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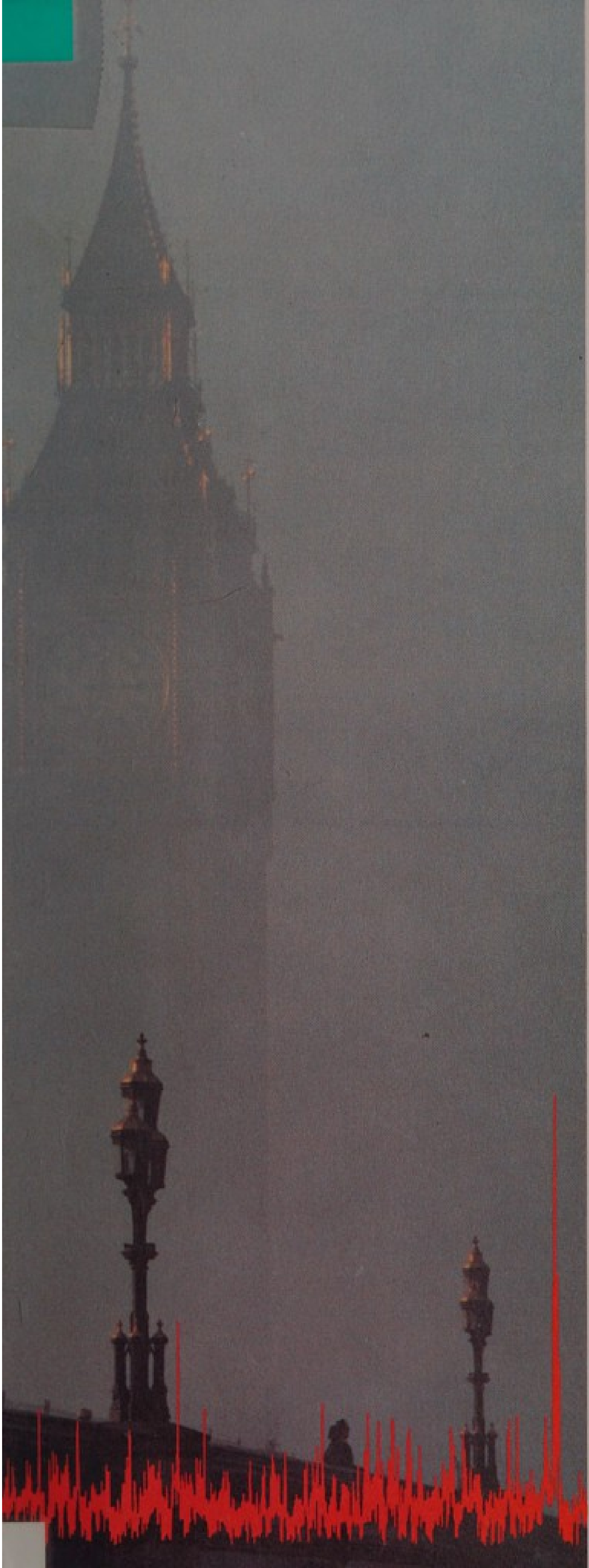

Urban Air Quality in the United Kingdom

January 1993

First Report of the
Quality of Urban Air Review Group

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Cover: A view of 'Big Ben' at midday on Saturday, December 14th 1991,
during the episode of high NO_2 concentrations.
(Photograph courtesy of the Sunday Times and Alan Wheeler)

The Quality of Urban Air Review Group

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The authors accept responsibility for the contents of this report but the views are their own and not necessarily those of the organisations to which they belong or the Department of the Environment

Executive Summary and Principal Recommendations

OVERVIEW

Forty years ago, smoke and sulphur dioxide pollution from domestic coal burning caused an air pollution episode that led to the premature deaths of 4,000 Londoners. These so-called smogs have been all but eliminated by a combination of measures of which the most important were the Clean Air Acts of 1956 and 1968, the move away from domestic coal burning for home heating and the centralisation of electricity generation in large power stations away from towns and cities.

Largely because of pollution emissions from motor traffic, urban air quality is once more causing public concern. Because of this concern, and to increase public awareness of air quality issues generally, the Government has established a public information system through which daily bulletins of air quality are issued via the media. These bulletins include health advice for the benefit of those whose health may be affected by high concentrations of air pollutants. Although the current situation is markedly less serious than the smogs of the 1950s, pollution concentrations regularly exceed international health guidelines in UK towns and cities, and on December 13th 1991 London experienced the most severe nitrogen dioxide pollution since regular monitoring began in 1971.

The UK Government and the European Community are responding to this problem with a range of pollution abatement measures designed to cut emissions from motor traffic, of which the three-way catalytic converter is the best known. This will cut emissions dramatically from each new petrol car and should result in marked improvements in air quality. Local authorities and non-Government organisations are also advancing abatement strategies such as traffic management and the promotion of public transport as well as developing local pollution alert systems.

However, the experience of other countries, most notably the United States of America, is that the growth of motor vehicle traffic will offset many of the air quality benefits accruing from better emission controls. For example, although three-way catalysts have been mandatory on cars in the US since 1983, the National Ambient Air Quality Standards are still regularly exceeded. In the UK, motor traffic is estimated to double by 2025 and there is real concern that even with the substantial financial investment in exhaust emission controls, the US experience will be repeated here.

The Government's Environment White Paper 'This Common Inheritance' marks a shift in Government thinking by signalling that effective pollution abatement must be shown to deliver acceptable air quality. The White Paper outlines an iterative strategy for achieving this goal, via:

- *improved urban air quality monitoring plus public information;*
- *the development of UK air quality standards;*
- *the integration of air quality standards and pollution control.*

As part of the scientific evaluation of this strategy, the Quality of Urban Air Review Group (QUARG) was invited by the Government to review the present state of urban air quality in the UK and to prepare scientific advice on the impact on our air quality of more stringent pollution control measures, such as the introduction of catalytic converters. This is the first report of the Group and outlines what we know about urban air quality and where further research is needed. The terms of reference and membership of the Review Group appear in *Annex A* of the Report.

The principal recommendations of the report are summarised in this *Executive Summary.* These should be read in conjunction with the detailed recommendations at the end of each of the chapters.

MAIN URBAN AIR QUALITY ISSUES

- The current expansion of UK urban pollution monitoring (the Enhanced Urban Network) has resulted in data being available for more pollutants at more sites. Real-time readings are now available for the following pollutants:
    - *benzene, 1,3-butadiene and other volatile organic compounds;*
    - *airborne fine dust (PM_{10});*
    - *carbon monoxide;*
    - *ozone;*
    - *sulphur dioxide;*
    - *nitrogen dioxide.*
- Motor traffic has played an ever increasing role in urban air pollution as the pollutants, such as smoke and sulphur dioxide, traditionally associated with coal combustion have declined to near-rural concentrations. Urban concentrations of nitrogen dioxide and carbon monoxide exceed international health guidelines in many heavily trafficked areas.
- Urban ozone concentrations occasionally exceed international health guidelines during summer pollution episodes. Whilst urban concentrations of ozone are usually lower than those in surrounding rural areas, the available monitoring data are few, and give no indication of spatial variations across our cities. However, average urban ozone concentrations are likely to *increase* as a result of the introduction of three-way catalytic converters.
- Whilst long-term average concentrations of sulphur dioxide have diminished greatly, concentrations can still exceed the World Health Organization 1-hour guideline in some urban areas.

- Certain weather conditions can lead to extreme concentrations of pollution generated by road traffic and other low level sources. For example, during the London pollution episode of December 1991 concentrations of nitrogen dioxide and benzene were unprecedented.

- There are few data to indicate long-term trends across the country, but those that are available suggest a general increase in nitrogen dioxide concentration over the last decade. However, recent data for a limited number of traffic-saturated inner-city sites have shown little change in concentrations. The expansion of urban monitoring via the Enhanced Urban Network, and national diffusion tube surveys will give a greatly improved view of future urban pollution trends.

- It is inevitable that over the next few decades, the beneficial impact on urban air quality of control measures such as the three-way catalyst will be considerably offset by the predicted growth in road traffic. It is however, not possible to quantify this impact precisely at present.

MONITORING RECOMMENDATIONS

- Although there is a growing UK urban air quality database, there remains a clear need for the expansion of air quality monitoring. The Group recognises the importance of the Government's Enhanced Urban Network in beginning this process and recommends that for adequate national coverage of the UK, the network be developed to monitor in at least 24 of the UK's major towns and cities.

- An interim list of 24 priority towns and cities, compiled by the Department of the Environment, is given in *Annex B* of the Report. The Group is currently reviewing the basis for selection of monitoring sites in the light of air quality survey data and developments in international legislation.

- The Group is concerned that to serve common policy and scientific objectives the Department's total urban monitoring effort is now in urgent need of rationalisation and review, subject to the requirements of international legislation.

- The Group recognises that in addition to the national networks, there is a considerable amount of monitoring being carried out at a local level by local authorities and other organisations. The Group considers that proper central scientific co-ordination of this effort will result in valuable additional information being collected and will make the best use of both local and national resources. The Group therefore recommends that the Government establishes such a co-ordination framework.

- The Group considers that the location of the Enhanced Urban Network stations within each urban area is adequate to reflect broadly the exposure of the general public. However, more research is needed involving monitoring, in conjunction with dispersion modelling, in order to quantify better the exposure of individuals to air pollutants. This should include measurements in different locations, such as inside cars and alongside busy roads.

- Urban monitoring at a more limited number of sites should also seek to measure concentrations and trends in other substances of health significance, most notably the following:

  - *acid aerosol;*
  - *toxic organic micropollutants such as polynuclear aromatic hydrocarbons and their derivatives, dioxins and dibenzofurans;*
  - *toxic metals such as mercury.*

- Current air quality monitoring in the UK is designed to provide information upon both central urban background and rural concentrations. However, there is a strong case for enhancement of monitoring at both roadside and suburban locations, which currently have very sparse coverage.

RESEARCH RECOMMENDATIONS

The Group considers that it is not possible with current knowledge to establish a quantitative link between changes in national pollutant emissions and changes in urban air quality. The Group recommends the establishment of a substantial programme of research aimed at understanding **urban** pollution emissions, chemistry and dispersion. This need is most acute in relation to nitrogen dioxide.

This programme should consider the following as priority research areas.

Atmospheric Chemistry and Dispersion Modelling

The behaviour and fate of pollutants in urban areas is poorly understood. Considerable effort needs to be devoted to this issue if the link between emissions abatement and improvements in air quality is to be fully quantified. It is particularly important to understand the relationship between emissions and measured concentrations of pollutants in urban areas.

New theoretical and experimental studies are required to understand the structure of the lower atmosphere in urban areas, how this is influenced by the character and distribution of buildings and open spaces, and how this structure influences the spatial and temporal distribution of pollution concentrations.

Emission Inventories

Accurate emission inventories, both current and predicted, are essential if changes in emissions resulting from control technologies and changes in vehicle use and fuel consumption are to be accurately incorporated into urban air quality models. For example, because the present catalysts do not operate when cold any growth in short journeys will have a detrimental effect on air quality. Hence projections in the pattern of vehicle use are important.

The existing UK emission inventories should be considerably refined by the development of growth forecasts with finer spatial and temporal resolution.

Vehicle Emissions and Alternative Fuels

There is currently inadequate information on in-service emissions from a range of vehicles using current and future emission control technology and different fuels. For new fuels it is important to carry out an in-depth study of environmental impacts from production through to ultimate fate of emissions.

The Influence of Weather

Peak air pollution concentrations are mediated by the prevailing weather conditions. However, this relationship is not fully understood largely as a result of inadequate monitoring of pollution coupled with the assessment of atmospheric conditions.

Airborne Fine Dust

Concentrations of airborne fine dust (PM_{10}) are now measured in real-time. Although some connection with road traffic is evident, the sources of PM_{10} are not fully known. In view of recent health effects studies in North America which show a correlation between PM_{10} and various adverse health outcomes, a better understanding of PM_{10}, and some of its specific components such as acid aerosol is of high priority.

Traffic Management

The only way to reduce concentrations of all vehicle exhaust pollutants is to reduce overall traffic levels. However, as a general rule, moving traffic generates less pollution than stationary traffic. The influence of traffic management on urban air quality, such as traffic lights, junctions, roundabouts, chicanes, red routes and traffic calming should be comprehensively assessed.

Public Information and Perception

Public alert systems allow sensitive individuals to avoid exposure to outdoor air pollution. There is, however, a need to assess the effectiveness with which the data are being communicated and the impact on driving behaviour of requests to curtail unnecessary journeys.

Further studies are required into soiling, nuisance and aesthetic aspects of urban air pollutants, particularly those from traffic, to ensure that improvements in air quality are perceived as such by the public.

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1 Introduction

1.1 BACKGROUND

Cities and towns are an essential part of everyday life and most of us either live in them or regularly use them for work, education, business and a range of other activities. The quality of urban life has dramatically improved during the twentieth century as measured by a wide range of indicators affecting our health and well being. Of increasing importance amongst these indicators is air quality.

Historically, the improvement in urban air quality throughout the United Kingdom has been dramatic. In little over a generation, the urban smogs or 'pea soupers' which led to 4000 additional premature deaths in London during the winter of 1952 have been all but eliminated. This success has been attributed to the Clean Air Acts of 1956 and 1968 and the 'smokeless zones' which cleaned up the main source of this kind of pollution — domestic coal burning.

More recently, as this problem has receded, our attention has focused increasingly on wider scale pollution issues such as acid rain, ground level ozone, stratospheric ozone depletion and global warming. A large amount of skill, effort and resources has been devoted to tackling these immensely important and challenging issues. Contemporary urban air quality issues have not attracted this same increasing commitment from the research community.

This shortfall in research effort is likely to become serious as new urban air quality problems emerge especially in relation to current and projected traffic levels. The Environment White Paper: This Common Inheritance(1) reflected a growing interest in the urban environment by promising increased air quality monitoring both in coverage of our major cities and of pollutants. Furthermore it made a commitment to the wider dissemination of air quality data to the general public together with health advice that they could use. Considerable detail has been added to urban air quality policy in two annual reports(2)(3) further to the original Environment White Paper.

As part of its response to the Environment White Paper, the Department of the Environment brought together a group of independent expert scientists to form the Quality of Urban Air Review Group. The membership and terms of reference of this Review Group are given in Annex A. This is the first report from the Group and its purpose is to set the scene, to put the currently perceived urban air quality problems into context and suggest a research and monitoring strategy covering the period up to 1995.

1.2 THE ISSUES

The foremost air quality issue in the mind of the general public is whether or not urban air is healthy. There is no straightforward answer to this question and this report clearly shows that much of the important information required is still not available. Nevertheless, the report attempts to show which pollutants still remain a cause for concern and points to those areas where past health problems are close to solution.

In terms of air quality and health, the following pollutants or groups of pollutants are described in general terms in this report:

- *nitrogen compounds;*
- *sulphur compounds;*
- *carbon monoxide;*
- *particulate matter;*
- *oxidants;*
- *metals;*
- *organic compounds.*

After human health, the next most important issue to focus upon is dirt, grime and urban soiling. Urban areas are increasingly becoming congested and full of motor traffic. Smoke from diesel vehicles has taken over from coal smoke as the major cause of blackening of building surfaces. Coal burning in homes and industrial boilers and furnaces together with industrial activities, still, in some areas, lead to grit and dust problems and the associated trace element contamination of soils and surfaces.

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(1) Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1990) HMSO, UK.
(2) Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1991) First Year Report, HMSO, UK.
(3) Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1992) Second Year Report, HMSO, UK.

It is important to mention issues that this report does not cover. Major scientific issues such as global warming and stratospheric ozone depletion caused by motor vehicles, urbanisation and urban lifestyles are covered by other advisory structures such as the Intergovernmental Panel on Climate Change and the Stratospheric Ozone Review Group. A number of urban welfare and planning and amenity problems are also beyond the scope of this report. They include specifically visual intrusion, noise and general disamenity. Neither does this Review Group deal with air quality problems in the vicinity of single industrial premises.

Whilst the Group felt qualified to consider the general exposure of the general population to air pollution, the specific effects of air pollution on health are also not dealt with here; this is the subject of the closely-related Advisory Group on the Medical Aspects of Air Pollution Episodes which, like QUARG, was formed in response to the Environment White Paper. Likewise, the Expert Panel on Air Quality Standards provides medical advice to the Department of the Environment on the setting of UK air quality standards for the pollutants discussed here.

REFERENCES

Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1990) HMSO, UK.

Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1991) First Year Report, HMSO, UK.

Her Majesty's Government **This Common Inheritance: Britain's Environmental Strategy** (1992) Second Year Report, HMSO, UK.

2 A Background to Urban Air Quality

2.1 INTRODUCTION

Approximately four in every five people in the United Kingdom live in urban areas, yet little scientific attention has been paid, in recent years, to urban air pollution. This report provides a summary of current understanding of the main issues, focusing on information from this country, and identifies gaps in scientific knowledge.

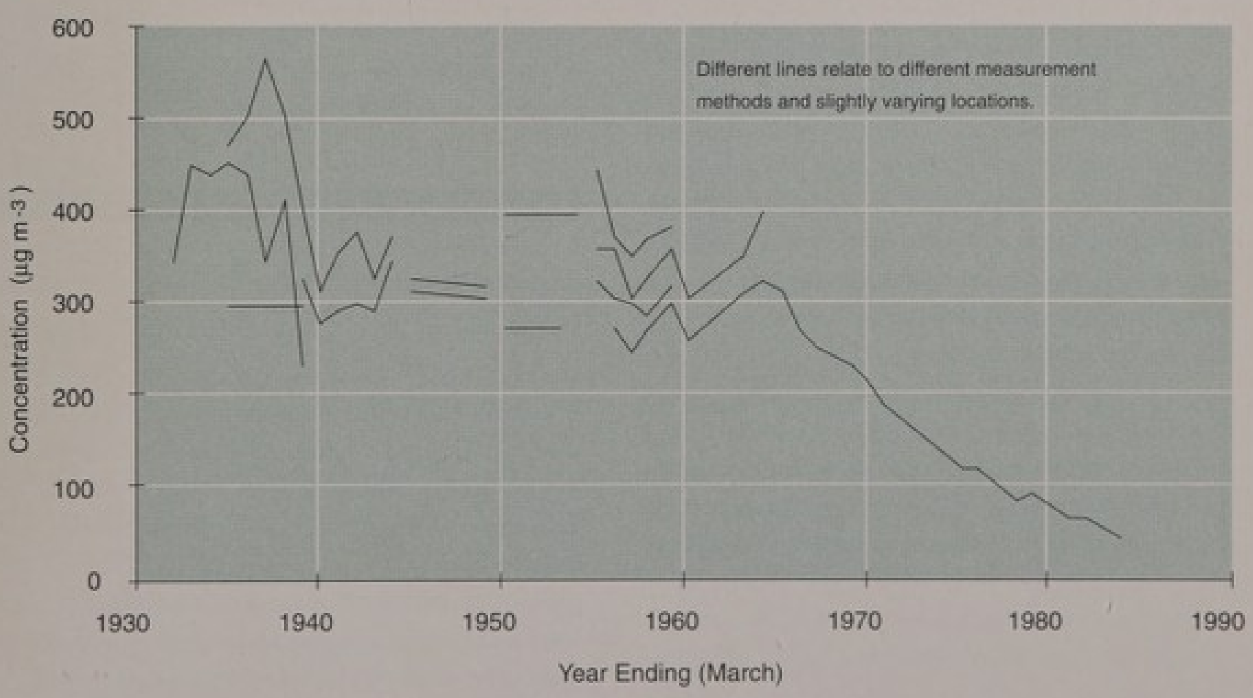
A number of different views exist on what air pollution is. In this report it is assumed that the air is polluted if it contains substances which have an adverse effect on human health, or the environment, or causes nuisance in urban areas. This broad definition could include the greenhouse gases, as well as indoor air pollution, but in this report the focus is on outdoor air quality, more specifically on the traditional toxic pollutants and those that cause public nuisance.

Concern about urban air quality is not new. Complaints were first recorded hundreds of years ago when coal was first used in London. For over 100 years, from the middle of the 19th century, the atmospheres of major British cities were regularly polluted in winter, giving rise to 'pea souper' fogs. However, it was not until 1952, when an estimated 4,000 people died prematurely in the two week period following a pollution episode in London, that air pollution was put firmly on the political agenda. This led to Parliament passing the first Clean Air Act in 1956 and the beginning of other measures to reduce emissions in urban areas.

These early urban pollution episodes — known as smogs from the words smoke and fog — were nearly all related to smoke and sulphur dioxide pollution from the widespread combustion of coal. High concentrations of these pollutants persisted in urban areas throughout the early decades of this century; with concentrations declining from about the middle of the century. This is shown for sulphur dioxide in Figure 2.1 for London(1). The dramatic reduction in concentrations of these pollutants was brought about as a result of the burning of cleaner fuels, especially the use of gas; the use of tall stacks on power stations, and their relocation outside cities; and the decline in heavy industry.

Despite these improvements in most urban areas, there are still a significant number of towns, chiefly around the coalfields, where coal is still widely used in the domestic and other sectors. In these areas, black smoke and sulphur dioxide concentrations, although much lower than three decades ago, can still approach, and in a few cases have exceeded the EC Directive limit values, eg Belfast and Durham. In all these areas the Department of the

Figure 2.1 Annual Mean Sulphur Dioxide (SO_2) Concentrations Measured at County Hall, London (1931-1985)(1)



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(1) Laxen DPH and Thompson MA (1987) **Sulphur Dioxide in Greater London 1931-1985** Environmental Pollution **43**, 103-114.

Environment has required local authorities to bring in or accelerate smoke control programmes to ensure compliance with the Directive by 1st April 1993 when derogations from meeting the limit values will end. With the completion of smoke control plans, levels should decrease even further in the next few years.

In most urban areas of the United Kingdom traffic generated pollutants — nitrogen oxides, carbon monoxide, hydrocarbons and particulates — have become the dominant pollutants. Although few definitive long-term monitoring data on these pollutants exist, it is likely that urban concentrations have increased over the past three or four decades. Lead is one traffic related pollutant that has not followed this pattern, with concentrations in the urban atmosphere having been reduced to about 20% of those in the 1970s.

Some pollutants are emitted directly into the atmosphere and are known as primary pollutants. Others are formed in the air as a result of chemical reactions with other pollutants and atmospheric gases, and are known as secondary pollutants. Carbon monoxide and sulphur dioxide are examples of primary pollutants, while ozone is a secondary pollutant. Some pollutants, such as nitrogen dioxide, can be both a primary and a secondary pollutants; that is some nitrogen dioxide is emitted into the atmosphere from power stations and vehicle exhaust and some is formed from the oxidation of nitric oxide in the air.

This distinction is important for understanding urban air pollution and devising appropriate control strategies. For primary pollutants there is likely to be a proportional relationship between emissions and ambient concentrations. However, with a secondary pollutant, reducing emissions of its precursors may not lead to a proportional reduction in its ambient concentration, and in some circumstances may actually lead to an increase in concentrations.

Air pollution is a problem for major conurbations throughout the world, in both developed and developing countries. International comparisons of urban air quality suggest that the concentrations found in conurbations in the United Kingdom are broadly similar to those found in similar sized conurbations elsewhere in northern Europe(1), except where concentrations are influenced by local point sources. This is not surprising since the factors that influence ambient concentrations, such as the vehicle stock and meteorological conditions, are largely similar.

The major urban pollutants are dealt with in detail in this report in the following chapters, pollutant by pollutant, in order to define the current understanding of urban air pollution in terms of ambient concentrations; their relationship to air quality criteria; and evidence of trends over time.

Prior to examining each pollutant in turn, this chapter brings together a number of more general issues which apply to several or all air pollutants. These include the following:

- *factors that influence urban air quality including the sources of pollutants and the meteorological influences on their dispersion;*
- *legislation introduced to reduce emissions and to set air quality standards;*
- *air quality criteria used to assess the significance of measured pollutant concentrations;*
- *models used to predict air quality;*
- *monitoring strategies;*
- *effects on buildings, and urban vegetation;*
- *public nuisance effects;*
- *the specific case of the exposure of the public to pollution from motor vehicles.*

2.2 SOURCES OF URBAN AIR POLLUTION

2.2.1 Introduction

Urban air pollutants arise from a wide variety of sources although in the main these consist of combustion processes. Each of the subsequent chapters on individual classes of pollutants describes where emissions arise in the urban environment. In order to quantify better the emissions and conduct an analysis of their impacts, it is common practice to assemble the known data into *emission inventories*. These can be at a national or local level and possess a degree of accuracy which reflects entirely the basis on which they are compiled.

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(1) Holman C (1992) **Personal Communication.**

Emissions of different pollutants are estimated from a knowledge of the processes which form them. For some pollutants this is relatively straightforward, as the emissions are dependent largely on the composition of the fuel. Thus in the case of sulphur dioxide they depend on the amount of sulphur in the fuel. For other pollutants, such as nitrogen oxides, emissions depend on the combustion conditions, such as temperature and pressure, and are thus more difficult to estimate. Emission inventories for these pollutants are therefore liable to be less accurate. Obviously, the use of pollution abatement technology such as flue gas desulphurisation will have an impact on emissions, but the effects of many of these technologies are well defined and thus can be taken into account.

Emissions from power stations are known with a fair degree of accuracy as there are a relatively small number of large sources. However, estimating emissions from a large number of small sources is more difficult and thus the estimates are less accurate.

In determining the contribution from road transport the emissions from nearly 25 million vehicles have to be considered. These depend on a wide range of factors, including the following:

- *fuel used;*
- *engine design/pollution control;*
- *maintenance;*
- *driver behaviour;*
- *traffic conditions;*
- *vehicle speeds;*
- *the number and the mileage of different types of vehicles.*

Figure 2.2 shows the effect of speed on emissions of carbon monoxide, nitrogen oxides and volatile organic compounds from petrol fuelled cars with and without catalytic converters. For cars without catalysts, emissions of carbon monoxide and VOCs decrease with increasing speed. Emissions are highest at the slow driving speeds characteristic of urban driving. For nitrogen oxides, the opposite generally occurs, with highest rates of emission at high speeds. Therefore highest emissions per vehicle kilometre are greatest for vehicles travelling at speed on motorways. Significant quantities are also produced by vehicles accelerating and decelerating in the stop-start driving conditions associated with urban traffic.

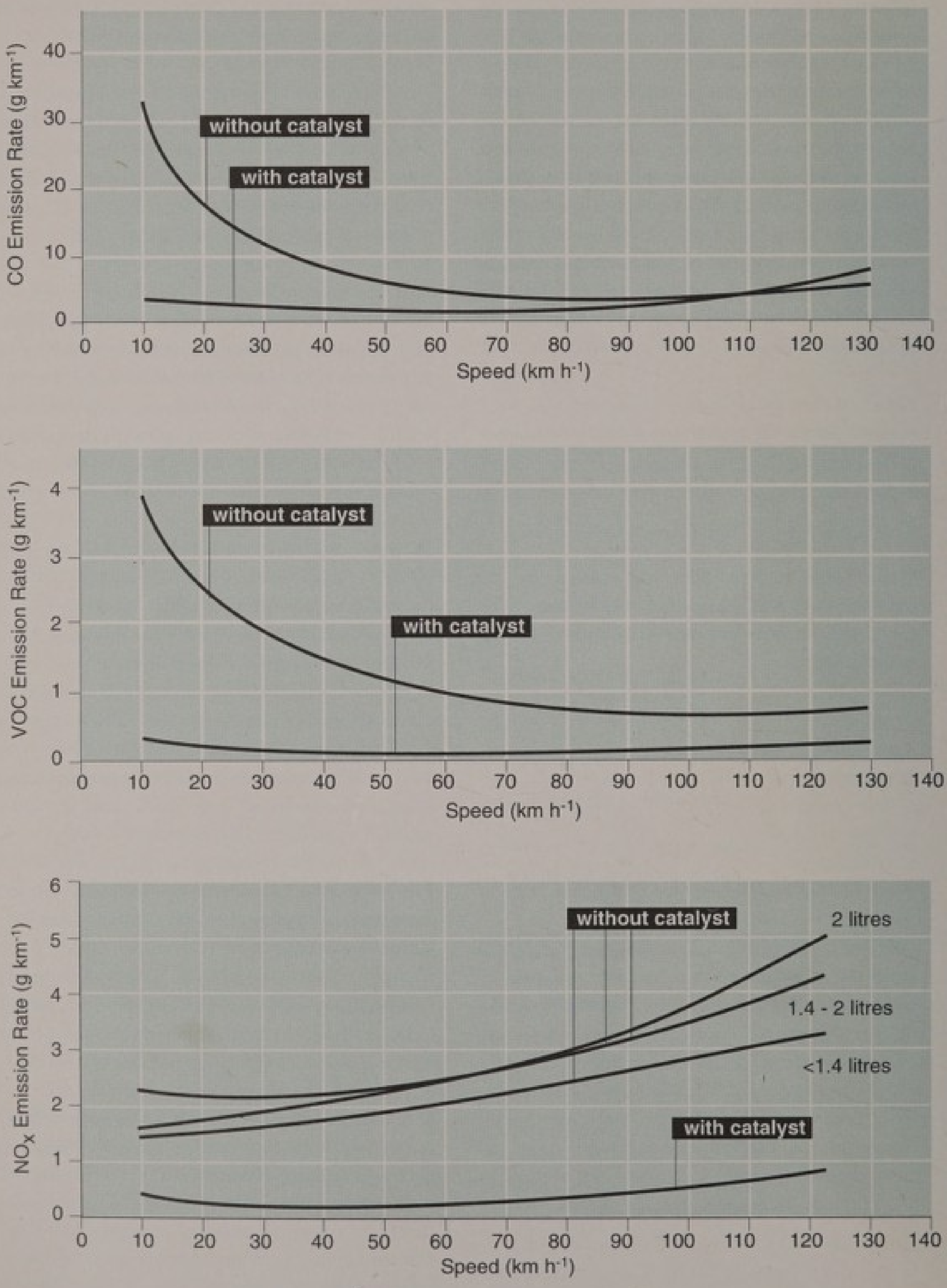
The effect on emissions of fitting a closed loop three way catalytic converters is dramatic, with emissions reduced by approximately 90% of those without a catalyst. Although less obvious from Figure 2.2 there remains a dependence on speed, with emissions of all three pollutants at their highest at high and low speeds.

These speed emissions curves do not, however, include the effect of cold starts on emissions. When the engine is cold, emissions, particularly of carbon monoxide, may be as much as an order of magnitude higher. For cars fitted with catalysts, emission reduction is only effective when the catalyst has reached its operational temperature of approximately 300°C. This is likely to take several minutes. Before the catalyst is lit-up the emissions are essentially uncontrolled.

Emission factors such as those in Figure 2.2 have been derived by measuring emissions from a relatively small number of vehicles as they are driven on the road. These are used together with information on the number of different types of vehicles in the national vehicle inventory; average vehicle speeds on different types of roads; and estimations of the distribution of cars, vans, lorries and buses between the various road types to give a national picture of emissions from the road transport sector.

The estimation of emissions of volatile organic compounds is probably the most difficult and their inventories are the least accurate of all the major pollutants. This is largely due to the problems of quantifying fugitive emissions, that is, those arising from leaks, and evaporation. Volatile organic compounds are a large group of chemicals that includes hydrocarbons, oxygenated compounds such as aldehydes, and halogenated compounds such as trichloroethane. These come from a range of point and diffuse sources including the evaporation and combustion of petrol. For most of these, relatively little is known of emission rates.

Figure 2.2 Speed Dependent Emission Rates for CO, VOC and NO_x for Petrol Engined Vehicles < 2.5T (all cylinder capacities unless otherwise indicated)[1]



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[1] Eggleston HS, Gaudioso D, Gorissen N, Joumard R, Rijkeboer RC, Samaras Z and Zierock KH (1991) **CORINAIR Working Group on Emission Factors for Calculating 1990 Emissions from Road Traffic Volume 1: Methodology and Emission Factors** Contract Number B4-3045 (91) 10PH, Commission of the European Communities, Belgium.

The UK emission inventories for all pollutants are under continual development as new methods, factors and statistics become available which improve the accuracy of the estimates(1). The most recent emission inventory was published in 1992(2).

2.2.2 National Emissions

Table 2.1 shows the relative importance of different sources of the pollutants sulphur dioxide; black smoke; nitrogen oxides; carbon monoxide; and volatile organic compounds in the United Kingdom in 1990.

At a national level road transport is the single most important source of most of these pollutants. The exceptions are sulphur dioxide and volatile organic compounds. In urban areas the contribution from road transport is likely to be greater than indicated by national emission data. This is because there is typically more traffic and less industry in urban areas, and emissions from traffic are at a lower height and thus have a greater impact on local air quality than higher level emissions from industrial sources.

Table 2.2 shows the importance of different fuels and other sources. Clearly, fossil fuel combustion is the main source of all the major pollutants with the exception of volatile organic compounds.

2.2.3 Urban Emission Inventories

Few emission inventories have been undertaken in the United Kingdom to determine the relative importance of different sources in urban areas. Those which have been completed have focused on the Greater London area.

Table 2.1 Sources of the Principal Pollutants (1990)(3)

	% of Total Emissions				
Source	Sulphur Dioxide	Black Smoke	Nitrogen Oxides	Carbon Monoxide	Volatile Organic Compounds(a)
Road Transport	2	46	51	90	41
Electricity Supply Industry	72	6	28	1	-
Other Industry	19	14	9	4	52
Domestic	3	33	2	4	2
Other	7	1	9	-	4
Total (kT)	3,774	453	2,719	6,659	2,396

(a) The term Volatile Organic Compounds does not include methane. The evaporation of petrol during production, storage and distribution is included under other industry. Its evaporation from the petrol tank and carburettors of petrol-engined vehicles is included under road transport.

Table 2.2: UK Emissions by Type of Fuel (1990)(3)

	% of Total Emissions				
Source	Sulphur Dioxide	Black Smoke	Nitrogen Oxides	Carbon Monoxide	Volatile Organic Compounds
Coal	75	37	29	4	2
Smokeless Fuels	1	3	-	2	-
Petroleum:					
Petrol	1	3	29	87	27
DERV	1	42	21	3	7
Gas Oil	2	2	6	-	-
Fuel Oil	19	3	6	-	-
Burning Oil	-	-	-	-	-
Other Petroleum	1	-	1	-	-
Other Gas	-	-	6	-	-
Other Emissions	-	9	1	3	62
Total (kT)	3,774	453	2,729	6,659	2,396

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(1) Eggleston HS and McInnes G (1987) **Methods for the Compilation of UK Air Pollution Emission Inventories** WSL Report LR634 (AP)M, Warren Spring Laboratory, Stevenage, UK.

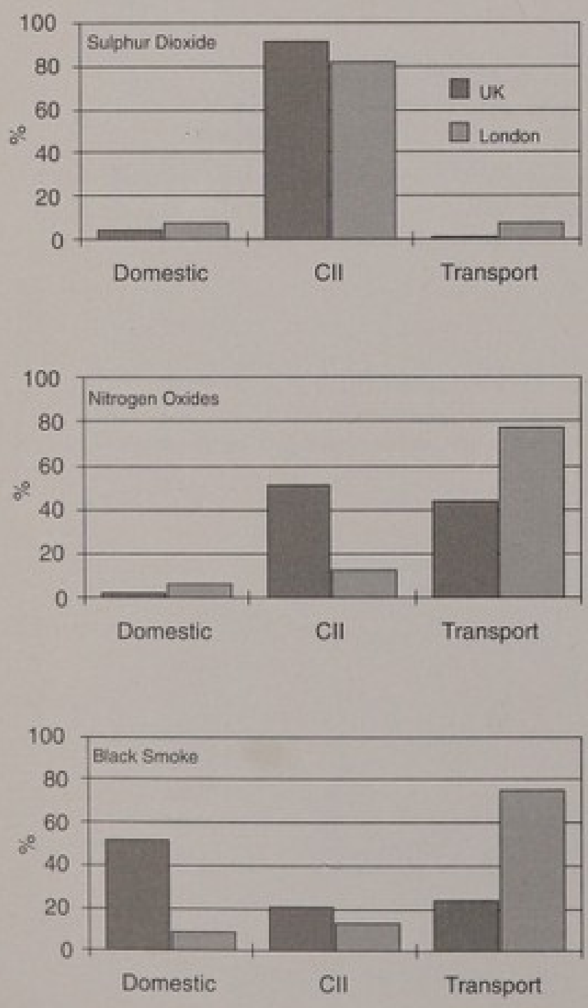
(2) Eggleston HS (1992) **Pollution in the Atmosphere: Future Emissions from the UK** WSL Report LR888 (AP), Warren Spring Laboratory, Stevenage, UK.

(3) Department of the Environment (1992) **Digest of Environmental Protection and Water Statistics No 14 1991**, HMSO, London.

The Greater London Council first undertook an emission inventory for sulphur dioxide for the year April 1975 to March 1976. This was repeated for 1983/84, and extended to include nitrogen oxides. Subsequently, Warren Spring Laboratory modified this London inventory to include more recent estimates of emissions from transport sources and extended it to include smoke emissions.

Figure 2.3 shows the relative importance of different sources of sulphur dioxide, nitrogen oxides and black smoke in Greater London for 1983/84 and nationally for the calendar year 1983, with data combined into three categories consistent across both studies.

Figure 2.3 Sources of SO_2, NO_x and Black Smoke in Greater London (April 1983-March 1984) and the UK (1983)(1)(2) (CII = Commercial, Industrial and Institutional)



Transport was clearly a more important source of sulphur dioxide, nitrogen oxides and black smoke in Greater London than in the United Kingdom as a whole. In Greater London nearly 80% of the nitrogen oxides and black smoke came from transport in 1983/4 compared to less than 50% and 25% respectively at a national level in 1983. Transport was a small source of sulphur dioxide both nationally and in Greater London.

Perhaps surprisingly, domestic sources of black smoke were more important at a national level than in Greater London. This will have been due to the domestic sector being an important source of black smoke in a few areas where coal was still being used widely. By 1983/84 most of London was covered by smoke control areas and thus the domestic sector was no longer a major source of black smoke in the capital.

Figure 2.4 shows the large changes in emissions of sulphur dioxide and nitrogen oxides over the short period from 1975/76 to 1983/84. Sulphur dioxide emissions declined, particularly from the commercial, industrial and institutional sectors. At the same time there was an increase in emission of nitrogen oxides in the domestic and transport sectors.

2.2.4 The Role of Vehicle Emissions

UK emissions from road transport have increased rapidly in recent years, despite the introduction of emission controls(2). This is due to the large increase in the number of vehicles on the roads, particularly during the last decade. Over the period 1980 to 1990 Great Britain's vehicle population increased by 28% to just under 25 million vehicles. Of these approximately 20 million were cars(2).

Table 2.3 shows the increase in United Kingdom emissions from the road transport sector during the same period.

Table 2.3 Increase in UK Estimated Emissions from Road Transport (1980-1990)(2)

Pollutant	% Increase
Carbon monoxide	46
Nitrogen oxides	72
Volatile organic compounds	12
Black smoke	75
Sulphur dioxide	50
Carbon dioxide	43

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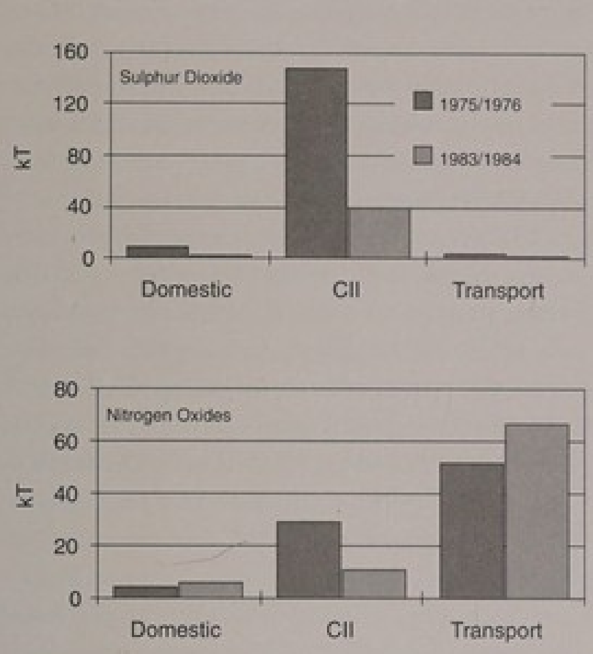
(1) Munday PK, Timmis RJ, and Walker CA (1989) **A Dispersion Modelling Study of Present Air Quality and Future Nitrogen Oxides Concentrations in Greater London** WSL Report LR 731 (AP)M, Warren Spring Laboratory, Stevenage, UK.

(2) Department of the Environment (1992) **Digest of Environmental Protection and Water Statistics No 14, 1991** HMSO, UK.

Figure 2.4 Emissions of SO_2 and NO_x in Greater London (1975/6 and 1983/4)(1)(2)
(CII = Commercial, Industrial and Institutional)



For most of the major pollutants, emissions increased by more than the increase in the number of vehicles in use. This may be explained by a combination of factors, but particularly the increasing distance travelled on average by vehicles. In the decade 1980 to 1990 vehicle usage increased by 50% to over 400 billion vehicle kilometres(3). The greater increase in emissions of nitrogen oxides can be explained by the trade off between emission controls for different pollutants. The tightening of emission limits for other pollutants can lead to an increase in emissions of nitrogen oxides.

2.3 EMISSION REGULATIONS

There are a number of pollution abatement methods available to governments. These include voluntary agreements between industry and the state; fiscal incentives to encourage consumers to buy less polluting products; and regulation. In recent years the latter has been the most widely used control instrument although there is growing interest in the use of fiscal incentives in Europe and elsewhere.

For many years the application of best practicable means (BPM) to prevent or minimise emissions from industrial processes was the basis of pollution control. This has been replaced in 1990 by the concept of best available technology (not entailing excessive costs). This approach assumes that technology is the only means of reducing emissions. Recently the Government has moved towards an effects-based approach to air pollution control in which pollution abatement policy is determined within the context of air quality standards and other environmental criteria(4).

Annex C lists the pollution abatement legislation introduced since the Clean Air Act, 1956 that is relevant to urban air quality.

2.4 AIR QUALITY CRITERIA

When discussing urban air quality it is useful to put ambient concentrations into context. This is generally done by comparing concentrations with internationally agreed air quality criteria. These criteria are based primarily on assessments of the human health effects of single pollutants. However, most of the major urban air pollutants also have adverse effects on plants, including food crops, and several air quality criteria have been adopted to protect vegetation, although these do not necessarily apply to urban vegetation. As adverse effects can occur on ecological systems at concentrations below those known to be harmful to humans, these vegetation air quality criteria have been adopted as guidelines or targets rather than as mandatory limit values.

When considering criteria set by the European Community (EC), it is important to distinguish between air quality limit values and air quality guide values. Limit values are mandatory, whereas guide values are designed to provide guidance. Air quality standards can contain both limit and guide values. Guidelines, as distinct from standards, have been proposed by other bodies such as the World Health Organization (WHO).

Individual response to a given concentration of air pollution varies considerably. For example, individuals with pre-existing lung disease may be more sensitive to

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(1) Munday PK, Timmis RJ, and Walker CA (1989) **A Dispersion Modelling Study of Present Air Quality and Future Nitrogen Oxides Concentrations in Greater London** WSL Report LR 731 (AP)M, Warren Spring Laboratory, Stevenage, UK.
(2) Department of the Environment (1992) **Digest of Environmental Protection and Water Statistics No 14, 1991** HMSO, UK.
(3) Department of Transport (1991) **Transport Statistics Great Britain** HMSO, UK.
(4) Her Majesty's Government (1992) **This Common Inheritance: Britain's Environmental Strategy** Second Year Report, HMSO, UK.

a given dose of pollution than healthy people. Differences in response can also be due to age, sex and the level of exercise taken. Air quality criteria generally aim to minimise the health impact on sensitive groups of people. A protection factor is often included to take account of current scientific and medical uncertainties.

There has been considerable discussion in recent years over what an adverse health effect is. Do all observable biological changes give rise to an adverse health effect? For example, it is known that exposure to certain concentrations of ozone gives rise to a change in certain indices of lung function, as measured in standard tests. What is less certain is whether these small changes in indices of lung function are actually important for the individual's ability to breathe. Such discussions, however, are outside the scope of this report. These issues are being discussed by other expert groups, particularly the Department of Health's Committee on Medical Effects of Air Pollution and the Department of the Environment's Expert Panel on Air Quality Standards, which have been set up to investigate the health effects of air pollutants and to recommend air quality criteria. The Department of Health's Advisory Group on the Medical Aspects of Air Pollution Episodes reported on ozone in 1991(1), and on sulphur dioxide acid aerosol and particulate matter in 1992(2). Further reports on the oxides of nitrogen and on the effects of exposures to mixtures of pollutants are expected in 1993 and 1994.

Effects of pollution on human health depend on duration of exposure as well as pollutant concentration. Thus there are different air quality guidelines/standards for different averaging times. For those pollutants for which long term (chronic) exposure is thought to be of most importance the air quality guidelines/standards are based on pollution concentrations averaged over one year. On the other hand, those pollutants for which short term (acute) exposure is thought to be most important have criteria based on concentrations averaged over much shorter periods, ranging from 10 minutes to 24-hours. Some pollutants have both chronic and acute effects and for these criteria are set for both short and long term averaging periods.

Some organisations have adopted maximum values for their guidelines/standards, while others have used the 98th percentile as the criterion. The latter approach allows for a few short lived pollution episodes. A 98th percentile of 1-hour average concentrations over one year allows the standard/guideline to be exceeded for 175 hours, while a 98th percentile of daily average values over one year allows the standard/guideline to be exceeded for 7 days. The 98th percentile criteria are set at levels that take account of the typical distribution of pollution concentrations and are therefore set at lower values than those produced using the maximum value approach. Thus the EC nitrogen dioxide air quality standard is a 98th percentile of 1-hour mean concentrations over a year and is set at 105 ppb (200 $\mu g\ m^{-3}$). The WHO's 1-hour guideline is set at 210 ppb (400 $\mu g\ m^{-3}$) and is slightly more stringent than the EC limit value. Basing control strategies on a 98th percentile standard will not, however, prevent abnormal pollution episodes from occurring, such as the episode in London in December 1991. The 98th percentile standard was met, despite concentrations reaching around 400 ppb (765 $\mu g\ m^{-3}$) for several hours.

One of the major shortcomings of the currently accepted air quality criteria is that they generally consider pollutants in isolation from each other rather than in combination. This is because little is known of the effects of mixtures of pollutants and thus there is insufficient information available to enable the setting of such criteria. The major exception to this is the sulphur dioxide and smoke/particulates air quality standard of the European Community and the WHO guideline.

The European Community adopted an air quality standard for smoke and sulphur dioxide in 1980 to stimulate the improvement of urban air quality. EC air quality standards for nitrogen dioxide and lead were adopted shortly after. These three standards have now been incorporated into UK legislation. In addition, an EC Directive on air pollution by ozone was adopted in September 1992 to standardise monitoring and exchange of information in Europe, and provide for a public information and warning system when ozone concentrations exceed certain threshold levels.

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(1) Advisory Group on the Medical Aspects of Air Pollution Episodes (1991) **First Report: Ozone** Department of Health, HMSO, UK.
(2) Advisory Group on the Medical Aspects of Air Pollution Episodes (1992) **Second Report: Sulphur Dioxide** Department of Health, HMSO, UK.

For effects other than cancer the World Health Organization's European Office has recommended air quality guidelines for 28 pollutants and groups of pollutants including sulphur dioxide and particulate matter, nitrogen dioxide, ozone, carbon monoxide, and a range of organic compounds and metals. These guidelines are 'intended to provide background information and guidance to governments making risk management decisions, particularly in setting standards' and 'may be used in planning processes and various kinds of management decision at community or regional level'. Indeed, the EC air quality Directive for nitrogen dioxide is based in part on dose/effect relationships derived by the WHO. The guidelines have also been widely used in the United Kingdom in assessing the possible impact of air quality for those pollutants for which there are no EC air quality standards.

In deriving the guideline values, protection factors have been applied by the WHO to allow for medical and scientific uncertainties. For certain air pollutants, the guidelines are only marginally above concentrations at which some effects have been recorded(1). Indeed, according to WHO, 'Compliance with recommendations regarding guideline values does not guarantee absolute exclusion of effects at levels below such values. For example, highly sensitive groups especially impaired by concurrent disease or other physiological limitations may be affected at or near concentrations referred to in the guideline values'(2).

The WHO have also derived risk assessments for pollutants that cause cancer, based on the work of the International Agency for Research on Cancer. Cancer risk assessment is a two-step procedure involving assessments firstly of how likely it is that a pollutant is a human carcinogen, and secondly of the rate at which the pollutant is likely to cause cancers for a given concentration and duration of exposure. Pollutants have been classified for carcinogenicity into the following groups:

- *Group 1: proven human carcinogens;*
- *Group 2A: limited evidence of carcinogenicity in humans but sufficient evidence for carcinogenicity in animals;*
- *Group 2B: inadequate evidence of carcinogenicity in humans but sufficient evidence for carcinogenicity in animals;*
- *Group 3: unclassified chemicals.*

It is generally accepted that for genotoxic carcinogens there is no threshold concentration below which the risk of cancer disappears. Thus there is no safe concentration of a genotoxic carcinogen. Instead of deriving guideline values the WHO have derived quantitative risk assessments for six proven or probable carcinogens. These are acrylonitrile, arsenic, benzene, chromium(VI), nickel, polynuclear aromatic hydrocarbons and vinyl chloride. The cancer risk estimates are based on a lifetime (70 years) exposure to a concentration of 1 $\mu g\ m^{-3}$. For benzene the risk estimate is 4 x 10^{-6}. This could be interpreted as meaning that if 1 million people were exposed to 1 $\mu g\ m^{-3}$ of benzene for 70 years there may be 4 additional cancers.

