MONITORING OF AIRBORNE PARTICULATE MASS AND NUMBER CONCENTRATIONS IN THE UK ATMOSPHERE

by

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ABSTRACT

An investigation of physical and chemical characteristics of atmospheric aerosols was conducted at sites in the South East of England in collaboration with Stanger Science and Environment, and in Birmingham as part of the PUMA collaborative programme. Data analyses were carried out on measurements by SMPS (particle numbers and size distribution in the range 11-450 nm) and TEOM ($PM_{2.5}$ and PM_{10}) at urban roadside, urban background, and rural sites. Chemical measurements were also made with Partisol and Dichotomous instruments at a rural and the Birmingham site.

PM_{10} was generally dominated by fine particles at all sites, but both fine and coarse particle concentrations were elevated at the roadside due to both exhaust emissions and re-suspension of dusts, influenced by both wind speeds and human activities. Whilst strong correlations were always observed between PM_{10} and $PM_{2.5}$ for all sites, the relationships between PM_{10}, $PM_{2.5}$ and particle numbers varied considerably with sites and seasons. The particle number size distribution was clearly distinct between urban and rural sites, indicating small number mode diameters at urban road (24.6-32.8 nm), slightly larger at urban background (26.4-50.5 nm) and great variations at the rural site (15-104 nm), where the formation of nuclei particles was identified. Extremely high nocturnal nitrate concentrations were observed at the rural site when huge differences in PM_{10} between TEOM and Partisol occurred.

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CHAPTER 1

INTRODUCTION

1.1. Background

The quality of everyday human life is closely related to the quality of air we breathe. Back in December 1952, high concentrations of smoke and SO_2 caused 4000 additional premature deaths in London during an air pollution episode. Black smoke concentrations are falling continuously due to the phase-out of coal combustion although another source of smoke has been noted from motor traffic, which arises particularly from the diesel vehicles including vans, taxis, light and heavy goods vehicles, buses and coaches (QUARG, 1993a&b).

In December 1991, another air pollution episode, with characteristic stagnant weather conditions occurred in London, and led an increase of about 10% in mortality compared with the same period in earlier years (Anderson et al., 1995). The concentrations of traffic-derived pollutants such as carbon monoxide, benzene and nitrogen dioxide reached unprecedented levels (Bower et al., 1994; Anderson et al, 1995). Black smoke concentrations were also elevated but the levels were about a factor of 20 lower than those recorded during the December 1952 episode. The Quality of Urban Air Review Group (QUARG) was established as part of the air pollution control strategy. Its first and second reports were produced in 1993, concluding that air pollution from motor vehicle traffic has become increasingly important in most cities and towns. The major vehicle emissions include carbon monoxide, oxides of nitrogen, hydrocarbons, black smoke and airborne particulate matter (PM).

Epidemiological studies, mostly carried out in the United States, have shown a clear link between elevated particulate mass concentrations and increased mortality and morbidity from all causes (Dockery et al., 1993; Pope et al., 1995; Vedal, 1997). A UK paper (Anderson et al, 1996) concluded "air pollution due to airborne particles and ozone may be associated with increased daily mortality in London." The Department of Health Committee on the Medical Effects of Air Pollution recommended that the demonstrated associations between daily concentrations of particle mass and the health effects are causal (DoH, 1995). PM_{10} emissions are thought to be responsible for 8,100 deaths annually in the UK (DETR, 1999). The UK Expert Panel on Air Quality Standards (EPAQS) recommended a standard - an upper limit PM_{10} (particles less than 10 micron metre in diameter) concentration of 50 $\mu g\ m^{-3}$ as a 24 hour rolling mean (EPAQS, 1995). At the present time, there are a large number of exceedences of the standard at urban locations across the UK.

To reduce the concentrations of particulate matter, a great deal of knowledge is required on its sources, behaviour, chemical and physical properties and factors influencing their concentrations, such as meteorological influence. The third report of QUARG (1996) reviewed some detailed knowledge of the particle sources, concentration levels and physical and chemical characterisations in the UK urban air. The national air quality monitoring network for urban areas was started in 1992 by the DETR. This network, designated the Automatic Urban Network (AUN), comprises of 11 former Statutory Urban Monitoring sites and 16 Enhanced Urban Network (EUN) sites. It was set up to monitor the levels of pollution to the public at sites representing the urban background concentrations located in the central areas of cities. The AUN sites are equipped to monitor five pollutants including oxides of nitrogen (NOx), sulphur dioxide (SO_2), carbon monoxide (CO), ozone (O_3) and particulate PM_{10}. The data from the AUN shows that the mean concentrations of PM_{10} are within the range 20-30 micrograms per cubic metre (QUARG, 1996). There is less rural PM_{10} data, which appears to be in the range 10-15 micrograms per cubic metre, reflecting mainly secondary particles. The numbers of sites that monitor air quality automatically in the UK have increased rapidly over the last ten years. Until December 2000, there have been 112 automatic sites in operation in the UK, but particulate PM_{10} measurements are made only at 52 urban and 3 rural sites.

This project was funded in 1997 by the Department of the Environment, Transport and the Regions (DETR), the former Department of Environment (DoE), and the present Department for Environment, Food and Rural Affairs (DEFRA). It was part of their Air Quality Research Programme to monitor airborne particulate mass, numbers and size distributions in the UK atmosphere. It is a collaborative project between the University of Birmingham and Stanger Science and Environment (SSE). The measurement of $PM_{2.5}$ and PM_{10} mass, particle numbers and particle size distributions was set up at two urban and two rural sites across the south east of England. The site and measurement details are illustrated in Chapter 2.

A key priority of the project was to analyse and interpret a considerable volume of data generated from the four selected sites during a two-year and seven-month period of continuous monitoring. The data generated within this study will be important for a better understanding of the nature of both particulate mass and numbers in different backgrounds in the UK atmosphere. It will be also a potentially extremely valuable resource for use in studies of the effects of airborne particulate matter on human health, particularly in terms of size-fractionated particle number data which has hitherto not been widely available. Therefore it will aid the government and any other key decision makers in the UK to set, monitor and enforce air quality policy, as well as those engaged in research into the medical aspects of particulate matter. Additional data from Birmingham, Hodge Hill, a site operated by Birmingham City Council, and the two URGENT (Urban Regeneration and the Environment) PUMA (Pollution of the Urban Midlands Atmosphere) campaigns within Birmingham University Campus, will be valuable contribution to the project. The gaseous pollutant data generated by the Automatic Urban and Rural Network (AURN) is also accessible through the air quality archive, which allows an overall assessment.

1.2. Health Effects

As a major air pollutant, airborne particles are thought to be related to human health, with effects including premature mortality, medical referrals, allergic reactions and lung dysfunction. The biological effects of inhaled particles are determined by their physical and chemical properties, by the sites of deposition, and by the mechanisms by which they injure the lung.

The aerodynamic size and associated composition of particles determines their behaviour in the respiratory system (i.e., how far the particles are able to penetrate, where particles are deposited, and how effective the body's clearance mechanisms are in removing them). According to different penetrations into the respiratory system, the International Standards Association (ISO, 1994) defined different particle-size conventions for the measurement of particulate matter. "Inhalable" particles are those which can enter the nose and mouth, and include particles up to 100 μm in aerodynamic diameter. "Thoracic" particles are those which can penetrate the respiratory system beyond the larynx and have a 50 % cut-off at 10 μm. The "respirable" particles include those particles, which can penetrate into the alveolar regions of the lungs and have a median cut-off at 4 μm. The "high risk" respirable convention is a definition of the respirable fraction for sick and children, which has a median cut-off at 2.5 μm corresponding to $PM_{2.5}$ in UK.

Many epidemiological studies have found a positive correlation between PM_{10} mass and respiratory illnesses and cardiovascular diseases (Braun et al., 1992; Dockery and Pope, 1994; Abbey et al., 1999). Other studies suggest that it is the finer particles, which have the greatest impact on health (Schwartz et al., 1996; Wilson and Suh, 1997; Cifuentes et al., 2000), which is supported by the fact that the human respiratory system retains the $PM_{2.5}$ fraction most strongly. Hoek et al. (2000) found that species within the finer particles (sulphate, nitrate and black smoke) were more consistently associated with total mortality (mostly death by pneumonia) than was PM_{10}. However, no consistent differences in relative risk were found between urban and rural areas. A study in London from 1992 to 1994 has identified the associations between various air pollutants and daily mortality. The results show that PM_{10} has the greatest effect on respiratory mortality (4% increase in deaths of all ages for a 10^{th}-90^{th}-percentile increment), while black smoke (fine particles of diesel origin) is associated with cardiovascular deaths (Bremner et al., 1999).

It will be cost-effective if $PM_{2.5}$ is used as a measure on the health effect since a smaller network of measurement is required for these more spatially uniform fine particles. Nevertheless, other studies have found that higher concentrations of coarse particles ($PM_{2.5-10}$) can also increase overall mortality rates (Castillejos et al., 2000). Miguel et al. (1999) suggests that re-suspended road dusts contain materials, which can potentially initiate allergic reaction.

Other researchers suggest that it is the ultrafine particles (those with a diameter of less than 0.1 μm) which affect human health (Seaton et al., 1995). The problem is the body's defensive reaction to particles diffusing onto the surface of the lungs. The immune system responds only to individual particles and not the overall mass concentration, therefore particle number and possibly chemical composition may be of great importance. Ultrafine titanium dioxide aerosol has been shown to have an adverse effect on the respiratory system of rats only at sizes smaller than 100 nm (Seaton, 1995). Research on asthmatic adults in Germany (Air Health, 1996) has found that their symptoms were provoked when they were exposed not to mass concentrations, but to increased particle numbers. Most recent studies on both rodents and humans demonstrate that ultrafine particles have a greater effect than larger particles (Oberdörster, 2001; Donaldson et al., 2000). However, another study on asthma patients performed in Germany and Finland (Wichmann and Peters, 2000) suggests that both fine and ultrafine particles have health effects which might be independent of each other.

The composition of airborne particles seems to be less important according to the previous research although it is an excellent guide to the source apportionment and hence an essential part for any control strategy. The Committee on the Medical Effects of Air Pollution (COMEAP, 1995) suggests that, according to classical mechanisms of toxicology, no single chemical component of the particles is responsible for the health effects observed. On the other hand, some studies show that the chemical composition of the aerosol may have health effects. Acidic particles may be irritant, PAHs (polycyclic aromatic hydrocarbons) potentially carcinogenic, and the trace metals delivered to the lungs on fine particles may catalyse production of tissue-damaging oxidants (Ghio et al., 1996; Dreher et al., 1997). Species (sulphate, nitrate and black smoke) associated with the finer particles have been found to be associated with total mortality (Hoek et al., 2000).

Since the mechanisms by which airborne particles cause adverse effects on human health are not well established, it may be assumed that some chemical or physical property of the particles, or a combination of the two, is responsible for the impacts on health. There are many suggestions as to which properties are important, but all are uncertain. It is useful to study a wider range of airborne particles of different physical and chemical species from both toxicological and epidemiological aspects. A large data set is therefore needed to explore the relative importance of particle variables or their different associations with human health. The long-term measurement of both particle mass and numbers, as well as the short-term chemical measurements from this project, can make a great contribution to studies on the health effects of particulate matter.

1.3. Control and Regulation of Emissions

The UK emission inventory for particulate matter accounts only for primary particulate matter (QUARG, 1996). The current emission inventory of sources of primary PM_{10} in the UK has shown that road transport is a major source of PM_{10} (25%) with other significant contributions from non-combustion processes (24%), industrial combustion plants and processes (17%), commercial and residential (16%) and power generation (15%). Emissions from vehicles account for about one fourth of PM_{10} nationally and 86 % of PM_{10} in the London area, highlighting the major difference observed in respect of traffic-generated pollutants between the national emission inventory and the emissions in urban areas. The primary $PM_{2.5}$, PM_1 and $PM_{0.1}$ emissions inventories have shown that road transport has become an increasingly important contributor of finer particles. There are significant uncertainties in the PM inventories, which may arise from use of emission factors, which are based on only a small number of measurements and assumed to be representative of the source category as a whole. Several important sources, which have not yet been considered, are re-suspension of dusts from road surfaces due to passage of vehicles, agricultural emissions of soil-derived and biological debris during ploughing and harvesting, and other biological sources, either natural or anthropogenic. Furthermore, the inventories only considered annual emission rates, taking no account of either seasonality or episodic events.

Road transport is the largest single source of the main air pollutants especially in urban areas and they are also the only source, which continues to grow. Innovation on cars has been undertaken in the past such as the fitting of catalytic converters on petrol cars, but this gain may in the longer term be offset by increasing traffic (Read et al., 1994). Another concern is the consequences of the more widespread use of diesel vehicles which have greater emissions of fine particles (QUARG, 1993b) and may become the major utility of transport. Previous work, carried out in Birmingham, has identified three main sources of variance using Principal Component Analysis (PCA). These are the primary emissions of vehicular pollutants, secondary pollutants and wind blown dust component including de-icing salt (Harrison et al., 1997b). Winter PM_{10} episodes include mostly $PM_{2.5}$ accompanied by NOx from traffic. However, coarse particles composed mainly of road dust are sometimes significant for elevated PM_{10} in summer, and are especially difficult to estimate (Deacon et al., 1997).

Secondary aerosol is not included in the UK emission inventory due to the uncertainty of its formation in the atmosphere. However its contribution to particulate matter is not negligible especially in summer time. Model predictions imply that about 9 $\mu g / m^3$ of PM_{10} on average are present as secondary particles in the Midlands, which represents about a third of the annual mean PM_{10} in Birmingham (QUARG, 1996). The total secondary aerosol (ammonium sulphate and ammonium nitrate) concentrations at rural sites were mapped using 3-year data from the European Measurement and Evaluation Programme (EMEP), a monitoring network for particulate sulphate in rural areas across Europe (Schaug et al., 1994). Estimations were made during the calculation of the nitrate concentrations due to lack of data (only two monitoring sites for nitrate at the time) and a scaled factor (Harrison and Allen, 1990) was used. The highest secondary concentrations were found in East Anglia, with a trend of decreasing concentrations towards the north and west of the UK. This was interpreted as: first, the prevailing south-westerly winds gave higher concentrations in the east; second, secondary aerosols were transported across from the European continent during long range transport episodes, which had the greatest influence on eastern parts of the UK (QUARG, 1996). Both sulphate and nitrate concentrations are affected by season. The highest sulphate concentrations tend to be in the summer and spring months, whilst nitrate levels are the highest during winter (Schaug et al., 1994). In this project, a Partisol Plus FRM 16 sampler (described in chapter 2) was used at the rural Harwell site during periods with varied air masses allowing secondary aerosols to be analysed.

In order to control airborne particulate emissions, the Royal Commission on Environmental Pollution (RCEP) produced a report on transport and the environment which called for a shift in emphasis away from road transport and setting of higher standards to reduce emissions (RCEP, 1994). The EPAQS published a proposed standard for PM_{10} in November 1995, which set an upper limit concentration of 50 μg / m^3 as a 24 hour rolling mean. In response, the Government produced the Air Quality Strategy (DoE, 1996) and in compliance with the EPAQS standard, a target of 99.5 percentile by 2005 was set, but was later changed to 99 percentile in the 1997 National Air Quality Strategy. To achieve the target in compliance with the standard, QUARG (1996) investigated the PM_{10} emissions and suggested that emissions must fall by around 60 % for the urban sites. This PM_{10} standard is now replaced with an objective based on that in the EU Air Quality Framework Directive (Table 1.1).

European air quality limit and guide values for SO_2 and suspended particles (using the black smoke procedure) were issued in 1980 (CEC, 1980). Monitoring of PM_{10} is required under the EU Framework directive on Air Quality Assessment and Management 96/62/EEC (CEC, 1996). The priority pollutants include SO_2, NO_x, particulate matter and lead, with O_3, benzene, CO, polycyclic aromatic hydrocarbons (PAH) and some trace metals to be addressed at a later stage. The current limit values for PM_{10} are specified by the EU Council Directive 1999/30/EEC (CEC, 1999) (Table 1.1). The stage 2 limit values are provisional and will be reviewed in 2003.

Table 1.1. EU limit values for atmospheric particulate matter

	Averaging period	Limit value	Application of limit value	Attainment date
PM_{10} Stage 1	24 hrs	50	Exceeded <35 times per year	1/1/05
PM_{10} Stage 1	Annual	40	Annual mean	1/1/05
PM_{10} Stage 2	24 hrs	50	Exceeded <7 times per year	1/1/10
PM_{10} Stage 2	Annual	20	Annual mean	1/1/10

In July 1997, the United States EPA announced the new National Ambient Air Quality Standards (NAAQS) for both PM_{10} and $PM_{2.5}$. These standards include annual and 24-hour average standards of 50 $\mu g\ m^{-3}$ and 150 $\mu g\ m^{-3}$ for PM_{10}, and annual and 24-hour average standards of 15 $\mu g\ m^{-3}$ and 65 $\mu g\ m^{-3}$ for $PM_{2.5}$ (USEPA, 1997). As in the UK, the revised 24-hour PM_{10} standard has to be based on the 99th percentile at single or multiple monitoring stations within an area. The new $PM_{2.5}$ annual standard form requires that the 3-year average of the annual arithmetic means should remain below 15 $\mu g\ m^{-3}$. The form of the 24-hour standard is based on the 98th percentile of the $PM_{2.5}$ concentrations averaged over 3 years. At present, there is no legislation towards the ultrafine particles although this is becoming a hotspot area of research due to its health effects suggested from epidemiological studies.

1.4. Physical Properties of Airborne Particles and Measurements

Airborne particulate matter represents a broad class of chemically and physically diverse substances, which consists of solid and liquid particles suspended in the air. It can be divided into primary particles emitted directly from sources such as vehicle exhaust and secondary particles formed in the atmosphere from condensation of vapours or by chemical reaction processes (QUARG, 1993a). Its size covers a wide range from a few nanometres to tens of micrometres, however only particles smaller than 10 micrometres in diameter have an adverse effect on human health. According to the current measurements, particulate matter can be classified as PM_{10} (50% cut-off aerodynamic diameter of 10 μm), $PM_{2.5}$ (fine particles, 50% cut-off diameter of 2.5μm), coarse particles ($PM_{2.5-10}$), $PM_{1.0}$ (50% cut-off diameter of 1.0μm) and ultrafine particles (diameter less than 0.1μm). Due to the mechanism of formation, particles are also classified roughly into three size modes, i.e., nucleation mode (0.01-0.1 μm), accumulation mode (0.1-2μm) and coarse mode (>2μm) (Whitby et al., 1975; Willeke and Whitby, 1975). Newly formed nucleation mode particles are very small, about 1-2 nm in diameter, but rapid growth occurs to form larger particles by coagulation and condensation. The nucleation mode particles show a number mode of 20-30 nm in diameter. Particles in the accumulation mode will not grow further significantly through coagulation due to low number concentration, and therefore possess a longer atmospheric life time of several days and travel over very long distances within the atmosphere. The coarse mode particles have rather shorter atmospheric lifetime, especially particles larger than 10 μm.

Airborne particles are produced from a variety of sources, including incomplete combustion processes, industry and construction, as well as naturally as a result of re-suspension of surface soil material, sea spray, volcanic activity, bio-mass burning, organic debris and reactions leading to condensation of volatile precursors. Combustion emissions include directly generated carbonaceous material, trace elements, nitrates and sulphates, while hydrocarbons, SO_2 and NO_x released from natural and anthropogenic sources are oxidised within the atmosphere forming products which may either nucleate new particles, or be removed to the surfaces of existing aerosols.

Fine and coarse particles possess distinct as well as similar mechanisms of formation, with a variable degree of source overlap. The former are often directly emitted as primary particles from combustion sources or formed by condensation of gaseous material through gas-particle conversion processes, or by coagulation and adsorption processes (secondary particles). Fine particles are often related to long-range transport, while large particles may be produced locally by mechanical attrition, disintegration processes (sea spray), industrial activities or re-suspension of surface material, particularly during drier conditions. In the UK urban areas, fine particles are dominated by vehicle exhaust emissions from road traffic and secondary particles, whereas coarse particles are less clearly defined, but major sources are re-suspended road dusts, windblown soils and sea spray particles (QUARG, 1996; Harrison et al., 1997b). In the US, some of the properties of these particles are summarised in Table 1.2.

Table 1.2. Properties of fine and coarse mode particles (Source: USEPA, 1995a)

	Fine Mode	Coarse Mode
Formed from	Gases	Large solids/droplets
Formed by	Chemical reaction; nucleation; condensation; coagulation; evaporation of fog and cloud droplets in which gases have dissolved and reacted.	Mechanical disruption (e.g. crushing, grinding, abrasion of surfaces); evaporation of sprays; suspension of dusts.
Composed of	Sulphate, $SO_4^{=}$; nitrate NO_3^-; ammonium, NH_4^+; hydrogen ion, H^+; elemental carbon; organic compounds (e.g., PAHs); metals (e.g. Pb, Cd, V, Ni, Cu, Zn, Mn, Fe); particle-bound water.	Resuspended dusts (e.g., soil dusts, street dust); coal and oil fly ash, metal oxides of crustal elements (Si, Al, Ti, Fe); $CaCO_3$, NaCl, sea salt; pollen, mould spores; plant/animal fragments; tire wear debris
Solubility	Largely soluble, hygroscopic and deliquescent	Largely insoluble and non-hygroscopic, except sea salt
Sources	Combustion of coal, oil, gasoline, diesel, wood; atmospheric transformation products of NO_x, SO_2 and organic compounds including biogenic species (e.g. terpenes) high temperature processes, smelters, steel mills, etc.	Resuspension of industrial dust and soil tracked onto roads; suspension from disturbed soil (e.g. farming, mining, unpaved roads); biological sources; construction and demolition; coal and oil combustion; ocean spray
Lifetimes	Days to weeks	Minutes to hours
Transport	100s to 1000s of kilometres	< 1 to 10s of kilometres

Particulate mass concentrations vary greatly from place to place and from time to time due to a wide diversity of geographical and meteorological conditions, as well as a variety of pollution sources. Measurements were made for PM_{10} and $PM_{2.5}$ from 1994 to 1996 in California covering 15 air basins (Dolislager and Motallebi, 1999). The maximum 24-hr PM_{10} concentration over the three years ranged from as low as 26 μg m^{-3} at Lake County up to as high as 524 μg m^{-3} at Great Basin Valleys, where dust storms dominated the very high PM concentrations in this desert environment. Salton Sea, South Coast and San Joaquin Valley showed the highest percent of sampling days when concentrations exceeded 50 μg m^{-3}, which were 72, 63 and 52 respectively. $PM_{2.5}$ concentrations also showed spatial variations although with a limited data set. Another study during the summers of 1992 and 1993 at eight sites within Metropolitan Philadelphia showed that PM_{10} and $PM_{2.5}$ concentrations were relatively uniform across Philadelphia due to the fact that PM_{10} was composed of mostly $PM_{2.5}$ approximately 75% (Suggs and Burton, 1983; Burton et al., 1996). Also sulphate and sulphate related species in Philadelphia were responsible for the variability in fine particles comprising approximately 65%, and as a result, in PM_{10} comprising about 50% (Spengler et al., 1990). Coarse particle concentrations comprising only one fourth of the PM_{10} were found to vary with site, and its variation was related to population density.

PM_{10} and black smoke (BS) measurements were made for two months in the winter of 1993/1994 at 28 sites (both urban and rural) across ten countries in Europe (Hoek et al., 1997). Greater differences were found in particle concentrations between countries than between urban and rural locations within countries, although urban PM_{10} was on average 22 % higher than at associated rural locations. Poor correlation was obtained between PM_{10} in western and central European countries, and either Scandinavia or southern Europe. The daily average mean PM_{10} and BS concentrations across countries ranged from 11 μg m^{-3} in Oslo to 99 μg m^{-3} in Athens and from 4 μg m^{-3} in Malmö to 109 μg m^{-3} in Athens respectively. Low particle concentrations were observed at the Scandinavian locations Umea, Malmö, Oslo and Kuopio, due to fewer emission sources in the absence of large industrial source areas and low population density. The highest particle concentrations appeared in the urban area of Athens due to industrial sources and, especially, diesel powered motorized traffic. Particle concentrations were generally higher at the urban sites than the rural sites, but at most cities the differences were below 11 μg m^{-3} for PM_{10} and 20 μg m^{-3} for BS, except in Teplice and Athens, where large differences were found (especially BS) probably due to geographical location. In Athens a mountain ridge separates the urban from the rural area while in Teplice the distance between the two sites exceeds 250 km.

Janssen et al. (1997) compared busy road and background sites in two cities in the Netherlands. Measurements of PM_{10}, $PM_{2.5}$, black smoke (BS) and elemental contents showed those differences between the street and background locations were due to traffic. Both PM_{10} and $PM_{2.5}$ were on average 1.3 times higher at the street site than the background site. A larger ratio of 2.6 was found for BS, which was highly correlated with elemental carbon/black carbon generated mainly from diesel exhausts (Edwards et al., 1983; Erdman et al., 1993; Ulrich and Israel, 1992). For the elemental species measured only Fe, Si and Cu showed a larger difference between road and background sites with 2-7 times higher at the road site than the background site. These differences were attributed to re-suspension of road dust. The contribution of $PM_{2.5}$ to PM_{10} was found to be 55 % on average in the Netherlands (Van Der Zee et al., 1998). Relative differences in concentrations between urban and non-urban areas were lowest during passage of polluted easterly air masses, and highest when air masses had a maritime origin.

Available data on PM_{10} concentrations in the UK is mainly obtained from the Automatic Urban and Rural Network (AURN), containing mostly urban sites and only a few rural sites. Deacon et al (1997) summarised the yearly mean and maximum PM_{10} concentrations from the 16 AUN urban stations between 1993 and 1995, and the exceedences of the EPAQS standard from 13 sites between 1992 and 1994. These data indicated that there were exceedences of the 50 $\mu g\ m^{-3}$ 24h rolling mean PM_{10} standard at all sites, showing as low as 3 days exceedence in Edinburgh during 1994, and as high as up to 91 days in Cardiff in the same year. The highest daily mean PM_{10} concentrations were found in Belfast (248 $\mu g\ m^{-3}$) in 1992 and the lowest values were found again in Edinburgh (62 $\mu g\ m^{-3}$) in 1994. The data also indicated that three major sources contribute to PM_{10} at UK urban sites, i.e., vehicle exhaust emissions, secondary sulphates and nitrates, and resuspended surface dusts and soils. Studies conducted in Birmingham from October 1994 to October 1995 again showed the three major sources dominating the PM_{10} concentrations as indicated from the study at the AUN sites (Harrison et al., 1997b).

Particle number concentration is dominated by particles smaller than 0.1 μm (ultrafine particles), and the mass concentration is dominated by particles in the size range 0.1-0.5 μm

(Whitby, 1978; QUARG, 1996; Tuch et al., 1997). On the other hand, ultrafine particles contribute very little to the overall particle mass concentration and so do particles larger than 0.5 μm to the total particle number concentration. There are two major sources of particle numbers. The first is primary emission from high temperature sources such as primary combustion-generated particles. The second is homogeneous nucleation of particles within the atmosphere from processes such as chemical conversion of sulphur dioxide to sulphate (QUARG, 1996). There are very limited data about particle number and size distribution measurement in the literature and even less data available on a long-term basis. The majority of PM measurements based upon mass concentration can not represent the variation of particle numbers.

During winter 1991/92 particle number and mass concentrations were measured in the city of Erfurt in Eastern Germany for size range 0.01-0.5 μm. Poor correlation was found between particle number and mass concentrations implying that both particle mass and numbers in at least the two size ranges 0.01-0.1 and 0.1-0.5 μm are required to be monitored when considering the health effects (Tuch et al., 1997).

Measurements were made from 30 November 1996 to 13 March 1997 at urban background sites in three European cities, including total particle number concentration in the range of 0.01-0.5 μm, number concentrations of ultrafine (0.01-0.1 μm) and accumulation (0.1-0.5) particles, as well as mass concentration of $PM_{2.5}$ (Ruuskanen et al., 2001). The mean ultrafine particle number concentrations were very similar from the three cities, which were 1.62×10^4, 1.77×10^4 and 1.83×10^4 particles cm^{-3} in Helsinki, Erfurt and Alkmaar respectively. However the mass concentrations of $PM_{2.5}$ were significantly different, showing a mean value of 9.42 μg m^{-3} in Helsinki, 41.9 μg m^{-3} in Erfurt and 27.0 μg m^{-3} in Alkmaar. Significant differences were also found in the concentrations of ultrafine particles and the total particle numbers between weekdays and weekends in all cities, which was similar to that found in Pasadena near Los Angeles, USA (Hughes et al., 1998). Poor correlation was observed between the $PM_{2.5}$ mass and the total as well as the ultrafine particle number concentrations consistent with the results from the study of Tuch et al (1997).

Spatial variation of particle number concentrations was investigated in Helsinki City, Finland (Buzorius et al., 1999). 10-minute average concentration varied from 10^3 to 10^5 particles cm^{-3} at different site, and there was a decrease in the concentration as distance of the measuring point from street increased. Diurnal variation on weekdays and weekends was quite different due to human activities. Li et al (1993) also identified traffic as a pollution source on particle number concentrations, which were as low as 1.0 x 10^4 particles cm^{-3} in the absence of traffic activity and as high as 4.35 x 10^4 cm^{-3} when an automobile or motor cycle passed the sampling location. The average NMD was found to be about 0.054 μm.

The most intensive measurement using a scanning mobility particle sizer (SMPS) started in 1995 in Brisbane City Australia. The average number median diameters (NMDs) were close to 40 nm in the size of 0.016-0.626 μm (Morawska et al., 1998), which was consistent with the result obtained from the automobile exhaust source spectra (Morawska et al., 1996). The average number concentration was 7.4 x 10^3 particles cm^{-3}. Relatively good correlation was found between the particle number concentrations and gaseous pollutants CO (R^2 =0.45) and NO_x (R^2 =0.45), but less with PM_{10} mass (R^2 =0.25). However, study by Morawska et al (1999a) did not observe any significant difference in particle number concentration with respect to distance from a busy road. A more detailed particle size distribution study for different aerosol was presented by Morawska et al (1999c) showing distinct nuclei modes in the number size distribution and bimodal mass/volume size distribution was observed for all cases.

Measurement in London found 1.0 x 10^4 particles cm^{-3} at background locations, 3.0-5.0 x 10^4 cm^{-3} in streets and 1.6 x 10^5 cm^{-3} in road tunnels and during fogs, indicating the influence of anthropogenic sources on particle number count (Waller, 1967). The study also identified particle mass median diameters between 0.4 and 0.8 μm, and number medians from 0.09 to 0.13 μm. Particle count and number size distribution measurements were carried out in Birmingham at background and roadside sites during 1994-1995 (Jones, 1996; Harrison et al., 1999a&b) and 1996-1997 (Shi et al., 1999a) but for only short periods. The average number counts were in the range 1.6-1.9 x 10^5 and 1.3-2.7 x 10^4 cm^{-3} at roadside and background locations respectively, showing that particle number concentration is clearly affected by road traffic. The earlier study showed a more consistent single mode at about 30 nm for particle number size distribution at the background site, whereas the roadside presented far greater variation showing modes often at about 30 and below 10 nm or between 20 and 50 nm. Significant correlation was observed between particle number and mass concentrations and particle count correlated better with $PM_{2.5}$ than with PM_{10}. Similar number modes were found (20-30 nm) in the later study.

1.5. Chemical Properties of Airborne Particles and Measurements

Chemical composition of PM is highly variable as was shown in many studies, due to pollution sources, chemical reactions in the atmosphere, long-range transport effect and meteorological conditions (Malm et al., 1994; Chow et al., 1994; Eldred et al., 1997; Müller, 1999). Their components include neutral and highly soluble substances such as $(NH_4)_2SO_4$, NH_4NO_3 and NaCl through to sooty particles composed of largely elemental carbon coated in organic compounds, and insoluble minerals such as particles of clay (Brook et al, 1997; Röösli et al., 2001).

The relative abundance of the major chemical components, termed as 'bulk chemical composition' was reviewed in the study of Harrison and Jones (1995) and Harrison and Yin (2000) for urban areas in the UK and around the world. These major components include sulphate, nitrate, ammonium, chloride, elemental and organic carbon, crustal materials and biological materials. Table 1.2 shows measurements of the bulk chemical composition around the world, and substantial variation was found at different locations even within one large country (e.g. in the eastern and western US) (USEPA, 1996). However in the UK the bulk chemical compositions from Leeds and Birmingham cities are very similar although they were measured at different times, in 1982 and 1995 respectively (Clarke et al., 1984; Harrison et al., 1997a).

In addition to the bulk composition, Harrison and Yin (2000) also discussed trace element and strong acid contents. The reviewed data does not show huge variation from major cities in the total trace element concentrations, but their speciation measurement is particularly important regarding their bio-availability and potential to affect human health. Strong acid content nitric acid and sulphuric acid are formed during the formation of nitrate and sulphate in the atmosphere from oxidation of nitrogen dioxide and sulphur dioxide. The loss of nitric acid is through the reaction with sea salt or ammonia to form sodium nitrate or ammonium nitrate, whereas sulphuric acid can only be subsequently neutralised by ammonia to form ammonium bisulphate or ammonium sulphate (Harrison and Allen, 1990).

Table 1.3. Bulk Chemical Composition (%) at Urban Areas around the World

Locations	References	Size(μm)	Total Mass ($\mu g\ m^{-3}$)	EC	OC	Organic	TC	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	Crustal	Minerals	Other
Eastern U.S.	USEPA (1996)	<10	-	3.3	6.1	8.5	9.4	1.2	27.8	10.7	-	-	19.6	28.9
		<2.5	-	3.9	14.9	20.9	18.8	1.1	34.1	13.0	-	-	4.3	22.8
		2.5-10	-	-	-	-	-	-	4.9	1.8	-	-	51.8	41.5
Western U.S.	USEPA (1996)	<10	-	5.1	21.4	30.0	26.5	24.0	4.6	6.7	-	-	36.3	0.0
		<2.5	-	14.7	27.8	38.9	42.5	15.7	10.8	7.5	-	-	14.6	0.0
		2.5-10	-	-	-	-	-	-	3.1	0.8	-	-	69.3	26.8
SouthWest U.S.*	Vasconcelos et al., (1994)	<2.5	3.4	-	-	-	29.3	-	13.3	26.7	-	24.0	-	6.7
		2.5- 15	4.8	-	-	-	-	-	1.3	2.5	-	88.5	-	7.7
Southern California (urban)*	Chow et al., (1994)	<10	71.7	3.5	-	20.0	-	12.7	13.2	5.7	1.3	18.2	-	19.3
		<2.5	37.0	5.0	-	26.5	-	9.8	20.9	9.0	0.4	2.5	-	23.9
Edison California*	Chow et al., (1996)	<10	52.5	5.7	19.7	27.6	25.4	3.0	6.3	2.0	-	46.1	-	4.3
		<2.5	49.6	6.0	31.4	44.0	37.4	3.0	6.0	2.0	-	35.0	-	0.0
Los Angeles*	Kao and Friedlander (1994)	<3.5	74.3	7.5	8.2	-	15.7	10.8	8.3	5.0	-	-	3.6	56.6
Leeds UK	Clarke et al., (1984)	<15	35.5	-	-	-	33.8	7.9	19.2	6.8	4.2	-	28.1	0.0
		<2.5	22.2	-	-	-	50.0	6.6	26.1	9.9	1.8	-	5.6	0.0
		2.5-15	13.3	-	-	-	13.3	5.8	7.4	2.5	8.2	-	62.8	0.0
Birmingham UK	Harrison et al., (1997)	<10	25.7	18.0	20.0	-	38.0	6.0	17.0	6.0	2.0	-	-	31.0
Brisbane Australia	Chan et al., (1997)	<10	18.9	10.0	-	21.0	-	-	3.0	6.0	18.0	22.0	-	20.0
		<2.5	7.3	19.3	-	27.0	-	2.6	5.0	10.0	9.7	6.1	-	20.3
		2.5-10	10.4	2.8	-	13.0	-	4.3	1.4	2.7	22.0	29.0	-	24.7
Sapporo Japan*	Kaneyasu et al., (1995)	<10	24.8	13.9	14.2	-	28.1	4.2	16.4	2.9	2.2	-	9.7	36.5
Lahore Pakistan*	Smith et al., (1996)	TSP	607	2.9	13.1	-	16.0	2.1	3.0	1.2	-	-	16.4	61.3
Hong Kong*	Qin et al., (1997)	RSP	66.2	-	-	-	57.1	2.8	14.4	3.3	2.3	-	6.1	14.0
Antwerp Belgium	Van Borm et al., (1989)	0.2-15	18.1	-	-	-	*21.3	-	18.9	-	3.2	-	30.0	26.6

Note: 1) TC = EC + OC; 2) "-" means not measured; 3) "*" indicates reconstructed

Sulphate is formed mainly through the oxidation of SO_2 in the atmosphere and is expected to be present mostly in the fine fraction as ammonium sulphate although some is present as sodium sulphate of marine origin (Harrison and Pio, 1983). The spatial gradient of sulphate is normally very small within areas of tens of miles (Burton et al., 1996), but over hundreds of miles it can be significant (QUARG, 1996). Brook et al (1997) found the spatial variation of SO_4^{2-} is very similar in eastern Canada since it accounted for 33% of the fine particles mass.

Nitrate is formed mainly from the oxidation of NO_x. One major form is ammonium nitrate generated through the reaction between gaseous nitric acid and ammonia, which is a major component in the fine particle fraction (Clarke et al, 1984). Other studies indicate a bimodal size distribution of nitrate (Kadowaki, 1976&1977). The coarse mode nitrate mainly consists of sodium nitrate, generated by the reaction between gaseous nitric acid and sea salt (e.g. NaCl) particles (Harrison and Pio, 1983; Wall et al., 1988; John et al., 1988; Solomon et al., 1992; Harrison et al., 1994; De Bock et al., 1994). In some environments such as coastal areas, sodium nitrate may be predominant. Larger spatial variation is expected for nitrate in comparison with sulphate.

Ammonium is formed through the neutralisation of sulphuric and nitric acids by atmospheric ammonia (Harrison and Kitto, 1992). A study from Leeds in the UK indicates that ammonium is mostly present in the fine fraction and very little or often zero is found in the coarse mode (Clarke et al., 1984).

Chloride is mainly primary emissions came as sea salt and during the winter months road de-icing salt. These contribute mostly to the coarse particles. Chloride may be also secondary in the form of ammonium chloride, which is in the fine mode and derived from the reaction of ammonia and hydrochloric acid vapour, emitted from combustion sources such as incinerators and power plants. Under normal atmospheric conditions, ammonium nitrate and ammonium chloride are unstable existing in the reversible phase equilibrium with the gaseous precursors, i.e., nitric acid, hydrochloric acid and ammonia (Allen et al., 1989). These equilibria are largely controlled by temperature and relative humidity (Stelson and Seinfeld, 1982a&b; Pio and Harrison, 1987a&b; Harrison and Pio, 1983; Harrison and Msibi, 1994). Dissociation of ammonium nitrate and ammonium chloride occurs at high temperature and low relative humidity. On the other hand, they are relatively stable under conditions of high relative humidity and low temperature.

Elemental carbon (EC) and organic carbon (OC) are major constituents of smoke from incomplete combustion processes, in urban areas mostly from road traffic. Elemental carbon, also termed as black carbon (BC), is responsible for the soiling characteristics of particles and possesses very good adsorptive properties, which may allow it to carry more harmful materials. Organic carbon is mostly produced from combustion processes as semi-volatile compounds or formed through chemical reactions (Bowman et al., 1997). It normally represents about 60-80% of total carbon (Harrison and Jones, 1995). The ratio of OC to EC varied at different locations but showed minimum values in the range 1.1-1.5 (Castro et al., 1999).

Crustal materials, confined mainly in the coarse fraction (Harrison et al., 1997a) are soil and wind blown dusts. Their compositions and concentrations can vary greatly due to local geology, surface conditions and meteorology, as well as human activities, like traffic and construction etc.

Biological particles include both small organisms like bacteria and spores, as well as larger particles such as pollens and fragments of cellulose plant materials (Matthias-Maser and Jaenicke, 1994). They are generally coarse in size except some viruses, and often classified as organic carbon instead of as individual components in most measurements.

1.6. Objectives of the Study

The specific objectives of the project and related chapters are outlined in this section as the following.

1) To measure the airborne particulate mass, number and size distributions at selected locations (urban background, urban roadside/kerbside and rural). The measurement methods are outlined in Chapter two.
2) To determine the relationships of PM_{10} to $PM_{2.5}$ and coarse particles using hourly and daily averages both for annual and seasonal datasets (Chapters3&4).
3) To assess temporal and spatial variations of particulate mass and number concentrations, as well as particle size distributions in the UK atmosphere using yearly, seasonal, monthly, daily and hourly averages (Chapters 3-5).

4) To assess meteorological influence on particle mass and number concentrations and to understand its affect, and thus to aid the interpretation of sources of particulate matter (Chapters 3-6).
5) To examine the pollution sources affecting particulate concentrations, particularly road traffic (Chapters 4-5) through the relationships between particle mass, particle number and traffic generated air pollutants at all sites.
6) To evaluate air pollution episodes through the analyses of exceedences of health-based standards for particle mass and the periods with high particle concentrations (Chapters 3&4).
7) To characterise particle number and size distribution at urban road, urban background and rural sites (Chapter 5).
8) To evaluate temporal variations of chemical species, particularly secondary ionic particulate concentrations at Harwell, and both secondary and primary species in Birmingham during periods of air pollution and non-pollution episodes, and their relationship to particle mass. (Chapter 6).

CHAPTER 2

MEASUREMENT METHODS

2.1. Introduction

A brief outline of the methodologies of air pollution data generation is shown in this chapter including sampling methods, equipment, site locations, chemical analyses and data collection and validation.

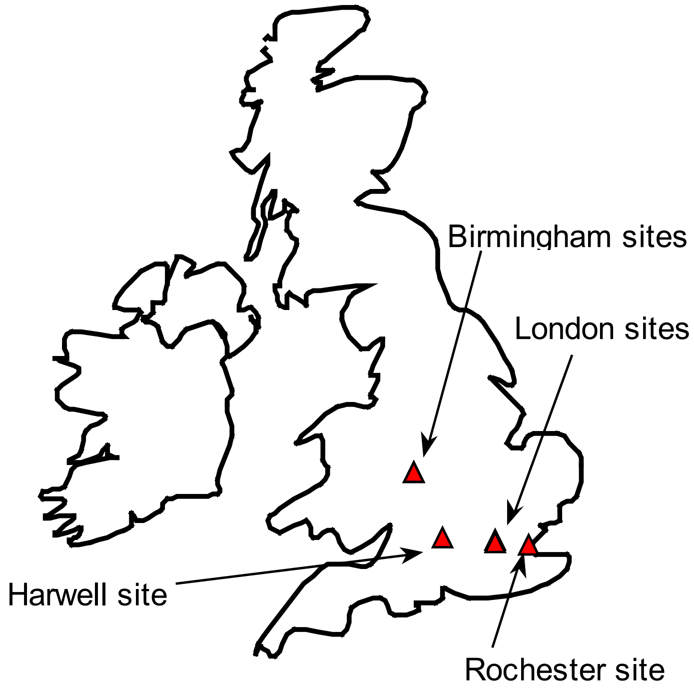
Various sampling sites were chosen for this project in order to collect air pollution data from different backgrounds. Different sampling instruments were located at these sites for monitoring particle mass, particle numbers, particle size distribution and particle chemical composition. The latter was derived from chemical analyses using various techniques. The measurement details are illustrated in Table 2.1. The methods of data collection and validation are also discussed at the end of the chapter.

In order to assist data interpretation, concentrations of gaseous pollutant nitrogen dioxide, nitric oxide, sulphur dioxide, carbon monoxide and ozone were downloaded from the AURN data archive. The meteorological data, wind speed and wind direction at the two London sites, originated from the monitoring site at the London Weather Centre (LWC), which is about 2 km south of the London Bloomsbury site. The wind speed anemometer is placed on top of the Ministry of Defence building in Whitehall at a real height of 35 m. The effective anemometer height is estimated to be 22 m (Personal communication, Meteorological Office, 1996). Wind data at Rochester and Harwell was measured on site.

2.2. Sampling Location

Seven different sampling locations (Figure 2.1) were involved in this study including four main sites set up for the DETR project and another three additional sites in Birmingham. The measurement parameters and equipment are shown in table 2.1.

Figure 2.1. Sampling locations



2.2.1. Main Sampling Sites

Instruments were located at four established sites, which form part of the DETR Automatic Urban and Rural Monitoring Networks (AURN). In all cases the monitoring equipment is housed in purpose built air-conditioned cabins with sample inlets approximately three metres from the ground level.

- **LM - London Marylebone Road**

This site is part of the London Air Quality Network and is operated by the South East Institute of Public Health. It is classified as an urban kerbside/roadside site, located around one metre from the kerbside of a major arterial route, which is one of the busiest roads in London with little perceived change in traffic flow throughout the day and the surrounding area forms a street canyon. Traffic flows of over 80,000 vehicles per day pass the site on six lanes with frequent congestion. The site is approximately 2 km from the London Bloomsbury site.

- **LB - London Bloomsbury**

This was the first site to be established in January 1992 in the National Automatic Urban Network and is classified as an urban background site. It is located within the south east corner of a small park in central London, generally laid to grass but with many mature trees. All four sides of the gardens are surrounded by a busy 2/4 lane one-way road system carrying approximately 35,000 vehicles per day, and subject to frequent congestion. The nearest road lies at a distance of approximately 35 metres but there are mature trees within about 5 metres.

- **RO - Rochester**

This site is located on the western boundary of a rural primary school on the outskirts of the village of Lower Stoke, Rochester, Kent. The area is generally open grass with some young trees within one metre. The nearest road is approximately 80 meters to the east of the monitoring station with a low traffic volume. The site is officially regarded as a rural site, but it is expected that human activities will be occasionally affecting the site.

- **HAR - Harwell**

This rural site is located within the grounds of the Harwell Science Centre, Didcot, Oxfordshire, in the middle of an unfarmed field and surrounded by predominantly agricultural land. There is limited activity in the area and the nearest road about 400 metres from the monitoring site is used only for access to buildings within the Science Park. The nearest trees are about 250 metres from the site. Distant sources include the busy A34 dual carriageway about 2 km to the east and the Didcot Power Station about 5 km to the north-east.

2.2.2. Additional Sites

Three additional sites in Birmingham are involved in the data analyses, one established continuous monitoring site run by Birmingham City Council and two other temporary sites, the URGENT PUMA site and a residential garden.

- **HH - Birmingham, Hodge Hill**

Hodge Hill, set up in 1994 by Birmingham City Council, is categorised as a suburban site close to the edge of the city located about 70 metres south to an elevated section of the very busy M6 motorway (approximately 160,000 v.p.d.). The sampling inlets are about 3.3 metres above ground level. PM_{10}, $PM_{2.5}$ and gaseous pollutants are monitored simultaneously at this site.

- **PUMA Site**

A temporary URGENT PUMA site was set up in Birmingham within a University car park. The sampling equipment was located on a tower about 10 metres above ground level to reduce the influence of traffic and the site is regarded as an urban background site. The nearest road is located about 15 meters with low traffic volumes.

- **RG – Residential Garden**

This site is situated in a home garden within a residential area in the suburb of Birmingham. The garden is surrounded by gardens and houses where the closest road busy A456 (dual carriageway) is located on the north-west about 200 metres away.

Table 2.1. Details of measurements

SITE	CLASSIFICATION	MEASUREMENT	EQUIPMENT
LM	Urban Kerbside/Roadside	PM_{10} and $PM_{2.5}$ particle count and size distribution	TEOM SMPS/CNC
LB	Urban Background	PM_{10} and $PM_{2.5}$ particle count and size distribution	TEOM SMPS/CNC
RO	Rural	PM_{10} and $PM_{2.5}$ Wind data	TEOM Met. Sensors
HAR	Rural	PM_{10} and $PM_{2.5}$ particle count and size distribution Wind data Chemical data	TEOM SMPS/CNC Met. Sensors Partisol
HH	Suburban	PM_{10} and $PM_{2.5}$ Wind data	TEOM Met. Sensors
PUMA	Urban Background	PM_{10} and $PM_{2.5}$ Chemical data	TEOM Partisol & Dichotomous Sampler
RG	Suburban	Chemical data	Partisol

2.3. Methodologies of Aerosol Sampling and Chemical Analyses

2.3.1. Measurement of Particle Mass

The concentrations of PM_{10} and $PM_{2.5}$ are measured continuously using Tapered Element Oscillating Microbalances (TEOMs) analyser which has provided the first widespread UK measurements of particulate air pollution as a mass concentration (QUARG, 1993a). At each site two TEOM's were installed, one fitted with a standard 16.7 $l\ min^{-1}$ PM_{10} impactor inlet validated according to the US EPA Federal Register requirements, whilst the other was fitted with a 16.7 $l\ min^{-1}$ cyclone manufactured by URG Inc, USA and reported by them to have a 50% cut-point at 2.5 μm.

At the exit of the sample head the flow is isokinetically split into a 3 $l\ min^{-1}$ sample stream, sent to the instrument's mass transducer, and a 13.7 $l\ min^{-1}$ exhaust stream. The main flow of 3 $l\ min^{-1}$ enters the sensor unit through a small Teflon-coated borosilicate glass-fibre filter about 13 mm held at the tip of an oscillating tapered glass tube and free to vibrate at its natural frequency. The oscillation frequency changes as the mass loading of the filter increases and the instrument monitors this change every 2 seconds by a computer and converted it to mass, then the concentration is calculated by dividing the mass changes by the air volume sampled. This information is then used to compute updated 15-minute average mass concentration values.

The TEOM heats the aerosol stream to the filter to 50^0C to prevent moisture affecting the mass measurement, which drive off some volatile species (Smith et al., 1997; Allen et al., 1997; Salter & Parsons, 1999) such as NH_4NO_3 and some organic carbon compounds.

2.3.2. Measurement of Particle Number and Size Distribution

Continuous measurements of particle numbers are made using a TSI Scanning Mobility Particle Sizer (SMPS) which use the electrical mobility detection technique to measure the number size distribution of particles. The SMPS system comprises an Electrostatic Classifier (EC) which separates the particles into known size fractions, and a Condensation Particle Counter (CPC) which measures their number concentration.

The sample inlet is taken from the output flow of a 16.7 l min^{-1} cyclone having a 50% cut-point at 1.0 μm, thus removing most of the large particles which can cause blockages in the system. The aerosol first enters an impactor where larger particles are removed due to their sufficient inertia by hitting the impaction plate, whilst smaller particles avoid the impaction and enter a small passage. The cut point diameter depends on the impactor flow rate and the nozzle diameter, which are 0.5 ℓ min^{-1} and 0.457 mm respectively. A bipolar charger in the EC is used to charge the particles in the incoming polydispersed aerosol to a known charge distribution, which are then classified according to their ability to traverse an electric field and counted with a model 3022 CPC. The EC was configured to allow particles in the range 11-450 nm diameter to be counted.

Such small particles cannot be detected by conventional light scattering techniques. In the CPC the monodispersed aerosol passes through a chamber which is saturated with n-butyl alcohol vapour and then to a cooled condenser where the alcohol condenses onto the particles. The resulting droplets grow to a diameter of about 10 μm and pass through a light beam where they are counted as a result of light scattered onto a photodetector.

The SMPS system is linked to a microcomputer and controlled using communication software. Particle count and size distribution data are stored on the computer in both graphical and statistical forms.

On an annual basis the SMPS systems were removed from site for servicing, and the CPC calibrated against an Aerosol Electrometer using a mono-disperse aerosol of 50 nm diameter sodium chloride particles.

2.3.3. Sampling and Measurement for Aerosol Ionic Chemical Components

Atmospheric particles constitute a large amount of source categories and chemical species. Secondary particulate matter, mainly in the form of ammonium sulphate and ammonium nitrate has been found as a major source in the atmosphere. During winter episodes secondary particulate matter does not appear to be a major contributor to urban PM_{10} concentrations, although there are observable effects during summer ozone episodes (Deacon et al., 1997). This is indicated by a clear relationship between increasing ozone concentrations and increases in PM_{10} during a summer month period at London Bloomsbury in 1994. To determine the contribution of these particulate material to PM_{10}, a R&P Partisol Plus FRM 16 sampler was used at a rural site, Harwell, an urban home garden and the PUMA sites for collecting hourly samples on PTFE filters during both periods of air pollution episodes and non episodes.

1) Sampling

The Partisol-Plus Model 2025 Sequential Air Sampler used in this project is the first model in Europe designed to meet the regulatory monitoring requirements for $PM_{2.5}$ and PM_{10} and other particulate sampling methods (R&P, 1997). It also contains a combination of innovative features for use in a wide variety of manual sampling applications. For example, it can be configured with a variety of inlet systems, such as PM_{10}, $PM_{2.5}$, PM_1 and TSP (total suspended particulate matter). An innovative filter storage and exchange system permits the operation of the device for up to 16 days of daily sampling and 16 hours of hourly sampling between site visits. 47mm diameter filters, which are available in a wide variety of materials, can be used with the Partisol sampler. In this project, the Time-Based Sequential Sampling, Continuous Type is used to allow an uninterrupted sampling of the ambient air, with each filter exposed for one hour until the supply filter cassette magazine becomes empty.

It is important to handle the filters carefully before and after exposure. Gloves and clean tweezers were used. Samples were stored in the freezer after exposure until being analysed to prevent volatility losses of nitrate and ammonium.

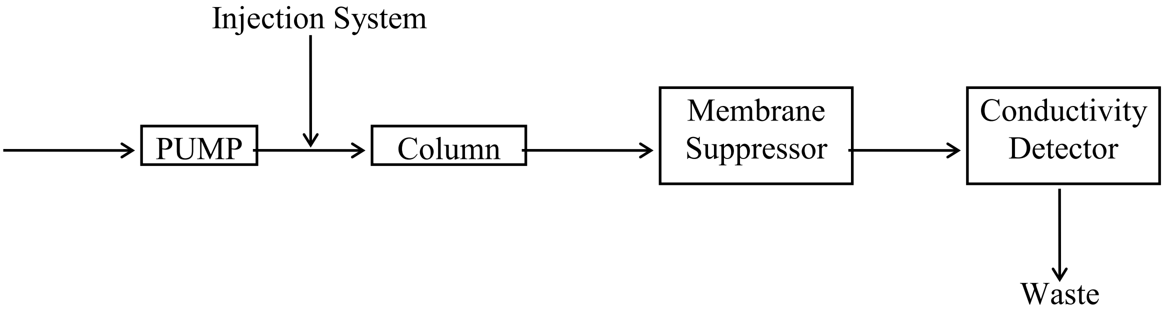
2) Chemical Analysis

Aerosol ions of nitrate, sulphate and chloride were analysed using an ion chromatography method and ammonium by a flow injection technique with fluorescence detection. The two techniques are described in detail below:

a) Ion Chromatography (IC)

Ion chromatography is a technique based on High Performance Liquid Chromatography, in which ions in solution are separated via a chromatography column (Reeve, 1995). It employs some well-established principles of ion exchange in a novel manner and uses electrical conductance for detection and quantitative determination of ions in solution after their separation (Jeffery et al., 1989). A feature of ion exchange chromatography is that ionic solutions are used as eluents, so that the eluted species are present in an electrolyte background, which produces interference in the conductivity measurement. A micromembrane suppressor is used to remove the interference and convert eluent ions into species giving low or zero conductance. The basic flow is illustrated below:

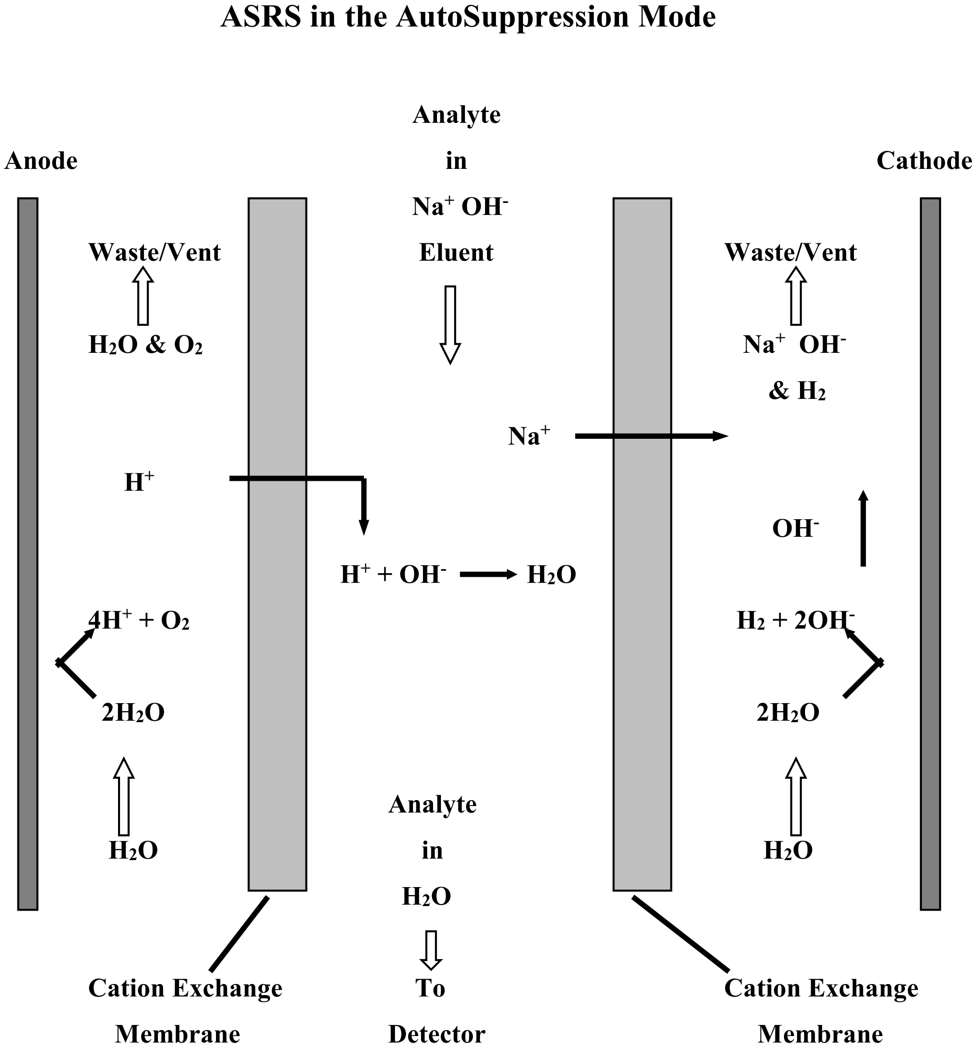
Figure 2.2. Schematic flow of basic Ion Chromatograph (Reeve, 1995)



The model used in this project was a Dionex DX-500 ion chromatograph fitted with a GP40 gradient pump, which generates one eluent from two different solutions, de-ionised, distilled water (DDW) and sodium hydroxide solution (0.1M). A 'mixing program' specified by the user determines how the ratio of these solutions may be varied with time. This implies a greater control over anion elution. An Anion Self-Regenerating Suppressor (ASRS) system can provide continuous recycling of regenerant (H_2O) through the ion exchange column and allows the suppression system to be used unattended indefinitely when in AutoSuppression Recycle Mode (ASRM). The ASRM uses the neutralised conductivity cell effluent as the source of regenerant (H_2O) for the regenerant chamber (Dionex, 1997). Figure 2.3 shows the principle of ASRS in the AutoSuppression Mode. The water regenerant undergoes electrolysis to form hydrogen gas and hydroxide ions in the cathode chamber while oxygen gas and hydronium ions are formed in the anode chamber. Cation exchange membranes allow hydronium ions to move from the anode chamber into the eluent chamber to neutralise hydroxide. Sodium ions in the eluent, attracted by the electrical potential applied to the cathode, move across the membrane into the cathode chamber to maintain electronic neutrality with the hydroxide ions at the electrode.

Samples present on teflon filters are extracted using a 10ml solution of de-ionised, distilled water (90% by volume) and propan-2-ol, HPLC grade. About 30 minutes mechanical agitation is needed to ensure thorough removal of the water-soluble aerosol. The resulting solutions were analysed using the Dionex.

Figure 2.3. Principle of ASRS in the AutoSuppression Mode (Dionex, 1997)



b) Ammonium Analysis

The method for ammonium analysis utilises a procedure based on the reaction of ammonia with o- phthalaldehyde (OPA) to form a fluorescent moiety (Roth, 1971). This reaction is most favoured in alkaline medium in the presence of a reducing agent. Detailed description of the technique has been given in previous studies (Rapsomanikis et al., 1988; Zhang and Dasgupta, 1989; Harrison et al., 1996). In this study, the OPA and a buffered sodium sulphite solution is introduced via a two peristaltic pump into a mixing coil, which is held in a 85 °C water bath. The samples are injected into the sample loop using a syringe fitted with an acrodisc filter, and are carried along by the reagents to the stage where the reaction takes place. The product is routed to the fluorescence detector where the excitation filter is set to expose the 'active' product to light with a wavelength of 370 nm whilst the emission filter is set to 418 to 700 nm. The reagents are prepared as follows:

i) OPA (o - phthaldialdehyde)

- Dissolve 1.3400g phthalic dicarboxaldehyde ($C_6H_6(CHO)_2$) in 250 ml methanol, then make up to 1000 ml solution with de-ionised distilled water (DDW).

ii) Buffered sodium sulphite

- Dissolve 13.41 g Na_2HPO_4 in 400 ml DDW. Adjust to pH 11 by adding 2 M NaOH using a pH meter and dilute to 500 ml with DDW.
- Dissolve 0.378 g Na_2SO_3 in 500 ml DDW.
- Mix the two above to make 1000 ml buffered solution.

The sample preparation is the same as for analysis using IC and the technique described above is used for analysing the particulate ammonium.

Quality control was maintained for analyses of SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ by comparing the analyte in the sample to the same analyte from a series of concentrations of standards. Calibration was made for each set of analysis with seven standard solutions ranged from 0.05 $\mu g\ ml^{-1}$ to 10 $\mu g\ ml^{-1}$, which reasonably covers all samples analysed. The detection limits were obtained for each species as three times the standard deviation, calculated from the analysis of at least seven blank filters. These were 0.026, 0.038, 0.017 and 0.015 $\mu g\ ml^{-1}$ for SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ respectively. The sample concentrations were mostly well above the detection limits, although on a few occasions only chloride gave lower values, which were treated as zero. The uncertainties of the analytical methods on determining the concentrations were approximately 6.3%, 3.5%, 4.2% and 5.1% (at 99% confidence level) on average for SO_4^{2-}, NO_3^-, Cl^- and NH_4^+ respectively.

2.3.4. Measurement of Carbon Species

In order to determine the contribution of airborne particulate carbon to PM_{10} mass, a Graseby Andersen dichotomous sampler fitted with a PM_{10} inlet was used at the PUMA site. Particles smaller than 10 micrometers are divided into two size fractions: 2.5 to 10 micrometers (coarse particles) and less than 2.5 microns (fine particles) by passing through a "virtual impactor" (Andersen, 1981). The aerosol can be accelerated through the virtual impactor nozzle and the coarse particles with greater inertia can impact into a straight receiver tube and then are collected on a 37 mm filter at a flow rate of 1.67 ℓ min^{-1}. The fine-particle flow passes around the receiver tube and is collected on a second 37 mm filter at a flow rate of 15 ℓ min^{-1}. A relatively small amount of fine particles collected on the coarse filter can be corrected through the ratio of the two air-flows, which are pre-set.

For analysing the carbonaceous material QMA filters were used and pre-heated at 400^0C for eight hours to eliminate the volatilizable impurities and reduce the carbon black values. Since the dichotomous sampler was designed to use any 37mm glass-fibre, cellulose-fiber or membrane filters which have higher pressure drop through the filters, a minor modification has to be made to use the quartz filter. A needle valve has been added into the fine particle flow stream just after the filter holder in order to keep both fine and coarse flow at the right levels required with an adjustment of the flow controller inside the pump.

The Leco Instruments Model RC412 Carbon Determinator was used in this analysis for identifying carbonaceous compounds according to the temperature at which they oxidise while exposed to an oxygen atmosphere in a programmable furnace. By measuring the emission of carbon dioxide as the temperature is raised a quantitative infrared absorption spectrum can be obtained. Two main phases of 100 to 350^0C, and 350 to 800^0C have been found to be suitable for identifying organic carbon (OC) and elemental carbon (EC) from previous work (Jones, 1996). For eliminating the moisture a short phase at 100^0C was used initially.

It is important to calibrate the RC412 instrument using a 12% carbon standard ($CaCO_3$) and at least three standard samples have been used for every day measurement. Also determining the background carbon within the instrument can give more accurate results by calibrating the carbon blank whenever the gas supply is changed. Sample calibration has been carried out using a series of $CaCO_3$ standard samples as the instrument can only produce relative carbon signals. The detection limits for OC and EC were 4.5 and 6.1 μg respectively, and the method uncertainty was about ±8.2% (at 99% confidence level).

2.4. Data Collection and Validation

2.4.1. Data Collection

Data collection and validation has been an important task for the continuous measurements of particle mass and numbers from TEOM and SMPS systems. From the four DETR sites, 15-minute averages of PM_{10} and $PM_{2.5}$ mass data are downloaded from the four main sites (LM, LB, RO and HAR) of this project via telemetry links and transferred to the University of Birmingham. The SMPS system at three of the main sites (LM, LB and HAR) is configured to perform a scan every 2.5 minutes and to compute 15 minute averages from this data. Large amounts of particle number and size distribution data, approximately 5 MB per site per week, were produced by the SMPS instruments, which made data transfer using a standard modem links impracticable. The adopted approach is to download on site at monthly intervals onto a removable storage media for subsequent processing and ratification. In addition daily instrument functional checks are made using communication software, which allows remote management and control of the SMPS site computers.

2.4.2. Data Capture and Quality Assurance

The level of data capture, the accuracy and precision of air pollution measurements are important factors for assessing results and providing information for the public. In many measurement programmes, instrument malfunction, human error, power failures, interference and a variety of other disturbances may result in the collection of spurious data. To ensure performing the most accurate analyses, effective data review and validation must be made to identify these data and then a removal or an adjustment can be applied as appropriate.

- **TEOM Instruments**

Relatively high data capture has been found for particle mass generated from the TEOMs, which have been used in the UK's Automatic Urban Network since 1991. Most data losses were caused as a result of electrical supply problems or vandalism rather than instrument malfunctions. In addition to the on-site instrument checks, the data were scrutinised to identify any periods where the data were erroneous or otherwise unacceptable. Error values often occur with TEOM instruments at the start of the measurement and these data are deleted. The instrument can also give abnormal readings occasionally whilst running when extreme negative or positive figures can be found. These again were deleted. Coarse fraction particle concentrations were obtained from the difference between simultaneous PM_{10} and $PM_{2.5}$ measurements. These can occasionally be negative due to noise in the PM_{10} and/or $PM_{2.5}$ data such that a peak in $PM_{2.5}$ noise coincides with a trough in PM_{10} noise. If calculated coarse particle concentrations were lower than –10 µg m^{-3} the coarse particle data were deleted. Meanwhile, the corresponding PM_{10} and $PM_{2.5}$ data were checked where they were deleted if there was an excessive increase or decrease in these data value comparing with the data before and after along that period or they were kept otherwise.

- **Scanning Mobility Particle Sizer**

The SMPS is the state-of-the-art method for sizing and counting ultrafine particles but, this was the first time in the UK and one of the first internationally when SMPS instruments had been used for continuous data collection. In this respect the use of the SMPS has been innovative and has experienced inevitably significant teething problems, most notably the blockage of the inlet impactor on the SMPS leading to a reduction in flow rate and hence in particle count. The instrument has no automatic diagnostic for this fault, and if the site visit identified a problem of impactor blockage, it would not be possible to know from any recorded variable when that blockage occurred, and indeed, it is likely that a steady reduction in flow rate and hence counting efficiency took place over a period of time. Latterly, such problems were largely overcome through more regular service visits especially at London Bloomsbury. There was also significant SMPS down-time due to the inadequacy of the instrument's software in relation to continuous operation. The data were scrutinised visually. There were on occasion very obvious spikes within size distributions, which were manually deleted and replaced with the average of data from neighbouring size bins. Data, which for any other reason appeared dubious, were deleted from the data set. Sometimes the data files were found wrongly labelled due to either software or human setting and usually they were corrected on the best of effort.

After data deletions, monthly data capture in terms of percentages at the DETR Sites is shown in Table 2.2. This represents the dataset used for analysis and data interpretation. High levels of data capture were obtained for particle mass, mostly above 80%, compared with particle numbers where the percentages of data capture were low and varied due to the SMPS instrument failure.

Table 2.2. Monthly data capture at various sites

	PM10				PM2.5				Particle Count		
	LM	LB	RO	HAR	LM	LB	RO	HAR	LM	LB	HAR
May-97	-	-	37%	-	-	-	37%	-	-	-	-
Jun-97	-	41%	99%	-	34%	41%	99%	-	-	-	-
Jul-97	48%	92%	99%	-	100%	100%	90%	-	-	-	-
Aug-97	97%	99%	91%	-	100%	63%	79%	46%	-	-	-
Sep-97	99%	100%	94%	9%	99%	76%	100%	38%	-	-	-
Oct-97	98%	99%	97%	100%	72%	74%	98%	100%	-	-	-
Nov-97	99%	99%	85%	92%	61%	82%	92%	59%	-	-	-
Dec-97	99%	100%	92%	100%	53%	29%	47%	100%	-	-	-
Jan-98	99%	89%	86%	100%	94%	99%	87%	100%	-	-	-
Feb-98	75%	95%	67%	100%	100%	99%	99%	100%	-	-	-
Mar-98	99%	89%	98%	60%	81%	47%	99%	100%	-	-	-
Apr-98	96%	99%	73%	100%	99%	100%	82%	100%	67%	87%	43%
May-98	100%	99%	89%	100%	100%	91%	97%	100%	100%	97%	81%
Jun-98	99%	99%	98%	100%	100%	99%	100%	100%	77%	70%	83%
Jul-98	99%	100%	97%	93%	99%	100%	94%	93%	74%	100%	65%
Aug-98	99%	78%	98%	99%	100%	78%	93%	100%	74%	52%	-
Sep-98	98%	84%	90%	99%	100%	92%	99%	100%	63%	-	20%
Oct-98	98%	99%	97%	100%	100%	100%	98%	100%	-	-	58%
Nov-98	99%	99%	99%	99%	100%	100%	99%	99%	13%	-	80%
Dec-98	99%	96%	99%	99%	100%	100%	99%	99%	35%	-	90%
Jan-99	96%	99%	99%	99%	100%	100%	100%	99%	-	-	65%
Feb-99	79%	99%	96%	99%	99%	90%	85%	99%	14%	39%	96%
Mar-99	96%	91%	94%	100%	99%	91%	100%	100%	45%	74%	77%
Apr-99	58%	100%	100%	94%	76%	100%	100%	92%	100%	100%	87%
May-99	71%	84%	98%	100%	89%	84%	98%	100%	68%	52%	74%
Jun-99	77%	100%	100%	93%	99%	100%	96%	82%	-	90%	50%
Jul-99	94%	100%	97%	100%	100%	100%	94%	100%	-	68%	68%
Aug-99	94%	99%	99%	100%	100%	99%	100%	100%	94%	68%	81%
Sep-99	80%	100%	92%	91%	84%	100%	97%	99%	13%	-	87%
Oct-99	93%	93%	99%	100%	100%	77%	99%	99%	-	90%	32%
Nov-99	90%	100%	98%	100%	100%	100%	98%	100%	-	57%	-
Dec-99	79%	92%	94%	100%	84%	99%	93%	100%	-	81%	-

CHAPTER 3

INTERPRETATION OF MEASUREMENTS OF PARTICLE MASS AND NUMBER AT THE FOUR DETR SITES

3.1. Introduction

Ambient particulate matter concentrations are influenced by a wide range of factors, such as site location, sampling period, sampling method, pollution sources etc. Hoek et al. (1997) compared the concentrations of PM_{10} and black smoke (BS) from both urban and rural sites across ten European countries. Substantial concentration differences were found between these countries due to very different meteorological conditions and air pollution sources. The median PM_{10} concentrations ranged from 11 to 92 $\mu g\ m^{-3}$, the median BS concentrations from 3 to 99 $\mu g\ m^{-3}$. In comparison, the differences in particle concentrations between urban and rural locations within the same country were smaller.

In the UK there has been increasing research on airborne particles since 1992 when monitoring of atmospheric particulate matter as PM_{10} commenced. However, many studies have concentrated on a short-term period or on a particular site or a pollutant species. Deacon et al. (1997) summarised PM_{10} concentration data for the period of 1993-1995 from 16 Automatic Urban Network Monitoring Stations as yearly mean and maximum values. The result showed that the yearly average concentrations are relatively uniform across the country at these urban background sites. The values ranged between 20 to 34 $\mu g\ m^{-3}$, although a slight tendency can be found for the mean concentrations to be higher at locations with large traffic densities (eg London Bloomsbury) or significant coal burning (eg Belfast Centre) or other activities (eg Cardiff). The latter was clearly seen from the yearly counts of exceedences of the EPAQS standard at these sites over the period of 1992-1994 showing the highest counts of 1075 and 1319 at the sites of Belfast in 1993 and Cardiff in 1994 respectively. The Cardiff site was influenced by a nearby building development between March and October 1994 (QUARG, 1996). Harrison and Deacon (1998) reported PM_{10} and gaseous pollutant concentrations from four urban background sites over the year of 1994 and suggested that the site representative for its similar type depend on the length of pollution period used in the calculation. The use of short-term maximum and exceedences of the threshold concentrations showed large differences between sites while longer-term averages gave a result of better spatial uniformity. Stedman (1997) studied a widespread PM_{10} episode in March 1996 across the UK monitoring sites, indicating that many sites had exceeded the PM_{10} EPAQS standard of 50 μg m^{-3} for over 10 days out of a 17 day period from 8th to 24th of March 1996. This episode was attributed to a significant long-range transport contribution from the European continent. The Quality of Urban Air Review Group released its third report in 1996 providing a general review of the UK urban airborne particulate matter concentrations (QUARG, 1996). The Expert Panel on Air Quality Standards also completed a report in 1999 to deal mainly with the sources of particulate matter. The most active studies have been conducted in Birmingham since 1994 and mainly focused on the two Birmingham AUN sites (Birmingham East and Birmingham Centre) and one local government site (Hodge Hill) (Jones, 1996; Harrison et al., 1997b, 1999a&b). These sites are all treated as urban background.

As mentioned in chapter two, four additional sites were set up in 1997 for measuring both PM_{10} and $PM_{2.5}$ mass concentrations. These include the two London sites – one roadside site (Marylebone Road) and one urban background site (London Bloomsbury), and the two rural sites – Rochester is located to the east and Harwell to the west of London. In addition to the mass concentration measurement, the two London sites and one of the rural sites, Harwell, were also equipped for particle number and size distribution measurements. Together with measurements of gaseous pollutants and meteorological parameters a fully comprehensive data assessment was enabled. This chapter reviews the airborne particle mass and number data collected from the four DETR sites, and both short-term and long-term variations and trends of the particle concentrations are studied. Comparison between sites and between pollutant species are also made. Estimates on the EPAQS exceedences have been made using the percentile distribution data.

3.2. Statistical Summary of Particle Mass and Number Data

Hourly seasonal average particle mass and gaseous pollutant concentrations measured at the four DETR sites are presented in Table 3.1. Due to the effect of road traffic substantial elevations of both PM_{10} and $PM_{2.5}$ concentrations have been observed from London Marylebone Road comparing with the nearby background site London Bloomsbury. Earlier studies made over the period from July to October 1995 compared PM_{10} concentrations between the roadsides Marylebone Road and Oxford Street with the site of London Bloomsbury and showed a typical elevation around 10-20 μg m^{-3} at the roadsides (QUARG, 1996). PM_{10} measurements made in Birmingham on a kerbside (A38) also showed an increase of about 20 μg m^{-3} above the average concentration at the AUN urban background site Birmingham Centre (Jones, 1996). This study shows that the average concentrations of PM_{10} and $PM_{2.5}$ over the whole period of two years and seven months are 34.7 and 21.8 μg m^{-3} at LM and 22.8 and 15.4 μg m^{-3} at LB. The observed PM_{10} elevation at the roadside site is about 11.9 μg m^{-3}, which is within the range from the previous result in London, but lower than that from the Birmingham site. The increase of $PM_{2.5}$ concentration at the roadside was 6.4 μg m^{-3}. Based on the two models of HARM (Metcalfe et al., 1995) and EMEP (Tarrason and Tsyro, 1998), if a regional average background about 10 μg m^{-3} secondary PM_{10} is considered, then very significant local elevation (about 100% of primary pollutant background) is seen at Marylebone Road. Substantial increment in coarse particle (5.5 μg m^{-3}) concentration was also found at London Marylebone Road presumably due to re-suspension relating to traffic induced turbulence (QUARG, 1996; Harrison et al., 2001). Clearly, the concentrations of both fine and coarse components are affected by road traffic activities. In comparison with the two urban sites, Rochester and Harwell exhibited much lower concentrations at 17.7, 11.4 and 6.3 μg m^{-3} in PM_{10}, $PM_{2.5}$ and coarse particles at Rochester and 14.4, 10.0 and 4.4 μg m^{-3} at Harwell. These results indicate that the impact of local sources within the urban area is very appreciable. The highest concentrations of gaseous pollutants of NO_x: 204.4 ppb and CO: 2.1 ppm again appeared at the kerbside site, influenced by vehicle exhaust emissions (QUARG, 1996).

Over a long-term period, similar particle mass concentrations were observed between the urban background site London Bloomsbury and the Birmingham sites. The average concentrations over a three-year period from October 1994 to November 1997 at Birmingham, Hodge Hill were 22.5, 14.4 and 8.2 μg m^{-3} for PM_{10}, $PM_{2.5}$ and coarse particles respectively (APEG, 1999), which are comparable to the long-term levels at LB. Birmingham Centre and Birmingham East also showed similar PM_{10} concentrations at 23.6 and 23.5 μg m^{-3} (Harrison et al., 1999a) although these figures are from a shorter term period between 1994 and 1995. These results indicate that the particle concentrations levels from one site can be representative for other sites of similar characteristics, particularly when results are based on long-term measurements. However large variations have been found at sites with different characteristics for both short and long-term periods from this study.

Table 3.1 Summary of concentration for particle mass and gaseous pollutants at four DETR sites

	PM10 ($\mu g/m^3$)	PM2.5 ($\mu g/m^3$)	Coarse ($\mu g/m^3$)	NOx (ppb)	CO (ppm)	SO_2 (ppb)
Whole period						
LM (20/6/97 - 31/12/99)	34.7	21.8	12.9	204.4	2.1	7.3
LB (20/6/97 - 31/12/99)	22.8	15.4	7.4	72.8	0.6	6.2
RO (20/6/97 - 31/12/99)	17.7	11.4	6.3	16.0	-	3.6
HAR (20/6/97 - 31/12/99)	14.4	10.0	4.4	16.6	-	1.4
Summer 97						
LM (20/6/97 - 31/8/97)	40.7	26.4	14.3	187.9	2.3	6.3
LB (20/6/97 - 31/8/97)	27.3	18.9	8.4	63.8	0.5	4.7
RO (20/6/97 - 31/8/97)	22.3	14.2	8.1	12.9	-	5.3
HAR (20/6/97 - 31/8/97)	-	-	-	-	-	-
Autumn 97						
LM (1/9/97 - 30/11/97)	37.6	23.3	14.3	221.7	2.5	9.6
LB (1/9/97 - 30/11/97)	29.4	19.3	10.1	109.1	0.9	7.7
RO (1/9/97 - 30/11/97)	19.1	13.2	5.9	22.0	-	4.2
HAR (28/9/97 - 30/11/97)	17.7	13.4	4.3	28.4	-	2.2
Winter 97/98						
LM (1/12/97 - 28/2/98)	36.0	22.8	13.2	222.1	2.5	11.8
LB (1/12/97 - 28/2/98)	23.7	15.9	7.8	81.9	0.6	9.5
RO (1/12/97 - 28/2/98)	18.1	13.0	5.1	22.4	-	4.9
HAR (1/12/97 - 28/2/98)	16.5	12.0	4.5	18.7	-	1.8
Spring 98						
LM (1/3/98 - 31/5/98)	31.8	20.0	11.8	167.1	1.7	6.9
LB (1/3/98 - 31/5/98)	23.7	16.8	6.9	63.2	0.6	6.5
RO (1/3/98 - 31/5/98)	18.8	13.0	5.8	12.9	-	3.8
HAR (1/3/98 - 31/5/98)	15.9	11.2	4.7	17.3	-	2.2
Summer 98						
LM (1/6/98 - 31/8/98)	31.9	19.4	12.5	186.1	2.0	6.6
LB (1/6/98 - 31/8/98)	20.6	13.5	7.2	48.3	0.6	4.7
RO (1/6/98 - 31/8/98)	16.5	10.0	6.5	10.6	-	2.5
HAR (1/6/98 - 31/8/98)	13.8	9.0	4.8	9.0	-	0.7
Autumn 98						
LM (1/9/98 - 30/11/98)	32.6	21.3	11.3	210.0	2.2	7.0
LB (1/9/98 - 30/11/98)	22.4	15.7	6.7	76.4	0.7	7.7
RO (1/9/98 - 30/11/98)	16.7	10.2	6.5	15.6	-	3.1
HAR (1/9/98 - 30/11/98)	14.6	10.3	4.3	16.1	-	1.0

Table 3.1 Summary of concentration for particle mass and gaseous pollutants at four DETR sites (con't)

	PM10 (μg/m³)	PM2.5 (μg/m³)	Coarse (μg/m³)	NOx (ppb)	CO (ppm)	SO_2 (ppb)
Winter 98/99						
LM (1/12/98 - 28/2/99)	29.7	19.0	10.7	211.0	2.0	6.6
LB (1/12/98 - 28/2/99)	20.3	14.4	5.9	74.7	0.8	8.5
RO (1/12/98 - 28/2/99)	15.9	9.4	6.5	19.5	-	3.9
HAR (1/12/98 - 28/2/99)	11.9	8.4	3.5	12.5	-	1.1
Spring 99						
LM (1/3/99 - 31/5/99)	31.7	21.0	10.7	182.4	1.7	5.7
LB (1/3/99 - 31/5/99)	23.4	15.4	8.0	74.5	0.6	5.4
RO (1/3/99 - 31/5/99)	19.9	11.9	8.0	13.5	-	2.6
HAR (1/3/99 - 31/5/99)	14.4	9.9	4.5	10.7	-	1.1
Summer 99						
LM (1/6/99 - 31/8/99)	36.6	21.5	15.1	178.2	1.8	7.9
LB (1/6/99 - 31/8/99)	22.0	14.8	7.2	64.8	0.5	3.2
RO (1/6/99 - 31/8/99)	19.1	11.6	7.5	11.0	-	4.2
HAR (1/6/99 - 31/8/99)	15.4	9.4	6.0	24.6	-	1.0
Autumn 99						
LM (1/9/99 - 30/11/99)	41.5	24.7	16.8	232.8	2.3	6.9
LB (1/9/99 - 30/11/99)	22.4	14.9	7.5	75.4	0.6	3.9
RO (1/9/99 - 30/11/99)	17.4	11.6	5.8	17.0	-	2.7
HAR (1/9/99 - 30/11/99)	14.0	9.7	4.3	21.2	-	1.7
Winter 12/99						
LM (1/12/99 - 31/12/99)	32.1	20.6	11.5	249.2	2.3	5.1
LB (1/12/99 - 31/12/99)	15.6	10.4	5.2	68.4	0.5	6.2
RO (1/12/99 - 31/12/99)	11.5	7.5	4.0	18.3	-	2.4
HAR (1/12/99 - 31/12/99)	9.2	6.5	2.7	8.1	-	0.9

3.2.1. Percentile Distributions of Particle Mass

Percentile distributions of PM_{10}, $PM_{2.5}$ and particle numbers have been calculated using fixed 24-hour averages (midnight to midnight) for all sites. Tables 3.2 and 3.3 contain data sets for every year and the whole period, and Figures 3.1 and 3.2 for the seasonal data set.

The results of particle mass percentile distribution (table 3.2) show that it is very likely for PM_{10} to exceed the EPAQS standard of 50 $\mu g\ m^{-3}$ taken as averages over a fixed 24 hour period rather than as the 24-hour running means at the site of London Marylebone Road. Regardless the data capture was not 100% (table 2.2), PM_{10} concentration has reached the upper limit of the standard for at least about 21.4 days within a seven-month period in 1997 and 18.3 and 36.5 days in the years 1998 and 1999 respectively. For the EU Council Directive Stage1 objectives of PM_{10} standard to be achieved by the year 2005, the 24h PM_{10} must not exceed 50 $\mu g\ m^{-3}$ more than 35 times per year. Clearly a reduction in PM_{10} levels at the roadside LM is needed to reach the target. The 99th percentiles far exceeded the standard value giving a figure of 82 $\mu g\ m^{-3}$ across the whole sampling period and the highest PM_{10} concentration of 134.0 $\mu g\ m^{-3}$ appeared in 1999 at 99.9th percentile. According to the Air Quality Strategy (DETR, 1997) produced by the UK government, by the year 2005 a target of 99th percentile in compliance with the EPAQS standard have to be achieved. Therefore, at the roadside site London Marylebone Road, PM_{10} emissions must fall by about 39% based on the whole period and 42% in relation to the emission levels in 1999 (99th percentile: 86.1 $\mu g\ m^{-3}$). In comparison, only a 12% cut in PM_{10} emissions is required at London Bloomsbury relating to pollution level during the whole period, and 19% based on the year 1997.

Table 3.2 Percentiles of PM_{10} and $PM_{2.5}$ calculated by annual and whole period using 24h-fixed data set

		50%	90%	95%	98%	99%	99.9%
	PM10						
LM	1997 (Jun-Dec)	36.2	57.8	65.2	76.3	82.9	94.6
	1998 (Jan-Dec)	31.6	45.3	51.8	57.6	62.1	69.4
	1999 (Jan-Dec)	33.2	51.7	60.3	78.9	86.1	134.0
	Whole period	33.2	50.1	58.2	69.0	82.0	132.9
LB	1997 (Jun-Dec)	23.0	40.9	48.9	57.4	61.9	83.9
	1998 (Jan-Dec)	21.3	32.8	41.0	44.2	48.6	61.1
	1999 (Jan-Dec)	19.5	31.9	39.0	44.2	48.6	57.0
	Whole period	21.1	36.0	41.6	48.7	56.6	81.5
RO	1997 (Jun-Dec)	16.8	31.0	38.0	41.2	43.2	60.6
	1998 (Jan-Dec)	15.3	27.5	32.5	36.0	39.3	55.9
	1999 (Jan-Dec)	16.0	27.1	30.1	37.3	39.0	51.6
	Whole period	16.0	28.2	33.7	38.9	41.7	57.2
HAR	1997 (Jun-Dec)	13.4	27.0	33.2	34.0	35.9	36.2
	1998 (Jan-Dec)	13.1	24.2	27.9	34.0	39.3	58.1
	1999 (Jan-Dec)	12.2	21.8	25.9	29.4	31.1	35.5
	Whole period	12.8	23.5	27.6	33.2	35.7	52.9
	PM2.5						
LM	1997 (Jun-Dec)	21.4	38.1	44.6	46.9	50.7	55.4
	1998 (Jan-Dec)	19.3	29.3	35.3	41.0	42.3	46.9
	1999 (Jan-Dec)	20.8	32.2	36.8	43.1	47.9	55.1
	Whole period	20.3	31.9	38.2	44.7	47.1	56.3
LB	1997 (Jun-Dec)	15.5	29.5	36.9	40.5	53.2	70.7
	1998 (Jan-Dec)	14.0	24.7	29.4	36.4	39.2	43.4
	1999 (Jan-Dec)	12.7	22.1	27.1	32.7	35.8	40.7
	Whole period	13.8	25.0	29.8	37.2	39.8	62.7
RO	1997 (Jun-Dec)	11.2	25.3	29.1	34.3	36.2	53.3
	1998 (Jan-Dec)	9.8	19.7	24.0	27.5	30.2	37.9
	1999 (Jan-Dec)	9.7	18.1	21.4	25.6	29.0	34.9
	Whole period	10.0	19.7	24.9	29.3	32.5	41.0
HAR	1997 (Jun-Dec)	9.7	22.5	26.4	29.4	35.5	37.8
	1998 (Jan-Dec)	8.9	18.3	20.7	25.7	29.2	39.9
	1999 (Jan-Dec)	8.0	15.6	18.6	23.2	24.5	26.8
	Whole period	8.5	17.8	21.2	25.5	28.4	39.0

As mentioned above, high levels of PM_{10} concentrations were related to both fine and coarse particle fractions on Marylebone Road highlighting the importance of both vehicle exhaust emissions mainly in the fine fraction (Harrison et al., 1997b) and resuspension effect from passing traffic, which increase the coarse particle concentrations (Harrison et al., 2001). Fine particles contribute at most up to two-thirds except occasionally coarse particles also play an important role, such as the year 1999, when the 99.9th percentile PM_{10} value exceeded 134.0 $\mu g\ m^{-3}$ but the percentile value for $PM_{2.5}$ was only 55.1 $\mu g\ m^{-3}$. Particle mass concentrations appeared to be lower in 1998, which is likely due to weather conditions as the year 1998 was the wettest year since 1996 reported by the BBC weather centre (www.bbc.co.uk). Fine particles may alone lead to an exceedence of the PM_{10} standard on Marylebone Road and London Bloomsbury, but for a very few days over a year period.

The numbers of exceedences of the standard for PM_{10} are significantly reduced at the urban background site London Bloomsbury as shown in the percentile distribution table. However, the contribution of fine particles to PM_{10} mass is somewhat higher in comparison with Marylebone Road. It is because this site, situated in the centre of London, is also affected by exhaust emissions from the surrounding moderately trafficked roads. The low contribution of coarse particles is due to a distance about 35m or greater between the site and roads making it hard for coarse particles suspended by traffic to reach the sampling inlet. It is very unlikely at Rochester and Harwell sites that PM_{10} will exceed the EPAQS standard based on the current data set.

Similar results of site variation were also observed from the seasonal data shown in Figure 3.1a&b. There are no clear indications of seasonal pattern for PM_{10} and $PM_{2.5}$ at all sites, but fluctuations in particle mass concentrations can be seen from season to season and year to year, which is largely based on meteorological conditions. However, autumn seasons are likely to show higher concentrations of both PM_{10} and $PM_{2.5}$, and hence enhance the number of exceedences of the EPAQS standard. Autumn 1999 has exhibited the highest number (26 days) of exceedences of the 50 $\mu g\ m^{-3}$ PM_{10} standard at Marylebone Road whereas only 2 days were observed in summer 1998. In autumn 1997 at London Bloomsbury, there were two days that fine particles alone exceeded the standard concentration value (Figure 3.1b). Extremely high PM_{10} concentrations were found both in summer and autumn 1999 at LM, which were attributed to very high coarse particle concentrations comprising around 50% of PM_{10} or higher. Overall, London Bloomsbury has much less chance to exceed the EPAQS standard but the chances still exist, unlike Rochester and Harwell where particle mass concentrations are much lower.

Figure 3.1a Seasonal percentile distribution of PM_{10} (24h-fixed data set) at four DETR sites

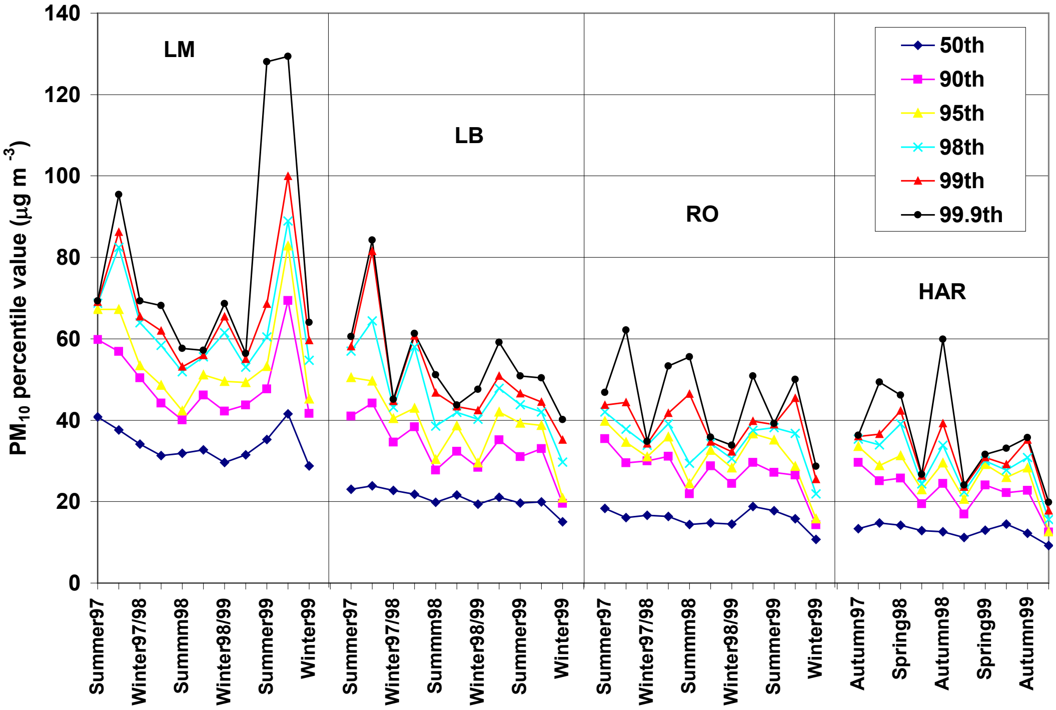
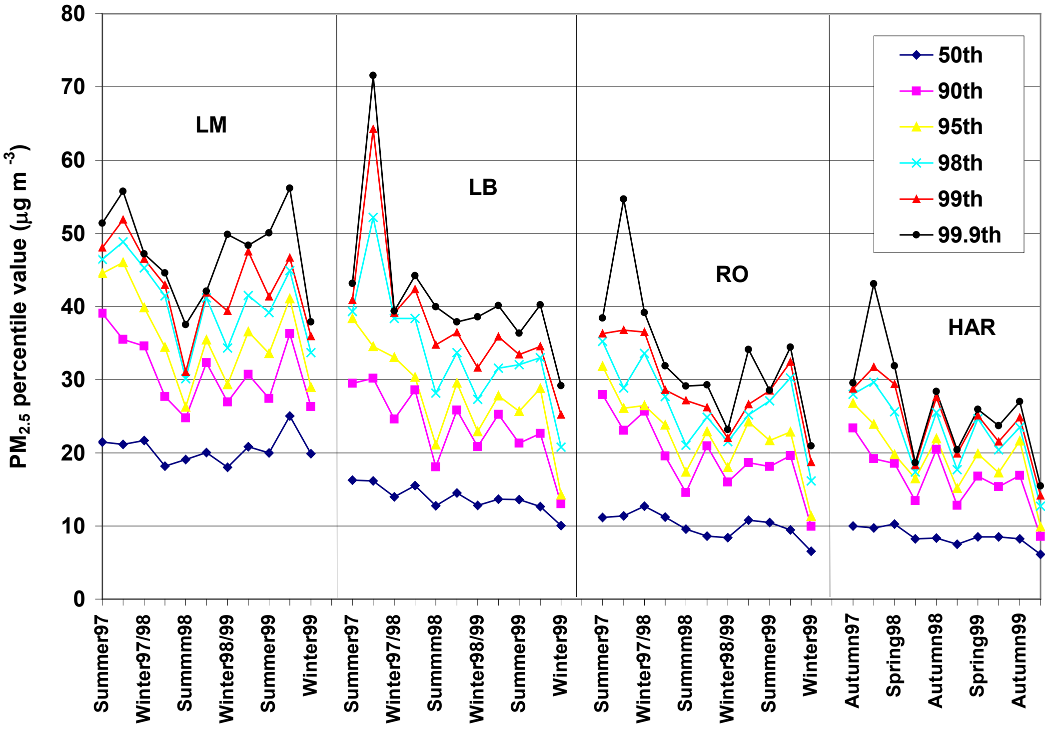


Figure 3.1b Seasonal percentile distribution of $PM_{2.5}$ (24h-fixed data set) at four DETR sites



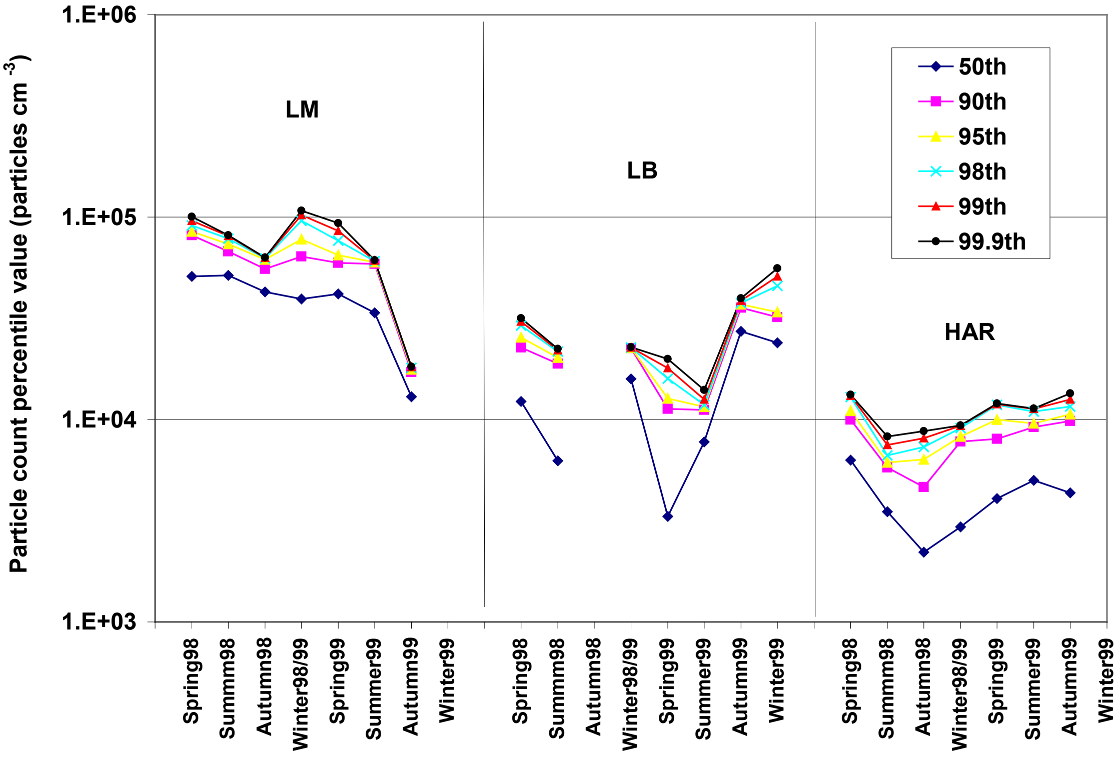
3.2.2. Percentile Distributions of Particle Numbers

In addition to particle mass, the percentile of particle number concentrations (particle count cm^{-3}) are also presented in Table 3.3 and Figure 3.2. There has been no standard yet proposed so far for particle numbers. However based on the measured particle number data set, it should be noted that a greater difference was observed in particle number concentrations between the three sites. Comparing data from the whole period, the ratio of Marylebone Road, London Bloomsbury and Harwell is about 8:4:1 according to the 99.9 percentiles, highlighting that particle number is a greater indicator for evaluating the site characteristics, particularly for assessing the levels of vehicle exhaust emissions (Harrison et al., 1999b). In comparison, the PM$_{10}$ ratio at the same percentile is about 2.5:1.5:1, showing much less variation between the three sites. The greater elevation in particle numbers at the roadside site Marylebone Road indicates that the site is heavily influenced by motor vehicle exhaust emissions. As a rural site, Harwell has the least effect from this source.

Table 3.3 Percentiles of particle count calculated by annual and whole period using 24h-fixed data set

		50%	90%	95%	98%	99%	99.9%
	Particle Count						
LM	**1997 (Jun-Dec)**	-	-	-	-	-	-
	1998 (Mar-Dec)	5.0×10^4	7.3×10^4	8.1×10^4	8.6×10^4	9.6×10^4	1.1×10^5
	1999 (Jan-Nov)	3.9×10^4	5.9×10^4	6.3×10^4	6.6×10^4	8.1×10^4	9.3×10^4
	Whole period	4.5×10^4	6.6×10^4	7.8×10^4	8.4×10^4	9.3×10^4	1.1×10^5
LB	**1997 (Jun-Dec)**	-	-	-	-	-	-
	1998 (Mar-Dec)	9.9×10^3	2.1×10^4	2.3×10^4	2.5×10^4	2.9×10^4	3.1×10^4
	1999 (Jan-Dec)	9.7×10^3	2.8×10^4	3.3×10^4	3.6×10^4	3.7×10^4	5.3×10^4
	Whole period	9.8×10^3	2.6×10^4	3.0×10^4	3.4×10^4	3.7×10^4	5.1×10^4
HAR	**1997 (Jun-Dec)**	-	-	-	-	-	-
	1998 (Mar-Dec)	3.4×10^3	7.7×10^3	9.1×10^3	1.0×10^4	1.2×10^4	1.3×10^4
	1999 (Jan-Nov)	4.3×10^3	8.5×10^3	9.6×10^3	1.1×10^4	1.2×10^4	1.3×10^4
	Whole period	3.8×10^3	8.3×10^3	9.5×10^3	1.1×10^4	1.2×10^4	1.3×10^4

Figure 3.2 Seasonal percentile distribution of particle counts (24h-fixed data set)



3.3 Seasonal Characteristics of Particle Mass and Numbers

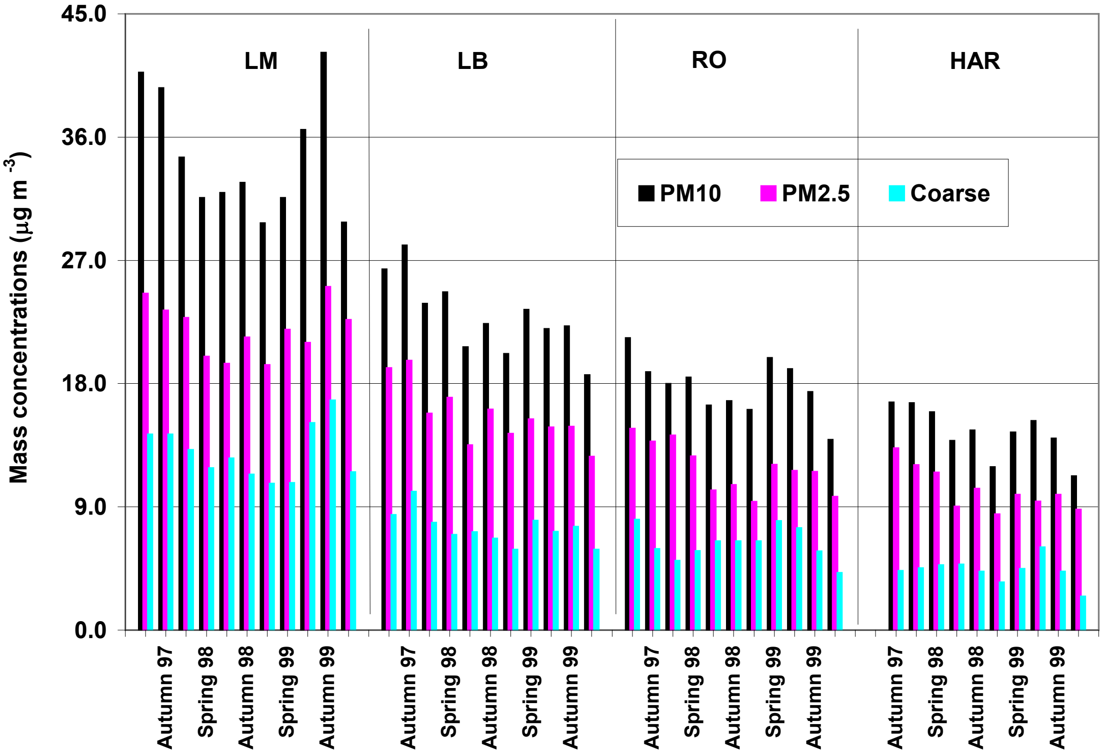
A full investigation of seasonal, monthly and diurnal characteristics of particle mass, number and gaseous pollutant concentrations has been conducted for all four sites in the following sections. Comparisons between sites and various pollutants were also made. Unlike previous work, here a year has been divided into four seasons as winter (December to February), spring (March to May), summer (June to August) and autumn (September to November).

3.3.1 Seasonal Variation in Particle Mass and Number Concentrations within Site

Seasonal average concentrations of particle mass and gaseous pollutants for a particular site are shown in figures 3.3a&c. There is no obvious seasonal pattern in the concentrations for particle mass PM_{10}, $PM_{2.5}$, and PM_{coarse} and for the gaseous pollutants NO_x, CO and SO_2. Instead, as mentioned earlier, the year 1998 exhibited lower particle mass concentrations at all sites, which was attributed to synoptic conditions although this is not clear in the gaseous pollutant concentrations.

Whilst there is a little seasonal variation in the concentration some features can be found for a given site or species. Higher coarse particle concentrations are likely to appear in summer, spring and autumn seasons when resuspension of dusts are favoured due to drier or windy whether conditions plus local activities such as traffic or construction. In London Marylebone Road, summer and autumn 1999 showed higher coarse concentrations, hence higher levels of PM_{10} (Figure 3.3a). Similarly higher coarse concentrations were observed from the Rochester site in spring 1999 and summer 1997&1999, whereas Harwell site showed higher coarse concentrations in summer 1998 and 1999. Seasonal variations of $PM_{2.5}$ were not apparent and higher concentrations may be present at any season of the year.

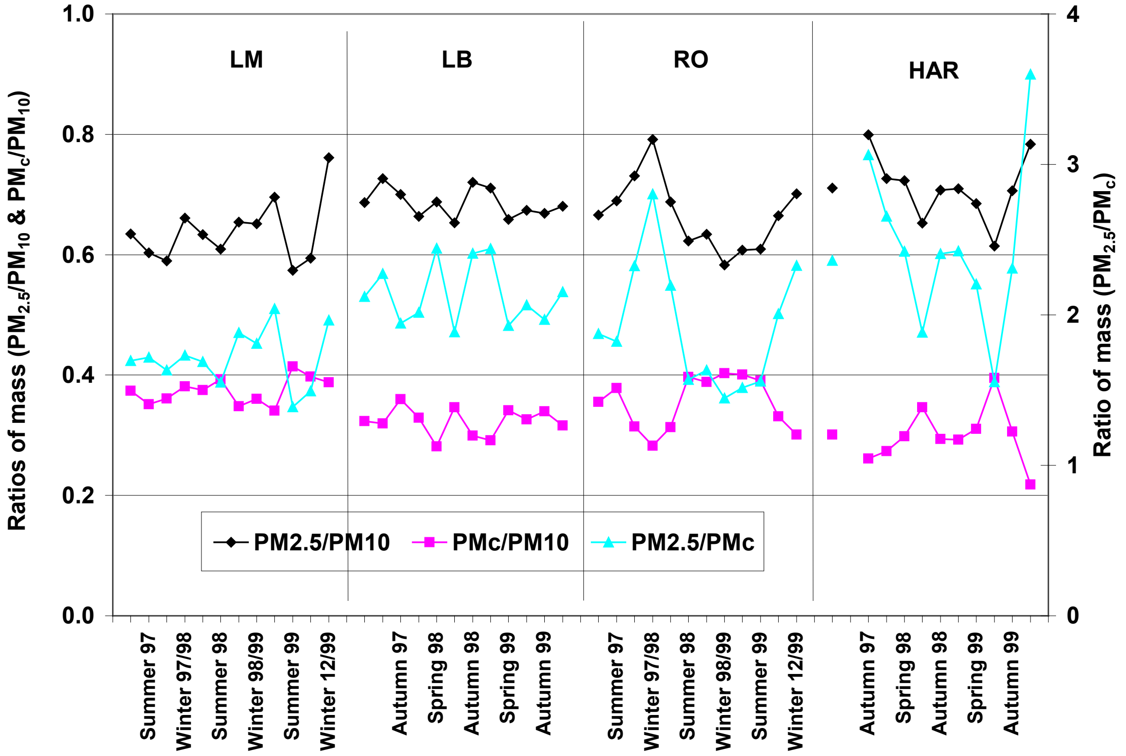
Figure 3.3a Seasonal average mass concentration at the four sites



In general, good correlation has been found between fine and coarse particles at London Marylebone Road showing fairly consistent ratio of $PM_{2.5}/PM_{coarse}$ around 1.7 (Figure 3.3b). Exceptions occurred in summer and autumn 1999 when the ratios were lower about 1.4 and 1.5 due to higher coarse components, and in spring and winter 1999 when the ratios were higher (2.0). This suggests that the two components have a similar source, which is important in affecting both fractions of the mass concentrations. In the case of London Marylebone Road, road traffic has been the major source responsible for the elevation of PM_{10}, $PM_{2.5}$, coarse particles and NO_x concentrations (APEG, 1999). Correlation between

$PM_{2.5}$ and coarse particle concentrations was also observed at LB but less well compared with London Marylebone Road since this site is less influenced by traffic. However the ratio (2.2 on average) of fine to coarse particle concentrations is higher at the urban background site than the roadside site relative to the differences of contribution from road traffic. At the Rochester and Harwell sites, fine and coarse particles appeared to be much less well correlated in comparison to the urban sites due to different pollution sources. It seems that PM_{10} and $PM_{2.5}$ are generally correlated at the London Bloomsbury, Rochester and Harwell sites showing a similar seasonal pattern. It suggests that particle concentrations at these sites are likely influenced by similar national weather conditions, which controlled the advection of polluted air-masses. In the case of Marylebone Road, local traffic has far greater impact on these particles. Detailed correlation analyses between concentrations of different size fractions are shown in chapter four.

