising an abatement strategy more complex. It will require an integrated approach to local emission control and larger scale national and international commitments.

6.3 Recommendations for Further Research

During the course of this study, various avenues have been opened up for development and investigation. Due to limitations of both time and resources, a number of them were not pursued further. The aim of this section is make suggestions that enhance this work or provide opportunities for further study.

Although URBNOX reproduces distribution of nitrogen dioxide and ozone within an urban area quite acceptably, it is acknowledged that a number of simplifications were made regarding the parameters and the structure of the model. Ideally, further consideration should be given to these. For example, one average wind speed is used for the entire column. However, as discussed previously, the wind speed changes with height and is generally lower in the lower layers of the boundary layer. This may have implications for the accuracy of pollutant levels in the upper layers of the column. In addition, the model could be developed to include the formation of an internal boundary layer over the urban area (Smith, pers. comm.) in order to more accurately represent the state of the atmosphere over an urban area and determine whether it has any effect on the behaviour of nitrogen dioxide.

The main criticism of the model is the very simple chemical scheme. Although it does produce reasonable results and does give a good indication of pollutant behaviour over an urban area, it does not make any provision for photochemical ozone production and this could affect the overall results of nitric oxide, ozone and nitrogen dioxide. The inclusion of a comprehensive photochemical scheme is a very complex task, running into several hundred reactions. One way of solving this would be to use the London Plume Model to calculate ozone production because it already set up with a very detailed photochemical scheme. The results from this would then be entered into URBNOX in a simplified manner and the model run as before. This would ensure that ozone production over the urban area is more accurately represented and the use of URBNOX will ensure more accurate dispersion in the lower few hundred metres of the boundary layer.

It is also recognised that the time version of URBNOX (URBNOX-T) needs further development, in terms of its parameters, in order to rectify the overprediction of nitrogen dioxide. In particular, the diurnal representation of some of the parameters, in particular the emissions and the diffusivities, needs to be investigated further. It also needs to be structured in order to make it more versatile in the way that it currently runs. A limitation of this modelling is the uncertainties concerning NO_x emissions and their spatial and temporal resolution. For this type of modelling, more than an annual average inventory is needed. Detailed diurnal patterns of emissions could be useful. This is one of the reasons for not pursuing this version of URBNOX further, but rather leaving it as a simple conceptual model.

It was not possible during the time available to incorporate the ideas in URBNOX into a more comprehensive urban model. Again, as explained above, URBNOX could be linked to the London Plume Model to combine detailed diffusion profiles with detailed photochemistry. However, this still does not allow for full, three dimensional windfields over an urban area. Consideration should also be given to how higher vertical resolution could be built into Eulerian airshed models. At the other extreme, research could be carried out to try and link URBNOX to smaller scale models, such as one single road in order to determine the influence it would have on the surrounding air quality. Ideally, in urban situations, models on different scales need to be nested in order to build up a complete picture of air quality.

Finally, a recommendation is made to undertake monitoring of the air mass overlying the city as well as at street level. In the case of secondary pollutants, this would aid the determination of the quantity of imported pollutants imported to an urban area. It would also characterise events occurring in the air mass overlying the city and aid the understanding of chemical processes. It would be especially useful to set up monitoring stations at a number of points to include results from within the street canyon, just above the street canyon and high above the street canyon, in order to produce detailed pollutant profiles. There are a number of high buildings that could be suitable, among which is the B.T. Tower. It would also be useful to have a number of monitoring stations situated just outside London in order to determine the levels of pollutants, especially ozone, entering the urban area. This could be considered alongside the integration of the London Air Quality Network with the national network.

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Appendix

A.1 URBNOX- Model Characteristics

URBNOX was based on a vertical diffusion model (TERN) which investigates the transport and dispersion of ammonia (ApSimon *et al,* 1994). It was written using FORTRAN-77 and compiled using the Prospero compiler. It is approximately 230 lines long. Using a standard 486 PC, the model has a run time of approximately 10 minutes. The model was verified with a line by line inspection and was tested against the R-91 Gaussian model using a comparable diffusion profile.

The model's inputs consist of DATA statements incorporated within the code and data entered via the keyboard once the model is set running. The parameters entered via the keyboard can be summarised as follows:

- Wind speed;
- Background concentrations of ozone, nitric oxide and nitrogen dioxide;
- Mixing height;
- Dissociation rate of nitrogen dioxide;
- Maximum Diffusivity (K_Z) value.

The inputs included within the code as DATA statements are:

- NO_x Emissions;
- Diffusion profile;
- Fraction of the NO_x emissions as nitrogen dioxide.

The output consists of concentrations of ozone, nitrogen dioxide and nitric oxide within the vertical air column every 5km across the city until the maximum distance of 40km. The output is written to an output file but the concentrations of ozone, nitrogen dioxide and nitric oxide for the lowest layer of the air column every 5km are also written to the screen as the model runs.

A flow chart of the structure of the model can be seen below in Figure A.1:

Figure A.1: URBNOX Flow Chart