There are problems with this approach as it assumes that there is a linear dose response relationship. In addition, these risk estimates involve the extrapolation of the results of animal studies to humans. In the UK, the Department of Health's Committee on Carcinogenicity has adopted a cautious approach to Quantitative Risk Assessment (QRA), holding that if these mathematical risk estimates are well founded they may be useful, but only as one component of a risk assessment.

An approach sometimes accepted for setting ambient air quality criteria is to divide occupational exposure standards by 40 to take account of potential sensitivity to air pollution of certain groups of the non-working population such as young children and the elderly, and their possible longer exposure time compared to that of the workplace.

The UK Department of the Environment has recently adopted a series of public information air quality criteria, in which pollution concentrations are banded into four categories: very good, good, poor and very poor. These informational criteria have been established for sulphur dioxide, nitrogen dioxide and ozone. They are used in

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(1) United Nations Economic Commision for Europe (1991) **Impact of Human Health of Air Pollution in Europe** A Report Submitted by the World Health Organization Regional Office for Europe to the Executive Body for the Convention on Long Range Transboundary Air Pollution, UNECE, Geneva.

(2) World Health Organization (1987) **Air Quality Guidelines for Europe** European Series No 23, WHO Regional Office for Europe, Copenhagen.

publicising air quality data via a public air pollution telephone information line (freephone 0800 556677); CEEFAX and the printed and broadcast media.

The EC air quality standards and guidelines; the WHO air quality guidelines and the UK DOE informational air quality criteria are given in the relevant chapters later in this report.

2.5 METEOROLOGICAL INFLUENCES

Pollution concentrations vary considerably from hour to hour and from one day to another. These variations are largely determined by meteorological factors. The extent to which pollutants are dispersed and diluted depends on wind speed, turbulence, mixing depth and urban topography. The role of wind speed is fairly self evident and, to a first approximation, concentrations are inversely related to speed, for ground level sources. Atmospheric turbulence determines how rapidly a parcel of polluted air is dispersed as it moves away from the source. Dispersion is less under stable atmospheric conditions, which occur largely at night-time, than under unstable conditions, which can occur during the middle of the day when heating of the ground causes thermal turbulence. Neutral stability, which is the most frequent condition, falls in between the two extremes. The mixing depth is the depth of the atmosphere into which the pollutants readily mix. Temperature inversions can restrict the depth of this mixed layer, and act as a lid to the atmosphere, allowing pollutants to build up underneath. Temperature inversions occur at night-time when there is rapid cooling of the ground, and also when warm air moves in over cold ground. In rural areas the inversion may lie only a few tens of metres above the ground, however, in large urban areas the 'heat island' effect created by the additional heat sources produces inversions more typically 100 to 200 m above the ground.

The greater surface roughness encountered in urban areas, due for example to buildings, generally acts to increase turbulence, and hence enhance dispersion. The exception is during periods of very light winds, when the air effectively stagnates close to the ground, especially in locations such as street canyons. The principal effect of the increased turbulence in urban areas is to reduce ground level concentrations. However, it can have the opposite effect for elevated point sources, such as individual chimney stacks, as the increased turbulence brings the plume down to ground more rapidly, giving rise to higher concentrations than would be found around a similar source in a rural area.

The conditions that favour pollution episodes in urban areas involve low wind speeds, stable atmospheric conditions and low mixing heights. These meteorological conditions normally occur during anticyclonic weather and mainly at night-time. During the day the temperature inversion is likely to break up as the sun warms the ground. However, during the winter months, it is possible for inversions to persist throughout the day and they may survive for several days before breaking up. It is conditions such as these that produced the smogs of the early part of this century and similar conditions were also responsible for the pollution episode in London in December 1991. This recent episode, which saw the highest concentrations occur during the night, is discussed more fully in Chapter 4.

2.6 MODELLING URBAN AIR QUALITY

Prediction of air quality in urban areas serves a number of important roles. At the local level it allows the impact of a new scheme to be assessed, eg a new road or a new industrial plant. This information can be used to determine the acceptability of a scheme or to help modify it to mitigate the impact. At the broader level, modelling can be used to help policy formulation by testing the impact of various policy options on air quality. An example of such an assessment is the modelling carried out for the whole of the London area to examine the effectiveness of the introduction of new regulations to control emissions from petrol vehicles during the 1990s (see below). Such regional/city scale models also help identify the main sources contributing to the air pollution problems, and thereby allow targeted control strategies to be developed. They also help in the design of monitoring networks by indicating locations where pollution levels can be expected to be highest.

The first models were developed to explain ground level concentrations of gaseous pollutants near a point source (a chimney) in open ground. In a commonly used approximation, the concentration across the plume follows a Gaussian distribution. The width and depth of the plume depend on windspeed and atmospheric turbulence and increase in the downwind direction. Two parameters characterise the dispersion, the vertical and horizontal (cross-wind) dispersion coefficients. These coefficients were initially measured in rural settings for 3-10 minute averaging times. In urban areas, however, there is far more turbulence induced by the varied layout of buildings and other structures. This increases dispersion and requires a different set of dispersion coefficients to be used. There have been few measurements of urban dispersion coefficients, thus there is a greater uncertainty in urban modelling compared with modelling of pollutants emitted in rural areas.

In the case of odours the period of interest is a few seconds, as human response to odorants is on this time scale. There are few measurements of peak concentrations over this time scale, but it is reasonable to assume that they will be about a factor of 10 higher than those predicted by models with their 3-10 minute averaging time.

Annual average concentrations are also of interest and these are usually modelled using a statistical representation of windspeed, wind direction and atmospheric stability. For city-wide modelling concentrations are calculated at a specific point by adding the contributions from each source.

A number of models have been developed for use in the UK. The early emphasis was on point source models. That developed by Warren Spring Laboratory for point and area sources has been applied to emissions from domestic, traffic and industrial sources in urban areas. The former Central Electricity Generating Board developed models to predict ground level concentrations from power stations, the greater emission height of modern power stations requiring special attention. More recently, Cambridge Environmental Research Consultants was commissioned by a number of UK organisations, including HMIP, to develop a model for emissions from point sources, to assist with regulatory requirements under the Environmental Protection Act. None of these UK models is commercially available, although the latter will be available shortly. Use has therefore been made by a number of organisations, of point source models commercially available from the United States of America. The most commonly used is a model called Industrial Source Complex (ISC) in either its short-term or long-term forms. An important parameter for all these point source models is the height to which the plume will rise. There are various procedures for estimating this plume rise, and this leads to some differences in results between models. The more sophisticated models allow the effect of plumes being caught up in building wakes to be taken into account as well as plumes impacting on high ground, both of these effects leading to higher ground level concentrations. They can also allow for deposition of particulate matter.

The Transport Research Laboratory has developed a simple model, which is largely empirical, to predict annual average peak hour carbon monoxide concentrations alongside roads. This has been widely used in road assessments in the UK. There is, however, a growing use of commercially available models from the USA. The one now commonly used is CALINE 4, which allows concentrations out to a few hundred metres from roads to be modelled. A simple model developed by Harwell Laboratory(1) closely predicts the rapid fall-off of average concentrations away from a road. Measured concentrations of lead-in-air alongside two busy roads agree closely with this model. The overall fall-off of modelled and measured concentrations (after subtracting local background) is shown in Figure 2.5. These modelled results refer to a road in an open setting. In urban areas, however, there are usually tall buildings to disturb the usual dispersion patterns. This is at its extreme in street canyons, where tall buildings line both sides of the road. Warren Spring Laboratory has developed a simple box model to predict concentrations in canyons, although its general applicability has not been tested. A model has also been developed in The Netherlands to deal with pollutants in street canyons, but as yet it has not been applied in the UK. Despite the existence of a number of models, modelling of pollution dispersion from road traffic in urban areas is not well developed in the UK.

Regional models are used to predict annual average concentrations. They are usually used to predict background concentrations over a large area, eg a city. The Greater London Council applied the commercially available CDM model from the USA to model concentrations across the Greater London area in the mid-1980s. The model included emissions from 1,600 square kilometres and several hundred point sources.

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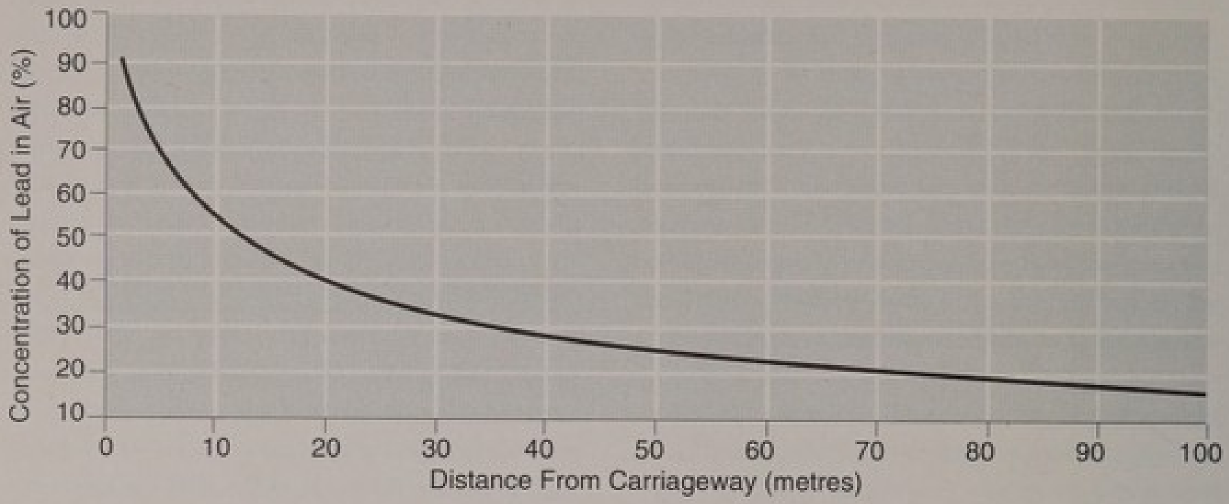
(1) Chamberlain AC, Heard MJ, Little P and Wiffen RD (1979) **Dispersion of Lead from Motor Exhaust** Phil. Trans. of the Royal Society of London **A290**, 577-589.

Figure 2.5 Average Decrease in Concentrations of Lead in Air With Distance from a Highway (results from monitoring and modelling studies expressed as a percentage of concentration at the hard shoulder)



Traffic emissions were included in the 1km x 1km area source emissions. Warren Spring Laboratory has applied its own model to Glasgow, Dublin and several towns where coal consumption is still high and also to the Greater London area, for which the predicted nitrogen oxides concentrations are described in Chapter 4. The city of Sheffield has recently acquired the commercially available Airviro model package to predict both short and long-term average concentrations from sources throughout the city. This model allows the user to input a windfield, incorporating, for example, valley effects.

A crucial element of all modelling studies is the input data. It is frequently difficult to obtain reliable emissions data for all sources (see Section 2.2), and this limits the reliability of the predicted concentrations. Meteorological data are also important and a representative nearby site must be found. There are a limited number of sites in the UK that provide the statistical data required as input to the long-term models, so the data may have to be for a site some distance from the area of interest. This is a further constraint on the accuracy of the predicted concentrations. Models are generally more reliable when they are used to compare the effectiveness of different control strategies, ie when relative concentrations are more important than absolute concentrations.

Finally, it is important to recognise that with all modelling it is essential to take account of background concentrations due to sources not included in the model. The background can represent a significant part of the measured concentration, both for whole urban areas, such as London, where sources from outside London are predicted to account for 20-40% of total nitrogen oxides concentrations(1), and for roadside locations, where the background is likely to represent 60-95% of measured roadside nitrogen dioxide concentrations(2).

2.7 MONITORING OF URBAN AIR QUALITY

2.7.1 Introduction

There are basically two types of air quality monitoring equipment. Firstly there are continuous automatic monitors using sophisticated electronic techniques to give more or less instantaneous measurements of air pollution concentrations. They allow peak concentrations to be established. Such equipment is used in most of the Department of the Environment's air quality networks including the Enhanced Urban Network. A particular advantage is that the data can readily be transferred to a central computer using telemetry. Secondly, there are simple techniques which are less sensitive; have longer averaging times, typically 24-hours to one month; and cannot be connected to a telemetric system, making data acquisition and rapid dissemination more difficult .

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(1) Munday PK, Timmis RJ, and Walker CA (1989) **A Dispersion Modelling Study of Present Air Quality and Future Nitrogen Oxides Concentrations in Greater London** WSL Report LR 731 (AP)M, Warren Spring Laboratory, Stevenage, UK.

(2) Laxen DPH, Jensen RA and Brooks K (1988) **Nitrogen Dioxide at the Building Facade in Relation to Distance from Road Traffic,** in 'Indoor and Ambient Air Quality' 40-45, Selper Limited, London, UK.

In general, automatic analysers have exacting requirements in terms of power supply, air conditioning and protective housing. In addition, they generally require regular visits, and calibration by trained operatives.

Traditionally, automatic analysers have been point monitors, drawing air from one particular location into the analyser. In the past few years, however, long-path optical techniques have become commercially available. These measure average ambient concentrations over the length of the optical beam, typically of the order of a few hundred metres. One generic method is Differential Optical Absorption Spectroscopy (DOAS). It has been employed commercially in the OPSIS instrument, which is now in use in a number of UK urban areas. In principle, the technique is powerful in that many pollutants can be measured in one installation, given appropriate spectroscopic absorptions, path lengths and instrument configuration.

When due care is take to scrutinise the performance and outputs of the instruments, particularly over a range of light levels, the method can produce good correlations with conventional analysers for SO_2, NO_2 and ozone, although several published correlations suggest the DOAS technique might systematically under-read for ozone. This technique is also applicable to a number of hydrocarbons, including benzene which is of current interest. Unfortunately, there have as yet been few suitable conventional hydrocarbon measurement systems with which to carry out comparisons for validation purposes.

As yet, calibration protocols have not been developed for routine application to the DOAS technique to ensure traceability of the measurements to primary standards. Given the growing use of automatic analysers for urban air quality monitoring by a variety of organisations, it would be of considerable value if guidance could be provided to help ensure the standardisation of both operational and quality assurance/ quality control procedures.

The second approach involves the use of less sophisticated techniques. For many years, inexpensive wet chemical methods for measuring air pollution have been used. These include the National Survey method for black smoke and sulphur dioxide and the potassium iodide method for total oxidants (including ozone), although the latter has rarely been used in the UK. Whilst these methods are intended to be specific to one pollutant, they can suffer from interferences from other chemicals present in the air. Thus the National Survey method for sulphur dioxide is affected by other acidic and alkaline compounds (unless the analysis is specific for sulphate). The potassium iodide oxidant method measures all the oxidants in the air including ozone, nitrogen dioxide and peroxyacetyl nitrate (PAN), but can give unreliable results if sulphur dioxide is not removed from the air stream due to a negative interference from this compound.

In recent years passive diffusion tubes that are specific to one pollutant have been developed, overcoming the problems outlined above. They have been widely used to measure ambient levels of nitrogen dioxide. They are cheap, simple to use, need no power supply or protective housing, and require no attention when in operation. However, they can only give long-term average concentrations and consequently the results cannot be directly related to the European Communities air quality Directive, which requires hourly measurements. They can, though, be used to infer 98th percentiles of hourly measurements. The accuracy of diffusion tubes has recently been called into question, as they may be affected by wind when used in exposed locations. It is important that the significance of this finding is fully explored, given the widespread use of diffusion tubes.

Diffusion tubes will continue to have an important role in monitoring urban air quality, despite their limitations, as they provide a cheap and convenient way of identifying the spatial distribution of pollution, highlighting hotspots, and identifying trends in average concentrations. More recently passive diffusion tubes have been developed for measurement of benzene, sulphur dioxide, ammonia and ozone, but as yet their use has been limited.

The location of air pollution monitoring stations is a critical element of any monitoring programme, as concentrations are likely to vary widely over an urban area. The siting criteria used will depend on the purpose of the monitoring. Thus measuring compliance with EC air quality Directives may require the use of different monitoring sites than a research programme undertaken to enhance scientific knowledge of atmospheric chemistry.

In addition to the use of fixed sites, a few surveys of air pollution in urban areas have been undertaken using mobile monitoring laboratories. These are generally specially fitted vans equipped with a range of automatic analysers and data logging equipment. As there can be large hour to hour and day to day variations in air pollution levels, data from mobile laboratories need to be handled with caution.

2.7.2 UK Networks

The DOE has a number of air quality monitoring networks in the UK including several in urban areas. These are shown in Table 2.4.

The EC Directive networks have been set up to measure concentrations of the pollutants nitrogen dioxide, sulphur dioxide and smoke, and lead, for which the European Community set standards in the 1980s. The locations of the automated monitoring stations are shown in Figure 2.6. Annex D gives further information on the location of automated monitoring stations.

The Enhanced Urban Network is currently being set up. It will consist in its initial phase of 12 stations in cities throughout the UK. They are urban background stations, being established in city centres where concentrations are expected to be highest, and in locations representative of people's exposure for significant periods of time. The current and forthcoming monitoring stations in the urban network have been chosen on the basis of two criteria; population and geographical spread. The first 12 stations are shown in Figure 2.6.

The Hydrocarbon Network is in the process of being established. It will use a continuously cycling gas chromatograph (GC), which will sample for about 30 minutes in each hour. Its purpose is to define concentrations of hydrocarbons such as benzene and 1,3-butadiene, which are carcinogens, and a range of other compounds, which are principally of interest because of their role in the formation of ozone and other secondary pollutants. The sites are also shown in Figure 2.6.

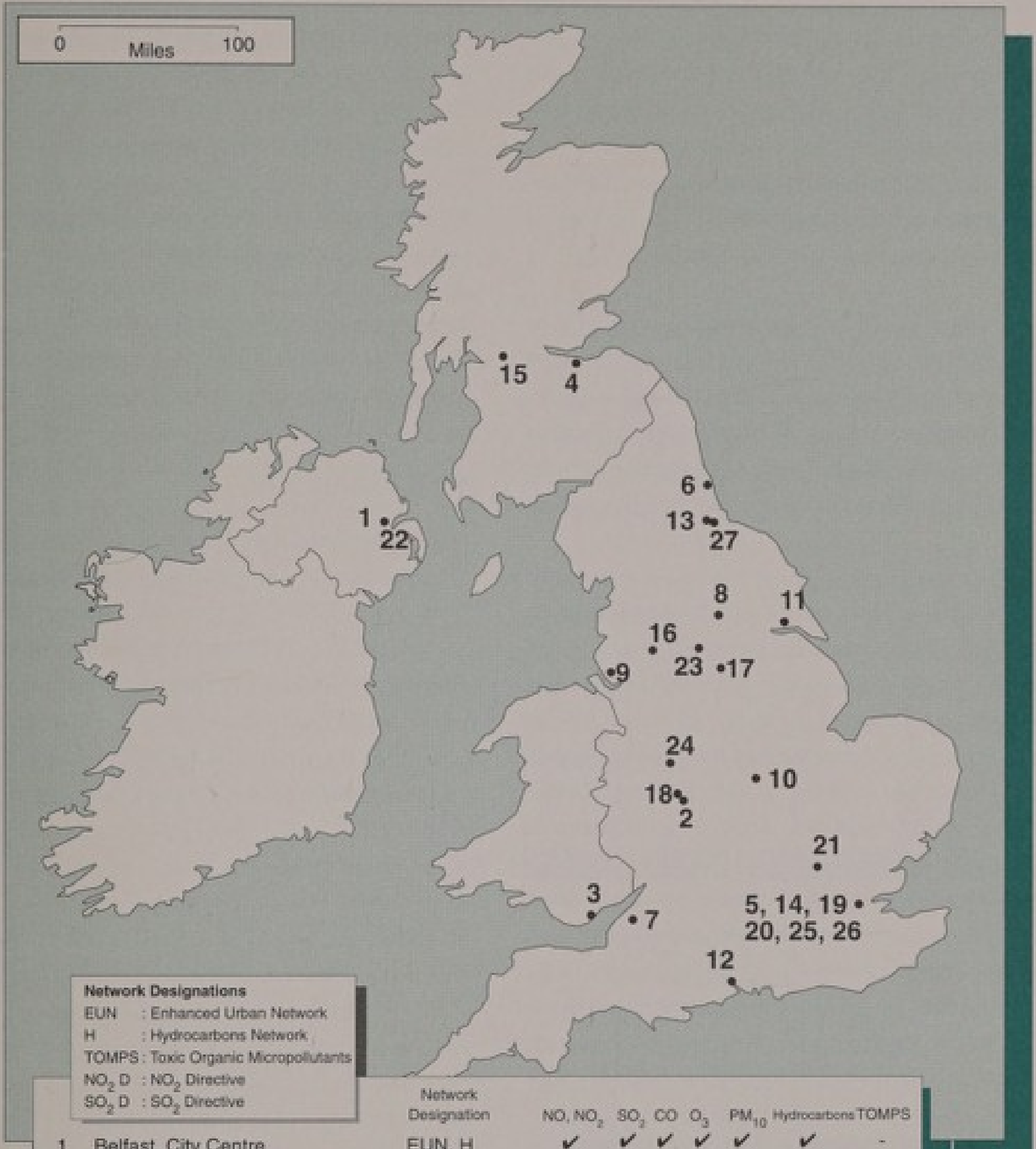
Table 2.4 Summary of National Air Quality Monitoring Networks in Urban Areas

Network	Pollutants	Type of Monitor	Number of Sites
EC Directive	nitrogen dioxide	chemiluminescence	7
	sulphur dioxide	uv fluorescence	3
	sulphur dioxide/smoke	bubbler/filter	166
	lead	filter	11
Enhanced Urban(a)	nitrogen dioxide	chemiluminescence	12
	sulphur dioxide	uv fluorescence	12
	carbon monoxide	infra-red absorption	12
	ozone	uv photometric	12
	PM_{10} particulates	TEOM	12
Hydrocarbon(b)	benzene	gas chromatography	6
	1,3-butadiene	gas chromatography	6
	other HCs	gas chromatography	6
TOMPS	PAHs	polyurethane filter	4
	PCBs	polyurethane filter	4
	dioxins/furans	polyurethane filter	4
Others (long-term, urban, etc)	nitrogen dioxide	chemiluminescence	2
	nitrogen dioxide	diffusion tube(b)	1,000
	sulphur dioxide	uv fluorescence	3
	sulphur dioxide/smoke	bubbler/filter	241
	carbon monoxide	infra-red absorption	6
	ozone	uv photometric	2
	lead	filter	7
	metals - urban	filter	5
	sulphate	filter	1

(a) 6 sites operational in 1992, 12 by 1994

(b) operational in 1993

Figure 2.6 Locations of Automated Urban Air Quality Monitoring Sites Funded by the DOE



Network Designations
EUN : Enhanced Urban Network
H : Hydrocarbons Network
TOMPS : Toxic Organic Micropollutants
NO_2 D : NO_2 Directive
SO_2 D : SO_2 Directive

		Network Designation	NO, NO_2	SO_2	CO	O_3	PM_{10}	Hydrocarbons	TOMPS
1	Belfast, City Centre	EUN, H	✓	✓	✓	✓	✓	✓	-
2	Birmingham	EUN, H	✓	✓	✓	✓	✓	✓	-
3	Cardiff	EUN, H, TOMPS	✓	✓	✓	✓	✓	✓	✓
4	Edinburgh	EUN, H	✓	✓	✓	✓	✓	✓	-
5	London- Bloomsbury	EUN, H	✓	✓	✓	✓	✓	✓	-
6	Newcastle	EUN	✓	✓	✓	✓	✓	-	-
7	Bristol	EUN	✓	✓	✓	✓	✓	-	-
8	Leeds	EUN	✓	✓	✓	✓	✓	-	-
9	Liverpool (planned)	EUN	✓	✓	✓	✓	✓	-	-
10	Leicester (planned)	EUN	✓	✓	✓	✓	✓	-	-
11	Kingston-upon-Hull (planned)	EUN	✓	✓	✓	✓	✓	-	-
12	Southampton (planned)	EUN	✓	✓	✓	✓	✓	-	-
13	Billingham	NO_2 D	✓	-	-	-	-	-	-
14	London - Bridge Place	NO_2 D	✓	✓	✓	✓	-	-	-
15	Glasgow	NO_2 D	✓	-	✓	-	-	-	-
16	Manchester	NO_2 D, TOMPS	✓	-	✓	-	-	-	✓
17	Sheffield	NO_2 D	✓	-	✓	-	-	-	-
18	Walsall	NO_2 D	✓	-	-	-	-	-	-
19	London - Earls Court	NO_2 D	✓	-	✓	-	-	-	-
20	London, Cromwell Road	-	✓	-	✓	-	-	-	-
21	Stevenage	TOMPS	✓	✓	✓	✓	-	-	✓
22	Belfast, East	SO_2D	-	✓	-	-	-	-	-
23	Barnsley	SO_2D	-	✓	-	-	-	-	-
24	Rugeley	SO_2D	-	✓	-	-	-	-	-
25	London - Greenwich	H	-	-	-	-	-	✓	-
26	Central London - Marsham Street	TOMPS	-	-	-	-	-	-	✓
27	Middlesbrough	H	-	-	-	-	-	✓	-

Another recent network has been set up to measure Toxic Organic Micropollutants (TOMPS) in urban areas. This is designed to give information on pollutants for which there is currently very little information but which are known to be toxic substances. Included are dioxins, which are present at very low concentrations, and which require careful and expensive analysis by gas-chromatography mass-spectrometry. This network is currently limited to 4 sites, as shown in Figure 2.6.

There are also various other networks in operation. One was set up in the mid 1980s to monitor the impact of the reduction of lead levels in petrol in 1985 and to follow the subsequent introduction of unleaded petrol. Another is a new network being established to monitor nitrogen dioxide using diffusion tubes in urban areas throughout the UK.

Until recently, all national air quality monitoring on behalf of the Department of the Environment was carried out by Warren Spring Laboratory. However, the DOE is now putting the operation of the Networks out to competitive tender. Part of the reason for this is to spread the experience and expertise in the rapidly expanding field of air quality monitoring. Another important reason has been to separate the quality assurance/quality control (QA/QC) functions from the day to day operations. Each network has a Central Management and Co-ordination Unit with overall responsibility for the network and a separate QA/QC Unit. There are variations for the day to day operational arrangements. For the Rural Network, there is a Site Management Unit with responsibility for a number of Local Site Operators and the Equipment Support Unit. For the Urban Network, the Central Management and Co-ordination Unit (CMCU) has direct responsibility for the Local Site Operators and the Equipment Support Unit. The structures and organisations involved are summarised in Table 2.5.

Despite a large investment in air quality monitoring in recent years by the Department of the Environment, the coverage of urban areas is still limited. There are many towns and cities of over a quarter of a million population that will remain outside the current and proposed automated monitoring networks.

2.7.3 Location Criteria

The locations of the monitoring stations are an important consideration in any air quality monitoring network. This is particularly so when the number of automatic monitoring sites that can be established is limited by financial considerations. There are broadly 6 categories of site in use in the UK:

- *industrial;*
- *roadside;*
- *urban background;*
- *suburban;*
- *rural;*
- *remote rural.*

Table **2.5 Structural Organisation of UK Urban Networks**

Network	**Structure**	**Organisations**
EC Directive	Centralised	Warren Spring Laboratory
	Local Site Operators(a)	Various
Enhanced Urban	CMCU	Rendel Science & Environment
	- Equipment Support Unit	Enviro Technology Services
	- Local Site Operators	Various
	QA/QC Unit	Warren Spring Laboratory
Hydrocarbon	CMCU	Harwell Laboratory
	QA/QC Unit	National Physical Laboratory
	Equipment Support Unit	Chrompack
	Local Site Operators	Various
TOMPS	Centralised	Warren Spring Laboratory
Others	Centralised	Warren Spring Laboratory
	Local Site Operators(b)	Local Authorities

(a) The sulphur dioxide and smoke network uses local authorities as local site operators, and the lead network is operated by Northern Environmental Consultants Limited.

(b) The nitrogen dioxide diffusion tube survey will co-ordinate data collected by local authorities.

Only the first four apply to urban areas. It is sometimes difficult to classify a site into one of these categories, but the basic features will be described to help interpret the results of monitoring surveys.

Industrial sites are rarely selected as part of a national network. Each industrial area will have its own features making it difficult to choose representative sites. The EC Directive Network has, however, included a nitrogen dioxide site designed to monitor emissions from the industrial area of Billingham. Industrial emissions are usually from chimney stacks and care needs to be taken in siting the monitoring station. The aim is usually to locate the station where concentrations can be expected to be highest. However, a site chosen to pick up the highest short-term (1-hour) concentrations will not necessarily be at the optimum position to pick up the highest annual mean concentrations.

Roadside sites are also of a somewhat specialist category, as each site will be individual in terms of its pollution concentrations. The traffic volume, the traffic mix and the traffic speed will all influence the concentrations, as will the setting, which may be a street canyon or an open road. In addition, concentrations fall-off rapidly away from the road, so the exact distance from the kerb is an important consideration. Some monitoring has been carried out at the 'kerbside', ie immediately above the kerb, and such a site is operated in central London, as part of the national monitoring programme. This is considered to represent extreme conditions and not to be very representative of the public's exposure. 'Roadside' monitoring is more usually carried out a few metres back from the kerb, often at the building facade, where it is considered to be more representative of people's exposure.

Urban background sites are the most common type found in urban areas. These represent typical exposure conditions for members of the public; in other words, conditions that significant numbers of people will be exposed to for significant periods of time. These sites are away from the immediate influence of local sources, but not uninfluenced by these sources, as the purpose of monitoring is usually to identify the highest background concentrations that might be experienced in urban areas. There is no clear guidance as to when a site moves from being 'roadside' to being 'urban background'. The new Enhanced Urban Network is based around 'urban background' sites and is using the following criteria to help in site selection:

The site should not be within:

- *30m of a very busy road (>30,000 vehicles/day);*
- *20m of a busy road (10,000 - 30,000 vehicles/day);*
- *10m of any other road (<10,000 vehicles/day).*

In a recent survey of nitrogen dioxide carried out by Warren Spring Laboratory, sites were defined as 'background' when they were more than 50 m from a major road (undefined). Studies in London have shown that, for nitrogen dioxide, local background is achieved at distances of around 25 m from busy roads.

Suburban sites fall between the urban and rural categories. They represent sites on the fringes of urban areas, where there will be a mix between housing and open land. The existing networks do not focus on such sites as they are generally of less interest in pollution terms. This may not be the case for ozone.

2.8 AIR QUALITY DATA DISSEMINATION

An important function of the air quality monitoring networks is the rapid provision of data to the public. This information is coupled with advice on the health effects. Currently, information is disseminated nationally on three pollutants: ozone, nitrogen dioxide and sulphur dioxide. The data are presented as air quality in one of four categories: very good; good; poor; and very poor, together with the highest 1-hour concentration in the last 24-hours. In addition a forecast is presented of air quality for the next 24-hours. No detailed evaluation has yet been carried out as to the effectiveness of this form of data presentation in conveying the information to the public. In addition to the immediate dissemination of data to the public, individuals and organisations can also have access to the longer term archives to enable research to be carried out. The mechanism for transferring data from several independent networks to the public is currently being re-evaluated by Logica UK.

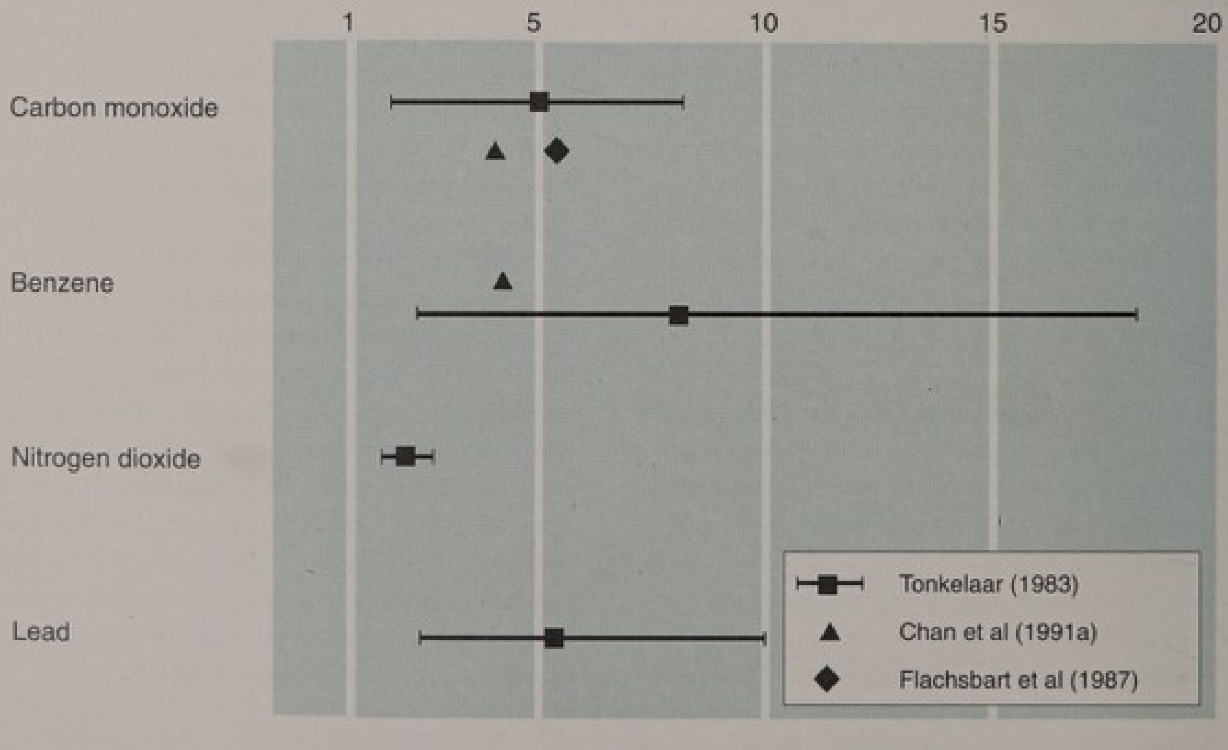
2.9 PUBLIC EXPOSURE TO URBAN POLLUTANTS

Monitoring is most commonly carried out at fixed locations in urban areas. These sites range from kerbside to urban background. They do not, however, cover the full range of conditions to which people are exposed. Considering traffic, which is the predominant source of urban air pollution, it is necessary when evaluating peak exposure to take into account exposure while travelling in cars, and on bicycles etc, as well as exposure in car parks, in tunnels and at petrol stations. The significance of exposure to pollutants in these locations will depend upon both the concentrations to which people are exposed and the duration of the exposure. Unfortunately, there have been relatively few studies to help quantify either of these two factors. In general, though, the pattern at the locations mentioned above is one of short lived exposure to high concentrations. Given the potential importance of these periods of exposure to high concentrations, and the multi-pollutant nature of the exposure, this aspect of urban air quality will be described in more detail here, rather than in the individual pollutant chapters.

2.9.1 Exposure in Vehicles

A reasonably consistent picture emerges from the few studies that have measured concentrations in cars while travelling on busy roads. These concentrations are essentially the same as those found immediately outside the car and significantly above urban background concentrations. Figure 2.7 summarises results for four pollutants from 3 studies carried out in different countries(1)(2)(3). The results have been standardised to concentrations measured over the same time period at nearby 'urban background' locations. On average, the concentrations of the primary pollutants CO and lead are 5 times higher in cars than at nearby urban background locations. Benzene concentrations appear to be more variable. This could be due to the additional role of evaporative emissions, which may well vary from one car to another. In the case of nitrogen dioxide, a secondary pollutant, concentrations in cars are a little under double those at urban background locations. This pattern is consistent with the ratios of roadside to local urban background concentrations, measured alongside a

Figure 2.7 Ratios of Pollutant Concentrations in Cars to that of the Urban Background



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(1) Tonkelaar W den (1983) **Exposure of Car Passengers to CO, NO, NO_x, Benzene, Toluene and Lead** Vth World Congress on Air Quality, Paris.

(2) Chan CC, Ozkaynak H, Spengler JD, and Sheldon L (1991a) **Driver Exposure to Volatile Organic Compounds, CO, Ozone and NO_2 Under Different Driving Conditions** Environmental Science and Technology **25**, 964-972.

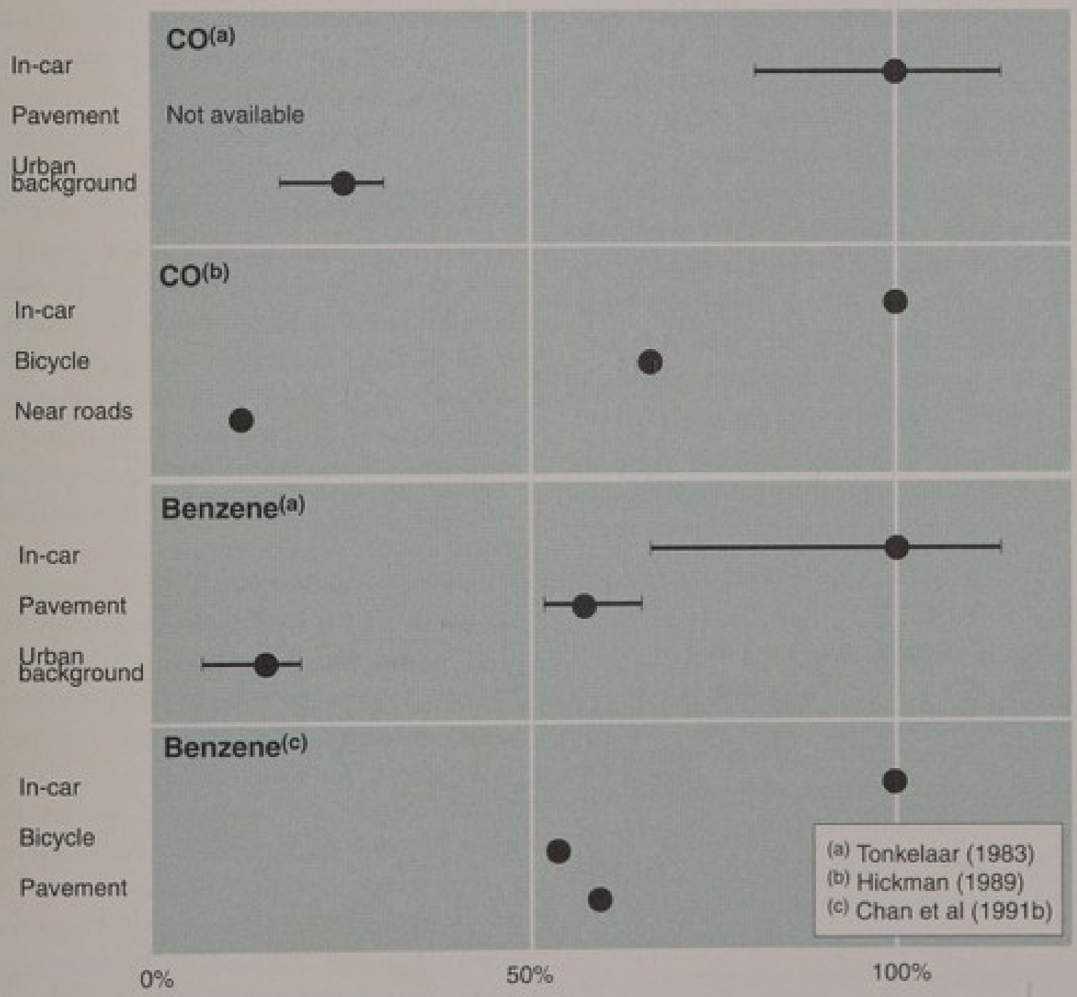
(3) Flachsbart PG, Howes JE, Mack GA and Rodes CE (1987) **Carbon Monoxide Exposures of Washington Commuters** Journal of the Air Pollution Control Association **37**, 135-142.

busy road (about 60,000 veh/day) in central London, which averaged around 3 for CO, around 4 for lead and only 1.4 for nitrogen dioxide.

Comparison of the in-car/urban background concentration ratios and the roadside/urban background ratios cited above suggests that exposure in cars is higher than that experienced alongside busy roads (except for ozone concentrations, which are depressed in cars, just as they are close to busy roads). This general pattern is repeated in a number of more specific studies, summarised in Figure 2.8, where both benzene and CO concentrations measured by personal exposure methods on pavements are on average around 50% of those measured in cars(1)(2)(3).

Concentrations in cars have been found to depend upon a number of factors, including vehicle speed, time of day and local background concentration. For both CO and VOCs (including benzene), concentrations are higher in congested slow moving traffic and they peak during the morning and evening rush hours. In-car concentrations are about 50% higher in the centre of towns than on fast motorway type roads, while the lowest concentrations are found on rural roads, although still elevated above local background. Nitrogen dioxide, on the other hand, displays a different pattern, with concentrations remaining high on the faster roads. The highest concentrations also occur during the middle of the day rather than during rush hour. These features are due to nitrogen dioxide being a secondary pollutant and to emissions of nitrogen oxides increasing with speed.

Figure 2.8 Relative Pollutant Concentrations Measured in Cars, on Pavements, on Bicycles and at Urban Background Sites (Average values for each are shown and where available the 25%-75%ile range; the in-car concentration is set to 100%)



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(1) Tonkelaar W den (1983) **Exposure of Car Passengers to CO, NO, NO_y, Benzene, Toluene and Lead Vth** World Congress on Air Quality, Paris.

(2) Chan CC, Spengler JD, Ozkaynak H and Lefkopoulou (1991b) **Commuter Exposure to VOCs in Boston, Massachusetts** Journal of the Air and Waste Management Association **41**, 1594-1600.

(3) Hickman AJ (1989) **Personal Exposures to Carbon Monoxide and Oxides of Nitrogen** TRRL Research Report 206, Transport and Road Research Laboratory, Crowthorne, UK.

2.9.2 Exposure of Cyclists

There have been few studies of people's exposure to traffic pollutants while on bicycles. Two investigations using personal samplers suggest that exposure of cyclists is less than that of people in cars, although concentrations are still well above urban background (Figure 2.8). It is difficult to tell from these studies whether the lower concentrations are due to cyclists using quieter roads or to concentrations in cars being higher than those experienced by cyclists on the same stretch of road. Cyclists generally operate at the side of the road, where concentrations, on average, can be expected to be lower than those experienced by motorists in the middle of a traffic lane. However, cyclists are breathing harder and therefore inhaling greater amounts of pollutants.

2.9.3 Exposure of Pedestrians

There have also been few studies of pedestrians' exposure to traffic pollutants alongside roads. Two studies of benzene using personal samplers suggest that on average pedestrians are exposed to about half the concentration experienced in cars along the same roads (Figure 2.8). Exposure of pedestrians can also be inferred from measurements made at fixed sites. Unfortunately, there are few roadside sites in the UK. Results for one busy roadside site in London (3 m from the kerb) showed annual mean concentrations to be 2–3 times higher than local background(1) for carbon monoxide; 4-5 times higher for nitric oxide; 1.1-1.8 times higher for nitrogen dioxide; around 3 times higher for lead; and 2–3 times higher for airborne particulates. Clearly pedestrians are exposed to traffic pollutant concentrations higher than the local urban background, although concentrations are still less than those experienced by people in cars.

2.9.4 Exposure in Car Parks

A limited number of studies have been carried out of pollution levels in car parks. An enclosed underground or multi-storey car park clearly has the potential for high concentrations of vehicle derived pollutants to build up. The concentrations encountered will be highly variable, depending on the number of vehicles using the car park; the occurrence, at peak periods, of queues; and the ventilation of the car park, whether forced or natural. It is therefore difficult to generalise about public exposure in car parks. Carbon monoxide emissions are particularly high from slow moving cars (see Figure 2.2) hence the focus on this pollutant in car park studies. Concentrations of over 100 ppm have been measured. These could be of significance if the exposure period is long enough. Insufficient attention has been paid to assessing the contribution this source makes to total exposure to traffic pollutants.

2.9.5 Exposure in Tunnels

It has been recognised for a long time that vehicle emissions build up in tunnels. For instance, fans had to be installed in the ventilation shafts of Blackwall Tunnel under the River Thames in London between 1922 and 1940, as the volume of motor traffic increased. A study in 1958/59 reported that the atmosphere in this tunnel was often irritating to the eyes(2). High concentrations of carbon monoxide, smoke and lead were measured in both this tunnel and the Rotherhithe Tunnel. The average carbon monoxide level was over 100 ppm (116 mg m^{-3}) during the rush hours, while airborne lead was around 15-20 μg m^{-3}. Further studies in the Rotherhithe Tunnel during the 1980s also demonstrated high levels of airborne lead, airborne particulates, and carbon monoxide. Lead concentrations were averaging around 15 μg m^{-3} prior to the reduction of lead in petrol in 1985, but subsequently fell by 50%. These concentrations were about 30-40 times higher than urban background levels. Airborne particulate (<10-15 μm) concentrations averaged 240 μg m^{-3} and were about 10 times urban background. The study of carbon monoxide involved measurements taken while driving through the tunnel. Concentrations measured outside the car varied along the tunnel between 3-94 ppm (3-109 mg m^{-3}). In contrast those measured in the car showed a steady build-up while driving through the tunnel to a peak of around 23 ppm (27 mg m^{-3}) as the car left the tunnel. High carbon monoxide concentrations were also found in a study carried out at the end of the road tunnel at Heathrow airport, although dispersion was rapid and the effect was limited to the proximity of the tunnel portal(3).

Given that most tunnels are artificially ventilated, it is not possible to generalise about concentrations, as the effectiveness of the ventilation will vary from one tunnel

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(1) London Scientific Services (1990) **London Air Pollution Monitoring Network Fourth Report 1989** (available from Rendel Science & Environment, London).

(2) Waller RE, Commins BT and Lawther PJ (1961) **Air Pollution in Road Tunnels** British Journal of Industrial Medicine **18** 250-259.

(3) Colwill DM, Hickman AJ and Waterfield VH (1982) **Atmospheric Pollution from Vehicle Emissions: Measurements Near the Tunnel Portal at London (Heathrow) Airport** TRRL Supplementary Report 769, Transport and Road Research Laboratory, Crowthorne UK.

to another. It is also clear from the studies that have been carried out, that concentrations vary along the length of the tunnel, so it is not possible to generalise from concentrations measured at one location.

2.9.6 Duration of Exposure

The exposure pattern of individuals will vary from person to person and from one day to another. It is reasonable to assume, however, that most urban drives will be of 10-60 minutes duration. A similar duration is likely for cyclists, although possibly somewhat lower.

There appears to be no information available on typical durations of exposure for pedestrians on busy roads, nor on the range of times that they are exposed in these locations. Exposure in car parks and tunnels, where even higher concentrations are experienced, will tend to be of shorter duration, probably of the order of 1 to 15 minutes, but again little detailed information exists. There are certainly occasions when exposure in car parks can be significantly longer, over one hour being reported in one instance.

2.10 EFFECTS ON BUILDINGS AND MATERIALS

Despite the large reductions in smoke levels in urban areas over the past thirty years, the soiling of buildings remains a problem. Diesel exhaust is a rich source of very fine carbon particles known as Particulate Elemental Carbon (PEC). It is now recognised that PEC emissions from diesel vehicles are the main source of soiling in most European towns.

These particles are very small and sticky due to their hydrocarbon content. Thus, a diesel particle landing on a surface is more likely to become strongly adhered to it than other particulate matter. It is also much less wettable than a suspended soil particle, and thus is less readily removed by rain.

The surface tension properties of PEC have implications for potentially damaging reactions which may occur within the patina of a building's facade. Acidic gases such as sulphur and nitrogen oxides can become easily absorbed onto the surface of such particles and once deposited on a soiled stone surface may act synergistically with it. Also, PEC may aid the catalytic conversion of such acidic gases to the sulphate and nitrate forms respectively.

The enhanced erosion of certain building stones, and the greater corrosion of metals, due to sulphur dioxide deposition, is well established. As is to be expected, the steady reduction of sulphur dioxide in urban areas has been matched by a reduction in the corrosion rate of metals. However, measurements of the erosion rates for stone have not demonstrated this same reduction. It is thought this may be due to a 'memory effect', whereby the erosion rate is determined by previous exposure. It is also possible that the increased urban concentrations of nitrogen oxides have compensated for the decline of sulphur dioxide, although there is no clear evidence as to the role, if any, that nitrogen oxides play in stone erosion.

In addition to causing soiling and enhanced corrosion/ erosion of building materials, air pollutants can affect a wide range of other materials used in urban areas. Of these pollutants, ozone is perhaps the most important. It is a very reactive gas, which causes the ageing of rubber. This ageing process can be reduced by adding anti-oxidants, but this may increase the material cost by 10 to 25%. Ozone can also attack the cellulose in textiles, reducing the strength of some items, and causing the fading of fabrics. Generally, however, the replacement of textiles due to changes in fashion occurs before significant damage from air pollution can take place. Furthermore, most textiles are kept indoors where levels of ozone are low. Ozone can also damage surface coatings such as paint. In this context, particular attention is paid to the protection of valuable paintings in art galleries from damage due to ozone.

Although little research has been undertaken in recent years on the damage to materials caused by ozone, there is evidence to suggest that the economic costs may be considerable. For instance, the cost of such damage in the United States of America was estimated in the 1970s to be in the region of $900 million per year (approximately equivalent to $2, 650 million in 1991).

2.11 IMPACTS OF URBAN AIR POLLUTION ON PARKS AND URBAN ECOSYSTEMS

Urban vegetation is characterised by amenity trees as found in public parks and alongside roads, and herbaceous plant species also typical of public parks in addition to private gardens and allotments.