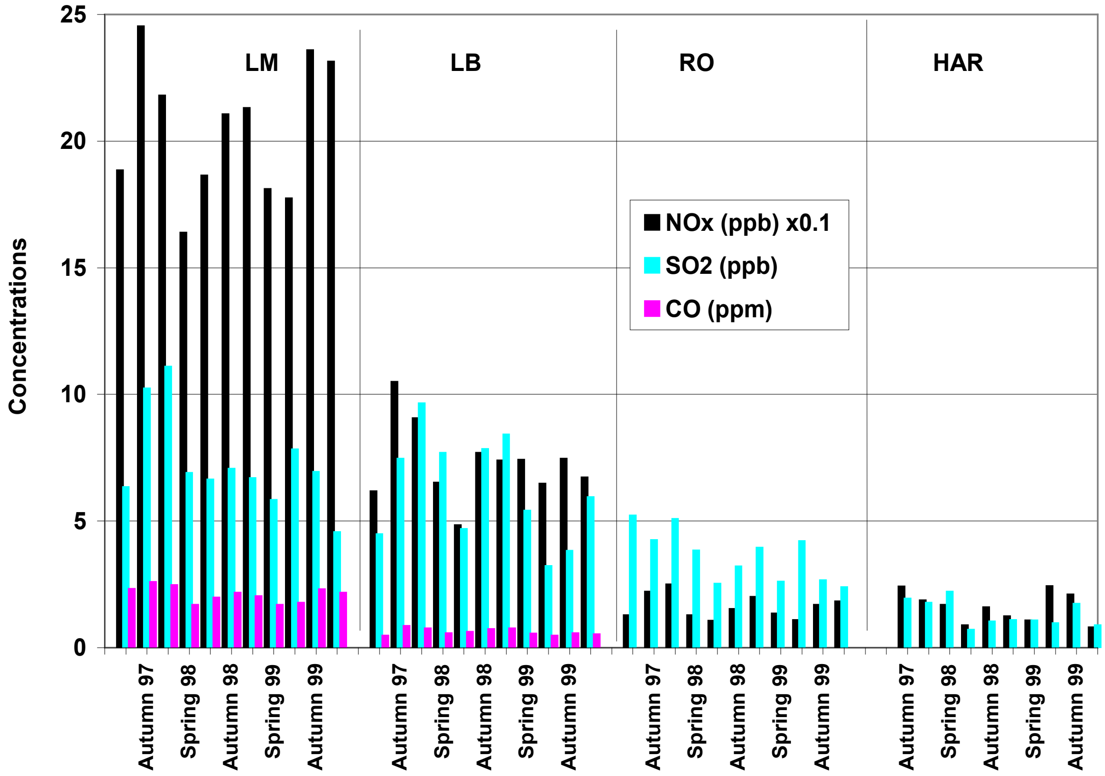
Figure 3.3b Seasonal average mass concentration ratios at the four sites



The gaseous pollutants behave differently for a particular site or species. A consistent seasonal variation was found for CO at both roadside and urban background sites (Figure 3.3c), where higher concentrations appeared in winter and autumn and lower values in spring and summer. This can be interpreted as due to incomplete exhaust combustion and poorer dispersion in colder weather conditions (QUARG, 1993a&b). The variation in NO_x

concentrations in LM is not obvious but generally shows higher levels in winter and autumn than in summer and spring. This is also true for Rochester where the impact of vehicular emissions is also present, however the Harwell site has exhibited the highest NO_x concentrations in both autumn (1997) and summer (1999). No seasonal dependence has been found in SO_2 concentrations for LM, RO and Harwell, although for LB SO_2 shows higher concentrations in colder seasons. Higher levels of SO_2 in warm seasons may be influenced by some point source plumes (Harrison and Deacon, 1998) from power stations, whereas winter maxima are likely due to sources at ground level which are less effectively dispersed particularly at urban sites. Very similar concentrations of SO_2 were found at the two urban sites (7.3 and 6.2 ppb on average at LM and LB), but the NO_x level at the roadside site is almost three times higher than that at the background site. This indicates that the contribution from traffic emissions to urban SO_2 is small in relation to the contributions from other sources. On the other hand, large differences in NO_x and CO concentrations between the two city sites highlight that road traffic has been a dominant source for both air pollutants. Lower concentrations of NO_x and SO_2 have been found at the Rochester and Harwell site, where both traffic and other pollution sources are dramatically reduced.

Figure 3.3c Seasonal gaseous pollutant concentration at the four sites



Particle number data were examined using monthly averages due to a low data capture (Figures 3.4a-c, where the data recovery is shown against each month as a percentage value). It is not advisable to draw a temporal trend using the data as only a few months have high data capture especially at London Bloomsbury, which has experienced the most problems (e.g. impactor blockage) at the beginning of measurement. Marylebone Road has also suffered some other difficulties through the end of the campaign. Regardless of the poor data capture, Marylebone Road demonstrated a decrease in particle number concentrations whereas London Bloomsbury showed the highest levels in the last three months. There may be a possibility that an underestimation of the particle number concentrations has occurred especially for the early months in London Bloomsbury due to an inclusion of some erroneous data caused by the factor of impactor blockage. In contrast, Harwell has shown the highest data collection and no clear trend can be drawn over the sampling period. It is worth mentioning that the rural site exhibited high number concentrations in May 1998 and August 1999, which is likely due to small particle formation through homogeneous nucleation processes involving photochemistry as there are increased photochemical activities in the warm seasons (Brook et al., 1997; Sweet and Gatz, 1998). More discussions on this issue can be found in chapter five.

Figure 3.4a Monthly average number concentration (particles cm^{-3}) at LM

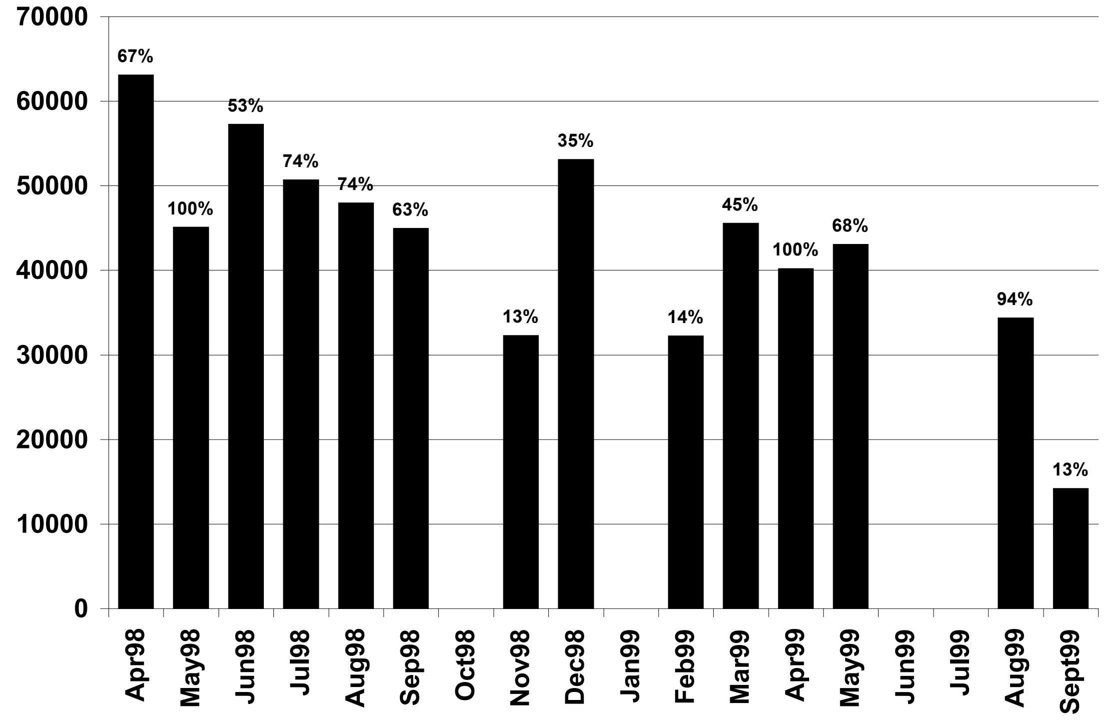


Figure 3.4b Monthly average number concentration (particles cm^{-3}) at LB

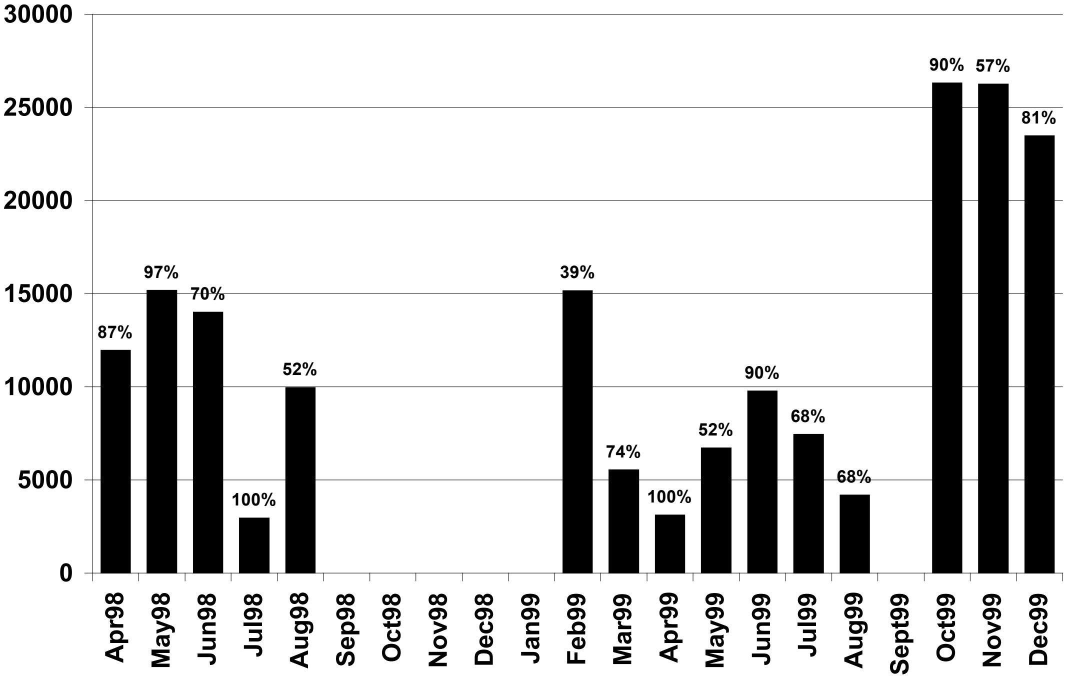
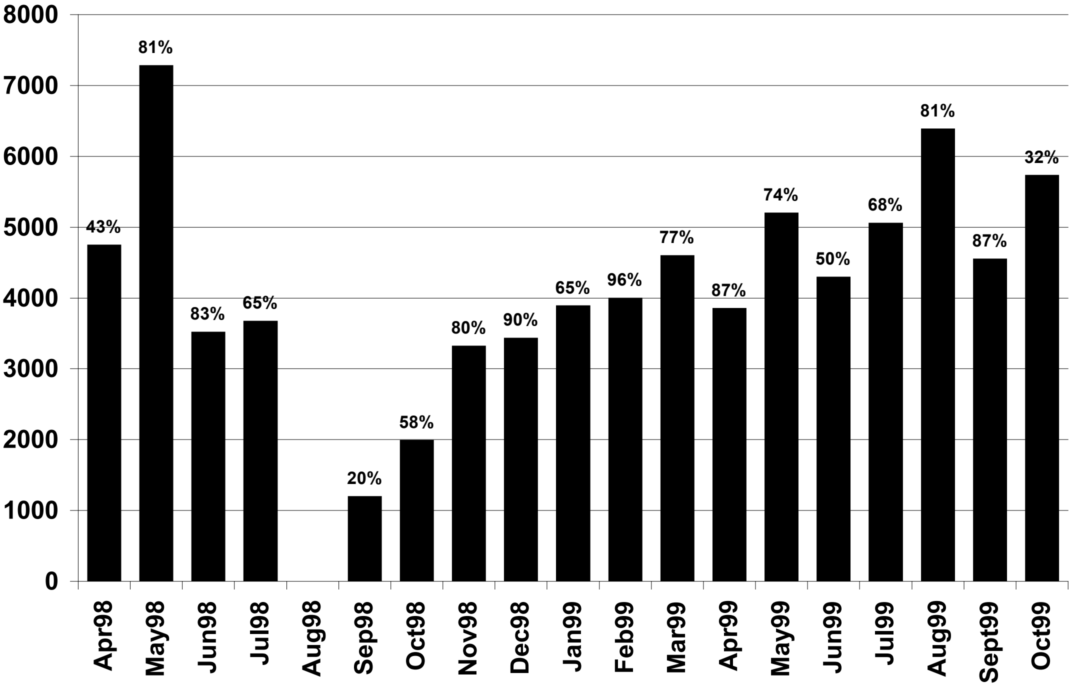


Figure 3.4c Monthly average number concentration (particles cm^{-3}) at HAR



3.3.2 **Seasonal Variation in Particle Mass and Number Concentrations between Site**

Further examination of the data has been made involving all sites and species for a given season shown in Figures 3.5a to 3.5k. The average concentrations of all pollutants generally follows the order of LM>LB>RO>HAR for all seasons as expected. Marylebone Road suffers the heaviest local traffic emissions, which can elevate all concentrations of particle mass, number and gaseous pollutants, whereas the urban background site London Bloomsbury is less influenced. Except encountering some local traffic influences from the nearest road, about 80 metres distant, Rochester is also affected by the advection of polluted London air-masses during frequent westerly winds or by long-range transport of continental pollution when there is an easterly wind. In the case of Harwell, the lowest pollution concentrations reflect the smallest influences from both local and long-range transport. Larger ratios between LM and LB in coarse particle concentrations can be found than in fine particles, highlighting the significance of local traffic sources contributing to large particles and the uniformity of fine particles controlled by both local and long-range sources. Again another interesting feature is that the greatest difference at these sites is for the particle number concentrations. This is in line with the large differences in CO and NO_x concentrations demonstrating that levels of particle number concentrations are important markers for assessing vehicle exhaust emissions particularly at urban locations. The differences in SO_2 do not appear to be great showing less effect from urban sources such as road traffic, so that non-urban sources, mainly from power stations, may well contribute to the SO_2 concentration levels in urban areas (Eggleston et al., 1992).

Figure 3.5 Seasonal average concentrations at the four DETR sites

Figure 3.5a Seasonal average concentration for summer 1997

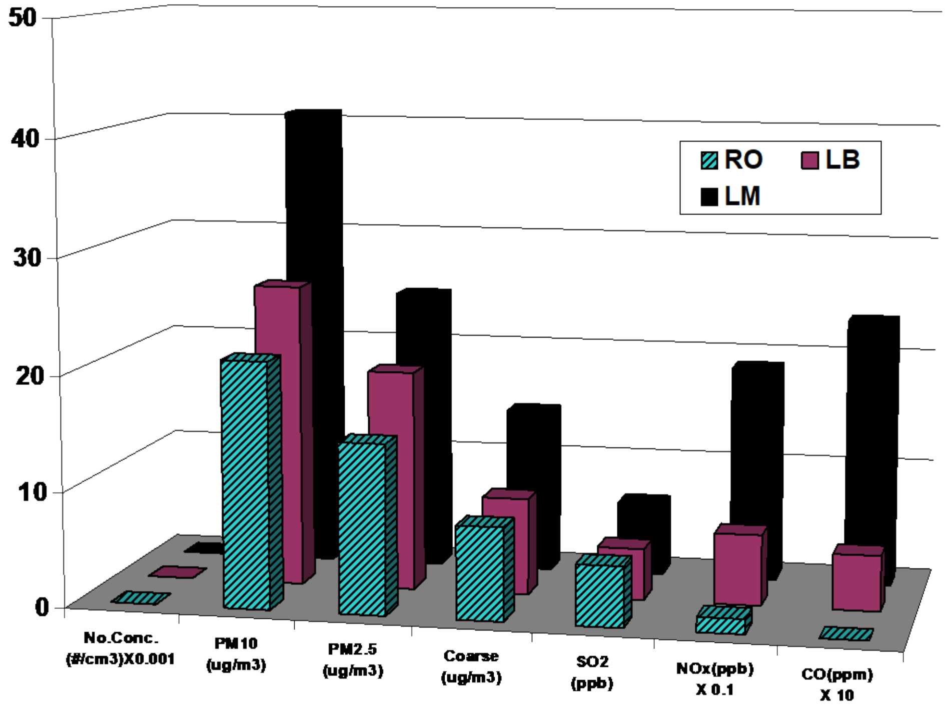


Figure 3.5b Seasonal average concentration for autumn 1997

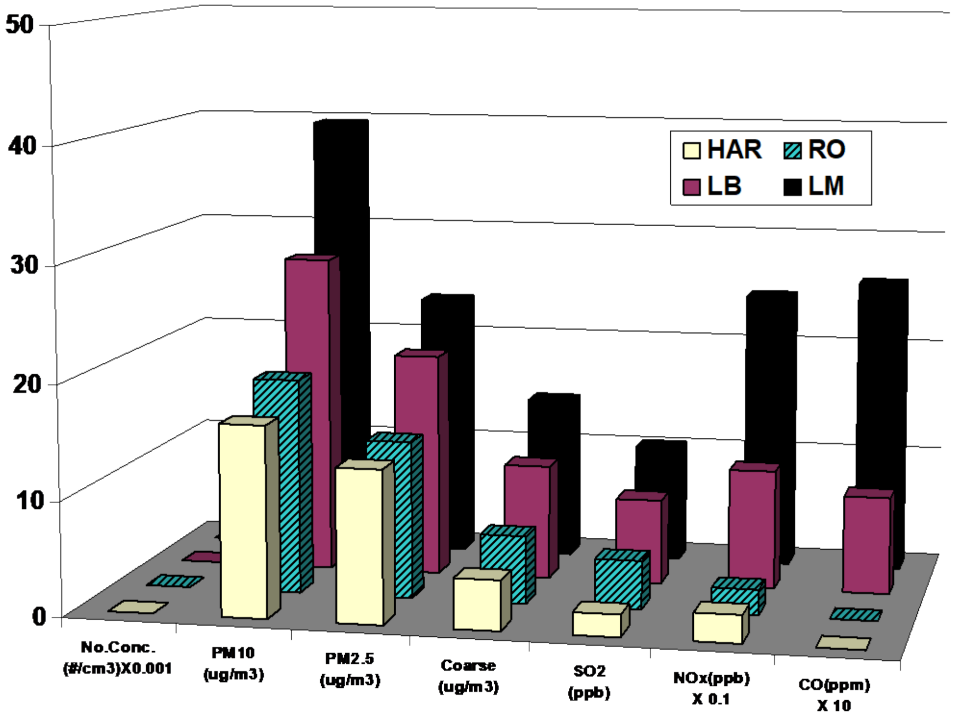


Figure 3.5c Seasonal average concentration for winter 97/98

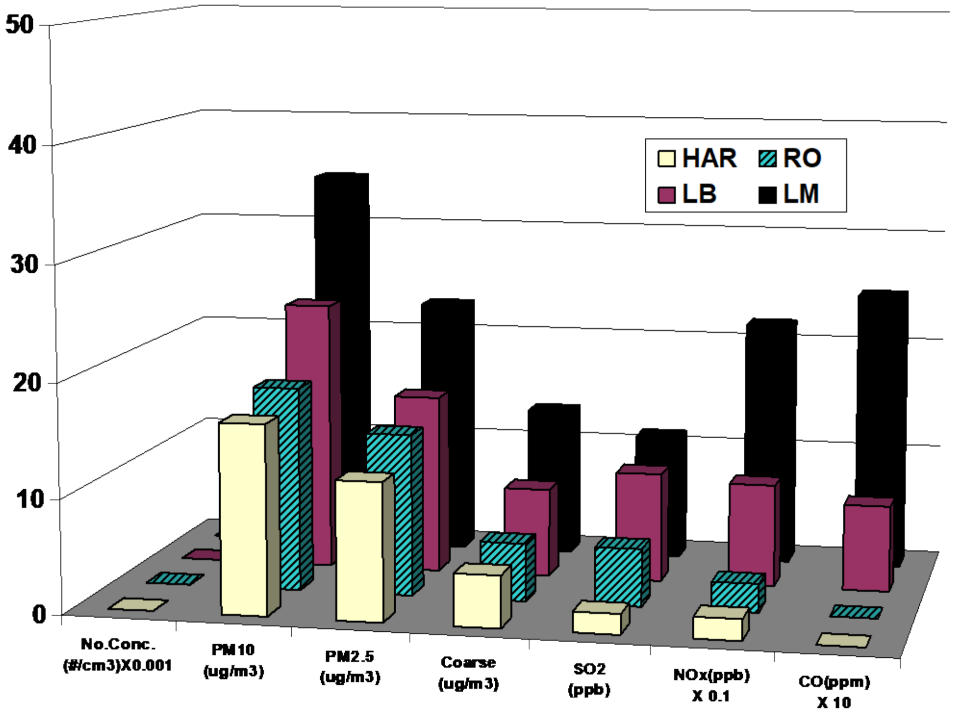


Figure 3.5d Seasonal average concentration for spring 1998

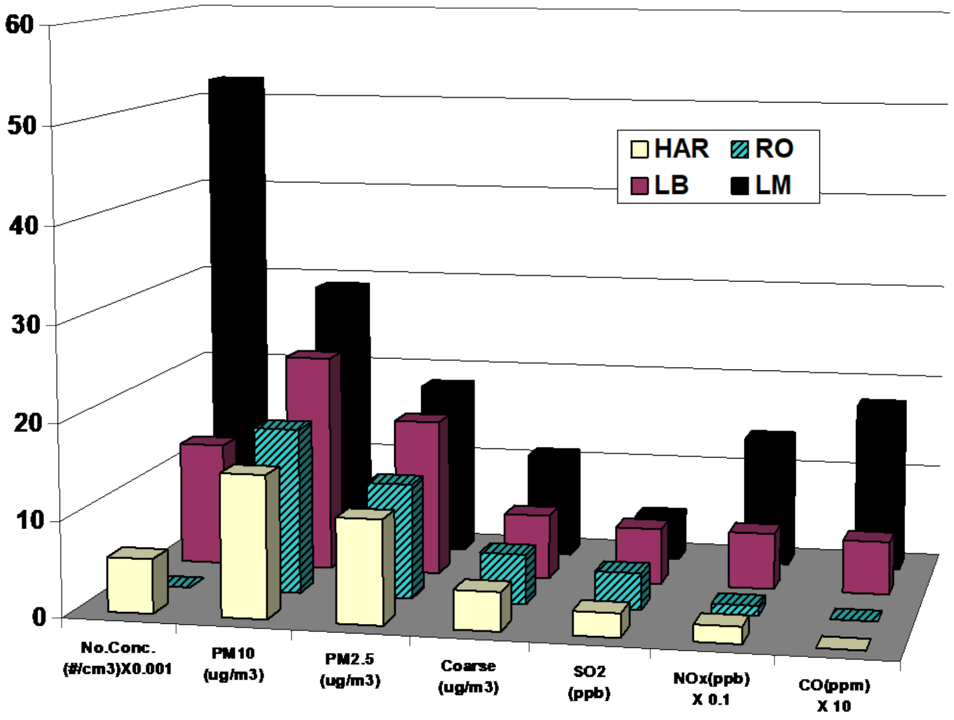


Figure 3.5e Seasonal average concentration for summer 1998

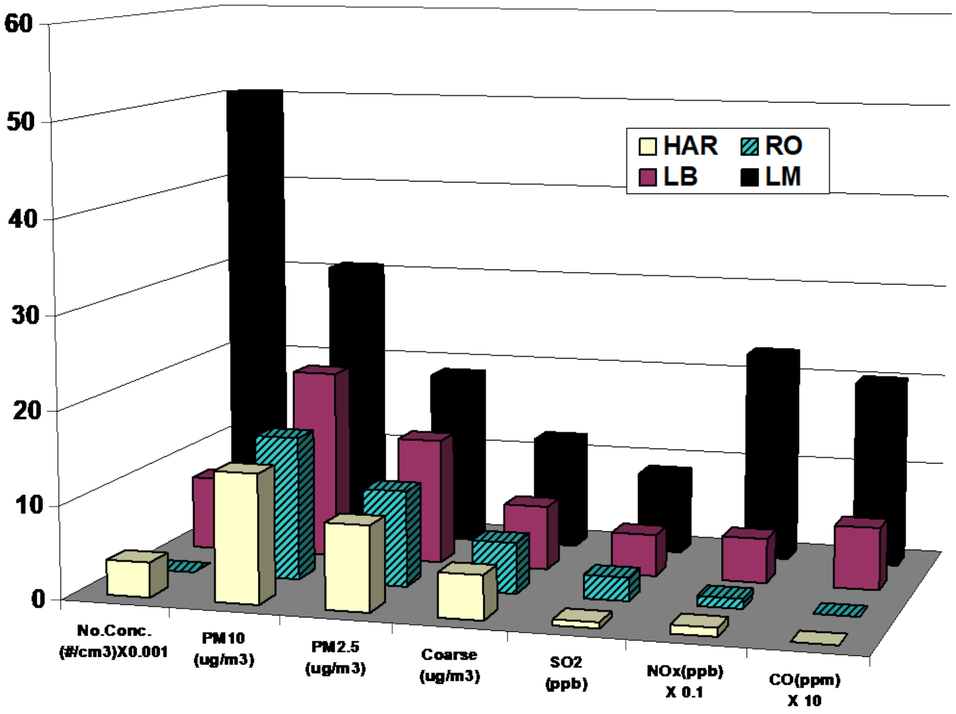


Figure 3.5f Seasonal average concentration for autumn 1998

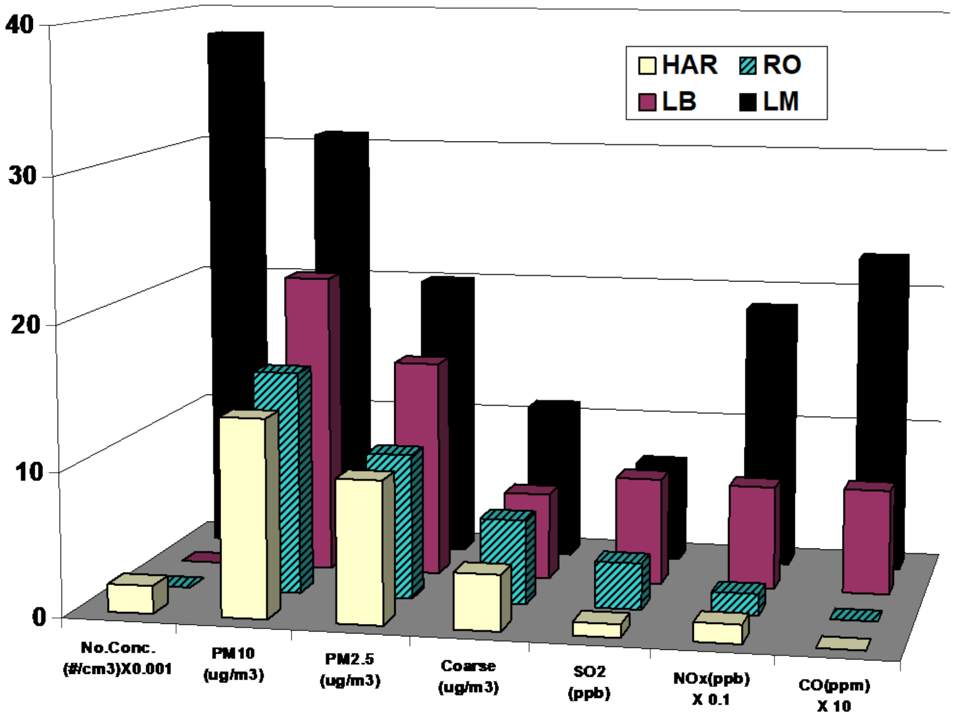


Figure 3.5g Seasonal average concentration for winter 98/99

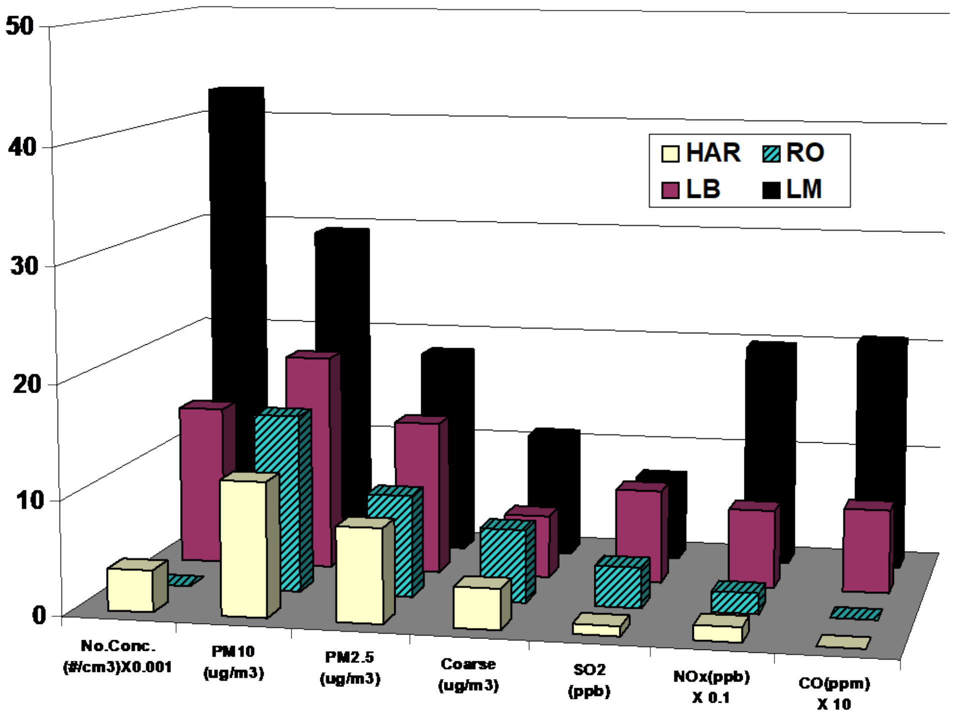


Figure 3.5h Seasonal average concentration for spring 1999

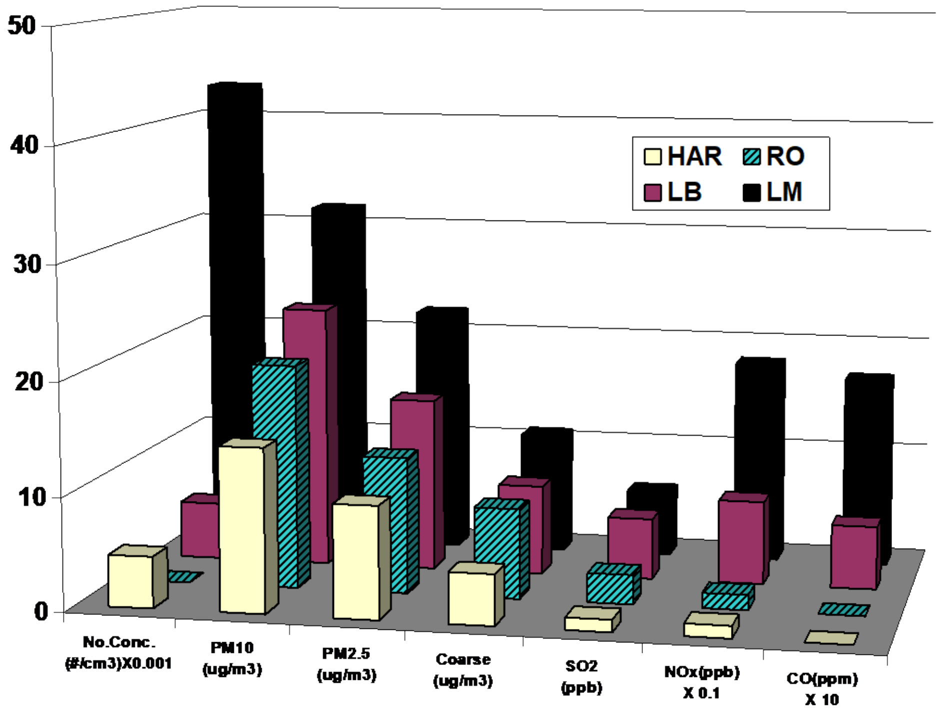


Figure 3.5i Seasonal average concentration for summer 1999

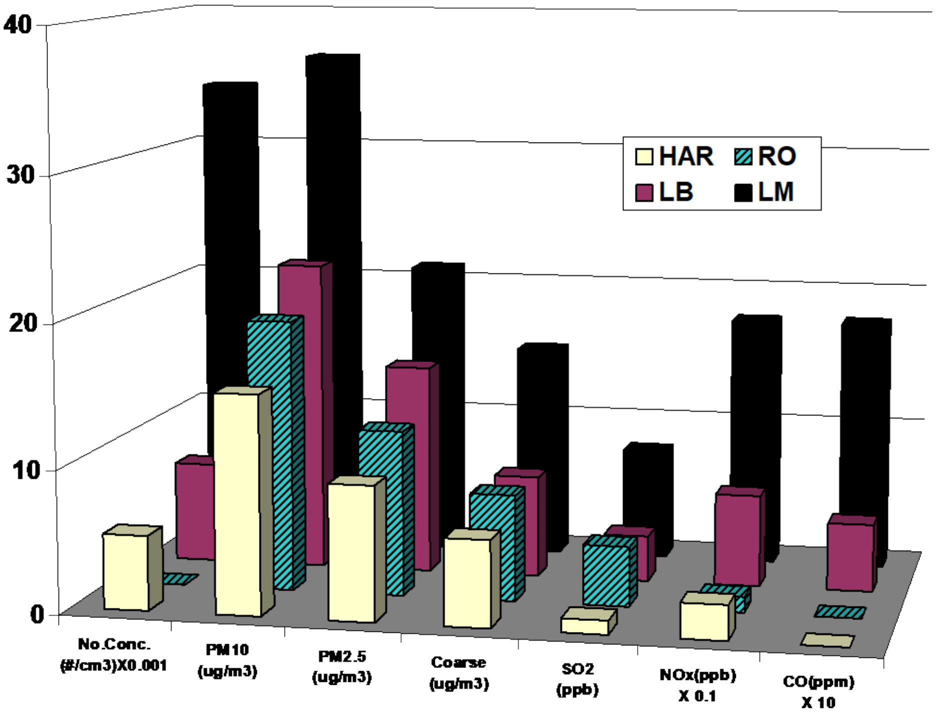


Figure 3.5j Seasonal average concentration for autumn 1999

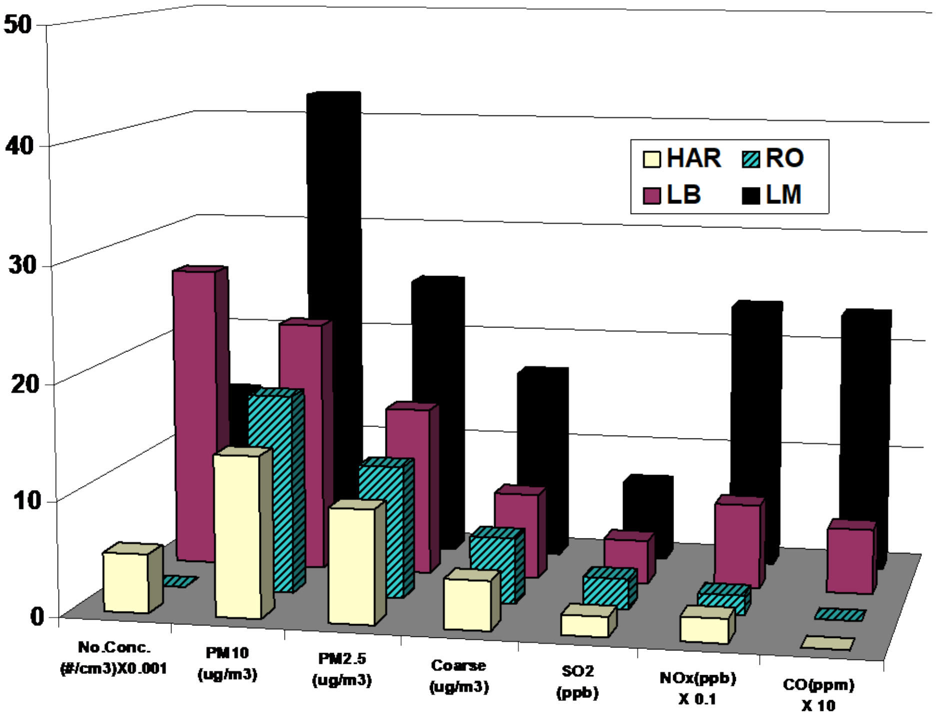
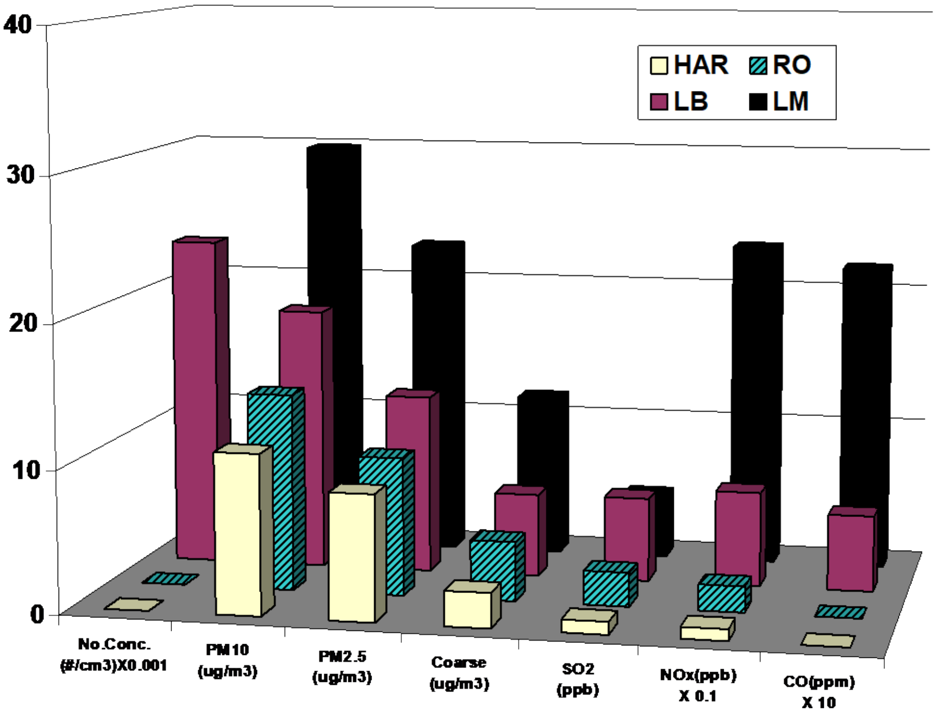


Figure 3.5k Seasonal average concentration for December 1999



3.4 Diurnal Characteristics of Particle Mass and Numbers

By aggregating all data available seasonally over the whole sampling period, diurnal characteristics of airborne particles can be investigated. The aggregated diurnal plots (Figures 3.6a to 3.6d) do not show very much difference between the four seasons for London Marylebone Road because, as mentioned earlier, this site is situated at one of the busiest roads in London with little perceived changes in traffic flow all year round. The concentrations of PM_{10}, $PM_{2.5}$ and particle numbers are seen to follow closely the diurnal pattern of vehicle exhaust related gaseous pollutants (NO_x and CO). There is a minimum concentration at the early hours in the morning when the profiles of human activities are the lowest. The pollutant levels start rising as early as 4 or 5 am and quickly reach the morning rush hour peak around 7-9 o'clock. A decrease was found in the concentrations towards the middle of the day due to an increase in wind speed, which is believed to have a dispersion effect on these pollutants (QUARG, 1996). Relatively consistent levels appeared for the rest of the day.

It is noted that the morning rush-hour peaks of number concentrations appeared slightly earlier than PM_{10} and $PM_{2.5}$. The rise in particle numbers is far quicker than the rise in other pollutants although the starting point is approximately coincident. Similar situations were also observed in Birmingham site (Harrison et al., 1997b; Jones, 1996), which is explained since freshly emitted particles from vehicle exhaust are very small in size and contribute mainly to particle count instead of particle mass, hence the faster response in particle numbers than in mass. Particle mass starts to increase due to coagulation or condensation processes of these small particles once the particle count reaches threshold levels.

There are no significant evening peaks found at Marylebone Road except for CO, which displayed an evening maximum in comparison with the morning peak. Although the reason for this is uncertain at present, it may however relate to the traffic patterns, i.e., vehicle types may have shifted from more diesels to petrol since petrol cars mainly generate three pollutants including CO, NO_x and hydrocarbons whereas diesel vehicles produce larger emissions of NO_x, particulate matter and black smoke (QUARG, 1993). Further investigation is shown using traffic data in Chapter 4.

Figure 3.6e shows that the diurnal variations of SO_2 are similar to NO_x, although the levels of concentrations are low, indicating that there is a relationship between SO_2 and road traffic. Coarse particles have minimum concentrations around 4-5 am when both wind speed and the volume of traffic are the lowest, and higher values through the middle of the day when higher wind speed and heavier traffic appeared (Figure 3.6f).

Diurnal variation of the data is examined using single season plots for the whole period. In general, earlier morning peaks appeared at 7 am in summer when winter months showed delayed morning rush-hour peaks around 9 am. In summer 1999, two peaks were found in PM_{10} mass around 8 o'clock in the morning and 12 at noon and those corresponded closely to coarse particles due to re-suspension of larger particles in the dryer and hotter summer months (Figure 3.6g). Particle numbers were found to have three high concentration peaks over a time period from 8 to 16 o'clock. The first and second number peaks were consistent with all other pollutants, corresponding closely to traffic activities which favour both pollutants from vehicle exhaust emissions and vehicle-induced re-suspension of dust. The third peak however displayed around 15-16h was not correlated with other pollutants although a slight increase was observed in the NO_x concentration (Figure 3.6h). Apart from vehicle exhaust emissions it may be also related to photochemical reactions as it occurred close to the diurnal peak in ozone concentration with a maximum around 2-3 p.m.

Autumn 1999 also showed a very good correlation of PM_{10} to coarse particles where three peaks in PM_{10} concentrations were observed at the morning rush hour, noon and early afternoon (Figure 3.6i). Unlike the previous situations, during December 1999 PM_{10} was consistently associated with fine particles originated from vehicle exhaust emissions, which is clearly seen from the good correlation between PM_{10} and the gaseous pollutants, NO_x and CO (Figure 3.6j).

Figure 3.6 Diurnal variation of concentrations at Marylebone Road

Figure 3.6a Diurnal variation at LM; spring 98/99

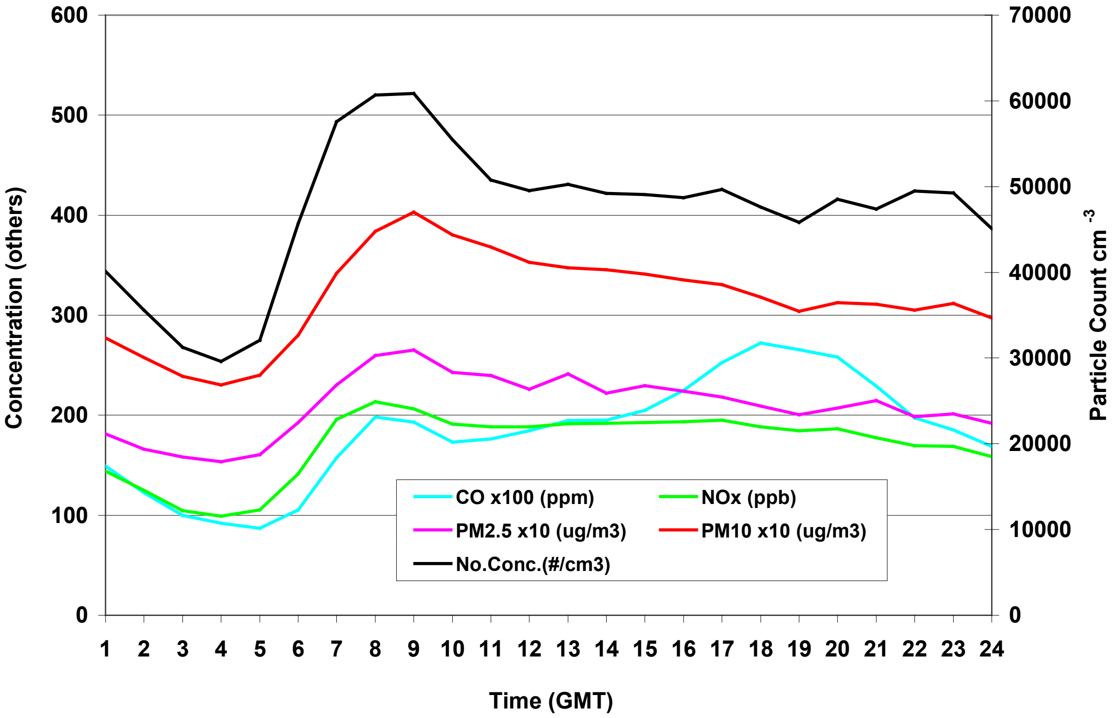


Figure 3.6b Diurnal variation at LM; summer 97/98/99

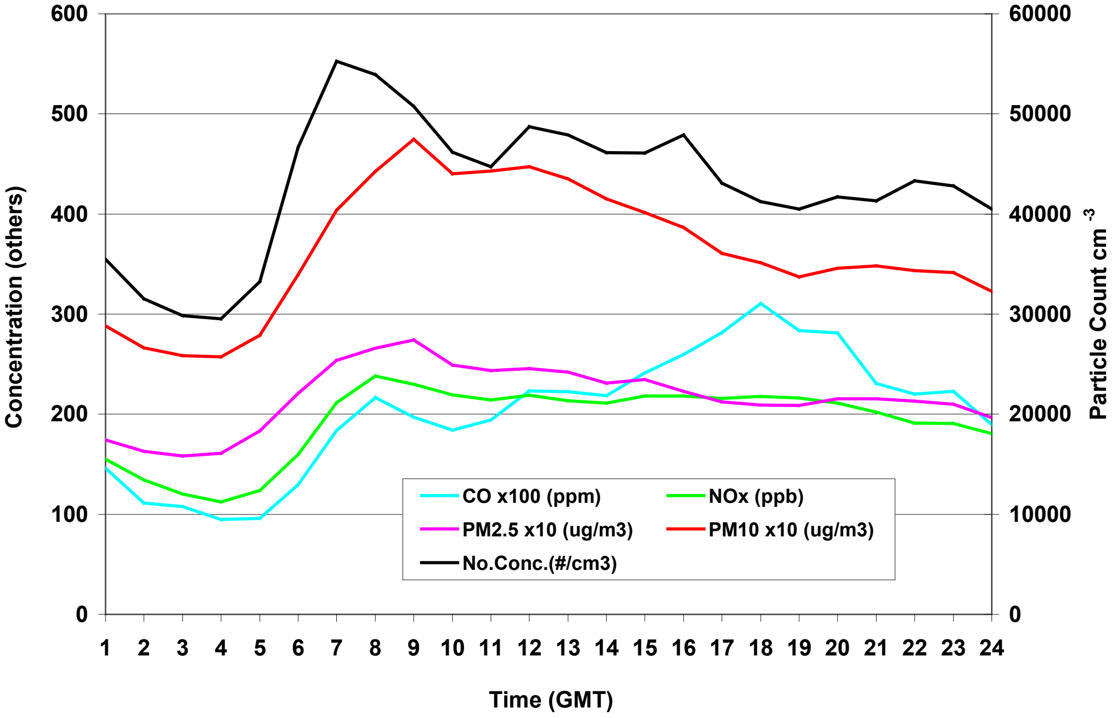


Figure 3.6c Diurnal variation at LM; autumn 97/98/99

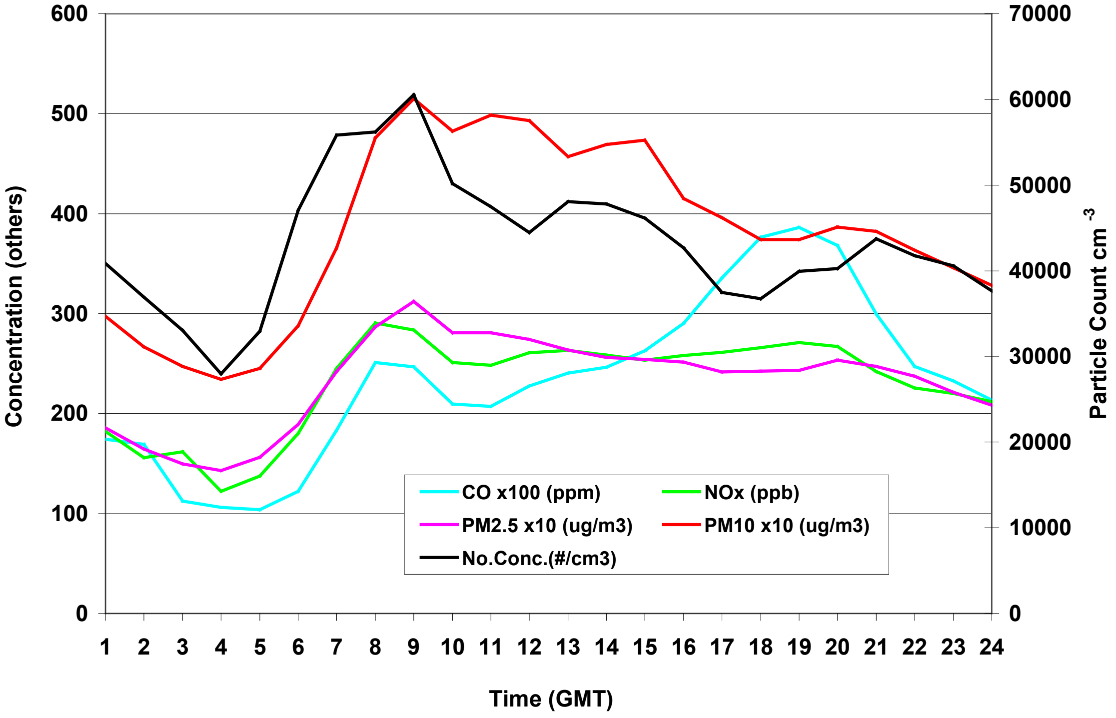


Figure 3.6d Diurnal variation at LM; winter 97/98/99

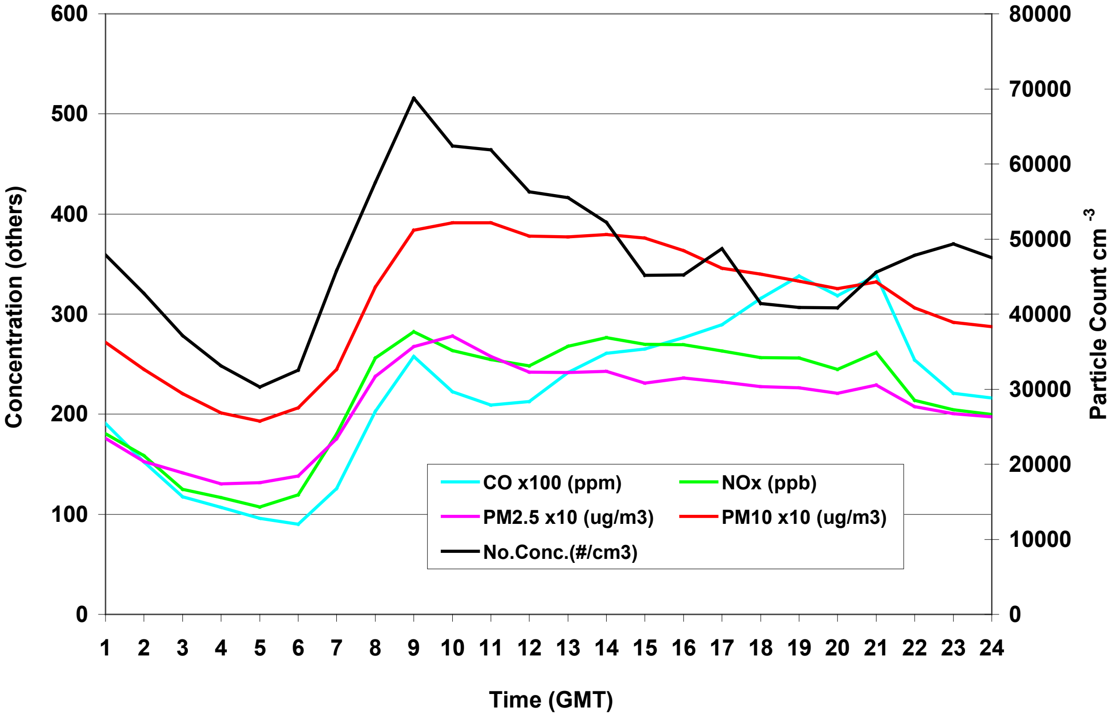


Figure 3.6e Diurnal variation of SO_2 concentration (ppb) at LM

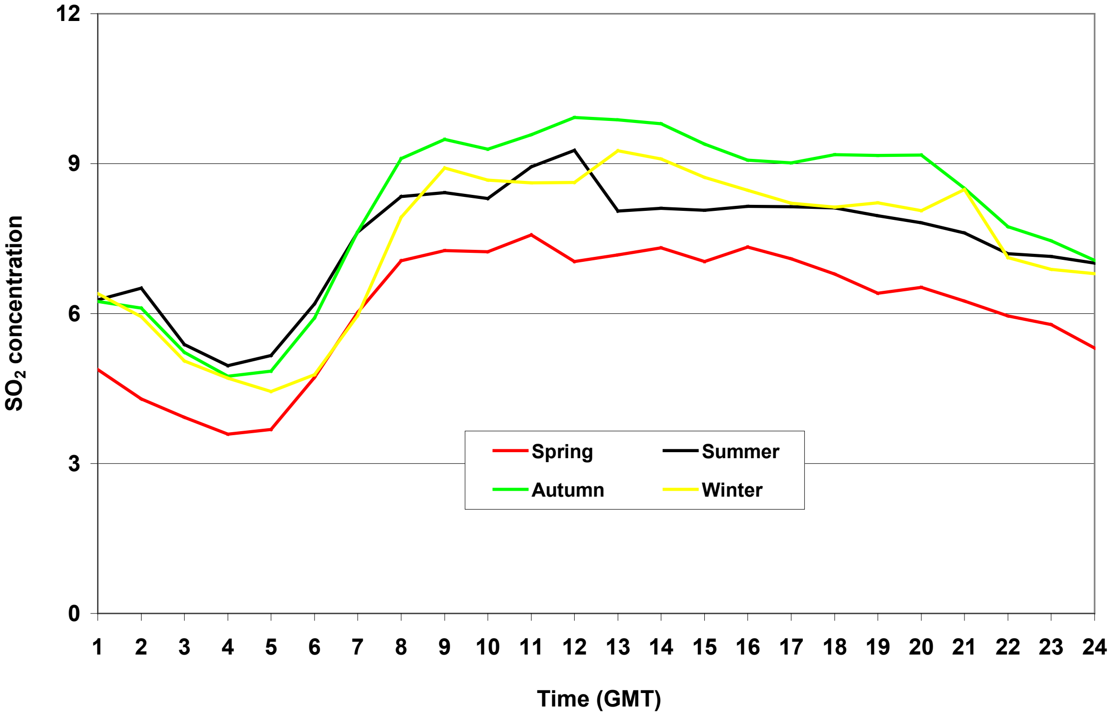


Figure 3.6f Diurnal variation of coarse particle concentration (μg m^{-3}) at LM

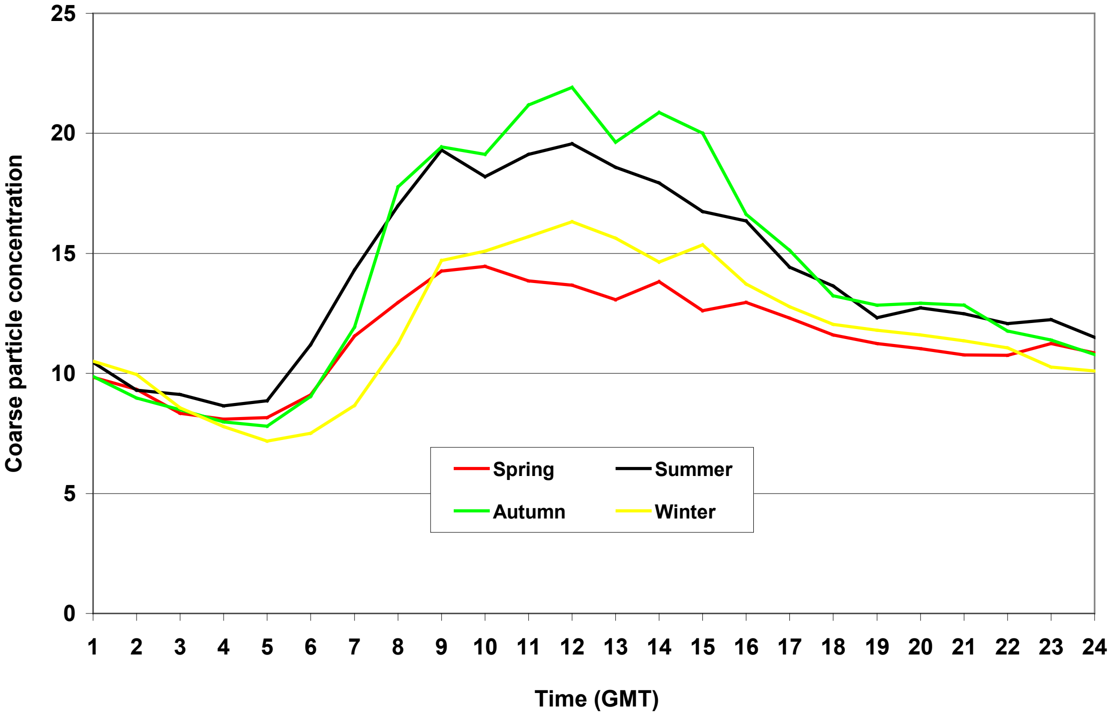


Figure 3.6g Diurnal variation at LM; summer 1999

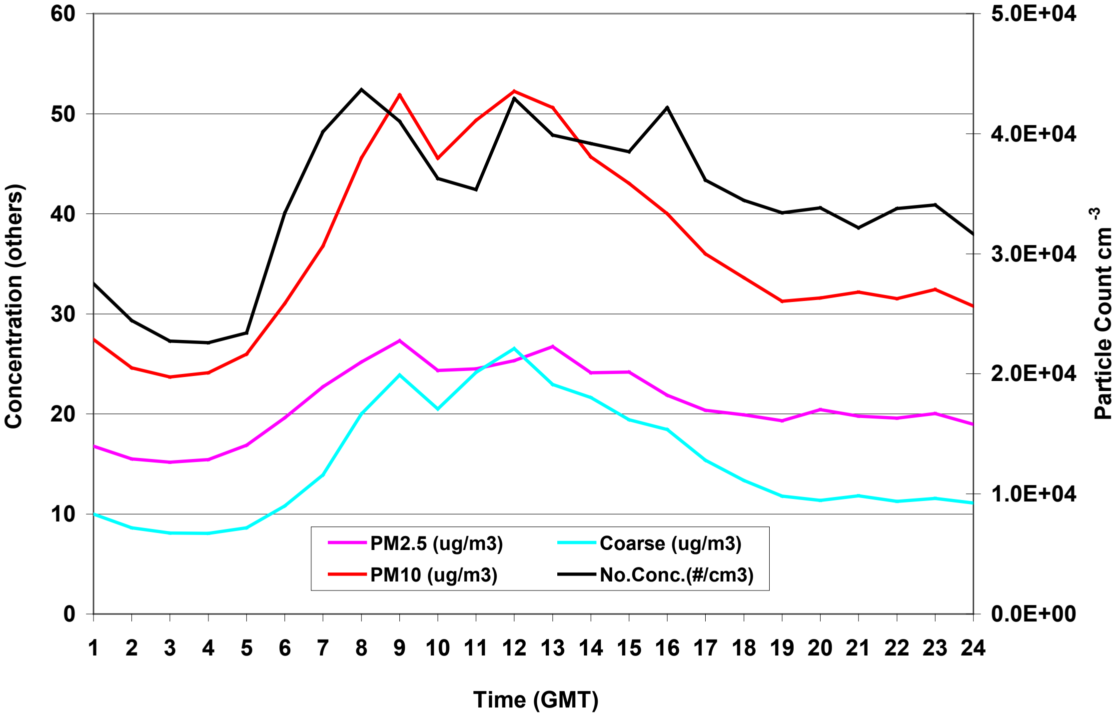


Figure 3.6h Diurnal variation at LM; summer 1999

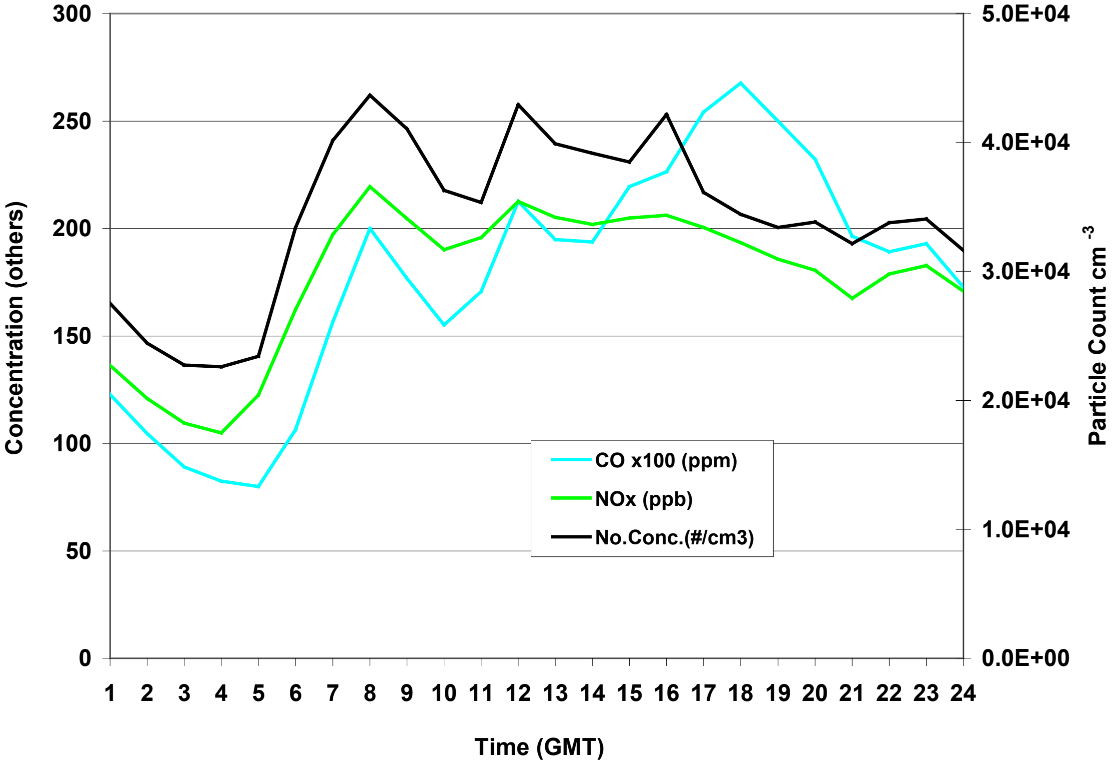


Figure 3.6i Diurnal variation at LM; autumn 1999

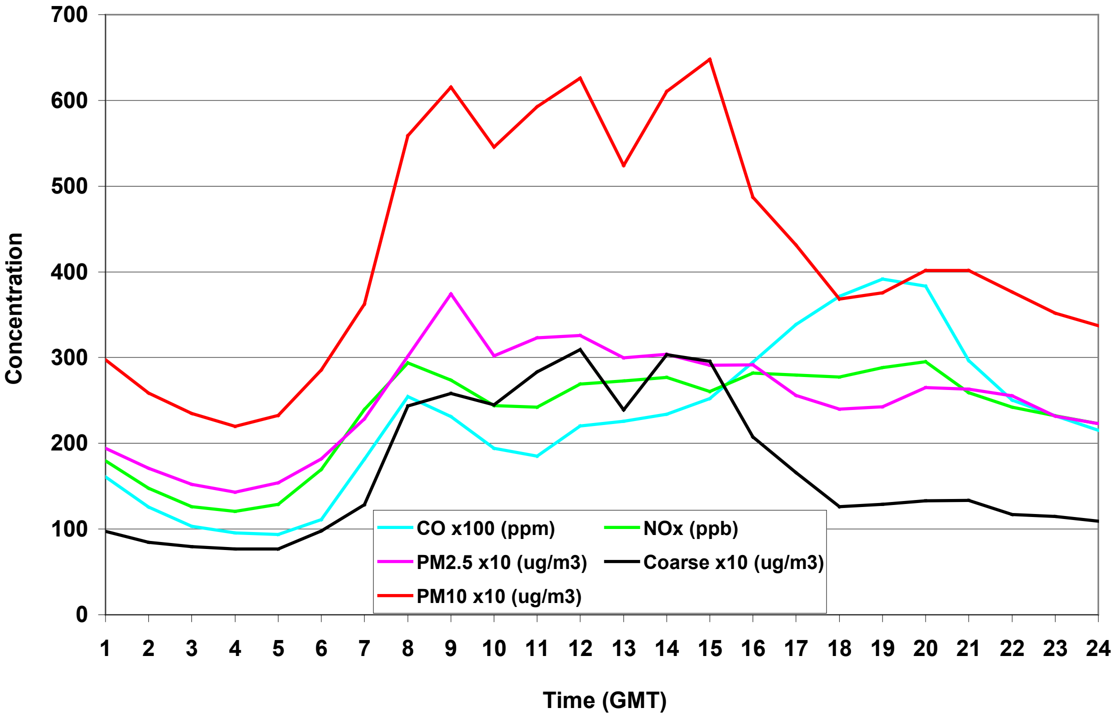
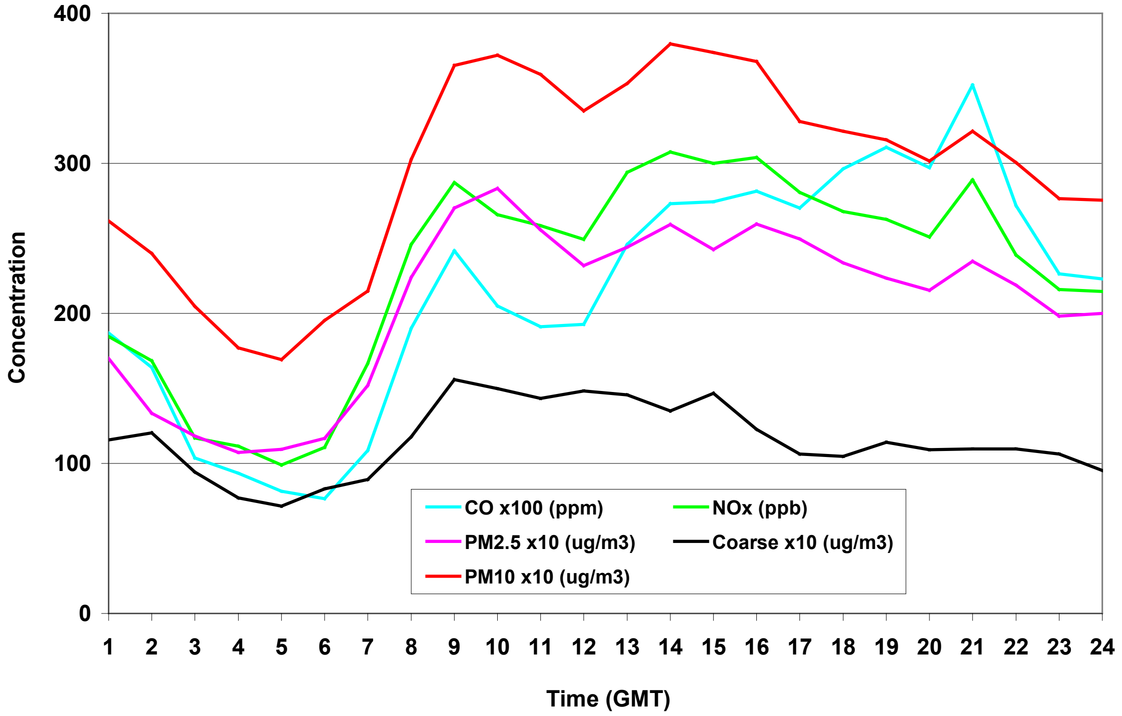


Figure 3.6j Diurnal variation at LM; December 1999



Similar diurnal variations were found at the urban centre London Bloomsbury site shown in figures 3.7a to 3.7f. Morning peaks in the concentrations of particle mass, number and gaseous pollutants were also observed as a result of airborne particles having a similar source as the gases, i.e., urban traffic. However the morning rush hour peaks at the background site occurred about one hour later (9-8 am) than the kerbside site showing the difference in traffic pattern between the two sites. In addition to CO, clear evening rush hour peaks in NO_x and particle concentrations were also observed for London Bloomsbury particularly in winter and autumn seasons (Figures 3.7e&f). Coarse particle concentration seems to be related to traffic but less marked in comparison with Marylebone Road showing a minimum in the early hours of the day and a small morning rush hour peak. Similar with LM, wind speed appeared to have re-suspension effect on the coarse particles since the concentrations are elevated over the middle of the day when wind speeds are higher. The diurnal variation of SO_2 concentration (not shown here) is slightly different from the other pollutants at the site indicating a small morning rush hour peak and following a gradual decrease for the rest of the day.

Figure 3.7 Diurnal variation of concentrations at London Bloomsbury

Figure 3.7a Diurnal variation at LB; spring 98/99

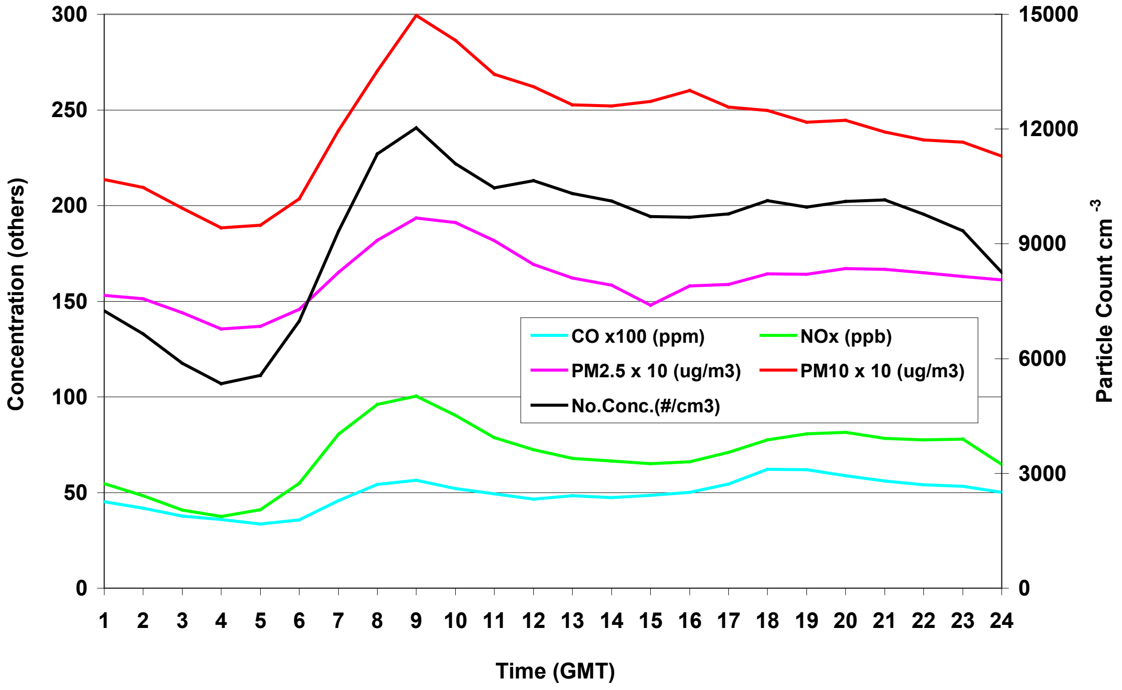


Figure 3.7b Diurnal variation at LB; summer 97/98/99

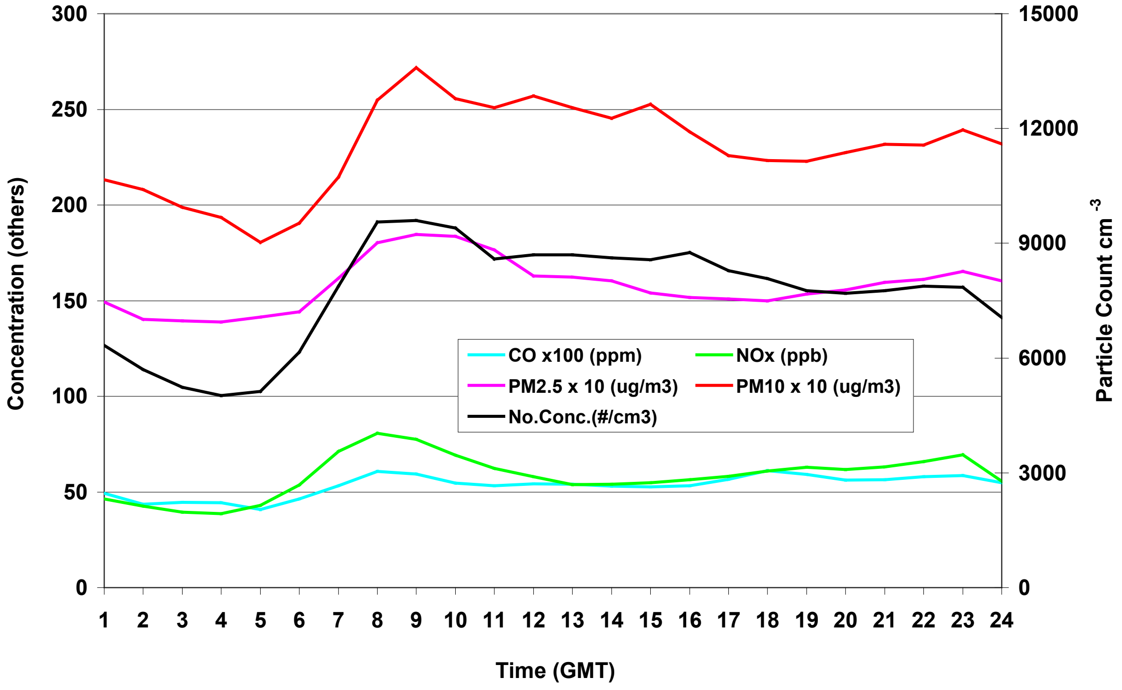


Figure 3.7c Diurnal variation at LB; autumn 97/98/99

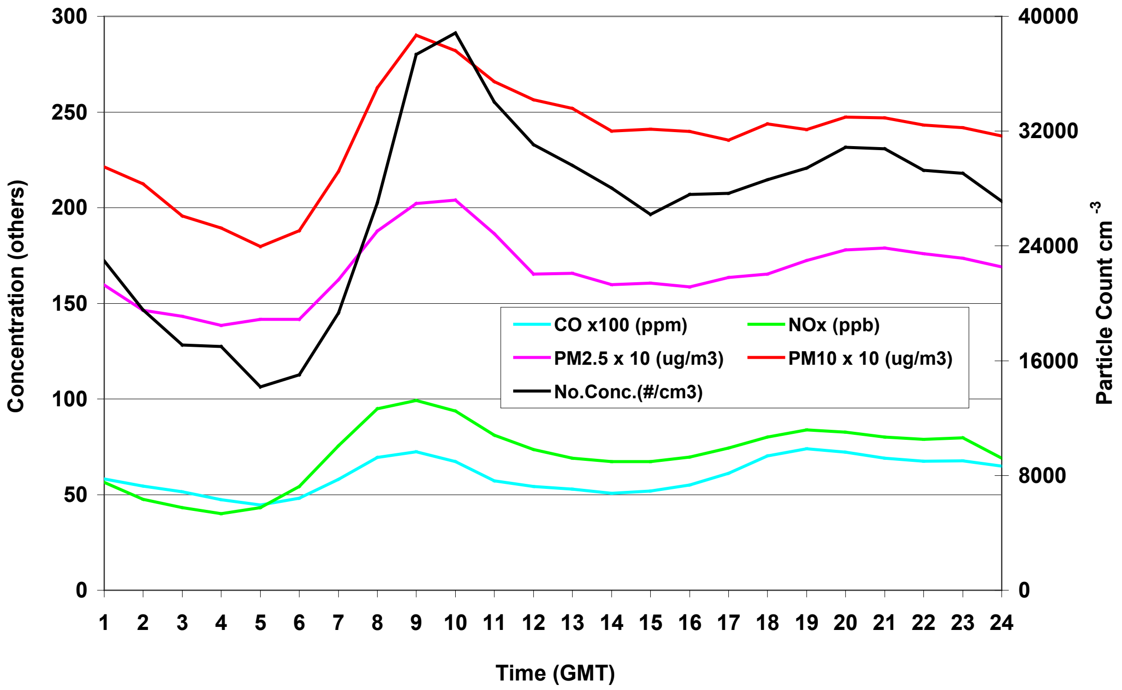


Figure 3.7d Diurnal variation at LB; winter 97/98/99

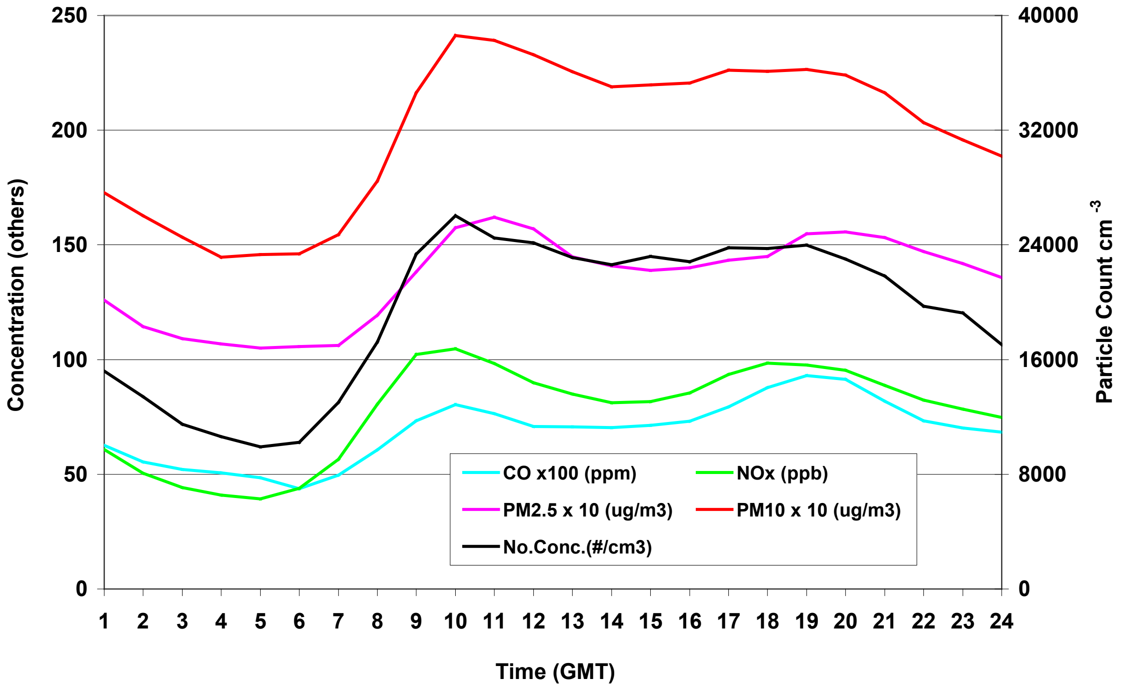


Figure 3.7e Diurnal variation at LB; winter 98/99

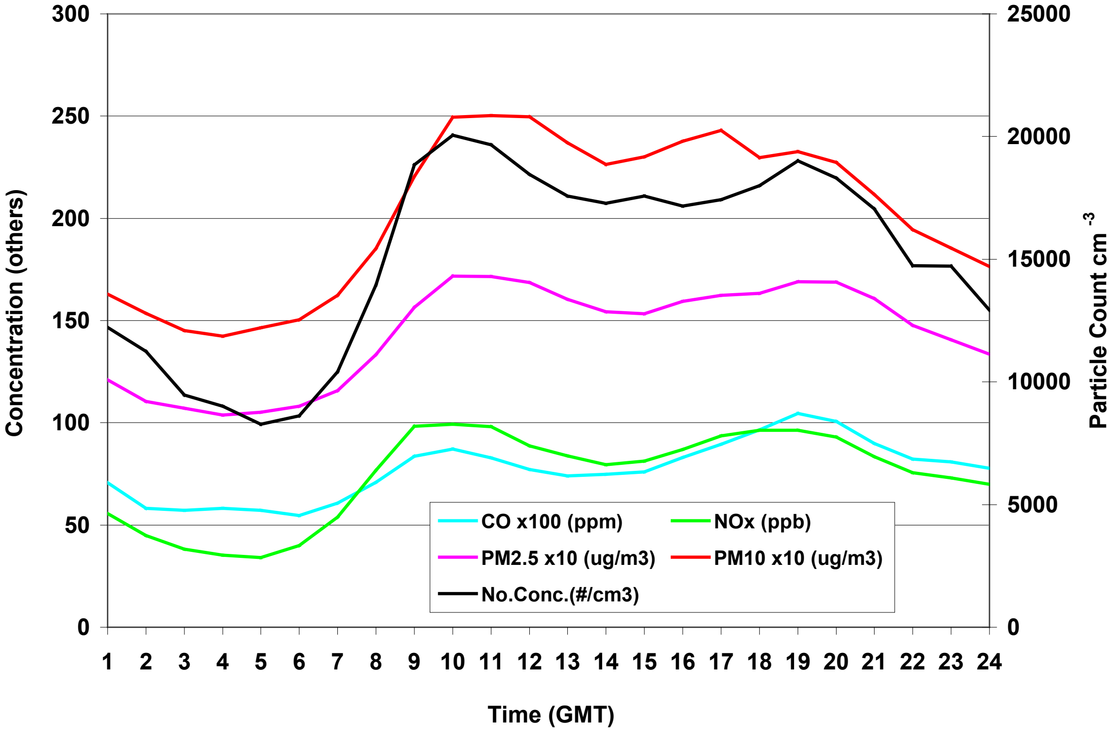
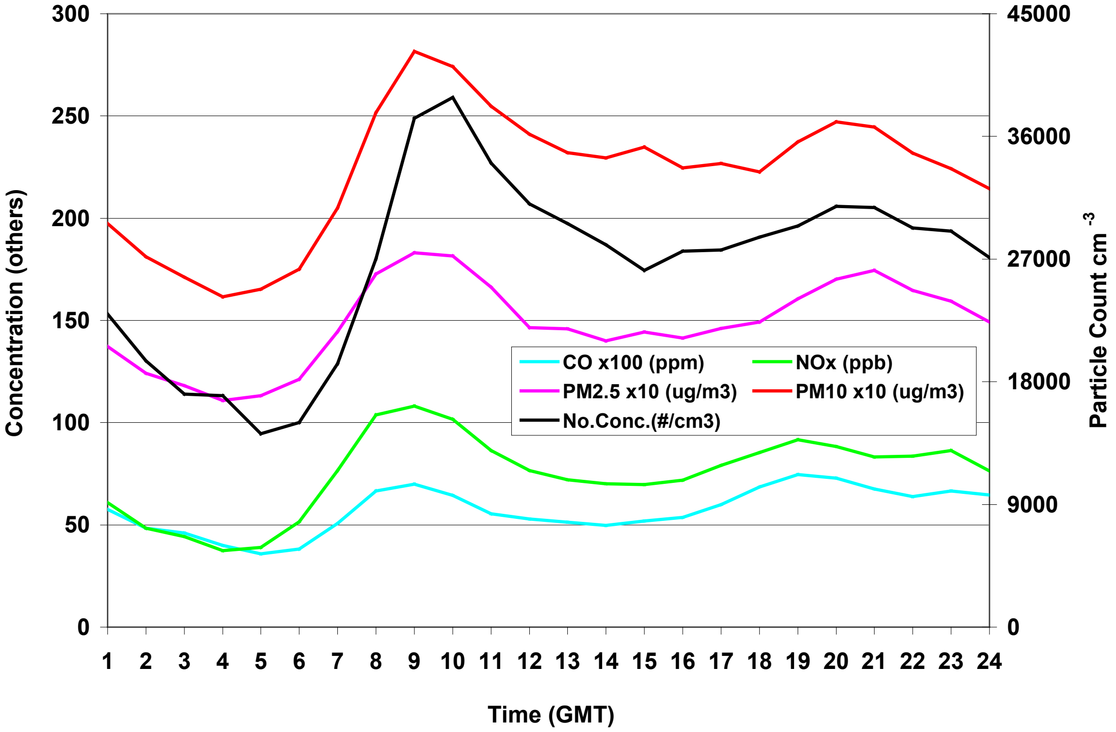


Figure 3.7f Diurnal variation at LB; autumn 1999



Diurnal patterns at the Rochester site are not clear marked and vary between seasons and species (Figures 3.8a-d). PM_{10} mass is dominated by fine particles during all seasons and its correlation to NO_x is weak. The nearest road from this site is located to the east and about 80 metres away with a low traffic volume and its influence on particle levels is largely controlled by weather conditions, like wind speed and wind direction. Therefore, pollution sources other than local traffic may dominate the particle concentrations at this site.

The levels of coarse particles also follow the wind profiles keeping low at night and high in the daytime. Surprisingly, SO_2 concentrations appeared to be high in the middle of the day (Figure 3.8e) and higher concentrations were observed in summer similar to the result found at the urban background site in Leeds where the highest concentrations appeared in summer and autumn (Harrison and Deacon, 1998). One of the possible sources is thought to be power station plumes from east London, which can easily travel down to the ground level when the inversion boundary layer depths are increased by solar radiation during the day and summer with the prevailing westerly wind. In winter or at the night the plumes are usually buoyant and may contribute nothing to ground level air quality due to shallow mixing boundary layers (Deacon et al., 1997).

Figure 3.8 Diurnal variation of concentrations at Rochester

Figure 3.8a Diurnal variation at RO; winter 97/98/99

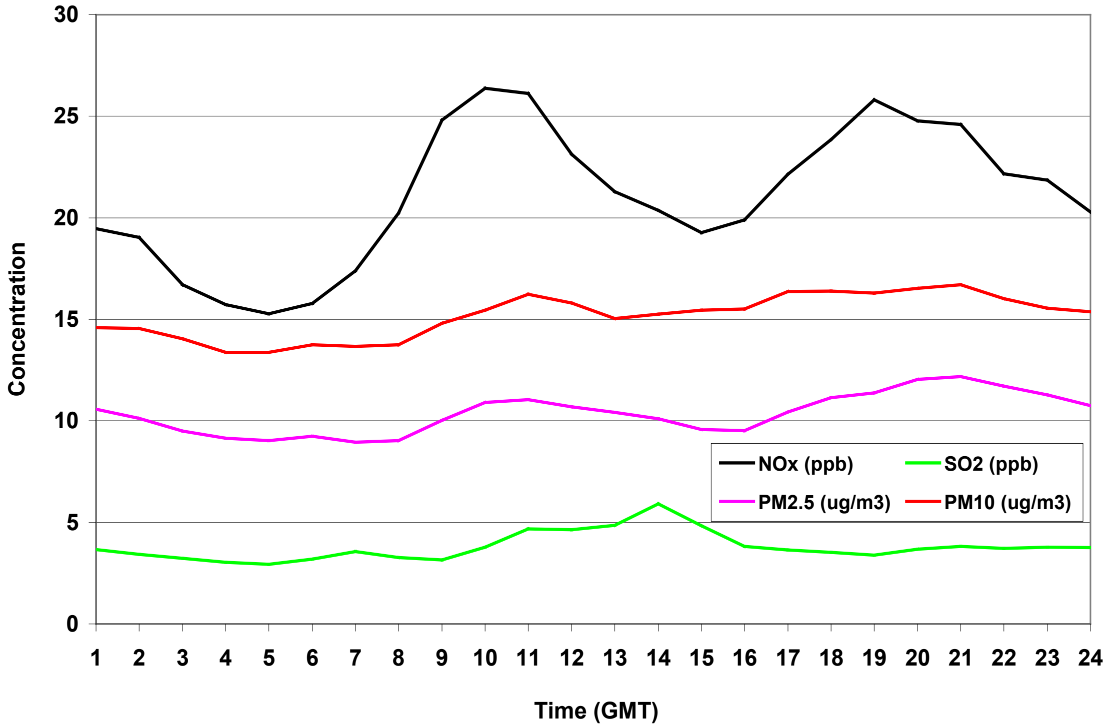


Figure 3.8b Diurnal variation at RO; autumn 97/98/99

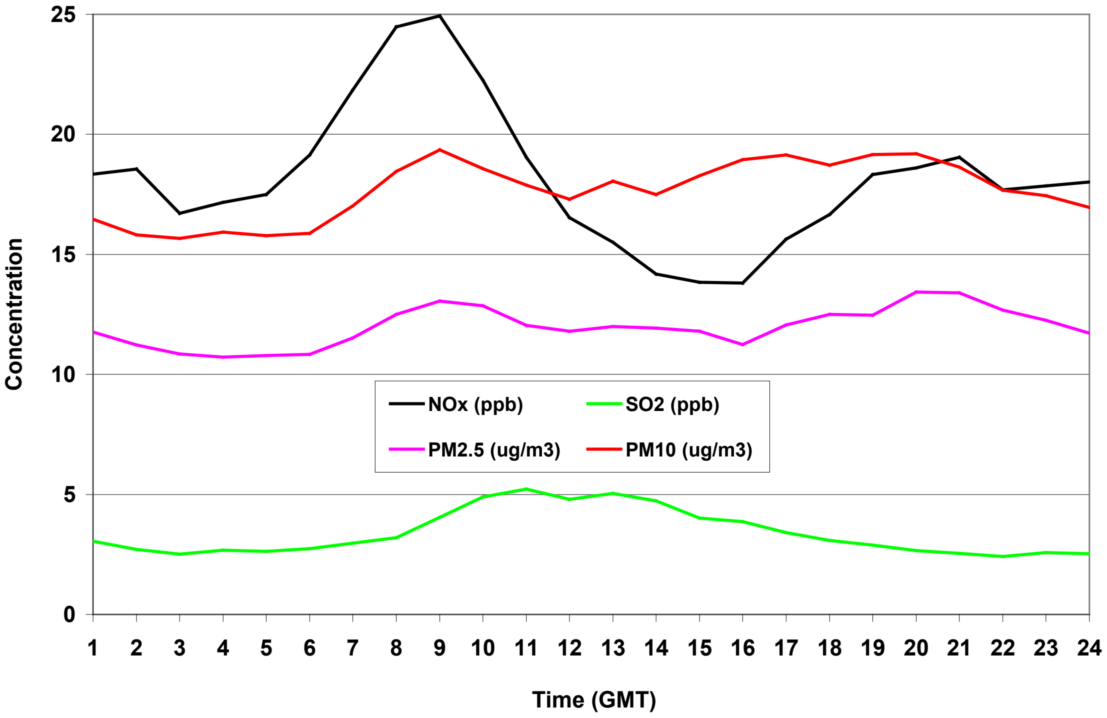


Figure 3.8c Diurnal variation at RO; summer 97/98/99

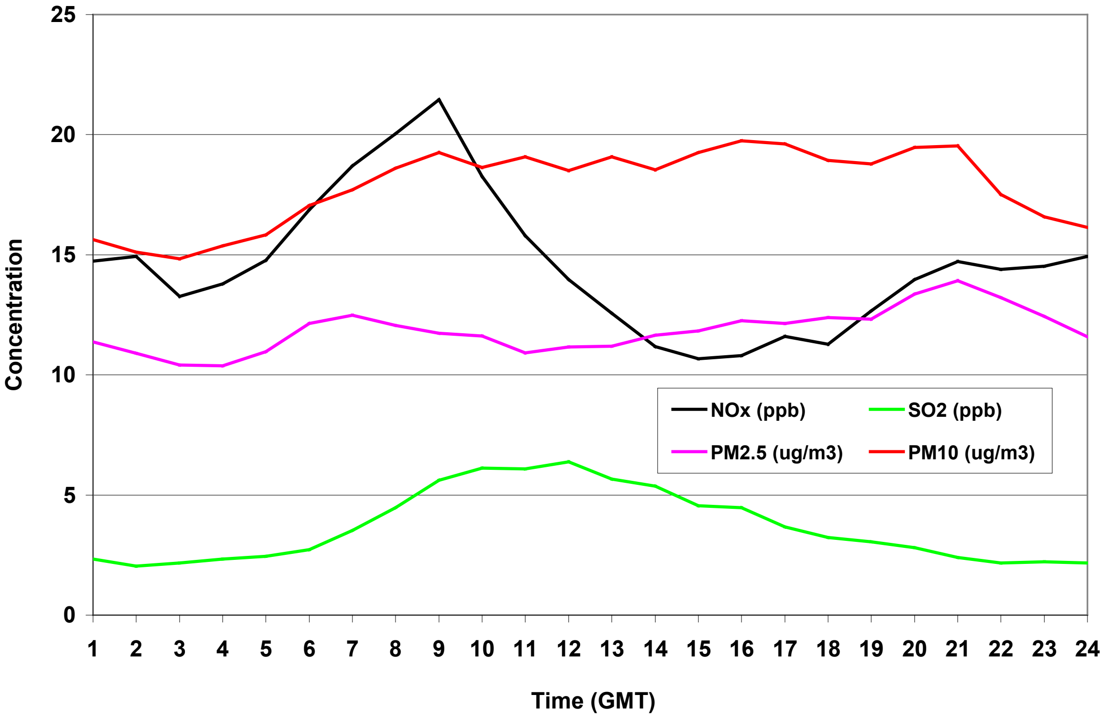


Figure 3.8d Diurnal variation at RO; spring 98/99

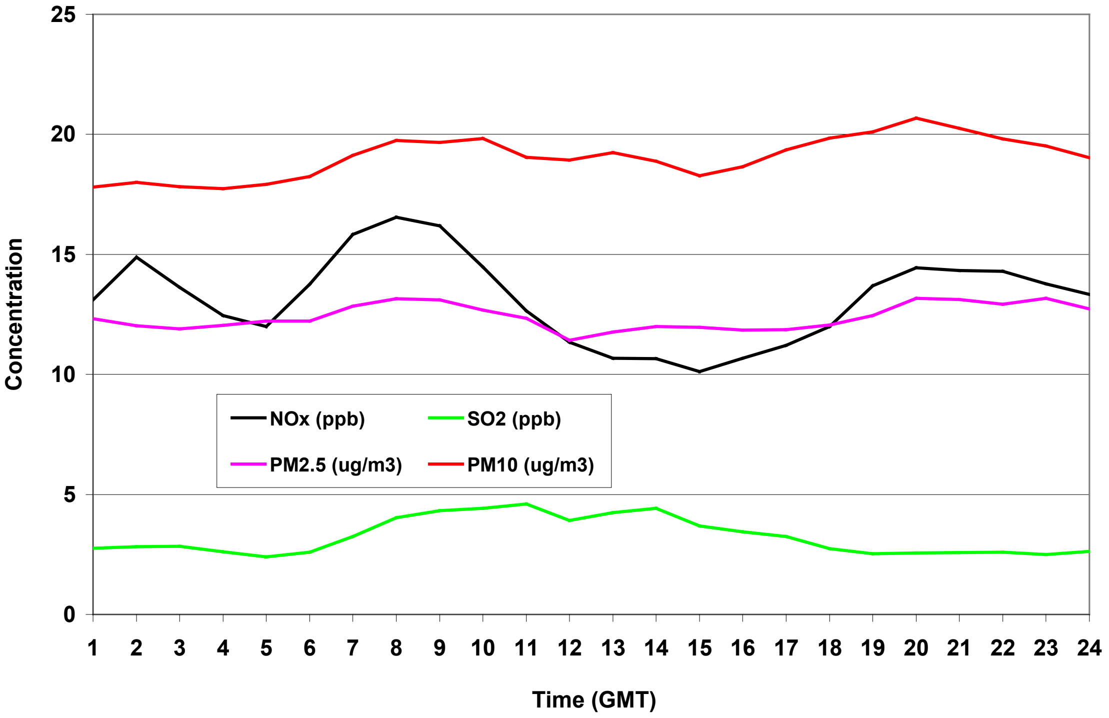
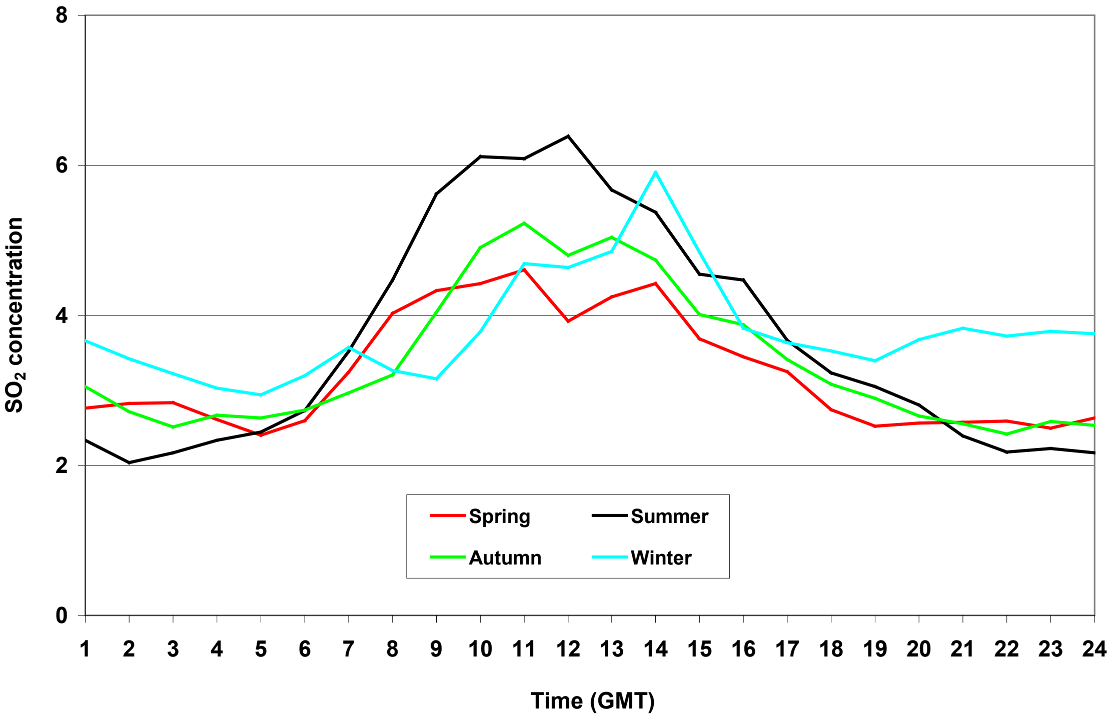


Figure 3.8e Diurnal variation of SO_2 concentration (ppb) at RO



At Harwell, fairly constant and stable concentrations were seen in particle mass whereas particle numbers and gaseous pollutant levels varied a lot throughout 24 hours (Figures 3.9a-d). Similar as Rochester, diurnal variation is not clearly marked and very little influence of road traffic was seen from these rural sites, although consistent morning and evening rush-hour peaks were clearly found in Autumn except SO_2 which showed midday maximum. Again the concentrations of SO_2 tended to be high in the middle part of the day, but were much lower than at the Rochester site. Particle numbers appeared to have a maximum at night in winter and autumn seasons whereas summer and spring showed peaks in the late at the night and in the early hours of the afternoon. The latter is likely to be related to new particle formation through homogeneous nucleation, such as chemical conversions of SO_2 to SO_4^{2-} under the condition of sunny and clear sky in summer and spring seasons (Birmili and Wiedensohler, 2000; Birmili et al, 2000). Figure 3.9e shows the diurnal profile of O_3 at the Harwell site, indicating that it is likely photochemical reactions have been involved in the new particle formation. These will be discussed in detail in Chapter 5. There is no clear indication for the night-time particle number concentration peaks, but heterogeneous nucleation processes may be involved.

Figure 3.9 Diurnal variation of concentrations at Harwell

Figure 3.9a Diurnal variation of concentration at HAR; spring 98/99

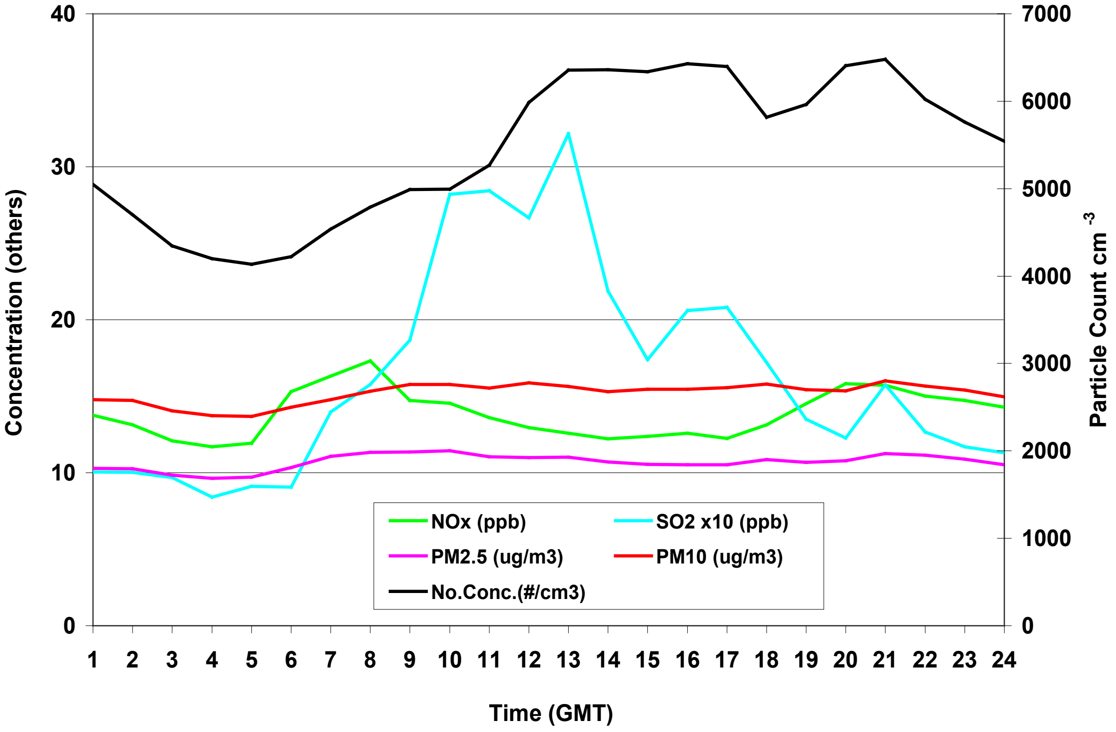


Figure 3.9b Diurnal variation of concentration at HAR; summer 98/99

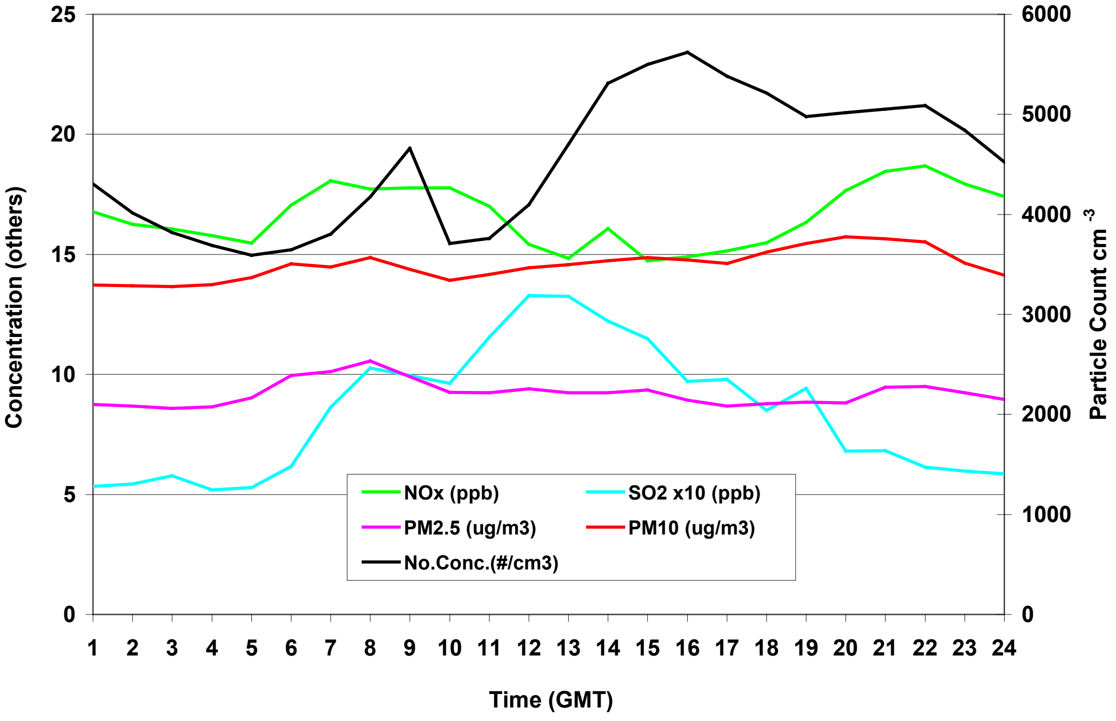


Figure 3.9c Diurnal variation of concentration at HAR; autumn 97/98/99

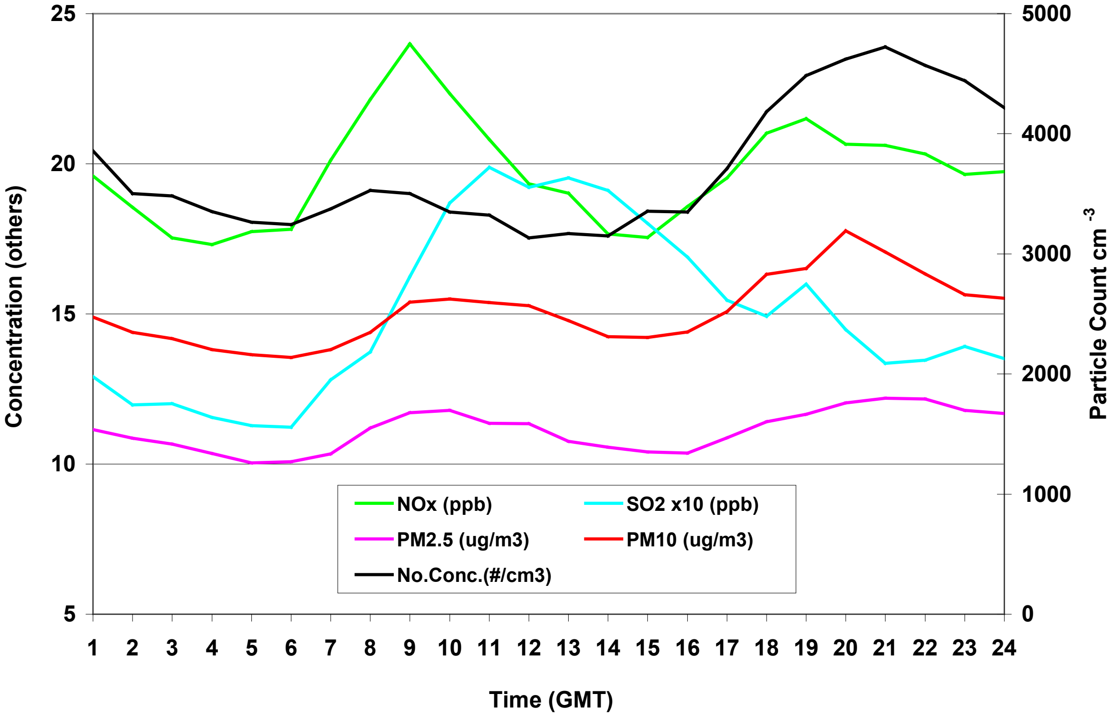


Figure 3.9d Diurnal variation of concentration at HAR; winter 97/98/99

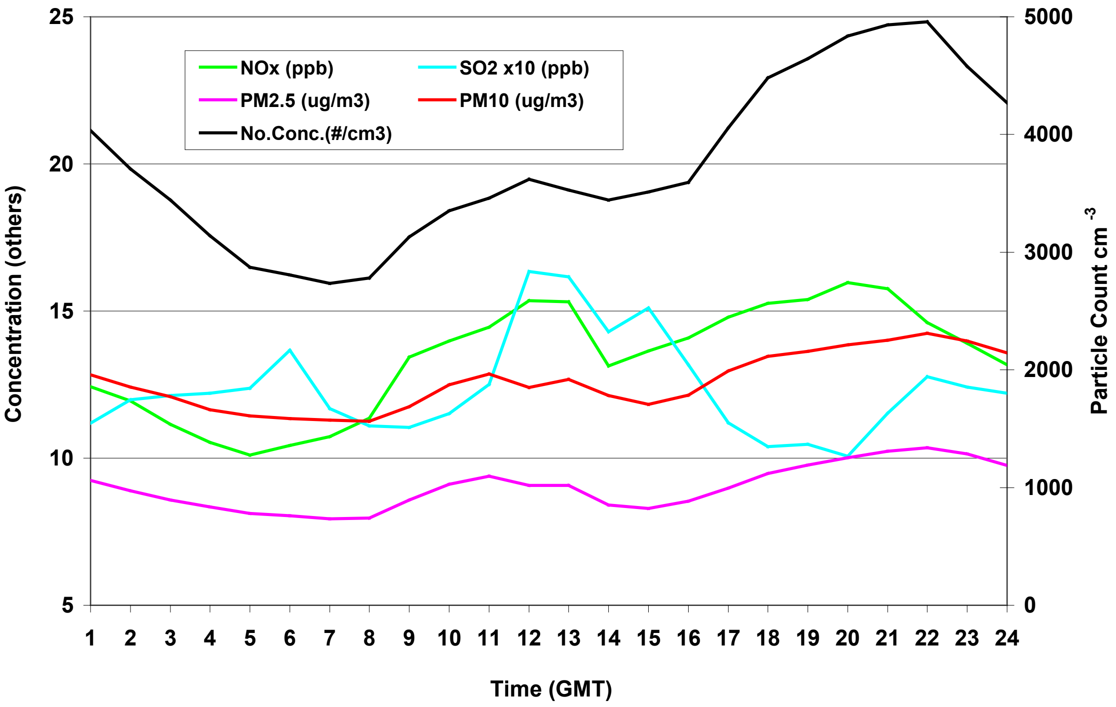
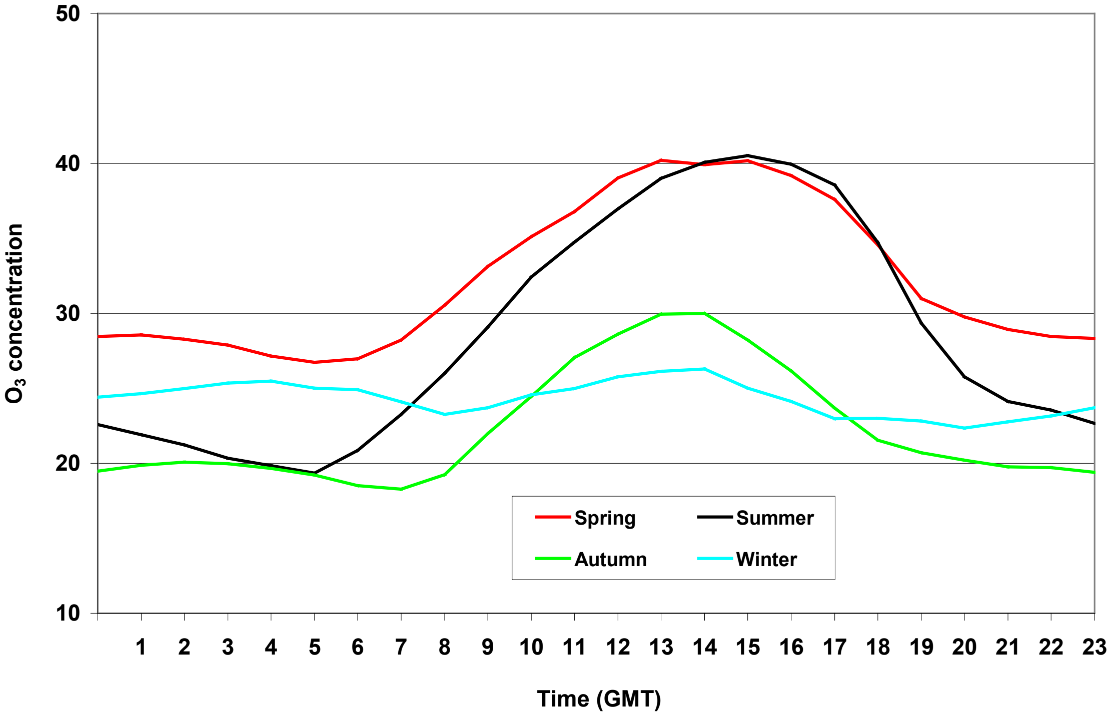


Figure 3.9e Diurnal variation of O_3 concentration (ppb) at HAR



3.5 Summary

An examination of airborne particle concentration levels and trends has been conducted using a two-year and seven-month data set from four U.K. sites. The results have given indications of the following:

Different particulate pollutant concentrations including particle mass, particle numbers and gaseous pollutants were found at these sites and the levels are in the order of London Marylebone Road > London Bloomsbury > Rochester > Harwell. Based on the average concentrations over the whole period, the local elevation was about 100% of primary pollutants at the roadside LM, relative to the urban background site LB. The increments in PM_{10}, $PM_{2.5}$ and coarse particle concentrations were 11.9, 6.4 and 5.5 $\mu g\ m^{-3}$ respectively, indicating that road traffic activities are very significant sources affecting PM_{10} concentrations of both fractions. The two rural sites Rochester and Harwell show much lower concentration levels due to the least influences from these local sources, mainly road transportation, which is clearly marked by greater differences in NO_x and CO concentrations between the urban and rural sites.

Larger ratios in coarse than in fine particle concentrations between the two London sites indicates the importance of local sources in contributing to large particles and the uniformity of fine particles controlled by both local and long-range sources. Consistent with traffic-generated pollutants NO_x and CO, greater differences occurred between sites in particle numbers than particle mass indicating that particle number is a better indicator for site comparison particularly for evaluating the levels of vehicle exhaust emissions. Similar PM_{10} concentrations have been found at the urban background sites London Bloomsbury, Birmingham Centre, Birmingham East and Birmingham, Hodge Hill, based on long-term measurements, which suggests that measurement at one site can represent similar sites on a fairly large scale.

Results from the percentile distributions of particle mass data show that London Marylebone Road suffers the greatest number of exceedences of the EPAQS standard. PM_{10} emissions would have to be reduced by about 39% and 42% for the whole period and the year 1999 respectively, to achieve the target of 99th percentile in compliance with the EPAQS standard. In comparison the count of exceedences of the standard is likely to be decreased significantly in London Bloomsbury whereas the chances are very small at the two rural sites.

Whilst very little seasonal variations can be found in the concentrations of particle mass, higher coarse particle concentrations are most likely to appear in summer seasons when hot and dry weather conditions favours the particle suspension processes influenced by wind speeds, traffic and any other local disturbance. London Marylebone Road is mainly affected by vehicle-driven particle resuspension while rural sites Rochester and Harwell are likely more related to wind or other local activities. In contrast higher fine particle concentrations may occur during both winter when cold weather favours building up pollutant concentrations mainly from primary sources like vehicle exhaust emissions, and summer when sunny weather favours secondary particle formation. Broadly similar seasonal patterns of particle mass concentrations were found at London Bloomsbury, Rochester and Harwell sites, suggesting that synoptic factors are important in affecting the advection of polluted air-masses.

Consistent seasonal variations were observed in CO concentrations at the two London sites showing higher levels in winter and autumn due to incomplete fuel combustion and lower levels in spring and summer. Generally, as a local vehicular source similar to CO, NO_x concentrations appeared to be higher in winter and autumn than in summer and spring at LM, LB and RO sites, but the Harwell site exhibited the highest levels in autumn 1997 and summer 1999. London Bloomsbury is the only site where SO_2 followed the patterns of other primary pollutants, giving higher concentrations in colder seasons, whereas this pattern may occur during any season of the year at the other sites. For winter seasons SO_2 is dominated by ground level sources particularly at sites polluted with road traffic, while summer seasons can also be affected by point source plumes from power stations which is easily transferred downward to ground level.

The temporal trend of particle numbers can not be outlined from the monthly averages due to severe data losses at the London sites. There is no clear trend at Harwell although the data capture was higher.

Broadly consistent diurnal variation was observed between PM_{10}, $PM_{2.5}$, particle number count and vehicle exhaust related gaseous pollutants NO_x and CO at the urban sites indicative of the influence of vehicle exhaust emissions. CO appeared to behave irregularly at LM, showing a higher evening peak, which was not observed at the other sites. Particle number concentrations tend to rise far more quickly than particle mass at the morning rush-hour as very small particles freshly emitted from vehicle exhaust will mainly contribute to particle count showing a quicker response, which is also observed in the earlier studies in Birmingham. The morning rush-hour peaks occurred one hour late at London Bloomsbury in comparison with Marylebone Road highlighting the differences in traffic characteristics between the two sites.

Less clear diurnal patterns appeared at the rural sites and poor correlation between particle mass and number concentrations with NO_x was found reflective of little influence of road traffic. Coarse particles tended to increase around the middle of the day when both wind speeds and human activities are the highest. Interestingly, SO_2 showed high concentrations in the middle of the day at Rochester and Harwell, which is likely related to power station plumes reaching ground level when the mixing layer depth is increased.

CHAPTER 4

RELATIONSHIP BETWEEN AIRBORNE PARTICLES AND GASEOUS POLLUTANTS AND FACTORS AFFECTING THEIR CONCENTRATIONS

4.1. Introduction

To understand the potential effects of air pollution, and to develop an appropriate strategy for controlling their extents, it is critical to have knowledge on the nature and the origins of airborne particulate pollutants and the atmospheric processes affecting their formation and fate. It has been recognised that aerosol consists of both man-made pollutants and material from natural sources. Earlier studies in Birmingham indicate that there are three main sources, which contribute to PM_{10} concentrations. They are primary fine particles from industrial and combustion sources, secondary aerosol and wind-blown soil and re-suspended street dust (QUARG, 1996; Harrison et al., 1996; Harrison et al., 1997b). Many studies both in the UK and other countries have identified road traffic as a major source of airborne particulate matter in the urban atmosphere (QUARG, 1996; Harrison et al., 1996; Harrison et al., 1997a&b; Rajkumar and Chang, 2000; Janssen et al., 1997; Olcese and Toselli, 1998). The airborne particulate concentrations in the UK are frequently over the EPAQS air quality standard as 50 $\mu g\ m^{-3}$ of 24h-running mean at urban sites. The statistical results from Chapter 3 show that the urban sites are most likely to exceed the standard, particularly at the roadside London Marylebone Road. Air pollution episodes can arise from both local or long range transport and are likely to be dominated by primary vehicular emissions in winter months while summer episodes may arise from both re-suspension of road dust or secondary particles (QUARG, 1996; Harrison et al., 1997b). In November 1995 the Birmingham site experienced an air pollution episode due to local bonfire night celebrations. Very high concentrations of particle mass, particle count, surface area and gaseous pollutants NO_x and CO were detected (Harrison et al., 1999a&b). Other studies have shown that PM_{10} concentrations are influenced by components which are long-rang transported. Two pollution episodes were identified in 1996 from January to February and March in the UK, when elevated PM_{10} was generally associated with air masses arriving from mainland Europe, whereas another episode in July 1996 was dominated by local sources (King and Dorling, 1997; Stedman, 1997; Malcolm et al., 2000). Hoek et al (1997) also reported a widespread episode across Europe in 1994 suggesting a long-range transported source.

Meteorology is another major factor influencing airborne pollutant concentrations. Wind speed and wind direction affect pollutant transport and suspension while temperature affects fuel usage and chemical reactions in the atmosphere. Solar radiation causes photochemical reaction among air pollutants and precipitation may remove pollutants from the atmosphere. Relative humidity influences the aerosol size, and hence their mass concentrations (Seinfeld and Pandis, 1998). The focus of this chapter is on presenting results related to correlation between particles and gaseous pollutants, air pollution episodes and EPAQS exceedences as well as sources and factors influencing the pollutant concentrations.

Linear regression analysis has been used to test associations between any two-air pollutant variables throughout Chapters 4 and 5. The Pearson's correlation coefficient (R) or the square of the Pearson's correlation coefficient (R^2) was used to measure the association between two air pollutants. A rough guide to the degree of the association given by some statistical references indicates that R, in the range 0.00-0.19, represents a very weak correlation, 0.20-0.39 a weak correlation, 0.40-0.69 a modest correlation, 0.70-0.89 a strong correlation and 0.90-1.00 a very strong correlation. In order to know whether the correlation is significant between two variables, the null hypothesis (H_0), a hypothesis of no correlation, was tested consulting a table for Pearson product moment correlation values at the 0.05 and 0.01 levels of significance, with the number of degrees of freedom $n - 2$ (n is the number of observations). In this study all of the coefficients are calculated based on pairs of data with at least 400 data points. Therefore, a minimum value at the 99% level of significance was obtained as 0.13 for R or 0.016 for R^2. Significant relationships have been found for most of the analyses performed.

It must be pointed out that three conditions should be met in order to apply the analyses. First, for all values on the independent variable the distribution of the values on the dependent variable must be approximately normal (*normality*). Second, for all values on the independent variable the distribution of the values on the dependent variable must be approximately equal in variability (*homoscedasticity*). In other words, the sum of squares of the distances from the points of the scatter diagram to the regression line in the y direction must be close to zero. Third, the regression should apply only within the range of the observed independent variable (x) values in the data, but not be extended below the minimum value of x or above the maximum value of x.

4.2 Intra-Site Pollutant Correlation

4.2.1 Correlation between PM_{10}, $PM_{2.5}$ and Coarse Particles

Some results from this project were presented in the APEG report (APEG, 1999) but only for a short period. The data showed generally strong correlation between PM_{10} and $PM_{2.5}$. A full data set covering the whole period from June 1997 to December 1999 has been investigated seasonally using both hourly and daily average concentrations. Table 4.1 shows the results of seasonal regression analyses between particle mass fractions using hourly data taking account of the whole sampling period. Generally, higher correlation (R^2 = 0.61-0.87) between PM_{10} and $PM_{2.5}$ was found at all sites in comparison with the correlation (R^2 = 0.39-0.84) of PM_{10} to coarse particles highlighting that fine particles are the major component of the PM_{10} mass.

Exceptionally at Marylebone Road in summer and autumn seasons, better correlations were observed between PM_{10} and coarse than fine particles. Higher gradients were found for coarse particles (0.53 in summer and 0.56 in autumn), whereas lower gradients were observed for fine particles (0.47 and 0.44). In fact, these exceptions were caused by very high hourly PM_{10} concentrations over 100 $\mu g\ m^{-3}$. Figures 4.1 and 4.2 show the regression plots for summer and autumn months respectively on Marylebone Road. Apparently, the higher gradients were related mainly to those hours when PM_{10} concentration exceeded the value of 100 $\mu g\ m^{-3}$ in summer and 130 $\mu g\ m^{-3}$ in autumn. For most of those points, PM_{10} were composed of a larger proportion of coarse than fine particles. Clearly at London Marylebone Road, both fine and coarse particles can contribute substantially to the PM_{10} episodes and the latter is particularly significant in the summer and autumn seasons.

Table 4.1 Seasonal results of regression analyses of $PM_{2.5}$ and PM_{10} data at DETR sites for hourly data

	$PM_{2.5} = m\ PM_{10} + c$	R^2	$PM_{coarse} = m\ PM_{10} + c$	R^2
Spring				
LM (98 & 99)	$PM_{2.5} = 0.63\ PM_{10} + 0.52$	0.80	$PM_{coarse} = 0.37\ PM_{10} - 0.53$	0.63
LB (98 & 99)	$PM_{2.5} = 0.58\ PM_{10} + 2.38$	0.75	$PM_{coarse} = 0.42\ PM_{10} - 2.26$	0.62
RO (98 & 99)	$PM_{2.5} = 0.59\ PM_{10} + 1.10$	0.69	$PM_{coarse} = 0.41\ PM_{10} - 1.02$	0.55
HAR (98 & 99)	$PM_{2.5} = 0.64\ PM_{10} + 0.83$	0.83	$PM_{coarse} = 0.36\ PM_{10} - 0.83$	0.61
Summer				
LM (97, 98 & 99)	$PM_{2.5} = 0.47\ PM_{10} + 4.86$	0.72	$PM_{coarse} = 0.53\ PM_{10} - 4.82$	0.77
LB (97, 98 & 99)	$PM_{2.5} = 0.61\ PM_{10} + 1.55$	0.75	$PM_{coarse} = 0.39\ PM_{10} - 1.46$	0.57
RO (97, 98 & 99)	$PM_{2.5} = 0.59\ PM_{10} + 0.51$	0.64	$PM_{coarse} = 0.41\ PM_{10} - 0.48$	0.48
HAR (98 & 99)	$PM_{2.5} = 0.59\ PM_{10} + 0.57$	0.72	$PM_{coarse} = 0.41\ PM_{10} - 0.56$	0.55
Autumn				
LM (97, 98 & 99)	$PM_{2.5} = 0.44\ PM_{10} + 6.86$	0.76	$PM_{coarse} = 0.56\ PM_{10} - 6.84$	0.84
LB (97, 98 & 99)	$PM_{2.5} = 0.61\ PM_{10} + 1.78$	0.73	$PM_{coarse} = 0.41\ PM_{10} - 1.20$	0.58
RO (97, 98 & 99)	$PM_{2.5} = 0.60\ PM_{10} + 1.15$	0.64	$PM_{coarse} = 0.41\ PM_{10} - 1.14$	0.46
HAR (97, 98 & 99)	$PM_{2.5} = 0.51\ PM_{10} + 3.04$	0.61	$PM_{coarse} = 0.49\ PM_{10} - 3.04$	0.59
Winter				
LM (97/98, 98/99 & 1299)	$PM_{2.5} = 0.62\ PM_{10} + 0.54$	0.86	$PM_{coarse} = 0.38\ PM_{10} - 0.52$	0.70
LB (97/98, 98/99 & 1299)	$PM_{2.5} = 0.69\ PM_{10} + 0.15$	0.80	$PM_{coarse} = 0.31\ PM_{10} - 0.04$	0.48
RO (97/98, 98/99 & 1299)	$PM_{2.5} = 0.66\ PM_{10} - 0.09$	0.73	$PM_{coarse} = 0.34\ PM_{10} + 0.16$	0.44
HAR (97/98, 98/99 & 1299)	$PM_{2.5} = 0.76\ PM_{10} - 0.60$	0.87	$PM_{coarse} = 0.24\ PM_{10} + 0.61$	0.39

Figure 4.1 Hourly correlation between PM_{10}, $PM_{2.5}$ and coarse particles for summer 1997, 1998 and 1999 at Marylebone Road

Fig. 4.1a

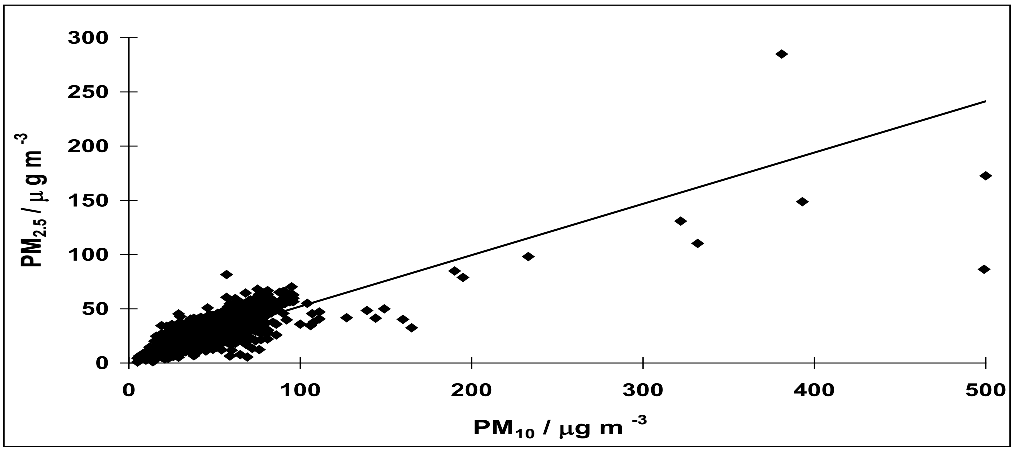


Fig 4.1b

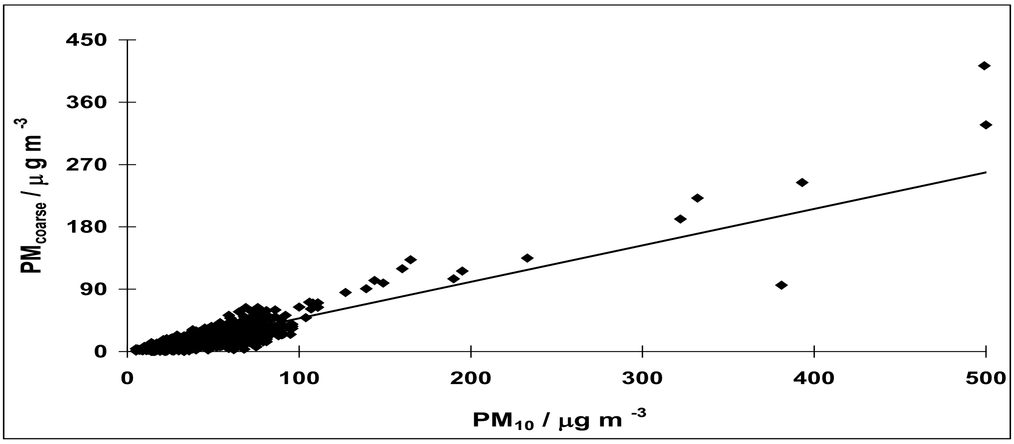


Figure 4.2 Hourly correlation between PM_{10}, $PM_{2.5}$ and coarse particles for autumn 1997, 1998 and 1999 at Marylebone Road

Fig. 4.2a

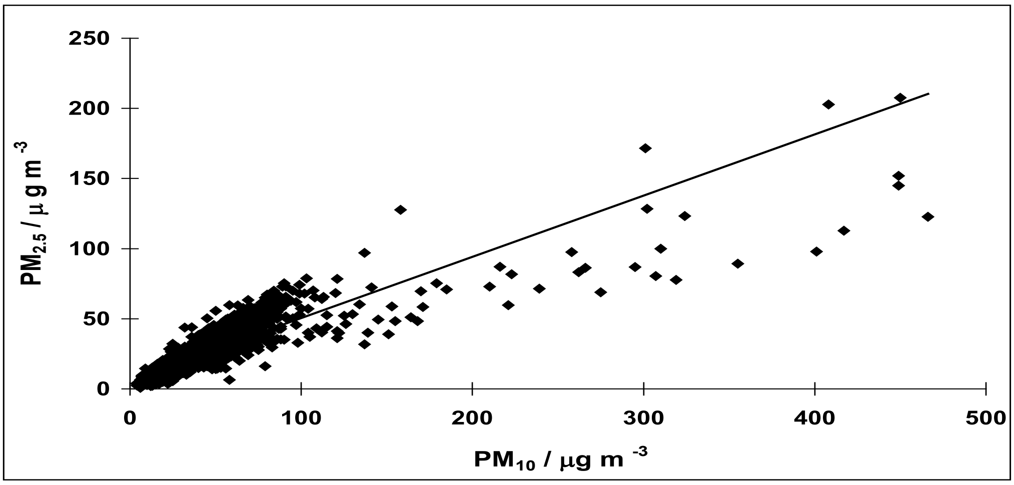
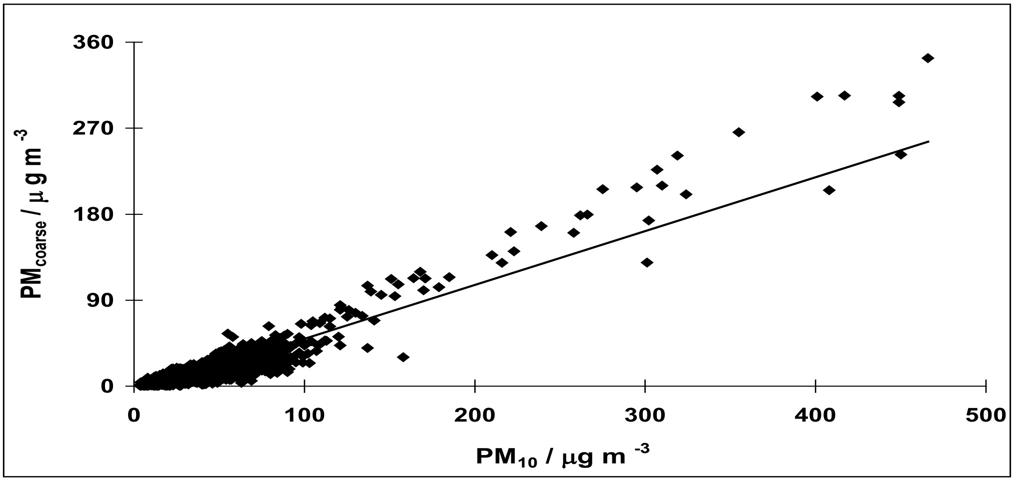


Fig. 4.2b



In addition to Marylebone Road, the other three sites also showed a higher coarse component in summer than in winter although the concentration levels of PM$_{10}$ were lower. Similarly, winter months have exhibited higher gradients in the correlation of PM$_{10}$ to the fine fraction at all four sites, giving a slope range of 0.62-0.76 (0.47-0.61 for coarse particles). The sample regression plots at Harwell (Figure 4.3) demonstrate the closest relationships between PM$_{10}$ and fine particles in the winter months. Figure 4.3a shows that most points lie close to the regression line and above when PM$_{10}$ reached 40 μg m^{-3} whereas figure 4.3b shows a rather scattered picture with points lying below the regression line against higher PM$_{10}$ concentrations. It is seen that at least two thirds of the PM$_{10}$ mass was made up of fine particles.

Individual seasonal hourly regression analyses have been conducted shown in table 4.2. Similar results have been found as discussed above. Generally higher correlations were observed between PM$_{10}$ and PM$_{2.5}$, however the coarse component can occasionally make higher contributions to very high PM$_{10}$ episodes especially in the summer months. Similar to that shown in the figures 4.1 and 4.2, higher coarse components have been observed in autumn 1997 and summer 1998 in Rochester when PM$_{10}$ exceeded 120 μg m^{-3} and 60 μg m^{-3} respectively, and in autumn 1998 in Harwell when PM$_{10}$ reached 100 μg m^{-3}. On using the averaged daily data, similar results were found but higher correlations were obtained between the particle mass fractions.

Figure 4.3 Hourly plots for winter 97/98, 98/99 and December 99 at Harwell

Fig. 4.3a

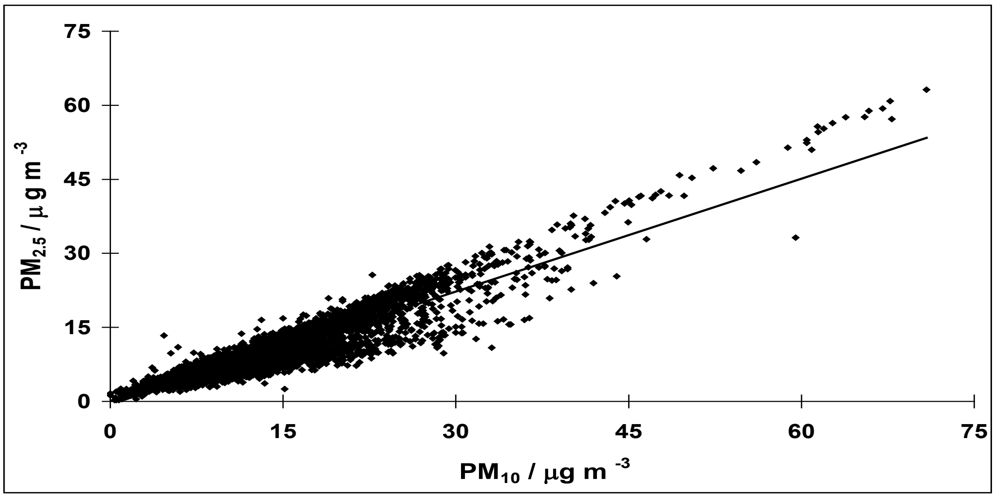


Fig. 4.3b

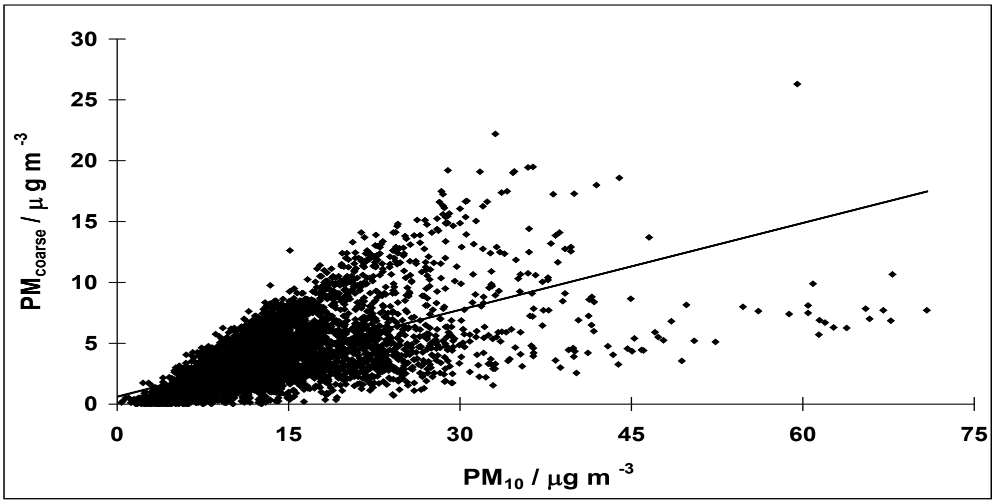


Table 4.2 Single seasonal results of regression analyses of $PM_{2.5}$ and PM_{10} data at DETR sites for hourly data

	$PM_{2.5}$ = m PM_{10} + c	R^2	PM_{coarse} = m PM_{10} + c	R^2
Summer 97				
LM (20/6/97 - 31/8/97)	$PM_{2.5}$ = 0.69 PM_{10} - 1.67	0.84	PM_{coarse} = 0.31 PM_{10} + 1.67	0.53
LB (20/6/97 - 31/8/97)	$PM_{2.5}$ = 0.59 PM_{10} + 3.07	0.71	PM_{coarse} = 0.41 PM_{10} - 2.69	0.57
RO (20/6/97 - 31/8/97)	$PM_{2.5}$ = 0.63 PM_{10} + 0.26	0.66	PM_{coarse} = 0.38 PM_{10} - 0.30	0.43
HAR (20/6/97 - 31/8/97)	-	-	-	-
Autumn 97				
LM (1/9/97 - 30/11/97)	$PM_{2.5}$ = 0.65 PM_{10} - 1.24	0.86	PM_{coarse} = 0.35 PM_{10} + 1.25	0.63
LB (1/9/97 - 30/11/97)	$PM_{2.5}$ = 0.54 PM_{10} + 3.80	0.63	PM_{coarse} = 0.48 PM_{10} - 4.05	0.61
RO (1/9/97 - 30/11/97)	$PM_{2.5}$ = 0.48 PM_{10} + 4.20	0.51	PM_{coarse} = 0.53 PM_{10} - 4.15	0.58
HAR (28/9/97 - 30/11/97)	$PM_{2.5}$ = 0.80 PM_{10} - 0.84	0.92	PM_{coarse} = 0.20 PM_{10} + 0.86	0.41
Winter 97/98				
LM (1/12/97 - 28/2/98)	$PM_{2.5}$ = 0.67 PM_{10} - 1.35	0.87	PM_{coarse} = 0.33 PM_{10} + 1.37	0.61
LB (1/12/97 - 28/2/98)	$PM_{2.5}$ = 0.68 PM_{10} + 0.12	0.70	PM_{coarse} = 0.32 PM_{10} + 0.32	0.36
RO (1/12/97 - 28/2/98)	$PM_{2.5}$ = 0.73 PM_{10} - 0.12	0.75	PM_{coarse} = 0.26 PM_{10} + 0.39	0.30
HAR (1/12/97 - 28/2/98)	$PM_{2.5}$ = 0.82 PM_{10} - 1.48	0.89	PM_{coarse} = 0.18 PM_{10} + 1.48	0.30
Spring 98				
LM (1/3/98 - 31/5/98)	$PM_{2.5}$ = 0.62 PM_{10} - 0.12	0.85	PM_{coarse} = 0.38 PM_{10} + 0.13	0.68
LB (1/3/98 - 31/5/98)	$PM_{2.5}$ = 0.57 PM_{10} + 3.40	0.71	PM_{coarse} = 0.43 PM_{10} - 3.18	0.61
RO (1/3/98 - 31/5/98)	$PM_{2.5}$ = 0.59 PM_{10} + 2.03	0.68	PM_{coarse} = 0.41 PM_{10} - 1.81	0.55
HAR (1/3/98 - 31/5/98)	$PM_{2.5}$ = 0.64 PM_{10} + 1.03	0.87	PM_{coarse} = 0.36 PM_{10} - 1.02	0.69
Summer 98				
LM (1/6/98 - 31/8/98)	$PM_{2.5}$ = 0.59 PM_{10} + 0.63	0.84	PM_{coarse} = 0.41 PM_{10} - 0.58	0.71
LB (1/6/98 - 31/8/98)	$PM_{2.5}$ = 0.55 PM_{10} + 2.17	0.69	PM_{coarse} = 0.45 PM_{10} - 2.2	0.61
RO (1/6/98 - 31/8/98)	$PM_{2.5}$ = 0.34 PM_{10} + 4.88	0.51	PM_{coarse} = 0.67 PM_{10} - 4.72	0.82
HAR (1/6/98 - 31/8/98)	$PM_{2.5}$ = 0.65 PM_{10} + 0.09	0.78	PM_{coarse} = 0.35 PM_{10} - 0.08	0.52

Table 4.2 Single seasonal results of regression analyses of $PM_{2.5}$ and PM_{10} data at DETR sites for hourly data (cont'd)

Autumn 98				
LM (1/9/98 - 30/11/98)	$PM_{2.5} = 0.62\ PM_{10} + 0.55$	**0.85**	$PM_{coarse} = 0.38\ PM_{10} - 0.58$	**0.68**
LB (1/9/98 - 30/11/98)	$PM_{2.5} = 0.69\ PM_{10} + 0.27$	**0.86**	$PM_{coarse} = 0.31\ PM_{10} - 0.27$	**0.55**
RO (1/9/98 - 30/11/98)	$PM_{2.5} = 0.59\ PM_{10} + 0.43$	**0.66**	$PM_{coarse} = 0.42\ PM_{10} - 0.48$	**0.51**
HAR (1/9/98 - 30/11/98)	$PM_{2.5} = 0.36\ PM_{10} + 5.07$	**0.44**	$PM_{coarse} = 0.64\ PM_{10} - 5.07$	**0.72**
Winter 98/99				
LM (1/12/98 - 28/2/99)	$PM_{2.5} = 0.59\ PM_{10} + 1.47$	**0.86**	$PM_{coarse} = 0.41\ PM_{10} - 1.46$	**0.76**
LB (1/12/98 - 28/2/99)	$PM_{2.5} = 0.70\ PM_{10} + 0.23$	**0.88**	$PM_{coarse} = 0.30\ PM_{10} - 0.23$	**0.58**
RO (1/12/98 - 28/2/99)	$PM_{2.5} = 0.56\ PM_{10} + 0.43$	**0.72**	$PM_{coarse} = 0.44\ PM_{10} - 0.43$	**0.61**
HAR (1/12/98 - 28/2/99)	$PM_{2.5} = 0.65\ PM_{10} + 0.69$	**0.76**	$PM_{coarse} = 0.35\ PM_{10} - 0.68$	**0.49**
Spring 99				
LM (1/3/99 - 31/5/99)	$PM_{2.5} = 0.61\ PM_{10} + 1.80$	**0.75**	$PM_{coarse} = 0.40\ PM_{10} - 1.89$	**0.63**
LB (1/3/99 - 31/5/99)	$PM_{2.5} = 0.60\ PM_{10} + 1.47$	**0.79**	$PM_{coarse} = 0.40\ PM_{10} - 1.47$	**0.64**
RO (1/3/99 - 31/5/99)	$PM_{2.5} = 0.60\ PM_{10} + 0.01$	**0.74**	$PM_{coarse} = 0.40\ PM_{10} - 0.01$	**0.56**
HAR (1/3/99 - 31/5/99)	$PM_{2.5} = 0.64\ PM_{10} + 0.69$	**0.78**	$PM_{coarse} = 0.36\ PM_{10} - 0.69$	**0.53**
Summer 99				
LM (1/6/99 - 31/8/99)	$PM_{2.5} = 0.39\ PM_{10} + 7.42$	**0.69**	$PM_{coarse} = 0.61\ PM_{10} - 7.32$	**0.85**
LB (1/6/99 - 31/8/99)	$PM_{2.5} = 0.64\ PM_{10} + 0.77$	**0.81**	$PM_{coarse} = 0.36\ PM_{10} - 0.77$	**0.57**
RO (1/6/99 - 31/8/99)	$PM_{2.5} = 0.59\ PM_{10} + 0.44$	**0.66**	$PM_{coarse} = 0.41\ PM_{10} - 0.44$	**0.49**
HAR (1/6/99 - 31/8/99)	$PM_{2.5} = 0.56\ PM_{10} + 0.76$	**0.68**	$PM_{coarse} = 0.44\ PM_{10} - 0.76$	**0.56**
Autumn 99				
LM (1/9/99 - 30/11/99)	$PM_{2.5} = 0.36\ PM_{10} + 9.61$	**0.79**	$PM_{coarse} = 0.64\ PM_{10} - 9.59$	**0.92**
LB (1/9/99 - 30/11/99)	$PM_{2.5} = 0.70\ PM_{10} - 0.79$	**0.87**	$PM_{coarse} = 0.30\ PM_{10} + 0.79$	**0.55**
RO (1/9/99 - 30/11/99)	$PM_{2.5} = 0.76\ PM_{10} - 1.62$	**0.81**	$PM_{coarse} = 0.24\ PM_{10} +1.62$	**0.29**
HAR (1/9/99 - 30/11/99)	$PM_{2.5} = 0.64\ PM_{10} + 0.77$	**0.79**	$PM_{coarse} = 0.36\ PM_{10} - 0.77$	**0.55**
Winter 99				
LM (12/99)	$PM_{2.5} = 0.58\ PM_{10} + 1.83$	**0.83**	$PM_{coarse} = 0.42\ PM_{10} - 1.83$	**0.72**
LB (12/99)	$PM_{2.5} = 0.71\ PM_{10} - 0.43$	**0.89**	$PM_{coarse} = 0.29\ PM_{10} + 0.43$	**0.57**
RO (12/99)	$PM_{2.5} = 0.67\ PM_{10} - 0.18$	**0.78**	$PM_{coarse} = 0.33\ PM_{10} + 0.18$	**0.47**
HAR (12/99)	$PM_{2.5} = 0.81\ PM_{10} - 0.26$	**0.79**	$PM_{coarse} = 0.20\ PM_{10} + 0.18$	**0.21**

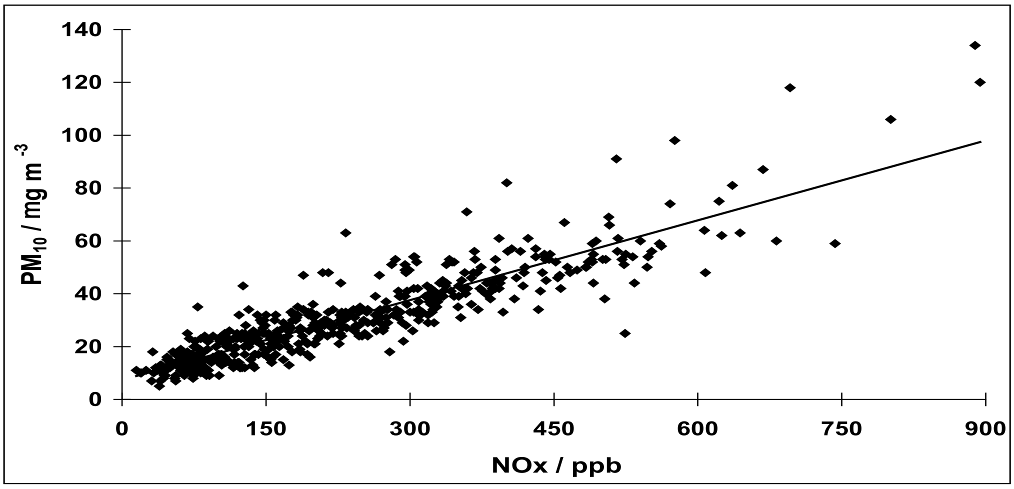
4.2.2 Correlation Between Particle Mass and Other Air Pollutants

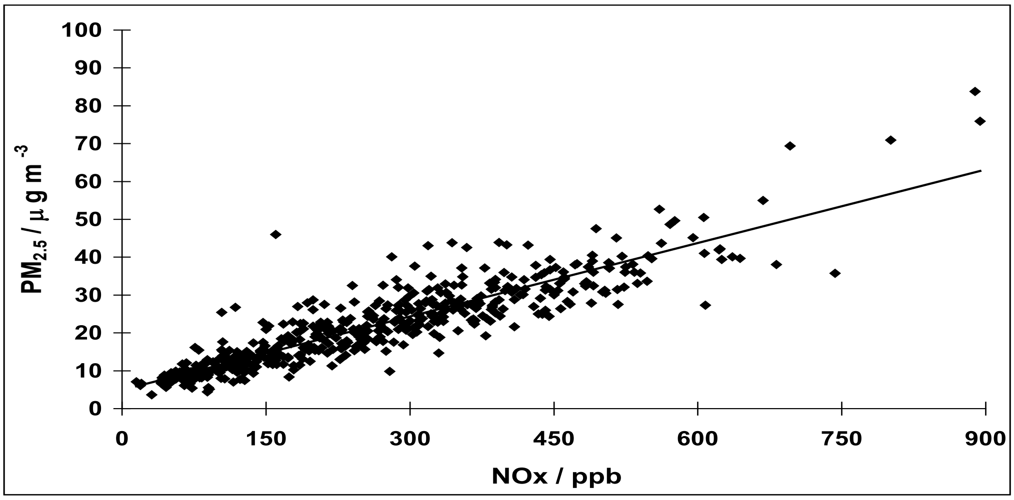
Relationships between PM_{10}, $PM_{2.5}$ and NO_x at the Birmingham Hodge Hill site have been examined in some detail (QUARG, 1996; APEG, 1999). The results show that winter months exhibited a higher correlation between PM_{10}, $PM_{2.5}$ and NO_x, indicative of a strong influence of traffic-related emissions on airborne particles. Here a detailed investigation on the relationship between various particle mass fractions and gaseous pollutants, such as NO_x, CO and SO_2, has been completed through a full data set from the four DETR sites. Comparison between the two London sites is particularly important to give a clear idea for what difference traffic could make for contributing to airborne particulate pollution levels.

Hourly single seasonal correlations of PM_{10}, $PM_{2.5}$, and coarse PM with NO_x, CO and SO_2 are shown in Table 4.3, 4.4 and 4.5. Large variations were found in the correlations between particle mass and these air pollutants for different sites and seasons. In general, higher correlations were observed from London Marylebone Road. PM_{10} and $PM_{2.5}$ were strongly related to NO_x particularly in winter and autumn seasons whereas coarse particles were rather weekly correlated with NO_x consistent with the result obtained from the Birmingham, Hodge Hill site. Most of the summer and spring months appeared to have only modest or weak correlations (Table 4.3).

In December 1999, the highest correlation was observed for PM_{10}, $PM_{2.5}$ and NO_x showing a same correlation coefficient of $R^2 = 0.81$ on Marylebone Road. The intercepts from these relationships were the lowest (5.0 for $PM_{2.5}$ and 7.4 for PM_{10}) among all seasons over the whole sampling period indicative of a strong influence on PM_{10} from the primary vehicle exhaust emissions with a higher average NO_x concentration (231.4 ppb). The average concentrations for that month are 29.8 $\mu g\ m^{-3}$ and 20.6 $\mu g\ m^{-3}$ for PM_{10} and $PM_{2.5}$ respectively. Assuming that NO_x is wholly responsible for the traffic related primary emissions, the traffic-induced primary PM_{10} and $PM_{2.5}$ can be calculated using the monthly average concentrations minus the background PM concentrations (the intercepts from the regression equation). The results show about 22.4 and 15.6 $\mu g\ m^{-3}$ from primary vehicle exhaust emissions, which accounts for more than two thirds of the total PM_{10} and $PM_{2.5}$ mass. The regression plots clearly show the strong relationships between PM_{10} and $PM_{2.5}$ with NO_x, whereas coarse particles are only modestly correlated although they can also be traffic related (figure 4.4a). Strong correlations were also found for PM_{10} and $PM_{2.5}$ with CO over the same period, as further evidence for the influence of traffic on Marylebone Road particularly during the winter period (Figure 4.4b).

Figure 4.4a Hourly Regression Plots for Marylebone Road; December 1999





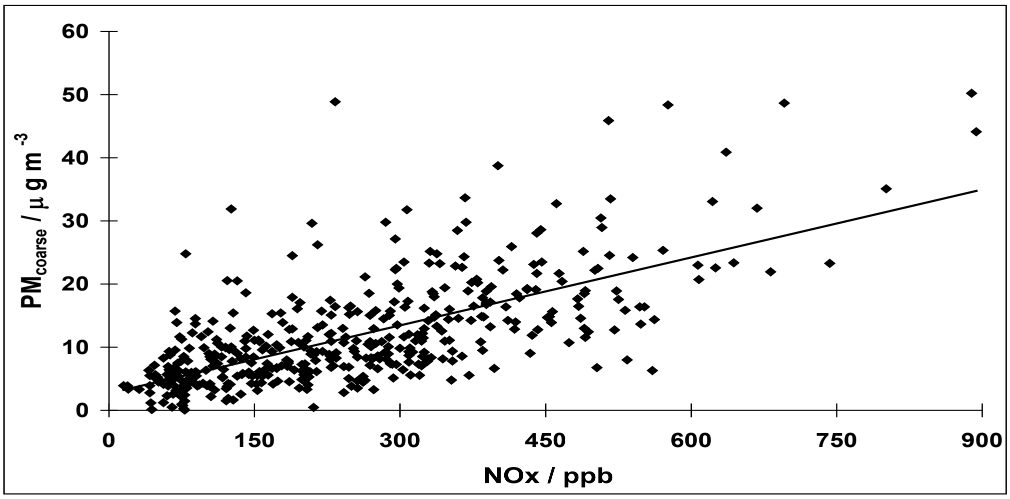
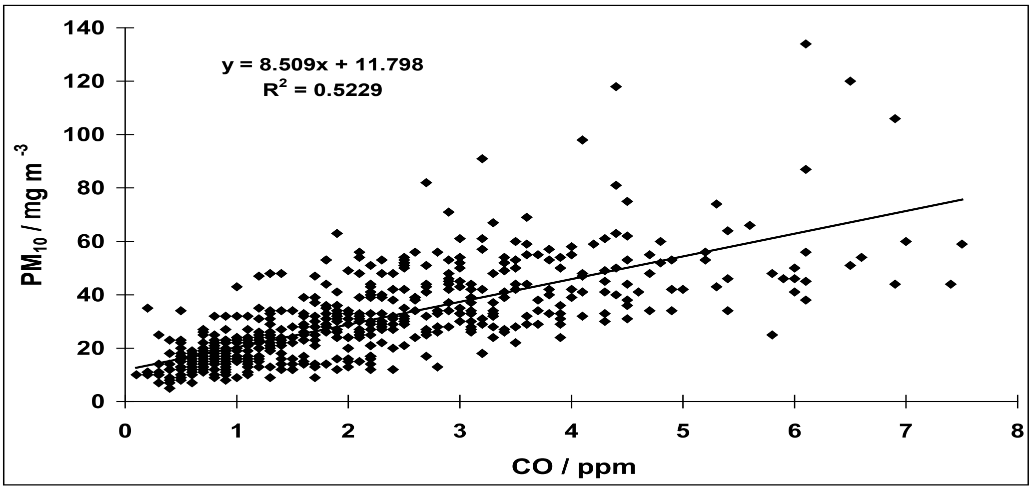


Figure 4.4b Hourly Regression Plots for Marylebone Road; December 1999



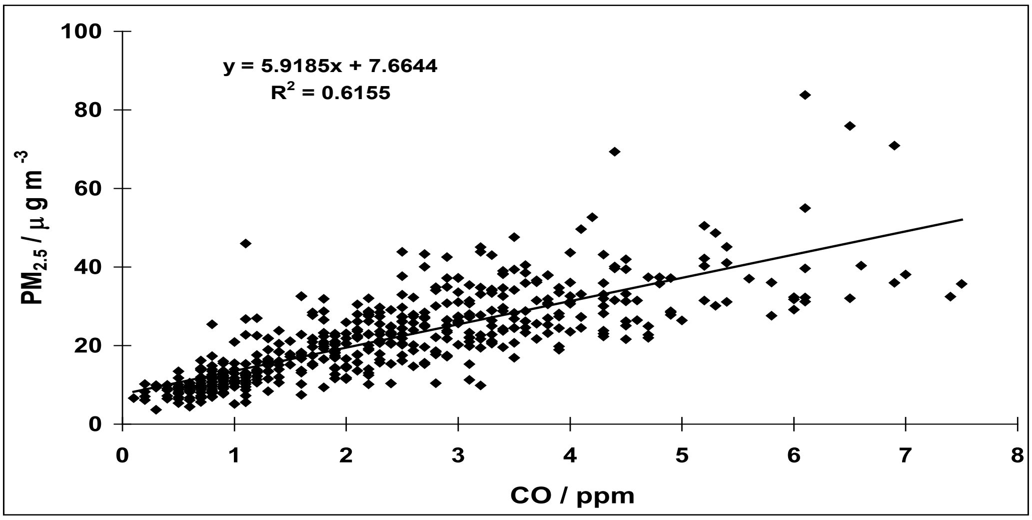


Table 4.3 Seasonal results of regression analyses of PM and NOx at DETR sites for hourly data

	$PM_{10} = m\ NO_x + c$	R^2	$PM_{2.5} = m\ NO_x + c$	R^2	$PM_{coarse} = m\ NO_x + c$	R^2
Summer 97						
LM (20/6/97 – 31/8/97)	$PM_{10} = 0.11\ NO_x + 20.15$	0.40	$PM_{2.5} = 0.07\ NO_x + 13.05$	0.29	$PM_{coarse} = 0.04\ NO_x + 7.18$	0.26
LB (20/6/97 - 31/8/97)	$PM_{10} = 0.24\ NO_x + 11.55$	0.23	$PM_{2.5} = 0.16\ NO_x + 8.80$	0.24	$PM_{coarse} = 0.07\ NO_x + 3.82$	0.08
RO (20/6/97 – 31/8/97)	$PM_{10} = 0.44\ NO_x + 15.60$	0.10	$PM_{2.5} = 0.35\ NO_x + 9.83$	0.11	$PM_{coarse} = 0.12\ NO_x + 6.39$	0.03
HAR (20/6/97 – 31/8/97)	-	-	-	-	-	-
Autumn 97						
LM (1/9/97 - 30/11/97)	$PM_{10} = 0.11\ NO_x + 13.98$	0.71	$PM_{2.5} = 0.07\ NO_x + 8.85$	0.52	$PM_{coarse} = 0.04\ NO_x + 6.34$	0.41
LB (1/9/97 - 30/11/97)	$PM_{10} = 0.14\ NO_x + 13.05$	0.46	$PM_{2.5} = 0.11\ NO_x + 7.26$	0.62	$PM_{coarse} = 0.03\ NO_x + 6.79$	0.05
RO (1/9/97 - 30/11/97)	$PM_{10} = 0.29\ NO_x + 12.19$	0.35	$PM_{2.5} = 0.25\ NO_x + 7.64$	0.56	$PM_{coarse} = 0.04\ NO_x + 4.96$	0.02
HAR (28/9/97 – 30/11/97)	$PM_{10} = 0.28\ NO_x + 9.84$	0.63	$PM_{2.5} = 0.22\ NO_x + 7.59$	0.61	$PM_{coarse} = 0.05\ NO_x + 3.15$	0.19
Winter 97/98						
LM (1/12/97 – 28/2/98)	$PM_{10} = 0.10\ NO_x + 11.97$	0.70	$PM_{2.5} = 0.07\ NO_x + 6.82$	0.65	$PM_{coarse} = 0.03\ NO_x + 5.79$	0.41
LB (1/12/97 - 28/2/98)	$PM_{10} = 0.12\ NO_x + 12.61$	0.45	$PM_{2.5} = 0.09\ NO_x + 8.58$	0.29	$PM_{coarse} = 0.05\ NO_x + 3.75$	0.20
RO (1/12/97 – 28/2/98)	$PM_{10} = 0.17\ NO_x + 13.98$	0.17	$PM_{2.5} = 0.20\ NO_x + 9.25$	0.27	$PM_{coarse} = 0.03\ NO_x + 4.36$	0.03
HAR (1/12/97 – 28/2/98)	$PM_{10} = 0.28\ NO_x + 11.27$	0.40	$PM_{2.5} = 0.27\ NO_x + 7.02$	0.48	$PM_{coarse} = 0.02\ NO_x + 4.26$	0.01
Spring 98						
LM (1/3/98 - 31/5/98)	$PM_{10} = 0.08\ NO_x + 18.66$	0.36	$PM_{2.5} = 0.05\ NO_x + 11.89$	0.28	$PM_{coarse} = 0.03\ NO_x + 6.99$	0.25
LB (1/3/98 - 31/5/98)	$PM_{10} = 0.18\ NO_x + 13.09$	0.24	$PM_{2.5} = 0.14\ NO_x + 8.30$	0.31	$PM_{coarse} = 0.05\ NO_x + 3.62$	0.07
RO (1/3/98 - 31/5/98)	$PM_{10} = 0.28\ NO_x + 14.50$	0.11	$PM_{2.5} = 0.21\ NO_x + 10.05$	0.12	$PM_{coarse} = 0.06\ NO_x + 4.77$	0.02
HAR (1/3/98 – 31/5/98)	$PM_{10} = 0.39\ NO_x + 9.29$	0.23	$PM_{2.5} = 0.29\ NO_x + 6.61$	0.29	$PM_{coarse} = 0.08\ NO_x + 3.38$	0.06
Summer 98						
LM (1/6/98 - 31/8/98)	$PM_{10} = 0.10\ NO_x + 12.89$	0.60	$PM_{2.5} = 0.06\ NO_x + 8.58$	0.47	$PM_{coarse} = 0.04\ NO_x + 4.36$	0.47
LB (1/6/98 - 31/8/98)	$PM_{10} = 0.19\ NO_x + 11.47$	0.21	$PM_{2.5} = 0.15\ NO_x + 6.29$	0.29	$PM_{coarse} = 0.04\ NO_x + 5.15$	0.03
RO (1/6/98 - 31/8/98)	$PM_{10} = 0.41\ NO_x + 12.10$	0.19	$PM_{2.5} = 0.33\ NO_x + 6.74$	0.19	$PM_{coarse} = 0.11\ NO_x + 5.37$	0.03
HAR (1/6/98 – 31/8/98)	$PM_{10} = 0.21\ NO_x + 12.71$	0.04	$PM_{2.5} = 0.23\ NO_x + 7.24$	0.10	$PM_{coarse} = -0.02\ NO_x + 5.43$	0.00

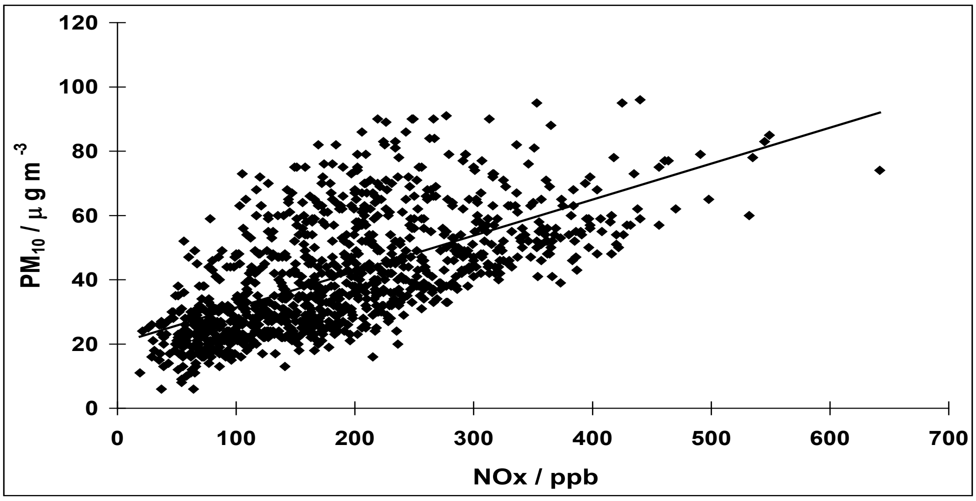
Table 4.3 Seasonal results of regression analyses of PM and NOx at DETR sites for hourly data (cont'd)

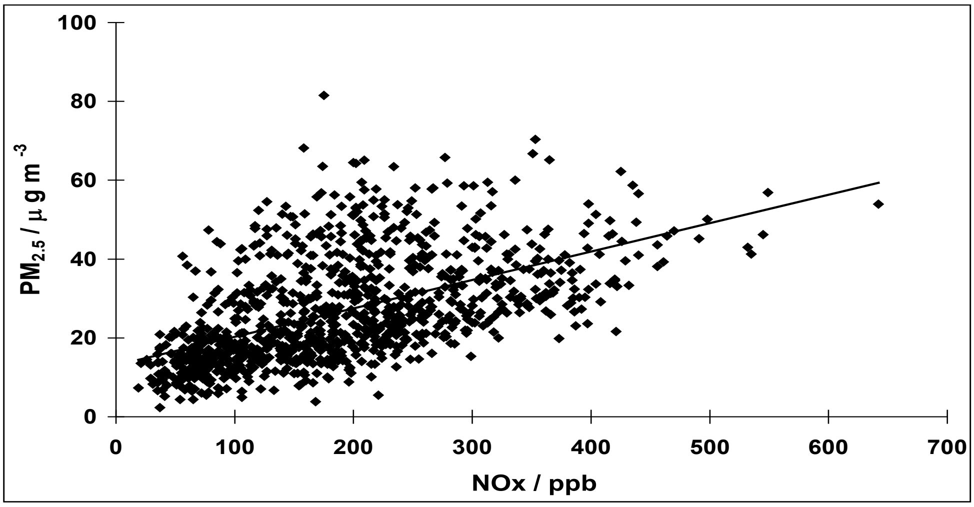
	$PM_{10} = m NO_x + c$	**R^2**	**$PM_{2.5} = m NO_x + c$**	**R^2**	**$PM_{coarse} = m NO_x + c$**	**R^2**
Autumn 98						
LM (1/9/98 – 30/11/98)	**$PM_{10} = 0.07 NO_x + 19.36$**	**0.36**	**$PM_{2.5} = 0.04 NO_x + 13.21$**	**0.28**	**$PM_{coarse} = 0.02 NO_x + 7.08$**	**0.21**
LB (1/9/98 – 30/11/98)	**$PM_{10} = 0.13 NO_x + 12.69$**	**0.40**	**$PM_{2.5} = 0.10 NO_x + 8.10$**	**0.42**	**$PM_{coarse} = 0.03 NO_x + 4.66$**	**0.10**
RO (1/9/98 – 30/11/98)	**$PM_{10} = 0.46 NO_x + 12.82$**	**0.23**	**$PM_{2.5} = 0.47 NO_x + 6.79$**	**0.20**	**$PM_{coarse} = -0.02 NO_x + 7.24$**	**0.00**
HAR (1/9/98 - 30/11/98)	**$PM_{10} = 0.60 NO_x + 9.18$**	**0.45**	**$PM_{2.5} = 0.50 NO_x + 6.09$**	**0.45**	**$PM_{coarse} = 0.09 NO_x + 3.20$**	**0.12**
Winter 98/99						
LM (1/12/98 – 28/2/99)	**$PM_{10} = 0.09 NO_x + 10.23$**	**0.65**	**$PM_{2.5} = 0.06 NO_x + 6.65$**	**0.62**	**$PM_{coarse} = 0.03 NO_x + 3.69$**	**0.38**
LB (1/12/98 – 28/2/99)	**$PM_{10} = 0.12 NO_x + 11.34$**	**0.46**	**$PM_{2.5} = 0.10 NO_x + 6.85$**	**0.59**	**$PM_{coarse} = 0.02 NO_x + 4.34$**	**0.08**
RO (1/12/98 – 28/2/99)	**$PM_{10} = 0.20 NO_x + 11.73$**	**0.25**	**$PM_{2.5} = 0.16 NO_x + 5.81$**	**0.40**	**$PM_{coarse} = 0.03 NO_x + 5.94$**	**0.01**
HAR (1/12/98 - 28/2/99)	**$PM_{10} = 0.17 NO_x + 9.33$**	**0.15**	**$PM_{2.5} = 0.19 NO_x + 5.64$**	**0.34**	**$PM_{coarse} = -0.02 NO_x + 3.70$**	**0.01**
Spring 99						
LM (1/3/99 – 31/5/99)	**$PM_{10} = 0.09 NO_x + 14.82$**	**0.54**	**$PM_{2.5} = 0.06 NO_x + 9.93$**	**0.41**	**$PM_{coarse} = 0.03 NO_x + 4.91$**	**0.26**
LB (1/3/99 – 31/5/99)	**$PM_{10} = 0.13 NO_x + 14.22$**	**0.35**	**$PM_{2.5} = 0.10 NO_x + 8.41$**	**0.47**	**$PM_{coarse} = 0.03 NO_x + 5.82$**	**0.07**
RO (1/3/99 – 31/5/99)	**$PM_{10} = 0.35 NO_x + 15.25$**	**0.19**	**$PM_{2.5} = 0.31 NO_x + 7.79$**	**0.31**	**$PM_{coarse} = 0.04 NO_x + 7.45$**	**0.01**
HAR (1/3/99 - 31/5/99)	**$PM_{10} = 0.09 NO_x + 13.28$**	**0.05**	**$PM_{2.5} = 0.08 NO_x + 8.95$**	**0.07**	**$PM_{coarse} = -0.002 NO_x + 4.37$**	**0.00**
Summer 99						
LM (1/6/99 – 31/8/99)	**$PM_{10} = 0.14 NO_x + 12.32$**	**0.21**	**$PM_{2.5} = 0.06 NO_x + 10.07$**	**0.22**	**$PM_{coarse} = 0.07 NO_x + 2.24$**	**0.14**
LB (1/6/99 – 31/8/99)	**$PM_{10} = 0.16 NO_x + 10.60$**	**0.36**	**$PM_{2.5} = 0.13 NO_x + 6.22$**	**0.40**	**$PM_{coarse} = 0.04 NO_x + 4.38$**	**0.10**
RO (1/6/99 – 31/8/99)	**$PM_{10} = 0.56 NO_x + 13.06$**	**0.23**	**$PM_{2.5} = 0.38 NO_x + 7.54$**	**0.20**	**$PM_{coarse} = 0.19 NO_x + 5.44$**	**0.08**
HAR (1/6/99 - 31/8/99)	**$PM_{10} = 0.16 NO_x + 11.71$**	**0.13**	**$PM_{2.5} = 0.09 NO_x + 7.18$**	**0.08**	**$PM_{coarse} = 0.09 NO_x + 4.14$**	**0.09**
Autumn 99						
LM (1/9/99 – 30/11/99)	**$PM_{10} = 0.10 NO_x + 16.87$**	**0.17**	**$PM_{2.5} = 0.06 NO_x + 9.86$**	**0.27**	**$PM_{coarse} = 0.04 NO_x + 7.43$**	**0.06**
LB (1/9/99 – 30/11/99)	**$PM_{10} = 0.13 NO_x + 12.44$**	**0.32**	**$PM_{2.5} = 0.10 NO_x + 7.19$**	**0.34**	**$PM_{coarse} = 0.03 NO_x + 5.35$**	**0.09**
RO (1/9/99 – 30/11/99)	**$PM_{10} = 0.16 NO_x + 14.87$**	**0.08**	**$PM_{2.5} = 0.15 NO_x + 9.24$**	**0.09**	**$PM_{coarse} = 0.01 NO_x + 5.67$**	**0.00**
HAR (1/9/99 - 30/11/99)	**$PM_{10} = 0.10 NO_x + 11.99$**	**0.07**	**$PM_{2.5} = 0.10 NO_x + 7.96$**	**0.11**	**$PM_{coarse} = 0.003 NO_x + 4.25$**	**0.00**
Winter 99						
LM (12/99)	**$PM_{10} = 0.10 NO_x + 7.36$**	**0.81**	**$PM_{2.5} = 0.06 NO_x + 4.95$**	**0.81**	**$PM_{coarse} = 0.04 NO_x + 2.72$**	**0.42**
LB (12/99)	**$PM_{10} = 0.14 NO_x + 6.11$**	**0.67**	**$PM_{2.5} = 0.10 NO_x + 3.47$**	**0.75**	**$PM_{coarse} = 0.04 NO_x + 2.81$**	**0.29**
RO (12/99)	**$PM_{10} = 0.21 NO_x + 7.78$**	**0.59**	**$PM_{2.5} = 0.18 NO_x + 4.34$**	**0.74**	**$PM_{coarse} = 0.04 NO_x + 3.44$**	**0.07**
HAR (12/99)	**$PM_{10} = 0.22 NO_x + 7.54$**	**0.42**	**$PM_{2.5} = 0.20 NO_x + 5.03$**	**0.60**	**$PM_{coarse} = 0.02 NO_x + 2.51$**	**0.02**

In comparison summer 1997 and 1999 exhibited higher background concentrations of PM_{10} and $PM_{2.5}$ showing an intercept of 20.2 and 13.1 μg m^{-3} in 1997 and 12.3 and 10.1 μg m^{-3} in 1999 (Table 4.3). The traffic induced fine primary particles become less significant, comprising only half of the total $PM_{2.5}$ of 26.4 μg m^{-3} in summer 1997 and less than half in summer 1999 (total $PM_{2.5}$: 21.5 μg m^{-3}). On the other hand summer 1999 showed very high traffic-related coarse particle concentrations of about 12.9 μg m^{-3}, which is about five sixths of the total coarse particle concentration of 15.1 μg m^{-3}. These results indicate that dry, hot and sunny weather in the summer months may promote the formation of fine secondary particles and also favours increased re-suspension of coarse particles. Figure 4.5 shows that PM_{10} and $PM_{2.5}$ are less related to NO_x in the summer months, with many data points lying reasonably high above the regression lines, and these points may be related to secondary fine particles. Comparatively, a rather closer relationship has been found between coarse particles and NO_x. Similar results were found in summer 1998 but a strong correlation for PM_{10}, modest for both $PM_{2.5}$ and coarse particle with NO_x, which highlights the significance of both fractions. Meanwhile, the lower background of $PM_{2.5}$ (intercept: 8.6 μg m^{-3}) may be due to the wet weather conditions in that summer mentioned earlier.

Interestingly, in the correlations between particle mass and CO in summer 1998, PM_{10} and $PM_{2.5}$ concentrations remained fairly constant when CO reached a level higher than about 5 ppm (Figure 4.6). This phenomenon was also observed from some other seasons, which seems to be consistent with the results obtained from the diurnal plots in which CO appeared to have a higher evening peak while the other pollutants did not at London Marylebone Road.

Figure 4.5 Hourly plots for Marylebone Road (20/6/97 – 31/8/97)





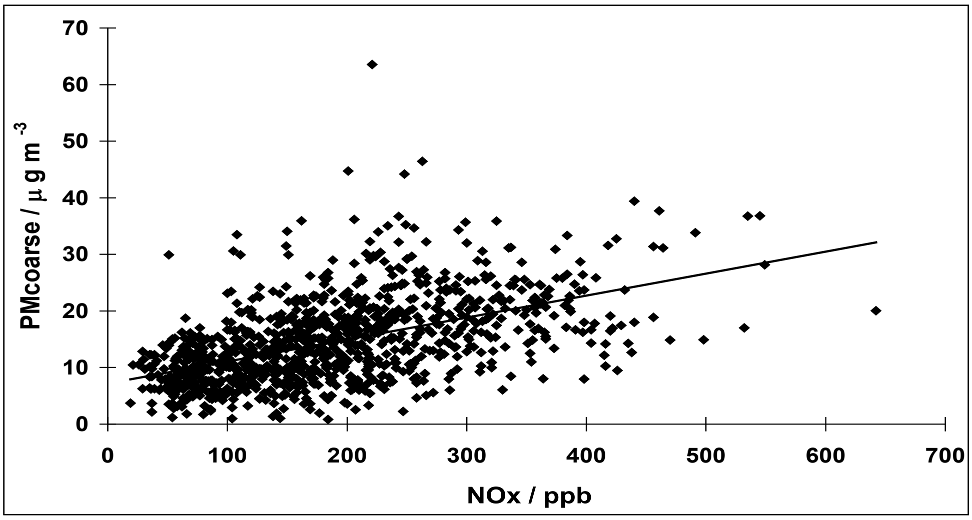
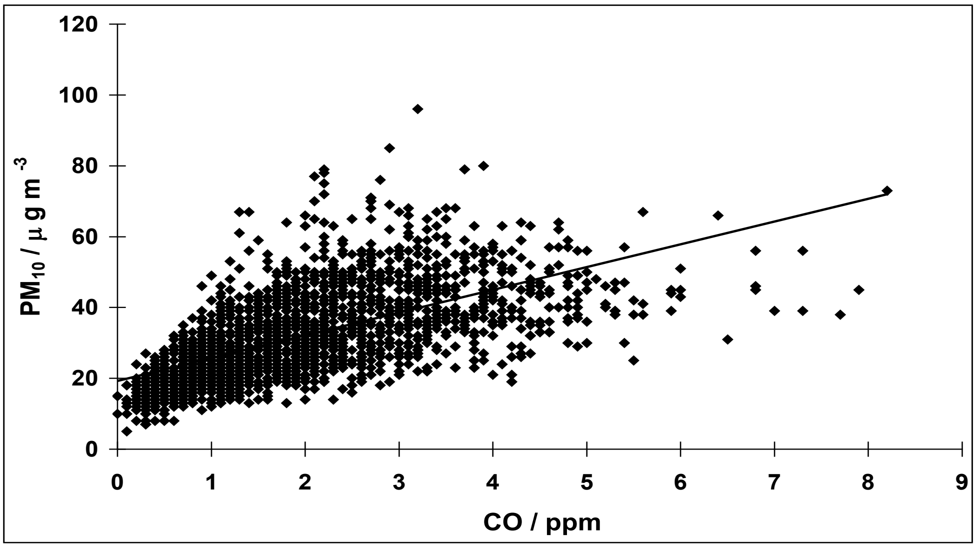
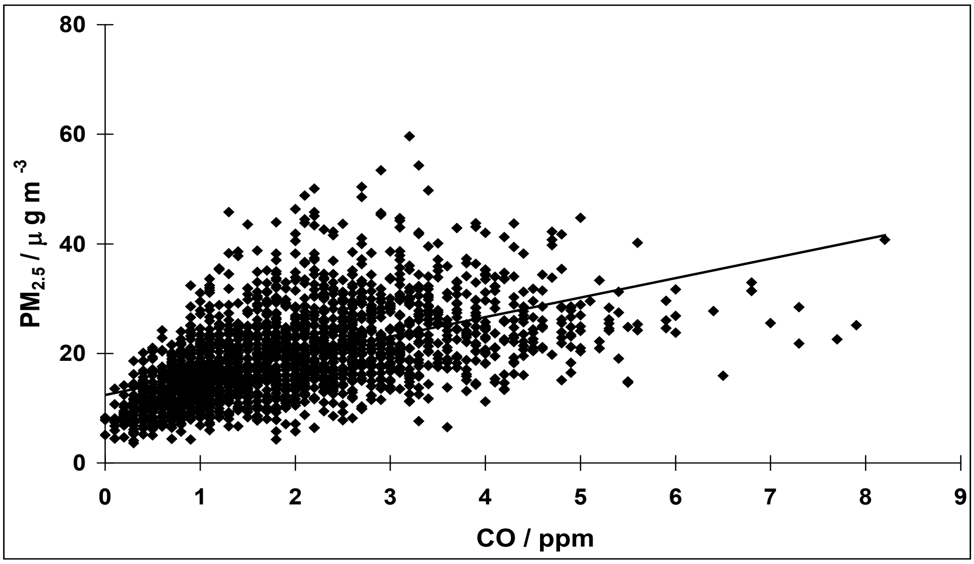


Figure 4.6 Hourly plots for Marylebone Road (01/06/98 – 31/8/98)





Strong correlations were also observed for PM_{10} and $PM_{2.5}$ with NO_x at London Bloomsbury especially in the winter and autumn months. Once again December 1999 demonstrated the highest correlation coefficient ($R^2 = 0.75$) and the lowest intercepts for both PM_{10} (6.1 μg m^{-3}) and $PM_{2.5}$ (3.5 μg m^{-3}) on this site over the whole period, however concentrations of both particle mass and NO_x are much lower compared to Marylebone Road (Figure 4.7). Similar to Marylebone Road, a weaker relationship was obtained in the summer and spring months between PM and NO_x, with correspondingly lower correlation coefficients (Table 4.3). In the case of the Rochester and Harwell sites, mostly weak or modest relationships were found.

Generally, modest correlations between PM_{10} and $PM_{2.5}$ with CO were observed for the two London sites but the roadside site has a closer relationship than the background site (Table 4.4). SO_2 is mostly related modestly or weakly to PM_{10} and $PM_{2.5}$ at the two London sites (table 4.5). Rochester and Harwell sites exhibited mostly weak relationships between SO_2 and PM.

Figure 4.7 Hourly plots for London Bloomsbury in December 1999

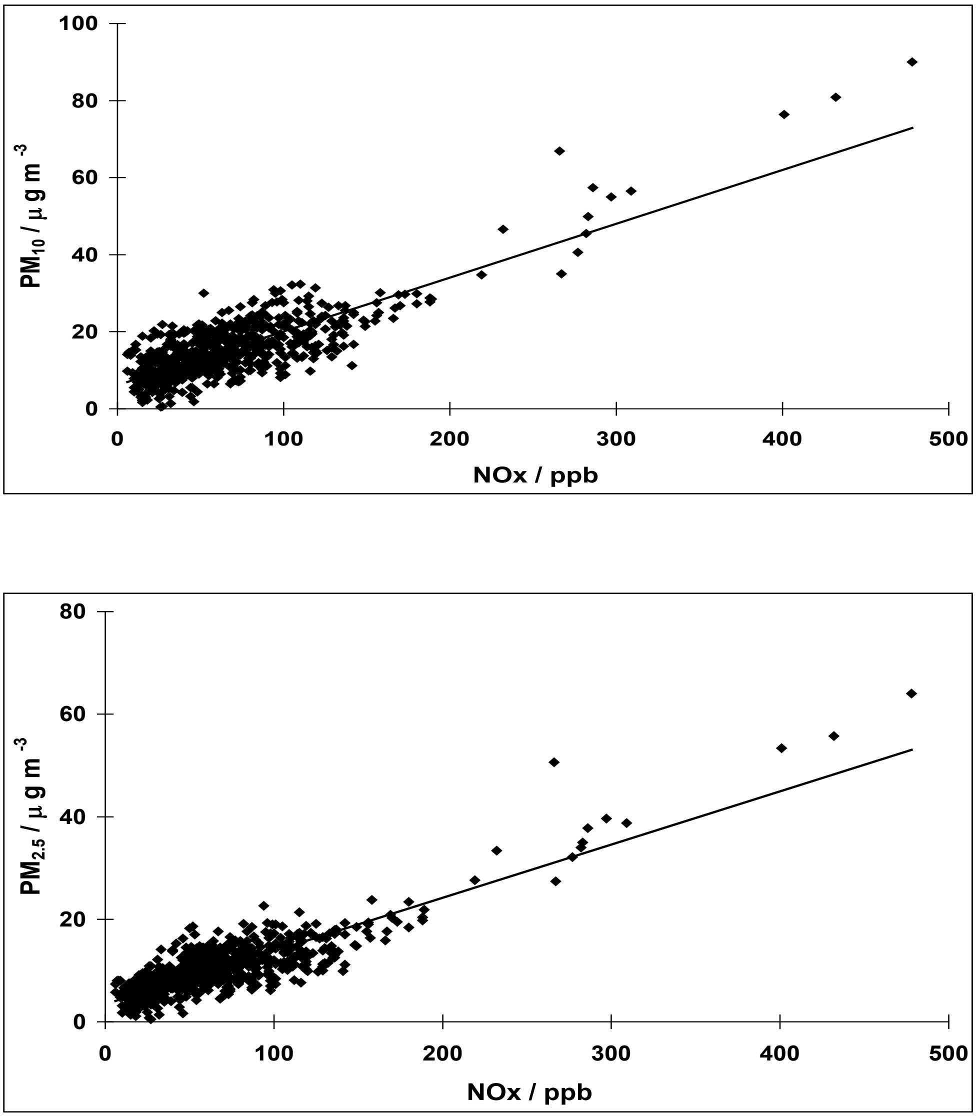


Table 4.4 Seasonal results of regression analyses of PM and CO at DETR sites for hourly data

	PM$_{10}$ = m CO + c	**R^2**	**PM$_{2.5}$ = m CO + c**	**R^2**	**PM$_{coarse}$ = m CO + c**	**R^2**
Summer 97						
LM (20/6/97 - 31/8/97)	**PM$_{10}$ = 6.59 CO + 25.83**	**0.25**	**PM$_{2.5}$ = 3.91 CO + 17.46**	**0.16**	**PM$_{coarse}$ = 2.47 CO + 8.73**	**0.19**
LB (20/6/97 - 31/8/97)	**PM$_{10}$ = 19.15 CO + 16.84**	**0.17**	**PM$_{2.5}$ = 14.71 CO + 11.53**	**0.24**	**PM$_{coarse}$ = 3.62 CO + 6.52**	**0.02**
Autumn 97						
LM (1/9/97 - 30/11/97)	**PM$_{10}$ = 7.22 CO + 21.31**	**0.44**	**PM$_{2.5}$ = 4.02 CO + 13.62**	**0.32**	**PM$_{coarse}$ = 2.32 CO + 8.60**	**0.27**
LB (1/9/97 - 30/11/97)	**PM$_{10}$ = 15.3 CO + 15.06**	**0.39**	**PM$_{2.5}$ = 12.85 CO + 8.36**	**0.60**	**PM$_{coarse}$ = 2.63 CO + 7.79**	**0.03**
Winter 97/98						
LM (1/12/97 - 28/2/98)	**PM$_{10}$ = 7.84 CO + 15.23**	**0.51**	**PM$_{2.5}$ = 5.58 CO + 9.10**	**0.46**	**PM$_{coarse}$ = 2.79 CO + 6.26**	**0.35**
LB (1/12/97 - 28/2/98)	**PM$_{10}$ = 7.61 CO + 18.02**	**0.16**	**PM$_{2.5}$ = 2.56 CO + 14.36**	**0.02**	**PM$_{coarse}$ = 4.70 CO + 4.77**	**0.16**
Spring 98						
LM (1/3/98 - 31/5/98)	**PM$_{10}$ = 5.72 CO + 21.79**	**0.26**	**PM$_{2.5}$ = 3.49 CO + 13.94**	**0.20**	**PM$_{coarse}$ = 2.17 CO + 8.09**	**0.19**
LB (1/3/98 - 31/5/98)	**PM$_{10}$ = 18.73 CO + 14.02**	**0.14**	**PM$_{2.5}$ = 16.24 CO + 7.41**	**0.24**	**PM$_{coarse}$ = 5.12 CO + 3.92**	**0.04**
Summer 98						
LM (1/6/98 - 31/8/98)	**PM$_{10}$ = 6.43 CO + 19.27**	**0.39**	**PM$_{2.5}$ = 3.56 CO + 12.42**	**0.29**	**PM$_{coarse}$ = 2.86 CO + 6.91**	**0.32**
LB (1/6/98 - 31/8/98)	**PM$_{10}$ = 11.64 CO + 13.33**	**0.17**	**PM$_{2.5}$ = 8.63 CO + 8.05**	**0.23**	**PM$_{coarse}$ = 2.94 CO + 5.31**	**0.03**
Autumn 98						
LM (1/9/98 - 30/11/98)	**PM$_{10}$ = 6.35 CO + 18.24**	**0.35**	**PM$_{2.5}$ = 3.75 CO + 13.16**	**0.24**	**PM$_{coarse}$ = 2.77 CO + 5.32**	**0.33**
LB (1/9/98 - 30/11/98)	**PM$_{10}$ = 11.34 CO + 14.06**	**0.19**	**PM$_{2.5}$ = 11.08 CO + 7.90**	**0.29**	**PM$_{coarse}$ = 0.96 CO + 5.98**	**0.01**
Winter 98/99						
LM (1/12/98 - 28/2/99)	**PM$_{10}$ = 8.06 CO + 13.21**	**0.48**	**PM$_{2.5}$ = 5.00 CO + 8.83**	**0.42**	**PM$_{coarse}$ = 2.94 CO + 4.69**	**0.33**
LB (1/12/98 - 28/2/99)	**PM$_{10}$ = 14.17 CO + 9.24**	**0.34**	**PM$_{2.5}$ = 11.83 CO + 5.16**	**0.43**	**PM$_{coarse}$ = 2.43 CO + 3.98**	**0.06**
Spring 99						
LM (1/3/99 - 31/5/99)	**PM$_{10}$ = 7.47 CO + 18.88**	**0.36**	**PM$_{2.5}$ = 4.93 CO + 13.26**	**0.24**	**PM$_{coarse}$ = 2.72 CO + 6.04**	**0.19**
LB (1/3/99 - 31/5/99)	**PM$_{10}$ = 18.31 CO + 12.76**	**0.22**	**PM$_{2.5}$ = 13.79 CO + 7.57**	**0.28**	**PM$_{coarse}$ = 4.50 CO + 5.19**	**0.05**
Summer 99						
LM (1/6/99 - 31/8/99)	**PM$_{10}$ = 7.59 CO + 23.16**	**0.09**	**PM$_{2.5}$ = 3.89 CO + 14.54**	**0.11**	**PM$_{coarse}$ = 3.66 CO + 8.66**	**0.05**
LB (1/6/99 - 31/8/99)	**PM$_{10}$ = 20.24 CO + 12.33**	**0.23**	**PM$_{2.5}$ = 16.52 CO + 6.95**	**0.30**	**PM$_{coarse}$ = 3.76 CO + 5.37**	**0.04**
Autumn 99						
LM (1/9/99 - 30/11/99)	**PM$_{10}$ = 7.21 CO + 24.56**	**0.10**	**PM$_{2.5}$ = 4.74 CO + 14.56**	**0.16**	**PM$_{coarse}$ = 2.42 CO + 10.55**	**0.03**
LB (1/9/99 - 30/11/99)	**PM$_{10}$ = 17.38 CO + 12.23**	**0.26**	**PM$_{2.5}$ = 14.18 CO + 6.64**	**0.30**	**PM$_{coarse}$ = 2.93 CO + 5.85**	**0.04**
Winter 99						
LM (12/99)	**PM$_{10}$ = 8.51 CO + 11.80**	**0.52**	**PM$_{2.5}$ = 5.92 CO + 7.66**	**0.62**	**PM$_{coarse}$ = 2.43 CO + 6.06**	**0.18**
LB (12/99)	**PM$_{10}$ = 16.02 CO + 7.15**	**0.30**	**PM$_{2.5}$ = 11.12 CO + 4.41**	**0.33**	**PM$_{coarse}$ = 3.95 CO + 3.11**	**0.13**

Table 4.5 Seasonal results of regression analyses of PM and SO_2 at DETR sites for hourly data

	$PM_{10} = m\ SO_2 + c$	R^2	$PM_{2.5} = m\ SO_2 + c$	R^2	$PM_{coarse} = m\ SO_2 + c$	R^2
Summer 97						
LM (20/6/97 – 31/8/97)	$PM_{10} = 3.01\ SO_2 + 22.02$	**0.52**	$PM_{2.5} = 2.09\ SO_2 + 13.36$	**0.44**	$PM_{coarse} = 0.96\ SO_2 + 8.42$	**0.28**
LB (20/6/97 – 31/8/97)	$PM_{10} = 1.50\ SO_2 + 19.47$	**0.24**	$PM_{2.5} = 0.96\ SO_2 + 14.43$	**0.22**	$PM_{coarse} = 0.45\ SO_2 + 6.25$	**0.08**
RO (20/6/97 - 31/8/97)	$PM_{10} = 0.42\ SO_2 + 18.80$	**0.05**	$PM_{2.5} = 0.30\ SO_2 + 12.36$	**0.05**	$PM_{coarse} = 0.15\ SO_2 + 7.30$	**0.02**
HAR (20/6/97 - 31/8/97)	**-**	**-**	**-**	**-**	**-**	**-**
Autumn 97						
LM (1/9/97 – 30/11/97)	$PM_{10} = 2.16\ SO_2 + 17.94$	**0.49**	$PM_{2.5} = 1.31\ SO_2 + 11.02$	**0.40**	$PM_{coarse} = 0.58\ SO_2 + 8.85$	**0.20**
LB (1/9/97 – 30/11/97)	$PM_{10} = 1.13\ SO_2 + 19.63$	**0.20**	$PM_{2.5} = 0.88\ SO_2 + 12.89$	**0.24**	$PM_{coarse} = 0.28\ SO_2 + 7.93$	**0.03**
RO (1/9/97 – 30/11/97)	$PM_{10} = 0.89\ SO_2 + 15.10$	**0.12**	$PM_{2.5} = 0.59\ SO_2 + 11.01$	**0.11**	$PM_{coarse} = 0.34\ SO_2 + 4.49$	**0.04**
HAR (28/9/97 - 30/11/97)	$PM_{10} = 0.88\ SO_2 + 14.88$	**0.11**	$PM_{2.5} = 0.60\ SO_2 + 11.94$	**0.08**	$PM_{coarse} = 0.14\ SO_2 + 4.03$	**0.03**
Winter 97/98						
LM (1/12/97 – 28/2/98)	$PM_{10} = 1.72\ SO_2 + 14.97$	**0.44**	$PM_{2.5} = 1.17\ SO_2 + 8.97$	**0.37**	$PM_{coarse} = 0.49\ SO_2 + 7.17$	**0.20**
LB (1/12/97 – 28/2/98)	$PM_{10} = 0.31\ SO_2 + 20.78$	**0.08**	$PM_{2.5} = 0.20\ SO_2 + 14.08$	**0.05**	$PM_{coarse} = 0.10\ SO_2 + 6.89$	**0.03**
RO (1/12/97 - 28/2/98)	$PM_{10} = 0.44\ SO_2 + 15.80$	**0.06**	$PM_{2.5} = 0.28\ SO_2 + 12.81$	**0.04**	$PM_{coarse} = 0.12\ SO_2 + 4.52$	**0.02**
HAR (1/12/97 - 28/2/98)	$PM_{10} = 1.22\ SO_2 + 14.39$	**0.27**	$PM_{2.5} = 1.07\ SO_2 + 10.15$	**0.28**	$PM_{coarse} = 0.14\ SO_2 + 4.25$	**0.03**
Spring 98						
LM (1/3/98 – 31/5/98)	$PM_{10} = 1.67\ SO_2 + 19.97$	**0.37**	$PM_{2.5} = 1.16\ SO_2 + 11.87$	**0.36**	$PM_{coarse} = 0.52\ SO_2 + 8.24$	**0.17**
LB (1/3/98 – 31/5/98)	$PM_{10} = 0.42\ SO_2 + 21.44$	**0.09**	$PM_{2.5} = 0.23\ SO_2 + 15.45$	**0.05**	$PM_{coarse} = 0.05\ SO_2 + 6.60$	**0.00**
RO (1/3/98 – 31/5/98)	$PM_{10} = 0.31\ SO_2 + 16.85$	**0.03**	$PM_{2.5} = 0.20\ SO_2 + 11.94$	**0.02**	$PM_{coarse} = 0.12\ SO_2 + 5.09$	**0.01**
HAR (1/3/98 - 31/5/98)	$PM_{10} = 0.32\ SO_2 + 15.20$	**0.05**	$PM_{2.5} = 0.26\ SO_2 + 10.94$	**0.05**	$PM_{coarse} = 0.08\ SO_2 + 4.59$	**0.01**
Summer 98						
LM (1/6/98 – 31/8/98)	$PM_{10} = 2.66\ SO_2 + 14.24$	**0.61**	$PM_{2.5} = 1.52\ SO_2 + 9.18$	**0.51**	$PM_{coarse} = 1.13\ SO_2 + 5.13$	**0.46**
LB (1/6/98 – 31/8/98)	$PM_{10} = 0.40\ SO_2 + 18.75$	**0.03**	$PM_{2.5} = 0.40\ SO_2 + 11.63$	**0.08**	$PM_{coarse} = 0.01\ SO_2 + 7.09$	**0.00**
RO (1/6/98 – 31/8/98)	$PM_{10} = 0.52\ SO_2 + 15.04$	**0.09**	$PM_{2.5} = 0.24\ SO_2 + 9.59$	**0.03**	$PM_{coarse} = 0.30\ SO_2 + 5.77$	**0.07**
HAR (1/6/98 - 31/8/98)	$PM_{10} = 0.48\ SO_2 + 13.42$	**0.03**	$PM_{2.5} = 0.43\ SO_2 + 8.70$	**0.04**	$PM_{coarse} = 0.06\ SO_2 + 4.70$	**0.00**

Table 4.5 Seasonal results of regression analyses of PM and SO_2 at DETR sites for hourly data (cont'd)

	$PM_{10} = m\,SO_2 + c$	R^2	$PM_{2.5} = m\,SO_2 + c$	R^2	$PM_{coarse} = m\,SO_2 + c$	R^2
Autumn 98						
LM (1/9/98 - 30/11/98)	$PM_{10} = 1.81\,SO_2 + 19.73$	0.35	$PM_{2.5} = 1.02\,SO_2 + 14.31$	0.22	$PM_{coarse} = 0.73\,SO_2 + 6.54$	0.27
LB (1/9/98 - 30/11/98)	$PM_{10} = 0.26\,SO_2 + 20.39$	0.06	$PM_{2.5} = 0.23\,SO_2 + 14.33$	0.07	$PM_{coarse} = 0.05\,SO_2 + 6.31$	0.01
RO (1/9/98 - 30/11/98)	$PM_{10} = 1.04\,SO_2 + 16.29$	0.13	$PM_{2.5} = 1.15\,SO_2 + 10.07$	0.13	$PM_{coarse} = 0.04\,SO_2 + 6.60$	0.00
HAR (1/9/98 - 30/11/98)	$PM_{10} = 5.26\,SO_2 + 12.08$	0.40	$PM_{2.5} = 4.22\,SO_2 + 8.73$	0.37	$PM_{coarse} = 1.04\,SO_2 + 3.42$	0.17
Winter 98/99						
LM (1/12/98 - 28/2/99)	$PM_{10} = 2.30\,SO_2 + 12.73$	0.44	$PM_{2.5} = 1.49\,SO_2 + 8.10$	0.43	$PM_{coarse} = 0.83\,SO_2 + 4.63$	0.26
LB (1/12/98 - 28/2/99)	$PM_{10} = 0.25\,SO_2 + 18.09$	0.06	$PM_{2.5} = 0.22\,SO_2 + 12.46$	0.08	$PM_{coarse} = 0.03\,SO_2 + 5.65$	0.00
RO (1/12/98 - 28/2/99)	$PM_{10} = 0.34\,SO_2 + 14.29$	0.04	$PM_{2.5} = 0.25\,SO_2 + 7.94$	0.05	$PM_{coarse} = 0.06\,SO_2 + 6.22$	0.00
HAR (1/12/98 - 28/2/99)	$PM_{10} = 1.05\,SO_2 + 10.99$	0.07	$PM_{2.5} = 1.32\,SO_2 + 7.29$	0.19	$PM_{coarse} = -0.25\,SO_2 + 3.72$	0.02
Spring 99						
LM (1/3/99 - 31/5/99)	$PM_{10} = 2.98\,SO_2 + 14.70$	0.52	$PM_{2.5} = 2.12\,SO_2 + 9.34$	0.44	$PM_{coarse} = 1.03\,SO_2 + 4.87$	0.24
LB (1/3/99 - 31/5/99)	$PM_{10} = 0.49\,SO_2 + 20.63$	0.05	$PM_{2.5} = 0.45\,SO_2 + 12.97$	0.10	$PM_{coarse} = 0.04\,SO_2 + 7.66$	0.00
RO (1/3/99 - 31/5/99)	$PM_{10} = 0.87\,SO_2 + 17.96$	0.07	$PM_{2.5} = 0.68\,SO_2 + 10.38$	0.09	$PM_{coarse} = 0.18\,SO_2 + 7.59$	0.01
HAR (1/3/99 - 31/5/99)	$PM_{10} = 0.38\,SO_2 + 13.93$	0.04	$PM_{2.5} = 0.31\,SO_2 + 9.43$	0.05	$PM_{coarse} = 0.07\,SO_2 + 4.44$	0.00
Summer 99						
LM (1/6/99 - 31/8/99)	$PM_{10} = 0.67\,SO_2 + 31.66$	0.04	$PM_{2.5} = 0.36\,SO_2 + 18.9$	0.05	$PM_{coarse} = 0.32\,SO_2 + 12.77$	0.02
LB (1/6/99 - 31/8/99)	$PM_{10} = 1.75\,SO_2 + 16.32$	0.24	$PM_{2.5} = 1.25\,SO_2 + 10.78$	0.24	$PM_{coarse} = 0.50\,SO_2 + 5.55$	0.09
RO (1/6/99 - 31/8/99)	$PM_{10} = 0.61\,SO_2 + 16.66$	0.13	$PM_{2.5} = 0.26\,SO_2 + 10.65$	0.04	$PM_{coarse} = 0.35\,SO_2 + 6.04$	0.12
HAR (1/6/99 - 31/8/99)	$PM_{10} = 0.79\,SO_2 + 14.77$	0.06	$PM_{2.5} = 0.54\,SO_2 + 8.97$	0.07	$PM_{coarse} = 0.23\,SO_2 + 5.98$	0.02
Autumn 99						
LM (1/9/99 - 30/11/99)	$PM_{10} = 2.46\,SO_2 + 24.27$	0.10	$PM_{2.5} = 1.57\,SO_2 + 14.46$	0.15	$PM_{coarse} = 0.94\,SO_2 + 9.65$	0.04
LB (1/9/99 - 30/11/99)	$PM_{10} = 0.61\,SO_2 + 19.64$	0.05	$PM_{2.5} = 0.55\,SO_2 + 12.56$	0.07	$PM_{coarse} = 0.07\,SO_2 + 7.20$	0.00
RO (1/9/99 - 30/11/99)	$PM_{10} = 0.67\,SO_2 + 15.81$	0.05	$PM_{2.5} = 0.39\,SO_2 + 10.73$	0.03	$PM_{coarse} = 0.27\,SO_2 + 5.11$	0.05
HAR (1/9/99 - 30/11/99)	$PM_{10} = 1.02\,SO_2 + 12.35$	0.04	$PM_{2.5} = 0.97\,SO_2 + 8.28$	0.07	$PM_{coarse} = 0.03\,SO_2 + 4.28$	0.00
Winter 99						
LM (12/99)	$PM_{10} = 3.90\,SO_2 + 14.33$	0.69	$PM_{2.5} = 2.30\,SO_2 + 10.67$	0.56	$PM_{coarse} = 1.61\,SO_2 + 4.10$	0.45
LB (12/99)	$PM_{10} = 0.49\,SO_2 + 12.70$	0.21	$PM_{2.5} = 0.38\,SO_2 + 8.19$	0.26	$PM_{coarse} = 0.11\,SO_2 + 4.58$	0.07
RO (12/99)	$PM_{10} = 0.59\,SO_2 + 10.14$	0.17	$PM_{2.5} = 0.47\,SO_2 + 6.46$	0.19	$PM_{coarse} = 0.13\,SO_2 + 3.77$	0.04
HAR (12/99)	$PM_{10} = 1.15\,SO_2 + 8.32$	0.23	$PM_{2.5} = 1.03\,SO_2 + 5.72$	0.33	$PM_{coarse} = 0.12\,SO_2 + 2.60$	0.01

4.3 EPAQS Exceedences and Episode Study

4.3.1 Number of Exceedences of the EPAQS Standard

The number of exceedences of the PM_{10} EPAQS standard are obtained as the number of times the 24h-running mean PM_{10} concentration exceeded 50 µg m^{-3}. A seasonal summary is shown in Table 4.6 for the period from summer 1997 to December 1999 at the four DETR sites. The EPAQS standard value of 50 µg m^{-3} was exceeded on a total number of 2069 occasions over a two-year and seven-month period in London Marylebone Road. In comparison London Bloomsbury showed a much lower EPAQS exceedence count of 391, whereas even lower numbers of exceedences were observed at the two rural sites, 96 in Rochester and 35 in Harwell. Similarly the highest 24h-running mean and the highest hourly mean also occurred at Marylebone Road (337 and 500 µg m^{-3}). The number of exceedences significantly decreased comparing with earlier studies for the UK AUN sites from 1992 to 1994, which reported that London Bloomsbury had an EPAQS exceedence count of 1901 over the three-year period (Deacon et al., 1997; QUARG, 1996).

There is no clear indication of seasonal trend of exceedences although it might be expected that winter and autumn should show a greater tendency of exceeding the standard when the dispersion of atmospheric pollution is poorer. Also sometimes contributions of coarse particles can raise the EPAQS count substantially, such as summer 1999 at Marylebone Road, summer 1998 at Rochester and autumn 1998 at Harwell.

Table 4.6 Number of exceedences of EPAQS standard at four DETR sites

Site & Period	No. of exceedences	Highest 24h-running Mean PM_{10} ($\mu g/m^3$)	Highest Hourly Average PM_{10} ($\mu g/m^3$)
Whole period			
LM (20/6/97 - 31/12/99)	2069	337.0	500.0
LB (20/6/97 - 31/12/99)	391	84.6	349.0
RO (20/6/97 - 31/12/99)	96	70.0	390.0
HAR (20/6/97 - 31/12/99)	35	64.0	371.9
Summer 97			
LM (20/6/97 – 31/8/97)	252	80.0	96
LB (20/6/97 – 31/8/97)	113	62.2	114
RO (20/6/97 – 31/8/97)	2	50.5	100
HAR (20/6/97 – 31/8/97)	-	-	-
Autumn 97			
LM (1/9/97 – 30/11/97)	341	102.7	166
LB (1/9/97 – 30/11/97)	143	84.6	349
RO (1/9/97 – 30/11/97)	28	66.8	267
HAR (28/9/97 – 30/11/97)	0	-	67.1
Winter 97/98			
LM (1/12/97 – 28/2/98)	220	77.3	103
LB (1/12/97 – 28/2/98)	8	52	77
RO (1/12/97 – 28/2/98)	0	-	174
HAR (1/12/97 – 28/2/98)	13	56.6	70.9
Spring 98			
LM (1/3/98 – 31/5/98)	97	71.4	158
LB (1/3/98 – 31/5/98)	61	73.5	188
RO (1/3/98 – 31/5/98)	11	54.6	72
HAR (1/3/98 – 31/5/98)	0	-	65.9
Summer 98			
LM (1/6/98 – 31/8/98)	52	63.7	96
LB (1/6/98 – 31/8/98)	17	54.6	81
RO (1/6/98 – 31/8/98)	24	70	390
HAR (1/6/98 – 31/8/98)	0	-	51.9
Autumn 98			
LM (1/9/98 – 30/11/98)	182	77.2	101
LB (1/9/98 – 30/11/98)	0	47.5	240.5
RO (1/9/98 – 30/11/98)	0	39	134
HAR (1/9/98 – 30/11/98)	22	64	371.9
Winter 98/99			
LM (1/12/98 – 28/2/99)	105	227	227
LB (1/12/98 – 28/2/99)	0	49.2	105
RO (1/12/98 – 28/2/99)	0	36.3	94.8
HAR (1/12/98 – 28/2/99)	0	28.6	36.4
Spring 99			
LM (1/3/99 – 31/5/99)	86	62	119
LB (1/3/99 – 31/5/99)	23	63.2	85.5
RO (1/3/99 – 31/5/99)	11	53.3	62.6
HAR (1/3/99 – 31/5/99)	0	33.6	92.8
Summer 99			
LM (1/6/99 – 31/8/99)	175	142.7	500
LB (1/6/99 – 31/8/99)	7	51.5	91.6
RO (1/6/99 – 31/8/99)	0	42.5	94.1
HAR (1/6/99 – 31/8/99)	0	35.8	54.6

Table 4.6 Number of exceedences of EPAQS standard at four DETR sites(cont'd)

Site & Period	No. of exceedences	Highest 24h-running Mean PM_{10} (μg/m^3)	Highest Hourly Average PM_{10} (μg/m^3)
Autumn 99			
LM (1/9/99 - 30/11/99)	**531**	**337**	**466**
LB (1/9/99 - 30/11/99)	**19**	**55.9**	**93.8**
RO (1/9/99 - 30/11/99)	**20**	**67.6**	**180.3**
HAR (1/9/99 - 30/11/99)	**0**	**39.9**	**121.4**
Winter 12/99			
LM (1/12/99 - 31/12/99)	**28**	**67.1**	**134**
LB (1/12/99 - 31/12/99)	**0**	**41.1**	**90**
RO (1/12/99 - 31/12/99)	**0**	**29.1**	**50.4**
HAR (1/12/99 - 31/12/99)	**0**	**20.1**	**41.3**

4.3.2 Particle Concentrations during Episodes

In addition to the EPAQS counts, very high hourly mean particle concentrations were observed at all four sites. The highest hourly PM_{10} concentrations reached 500, 349, 390 and 372 μg m^{-3} at LM, LB, RO and HAR respectively (Table 4.6). By examining these high hourly concentrations, it is found that PM_{10} episodes are mostly dominated by fine particles but coarse particles can contribute considerably to episodes on some occasions. At LM hourly PM_{10} concentrations frequently exceeded 50 μg m^{-3} and were dominated by either fine or coarse particles or both. For PM_{10} concentrations in the range 80-100 μg m^{-3}, the fine fraction contributes approximately two thirds (Figure 4.8) although coarse particles make a higher contribution on a few occasions. Similar composition was also found from PM_{10} concentrations between 50 and 80 μg m^{-3}. Comparatively very high PM_{10} concentrations (over 100 μg m^{-3}) are likely to occur in summer and autumn seasons, and composed of a higher component of the coarse fraction, which contributes anything between half and up to four fifths (Figure 4.9a). It seems that these higher coarse components are temporally related to higher wind speeds (4.9b), but not in all cases. In addition to wind, traffic is another important factor, which elevates the coarse particle concentrations through re-suspension on Marylebone Road. Similarly, any construction work, which is unidentified, may also cause occasional very high coarse particle concentrations. There are situations that high PM_{10} levels can sometimes arise from similar contributions of fine and coarse particles, indicating that both fine and coarse particle concentrations are elevated on Marylebone Road due to a similar source from road traffic (Harrison et al., 2001; APEG, 1999).

In LB the highest PM_{10} levels (> 80 μg m^{-3}) occurred mostly in autumn and spring, and were associated either with higher coarse or fine components (Figure 4.10a). Similar to LM there is a temporal relationship between the higher coarse concentrations and wind speeds (Figure 4.10b). For most of the hours with concentrations between 60 and 80 μg m^{-3}, PM_{10} composed of higher $PM_{2.5}$ than coarse particles (Figure 4.11). Rochester and Harwell also exhibited the highest hourly PM_{10} concentrations (>100 μg m^{-3}) in the autumn seasons, often associated with a higher mass of coarse particles (Figures 4.12a and 4.13a). Fine particles may be the dominant component for PM_{10} concentrations less than 100 μg m^{-3}. The high coarse particle concentrations sometimes were related to higher wind speeds but other times were not (Figures 4.12b and 4.13b). A possible interpretation for the latter is due to local constructions or some other as yet unidentified events.

In general, high PM_{10} concentrations were related very well to fine particles at LB, RO and HAR, which made the greatest contributions to the most of the PM_{10} episodes. However, coarse particles predominated on occasions when PM_{10} concentrations exceeded about 100 μg m^{-3}, and these very high concentrations only lasted for a short period of a few hours. In comparison the PM_{10} episodes at LM were mostly affected by both fine and coarse particles, although very high coarse components were also observed during periods of extremely high concentrations.