Since the implementation of the Clean Air Act in 1956, urban air quality has altered considerably, as both SO_2 and smoke levels have sharply declined. Prior to this legislation very few tree species were able to grow and thrive in urban areas, whereas nowadays a much greater diversity of trees can be seen. The colonisation of lichen species which has been observed in some areas of London is consistent with falling SO_2 levels. However this improvement in urban air quality has been negated to a large extent by the dramatic increases in vehicle exhaust emissions, resulting in elevated levels of NO_x and hydrocarbons, both precursors of O_3. Both NO_2 and O_3 have been demonstrated to affect tree growth and performance at concentrations typical of those recorded during pollution episodes which characterise urban air quality.

So far it has not been possible to quantify the contribution made by air pollution to damage to amenity trees. This is a complex problem as it is difficult to separate effects attributable to air pollution from those caused by other stress factors such as road salt, drought and pest infection. These other stresses may in fact predispose trees to damage by air pollutants or vice-versa.

Several studies have provided strong evidence that air quality in urban areas is a major factor influencing growth of herbaceous species. Studies in which crop plants have been exposed along transects from suburban areas into central London have shown clear trends of decreasing yield on moving into the city centre. However it is difficult to single out the effects of any one pollutant as although visible damage attributable to high ozone episodes has been recorded, effects on yield for example are mainly attributable to pollutant mixtures.

The fact that the influence of urban air quality on vegetation has not been fully defined highlights the need for continued scientific research in this area. In recognition of this need, the DOE Directorate of Rural Affairs is currently commissioning a pilot study to identify main stress factors affecting amenity trees. Such innovations will then permit a more detailed assessment of the extent of the problem. Furthermore it may then be possible to make confident predictions concerning future impacts of air quality on vegetation in the light of the widespread use of catalytic converters.

2.12 PUBLIC NUISANCE EFFECTS

The focus of most air quality standards, emission control regulations and other legislation is on the protection of human health or on the prevention of harm to the environment. However, the aspect of air pollution that often causes most direct concern to the public is the nuisance effects arising from fumes, odours, dust and dirt. Traffic is the most widespread source of these nuisance effects, although certain industries and construction/demolition activities can contribute to localised effects.

Public attitude surveys since the early 1970s have consistently revealed public concern about 'dust and dirt' or 'fumes and odours' arising from traffic, with these effects ranking alongside noise nuisance from traffic. Despite this concern, very little by way of objective study has been carried out. As controls are focused largely on gaseous emissions from motor vehicles, it is possible that without any control of nuisance effects the public will not perceive the improvement in air quality. A control programme on nuisance aspects of air quality will require a far greater understanding of the nature and sources of the nuisance.

Studies by the Transport Research Laboratory of the environmental effects of a number of schemes that changed traffic flow have shown a strong link between nuisance and both the number of lorries and the change in total traffic flow(1). Road schemes that reduced traffic by 60% on average, were found to reduce the number of people bothered by dust and dirt at home, either 'very much' or 'quite a lot', by half, from 56% to 28%. In one case, the percentage bothered by dust and dirt was reduced from 55% to 16% following implementation of a scheme that reduced lorry traffic, but which did not reduce total traffic flow. The significant role of lorries identified in this study probably represents a combination

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(1) Mackie AM and Davies CH (1981) **Environmental Effects of Traffic Changes** TRRL Report LR1015, Transport and Road Research Laboratory, Crowthorne, UK.

of effects, including noise/vibration and the perceived physical danger, but is also likely to relate to the more smoky and odorous nature of emissions from diesel engines. In another case a 16% increase in traffic doubled the number of people bothered by dust and dirt, from 33% to 63%.

Dust and dirt from traffic will include direct exhaust emissions of particulates (mainly from diesels) and dust resuspended from the road by passing traffic. The resuspended material will include soil material that predominates on road surfaces; products of vehicle wear ie rust, tyre rubber etc; and de-icing salt in winter months. The nuisance effect of this dust and dirt is related to its deposition onto surfaces. It is most noticeable on windows and window sills; on cars; and on washing and indoor fabrics. The soiling effect of the carbonaceous particulates emitted from diesel engines is considered to be particularly important, however, little is known of which sources of dust and dirt are most important.

A recent major study in Norway has examined the relationship between public nuisance impacts of traffic and the characteristics of the traffic(1). The degree of nuisance from dust and dirt was found to depend on traffic flow in the nearby street, but an improved relationship was found if account was taken of the general traffic in the area. Thus a given traffic flow on the nearby road caused more concern in a major urban area than the same traffic flow in a suburban area. This, and other studies, has shown that the nuisance effect of traffic applies both indoors and outdoors.

A study in London has shown that soiling levels alongside busy roads are on average double those measured away from the road(2). The average soiling rate alongside roads was 16% per week, with a number of sites showing levels above the 20 to 25% per week threshold that has been established as the level at which there is a clear nuisance effect. High soiling rates above the nuisance threshold have also been measured around construction sites.

Fumes and odours appear to be of less significance as a source of nuisance. The term 'fumes' is very difficult to define. It includes gases as well as fine aerosol particles (ie less than 2 μm in diameter) and often implies the odorous component of these. Surveys suggest that the public associate the term 'fumes' with health effects, as well as nuisance. A public opinion survey by the Department of the Environment in 1989 found that 33% were 'very worried' and 42% 'quite worried' by traffic exhaust fumes.

Odour from vehicles will contribute to the unpleasantness of being in the vicinity of traffic. It is the nature of the perception of odours that a response is elicited from exposure over a period of a few seconds, and concentrations over this time period can be a factor of 10-20 times higher than those measured over one hour. There has been little work on characterising the odorants in vehicle exhaust. Aldehydes are thought to play an important role and one study has suggested benzaldehyde as a marker for diesel exhaust odorants. The use of catalytic converters has added an odorant to the roadside environment, in the form of hydrogen sulphide. This is created in the catalyst from the small amounts of sulphur present in petrol.

Odours are one of the main sources of public complaint about air pollutants. These complaints arise from specific sources, ranging from major industry to small catering outlets. An example of a source of complaint in urban areas is the small vehicle paint spray operator. The Environmental Protection Act has streamlined procedures for bringing nuisance actions against offenders. It also requires both small and large industrial premises not to create an odour nuisance outside the boundary fence.

2.13 VISIBILITY

One of the most obvious impacts of air pollution is loss of visibility; and for many people the associated loss of amenity is a serious concern. Air pollution reduces visibility by introducing particles and gases, which absorb and scatter light, between the observer and the observed object. Fogs are the most extreme instance of visibility loss, and there is much evidence that air pollution increases the prevalence of urban fogs. This is associated especially with pollution by airborne particles, which act as nuclei for the condensation of fog droplets. Smogs of the classical London type, which could reduce

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(1) Institute of Transport Economics (1992) **Traffic and the Environment (English Version)** Institute of Transport Economics, Norway.
(2) Moorcroft SM and Laxen DPH (1990) **Assessment of Dust Nuisance** Environmental Health, August 1990, 215-217.

visibility to a few metres, are now a thing of the past. However, less intense winter smogs still occur occasionally, related largely to the build-up of traffic related pollutants. Reduced visibility is now more commonly associated with summer smogs due to photochemical air pollution (Los Angeles type smog). The reasons for visibility degradation are discussed in more detail in Chapter 6.

2.14 SUMMARY AND KEY ISSUES

- *The nature of urban air pollution has changed over recent decades. Motor vehicles are now the dominant source.*
- *There are a growing number of legislative measures available to control urban air pollution. The efficacy of these measures, especially those related to motor vehicles, has not been adequately evaluated.*
- *Meteorological conditions are important in determining day to day and seasonal variations in pollution concentrations. They also determine the occurrence of pollution episodes.*
- *Air quality monitoring has increased in recent years both in terms of the number of pollutants monitored and the number of sites. However coverage of urban areas is still limited.*
- *Models are useful for developing, and assessing the impact of, pollution abatement strategies. However, models are not well developed and tested for predicting the localised impact of roads in urban areas.*
- *Pollution concentrations measured in cars are generally higher than those found elsewhere in urban areas. They are also elevated in carparks and tunnels. There has been little work to quantify public exposure to air pollutants in these and other hot-spots.*
- *Dust and dirt represent important sources of public concern about air pollution in urban areas, yet little quantitative work has been carried out on the subject. There is no strategy to tackle this form of air pollution.*

2.15 RESEARCH RECOMMENDATIONS

- *Urban air quality monitoring should be extended to cover all major UK urban areas. It is envisaged this would involve an additional 10-15 stations, located in urban centres with a population in excess of 200,000-250,000. Establishing these stations sooner rather than later is to be encouraged, as it will enable the effectiveness of current control measures to be determined.*
- *There is a need to supplement the one kerbside site in the UK with a number of fully instrumented roadside monitoring stations. These should be in more than one urban area. They will help define the role of road traffic as a determinant of urban air quality. The pollutants monitored should include NO_2, SO_2, CO and PM_{10}. These stations should be established as soon as possible so as to establish the effectiveness of the introduction of catalytic converters.*
- *Lack of long-term monitoring data has hampered our understanding of urban air quality. There should therefore be a commitment to maintaining a number of air quality monitoring stations at fixed locations for extended periods, so as to adequately follow trends.*
- *The substantial commitment to air quality monitoring in the UK must be matched by the provision of adequate resources for the scientific and policy evaluation of the vast amount of data that will become available.*
- *Given the importance of predicting air quality impacts of specific road proposals in urban areas, there is a need to validate existing dispersion models, including those specifically designed for street canyons.*
- *Local authorities are increasingly undertaking their own air quality monitoring. They should be given guidance, in the form of a manual, to ensure that measurements are made and presented in a consistent way. This should include recommendations for equipment selection and detailed operational and quality assurance/quality control procedures.*
- *Fixed monitoring stations do not provide sufficient information to fully characterise the public's exposure to air pollution. Studies should be carried out to define the importance of exposure in different*

locations, such as in cars and alongside busy roads, so as to develop adequate measures to protect human health.

- *Although the DOE has increased the dissemination of air quality data to the public through the provision of a freephone line; through CEEFAX; and through the printed and broadcast media, no study has been carried out as to the effectiveness of the current presentation. Research should be undertaken to establish the effectiveness with which the data are being communicated.*
- *Urban emission inventories have only been undertaken for the Greater London area. The capital may not necessarily be representative of other urban areas and therefore inventories should be undertaken for a number of other urban areas of various sizes and types.*
- *Further studies are required into nuisance aspects of urban air pollutants, particularly those from traffic, to ensure that improvements in air quality are perceived as such by the public.*

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3 Nitrogen Compounds

3.1 INTRODUCTION

The most important nitrogen compounds present in urban locations are nitric oxide (NO) and nitrogen dioxide (NO_2), referred to collectively as NO_x. The main source of these pollutants in urban areas is vehicle emissions and, arguably, NO_2 has become the most significant urban air pollutant in the UK.

Other nitrogen oxides, such as N_2O, N_2O_3 and N_2O_4, do not contribute significantly to urban air pollution. However, nitrogen pentoxide (N_2O_5), nitrogen trioxide (NO_3), nitric acid (HNO_3) and nitrous acid (HNO_2) may be important in the chemistry of pollution episodes which may develop over several days. Peroxyacetyl nitrate (PAN) and other organic nitrates are also important in the atmospheric chemistry of such episodes. Nitrogen compounds also contribute to the wet and dry deposition of acid species on buildings. This chapter principally is concerned with NO and NO_2 and includes the following:

- *their sources;*
- *relevant EC legislation and WHO guidelines;*
- *typical concentrations in urban locations;*
- *projected future trends.*

Nitrogen dioxide has been shown to have an adverse impact on health. Its main effect is on the respiratory system, with young children and asthmatics being the groups most at risk.

The oxide emitted in largest quantities into the atmosphere is NO which is relatively innocuous. However, once emitted into the atmosphere NO is oxidised to NO_2 by oxidants such as ozone. The proportion of NO which is converted to NO_2 and the reaction rate depend upon the concentration of ozone available for reaction and the concentration of NO to be oxidised (see Chapter 7). This reaction is fast and approaches completion in approximately one minute. However, close to large sources of NO, such as power station plumes, busy road junctions or street canyons, the supply of ozone may be rapidly exhausted and a large proportion of the NO is left unoxidised. Nevertheless, at increased distances downwind of large sources, as the highly polluted air gradually mixes with cleaner air and more ozone becomes available, the majority of the NO is ultimately converted to NO_2.

The conversion of NO to NO_2 is an important feature of the chemistry of NO_x in urban air and one which is not fully understood, as yet, because there are conditions under which NO_2 may be created by routes other than oxidation of NO by ozone. As NO_2 is a pollutant of great concern in urban environments, this is an aspect which will require further investigative work.

3.2 SOURCES

Nitrogen oxides are formed at high temperature during combustion processes from the oxidation of nitrogen in the air and any nitrogenous components of the fuel or other material being burned. Generally, it is the oxidation of nitrogen in air which produces the majority of NO_x. The most important sources are the combustion of fossil fuels in power generation and the combustion of petrol and diesel in vehicles. The proportion of NO produced compared to NO_2 varies from process to process, being a function of combustion temperature, combustion conditions and other factors. For some processes it is sometimes difficult to determine accurately the proportion of NO_2 produced and in such cases it is often assumed to be approximately 10% of the total. Particularly with regard to vehicle emissions, this is an area which needs further examination. Since it is NO_2 which can affect health and because a large proportion of NO may ultimately be converted to NO_2, it is common practice to describe all of the NO_x as NO_2 in estimates of emissions by mass.

Estimated UK emissions of NO_x for the period 1980-90 are presented in the form of a histogram in Figure 3.1, taken from the 1991 Digest of Environmental Protection and Water Statistics(1). These figures are likely to be less accurate than those estimated for some other emissions, such as SO_2, because they are based on relatively few measurements and combustion conditions can vary widely. Furthermore, emissions estimates from vehicles depend upon the age distribution of vehicles in use, their state of maintenance and the distribution of speeds, each of which have a degree of uncertainty. It is estimated that the accuracy of the figures is approximately thirty percent. Estimates have been revised upwards in recent years because of changes to the Department of Transport's figures for vehicle kilometres and on a number of other issues such as the age distribution of vehicles on the road.

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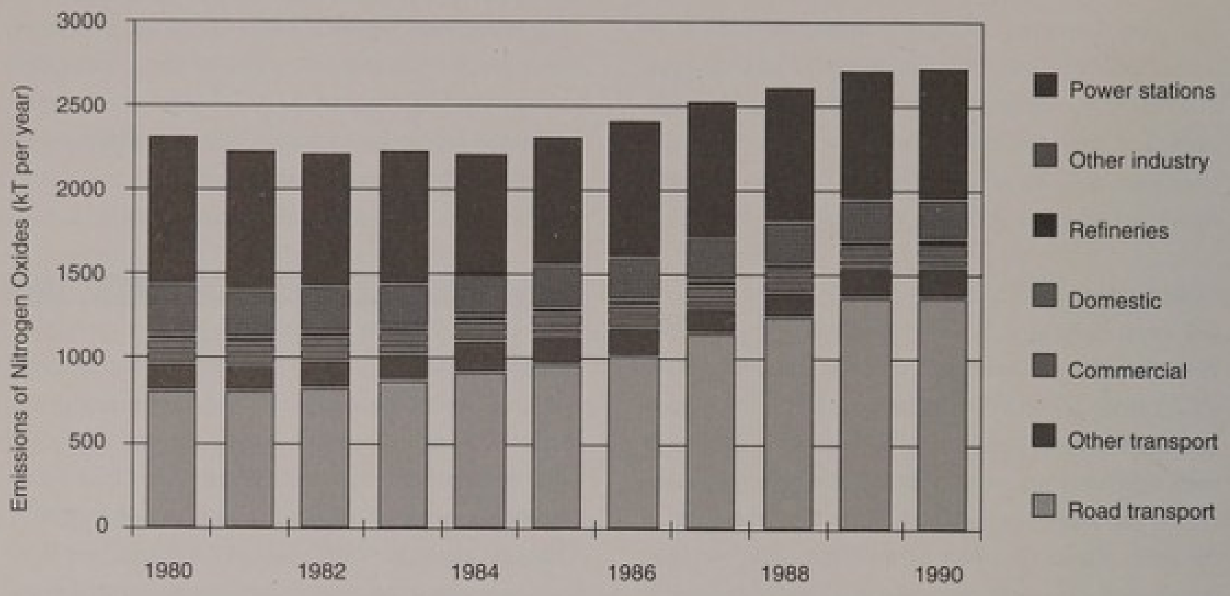
(1) Department of the Environment (1992) **Digest of Environmental Protection and Water Statistics No 14, 1991** HMSO, UK.

Figure 3.1 Estimated UK Emissions of NO_x, by Source Category



All of the emissions arise from combustion of various fuel types. For 1990, coal and petrol each account for 29% of emissions and DERV for a further 21%. However, it should be borne in mind that the estimates are for emissions on a national scale. Relative contributions to the concentrations of NO_x in urban areas will be different, with the contribution from vehicles assuming a higher proportion than indicated by the national average. In locations where the highest concentrations are found, emissions at ground level from vehicles are likely to dominate.

Figure 3.1 also indicates changes in emissions during the period 1980-1990. Total emissions were stable during the early 1980s, at approximately 2.2 MT per annum. However, since 1985 they have risen steadily to 2.7 MT per annum in 1990. Total NO_x emissions from road transport have risen by approximately 40% during this period. In addition, the proportion of the total attributable to road transport has risen, from 35% in 1980 to 51% in 1990, whereas that from power generation has declined from 38% to 28% during the same period.

Future trends in emissions will be affected by following factors:

- *the introduction of catalytic converters which are required on new cars from the end of 1992*(1)*;*
- *growth in the number of vehicles on the road;*
- *the reduction in emissions from large combustion plant*(2)*;*
- *the introduction of gas fired plant for power generation.*

3.3 STANDARDS AND GUIDELINES

Limit and guide values for the concentration of NO_2 in air have been specified by the European Community(3) and incorporated into UK law by the Air Quality Standards Regulations (1989)(4). The limit value, 105 ppb (200 $\mu g\ m^{-3}$) expressed as the 98th percentile of hourly averages over a period of one year, should not be exceeded and is set at a level so as to protect human health. The guide values are intended as longer term objectives and are set to improve the protection of health and to contribute to the protection of the environment. Guide values are 26 ppb (50 $\mu g\ m^{-3}$), as a 50th percentile of hourly averages, and 71 ppb (135 $\mu g\ m^{-3}$), as a 98th percentile of hourly averages.

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(1) **Council Directive of 26 June 1991 Amending Directive (70/220/EEC) on the Approximation of the Laws of the Member States Relating to Measures to be Taken Against Air Pollution by Emissions from Motor Vehicles** (91/441/EEC) Council of the European Communities, Belgium.

(2) **Council Directive of 24 November 1988 on the Limitation of Emissions of Certain Pollutants into the Air from Large Combustion Plants** (88/609/EEC) Council of the European Communities, Belgium.

(3) **Council Directive of 7 March 1987 on Air Quality Standards for Nitrogen Dioxide** (85/203/EEC) Council of the European Communities, Belgium.

(4) Her Majesty's Government (1989) **The Air Quality Standards Regulations** Statutory Instrument Number 317, HMSO, UK.

Table 3.1a Air Quality Limit Values and Guidelines for Nitrogen Dioxide (ppb)

Organisation	50th Percentile	98th Percentile	24-hour Average	1-hour average
EC Directive(a)(b)				
Limit Value	-	105	-	-
Guide value	26	71	-	-
World Health Organization	-	-	78	209

(a) EC Directive (85/203/EEC) refers to hourly mean measurements

(b) The original Directive specified values in µg m^{-3}, as do the WHO. They have been converted to ppb here using a factor of 0.523 (assuming a temperature of 20°C)

Table 3.1b Department of the Environment Air Quality Bands for Nitrogen Dioxide (hourly average concentration)

Category	Concentration (ppb)
Very good	<50
Good	50-99
Poor	100-299
Very poor	≥300

The World Health Organization (WHO) also recommend guidelines. These have been set with regard to the lowest observed effect level on asthmatics and 'allow for a further margin of protection'. The guidelines are 210 ppb (400 µg m^{-3}) as a maximum one hour average and 80 ppb (150 µg m^{-3}) maximum 24-hour average. The standards and guidelines are summarised in Table 3.1.

3.4 CONCENTRATIONS OF NO_2 AND NO IN THE UK

3.4.1 A Brief Introduction to the Principal Measurement Techniques

Nitrogen dioxide is a significant pollutant in urban air, primarily because it arises from vehicle emissions. As a result, a considerable amount of data exist on urban concentrations of NO_2, although compared to the long history of SO_2 and smoke monitoring, many of the measurements are relatively recent. Many of the datasets have been obtained in short-term 'diffusion tube' surveys lasting some weeks or months, although a number of longer-term networks have been in operation since 1986. Diffusion tubes have proved very popular because they are cheap and hence can be deployed in large numbers over a wide area. They have, therefore, provided a cost-effective means of measuring spatial distributions of NO_2.

The diffusion tube is a 'passive' sampler and as such measures a mean concentration over the period for which it is exposed, usually one to four weeks. For measurement of long-term mean concentrations this poses no difficulties, but clearly it is impossible to measure hourly averages, and hence short-term peak concentrations, by this method. The 98th percentile may only be estimated, based on measurements of the 98th percentile/annual average ratio using chemiluminescent analysers.

For the measurement of NO_2 concentrations, the EC Directive states as a reference method an analyser which uses the 'chemiluminescent' technique. Such an instrument samples the ambient air continuously and the results are usually reported as hourly averages. In this way, a year of such data can be used to measure directly the 98th percentile as defined in the EC Directive.

Analysers of this type are expensive to purchase and operate, relative to the diffusion tube, and as a consequence they are deployed at a much more limited number of sites. On the other hand, they are usually part of a fixed monitoring station and thus provide trend data over a period of time.

Much recent interest has focused upon the comparability of chemiluminescence instruments and diffusion tubes for measurement of NO_2. A detailed intercomparison(1) indicated that there is a tendency for diffusion tubes to over-read relative to chemiluminescence instruments, which is the reference technique for EC Directive monitoring. Whilst on average the diffusion tubes gave results around 30% higher, the factor was extremely variable and at some sites the two techniques were in

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(1) Campbell GW, Cox J, Downing CEH, Stedman JR and Stevenson K **A Survey of Nitrogen Dioxide Concentrations in the United Kingdom Using Diffusion Tubes: July to December 1991** WSL Report LR893, Warren Spring Laboratory, Stevenage, UK.

good agreement. Some other users of diffusion tubes have reported relatively close agreement between the two techniques at their sites.

There are physical reasons why diffusion tubes may over-read in a site-specific manner. The influence of wind can cause turbulence at the tube inlet which reduces the effective diffusion length, leading to more rapid NO_2 uptake. This effect is wind-speed dependent and hence intimately related to diffusion tube siting. For this reason, any over-reading is highly site-specific and no general correction factor can be recommended. Diffusion tube data in this report are for this reason presented uncorrected, but the reader should be aware of this potential difficulty and the consequent positive bias in some data.

3.4.2 Trends in Annual Average NO_2 Concentrations

Data from chemiluminescent analysers are shown in Figure 3.2 for a number of monitoring sites in cities which form part of the DOE's 'NO_2 Directive' network managed and operated by Warren Spring Laboratory, (except for the County Hall site which was operated by London Scientific Services.)

There are no clearly identifiable trends in most of these data for either NO_2 or NO, although the period of measurement at Glasgow and Manchester is, as yet, somewhat limited. Analysis of trends at other sites where chemiluminescent monitors have been deployed over the period 1976 to 1991 indicates a similar lack of trend.

The majority of these sites for which several years chemiluminescence data are available are part of the EC Directive network and hence located at either heavily-trafficked city centre sites, or at sites influenced by industrial emissions of NO_x. The elevated concentrations of NO_2 and NO_x at these sites have remained broadly constant over the limited time period (mostly five years) for which data are available. This is not surprising in the light of very slow rates of traffic growth in heavily congested areas and little change in industrial emissions.

There are exceptions to this pattern. One is the non-Directive Stevenage site which has shown a steady upward trend in NO_x over many years, and NO_2 since 1978. This behaviour is consistent with traffic growth on the nearby A1(M) causing an increase in NO_x. This increase in NO_2 was smaller than that in NO_x which is consistent with our understanding of the conversion of the NO to NO_2 in the atmosphere. Additionally, the County Hall rooftop site in central London showed an increase in NO_2 and NO_x over the period 1978 to 1989, when monitoring ceased (see Figure 3.2). Because of its elevated location, this site may be more representative of pollution of London as a whole than the roadside sites. Some rural sites (eg Bush, near Edinburgh) have also shown increases in NO_2 over recent years, although the majority have not.

The measurements from diffusion tube surveys are also equivocal on this issue. The survey of Campbell et al(1), (1992) covered 240, mainly urban, sites and produced concentration fields for NO_2 for the periods July-December 1986 and July-December 1991: the latter were, on average, 35% higher than the former. The authors drew attention to the fact that the observed difference was well within the interannual variability in NO_2 observed at UK sites and that it was not necessarily indicative of an upward trend in NO_2, but noted that the difference was consistent with the increase in NO_x emissions from low-level sources over this period. Diffusion tube surveys in specific urban areas including London and Manchester which have sampled over the entire six year period have not shown a significant trend in NO_2. These surveys have generally used relatively high-NO_x sites and it is possible that NO_x levels have increased, whilst NO_2 has not. It is therefore possible that urban NO_2 concentrations will not diminish in line with NO_x emissions. Some of these data are presented in Figure 3.3.

3.4.3 Spatial Distributions of Annual Average Nitrogen Dioxide Concentrations

The continuous analysers used in the Directive network provide excellent data on the temporal variation of NO and NO_2 concentrations but these are, of necessity, too sparsely distributed to describe accurately spatial distributions in individual towns and cities. The use of diffusion tubes in surveys goes a long way to solving this problem.

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(1) Campbell GW, Cox J, Downing CEH, Stedman JR and Stevenson K **A Survey of Nitrogen Dioxide Concentrations in the United Kingdom Using Diffusion Tubes: July to December 1991** WSL Report LR893, Warren Spring Laboratory, Stevenage, UK.

Figure 3.2 Annual Mean Concentrations of NO and NO_2 in London (Victoria), Glasgow, Manchester and London (County Hall Rooftop) in Recent Years, for which data are available

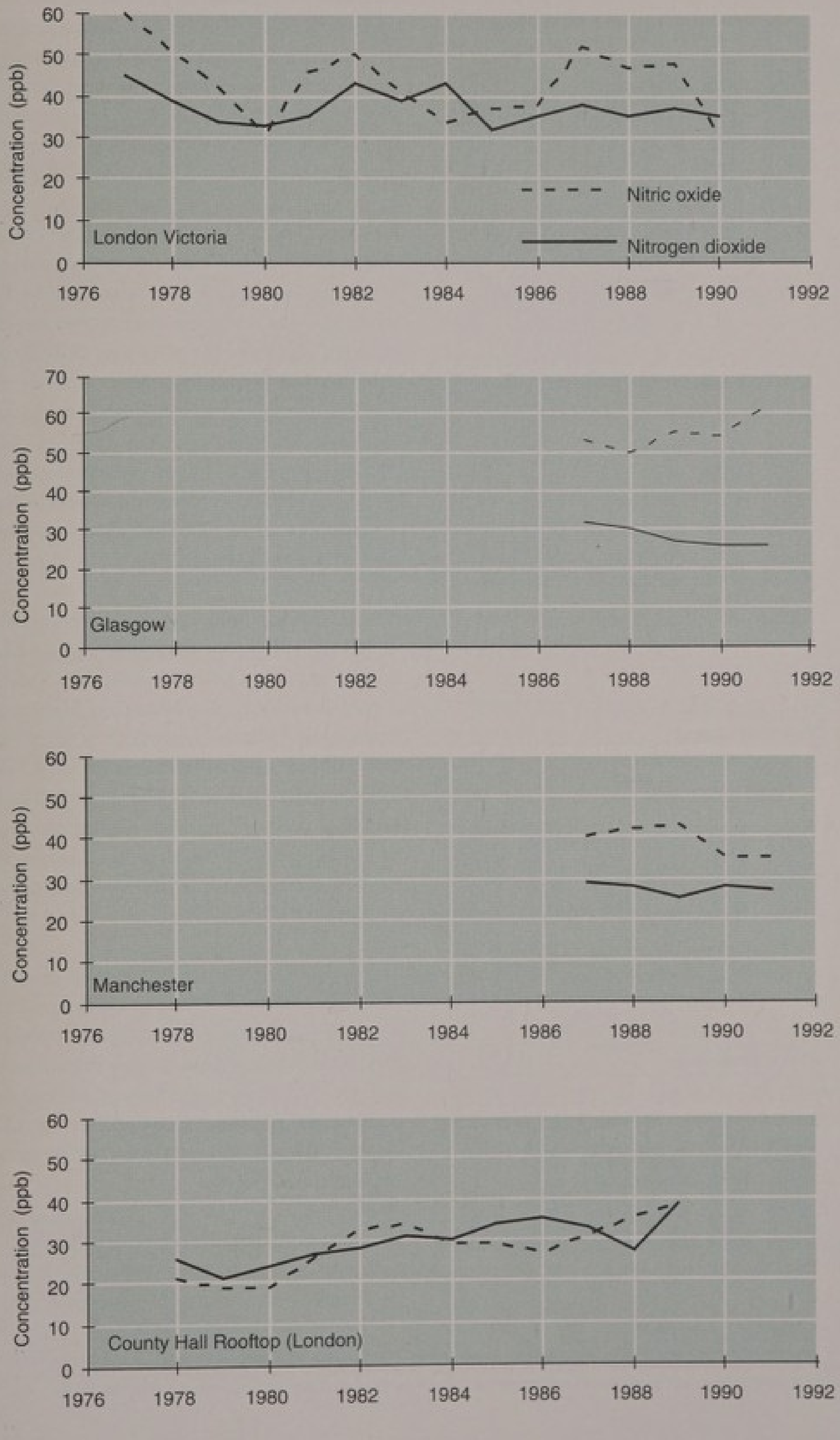
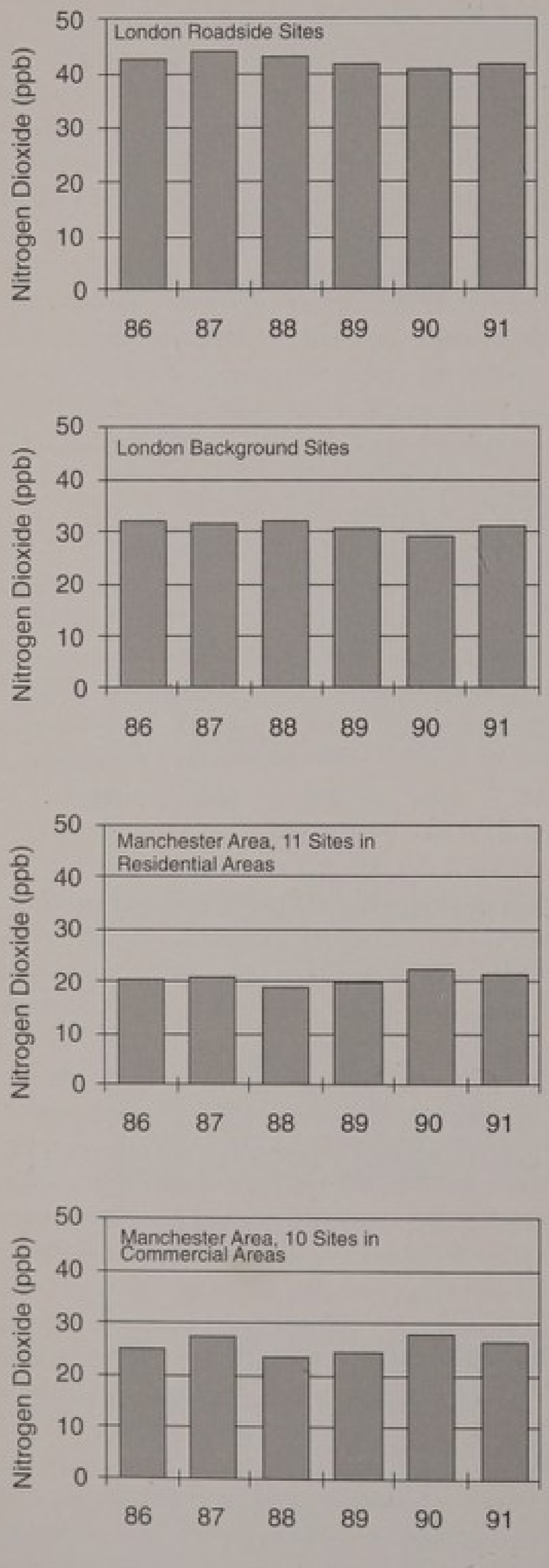


Figure 3.3 Mean NO_2 Concentrations Averaged over Several Sites in London and Manchester (1986-1991), Measured by Diffusion Tubes



Diffusion tube surveys have been carried out on several occasions in the last ten years by a variety of organisations. Typically, they have tended to consist of a deployment of the samplers for a limited period, either several weeks or several months. Local authorities, not unreasonably, restrict surveys to their own area of interest, although in the case of London, individual Boroughs contribute to a London-wide survey and also have maintained the survey over a number of years.

For consideration of the spatial distribution of NO_2 concentration across a large city, studies carried out in Manchester and London are particularly useful. The former refers to work carried out by the Atmospheric Research and Information Centre (ARIC), for the Association of Greater Manchester Authorities⁽¹⁾. As part of their network of 17 sites in the Greater Manchester Acid Deposition Survey (GMADS), ARIC have measured NO_2 for a number of years, with diffusion tubes exposed and collected on a weekly basis. A 'contour' plot of the NO_2 concentrations for the year 1991 is presented in Figure 3.4.

One of the largest diffusion tube surveys carried out in the UK for one city for a whole year was that for London in 1984 to 1985. Carried out jointly by The Greater London Council and AEA Technology, Harwell and the Environmental Health Departments of the thirty-three London Local Authorities, the survey used 115 sites; some 'roadside' and some 'background'. The results have been presented in several publications, including the second report of the Photochemical Oxidants Review Group. Another version is presented here, taken from Clark et al⁽²⁾, in Figure 3.5.

Both of these surveys and the resulting contour plots show very clearly that highest concentrations are found in city centres, with generally decreasing concentrations towards the outskirts. Similar urban patterns have been observed in diffusion tube surveys in Birmingham, Glasgow and Swansea. A plot of the 1986 Glasgow survey is given in the second report of Photochemical Oxidants Review Group.

Hewitt⁽³⁾ reports the results of a year long diffusion tube survey in Lancaster (January 1989 to January 1990). In all, 49 measurement sites, mostly roadside, grouped in

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(1) Conlan DE, Longhurst JWS and Gee DR (1992) **Urban Acid Deposition: Results from the GMADS Network 1991** Atmospheric Research Information Centre (ARIC), UK.
(2) Clark RG and White JR (1986) **Environmental Health Aspects of the 1984/85 London Diffusion Tube Survey** London Environmental Supplement Number 14, UK.
(3) Hewitt CN (1991) **Spatial Variations in Nitrogen Dioxide Concentrations in an Urban Area** Atmospheric Environment Part B Urban Atmosphere **25B**, 429-434.

Figure 3.4 Spatial Distribution of Annual Mean NO_2 Concentrations in Greater Manchester (1991)

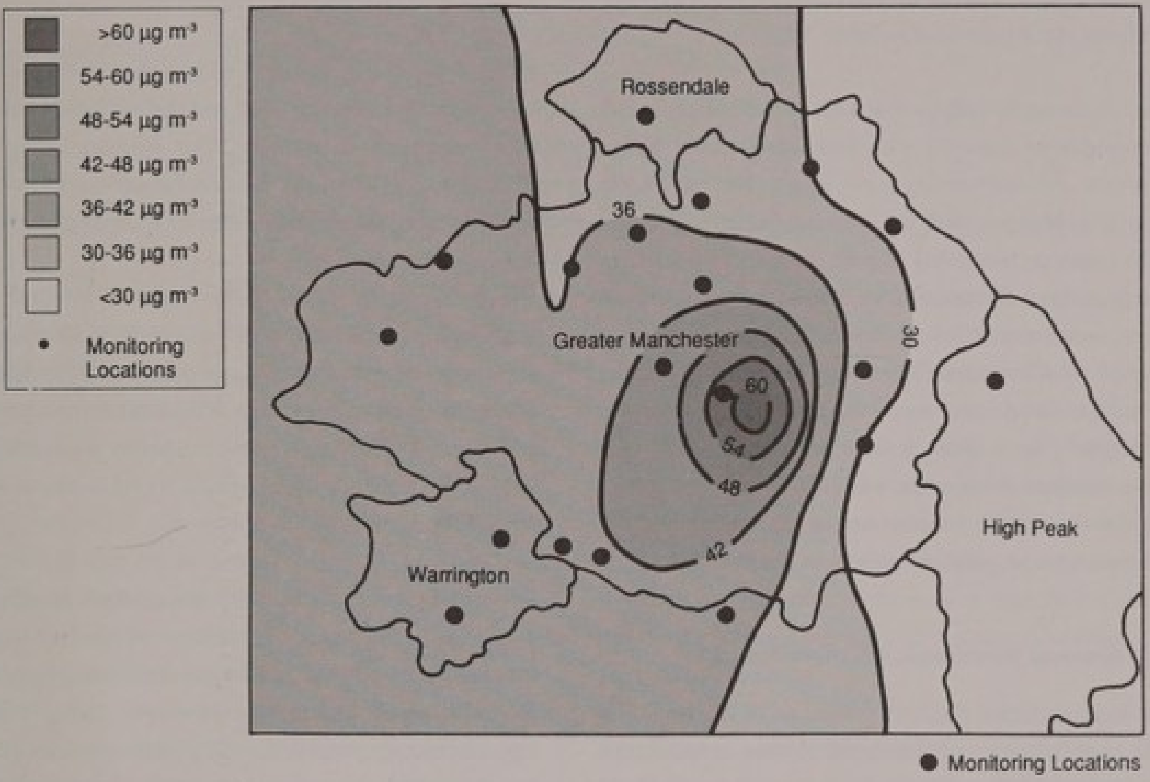
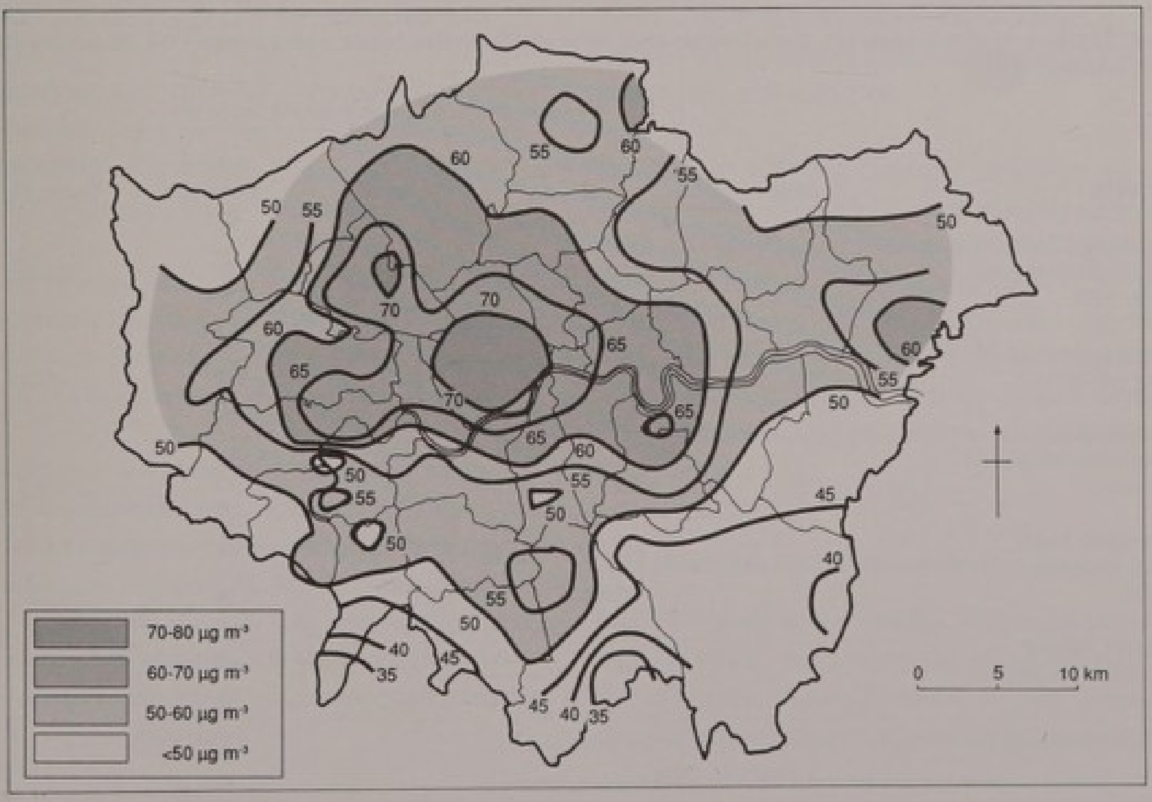


Figure 3.5 Spatial Distribution of Annual Mean NO_2 Concentrations in Greater London (1984-1985)



five locations were used. The survey was an attempt to investigate a possible relationship between NO_2 concentration and traffic flows. A summary of the results of the survey is presented in Table 3.2.

The results are broadly in line with expectations, ie that concentrations increase with increasing traffic flows. However, the relationship is not direct. The city centre pedestrian precinct, with little passing traffic, had higher concentrations compared to both the suburban sites. In addition, the suburban residential street has an annual mean concentration of 15.7 ppb (30 $\mu g\ m^{-3}$) with a traffic flow of less than 800 vehicles per day, whereas the suburban main road shows a mean of 19.9 ppb (38 $\mu g\ m^{-3}$) for a daily flow of 10,500 vehicles. This study confirms other work which indicates that spatial distributions of NO_2 in cities are not purely a function of the road network and the traffic flows on those roads.

3.4.4 Seasonal Variations in NO_2 Concentrations

It is to be expected that concentrations of NO and NO_2 will vary between summer and winter, because the conversion of NO to NO_2 is dependent on the available oxidants, which are themselves a function of the available sunlight. In addition, the surface based inversion layers more prevalent in winter will confine NO_x emissions and suppress mixing, thereby increasing NO_x concentrations but reducing the opportunity for NO to react with oxidants.

In rural locations, monitoring has shown that winter concentrations of both NO and NO_2 clearly exceed those observed in summer. The Second Report of Photochemical Oxidants Review Group quotes winter/summer ratios for mean NO and NO_2 concentrations of 2.3 and 1.6 respectively.

For urban locations the situation is much more complex and the winter/summer ratios depend on the proximity of the monitoring site to the NO_x emission source. In addition, the urban atmosphere's capacity to oxidise NO to NO_2 is limited by the availability of oxidants such as ozone.

Generally, emissions of NO_x are at their greatest in winter and the higher incidence of surface based inversions tends to increase concentrations relative to those observed in summer. However, there is little seasonal change observed in NO_2 concentrations, partly because, although emissions of NO_x are increased in winter, there is less ozone to cause oxidation of NO to NO_2.

Table 3.2 Summary of Fortnightly NO_2 Concentration obtained at 49 Sites in Five Locations in Lancaster, UK, 22 January 1989 to 21 January 1990

		Nitrogen Dioxide Concentrations ($\mu g\ m^{-3}$)[a]			
Location	**No of Sites**	**Annual mean ±sd**	**2-Week Minimum**	**2-Week Maximum**	**Mean Daily Traffic Flow**
King Street/China Street - city centre one way main road	12	63±24	12	222	30,000
Meeting House Lane - city centre road	6	58±17	5	107	-9000
Market Street - city centre pedestrian precinct	6	45±17	5	111	<100[b]
Bowerham Road - suburban main road	11	38±16	10	96	10,500
Palatine Avenue - suburban residential street	14	30±13	7	67	<800[c]

(a) Concentrations given in $\mu g\ m^{-3}$. Convert to ppb using a factor of 0.523.

(b) Pedestrian precinct, but all sites within 75 m of main road.

(c) Estimated.

Table 3.3 Seasonal Variations of NO_2 Concentrations (ppb) at the Urban NO_2 Directive Sites, 1990

Site	Winter Mean		Summer Mean		Ratio (Winter/Summer)	
	NO	NO_2	NO	NO_2	NO	NO_2
London, Bridge Place	64	40	38	37	1.68	1.08
London, Earls Court	66	35	35	37	1.89	0.94
Glasgow	95	28	37	28	2.57	1.00
Manchester	52	33	26	27	2.00	1.22

The summer to winter ratios for the urban sites in the NO_2 Directive Network are shown in Table 3.3. These data demonstrate very clearly that there is little variation in the mean concentration of NO_2 between summer and winter.

Other ways of presenting data from continuous monitoring sites are as a straightforward time series of hourly average concentrations, as a cumulative frequency distribution and as diurnal average concentrations. A comparison of these plots for different sites reveals some interesting differences, particularly in the cumulative frequency distributions and diurnal average concentrations. A summary of results from the continuous monitoring sites operated by Warren Spring Laboratory is given by Broughton et al(1). Time series of hourly concentrations of NO and NO_2 at Manchester and Glasgow are presented in Figures 3.6 and 3.7.

A distinct increase in the peak concentrations of NO can be observed during the winter months relative to the summer months. By contrast, the time series for NO_2 do not show an obvious increase during the winter months.

Further evidence for this lack of a seasonal variation of NO_2 concentrations in urban locations can be seen from a comparison of the cumulative frequency distributions for NO and NO_2 as presented Figure 3.8.

Both Glasgow and Manchester show a clear increase in winter concentrations over summer concentrations for NO, with the difference being most marked at the higher percentiles, ie occasions of peak concentrations. For NO_2, however, this is not the case. The winter/summer difference is not exhibited at the higher percentiles and a difference, if it exists at all, is most pronounced in the 20th to 50th percentile range.

An examination of diurnal concentrations also shows some interesting features, (Figure 3.9). It is immediately noticeable that the NO concentrations in winter are greater than those in summer, particularly in the daytime after the peak early morning 'rush hour'. For NO_2, however, the two sites show different characteristics. At the Glasgow site, as in the cumulative distribution, there is no difference in summer/winter concentrations, whereas at Manchester there is a significant mean difference between winter and summer concentrations throughout the day.

Diurnal concentration plots of NO_2 for other urban sites operated by Warren Spring Laboratory show varying degrees of similarity to those of either Manchester or Glasgow. However, in most cases the winter/summer difference is quite small. The industrial site of Billingham displays the largest winter/summer difference and the kerbside site in Cromwell Road behaves quite differently, as discussed in Section 3.4.6.

In terms of the winter/summer difference in NO concentrations, all the sites considered by Broughton et al show similar characteristics, which suggest that there are subtle differences in the conversion from NO to NO_2 at each monitoring site. In their discussion of these monitoring sites, Bower et al(2) attribute the lower concentrations at Manchester to its elevated location (25m), and consequent greater separation from ground level sources.

3.4.5 Short-term, Peak Concentrations

The EC Directive for ambient NO_2 concentrations specifies a limit value and a guide value in terms of the 98th percentile of hourly means. In other words, a concentration which is not to be exceeded for more than 175 hours in a year.

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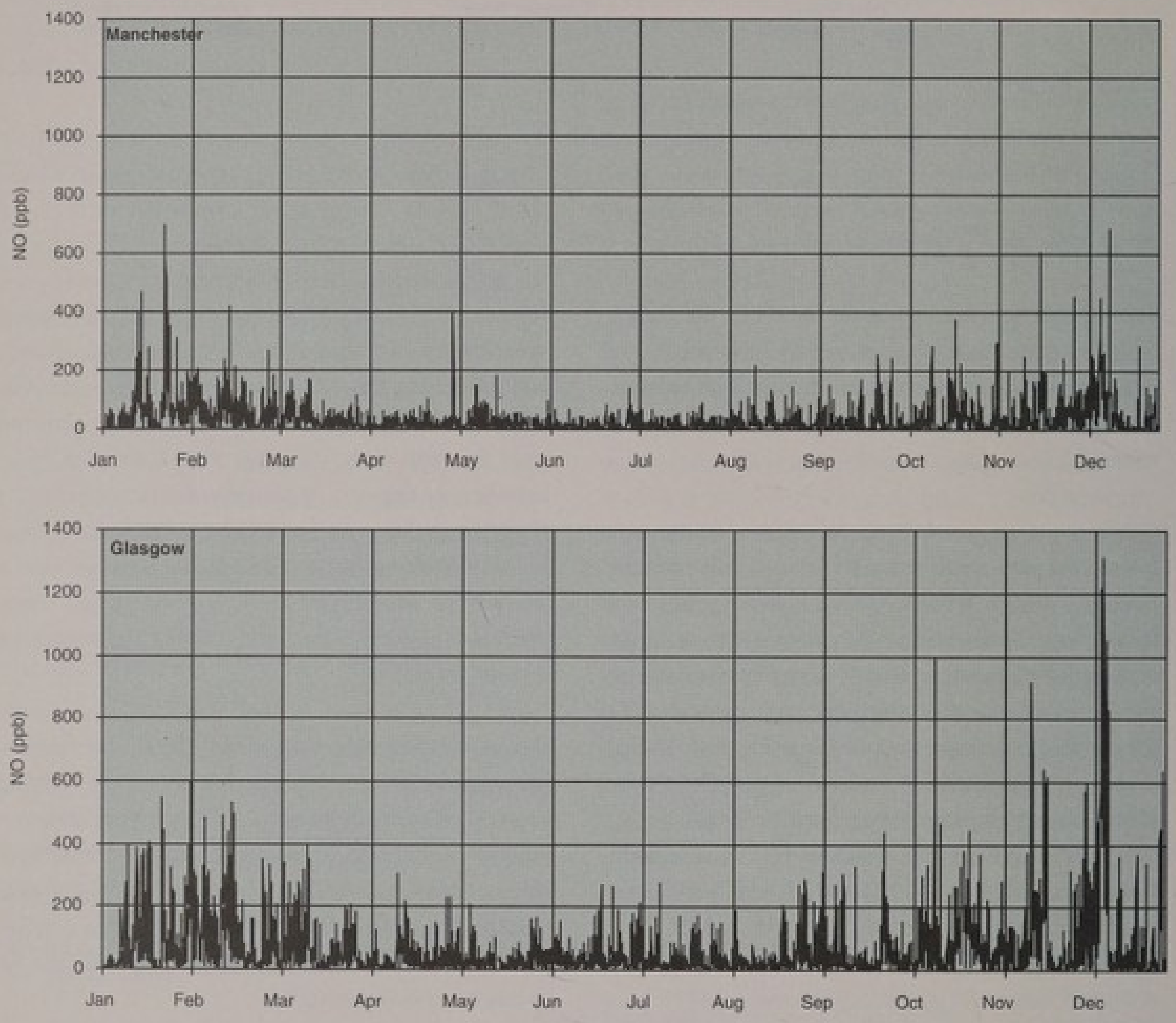
(1) Broughton GFJ et al (1992) **Air Quality in the UK: A Summary of Results from Instrumental Networks in 1990/91** WSL Report LR883, Warren Spring Laboratory, Stevenage, UK.
(2) Bower JS et al (1991) **Urban NO_2 Concentrations in the UK in 1987** Atmospheric Environment Part B Urban Atmosphere 1991 **25B**, 267-284.