Figure 4.8 Hourly PM concentrations (PM_{10} = 80-100 µg m^{-3}) at LM

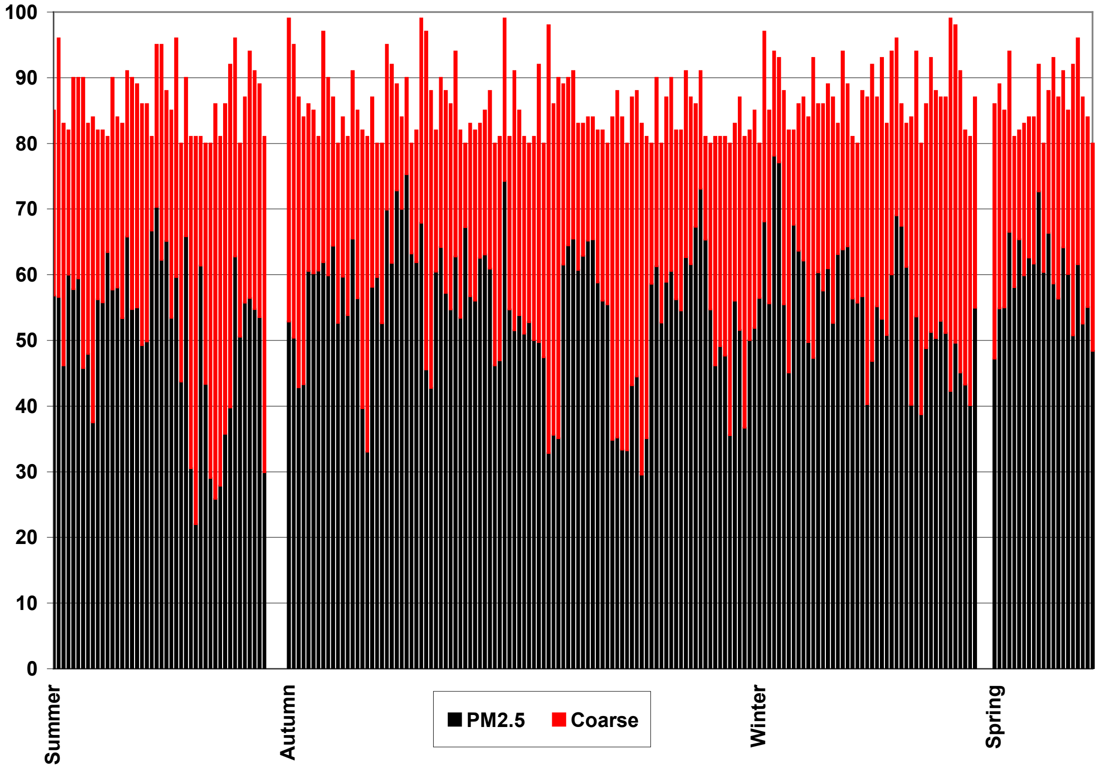


Figure 4.9a Hourly PM concentrations (PM_{10} > 100 µg m^{-3}) at LM

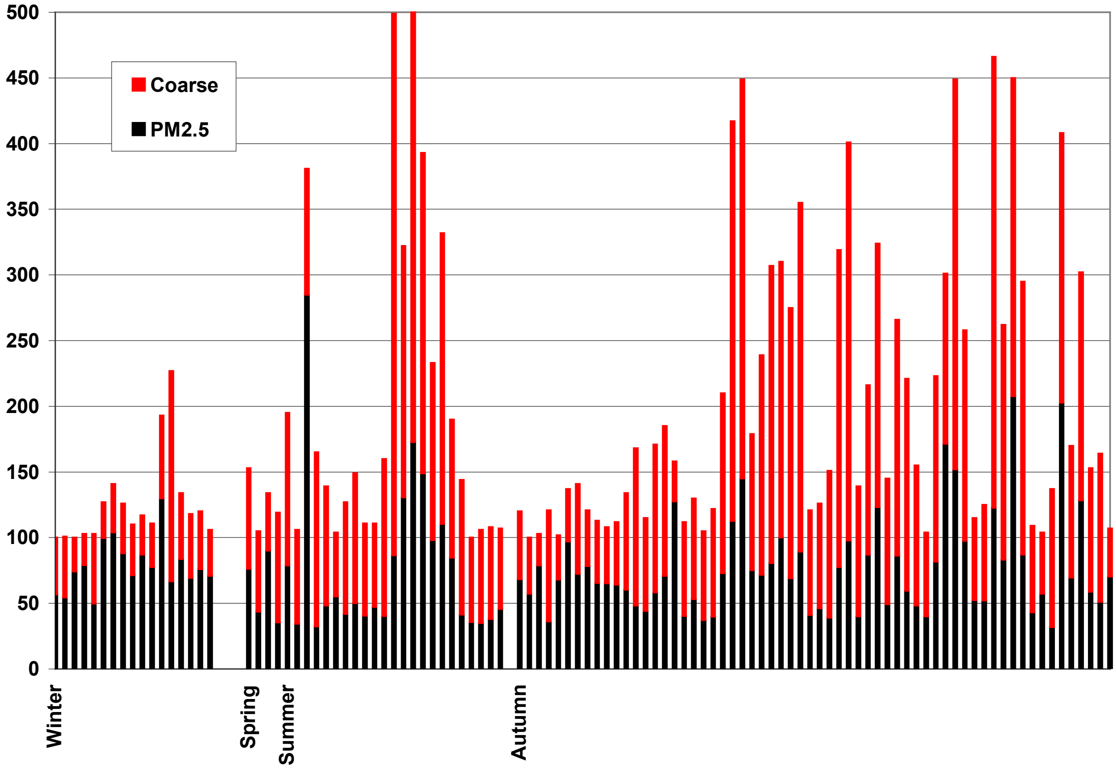


Figure 4.9b Hourly wind speeds (PM$_{10}$ > 100 µg m^{-3}) at LM

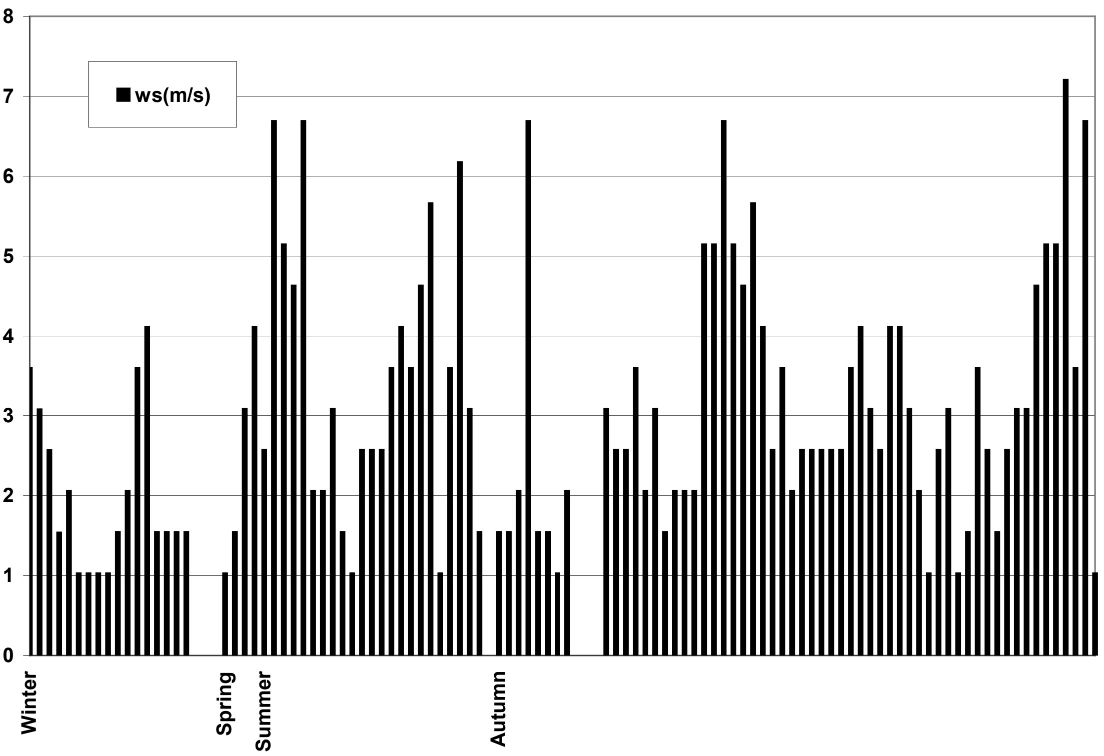


Figure 4.10a Hourly PM concentrations (PM$_{10}$ > 80 µg m^{-3}) at LB

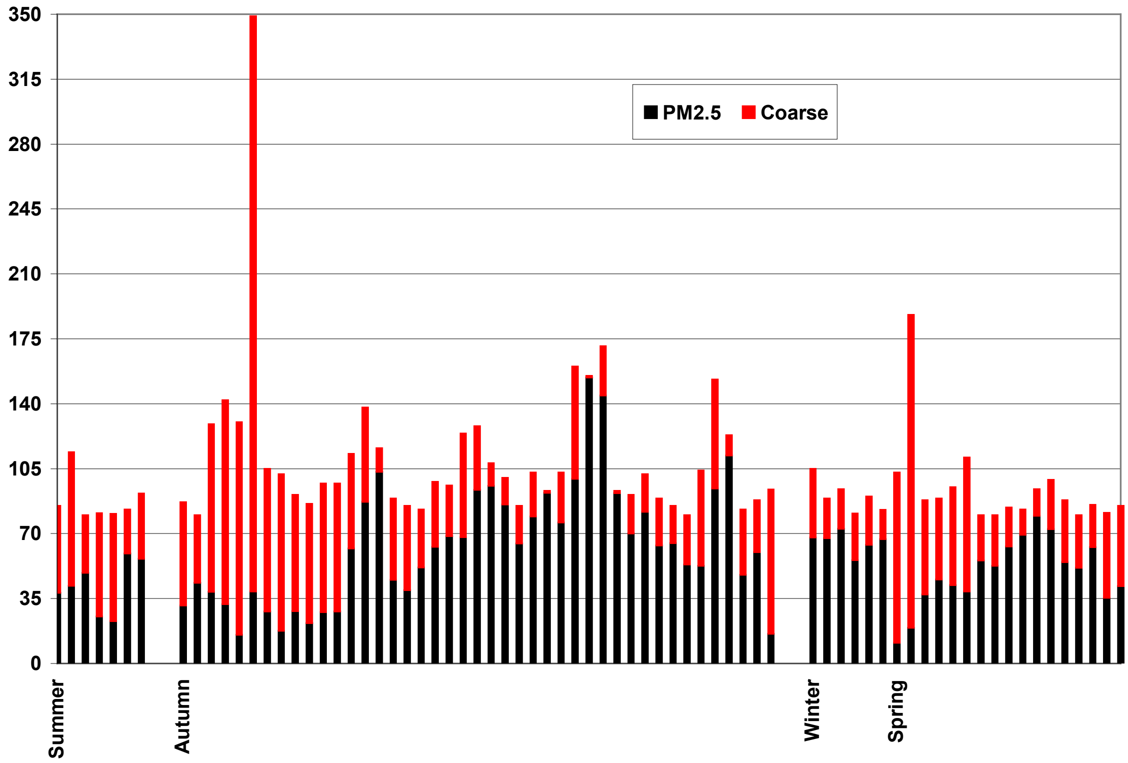


Figure 4.10b Hourly wind speeds (PM$_{10}$ > 80 μg m^{-3}) at LB

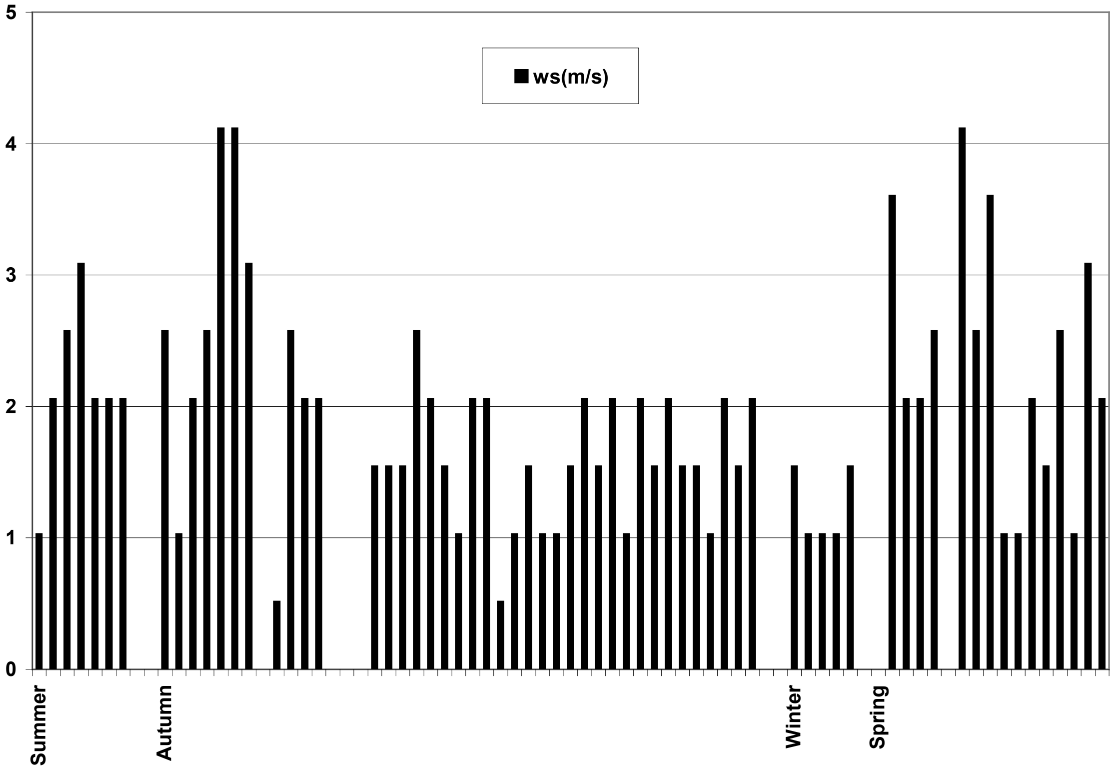


Figure 4.11 Hourly PM concentrations (PM$_{10}$ = 60- 80 μg m^{-3}) at LB

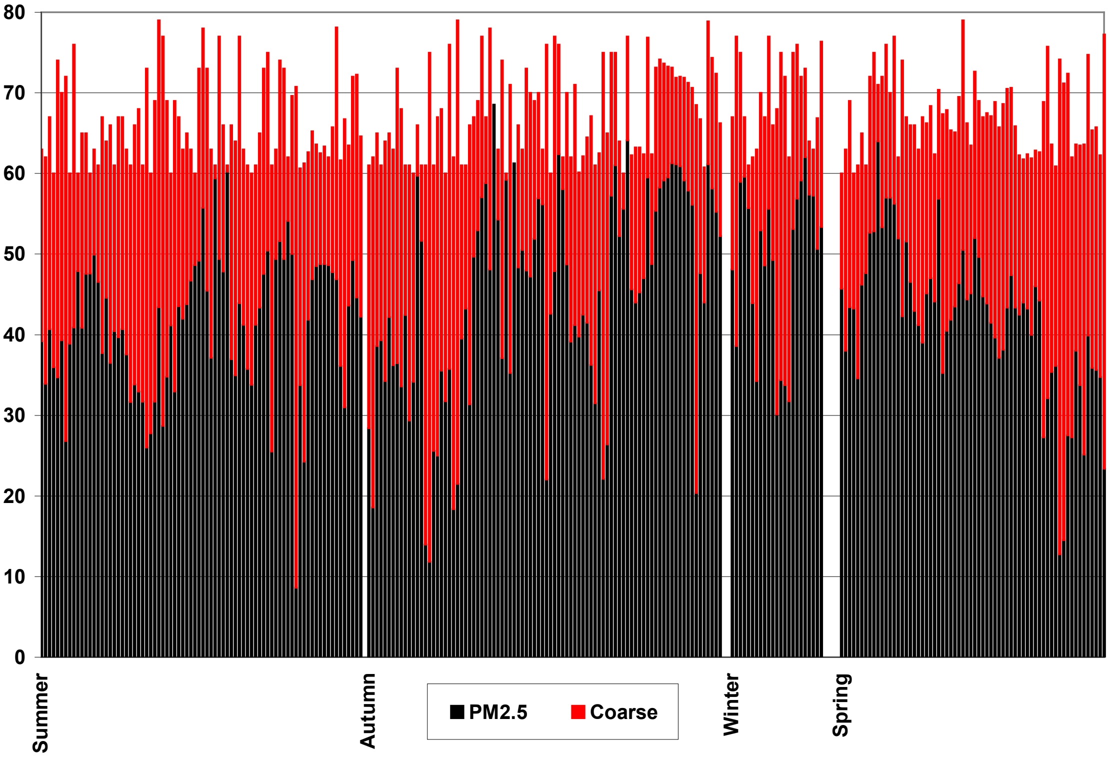


Figure 4.12a Hourly PM concentrations ($PM_{10} > 60$ µg m^{-3}) at Rochester

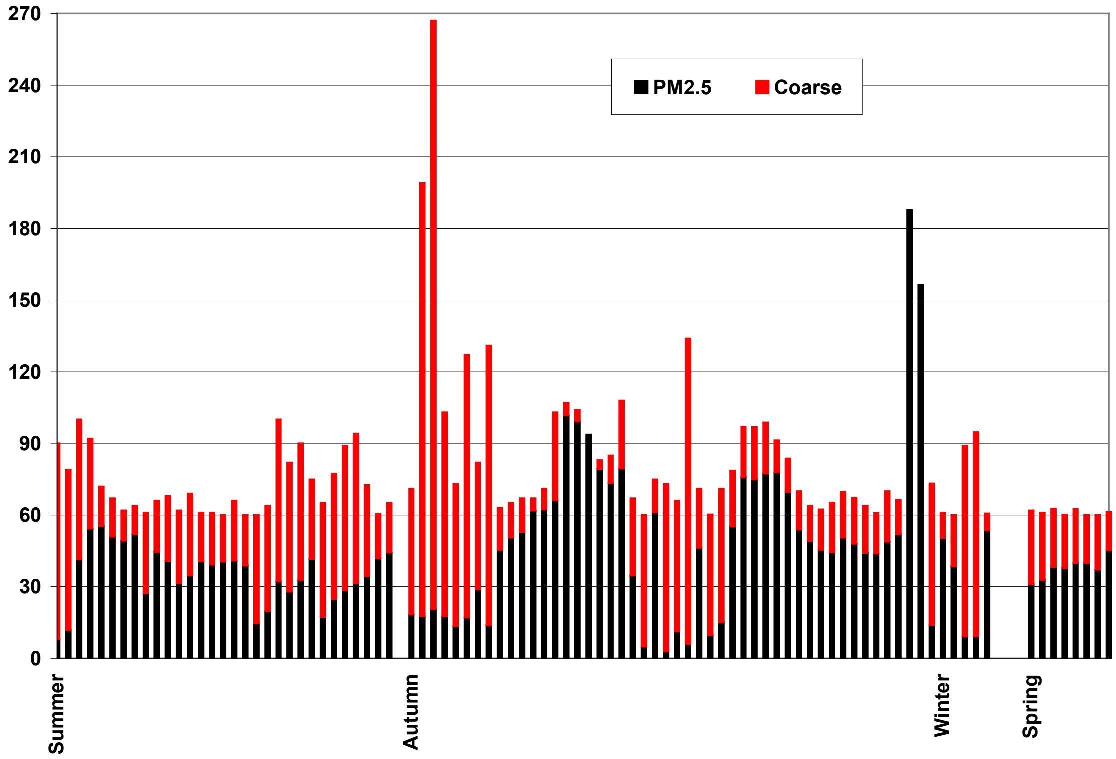


Figure 4.12b Hourly wind speeds ($PM_{10} > 60$ µg m^{-3}) at Rochester

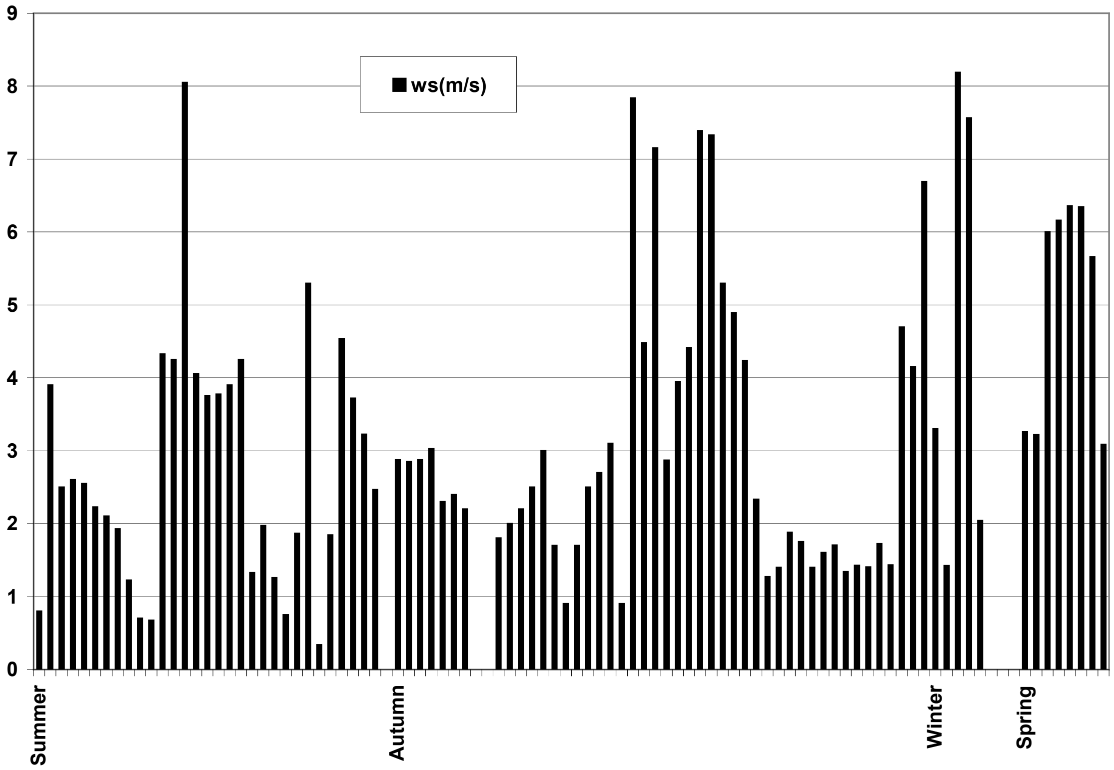


Figure 4.13a Hourly PM concentrations ($PM_{10} > 50\ \mu g\ m^{-3}$) at Harwell

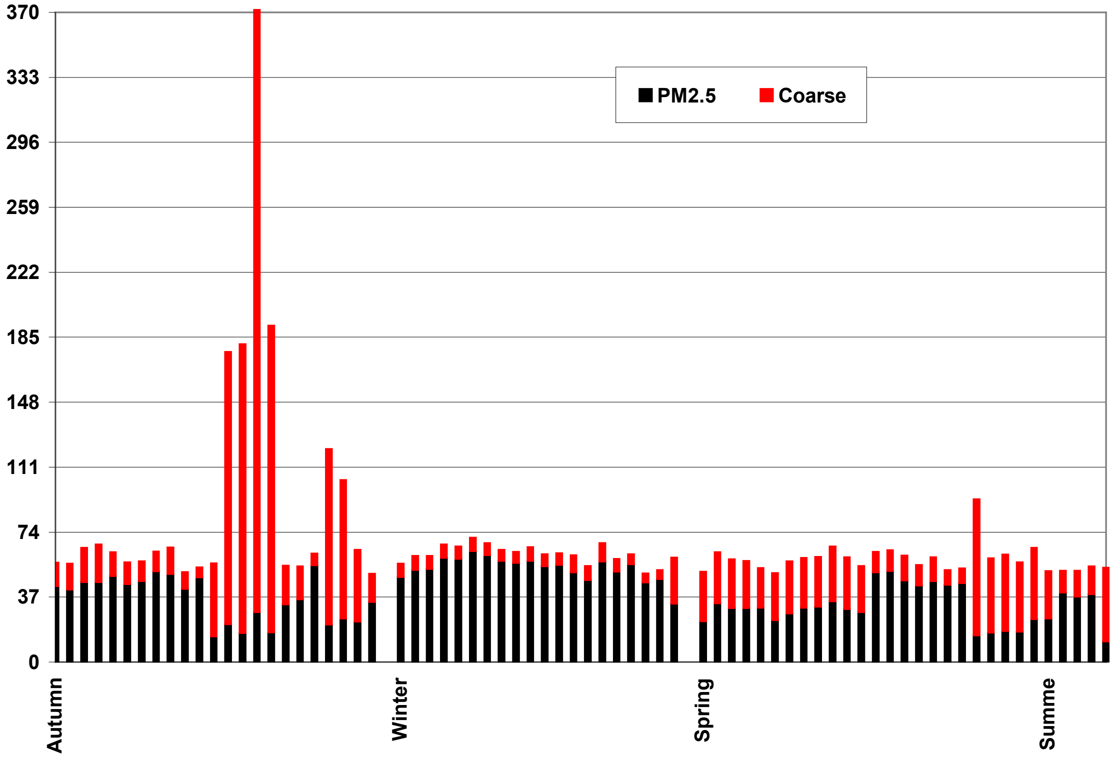
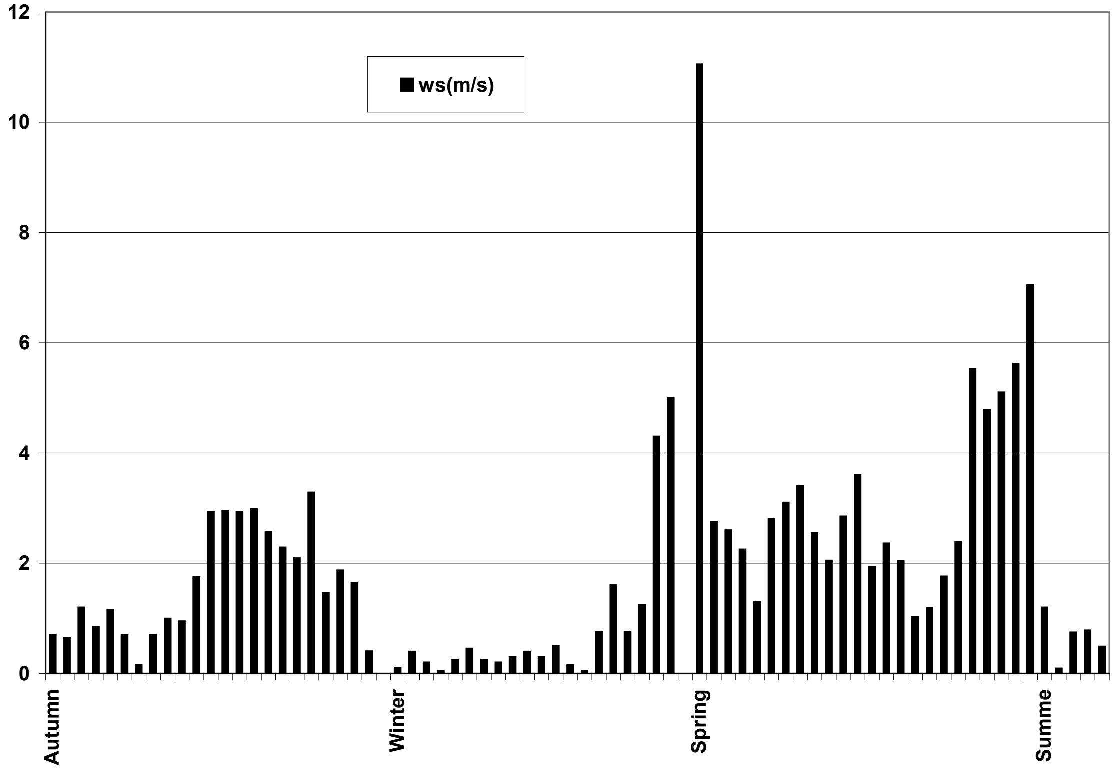


Figure 4.13b Hourly wind speeds ($PM_{10} > 50\ \mu g\ m^{-3}$) at Harwell



Additional investigation was performed for two chosen periods. The first is from the 5th to the 21st August 1997, when PM_{10} levels were elevated at all three sites LM, LB and RO (no measurement was made at HAR). This was clearly a fine particle dominated episode consisting of more than two thirds of the fine fraction at all sites. The average PM_{10} concentrations over the period were 53.0, 41.2 and 35.1 µg m^{-3} (Table 4.7) at LM, LB and RO, respectively, which were much higher than the typical average concentrations of 34.7, 22.8 and 17.7 µg m^{-3} (Table 3.1). On examining the levels of the other pollutants, it was found that the average concentrations of CO, NOx and SO_2 were identical to those typical values apart from Rochester where the concentration of SO_2 was 15.7 ppb, nearly three times of the normal average of 3.6 ppb. On the contrary, O_3 levels were increased considerably over the period in comparison with normal levels. The maximum values at LM, LB and RO were 60, 70 and 111 ppb respectively indicating that there was high photochemical activity during this episode. There were frequently easterly or south-easterly winds over the period and the wind speeds remained low or medium in London areas, on average between 2-5 m/s, and higher in Rochester between 2-9 m/s (Figure 4.14). Therefore, another component, which contributed to the episode, could be long-range transport from continental Europe. From the analyses above, it is concluded that episode one was mostly related to components from both long-range transport and secondary particle formation through photo-chemistry, whereas local primary emissions were less significant. In comparison, the winter and spring episodes from 19 January to 4 February 1996 and March 1996 reported by King and Dorling (1997) and Stedman (1997) were mainly due to long-range transport contributions from the continental Europe.

Table 4.7 Pollutant concentrations during episode period

	PM10 (µg/m^3)	**PM2.5 (µg/m^3)**	**Coarse (µg/m^3)**	**CO (ppm)**	**NOx (ppb)**	**SO2 (ppb)**	**O3 (ppb)**
Episode One (5/8/97 -21/8/97)							
LM							
Average	53.0	36.0	16.8	2.4	197.0	7.8	9.9
Max.	95.0	81.6	63.6	8.7	438.0	37.0	60.0
LB							
Average	41.2	28.2	12.6	0.7	71.8	7.1	17.9
Max.	114.0	60.2	72.1	3.0	237.0	62.0	70.0
RO							
Average	35.1	25.3	11.2	-	15.7	6.1	40.7
Max.	100.0	57.3	58.5	-	56.0	39.0	111.0

Episode Two (29/10/97 - 14/11/97)

LM							
Average	53.3	41.8	26.9	3.9	378.4	14.2	5.4
Max.	167.0	97.1	68.7	12.9	1357.0	51.0	15.0
LB							
Average	36.9	27.9	10.0	1.6	191.3	11.9	6.6
Max.	171.0	155.9	60.5	8.7	943.0	77.0	26.0
RO							
Average	24.3	18.3	5.8	-	45.2	6.3	13.7
Max.	108.0	101.7	36.8	-	270.0	55.0	46.0
HAR							
Average	29.9	23.9	6.0	-	66.2	6.4	5.5
Max.	67.1	51.7	30.7	-	209.1	41.6	23.0

The second period is from 29/10/97 to 14/11/97 (Figure 4.15), which is again a fine fraction dominated episode. Similar analyses were applied and the major difference from the first episode is that low levels of O_3 and high levels of other air pollutants were observed. The NO_x, CO and SO_2 concentrations were greatly elevated at all four sites giving average concentrations around 2-4 times higher than the typical average values (Table 4.7). The wind profiles were only fully available for the Rochester site, and show that the wind directions over this period were varied. The prevailing wind was in a westerly or north-westerly direction between 29th of October to the 2nd of November, south-easterly to southerly from the 3rd to 5th of November, and finally south-westerly or westerly from 6th to 14th of November. It is noted that the only days with south and south-easterly wind but higher wind speeds did not show significantly elevated concentrations of PM indicating that this episode is not due to long-range transport from the European continent.

There are two noted periods when PM_{10} concentrations were elevated substantially showing identical peaks at LM, LB and RO sites (Figure 4.15). One is from the 29th of October to 3rd of November and another is from 11th to 14th of November when the wind speeds were very low about 1-2 m/s at London sites and 1-3 m/s at Rochester (Figure 4.14). Harwell seems to behave differently from the others and only shows high PM_{10} concentrations during the first period but on a slightly different time scale when a very low wind speed prevailed (about 1-2 m/s). The highest levels of PM_{10} reached up to 167, 171 and 108 $\mu g\ m^{-3}$ on the 2nd of November 1997 at LM, LB and RO, respectively, accompanied with the highest NO_x (about 1357, 870 and 270 ppb) and CO (about 14 and 9 ppm) concentrations. Clearly, primary pollutants mainly from vehicle exhaust emissions dominated the second episode particularly at the two urban sites. Comparing with the London sites, the concentrations at Rochester and

Harwell were much lower, which were likely influenced by the polluted airmasses from London at Rochester during westerly wind, and from the midlands at Harwell during north-westerly wind. Concentrations were lowest between days 8-10 November due to winds of south-westerly direction and higher speed. Similarly other air pollutant levels were also low on these days. It is clear that episode two was on a regional scale consisting of a predominant component of local primary vehicle exhaust emissions characterised by high concentrations of NO_x and CO. It was largely controlled by weather conditions, which favoured pollutant build up.

Similar to these two periods analysed above, other fine particle dominated PM_{10} episodes are generally due to either primary pollutants arising mainly from local sources or long-range transport, or secondary pollutants formed through chemical reactions. The latter is likely to occur in summer and spring whereas winter and autumn pollution episodes are generally related to primary sources.

Figure 4.14 Wind profile at London and Rochester sites

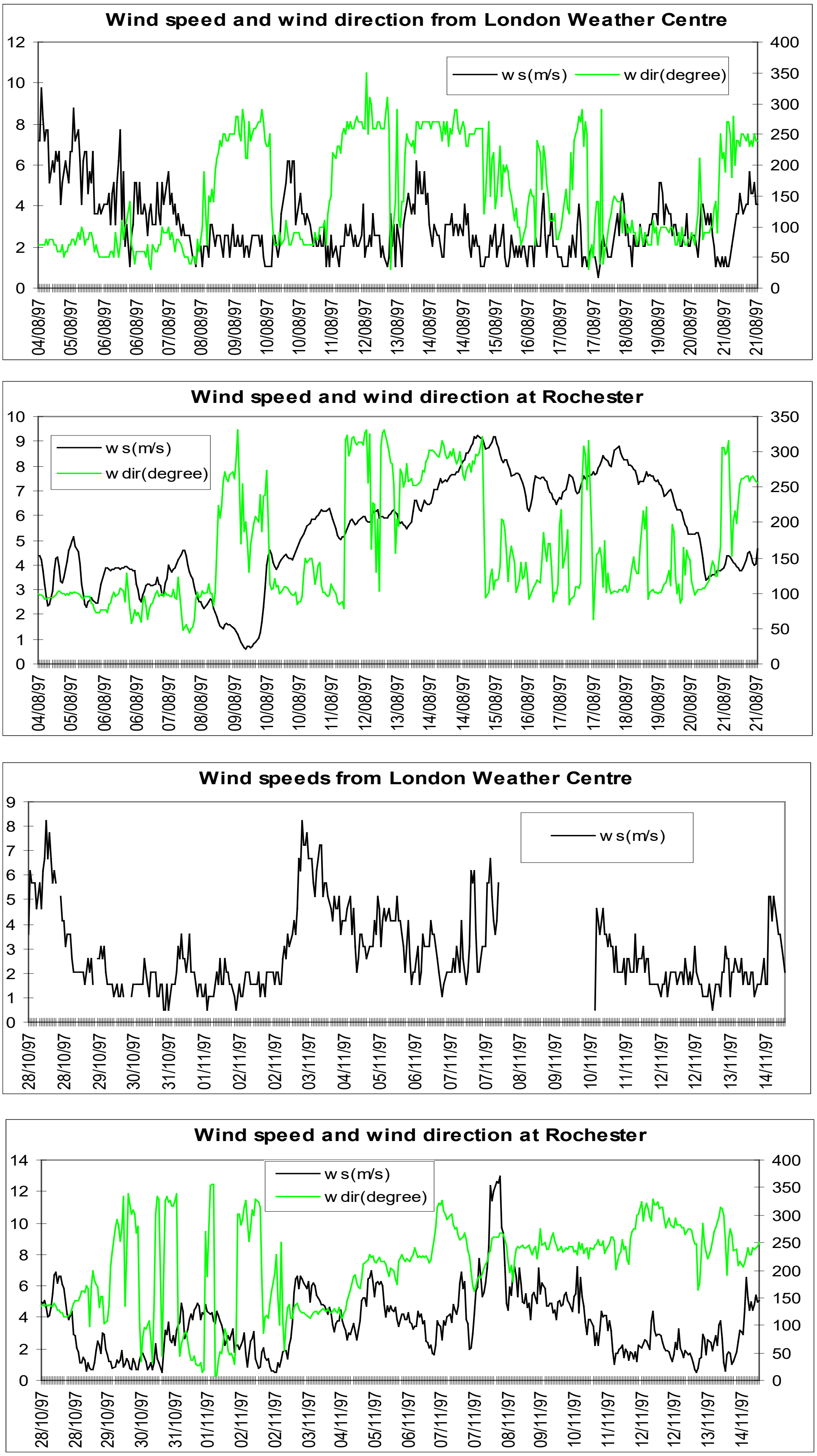
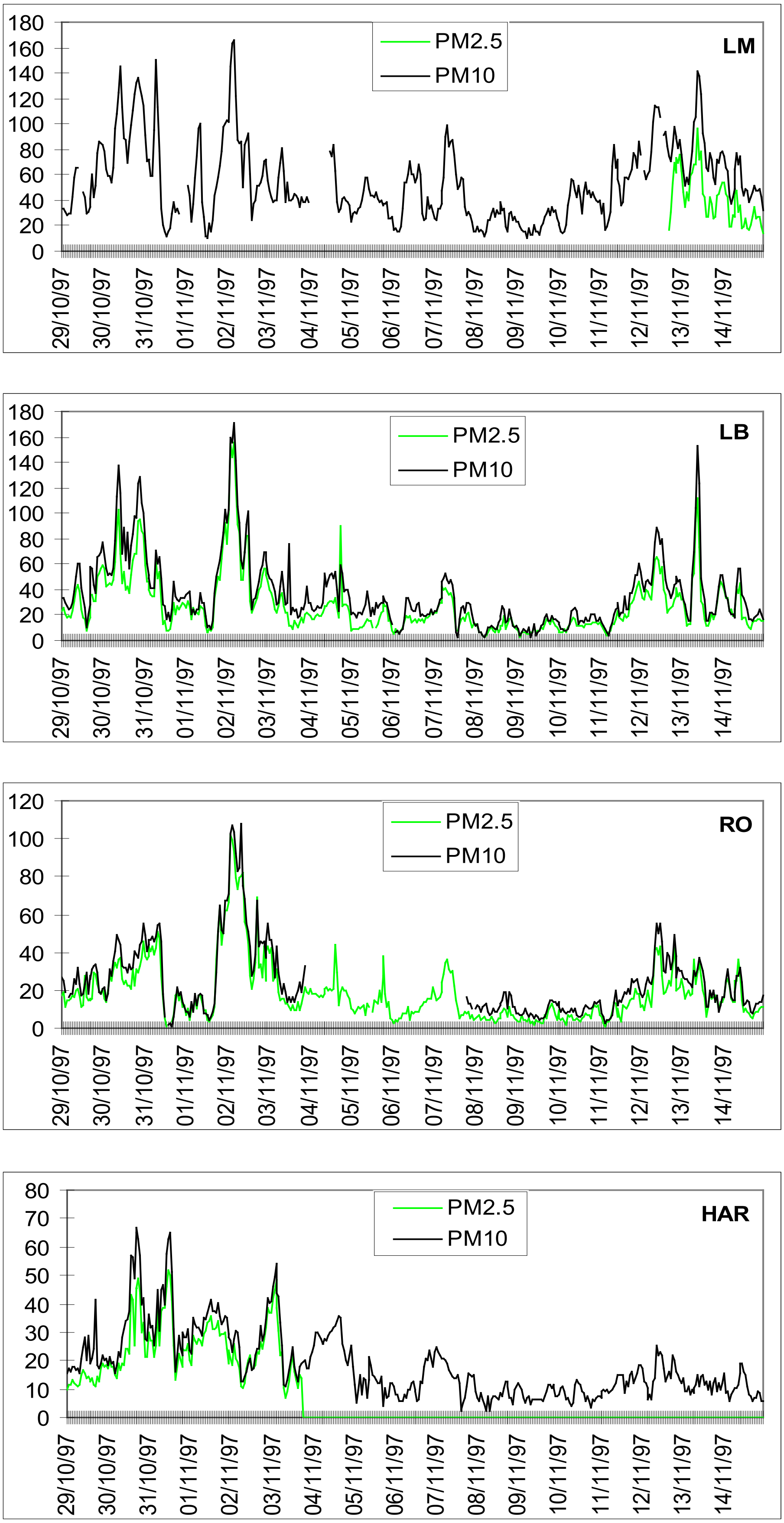


Figure 4.15 High PM concentrations at the four DETR sites on a wide spread episode



4.4 Airborne Particulate Concentrations and Traffic

To control PM_{10} concentrations to be within the limit of the EPAQS standard, the major sources of emissions need to be identified. Table 4.6 discussed above clearly shows that the urban sites LM and LB are most likely to exceed the standard. Early studies from Hodge Hill, Birmingham show that exhaust emissions from road traffic are major contributors to PM_{10} episodes in winter in urban areas. This section seeks to evaluate the relationship between traffic-induced pollutants using the two London sites and the correlation of traffic to airborne particles.

4.4.1 Correlation between Traffic Induced Pollutants

A comparison of daily mean concentrations of PM_{10}, $PM_{2.5}$, PM_{coarse} and NO_x at Marylebone Road has been made for the period from June 1997 to September 1998 using the roadside enhancement data (roadside enhancement = roadside measurement – background measurement). London Bloomsbury was chosen as the background site (APEG, 1999; Harrison et al., 2001). Very strong correlation was found between traffic-induced PM_{10}, $PM_{2.5}$ and NO_x (R = 0.87 and 0.79). The results show that it is reasonable to choose LB as a background site as the intercepts from the regression equations are very small. Also the roadside PM_{10} concentrations are composed of about equal halves of fine and coarse particles addressing the importance of both exhaust emissions and re-suspended particles. Similar analyses are applied here for a longer period to evaluate the roadside increment of both particle mass and numbers. Hourly differences between the two London sites were calculated and the relationship between elevation of particle concentrations and gaseous pollutants was investigated.

The results indicated that the traffic increment of NO_x and CO has strong or very strong correlation with the traffic increment of particle numbers and strong or modest correlation with particle mass (PM_{10} and $PM_{2.5}$) (Figure 4.16). The higher correlation for particle numbers with NO_x and CO than for particle mass highlights that particle number is a better parameter for assessing vehicle exhaust emissions. Also NO_x correlates better with particle numbers and mass than CO. Particle number concentrations correlate strongly with PM_{10} and $PM_{2.5}$ during all seasons (R^2 = 0.51 – 0.83) showing that road traffic as a main pollution source on Marylebone Road affected the particle concentrations in both number and mass forms. Winter months, such as February 1999, gave the closest relationship between the particle number with PM_{10}, $PM_{2.5}$ and NO_x (Figure 4.17).

Figure 4.16 Hourly mean concentrations of traffic increment (summer99)

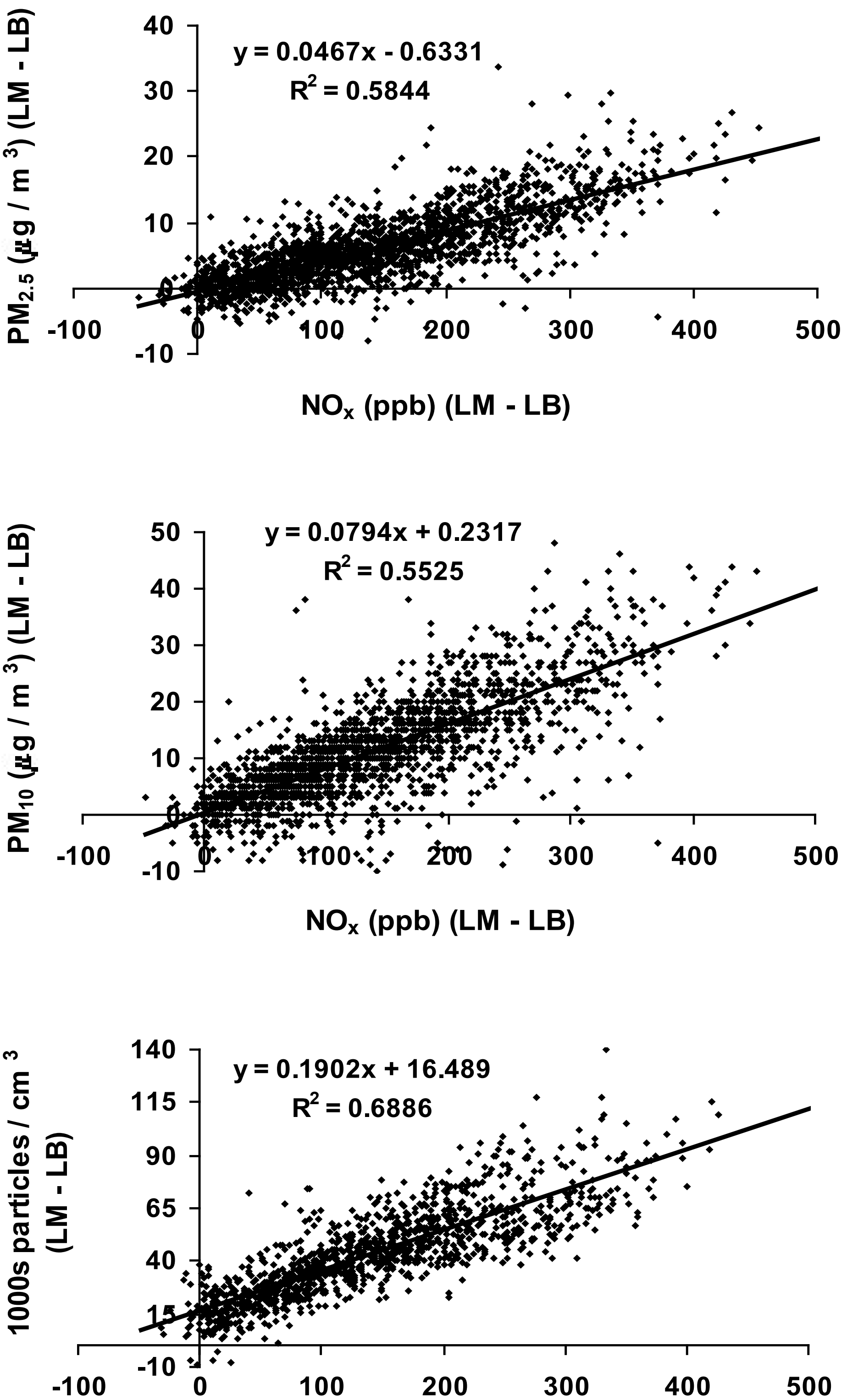
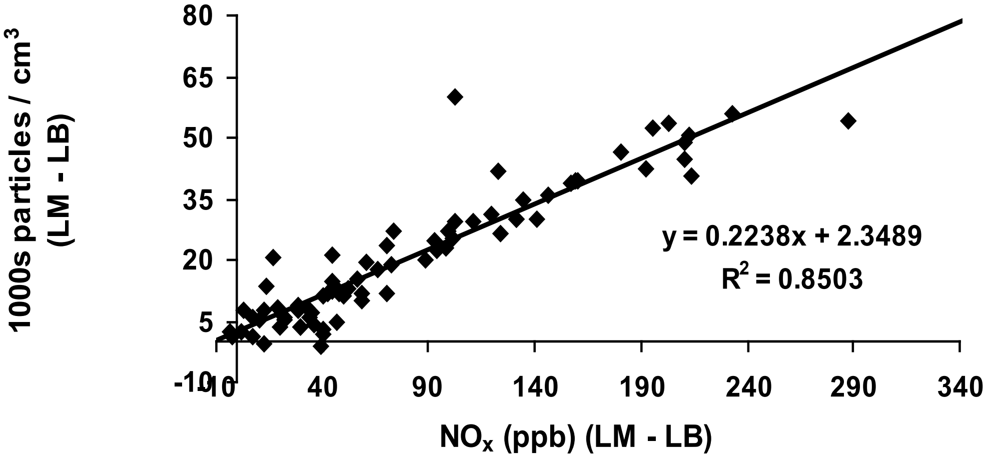
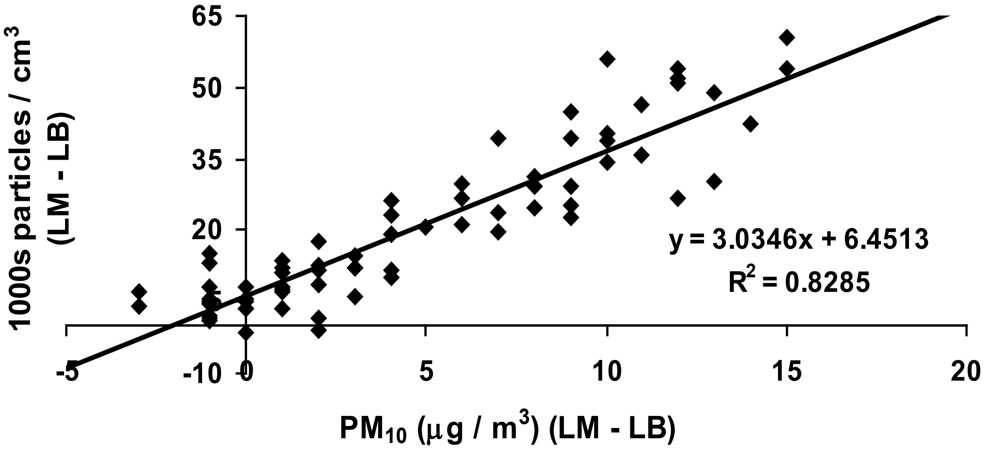
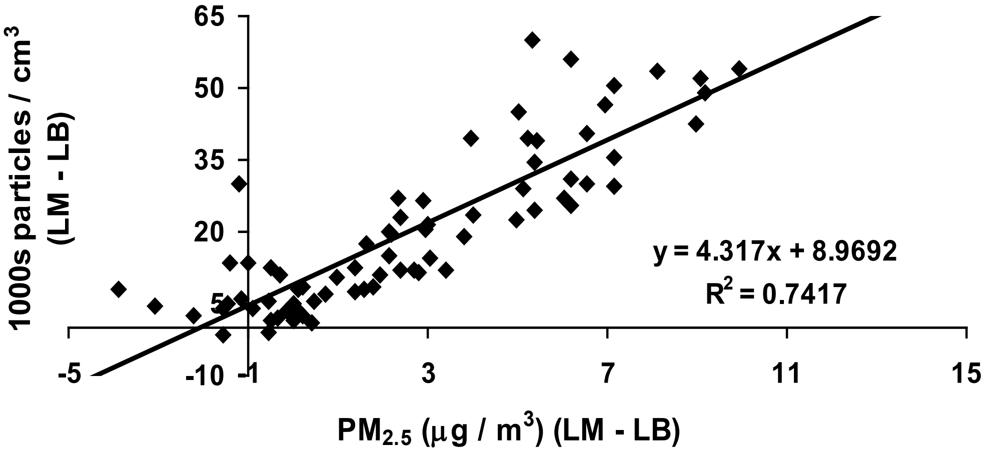


Figure 4.17 Hourly mean concentrations of traffic increment (February99)







4.4.2 PM and Total Traffic Count

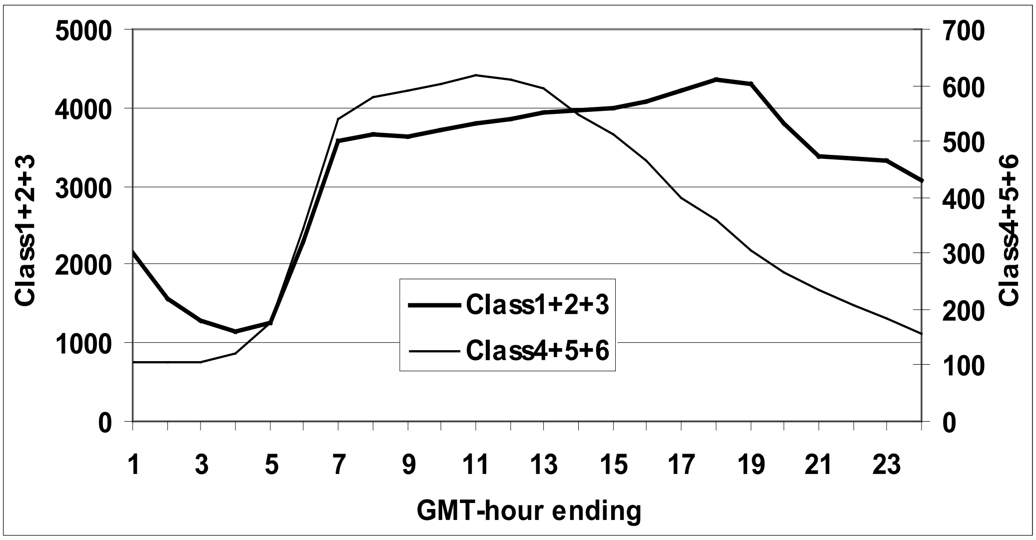
Since September 1998 traffic measurement has been made by South East Institute of Public Health (Seiph) at London Marylebone Road, including traffic volume, traffic type and traffic speed. There are six lanes on the road and each one was equipped with two counting systems. All vehicles are divided into six classes according to the European six bin scheme accounting for class1 -motorcycle, class2 - car or light van, class3 - car with trailer, class4 - rigid lorry or heavy van or mini bus, class5 - articulated lorry and class6 - bus or coach. Traffic speed was separated into bins at every 5 kph.

Seasonal correlation of total traffic volume to particle mass, particle numbers and the gaseous pollutants was examined here using the hourly averages for the period from September 1998 to December 1999. The results showed positive but relatively weak correlations between various particle mass fractions, particle numbers and traffic count with coefficient R ranging from 0.10 to 0.41. The closest and still modest association was observed only for $PM_{2.5}$ in December 1999 (R = 0.41). Other researchers also found weak associations between traffic volume and particle mass (Lam et al., 1999; Rajkumar and Chang, 2000). A possible explanation made by Rajkumar and Chang for the low correlation was the sampler being located far from the road (5-20m), however this is not the case reported from Lam et al (about 1m) nor for London Marylebone Road (next to the traffic). The highly variable meteorology may be related to the poor correlation. Weak correlation was also seen between traffic volume and the gaseous pollutants when CO exhibited a closer relationship to traffic than NO_x. In addition, obvious seasonal trends were observed indicating better correlations in the winter and autumn months than in the spring and summer months.

4.4.3 Diurnal Traffic Count

Hourly traffic volume was aggregated into two groups regarding vehicle type. Group one covers mainly petrol vehicles of class1, class2 and class3 while group two includes mainly diesel vehicles i.e., class4, class5 and class6. During all seasons Marylebone Road experiences more petrol (1200-4300 vehicles per hour) than diesel vehicles (100-600 vehicles per hour). It is noted that there is a clear divergence between the two groups (Figure 4.18) where petrol vehicles show a predominant evening peak around 18 to 19 hours. It is identical to the evening CO peak observed earlier (Chapter 3) confirming that this peak is due to increasing numbers of petrol vehicles generating more CO emissions. Conversely, the diesel vehicle-count started dropping after lunch from about 600 h^{-1} to 150 h^{-1} by midnight. Therefore NO_x produced by both diesel and petrol vehicles did not show a clear evening peak. This diurnal behaviour may also explain the phenomenon observed in the regression plot between PM and CO, which shows that PM_{10} and $PM_{2.5}$ concentrations did not rise following the increase in CO concentrations above 5ppm (Figure 4.6).

Figure 4.18 Diurnal traffic flow on Marylebone Road in summer 1999



4.5 Wind-induced Re-suspension of Dust

To understand the influence of meteorology on airborne particle mass concentrations and elucidate the sources of PM, the relationship between PM and wind speed was evaluated using the Hodge Hill data and examined further using the data from the four DETR sites. Analysis of the winter 94/95, 95/96 and 96/97 data for Hodge Hill using a curved fitting procedure shows that $PM_{2.5}$ concentrations have a marked power relationship, decreasing with increasing wind speed (Figure 4.19a) due to a dilution effect. This is consistent with the widely-utilised Gaussian dispersion model of turbulent diffusion which predicts just such a marked decline (Landsberg, 1981). Note however that the results do not approach a limiting value of zero at the highest wind speeds. This may be explained by the fact that ‘clean’ air being advected into the system, itself has an associated background value of $PM_{2.5}$. Therefore, despite ventilation by the wind, the wind itself carries in a background value of fine particles. The coarse fraction relation (Figure 4.19b) is less marked and the fit is polynomial with an upturn in particle concentrations at the highest wind speeds, which may reflect a shift in the source inventory i.e. away from vehicular emissions toward particulate emissions dislodged from urban surfaces. Also, high winds will tend to enhance atmospheric residence times of larger particles, which may not otherwise have reached the sampling site (Butcher and Charlson, 1972). The curved ratio fit (Figure 4.19c) indicates a significant positive gradient when the dilution effect is controlled and shows that higher wind speeds are associated with an increase in coarse particle concentrations which is consistent with the re-suspension of dust.

Figure 4.19. Daily average plots for winter 94/95, 95/96 & 96/97 at Hodge Hill, Birmingham.

Fig. 4.19a

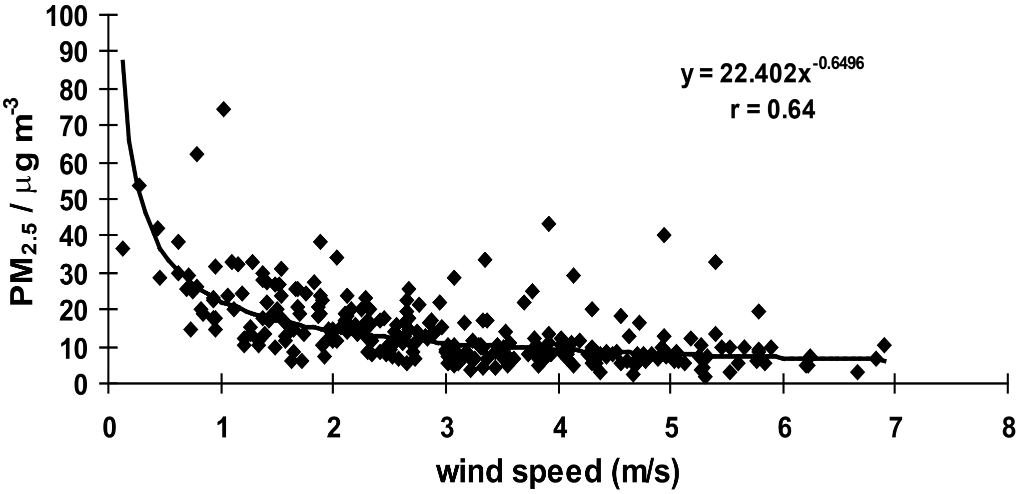


Fig. 4.19b

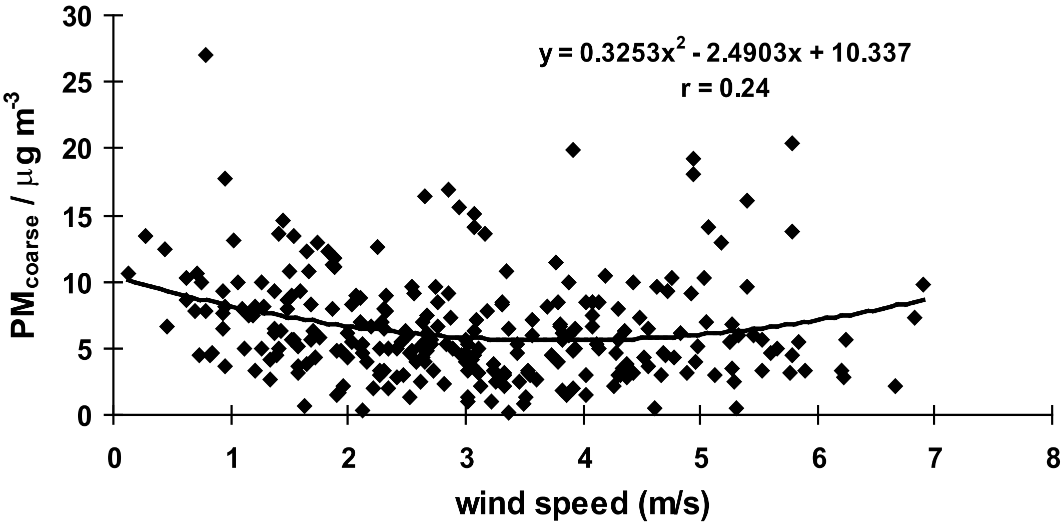
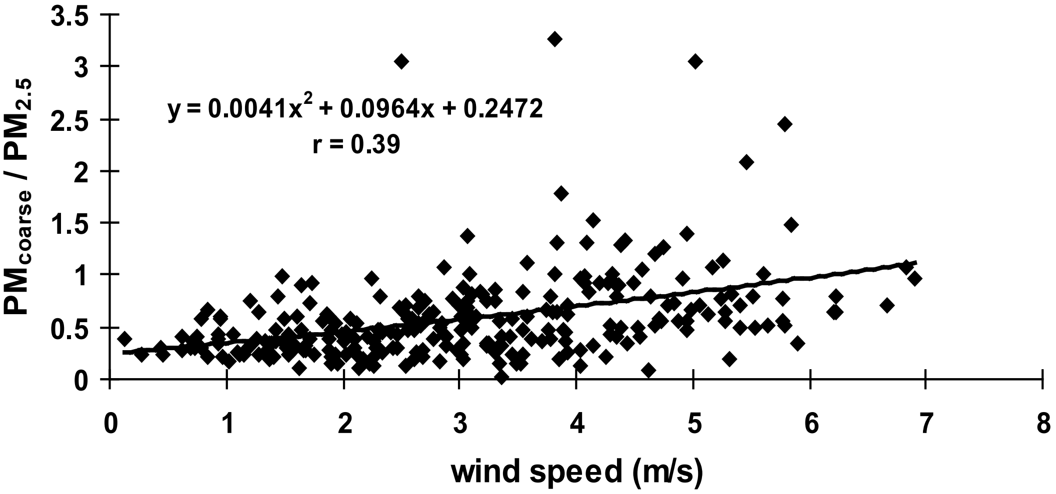


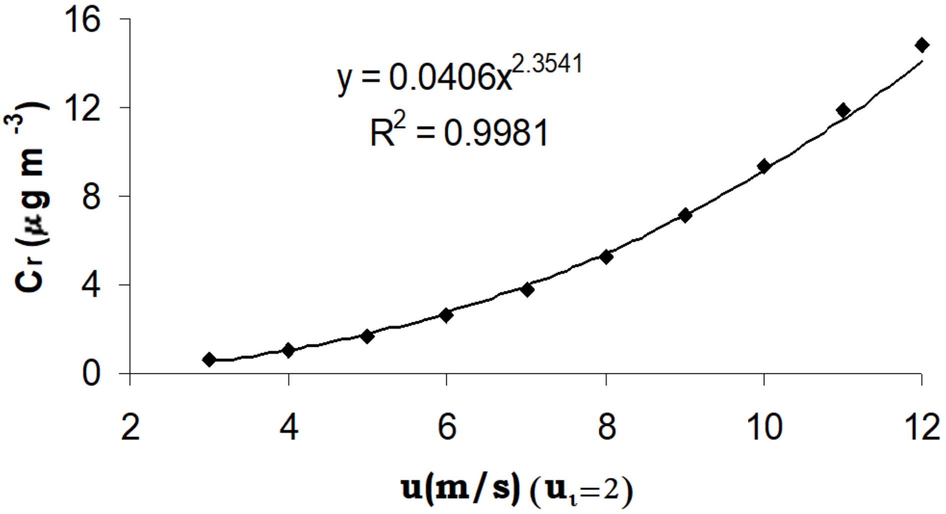
Fig. 4.19c



From the above result, it is clear that the influence of the wind on fine particles is a dilution, whereas in the case of coarse particles, the effect is one of both dilution and re-suspension. Suppose that the total coarse particle concentration Ct is related to two components Cb and Cr, due to the two different wind effects of dilution and re-suspension processes. Assuming that component Cr is insignificant at very low wind speeds, component Cb may be calculated from the relationships of the ratio and $PM_{2.5}$ fits (Figure 4.19c&a). Therefore component Cr, representing the re-suspension effect, can be obtained as Cr = Ct – Cb. By applying this method, an estimation of coarse particle concentrations due to re-suspension at various wind speeds can be made.

Figure 4.20 shows the resultant relationship, and clearly indicates that re-suspended coarse particle concentrations increase with wind speeds. The curve in figure 4.20 is the best fit of a power relationship $Cr = au^b$, where u is the wind speed, and a and b are constants. A threshold wind speed u_t is defined through the curve fitting at which particle suspension processes are assumed to be negligible. This method has been applied to both Hodge Hill and the four DETR sites. It must be pointed out that the method should be applied for best results using a longer term data-set due to the high degree of scatter in individual data seen in figure 4.19. Seasonal estimates of wind suspended coarse component concentrations and the exponent b from the best curve fittings are shown in Table 4.8. The threshold wind speed was slightly lower in the summer and higher in the winter months, consistent with the earlier results showing that dry summer months favour the re-suspension processes. The exponents ranged from 1.23-3.92 showed clear seasonal variations, which was generally higher in the warmer and drier months. As expected, the wind re-suspended coarse particle concentration C_r is also higher for most of the summer months.

Figure 4.20. Estimated dependence of re-suspended concentration upon wind speed at HH, Birmingham; winter 94/95, 95/96 &96/97



Sehmel (1980a) and Nicholson (1988) have reviewed many published data about particle suspension processes. They reported that many authors have found that increasing wind speeds are associated with rapid increase in re-suspension rate or factor (defined as the ratio of airborne concentrations to surface concentration). Usually a power relationship was fitted. For the wind-caused re-suspension processes, the exponent b is in the range 1-6 and typically 3 or 4 (Nicholson, 1993). The values determined from the current work lie within the range from the literature but towards the lower end. The reason is presumably due to factors affecting the re-suspension by wind, like weather conditions, mechanical disturbances and the type of surface and other environmental conditions, which could make re-suspension processes complicated. Acknowledging these uncertainties, however, Table 4.8 may provide a useful indication about the possible magnitude of wind-induced re-suspension.

Table 4.8. Seasonally-averaged estimates of "wind-resuspended" and "background" components of coarse particles (hourly data)*

Site/Season	Threshold wind speed (m s $^{-1}$)	a	b	C_r (μg m $^{-3}$)	C_t (μg m $^{-3}$)	C_b (μg m $^{-3}$)
LM						
Summer 97	2	0.43	1.50	2.9	14.3	11.4
Autumn 97	2	0.04	2.51	1.6	14.3	12.7
Winter 97/98	-	-	-	-	13.2	-
Spring 98	2	0.15	1.85	1.6	11.8	10.2
Summer 98	1	0.08	2.22	1.9	12.5	10.6
LB						
Summer 97	3	0.02	2.26	0.6	8.4	7.8
Autumn 97	3	0.11	1.64	1.2	10.1	8.9
Winter 97/98	3	0.13	1.53	1.5	7.8	6.3
Spring 98	2	0.04	2.18	1.1	6.9	5.8
Summer 98	1.5	0.06	2.37	1.9	7.2	5.3
RO						
Summer 97	2	0.001	3.92	1.4	8.1	6.7
Autumn 97	3	0.17	1.23	1.3	5.9	4.6
Winter 97/98	3	0.05	1.77	1.4	5.1	3.7
Spring 98	3	0.14	1.28	1.4	5.8	4.5
Summer 98	3	0.02	2.17	1.1	6.5	5.4
HAR						
Autumn 97	2	0.001	3.62	0.3	4.3	4.0
Winter 97/98	3	0.08	1.42	0.8	4.5	3.7
Spring 98	3	0.00	2.68	0.3	4.8	4.4
Summer 98	2	0.02	2.44	0.6	4.8	4.2
HH						
Winter 94/95, 95/96 & 96/97	2	0.04	2.35	1.1	6.5	5.4
Spring 95, 96 & 97	1.5	0.19	1.90	2.3	8.5	6.2
Summer 95, 96 & 97	1	0.17	2.47	2.6	9.4	6.8
Autumn 95, 96 & 97	2	0.02	2.75	0.8	7.4	6.6

*** C_t - total coarse particle concentration; C_r - resuspended coarse particle concentration;**
C_b - background coarse particle concentration; - - poor fit to data;
Values of a and b derive from exponential curve fit (see text)

Further analyses shown in table 4.9 has been conducted by aggregating the data into weekday, weekend, day and night for the two London sites. Interestingly, the results show that at all seasons, there is a large difference for the re-suspended concentrations between weekdays and weekends and also between days and nights. This could be explained as re-suspension is not solely related to the action of wind, but also due to other mechanical processes, which can initiate or enhance particle re-suspension by wind. In the case of the two London sites, the mechanical processes affecting the re-suspended coarse particle concentrations are mainly road traffic and pedestrians. Obviously, greater concentrations on the weekdays than during the weekends is likely due to the traffic flow patterns whereas both wind and mechanical actions have effect on the concentrations obtained between day and night. The latter effects resulted in the higher concentrations during the days and very little mass at night when both traffic is light and wind speed is lower. Very consistent results were found at the Birmingham, Hodge Hill site, whereas the suburban site Rochester and rural site Harwell exhibited a less marked but still observable effect.

This weekday-to-weekend and day-to-night difference was also observed for the "background" component of coarse particles, which is probably related to emission from industry, construction activities, traffic-induced re-suspension, biological particles and sea spray. It is likely that this component is mainly attributed to road traffic generated re-suspended particles at urban sites, since a close parallel of the weekday/weekend and day/night variation has been found between the "background" component and $PM_{2.5}$ arising from exhaust emissions. Wind driven sea salt aerosol can travel long distances inland (Gustafsson and Franzen, 2000) and the typical concentrations in the UK are about 1-3 $\mu g\ m^{-3}$ (APEG, 1999), but it is unlikely that this component can have a strong influence on the above variations. On the other hand a strong relationship with traffic pattern has been observed at urban locations. A study from Australia (Chan et al., 1997) reported a similar weekday-to-weekend variation in coarse particle concentrations, considered to be related to the contribution of road dust. Tsai and Wu (1995) studied the contribution of road dust re-suspension to airborne particle concentrations in Taipei and found higher concentrations near the ground due to the effects of re-suspension from road dust. The current study shows clearly that coarse particles comprise an appreciable proportion of PM_{10} at UK urban sites. In comparison, the proportion of coarse particles is much lower at the rural Harwell site indicating that urban activities are significant factors affecting the coarse particle concentrations. In other words, purely wind-driven re-suspension is not the only process producing high concentrations of coarse particles. This is particularly evident from the weekday/weekend data.

Table 4.9 Seasonally-averaged estimates of "wind-resuspended" and "background" components of coarse particles (hourly data) at the two London sites*

Site	Season	Period	Threshold wind speed (m s $^{-1}$)	a	b	C_r (μg m $^{-3}$)	C_t (μg m $^{-3}$)	C_b (μg m $^{-3}$)
LM	Summer 97	*Week-day*	2	0.50	1.48	3.4	16.3	12.9
		Weekend	3	0.24	1.36	1.5	10.8	9.3
		Day	2	0.21	1.91	2.9	15.6	12.7
		Night	3	0.39	1.28	1.7	12.3	10.6
	Autumn 97	*Week-day*	2	0.09	2.06	1.6	16.0	14.4
		Weekend	4	0.03	1.94	0.5	10.8	10.3
		Day	3	0.13	1.90	2.4	17.5	15.1
		Night	3	0.10	1.73	0.9	11.8	10.9
	Winter 97/98	*Week-day*	3	0.34	1.05	1.7	13.7	11.9
		Weekend	-	-	-	-	11.7	-
		Day	4	0.22	1.21	1.6	15.9	14.3
		Night	-	-	-	-	11.6	-
	Spring 98	*Week-day*	2	0.17	1.55	1.5	12.6	11.1
		Weekend	3	0.04	2.34	1.5	11.3	9.9
		Day	2	0.58	1.00	2.4	13.1	10.7
		Night	2	0.03	2.56	1.1	10.9	9.9
	Summer 98	*Week-day*	2	0.02	2.94	1.7	13.3	11.6
		Weekend	2	0.15	1.62	1.4	10.6	9.2
		Day	1.5	0.04	2.45	1.9	13.6	11.7
		Night	3	0.24	1.15	1.0	9.9	9.0
LB	Summer 97	*Week-day*	2	0.01	2.92	0.7	9.3	8.7
		Weekend	2	0.02	2.77	0.9	7.5	6.6
		Day	2	0.05	2.33	1.2	8.4	7.2
		Night	3	0.01	2.75	0.2	9.8	9.6
	Autumn 97	*Week-day*	3	0.04	2.26	1.3	11.2	9.9
		Weekend	-	-	-	-	8.1	-
		Day	3	0.13	1.72	1.8	11.4	9.6
		Night	-	-	-	-	8.7	-
	Winter 97/98	*Week-day*	3	0.03	2.16	1.2	8.4	7.3
		Weekend	4	0.29	1.27	1.4	6.4	5.0
		Day	3	0.09	1.01	1.7	9.2	7.5
		Night	3	0.12	1.55	1.4	7.1	5.7
	Spring 98	*Week-day*	2	0.01	2.75	0.7	7.0	6.3
		Weekend	2	0.20	1.58	2.1	6.8	4.7
		Day	3	0.01	2.85	1.0	8.2	7.2
		Night	3	0.05	2.12	0.6	5.2	4.6
	Summer 98	*Week-day*	1	0.09	2.20	2.3	7.6	5.2
		Weekend	3	0.01	2.87	0.7	6.0	5.3
		Day	1.5	0.09	2.17	2.3	7.6	5.2
		Night	2	0.04	2.34	1.0	6.2	5.2

*** C_t - total coarse particle concentration; C_r - resuspended coarse particle concentration;
C_b - background coarse particle concentration; - - poor fit to data;
Values of a and b derive from exponential curve fit (see text)**

4.6 Summary

Generally, PM_{10} is dominated by fine particles at the DETR sites, showing strong or very strong correlation between $PM_{2.5}$ and PM_{10} (Table 4.1), which is consistent with the result drawn from the Birmingham, Hodge Hill site (QUARG, 1996 and Harrison at el., 1997b). An obvious seasonal variation was observed indicating that in the winter months a large proportion of fine particles was present but in the summer months, coarse particles may comprise more of the PM_{10} mass due to re-suspension of dusts driven by wind or human activities such as road traffic.

Strong correlations have been observed for both PM_{10} and $PM_{2.5}$ with NO_x at the two London sites, particularly over the winter period emphasising that particles at the urban site are associated with NO_x in line with a road traffic source (LRC, 1997). On the other hand the modest or weak correlation observed in the summer period shows less evidence of the primary pollutant than in the winter data due to better dispersion or a change over of pollution source from primary particles to secondary sources. The degree of correlation of both fine and coarse particle mass to NO_x tends to decrease from London Marylebone Road to London Bloomsbury to Rochester, and to Harwell reflecting the differences of traffic induced fine and coarse particles at the four sites. Similar results can be drawn for CO at the two London sites (no data is available at the other two sites). SO_2 exhibited mostly modest or weak relationship to particle mass.

The EPAQS standard was most frequently exceeded at London Marylebone Road, again highlighting the significance of the local source from road traffic. London Bloomsbury shows a much lower number of exceedences due to lesser influence of road transport and only a small number of exceedences were found at the Rochester and Harwell sites. By examining the high PM concentrations, it was found that PM_{10} episodes were mostly associated with fine particles at LB, RO and HAR sites although occasionally there were short periods when elevated coarse particle concentrations were dominant particularly in summer or autumn seasons. However, at London Marylebone Road, both fine and coarse particles can contribute to PM_{10} episodes due to a major source from road transport, which produces both fine vehicle exhaust emissions and re-suspended road dust. Very high PM_{10} concentrations over 100 $\mu g\ m^{-3}$ are likely to occur in summer and autumn seasons associated with a larger proportion of the coarse fraction related to both traffic and wind. In the UK atmosphere, fine particle dominated PM_{10} episodes are generally due to either primary pollutants derived from mainly local sources like traffic or long-range transport, or secondary pollutants formed locally or during transportation from a long distance (e.g. continental Europe). The latter is likely to occur in summer and spring whereas winter and autumn pollution episodes are generally related to primary sources. Coarse particles alone can lead to an exceedence of the 24-hour running mean concentration of 50 μg m^{-3}, particularly in summer and autumn seasons, but only for short periods.

Correlations of traffic volume to particle mass, NO_x and CO are positive but relatively weak although studies show strong correlations between particle concentrations and the traffic related air pollutants (NO_x and CO), and very strong association between particle numbers and these pollutants when using the traffic increment. The diurnal traffic count shows a marked difference between the two groups of vehicles indicating a clear evening peak for petrol vehicles, which explains the abnormal behaviour of CO observed in both pollutant diurnal variation and the poorer correlation of CO to particle concentrations than for $NO_{x.}$

Fine particle concentrations correlate inversely with wind speed due to dilution and ventilation effects. However, the influence of wind speed on coarse particle concentrations consists of dilution and re-suspension. Higher wind speeds are associated with increasing coarse particle concentrations, which is evidenced by the estimates of re-suspended coarse particles, which is higher in the summer months when the process was favoured by the hot and drier climate. The influence of wind speed upon coarse particle concentrations has shown a consistent weekday/weekend and day/night pattern at all sites discussed and was especially apparent at the urban sites. It is clear that apart from wind speed human activities, such as transports, pedestrians, mechanical processes are also responsible for the process of coarse particle re-suspension. However, in drier weather conditions dust storms are known to be associated closely with wind action (Kanbour et al., 1990). A similar conclusion was also drawn from site comparison where the re-suspended coarse components are higher at the three urban sites and lower at the two rural sites, which also indicates that the contribution of sea salt as a wind related component at these sites is not significant.

CHAPTER 5

PARTICLE SIZE DISTRIBUTIONS AND NUMBER COUNT AT THREE TYPICAL UK SITES

5.1 Introduction

Ultrafine particles with diameter smaller than 100 nm have only recently received serious attention on both their physical and chemical characterisations. They account for a very large proportion of the number of particles, but only a small amount of the mass (Jaenicke, 1993), and are present at typical concentrations of about 10^4 particles per cm^3 of air in the city atmosphere (Harrison et al., 1999b). Studies in America show that, in urban areas, road transport is the main source of these particles, which are predominantly organic compounds in nature, with further contribution from elemental carbon, trace metals, sulphate, nitrate and ammonium (Hughes et al., 1998; Cass et al., 2000). Current measurements in the UK are mainly focused on particle mass concentrations of PM_{10} and $PM_{2.5}$ conducted by the AUN (the Automatic Urban Network) and local environmental health authorities. Only very limited measurements have been made on ultrafine particle numbers prior to this project, and there have been no long-term measurements of particle size distributions previously reported in the UK. Work conducted in urban areas, but only for a short period, has been described by Harrison et al (1999a&b), and Jones (1996), who showed that particle number concentrations could give a better indication of traffic emissions, a predominant PM_{10} source in urban areas.

Measurements of particle number and size distribution have been made on a continuous basis at three locations in the UK atmosphere using a Scanning Mobility Particle Sizer (SMPS). London Marylebone Road is a site located next to one of the busiest roads in central London, carrying about 80,000 vehicles per day. London Bloomsbury, located within a central London garden and about 35 metres from the surrounding roads, is about 2 kilometres distant from Marylebone Road and is classified as an urban background site. Harwell is a rural site and situated within an open agricultural field. Data were stored on an hourly basis and investigated for the levels of particle number concentrations (Chapter 3) and size distributions at different locations, and their relationship to particle mass and other gaseous pollutants especially traffic related such as NOx and CO. Hence, a better knowledge of particulate mass and numbers over various size ranges could be developed which will have a great benefit to epidemiological research. Some details of the particle number concentrations have been discussed in chapter 3 showing monthly average variations, seasonal percentile distributions, and seasonal diurnal trends, at the three locations.

Whilst no significant temporal trends within the monthly particle count data have been found at all three sites, clear divergence of particle count levels between the sites was found to exist. The average hourly number concentrations (particles cm^{-3}) over the whole period were about 4.6×10^4 (range: 2.5×10^3 - 1.8×10^5) at LM; 1.2×10^4 (range: $2.2 \times 10^2 - 1.1 \times 10^5$) at LB; and 4.4×10^3 (range: $1.6 \times 10^2 - 4.7 \times 10^4$) at the rural site. The long-term mean number concentration at the urban background site LB is comparable with the results obtained from three European cities, which were 1.62×10^4, 1.77×10^4 and 1.83×10^4 particles cm^{-3} in Helsinki, Erfurt and Alkmaar respectively (Ruuskanen et al., 2001). However, the roadside site is about 2-3 times higher than those from the background sites. Buzorius et al (1999) studied the spatial variation of particle number concentrations in Helsinki City. The measurement shows a decrease in the concentrations as distance of the measuring point from the street increased. Similar results have been found from other researchers highlighting the significance of traffic on influencing particle number concentrations (Li et al., 1993; Jones,1996; Harrison et al., 1999a&b; Shi et al., 1999a).

5.2 Particle Number, Particle Mass and Traffic Related Air Pollutants

5.2.1 Particle Number and Mass Concentrations

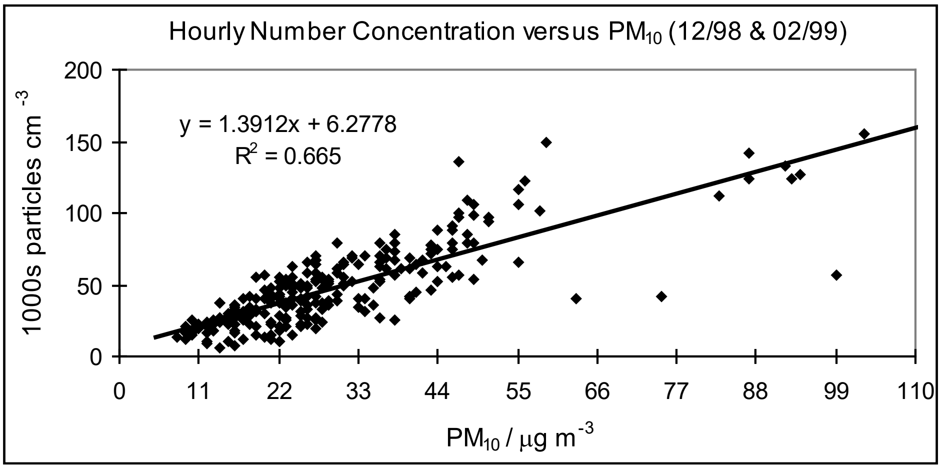
Studies from the current project (chapter 4), and previous research in the UK, as well as many other countries (APEG, 1999), showed that the particle mass concentrations of PM_{10} and $PM_{2.5}$ are highly correlated, making it difficult to distinguish the two variables in epidemiological studies since they do not behave independently. The introduction of ultrafine particles of less than 100 nm, measured as particle numbers rather than mass, could enhance the degree of the above difficulty, therefore, investigation for the relationship between the three metrics, PM_{10}, $PM_{2.5}$ and particle number becomes very important.

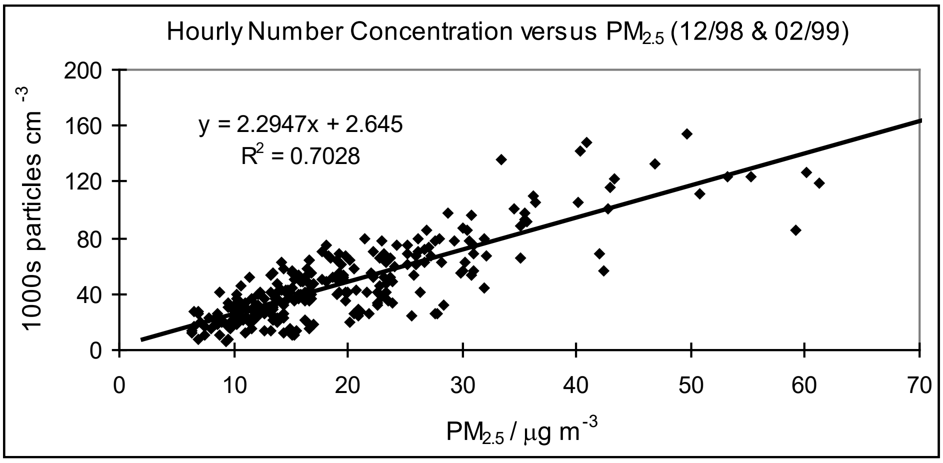
Hourly seasonal regression analyses were conducted for particle numbers and mass at the three sites. The results show that better correlation (mostly strong or modest) (R^2 = 0.18-

0.72) was found at Marylebone Road between particle numbers and particle mass as PM_{10} and $PM_{2.5}$ than at the other two sites, London Bloomsbury with strong or modest or weak correlation (R^2 = 0.14-0.71) and Harwell with modest or weak correlation (R^2 = 0.03-0.49). The gradients from the regression lines of particle count/PM, with a unit of particles per microgram at the roadside site are about 1.2 x 10^{9} and 1.9 x 10^{9} on average for PM_{10} and $PM_{2.5}$ respectively. These are higher comparing with London Bloomsbury (gradients: 4.6 x 10^{8} particles μg^{-1} for PM_{10} and 7.1 x 10^{8} particles μg^{-1} for $PM_{2.5}$) and Harwell showing even lower gradients about 2.3 x 10^{8} and 3.3 x 10^{8} particles per microgram PM_{10} and $PM_{2.5}$. This indicates that the average particle size at the roadside site is smaller as they are mostly freshly emitted particles from the vehicle exhaust. However, the gradients calculated here at the two London sites are lower than observed earlier at the Birmingham sites where the gradient was around 2.2-2.6 x 10^{9} particles μg^{-1} for PM_{10} at the Birmingham East site, 12.5 x 10^9 for PM_{10} and 14.3 x 10^9 for $PM_{2.5}$ at Hodge Hill (Harrison et al, 1999a).

Winter months exhibited better correlation between particle numbers and mass, especially for fine particle mass. Figure 5.1 shows the measurements on Marylebone Road for the period of winter 98/99, when the highest correlation coefficient was found. As expected, particle numbers correlated better with $PM_{2.5}$ than PM_{10}, which confirms that particle count was mostly influenced by fine particles. The coarse particles contributed very little to particle count and therefore the plots appear more scattered in the correlation of both PM_{10} and coarse particle to particle count. Strong correlation was also observed in summer 1998 on Marylebone Road shown in figure 5.2. A higher correlation coefficient was found in the relation of particle count and PM_{10}, than particle count and $PM_{2.5}$, reflecting that the average particle size is larger in summer than in winter due to traffic-driven re-suspension of dust from a same pollution source. The intercept in the correlation of particle count to $PM_{2.5}$ is about 4 times larger in summer than in winter (Figure 5.1&5.2), indicating that ultrafine particles may be formed through chemical conversion under fine weather conditions in the summer, in addition to direct emissions from vehicle exhaust. An early study in Birmingham found clear indications that solar radiation could cause a substantial increase in particle numbers due to photochemical gas-to-particle conversion (Jones, 1996).

Figure 5.1 Hourly plots for Marylebone Road (12/98 & 02/99)





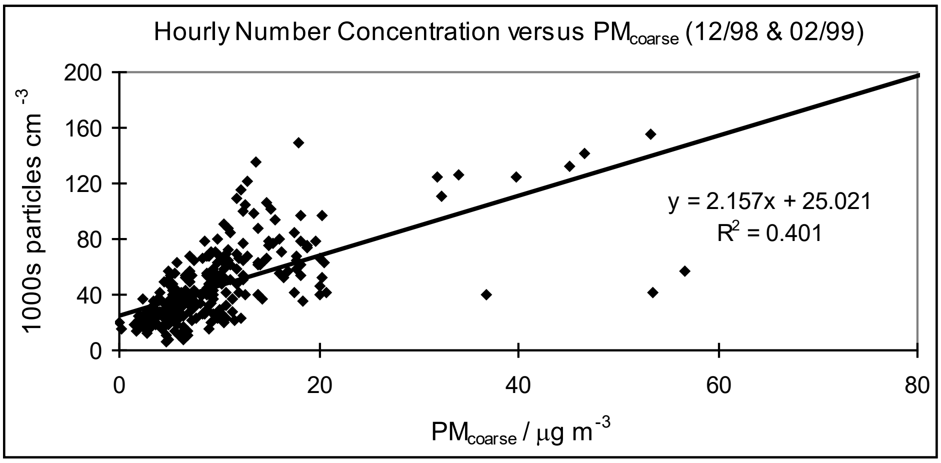
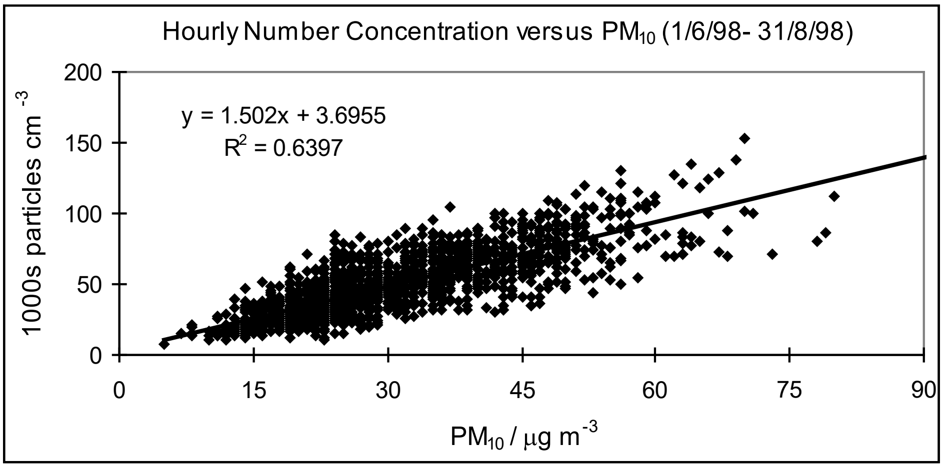
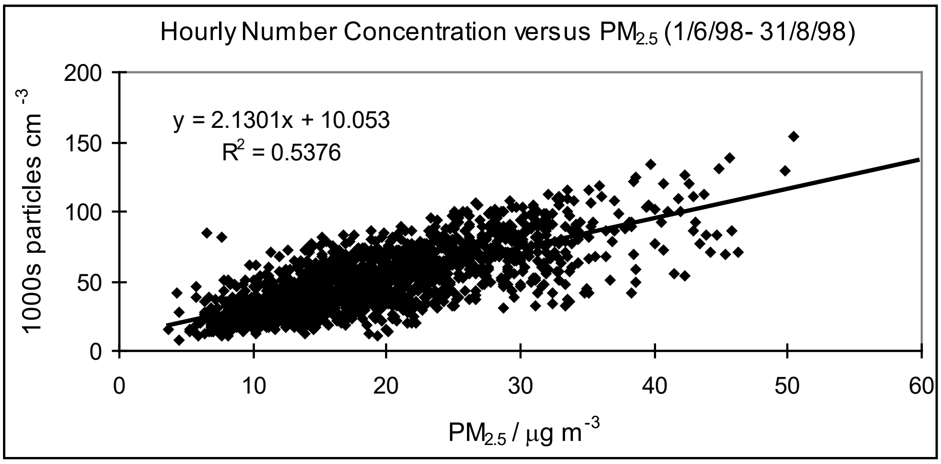
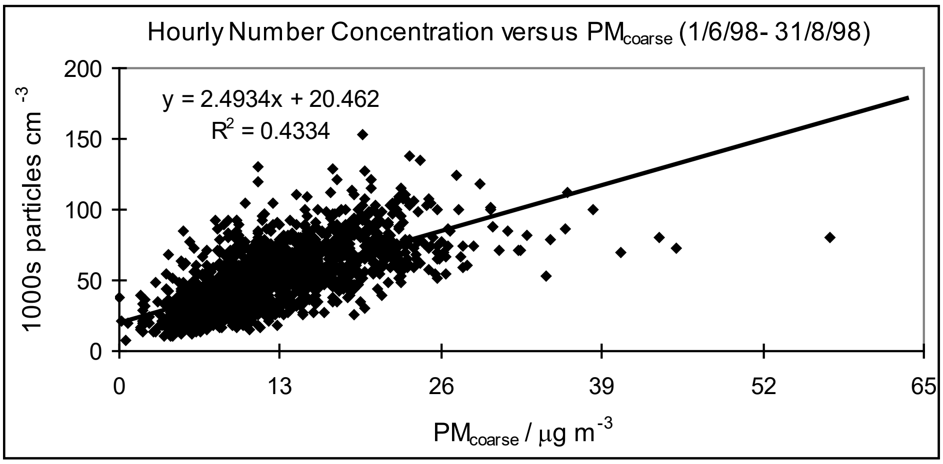


Figure 5.2 Hourly plots for Marylebone Road (1/6/98 – 31/8/98)

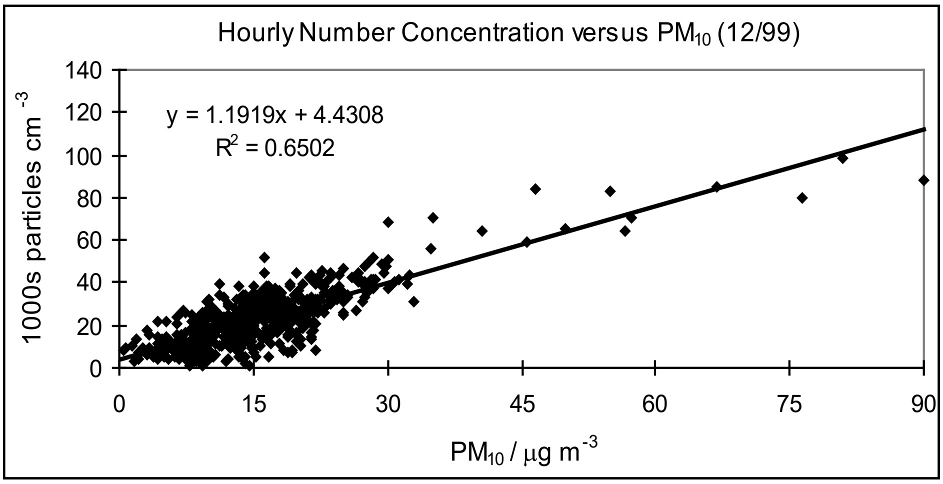






Similarly, the results from London Bloomsbury showed strong correlation for particle count and mass in the winter periods, such as December 1999 (Figure 5.3). London Bloomsbury is also influenced by the emissions from road traffic, which can be verified through the strong correlation between particle numbers and traffic-related NO_x (Section 5.2.2). Results from the Harwell site showed more scatter in the regression plots (figure 5.4) although consistent seasonal variation was also found. In summer 1999, the correlation was clearly influenced by both larger particles, when coarse particle concentrations increased without a corresponding rise in particle count, and very small particles, when particle numbers reached their highest values with low PM_{10} and $PM_{2.5}$.

Figure 5.3 Hourly plots for London Bloomsbury in December 1999



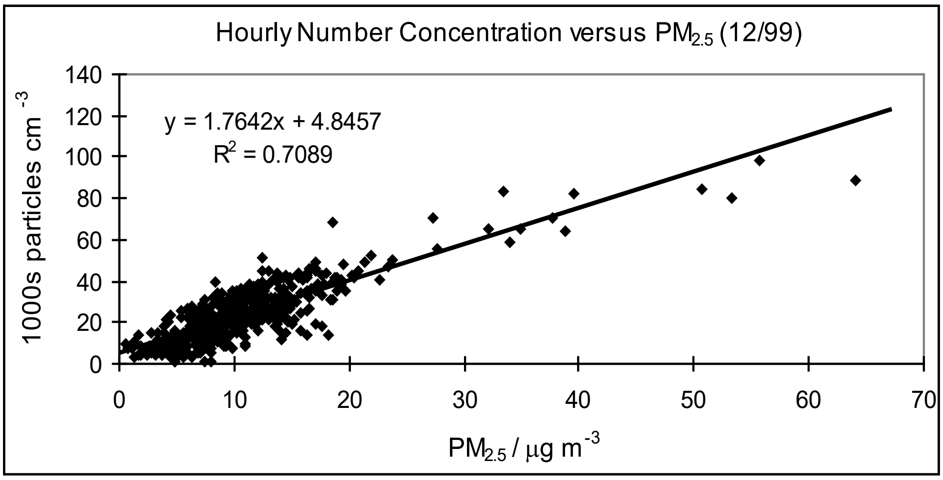
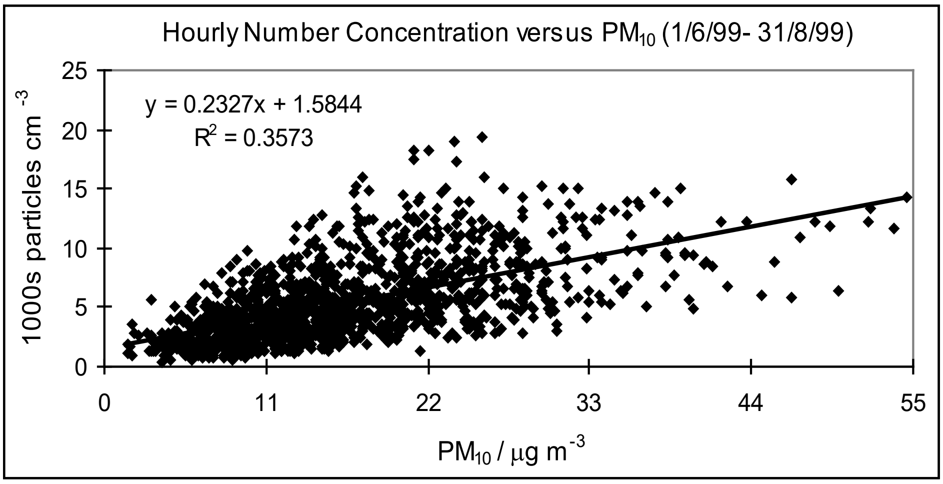
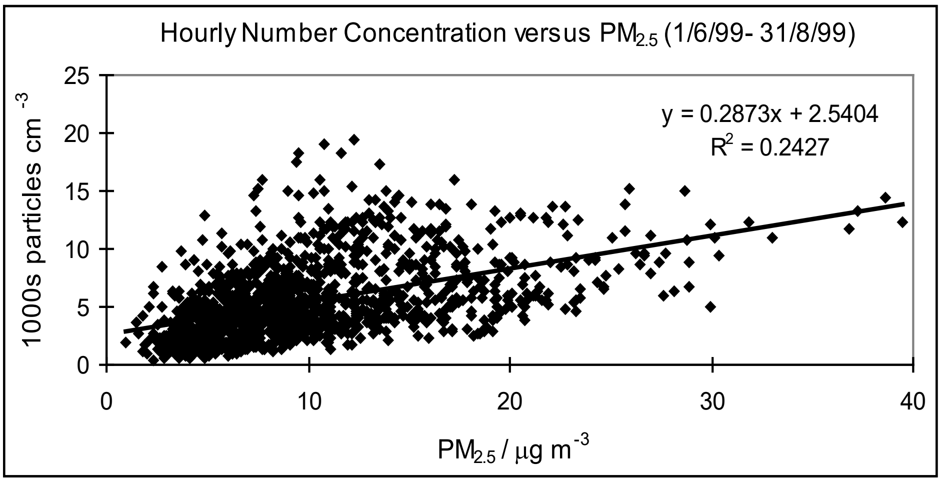
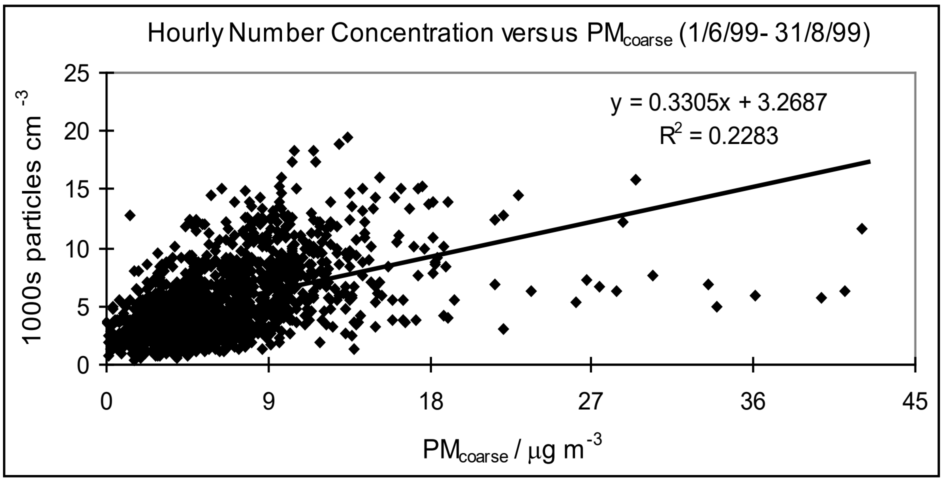


Figure 5.4 Hourly plots for Harwell in summer 1999







A previous study from three European cities found poor correlations (R^2 = 0.002-0.34) between the total particle number (0.1-0.5 μm) and the $PM_{2.5}$ mass concentrations (Ruuskanen et al., 2001). A similar result was observed in Brisbane City, Australia with a weak correlation between the number and PM_{10} mass (R^2 = 0.25) (Morawska et al., 1998). Another study in the same city of Erfurt, Eastern Germany showed a relatively good relationship of particle number and mass concentrations (R^2 = 0.5) during an earlier time period in 1991/92 (Tuch et al., 1997). These results highlight the importance of both particle numbers and mass in assessing urban air quality. On the other hand, strong correlations between particle number and mass concentrations have been found for both Marylebone Road and London Bloomsbury, especially for winter periods. These results are likely to cause a problem for epidemiological studies seeking to differentiate between PM_{10} mass and particle numbers as a causal agent on adverse health outcomes. This was also true at a background site in central Birmingham where a strong correlation between particle count and PM_{10} mass (r = 0.66) was observed (Harrison et al., 1999a). However, significant variation both spatially and temporally also has been found in the correlations due to pollution sources and meteorological conditions as a result from this study. Only modest or weak correlation was found from the rural site Harwell while a stronger relationship was observed between the two mass fractions of PM_{10} and $PM_{2.5}$.

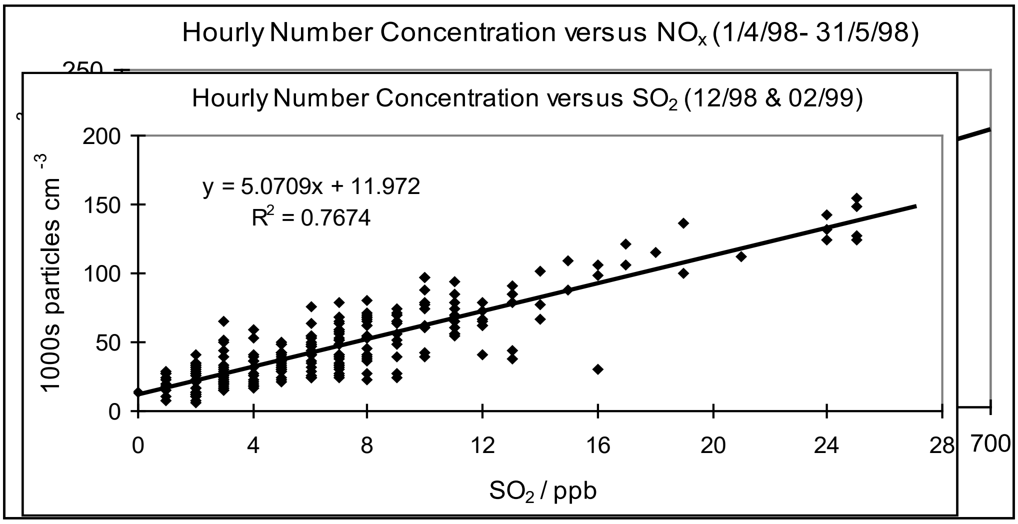
5.2.2 Particle Number and Traffic Related Air Pollutants

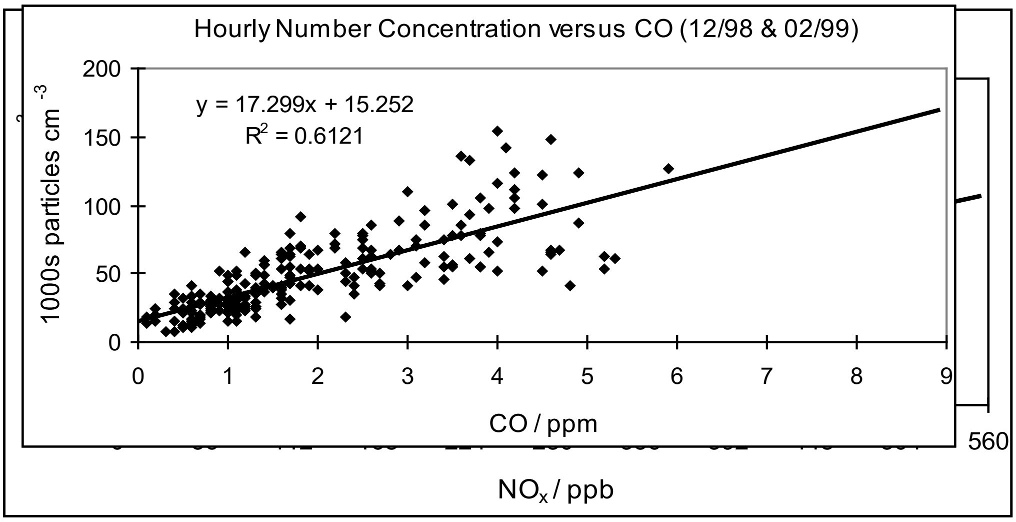
As very small particles are highly abundant in urban areas as a result of vehicle exhaust emissions, further investigation on the correlation between particle numbers and the various air pollutants is made.

Overall, particle number correlates better with NO_x and CO than particle mass at Marylebone Road, indicating that particle number is a better metric for vehicle exhaust emissions, similar to the result found from a previous study at a Birmingham site (Harrison et al., 1999b). Strong or very strong correlation (R^2 = 0.42-0.84) was observed from Marylebone Road, between particle numbers and NO_x (e.g. figure 5.5). The winter plot exhibited the lowest background particle number when local primary exhaust emissions were predominant. Apart from NO_x, CO and SO_2 also correlated strongly with particle numbers at this site particularly in the winter period (Figure 5.6). Good correlation was also found between the number concentrations and gaseous pollutants CO ($R^2 = 0.45$) and NO_x ($R^2 = 0.45$) from a study in Brisbane, Australia (Morawska et al., 1998).

Similar to PM_{10} and $PM_{2.5}$ as discussed in chapter 4, figure 5.7 also shows that particle number appeared to stay unchanged when carbon monoxide exceeded about 5 ppm. One reason for this phenomenon might be that freshly emitted very small particles from the vehicle exhaust could form larger particles through accumulation or coagulation processes when the pollution levels are very high, so that particle numbers drop or stay unchanged. However if this were the case, one would wonder why the other air pollutants like nitrogen oxides did not give similar indication. Another reason (section 4.3.3) may be the differences in traffic type, which produces different pollutants. Since diesel vehicles produce more particulate and NO_x whereas petrol cars produce more CO (QUARG, 1993b), higher levels of CO due to petrol vehicles would not correspond with an increase in the concentrations of particles or NO_x.

Figure 5.5 Hourly plots for particle numbers and NO_x (LM)





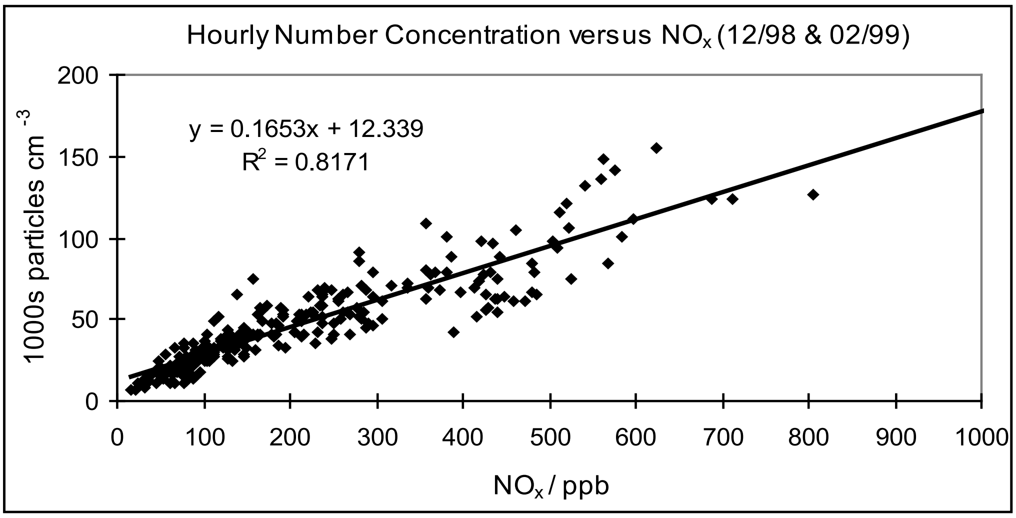
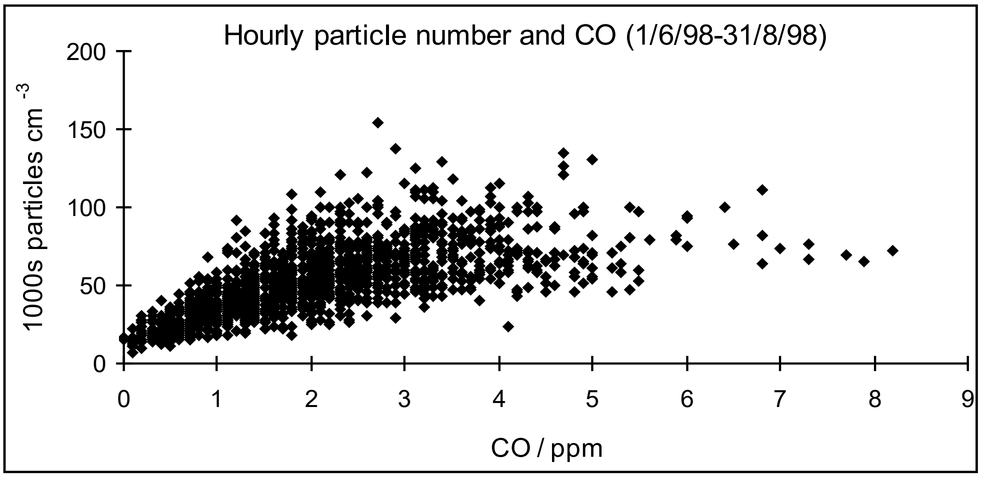


Figure 5.6 Hourly plots for particle numbers and SO_2 and CO (LM)



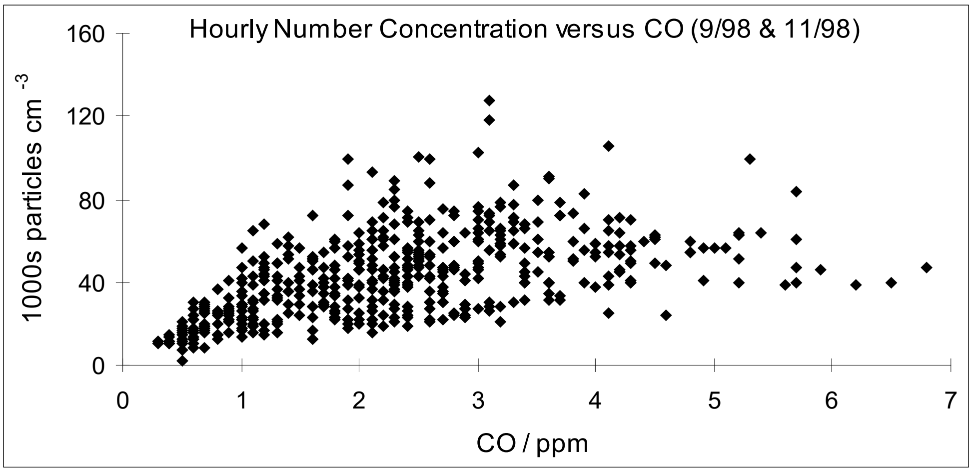


Figure 5.7 Hourly plots for particle numbers and CO at LM

The urban background site London Bloomsbury showed a much weaker relationship between particle numbers and the gaseous pollutants, and a strong correlation was only observed for NO_x in the winter months (R^2 = 0.61&0.80 in February and December 1999). Similar to the Marylebone Road results, NO_x correlates better (R^2 = 0.17-0.80) with particle numbers than CO (R^2 = 0.04-0.46) and SO_2 (R^2 = 0.01-0.40) as they are mostly generated from diesel traffic, which produces the most of NO_x. In the case of the rural site Harwell, mostly weak or modest correlations were found for particle numbers with NO_x (R^2 = 0.10-0.63) and all weak with SO_2 (R^2 = 0.10-0.24).

5.3 Particle Number Mode Diameter at Three Sites

By calculating the average particle number size distribution seasonally, or for a particular period, from the data available, the characterisation of particle size at different locations and different periods can be determined, and thus the sources of particles may be related and investigated. The monthly average particle number mode diameters at different sites were calculated and the results are shown in table 5.1. The smallest mode diameters appeared generally at Marylebone Road and ranged from about 24.6 to 32.8 nm. This indicates that motor vehicle exhausts produce particles with smaller size, and in higher total numbers of about 4.3 x 10^4 per cubic centimetre of air on average. These results are consistent with the studies of emissions from diesel engines using high exhaust dilution ratios, which can represent the real atmospheric conditions (Shi et al., 1999b; Shi and Harrison, 1999; Shi et al., 2000). Shi et al. (1999a) measured ambient particle size distributions at three locations in Birmingham. A consistent particle number mode in the range of 20-30 nm was found near a busy road, but with a larger average number count of about 1.6 x 10^5 particles cm^{-3} due to a difference of instruments employed.

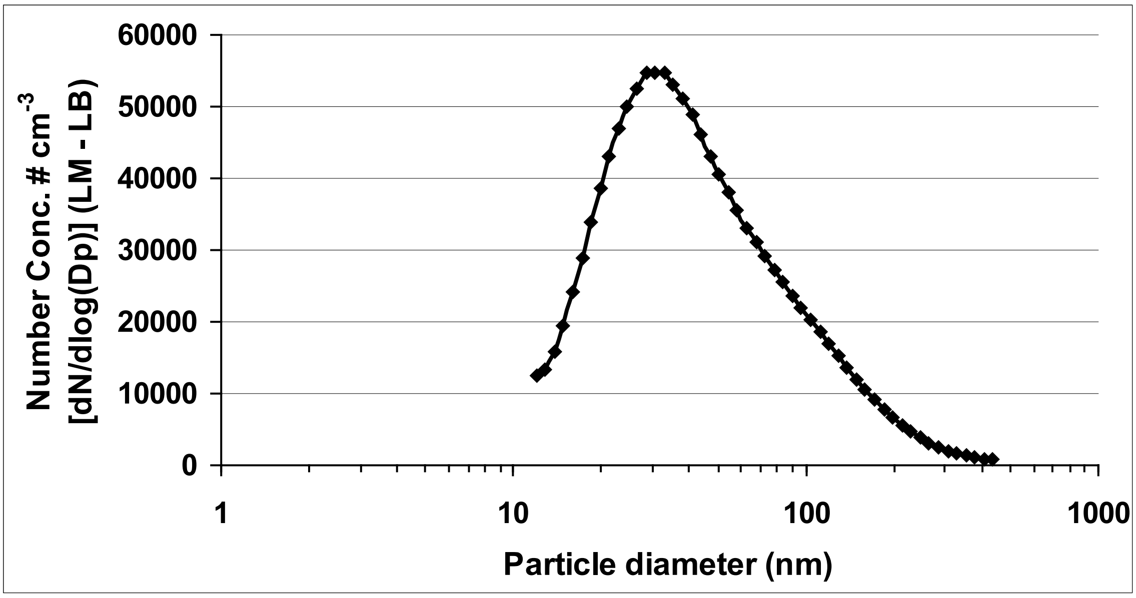
Slightly larger particle number mode diameters were observed (26.4 -50.5 nm) at London Bloomsbury, and the corresponding average number concentration was lower at about 1.2 x 10^4 cm^{-3}. Clearly this site is also influenced by local traffic emissions but the effect is relatively small in comparison with the roadside site, reflecting a rather coarser background particle loading. Similar results were found from other studies (Li et al., 1993; Morawska et al., 1996 and 1998), showing an average number mode diameter of 54 nm and 40 nm respectively.

As discussed in section 4.3.3 and APEG (1999), the increments in particle numbers due to traffic can be calculated from the differences between the two London sites on an hourly basis. The data shows a highly elevated particle number concentration about 5.5 x 10^4 cm^{-3} at Marylebone Road with a particle number size distribution having a mode diameter around 20-30 nm (figure 5.8). This is much smaller than that reported in many of the studies of engine exhaust using conventional dilution tunnel methods, which gave an unreliable estimate of particle size distribution with a mode at about 100 nm diameter.

Table 5.1 Average particle number mode diameters (nm)

	LM	LB	HAR
Apr-98	24.6	26.4	21.3
May-98	26.4	26.4	43.7
Jun-98	26.4	26.4	62.6
Jul-98	26.4	32.8	26.4
Aug-98	26.4	30.5	-
Sep-98	26.4	-	103.7
Oct-98	-	-	43.7
Nov-98	30.5	-	96.5
Dec-98	28.4	-	72.3
Jan-99	-	-	14.9/72.3
Feb-99	26.4	30.5	67.3
Mar-99	30.5	30.5	77.7
Apr-99	30.5	35.2	50.5
May-99	32.8	35.2	67.3
Jun-99	-	35.2	43.7
Jul-99	-	50.5	35.2/83.5
Aug-99	30.5	40.7	58.3
Sep-99	32.8	-	72.3
Oct-99	-	32.8	67.3
Nov-99	-	30.5	-
Dec-99	-	30.5	-
Average	27.9	33.1	53.4
Range	24.6-32.8	26.4-50.5	14.9-103.7

Figure 5.8 Particle number size distribution of traffic increment (March & April 1999)



The results from the Harwell site showed far more variations in the number mode diameter (15-104 nm) reflecting an occasionally bimodal distribution. Figure 5.9 shows a typical particle number size distribution for comparison between the three sites. Interestingly at Harwell, an upturn at the smaller end of the size distribution was observed sometimes indicative of new particle (very fine particles less than 10 nm) formation (Figure 5.10). Particles smaller than 10 nm were not detected as the SMPS system utilised in this study contains a CPC (Model 3022) with a minimum particle size detection of 7 nm. In practice, the minimum measurable particle size is larger due to the channel resolution of the measurement. The predominant mode (50-100 nm) at Harwell generally reflects the advected accumulation mode aerosol indicating little or no local influence from road traffic. In the case of small mode diameters, they were believed due to either local primary sources or homogeneous nucleation, which will be discussed later in this chapter.

Figure 5.9 Particle number size distribution at three sites (April & May 1998)

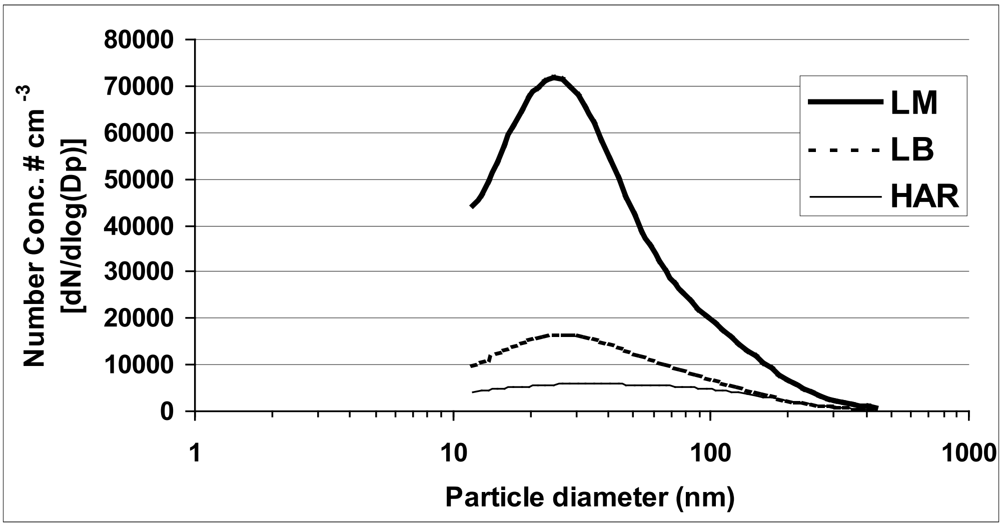
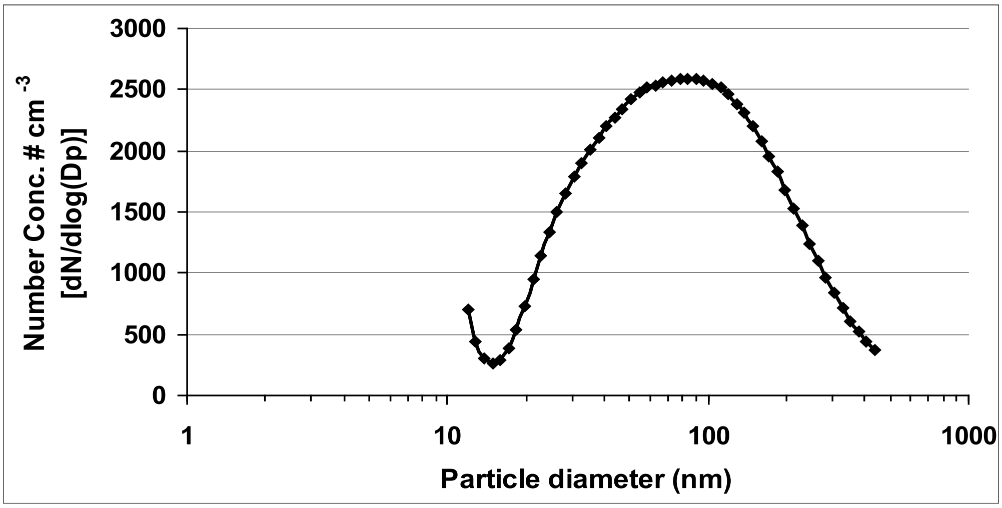


Figure 5.10 Particle number size distribution at Harwell (autumn98)



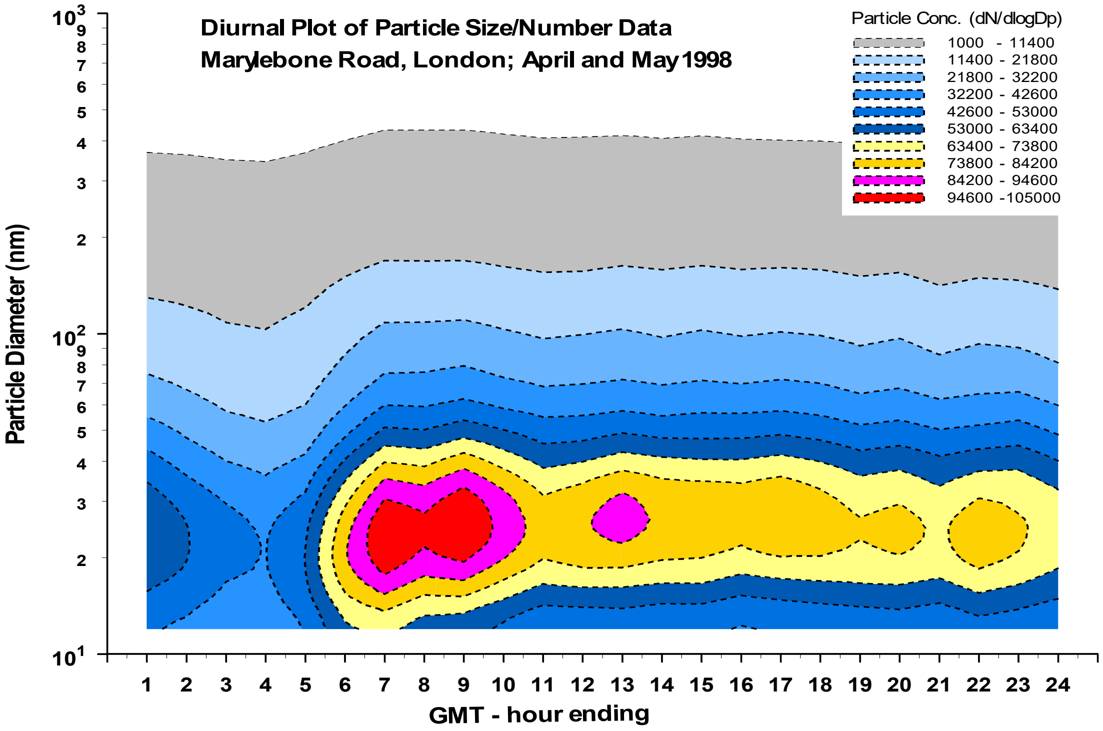
5.4 Diurnal Variation in Particle Size and Numbers

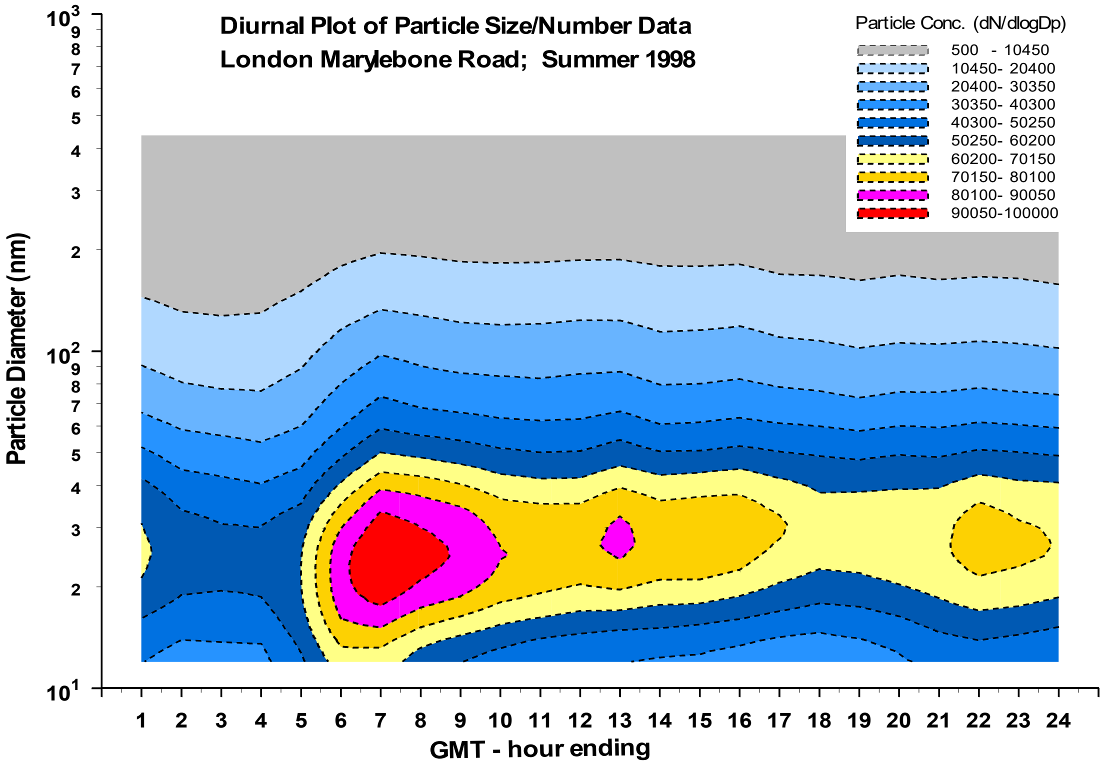
In order to conduct a full investigation of particle size distribution data, hourly averages have been calculated and examined by constructing a diurnal contour plot, which allows easy visualisation of processes affecting the particles. Within these plots, the y axis represents particle diameter and the x axis represents the time of day. The particle count measured as $dN/dlogD_P$ is represented by using different colours. These plots have been applied to different periods and sites, and comparisons have also been made.

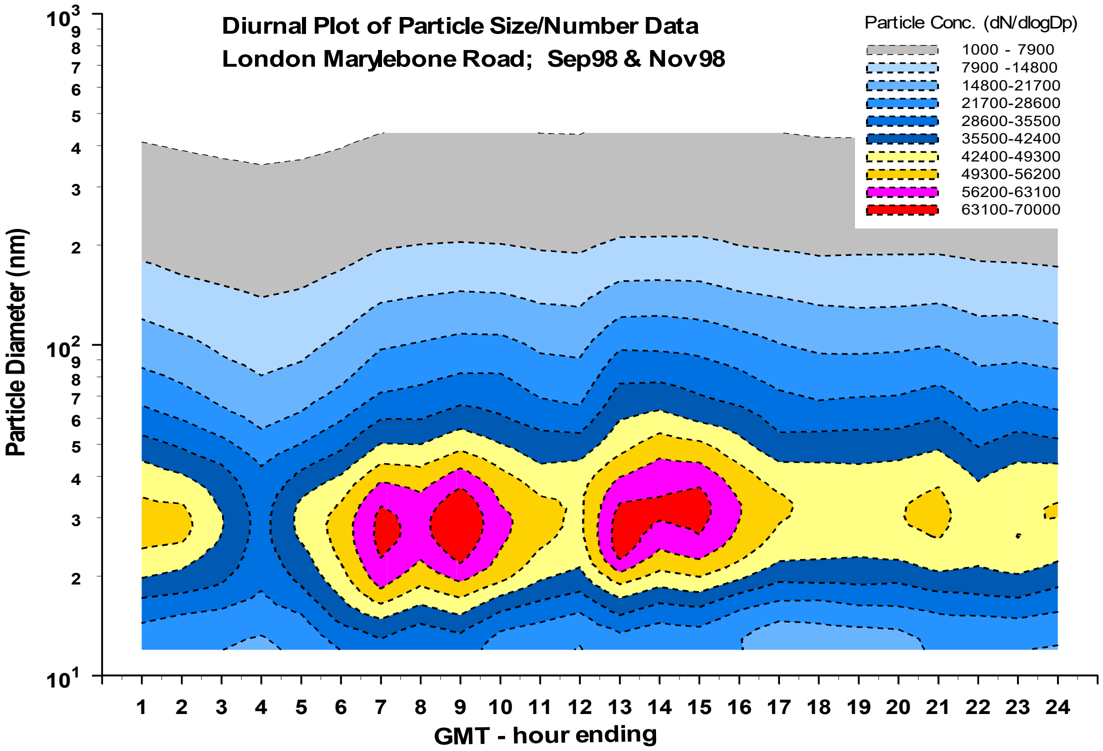
5.4.1 Particle Size and Numbers at Marylebone Road

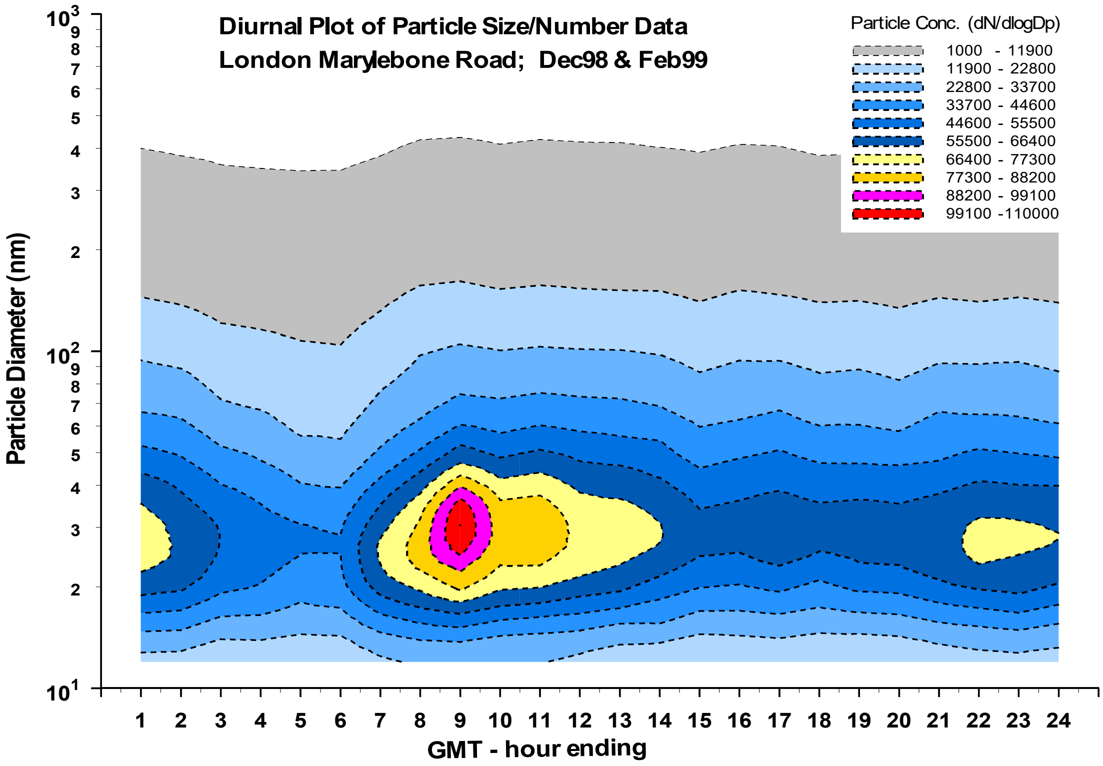
Seasonal average data for Marylebone Road is shown in Figure 5.11. These plots show a clear diurnal variation in particle number size distribution, representative of the pattern of traffic activity and prevailing meteorological variations. Within the plot for April and May 1998, a large morning rush hour peak appeared at 6:00-10:00 a.m. with a maximum in particle count of up to 10^5 expressed as $dN/dlogD_P$ with a modal particle size of 20-30 nm. There is a smaller peak in particle count around 1:00 p.m., and a steady elevation in the 20-30 nm region for the remainder of the day until midnight due to little perceived changes in traffic flow throughout the day at this site. Similar morning rush hour modes in particle number concentration have been observed during all seasons, although they appear at a slightly earlier or later times due to weather conditions. Summer 1998 showed an earlier morning rush hour particle number peak at a slightly smaller size (20 nm), whereas the winter period for December 1998 and February 1999 showed a late morning rush hour number mode with a slightly larger size around 30 nm. Clearly winter months have less influence from human activities, reflected by the diurnal plot showing a clear single morning peak, but with a higher particle count of up to 1.1 x 10^5 due to less dispersion. The rest of plots for September and November 1998, and spring 1999, also show a trend towards a coarser particle mode. In addition to the predominant morning rush hour peak, September and November 1998 shows a prominent afternoon peak around 1:00-3:00 p.m. and spring 1999 shows a small peak at the end of the evening around 10:00-12:00 p.m.

Figure 5.11 Seasonal diurnal plots of particle size and number data (LM)




Diurnal Plot of Particle Size/Number Data
London Marylebone Road; Summer 1998
Particle Conc. (dN/dlogDp)
500 - 10450
10450- 20400
20400- 30350
30350- 40300
40300- 50250
50250- 60200
60200- 70150
70150- 80100
80100- 90050
90050-100000
Particle Diameter (nm)
10^3
10^2
10^1
9
8
7
6
5
4
3
2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; Sep98 & Nov98
Particle Conc. (dN/dlogDp)
1000 - 7900
7900 -14800
14800-21700
21700-28600
28600-35500
35500-42400
42400-49300
49300-56200
56200-63100
63100-70000
Particle Diameter (nm)
10^3
10^2
10^1
9
8
7
6
5
4
3
2
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; Dec98 & Feb99
Particle Conc. (dN/dlogDp)
1000 - 11900
11900 - 22800
22800 - 33700
33700 - 44600
44600 - 55500
55500 - 66400
66400 - 77300
77300 - 88200
88200 - 99100
99100 -110000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

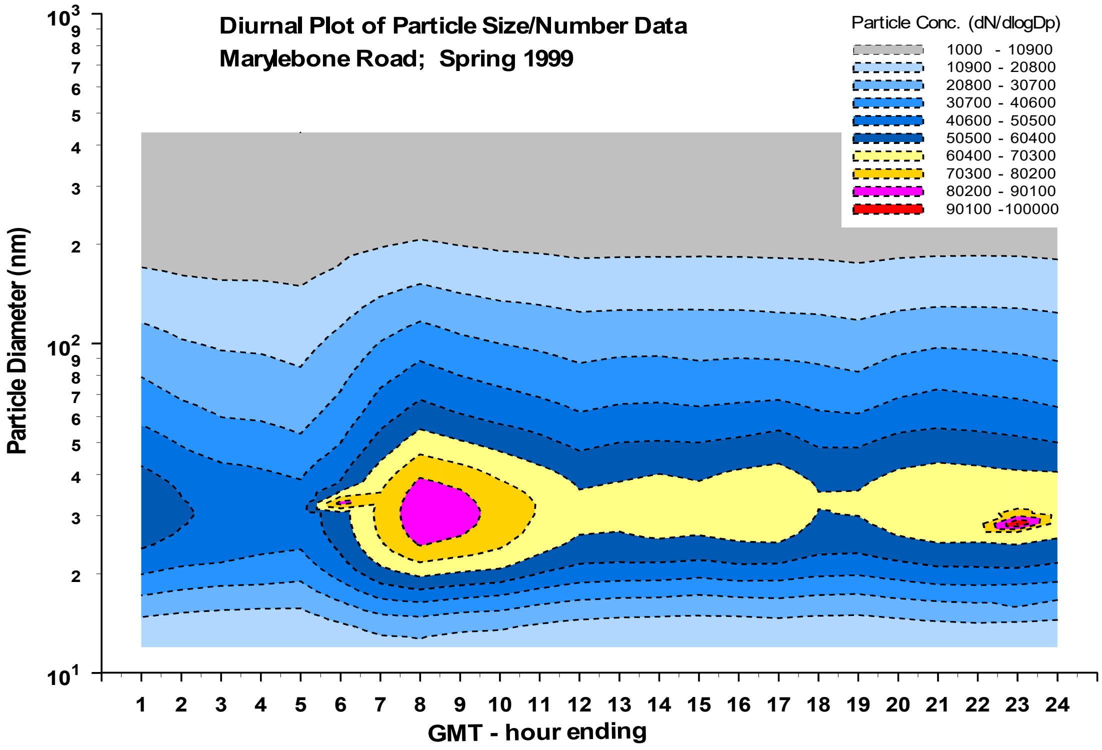
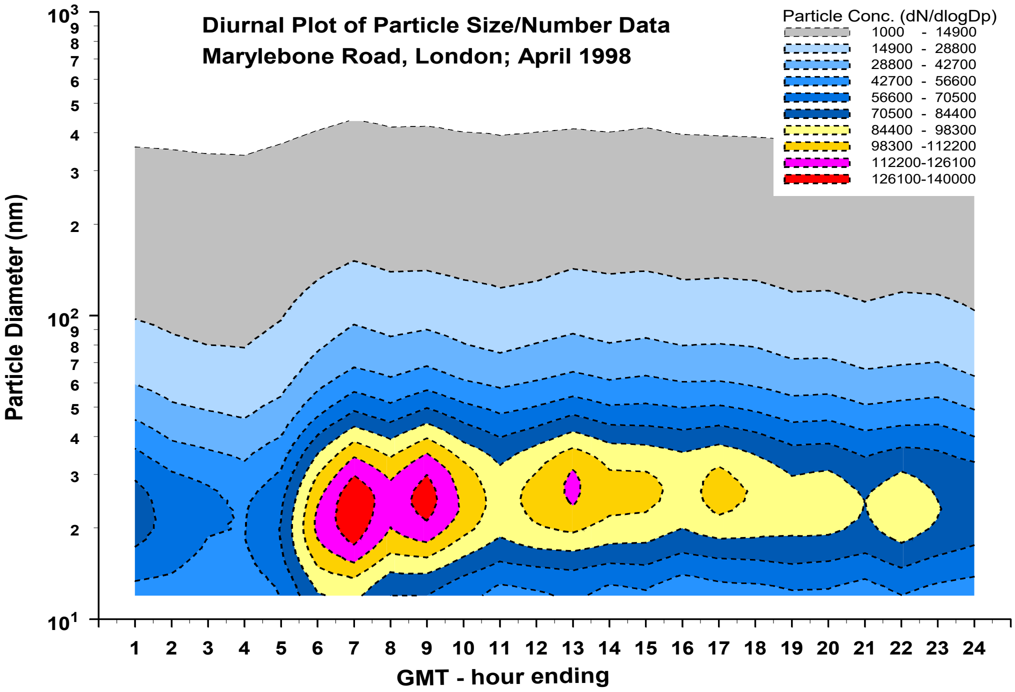
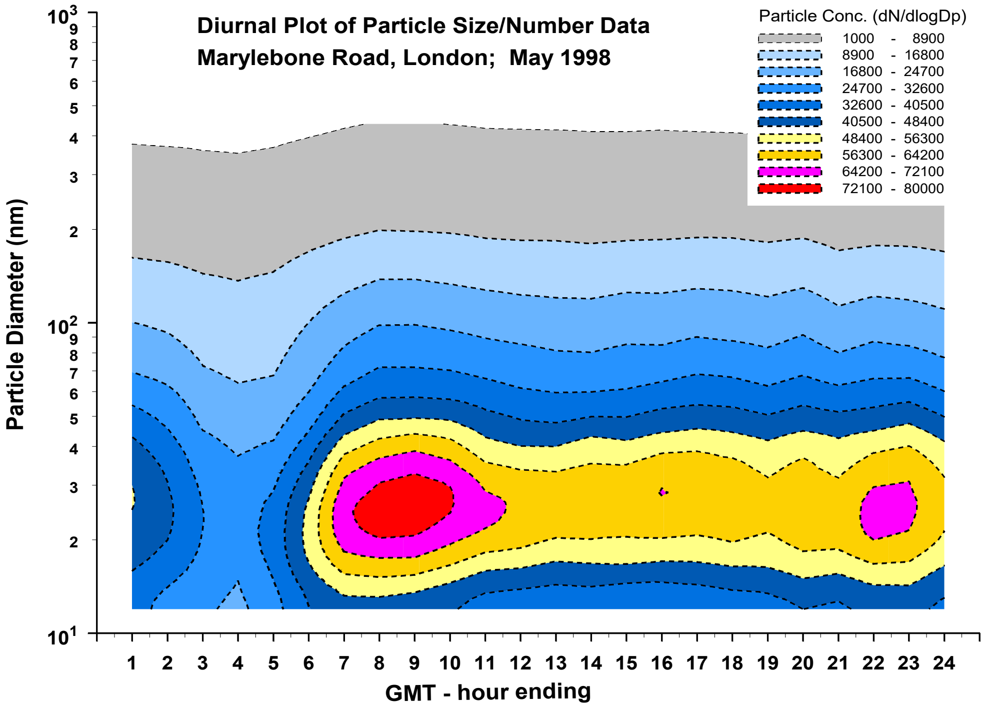

Diurnal Plot of Particle Size/Number Data
Marylebone Road; Spring 1999
Particle Conc. (dN/dlogDp)
1000 - 10900
10900 - 20800
20800 - 30700
30700 - 40600
40600 - 50500
50500 - 60400
60400 - 70300
70300 - 80200
80200 - 90100
90100 -100000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

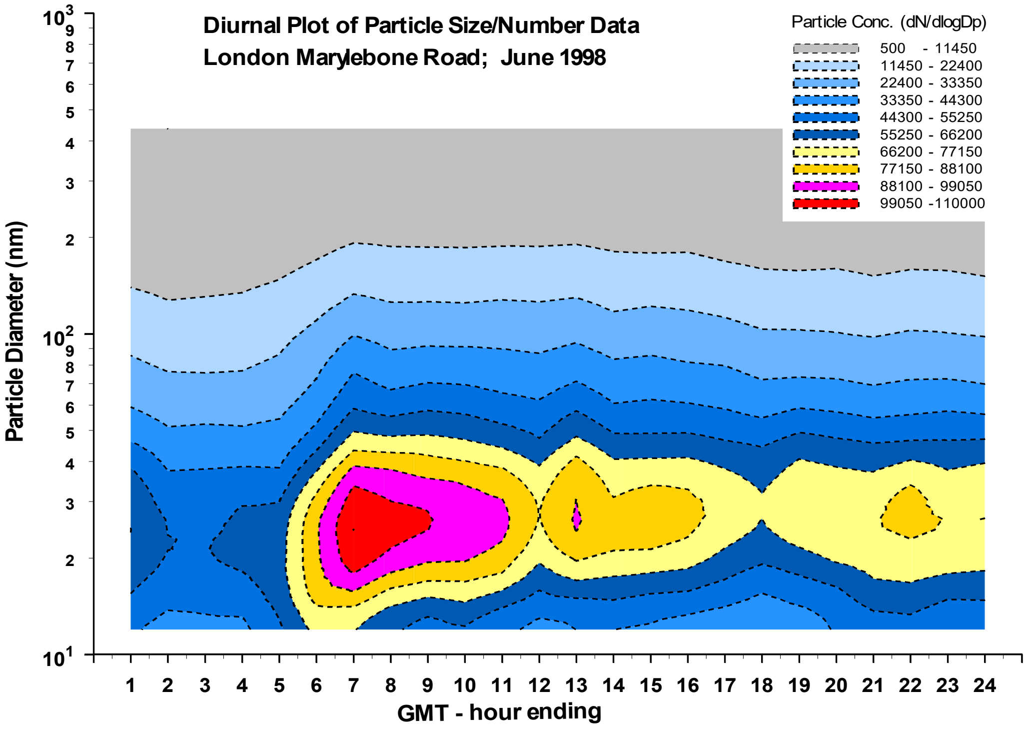
Figure 5.12 shows plots of monthly average data at LM from April 1998 to August 1999. These are broadly similar to the seasonal average plots. As an exception, July 1998 showed three obvious particle number modes. There was a morning peak comprising of particles of smaller size at 20 nm; a wider afternoon peak from 12:30 to 16:30 representing particles at 30 nm; and a small late evening peak around 23:00 with similar particle size as the second peak. All three number peaks have similar size in the nucleation mode presumably from a same source of traffic. In addition, August 1999 also showed three peaks around morning at 8:00, lunch-time at 12:00 and early afternoon at 16:00, which correlated well with the traffic induced pollutant NO_x (see figure 3.6g&h).

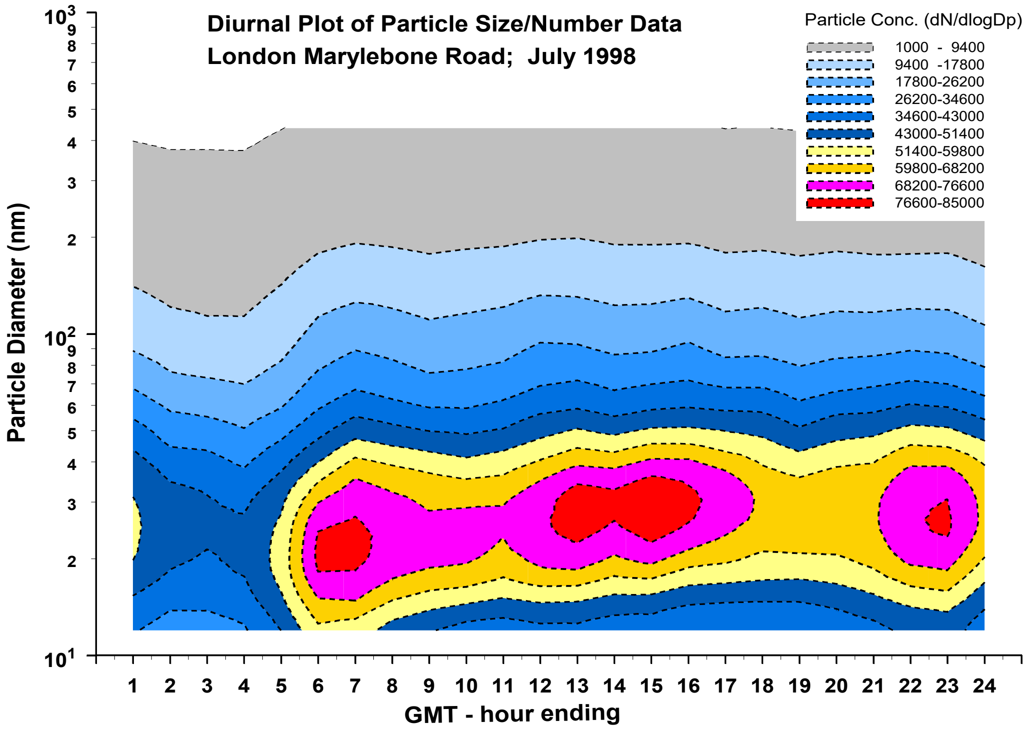
On aggregating the weekday and weekend data for each month, evidence of human activity affecting the particle number concentration is clearly seen (figure 5.13). The main features differentiating the weekdays and weekends are: a) higher particle count on weekdays than on weekends; b) a delayed and smaller morning peak on weekends comparing with weekdays; c) a late afternoon peak with continuous increase in particle numbers until midnight on weekends. The weekday/weekend variation in particle number concentrations have been observed from the other studies (Hughes et al., 1998; Ruuskanen et al., 2001).

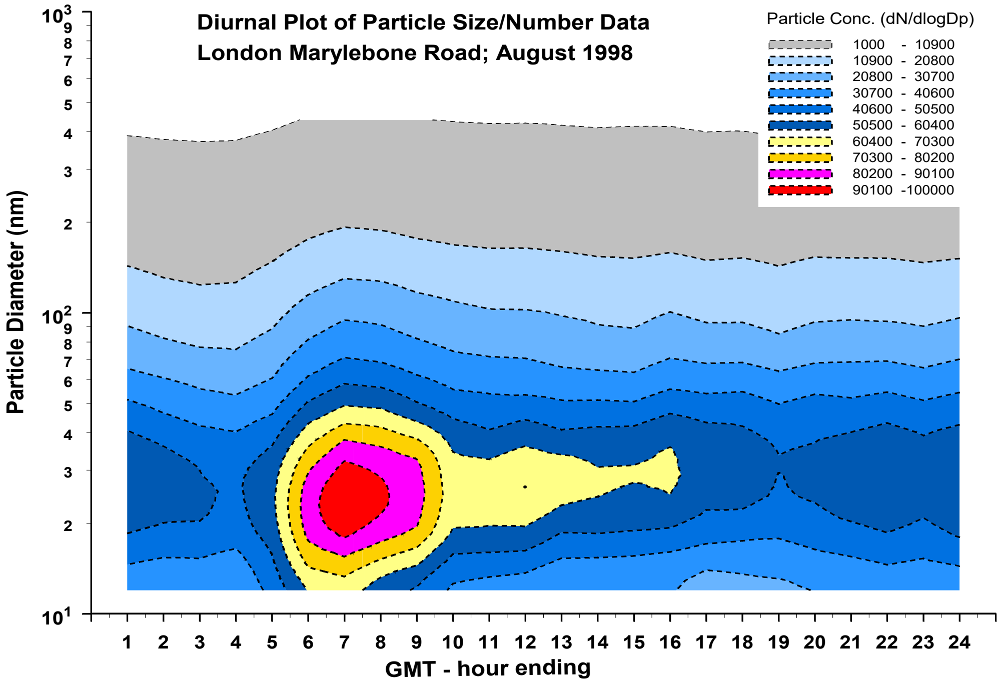
Figure 5.12 Monthly diurnal plots of particle size and number data (LM)

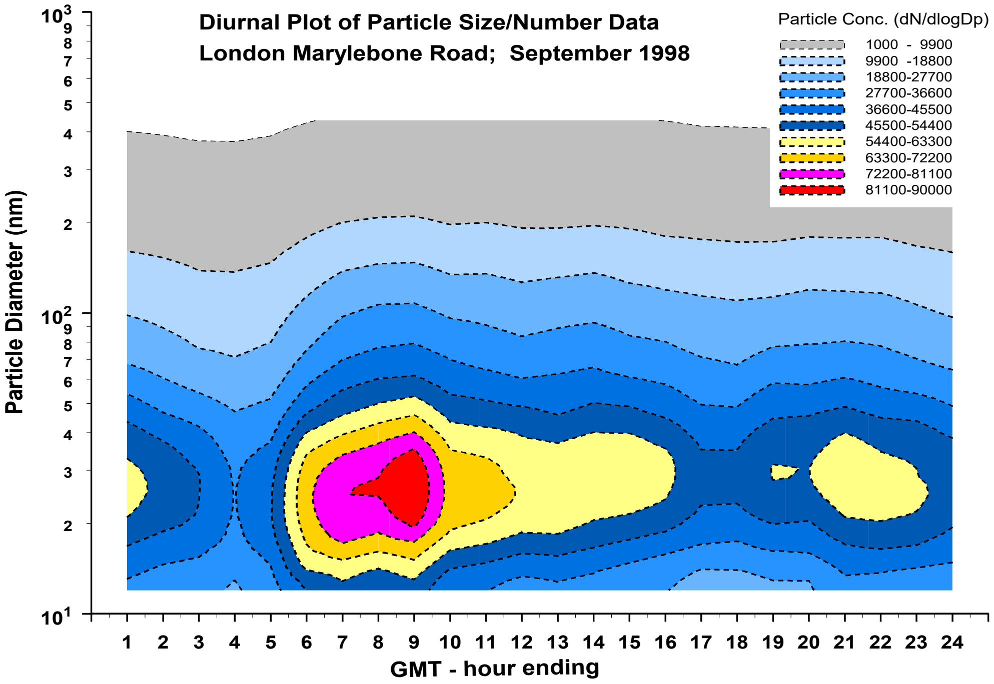

Diurnal Plot of Particle Size/Number Data
Marylebone Road, London; April 1998
Particle Conc. (dN/dlogDp)
1000 - 14900
14900 - 28800
28800 - 42700
42700 - 56600
56600 - 70500
70500 - 84400
84400 - 98300
98300 -112200
112200-126100
126100-140000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

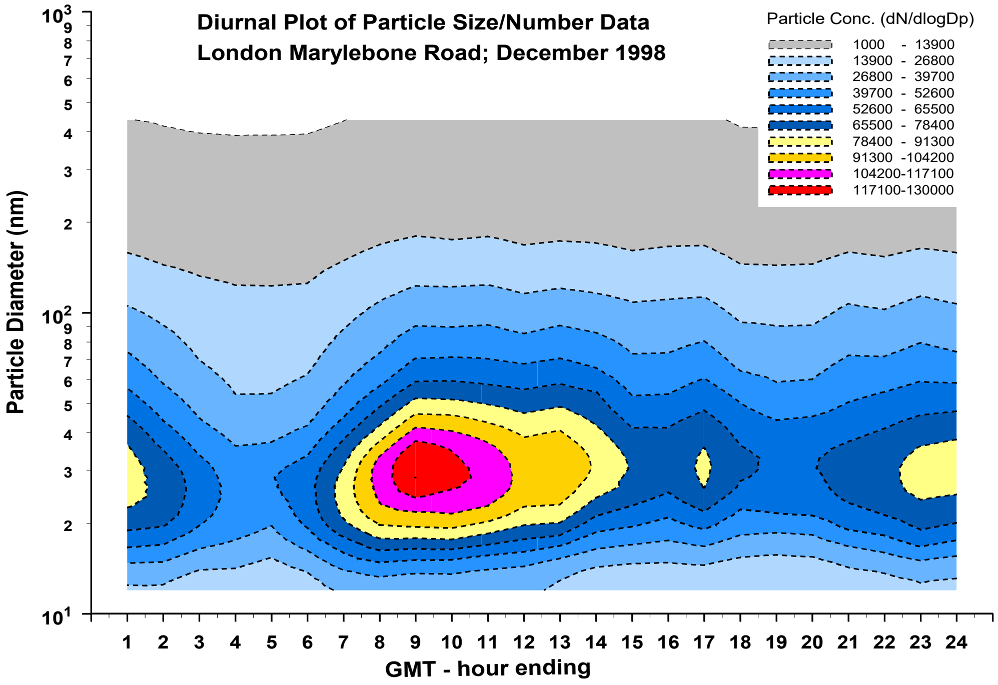

Diurnal Plot of Particle Size/Number Data
Marylebone Road, London; May 1998
Particle Conc. (dN/dlogDp)
1000 - 8900
8900 - 16800
16800 - 24700
24700 - 32600
32600 - 40500
40500 - 48400
48400 - 56300
56300 - 64200
64200 - 72100
72100 - 80000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

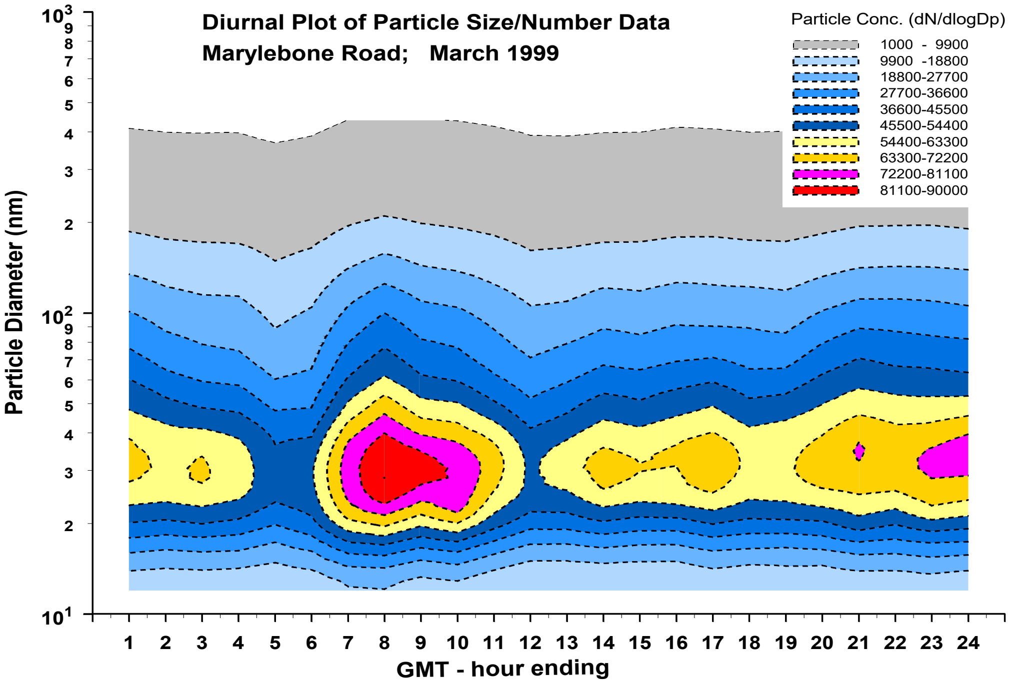

Diurnal Plot of Particle Size/Number Data
London Marylebone Road; June 1998
Particle Conc. (dN/dlogDp)
500 - 11450
11450 - 22400
22400 - 33350
33350 - 44300
44300 - 55250
55250 - 66200
66200 - 77150
77150 - 88100
88100 - 99050
99050 -110000
Particle Diameter (nm)
10^1
10^2
10^3
2
3
4
5
6
7
8
9
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

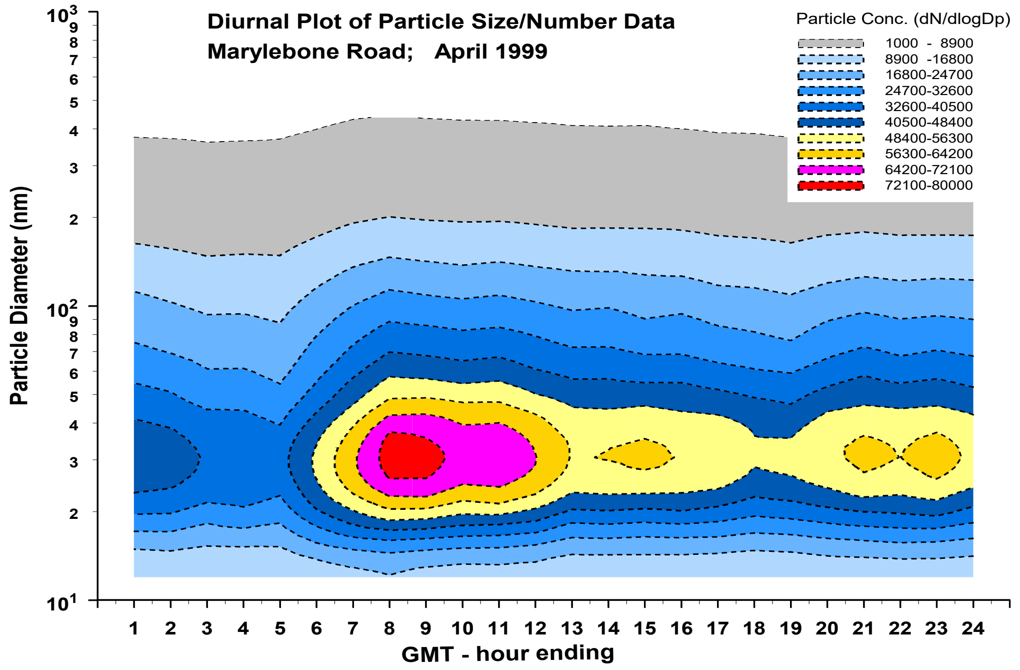

Diurnal Plot of Particle Size/Number Data
London Marylebone Road; July 1998
Particle Conc. (dN/dlogDp)
1000 - 9400
9400 -17800
17800-26200
26200-34600
34600-43000
43000-51400
51400-59800
59800-68200
68200-76600
76600-85000
Particle Diameter (nm)
10^1
10^2
10^3
2
3
4
5
6
7
8
9
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

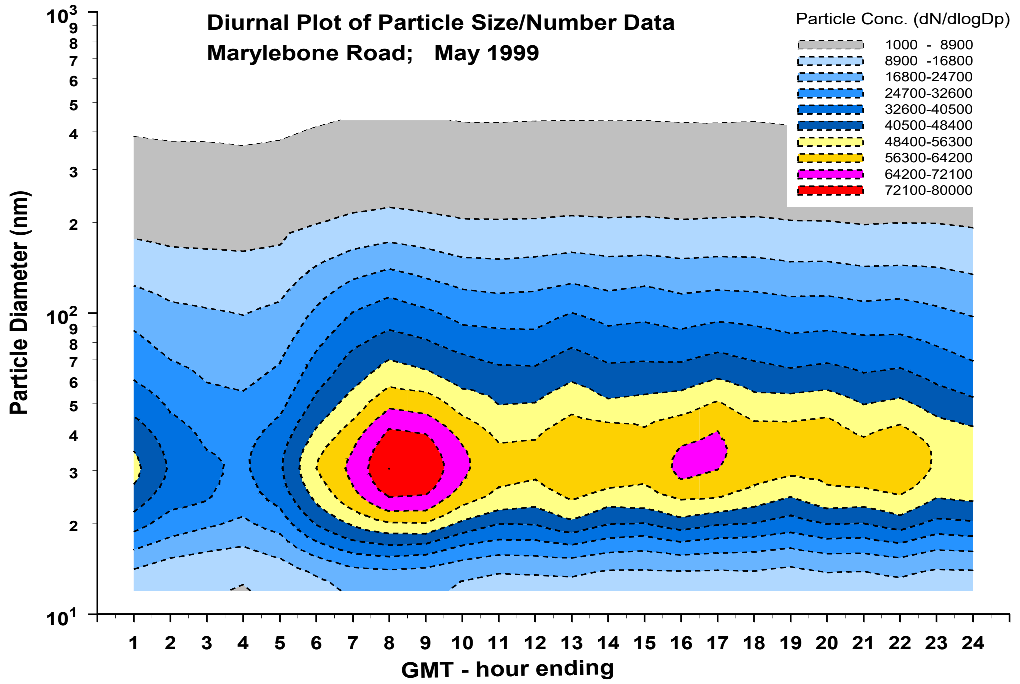

Diurnal Plot of Particle Size/Number Data
London Marylebone Road; August 1998
Particle Conc. (dN/dlogDp)
1000 - 10900
10900 - 20800
20800 - 30700
30700 - 40600
40600 - 50500
50500 - 60400
60400 - 70300
70300 - 80200
80200 - 90100
90100 -100000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; September 1998
Particle Conc. (dN/dlogDp)
1000 - 9900
9900 -18800
18800-27700
27700-36600
36600-45500
45500-54400
54400-63300
63300-72200
72200-81100
81100-90000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; December 1998
Particle Conc. (dN/dlogDp)
1000 - 13900
13900 - 26800
26800 - 39700
39700 - 52600
52600 - 65500
65500 - 78400
78400 - 91300
91300 -104200
104200-117100
117100-130000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
Marylebone Road; March 1999
Particle Conc. (dN/dlogDp)
1000 - 9900
9900 -18800
18800-27700
27700-36600
36600-45500
45500-54400
54400-63300
63300-72200
72200-81100
81100-90000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
Marylebone Road;   April 1999
Particle Conc. (dN/dlogDp)
1000 - 8900
8900 -16800
16800-24700
24700-32600
32600-40500
40500-48400
48400-56300
56300-64200
64200-72100
72100-80000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
Marylebone Road;   May 1999
Particle Conc. (dN/dlogDp)
1000 - 8900
8900 -16800
16800-24700
24700-32600
32600-40500
40500-48400
48400-56300
56300-64200
64200-72100
72100-80000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

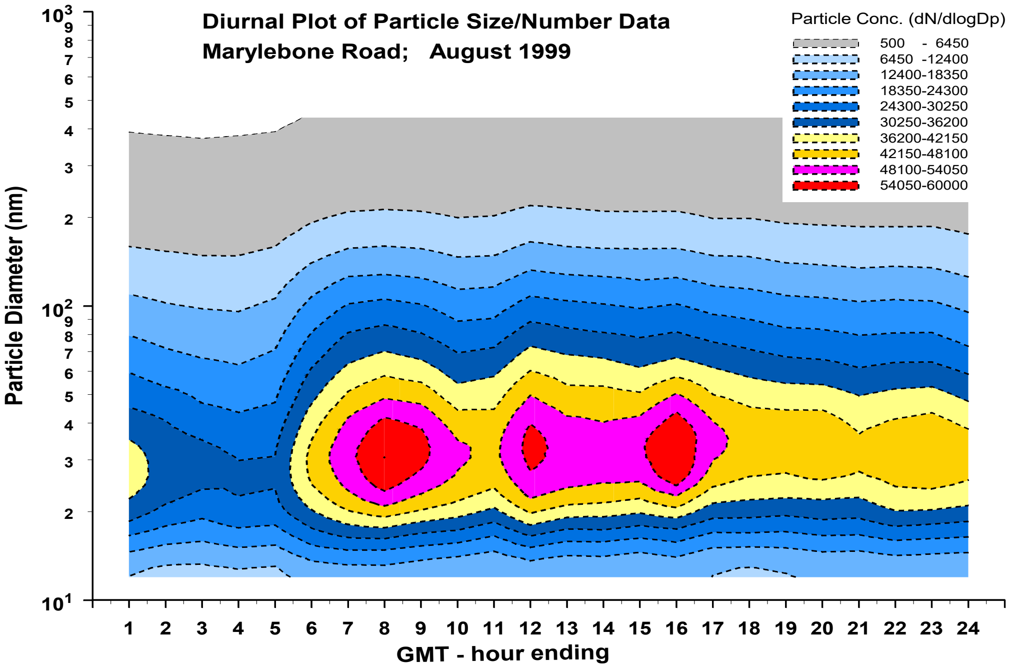
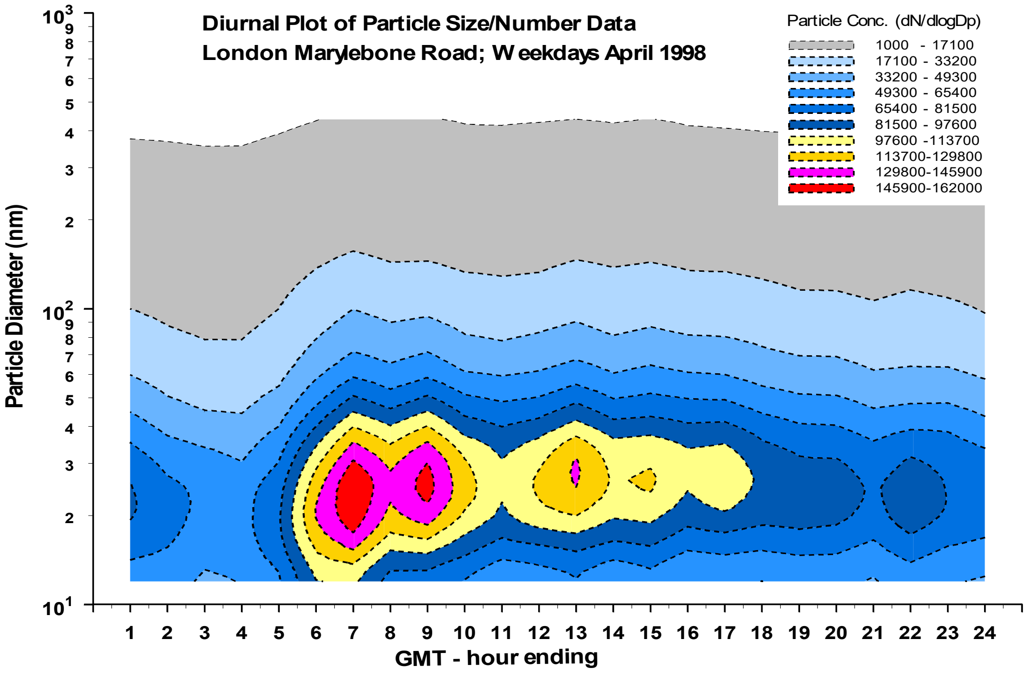
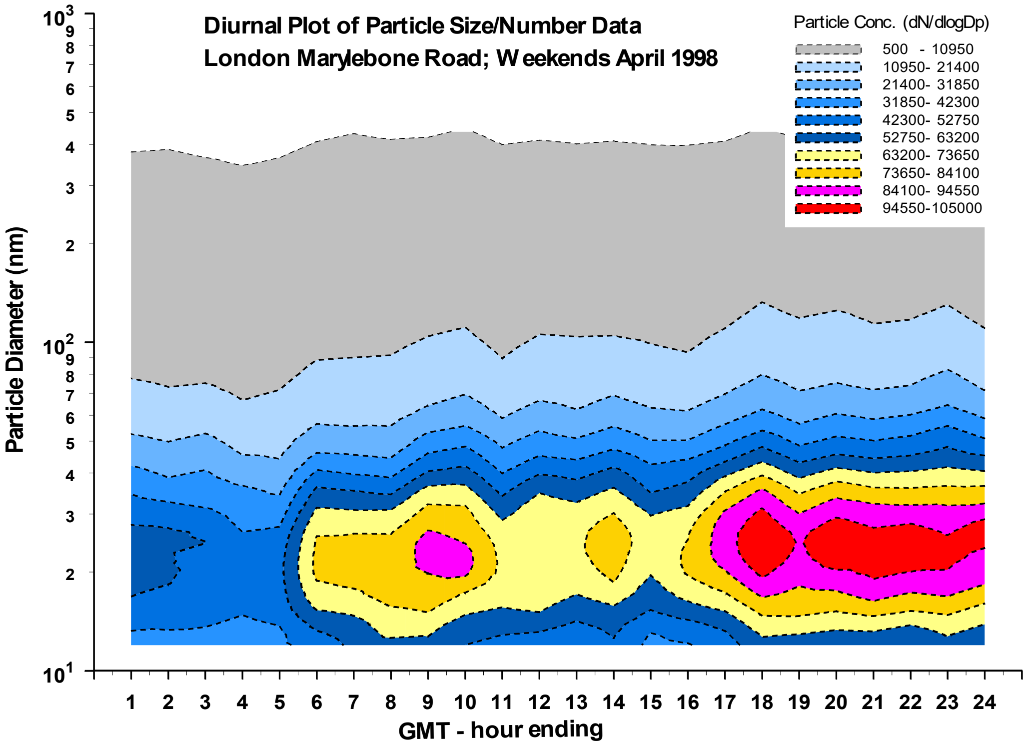
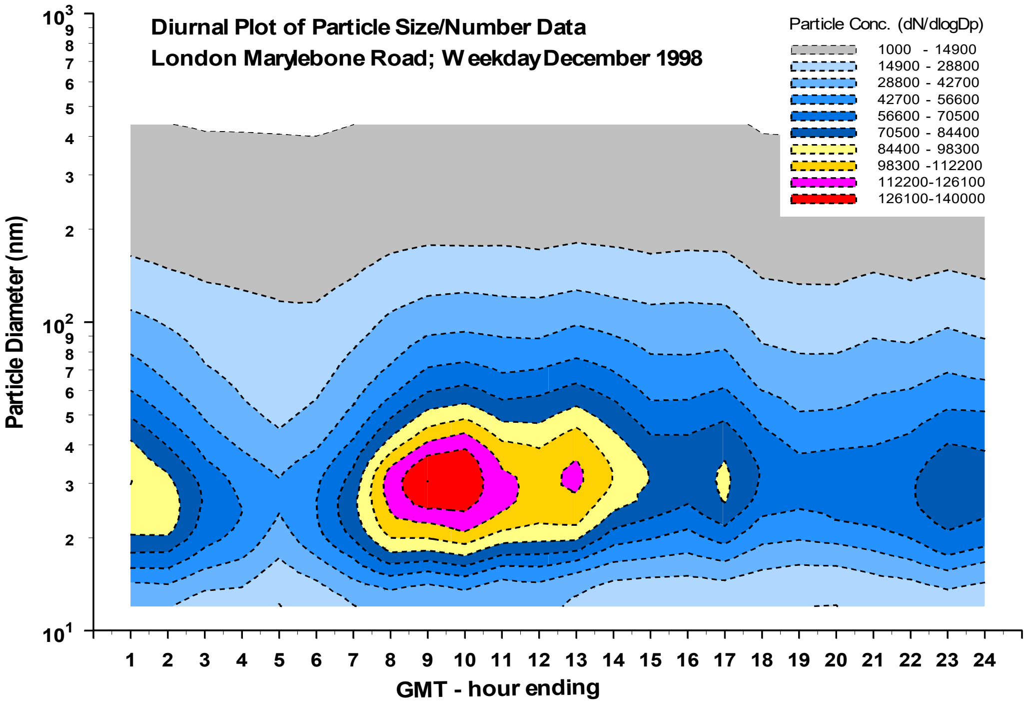
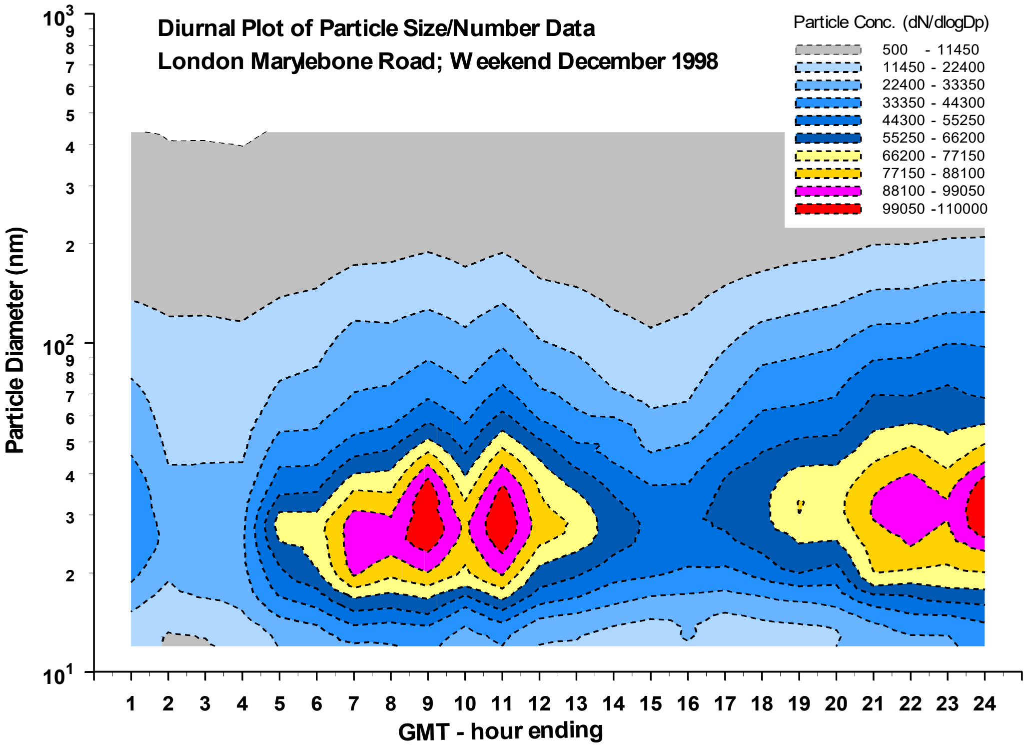


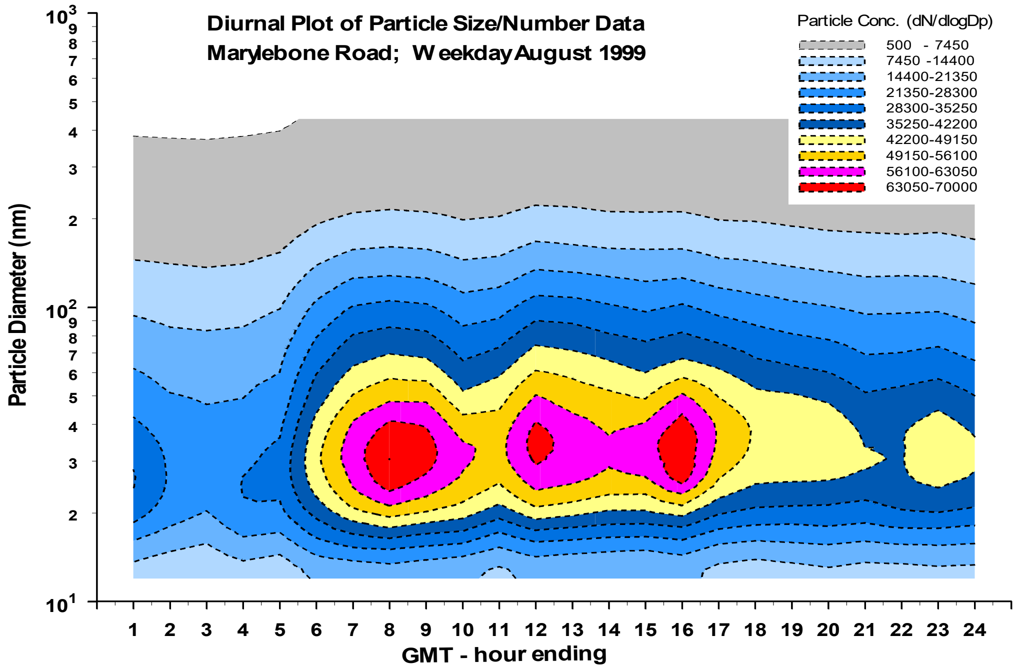
Figure 5.13 Weekday/Weekend diurnal particle size and number data (LM)

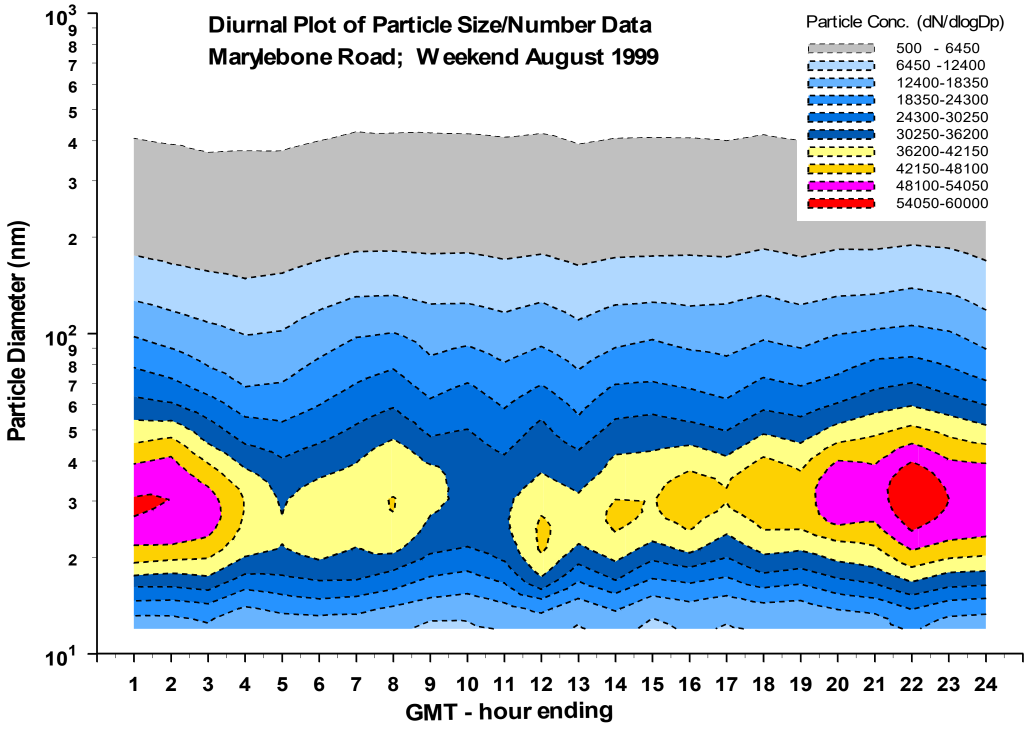



Diurnal Plot of Particle Size/Number Data
London Marylebone Road; W eekends April 1998
Particle Conc. (dN/dlogDp)
500 - 10950
10950- 21400
21400- 31850
31850- 42300
42300- 52750
52750- 63200
63200- 73650
73650- 84100
84100- 94550
94550-105000
Particle Diameter (nm)
10^3
10^2
10^1
9
8
7
6
5
4
3
2
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; W eekday December 1998
Particle Conc. (dN/dlogDp)
1000 - 14900
14900 - 28800
28800 - 42700
42700 - 56600
56600 - 70500
70500 - 84400
84400 - 98300
98300 -112200
112200-126100
126100-140000
Particle Diameter (nm)
10^3
10^2
10^1
9
8
7
6
5
4
3
2
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24


Diurnal Plot of Particle Size/Number Data
London Marylebone Road; Weekend December 1998
Particle Conc. (dN/dlogDp)
500 - 11450
11450 - 22400
22400 - 33350
33350 - 44300
44300 - 55250
55250 - 66200
66200 - 77150
77150 - 88100
88100 - 99050
99050 -110000
Particle Diameter (nm)
10^1
2
3
4
5
6
7
8
9
10^2
10^3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
Marylebone Road; Weekday August 1999
Particle Conc. (dN/dlogDp)
500 - 7450
7450 -14400
14400-21350
21350-28300
28300-35250
35250-42200
42200-49150
49150-56100
56100-63050
63050-70000
Particle Diameter (nm)
10^1
2
3
4
5
6
7
8
9
10^2
10^3
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending



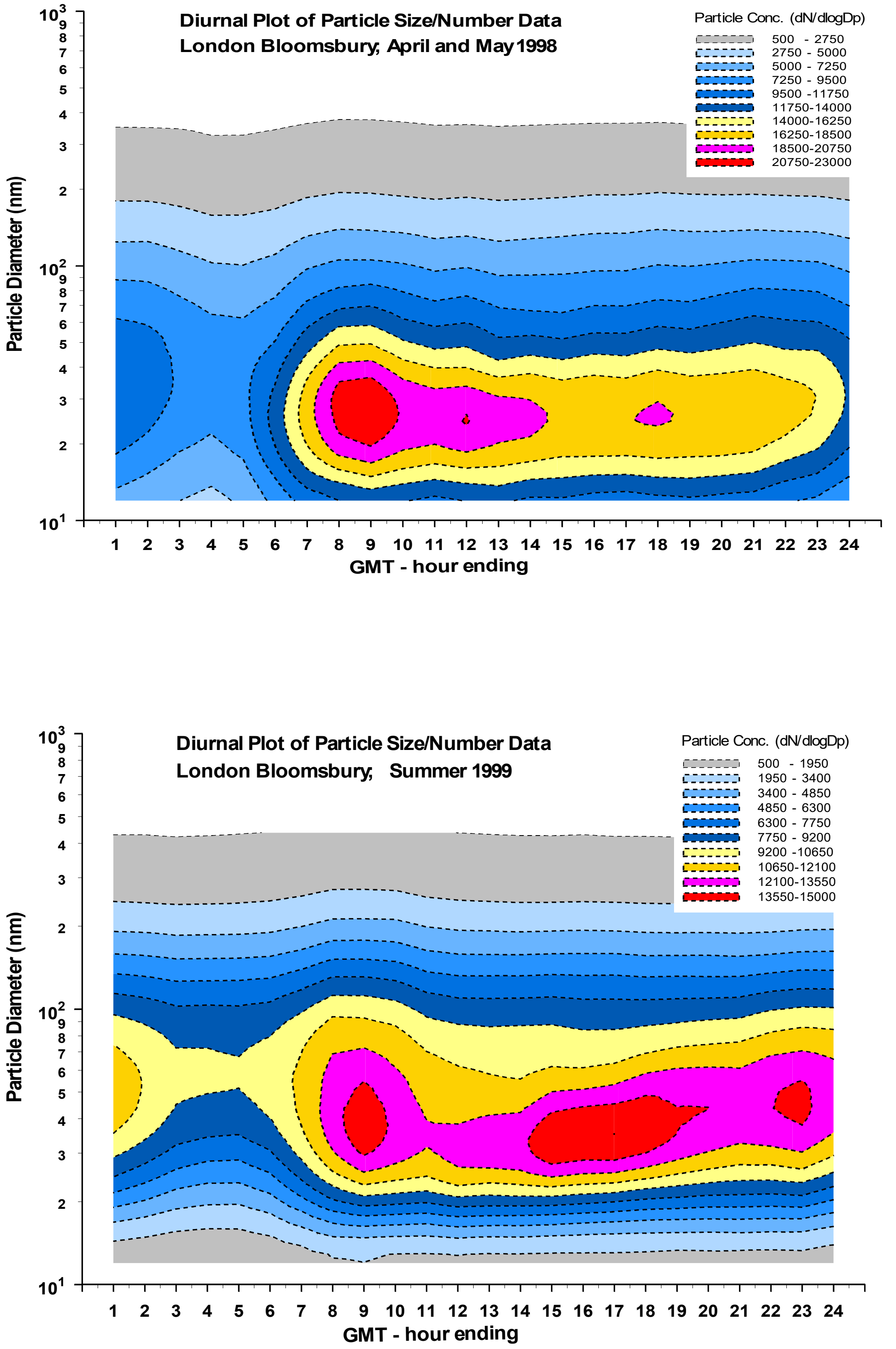
5.4.2 Particle Size and Numbers at London Bloomsbury

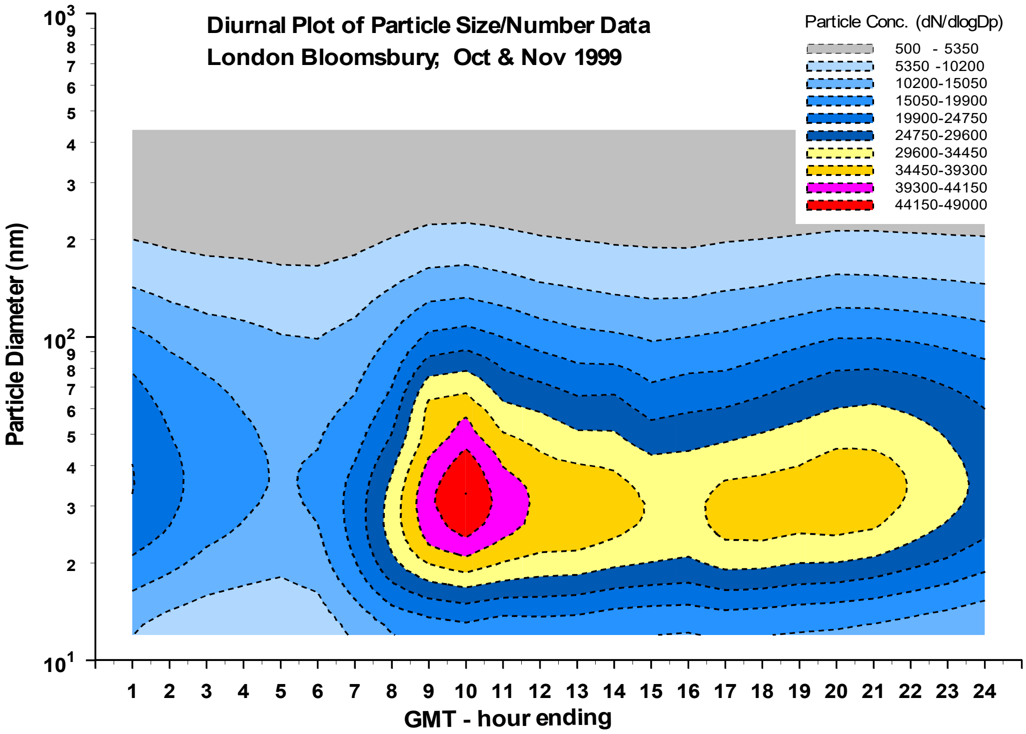
Some selected seasonal, monthly and daily average plots of particle number size distribution at LB are shown in Figure 5.14. These are broadly similar to LM, but with a tendency to a lower particle number count and a slightly coarser mode in the size distribution. This is because the background site is located about 35 m from the surrounding roads with moderate traffic levels. Data from individual months show greater variability due to traffic activity and meteorology than the seasonal data. The weekday/weekend (figure 5.15) difference at LB is also clearly marked revealing higher particle number concentration on weekdays than weekends and the existence of an evening/night-time peak in traffic at the weekends.

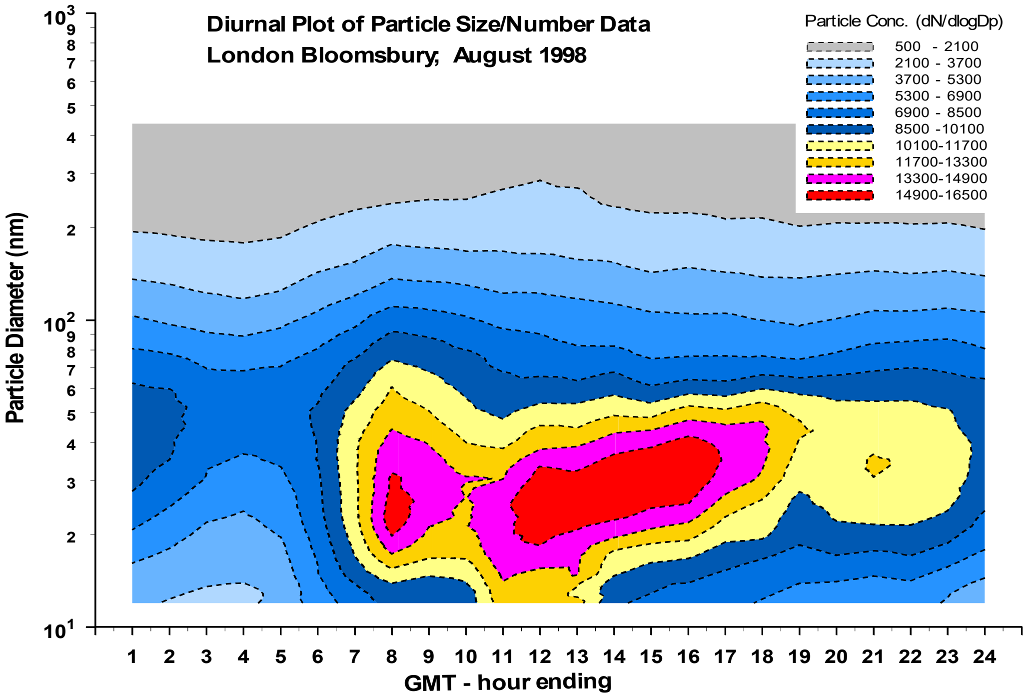
Apart from the similarity of these plots, the period of August 1998 stands out showing a wide number peak relating to particles of smaller size below 20 nm. The daily plot on the 7th August indicated clearly that very small particles less than the measurable size of 10 nm were formed at about 11 to 14 o'clock. Relatively higher number concentrations were observed at the time (5.2×10^4 cm^{-3}). These particles are likely related to homogeneous nucleation processes, but the precursor gaseous pollutant concentrations of SO_2 and NO_x did not show an increase. O_3 concentration was slightly higher than usual and the wind was westerly with lower speeds at 2-3 metres per second. A similar situation occurred on the 24th August (not shown, as the data were not complete). The peak was observed at about 11 with a number concentration about 2.8 x 10^4 cm^{-3}. This time the SO_2 and NO_x concentrations were slightly elevated while the wind was also westerly before the event, and then changed to northerly with speeds around 3-5 metres per second.

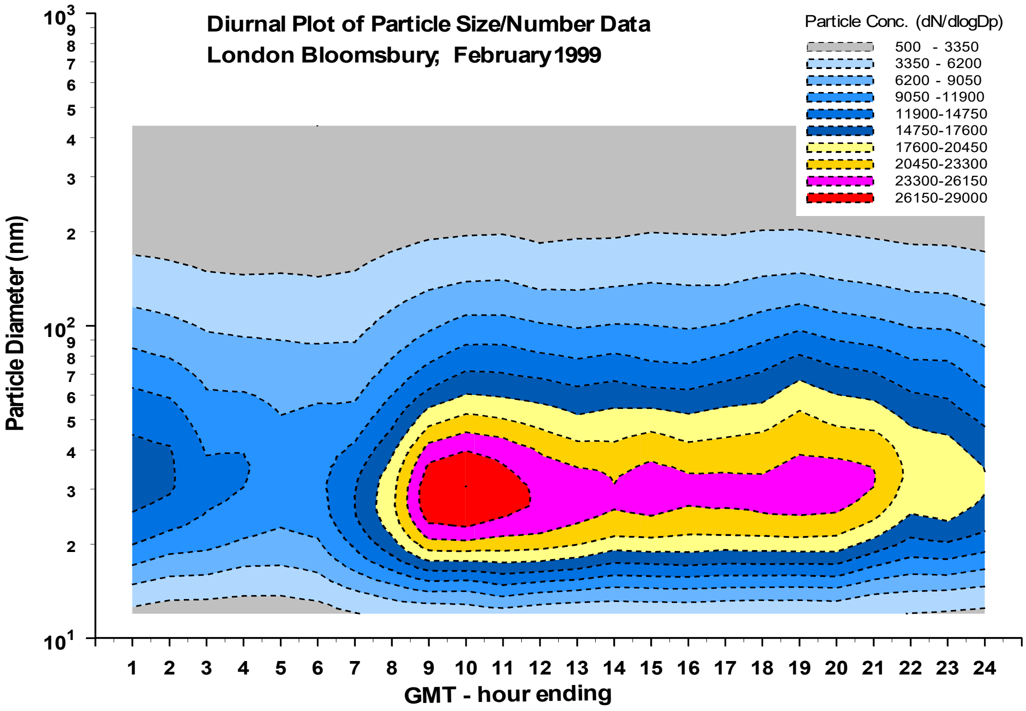
New particle formation through homogenous nucleation has been mostly observed in remote areas, such as coastal sites (Allen et al., 1999; O'Dowd et al., 1999) and rural sites (Hugh et al., 2000; Birmili et al., 2000; Birmili and Wiedensohler, 2000). Only few studies show that the processes can occur in urban areas (e.g. Harrison et al., 2000). Early studies in Birmingham (Shi et al., 1999a &2001) have found that very small particles (3-7 nm) were generated from vehicle exhaust. These nanoparticles are formed through homogeneous nucleation and growth of semi-volatile organics and H_2SO_4-H_2O (Baumgard and Johnson, 1996; Shi and Harrison, 1999). These particles can grow rapidly through coagulation and condensation. At the roadside site (LM), the speed of growth of these nanoparticles is greatly enhanced under conditions of very high particle number count due to heavy traffic, such as the growth by condensation of semi-volatile organic compounds (Marti et al., 1997), which are abundant at the roadside site. Therefore only particle number size modes around 20-30 nm were observed on Marylebone Road. The urban background site (LB) has a slightly larger number size mode (30 nm) due to a distance from road. Newly generated very small particles from traffic generally will grow to the observed size before reaching the sampling point. The smaller particles detected on the 7th and 24th August 1998 may indicate a different pollution source other than traffic although the evidence is inconclusive.

Figure 5.14 Seasonal, monthly and daily particle size and numbers data (LB)




Diurnal Plot of Particle Size/Number Data
London Bloomsbury, Oct & Nov 1999
Particle Conc. (dN/dlogDp)
500 - 5350
5350 -10200
10200-15050
15050-19900
19900-24750
24750-29600
29600-34450
34450-39300
39300-44150
44150-49000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Bloomsbury, August 1998
Particle Conc. (dN/dlogDp)
500 - 2100
2100 - 3700
3700 - 5300
5300 - 6900
6900 - 8500
8500 -10100
10100-11700
11700-13300
13300-14900
14900-16500
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending


Diurnal Plot of Particle Size/Number Data
London Bloomsbury, February 1999
Particle Conc. (dN/dlogDp)
500 - 3350
3350 - 6200
6200 - 9050
9050 -11900
11900-14750
14750-17600
17600-20450
20450-23300
23300-26150
26150-29000
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

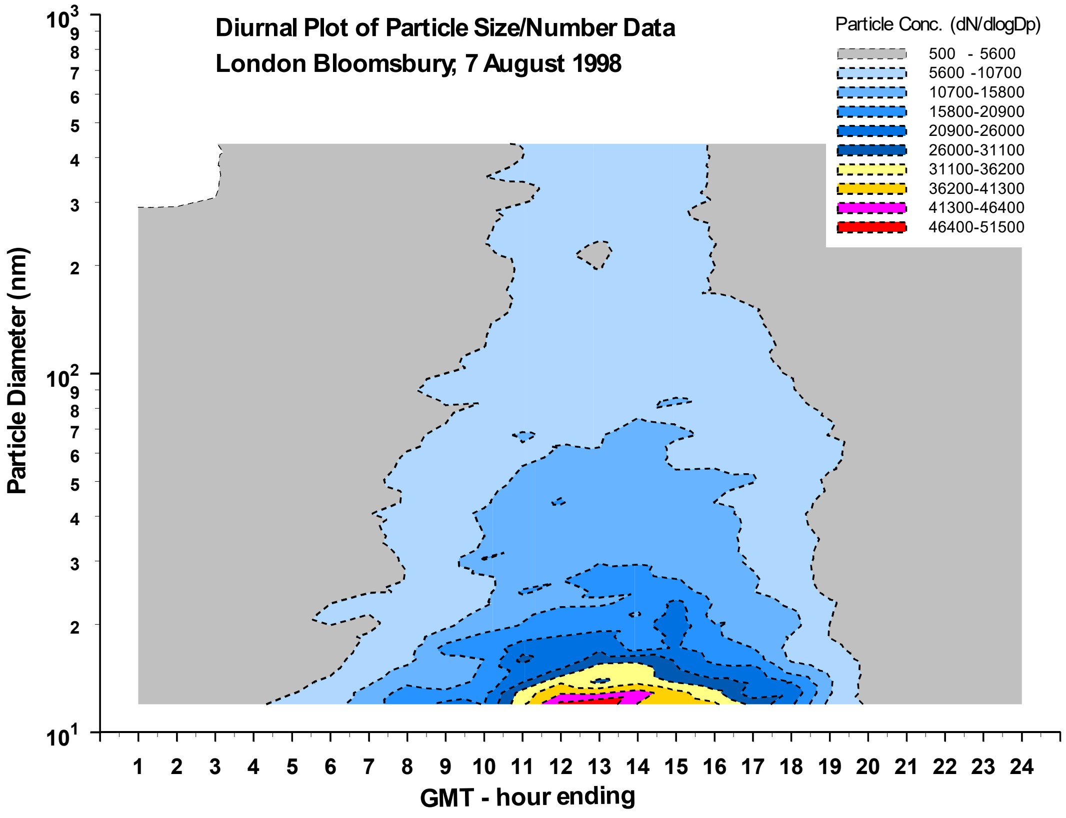
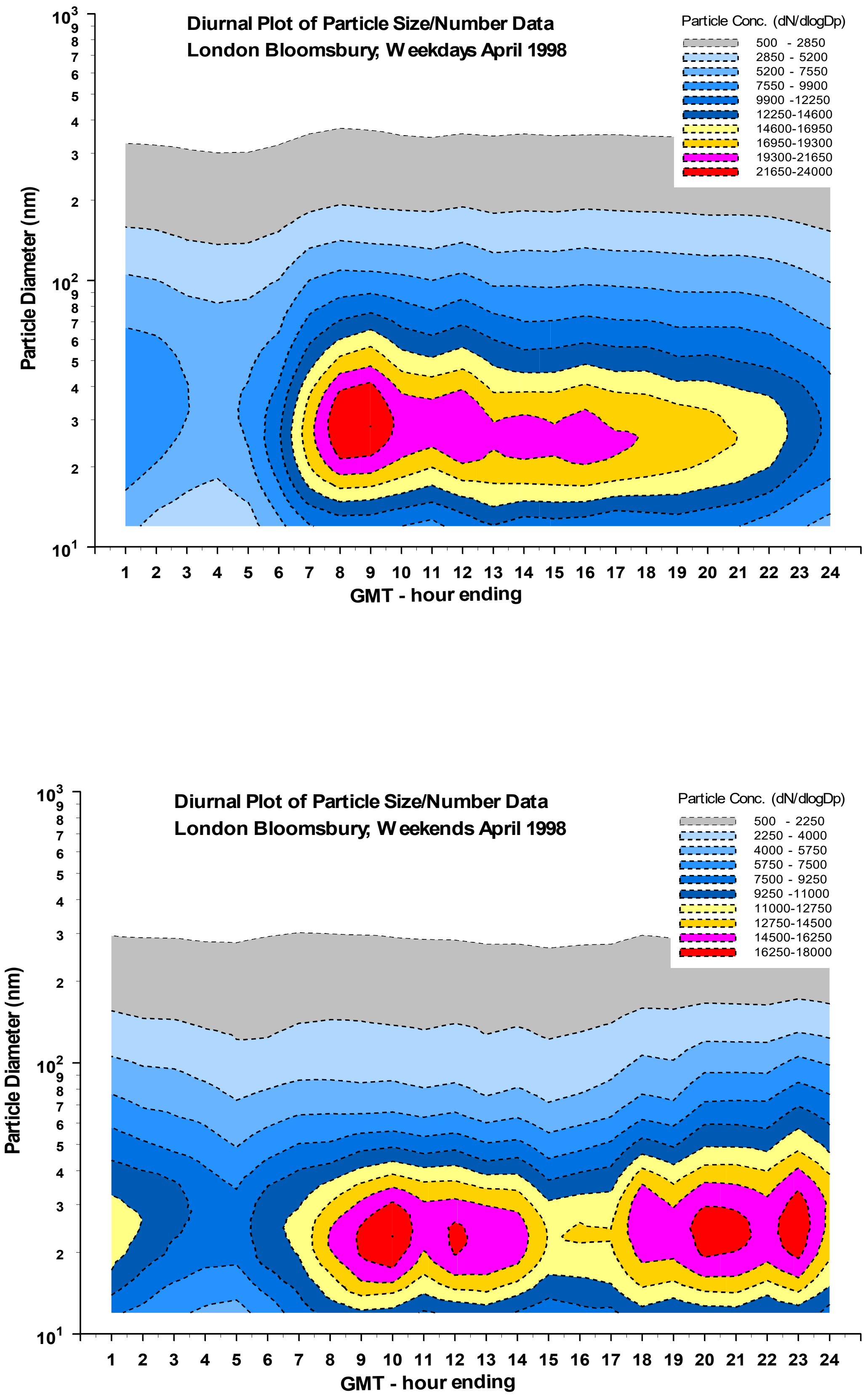
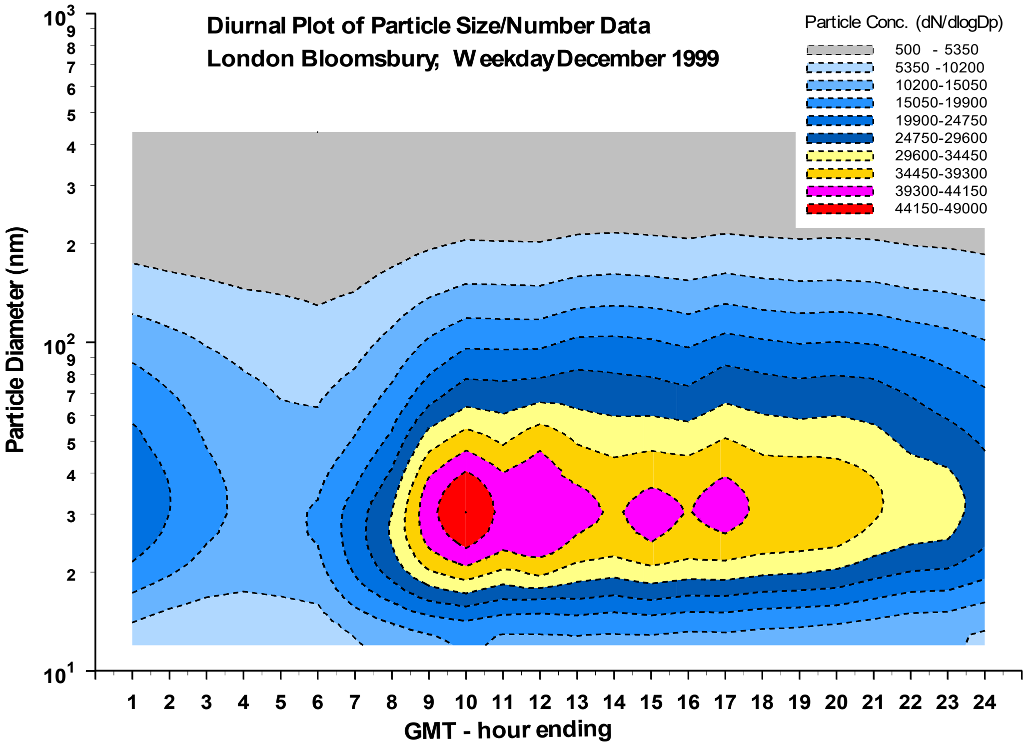
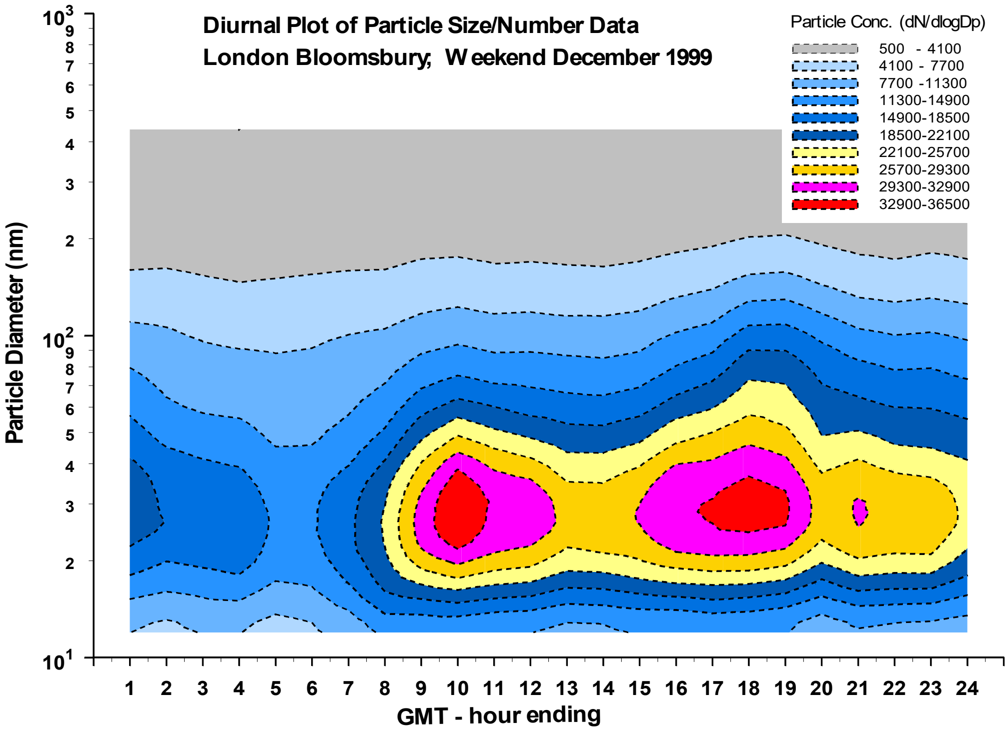

Diurnal Plot of Particle Size/Number Data
London Bloomsbury, 7 August 1998
Particle Conc. (dN/dlogDp)
500 - 5600
5600 -10700
10700-15800
15800-20900
20900-26000
26000-31100
31100-36200
36200-41300
41300-46400
46400-51500
Particle Diameter (nm)
10^3
9
8
7
6
5
4
3
2
10^2
9
8
7
6
5
4
3
2
10^1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
GMT - hour ending

Figure 5.15 Weekday/Weekend diurnal particle size and number data (LB)



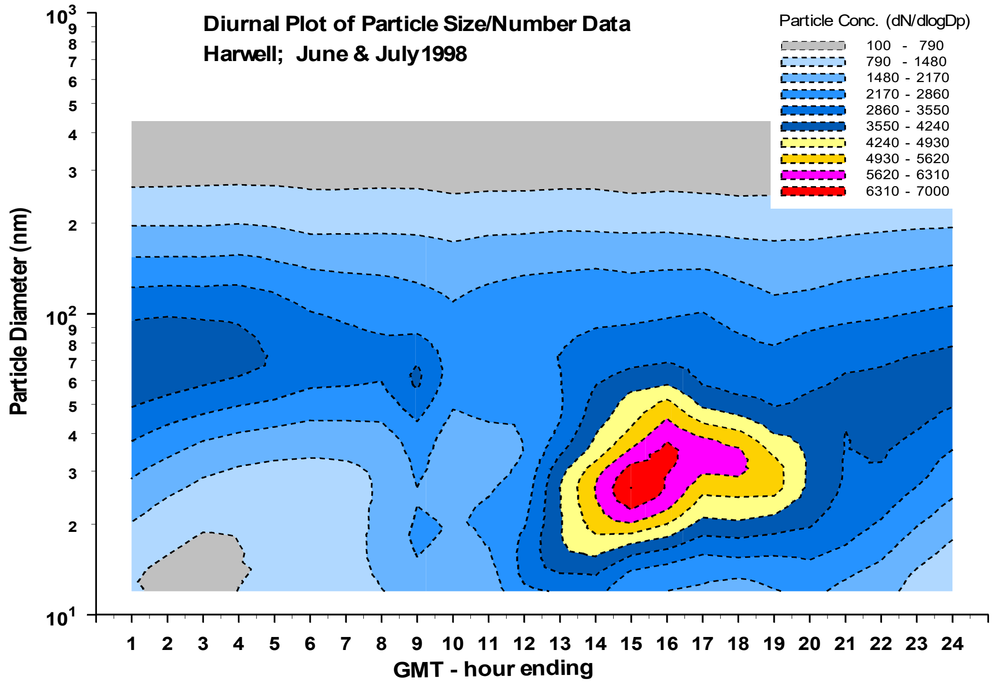


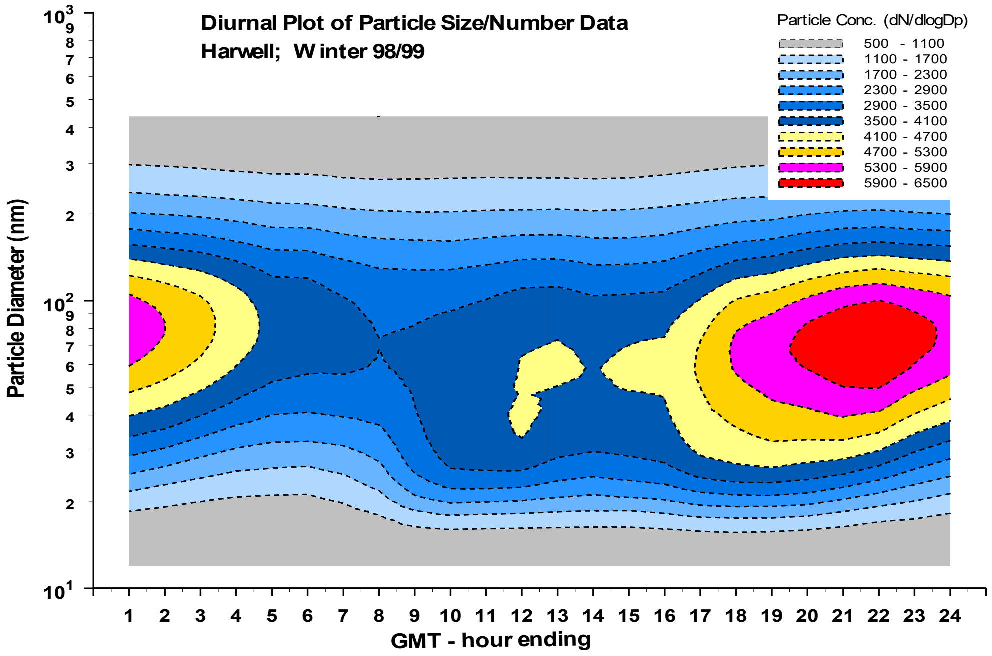


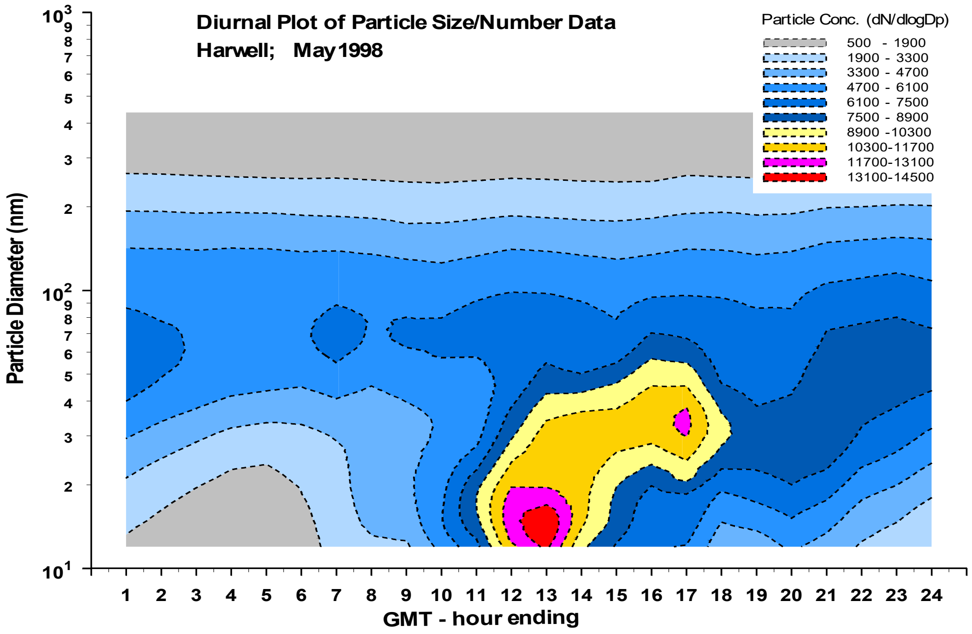
5.4.3 Particle Size and Numbers at Harwell

In contrast to LM and LB, the Harwell site exhibited totally different diurnal patterns in the particle size distribution with low particle count and a wide variation in particle size mode over different periods. No obvious relationship was found between the diurnal variation and traffic activity as expected at this rural site some distance from major roads. Figure 5.16 shows a few seasonal and monthly plots at the Harwell site. In general, particle number modes appeared mostly at daytime i.e. midday or early afternoon, in spring and summer with a smaller particle size and higher particle count. The plot for June and July 1998 shows a number mode around 3:00 p.m. at a size about 20-30 nm, while the plot for May 1998 indicates a peak at about 1:00 p.m. with high particle number concentration up to 1.5 x 10^4 cm^{-3} and a very small particle size about 10 nm. In comparison, winter and autumn months sometimes show peaks in the late night (e.g. winter 98/99) in the accumulation mode at 50-100 nm diameter with a low particle count.

Figure 5.16 Seasonal and monthly particle size and number data (HAR)

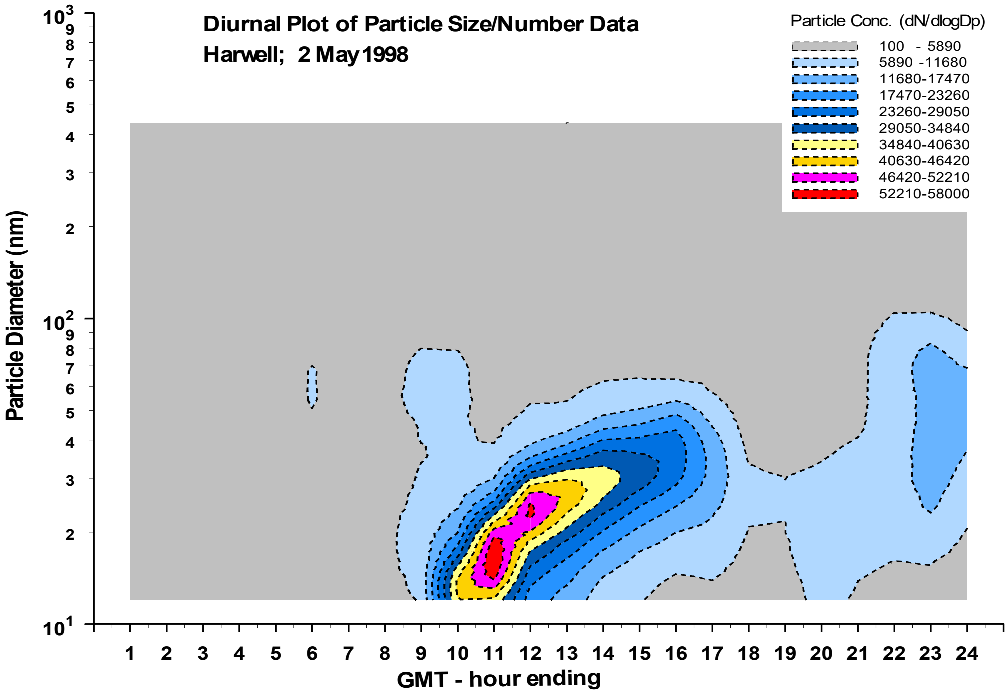


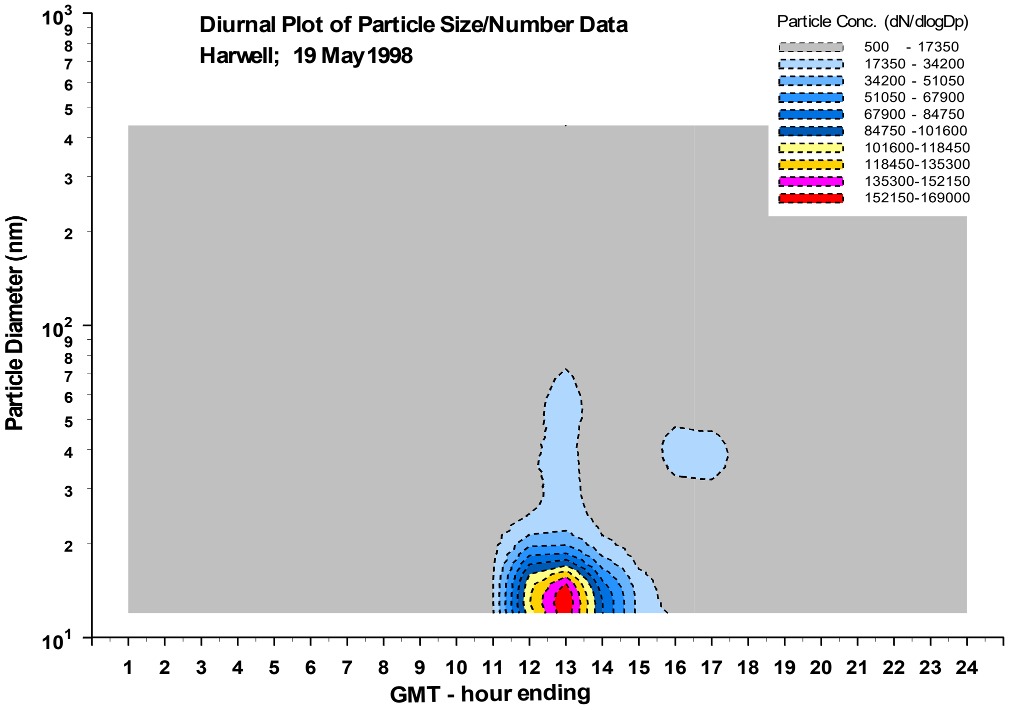


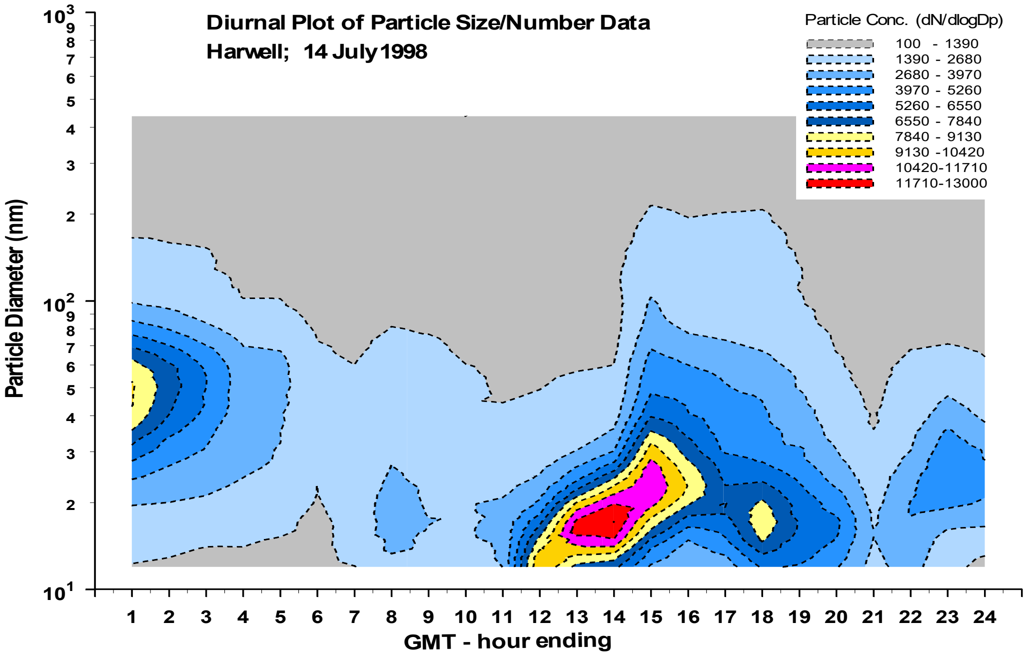


In order to reveal more details of the process, daily average particle size distribution are plotted. Examples from the spring and summer months are shown in figure 5.17 indicating that homogeneous nucleation processes were involved. On the 2nd and 19th of May 1998, substantial bursts occurred in particle number concentration with values up to 5.8 x 10^4 cm^{-3} and 1.7 x 10^5 cm^{-3} respectively. The day of May 2nd has a number mode starting around 10:00-11:00 a.m. with particles just over 10 nm and growing slowly over a 4 hour period to about 30 nm by 2:00-3:00 p.m. On the 19th of May, the number peak appeared around 1:00 p.m. with extremely small particles below the observable size of 11 nm. Similar to the plot for 2nd May, the plot for 14th July 1998 also shows a typical increase in particle number distribution starting with sub-10 nm particles at about 12 noon and growing to about 30 nm by 3:00 p.m. These types of nucleation and growth phenomenon were also observed from a suburban site in Birmingham with a significant higher particle number count (Harrison et al., 2000) and two rural continental sites Hohenpeissenberg and Melpitz, Germany (Birmili et al., 2000a; Birmili et al., 2000). On the days of 2nd and 19th May, the prevailing wind was from a north-easterly direction, which suggests that pollution from the nearby power station or A34 located to the north-east may be involved in the new particle formation. The O_3 level was higher on those two days and so were the SO_2 concentrations. Birmili and Wiedensohler (2000) detected new particle formation at Melpitz, Germany on 7th June 1997 suggesting that both SO_2 and solar radiation can influence the formation of these new particles. On 14th July there was a westerly wind and lower SO_2 and NO_x concentrations when a relatively higher particle number count was observed around 1:00 p.m. and the source origin of these particles was not clear.