Figure 3.6 Time Series of Hourly NO Concentrations at Manchester and Glasgow (1991)



Values for the 98th percentile of NO and NO_2 concentrations at three of the NO_2 Directive sites operated by Warren Spring Laboratory are presented in Figure 3.10. As with the annual mean data, the values for this statistic show no trend at these sites, although the period is short for all sites except London, Victoria. The trend in the 98th percentile for the rooftop site at County Hall reflects that of the annual mean.

Data from continuous analysers for the period 1986-89 are also available from other sites in London, as part of the London Boroughs network, operated by London Scientific Services. The four sites were able to provide similar statistics to those of the DOE networks and are summarised for NO_2 in Table 3.4.

Interest in the 98th percentile obviously arises because the EC Directive for NO_2 frames the limit and guide value in this way. Because the 98th percentile is measured at relatively few locations in the UK, it has become common practice to infer the 98th percentile from the annual mean concentration. This is done using an average factor of 2.4 or similar, based on the fact that the ratio of the 98th percentile to the annual mean, as measured by chemiluminescent analysers, is equal to this factor. Some data from the NO_2 Directive network are presented in Table 3.5 which illustrate the variation of this site-specific ratio for a selection of sites.

This factor of 2.4 has been widely used to infer 98th percentile values from the 1986 and 1991 six monthly diffusion tube surveys carried out by Warren Spring Laboratory. The accuracy of employing this factor to a

Figure 3.7 Time Series of Hourly NO_2 Concentrations at Manchester and Glasgow (1991)

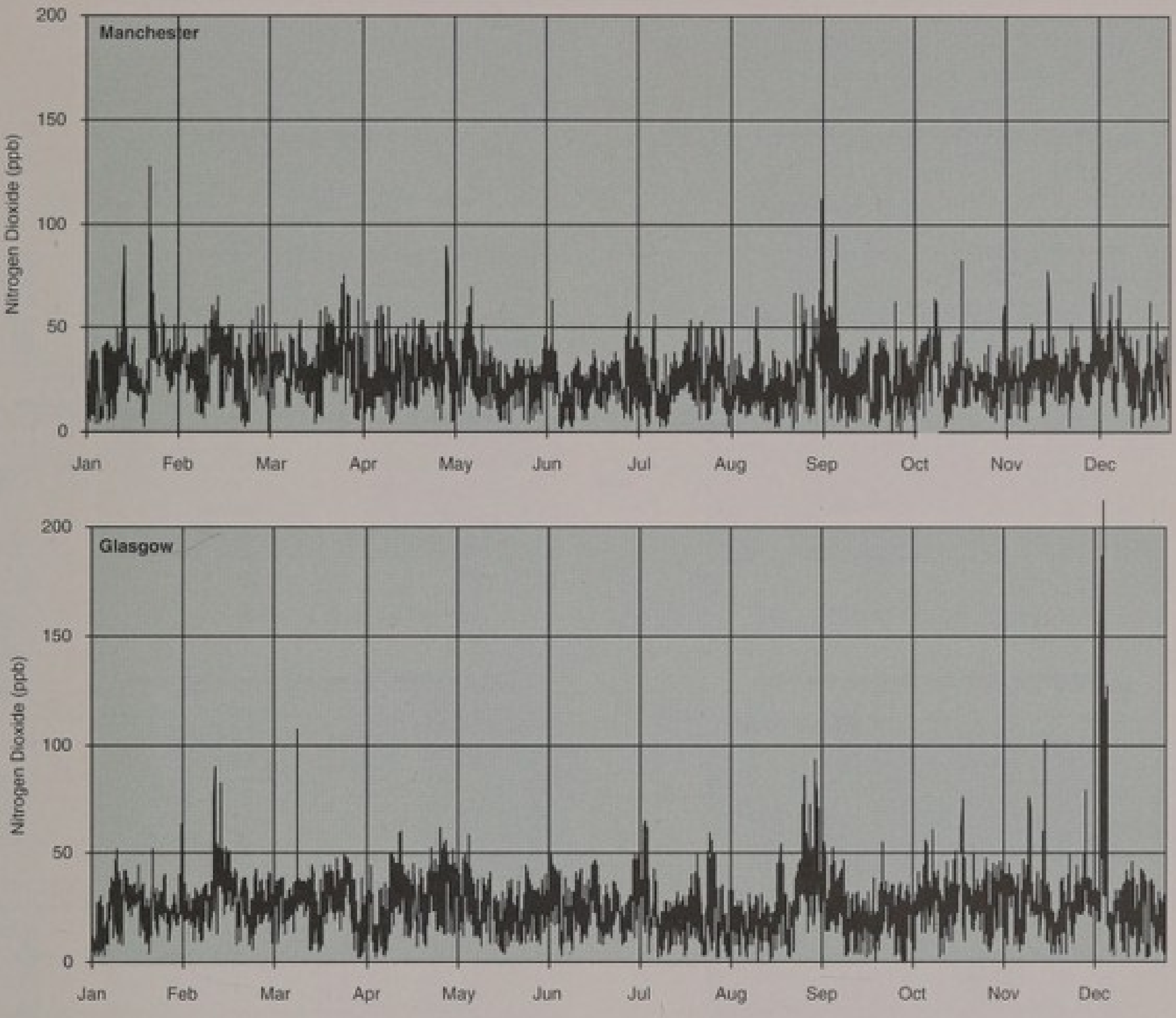


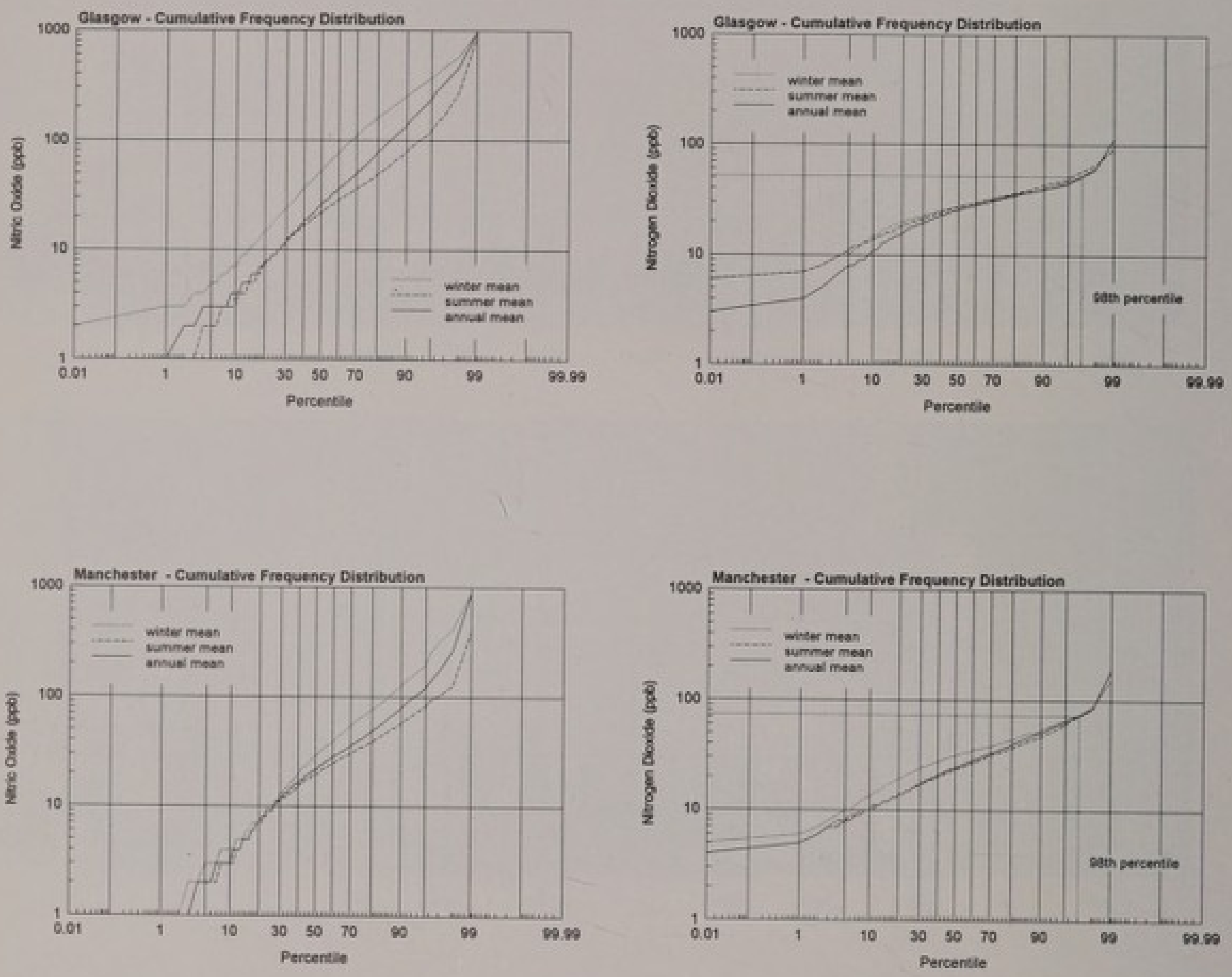
Table 3.4 Summary of Peak NO_2 Concentrations Recorded by the London Boroughs Network, 1986 to 1989

	98th Percentile				Highest hourly value			
Site	1986	1987	1988	1989	1986	1987	1988	1989
West London	54	75	68	76	93	209	177	211
Central London	87	102	71	93	288	213	179	244
East London	58	60	-	-	123	176	164	143

six monthly rather than an annual mean as illustrated by Figure 3.11. This shows that as the number of monthly means is reduced there is a corresponding increased deviation from the estimated annual mean. Thus a six month mean would be within ±10% of the annual mean.

Also of interest are the extreme values recorded for the hourly average concentration at each site where continuous monitoring takes place. Figure 3.12 shows the extreme value recorded at each of the urban sites operated by Warren Spring Laboratory for which data are available to 1991.

Figure 3.8 Cumulative Frequency Distributions of NO and NO_2 Concentrations at Glasgow and Manchester (January 1990-March 1991)

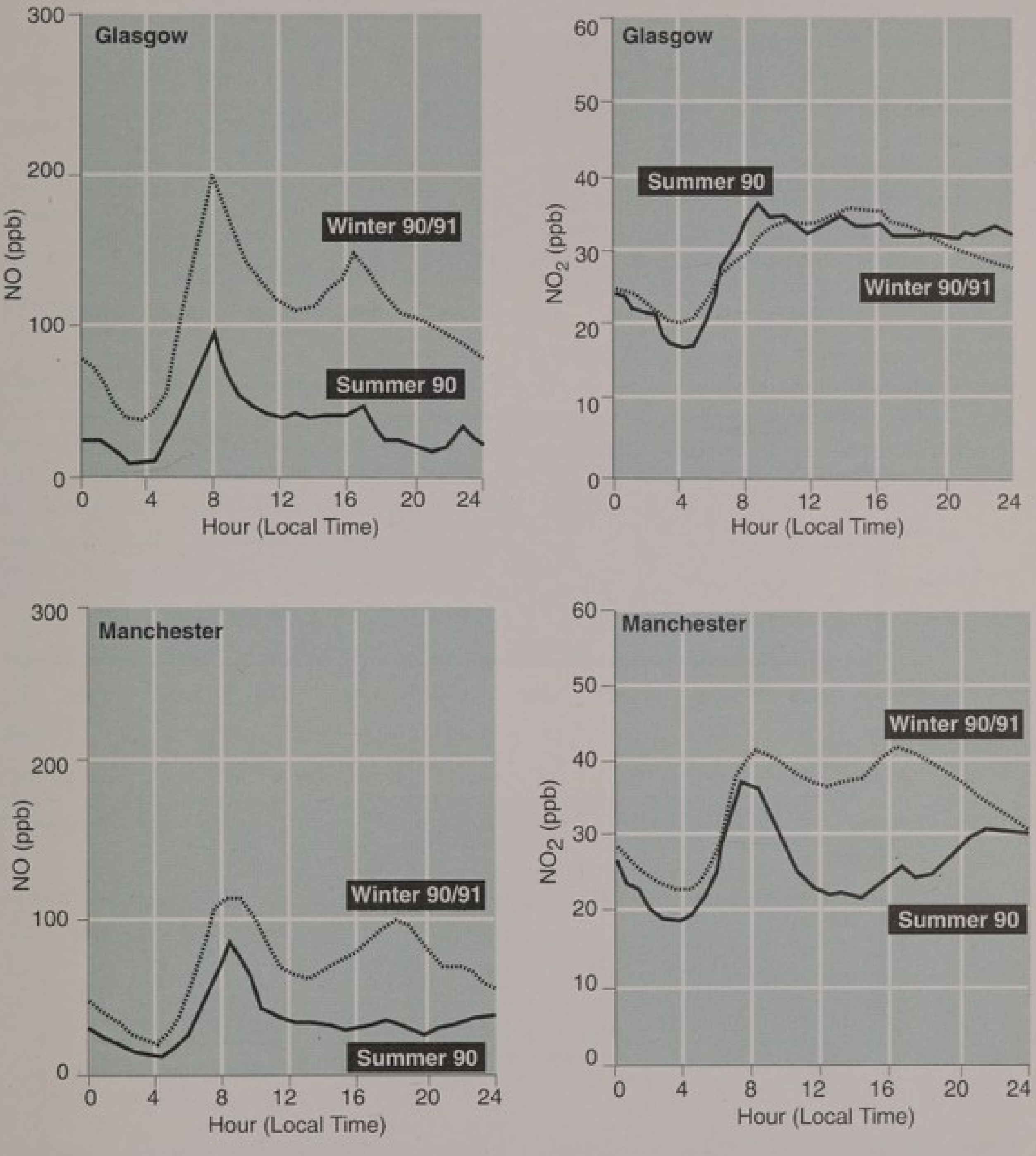


3.4.6 Concentrations in Streets and in Relation to Traffic Flows

Much of the preceding material presented in this chapter has concentrated on data from monitoring sites which have been deliberately located so as not to be influenced unduly by one individual source, such as a road. Many measurements are also made, however, of concentrations around roads, as this is an environment where high concentrations might be anticipated. A comparison of NO and NO_2 concentrations at roadside sites and urban background sites illustrates the complex nature of the reactions involving nitrogen oxides which occur in urban environments.

Continuous monitoring of NO and NO_2 concentrations has been carried out at two sites in London adjacent to heavily trafficked roads. On Cromwell Road, the sampling point operated by Warren Spring Laboratory is situated only 0.5 m from the kerbside of a road carrying 50,000-60,000 vehicles per day. This site has recorded

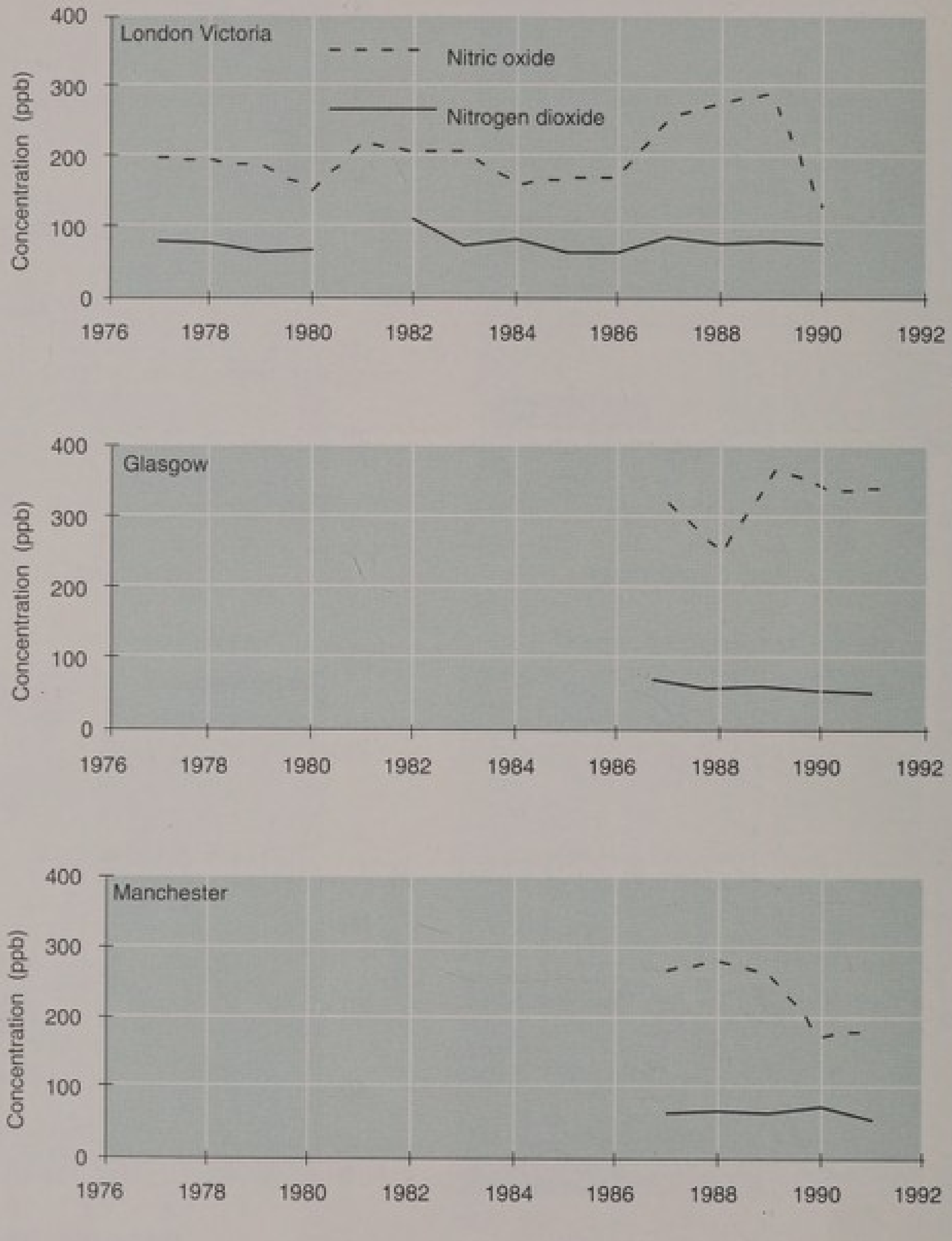
Figure 3.9 Average Diurnal Variations in Hourly Mean NO and NO_2 Concentrations at Glasgow and Manchester (January 1990-March 1991)



the highest concentrations of NO and NO_2 in the UK, being 2,200 ppb (3477 μg m^{-3}) and 1,817 ppb (3476 μg m^{-3}), respectively in 1983. London Scientific Services also maintained a continuous roadside site in central London situated 3 m from the kerb of a road carrying 50,000 to 60,000 vehicles per day. The results from this and Cromwell Road are summarised in Table 3.6.

The annual mean concentrations of NO and NO_2 at the Cromwell Road site show that concentrations of NO are approximately 4.5 times those for NO_2. This is not unexpected since the primary emission from vehicle exhausts is mainly in the form of NO. The time series for NO and NO_2 concentrations are presented in Figure 3.13 for the calendar year, 1991.

Figure 3.10 98th Percentiles of Hourly Mean NO and NO_2 Concentrations at Three EC Directive Sites — London (Victoria), Glasgow and Manchester



An immediate observation of these data when viewed in this manner is that the NO concentrations are dramatically higher than those for Glasgow and Manchester with higher mean and peak values. Concentrations of NO_2, however, show only a slight increase relative to the Manchester and Glasgow sites.

The cumulative frequency distributions and the diurnal average concentration plots, as presented in Figure 3.14, show a distinct contrast in the winter/summer differences between NO and NO_2 concentrations. As for the Manchester and Glasgow data, winter concentrations of NO are higher than in summer, particularly for the peak concentrations and in the daytime hours. For NO_2, on the other hand, the concentrations observed in summer are markedly greater than those in winter; most likely being a reflection of the greater availability of ozone in the spring and summer months. By comparison, the Glasgow site showed no significant difference between summer and winter, whereas the Manchester site showed higher concentrations during the winter (Section 3.4.4).

Table 3.5 Ratios of 98th Percentile to Annual Mean for NO_2 Concentrations at Sites Operated by Warren Spring Laboratory

	Ratio of 98th Percentile/Annual Mean			
Site	**1987**	**1988**	**1989**	**1990**
London, Victoria	2.18	2.11	2.16	2.14
London, Earls Court	2.40	2.49	2.60	2.23
Cromwell Road	-	-	2.33	2.36
Stevenage	2.67	2.21	2.24	2.24
Glasgow	2.23	1.90	2.26	2.04
Manchester	2.24	2.39	2.48	2.64

There is also a marked variation in the diurnal NO concentrations between weekday and weekends, as can be seen in Figure 3.15. Not only are concentrations of NO lower during the daytime at weekends as compared to weekdays, but the peak concentrations associated with peak vehicle flows during weekday mornings is absent at the weekends.

Diffusion tube surveys often include a mix of roadside and background sites. In the 1991 diffusion tube survey carried out by Warren Spring Laboratory, sites were classified according to their distance from the nearest road. 'Near road' sites were defined as 'facing directly on to a major road' of which there were 19. 'Background' sites were those over 50 m from a major road. Not surprisingly, it is the near-road sites which consistently show higher concentrations, when compared with background sites in the same urban area. The three sites with the highest mean concentration over the six month period were all near-road sites in London.

The second report of the Photochemical Oxidants Review Group presents the results from diffusion tube studies of NO_2 concentrations adjacent to busy roads. One study demonstrated that for a road with traffic flows of 50,000 vehicles a day, the NO_2 concentrations varied as follows:

Table 3.6 Peak Hourly Average NO and NO_2 Concentrations (ppb) Recorded at Two Roadside Sites in London

	1986		1987		1988		1989		1990	
Site	NO	NO_2	NO	NO_2	NO	NO_2	NO	NO_2	NO	NO_2
Cromwell Road	1,126	195	N/A	N/A	N/A	N/A	1,767	271	1,336	245
Central London	N/A	468	N/A	264	N/A	345	N/A	212	-	-

Figure 3.11 Difference Between True NO_2 Annual Mean and Average Over Different Numbers of Monthly Means

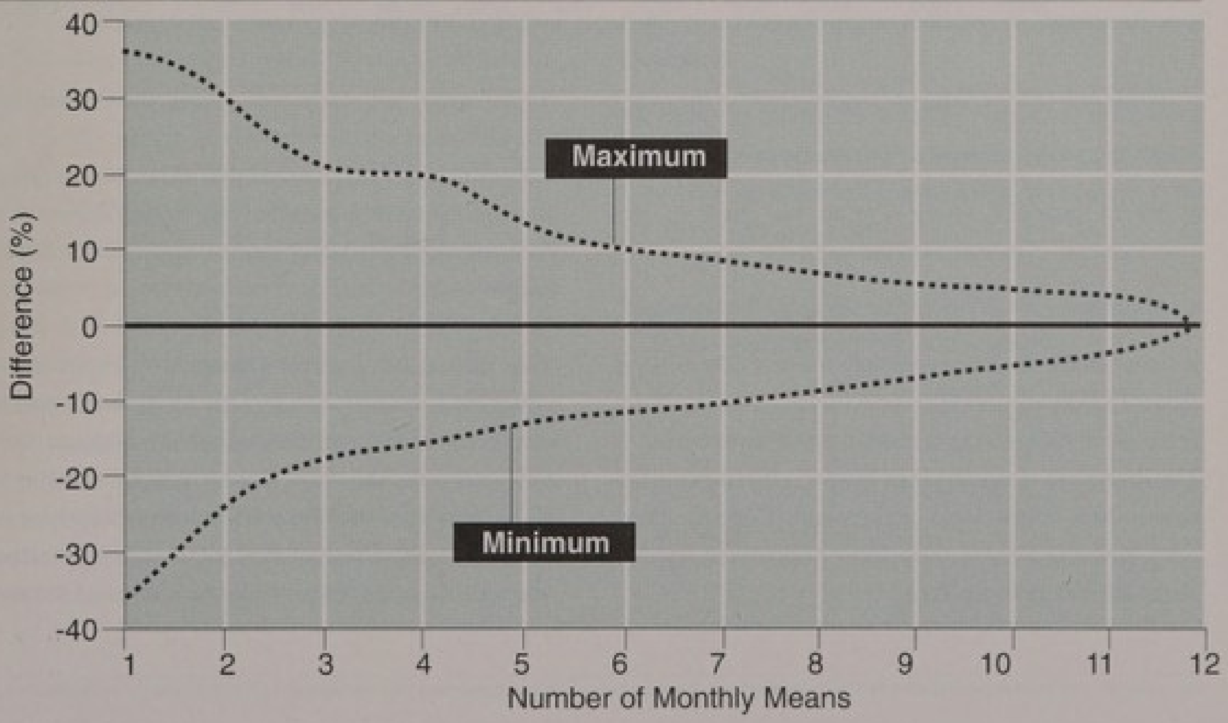
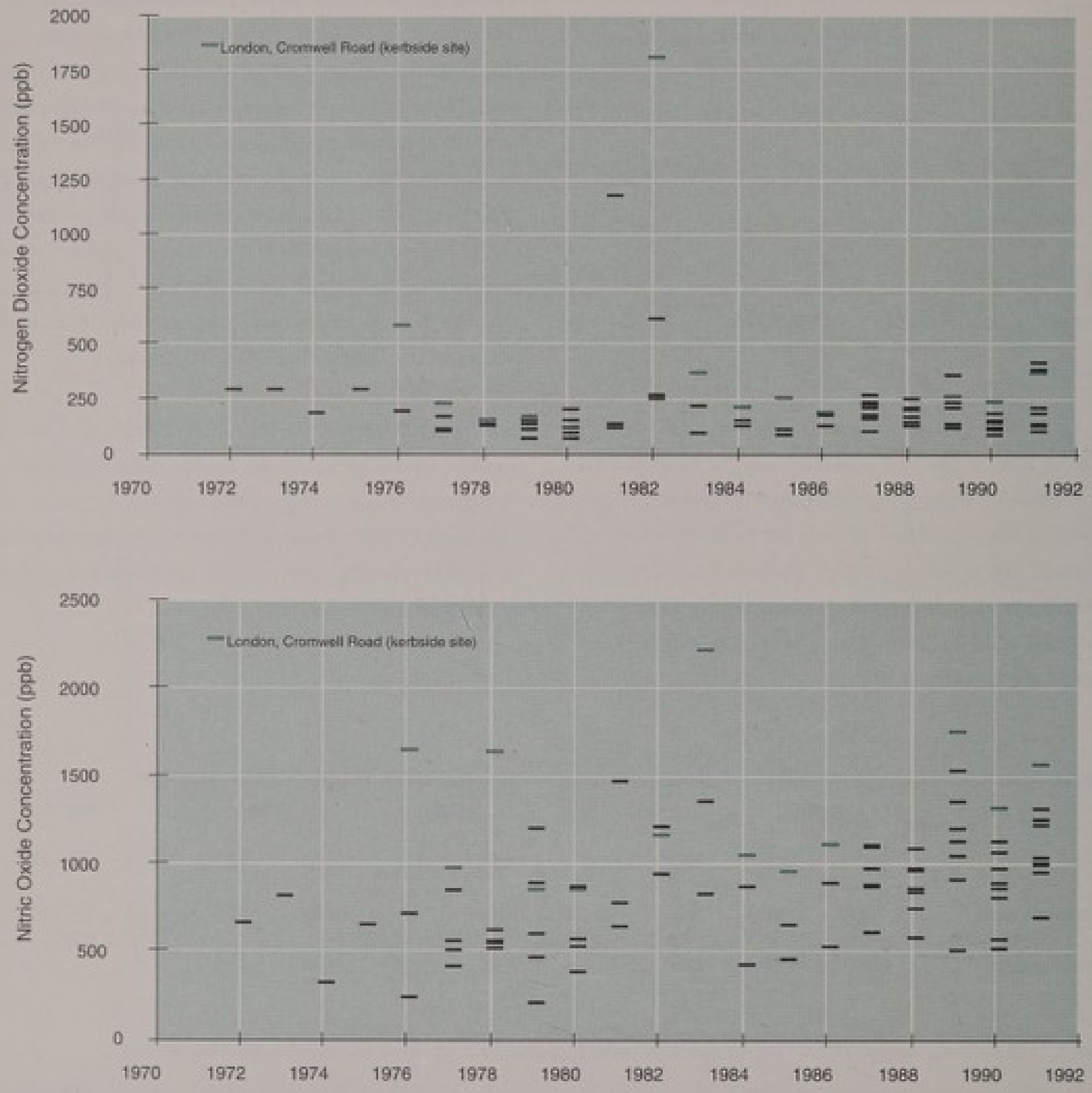


Figure 3.12 Extreme Values of NO and NO_2 Concentrations at Urban Sites Operated by Warren Spring Laboratory



- *80-90 ppb (153–172 µg m^{-3}) in the centre of the road;*
- *50-60 ppb (96–115 µg m^{-3}) at the kerb;*
- *40-50 ppb (77–96 µg m^{-3}) at the back of the pavements, 3 metres from the kerb;*
- *30-40 ppb (57–77 µg m^{-3}) in the local 'background'.*

Another study of roads with daily traffic flows ranging from 16,000 to 160,000 in London examined the decrease in NO_2 concentrations away from the road⁽¹⁾. The results are summarised in Figure 3.16, showing the excess NO_2 above local background. Concentrations were indistinguishable from local background beyond about 20-30m from the kerb.

Significantly, the study was unable to demonstrate a simple relationship between traffic flows and concentration. This is ascribed to either the inability to account for vehicle speed as well as traffic flow or the formation of NO_2 being limited by the availability of ozone.

This latter point is partly illustrated by Figure 3.17 in which the frequency distributions for three categories of continuous monitoring sites operated by Warren Spring Laboratory are shown. It is clear that the kerbside site (Cromwell Road) has a much lower NO_2/NO_x ratio than the urban sites, which in turn is lower than at the rural sites. Although this effect could be accounted for partly

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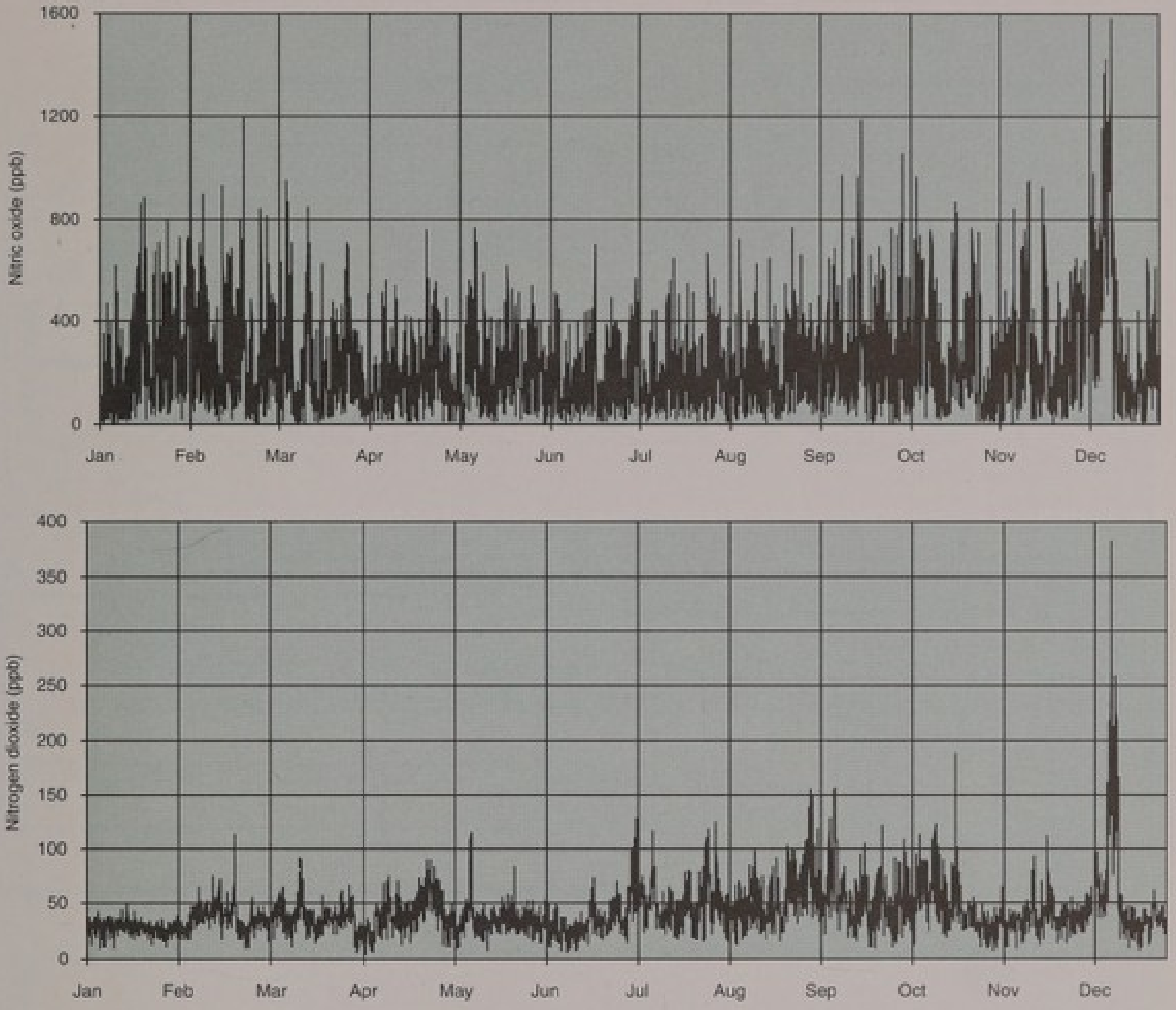
(1) Laxen DPH and Noordally E (1989) **Nitrogen Dioxide Distribution in Street Canyons** Atmospheric Environment **21**, 1899-1903.

Figure 3.13 Time Series of NO and NO_2 Concentrations at Cromwell Road, London (1991)



by the proximity of the source to the monitor, it is also likely that the ratio at the kerbside is reduced by the lack of available ozone.

The second report of Photochemical Oxidants Review Group[(1)] also includes an interesting result from remote sensing measurements of the vertical distribution of NO_2 in a street in central London. This is illustrated in Figure 3.18 which shows a vertical profile of NO_2 concentrations in a London street with dense traffic. This profile indicates that two maxima are present. One is in the street at ground level where the emissions are located and the second is elevated, above the building. The secondary maximum is thought to arise because of the oxidation of NO to NO_2 where additional ozone is available.

3.4.7 Concentrations in Relation to Standards and Guidelines

Measured exceedances of the EC Directive limit value for NO_2 (105 ppb as a 98th percentile of hourly means) have been confined to London and in particular for the following sites and years:

- *London, Earls Court, 1989 (later shown to be due to undue interference from local sources);*
- *London, Cromwell Road, 1989 (a value of 105 ppb, ie just at the limit value);*
- *Central London roadside site for the London Boroughs' network, 1988.*

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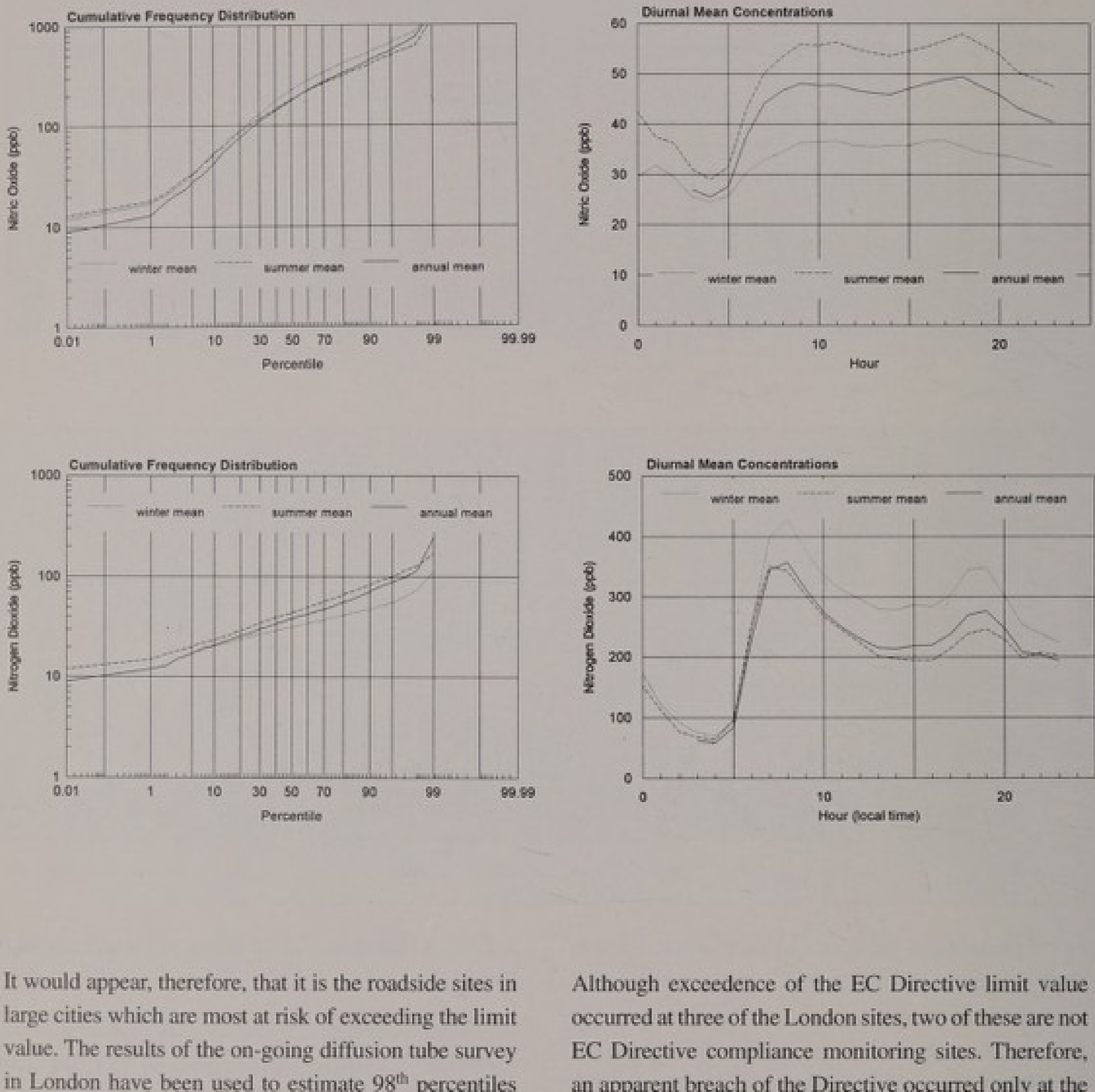
(1) United Kingdom Photochemical Oxidant Review Group (1990) **Second Report; Oxides of Nitrogen in the United Kingdom** AEA Technology, Harwell, Oxon, UK.

Figure 3.14 Cumulative Frequency Distributions and Diurnal Concentrations of NO and NO_2 at Cromwell Road, London (1990 - 1991)



It would appear, therefore, that it is the roadside sites in large cities which are most at risk of exceeding the limit value. The results of the on-going diffusion tube survey in London have been used to estimate 98th percentiles and show that the limit value is only likely to be exceeded within about 10 m of the kerb of a busy road.

EC guide values have been exceeded at the London sites operated by Warren Spring Laboratory in each of the years 1988-91, both for the 50th percentile and the 98th percentile. Exceedence in other cities is much less frequent, although still in evidence for occasional years in Manchester and Glasgow.

The WHO guidelines are more stringent and therefore are exceeded a few times a year at several of the monitoring sites. A summary of the various exceedences of the limit and guideline values is given in Table 3.7.

Although exceedence of the EC Directive limit value occurred at three of the London sites, two of these are not EC Directive compliance monitoring sites. Therefore, an apparent breach of the Directive occurred only at the London Earls Court site during 1989. However, investigations following this breach of the Directive demonstrated that this was due to poorly controlled vehicle emissions from inside the building which houses the monitoring station.

The 1991 diffusion tube survey identified sites where the six monthly concentrations exceeded 26 ppb, a figure which was taken as an approximation to the EC guide value of 50 µg m^{-3}, as a 50th percentile of hourly means. However, as discussed in Section 3.4.5, care should be taken when using six monthly means in this way. Nevertheless, using this criterion, 107 of the 316 sites

Figure 3.15 Diurnal Variation of Hourly Mean NO Concentrations for Weekdays and Sundays at London, Earls Court (1987)

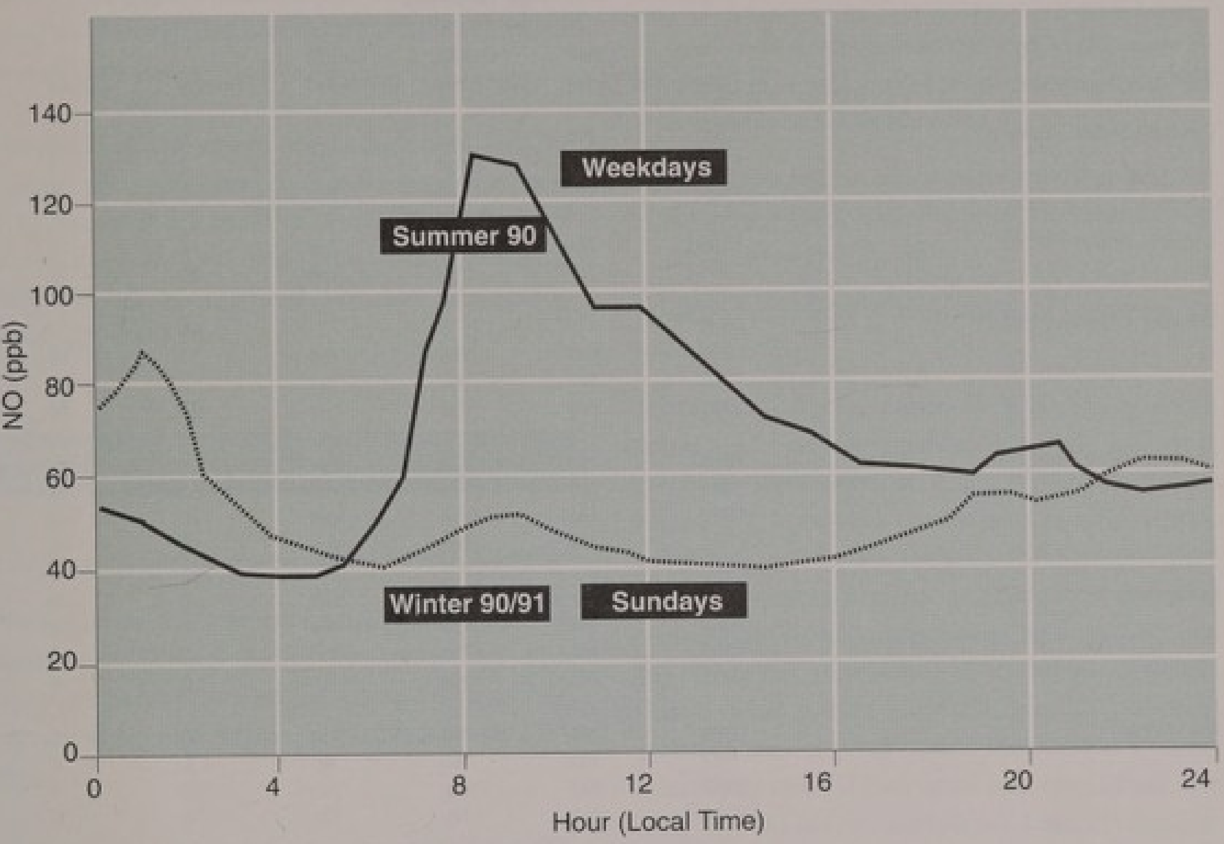


Figure 3.16 Variation of Annual Mean NO_2 Concentration Against Background With Distance From Kerb

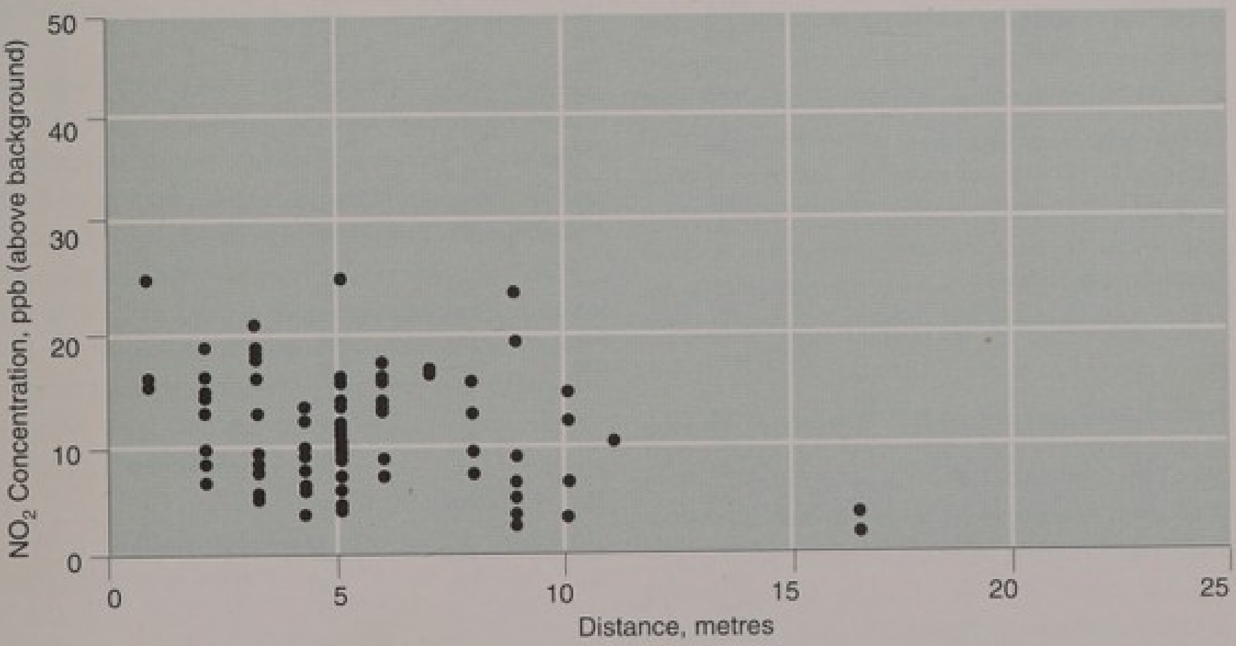


Table 3.7 Exceedences of Limit Values, Guide Values and Guidelines for NO$_2$ in Recent Years

		EC Directive			WHO	
Site	Year	Limit (98th%ile)	Guide (98th%ile)	Guide (50th%ile)	Hourly	Daily
Central London, Victoria(a)	1988	No	Yes	Yes	0	3
	1989	No	Yes	Yes	1	1
	1990	No	Yes	Yes	0	0
London, Bridge Place(a)	1990	No	Yes	Yes	0	5
	1991	No	Yes	Yes	23	9
London, Cromwell Road(b)	1988	-	-	-	0	-
	1989	Yes	Yes	Yes	11	15
	1990	No	Yes	Yes	0	12
	1991	Yes	Yes	Yes	27	18
London, Earls Court(a)	1988	No	Yes	Yes	1	9
	1989	Yes	Yes	Yes	25	9
	1990	No	Yes	Yes	0	4
	1991	No	Yes	Yes	16	5
Glasgow(a)	1988	No	No	Yes	0	0
	1989	No	No	No	2	3
	1990	No	No	No	0	0
	1991	No	No	No	0	0
Manchester(a)	1988	No	No	No	8	5
	1989	No	No	No	2	1
	1990	No	Yes	No	0	1
	1991	No	No	No	0	0
Walsall(a)	1988	No	No	No	0	0
	1989	No	No	Yes	1	1
	1990	No	No	No	0	0
	1991	No	No	No	0	0
Billingham(a)	1988	No	No	No	1	0
	1989	No	No	No	0	0
	1990	No	No	No	0	0
	1991	No	No	No	0	0
Central Londound (Background)(c)	1986	No	Yes	Yes	-	-
	1987	No	Yes	Yes	-	-
	1988	No	Yes	Yes	-	-
	1989	No	Yes	Yes	-	-
Central London (Roadside)(c)	1986	Yes	Yes	Yes	-	-
	1987	Yes	Yes	Yes	-	-
	1988	Yes	Yes	Yes	-	-
	1989	No	Yes	Yes	-	-
West London(c)	1986	No	No	No	-	-
	1987	No	Yes	Yes	-	-
	1988	No	No	No	-	-
	1989	No	Yes	No	-	-
East London(c)	1986	No	No	No	-	-
	1987	No	No	No	-	-
	1988	-	-	-	-	-
	1989	-	-	-	-	-

(a) EC Directive compliance monitoring sites

(b) Kerbside site

(c) London Boroughs Network sites, operated by London Scientific Services (now Rendel Science & Environment) used in the survey equalled or exceeded the EC guide value. Of the 19 near-road sites, 13 were included in this group and the three sites with the highest concentrations were all near-road sites in London.

The diffusion tube survey results have been used by Warren Spring Laboratory to compile maps of average NO_2 concentrations based on a relationship between population density and NO_2 concentrations. Interpretations for 1986 and 1991 are presented in Figure 3.19 and 3.20.

3.5 EPISODES OF ELEVATED NO_2 CONCENTRATIONS

3.5.1 Episodes of High Concentrations of NO and NO_2

From time to time the continuous monitoring sites operated by Warren Spring Laboratory and other organisations have recorded high concentrations of NO_2 over durations of a few hours or, on occasion, over a few days.

As most of the long period monitoring of NO and NO_2 by continuous analysers has taken place in London and it is here that highest concentrations are observed, much of our understanding of NO_2 episodes stems from data recorded at sites in London.

Simpson(1) has carried out analysis of episodes, as recorded at the London Victoria monitoring site. Although the dataset considered in this study is a little distorted by some exceptional concentrations in 1982, it is clear that episodes are most likely to occur in summer, when a greater potential for photochemical oxidation of NO to NO_2 exists and in winter, emissions are greatest and the dispersion of emissions from ground level sources is most restricted. Therefore, two types of episodes exist, and are categorised as either being 'winter' or 'summer'.

Some conclusions and observations arising from the study are given as being:

- *photochemical oxidation of NO to NO_2 can account for much of the NO_2 observed in summer and early autumn;*
- *NO_2 or ozone produced on one day can add to the NO_2 concentrations on the next day;*
- *some of the kerbside measurements in episodes can only be explained by high primary emissions of NO_2 or some unknown mechanism;*
- *traffic appears to be the main contributor to the episodes studied; modelling work has estimated the contribution as being 90%;*
- *there are no typical meteorological conditions for NO_2 episodes.*

The highest hourly concentrations of NO_2 typically arise during winter episodes; the December 1991 episode is one of the more severe examples. Winter episodes are caused by low wind speeds and mixing depths, conditions which are unfavourable for pollutant dispersal. Frequently, but not invariably, the episodes are characterised by low temperatures, high humidity and fog. These are meteorological conditions classically linked with progressive build-up of pollutant concentrations in urban areas. The London episodes show highly elevated concentrations of carbon monoxide and NO_x. The hitherto unexplained feature is the large extent of conversion of NO to NO_2, which is far beyond that which can be explained by reaction of NO with ozone. A number of explanations have been advanced; under very cold conditions, enhanced homogeneous reactions of NO with O_2 molecules in freshly discharged exhaust gas under conditions of low dilution associated with low wind speeds and slowly moving traffic, or heterogeneous reactions of NO with O_2 on the surface of airborne particles, including fog droplets. The actual mechanism is currently unknown and may involve more than one of the above processes. Since winter episodes are often responsible for the largest concentrations of NO_2, further research is strongly recommended.

3.5.2 The December 1991 Episode in London

In the period 12th to 15th December, 1991, the monitoring stations operating in London recorded a major winter pollution episode, with unusually high concentrations of NO_2. A time series of the concentrations recorded throughout the whole of 1991 at London, Bridge Place, demonstrates the relative magnitude of the peak concentrations and is presented in Figure 3.21. In addition, the NO_2 concentrations at the

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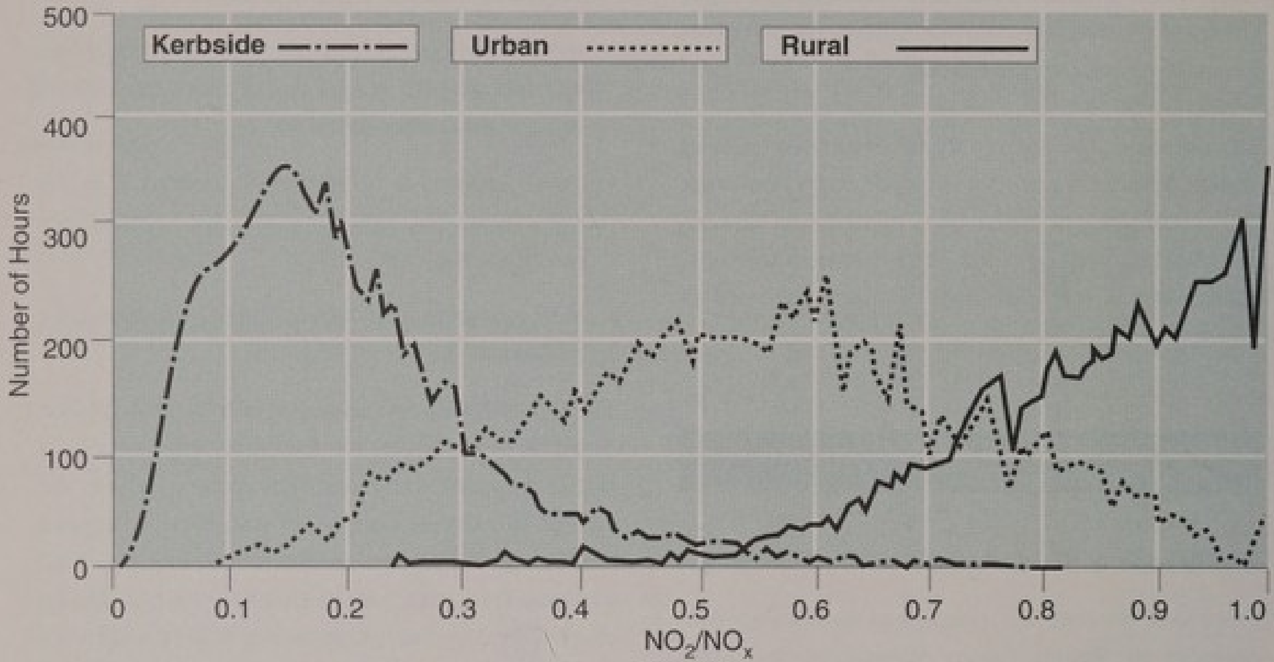
(1) Simpson D (1987) **An Analysis of Nitrogen Dioxide Episodes in London** WSL Report LR675, Warren Spring Laboratory, Stevenage, UK.

Figure 3.17 Frequency Distribution of the Ratio of NO_2/NO_x at Three Categories of Monitoring Sites



three monitoring sites operated by Warren Spring Laboratory for the period of the episode are presented in Figure 3.22.

An interesting feature of the episode was that highest concentrations of NO_2 were observed at non-kerbside monitoring sites. Indeed, the peak concentration of 423 ppb (809 µg m^{-3}) on Friday, 13th December was the highest ever recorded at a non-kerbside site in the UK. The highest concentration recorded at the Cromwell Road kerbside site during this episode was 382 ppb (731 µg m^{-3}), whereas the highest ever concentration observed at this site was 1,817 ppb (3,476 µg m^{-3}) in 1982. Although a concentration of 105 ppb (200 µg m^{-3}) was exceeded at all three sites during this period, this did not lead to an exceedence of the 98th percentile limit value during 1991. Therefore, there was no breach of the EC Directive for either of the compliance monitoring sites, Bridge Place or Earls Court, despite the extreme hourly concentrations recorded.

Some immediately obvious features are that the worst day during the episode was the 13th December and that the highest concentrations were observed in the early hours of the morning. This is inconsistent with previous episodes, ie the highest concentrations are not obviously correlated with peak traffic flows.

Examination of all available data resulted in the following observations:

- *The NO_2/NO_x ratio varied between 0.08 and 0.20 at Cromwell Road but was consistently higher, between 0.33 and 0.40 for the two 'background' sites. Given the limited ozone availability during this period, it is difficult to understand how so much NO could have been oxidised to NO_2, assuming primary NO_2 emissions were 5 to 10% of the total NO_x.*
- *The elevated NO concentrations were well correlated with the CO concentrations, but not those of SO_2. This strongly suggests that motor vehicle emissions were the dominant source of pollution during this episode.*
- *Concentrations of NO_2 were high across the whole of the London basin, but outside of London NO_2 concentrations were not elevated during this period.*
- *Meteorological conditions during the episode were of low wind speeds (0 to 3 m s^{-1}), low temperatures, mist and high stability. The overall synoptic pattern was of an anticyclone centred over the Alps and affecting south-east England.*

This episode appears to have many interesting and unusual features and will be the subject of further investigative work.

Figure 3.18 Spatial Profile of NO_2 Concentrations in a London Street With Dense Traffic

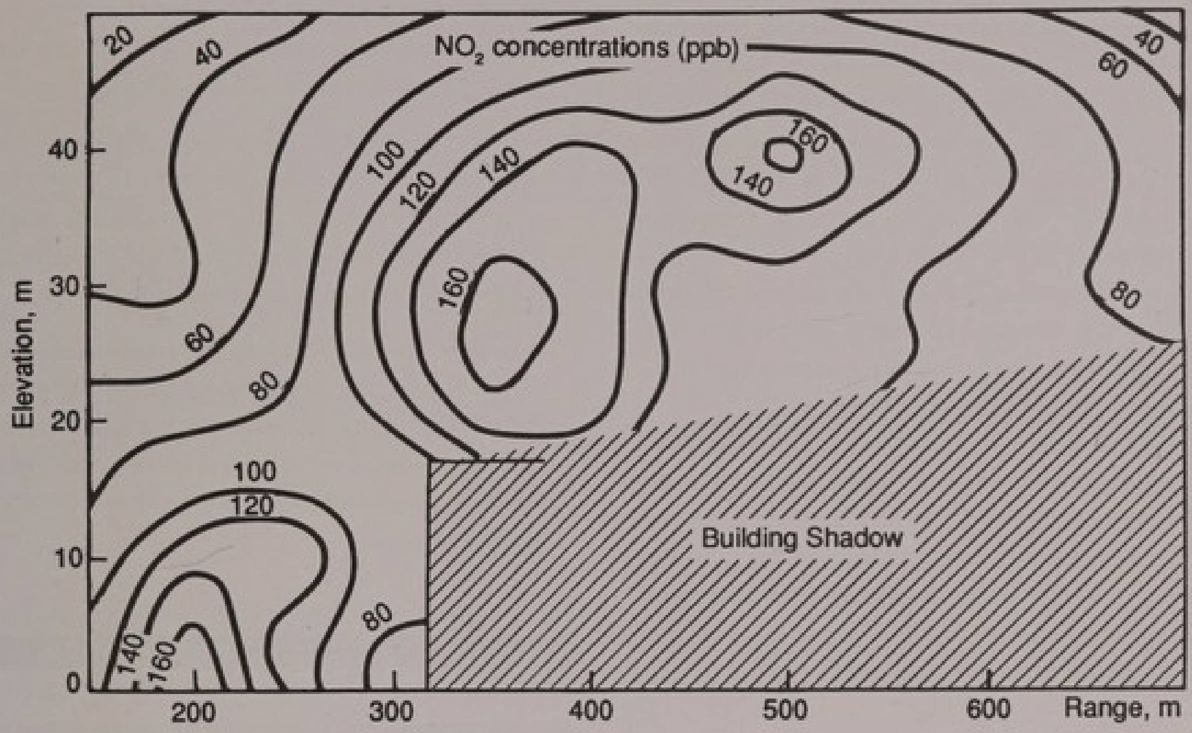


Figure 3.19 Estimated NO_2 Concentrations (ppb) in Great Britain (July-December 1986)

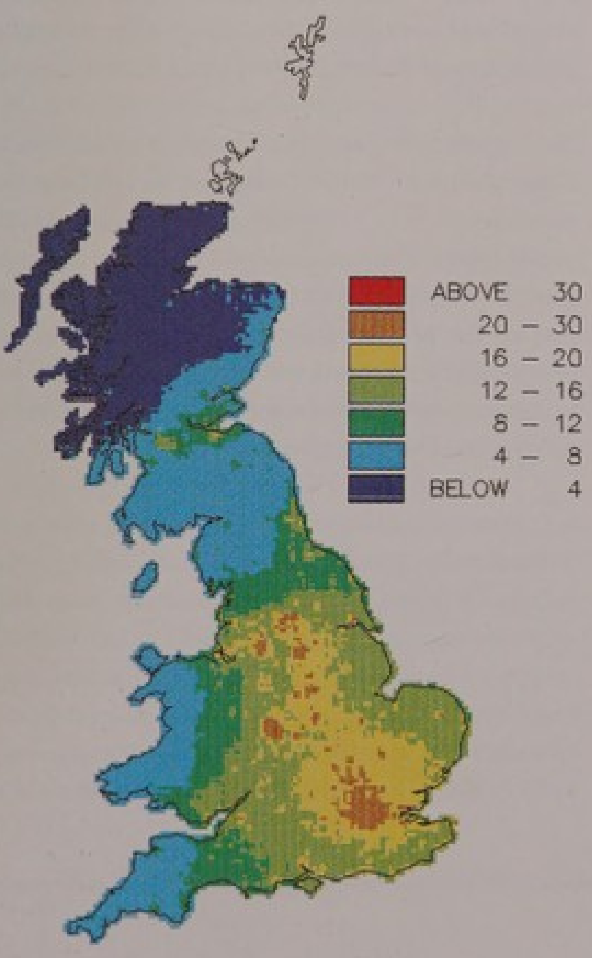
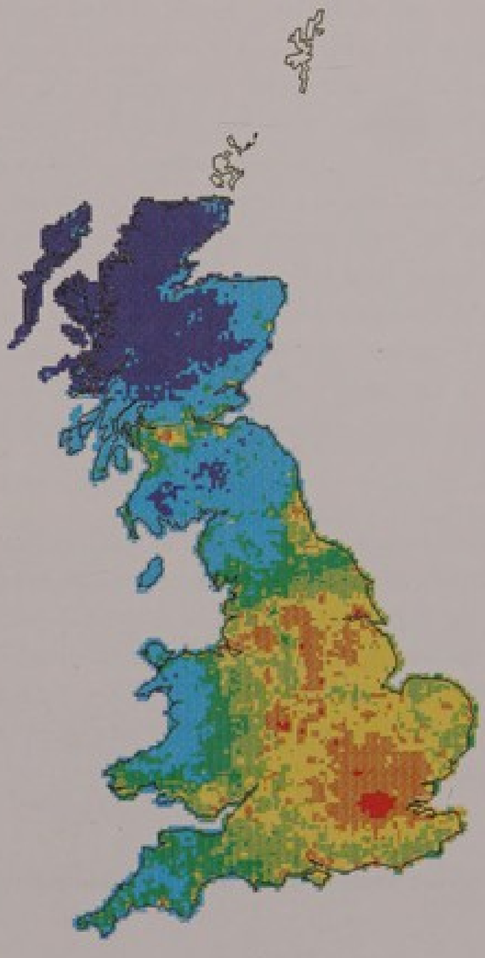


Figure 3.20 Estimated NO_2 Concentrations (ppb) in Great Britain (July-December 1991)



3.5.3 Issues Raised by Episodes

The dominant source of NO_x during episodes is undoubtedly vehicle emissions. However, the proportion of NO_2 to NO_x found at urban monitoring sites raises a number of interesting issues. In particular, why is the ratio of NO_2/NO_x sometimes very high at kerbside locations? Scatter plots of the hourly average NO_2 and NO_x concentrations at the Cromwell Road kerbside monitoring site during summer and winter, 1991 to 1992, are presented in Figure 3.23. During the winter, however, the NO_2/NO_x ratios are generally lower. High NO_x concentrations in the winter plot are attributed to the December episode.

A comparison of the frequency distribution of NO_2/NO_x ratio at Warren Spring Laboratory kerbside urban and rural monitoring sites during 1990 to 1991 is presented in Figure 3.17. These data illustrate that further from the NO_x source the ratio of NO_2/NO_x increases as more of the NO is oxidised to NO_2 by ozone.

Currently, there is considerable uncertainty over the ratio of NO_2 to NO_x in vehicle emissions and both the emission rate and the ratio vary widely with driving conditions and the state of engine maintenance. For normal open road driving it is generally assumed that the proportion of NO_2 in the exhaust from petrol combustion is less than 10%. In cold weather for an idling engine one study in Sweden has found that it may be higher(1). However, there are a significant number of episodes in which NO_2 concentrations in the air are very high and in which the NO_2/NO_x ratio is much higher than 0.3. Notable among these have been episodes recorded in Glasgow in December 1981 and at the Cromwell Road site in November 1982 where NO_2 concentrations reached 1,180 ppb (3,482 $\mu g\ m^{-3}$) and 1,820 ppb (2,257 $\mu g\ m^{-3}$) respectively with NO_2/NO_x ratios of 0.68 and 0.88.

This raises the question of where the NO_2 comes from. There is little doubt that vehicle exhausts are sufficient to produce the high concentrations of total NO_x under suitable meteorological conditions and close to heavy traffic but it is the conversion of NO to NO_2 which is difficult to explain. Issues which need to be considered include the following.

- *Is it possible for the ratio NO_2/NO_x to be higher than assumed in vehicle exhausts? If so, what are the combustion conditions responsible or what processes occur between combustion and emission which produce the high ratios?*
- *Why is it that high concentrations of NO_x do not always produce high concentrations of NO_2 and why is it that even under winter conditions when photochemistry and oxidation by ozone are reduced the ratio NO_2/NO_x is so variable?*
- *What are the atmospheric processes which could be responsible for the conversion? Mechanisms to be considered include catalysis of the three body reaction with oxygen at wet or dry or cold surfaces, reactions involving particulates and reactions involving water droplets or vapour.*

3.6 FUTURE TRENDS AND SCENARIO STUDIES

As it is perhaps the pollutant of greatest concern, concentrations of NO_2 in urban areas in the next ten years are of prime importance. Although the improvement of NO_x emissions from industry will have some impact on some urban areas, it is undoubtedly the emissions from motor vehicles which will be the largest determinant of future urban NO_2 concentrations.

The introduction of catalytic converters to the vehicle fleet, scheduled for 1993 will have some impact on emissions of NO_x. Estimated vehicle emissions in the period 1986 to 2010 are shown in Figure 3.24. They are predicted to peak in 1992 and then decline. However, it may be that at some time beyond the year 2010, an increase in traffic growth will cause the NO_x emissions to increase once more and possibly neutralise the benefits brought about by catalytic converters.

It is, however, unlikely that a decrease in NO_x emissions will lead to an equal decrease in NO_2 concentrations, or arguably a decrease at all in some urban areas. Our understanding of the chemistry of the NO to NO_2 conversion in the urban environment is insufficient to make accurate predictions with complete confidence. Should the urban atmosphere be 'saturated' with respect to NO_2 at the present time, then it is possible that a

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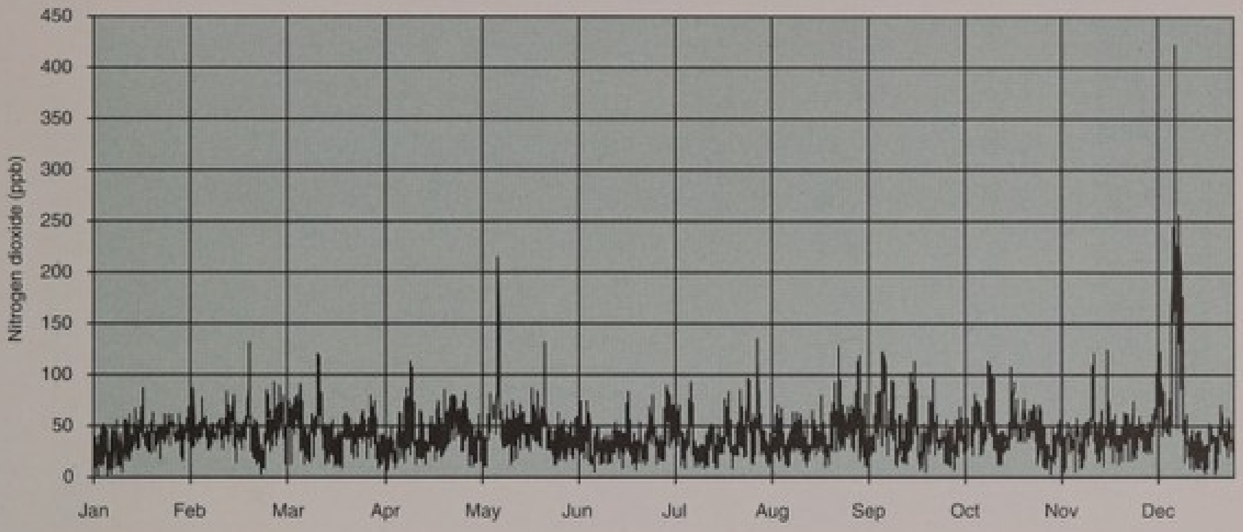
(1) Lenner M, Lindquist O and Rosen A (1983) **The NO_2/NO_x Ratio in Emission from Gasoline Powered Cars: High NO_2 Percentage in Idle Engine Measurements** Atmospheric Environment 17, 1395-1398.

Figure 3.21 Time Series of Hourly NO_2 Concentrations at London, Bridge Place (1991)



reduction in NO emissions will not result in a decrease in NO_2 concentrations. Evidence for this is presented in Figure 3.25 which shows that, at kerbside monitoring sites in particular, the NO_2/NO_x annual mean ratio decreases at higher NO_x concentrations.

Notwithstanding some of these difficulties in modelling future concentrations of NO_2, such an exercise has been undertaken by Munday et al⁽¹⁾ for Greater London. The area of interest for this modelling is determined by the fact that a detailed inventory of sources exists for Greater London and the monitoring activity there has allowed a good picture of the spatial distribution of existing NO_2 concentrations to be mapped.

Using this inventory, with projected NO_x emissions for the year 2000 and an empirical relationship between observed NO_x concentrations and NO_2 concentrations, a Gaussian plume model has been used to predict both current and future NO_2 concentrations. The prediction for the year 2000 is shown in Figure 3.26.

The predictions show a substantial decrease relative to the measured concentrations in the 1984/85 London-wide diffusion tube survey. However, it should be borne in mind that the same modelling techniques produced an underestimate of the 1984/85 case. Taking all factors into account, the conclusion from this study was that NO_2 concentrations are only likely to decrease by 5% in Central London, as compared to those experienced in 1984/5, despite the introduction of vehicle emission control measures.

3.7 NITRIC AND NITROUS ACIDS IN UK AIR

Nitric acid, HNO_3 is a strong acid which exists in the atmosphere as a vapour. It arises from oxidation of nitrogen dioxide; during daytime by reaction with the hydroxyl radical, and at night through a sequence of reactions first involving nitrogen dioxide and ozone. Conversion of NO_2 proceeds at approximately 10% per hour and thus nitric acid is a regional rather than a localised pollutant, with formation occurring predominantly well downwind of urban source regions.

Atmospheric concentrations of nitric acid are determined to some degree by its rate of production from NO_2 and its rate of loss by rapid dry deposition. However, the main controlling factor appears to be the reversible equilibrium reaction with ammonia to form ammonium nitrate aerosol.

$$NH_3 + HNO_3\ (\text{gas}) \Leftrightarrow NH_4NO_3\ (\text{aerosol})$$

The position of equilibrium in this reaction is heavily dependent upon temperature, and upon humidity due to the deliquescent nature of the aerosol. Whilst due to

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(1) Munday PK et al (1990) **A Dispersion Modelling Study of Present Air Quality and Future Nitrogen Oxides Concentrations in Greater London 1989** WSL Report LR731, Warren Spring Laboratory, Stevenage, UK.

Figure 3.22 Hourly Mean NO_2 Concentrations at Cromwell Road, Bridge Place and Earls Court, London, During the December 1991 Episode

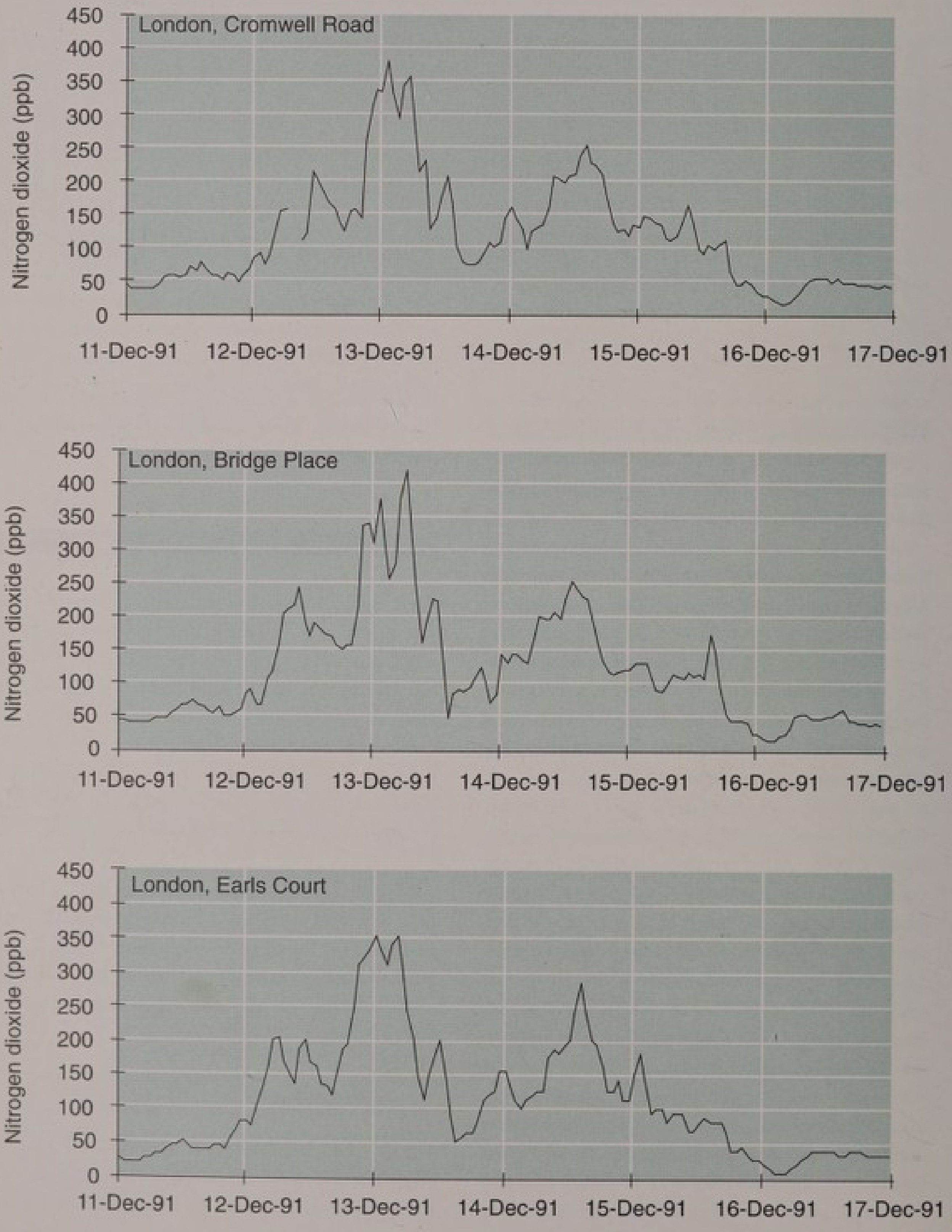


Figure 3.23 Scatter Plots of NO_2/NO_x at Cromwell Road, London

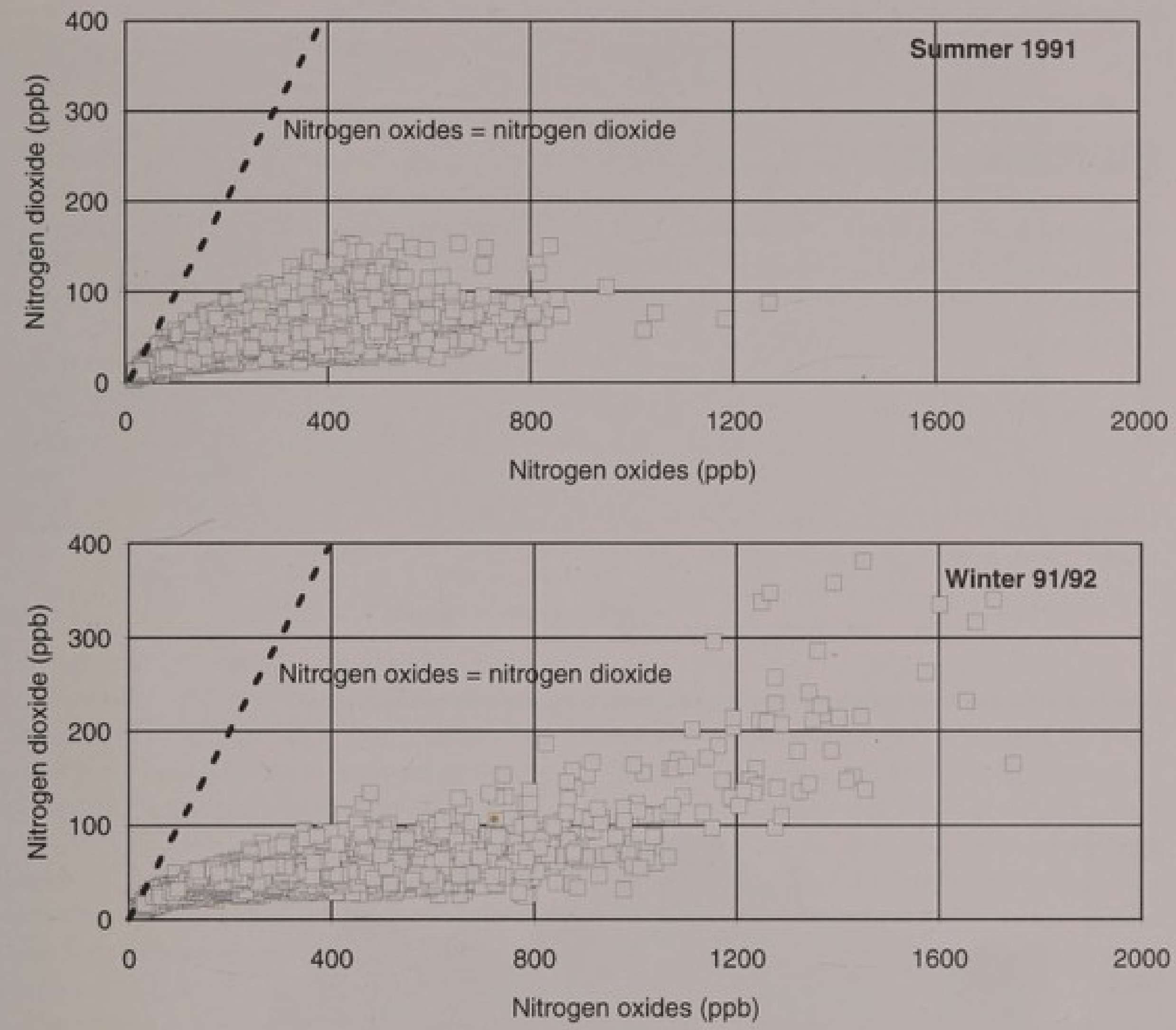


Figure 3.24 Estimates of Vehicular NO_x Emissions (1985-2010)

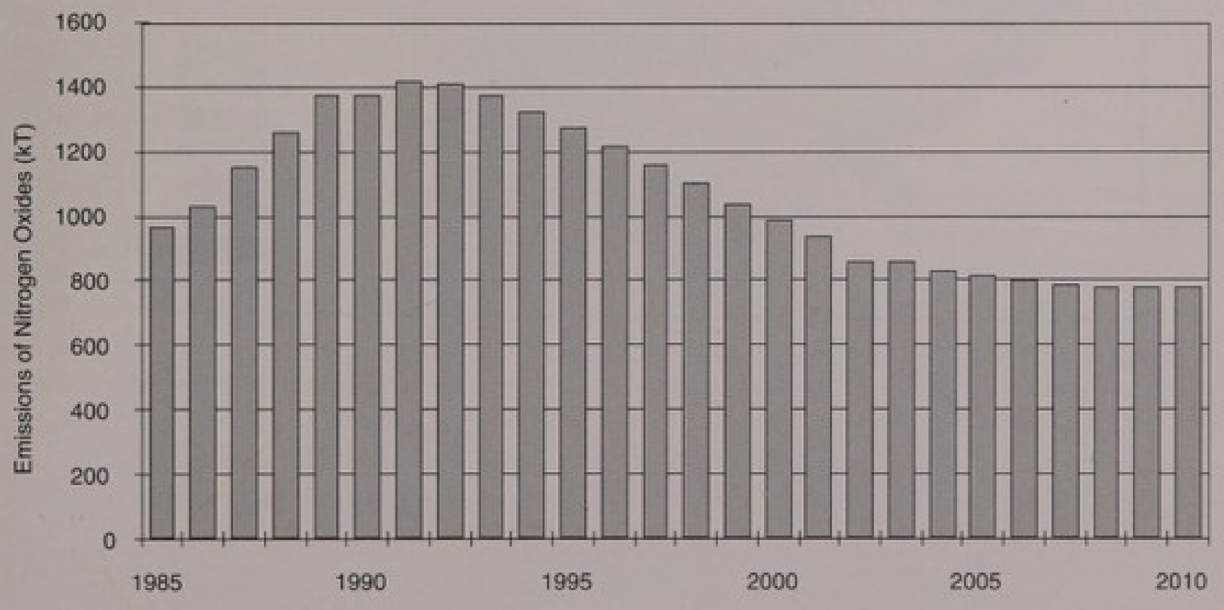


Figure 3.25 The Relationship Between Annual Mean NO_2 and NO_x Concentrations at UK Monitoring Sites (1976-1991)

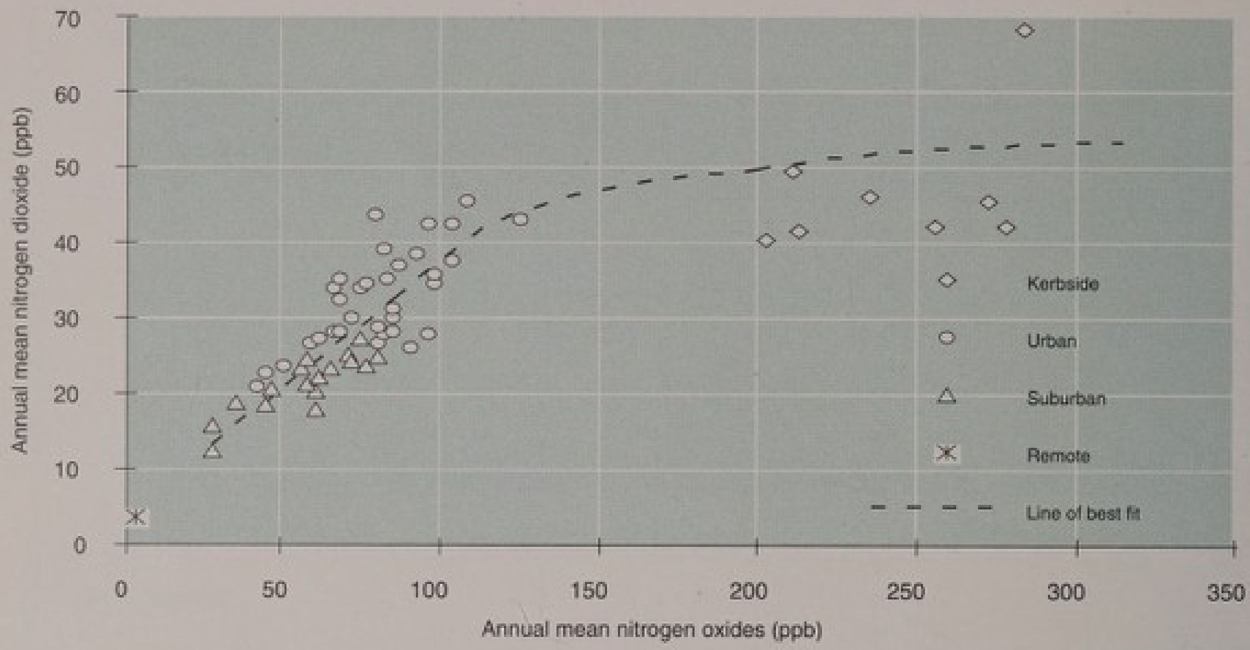
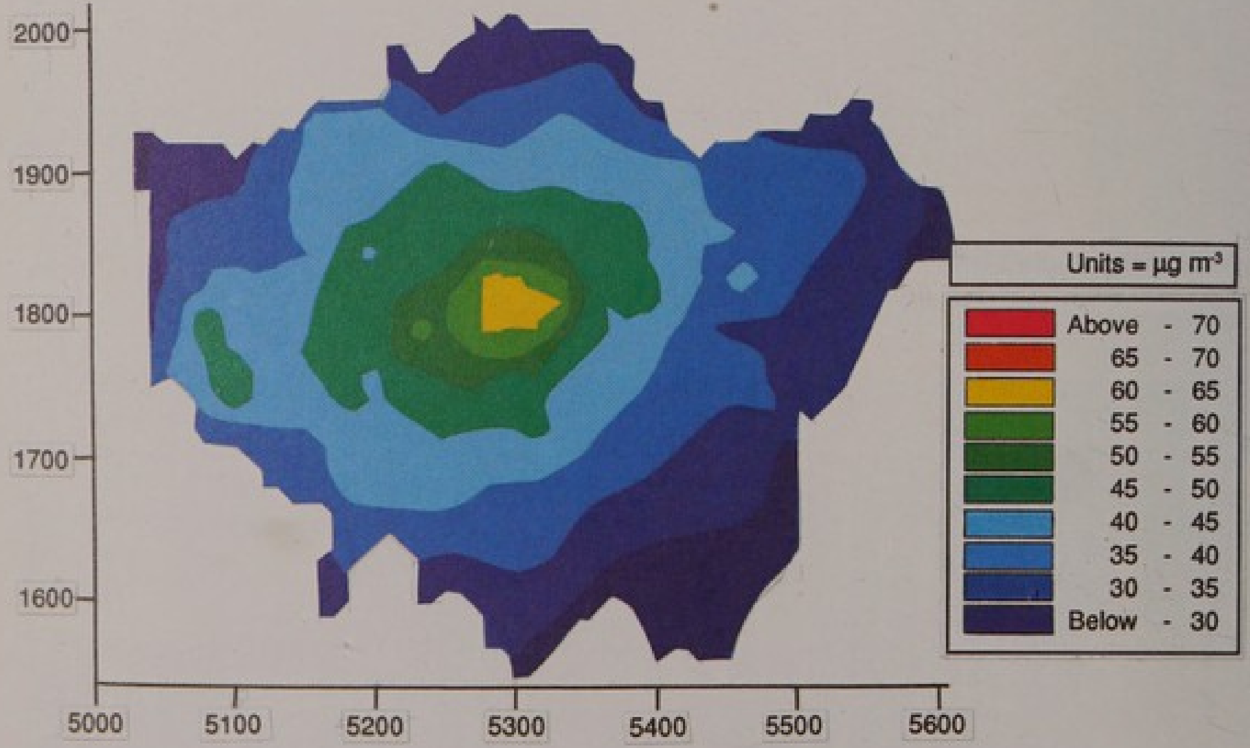


Figure 3.26 Predicted NO_2 Concentrations in Greater London in the year 2000 (values in µg m^{-3})



kinetic limitations, this reaction system is not always in perfect equilibrium, often it is close(1). Thus the main determinants of the HNO_3 concentration in air are the ammonia concentration, the air temperature and humidity.

Concentrations of nitric acid in rural air have been measured in a number of studies, particularly focused on eastern England(2). Urban data are few, and Table 3.8 shows concentrations of HNO_3, particulate nitrate and NH_3 measured in Birmingham in April-June 1991.

Table 3.8 Nitric Acid, Particulate Nitrate and Ammonia Measured in Birmingham

	HNO_3	Partic NO_3	NH_3
Range	0.4-2.5 ppb (1.1-6.6 $\mu g\ m^{-3}$)	0.5-6.5 $\mu g\ m^{-3}$	3.0-9.7 ppb (2.1-6.9 $\mu g\ m^{-3}$)
Mean	1.2 ppb (3.2 $\mu g\ m^{-3}$)	1.4 $\mu g\ m^{-3}$	5.5 ppb (3.9 $\mu g\ m^{-3}$)

The weather during the work was generally warm, which explains the high HNO_3/particulate nitrate ratios, due to enhanced NH_4NO_3 dissociation. The concentrations measured are broadly similar to those encountered at rural sites during the warmer parts of the year.

Nitrous acid, HONO, is also a product of atmospheric reactions of nitrogen oxides. Its major source is not clearly known, but appears to be related to heterogeneous reactions of NO_2, and possibly NO, upon surfaces such as the ground and airborne particles. The main significance of HONO is as a source of hydroxyl radical, OH, by photolysis.

$$HONO + h\nu \rightarrow OH + NO$$

Thus concentrations of HONO build up overnight causing a substantial production of OH at sunrise, important in starting the chemistry responsible for photochemical air pollution. Daytime concentrations are low, due to photolysis.

No UK urban data are available for HONO, although rural data show concentrations similar to those of HNO_3, representing about 10% of the NO_2 concentration(3). The average 24-hour concentration in that work was 0.45 ppb (0.88 $\mu g\ m^{-3}$). Appreciably higher concentrations have been measured in Mainz (Germany) and Los Angeles (USA) suggesting that urban levels may considerably exceed rural concentrations. Urban measurements are needed in the UK to resolve this question.

3.8 SUMMARY AND KEY ISSUES

Whilst there are a range of nitrogen compounds found in urban air, it is the two principal oxides of nitrogen, NO and NO_2, which are of prime concern for the urban environment. Of these, it is nitrogen dioxide, NO_2, which is of potential concern for human health. Nitric oxide, NO, is relatively innocuous, but is oxidised in the atmosphere to produce NO_2.

Nationally, the two main sources of NO_x are motor vehicles and power stations. In urban areas, vehicles dominate as a contributor to concentrations, by up to 90% in episode conditions.

Air quality standards for NO_2 have been set by the EC and incorporated into UK law. In addition, the World Health Organization has published guidelines for concentrations below which health effects are not likely to be observed in the most sensitive members of the population. A breach of the Directive has only occurred at the London, Earls Court, site in 1989 and this was as a result of vehicle emissions within the building housing.

Continuous monitoring of NO_2 in the UK suggests that the EC limit value, of 105 ppb (200 $\mu g\ m^{-3}$) as a 98th percentile of hourly means, is only exceeded close to busy roads. Diffusion tube studies also suggest that the limit value will only be exceeded within about 10 m of the kerb of busy roads.

Monitoring of NO and NO_2 has not taken place on a widespread basis until relatively recently and is still rather limited. Therefore, assessment of long term trends is confined to a small number of sites. At present, the continuous monitoring of NO and NO_2 is increasing in towns and cities and many more data are becoming available. Allied to this, use of the passive diffusion tube sampler has allowed a considerable body of information to be collected at low cost on the spatial distribution of NO_2 in urban areas.

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(1) Allen AG, Harrison RM and Erisman JW (1989) **Field Measurement of the Dissociation of Ammonium Nitrate and Ammonium Chloride Aerosols** Atmospheric Environment **23**, 1591-1599.

(2) Harrison RM and Allen AG (1990) **Measurements of Atmospheric HCl, HNO_3 and Associated Species on a Small Network in Eastern England** Atmospheric Environment **24A**, 369-376.

(3) Kitto A-MN and Harrison RM (1992) **Nitrous and Nitric Acid Measurements at Sites in South-East England** Atmospheric Environment **26A**, 235-241.

Monitoring of NO and NO_2 concentrations by the use of continuous chemiluminescent analysers has allowed researchers to examine aspects of their temporal variations, seasonal variations and relationships to traffic flows. Unfortunately, there is still much to understand regarding the behaviour of NO and NO_2 in the atmosphere, especially with their chemistry and the conversion of NO to NO_2. Several features of episodic high NO_2 concentrations are not explicable with current theories.

Emission inventories indicate an increase in UK NO_x emissions of 16% over the period 1986-1991, and 37% in road traffic emissions. Because of the non-linear relationship between NO_x and NO_2 concentrations, the impact upon NO_2 would be expected to be less than upon NO_x. The pattern in traffic growth has been very spatially non-uniform, with the greatest growth in vehicle miles taking place on motorways and trunk roads, and rather little in urban centres. In this context, the siting of the EC Directive and other older monitoring stations gives a very incomplete picture of NO_2 in the UK and it is not possible to be clear about trends. Additionally, because of substantial inter-annual variability due mainly to meteorological factors, it may take many years (10 plus) before even quite substantial trends become entirely clear. It is therefore likely on the basis of the emission inventories that NO_2 concentrations are increasing, although this is not seen at all sites. While some long-running sites in urban and rural areas show upward trends, it appears to be the central urban sites which are showing the smallest growth in NO_2. The newly established EUN sites will provide an excellent facility for determining trends in NO_2 at central urban background locations over the future years.

Future trends in urban concentrations of NO_2 are almost exclusively dictated by the motor vehicle activity in the urban environment, whether they are equipped with improved emission controls and how effective these might be. Even if the primary emissions of NO are substantially reduced, it is by no means clear the extent to which this will translate into lower concentrations of NO_2.

3.9 RESEARCH RECOMMENDATIONS

The following are recommendations for further research in the UK.

- *As a priority, the mechanisms for producing high concentrations of NO_2, in the apparent absence of ozone, must be investigated.*
- *The microscale variations of NO_2 concentrations in urban areas, eg at road intersections, should be investigated.*
- *Comprehensive data should be gathered on the ratio of NO_2 to NO_x in vehicle exhausts, for a range of vehicles, vehicle speeds and ambient temperatures.*
- *The diffusion tube passive sampling technique needs to be comprehensively assessed and guidance on its proper use made available to all interested parties.*
- *NO_2 concentrations should be monitored in areas which become vehicle free, eg pedestrianised areas.*
- *Further long-term monitoring is required at fixed locations, including suburban areas.*

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Council Directive of 7 March 1987 on Air Quality Standards for Nitrogen Dioxide (85/203/EEC) Council of the European Communities, Belgium.

Council Directive of 26 June 1991 Amending Directive (70/220/EEC) on the Approximation of the Laws of the Member States Relating to Measures to be Taken Against Air Pollution by Emissions from Motor Vehicles (91/441/EEC) Council of the European Communities, Belgium.

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4 Sulphur Compounds

4.1 INTRODUCTION

Sulphur dioxide (SO_2) and smoke are the two pollutants which have been most closely associated with urban air pollution. They are also the most widely measured pollutants with records going back to before 1914 from the use of lead dioxide candles for the measurement of SO_2. It was the urban smogs of the 1950s, culminating in the great London smog in December 1952, (associated with 4,000 premature deaths) which led to the introduction of the Clean Air Acts (1956 and 1968); themselves partly responsible for the subsequent dramatic improvement in urban air quality in the UK.

This profoundly disturbing event and the subsequent legislation also prompted the establishment of a national network of SO_2 measurement sites, primarily in urban locations and operated by local authorities. This was the 'National Survey' which commenced in 1961, for the purpose of monitoring SO_2 and smoke concentrations. For many urban areas in the UK, this measurement programme has constituted the sole monitoring activity for atmospheric pollution. At its largest, the National Survey was composed of over a thousand sites, but has since been reduced to around 170. This reflects the relative decline in the urban concentrations of SO_2 and smoke. However, SO_2 is still a pollutant of significance in urban areas and the role and importance of acid aerosols is being increasingly debated.