Figure 5.17 Daily plots from spring and summer at Harwell site



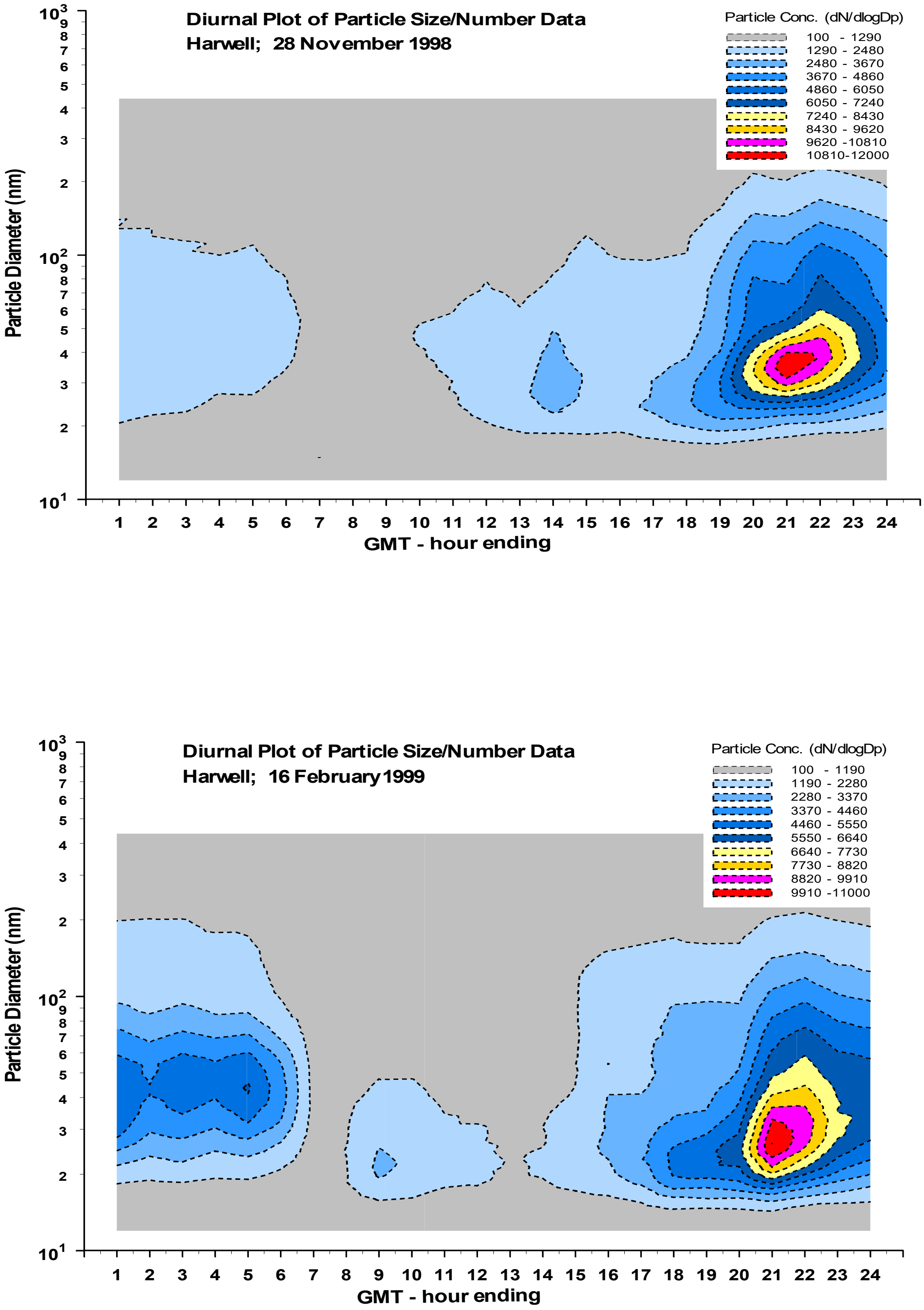

Diurnal Plot of Particle Size/Number Data
Harwell; 19 May 1998
Particle Conc. (dN/dlogDp)
500 - 17350
17350 - 34200
34200 - 51050
51050 - 67900
67900 - 84750
84750 -101600
101600-118450
118450-135300
135300-152150
152150-169000
Particle Diameter (nm)
10^1
10^2
10^3
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24


Diurnal Plot of Particle Size/Number Data
Harwell; 14 July 1998
Particle Conc. (dN/dlogDp)
100 - 1390
1390 - 2680
2680 - 3970
3970 - 5260
5260 - 6550
6550 - 7840
7840 - 9130
9130 -10420
10420-11710
11710-13000
Particle Diameter (nm)
10^1
10^2
10^3
GMT - hour ending
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

Interestingly, Figure 5.18, from 28th of November 1998 and 16th of February 1999, shows nocturnal peaks in the nano-particle range around 21:00 hours, which cannot be associated with homogeneous nucleation. The processes of formation of these particles are not clear and there were no direct relations to any kind of pollution source such as the nearby power station or the A34 road as the wind was southerly or westerly for these two periods. Instead, it was found that the particle number count correlates very well to NOx concentrations both having a night-time peak on the 28th of November, whereas less clues was found on the 16th of February. It is suggested that these particles may be formed through heterogeneous nucleation processes involving $N_2O_5 + H_2O$ as the chemical data in Harwell has identified frequent night-time nitrate peaks all year round (Chapter 6). Unfortunately, no chemical data is available for those two days.

Some other winter and autumn periods exhibited peaks at night but with a larger particle size around 100 nm. These particles may be formed locally from the coagulation of smaller particles or transported from a source, which is very distant since particles at this size could have a long lifetime and therefore travel over long distances. These data will be discussed subsequently in the light of chemical measurements at the site (Chapter 6). The summer phenomenon influencing particles of 10-20 nm generates insufficient mass to influence the chemical concentration data. However, the peak in the accumulation mode should be associated with significant particle mass, and therefore the diurnal variations in particle chemical composition may be helpful in elucidating the processes responsible for the diurnal variation in particle size distribution in the winter months. As expected, there was no clear weekday/weekend variation at Harwell site.

Figure 5.18 Daily plots from autumn and winter at Harwell site



5.5 Conclusions

Strong or modest correlation between particle number and PM_{10} and $PM_{2.5}$ mass concentrations has been observed for both Marylebone Road and London Bloomsbury during the winter period. These results may cause confusion for epidemiological studies in differentiating between PM_{10}, $PM_{2.5}$ mass and particle numbers as a causal agent on adverse health outcomes. However, weaker correlation was also found during the other seasons at the two urban sites. Further evaluation for the relationship between particle mass and number is needed using a continuous larger data set, as a rather limited and incoherent data set was available here. In contrast, only modest or weak correlation was found at the rural site Harwell, while a stronger relationship was observed between the two mass fractions of PM_{10} and $PM_{2.5}$. The gradients from the correlation of particle number and mass for Marylebone Road are higher than for London Bloomsbury and Harwell, indicating that the average particle size at the roadside site is smaller as it is mainly freshly emitted from vehicle exhaust. There is a seasonal trend in the correlation at all sites, showing higher correlations between particle number and mass in winter months dominated by fine primary pollution, whereas during summer periods the correlation may be influenced by both fine and coarse particles.

As expected, the correlation between particle number and NO_x and CO is very strong at the LM site, weaker but still strong at the LB site, and weak at the Harwell site due to the influence of traffic. Particle number concentrations correlate more strongly with gaseous pollutant emissions from traffic than particle mass concentrations, particularly for the kerbside site at Marylebone Road, confirming that ultrafine particles are a better tracer for vehicle exhaust emissions. Similar seasonal variations were also found in the correlation for particle number and the air pollutants, as for particle number and mass.

The particle size distributions have been calculated as daily, monthly and seasonal means. Results from the two London sites exhibited a clear diurnal trend in the particle number count highly reflective of the road traffic influence. The monthly average particle number mode diameter is small at the LM site in the range of 24.6-32.8 nm, reflecting particles directly emitted from the vehicle exhaust. Slightly larger particles are recorded at the LB site with average number mode diameter around 26.4-50.5 nm, showing a coarser background aerosol due to a lesser and more distant traffic influence. In comparison, the data from the Harwell site show no consistent diurnal patterns, indicating no clear relationship to traffic with wide variation in the number mode diameters (15-104 nm). Generally, in the winter and autumn months, there tended to be a particle number peak in the early evening or late night with particle sizes relatively coarse at 80-100 nm, reflecting advected or aged aerosol in the accumulation mode. During the summer and spring months, however, the data show strong evidence of new particle formation from homogeneous nucleation processes, often characterised by an increase in very fine particle numbers in the midday or early afternoon, with a steady increase in the modal diameter.

Clear weekday/weekend variations at the two London sites were also recorded, indicating a different pattern of human activities between weekdays and weekends. The main features are higher particle counts on weekdays than on weekends, and a delayed, smaller morning number peak and a late afternoon or evening peak until midnight on weekends.

CHAPTER 6
ANALYSIS OF HIGH TEMPORAL RESOLUTION CHEMICAL COMPOSITION DATA

6.1 Introduction

Hourly PM_{10} samples were collected on PTFE filters with a R&P Partisol Plus FRM 16 sampler at the Harwell site over a seventeen-month period from May 1998 to September 1999. The instrument was operated on a campaign basis during periods when air quality was predicted to deteriorate and samples were analysed for sulphate, nitrate, chloride and ammonium for studying the contribution of these ionic species to particulate PM_{10}. Altogether there were eight sampling periods from 1-6 days continuously (Table 6.1). Identical measurement was conducted in a home garden in Birmingham in November 1999 during the bonfire night period.

Daily and hourly measurements were also made during the URGENT PUMA campaign, on the University of Birmingham campus during summer 1999 and winter 2000 periods. In addition to the Partisol sampler, other sampling equipment was also involved. A Graseby Andersen dichotomous sampler fitted with a PM_{10} inlet was used to collect fine and coarse fraction of PM_{10} particles on a quartz filter for particulate carbon analysis. A 10-stage MOUDI sampler was installed capable of collecting particles less than 15 μm on separate size stages, with PTFE filters for similar analysis as the Partisol samples. A single TEOM for measuring PM_{10} in summer and two TEOMs for measuring both PM_{10} and $PM_{2.5}$ in winter were also installed. All equipment was located on a tower about 10 metres above ground level to reduce the influence of traffic and the site was regarded as an urban background site. The nearest road was about 20 meters away with low traffic volumes. Daily samples were collected during the campaign except 2-3 days with hourly measurements when pollution levels were thought to be higher. This chapter describes the results of those chemical analyses, with comparison made between rural and urban sites.

Table 6.1. Sampling and chemical measurement record at the three sites

Site	Date	Instrument	Chemical data
Harwell - rural	14/05/98	Partisol	Cl^-, SO_4^{2-}, NO_3^- and NH_4^+
	04/06/98 - 07/06/98		
	05/08/98 - 09/08/98		
	22/09/98 - 25/09/98		
	01/12/98 - 03/12/98		
	30/01/99 - 04/02/99		
	02/04/99 - 03/04/99		
	03/09/99 - 08/09/99		
Home garden (Birmingham) - suburban	04/11/99 - 08/11/99	Partisol	Cl^-, SO_4^{2-}, NO_3^- and NH_4^+
PUMA (Birmingham) - urban background	15/06/99 - 12/07/99	Partisol, MOUDI and Dichotomous	Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, OC and EC
	20/01/00 - 17/02/00		

6.2 Measurement at Harwell

The Harwell site is approximately 2 km to the west of the heavily trafficked A34 road, which will occasionally affect the site although the influence is believed to be small except in a very stable atmosphere or during a downwind situation. Another pollution source is the coal-fired Didcot power station located at a distance of 7.6 km on a wind bearing of 40º from the sampling site. It is expected that there will be conditions when the power station plume will affect the site. Apart from these influences, there are no other major point sources considered likely to influence the site. Plumes from major urban areas such as London to the east, Bristol to the west and Oxford/Abingdon to the north may at times influence the site. It is likely that at this rural location, long-range pollutant transport has more influence over ground-level concentrations than local sources. Air mass back trajectories were therefore produced (see Appendix A) at every six hours for each sampling period to aid elucidating the variation of concentrations of these particles. Meteorological data such as wind speeds and wind direction, and gaseous pollutant concentrations, are also presented.

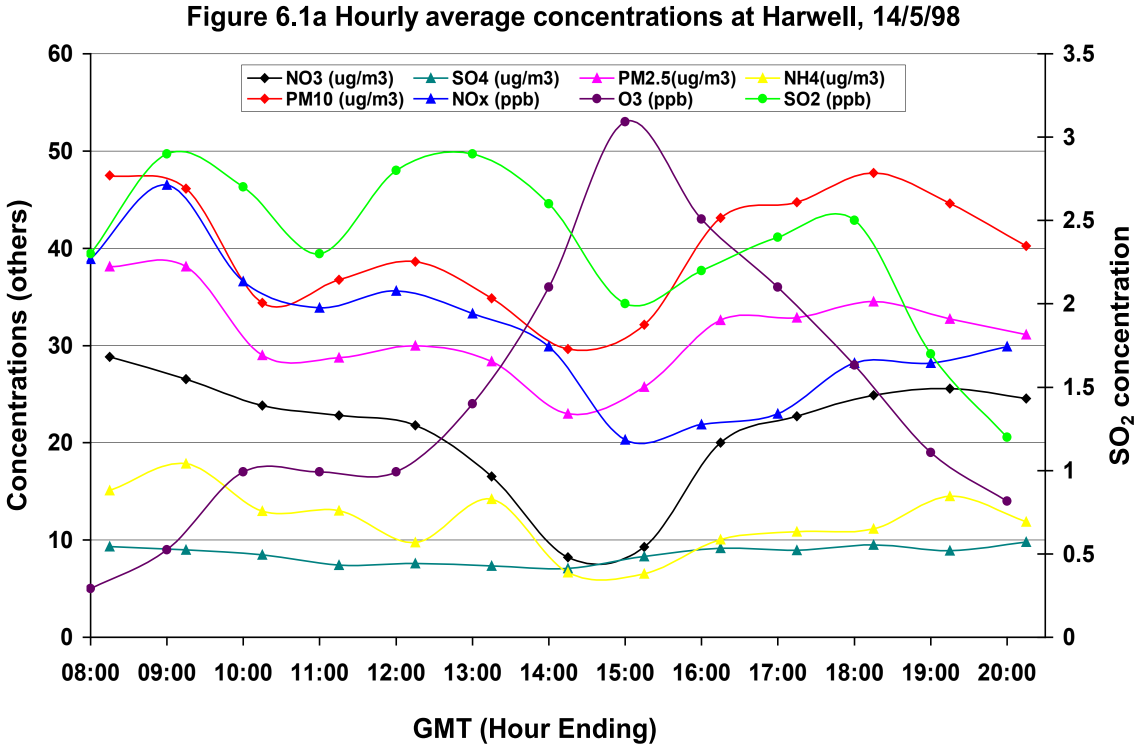
To aid the data interpretation, other meteorological data including temperature, pressure, relative humidity and cloud were adopted from a nearby site, Benson_samos, situated at a distance about 13 km away from the Harwell site to the north-east. The mixing layer height was derived from the UK high resolution radiosonde data from three sites, Larkhill about 50 km to the south-west, Herstmonceux_west_end about 140 km to the south-east and Hemsby about 240 km to the north-east of the Harwell site.

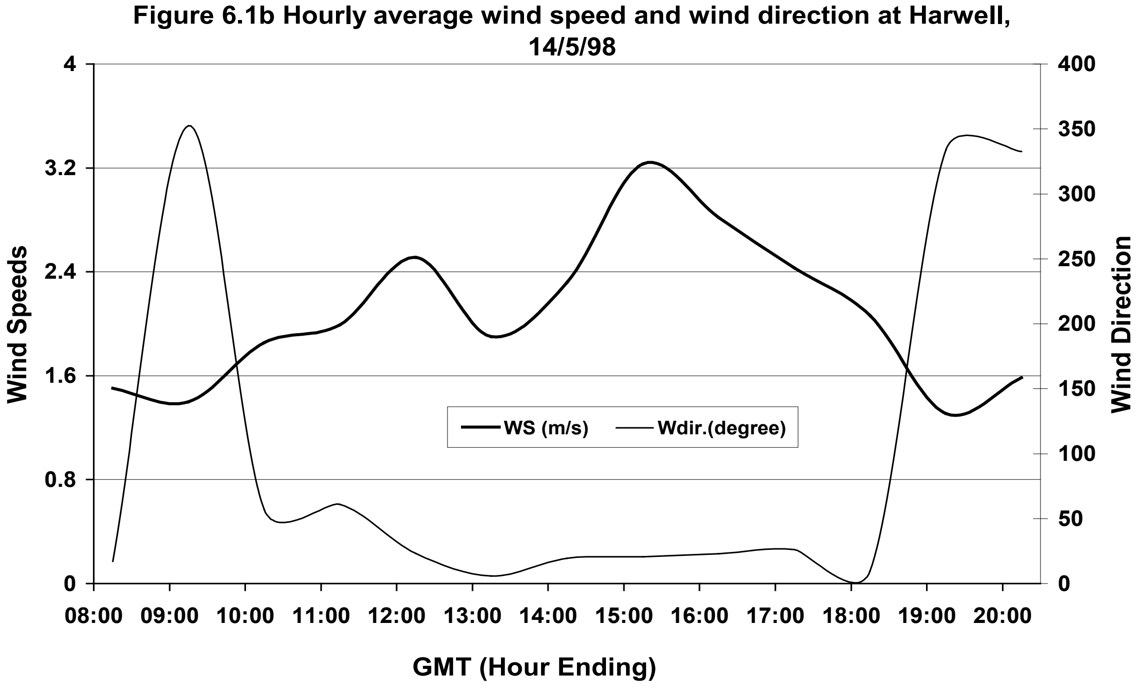
6.2.1 Data from Individual Sampling Period

1. Particles collected at Harwell in May 1998

On the 14th of May 1998, very high concentrations of PM_{10}, $PM_{2.5}$, nitrate and ammonium were observed (Figure 6.1a) and the concentrations of sulphate were rather higher than normal levels. This can be explained by the back trajectories, which show that polluted air came from the European continent, travelling across Northern Germany or The Netherlands. The power station plume may also have affected the site since the local wind directions were close to north or north-easterly during the sampling period. However, the particle size distribution data indicated peaks showing particles in the accumulation mode between 100-200 nm, indicative of long-range transported aerosol. There was a drop in the particle concentrations in the middle of the day, which is related to the higher wind speeds (Figure 6.1b).

Figure 6.1 Hourly measurements at Harwell, 14/05/98





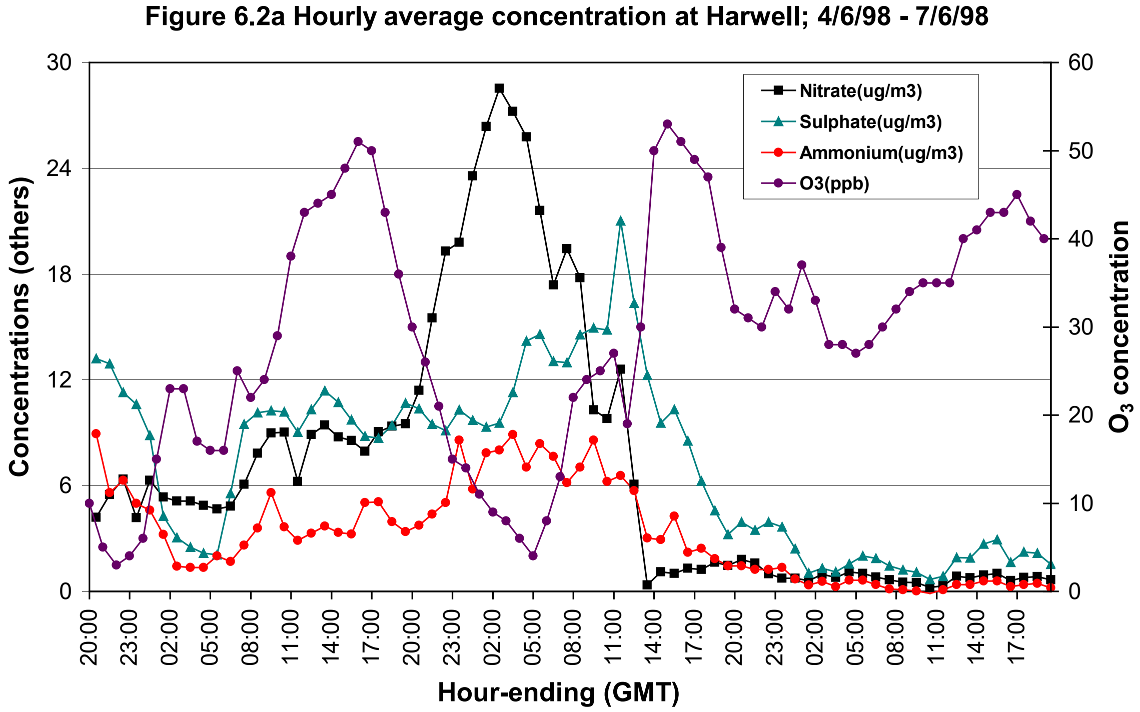
2. Particles collected at Harwell in June 1998

Data appear to be of greater interest in the period 4-7 June 1998 (Figure 6.2) although the particle concentrations were generally lower than the concentrations on the 14th of May. On the 4th of June the back trajectories indicate that the air-mass originated from the north marine regions travelling across the UK before approaching the site from the northwest. By the time of 1800 it had diverged to cover regions of northern France and southern England. On the 5th and 6th of June it started over the north marine areas and transited southern England before reaching the site from the east. By 1800 on the 6th of June it deviated to show that the predominant circulation was a westerly maritime air-mass, which remained till the end of the measurement period.

There was a massive nighttime peak in nitrate concentrations centred at 0300 on the 6th of June (Figure 6.2a), at which time the site was influenced by an air mass arriving from the Netherlands and most probably traversing London. The local wind direction at the time was around 100^0 and wind speed was about 1.5 m s^{-1} (Figure 6.2d), which was the lowest over the sampling period. Anti-correlation has been found between nitrate and O_3 during this period. Similar increase was also observed in NO_x concentrations over the high nitrate period (Figure 6.2b). Figure 6.2c shows that at the time of high nitrate, the nitrate concentrations alone exceeded that of the PM_{10} measured using TEOM, which typically drives off around 15-30% of the particle mass by heating up the incoming air to 50^0C (APEG, 1999). Ammonium nitrate, as a semi-volatile species, could be lost easily in the TEOM measurement (Pang et al., 2001), but not in the Partisol sampler unless due to incautious sample handling.

Sulphate peaked at a later time around 1200 on the 6th of June when air-mass trajectory was similar to that for the nitrate peak. Poor correlation was found between sulphate and SO_2 (Figure 6.2e). All concentrations started to decrease afterwards when wind direction became south-westerly, and reached the lowest over the whole period when the air-mass became predominantly westerly after 1400 on the 6th of June. Generally, ammonium appeared to have a better correlation with sulphate than nitrate during the sampling period. PM_{10} and $PM_{2.5}$ concentrations closely correlated to sulphate indicating the dominance of long-range transport in influencing the PM_{10} concentrations measured with the TEOM. The high nitrate period indicated that the TEOM is incapable of measuring the major part of the nitrate, which is likely in the form of ammonium nitrate.

Figure 6.2 Hourly measurements at Harwell, 04/06/98 – 07/06/98



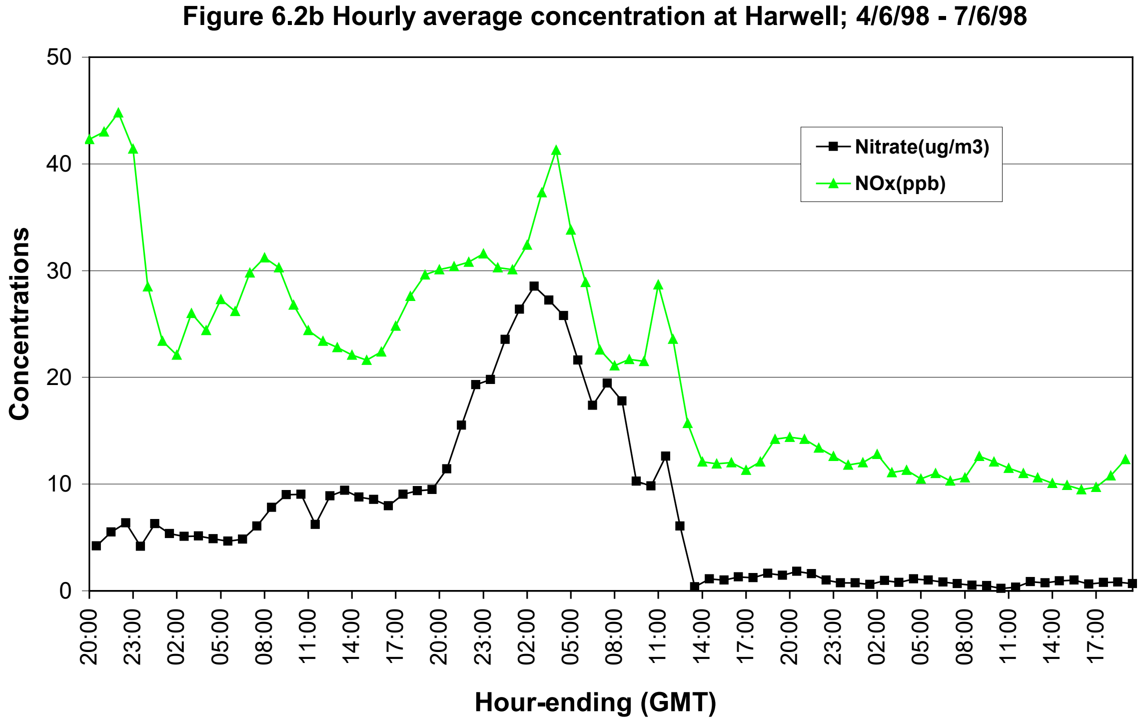


Figure 6.2c Hourly average concentration at Harwell; 4/6/98 - 7/6/98

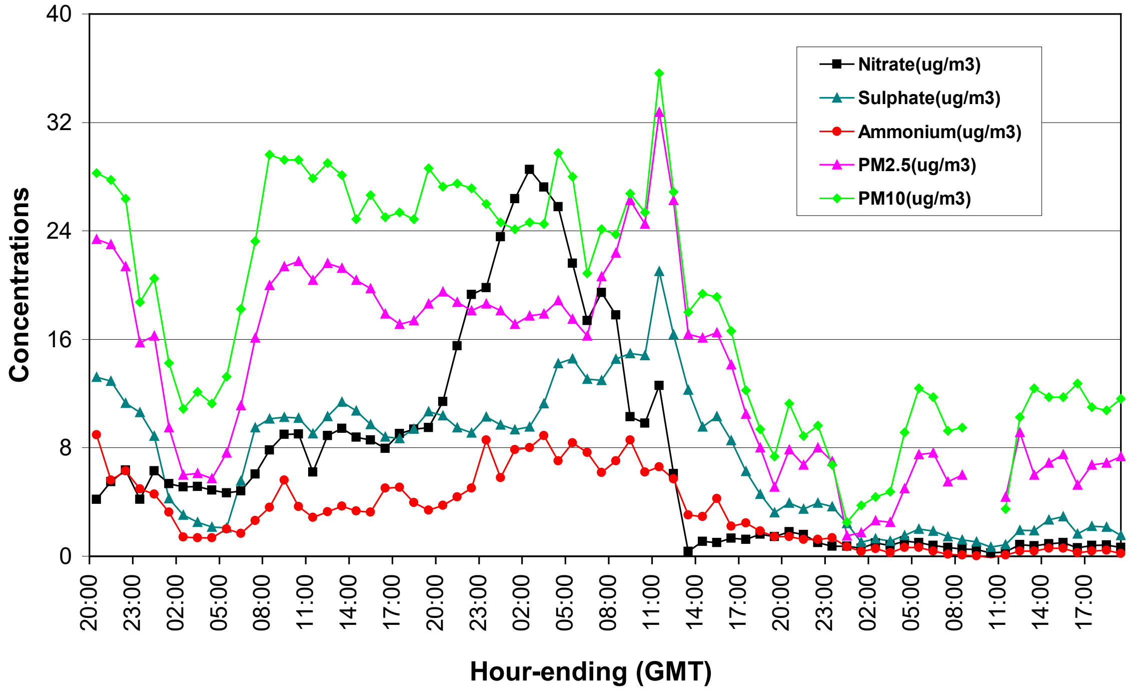


Figure 6.2d Hourly average wind speed and wind direction at Harwell; 4/6/98 - 7/6/98

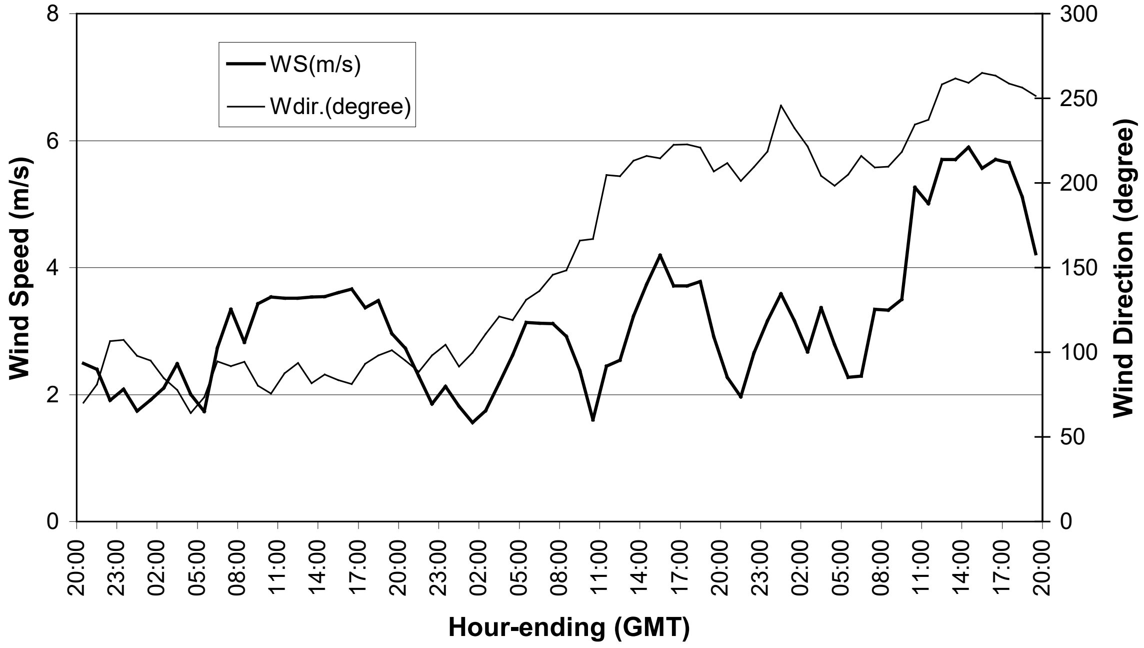
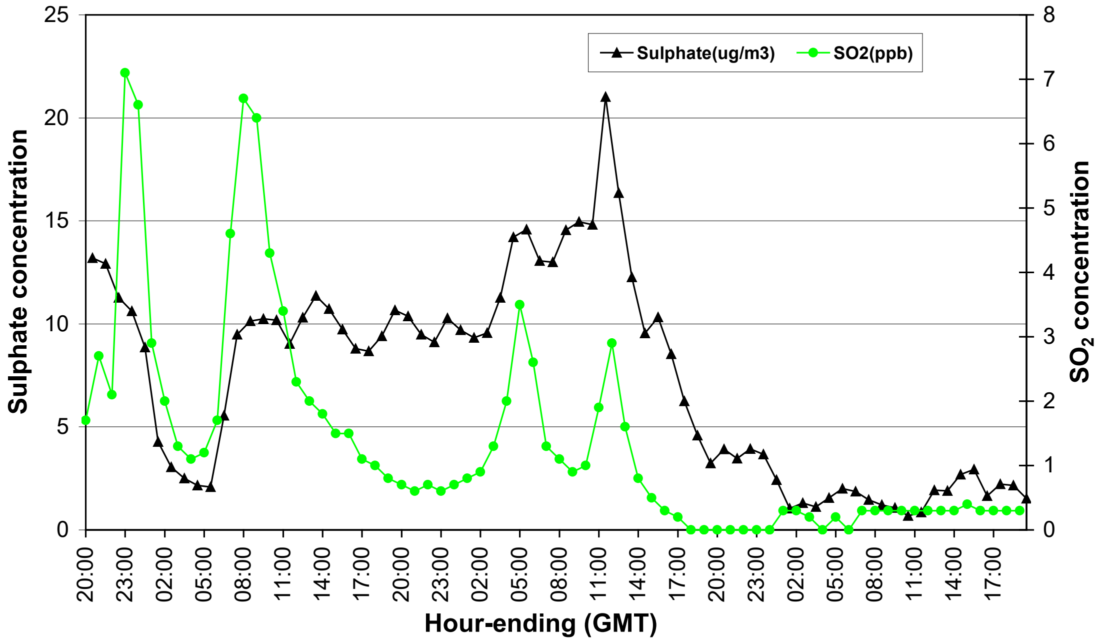


Figure 6.2e Hourly concentration at Harwell; 4/6/98 - 7/6/98



3. Particles collected at Harwell in August 1998

Particle concentrations are generally low over the sampling period 5-9 August 1998 (Figure 6.3) as clean air was advected from the west. Airmass back trajectories indicate that during 5th and 6th August the airmasses arrived from the west across southern Ireland, on 7th and 8th August, moving slightly south and approaching over the Bristol area. By August 9th the still westerly originated airmass travelled across the UK reaching Harwell over London from the east. The prevailing local winds were westerly until around 2200 on 8th August when they changed to easterly (Figure 6.3e).

The main feature in the ionic concentration data is for night-time peaks in sulphate, nitrate and ammonium, anti-correlated with the daytime peaks in ozone concentration (Figure 6.3a). Generally, sulphate was dominant and peaking during periods in the early hours on 7th and 8th August when the airmass was arriving from the west, whereas nitrate became dominant on the last night peaking at 0600 on 9th August when the airmass was approaching from the east. According to the local wind direction, the local Didcot power station to the north east was unlikely to affect sulphate peak concentrations, although sulphur dioxide showed a similar temporal trend to sulphate (Figure 6.3b).

Nitrate concentrations generally correlated with NO_x (Figure 6.3c), and showed diurnal variations with night-time peaks. It is suggested from the data that a fairly rapid formation of nitrate occurred in response to NO_x concentration fluctuations. The highest nitrate peak on the last day was likely influenced by polluted air transferred from the City of London due to an easterly wind direction. Ammonium concentrations were correlated fairly well with both sulphate and nitrate, but most closely with sulphate. During the high concentration period, the $PM_{2.5}$ mass is largely accounted for by the sum of sulphate, nitrate and ammonium particles (Figure 6.3d), indicative the secondary nature of these fine mode particles.

Figure 6.3f shows that the diurnal variations of nitrate, ammonium and sulphate are generally related to the variation of temperature and relative humidity. The concentrations are higher during the night when the temperature is low and the relative humidity is higher and lower during the day when temperature is high and relatively humidity is lower. Previous studies indicate that ammonium nitrate is volatile under high temperature and low relative humidity (Stelson and Seinfeld, 1982a&b; Pio and Harrison, 1987a&b; Harrison and Msibi, 1994). The formation of sulphate is also favoured under the condition of high relative humidity (Motallebi, 1999), however, the rapid declines in sulphate concentrations during the days are due to increasing mixed layer depth.

Figure 6.3 Hourly measurements at Harwell, 05/08/98 – 09/08/98

Figure 6.3a Hourly average concentration at Harwell; 5/8/98 - 9/8/98

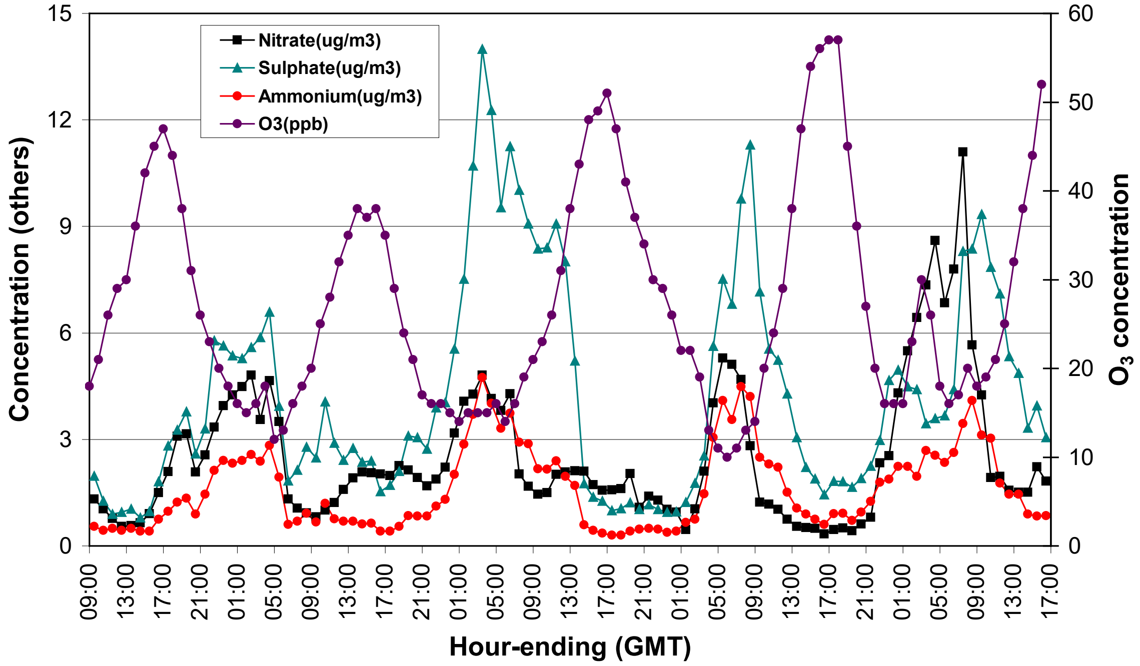


Figure 6.3b Hourly average concentration at Harwell; 5/8/98 - 9/8/98

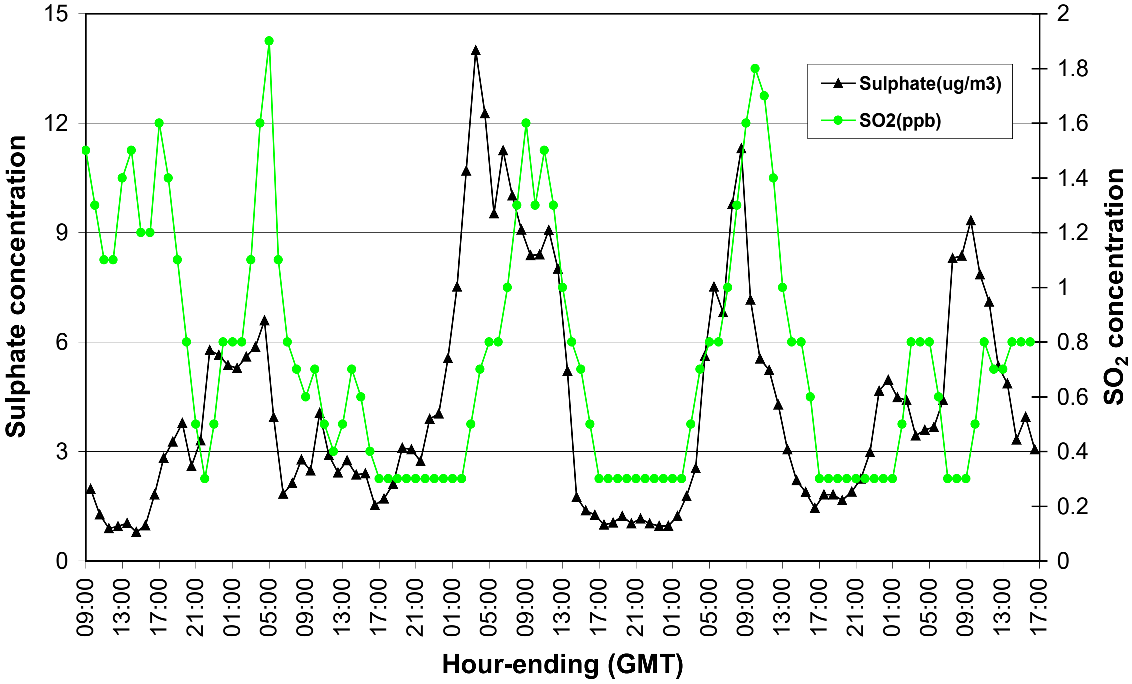


Figure 6.3c Hourly average concentration at Harwell; 5/8/98 - 9/8/98

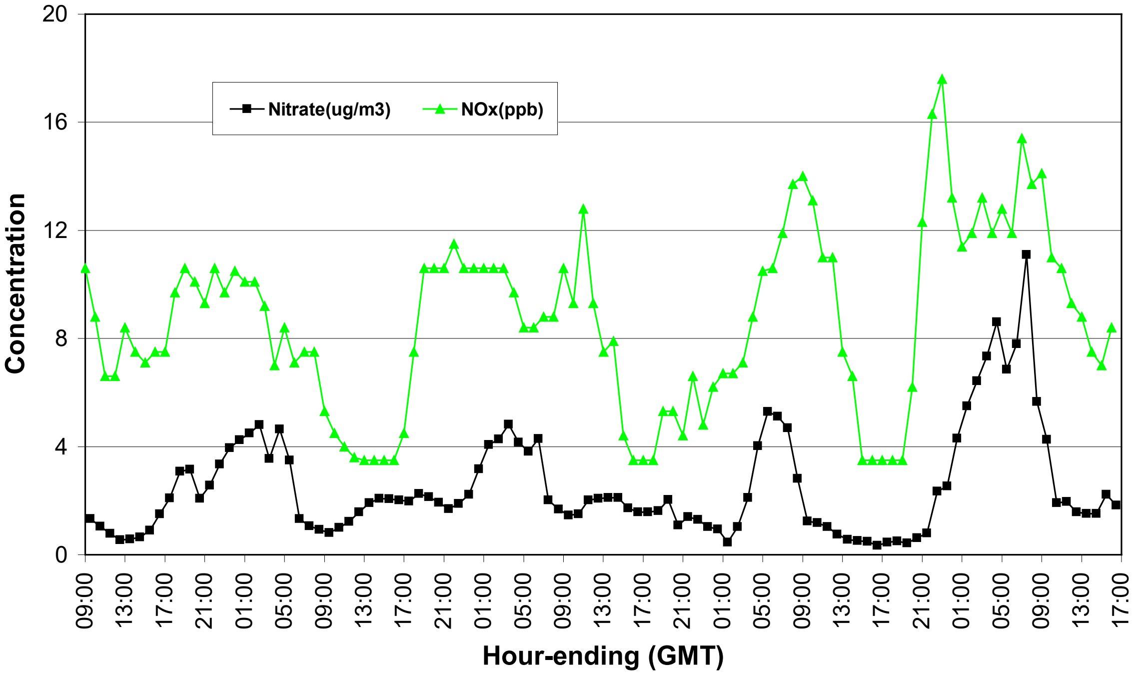


Figure 6.3d Hourly average concentration at Harwell; 5/8/98 - 9/8/98

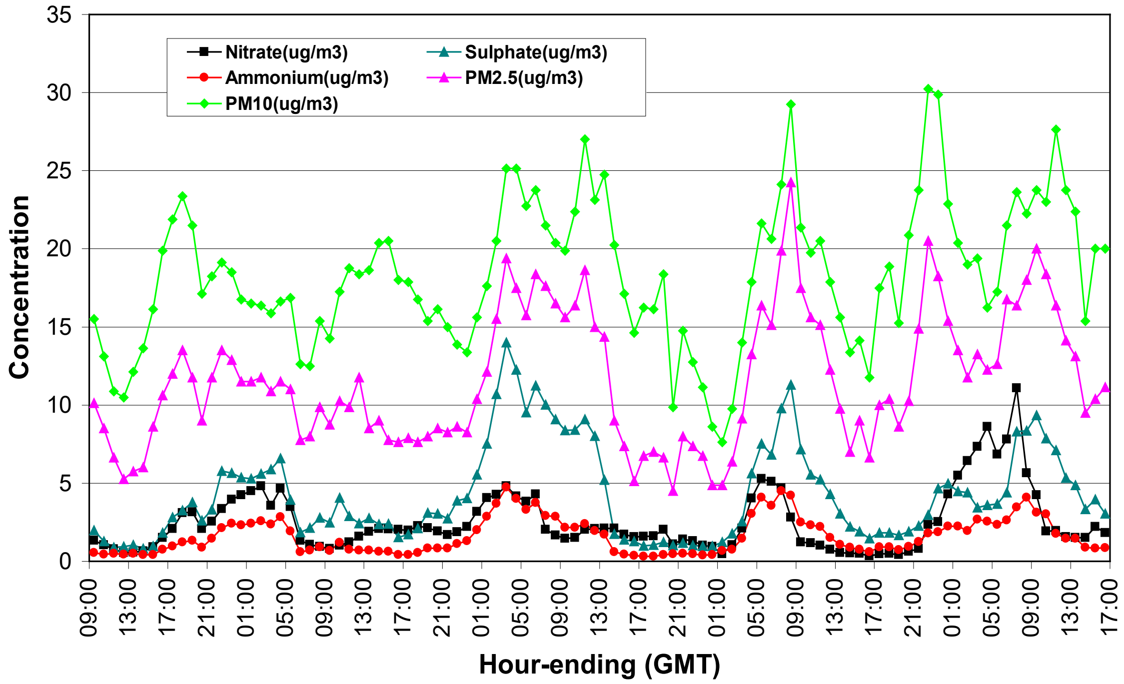


Figure 8.3f Hourly average wind data at Harwell; 5/8/98 - 9/8/98

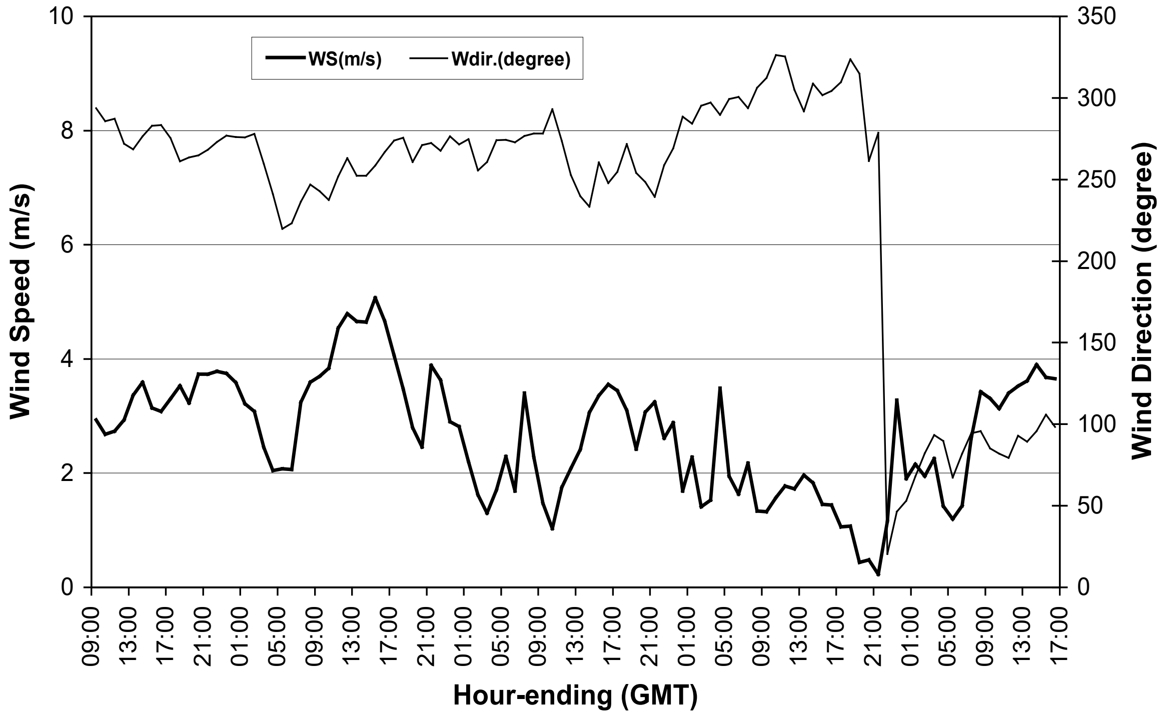
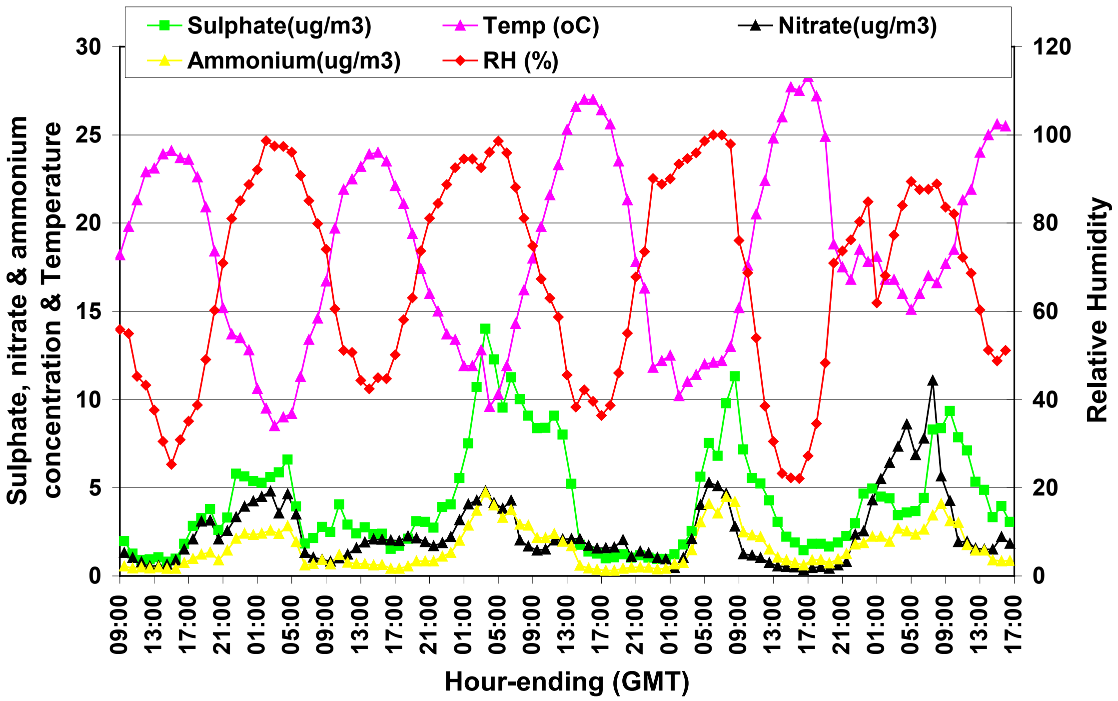


Figure 6.3f Hourly average data in Harwell; 5/8/98 - 9/8/98



4. Particles collected at Harwell in September 1998

The most polluted period was 22-25 September 1998 when airmasses approached the site from the east crossing Germany or France. At the beginning of the period, the airmass originated over marine areas, travelled across northern Germany and arrived at Harwell through the Netherlands and London. From 0600 on September 23rd, the trajectory was moved gradually to a more southerly direction approaching from south Germany over northern France. By 1800 on September 24th the airmass approached from south-east France and moved further south on September 25th. Similar changes can be seen in the local wind directions, which generally remained easterly in the sector of 60-140º (Figure 6.4h).

The major feature in the ion concentration data was massive nocturnal nitrate peaks anti-correlated with ozone with a strong diurnal variation (Figure 6.4a). The nitrate peak concentrations reached 22 µg m^{-3} on 23rd, 46 µg m^{-3} on 24th and 53 µg m^{-3} on 25th September in the early morning respectively. Sulphate concentrations were slightly increased (around 10 µg m^{-3}) with little diurnal pattern. Ammonium was strongly correlated with nitrate with a NO_3^-/NH_4^+ ratio of 3.75 close to the ratio of the molecular weight (3.4) (Figure 6.4b), indicating that nitrate is mostly presented as ammonium nitrate. Chloride concentrations were relatively low, but correlated with ammonium suggestive of the presence of ammonium chloride (Figure 6.4c), which cannot be verified without data on the gas phase precursors. Nitrate concentrations are related to NO_x temporally (Figure 6.4d), and tend to increase at night, reaching the highest in the morning around 0800 hours. The data indicate that there is a rapid nocturnal formation of nitrate in the stable shallow boundary layer. The high relative humidity approaching up to 100%, low temperature and low wind speeds are all favourable for heterogeneous formation of secondary particles and for building up higher concentrations.

There is a peak in sulphur dioxide concentrations during the afternoon on 23rd September (Figure 6.4e), but this is not correlated with sulphate and the wind direction does not show any influence from the local power station. PM_{10} and $PM_{2.5}$ concentrations were better correlated with sulphate (Figure 6.4f) which accounted for up to about one third of the PM_{10} mass, but less with nitrate and ammonium (Figure 6.4g). Similar to the period in June 1998, underestimation of the PM mass by the TEOM is clearly seen during high nitrate periods.

Figure 6.4 Hourly measurements at Harwell, 22/09/98 – 25/09/98

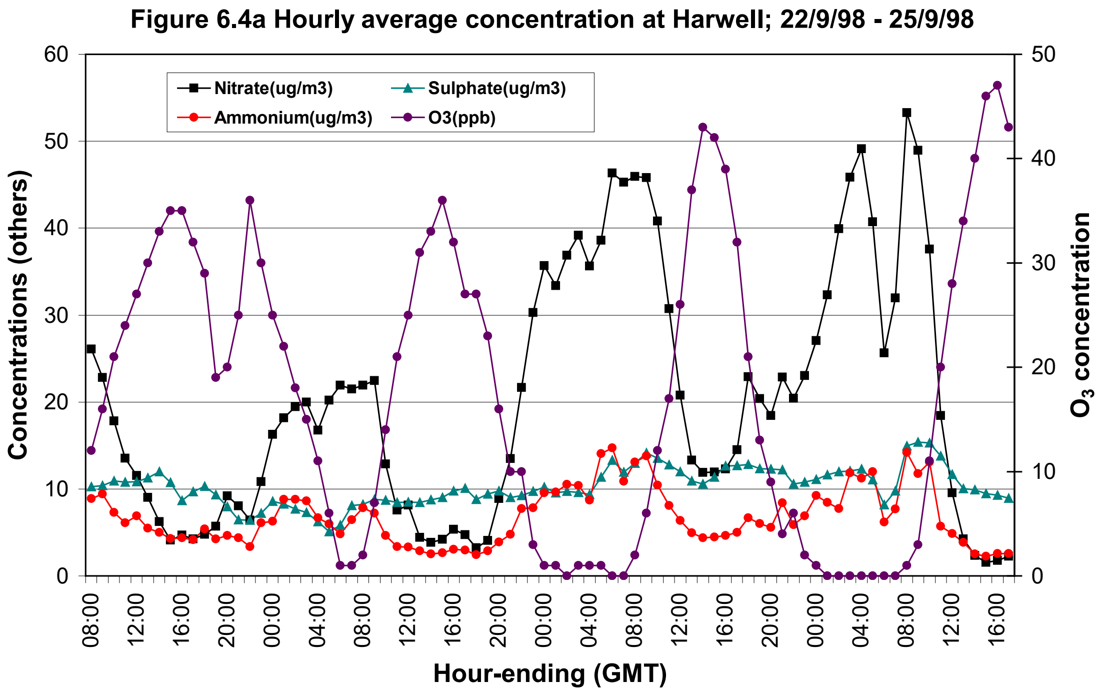


Figure 6.4b Hourly average concentration at Harwell; 22/9/98 - 25/9/98

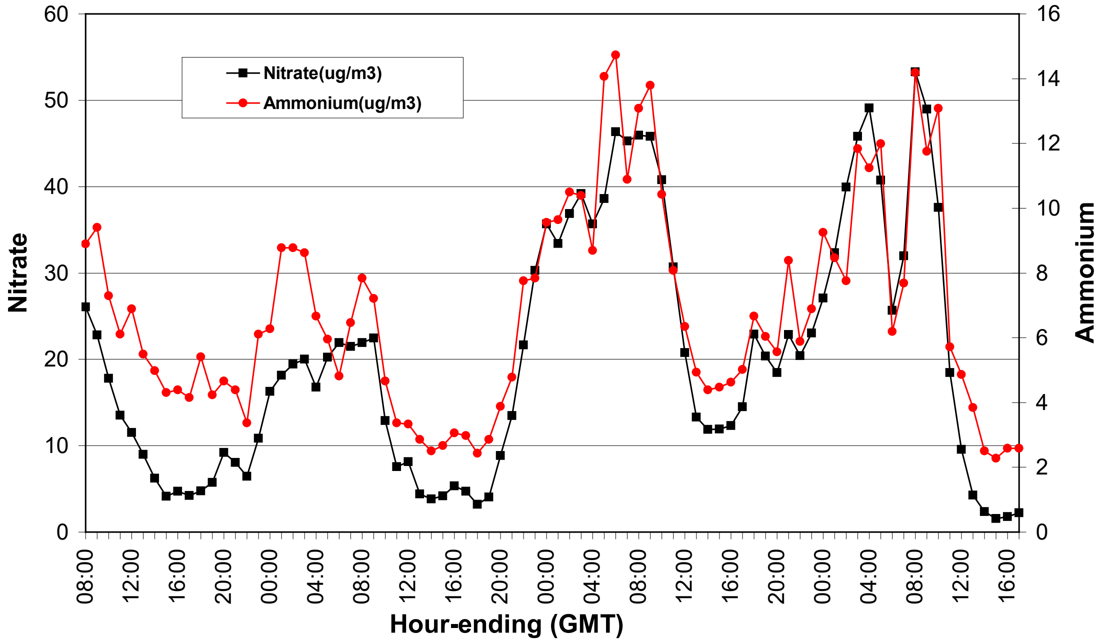


Figure 6.4c Hourly average concentration at Harwell; 22/9/98 - 25/9/98

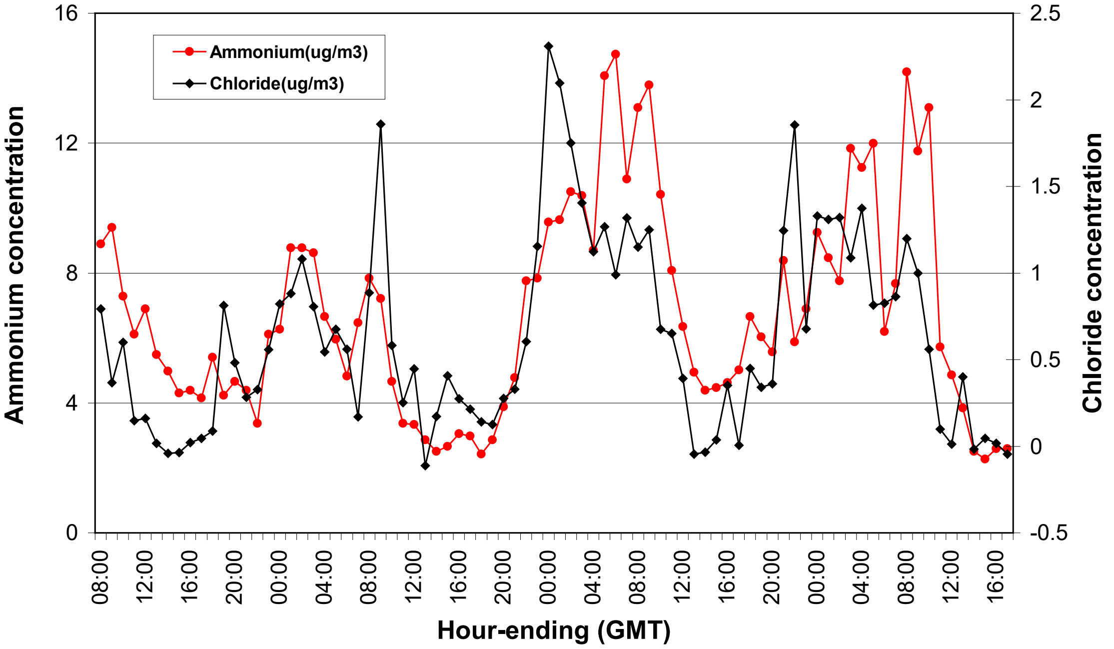


Figure 6.4d Hourly concentration in Harwell; 22/9/98 - 25/9/98

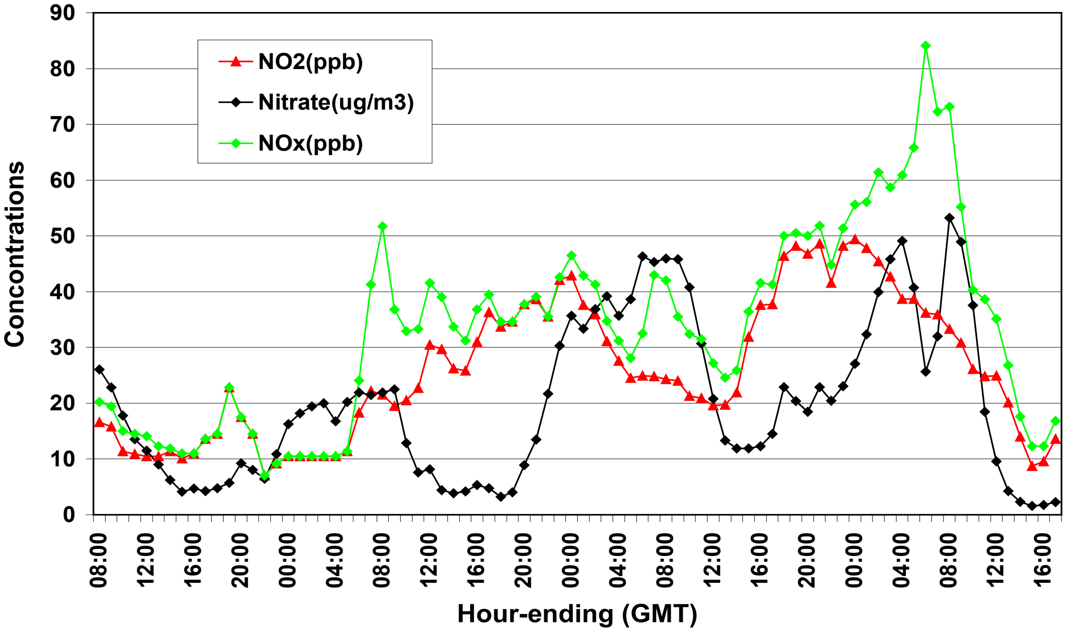


Figure 6.4e Hourly average concentration at Harwell; 22/9/98 - 25/9/98

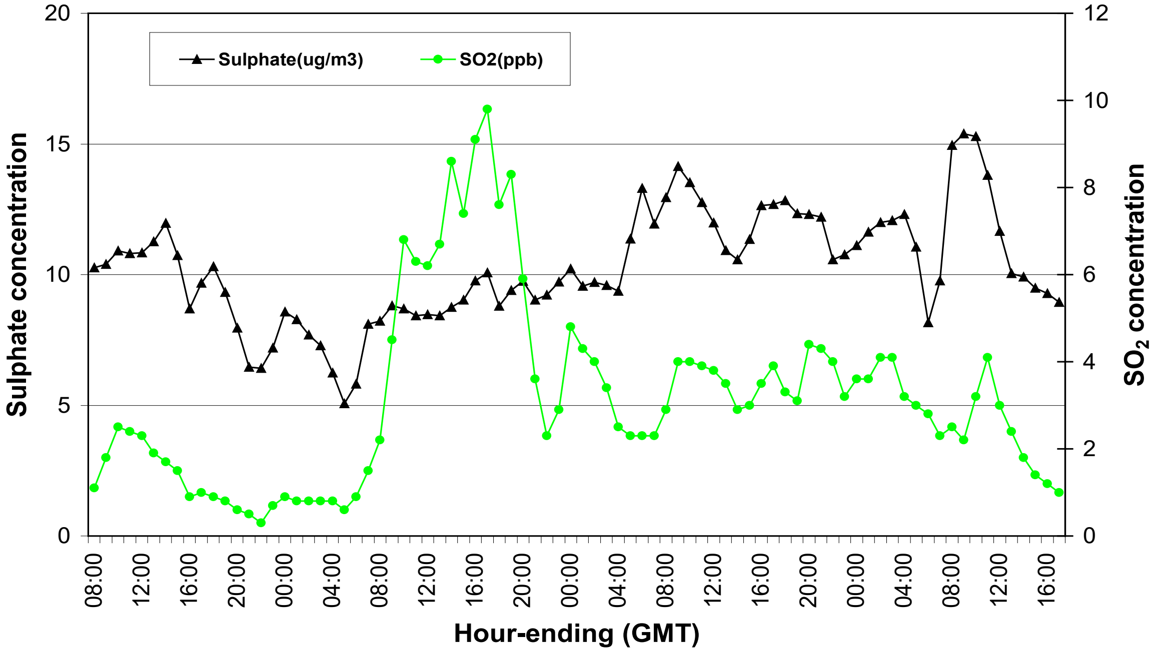


Figure 6.4f Hourly average concentration at Harwell; 22/9/98 - 25/9/98

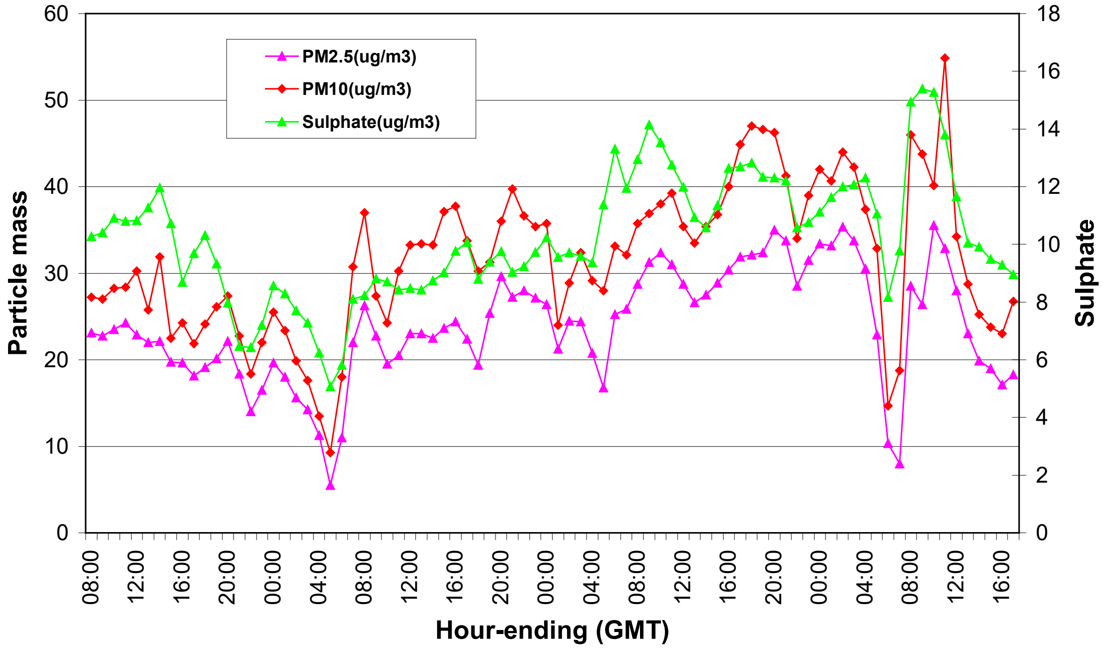


Figure 6.4g Hourly average concentration at Harwell; 22/9/98 - 25/9/98

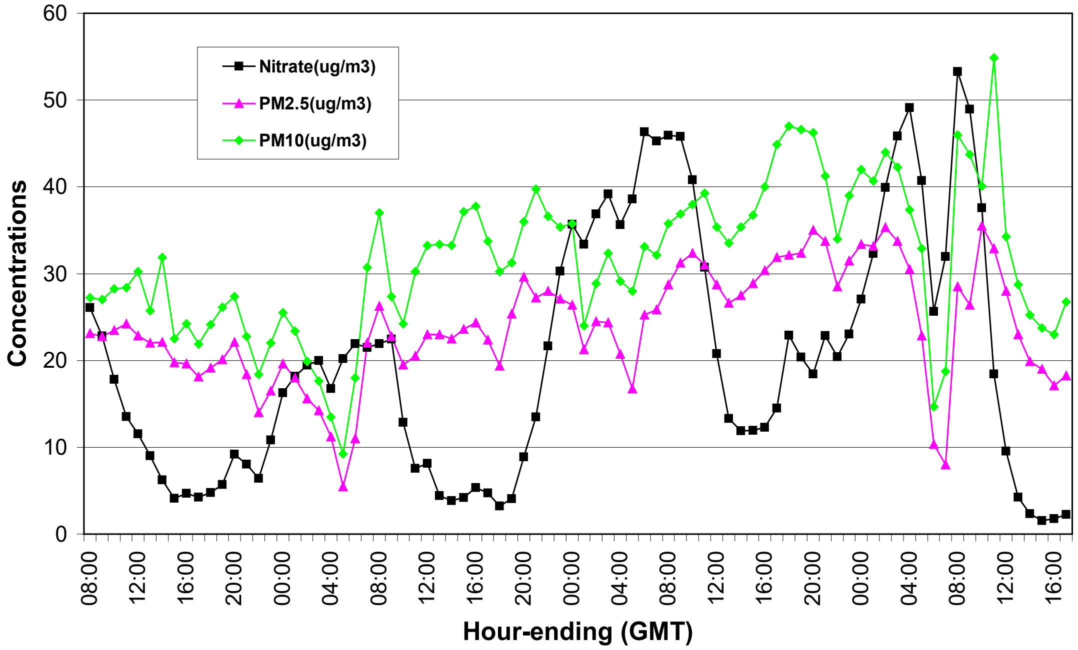
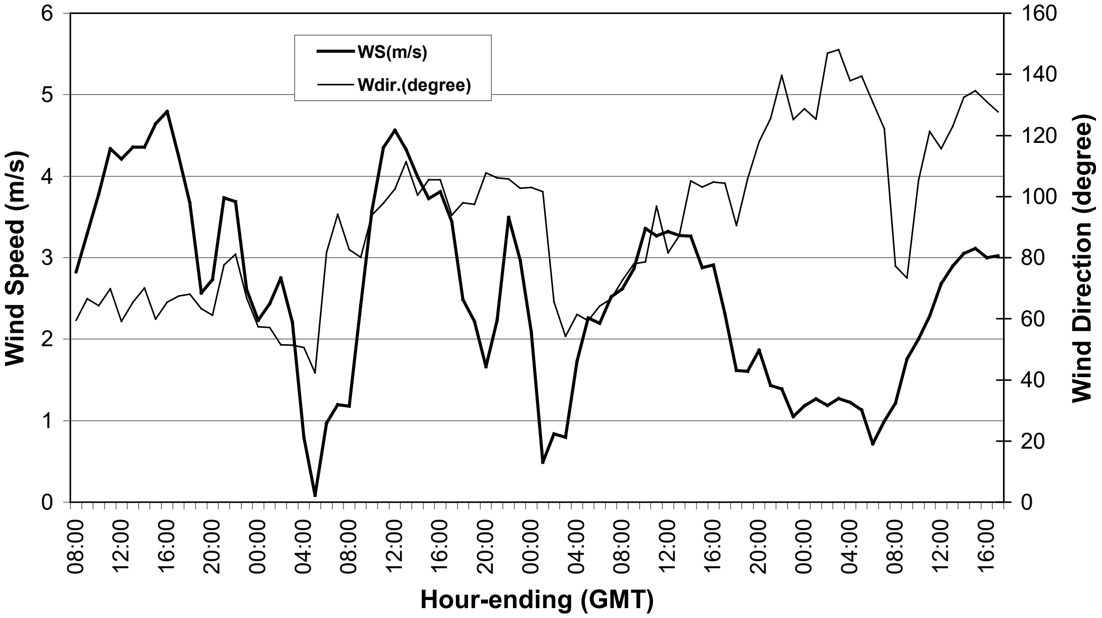


Figure 6.4h Hourly average wind speed and wind direction at Harwell; 22/9/98 - 25/9/98



5. Particles collected at Harwell in December 1998

Figure 6.5 shows data from a winter period 1st-3rd December 1998. On the 1st of December the airmass approached from the east over northern Germany, and gradually deviated further north on the 2nd arriving at the site from the northeast, and by 1200 on the 3rd the airmass approached from the north. The local wind direction was approximately 50° until 1100 on December 3rd when it moved to approximately 330°. PM_{10} concentrations were moderate during this period, on average about 22 µg m^{-3}. There was an elevation in the chloride concentration, which likely followed the trend in the coarse particle concentrations, probably indicative of a winter source of de-icing salt from the nearby A34 road. There were no other obvious features within this incomplete data-set.

Figure 6.5 Hourly measurements at Harwell, 01/12/98 – 03/12/98

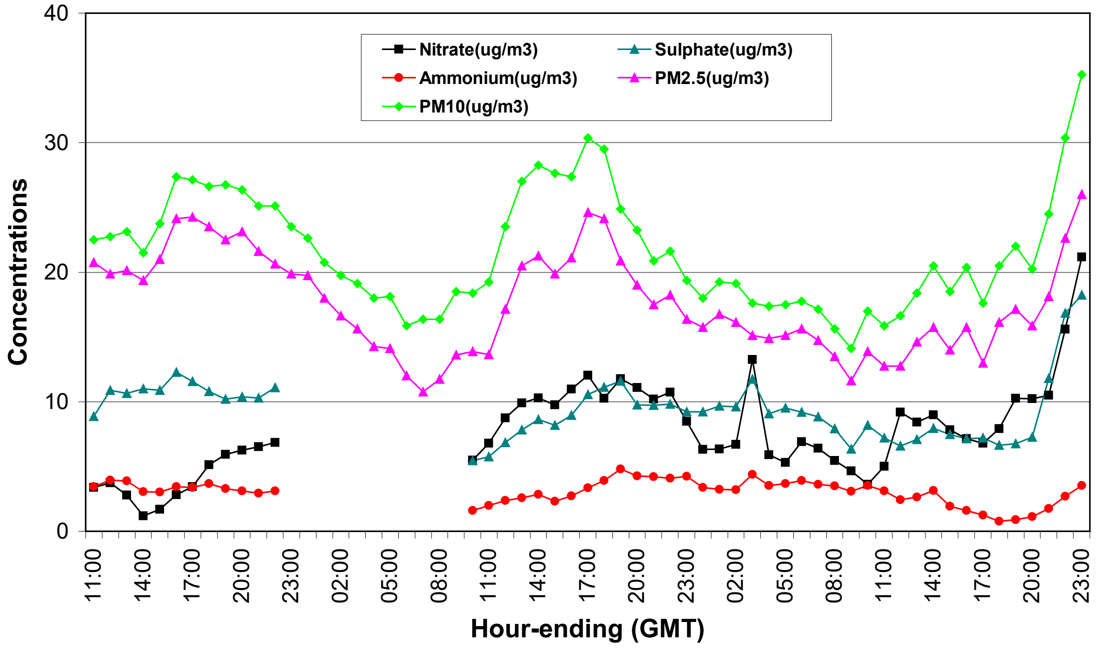


Figure 6.5a Hourly average concentration at Harwell; 1/12/98 - 3/12/98

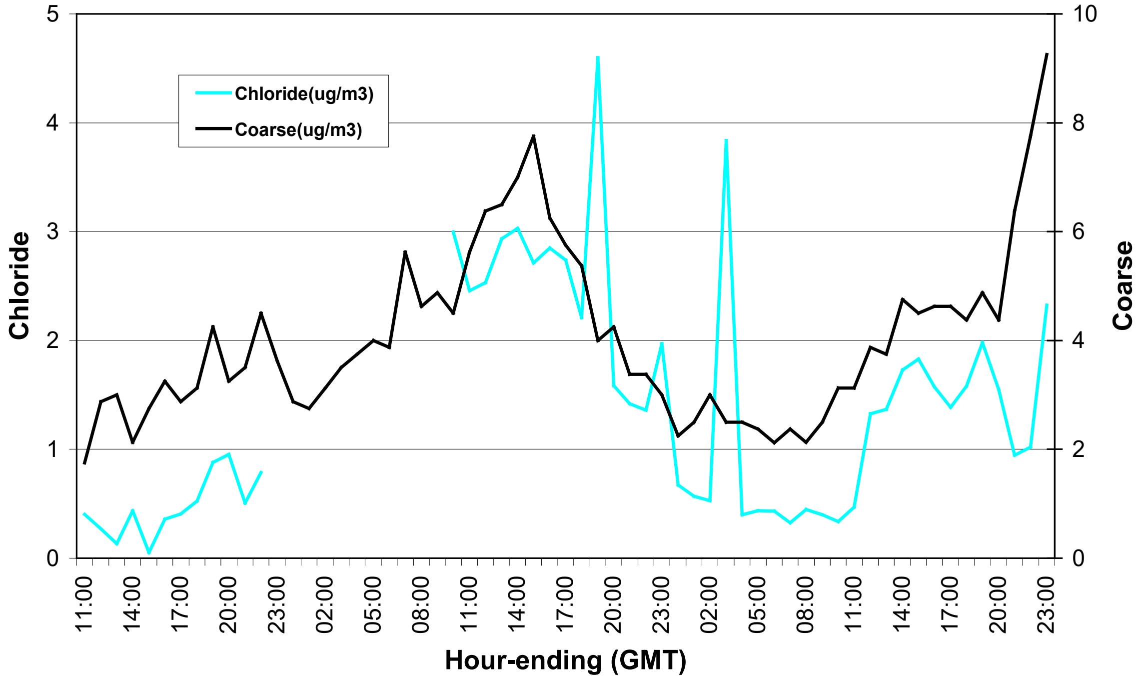
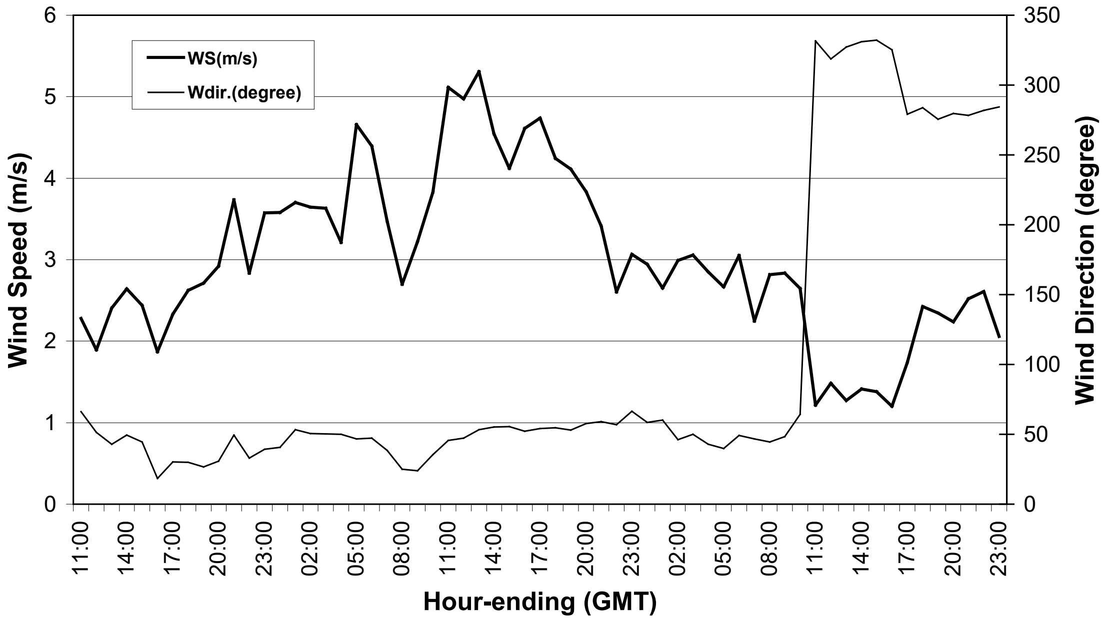


Figure 6.5b Hourly average concentration at Harwell; 1/12/98 - 3/12/98

Figure 6.5c Hourly average wind speed and wind direction at Harwell; 1/12/98 - 3/12/98



6. Particles collected at Harwell in January-February 1999

Data from another winter period, January 30th to February 4th 1999, is shown in Figure 6.6. The airmass originated from the Atlantic, travelled across northern Ireland and then the Midlands, approaching Harwell from the north-west on January 30-31st, moving more northerly on February 1st. Starting from February the 2nd the airmass back trajectories became more complex, circling across the UK at the start, and then the continent before approaching Harwell from the west. The local wind directions were around 200° on January 30th, increasing gradually to 340° on February 1st, and then stabilising at around 270° from February 2nd to 4th (Figure 6.6g).

The ion concentration anti-correlated with ozone (Figure 6.6a) and showed a clear decrease after around midnight on February 2nd due to both a clean westerly circulation and a higher wind speed. Much higher nitrate concentrations were observed prior to that, showing a massive peak (up to 25 μg m^{-3}) centred at 2300 on the 31st of January when air came across the Midlands and the wind speeds were low. This again suggests that nitrate can be produced highly efficiently at night when the atmosphere is stable. The particle number data also showed a peak that night with particle size in the accumulation mode around 60-70 nm in diameter. Sulphate and ammonium concentrations were generally low on an average around 4 and 3 μg m^{-3} over the sampling period. Local wind directions indicated no influence from the Didcot power station and the A34 road. There was a temporal correlation between nitrate and NO_2 and NO_x (Figure 6.6b), and also between SO_2 and sulphate (Figure 6.6c), which accounted for only a modest proportion of PM_{10}. Ammonium was better correlated with sulphate than with nitrate (Figure 6.6d), suggesting that some of the nitrate may be in forms other than ammonium nitrate, which appeared temporarily to dominate the $PM_{2.5}$ and PM_{10} concentrations measured with the TEOM instruments (Figure 6.6e). There was a notable increase in chloride concentrations, which was temporally related to coarse particles (Figure 6.6f), and an elevation on the last two days presumably due to the high wind, causing an advection of sea salt or road de-icing salt.

Figure 6.6 Hourly measurements at Harwell, 30/01/99 – 04/02/99

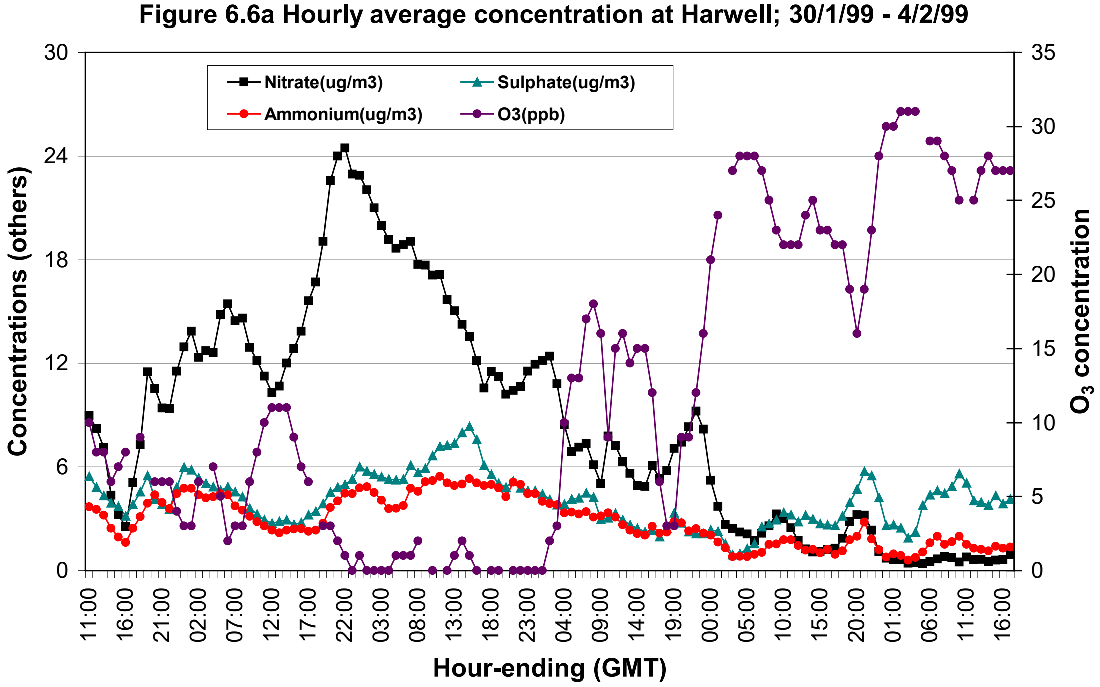


Figure 6.6b Hourly concentration in Harwell; 30/1/99 - 4/2/99

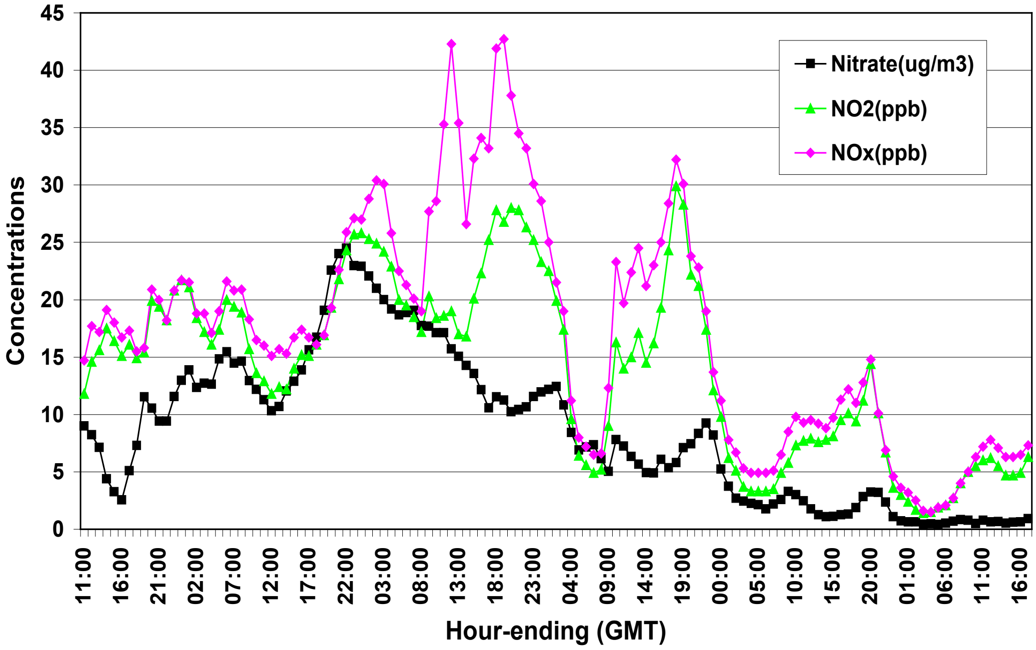


Figure 6.6c Hourly average concentration at Harwell; 30/1/99 - 4/2/99

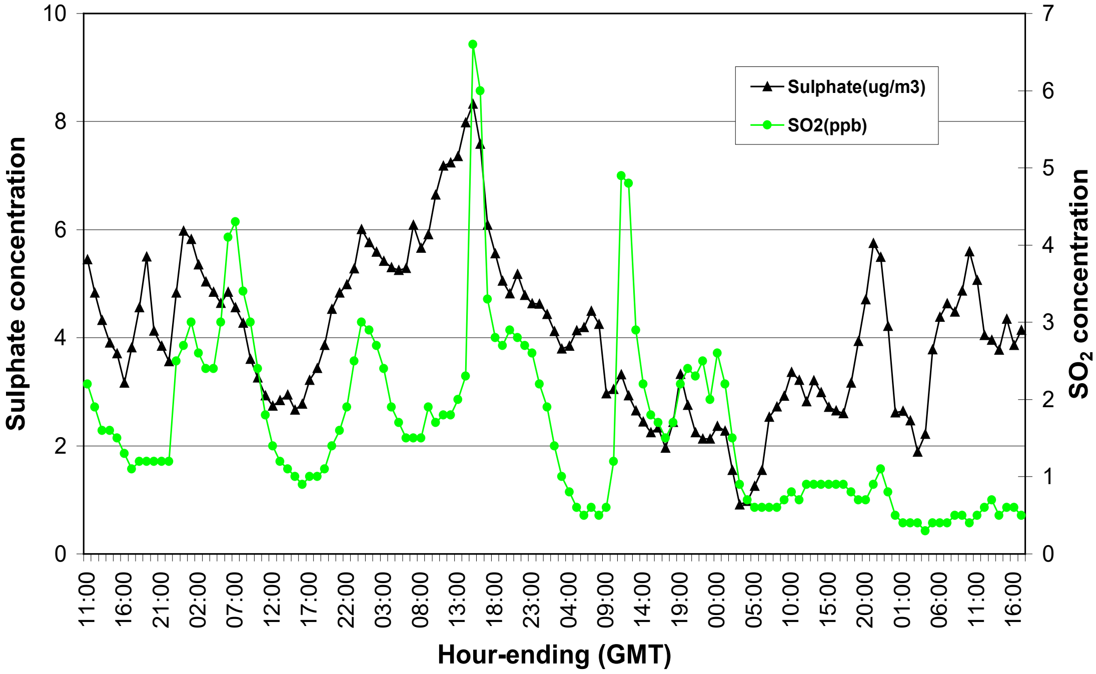


Figure 6.6d Hourly average concentration in Harwell; 30/1/99 - 4/2/99

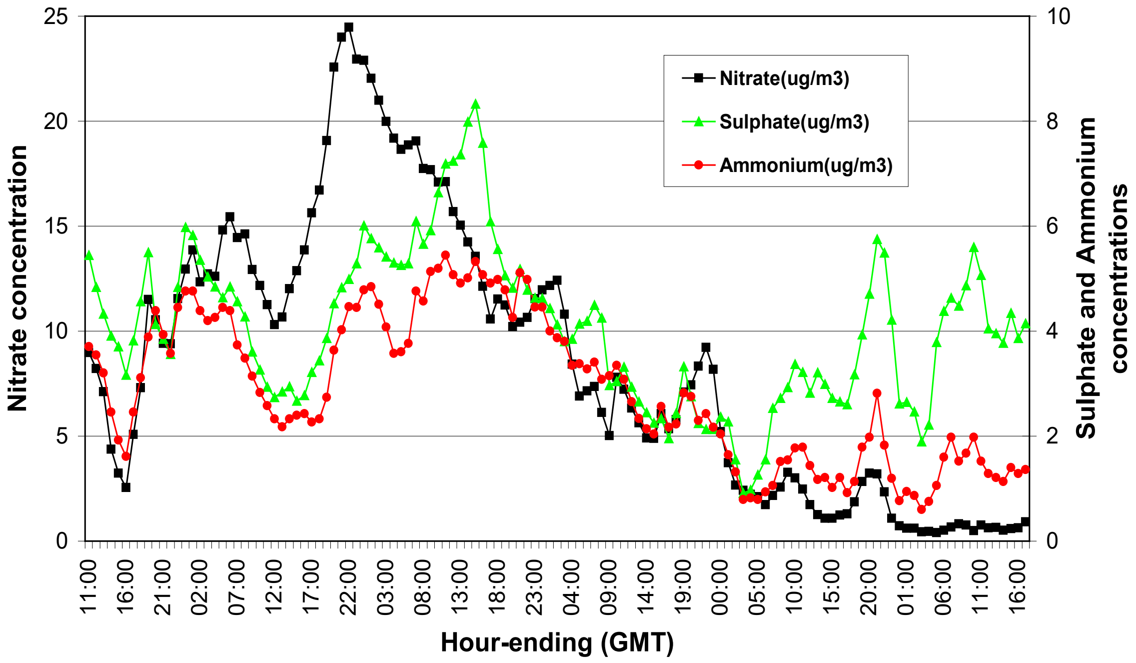


Figure 6.6e Hourly average concentration at Harwell; 30/1/99 - 4/2/99

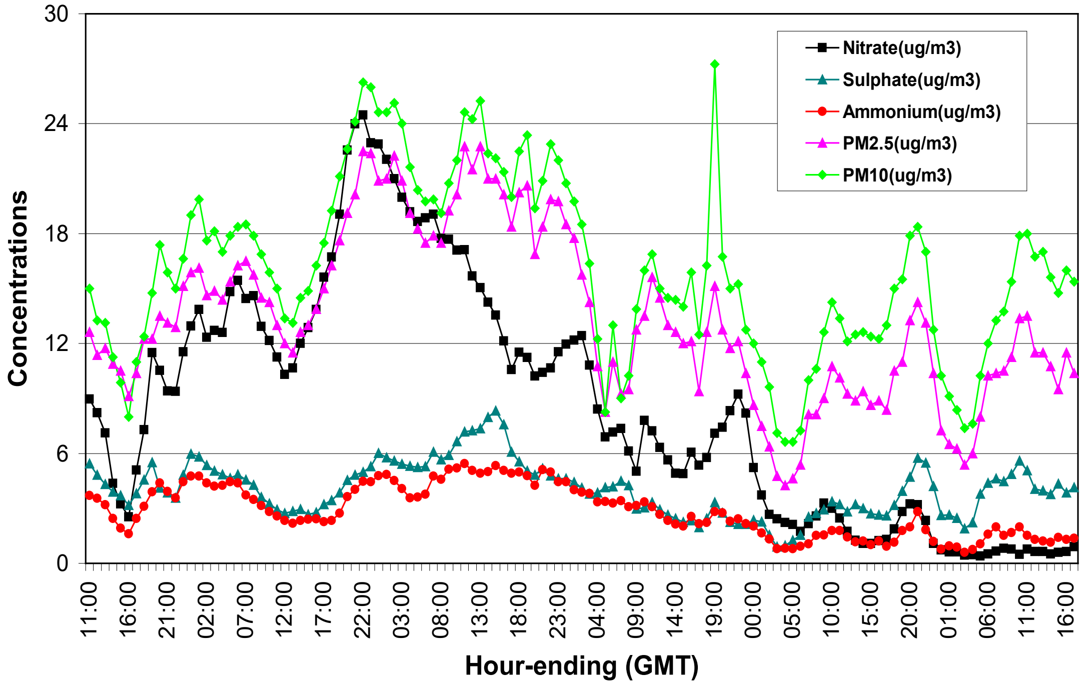


Figure 6.6f Hourly average concentration at Harwell; 30/1/99 - 4/2/99

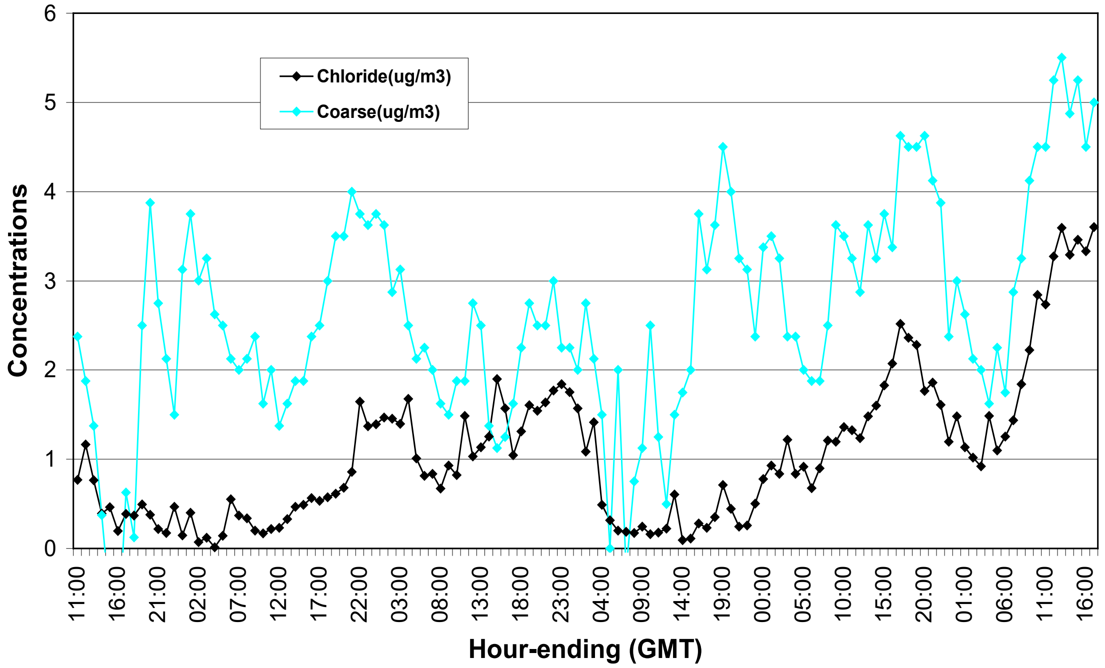
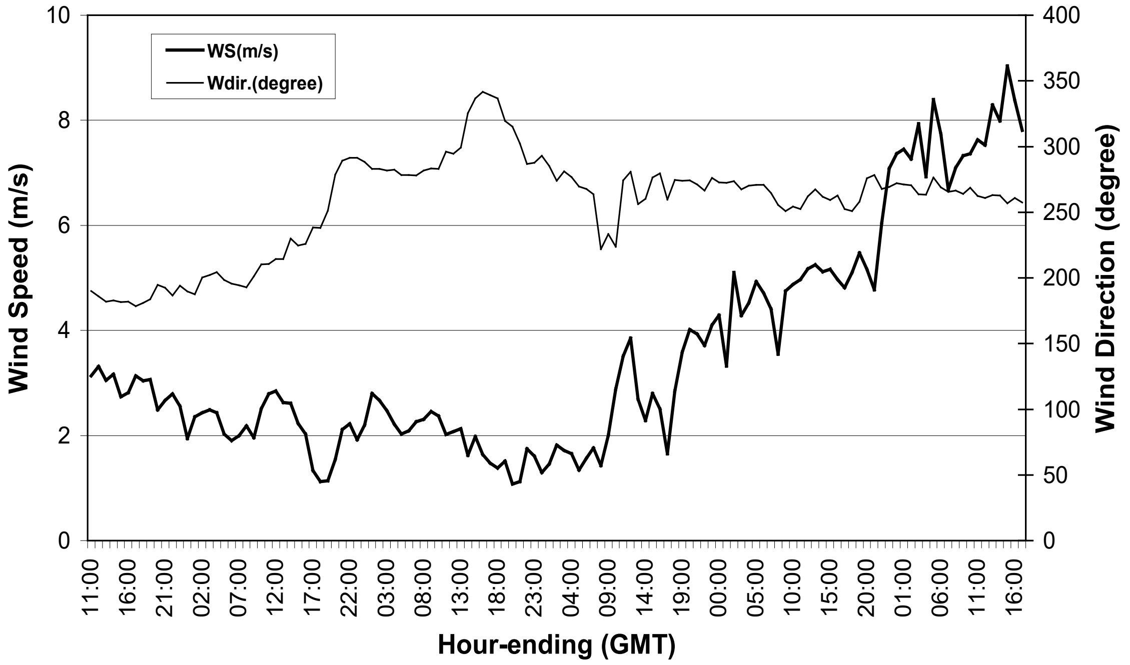


Figure 6.6g Hourly average wind speed and wind direction at Harwell; 30/1/99 - 4/2/99



7. Particles collected at Harwell in April 1999

Figure 6.7 shows the results for a short period of measurement made on 2nd-3rd April 1999. No airmass back trajectories were available from the BADC. There were south-westerly winds from 1000 to 1400 on the 2nd April when ion concentrations were low. The wind direction started changing gradually afterwards to easterly when a nitrate concentration peak occurred at around 0900 on April 3rd, and until 1400 when the wind direction became westerly. Ammonium was correlated with both nitrate and sulphate, which was only responsible for about less than 30% of the PM_{10} mass. Again, PM_{10} measured with the TEOM seems not influenced by the nitrate peak on the second date. Both sulphur dioxide and sulphate and NO_x and nitrate appeared to be broadly correlated, probably reflecting the general level of pollution of the various airmasses sampled over this period.

Figure 6.7 Hourly measurements at Harwell, 02/04/99 – 03/04/99

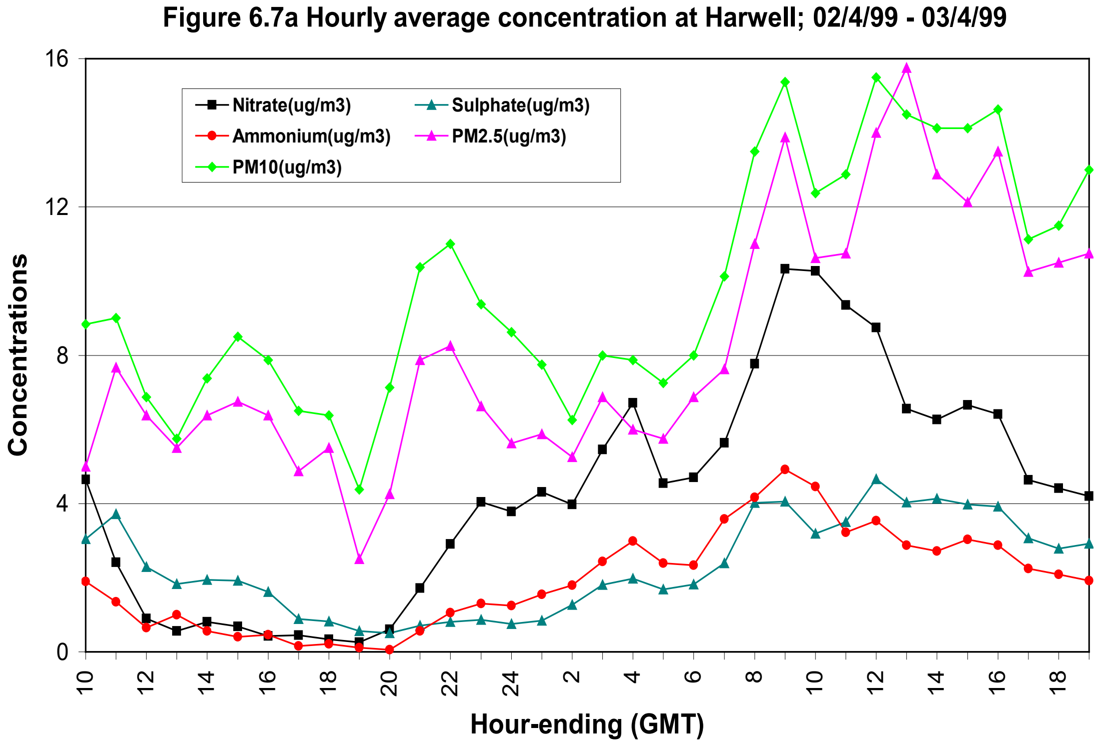


Figure 6.7b Hourly average concentration at Harwell; 02/4/99 - 03/4/99

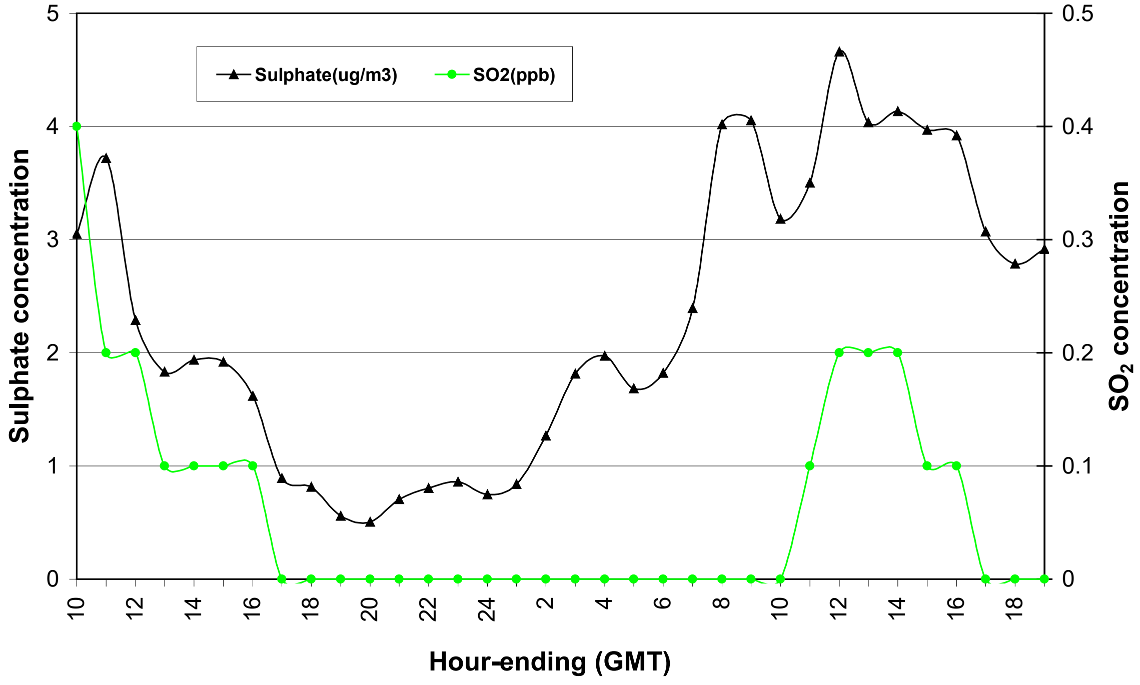


Figure 6.7c Hourly average concentration at Harwell; 02/4/99 - 03/4/99

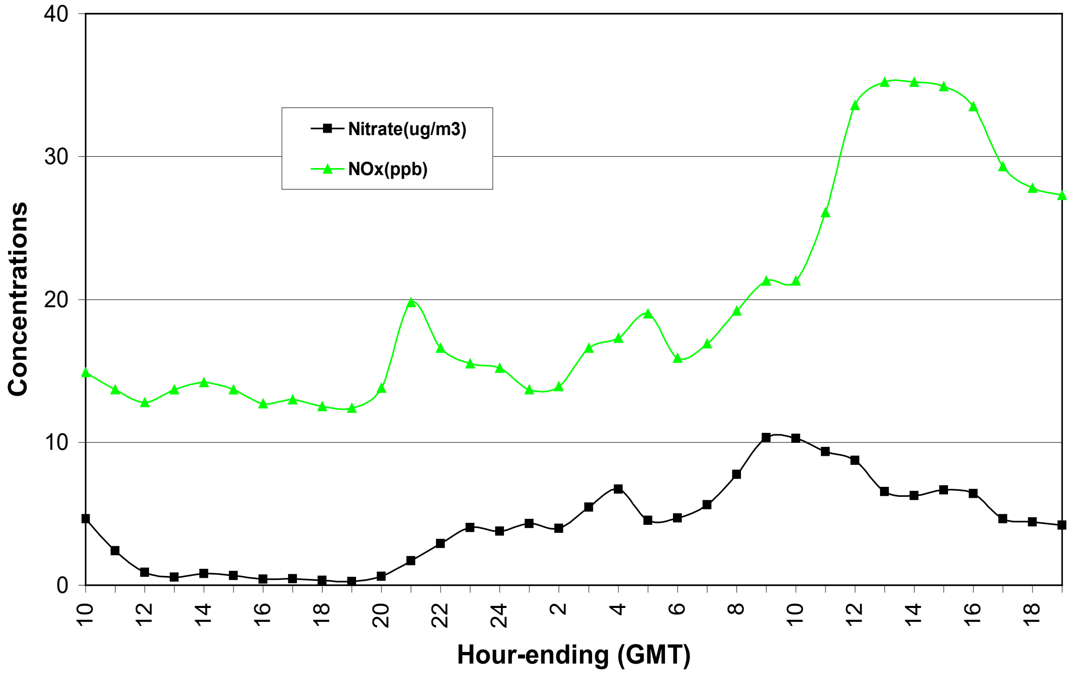


Figure 6.7d Hourly average concentration at Harwell; 02/4/99 - 03/4/99

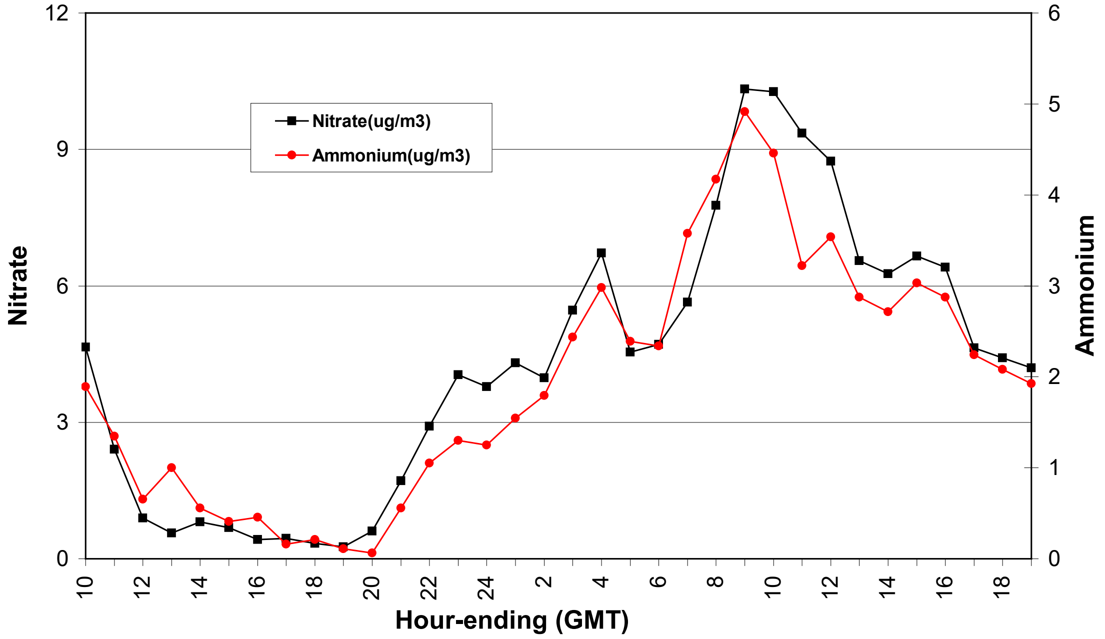
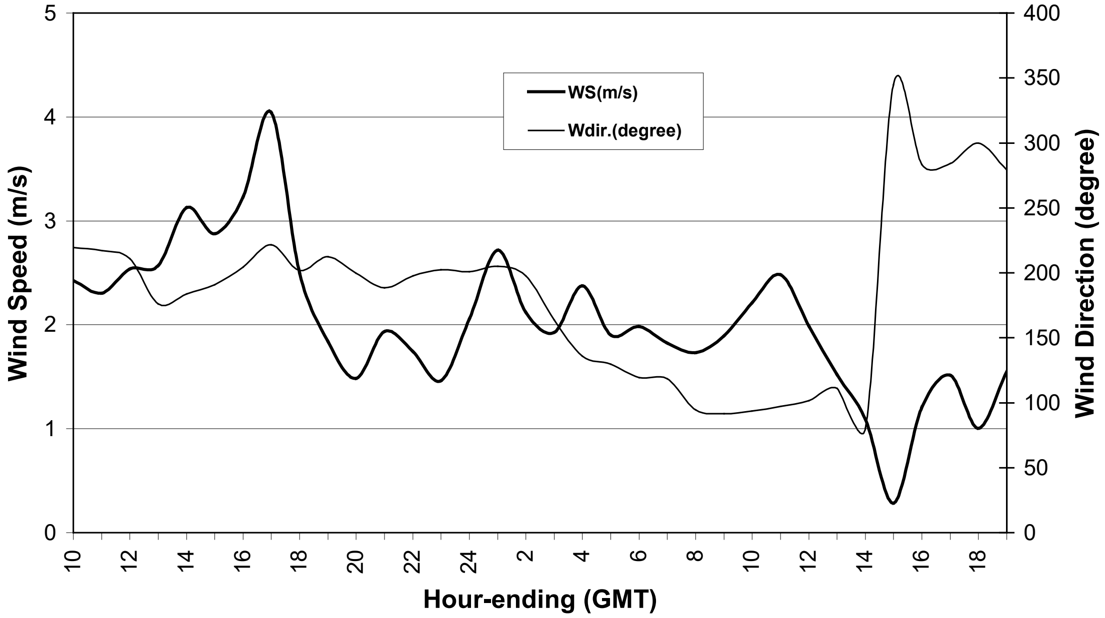


Figure 6.7e Hourly average wind speed and wind direction at Harwell; 02/4/99 - 03/4/99

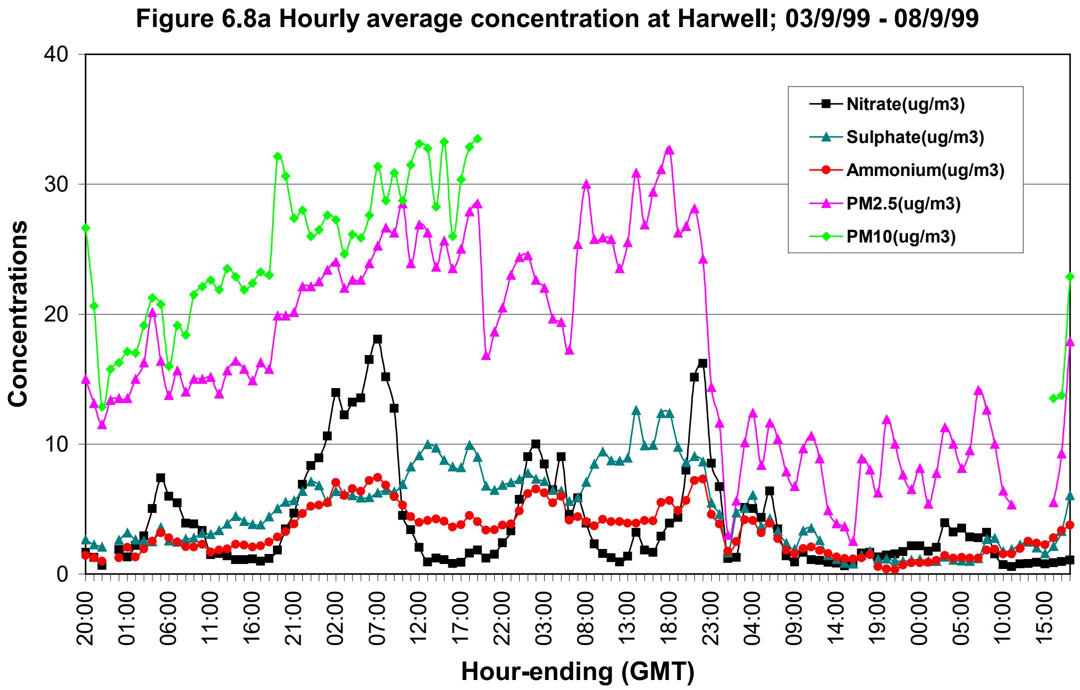


8. Particles collected at Harwell in September 1999

Figure 6.8 shows data from a more extensive period between 3rd and 8th September 1999. On September 3rd the air mass originated from the Atlantic, but travelling eastwards and approached the site from the south-east. On September 4th-6th it altered to the continent, travelling through Germany, Netherlands and probably London before reaching Harwell. On September 7th and 8th the air mass generally came from the west, and approached the site from the west or the south. The variation of the local wind direction was complex, but generally changing from the east to the west through this sampling campaign (Figure 6.8f).

During the period of easterly air masses from 4-6 September higher concentrations of PM_{10}, $PM_{2.5}$ and ions were observed (Figure 6.8a). Very high ozone concentrations also occurred at the time reaching up to 80 ppb on September 4th in the afternoon. High concentrations of nitrate appeared at night when the relative humidity was higher over 90%, and anti-correlated with ozone (Figure 6.8b) and temperature. On the other hand, peak concentrations of sulphate were well correlated with ozone (Figure 6.8c) increasing during daytime rather than at night on the 5-6 September. Nitrate was well associated with ammonium showing a consistent rise in the peak concentrations (Figure 6.8d), whereas sulphate peaks were not well correlated to ammonium (Figure 6.8e). Concentrations of PM_{10} and $PM_{2.5}$ were more related to the temporal variation of sulphate than to nitrate, but sulphate accounted for only about one third of the PM_{10} mass.

Figure 6.8 Hourly measurements at Harwell, 03/09/99 – 08/09/99



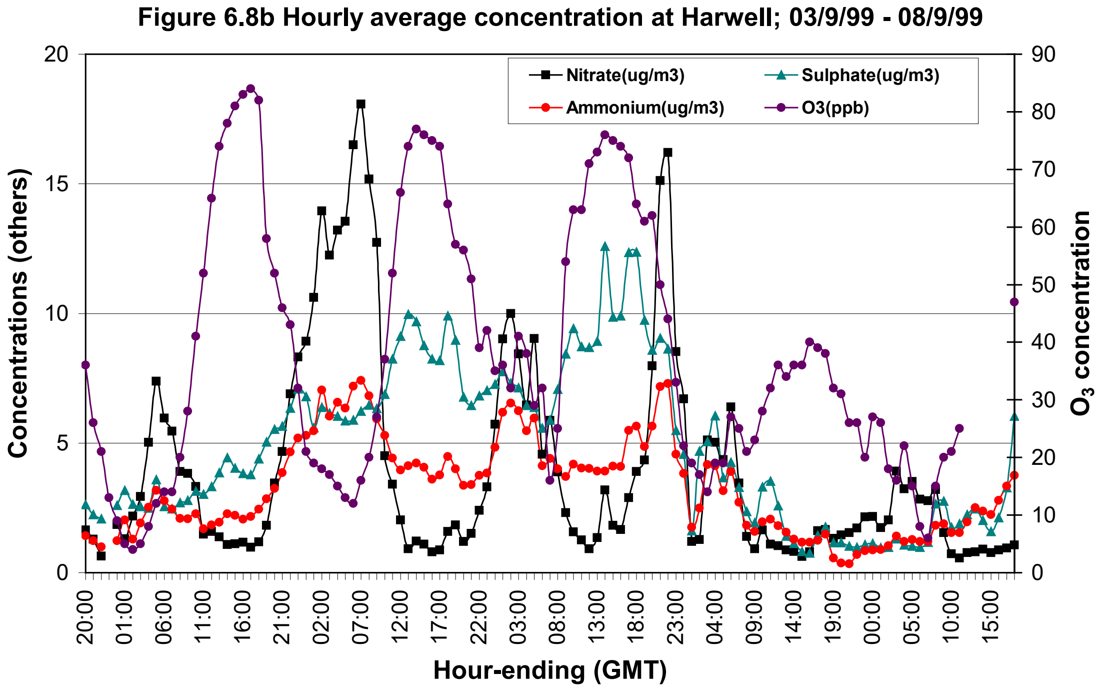


Figure 6.8c Hourly average concentration at Harwell; 03/9/99 - 08/9/99

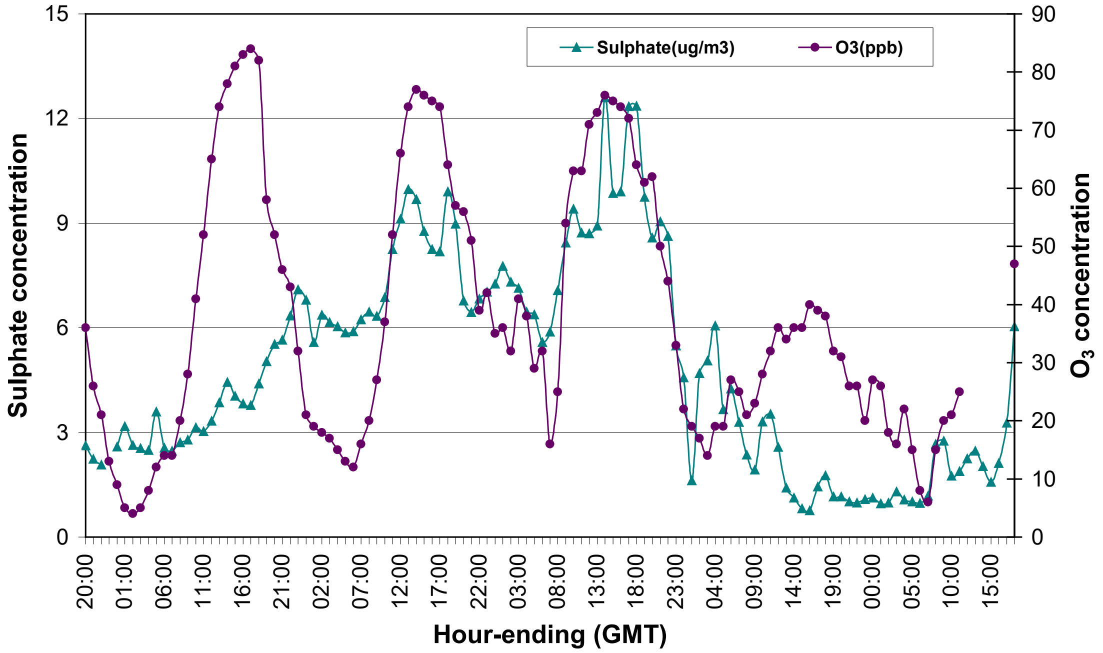


Figure 6.8d Hourly average concentration at Harwell; 03/9/99 - 08/9/99

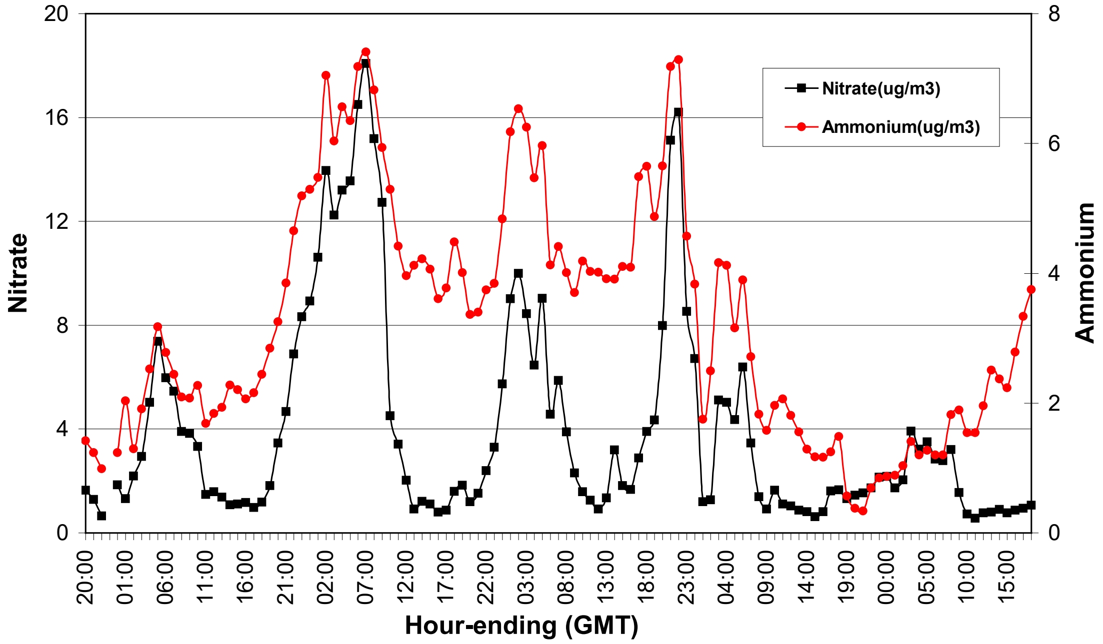


Figure 6.8e Hourly average concentration at Harwell; 03/9/99 - 08/9/99

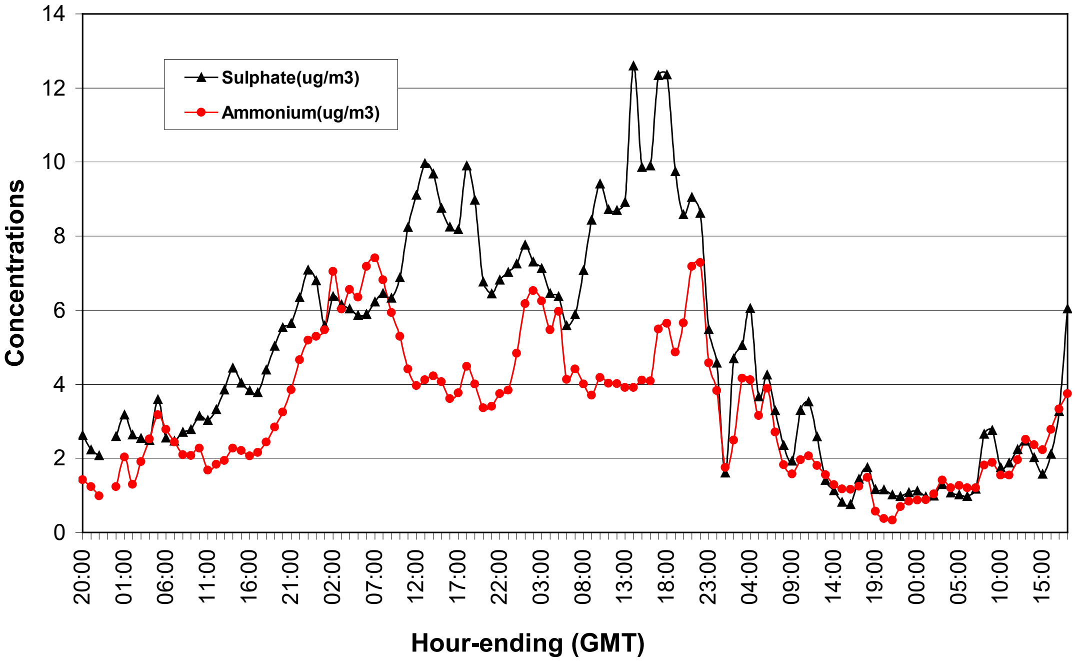
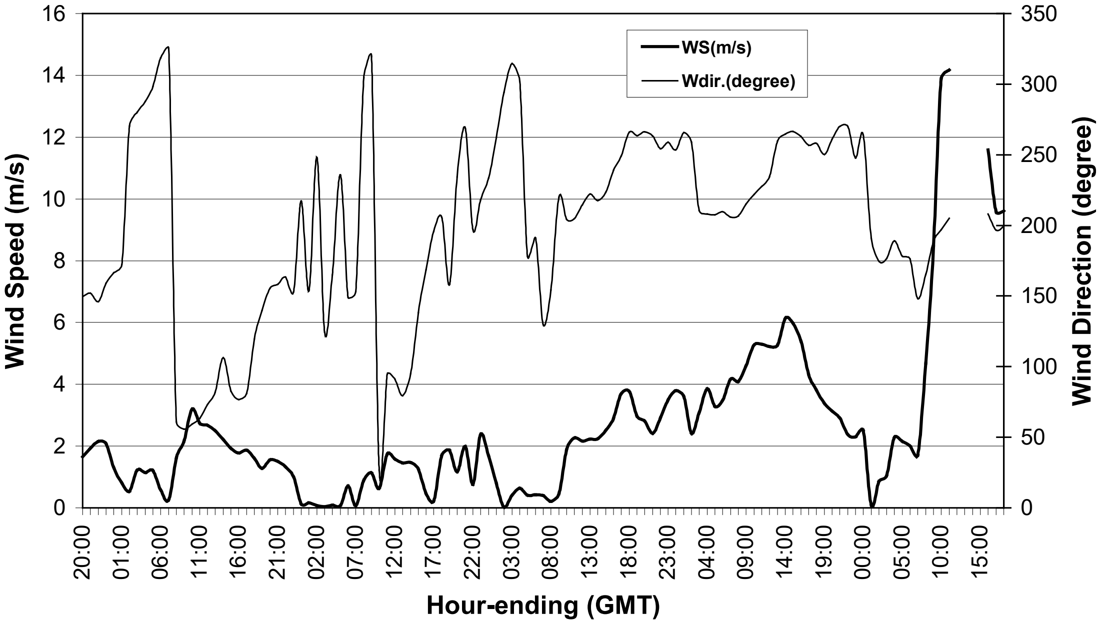


Figure 6.8f Hourly average wind speed and wind direction at Harwell; 03/9/99 - 08/9/99



6.2.2 General Discussion and Conclusions from the Harwell Data

Air sampling has covered some diverse atmospheric conditions in different seasons and with varied air-mass back trajectories. In general, aerosol at this rural site is mainly affected by airmasses transported from either a long distance like continental Europe or the nearby cities like the London conurbation.

The most interesting feature was the ability of the atmosphere to generate extremely high nocturnal nitrate concentrations anti-correlated strongly with ozone, which shows its typical afternoon maximum. There is a strong tendency for high nitrate concentrations to be associated with air masses with easterly origins (June 1998, September 1998 and September 1999) either from the continent or the London conurbation. However, for the period of Jan-Feb 1999 the higher nitrate peak was associated with westerly or north-westerly wind, which was likely due to an unidentified local source, or transported from Bristol or the Midlands. Previous study in the eastern England also observed nocturnal formation of NO_3^- (Harrison and Allen, 1990), and suggests a nighttime source of HNO_3 or NO_x. The often better correlation between nitrate and NO_x during high nitrate peaks from this study is strongly suggestive of a rather local and rapid nocturnal formation of nitrate in the stable boundary layer, when the wind speeds are consistently low. With easterly winds, polluted air can be transported from London, or continental Europe and result in the formation of ammonium nitrate from NO_x and NH_3, emitted in the urban and surrounding agricultural areas, during its transport to the site. Studies in California identified nitrate as the largest source contributor to particle mass (Motallebi, 1999; Dolislager and Motallebi, 1999) and suggested that cool temperatures, low wind speeds, low inversion layers and humid conditions would favour the formation of nitrate. The presence of oxidants and hydroxyl radicals in the air is more important in the formation of sulphate, although it can be speed up under humid conditions.

During nighttime, the important path of chemical conversion from NO_x to NO_3^- is through the reactions of

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{1}$$

$$NO_2 + NO_3 \leftrightarrows N_2O_5 \tag{2}$$

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \tag{3}$$

$$NH_3 + HNO_3 \leftrightarrows NH_4NO_3 \tag{4}$$

Due to Dalton's Law the partial pressure of a gas depends on the fractional amount of the gas present. At atmospheric pressure 1ppb gas will have a partial pressure of 10^{-9} atm. Also at atmospheric pressure 1 cm^3 of gas contains 2.69×10^{19} molecules (Loschmidt's number). The concentration of NO_2 and O_3 can be converted from ppb to the number of molecules of gas per cubic centimetre, i.e. molecule cm^{-3} by obtaining the product of the Loschmidt's number and the partial pressure of the gas as follows

$$1ppb = 2.69 \times 10^{19} \times 10^{-9} = 2.69 \times 10^{10} \text{ molecule cm}^{-3}$$

Considering the real time pressure and temperature, the corrected conversion is

$$1ppb = 2.69 \times 10^{10} \times (273/T) \times (1013/P) \text{ molecule cm}^{-3}$$

Where T and P are temperature (^{0}K) and pressure (mb) respectively.

The reaction rate constant *k* for reaction (1) at different temperature is calculated as $1.4 \times 10^{-13} \exp(-2470/T)$ cm^3 $molec^{-1}$ s^{-1} (IUPAC, 1997). In theory the NO_3 radical lifetimes are a strong function of relative humidity. The observed NO_3 lifetimes are the order of 40 minutes below about RH = 50%, and drop to the order of a few minutes when the RH is above about 50%. The latter is most consistent with a loss of N_2O_5 to form HNO_3, which would lead to an irreversible loss of NO_3 (Platt and Heintz, 1994). However, in practice it is likely that some of the N_2O_5 decomposes back to $NO_2 + NO_3$, and some fraction of it is continuously lost to HNO_3 formation.

Assuming a humid and foggy night, the loss of NO_3 or the formation of HNO_3 would be complete, and the maximum formation rate of total nitrate ($HNO_3 + NO_3^-$) can be estimated as

$$d[NO_3^-] / dt = 2 \times d[NO_3] / dt = 2\, k\, [NO_2][O_3] \qquad (5)$$

One mole of a substance contains 6.02×10^{23} molecules, and the unit of the rate, which is molecule cm^{-3} s^{-1}, can be converted to g cm^{-3} s^{-1} by dividing the number by 6.02×10^{23} and then multiplying by the molecular weight. The above calculation was applied to some periods with high nighttime nitrate peaks and the results are detailed individually as follows.

High nitrate peak was observed over the night-time from 20 hours on the 5th to 9 hours on the 6th of June 1998 when there was an easterly wind (Figure 6.2). The relative humidity during the time was high at 80-96.5%. Ammonia, which was not measured here, is likely to be present in excess at ground level in rural areas of the UK for the formation of particulate nitrate (Harrison and Allen, 1990). NO_x concentration was used in the calculation instead of NO_2 for this particular period, since it was not available from the National Air Quality Information Archive, from where the O_3 concentration was obtained. The averaged total nitrate formation rate calculated using equation (5) is 7.7 $\mu g\ m^{-3}\ h^{-1}$. At a wind speed of 3 $m\ s^{-1}$, approximately 9 hours were needed for pollutant transportation from London to Harwell at a distance of 100 km. Therefore, the estimated total nitrate concentration, at a formation rate of 7.7 $\mu g\ m^{-3}\ h^{-1}$, was about 69 $\mu g\ m^{-3}$, which is 2.4 times the measured particulate nitrate peak concentration.

The result indicates that fast formation of nitrate can occur during the night under conditions of high humidity and stable atmosphere with low temperature, low wind speeds and low inversion layer down to an average of about 100 metres. On the other hand, the higher ratio of the total nitrate to the particulate nitrate concentrations may be due to three possible factors. First, in the real atmosphere the NO_3 radical is not completely lost to the formation of HNO_3 due to reaction (2). Second, the HNO_3 formed is not entirely neutralised by NH_3 due to the reversible equation (4) although high humidity and lower temperature (around 13^0C) favours the particle phase. Third, NH_3 is not in excess for completing the neutralisation of HNO_3 especially at night. Measurements of other precursor pollutant concentrations, such as NH_3 and HNO_3, and weather data including relative humidity and temperature at the same site are needed in future studies to aid interpretation of the data.

Consistent nighttime nitrate peaks occurred during the period 22/9/98 – 25/9/98 with easterly winds (Figure 6.4). The same calculation was conducted and the average formation rates for total nitrate were 3.0 $\mu g\ m^{-3}\ h^{-1}$ during the night on 22nd –23rd, 3.3 $\mu g\ m^{-3}\ h^{-1}$ for the night of 23rd–24th, and 3.9 $\mu g\ m^{-3}\ h^{-1}$ at the night of 24th-25th. The estimated total nitrate concentrations were 22.5, 36.6 and 67.9 $\mu g\ m^{-3}$, at a wind speed of 3.7, 2.5 and 1.6 $m\ s^{-1}$ for the three nights respectively. The estimate was less by one fifth than the measured peak value during the second night, and 1.4 times the measured peak concentration during the last night, but very similar concentrations were observed during the first night-time period. Previous measured ratio of the total nitrate ($HNO_3 + NO_3^-$) to NO_3^- in Eastern England was about 1.0-1.3 (Harrison and Allen, 1990), close to that found on the first and the last nights. The ratios are all lower than that obtained from the summer period in June 1998. This may be related to the lower temperature, which reduces the dissociation of ammonium nitrate.

However, the higher measured NO_3^- concentrations in September were generally due to a more stable atmosphere, showing the mixing layer height below 60 metres.

Unlike the above two periods, the winter campaign in January and February 1999 showed high nitrate peak with westerly air masses (Figure 6.6). The humidity was greater than 90% at night with high nitrate concentrations, and the temperature and inversion layer are also low at 4-5 ^{0}C and 10-50 metres respectively. Interestingly, the estimated total formation rate is very low at 0.82 $\mu g\ m^{-3}\ h^{-1}$. If assuming that this period was affected by plumes from the Bristol City at a distance about 110 km to the west, an estimate of about 10 $\mu g\ m^{-3}$ nitrate was obtained, which was much lower than the measured peak concentration (24 $\mu g\ m^{-3}$). This indicates that additional particulate nitrate may be formed through other routes such as direct reaction between NO_2 and NaCl (Mamane and Gottlieb, 1992; Harrison et al., 1994), which is higher during the winter period as a source of either sea salt or de-icing salt.

The concentrations of sulphate and ammonium are also higher during periods of easterly air masses, whereas chloride only shows appreciable concentrations in the winter periods. It is presumably due to either a source of de-icing salt from the nearby A34 in December 1998 with a north-easterly wind, or both road salt and sea salt in Jan-Feb 1999 with a westerly winds, reaching up to 9 m s^{-1} on the last day, when the chloride concentration increased up to 3.6 $\mu g\ m^{-3}$.

The other feature is that for most of the sampling periods the nitrate was mainly in the form of ammonium nitrate, judging from the correlation of the two species. However in Jan-Feb 1999 there was little association between the two, suggesting that the nitrate was present as sodium or calcium salts, which is supported by the results on estimating the formation of nitrate. On the other hand, good correlation between sulphate and ammonium was observed only from periods with westerly air masses or wind (August98 and Jan-Feb99). In some instances, sulphate correlates with nitrate in its diurnal behaviour. In others it shows no diurnal variation, and in other circumstances sulphate peaks during daytime in a similar manner to ozone and anti-correlated with nitrate (Sept99). PM_{10} measured with the TEOM correlates better with sulphate than with nitrate, and consists of anything between about 15% and 60% of sulphate.

For periods in June 1998, September 1998 and Jan-Feb 1999 massive nitrate concentrations determined from the Partisol instruments went wholly unobserved by the TEOM. It shows that the TEOM instruments report lower concentrations of particulate matter than the Partisol due to losses of semi-volatile species by heating up the aerosol to 50^0C (Salter and Parsons, 1999; APEG, 1999; Allen et al., 1997; Smith et al., 1997). However, the difference is expected to vary both temporally and geographically. A typical correction factor of 1.3 was applied when assessing the likelihood of areas exceeding the EU limit values (DETR, 1999) according to previous studies, which concluded that TEOM instruments underestimated the Partisol PM_{10} by 15-30% at concentrations around the air quality standard of 50 μg m^{-3} (APEG, 1999). Rickard and Ashmore (1996) found the TEOM to give PM_{10} concentrations on average 6.9 μg m^{-3} lower than those obtained from a cascade impactor. This study shows clearly that a huge difference in the particle mass concentrations between the Partisol and the TEOM samplers may occur when very high levels of nitrate appeared, and also confirms that a single correction factor for the TEOM instrument is not adequate (Green et al, 2001).

6.3 Measurements in Birmingham

6.3.1 Particles Collected from a Home Garden in Birmingham

Hourly data obtained from a suburban garden in Birmingham during the bonfire night period on 4-8 November 1999 is presented in figure 6.9. The PM_{10} data was taken from the Birmingham Central AURN monitoring site. From the afternoon on November 4th the airmass (Appendix B) came from the west travelling over northern France and approaching Birmingham from the south. By 1200 on November 5th it changed to south westerly, then to north westerly on November 6th, westerly on November 7th and north westerly again on November 8th. The local wind data taken from the nearest site, Birmingham University, indicate a general westerly direction and high speeds on November 4-5th, medium on 6th and lower from the evening on 6th and afterwards (Figure 6.9e). PM_{10} concentrations peaked on the evenings of November 5th and 6th with higher contributions from chloride (Figure 6.9a-b), which was related to the bonfire night activities (Aldape et al., 1999). However these elevations in particle concentrations were very modest due to high wind and wet weather conditions in comparison with those occurring on days with stagnant air observed during the bonfire night in 1995 at the Birmingham East AURN site (Jones, 1996). There was a temporal correlation between the ionic species, especially between ammonium, chloride and nitrate (Figure 6.9c-d). The average total contribution from the measured species to PM_{10} was about 38%. Generally, this period was influenced by local activities.

Figure 6.9 Hourly measurements in Birmingham, 04/11/99 – 08/11/99

Figure 6.9a Hourly average concentration in a residential garden, Birmingham; 04/11/99 - 08/11/99

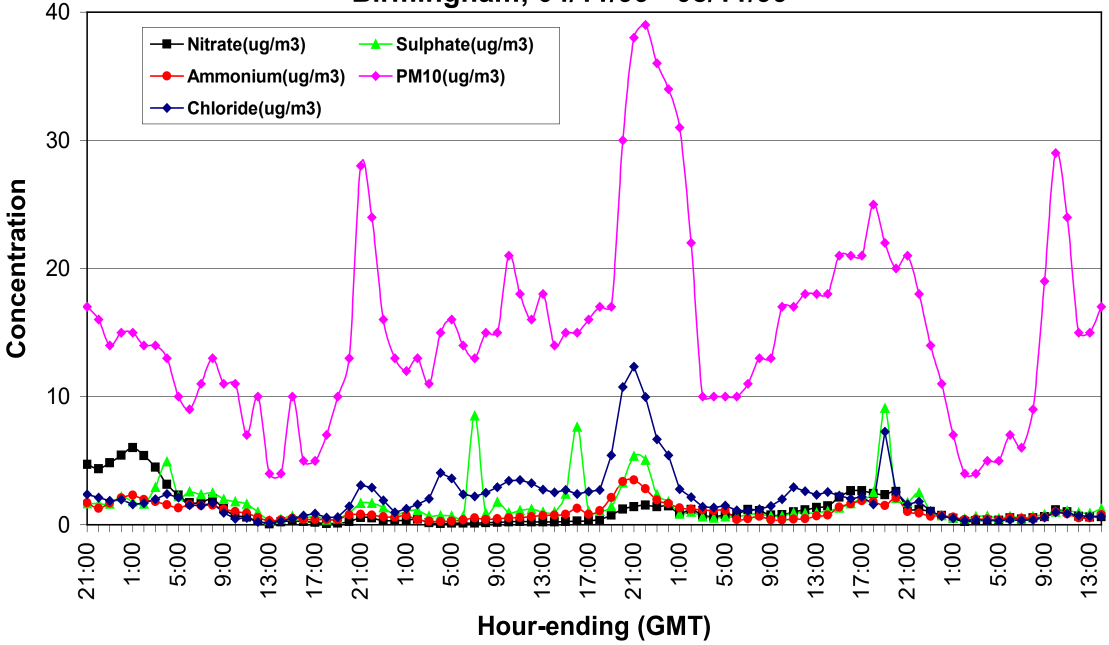


Figure 6.9b Hourly average concentration in a residential garden, Birmingham; 04/11/99 - 08/11/99

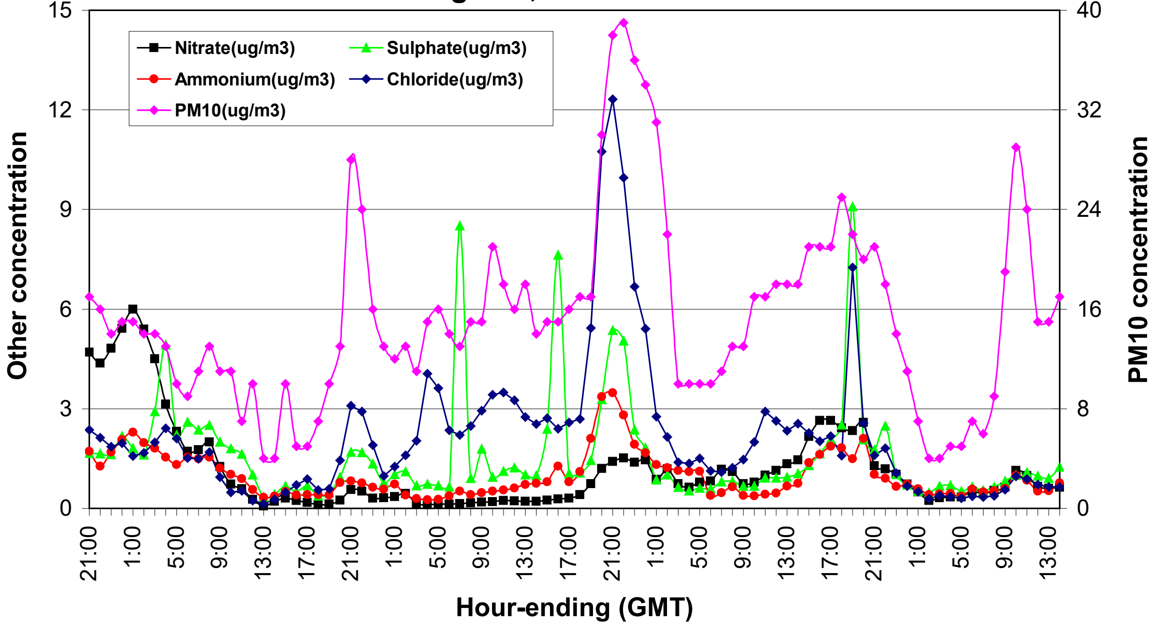


Figure 6.9c Hourly average concentration at a residential garden, Birmingham; 04/11/99 - 08/11/99

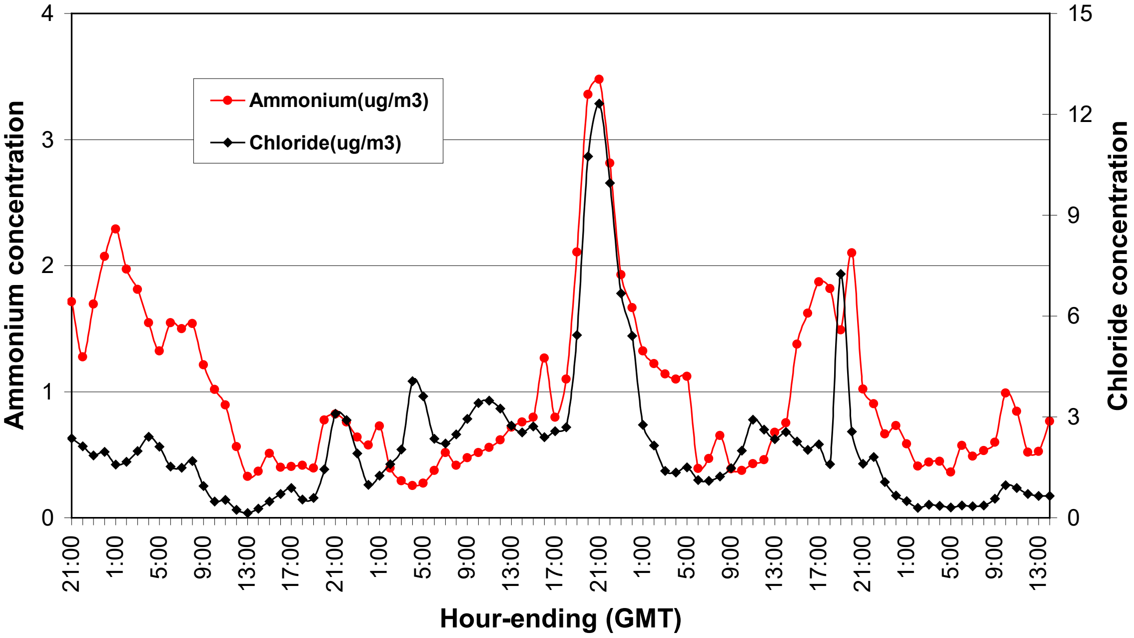


Figure 6.9d Hourly average concentration at a residential garden, Birmingham; 04/11/99 - 08/11/99

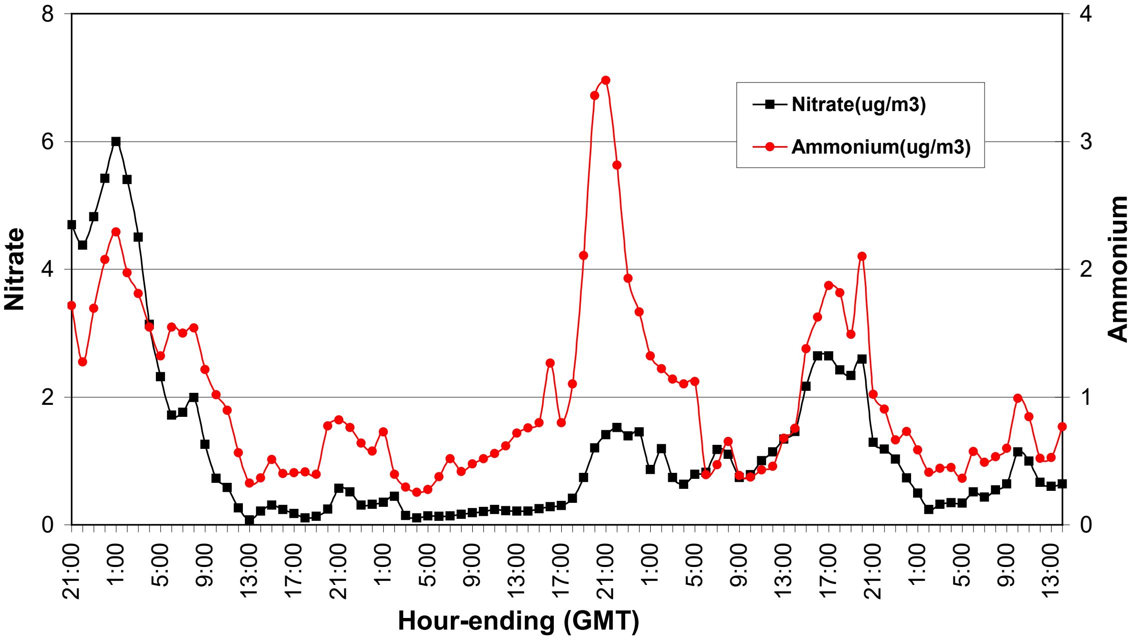
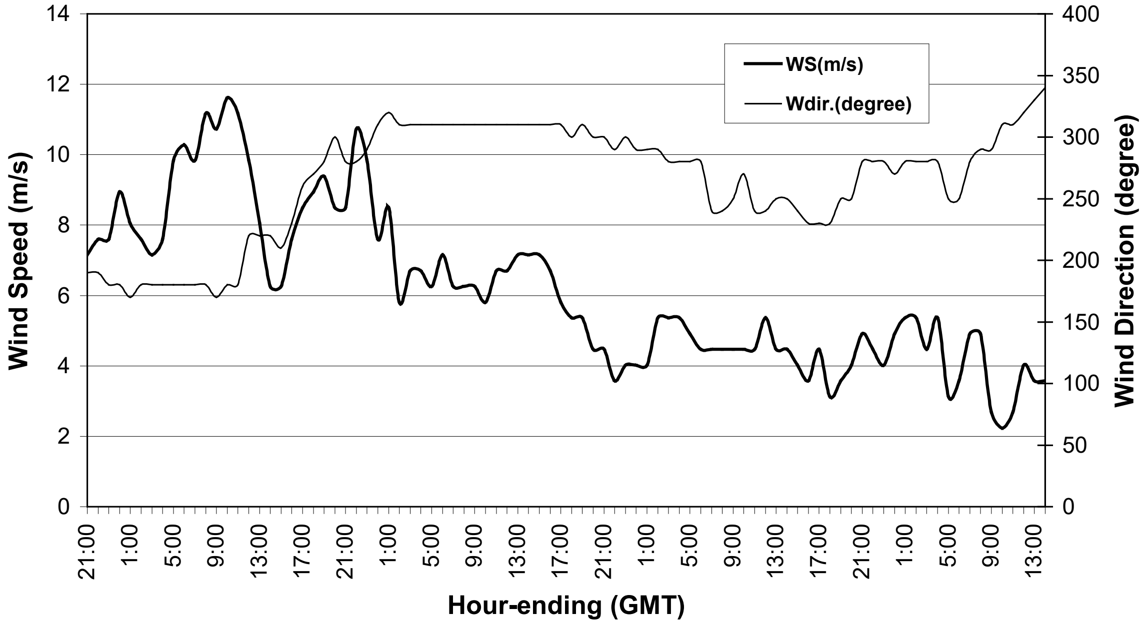


Figure 6.9e Hourly average wind speed and wind direction at the University of Birmingham site; 04/11/99 - 08/11/99



6.3.2 Particles Collected during the PUMA campaign in Birmingham

6.3.2.1 Summer Campaign

Ionic species measurements

Hourly measurements were made for four intensive sampling periods in addition to the 24-hour sample collection in the summer of 1999. The hourly concentrations of ionic species and PM_{10} are presented in Figure 6.10, and air mass back trajectories shown in Appendix B for those four hourly one-day periods. Figure 6.11 shows data from the whole summer campaign on a 24-hour basis, where hourly samples were aggregated into daily averages.

Higher PM_{10} concentrations were observed at periods on days of 25-26th June 1999, 9th of July and 11-12th of July, showing up to 31, 40 and 35 $\mu g\ m^{-3}$ respectively (Figures 6.10a,c&d). The air mass, originated from the west, circulated over the UK and approached the site from the south-east on the 25-26th of June and from the east on the 9th of July, whereas a north-easterly air mass approached on the last intensive day of 11-12th of July. The particle concentration was very low on the day over 30-June and 01-July when a clean westerly or south westerly air mass was present (Figure 6.10b). It is noticed that the ionic species make a much lower contribution to the overall PM_{10} concentration during the whole sampling period (Figure 6.11) in comparison with the rural Harwell site, and about only one third or much less of the PM_{10} was collected as sulphate. At this typical urban location, a large contribution is likely to be the local road traffic emissions of carbonaceous aerosols shown later in this chapter. In addition, re-suspension and windblown dusts could also account for an appreciable proportion of the PM_{10} mass in the summer period. Nitrate concentrations at the urban site were much lower, which do not give any indication of influencing the PM_{10} concentrations measured with the TEOM. There is a good consistency between sulphate and ammonium while nitrate tends to stand-alone until the last week of the sampling period. The concentration of chloride was generally low but significant levels were observed.

Figure 6.10 Hourly measurements from the summer PUMA Campaign

Figure 6.10a Hourly average concentration at a PUMA Site in Birmingham; 25/6/99 - 26/6/99

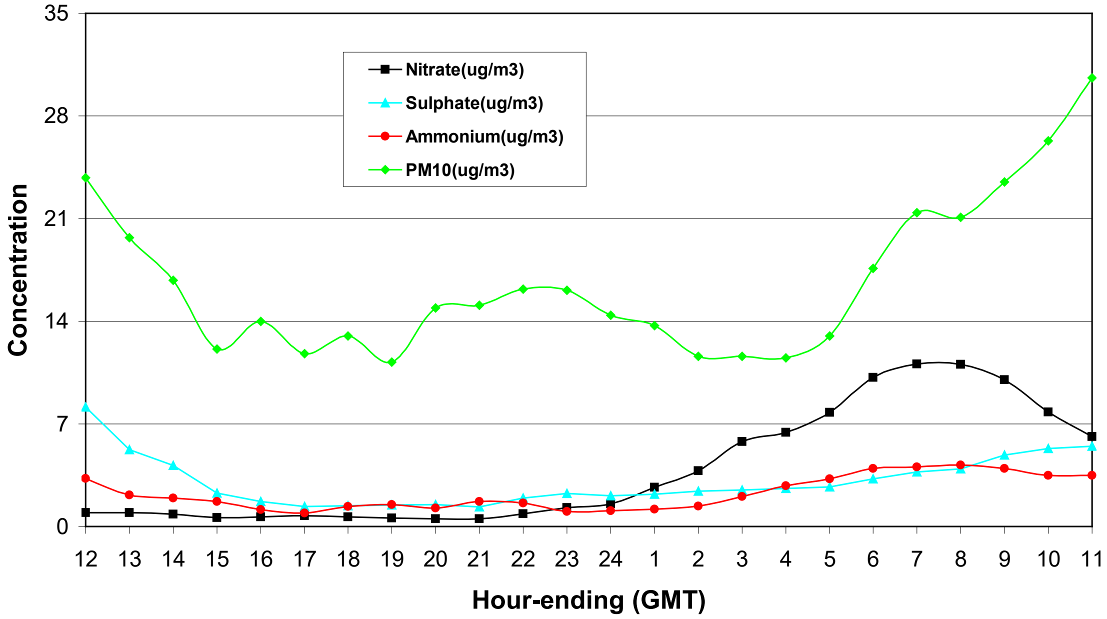


Figure 6.10b Hourly particle concentration at a PUMA Site in Birmingham; 30/6/99 - 01/7/99

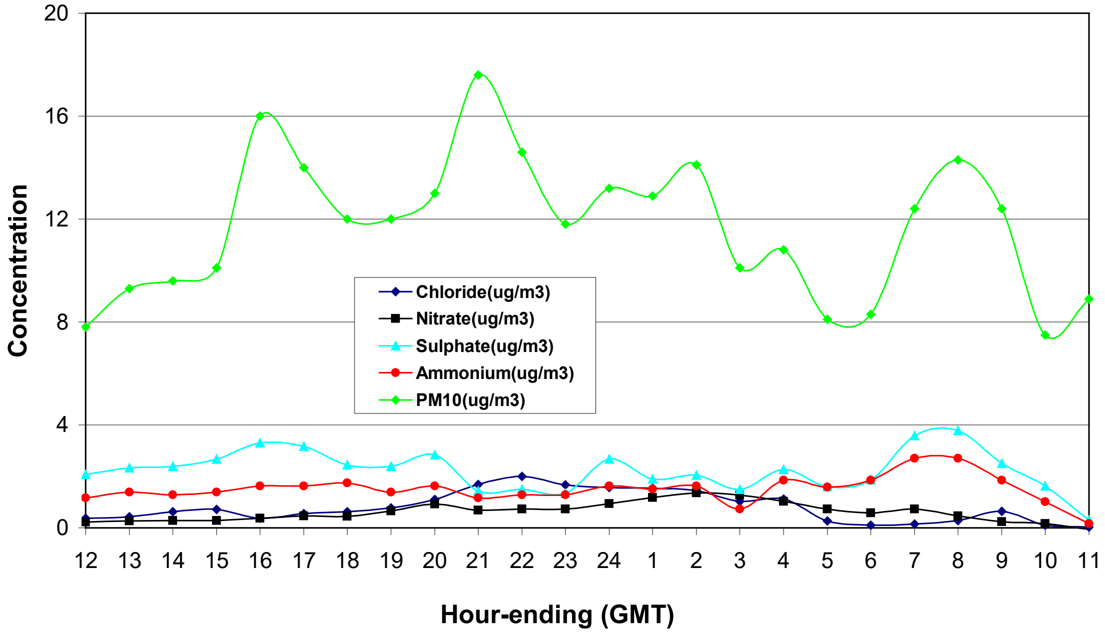


Figure 6.10c Hourly particle concentration at a PUMA Site in Birmingham; 09/7/99

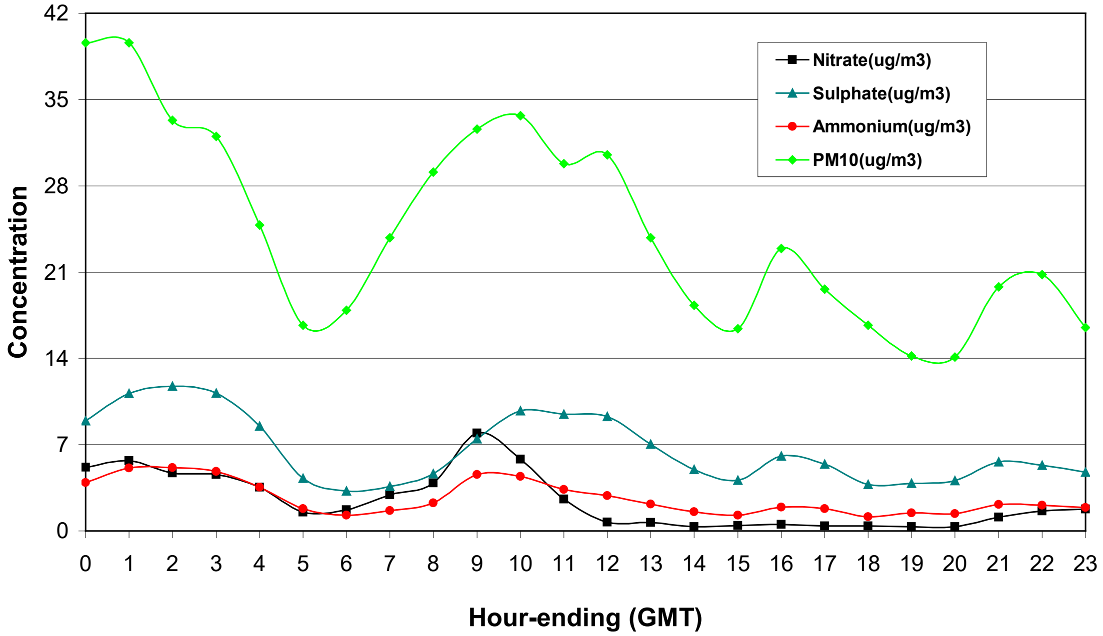


Figure 6.10d Hourly particle concentration at a PUMA Site in Birmingham; 11/7/99 - 12/7/99

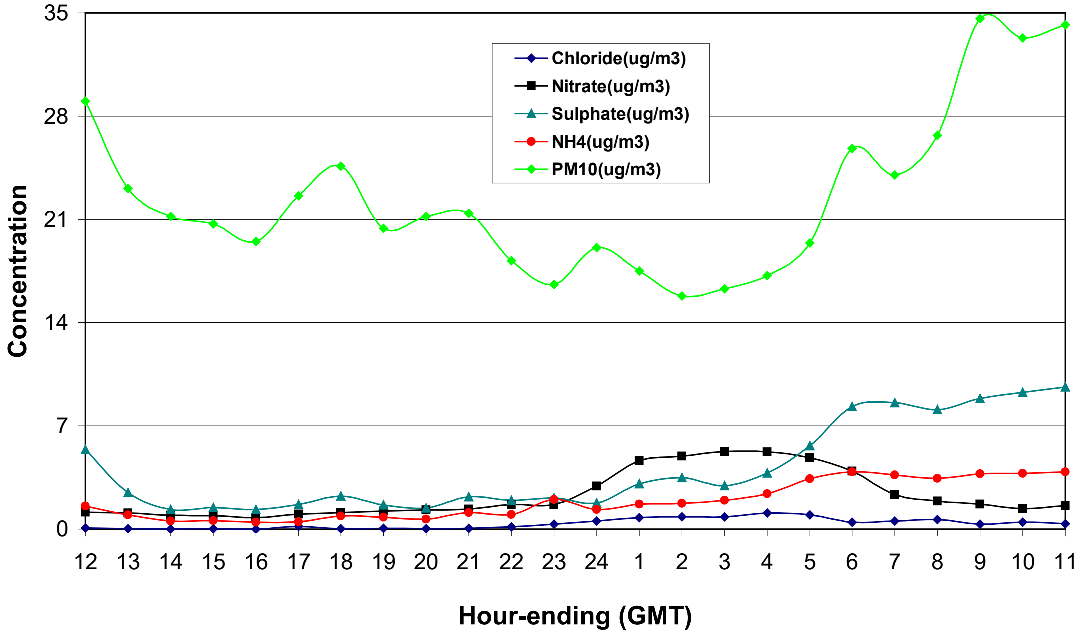
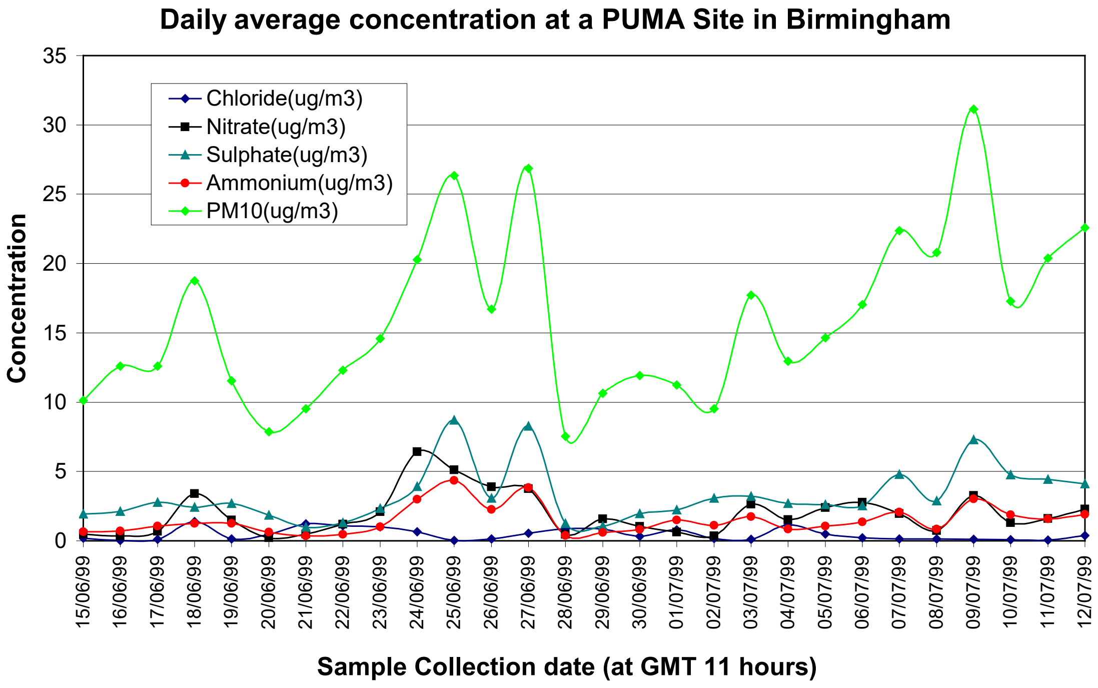


Figure 6.11 Daily measurements from the summer PUMA Campaign



Carbon measurements

Over the period from the 11th June to the 12th July, daily samples were collected using a Graseby Andersen dichotomous sampler fitted with PM_{10} inlet. Fine and coarse particles were collected on QMA filters, which were analysed for organic carbon (OC) and elemental carbon (EC) using a Leco Instruments Model RC412 Carbon Determinator.

The average concentrations of organic and elemental carbon specified for both coarse and fine particle fractions over the campaign period are listed in table 6.2. The results show that the concentration of organic carbon is higher than elemental carbon, suggesting that summer periods are more favourable for the formation of secondary organic carbon through the process of gas/particle conversion of VOCs as a result of photochemical activity (Castro et al., 1999). Figure 6.12 clearly show that nearly all points lie above the ratio of 1:1 line for the correlation between OC and EC. The ratios of the mean organic to elemental carbon are comparable to the previous daily results (coarse- 3.1, fine- 1.3, PM_{10}- 1.4) but much higher than the weekly results (coarse- 1.4, fine- 0.7, PM_{10}- 0.8) from Birmingham, Hodge Hill (Jones, 1996). This suggests that there was a significant loss of some volatile organic carbon from the longer period of sampling.

Use of PM_{10} particle mass concentration obtained from a TEOM instrument enabled estimation of the average chemical composition for the site, considering both ionic and carbon species (Figure 6.13). As mentioned above, carbonaceous particles accounted for a large proportion, about 36%, of the PM_{10} mass on average, which is similar to the results from other two UK urban sites, Leeds (33.8% of PM_{15}) (Clarke et al., 1984) and Birmingham, Hodge Hill (38% of PM_{10}) (Harrison et al., 1997a). The sum of total carbon and ionic species explains about 82% of the PM_{10} particle composition, with 46% of total ionic materials, however, this value may be overestimated considering PM_{10} mass underestimation from the TEOM.

Table 6.2. Average concentrations ($\mu g\ m^{-3}$) of carbonaceous particles from the summer PUMA campaign; 12/6/99 – 12/7/99

Fraction	OC	EC	TC	OC/EC (Range)
Coarse particles	0.8	0.3	1.1	2.5 (0.3 – 13.8)
Fine particles	2.0	1.3	3.3	1.5 (0.4 – 3.2)
PM_{10}	2.8	1.6	4.4	1.7 (0.9 – 3.9)

Figure 6.12 Daily concentration of organic and elemental carbon from the summer PUMA campaign; 12/6/99 – 12/7/99

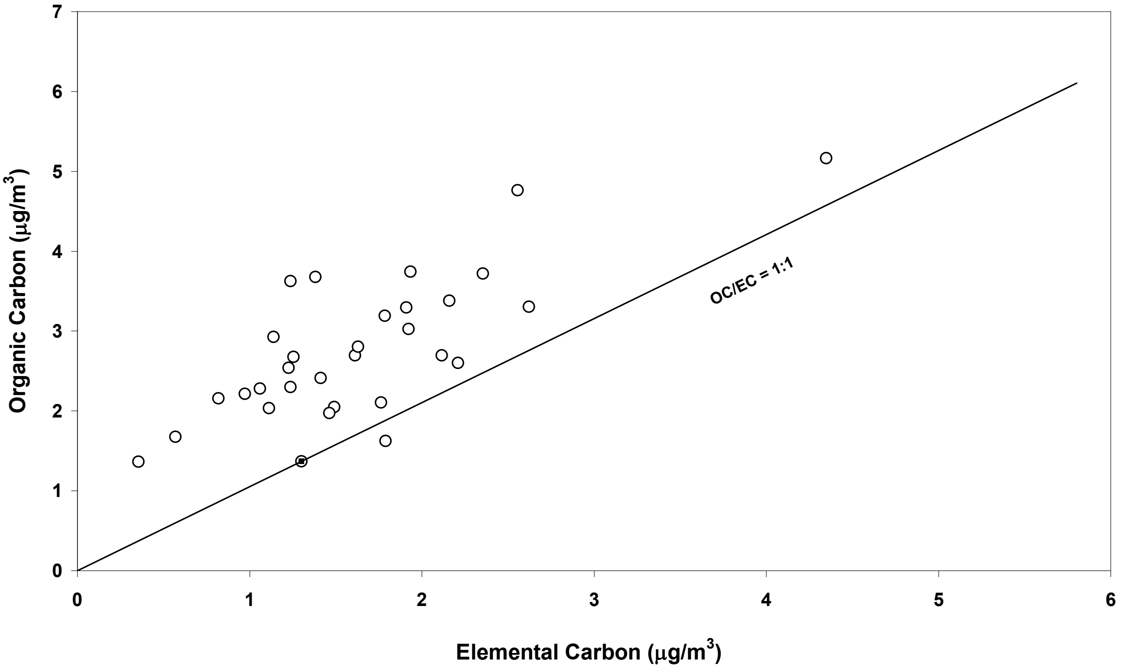
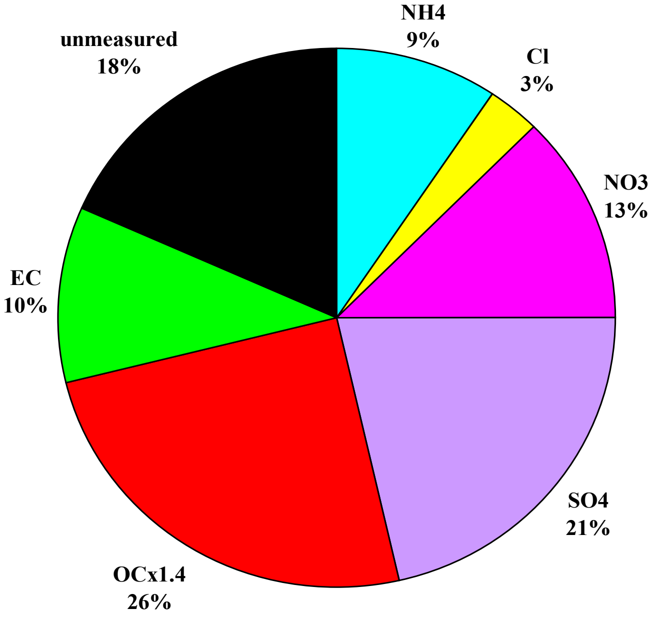


Figure 6.13. PM_{10} mean composition (%) from the summer PUMA campaign; 12/6/99-12/7/99



6.3.2.2 Winter Campaign

Ionic species measurements

The winter PUMA campaign was conducted during the period from 20th January 2000 to 17th February 2000. Two intensive days of hourly measurements were made (Figure 6.14a-b). On the first intensive day, 25-26th January 2000, the air-mass originated from the marine area and reached the site over northern England. The local wind speed was very low down to zero with westerly direction. On the second intensive day, 9-10th February 2000, at the beginning of measurement the air-mass travelled across northern Germany and the Netherlands before approaching the site, and then moved to north arriving at the site over the sea from the north-east. Local wind data is not available. Particle mass concentrations of PM_{10} and $PM_{2.5}$ were found to be higher in the afternoon during both intensive periods (Figures 6.14a&b), but the contribution of ionic species was generally low. Once again the ionic species alone composed a lower proportion of the PM_{10} mass on most of the days (Figure 6.14c) during the winter campaign, compared with the Harwell data. Organic and elemental carbon accounted for up to 40-50% of the PM_{10} mass on 24-25th and 25-26th January, and 13-14th February when the pollution levels were higher. The chloride concentrations were much higher throughout the winter period, presumably due to mainly de-icing salt, representing about 50-100% of the coarse fraction. Sulphate, nitrate and ammonium were generally correlated, but not with chloride.

Figure 6.14 Hourly and daily measurements from the winter PUMA Campaign

Figure 6.14a Hourly average concentration (μg m^{-3}) at a PUMA Site in Birmingham; 25/1/00 - 26/1/00

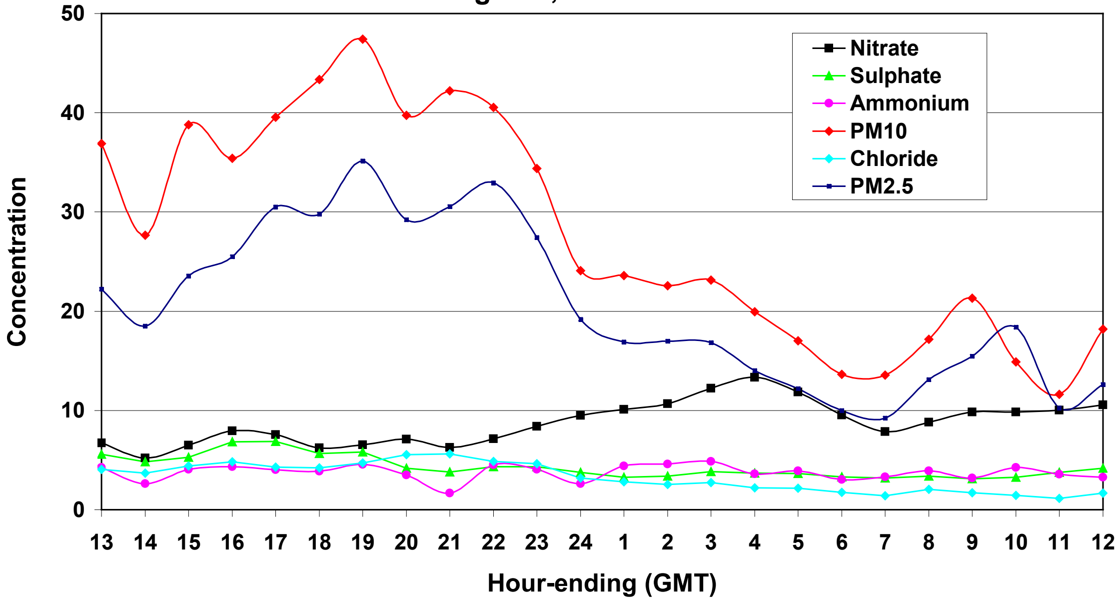


Figure 6.14b Hourly average concentration (μg m^{-3}) at a PUMA Site in Birmingham; 09/2/00 - 10/2/00

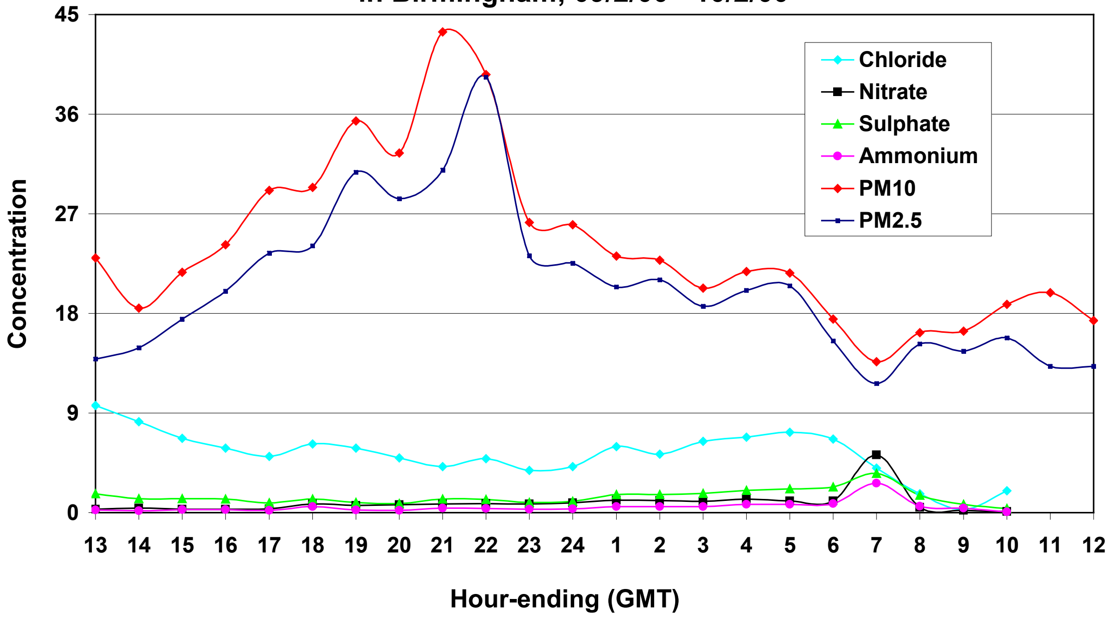
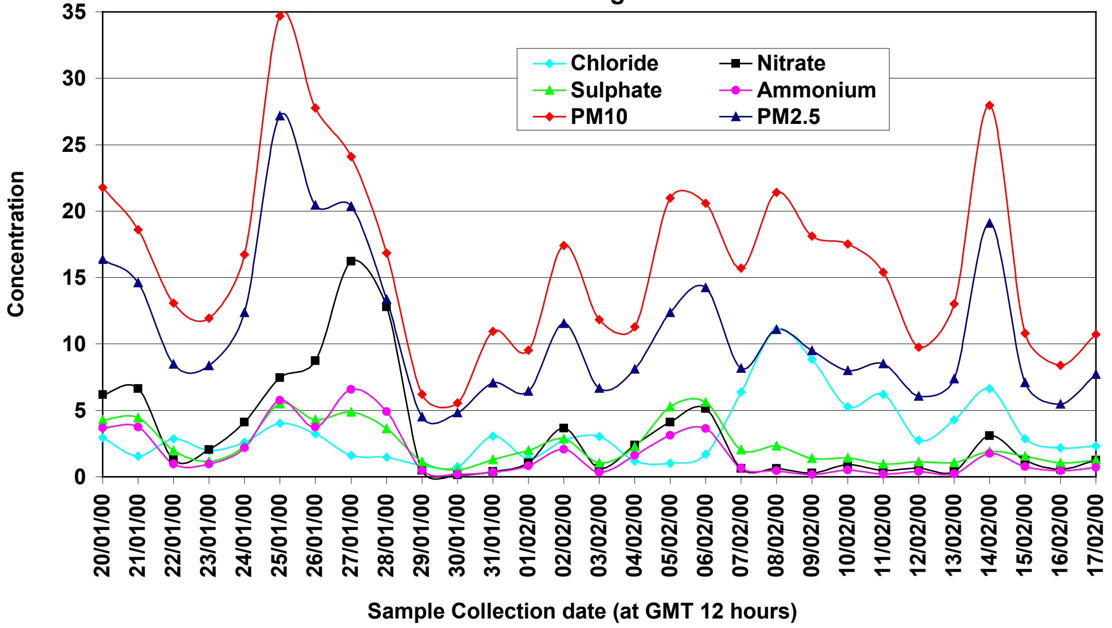


Figure 6.14c Daily average concentration from the winter PUMA campaign in Birmingham



Carbon measurements

Carbon measurements were also made during the winter campaign. The average elemental carbon concentrations are comparable to the summer results, however the average organic carbon concentrations are significantly less (Table 6.3), showing a ratio of OC/EC close to 1 (Figure 6.15).

The average PM_{10} composition in the winter period (Figure 6.16) indicated that the total of all measured species accounted for 91% of the PM_{10} mass from the TEOM, including 24% of carbonaceous and 67% of ionic materials. Clear differences between summer and winter were seen for most components. Significantly larger contributions of chloride (21%) and nitrate (20%) were observed in winter than in summer chloride (3%) and nitrate (13%). On the contrary, summer months showed much larger proportion of sulphate (21%) and organics (26%) comparing with the winter contribution of sulphate (15%) and organics (14%). The higher value of unmeasured component in summer is presumably due to re-suspension or wind blown dusts.

Table 6.3. Average concentrations (µg m^{-3}) of carbonaceous particles from the winter PUMA Campaign; 20/1/00 – 17/2/00

Fraction	OC	EC	TC	OC/EC (Range)
Coarse particles	0.19	0.22	0.41	0.84 (0.03 – 14.10)
Fine particles	1.46	1.47	2.93	0.99 (0.21 – 4.91)
PM_{10}	1.65	1.69	3.34	0.97 (0.40 – 2.67)

Figure 6.15 Daily measurements of organic and elemental carbon from the winter PUMA Campaign; 20/01/00 – 17/02/00

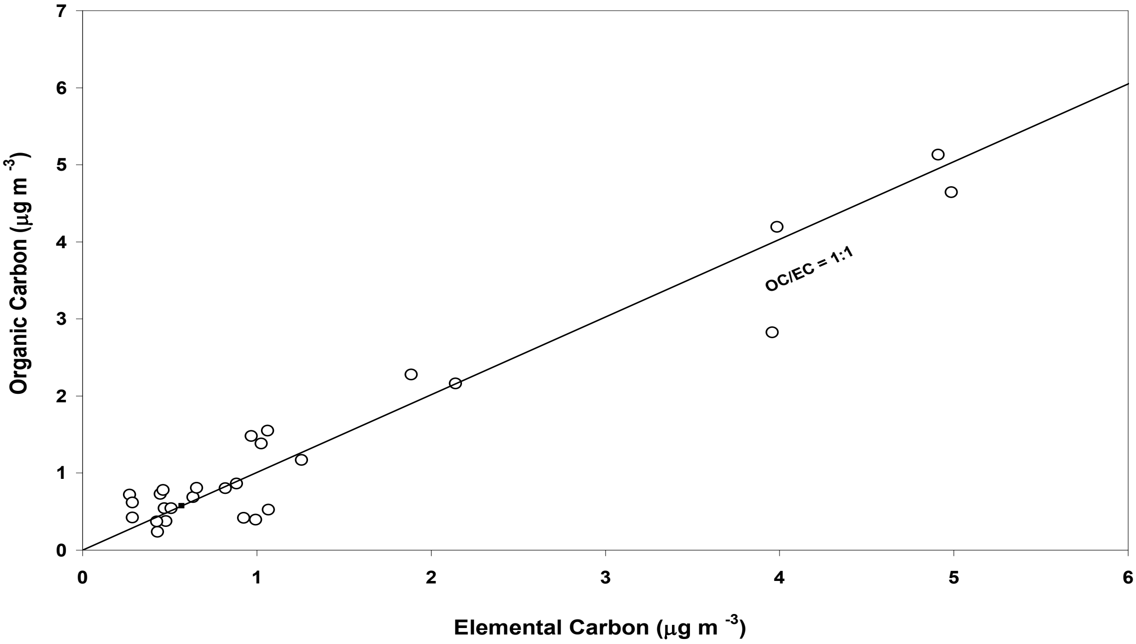
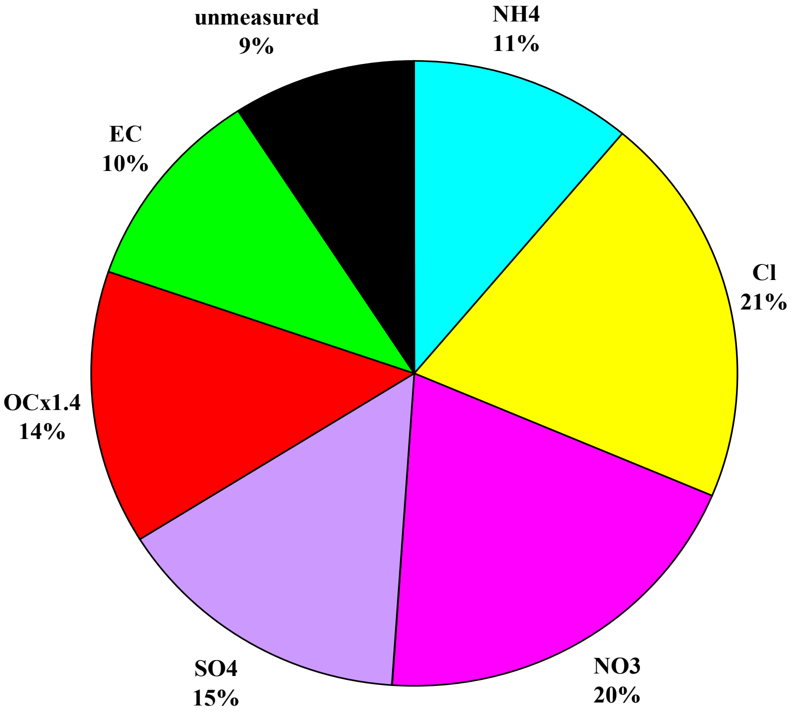


Figure 6.16. PM_{10} mean composition (%) from the winter PUMA Campaign; 20/01/00-17/02/00



6.3.2.3 Mass Closure Analyses at the PUMA Site

Mass closure analysis has been conducted for daily measurements including organic and elemental carbon measured with the dichotomous sampler, along with chloride, nitrate, sulphate and ammonium data as a combination from the Partisol and MOUDI. PM_{10}, $PM_{2.5}$ and coarse ($PM_{2.5-10}$) particle mass data were derived from the TEOMs, where $PM_{2.5}$ in summer was obtained as an average from West Bromwich, Springfield and Firtree around the West Midlands.

Initially, the 10 stage MOUDI impactor data were inverted, considering the daily mean flow rate, which influences the stage cut points and thus the particle mass. Then, the data was split into fine and coarse fractions for all components measured. Finally, the PM_{10} Partisol data was apportioned into fine and coarse fractions using the MOUDI proportions, and applied to the mass closure analyses for eliminating evaporative losses which may have affected the

MOUDI data. The organic material was obtained by applying a factor of 1.4 to the organic carbon fraction. Sea salt, NaCl was also derived considering the counter ion, Na^+.

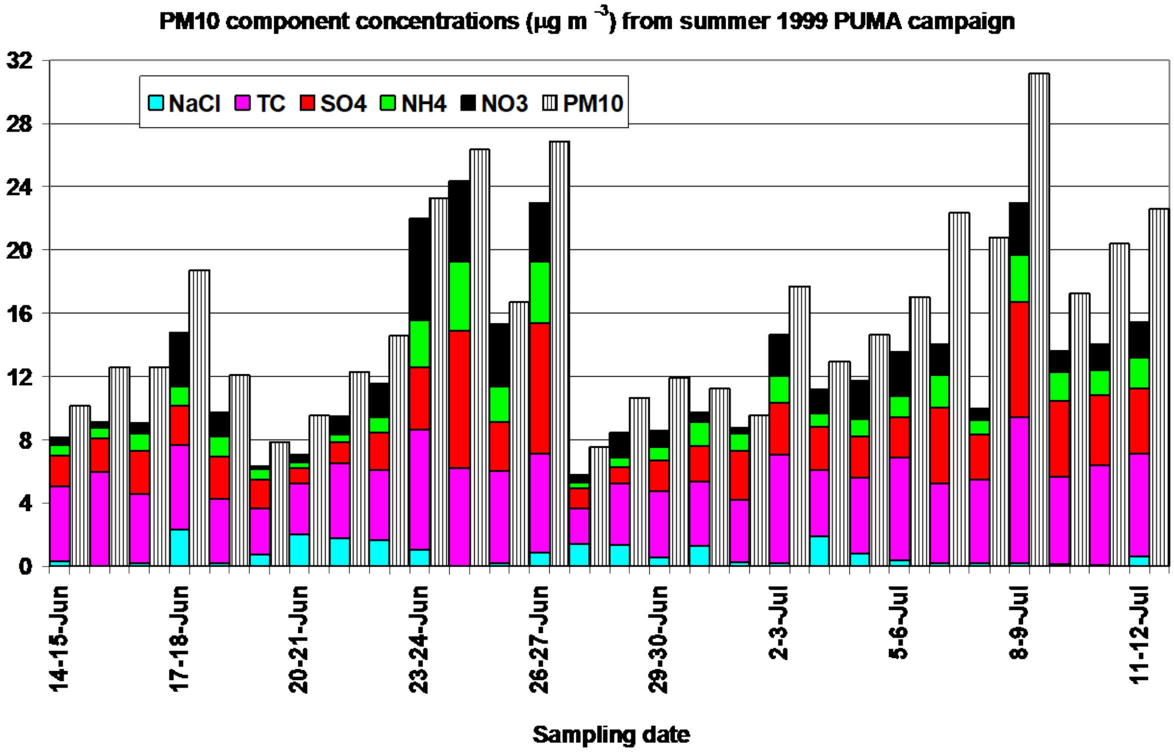
The sums of all components as defined above were compared with the particulate mass from the TEOM for PM_{10}, $PM_{2.5}$ and coarse fractions in both summer and winter periods, and the data is shown in Figure 6.17. Only ten days of data were analysed from the winter campaign due to fewer measurements with the MOUDI. Apart from the underestimation of the PM mass from the TEOM, both summer and winter campaigns showed better mass closure for the fine than the coarse fraction, largely due to unmeasured re-suspended materials. In the case of fine particles, winter mass closure is generally better than that in summer on average, mainly due to losses of ammonium nitrate or semi-volatile organic compounds especially on days with higher pollution levels. Losses of semi-volatile species may apply to both TEOM and MOUDI measurements when the weather is hot in summer, but less or no losses should occur from the MOUDI in winter due to cooler weather. On the 25-26th of January 2000, the $PM_{2.5}$ components were over estimated, which may have been solely due to the loss of NH_4NO_3 from the TEOM. In the case of coarse particles, better mass closure in winter than in summer is generally related to unmeasured particles due to re-suspension, and also to the loss of nitrate affected by weather conditions.

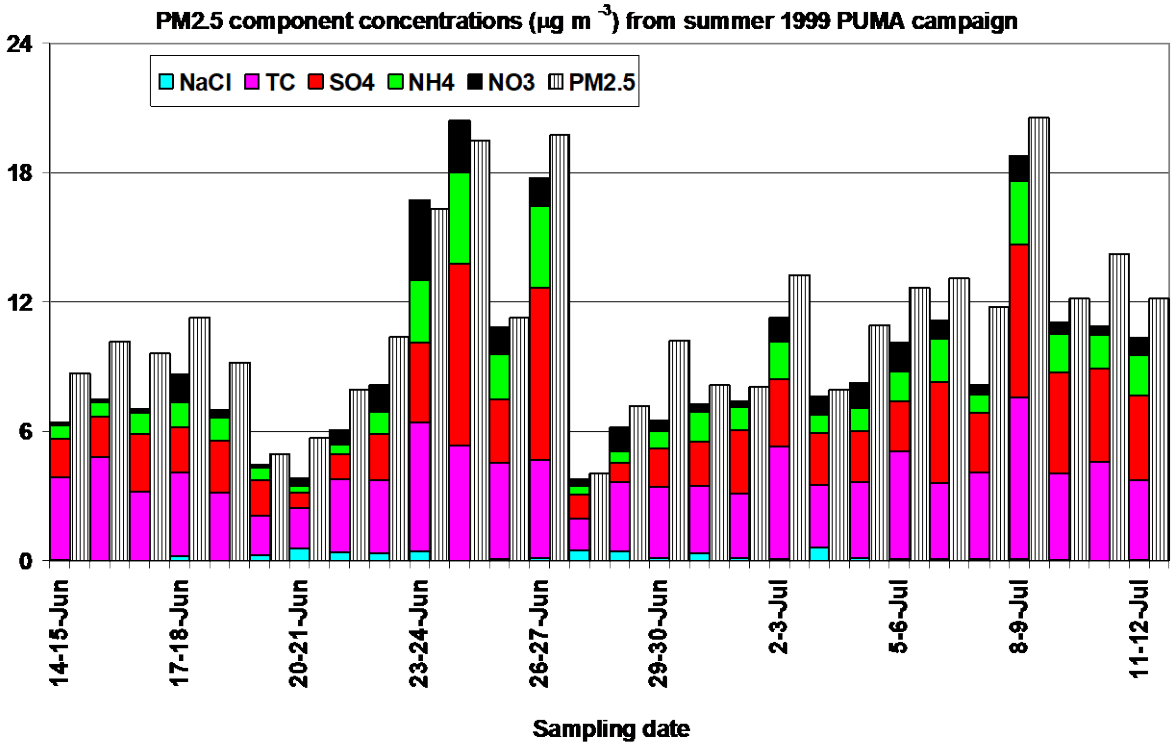
Table 6.4 shows averaged chemical compositions as percentages for $PM_{2.5}$ and coarse particles. In both campaigns, sulphate and ammonium are mainly present in the fine fraction, contributing 28% and 13% in summer, and 22% and 15% in winter. In the coarse fraction, sulphate only accounts for 4% in summer and 5% in winter, and ammonium accounts for 1% in both seasons. Nitrate was present in both fine and coarse fractions, with a higher contribution to the fine fraction in winter. Carbon materials were present mostly in the fine particles in winter contributed 27% to $PM_{2.5}$ and 8% to $PM_{2.5-10}$, whereas in the summer time the difference of contribution to the two fractions is smaller. NaCl is clearly found mostly in the coarse fraction in both seasons, but much higher concentrations were observed in the winter than in the summer period. The unexplained proportion is larger for coarse particles than for fine, and in summer than in winter largely due to re-suspended materials at the urban site. Higher unmeasured proportion of fine particles in summer than in winter may be associated with a loss of semi-volatile species in both the Partisol and MOUDI samplers during warm weather conditions.

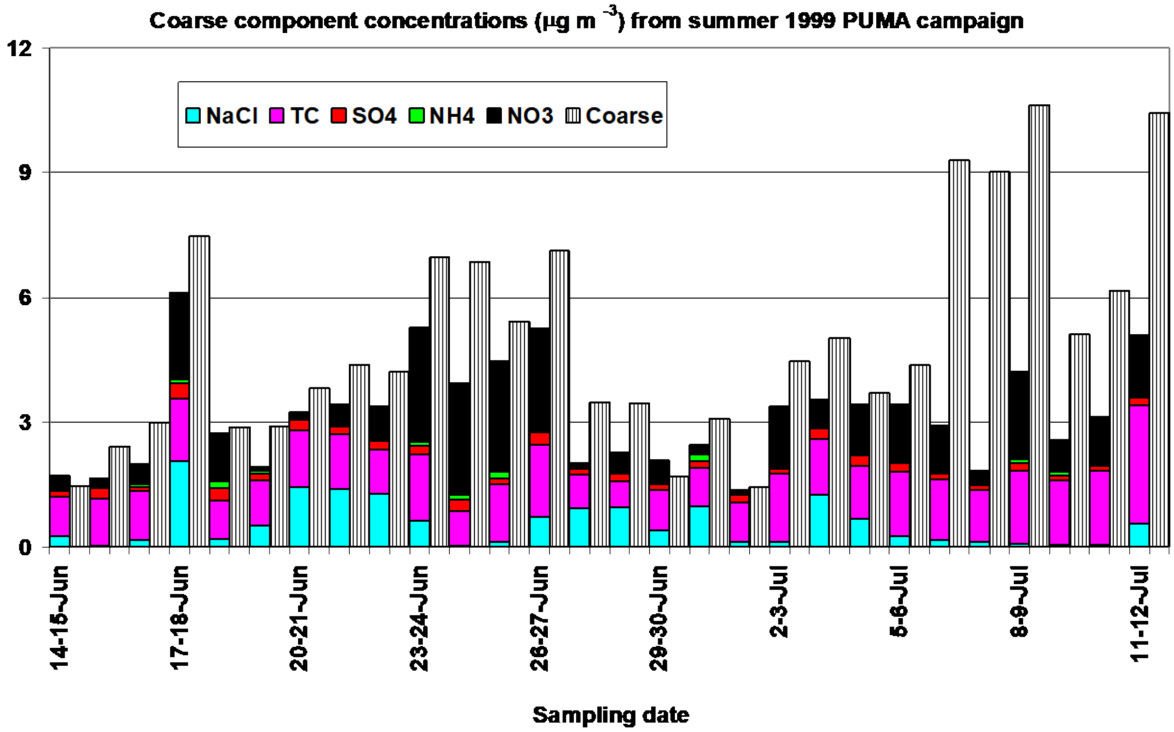
Table 6.4 Average chemical composition (%) from the PUMA site

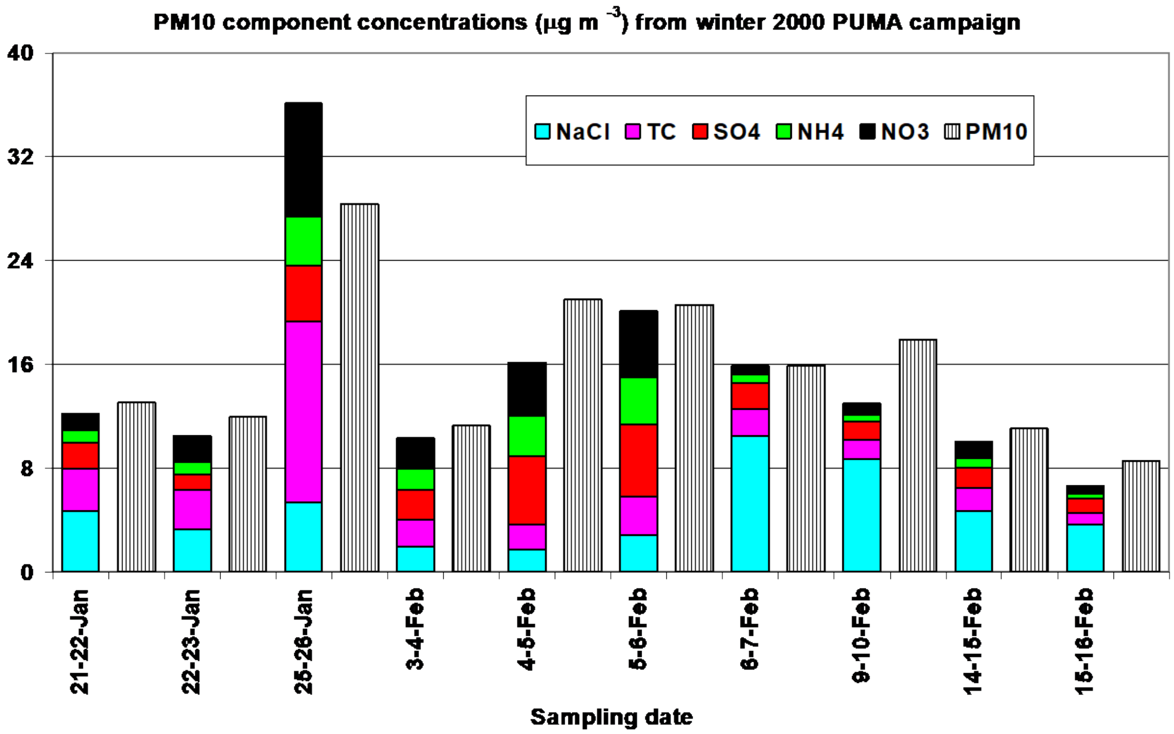
	NaCl	TC	SO_4	NH_4	NO_3	Other
Summer						
$PM_{2.5}$	2	35	28	13	8	16
Coarse	11	26	4	1	22	36
Winter						
$PM_{2.5}$	19	27	22	15	16	1
Coarse	53	8	5	1	21	13

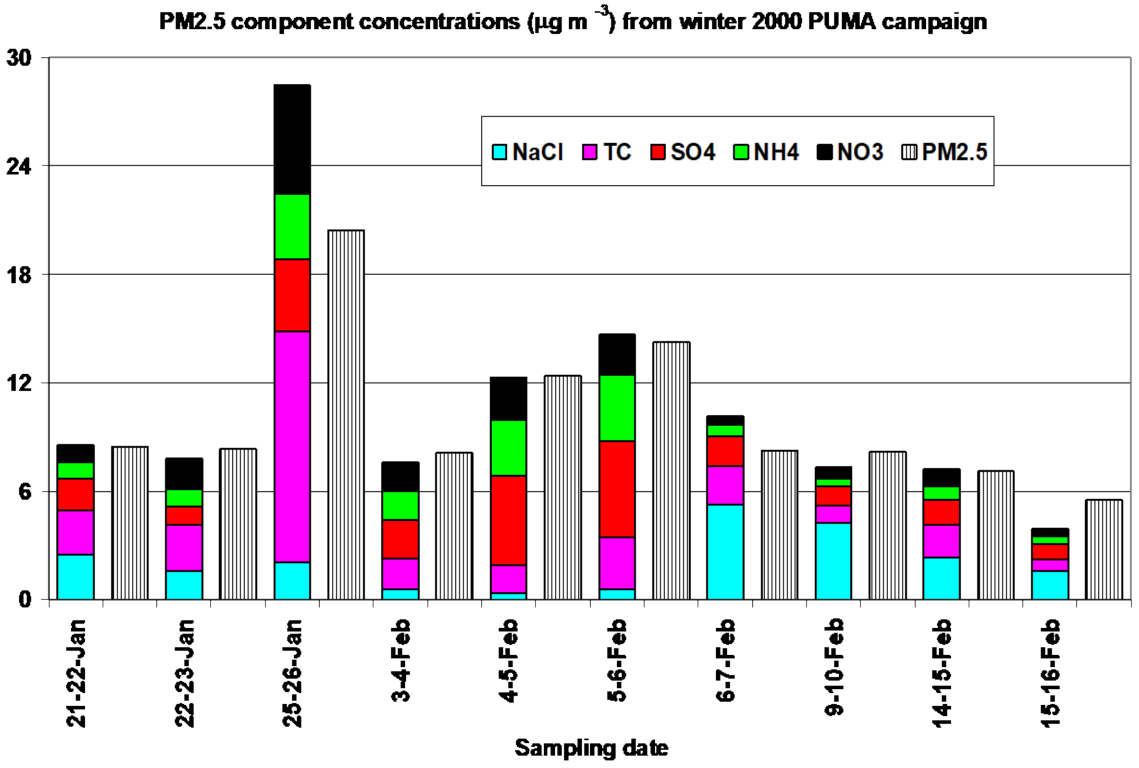
Figure 6.17 Mass closure at the PUMA site

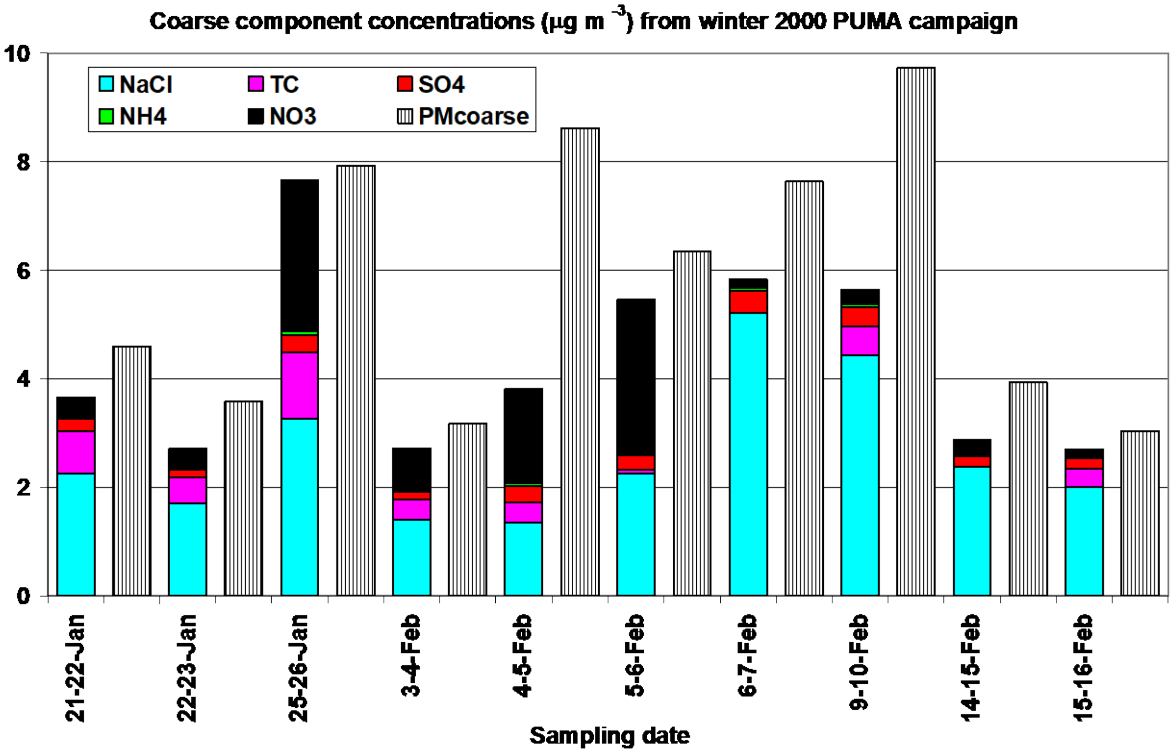



PM2.5 component concentrations (µg m $^{-3}$) from summer 1999 PUMA campaign


Coarse component concentrations (µg m $^{-3}$) from summer 1999 PUMA campaign


PM10 component concentrations (µg m -3) from winter 2000 PUMA campaign
40
32
24
16
8
0
NaCl
TC
SO4
NH4
NO3
PM10
21-22-Jan
22-23-Jan
25-26-Jan
3-4-Feb
4-5-Feb
5-6-Feb
6-7-Feb
9-10-Feb
14-15-Feb
15-16-Feb
Sampling date


PM2.5 component concentrations (µg m -3) from winter 2000 PUMA campaign
30
24
18
12
6
0
NaCl
TC
SO4
NH4
NO3
PM2.5
21-22-Jan
22-23-Jan
25-26-Jan
3-4-Feb
4-5-Feb
5-6-Feb
6-7-Feb
9-10-Feb
14-15-Feb
15-16-Feb
Sampling date



6.3.3 Conclusions from Birmingham Data

The Birmingham air sampling was less focussed on episodic periods than that from Harwell and was also more representative of an urban location. The data do not give clear indication of whether nitrate influenced PM_{10} measured by the TEOM in the same way as the rural site, although there are suggestions in the trends that it did not do so, presumably due to the usual volatilisation problems. The total ionic components represent less proportion of PM_{10} mass in comparison with the data from the rural site, which is typical of the central urban situation within the UK. Emissions from local sources such as road traffic, re-suspension and windblown dusts account for a significant proportion of the PM_{10} mass, although easterly air masses are also related to higher concentration levels.

In summer, 82% of the PM_{10} mass was explained including 36% of carbonaceous materials (26% of OC and 10% of EC), 21% of sulphate, 13% of nitrate, 9% of ammonium and 3% of chloride. 91% of PM_{10} in winter was measured consisting of 24% of total carbon (14% of OC and 10% of EC), 21% of chloride, 20% of nitrate, 15% of sulphate and 11% of ammonium. Much higher proportions of OC, sulphate and unexplained materials were observed in summer than in winter, indicating that summer time favours the secondary formation of organic compounds and sulphate by gas-to-particle conversion, and also the re-suspension of dust. On the other hand lower contributions from nitrate and chloride were found in summer than in winter. Nitrate as a cooler product (Dolislager and Motallebi, 1999; Motallebi, 1999) is more likely produced by the transformation of gaseous precursor pollutant to secondary aerosol through aqueous-phase oxidation during the winter period (Brauer et al., 1995). The higher chloride proportion in winter-time is clearly due to road salt. Harrison and Allen (1990) also found that chloride concentrations were 3 times higher in winter than in the summer period in Essex.

Mass closure covering the components NaCl, TC, SO_4^{2-}, NO_3^- and NH_4^+ was performed separately for fine and coarse particles at the PUMA site using a combination of data from the Partisol and MOUDI instruments. The result shows better mass closure in winter than in summer and for $PM_{2.5}$ than for coarse particles. The averaged chemical composition shows different characteristics of source strength for different size fractions in different seasons. 94% of the sulphate in summer and 91% in winter is present in the fine particles, which is close to that measured in Leeds in 1982 (85%) for both urban and rural sites (Clarke et al., 1984). The contribution of SO_4^{2-} to $PM_{2.5}$ composition (28% in summer and 22% in winter) is also similar to the typical UK urban fine composition of 25% of sulphate summarised by Harrison and Jones (1995). Ammonium is almost entirely present in $PM_{2.5}$ in both summer and winter periods, consistent with the previous results (Clarke et al., 1984; Harrison and Pio, 1983). 64% of nitrate appeared to be in the fine fraction in winter, which is close to the percentage of 61% and 68% found in Leeds, but only 32% of NO_3^- was found to be in the fine particles in summer time. Chloride, mostly in the form of NaCl, has a higher contribution to coarse than to fine particles, and in winter than in summer month. The total carbonaceous material is mostly in the fine particle form (75% in summer and 88% in winter). 63% of TC is in organic form in summer, which is within the range found in previous work (60-80%) (Harrison and Jones 1995), but during the winter campaign only 49% of OC was found.

CHAPTER 7

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

7.1 General Conclusions

Long-term continuous measurements of PM_{10}, $PM_{2.5}$ mass, particle count and particle size distributions have been conducted at two urban sites, London Marylebone Road (LM) and London Bloomsbury (LB), two rural sites, Rochester (RO – mass only) and Harwell (HAR) in the UK atmosphere. Data for gaseous pollutants, NO_x, CO, SO_2 and O_3 were adopted from the Automatic Urban and Rural Network data archive to assist the data analyses. Meteorological data, wind speeds and wind direction for the London sites were originated from the London Weather Centre, whereas the rural site measurements were made on site. In addition, hourly measurement of PM_{10} chemical species SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- was made at Harwell on a campaign basis during both air pollution episodes and non-episodes when the site was influenced with different air masses. Chemical data including the major ions, organic (OC) and elemental carbon (EC) were also obtained from campaigns in Birmingham, and comparison between rural and urban locations was made. PM_{10}, $PM_{2.5}$ mass and the wind data from the Birmingham Hodge Hill (HH) site were also used in the study for assessing the relationship between the particle mass and wind speeds. A considerable volume of data has been generated from both the long-term and the short-term measurements, and a detailed examination has been made. Results have been used for a better understanding of the nature of both particulate mass and numbers in different backgrounds in the UK atmosphere. It provides a resource for the government in the UK to set, monitor and enforce air quality policy, as well as for those engaged in research into the medical aspects of particles.

1. Spatial and Temporal Variations in Particle Mass, Number and Gaseous Pollutant Concentrations at the Four DETR Sites

According to both long and short-term averages, the concentrations of particle mass, particle number and gaseous pollutants appeared to be in the order of LM>LB>RO>HAR over a two year and seven month period. The increments in the PM_{10}, $PM_{2.5}$ and the coarse particle mass between LM and LB were 11.9, 6.4 and 5.5 $\mu g\ m^{-3}$, respectively, indicating that both fine and coarse particle concentrations were elevated at the roadside site due to mainly traffic activities. The two rural sites showed much lower but similar concentration levels due to the least influences from local sources, which is clearly marked by the larger differences in the NO_x and CO concentrations between sites. Consistent with NO_x and CO, larger ratios were observed in particle numbers than particle mass between LM, LB and HAR confirming that particle number is a better metric for evaluating vehicle exhaust emissions.

Whilst there was a little seasonal dependence for particle mass and numbers within each site, broadly similar seasonal variations in the particle mass at LB, RO and HAR sites suggested that synoptic factors are important in affecting the advection of polluted air masses. Generally consistent seasonal variations were observed in CO and NO_x concentrations showing higher levels in winter and autumn than in spring and summer. However higher SO_2 concentrations may occur at any seasons of the year. The temporal trend of particle numbers cannot be drawn from the monthly averages due to severe data losses at the London sites. There was no clear trend at Harwell although the data capture was higher.

Broadly similar diurnal variations appeared in PM_{10}, $PM_{2.5}$, particle count, CO and NO_x at the urban sites with a larger morning rush-hour peak and a smaller evening peak, indicative of the influence of vehicle exhaust emissions. CO showed a higher evening peak due to a shift of the vehicle type. Diurnal fluctuations were reduced at the rural sites due to the least influences from traffic. Coarse particles tended to increase around the middle of the day at all sites when both wind speeds and human activities were highest and similar pattern in SO_2 at the rural sites was likely related to the atmospheric stability.

2. Exceedences of the EPAQS and Characterisation of PM_{10} Episodes

The Expert Panel for Air Quality Standard (EPAQS) was most frequently exceeded at Marylebone Road, showing a minimum EPAQS count of 2069 during a two-year and sever-month period. PM_{10} emissions would have to be reduced by about 39% and 42% to achieve the target of the 99th percentile in compliance with the standard based on the whole period and a single year 1999 respectively. In London Bloomsbury the number of exceedences was significantly lower due to less traffic (EPAQS count: 391), whereas only small chances of exceedences existed in the rural sites Rochester (EPAQS count: 96) and Harwell (EPAQS count: 35).

The PM_{10} episodes were generally dominated by fine particles at all sites, but the contribution of coarse particles was also significant at the urban roadside. Coarse particles tend to dominate the PM_{10} when its concentrations were over 100 µg m^{-3}. Fine particle dominated PM_{10} episodes were generally due to either primary emissions from local sources like traffic or long-range transport, or secondary pollutants formed locally or transported from a long distance (e.g. continental Europe).

3. **Correlations for Particle Mass, Particle Number and Gaseous pollutants**

Whilst strong relationships have always been observed between PM_{10} and $PM_{2.5}$, the correlations between particle number and PM_{10} or $PM_{2.5}$ mass were found to vary considerably with sites and seasons, i.e. better correlations at urban than at rural and in winter than in summer periods. The strong correlations at the urban sites in winter may cause confusion for epidemiological studies in differentiating between particle mass and particle number as a causal agent on adverse health outcomes. However, poor correlations in other seasons indicate that the two metrics are clearly distinguished. In contrast, only modest or weak correlation was found at the rural site, while stronger relationships were observed between the two mass fractions.

The correlations between both particle mass and number with NO_x and CO were higher at urban than at rural site, reflecting the influences of traffic on both mass and numbers. However, particle number correlates more strongly with NO_x and CO than particle mass, particularly at Marylebone Road, confirming that ultrafine particles are a better tracer for vehicle exhaust emissions. Strong or very strong correlations were observed at urban sites for PM_{10}, $PM_{2.5}$ and particle count with NO_x and CO in winter and autumn seasons, whereas most of the summer and spring months appeared to have only modest or weak relationship. The less evidence of the primary vehicle exhaust emissions in the summer than in the winter data was due to a better dispersion or a shift in pollution sources from vehicle exhaust emissions to secondary formation or re-suspended dusts. SO_2 exhibited mostly modest or weak relationship to particle mass and numbers.

Even stronger correlations were observed between the hourly traffic increment concentrations (LM-LB) for particle mass (PM_{10} and $PM_{2.5}$) and number, and for particle mass and number with NO_x and CO. These results confirm that road traffic as a major pollution source at Marylebone Road has dominated the particle concentrations in both mass and numbers, particularly during the winter periods. However traffic volume showed positive but relatively weak relationships with particle mass, NO_x and CO at LM. The diurnal traffic count showed a marked difference between the two groups of vehicles indicating a clear larger evening peak in petrol vehicles, which explains the abnormal diurnal behaviour of CO and its weaker correlation to particle concentrations than $NO_{x.}$

4. Particle Concentrations and Wind Speeds

The relationships between particle mass and wind speeds were examined using data from the Birmingham, Hodge Hill and the four DETR (the Department of the Environment, Transport and the Regions) sites. Fine particle concentrations correlate inversely with wind speed due to a dilution effect. However, the influence of wind speed on coarse particle concentrations consists of both dilution and re-suspension. Seasonal estimation of coarse particle concentrations due to the re-suspension effect at various wind speeds has been made showing that higher wind speeds were associated with increasing coarse particle concentrations. The estimates of re-suspended coarse particles were higher in summer when the process was favoured by the hotter and drier climate, and higher also at the three urban sites than at the two rural sites indicating that human activities were also responsible for the re-suspension process. The data also shows a consistent weekday/weekend and day/night pattern, especially apparent at the urban sites.

5. Characterisation of Particle Size Distributions at the LM, LB and Harwell Sites

The particle size distributions have been calculated as daily, monthly and seasonal means. Clear diurnal trends in both particle count and size have been observed from the two London sites, highly reflective of the road traffic influence. The monthly average particle number mode diameter is small at LM in the range 24.6-32.8 nm, reflecting particles directly emitted from the vehicle exhaust. Slightly larger average number mode diameters (26.4-50.5 nm) were recorded at LB, indicating a coarser background aerosol due to less and more distant traffic. In comparison, the rural site Harwell shows no consistent diurnal patterns relative to the traffic and wide variations in the number mode diameters (15-104 nm). The traffic increment (LM-LB) in the size distributions showed an even smaller number mode diameter, around 20-30 nm. Clear weekday/weekend variations were also recorded at the two London sites. The major features are a higher particle count on weekdays than on weekends and a delayed, smaller morning number peak and a late evening or night-time peak on weekends reflective of human activities.

Generally at Harwell, winter and autumn months tended to show particle number peaks in the early evening or late at night with particle sizes relatively coarse at 80-100 nm, reflecting advected or aged aerosol in the accumulation mode. However, the summer and spring months showed strong evidence of new particle formation through homogeneous nucleation processes, often characterised by an increase in very fine particle numbers at midday or in the early afternoon, with a steady increase in the modal diameter.

6. Temporal Variation of Chemical Species and Their Relationship to Particle Mass at the Harwell and Birmingham Sites

- **At Harwell**

Hourly PM_{10}, particulate sulphate, nitrate, ammonium and chloride concentrations were measured at the rural Harwell site, covering diverse atmospheric conditions in different seasons and with varied air mass origins. In general, higher concentrations were mainly affected by air masses transported from either continental Europe or the nearby cities particularly the London conurbation.

A notable feature has been the ability of the atmosphere to generate extremely high nocturnal nitrate concentrations anti-correlated strongly with ozone, which shows its typical afternoon maximum. A strong tendency for high nitrate concentrations was associated with air masses of easterly origins (June 1998, September 1998 and September 1999). However, the period of Jan-Feb 1999 showed higher nighttime nitrate peak associated with westerly wind, which was likely related to air masses from Bristol or the Midlands. The often better correlation between nitrate and NO_x during high nitrate peaks from this study is strongly suggestive of a rather local and rapid nocturnal formation of nitrate in the stable boundary layer. When there is an easterly wind, polluted air can be transported from London, or continental Europe, and results in the formation of ammonium nitrate from NO_x and NH_3, emitted in the urban and surrounding agricultural area, during transport to the site. The estimated maximum formation rate at night for total nitrate (NO_3^- + HNO_3) varied temporally and was largely controlled by both meteorological conditions and the levels of gaseous precursor pollutants. However, the results indicate that fast formation of nitrate can occur during the night under conditions of high humidity and stable atmosphere with low temperature, low wind speeds and low inversion layer down to typically about 100 metres. The concentrations of sulphate and ammonium were also higher during periods of easterly air-masses, whereas chloride only showed appreciable concentrations in the winter periods due to either a source of de-icing salt or sea salt when there is a higher westerly wind.

For most of the sampling periods the nitrate was mainly in the form of ammonium nitrate, shown from the correlation of the two species. However in Jan-Feb 1999 there was little association between the two, suggesting that the nitrate was present as sodium or calcium salts, which is supported by the results from the nitrate formation rate analyses. On the other hand, good correlation between sulphate and ammonium was observed during periods with westerly air masses (August98 and Jan-Feb99). PM_{10} measured with the TEOM (Tapered Element Oscillating Microbalance) correlated better with sulphate than with nitrate, and consisted of anything between about 15% and 60% of sulphate.

Another important feature was that during periods with polluted air masses, massive nitrate peak concentrations, determined by the Partisol instrument, went wholly unobserved by the TEOM. It confirms that the TEOM instruments provide lower concentrations of particulate matter than the Partisol, due to losses of semi-volatile species by heating up the aerosol to 50^0C. It also indicates that a huge difference in the particle mass concentrations between the two samplers can occur when very high levels of nitrate are present.

- **At Birmingham**

Whilst long-range transported air masses are the dominant pollution sources at the rural Harwell site, the Birmingham data is more representative of an urban location influenced by mainly local activities. The total ionic components represent a lower proportion of the PM_{10} mass in comparison with the data from the rural site. Emissions from local primary sources, such as road traffic and re-suspension of dust account for a significant proportion of PM_{10} mass although easterly air masses are also related to higher concentration levels.

In summer, the measured chemical components accounted for 82% of the TEOM PM_{10} mass, including 36% of carbonaceous materials (26% of OC and 10% of EC), 21% of sulphate, 13% of nitrate, 9% of ammonium and 3% of chloride. 91% of PM_{10} in winter was measured, consisting of 24% of total carbon (14% of OC and 10% of EC), 21% of chloride, 20% of nitrate, 15% of sulphate and 11% of ammonium. Much higher proportions of OC, sulphate and unexplained materials were observed in summer than in winter period, indicating that summer time favours the secondary formation of organic compounds and sulphate and the re-suspension of dust. On the other hand higher nitrate and chloride contribute the most in winter due to more production of nitrate and the presence of de-icing salt.

Mass closure, covering the components NaCl, TC (total carbon), SO_4^{2-}, NO_3^- and NH_4^+, has been performed for both fine and coarse fractions at the PUMA site, showing better closure in winter than in summer and for $PM_{2.5}$ than for coarse particles. The average chemical composition shows different characterisations of source strength for the two size fractions and for different seasons. The largest contribution to fine particles is TC in both summer and winter associated with local sources like traffic. Secondary sulphate is another significant source for the fine fractions. On the contrary, coarse particles consist of largely sodium chloride in winter, and both TC and the unexplained component (most likely re-suspended dusts) in summer.