4.2 SOURCES

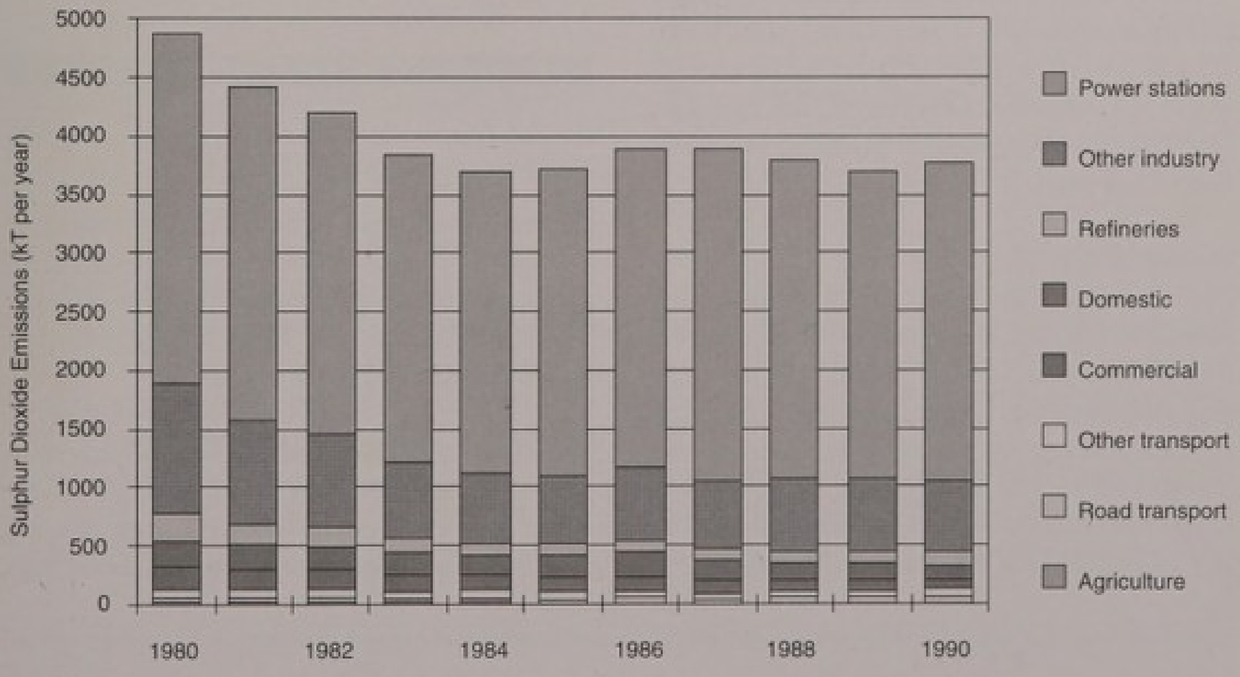
Sulphur dioxide can be found naturally occurring in the earth's atmosphere, mainly as a result of volcanic activity. However, its concentrations in the UK, and particularly in urban areas, arise principally as a result of the combustion of fossil fuels. Coal, oil and natural gas all contain greater or lesser amounts of sulphur and therefore all produce SO_2 when burnt.

Natural gas, as sold by British Gas, contains only trace amounts of sulphur, but coal and heavy fuel oil contain significant amounts of sulphur. The average sulphur content of UK coal is 1.7% by weight and for heavy fuel oil the figure may be as high as 3%. Other forms of oil usually contain lesser amounts of sulphur and the sulphur content is often defined by legislation. For example, the sulphur content of distillate fuel oil is currently limited to 0.3%.

National emissions of SO_2 are presented in Figure 4.1, categorised by sector.

Emissions of SO_2 declined from 6.3 MT in 1970 to around 3.7 MT in 1984 since when they have levelled off with the 1990 figures also being 3.7 MT. These figures are compiled by the Warren Spring Laboratory (WSL) and are based on fuel consumption and composition and are estimated to have an accuracy of

Figure 4.1 Estimated UK Emissions of SO_2, by Source Type



± 10% to 15%. Over 90% comes from industrial sources with power generation accounting for 72%. Power station emissions have declined slightly since 1970 whereas emissions from industry have reduced significantly being only 25% of their 1970 value by 1991. Coal and fuel oil are the major fuel contributors to emissions with coal contributing 75% in 1990 and fuel oil 18%. In the longer term the prospects are that national emissions will decline still further as a result of the use of natural gas for electricity generation, the progressive introduction of flue gas desulphurisation in power stations and an increase in imported low sulphur fuel. The EC Large Combustion Plant Directive will have an influence in promoting lower emissions and on a longer time scale the development of alternative technologies and the non-fossil fuel obligation may also have an effect.

As with NO_x, the levels and trends in national emissions can be misleading if applied directly to urban areas. This is particularly so for SO_2 where the major source is electricity generation. Large power stations are no longer sited in urban centres and emissions are generally from tall stacks, with the result that they rarely contribute to the worst urban pollution episodes which occur when emissions from low level sources are trapped by inversions in a shallow mixing layer. It is for this reason that smaller local sources can have a disproportionate effect on air quality.

Vehicles are not a significant source of SO_2 emissions in general, since the sulphur content of petrol is small (0.04% by mass). Diesel however, does contain larger amounts of sulphur (0.2% by mass) which results in SO_2 emissions from diesel engined vehicles, eg lorries, buses and taxis. Catalytic converters can be associated with emissions of hydrogen sulphide, which may constitute a local nuisance rather than a health issue.

Because SO_2 is primarily a result of combustion, concentrations in urban areas reflect the extent to which coal and fuel oil is burnt. For domestic heating, coal has been replaced in most UK towns and cities by natural gas (which contains negligible amounts of sulphur) and electrical forms of space heating. Exceptions to this general rule remain, however, and in these places combustion of coal in domestic premises still produces high concentrations of SO_2 in the local atmosphere.

4.3 STANDARDS AND GUIDELINES

Because SO_2 is a relatively common and well recognised pollutant, it is well regulated in terms of ambient air quality standards and guidelines. In the UK, the Air Quality Standards Regulations of 1989(1) (Statutory Instrument 317) incorporated the 1980 EC Directive which defined 'limit' and 'guide' values for concentrations of SO_2. The limit values are mandatory and should not be exceeded anywhere, whereas the guide values are 'intended to serve as long-term precautions for health and the environment'.

The EC derived standards are based on daily means of SO_2 concentrations, which reflects the measurement technique used in the national monitoring network, ie the 'bubbler' method described in Section 4.4. A consequence of this is that the limit and guide values are unable to take into account very short-term peak concentrations, of a few hours duration, in the same way that the EC Directive for nitrogen dioxide does.

The World Health Organization has proposed guidelines for SO_2 concentrations which incorporate a safety margin below those at which effects may be recorded in sensitive individuals. These guidelines are based on one hour averages and ten minute averages as well as daily means and hence consider the effects of short term episodes. They have no legal status.

The numerical values of these standards and guidelines are presented in Table 4.1.

4.4 MEASURED CONCENTRATIONS OF SO_2

4.4.1 Monitoring of SO_2

Sulphur dioxide is one of the more widely monitored pollutants considered in this report. Warren Spring Laboratory has a long history of managing networks, starting with the National Survey in 1961. Individual sites are maintained by local authorities.

When the National Survey of smoke and SO_2 was set up in 1961 it had around 500 monitoring sites, a number which grew to around 1,200 by 1966, most of which were in urban or industrial areas. The number then

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(1) Her Majesty's Government **The Air Quality Standards Regulations** (1989) Statutory Instrument 317 HMSO, UK.

Table 4.1a Air Quality Standards and Guidelines for Sulphur Dioxide (ppb)

Source/ Organisation	Annual Averages	98th Percentile	24hr Average	1hr Average	10 min Average
EC Directive					
- Limit Values	30(>34)	94(>128)	-	-	-
	45(≤34)	132(≤128)	-	-	-
- Guide Values	15-23		38-56		
World Health Organization				130	188

Notes regarding EC Directive (80/779/EEC):

- refers to daily mean measurements;
- annual-average limit value is expressed as the median value; annual average guide values are arithmetic means;
- two limit values quoted depending upon associated smoke concentrations, (given in brackets as $\mu g\ m^{-3}$)
- values here are given in ppb, the EC Directive specifies values in $\mu g\ m^{-3}$ and they have been converted in this table using a factor of 0.376, (assuming a temperature of 20°C)

remained more or less constant until 1982 when they were reorganised into the Basic Urban and EC Directive networks. These networks are funded by the DOE.

The objective of the Basic Urban network is to provide information on long term trends on a national scale. Monitoring stations were chosen to provide coverage in all the major conurbations, in most of the larger towns and from a sample of smaller towns, with an emphasis on commercial town centres and heavily populated areas. The number of sites in the network has remained fairly steady at about 175 from its inception to the present day.

The EC Directive network was set up to monitor air quality in areas where the results of the National Survey indicated that the Directive limits could be breached, and in order to comply with the requirements of EC Directive 80/779/EEC. Some of the monitoring sites are included in both the Basic Urban and EC Directive networks. However, the intention has been to discontinue EC monitoring when, over a period of time and in response to the implementation of smoke control orders air quality improves to a point where the limit values will not be exceeded. The DOE criterion for the closure of a site is that concentrations should be below the upper EC guide value for three years or more. When the EC network was established in 1982 it consisted of about 370 sites. By 1986/87 the number was 377, but since then the number has been reduced to 166.

Table 4.1b Department of the Environment Air Quality Bands for Sulphur Dioxide (hourly average concentrations)

Category	Concentration (ppb)
Very good	<60
Good	60-124
Poor	125-399
Very poor	≥400

The method used to measure SO_2 in both networks is sometimes known as the twenty-four hour 'bubbler'. The technique is more correctly termed the 'net acidity' method and is defined by a British Standard (BSI 1747 Part 3, 1969)(1). This method produces daily means for SO_2 concentrations, but is not identical to that described in the EC Directive, although both methods rely on absorption of SO_2 in a reagent exposed to the ambient air over a period of 24 hours. In the UK's net acidity method, filtered air is 'bubbled' through a dilute solution of hydrogen peroxide held in a glass 'Drechsel' bottle. Any SO_2 reacts with the hydrogen peroxide to form sulphuric acid. After a week's operation, a bottle for each day is analysed in a laboratory to determine the amount of sulphuric acid present. It is assumed that all the acid was formed by SO_2 in the air and hence a concentration is established. An obvious difficulty with this technique is that any acid or alkali in the air will affect the result. Nevertheless, despite this, the net acidity method has provided meaningful results over a long period of time.

A somewhat more advanced method of monitoring SO_2 concentrations is the ultraviolet fluorescence (UVF) technique, which allows continuous monitoring of SO_2

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(1) British Standards Institution (1969) **Methods for the Measurement of Air Pollution** BS 1747 Part 3 BSI, UK.

concentrations in situ by an analyser. Such an instrument allows hourly and ten minute average concentrations to be measured and hence provides a more detailed analysis of short-term peak concentrations than the more traditional net acidity method.

Because of the potential differences in accuracy that might arise from the use of different techniques to those specified by the EC Directive, WSL have conducted an intercomparison between the net acidity method and the UVF method (which is recognised and approved by the EC). The study(1) showed that in general, the net acidity method produced higher readings. The exception to this appeared to be several sites where the net acidity method gave lower readings at peak concentrations, as indicated, for example by the 98th percentile.

Some local authorities are also active in monitoring SO_2 by means other than the bubblers. Several now have continuous UVF analysers and others have invested in 'OPSIS', a Swedish instrument which employs the technique of Differential Optical Absorption Spectrometry (DOAS). Some of these local authorities then make the information on SO_2 concentrations available to the public using local news media.

The DOE's new Enhanced Urban Network includes measurements of SO_2 and therefore is currently providing valuable additional data on urban SO_2 concentrations, using continuous analysers.

4.4.2 Temporal Trends in Sulphur Dioxide Concentrations

When discussing temporal trends and current concentrations, it is worthwhile recalling the concentrations of SO_2 recorded in major urban areas during the smog episodes of the 1950s and 1960s. During the well known smog of 4 to 10 December 1952, daily average SO_2 concentrations were in the range 1,000 to 1,400 ppb (3,000 to 4,000 $\mu g\ m^{-3}$) on 3 days; the highest reported concentration in the UK was 1,340 ppb (3,830 $\mu g\ m^{-3}$) in Lambeth, in London. As this was the average over 7 to 8 December, it is possible that a daily level could have approached or exceeded 1,400 ppb (4,000 $\mu g\ m^{-3}$) . In the 1962 smog which occurred on 3 to 7 December, there were two days in which two or more sites recorded daily mean SO_2 concentrations above 4,000 $\mu g\ m^{-3}$ (1,400 ppb).

In urban areas, concentrations of sulphur dioxide have shown a clear and marked decline since the mid-1960s, as shown by measurements in London, illustrated in Figure 2.1 of Chapter 2, and also in other cities. Figure 4.2 shows the decline, over the same time period, in Lincoln while concentrations in rural Lincolnshire remained steady until the early 1980s. The immediate conclusion to be drawn from these data is that urban concentrations of SO_2 are now reduced to near rural levels in Lincoln, which suggests that the contribution of emission sources within the city is now small in relation to those external to the city.

The dramatic reduction in SO_2 concentrations during the 1960s and 1970s is due to changes in fuel use. In London, work by Warren Spring Laboratory and the former Greater London Council, has shown that there was a reduction in the emissions from solid fuel burning from 1962 to 1975 and then a reduction in the use of fuel oil from 1975 to 1988.

A further indication of the trend away from coal burning may be found in the ratio of summer to winter means and also the ratio of SO_2 to smoke. The summer/winter ratio has, in most locations, moved towards a value of 1.0 and the SO_2/smoke ratio has, for example in York, risen from 1.0 (in the early 1960s) to approximately 5 in 1992.

4.4.3 Variations in Sulphur Dioxide Concentrations in UK Towns and Cities

The geographically widespread distribution of SO_2 monitoring sites in urban areas in the DOE networks permits a good description of SO_2 concentrations in the UK. Urban concentrations are determined by local emissions at low level and are highest where fossil fuels such as coal are still used in significant quantities for domestic and space heating requirements. In contrast, the spatial pattern in rural areas is defined by the emissions of elevated point sources, ie power stations.

In many UK towns and cities, average concentrations of SO_2 are relatively low, typically in the range 5 to 15 ppb. However, in those places where fossil fuel burning

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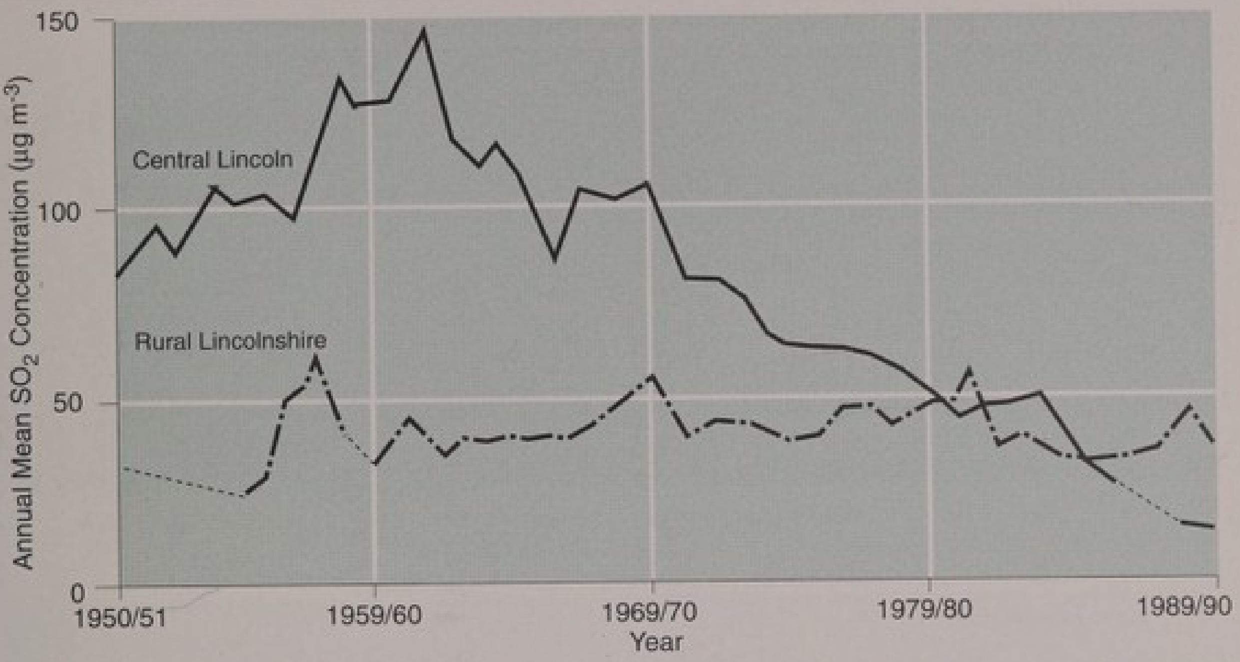
(1) McInnes G (1988) **Report on the Assessment of the Comparability of the United Kingdom's Net Acidity Method for Monitoring Sulphur Dioxide Against the UV Fluorescence Method** WSL Report LR653, Warren Spring Laboratory, Stevenage, UK.

Figure 4.2 Comparison of SO_2 Concentrations Measured in the City of Lincoln and Rural Lincolnshire



strongly influences SO_2 concentrations the average tends to be higher. In particular, the winter seasonal average is high, reflecting the continuing use of coal and oil for heating purposes. A good example of a city in this category is Belfast, where coal and smokeless fuel is used in domestic premises, in the absence of natural gas as an alternative. However, Belfast is atypical of the UK in general, where natural gas is widely available.

Figure 4.3 presents data recorded in Belfast for the period January 1990 to March 1991 as a time series of hourly averages. In the same figure, SO_2 concentrations at London, Bridge Place, are presented, although data are only available for the period September to March. (Prior to September the equivalent site in London was at a different location nearby, denoted 'London, Victoria', where measurements have been made since 1972. Concentrations at the two London sites are broadly comparable.)

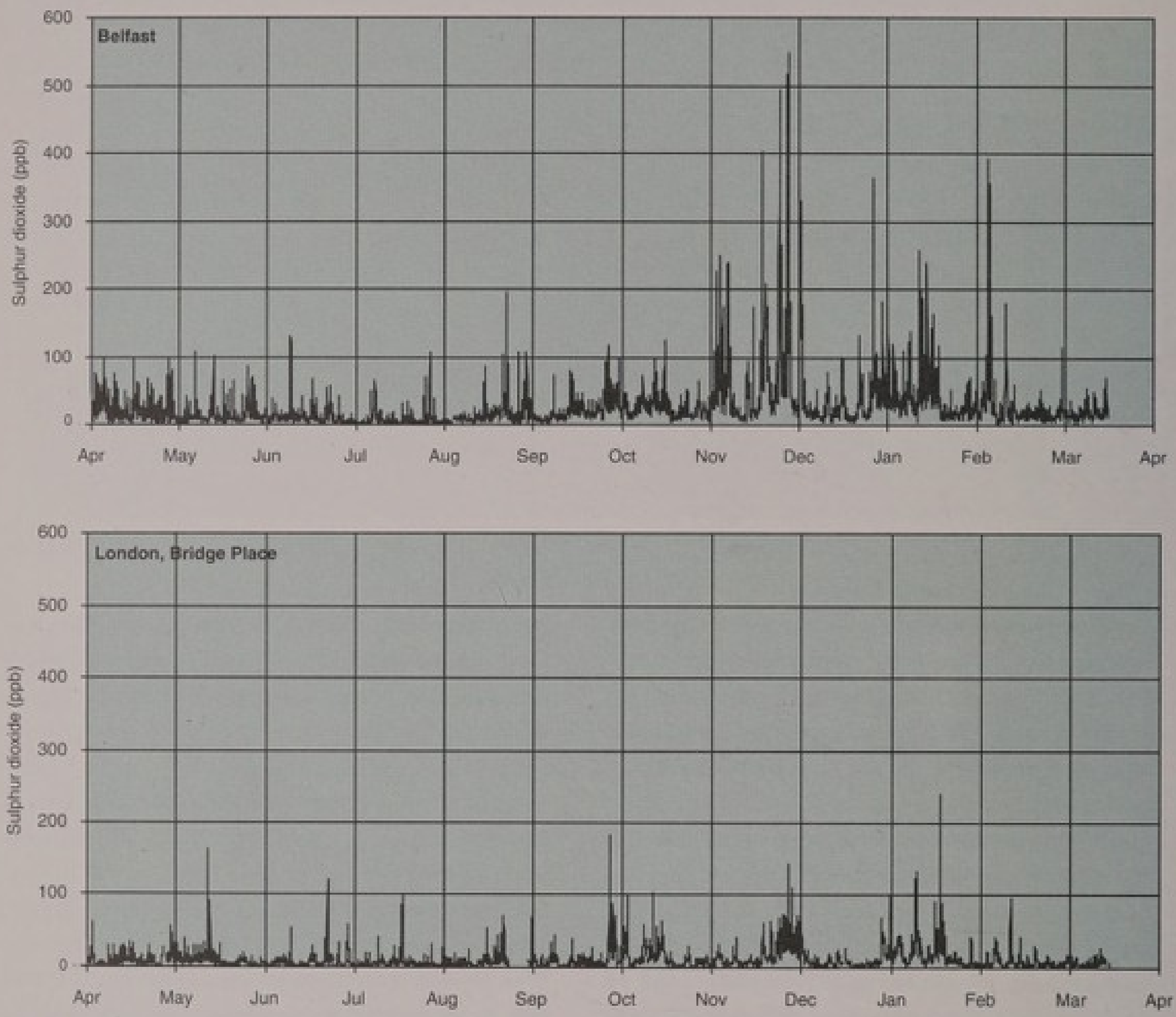
The difference in winter concentrations between London and Belfast is striking. Not only does the mean concentration at Belfast increase during the winter months, but also there are very significant peak concentrations. In London, vehicles, mainly diesel-engined, are the most significant source. Figure 4.4 for Cromwell Road, London presents a similar time series, and also the average diurnal concentration. At the Cromwell Road site, continuous measurement of SO_2 concentrations are made at the kerbside and as such these recordings reflect the influence of vehicles. Consequently, there is no obvious seasonal variation in concentrations. Mean values are higher than for Bridge Place.

In London, SO_2 concentrations are occasionally elevated for short periods of a few hours at specific locations when plumes from the power stations in the Thames Estuary are transported over the city in easterly winds. London Scientific Services (now Rendel Science & Environment) operated continuous SO_2 analysers at four sites in London during the period 1986 to 1989. They report that occasional hourly average peaks in excess of 350 ppb were observed at the East London site in Bexley and the Central London site in association with light easterly winds. Therefore, although in general urban concentrations of SO_2 are not influenced by industrial emissions, there are infrequent occasions when this might be the case.

Analysis of the data obtained from the continuous monitoring site at Belfast shows that over a twenty-four period in winter, concentrations are highest in the late evening and night with a subsidiary peak between about 7 am and 10 am. This pattern is consistent with the major contribution being from space heating.

If an episode is defined as occurring when the hourly concentration exceeds 122 ppb (350 µg m^{-3}), then episodes may be examined in terms of their duration and

Figure 4.3 Time Series of Hourly Mean SO_2 Concentrations at Belfast and London, Bridge Place (1991–1992)



frequency of occurrence. The results of this analysis for Belfast, hourly and daily episodes, is presented in Figures 4.5 and 4.6, respectively.

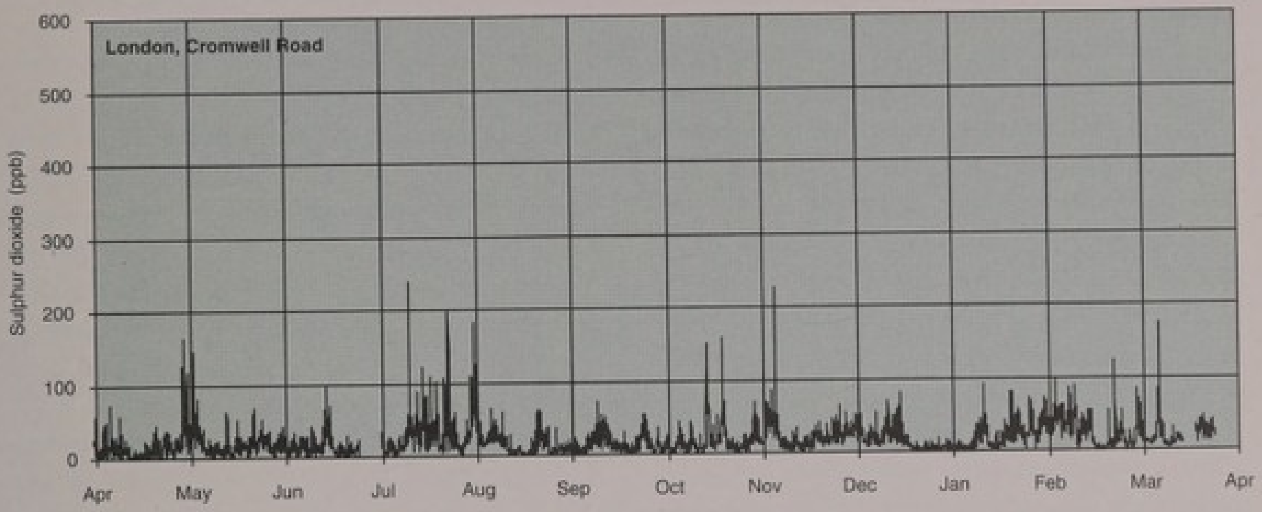
For the consecutive hourly concentration plots, it is readily apparent that the highest frequencies are for duration of 1 to 7 hours. This relates to the diurnal cycle of emissions. In the case of the daily plots, episodes show a duration of 1 to 5 days, which is a reflection of the fact that elevated SO_2 concentrations occur in anticyclonic weather conditions, which typically persist for this length of time.

The pattern will be different for the occurrence of episodes caused by power stations or other point source emissions.

4.4.4 Exceedences of Standards and Guidelines

The EC Directive limit and guide values, as given in Section 4.3, are expressed in terms of daily mean concentrations. As a result, the DOE's extensive network of 'bubblers', managed by Warren Spring Laboratory, is able to provide clear guidance on those urban areas where exceedences are occurring. In terms of the Directive, several sites have in the past exceeded the limit specified for black smoke, especially for the criterion that the numerical value for the 98th percentile should not be exceeded for more than three consecutive days. Judged purely in terms of the limit value for SO_2, however, the number of exceedences is relatively few. In 1990/91, the only exceedence reported was at Belfast 42, where the 98th percentile of daily means was recorded as 374 $\mu g\ m^{-3}$.

Figure 4.4 Time Series of Hourly Mean SO_2 Concentrations at Cromwell Road, London (1990–1991) and Diurnal Variation Plot for the Same Site



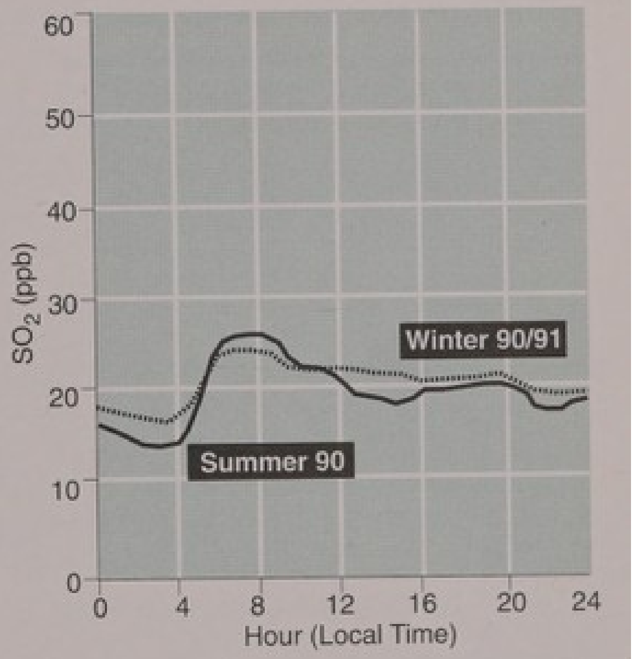


Figure 4.5 SO_2 Episode Durations (Consecutive Hour > 122 ppb) in Belfast (October 1989-March 1991)

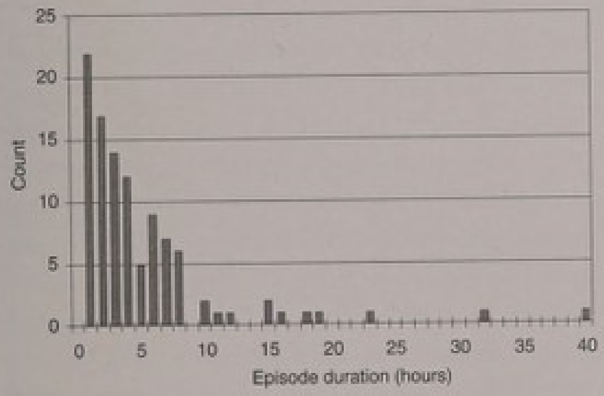
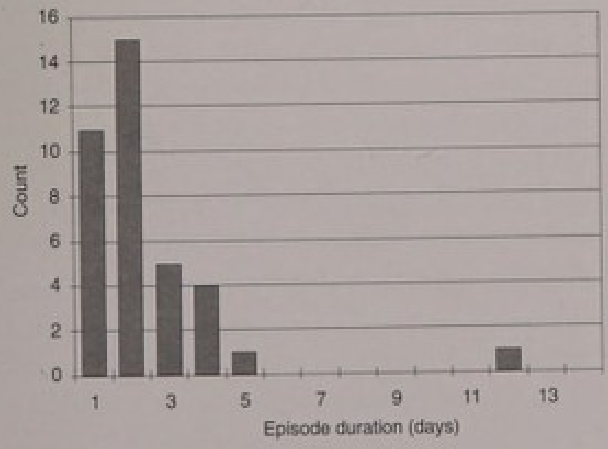


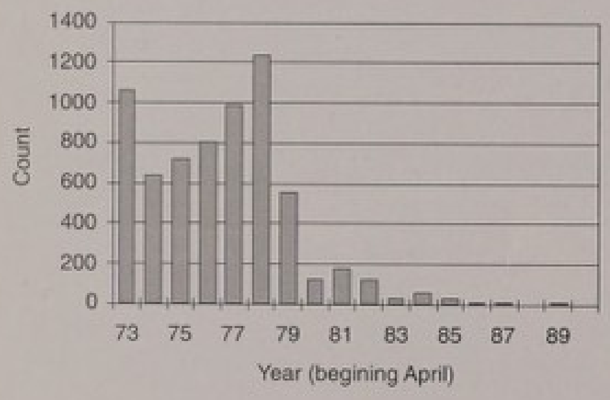
Figure 4.6 SO_2 Episode Durations (Consecutive Days with one hour or more > 122 ppb) in Belfast (October 1989-March 1991)



The WHO guideline of 122 ppb (350 µg m^{-3}) as an hourly average is more stringent than the EC limit values, although much less information is available on hourly average concentrations. Continuous monitoring by the DOE is currently limited to the site in central London; Cromwell Road in London, Belfast; and four relatively recently established sites where it is judged that SO_2 may be a problem. These are at Bircotes (Nottinghamshire), Featherstone, Rugeley and Barnsley. Occasional exceedences of the guideline are observed at all these sites, usually in the range 5 to 20 hours in one year. In Belfast, the figure is much higher, for example, 269 hours in 1990 to 1991.

At the London Victoria site, measurements were made continuously in the period 1973 to 1991. It is interesting to examine the number of occasions when the hourly mean was in excess of 122 ppb during this period. These data are presented in Figure 4.7.

Figure 4.7 Exceedences of WHO Hourly Mean Sulphur Dioxide Guideline Value in Central London (1973-1991)



The decline in the number of hours when the guideline was exceeded in this period is striking and confirms the trend shown by the daily mean measurements of the net acidity method in UK towns and cities.

Now that the Enhanced Urban Network is in place and expanding, much more information will become available on hourly average concentrations of SO_2 in urban areas.

4.5 ACID AEROSOL CONCENTRATIONS IN THE UK

There has been a continuing interest, dating from at least the time of the smogs in London in the 1950s and 1960s, in the effects on health of the acidic aerosol particles in urban atmospheres. The characterisation and measurement of these acidic particles is not straightforward and measurements have not been widely carried out. Measurements were made by the Air Pollution Research Unit (APRU) of the Medical Research Council (MRC) at St Bartholomew's Hospital during air pollution episodes from 1957 and daily measurements were carried out from 1963 to 1972, inclusive. The method used was to collect airborne particulate matter on a filter through which air was drawn at a rate of 10 to 20 litres per minute. The filter was then immersed in an excess of sodium tetraborate and the solution titrated back to neutrality with sulphuric acid. Although this method measured the total acidity of the material, most appeared to be present as H_2SO_4. A summary of the average and maximum daily concentrations is presented in Figure 4.8.

During this period, the highest daily mean concentration observed was 134.1 µg m^{-3} H^+ as H_2SO_4. Prior to this, the highest daily and hourly values recorded were 347 µg m^{-3} and 678 µg m^{-3}, respectively, on an episode day in December 1962. As is clear from Figure 4.8, these measurements in London showed the highest concentrations in winter, but it is interesting to note that the winter/summer ratios for H_2SO_4 are relatively small compared with those for the primary pollutant SO_2, where ratios of 1.8 to 2.0 were typical in central London in the mid 1960s. This suggests that summertime production of H_2SO_4 was probably significant in London in the 1960s and 1970s.

The only other historical urban sulphate measurements available in the UK are those measured by AEA Technology, Harwell in Teesside in 1969 to 1970. The mean total sulphate aerosol concentration in the period June to December 1969 and May to October 1970 was 15 µg m^{-3} compared with the rural Harwell value for the same period of 9.8 µg m^{-3}. Measurements of daily mean total sulphate are carried out by WSL in central London and recent data are presented in Figure 4.9.

Figure 4.8 Mean and Maximum Daily Acid Aerosol Concentrations in London (St Bartholomews Hospital)

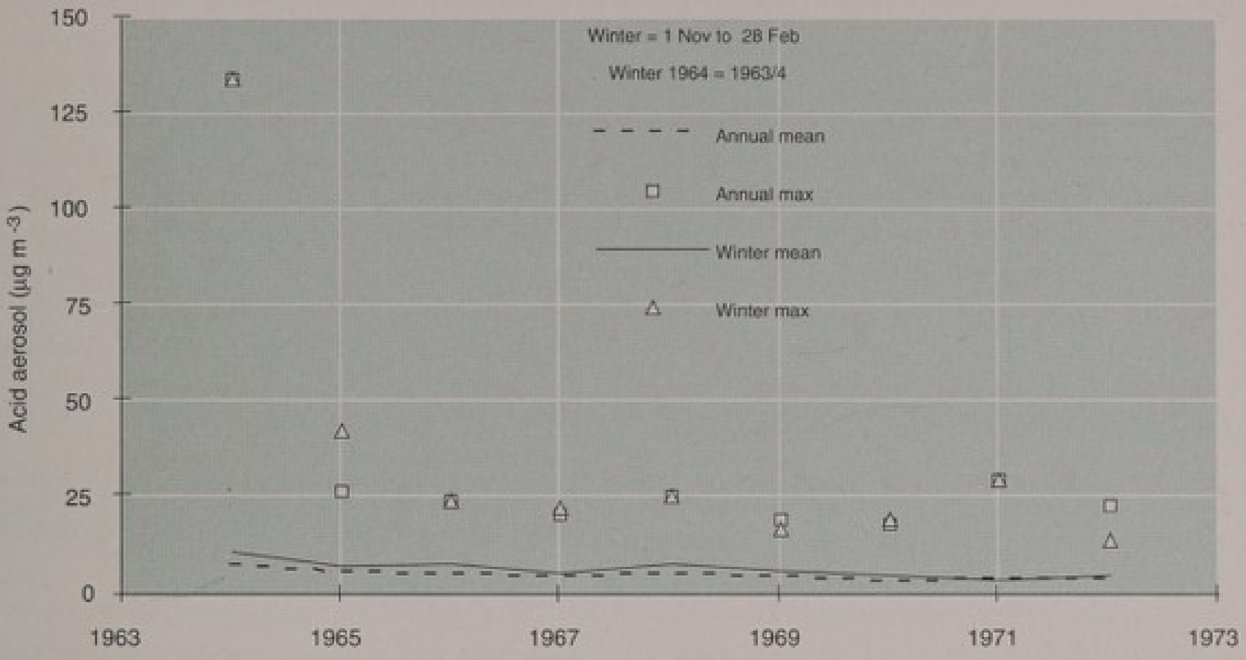
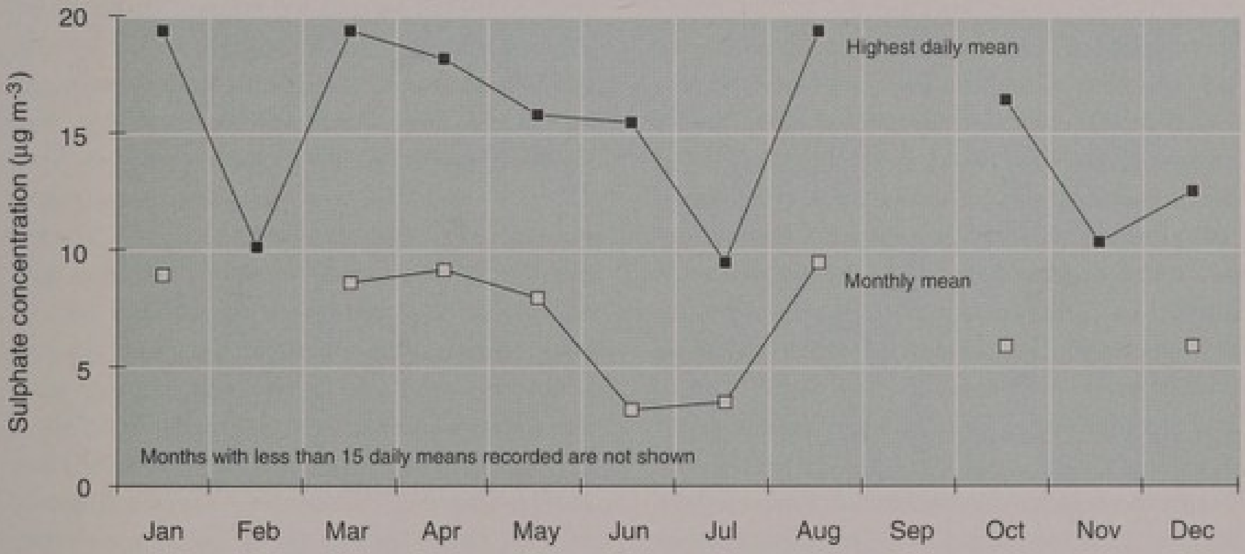


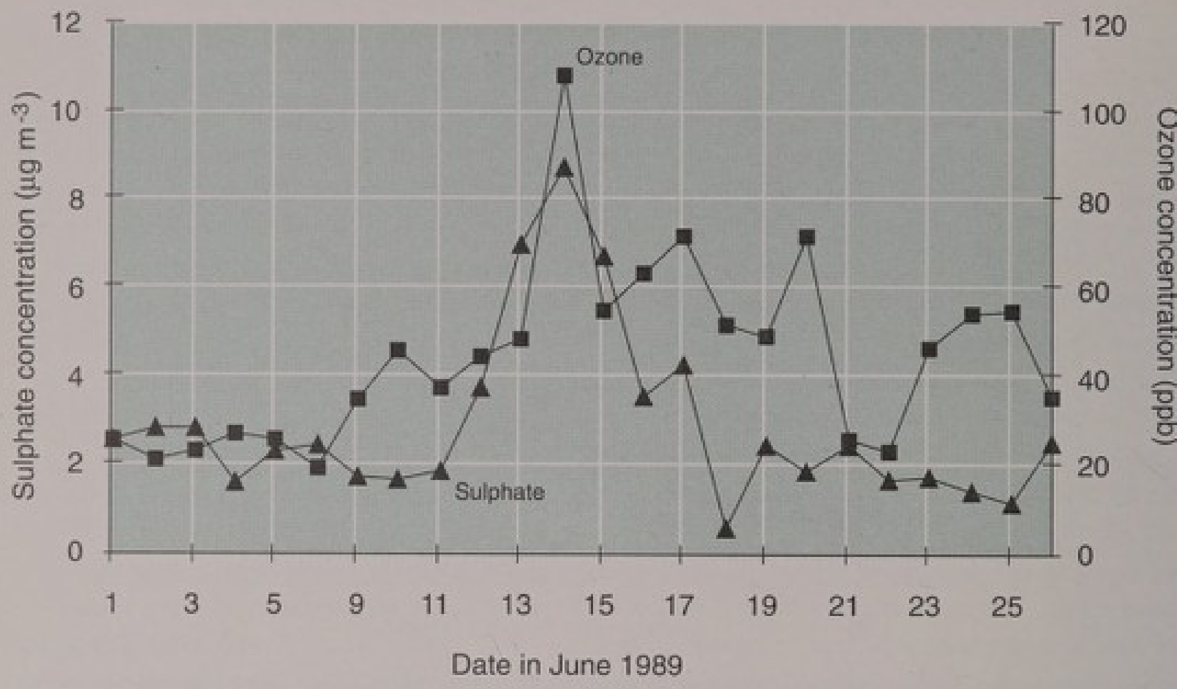
Figure 4.9 Average and Maximum Sulphate Concentrations in Central London (1990) (London, Victoria for Jan-Aug and for London, Bridge Place for Sept-Dec)



These total sulphate concentrations give an upper limit to acid sulphate concentrations. Bearing this in mind and comparing these data with the mean values in rural Essex, there may be only a small difference between urban and rural values of acid sulphates. This is consistent with the timescale of production of H_2SO_4 in the atmosphere. However, it should be stressed that no current urban data are available to confirm this. Data presented in Figure 4.9 show lower mean total sulphate values in summer months but broadly similar maximum daily values throughout the year. This suggests that two sulphate production mechanisms may be operating. Evidence for one of these mechanisms, photochemical production, is presented in Figure 4.10 which shows the good correlation between total sulphate aerosol and ozone in Central London during an ozone episode in June 1989.

Few other measurements have been made in the UK apart from at Harwell (see below) but a considerable amount of work has been carried out in the USA, the measurements being carried out using denuder tubes and filter packs. These measurements in the USA find that periods of elevated acidic aerosols occur more frequently in summer months, in contrast to the earlier measurements in London. It is possible, as

Figure 4.10 Mean Daily Ozone and Total Sulphate Aerosol Concentrations in London



concentrations of SO_2 in London have decreased so markedly, that summer concentrations of acid aerosol are now higher in London than in winter, but no data are available to confirm this. The chemistry of H_2SO_4 aerosol formation and neutralisation is complex, but the primary gas phase route is the reaction of SO_2 with OH radicals (whose concentrations are highest during photochemical episodes). The sulphuric acid formed can then react with ammonia to form the neutral ammonium sulphate, so that the amount of H_2SO_4 persisting in the atmosphere will be a function of ambient ammonia concentrations. Reactions with other species such as calcium carbonate and sodium chloride can also occur.

The timescale of the SO_2 oxidation is of the order of a few percent per hour, so that like ozone, sulphate aerosol is a regional pollutant rather than specifically an urban one. Measurements of aerosol sulphate and nitrate have been made since the 1950s at Harwell and bearing in mind the timescales of sulphate production, these data should be broadly representative of much of southern England. However, it should nonetheless be noted that no recent urban data on acid aerosols exist in the UK, to assess the concentrations in densely populated areas.

Data collected at Harwell provide an excellent and unique record of the sulphate and nitrate aerosol concentrations from 1954 to the present day, H^+ ion concentrations were not measured directly but have been obtained by assuming an ion balance between SO_4^{2-}, NO_3^-, NH_4^+ and H^+, with H^+ given by $(SO_4^{2-} + NO_3^-)$ - NH_4^+ (in equivalents). The absolute values of the annual mean concentrations are currently about 3 to 5 µg H_2SO_4 m^{-3} (about 0.03- 0.05 µeq m^{-3}).

In recent years, other than the AEA Technology, Harwell data referred to above, few measurements have been made in the UK. In the two year period 1979 to 1981, 65 daily samples were collected at a rural site near Lancaster, a small city in northwest England. Some recent measurements have been made simultaneously at three rural sites in Essex using denuders(1). Twenty-four hour samples were collected for 33 days in the period 1987 to 1989. The average H^+ ion concentrations observed were 11.5 to 28.7 neq m^{-3} or 1.1 to 2.8 µg H_2SO_4 m^{-3}. The highest daily H^+ ion values observed at the three sites ranged from 50.5 to 110 neq m^{-3} (4.9 to 10.8 µg H_2SO_4 m^{-3}). These levels are similar to those found in the Netherlands, where in both cases ammonia neutralisation may be important . In this context it is worth noting that published data from North America tend overall to be higher than those reported in Europe, probably due to lower ammonia concentrations at the North American sites. Data from rural sites in North America show that maximum daily mean values of about

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(1) Kitto A-MN and Harrison RM (1992) **Processes Affecting Concentrations of Aerosol Strong Acidity at Sites in Eastern England** Atmospheric Environment **26A**, 2389-2390.

5 to 15 µg H_2SO_4 m^{-3} were observed in summer months from 1983 to 1986 and values of up to 27 µg H_2SO_4 m^{-3} were observed over shorter periods in the late 1970s.

It is difficult to assess the significance of these concentrations as no health-related standards or guidelines presently exist for acid aerosols. The WHO, for example, in their 1987 publication, felt that insufficient data were then available to establish a numerical guideline. They did however suggest that monitoring is warranted when levels of sulphuric acid are likely to exceed 10 µg m^{-3}.

4.6 MODELLING STUDIES OF SO_2 CONCENTRATIONS

The 1980 EC Directive on smoke and SO_2 concentrations made a provision for those areas which did not meet the limit values for smoke and SO_2 to implement smoke control programmes in order that concentrations were less than limit values by April 1993 at the latest. At a number of such towns, Warren Spring Laboratory have carried out modelling studies to identify those outstanding areas requiring smoke control and assess the likely success of existing policies. Modelling studies have included the following towns:

- *Dunfermline;*
- *Leek, Staffordshire;*
- *Perth;*
- *Kirkcaldy;*
- *Fife;*
- *Sunderland;*
- *Belfast.*

In all these cases, a detailed emission inventory was compiled for the study area, based on fuel usage and mapped on a 1km x 1km grid. Using these data and appropriate climate data as inputs, a long period Gaussian plume dispersion model was used to predict present and future concentrations of smoke and SO_2.

The most recent of these reports(1) was able to show that in Sunderland the implementation of smoke control areas would result in decreased SO_2 concentrations, as would be expected. The benefit of the modelling was that the optimum smoke control areas could be identified and the risk of exceeding the Directive limit values quantified.

As an example of what may be achieved with this approach and an illustration of the spatial distribution of SO_2 across an urban area, the contour map of calculated winter average SO_2 concentrations for 1983 to 1984 is presented in Figure 4.11, taken from Timmis and Walker(2).

4.7 SUMMARY AND KEY ISSUES

Along with black smoke, sulphur dioxide is the pollutant most commonly associated with atmospheric pollution in urban areas when a historical perspective is taken. The severe episodes seen in the 1950s and 1960s in UK cities and their sometimes tragic effects stimulated legislation to minimise the problem and the establishment of a national monitoring network in 1961.

Concentrations of SO_2 in urban areas are determined by combustion of fossil fuels, chiefly coal and fuel oil, but with diesel-engined vehicles also making a significant contribution. Although concentrations have dramatically declined in most UK towns and cities during the 1970s and 1980s, some locations still exhibit high concentrations. These are exclusively associated with the burning of coal for space heating in domestic premises. Belfast is the prime example of this.

In 1990/91 there was only one monitoring site which exceeded an EC Directive limit value. This was at Belfast, where the 98th percentile was recorded as 141 ppb (374 µg m^{-3}).

The frequency with which the hourly mean WHO guideline value of 122 ppb was exceeded at the London Victoria site has declined dramatically between the period 1973 to 1974 and 1990 to 1991.

Acid aerosols are increasingly being thought of as significant in urban air pollution, but as yet little data exists on their concentrations. The little evidence that is available suggests concentrations were appreciably higher during the smogs of the 1950s than present levels.

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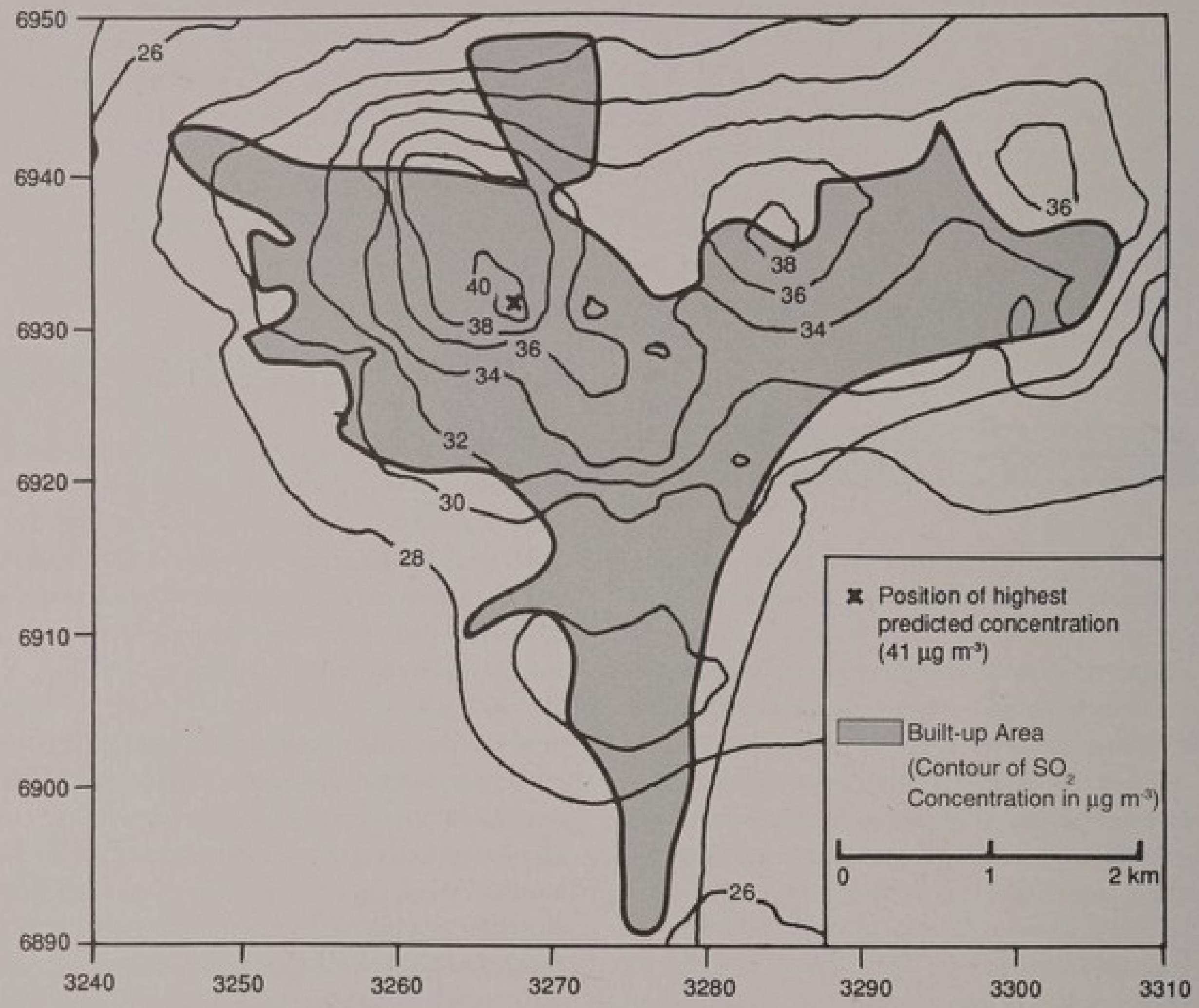
(1) Roberts CS (1992) **Dispersion Modelling of Smoke and Sulphur Dioxide in Sunderland 1991** WSL Report LR864, Warren Spring Laboratory, Stevenage, UK.

(2) Timmis RJ and Walker CA (1989) **Dispersion Modelling of the Effect of Smoke Control on Air Quality in Kirkcaldy** WSL Report LR729, Warren Spring Laboratory, Stevenage, UK.

Figure 4.11 Contour Map of Calculated Winter Mean SO_2 Concentrations in Kirkcaldy



4.8 RESEARCH RECOMMENDATIONS

- *For SO_2, future work should be directed at emissions from diesel engined vehicles and predicting the effect of fuel changes in urban environments.*
- *It is clear that there is insufficient knowledge and understanding of the concentrations and behaviour of acid aerosols in the urban environment. Significantly more data are required.*

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McInnes G (1988) **Report on the Assessment of the Comparability of the United Kingdom's Net Acidity Method for Monitoring Sulphur Dioxide Against the UV Fluorescence Method** WSL Report LR653,Warren Spring Laboratory, Stevenage, UK.

Roberts CS (1992) **Dispersion Modelling of Smoke and Sulphur Dioxide in Sunderland 1991** WSL Report LR864, Warren Spring Laboratory, Stevenage, UK.

Timmis RJ and Walker CA (1989) **Dispersion Modelling of the Effect of Smoke Control on Air Quality in Kirkcaldy** WSL Report LR729, Warren Spring Laboratory, Stevenage, UK.

Her Majesty's Government **The Air Quality Standards Regulations** (1989) Statutory Instrument 317 HMSO, UK.

5 Carbon Monoxide

5.1 SOURCES

Carbon monoxide (CO) is produced by the incomplete combustion of fossil fuel. Most combustion systems, in stationary or mobile sources, are designed to operate most efficiently at stoichiometric air/fuel ratios when CO emissions will normally be at or near a minimum. However it is often necessary for combustion systems to operate away from these optimal conditions and in such cases, CO emissions can vary quite significantly from the optimal values. Such situations can occur for example when starting boilers from cold, or when motor vehicles are idling or moving very slowly. CO emissions can therefore be dependent upon combustion conditions and can readily reflect the condition, state of wear or misadjustment of the combined fuel/combustion system.

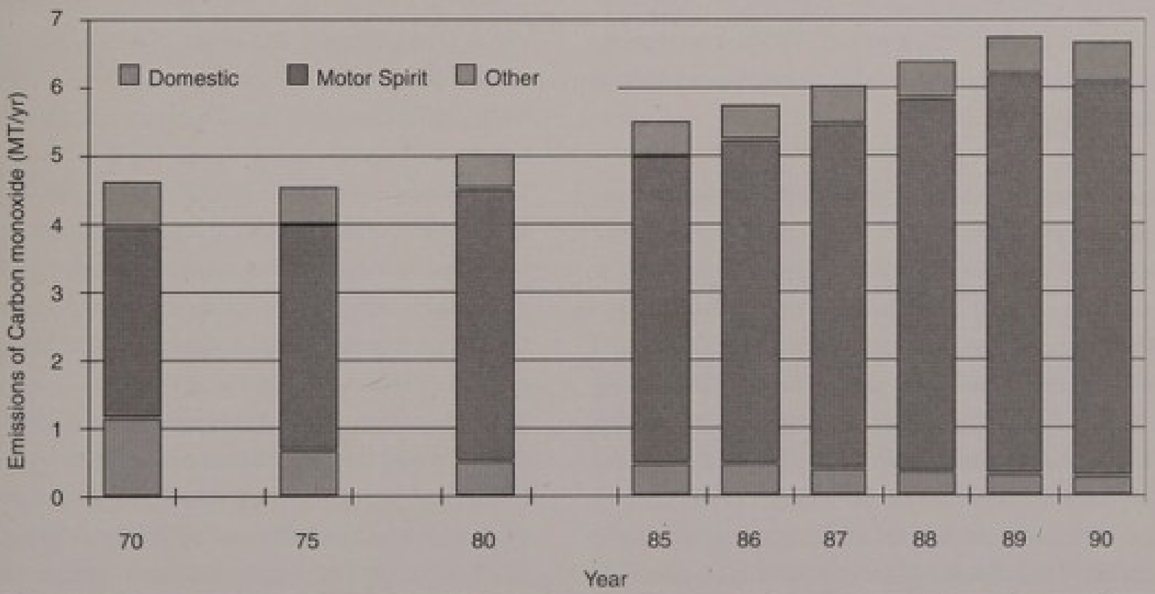
Emission estimates embodied in the National Atmospheric Emissions Inventory are obtained from a large number of measurements of motor vehicle emissions during realistic on-the-road drives in UK conditions. Emissions from stationary sources are also obtained from in-situ measurements of emission factors for a range of combustion installations. These factors are then applied to national fuel use and traffic activity statistics to produce annual UK emission estimates.

Emissions are dominated by the contribution from road transport, Figure 5.1, particularly petrol-engined vehicles(1). There has been a steady increase in this contribution as traffic has increased. The 1990 contribution amounts to 87% of the total compared to 61% in 1970. The contribution from domestic sources has fallen as coal consumption has decreased. The 1990 contribution being 4% compared to 25% in 1970. The overall upward trend in emissions is shown in Figure 5.1. Future emissions of carbon monoxide will be reduced as a result of the EC vehicle directives.

Measurements of CO emissions from in-service vehicles can show wide variations, particularly in some vehicles with carburettor-based fuelling systems which may be poorly adjusted. Such variations should decrease as fuel injection and engine management systems become more common, but at present emission estimates are based on means of distributions of data which contain some large variations. This phenomenon has also been noted in the USA, by Stedman and co-workers, where the potential for some vehicles to emit much larger quantities than the bulk of the fleet is rather greater than currently is the case in the UK, since the US car fleet is completely catalyst equipped. However similar conclusions have been noted by Stedman in two short studies in the UK.

Bailey and Eggleston(2) made a preliminary investigation of this effect on the accuracy of the UK road transport emission estimates of speciated hydrocarbons. They concluded that sampling from the actual distribution of emission measurements could lead to overall emission estimates from 13% to 55% higher than simply averaging

Figure 5.1 UK Emissions of CO (1970-1990)



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(1) Gillham CA, Leech PK and Eggleston HS (1992) **UK Emissions of Air Pollutants 1970-1990** WSL Report LR887(AP), Warren Spring Laboratory, Stevenage, UK.

(2) Bailey JC and Eggleston HS (1992) **The Generation of Speciated Hydrocarbon Emission Data and its Use in the Compilation of Emission Inventories** Paper to Fisita Conference, I Mech E, UK.

the results. Similar conclusions in a qualitative sense at least are likely to apply to CO so that it is possible that current emission inventories may underestimate the true emissions. This is discussed further in Section 5.5.

5.2 THE MONITORING OF CO CONCENTRATIONS

Since July 1972, measurements of hourly average carbon monoxide concentrations have been performed with continuous analysers at 22 fixed-point locations in the UK. (Current sites are described in Annex D.) The Department of the Environment funded the operation of 18 of these sites, while the Greater London Council (GLC) and later London Scientific Services (LSS) operated a further 4 sites in London. The distribution of measurements sites throughout the UK and the instrumentation employed, has varied considerably throughout the 20 years of measurements.

Some data have been published for mobile monitoring within the moving traffic stream. However, this short-term monitoring is generally insufficient to determine the micro-scale concentration variations within cities.

Most of the measurements performed in the 1970s were made at the London Victoria urban background site and on the kerbside of five cities. During the mid- 1980s, the DOE monitoring network centred on the London sites. Since 1989, the size and geographical spread of the network has rapidly expanded in two stages. Firstly, monitoring was initiated at five NO_2 Directive sites. Secondly, Enhanced Urban Network (EUN) sites were established during 1992. Further EUN sites are planned for future years. The monitoring network as of 1992 is shown in Figure 5.2.

Figure 5.2 Current UK Carbon Monoxide Monitoring Stations

Measurements in central London at urban background locations have been performed by Warren Spring Laboratory on behalf of DOE at three separate sites: Endell Street (1972 - 76); Vauxhall Bridge Road (1976 - 90) and Bridge Place (1990 onwards). These three sites when combined produce a unique dataset commencing in 1972. Overlapping periods during site relocation indicate that concentrations of CO and other pollutants are broadly similar. Collectively throughout this chapter, these three sites are known as Central London. Three methods of detection have been employed between 1972 and 1991: Non-Dispersive Infra-Red (NDIR); Coulometry and Gas Filter Correlation (GFC). A fourth method, Cross Flow Correlation (CFC) has been in use since 1992. The period of operation of each method is shown in Table 5.1 (and graphically in Figure 5.6). In general terms, the network operated NDIR instruments during 1972 to 1980, coulometry 1980 to1985, and GFC 1985 to 1991.

The primary standards for the CO monitoring network are gravimetrically produced cylinders of CO in nitrogen. These are used to calibrate a set of CO cylinder transfer standards. Prior to 1987, these transfer standards were also CO in nitrogen. CO in air cylinders are now in normal use. Zeroing the analysers was either performed with scrubbed ambient air or by a zero air cylinder.

The practice of calibrating NDIR instruments with CO in nitrogen transfer standards, and the use of zero air cylinders has led to a serious interference problem. NDIR is known to suffer from interference with CO_2 which is present in ambient air, but was not contained in the transfer cylinders. Also, the zero cylinders in use at the time did not contain atmospheric concentrations of CO_2. On an annual average basis, it appears that the NDIR instruments were over-reading by 1 to 2 ppm. However, this range is not an offset on all hourly averages. The

Table 5.1 UK Carbon Monoxide Monitoring Sites their Instrumentation and Monitoring Period

Site	Instrument	Start	End
Stevenage	Non-Dispersive Infra-Red	Nov 78	July 79
	Coulometric	Aug 79	Mar 89
	Gas Filter Correlation	Apr 89	
London, Victoria	Non-Dispersive Infra-Red	June 72	Oct 79
(Endell Street and	Coulometric	Nov 79	Dec 84
Vauxhall Bridge Road)	Gas Filter Correlation	Jan 85	Aug 90
London, Cromwell Road	Non-Dispersive Infra-Red	Feb 73	Feb 80
	Coulometric	Mar 82	Dec 84
	Gas Filter Correlation	Apr 89	
Cardiff (kerbside)	Non-Dispersive Infra-Red	July 73	Nov 76
Glasgow, Hope Street	Non-Dispersive Infra-Red	June 73	Oct 82
Birmingham (kerbside)	Non-Dispersive Infra-Red	Mar 74	Jan 78
Cambridge	Non-Dispersive Infra-Red	Nov 74	Mar 78
Harrow	Coulometric	Aug 79	Oct 80
Canvey	Non-Dispersive Infra-Red	Oct 77	Feb 80
London, Earls Court	Gas Filter Correlation	Aug 89	
Glasgow	Gas Filter Correlation	July 89	
Manchester	Gas Filter Correlation	Aug 91	
Sheffield	Gas Filter Correlation	Aug 91	
London, Bridge Place	Gas Filter Correlation	Aug 90	
London, Bloomsbury	Gas Filter Correlation	Jan 92	
Cardiff	Gas Filter Correlation	May 92	
Belfast 2	Gas Filter Correlation	Mar 92	
Birmingham	Gas Filter Correlation	Mar 92	
Newcastle	Gas Filter Correlation	Mar 92	
West London	Gas Filter Correlation	Jan 86	Dec 90
Central London (background)	Gas Filter Correlation (86 onwards)	Jan 78	Dec 90
Central London (kerbside)	Gas Filter Correlation (86 onwards)	Jan 82	Dec 90
East London	Gas Filter Correlation	Jan 86	Dec 90

effect of the interference on ambient measurements is not straightforward and should always be borne in mind when assessing NDIR data.

5.3 COMPLIANCE WITH GUIDELINES

5.3.1 Introduction

Since there is presently no EC Directive on carbon monoxide, the World Health Organization guidelines for this pollutant are considered here. These are the most widely and internationally recognised criteria for CO. The WHO Regional Office for Europe has established air quality guidelines with the primary aim of providing a basis for protecting human health (1).

The WHO considered the best available scientific evidence on the health implications of CO exposure, particularly in relation to likely cardiovascular, neurobehavioural, fibrinolysis and perinatal effects. It recommended a maximum blood carboxyhaemoglobin (COHb) level of 2.5-3.0% for the protection of the general population, including sensitive groups such as the elderly, infirm, pregnant women, young infants and patients with cardiac or respiratory difficulties.

To prevent COHb levels exceeding this threshold, the WHO has proposed the following time-weighted exposure guidelines, using the Coburn mathematical equation to predict blood CO uptake as a function of time:

- *100 mg m^{-3}(87 ppm) over 15 minutes;*
- *60 mg m^{-3} (50 ppm) over 30 minutes;*
- *30 mg m^{-3} (25 ppm) over 1-hour;*
- *10 mg m^{-3} (10 ppm) over 8-hours.*

Note that the ppm/mg m^{-3} conversion factors used here are inconsistent. However, for the purpose of comparing UK CO levels with these guidelines, the ppm equivalents in brackets have been utilised. In Table 5.2, where CO concentrations from 1972 onwards are compared with the four guidelines, it should be noted that, following an

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(1) World Health Organization Regional Office for Europe (1987) **Air Quality Guidelines for Europe** WHO Regional Publications, European Series Number 23, WHO, Copenhagen.

Table 5.2 Carbon Monoxide Exceedences of WHO Guidelines (Pollution years)

		8-hour mean ≥10 ppm		1-hour mean ≥25 ppm		30 min ≥50 ppm		15 min ≥87 ppm		Data Capture
Site	Year	count	days	count	days	count	days	count	days	(%)
STE	78/79	0	0	0	0	—	—	—	—	16
STE	79/80	0	0	0	0	—	—	—	—	39
STE	80/81	0	0	0	0	—	—	—	—	96
STE	81/82	0	0	0	0	—	—	—	—	88
STE	82/83	0	0	0	0	—	—	—	—	75
STE	83/84	0	0	0	0	—	—	—	—	29
STE	84/85	1	1	0	0	—	—	—	—	6
STE	85/86	—	—	—	—	—	—	—	—	0
STE	86/87	—	—	—	—	—	—	—	—	0
STE	87/88	—	—	—	—	—	—	—	—	0
STE	88/89	0	0	0	0	0	0	0	0	0
STE	89/90	0	0	0	0	0	0	0	0	70
STE	90/91	0	0	0	0	0	0	0	0	83
STE	91/92	0	0	0	0	0	0	0	0	99
LV	72/73	1	1	0	0	—	—	—	—	70
LV	73/74	0	0	0	0	—	—	—	—	76
LV	74/75	3	3	0	0	—	—	—	—	70
LV	75/76	3	2	0	0	—	—	—	—	55
LV	76/77	5	2	0	0	—	—	—	—	41
LV	77/78	0	0	1	1	—	—	—	—	33
LV	78/79	1	1	0	0	—	—	—	—	56
LV	79/80	0	0	0	0	—	—	—	—	80
LV	80/81	0	0	0	0	—	—	—	—	92
LV	81/82	0	0	0	0	—	—	—	—	87
LV	82/83	0	0	0	0	—	—	—	—	77
LV	83/84	0	0	0	0	—	—	—	—	61
LV	84/85	0	0	0	0	—	—	—	—	78
LV	85/86	0	0	0	0	—	—	—	—	65
LV	86/87	0	0	0	0	—	—	—	—	48
LV	87/88	0	0	0	0	0	0	0	0	14
LV	88/89	1	1	0	0	0	0	0	0	88
LV	89/90	1	1	0	0	0	0	0	0	82
LV	90/91	0	0	0	0	0	0	0	0	32
CRD	73/74	137	77	10	4	—	—	—	—	74
CRD	74/75	30	26	2	2	—	—	—	—	77
CRD	75/76	105	68	28	10	—	—	—	—	74
CRD	76/77	207	122	92	43	—	—	—	—	85
CRD	77/78	55	40	13	4	—	—	—	—	68
CRD	78/79	20	13	5	2	—	—	—	—	21
CRD	79/80	26	17	3	1	—	—	—	—	48
CRD	80/81	—	—	—	—	—	—	—	—	0
CRD	81/82	0	0	0	0	—	—	—	—	8
CRD	82/83	7	6	0	0	—	—	—	—	77
CRD	83/84	3	2	0	0	—	—	—	—	84
CRD	84/85	0	0	0	0	—	—	—	—	40
CRD	85/86	—	—	—	—	—	—	—	—	0
CRD	86/87	—	—	—	—	—	—	—	—	0
CRD	87/88	—	—	—	—	—	—	—	—	0
CRD	88/89	—	—	—	—	—	—	—	—	0
CRD	89/90	8	7	0	0	0	0	0	0	88
CRD	90/91	3	2	0	0	0	0	0	0	98
CRD	91/92	8	4	0	0	0	0	0	0	99
CAR	73/74	151	96	108	62	—	—	—	—	57
CAR	74/75	162	101	67	41	—	—	—	—	91
CAR	75/76	119	84	61	47	—	—	—	—	71
CAR	76/77	1	1	0	0	—	—	—	—	32
GLAS	73/74	34	23	0	0	—	—	—	—	61
GLAS	74/75	18	15	0	0	—	—	—	—	73
GLAS	75/76	31	29	1	1	—	—	—	—	55
GLAS	76/77	92	68	20	8	—	—	—	—	70
GLAS	77/78	40	34	2	2	—	—	—	—	67
GLAS	78/79	39	33	3	3	—	—	—	—	87
GLAS	79/80	30	24	4	2	—	—	—	—	84
GLAS	80/81	2	2	0	0	—	—	—	—	40
GLAS	81/82	23	14	0	0	—	—	—	—	59
GLAS	82/83	0	0	0	0	—	—	—	—	45

(Continued)

Table 5.2 Carbon Monoxide Exceedences of WHO Guidelines (Pollution years) (Continued)

Site	Year	8-hour mean ≥10 ppm		1-hour mean ≥25 ppm		30 min ≥50 ppm		15 min ≥87 ppm		Data Capture (%)
		count	days	count	days	count	days	count	days	
BHAM	74/75	39	26	1	1	—	—	—	—	64
BHAM	75/76	116	74	10	5	—	—	—	—	77
BHAM	76/77	149	89	46	18	—	—	—	—	76
BHAM	77/78	70	56	3	3	—	—	—	—	67
CAMB	74/75	56	45	8	5	—	—	—	—	39
CAMB	75/76	29	25	2	2	—	—	—	—	86
CAMB	76/77	64	48	21	11	—	—	—	—	59
CAMB	77/78	76	60	1	1	—	—	—	—	63
HARR	79/80	0	0	0	0	—	—	—	—	60
HARR	80/81	0	0	0	0	—	—	—	—	44
CAN	77/78	0	0	0	0	—	—	—	—	25
CAN	78/79	0	0	0	0	—	—	—	—	42
CAN	79/80	0	0	0	0	—	—	—	—	43
LEC	89/90	2	1	0	0	0	0	0	0	29
LEC	90/91	1	1	0	0	0	0	0	0	91
LEC	91/92	6	4	0	0	0	0	0	0	91
GLA	89/90	3	2	0	0	0	0	0	0	67
GLA	90/91	1	1	0	0	0	0	0	0	86
GLA	91/92	2	2	0	0	0	0	0	0	99
MAN	91/92	0	0	0	0	0	0	0	0	61
SHE	91/92	0	0	0	0	0	0	0	0	64
LBRI	90/91	0	0	0	0	0	0	0	0	61
LBRI	91/92	2	2	0	0	0	0	0	0	99

Site abbreviations

STE	Stevenage
LV	London, Victoria
CRD	London, Cromwell Road
CAR	Cardiff (kerbside)
GLAS	Glasgow, Hope Street
BHAM	Birmingham (kerbside)
CAMB	Cambridge
HARR	Harrow
CAN	Canvey
LEC	London, Earls Court
GLA	Glasgow
MAN	Manchester
SHE	Sheffield
LBRI	London, Bridge Place

upgrade of Warren Spring Laboratory database structures, exceedences of the short-term 15 and 30 minute criteria are available only after 1987. Exceedences of the 8-hour guideline are calculated on the basis of fixed rather than running averages (0000-0700, 0800-1500, 1600-2300 hrs).

In assessing the guideline exceedence statistics in Table 5.2, data from NDIR-equipment sites should be regarded with caution (as noted in Section 5.2). The most reliable results therefore comprise the Stevenage and Central London datasets from 1980, Cromwell Road measurements from 1982, and all other data from 1983.

5.3.2 Exceedence of Hourly and Short-Term Guidelines

There were no recorded exceedences of the 1-hour, 30-minute or 15-minute guidelines at UK monitoring sites during these non-NDIR periods. All these criteria are established as maximum values during a year, and may therefore be exceeded by a single extreme value. Since such extreme values are highly variable in space and time, it may be unwise to attempt to predict future compliance with short-term guidelines on the basis of previous experience. However, the data in Annex E show maximum hourly averages at urban and kerbside sites have approached 25 ppm in recent years, with peaks of 24.8 ppm at Cromwell Road, 20.9 ppm at Central London, 18.0 ppm at London Earls Court and 19.2 ppm at Glasgow. The discussion of future emission trends and urban air quality elsewhere in this report, suggests that CO concentrations should begin to decrease from about 1992 onwards. It is therefore unlikely that these short term guidelines would be exceeded in the future at UK sites.

Elevated hourly average CO concentrations are strongly associated with winter stagnation episodes. The December 1991 episode provides a good example of such an event. During the period from 11-15 December, peak hourly concentrations reached 13.9 ppm at Bridge Place, London, 18.0 ppm at London Earls Court, 16.7 ppm at kerbside Cromwell Road and 15.2 ppm in Glasgow. One-hour guideline exceedences are, clearly, most likely to occur in urban environments during episode conditions when low wind speeds and stable boundary layers lead to inefficient dispersion of vehicle emissions.

Figure 5.3 demonstrates that maximum hourly average CO concentrations in any year correlate well with annual averages for non-kerbside urban sites. Note the different peak/mean relationship evident for urban and kerbside data: kerbside CO measurements are less time-variant throughout the year and show reduced peak/mean ratios overall. The relationship graphed in Figure 5.3 suggests that exceedences of the hourly guideline may be expected for non-kerbside urban sites with annual average CO concentrations exceeding ~2.5 ppm, as well as in kerbside locations. As the emission pattern for motor vehicles changes with increasing catalyst use, this relationship will also change.

5.3.3 Exceedences of the 8-Hour Guideline

The 8-hour WHO guideline for CO is clearly more stringent than the corresponding 1-hour criterion; this was noted in a previous analysis of the UK position in relation to a range of WHO guidelines(1). Using the Larsen model for log-normally distributed pollutants (which is a good approximation for CO concentrations above the 50th percentile) and assuming a standard geometric deviation typical of London sites of 1.8, we derive a maximum 8-hour concentration of 15 ppm equivalent to a maximum 1-hour concentration of 25 ppm (the WHO 1-hour guideline). The WHO 8-hour guideline of 10 ppm is therefore considerably more stringent than the 1-hour value. The 8-hour guideline is frequently exceeded at UK urban or kerbside locations. One or more exceedences have been observed for 9 out of 20 (45%) of urban site years and 5 out of 7 (71%) of kerbside site years since 1980 at the sites operated by Warren Spring Laboratory. It is interesting to note that all exceedences at these urban sites have occurred since 1988/89.

As was the case for elevated hourly average CO concentrations, elevated 8-hour concentrations and resulting guideline exceedences are strongly associated with cold, stable winter pollution episodes. For instance, all 16 such exceedences observed at London monitoring stations in 1991 occurred during the 4-day episode period from 12 to 15 December 1991.

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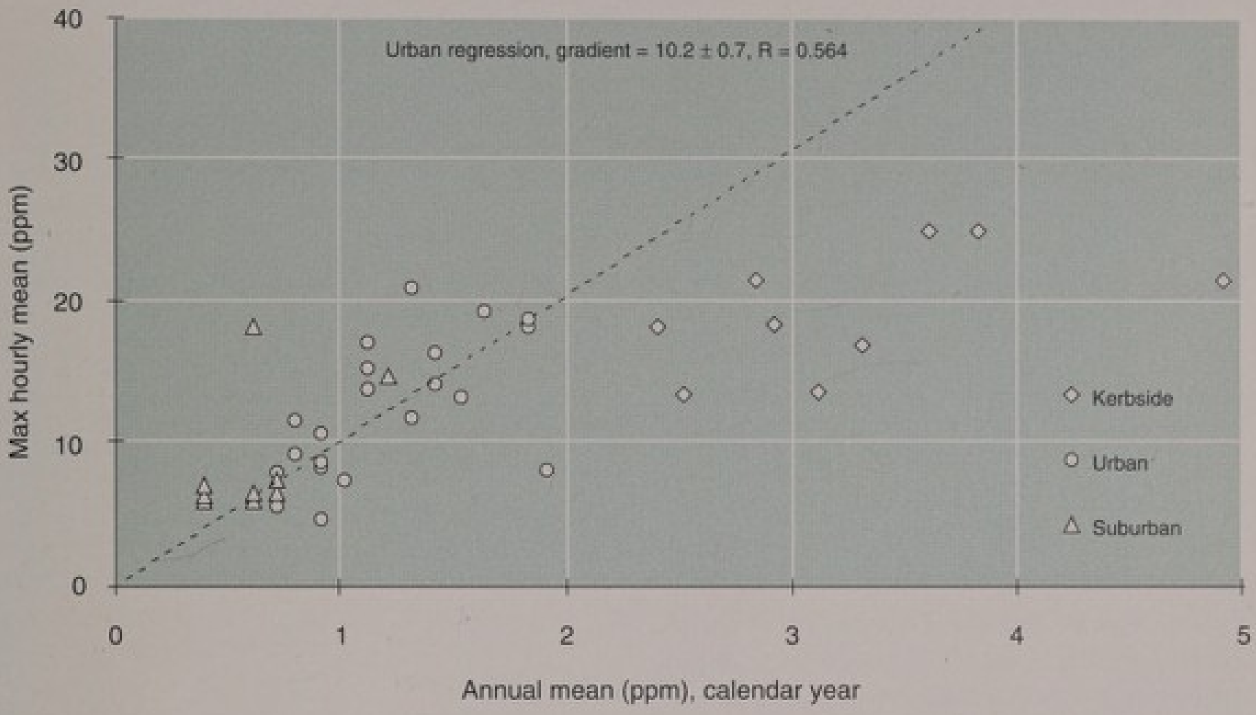
(1) Williams ML (1988) **An Assessment of the UK Position with Respect to the 1987 WHO Guidelines** WSL Report LR650(AP), Warren Spring Laboratory, Stevenage, UK.

Figure 5.3 Annual Mean CO Concentrations Compared to Maximum Hourly Mean Concentrations, by Type of Site (1980-1991)



In Figure 5.4 the maximum 8-hour mean CO concentration is plotted against the annual mean for a range of site types. There is some scatter but a reasonably good relationship is observed, particularly for the non-kerbside data. At such sites the data suggests that for annual means of ~1.25 ppm exceedences of the 8-hour WHO guideline may occur. In this plot, the different peak/mean ratios at the kerbside site are also clearly apparent.

5.4. SPATIAL AND TEMPORAL DISTRIBUTIONS

5.4.1 Spatial and Temporal Distribution

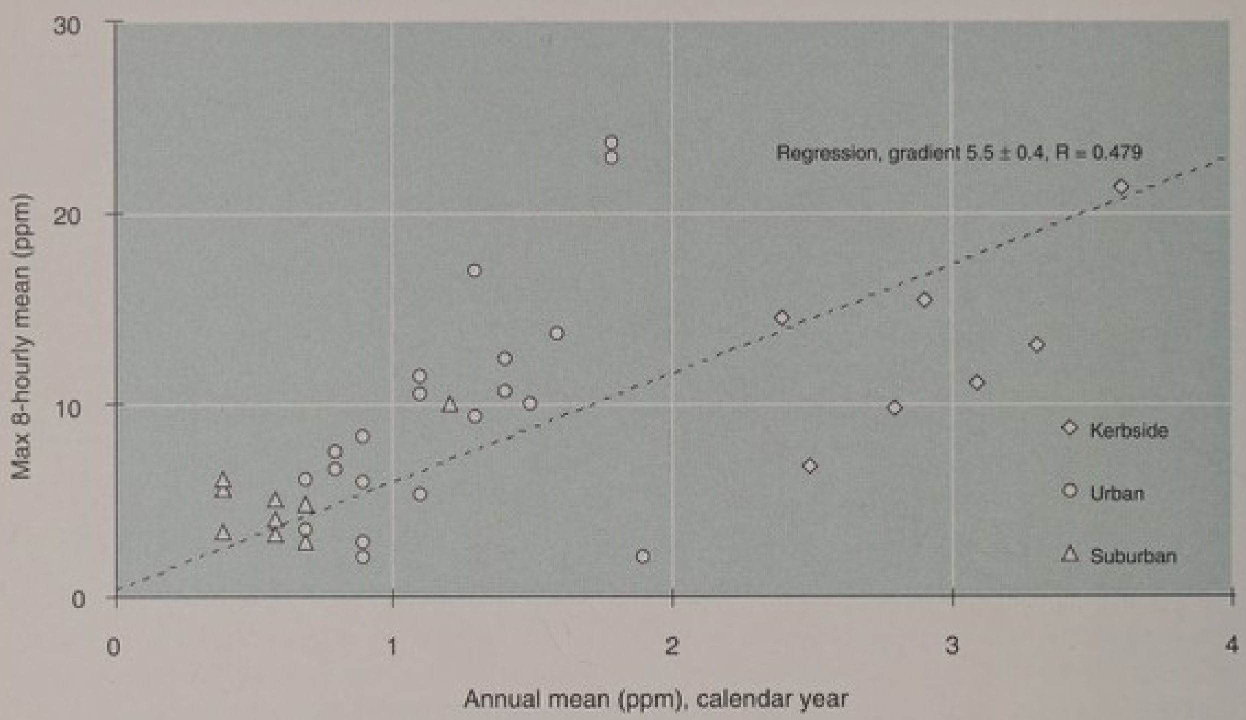
The relatively limited number of CO measurement sites operational up to 1991 precludes any direct derivation of a UK-wide spatial distribution of this pollutant. Monitoring site numbers have, however, increased substantially since 1991. Thirteen automatic measurement stations are operational as of the end of 1992 (Figure 5.2). The sites include five established to determine compliance with the EC NO_2 Directive, a kerbside location in central London, a suburban site in Hertfordshire and six Enhanced Urban Network (EUN) monitoring stations (Annex D).

It should be noted that the urban EUN and NO_2 Directive sites have been selected using different locational criteria: EUN sites are established to assess broad population exposure, whilst Directive sites are targeted at worst-case urban environments complying with the precise requirements of the EC Directive for NO_2.

Even with projected increases in EUN site numbers over the coming years, national-scale CO distributions will not be readily deducible from direct measurements. To establish such spatial patterns with confidence would require a comprehensive passive sampling survey such as that undertaken for NO_2 in 1986 and 1991. Diffusion tube samplers for CO have recently been developed and such an exercise may, therefore, be feasible in future.

Although insufficient direct measurements of CO concentrations are available for a UK mapping exercise, a useful approximation can be obtained making use of the recent national NO_2 diffusion tube survey and a knowledge of the CO and NO_x emissions from motor vehicles and the good correlation between CO and NO_x observed at urban sites in the UK. The assumptions made were that the CO/NO_x ratio (by volume) is 12 and that in 5 km grid squares with population greater than 5,000, NO_x = 2.5 NO_2 and elsewhere NO_x = 1.2 NO_2. The resulting distribution is shown in Figure 5.5.

Figure 5.4 Annual Mean CO Concentrations Compared to Maximum 8-Hourly Mean Concentrations, by Type of Site (1980-1991)



Apart from national patterns of CO concentrations, some work has been undertaken — using mobile laboratories — to assess city wide and micro-scale (near road) concentration variations within cities. As a primary pollutant for which motor vehicles are the dominant source (Section 5.1), both peak and average concentrations will depend very much on location type within cities. CO gradients are also likely to be very marked near to roads. Mobile laboratory monitoring results demonstrate this clearly. However, there is currently little UK-based information on such concentration variations.

A survey was undertaken by the Warren Spring Laboratory mobile laboratory in 1985 which showed that the existing London Victoria site was suitable for compliance monitoring for the purposes of the EC Directive on NO_2[1]. Measurements of NO_2, NO_x, SO_2, ozone and CO were performed while driving within the moving traffic stream on 15 and 24 October 1985. These data were compared with the concentrations measured simultaneously at the fixed site.

A number of circuits of the area surrounding Victoria were performed covering the major routes together with adjacent minor roads where very little traffic was observed. The average concentrations which were recorded are summarised in Table 5.3. The results show a relatively high gradient in NO and CO concentrations (30 - 40%) between the major thoroughfares and the adjacent minor roads. A shallower gradient (60%) was recorded for NO_2 indicating a more uniform spatial distribution of NO_2.

Rapid increases in CO and NO concentrations were regularly recorded while crossing a road intersection. CO concentrations were measured to rise on one occasion, from approximately 10 ppm to 20 ppm while the mobile laboratory moved at walking pace, a few tens of metres along a minor road towards a major road.

5.4.2 Long Term Trends

Only one site — London Victoria — has a sufficiently extended history of relatively unbroken data capture to facilitate meaningful trend analysis of measured concentrations. In 1990, this monitoring station was relocated 200m to a nearby location in Bridge Place, as a

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(1) Broughton, G (1988) **A Mobile Laboratory Survey of Gaseous Air Pollutants Surrounding the Proposed European Community Nitrogen Dioxide Directive Central London Site at Victoria, 1986** WSL Report LR556, Warren Spring Laboratory, Stevenage, UK.

Table 5.3 Summary of Mobile Laboratory Survey in Central London, 15 and 24 October 1985

Road Section	NO Average (ppb)	Rank	Average relative to highest	NO_2 Average (ppb)	Rank	Average relative to highest	CO Average (ppm)	Rank	Average relative to highest
Vauxhall Bridge Road	315	4	67	84	3	90	6.5	3	66
Vauxhall Bridge Road north	312	5	62	81	5	87	4.6	5	47
Hyde Park Corner roundabout	501	1	100	93	1	100	9.8	1	100
Grosvenor Place	498	2	99	90	2	97	8.6	2	88
The minor roads	169	6	34	59	6	63	4.2	6	43
Victoria Street	409	3	82	82	4	88	6.1	4	62

result of property development of the original Minster House site. As part of the relocation exercise, parallel monitoring at both locations demonstrated closely tracking measured pollutant concentrations. As a result, it is believed that the relocation should not significantly affect data continuity from 1990.

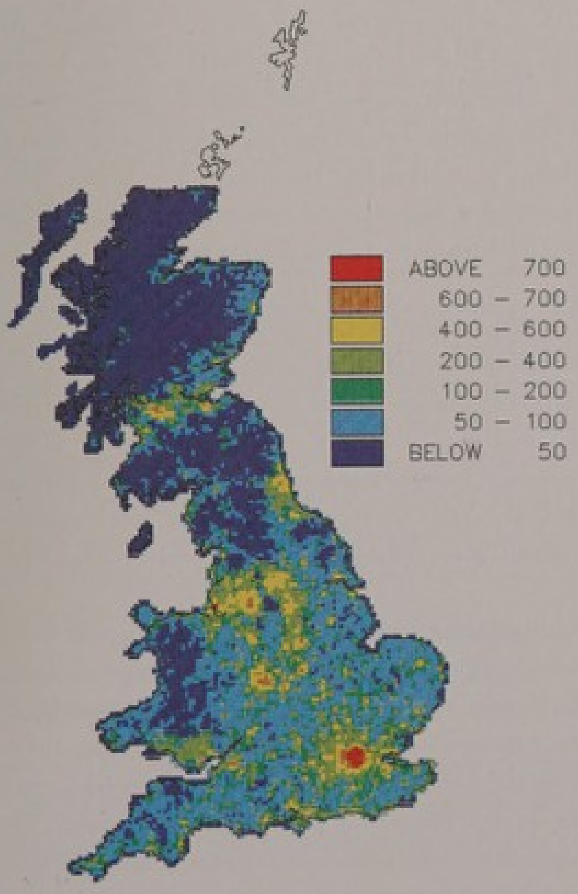


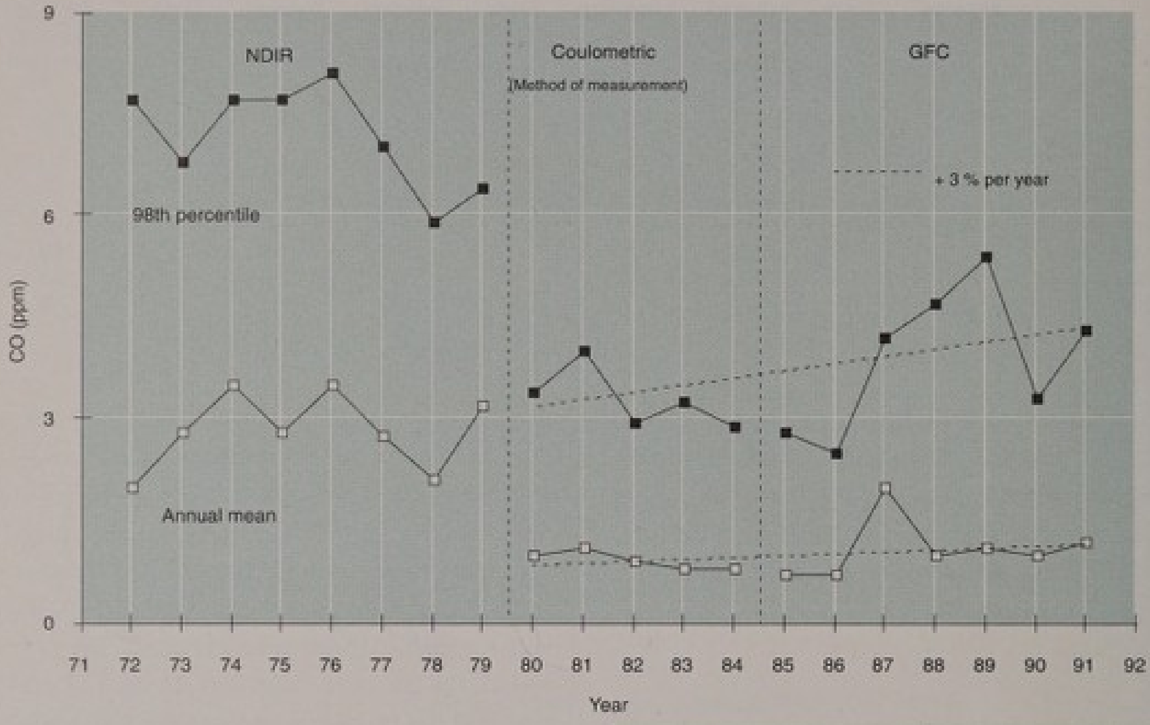
Figure 5.5 Estimated CO Concentrations (ppb) in the UK (1991)

Annual average and 98th percentile hourly average concentrations at the Central London sites from 1972 to 1991 are graphed in Figure 5.6. Any air quality trends deduced from such a time series should always be regarded with caution. Changes in monitoring methodology, instrumentation and operational practice will invariably occur over extended measurement periods. As discussed in Section 5.2, the CO analyser type deployed at Central London changed from NDIR to coulometric in 1980 and then to Gas Filter Correlation in 1985. Unfortunately, the NDIR method was subsequently shown to be subject to a degree of CO_2 interference, likely to cause over-reading of measured concentrations. Since the degree of this over-reading is not now readily quantifiable, the results of this earliest period of monitoring should be regarded as suspect.

Also of significance in attempting to determine and assess long-term trends is the fact that UK gas primary reference standards and calibration methodologies have evolved and advanced considerably over time, resulting in improvements in measurement accuracy, precision and reproducibility. Incomplete data capture during some years should also be recognised when deducing such trends.

Consideration of the entire Central London dataset from 1972 to 1991 (Figure 5.6) would suggest a significant downward trend in both annual average and 98th percentile concentrations. However, excluding the relatively unreliable 1972-1980 NDIR results produces a different picture: from 1980 to 1991, linear regression analysis demonstrates an increase in average concentrations of 0.04 ppm yr^{-1} (with a standard error of ± 0.03 ppm). In 1991, this corresponds to $3 \pm 2\%$ yr^{-1}. The corresponding annualised 1991 rate of increase for 98th percentiles is also $3 \pm 2\%$ yr^{-1}. This overall increase

Figure 5.6 Annual Mean and Annual 98th Percentile of CO in Central London (1972-1991)



in CO concentrations in Central London is consistent in broad terms with the corresponding UK-wide 32% increase in CO emissions from 1980 to 1990 (Table 5.1).

It should be recognised that completely different trends can be attributed to the same time series by considering different periods of time from the overall dataset. For instance, a downward trend in concentrations is evidenced from 1980 to 1985 (Figure 5.6), but a rise of 3 ± 8% per year and 5 ± 3% per year (at 1991) is shown for average and 98th percentile levels from 1986 to 1991.

In conclusion, the limited national CO dataset renders long-term trend analysis difficult. Only one site - Central London - has sufficient data and much of the early results from this location must be regarded as unreliable. Analysis of the remaining data suggests an overall 0.04 ppm per annum increase in average levels from 1980 to 1991. It would be unwise to derive any conclusions for national CO trends from these results.

5.5 DIURNAL AND SEASONAL CHARACTERISTICS

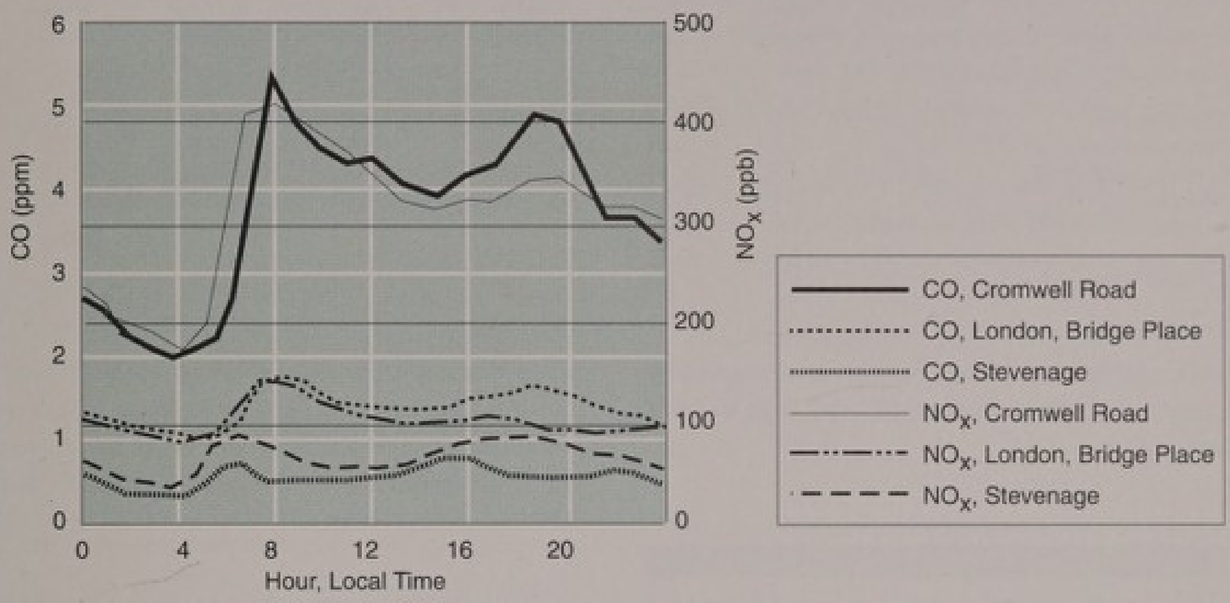
5.5.1 Diurnal Variations

CO diurnal average graphs for a number of representative site types during 1991 are shown in Figure 5.7. The sites covered include a kerbside site (Cromwell Road), together with background urban (London, Bridge Place) and suburban (Stevenage) locations. For comparative purposes, the corresponding NO_x diurnal graphs for these sites are also included.

The major source of both pollutants in urban areas is motor vehicle traffic. As a result, therefore, it is not surprising that the diurnal variations of both pollutants are very similar. This is particularly marked at the kerbside Cromwell Road site. The twin peaks centred on 0800 and 1800 are typical of pollutant concentrations influenced by morning and evening rush hour emissions.

It is interesting to note that the morning NO_x peak at the urban and kerbside sites is sharper and higher than during the evening rush hour period. This time of day tends to be associated with poorer dispersion conditions, due to generally lower wind speeds and mixing heights, than the corresponding early evening period. However, this seems to have less effect on CO levels, which are similar at all sites during the morning and evening rush hours.

Figure 5.7 Diurnal Variations of CO and NO_x Concentrations (1991)



5.5.2 Seasonal Variations

Emissions of CO are dominated by the influence of petrol driven motor vehicles (87% in 1990), and are therefore, relatively unaffected by seasonal variations. However, cold start emissions in winter and holiday activity in summer will cause some variation. Due to the effects of atmospheric dispersion and of these emission changes, ambient concentrations do show considerable variations between summer and winter period. Ratios measured at CO monitoring sites during 1991 are given in Table 5.4.

The effect of the seasonal changes in dispersion may be expected to be at a minimum nearest the source, with winter concentrations being highest. Measurements indicate that the highest ratio (0.83) ie the least variation, occurred at the Cromwell Road kerbside. The highest concentrations were also recorded at the kerbside, and there is an indication that the ratios are proportional to concentration, ie distance from source. Measurements from localities more distant from road traffic are not available.

5.5.3 CO/NO_x Ratios

CO and NO_x are primary pollutants, emitted at source, and are conserved during the short timescales within cities. NO_x is also heavily influenced by traffic, but not to the same extent as for CO. The ratio of CO to NO_x may therefore be expected to be broadly similar between seasons, but approach the emission ratios for motor vehicles nearest the source where concentrations are highest.

The ratios given in Table 5.4 show a general decrease in CO to NO_x ratios from summer to winter periods, which is probably due to the non-vehicular component of NO_x arising from space-heating. An approximate estimate of this component of NO_x may be obtained if we assume that, in the absence of space-heating NO_x, the CO/NO_x ratios should be the same in summer and winter. Excluding Cromwell Road and Stevenage from the analysis (as they are very heavily dominated by traffic sources - compare the summer and winter CO/NO_x ratios at these sites) and the sites for which no summer CO data are available, we can derive the non-vehicular NO_x component as ~15-30% of the total NO_x. This is in good agreement with previous modelling estimates.

Bearing these results in mind, it is interesting to compare the measured CO/NO_x ratios with the emission estimates from road transport in the National Atmospheric Emissions Inventory. For 1990, the CO/NO_x emission ratio by volume is 7.1 which is somewhat lower than the measured urban values (except for the Stevenage site). This finding is consistent with the earlier suggestion of Bailey and Eggleston(1) that CO emissions from road

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(1) Bailey JC and Eggleston HS (1992) **The Generation of Speciated Hydrocarbon Emission Data and its Use in the Compilation of Emission Inventories** Paper to Fisita Conference, I Mech E, UK.

Table 5.4 Concentrations and Ratios of Carbon Monoxide and NO_x

Site	CO Summer (ppm)	Winter (ppm)	NO_x Summer (ppb)	Winter (ppb)	CO Summer/ (Winter) Ratio	CO / NO_x Summer (Ratio)	CO / NO_x Winter (Ratio)
Stevenage	0.5	0.9	58	104	0.56	8.6	8.7
Cromwell Road	3.0	3.6	239	300	0.83	12.6	12.0
London, Earls Court	1.4	1.7	71	122	0.82	19.7	13.9
Glasgow	1.1	1.7	60	107	0.65	18.3	15.9
Manchester	—	1.1	45	91	—	—	12.1
Sheffield	—	1.1	64	130	—	—	8.5
London, Bridge Place	1.1	1.6	73	133	0.69	15.1	12.0

traffic may be underestimated and merits a more detailed investigation of emissions of CO and NO_x in urban areas.

5.6 AREAS OF INSUFFICIENT KNOWLEDGE

Although sources and temporal variations in ambient CO concentrations are relatively well understood, we have no information on spatial patterns of this pollutant over a national scale. It would be reasonable to expect spatial variations in urban CO concentrations to be similar to those of NO_x. More data on urban CO concentrations would improve the picture of UK-wide vehicle emission impacts.