7.2 Recommendations for Further Work

- The chemical measurement at the rural Harwell site has identified a frequent nocturnal formation of nitrate. However, the estimates of the maximum formation rate at night for total nitrate (NO_3^- + HNO_3) were not consistent with the measured particulate nitrate formation rates, which varied temporally and were largely controlled by both meteorological conditions and the levels of gaseous precursor pollutants. Measurements of other gaseous precursor pollutants such as NH_3 and HNO_3, as well as weather data including relative humidity and temperature at the same site, are recommended in future studies to aid interpretation of the data. More episodic measurements are also important including gravimetric analyses using the Partisol sampler in order to estimate how much particle mass is lost from the TEOM during high nitrate periods. In addition, measurements at another upwind rural site would be extremely useful to the above analyses, particularly in relation to pollution sources and its transportation aspect.

- It was difficult to identify the relationship between traffic volume and particle mass and number concentrations at Marylebone Road from the current data, presumably due to an influence of complex meteorology within the street canyon. Continuous on-site measurements of both wind and traffic data may be significant for elucidating the data.

- Whilst the production of ultrafine nuclei particles through homogeneous nucleation was identified at the rural site, evidence for this at the urban background site was small and did not exist at the roadside site. One of the considerations is that the Condensation Particle Counter (CPC) (Model 3022) used in this project was unable to measure particles smaller than 11 nm, therefore measurement with another CPC (Model 3025) to cover smaller particles would enable a more detailed investigation on the process of new particle formation. In addition, the rural site data also showed a nucleation mode during the night-time in winter and autumn seasons, which may be related to heterogeneous nucleation processes. High resolution chemical data, which was not available during this study, including secondary aerosol constituents, may throw light on the observed phenomena.

- The both strong and weak correlations between particle number and PM_{10} and $PM_{2.5}$ mass found in this study are likely to cause confusions for epidemiological studies in differentiating between the mass and particle numbers as a causal agent on adverse health outcomes. Further investigation on this issue using a larger data set is warranted.

REFFERENCES

Abbey DE, Nishino N, McDonnell WF, Burchette RJ, Knutsen SF, Beeson WL and Yang JX (1999) *Long-term inhalable particles and other air pollutants related to mortality in nonsmokers,* AM. J. Resp. Crit. Care Med., 159, 373-382.

Air Health (1996) *Particle numbers,* Air Health Strategy: September 1996, Information for Industry, London, UK.

Aldape F, Flores MJ, Díaz RV, Hernández-Méndez B, Montoya ZJM, Blanco EE, Fuentes AF and Torres-Martínez LM (1999) *PIXE analysis of airborne particulate matter from Monterrey, Mexico. A first survey,* Nucl. Instr. and Meth. B, 150, 439-444.

Allen AG, Grenfell JL, Harrison RM, James J and Evans MJ (1999) *Nanoparticle formation in marine airmasses: contrasting behaviour of the open ocean and coastal environments,* Atmos. Res., 51, 1-14.

Allen AG, Harrison RM and Erisman JW (1989) *Field measurements of the dissociation of ammonium nitrate and ammonium chloride aerosols*. Atmos. Environ., 23, 1591-1599.

Allen G, Sioutas C, Koutrakis P, Reiss R, Lurmann FW and Roberts PT (1997) *Evaluation of the TEOM method for measurement of ambient particulate mass in urban areas*, J. Air & Waste Manage. Assoc., 47, 682-689.

Andersen (1981) Instruction Manual, Series 244, Andersen Samplers Incorporated.

Anderson HR, Limb ES, Bland JM, Ponce de Leon A, Strachan DP and Bower JS (1995) *The health effects of an air pollution episode in London, December 1991.* Thorac, 50, 1188-1193.

Anderson HR, Ponce de Leon A, Bland JM, Bower JS and Strachan DP (1996) *Air pollution and daily mortality in London: 1987-1992*. British Medical Journal 312, 665-669.

APEG (1999) *Source Apportionment of Airborne Particulate Matter in the United Kingdom,* Report of the Airborne Particle Expert Group, DETR, UK.

Baumgard K and Johnson JH (1996) *The effect of fuel and engine design on diesel exhaust particle size distributions,* SAE Technical Paper 960131.

Birmili W and Wiedensohler A (2000) *New particle formation in the continental boundary layer: Meteorological and gas phase parameter influence,* Geophys. Res. Lett., 27, 3325-3328.

Birmili W, Wiedensohler A, Plass-Dülmer C and Berresheim H (2000) *Evolution of newly formed aerosol particles in the continental boundary layer: A case study including OH and* H_2SO_4 *measurements,* Geophys. Res. Lett., 27, 2205-2208.

Bower JS, Broughton GFJ, Stedman JR and Williams ML (1994) *A winter smog episode in the UK.* Atmospheric Environment 28, 461-476.

Bowman FM, Odum JR, Seinfeld JH and Pandis SN (1997) *Mathematical Model for Gas-Particle Partitioning of Secondary Organic Aerosols*, Atmos. Environ., 31, 3921-3931.
Brauer M, Dumyahn TS, Spengler JD, Gutschmidt K, Heinrich J and Wichmann HE (1995) *Measurements of acidic aerosol species in Eastern Europe: implications for air pollution epidemiology, Environ. Health Persp.,* 103, 482-488.

Braun-Fahrlander C, Ackermann-Liebrich U, Schwartz J, Gnehm HP, Rutishauser M and Wanner HU (1992) *Air Pollution and Respiratory Symptoms in Preschool Children*, Am. Rev. Respir. Dis., 145, 42-47.

Bremner SA, Anderson HR, Atkinson RW, McMichael AJ, Strachan DP, Bland JM and Bower JS (1999) *Short term associations between outdoor air pollution and mortality in London, 1992-4,* Occup. Environ. Med., 56, 237-244.

Brook JR, Dann TF and Burnett RT (1997) *The relationship among TSP, PM_{10}, $PM_{2.5}$, and inorganic constituents of atmospheric particulate matter at multiple Canadian locations*, J. Air & Waste Manage. Assoc., 47, 2-19.

Burton RM, Suh HH and Koutrakis P (1996) *Spatial Variation in Particulate Concentrations within Metropolitan Philadelphia,* Environ. Sci. Technol., 30, 400-407.

Butcher SS and Charlson RJ (1972) *An Introduction to Air Chemistry*, London: Academic Press.

Buzorius G, Hämeri K, Pekkanen J and Kulmala M (1999) *Spatial Variation of aerosol Number Concentration in Helsinki City,* Atmos. Environ., 33, 553-565.

Cass GR, Hughes LA, Bhave P, Kleeman MJ, Allen JO and Salmon LG (2000) *The chemical composition of atmospheric ultrafine particles,* Phil. Trans. R. Soc. Lond. A, 358, 2581-2592.

Castillejos M, Borja-Aburto VH, Dockery DW, Gold DR and Loomis D (2000) *Airborne coarse particles and mortality,* Inhal. Toxicol., 12, 61-72.

Castro LM, Pio CA, Harrison RM and Smith DJT (1999) *Carbonaceous Aerosol in Urban and Rural European Atmospheres: Estimation of Secondary Organic Carbon Concentrations,* Atmos. Environ., 33, 2771-2781.

CEC (Council of the European Communities) (1980) Council Directive 80/779/EEC: *Air quality limit values and guide values for sulphur dioxide and suspended particles,* O.J.L 229.

CEC (Council of the European Communities) (1996) Council Directive 96/62/EEC: *Ambient air quality assessment and management,* O.J. L 296.

CEC (Council of the European Communities) (1999) Council Directive 1999/30/EEC: *Limit values for sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air,* O.J. L 163.

Chan YC, Simpson RW, McTainsh GH, Vowles PD, Cohen DD and Bailey GM (1997) *Characterisation of Chemical Species in $PM_{2.5}$ and PM_{10} Aerosols in Brisbane, Australia*, Atmos. Environ., 31, 3773-3785.

Chow JC, Watson JG, Fujita EM, Lu Z and Lawson DR (1994) *Temporal and Spatial Variations of PM2.5 and PM10 Aerosol in the southern California Air Quality Study*, Atmos. Environ., 28, 2016-2080.
Chow JC, Watson JG, Lu Z, Lowenthal DH, Frazier CA, Solomon PA, Thuillier RH and Magliano K (1996b) *Descriptive Analysis of PM2.5 and PM10 at Regionally Representative Locations During SJVAQA/AUSPEX*, Atmos. Environ., 30, 2079-2112.

Cifuentes LA, Vega J, Kopfer K and Lava LB (2000) *Effect of the fine fraction of particulate matter versus the coarse mass and other pollutants on daily mortality in Santiago, Chile*, J. Air Waste Mgt. Assoc. 50, 1287-1298.

Clarke AG, Willison MJ and Zeki EM (1984) *A Comparison of Urban and Rural Aerosol Composition Using Dichotomous Samplers*, Atmos. Environ., 18, 1767-1775.

COMEAP (1995) *Health Effects of Non-Biological Particles*, Committee on the Medical Effects of Air Pollutants, Department of Health, UK.

Deacon AR, Derwent RG, Harrison RM, Middleton DR and Moorcroft S (1997) *Analysis and Interpretation of Measurements of Suspended Particulate Matter at Urban Background Sites in the United Kingdom,* Sci. Total Environ., 203, 17-36.

De Bock LS, Van Malderen H and Van Grieken RE (1994) *Individual aerosol particle composition variations in air masses crossing the North Sea,* Environ. Sci. Technol., 28, 1513-1520.

DETR (1997) *The United Kingdom National air quality strategy,* DETR, The Stationary Office, CM 3587.

DETR (1999) *Assistance with the review and assessment of PM_{10} concentrations in relation to the proposed EU stage 1 limit values*, HMSO, London.

Dionex (1997) *Installation instructions & troubleshooting guide for the Anion Self-regeneration Suppressor.*

Dockery DW and Pope CA (1994) *Acute respiratory effects of particulate air pollution,* Annual Review of Public Health, 15, 107-132.

Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG and Speizer FE (1993) *An Association Between Air Pollution and Mortality in Six US Cities*, N. Engl. J. Med., 329, 1753-1759.

DoE (1996) *An air quality strategy for the UK draft strategy for consultation,* Department of the Environment, UK.

DoH (1995) *Non-biological particles and health,* Department of Health, Committee on the Medical Effects of Air Pollutants.

Dolislager LJ and Motallebi N (1999) *Characterisation of particulate matter in California,* J. Air & Waste Manage. Assoc., 49, 45-56.

Donaldson K, Stone V, Gilmour PS, Brown DM and MacNee W (2000) *Ultrafine particles: mechanisms of lung injury,* Phil. Trans. R. Soc. Lond. A, 358, 2741-2749.

Dreher KL, Jaskot RH, Lehmann JR, Richards JH, McGee JK, Ghio AJ and Costa DL (1997) *Soluble transition metals mediate residual oil fly ash induced acute lung injury*, J. Toxicol. Environ. Hlth. 50, 285-305.

Edwards JD, Ogren JA, Weiss RE and Charlson RJ (1983) *Particulate air pollutants: a comparison of British "smoke" with optical absorption coefficient and elemental carbon concentration*, Atmos. Environ., 17, 2337-2341.

Eggleston S, Hackman MP, Heyes CA, Irwin JG, Timmis RJ and Williams ML (1992) *Trends in Urban Air Pollution in the United Kingdom during Recent Decades,* Atmos. Environ., 26B, 227-239.

Eldred RA, Cahill TA and Floccini RG (1997) *Composition of* $PM_{2.5}$ *and* PM_{10} *aerosols in the IMPROVE network,* J. Air & Waste Manag. Assoc., 47, 194-203.

EPAQS (1995) *Particles*, *Recommendation of the Expert Panel on Air Quality Standards,* HMSO, London, UK.

Erdman A, Israel GW and Ernst U (1993) *Comparative measurements of atmospheric elemental carbon using the British Black Smoke sampler and a thermal carbon analyser,* Staub 53, 187-191 (in German).

Ghio AJ, Stonehuerner J, Pritchard RJ, Piantadosi CA, Quigley DR, Dreher KL and Costa DL (1996). *Humic-like substances in air pollution particulates correlate with concentrations of transition metals and oxidant generation*. Inhal. Toxicol., 8, 479-494.

Green D, Fuller G and Barratt B (2001) *Evaluation of TEOM 'correction factors' for assessing the EU stage 1 limit values for* PM_{10}, Atmos. Environ., 35, 2589-2593.

Gustafsson MER and Franzen LG (2000) *Inland transport of marine aerosols in southern Sweden,* Atmos. Environ., 34, 313-325.

Harrison RM and Allen AG (1990) *Measurements of atmospheric* HNO_3, *HCl and associated species on a small network in Eastern England,* Atmos. Environ., 24, 369-376.

Harrison RM and Deacon AR (1998) *Spatial Correlation of Automatic Air Quality Monitoring at Urban Background Sites: Implications for Network Design,* Environmental Technol., 19, 121-132.

Harrison RM, Deacon AR, Jones MR and Appleby RS (1997b) *Sources and Processes Affecting Concentrations of PM10 and PM2.5 Particulate Matter in Birmingham (U.K.)*, Atmos. Environ., 31, 4103-4117.

Harrison RM and Jones MR (1995) *The Chemical Composition of Airborne Particles in the UK Atmosphere, Sci. Total Environ*., 168, 195-214.

Harrison RM, Jones MR and Collins G (1999a) *Measurements of the Physical Properties of Particles in the Urban Atmosphere*, Atmos. Environ., 33, 309-321.

Harrison RM and Kitto AMN (1992) *Estimation of the Rate Constant for the Reaction of Acid Sulphate Aerosol with NH_3 Gas from Atmospheric Measurements*, J. Atmos. Chem., 15, 133-143.

Harrison RM and Msibi IM (1994) *Validation of Techniques for Fast Response Measurement of HNO_3 and NH_3 and Determination of the $[NH_3][HNO_3]$ Concentration Product*, Atmos. Environ., 28, 247-255.

Harrison RM, Msibi IM, Kitto AMN and Yamulki S (1994) *Atmospheric chemical transformations of nitrogen compounds measured in the North Sea experiment*, Atmos. Environ., 28, 1593-1599.

Harrison RM, Peak JD and Msibi MI (1996) *Measurements of Airborne Particulate and Gaseous Sulphur and Nitrogen Species in the Area of the Azores, Atlantic Ocean,* Atmos. Environ., 30, 133-143.

Harrison RM. and Pio CA (1983) *Major ion chemical composition and chemical associations in inorganic atmospheric aerosols,* Environ. Sci. Technol., 17, 169-174.

Harrison RM and Pio CA (1983) *Size-differentiated composition of inorganic atmospheric aerosols of both marine and polluted continental origin,* Atmos. Environ., 17, 1733-1738.

Harrison RM, Shi JP and Jones MR (1999b) *Continuous Measurements of Aerosol Physical Properties in the Urban Atmosphere,* Atmos. Environ., 33, 1037-1047.

Harrison RM, Shi JP, Xi S, Khan A, Mark D, Kinnersley R and Yin J (2000) *Measurement of number, mass and size distribution of particles in the atmosphere,* Phil. Trans. R. Soc. Lond. A, 358, 2567-2580.

Harrison RM, Smith DJT, Pio CA and Castro LM (1997a) *Comparative Receptor Modelling Study of Airborne Particulate Pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan)*, Atmos. Environ., 31, 3309-3321.

Harrison RM and Yin J (2000) *Particulate matter in the atmosphere: which particle properties are important for its effects on health?* Sci. Total Environ., 249, 85-101.

Harrison RM, Yin J, Mark D, Stedman J, Appleby RS, Booker J and Moorcroft S (2001) *Studies of the coarse particle (2.5-10 μm) component in UK urban atmospheres,* Atmos. Environ., 35, 3667-3679.

Hoek G, Brunekreef B, Verhoeff A, Van Wijnen J and Fischer P (2000) *Daily mortality and air pollution in the Netherlands,* J. Air Waste Mgt. Assoc. 50, 1380-1389.

Hoek G, Forsberg B, Borowska M, Hlawiczka S, Vaskövi E, Welinder H, Branis M, Benes I, Kotesovec F, Hagen LO, Cyrys J, Jantunen M, Roemer W and Brunekreef B (1997) *Wintertime PM_{10} and black smoke concentrations across Europe: results from the peace study*, Atmos. Environ., 31, 3609-3622.

Hugh C, Williams PI, McFiggans G, Gallagher MW, Beswick KM, Bower KN and Choularton TW (2000) *Behavior of ultrafine particles in continental and marine air masses at a rural site in the United Kindom,* J. Geophys. Res., 105, 26891-26905.
Hughes LS, Cass GR, Gone J, Ames M and Olmez I (1998) *Physical and Chemical Characterization of Atmospheric Ultrafine Particles in the Los Angeles Area,* Environ. Sci. Technol., 32, 1153-1161.

ISO (1994) *Air quality – particle size fraction definitions for health-related sampling,* IS 7708, ISO, Geneva.

IUPAC (1997) *Summary of evaluated kinetic and photochemical data for atmospheric chemistry,* J. Phys. Chem. Ref. Data, 26, 1329-1499.

Jaenicke R (1993) *Tropospheric aerosols,* In Hobbs PV (ed): Aerosol-Cloud-Climate Interactions, Academic Press, New York.

Janssen NAH, Mansom KFMV, Jagt KVD, Harssema H and Hoek G (1997) *Mass Concentration and Elemental Composition of Airborne Particulate Matter at Street and Background Locations*, Atmos. Environ., 31, 1185-1193.

Jeffery GH, Bassett J, Mendham J and Denney RC (1989) Vogel's textbook of q*uantitative chemical analysis*. John Wiley & Sons pp.197-215.

John W, Wall SM and Ondo J (1988) *A new method for nitric acid and nitrate aerosol measurement using the dichotomous sampler,* Atmos. Environ., 22, 1627-1635.

Jones MR (1996) *Physical and chemical properties of airborne particulate matter in Birmingham, UK,* PhD thesis, the University of Birmingham.

Kadowaki S (1976) *Size distribution of atmospheric total aerosol, sulfate, ammonium and nitrate particulate in the Nagoya area,* Atmos. Environ., 10, 39-43.

Kadowaki S (1977) *Size distribution and chemical composition of atmospheric particulate nitrate in the Nagoya area,* Atmos. Environ., 11, 671-675.

Kanbour FJ, Altai FA, Yassin S, Harrison RM and Kitto AMN (1990) *A comparison of smoke shade and gravimetric determination of suspended particulate matter in semi-arid climate (Baghdad, Iraq),* Atmos. Environ., 24A, 1297-1301.

Kaneyasu N, Ohta S and Murao N (1995) *Seasonal Variation in the chemical Composition of Atmospheric Aerosols and Gaseous Species in Sapporo, Japan*, Atmos. Environ., 29, 1559-1568.

Kao AS and Friedlander SK (1994) *Chemical Signatures of the Los Angeles Aerosol* ($dp < 3.5$ μm), Aerosol Sci. Technol., 21, 283-293.

King AM and Dorling S (1997) *PM_{10} Particulate Matter – The Significance of Ambient Levels,* in New Directions, Atmos. Environ., 31, 2379-2383.

Lam GCK, Leung DYC, Niewiadomski M, Pang SW, Lee AWF and Louie PKK (1999) *Street-level concentrations of nitrogen dioxide and suspended particulate matter in Hong Kong,* Atmos. Environ., 33, 1-11.

Landsberg HE (1981) *The Urban Climate,* Academic Press.
Li CS, Lin WH and Jenq FT (1993) *Characterisation of outdoor submicron particles and selected combustion sources of indoor particles,* Atmos. Environ., 27B, 413-424.

LRC (1997) *West Midlands Atmospheric Emissions Inventory,* London Research Centre, London, UK.

Malcolm AL, Derwent RG and Maryon RH (2000). *Modelling the long-range transport of secondary PM_{10} to the UK,* Atmos. Environ., 34, 881-894.

Malm WC, Sisler JF, Huffman D, Eldred RA and Cahill TA (1994) *Spatial and seasonal trends in particle concentration and optical extinction in the United States*, J. Geophys. Res., 99, 1346-1370.

Mamane Y and Gottlieb J (1992) *Nitrate formation on sea salt and mineral particles – a single particle approach,* Atmos. Environ., 26, 1763-1769.

Marti JJ, Weber RJ and McMurry PH (1997) *New particle formation at a remote continental site: assessing the contributions of SO_2 and organic precursors,* J. Geophys. Res., 102, 6331-6339.

Matthias-Maser S and Jaenicke R (1994) *Examination of atmospheric bioaerosol particles with radii > 0.2 μm,* J. Aerosol Sci., 25, 1605-1613.

Metcalfe SE, Whyatt JD and Derwent RG (1995) *A comparison of model and observed network estimates of sulphur deposition across Great Britain for 1990 and its likely source attribution,* Q. J. Royal Met. Soc., 121, 1387-1411.

Met Office (1996) *Personal communication*, Meteorological Office, 1996.

Miguel AG, Cass GR, Glovsky MM and Weiss J (1999) *Allergens in paved road dust and airborne particles,* Environ. Sci. Technol., 33, 4159-4168.

Morawska L, Thomas S, Bofinger D, Wainwright D and Neale D (1998) *Comprehensive characterisation of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants,* Atmos. Environ., 32, 2467-2478.

Morawska L, Thomas S, Bofinger N D, Neale D and Wainwright D (1996) *Characterisation of airborne particulate pollution,* 13th International Clean Air Conference Proceedings.

Morawska L, Thomas S, Gilbert D, Greenaway C and Rijnders E (1999a) *A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road,* Atmos. Environ., 33, 1261-1274.

Morawska L, Thomas S, Jamriska M and Johnson G (1999c) *The modality of particle size distributions of environmental aerosols,* Atmos. Environ., 33, 4401-4411.

Motallebi N (1999) *Wintertime PM2.5 and PM10 source apportionment at Sacramento, California,* J. Air & Waste Manage. Assoc., 49, 25-34.

Müller K (1999) *A three year study of aerosol in northwest Saxony (Germany),* Atmos. Environ., 33, 1679-1685.
Nicholson KW (1988) *A Review of Particle Resuspension,* Atmos. Environ., 22, 2639-2651.

Nicholson KW (1993) *wind tunnel experiments on the resuspension of particulate material,* Atmos. Environ., 27A, 181-188.

Oberdörster G (2001) *Pulmonary effects of inhaled ultrafine particles,* Int. Arch. Occ. Environ. Health, 74, 1-8.

O'Dowd C, McFiggans G, Creasey DJ, Pirjola L, Hoell C, Smith MH, Allan BJ, Plane JMC, Heard DE, Lee JD, Pilling MJ and Kulmala M (1999) *On the photochemical production of new particles in the coastal boundary layer,* Geophys. Res. Lett., 26, 1707-1710.

Olcese LE and Toselli BM (1998) *Statistical Analysis of PM_{10} Measurements in Cordoba City, Argentina,* Met. Atmos. Phys., 66, 123-130.

Pang Y, Ren Y, Obeidi F, Hastings R and Eatough DJ (2001) *Semi-volatile species in $PM_{2.5}$: Comparison of integrated and continuous samplers for $PM_{2.5}$ research or monitoring*, J. Air & Waste Manage. Assoc., 51, 25-36.

Pio CA and Harrison RM (1987a) *The equilibrium of ammonium chloride aerosol with gaseous hydrochloric acid and ammonia under tropospheric conditions,* Atmos. Environ., 21, 1243-1246.

Pio CA and Harrison RM (1987b) Vapour pressure *of ammonium chloride aerosol: effect of temperature and humidity,* Atmos. Environ., 21, 2711-2715.

Platt U and Heintz F (1994) *Nitrate radicals in tropospheric chemistry*, Israel, J. Chem., 34, 289-300.

Pope CA, Thunn MJ, Namboodiri MM, Dockery DW, Evans JS, Speizer FE, Heath CW (1995) *Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of US Adults*, Am. J. Respir. Crit. Care Med., 151, 669-674.

Qin Y, Chan CK and Chan LY (1997) *Characteristics of Chemical Compositions of Atmospheric Aerosols in Hong Kong: Spatial and Seasonal Distributions*, Sci. Total Environ., 206, 25-37.

QUARG (1993a) *Urban air quality in the United Kingdom,* First Report of the Quality of Urban Air Review Group, Department of the Environment, UK.

QUARG (1993b) *Diesel vehicle emissions and urban air quality*, The Second Report of the Quality of Urban Air Review Group, Department of the Environment, UK.

QUARG (1996*) Airborne Particulate Matter in the United Kingdom*, The Third Report of the Quality of Urban Air Review Group, Department of the Environment, UK.

Rajkumar WS and Chang AS (2000) *Suspended particulate matter concentrations along the East-West Corridor, Trinidad, West Indies,* Atmos. Environ., 34, 1181-1187.

Rapsomanikis S, Wake M, Kitto Amn and Harrison RM (1988) *Analysis of atmospheric ammonium and particulate ammonium by a sensitive fluorescence method,* Environ, Sci. Technol., 22, 948-952.

RCEP (1994) Royal Commission on Environmental Pollution, Eighteenth Report, Transport and the Environment, HMSO, UK.

Read et al (1994) *How vehicle pollution affects our health,* Editor Dr C. Read, Summary of papers presented at a symposium for the Ashden Trust, May 1994.

Reeve RN (1995) *Environmental Analysis – ACOL,* John Wiley & Sons, 76-82.

Röösli M, Theis G, Künzli N, Staehelin J, Mathys P, Oglesby L, Camenzind M and Braun-Fahrländer Ch (2001) *Temporal and spatial variation of the chemical composition of* PM_{10} *at urban and rural sites in the Basel area, Switzerland,* Atmos. Environ., 35, 3701-3713.

Roth M (1971) *Fluorescence reaction for amino acids,* Analytical Chem., 43, 880-882.

R & P (1997) Partisol - Plus Model 2025, Operating Manual. Rupprecht & Patashnick Co., Inc. USA.

Ruuskanen J, Tuch Th, Brink H Ten, Peters A, Khlystov A, Mirme A, Kos GPA, Brunekreef B, Wichmann HE, Buzorius G, Vallius M, Kreyling WG and Pekkanen J (2001) *Concentrations of ultrafine, fine and* $PM_{2.5}$ *particles in three European cities,* Atmos. Environ., 35, 3729-3738.

Salter LF and Parsons B (1999) *Field Trials of the TEOM (R) and Partisol for* PM_{10} *Monitoring in the St Austell China Clay Area, Cornwall, UK,* Atmos. Environ., 33, 2111-2114.

Schaug J, Pederson U, Skjelmoen JE and Kvalvagnes I (1994) *EMEP Data Report 1992***,** EMEP.

Schwartz J, Dockery DW and Neas LM (1996) *Is Daily Mortality Associated Specifically with Fine particles?* J. Air Waste Manage. Assoc., 46, 927-939.

Seaton A, MacNee W, Donaldson K and Godden D (1995) *Particulate Air Pollution and Acute Health Effects,* Lancet, 345, 176-178.

Sehmel GA (1980a) *Particle resuspension: A review*, Environ. Int., 4, 107-127.

Seinfeld JH and Pandis SN (1998) *Atmospheric chemistry and physics,* John Wiley & Sons, INC., New York.

Shi JP, Khan AA and Harrison RM (1999a) *Measurement of ultrafine particle concentrations and size distributions in urban air,* Sci. Total Environ., 235, 51-64.

Shi JP and Harrison RM (1999) *Investigation of ultrafine particle formation during diesel exhaust dilution*, Environ. Sci. Technol., 33, 3730-3736.

Shi JP, Harrison RM and Evans D (2001) *Comparison of ambient particle surface area measurement by epiphaniometer and SMPS/APS*, Atmos. Environ., 35, 6193-6200.

Shi JP, Harrison RM and Brear B (1999b) *Particle Size Distribution from a Modern Heavy Diesel Engine,* Sci. Total Environ., 235, 305-317.

Shi JP, Mark D and Harrison RM (2000) *Characterization of particles from a current technology heavy-duty diesel engine*, Envoron. Sci. Technol., 34, 748-755.

Smith DJT, Harrison RM, Luhana L, Pio CA, Castro LM, Tariq MN, Hayat S and Quraishi T (1996) *Concentrations of Particulate Airborne Polycyclic Aromatic Hydrocarbons and Metals Collected in Lahore, Pakistan*, Atmos. Environ., 30, 4031-4040.

Smith S, Stribley T, Barratt B and Perryman C (1997) *Determination for Partisol, TEOM, ACCU and cascade impactor instruments in the London Borough of Greenwich*, Clean Air, 27, 70-73.

Solomon PA, Salmon L, Fall T and Cass GR (1992) *The spatial and temporal distribution of atmospheric nitric acid and particulate nitrate concentrations in Los Angeles,* Environ. Sci. Technol., 26, 1594-1601.

Spengler JD, Brauer M and Koutrakis P (1990) *Acid air and health,* Environ. Sci. Technol., 24, 946-956.

Stedman JR (1997) *A U.K.-Wide Episode of Elevated Particle (PM_{10}) Concentration in March 1996,* in New Directions, Atmos. Environ., 31, 2381-2383.

Stelson AW and Seinfeld JH (1982a) *Relative humidity and temperature dependence of the ammonium nitrate dissociation constant,* Atmos. Environ., 16, 983-992.

Stelson AW and Seinfeld JH (1982b) *Relative humidity and pH dependence of the vapour pressure of ammonium nitrate-nitric acid solutions at 25°C,* Atmos. Environ., 16, 993-1000.

Suggs JC and Burton RM (1983) *Spatial characteristics of inhalable particles in the Philadelphia Metropolitan area,* JAPCA, J. Air & Waste Manage. Assoc., 33, 688-691.

Sweet CW and Gatz DF (1998) *Summary and analysis of available $PM_{2.5}$ measurements in Illinois,* Atoms. Environ., 32, 1129-1133.

Tarrason L and Tsyro S (1998) *Long-range transport of fine secondary particles as presently estimated by the EMEP Lagrangian model.* EMEP/Msc-W Note 2/98.

Tsai JH and Wu YL (1995) *Contributions of Road Dust Resuspension to the Airborne Particle Concentrations in Taipei,* Particul. Sci. Technol., 13, 55-67.

Tuch TH, Brand P, Wichmann HE and Heyder J (1997) *Variation of Particle Number and Mass Concentration in Various Size Ranges of Ambient Aerosols in Eastern Germany,* Atmos. Environ., 31, 4193-4197.

Ulrich E and Israel GW (1992) *Diesel soot measurements under traffic conditions,* J. Aerosol Sci., 23, S925-S928.

USEPA (1995a) *National air pollutant emission trends 1994*, Report number EPA-454/R-95-014, USEPA Office of Air Quality Planning and Standards, Research Triangle Park, NC, USA.
USEPA (1996) *Review of the Ambient Air Quality Standard for Particulate Matter: Policy Assessment of Scientific and Technical Information*, OAQPS Staff Paper, EPA-452/R-96-013, Research Triangle Park, North Carolina.

USEPA (1997) *National Ambient Air Quality Standards for Particulate Matter; Final Rule.* United States Environmental Protection Agency / 40 CFR Part 50, Federal Register 62, No. 138.

Van Borm WA, Adams FC and Maenhaut W (1989) *Characterisation of Individual Particles in the Antwerp Aerosol*, Atmos. Environ., 23, 1139-1151.

Van Der Zee SC, Hoek G, Harssema H and Brunekreef B (1998) *Characterization of particulate air pollution in urban and non-urban areas in the Netherlands*, Atmos. Environ., 32, 3717-3729.

Vasconcelos LAD, Macias ES and White WH (1994) *Aerosol composition as a function of haze and humidity levels in the southwestern US,* Atmos. Environ., 28, 3679-3691.

Vedal S (1997) *Ambient particles and health: Lines that divide*, J. Air & Waste Manage. Assoc., 47, 551-581.

Wall SM, John W and Ondo JL (1988) *Measurement of aerosol size distributions for nitrate and major ionic species,* Atmos. Environ. 22, 1649-1656.

Waller RE (1967) *Studies on the nature of air pollution,* London Conference on Museum Climatology, International Institute for Renovation of Works of Art, 65-69.

Whitby K (1978) *The physical characteristics of sulphur aerosols,* Atmos. Environ., 12, 135.

Whitby KT, Clark WE, Marple VA, Sverdrup GM, Sem GJ, Willeke K, Liu BYH and Pui DYH (1975) *Characterisation of California aerosols – I. Size distributions of freeway aerosol,* Atmos. Environ., 9, 463-482.

Wichmann HE and Peters A (2000) *Epidemiological evidence of the effects of ultrafine particle exposure,* Phil. Trans. R. Soc. Lond. A, 358, 2751-2769.

Willeke K and Whitby KT (1975) *Atmospheric aerosols: size distribution interpretation,* J. Air Pollution Control Assoc., 25, 529-534.

Wilson WE and Suh HH (1997) *Fine particles and coarse particles: concentration relationships relevant to epidemiological studies*, J. Air & waste Manage. Assoc., 47, 1238-1249.

Zhang GF and Dasgupta PK (1989) *Fluorometric measurement of aqueous ammonium ion in a flow injection system,* Analyt. Chem., 61, 408-412.

APPENDIX A

AIR MASS BACK TRAJECTORIES AT THE HARWELL SITE

(Pressure height = 950 hPa)

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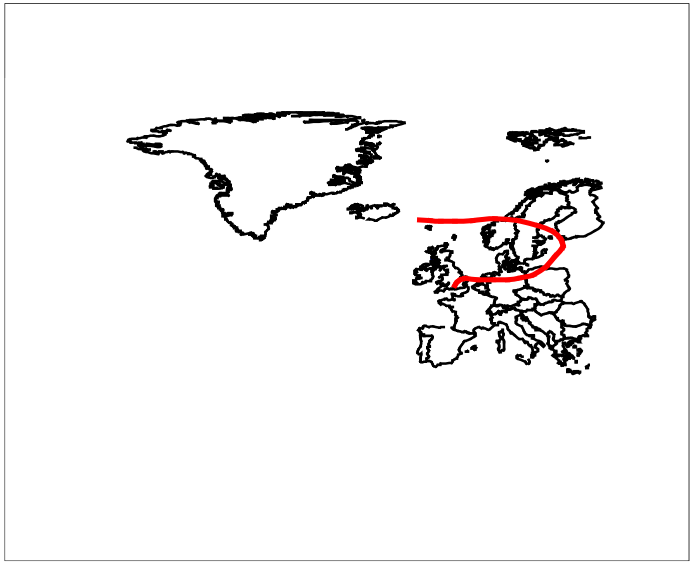

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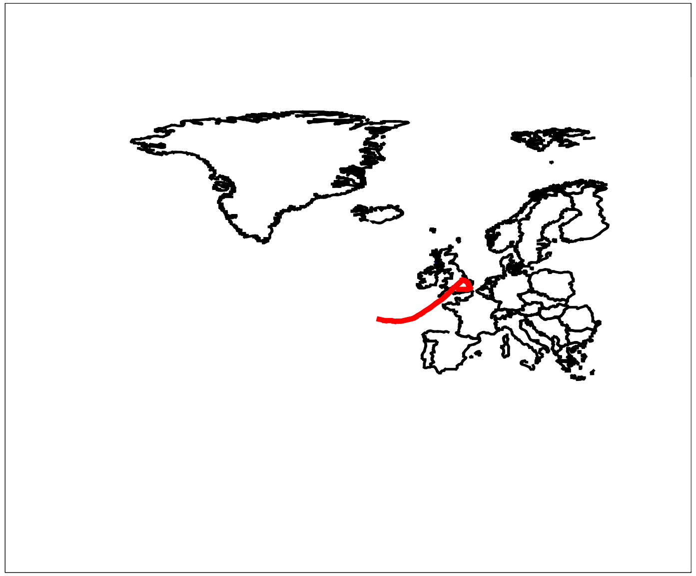

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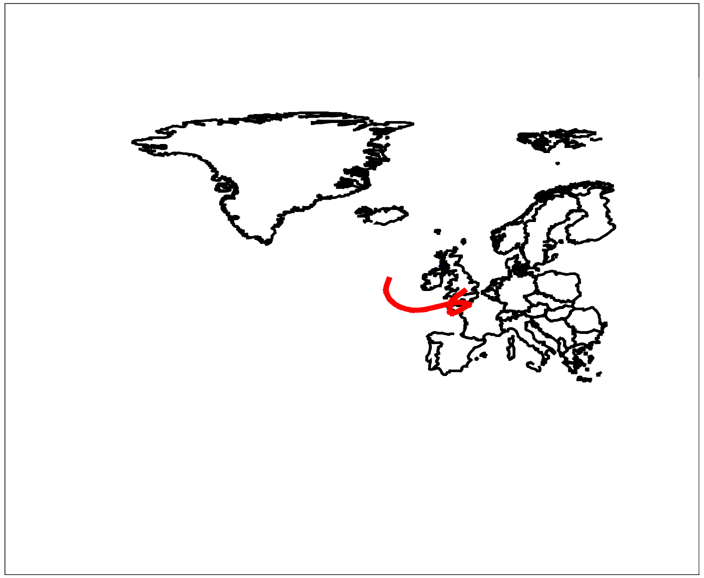

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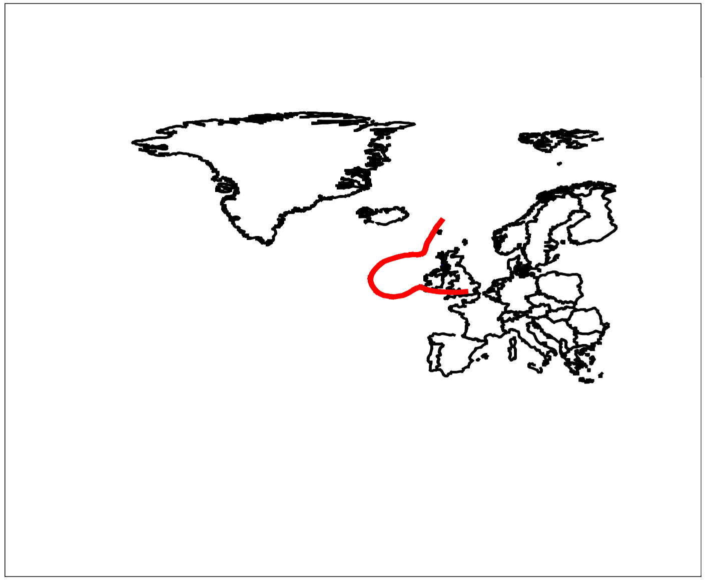

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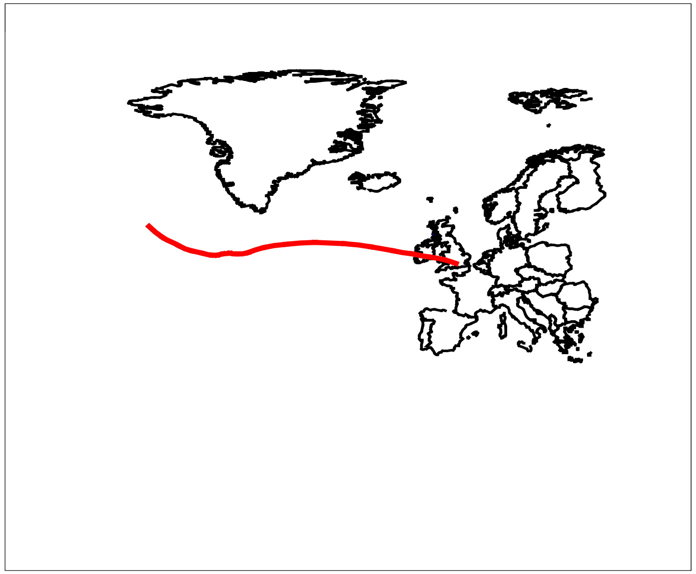

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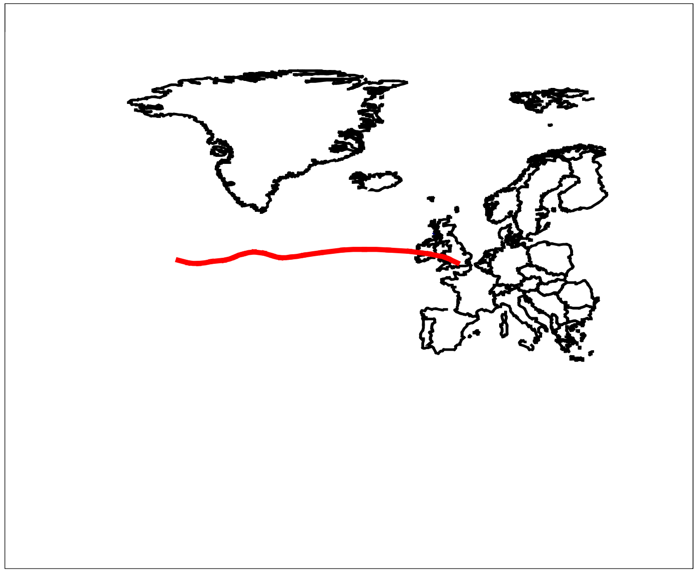

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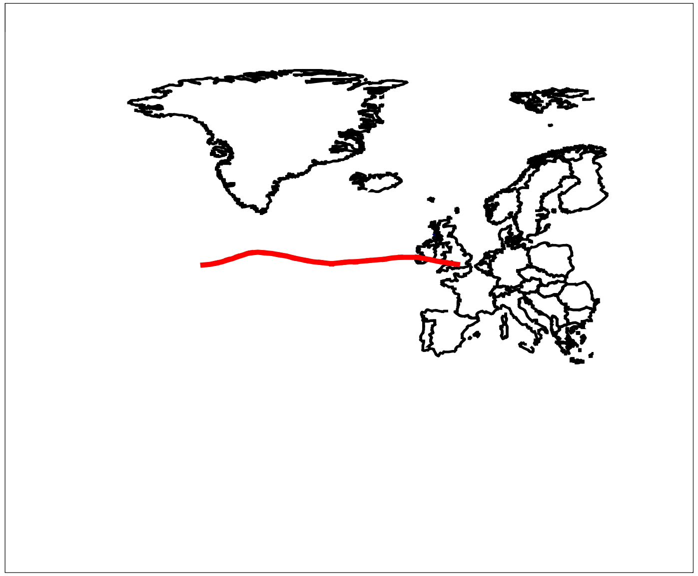

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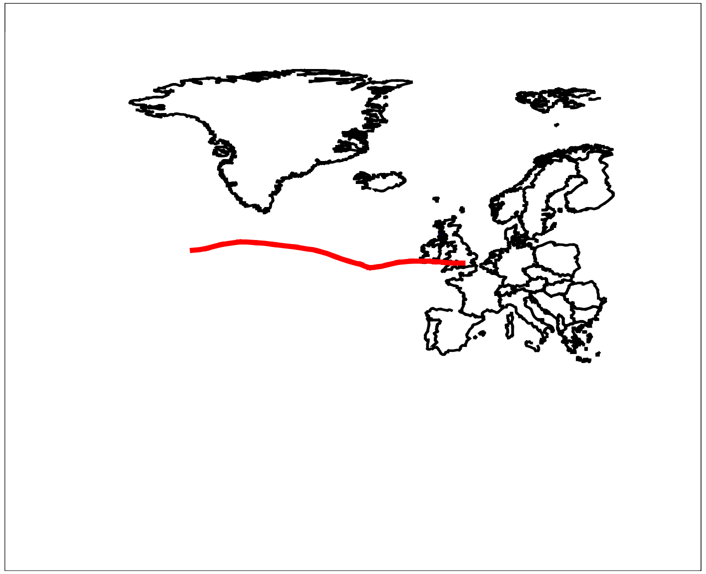

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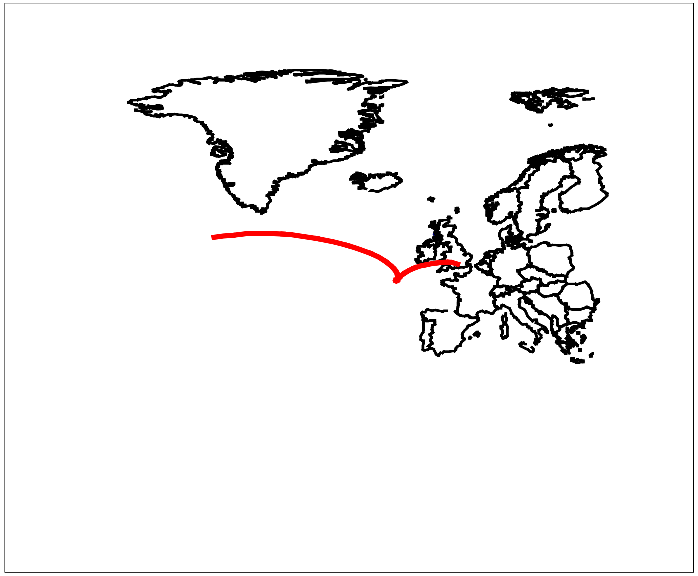

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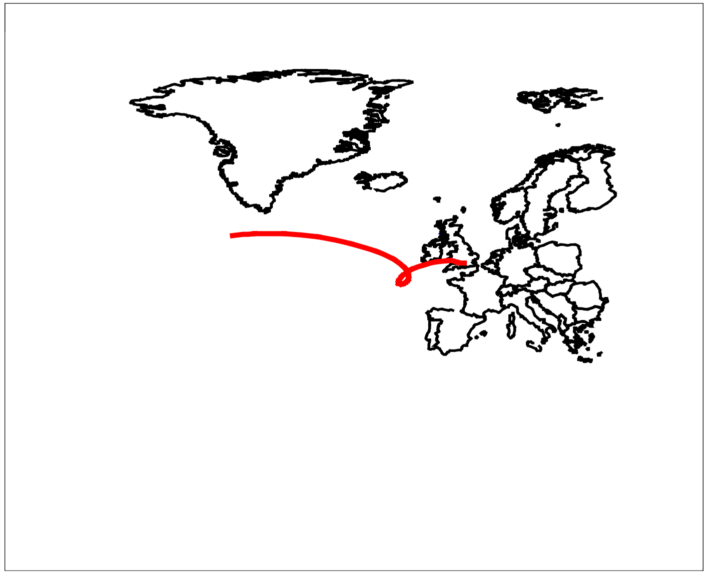

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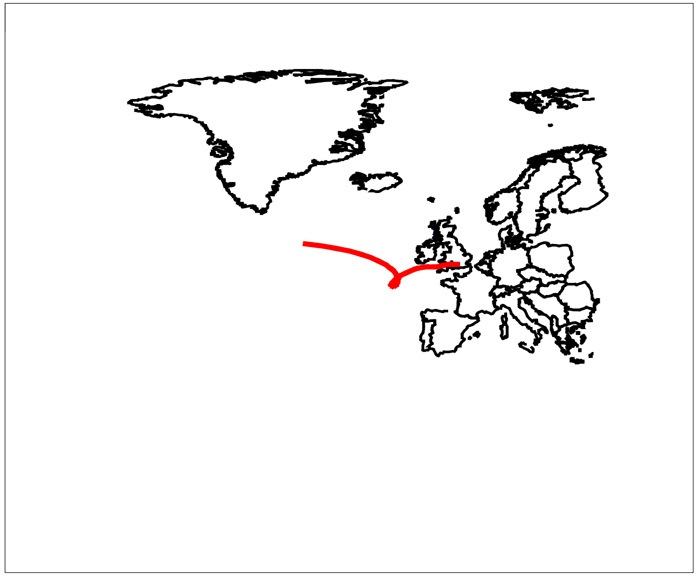

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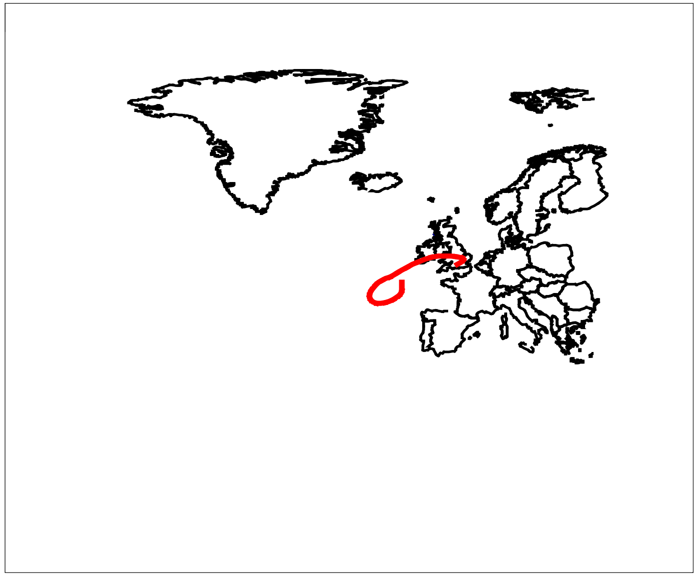

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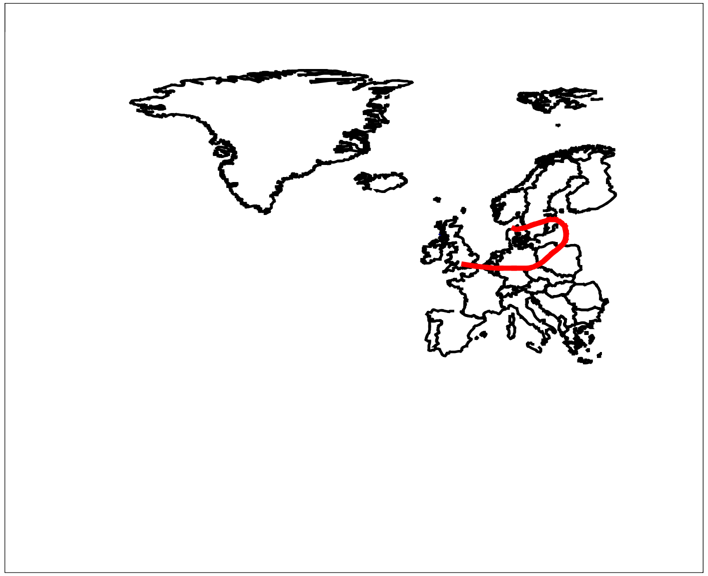

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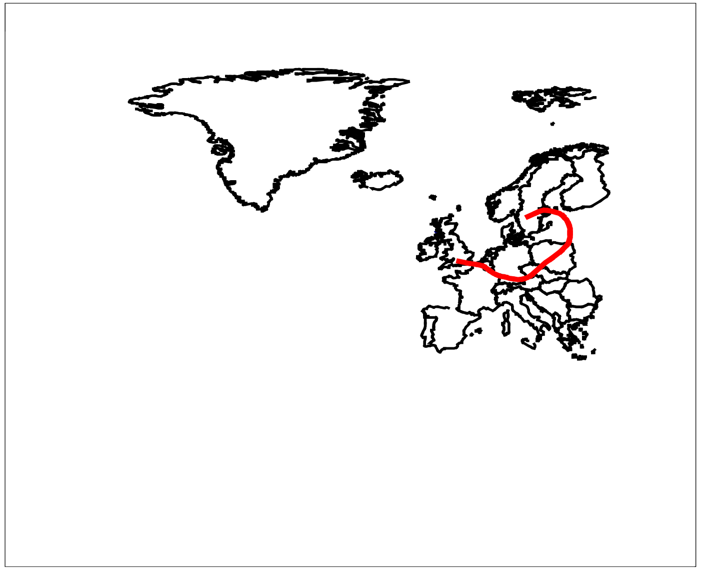

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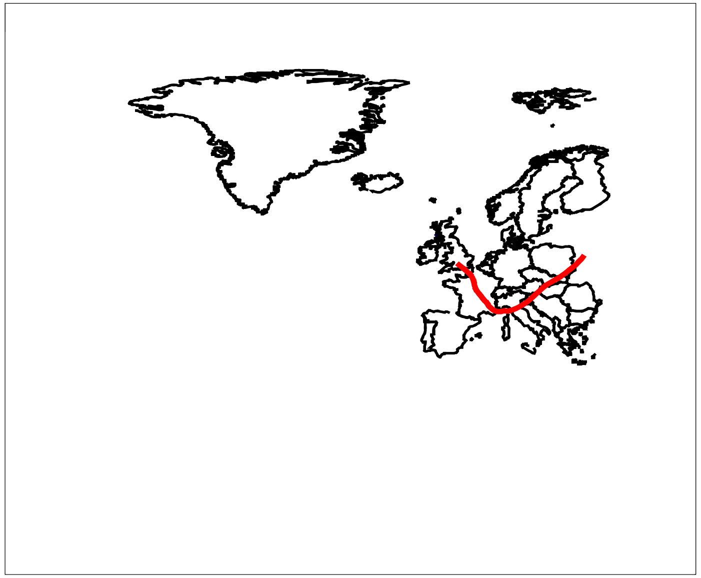

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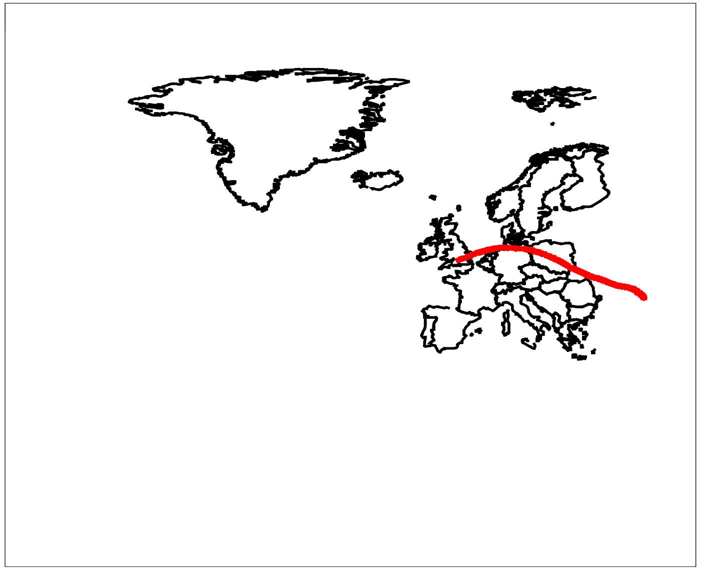

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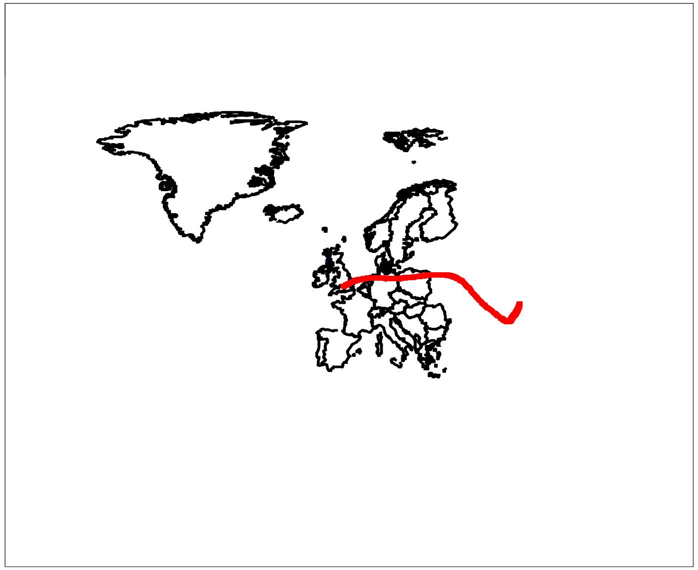

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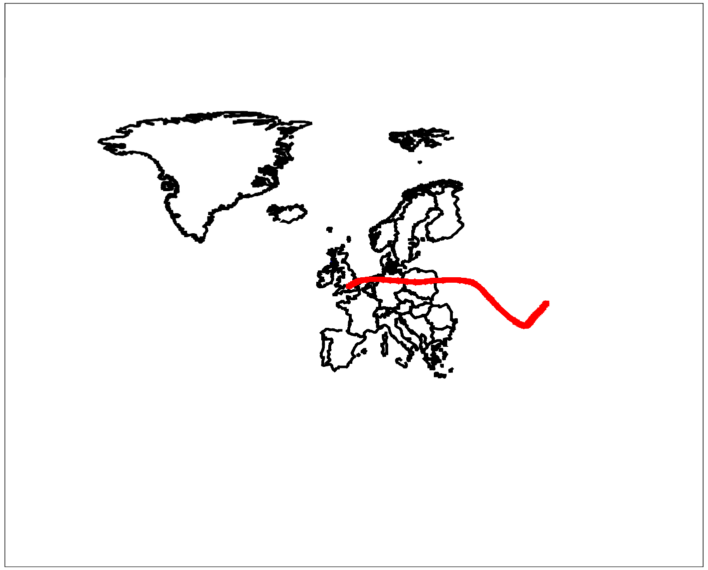

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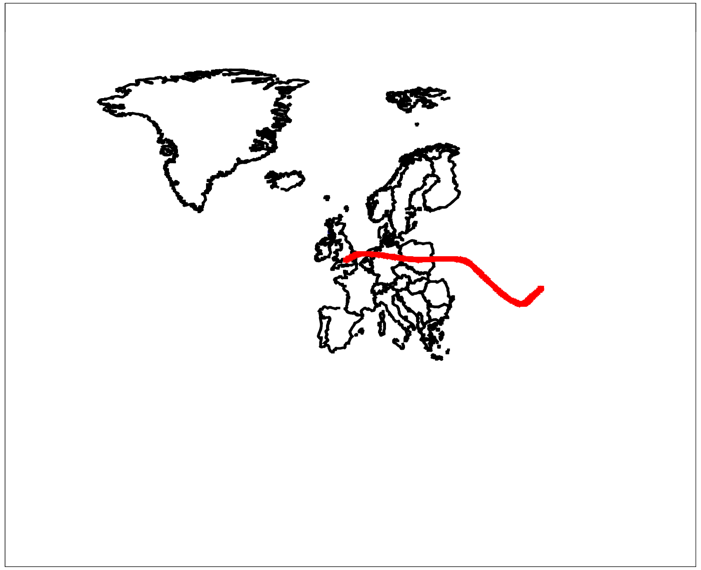

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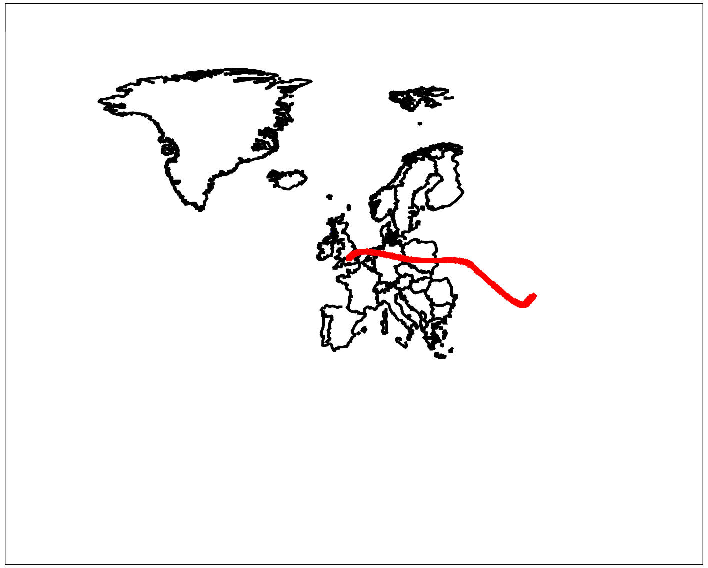

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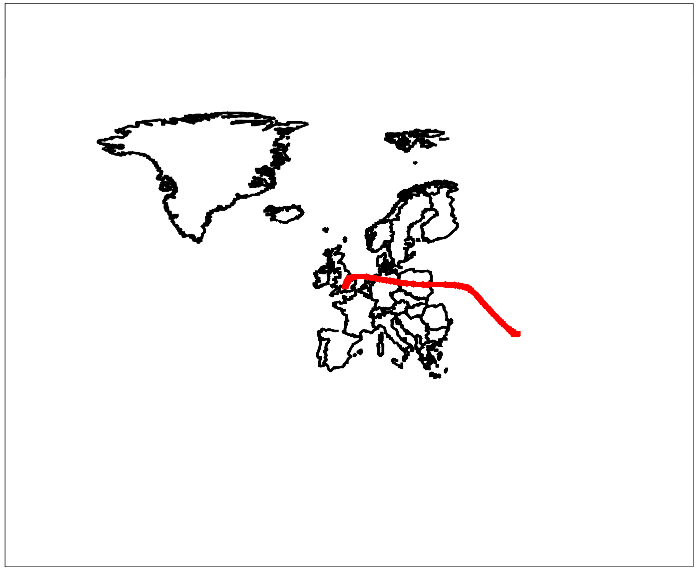

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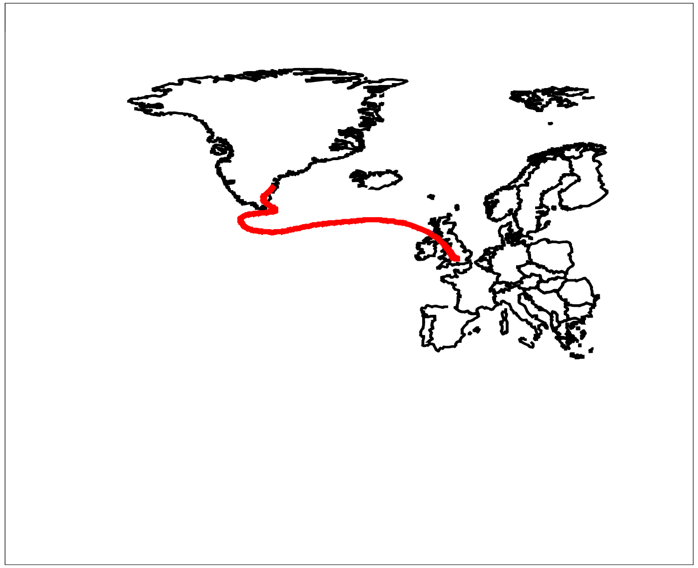

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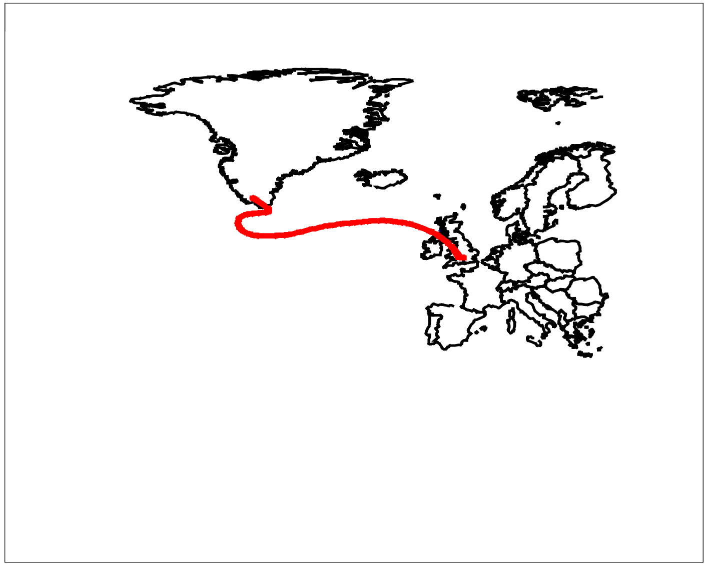

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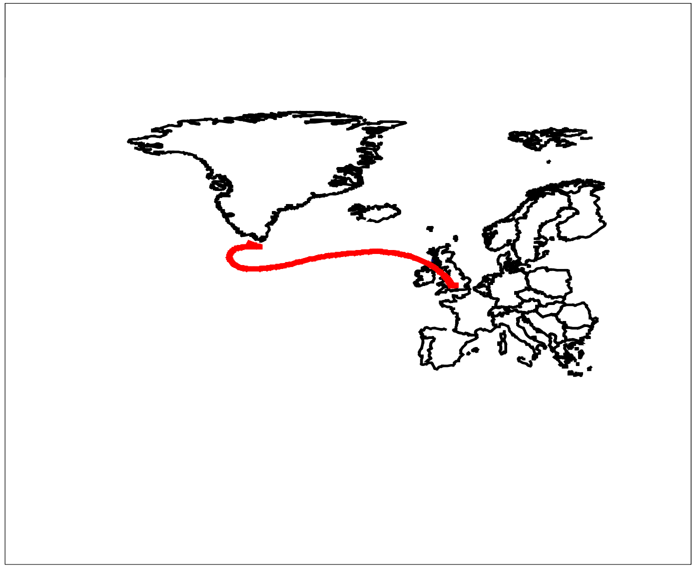

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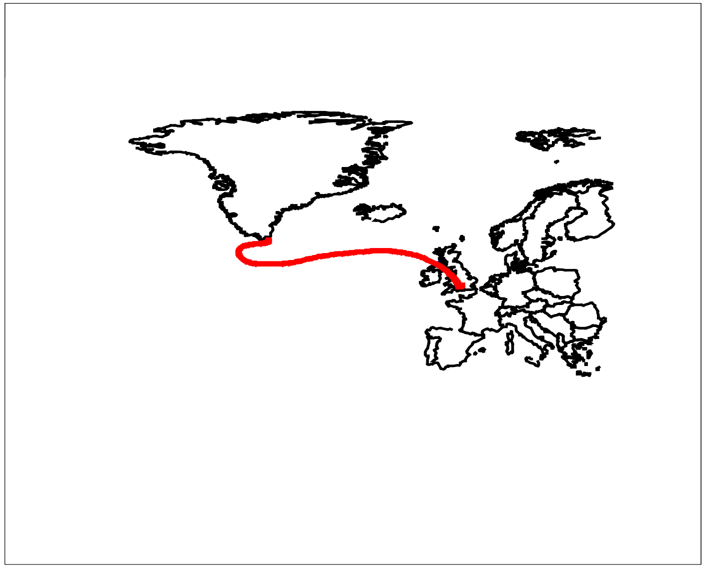

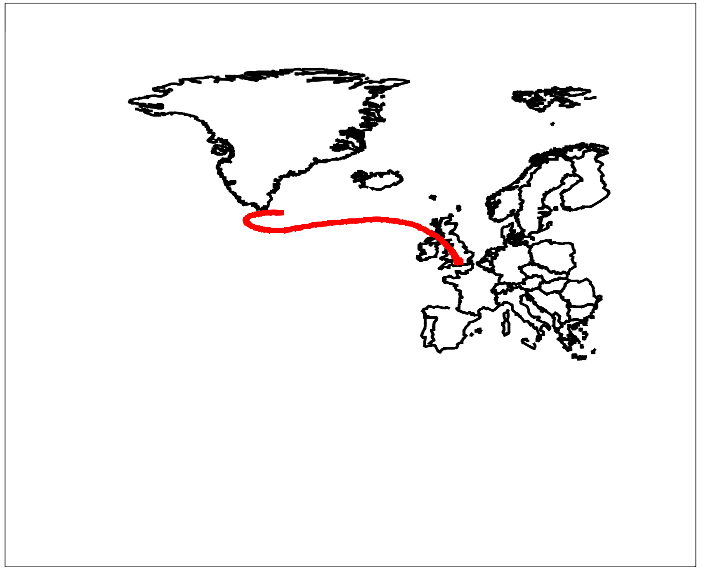
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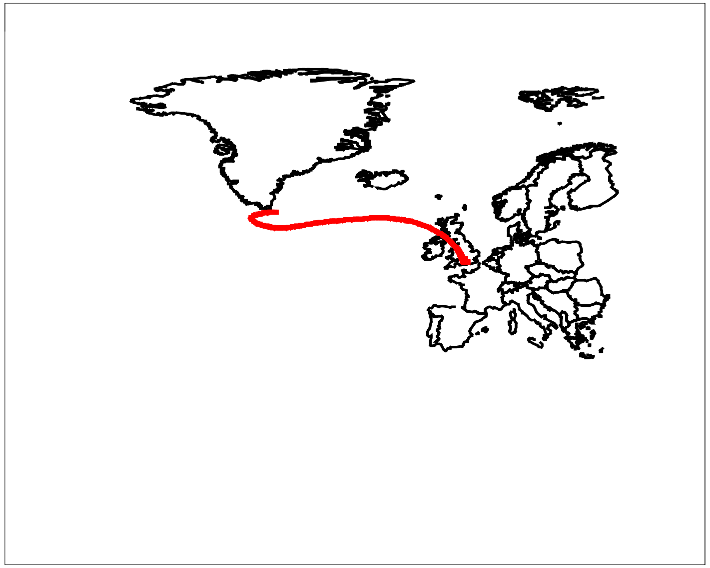
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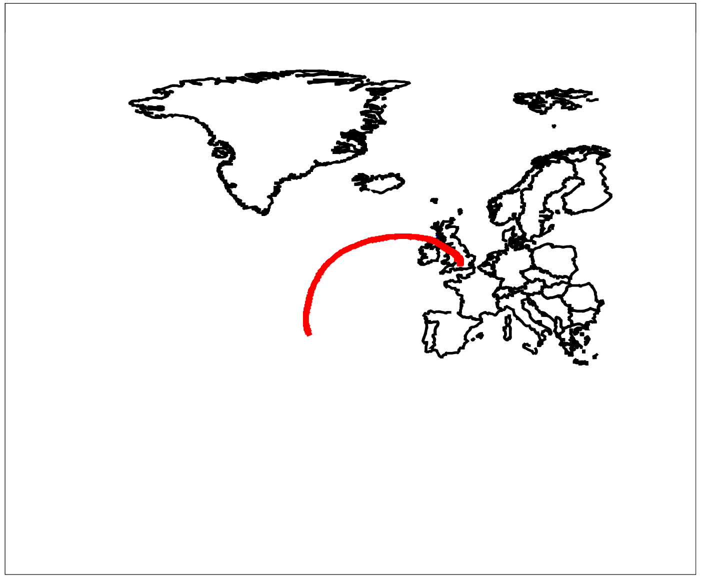

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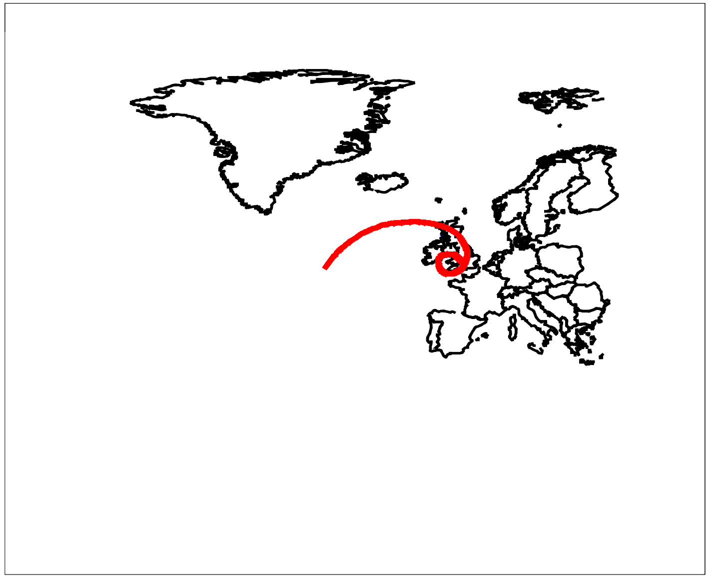

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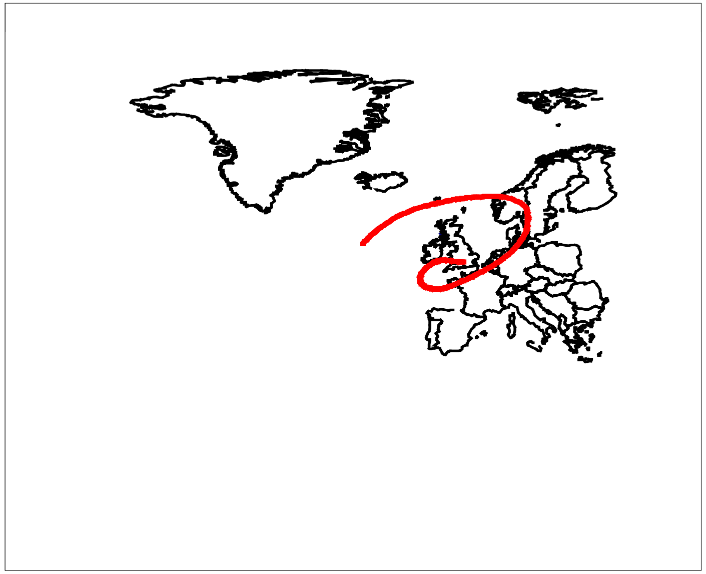

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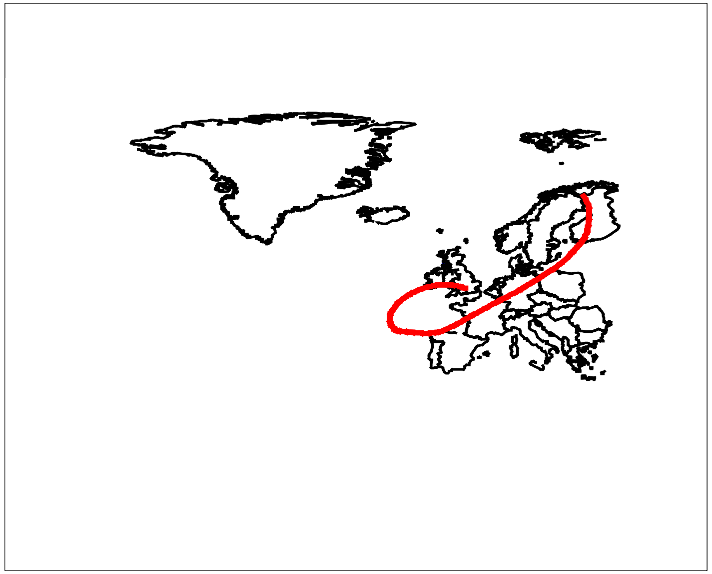

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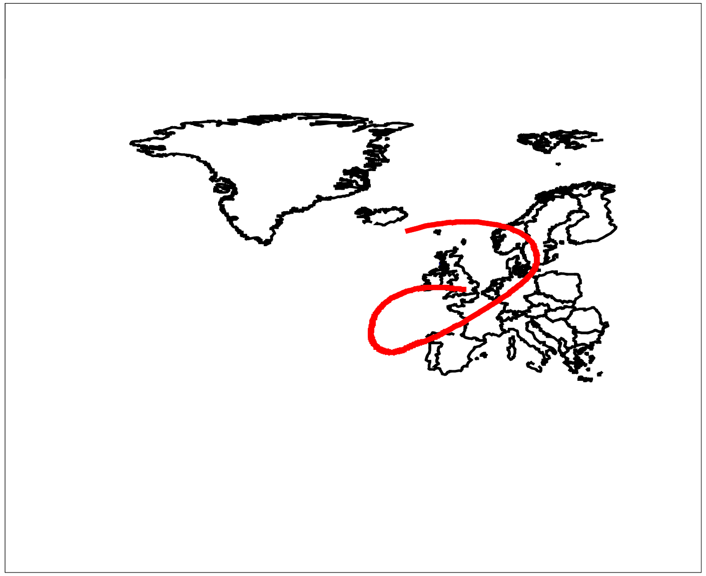

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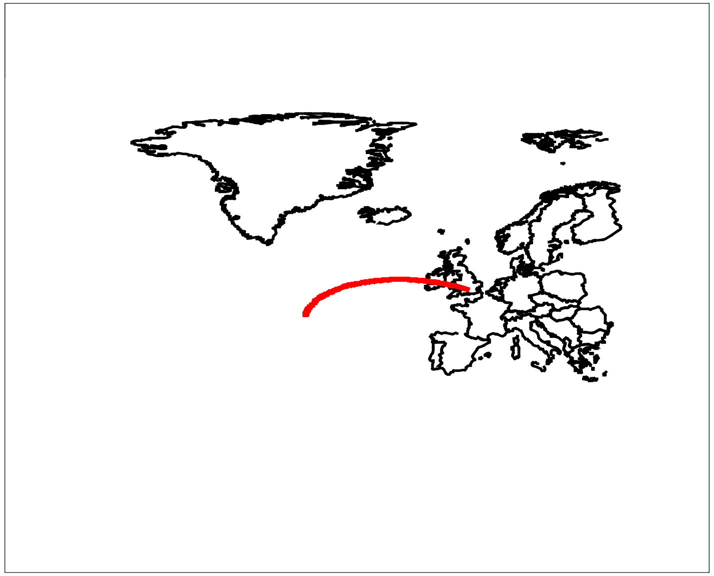

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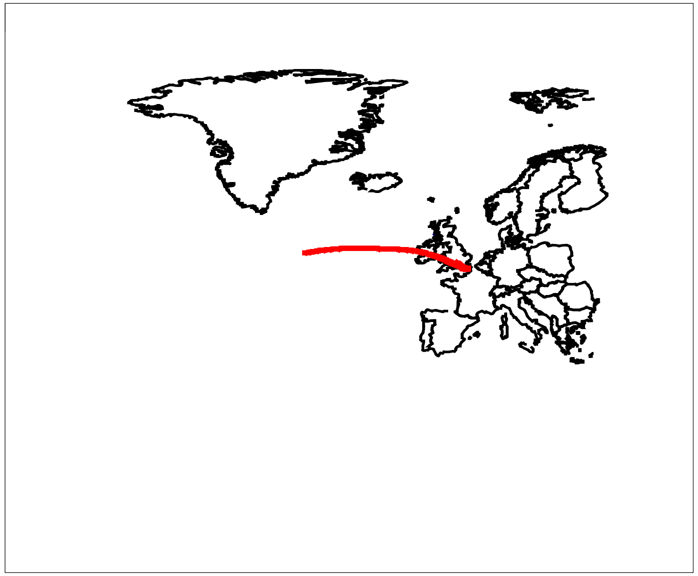

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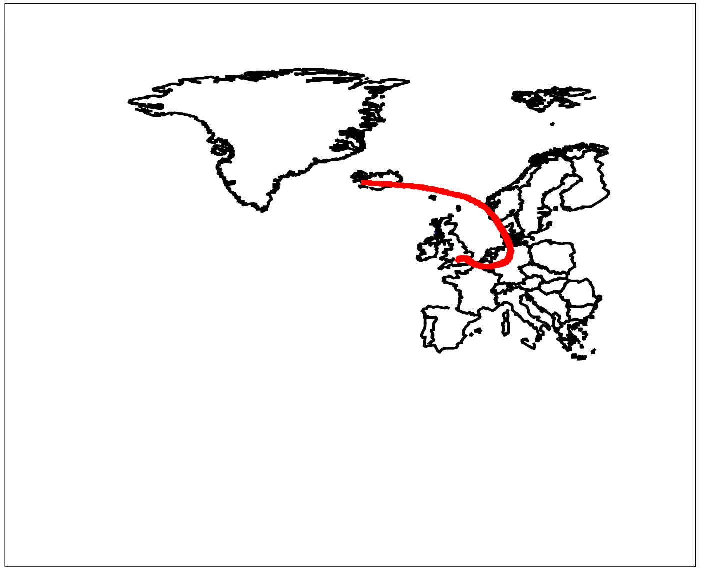

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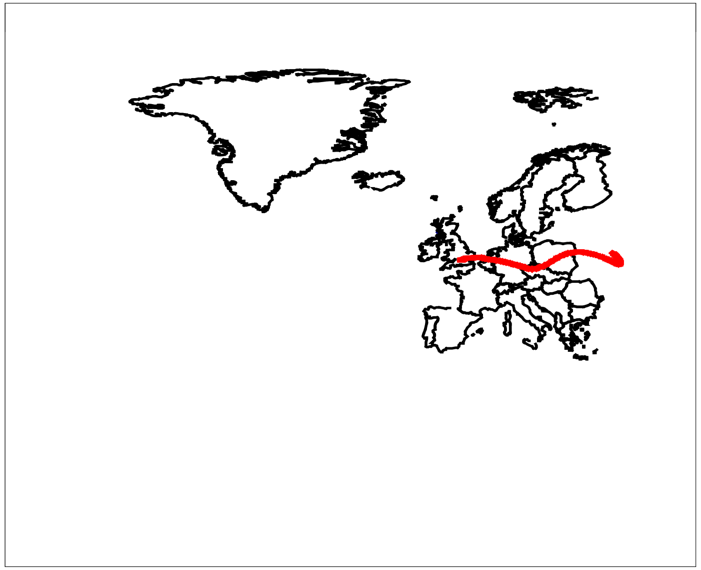

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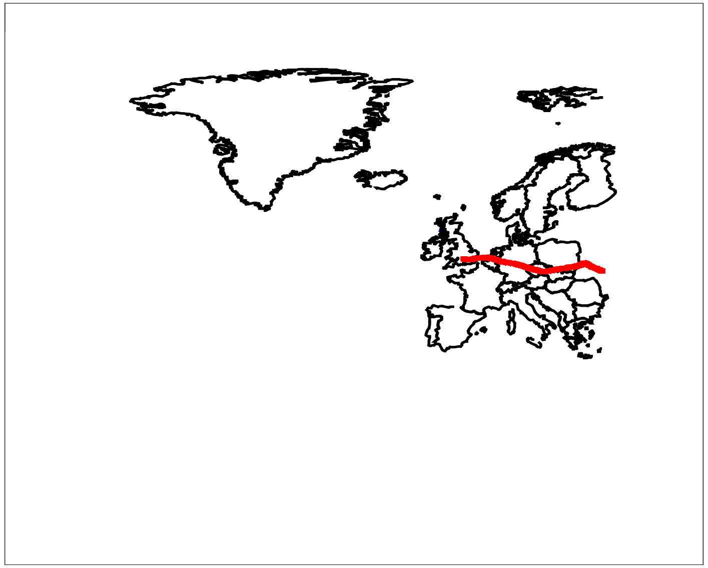

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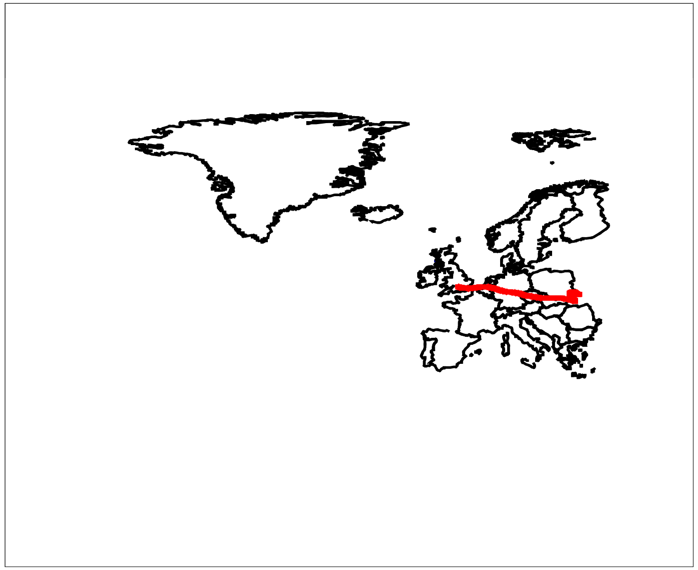

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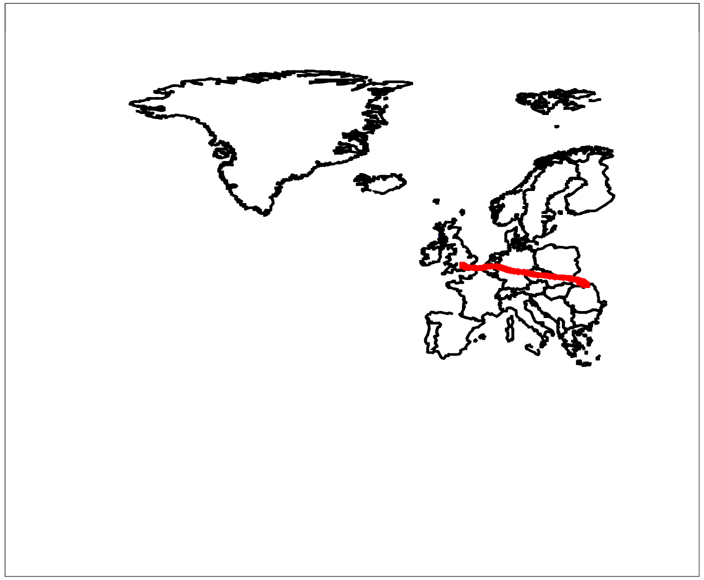

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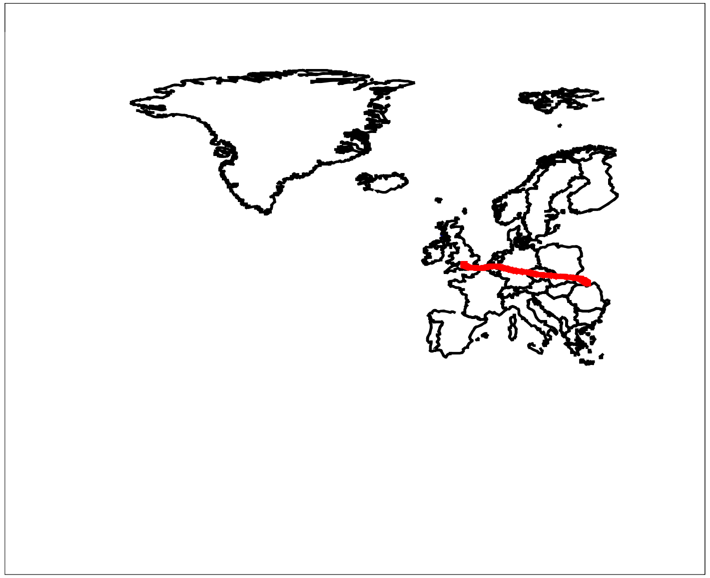
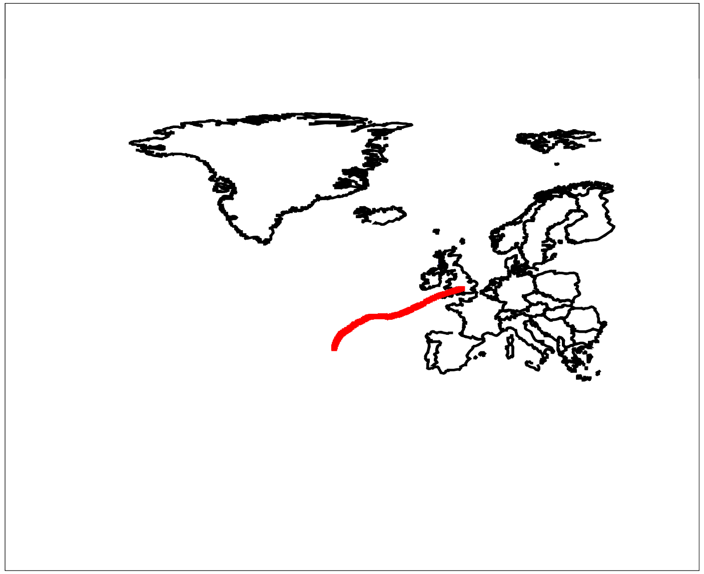


06/09/99 12:00

06/09/99 18:00


07/09/99 00:00


07/09/99 06:00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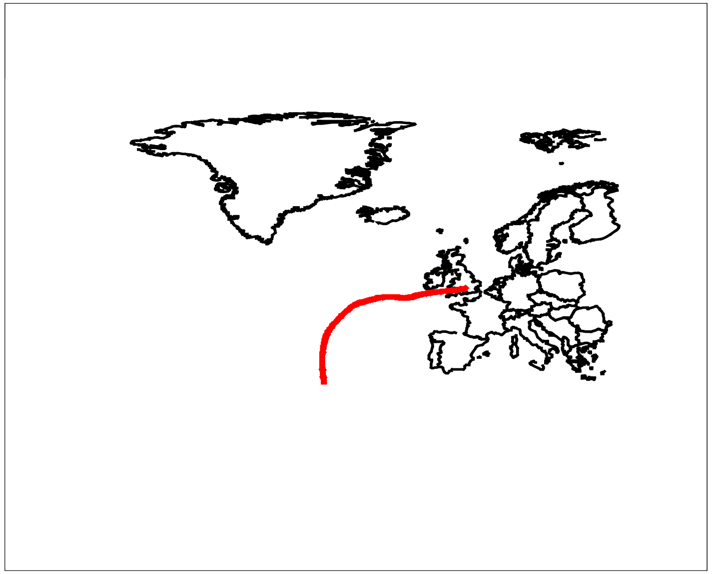
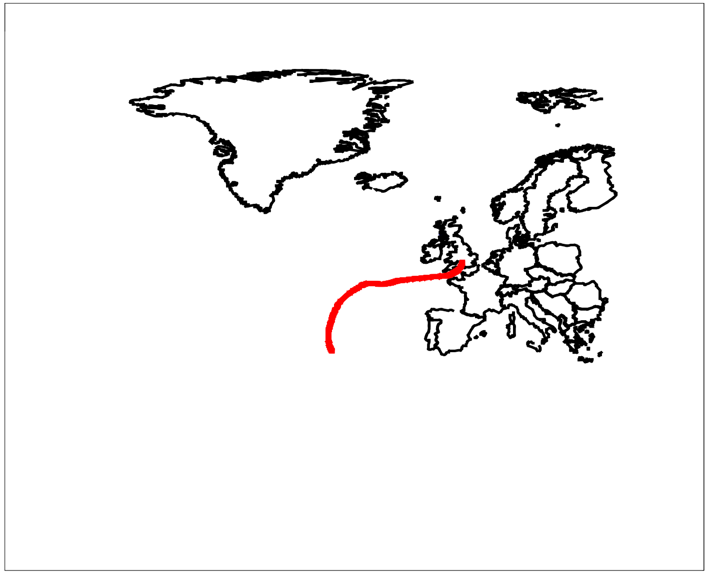

07/09/99 18:00

08/09/99 00:00

08/09/99 06:00



08/09/99 12:00

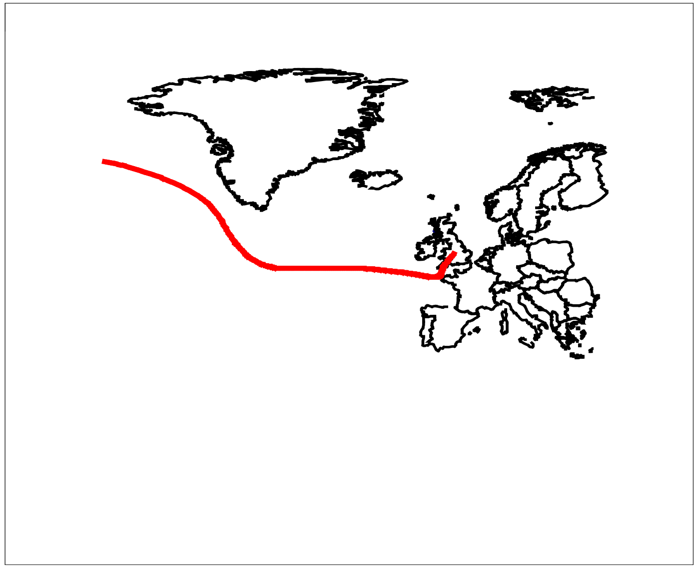
08/09/99 18:00

APPENDIX B

AIR MASS BACK TRAJECTORIES FROM THE BIRMINGHAM SITE

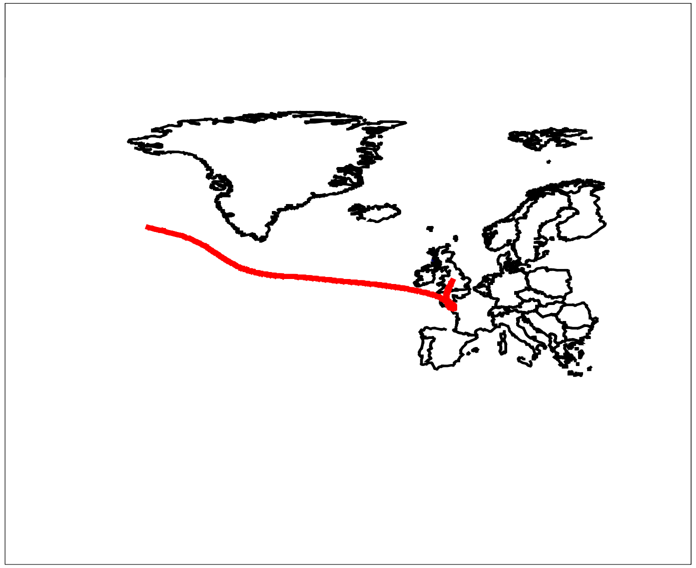
(Pressure height = 925 hPa)

04/11/99 00:00



04/11/99 06:00

04/11/99 12:00



04/11/99 18:00

05/11/99 00:00

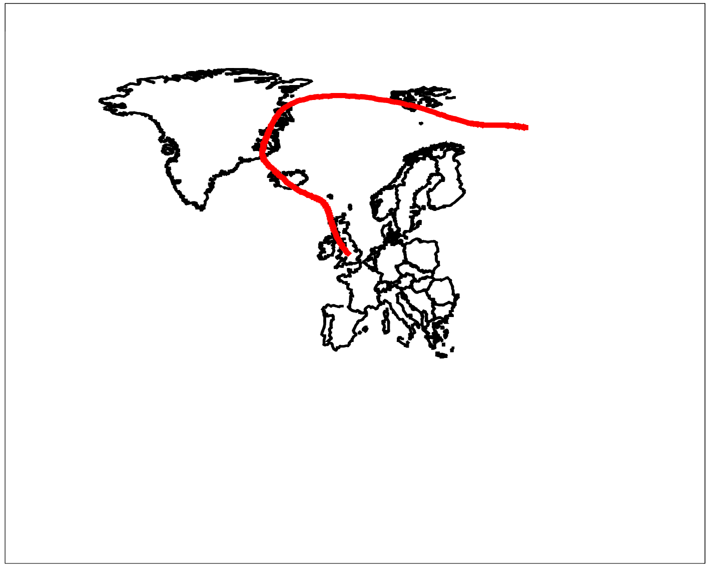
05/11/99 06:00

05/11/99 12:00

05/11/99 18:00

06/11/99 00:00

06/11/99 06:00



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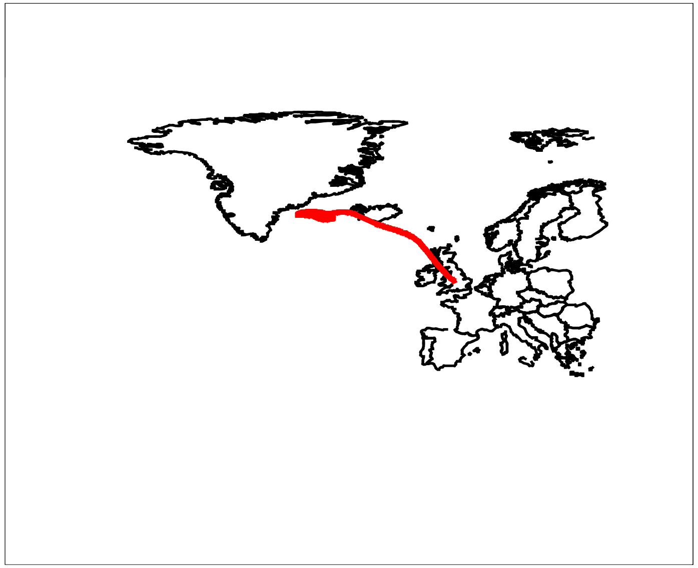
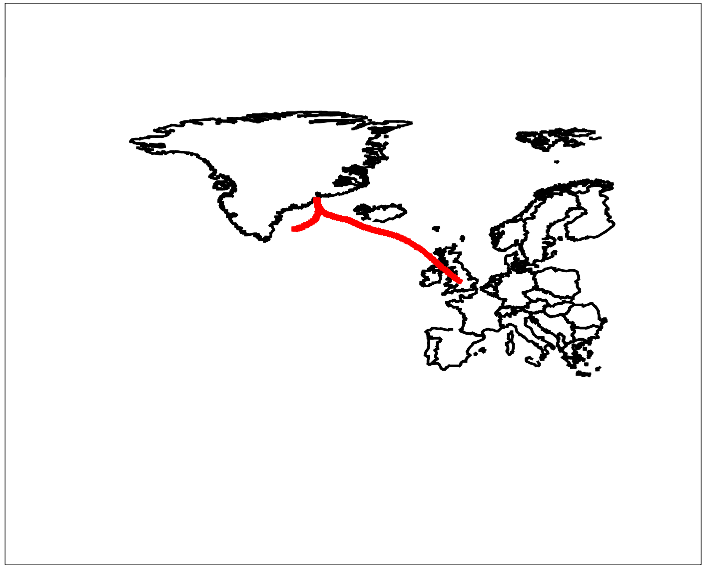
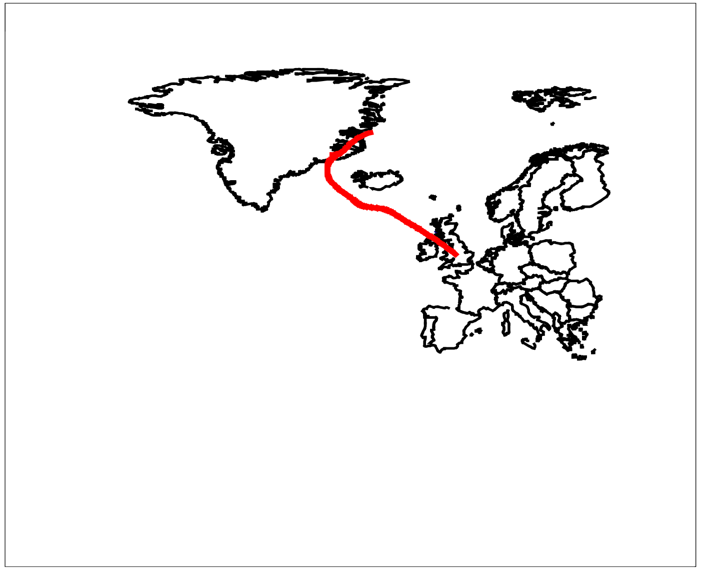


06/11/99 18:00



07/11/99 00:00



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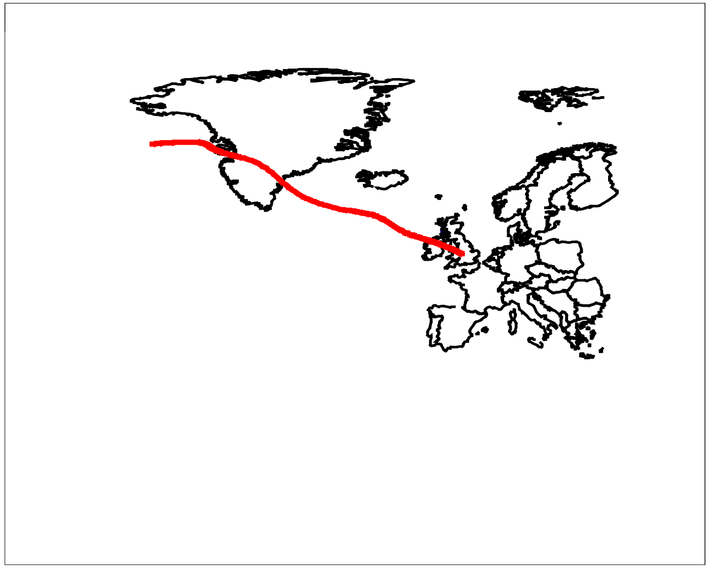

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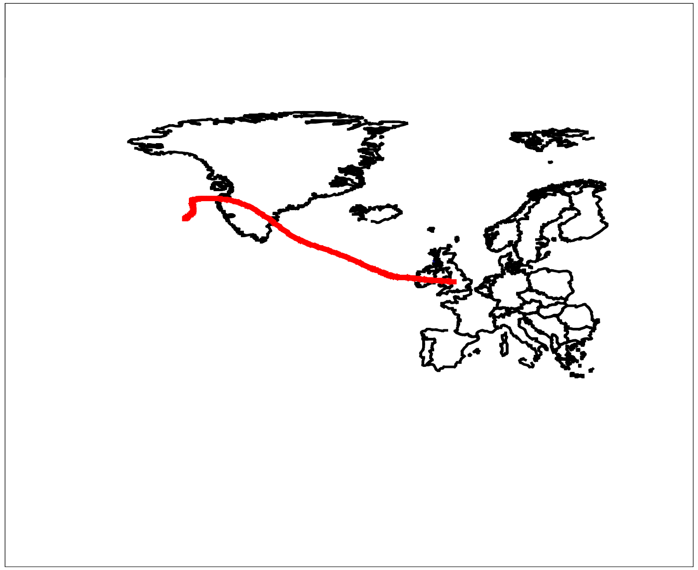

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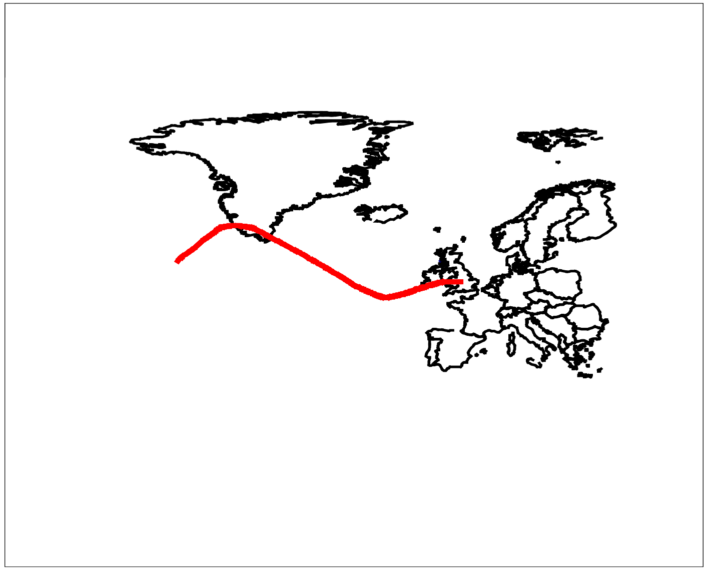
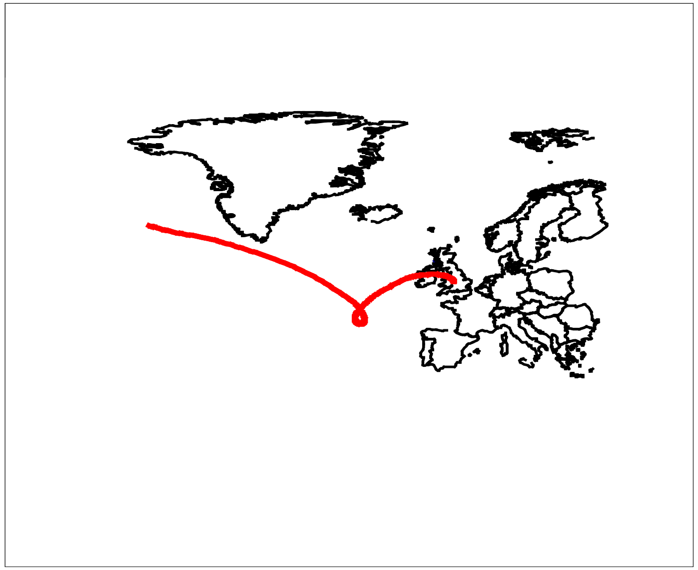


08/11/99 00:00

08/11/99 06:00

08/11/99 12:00



08/11/99 18:00

25/06/99 00:00

25/06/99 06:00

25/06/99 12:00

25/06/99 18:00

26/06/99 00:00

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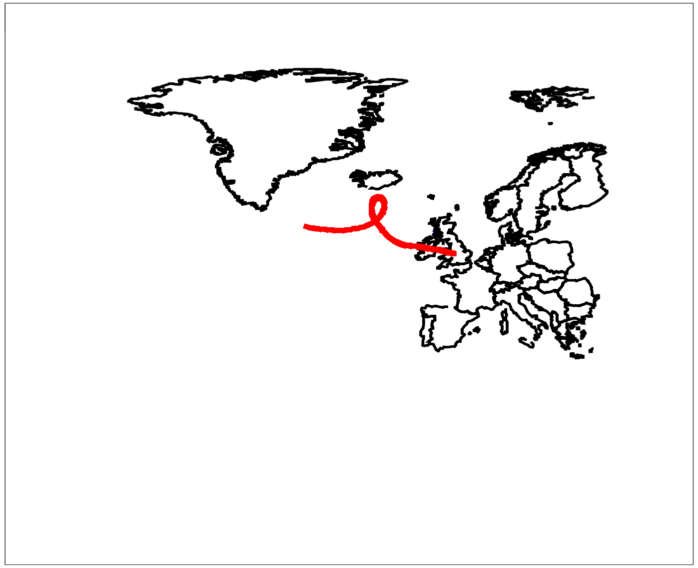
26/06/99 18:00

30/06/99 00:00



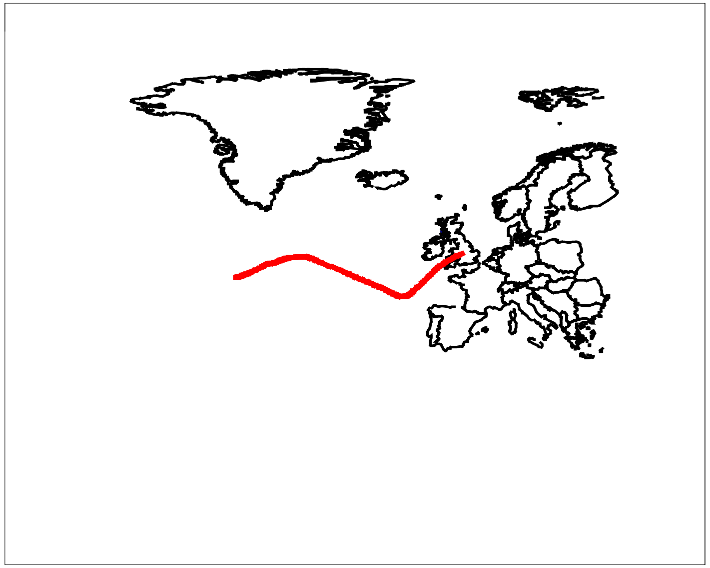
30/06/99 06:00

30/06/99 12:00

30/06/99 18:00

01/07/99 00:00

01/07/99 06:00



01/07/99 12:00

01/07/99 18:00

08/07/99 18:00

09/07/99 00:00

09/07/99 06:00

09/07/99 12:00

09/07/99 18:00

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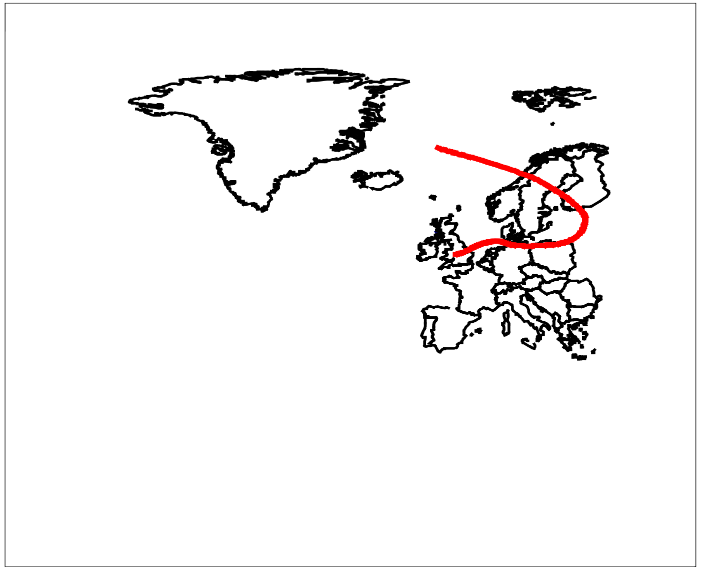
11/07/99 18:00

12/07/99 00:00



12/07/99 06:00

12/07/99 12:00

12/07/99 18:00


25/01/00 00:00


25/01/00 06:00


25/01/00 12:00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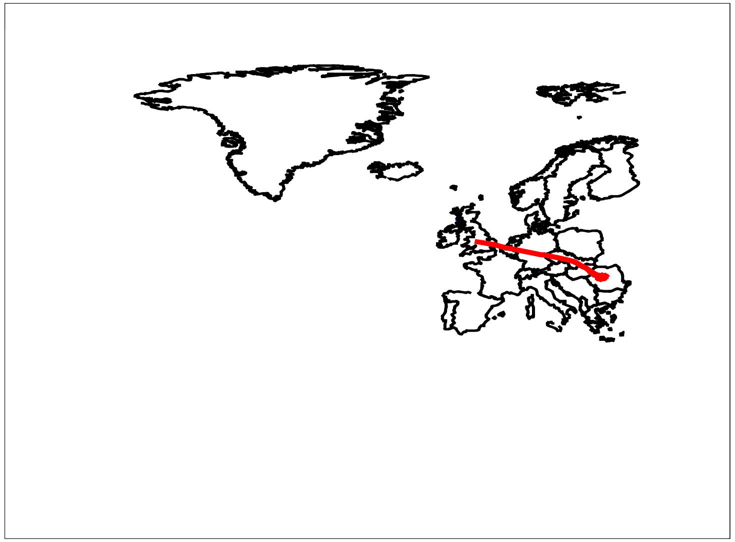
26/01/00 18:00

9/02/00 00:00



9/02/00 06:00

9/02/00 12:00

9/02/00 18:00

10/02/00 00:00

10/02/00 06:00

10/02/00 12:00

10/02/00 18:00

APPENDIX C

PUBLICATIONS RELATED TO THE STUDY

- Harrison RM, **Yin J**, Mark D, Stedman J, Appleby RS, Booker J and Moorcroft S (2001) *Studies of the coarse particle (2.5-10 μm) component in UK urban atmospheres,* Atmos. Environ., 35, 3667-3679.

- Harrison RM and **Yin J** (2000) *Particulate matter in the atmosphere: which particle properties are important for its effects on health?* Sci. of the total Environ., 249, 85-101.

- Harrison RM, Shi JP, Xi S, Khan A, Mark D, Kinnersley R and **Yin J** (2000) *Measurement of number, mass and size distribution of particles in the atmosphere,* Phil. Trans. R. Soc. Lond. A, 358, 2567-2580.

- Mark D, **Yin J**, Harrison RM, Booker J and Moorcroft S (1998) *Measurements of PM_{10}, $PM_{2.5}$ particles at four outdoor sites in the UK.* J. Aerosol Sci., Vol. 29, Suppl. 1, pp. S95-S96.