A passive diffusion tube sampler for CO has recently been developed. Should this prove sufficiently accurate and usable, a national-scale survey — along the lines of the successful NO_2 surveys carried out in 1986 and 1991 — would become practicable.

Diffusion tube surveys, as well as providing a national picture of CO concentrations, could also be readily used to investigate city-scale spatial variations and assess the representativeness of results from the relatively limited number of fixed automatic monitoring stations.

Data on micro-scale spatial variations of CO concentrations are also lacking. Concentration gradients may be expected to be particularly high in urban kerbside or near-road environments. Data on such variations would be useful in assessing resulting health implications of short-term exposure to this pollutant.

Although passive samplers could be used to assess micro-scale variations in long-term average concentrations, automatic analysers would be required to quantify corresponding changes in short-term and peak concentration patterns.

As noted in Section 5.4.2, little reliable information exists on long-term CO trends in the UK. The increased number of automatic monitoring stations established since 1989 will provide more robust baseline trend information in future. National-scale passive sampler surveys could also be used to provide trend information over a more broadly-based range of UK urban environments.

The accuracy of the National Atmospheric Emission Inventory estimates for CO is largely unknown. Some preliminary work has suggested that the emissions of CO may be underestimated and this merits further investigation.

5.7 SUMMARY AND KEY ISSUES

- *Urban emissions of CO are dominated by motor traffic, and particularly from petrol-engined vehicles. Future emissions will decline due to EC vehicle directives.*
- *Ambient CO measurements have been made using automatic analysers at 22 UK sites since 1972. The longest data record is from London.*
- *Measurement and calibration methods have changed a number of times during this period. Early measurements using NDIR analysers may be suspect due to CO_2 interference.*
- *Current CO levels do not exceed short-term WHO guidelines, and are unlikely to do so in future.*

- *The 8-hour WHO guideline is more stringent, and is relatively frequently exceeded at urban and kerbside locations. This is most often associated with cold, stable winter episode periods.*
- *Insufficient measurement sites are available to establish UK-wide spatial distributions of CO. However, estimates can be made using NO_2 and vehicle emission data.*
- *Current city and micro-scale CO variations are not well established, although previous measurement campaigns using a mobile laboratory show significant local variations.*
- *Only one site in Central London has a sufficiently long dataset to enable trend analysis, and measurements here show a slight rise in levels from 1980 to 1991. This cannot, however, be considered to represent a national trend.*

5.8 RESEARCH RECOMMENDATIONS

- *A more detailed investigation of urban CO and NO_x emissions is needed to establish whether vehicle CO emissions are being underestimated.*
- *An extended CO diffusion tube survey should be undertaken to provide a national picture of concentrations.*
- *Urban-scale diffusion tube surveys could, similarly, establish CO patterns within cities and assess the representativeness of fixed point measurements.*
- *Studies of micro-scale CO variations, using automatic analysers, would assist in the assessment of short-term health impacts.*

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6 Particulate Matter

6.1 INTRODUCTION

6.1.1 Particulate Matter in the Urban Atmosphere

Airborne particulate matter is one of the most obvious forms of pollution. Close to source (eg a diesel engine exhaust) it can be clearly visible and even when thoroughly mixed with the surrounding air it is the primary cause of visibility loss on hazy days. Airborne particles are the most evident indicator of the presence of 'smog' (= smoke and fog), although the causes and characteristics of the London smogs which were most prevalent in the 1950s, and the Los Angeles smogs are almost entirely different.

Soiling effects on buildings arise principally from particulate matter. As well as contributing to poor visibility and soiling effects, particulate matter also has effects on human health. Lead in the atmosphere is present in particulate form as are other metals such as cadmium, nickel and chromium (Chapter 8). Many organic species including polynuclear aromatic hydrocarbons and dioxins also appear in airborne particles (Chapter 9).

In the 1950s and 1960s smoke played a major role in the pollution of UK towns and cities. At that time, it largely comprised carbonaceous soot from coal burning. As domestic coal combustion declined to be replaced by cleaner fuels the concentrations of black sooty smoke fell just as concentrations of secondary particulate pollutants such as ammonium sulphate were rising due to increased emissions of sulphur dioxide over Europe. Thus black smoke pollution changed over 10 years or so into a predominance of white particles which still reduce visibility but have much reduced soiling effects. In recent years growth in the number of diesel vehicles, which emit black smoke, has led to some increase in the blackness of smoke at heavily trafficked sites and it is diesel vehicles rather than coal combustion which are now the major source of black smoke particles in UK urban air.

6.1.2 Origins and Size of Airborne Particulate Matter

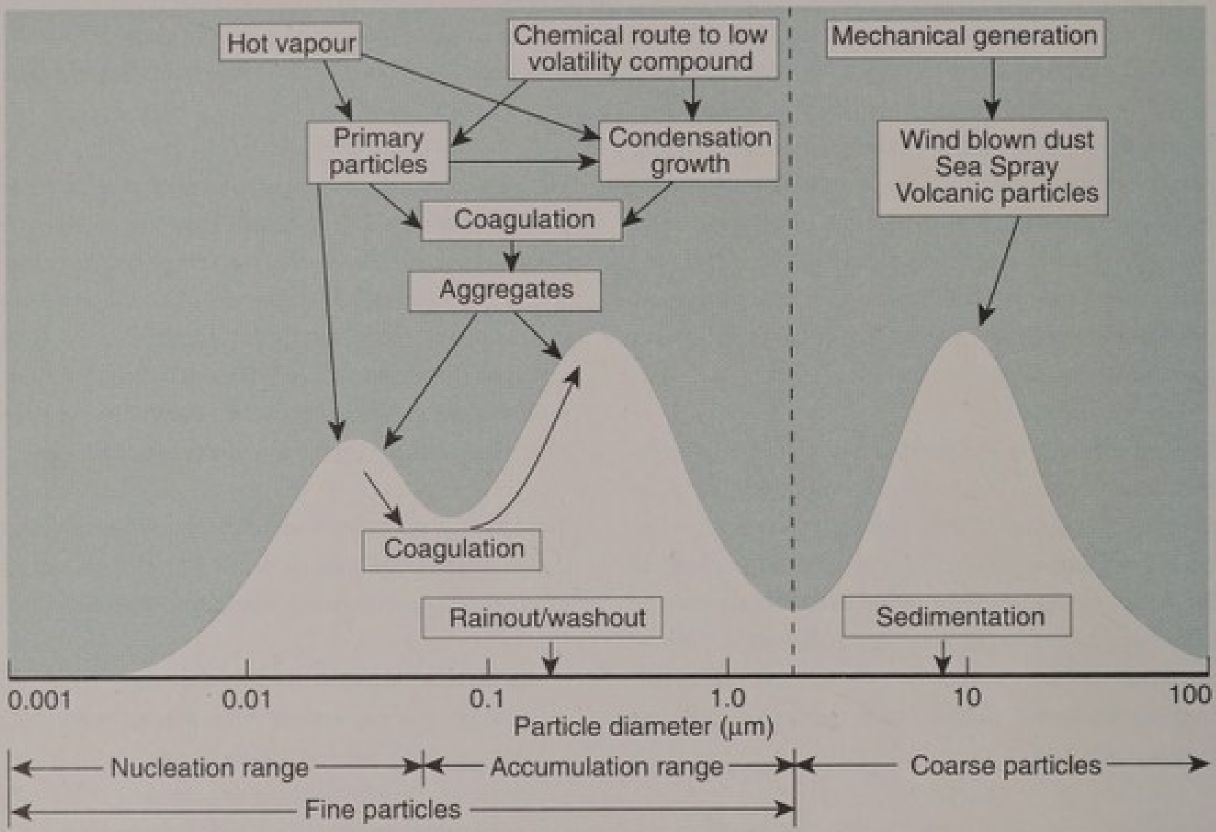
One of the most important distinctions to be drawn in relation to airborne particles reflects their origin. They may be either: primary - these are emitted directly from sources such as power stations, motor vehicles and cement factories; or secondary - particles formed within the atmosphere from condensation of vapours, or as a result of chemical reaction processes. The most abundant secondary constituent is frequently ammonium sulphate, formed from the reaction of ammonia gas with sulphuric acid, itself a product of atmospheric oxidation of sulphur dioxide gas.

The main determinant of the behaviour of an atmospheric particle is its size. This is usually expressed in terms of the 'aerodynamic diameter' which refers to unit density spherical particles with the same aerodynamic properties, such as falling speed. In practice, except for very dense materials and clusters, the aerodynamic diameter is very similar to the geometric diameter as might be measured with a light microscope or electron microscope.

Measurements of particle size distributions usually show up to three groups of particles (or modes), shown schematically in Figure 6.1. These are as follows.

- ***nucleation mode, < 0.2 µm diameter.*** *These are particles recently emitted from processes involving condensation of hot vapours (eg incinerators, smelters), or particles freshly formed within the atmosphere by gas to particle conversion (eg sulphuric acid particles from sulphur dioxide oxidation). Nucleation mode particles have a rather transient existence, as they rapidly coagulate into larger particles; hence in many situations the nucleation mode is not found.*
- ***accumulation mode, 0.2 - 2 µm diameter.*** *This mode comprises particles which have grown from the nucleation mode by coagulation or condensation of vapours. These are the most stable and long-lived of atmospheric particles with a lifetime of some 7-30 days, as they are not subject to efficient removal by gravitational settling, scavenging by rain, or any of the other mechanisms which remove smaller and larger atmospheric particles.*
- ***coarse mode, > 2 µm diameter.*** *These particles are mainly formed by mechanical attrition processes, and hence soil dust, sea spray and many industrial dusts fall within this mode. Because of their large size and high settling speeds, their atmospheric lifetime tends to be short.*

Figure 6.1 Schematic Representation of a Typical Size Distribution for Atmospheric Particles, Indicating some Formation Pathways



Frequently a simple distinction is drawn between fine particles, usually < 2 µm diameter and coarse particles, > 2 µm. The former are those most commonly connected with adverse health effects, whilst the latter may make a major contribution to soiling due to their rapid deposition, and the disamenity consequent upon it. In years gone by, deposition of coarse particles from industry and mining activities was a major cause of local soiling problems; fortunately due to stricter controls such problems now occur infrequently.

6.1.3 Classification of Particulate Matter

Over the years many terms have been adopted to describe airborne particles. Some are linked to specific sampling devices, whilst others are connected with human respiratory exposure; not all have single explicit definitions.

Terms used here are as follows.

Suspended Particulate Matter (SPM), a general term embracing all airborne particles.

Aerosol, a suspension of particles in a gas.

Total Suspended Particulates (TSP), a term describing the gravimetrically determined mass loading of airborne particles, most commonly associated with use of the U.S. high volume air sampler in which particles are collected on a filter for weighing.

PM_{10}, particulate matter less than 10 µm aerodynamic diameter (or, more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter).

Smoke, particulate matter, < 15 µm, derived from the incomplete combustion of fuels.

Black Smoke, non-reflective (dark) particulate matter, associated with the smoke stain measurement method, described later.

Inhalable Particles (also termed inspirable), particles which may be breathed in - inhalability is the orientation-averaged aspiration efficiency for the human head.

Respirable particles, particles which can penetrate to the unciliated regions of the deep lung.

Thoracic particle mass, describes that fraction of the particles which penetrates beyond the nasopharynx and larynx. A standard curve of thoracic aerosol as function of particle aerodynamic diameter takes the form indicated in Figure 6.2.

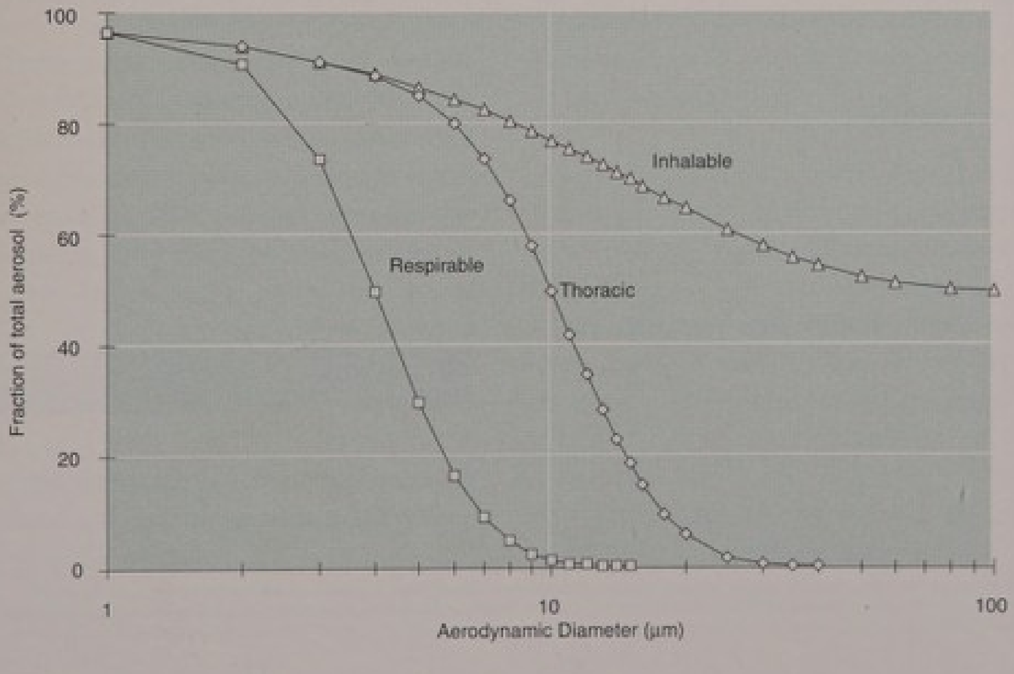
The difference between inhalable and respirable particles arises from their behaviour when they are inhaled. Because of inertial and gravitational effects, very large particles do not readily enter the human nose or mouth. Those that do enter during normal breathing are termed 'inhalable'. Figure 6.2 shows the efficiency with which particles of different size may be inhaled, according to the curve recommended by the International Standards Organisation (ISO). Particles which pass this first barrier to entry may then deposit in one of three regions, or be exhaled undeposited. The three defined regions of deposition are described as naso-pharyngeal, tracheo-bronchial and alveolar. Both of the former regions are cleared to the stomach and components of the particles may be absorbed therein, or excreted. Particles which deposit in the alveolar, or deepest region of the lung are not cleared efficiently and may be absorbed into the blood stream (eg lead), or if insoluble and inhaled in sufficiently large amounts may cause lung conditions such as emphysema, pneumoconiosis or carcinoma (eg asbestos). The particles capable of entering the alveolar region are termed respirable and a curve indicating the extent to which different particle sizes are typically respirable appears in Figure 6.2. Whilst there is no agreed definition, particles of less than 2.5 µm aerodynamic diameter are frequently described as respirable.

6.1.4 Effects on Health

In the days of urban smogs it was the carbonaceous soot in association with SO_2 which was identified as the major health hazard. More recently, attention has turned both to PM_{10} as well as specific toxic components of airborne particles, both inorganic (eg lead, cadmium) and organic (dioxins, polynuclear aromatic hydrocarbons etc).

One area of recent concern is that of the effects of exposure to low concentrations of fine particulates. Recent studies in this area have concentrated upon the effects of fine particulates measured as PM_{10}. At concentrations which hitherto would have been disregarded, associations with mortality, morbidity and changes in indices of lung function have been demonstrated. The consistency of the associations

Figure 6.2 Typical Curves Defining Respirable, Thoracic and Inhalable Particle Fractions



demonstrated and the fact that indices of lung function, respiratory morbidity and deaths in patients suffering from chronic obstructive respiratory disease, seem to form some sort of dose-response relationship, have led some researchers to speculate that the association may be causal. However, to date, no convincingly plausible biological hypothesis to explain the effects has been put forward. This lack of a plausible hypothesis has been seen by some as a serious flaw in the proposition of causality. As in all studies of this kind, the possibility that variations in some other parameter, itself related to PM_{10}, is causally related to the effects recorded cannot be dismissed. That this might be the case has been strengthened recently by the comment that as the composition of PM_{10} is almost certain to vary from place-to-place then, despite an apparently consistent association with effects, it is unlikely that a single biological hypothesis regarding mechanism of effect will be adequate. On the other hand the notion that a series of different mechanisms could explain such a consistent set of demonstrated associations seems also unlikely and the idea of a critical, as yet unidentified, covariate has become more appealing.

Clearly, before this last argument can be accepted, analysis of the components of PM_{10} in a number of different areas will need to be undertaken. If the composition is found to vary widely from place-to-place then the suggestion that PM_{10} is causally related to various effects will be substantially weakened. It is suggested that consideration is given to putting this sort of analysis in hand. The measurement of PM_{10} at 12 sites in the UK will provide an excellent basis for these studies.

6.1.5 Effect on Visibility

Prevailing visibility is defined as the greatest distance in a given direction at which it is just possible to see and identify a prominent dark object during daytime, and an unfocussed moderately intense light source at night. Degradation of visibility arises when gases and particles between the observer and the observed object either absorb or scatter the light which carries the image to the observer.

Clean particle-free air is essentially transparent in the visible light region and visibility is restricted only by Rayleigh scattering by gas molecules. At sea level, in the total absence of particles, Rayleigh scattering limits visibility to around 300 km. Air pollution reduces visibility by three main mechanisms:

- *absorption of light by gases;*
- *scattering of light by particles;*
- *absorption of light by particles.*

The only gas which absorbs visible light to a significant degree is nitrogen dioxide, which can impart a brown colour to the air. However, appreciable concentrations are required and this is overall only a minor contribution. By far the major factor is light scattering by particles. This is at a maximum for particles whose radius is similar to the wavelength of visible light, ie 0.1 to 1 µm diameter. A study in North-West England(1) showed a strong negative correlation of visibility with concentrations of ammonium ($r = -0.77$; $p = 0.001$), non-marine sulphate ($r = -0.70$; $p = 0.001$) and nitrate ($r = -0.53$; $p = 0.001$), all major constituents of particles in this size range. The only particles with an appreciable ability to reduce visibility by absorption of light are those containing elemental carbon or iron oxide. In practice, at lower relative humidities, the total suspended particle concentration is an excellent predictor of visibility. A further consequence of light absorption and scattering by air pollutants is a reduction in both sunshine intensity and duration; when the sun is low in the sky and the pathway through the atmosphere long, the sun may be entirely obscured at the start and end of the day.

At high relative humidities, water soluble particles deliquesce and consequently increase in size. They form the nuclei upon which water condenses to form a fog. It is thus no coincidence that the decrease in urban smoke concentrations since the 1950s has been accompanied by a decrease in the frequency of urban fogs(2).

6.2 CHEMICAL COMPOSITION OF PARTICULATE MATTER IN URBAN AIR

Chemical composition is one of the key variables in understanding airborne particles. This is because:

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(1) Colbeck I and Harrison RM (1984) **Ozone-Secondary Aerosol - Visibility Relationships in North-West England** Science of the Total Environment **34,** 87-100.

(2) 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** Atmospheric Environment **26B,** 227-240.

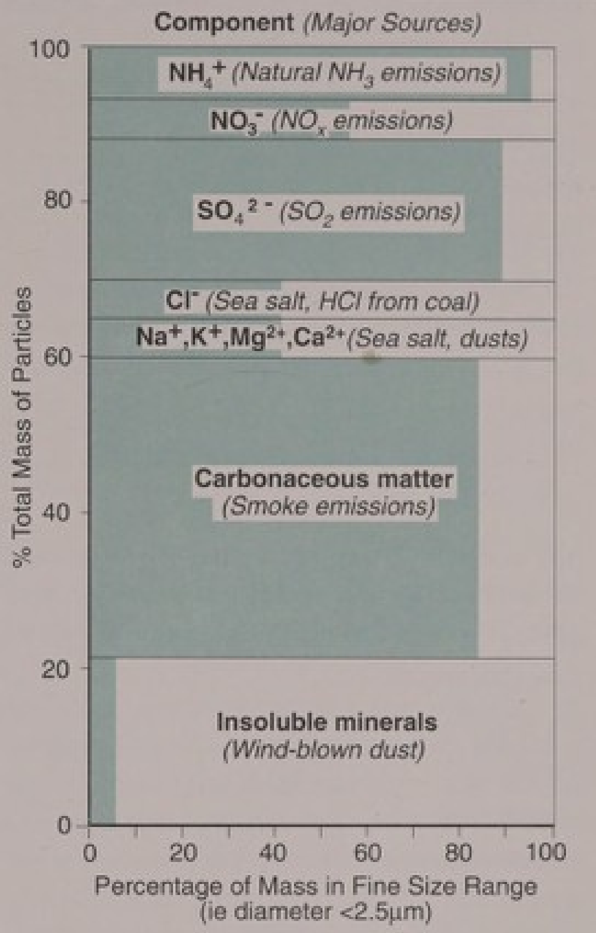
- *some health effects depend upon specific chemical components:eg polynuclear aromatic hydrocarbons with carcinogenicity; lead with lead poisoning, etc*
- *the chemistry usually gives the best clue as to particle source. Thus, for example, lead is associated with leaded petrol and smelters, whilst polynuclear aromatic hydrocarbons are associated with combustion sources, the ratios of individual compounds reflecting the type of source.*

Figure 6.3 presents a typical breakdown of the components of the total suspended particulates for an urban area, based largely upon data collected in Leeds (1982/3)⁽¹⁾. The main components are:

- *soil-derived minerals, due to resuspension;*
- *elemental carbon, from combustion processes;*
- *organic compounds, mainly partially or unburned combustion products;*
- *ammonium salts, from ammonia neutralisation of airborne acids;*
- *sodium and magnesium chloride, from marine sources;*
- *calcium sulphate, from building materials and rocks/ soils;*
- *sulphates from SO_2 oxidation;*
- *nitrates from NO_x oxidation.*

One approach to identifying chemical substances in atmospheric particles involves using X-ray powder diffraction (XRD). This technique identifies only crystalline components, representing about 50% of urban particle mass. One, perhaps surprising, finding is that many of the compounds are found in many different parts of the world⁽²⁾. Table 6.1 shows a summary of published data indicating the ubiquitous nature, particularly of rock/soil minerals such as α-quartz, calcite, dolomite, gypsum and feldspar, ammonium salts, and lead salts (from leaded petrol combustion).

Figure 6.3 Composition of Atmospheric Particles Collected in Leeds (1982/3) (Fine Particles < 2.5 μm, coarse 2.5-15 μm)



A wide variety of organic species are found in urban particles. These sub-divide approximately into two groupings, which are as follows:

- *Primary condensates:*
  - *Alkanes (C_{17} - C_{36})*
  - *Alkenes*
  - *Aromatics*
  - *Polyaromatics*
- *Oxidised hydrocarbons, either as primary condensates or secondarily produced as a result of atmospheric oxidation reactions:*
  - *Acids*
  - *Aldehydes*
  - *Ketones*
  - *Quinones*
  - *Esters*
  - *Phenols*
  - *Dioxins*
  - *Dibenzofurans*

In addition, traces of nitro-organics and heterocyclic sulphur may be found in particulate material.

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(1) Clarke AG, Willson MJ and Zeki EM (1984) **A Comparison of Urban and Rural Aerosol Composition Using Dichotomous Samplers** Atmospheric Environment **18**,1767-1775.

(2) Sturges WT, Harrison RM and Barrie LA (1989) **Semi-quantitative X-ray Diffraction Analysis of Size-fractionated Atmospheric Particles** Atmospheric Environment **23**, 1083-1098.

Table 6.1. Comparison of Chemical Components of Airborne Particles Identified by X-ray Powder Diffraction in Various Studies

Compound	Toronto, Canada	NW England	Northern England	Denver US	US	St Louis US	Japan
α-Quartz	√	√	√	√	√	√	√
Calcite	√	√	√	√	√	√	√
Dolomite	√				√	√	
Gypsum	√	√	√	√	√		√
Feldspar	√			√		√	√
NaCl	√	√	√	√	√	√	√
NH_4Cl	√		√				√
$(NH_4)_2SO_4$	√	√	√	√	√	√	√
NH_4NO_3		√					
$(NH_4)_2SO_4.2NH_4NO_3$	√		√		√		√
$(NH_4)_2.SO_4.3NH_4NO_3$	√		√		√		
$CaSO_4.(NH_4)_2SO_4.H_2O$	√	√	√		√		
$PbSO_4.(NH_4)_2SO_4$	√	√	√	√	√	√	
$PbSO_4$	√		√				
$3(NH_4)_2SO_4.NH_4HSO_4$	√				√	√	
NH_4HSO_4			√				
Chlorite	√						√
Kaolinite	√			√			
Magnetite/Haematite	√			√			√
$NaNO_3$		√					
Na_2SO_4	√						
$Na_2SO_4.NaNO_3.H_2O$			√				
$Na_2SO_4.(NH_4)_2SO_4.4H_2O$			√				
$ZnSO_4.(NH_4)_2SO_4.6H_2O$				√		√	
$Fe_2(SO_4)_3.3(NH_4)_2SO_4$		√					

There has been virtually no research in the UK upon the organic composition of atmospheric particles other than for a few specific groups of compounds such as PAH, described in Chapter 9.

6.3 SOURCES OF URBAN PARTICULATE MATTER

6.3.1 Primary Particulate Matter

Emissions may arise from both stationary and mobile sources.

Mobile Sources

These are both petrol and diesel vehicles, the latter being responsible for the majority of black smoke.

Stationary Sources

These fall into two groups:

- *controlled emissions from chimney stacks;*
- *uncontrolled or 'fugitive' emissions.*

Fugitive emissions, however, are both difficult to measure and control, and may include:

- *wind blown dusts from open storage areas and spoil heaps;*
- *emissions from buildings via natural or fan assisted ventilation;*
- *emissions from roadways as a result of local air turbulence;*

- *emissions from the handling of materials, eg when loading/unloading.*

6.3.2 Secondary Particulate Matter

Particles may be formed when two volatile and noncondensible vapour species react to give rise to a product with a very low vapour pressure, and such a product may be regarded as a secondary particle in order to differentiate it from those arising from the reactions of solids and liquids.

The main source of secondary particles is the atmospheric oxidation of SO_2 to sulphuric acid, and of NO_2 to nitric acid. Whilst sulphuric acid exists in air in particle form, nitric acid is present as a vapour. Both nitric acid and hydrochloric acid vapour, the latter arising mainly from refuse incineration and coal combustion, react reversibly with ammonia gas, largely arising as a product of decomposition of animal urine, to form ammonium salts⁽¹⁾. Ammonium nitrate and sulphate exist in air as solid particles at low humidities, or as solution droplets at higher humidities.

$$NO_2 \rightarrow HNO_3$$

$$HNO_3 + NH_3 \Leftrightarrow NH_4NO_3$$

$$HCl + NH_3 \Leftrightarrow NH_4Cl$$

Sulphuric acid reacts irreversibly in two stages to form either ammonium bisulphate or ammonium sulphate

$$H_2SO_4 + NH_3 \rightarrow NH_4HSO_4$$

$$+ NH_3 \rightarrow (NH_4)_2SO_4$$

These ammonium salts form progressively as SO_2 and NO_2 are oxidised on a timescale of hours, and ammonia becomes available for neutralisation. They are not, therefore, a specifically urban problem, but are part of a regional-scale pollution phenomenon affecting both rural and urban sites. Ammonium salts comprise a major part of the accumulation mode particles in the UK air.

6.3.3 Airborne Particulate Elemental Carbon (PEC)

In most ambient atmospheric situations, carbon contributes 10-20% of total aerosol mass. The main forms in which carbon occurs are:

- *carbonates; normally less than 5% of total carbon mass;*
- *organic carbon; normally contributes 60-80% of total carbon mass and is a matter of some concern because of the possible mutagenic and carcinogenic effects of some compounds; and*
- *particulate elemental carbon (PEC); also known as black carbon or graphitic carbon.*

There have been few measurements of atmospheric PEC levels in the U.K. A selection of levels reported in the literature⁽²⁾ for other urban locations is given in Table 6.2.

The main adverse effects associated with PEC are reduction of visibility and soiling of surfaces. The size of the particulates peaks in the submicron range and this determines their light scattering capability. In addition, they have a high optical absorption coefficient. A number of studies have investigated visibility reduction by identifying the physical and chemical composition of the atmosphere and applying the extinction coefficients for each of the components. These studies suggest that scattering is the dominant process for light extinction, with about 20% of the scattering caused by PEC. Absorption is responsible for between 10% (rural areas) and 30% (urban areas) of light extinction with PEC responsible for more than 90% of the absorption. On this basis, PEC is responsible for between 25% and 45% of visibility reduction⁽²⁾.

To approach the problems of identifying PEC sources in the urban aerosol, a PEC inventory for the area of concern can be calculated from annual consumption of fuels and their PEC emission factors. The results for London in 1980 are presented in Table 6.3. Likewise similar calculations have been made to estimate the total mass of PEC for the UK according to fuel usage for the period 1971-86. The data were derived using annual fuel consumption and the emission factors for PEC in Table 6.3. The total emissions of PEC and the estimated

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(1) Allen AG, Harrison RM and Erisman JW (1989) **Field Measurements of the Dissociation of Ammonium Nitrate and Ammonium Chloride Aerosols** Atmospheric Environment 23, 1591-1599.

(2) Hamilton RS and Mansfield TA (1991) **Airborne Particulate Elemental Carbon: its Sources, Transport and Contribution to Dark Smoke and Soiling** Atmospheric Environment 23, 1591-1599.

relative contribution of DERV during this period is given in Figure 6.4. The mass emitted from power stations has not been included as the mass of smoke they emit into the atmosphere is very small. The disparity between the two bar lines has comparatively lessened since 1982 due mainly to the increased contribution from diesel sources. The percentage contribution of PEC mass emissions from fuel type during this period is illustrated in Figure 6.5. The percentage contributions from coal and solid smokeless fuels are not shown in Figure 6.5 as their contribution to the total was less than 1%. These estimates show that diesel emissions make the major contribution (80-95%) to PEC at both urban and national level (whereas their contribution to dark smoke is substantial only at the urban level). Less than 3% of the total mass of smoke emitted for the UK in 1985 was PEC and for London (1980) PEC accounted for 7% of the total smoke emitted. However, this comparison does not take account of the darkness of PEC.

Table 6.2. Ambient Concentrations of Particulate Elemental Carbon (in µg m^{-3}) Reported for a Variety of Locations

	Concentration (µg m^{-3})
Rural and Remote Areas	
Average 20 rural sites, USA	1.3
Cities	
New York	4.2-13.3
Portland	10
Washington	6.5
Los Angeles	3.1-4.1
Denver	5.4
Hamburg	2.4
Hamburg (during smog)	24
Leeds, England	6
Athens	9.1-12.2
Los Angeles	3.4-5.7
Los Angeles	0.4-13.1
Paris	1.6-10.2
Average 46 urban sites, USA	3.8

6.3.4 Nuisance Dust

Surveys of the public perception of air pollution from traffic show that the aspect that causes the most direct concern is dust and dirt. However, very little work has been carried out on traffic as a source of nuisance dust. (The term 'nuisance dust' is used to describe dust that causes soiling of windows, cars, paintwork etc It does not cover dust that causes health effects). One study, using the glass slide technique for measuring soiling rates(1), has shown that alongside busy roads soiling rates are typically double the local background. A significant proportion of the roadside sites in this study produced soiling rates considered to be unacceptable by the public.

The source of roadside dust will be particulate matter emitted in vehicle exhausts and particles raised from the road surface by passing traffic. In addition to road traffic, construction/demolition activities can be an important, and fairly widespread, source of nuisance dust in urban areas. Other sources, such as waste transfer stations and concrete batching plant can contribute to more localised nuisance dust problems.

6.4 AIR QUALITY STANDARDS

Guidance in the assessment of ambient concentrations is available from a number of sources including the World Health Organization, the European Community and USEPA. Since most health effects research on suspended particles has involved exposure to both particles and sulphur dioxide simultaneously, air quality standards have been framed in terms of both.

Table 6.3. Mass of Particulate Elemental Carbon (PEC) Emissions (in Tonnes) According to Fuel Use for London (1980)

Fuel type	Amount of fuel consumed (kT)	PEC emission factor (% by mass)	Amount of PEC emitted (T)	% of PEC total by fuel type
Coal: domestic	50	0.0001	0.05	0.004%
Coal: industrial	250	0.0001	0.25	0.02%
Solid smokeless fuel	350	0.0001	0.35	0.3%
Gas oil	1000	0.01	100	8%
Fuel oil	600	0.02	12	1%
Petrol	2200	0.002	44	4%
Diesel	520	0.2	1040	87%

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(1) Moorcroft JS, Laxen DPH (1990) **Assessment of Nuisance Dust** Environmental Health, August 1990, 215-217.

Figure 6.4 Diesel Contribution to Total Mass Emissions of Particulate Elemental Carbon in the UK (1971-1986)

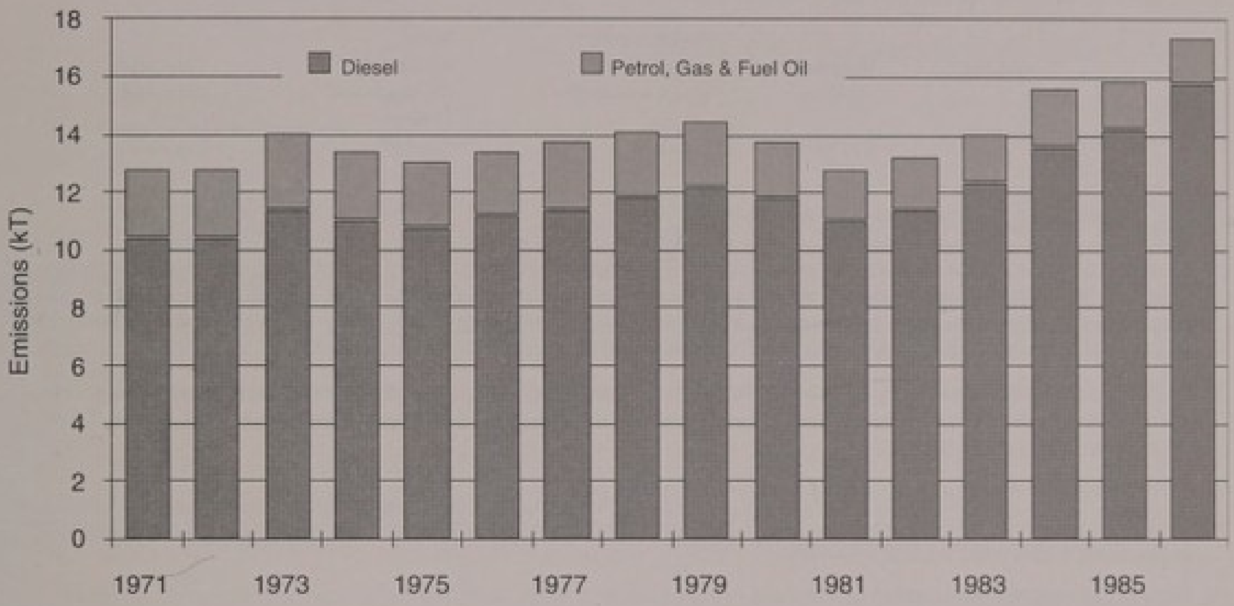
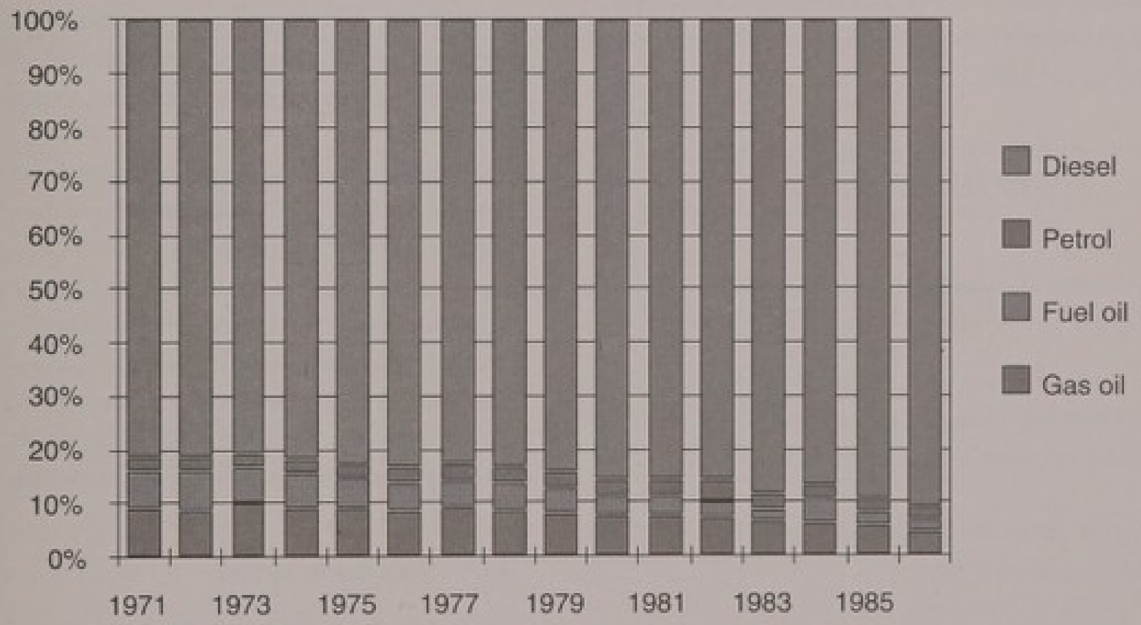


Figure 6.5 Percentage Distribution of Particulate Elemental Carbon Emissions, by Fuel Source, in the UK (1971-1986)



The WHO Guidelines[1] appear in Table 6.4.

In the UK statutory air quality standards were introduced by the Air Quality Standards Regulations 1989, which gave effect to the terms of the EC Directive 80/779/EEC on air quality limit values and guide values for sulphur dioxide and suspended particulates, as amended by 89/427/EEC.

Table 6.5 shows limit values for suspended particles determined by the black smoke method, whilst Table 6.6 shows the Guide Values by this method. Limit values for gravimetrically determined particle mass appear in Table 6.7.

In the USA the Environmental Protection Agency ambient quality standards for particulate matter are:

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[1] World Health Organization Regional Office for Europe **Air Quality Guidelines for Europe** (1987) European Series Number 23, World Health Organization, Copenhagen.

Table 6.4. WHO Guidelines for Combined Exposure to Sulphur Dioxide and Particulate Matter[a]

				Gravimetric assessment	
	Averaging time	**Sulphur dioxide** ($\mu g\ m^{-3}$)	**Reflectance assessment: black smoke[b]** ($\mu g\ m^{-3}$)	**Total suspended particulates (TSP)[c]** ($\mu g\ m^{-3}$)	**Thoracic particles (TP)[d]** ($\mu g\ m^{-3}$)
Short Term	24-hours	125	125	120[e]	70[e]
Long Term	1 year	50	50	-	-

(a) No direct comparisons can be made between values for particulate matter in the right and left-hand sections of this table, since both the health indicators and the measurement methods differ. While numerically TSP/TP values are generally greater than those of black smoke, there is no consistent relationship between them, the ratio of one to the other varying widely from time to time and place to place, depending on the nature of the sources.

(b) Nominal $\mu g\ m^{-3}$ units assessed by reflectance. Application of the black smoke value is recommended only in areas where coal smoke from domestic fires is the dominant component of the particulates. It does not necessarily apply where diesel smoke is an important contributor.

(c) TSP: measurement by high volume sampler, without any size selection.

(d) TP: equivalent values as for a sampler with ISO-TP characteristics (having 50% cut-off point at 10 μm): estimated from TSP values using site-specific TSP/ISO-TP ratios.

(e) Values to be regarded as tentative at this stage being based on a single study (involving sulphur dioxide exposure also).

Primary Standards (for the protection of human health)

24-hour mean, not to be exceeded on more than 0.27% of occasions (1 in 365) 150 $\mu g\ m^{-3}$ PM_{10} (previously 260 $\mu g\ m^{-3}$ TSP).

Annual arithmetic mean 50 $\mu g\ m^{-3}$ PM_{10} (previously 75 $\mu g\ m^{-3}$ TSP annual geometric mean).

Secondary Standards (for protection of the environment, amenity, etc)

24-hour mean, not to be exceeded on more than 0.27% of occasions (1 in 365); previously 150 $\mu g\ m^{-3}$ TSP annual geometric mean.

Annual arithmetic mean; previously 60 $\mu g\ m^{-3}$ TSP annual geometric mean.

Both are now as per primary standards.

6.5 MEASUREMENT OF PARTICULATE MATTER CONCENTRATIONS

6.5.1 Particle Sampling and PM_{10} Measurement

A wide variety of techniques is available to collect and analyse particulate material in the atmosphere. The most widely used is filtration, in which the air to be sampled is drawn through a filter using an electric pump. Particulate matter is trapped on the filter and can then be analysed in a number of ways depending on whether details of the composition of the particles are required or whether a more general measurement of total mass is needed.

An important feature of particulate measurement is the size range of particles collected for analysis. This is controlled by the sampling flow rate and the aerodynamics of the orifice through which the sample is collected. For health effects it is respirable particles which are important and in recognition of this sampling procedures are being standardised to have a 50% cut-off for particles with an aerodynamic diameter of 10 μm. Such measurements are termed PM_{10} measurements.

6.5.2 Black Smoke Method

In the UK the technique which has been used most widely and for the longest period of time is the black smoke method. Air is drawn through a white filter on which the particles produce a stain the darkness of which is measured using a portable reflectometer. A standard calibration curve is used to convert the measurement into the concentration of particles in the air. The method is covered by a British Standard[1] and samples respirable particles together with some larger particles with diameters up to around 10-15 μm. The British Standard method is not the same as that defined in the EC Directive on particulate concentrations but is related to it through:

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(1) British Standards Institution (1969) **Determination of the Concentration of Suspended Matter** BS1747, Part 2, BSI, UK.

Table 6.5. EC Limit Values for Suspended Particulates (as Measured by the Black Smoke Method),(a) Expressed in µg m^{-3}

Reference period	Limit value for suspended particulates
Year	68 (median of daily mean values taken throughout the year)
Winter (1 October to 31 March)	111 (median of daily mean values taken throughout the winter)
Year (made up of units of measuring periods of 24-hours)	213(b) (98 percentile of all daily mean values taken throughout the year)

(a) Converted to British Standard Smoke

(b) Member States must take all appropriate steps to ensure that this value is not exceeded for more than three consecutive days. Moreover, member States must endeavour to prevent and to reduce any such instances in which this value has been exceeded.

Table 6.6. EC Guide Values for Suspended Particulates (as Measured by the Black Smoke Method (a)) Expressed in µg m^{-3}

Reference period	**Guide value for suspended particulates**
Year	34 to 51 (arithmetric mean of daily mean values taken throughout the year)
24-hours	85 to 128 (daily mean value)

(a) Converted to British Standard Smoke

Table 6.7. EC Limit Values for Suspended Particulates as Measured by the Gravimetric Method. Expressed in µg m^{-3}

Reference period	**Limit value for suspended particulates**
Year	150 (arithmetric mean of daily mean values taken throughout the year)
Year (made up of units of measuring periods of 24-hours)	300 (95 percentile of all daily mean values taken throughout the year)

$$\text{BS value} = 0.85\text{xEC value}$$

This approach to particulate measurement has the advantages of simplicity and low cost which have permitted its use in the extensive national networks for the measurement of smoke and SO_2. However, its disadvantages are many and it is particularly significant that its validity depends on the predominance of carbonaceous airborne matter. Where the proportion of carbonaceous (ie black) material is reduced or where unusually reflective material (eg crystalline matter) is collected the standard curve becomes inapplicable and a site specific mass/darkness relationship must be established. Nowadays, black smoke measurements are not in any meaningful way comparable with gravimetric.

A further advantage of these measurements is that they give a direct measure of the soiling potential of airborne particles. The method is therefore most effective where elemental carbon forms a high proportion of the collected material and in this respect the following relationship has been established(1):

$$\text{Elemental Carbon } (\mu g\ cm^{-2}) = 0.13\text{xBS} - 0.1$$

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(1) 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** Atmospheric Environment **17**, 2337-2341.

where BS is the British Standard smoke value in $\mu g\ cm^{-2}$.

6.5.3 Gravimetric Techniques

In the UK the most commonly used gravimetric sampler is the Warren Spring Laboratory Metal Particulate (M-Type) Sampler. This is designed to sample fine airborne particulate material for subsequent metal analysis. It consists of a sampling head containing the filter holder, a pump incorporating a flow controller, and a dry gas meter. The characteristics of the sampling head conform to the specification given in the EC Directive 82/884/EEC on a Limit Value for Lead in Air. The inlet efficiency is very high for particulates <5 µm diameter but falls for larger diameters, especially at high wind speeds. The maximum particle diameter to be sampled with 50% efficiency is related to wind speed as follows: wind speed 1 $m\ s^{-1}$, 17 µm; 3 $m\ s^{-1}$, 14 µm and 5 $m\ s^{-1}$, 13 µm.

The High Volume PM_{10} sampler is the US Environmental Protection Agency reference method for sampling PM_{10} particulate matter and is the principal method of measuring ambient levels in the USA. It is essentially similar to the previously used high volume TSP sampler but with the addition of a 10 µm particle size selective inlet.

The above methods are all subject to three principal disadvantages.

- *They are labour intensive, due to the need to pre and post-weigh filters and to attend on site at frequent intervals in order to remove and refit filters.*
- *The reporting of results is delayed.*
- *Under typical conditions, hourly results cannot be obtained since insufficient particulate matter would be collected in this time to give a statistically significant weight increase. Even if the weight increase were significant, the hourly changeover of filters would be prohibitively labour intensive.*

6.5.4 The Tapered Element Oscillating Microbalance (TEOM)

Two solutions are available to the above problems, both providing near real-time particulate mass, typically at hourly intervals.

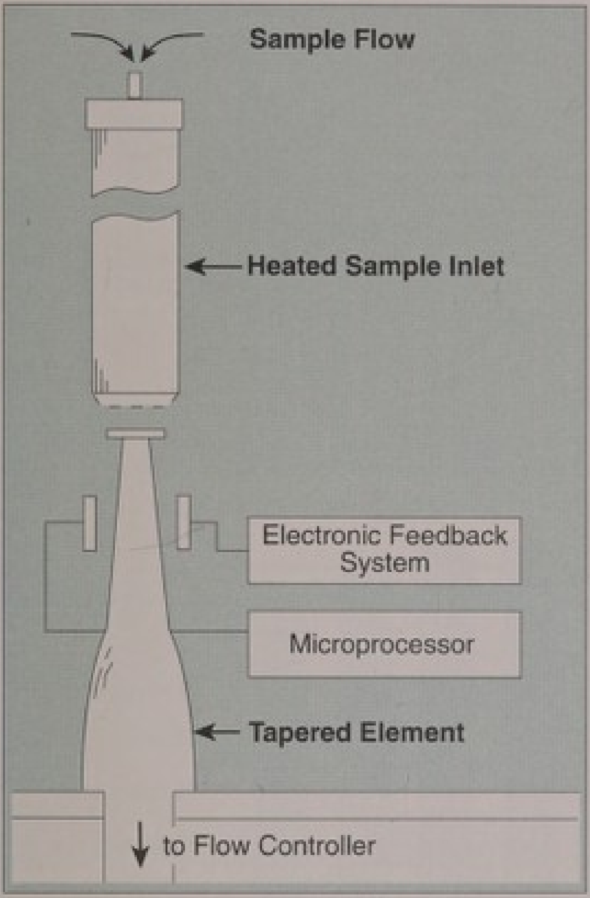
- *Beta Attenuation Monitoring*
- *Tapered Element Oscillating Microbalance (TEOM)*

Both are recognised by the USEPA as equivalent to their Reference Method. Of these, only the TEOM is widely used in the UK.

The TEOM consists of an electronic processing system designed around a tapered piezo-electric element with an exchangeable PM_{10} filter cartridge mounted on its tip. The tapered element is induced to vibrate at its natural frequency, determined by the stiffness of the mounting and the mass of the filter. The particulate laden air stream is drawn through a heated inlet to a cartridge containing a teflon-coated glass fibre filter. The particulate mass collects on the filter and the filtered air then proceeds through a flow controller. This is directed by a microprocessor to maintain the air flow at a constant rate. (Figure 6.6). As the mass on the filter increases, the natural frequency of oscillation decreases. The processor detects this change in frequency and computes the total mass accumulation on the filter. The rate of accumulation and the equivalent air concentration are calculated in near-real time with results provided at user-defined intervals. At a sample flow rate of 2 litres/min and mean suspended particulate concentration of 50 $\mu g\ m^{-3}$, four weeks of unattended operation is possible. Hourly results are of particular value because they match the typical temporal resolution of other environmental data such as wind speed, direction, etc, and are of value when attempting to validate the predictions of some of the widely used short-term dispersion models which compute hourly ground level concentrations, or when using a source-apportionment model.

The TEOM sampler is a recent development which has been adopted for the Enhanced Urban Network. It offers great advantages due to the very short time response allowing provision of near-real-time data. The disadvantage is that unlike the gas analysers it cannot be recalibrated with primary or transfer standards in the

Figure 6.6 Schematic Diagram of the TEOM Ambient Particle Monitor



field, and hence data will be viewed with some circumspection until reliability has been fully established.

6.5.5 Measurements of Deposition Rates

While suspended particle concentrations are of interest in relation to possible health effects, particle deposition may give rise to soiling on buildings and other problems. Traditionally, deposition rates in the UK have been measured using the British Standard Deposit Gauge(1). Unfortunately, it is subject to many problems in use, being large and cumbersome, and having a fairly low collection efficiency even at low wind speeds. An improved gauge has been developed utilising an aerodynamically profiled collection dish, designed to ensure that air flow over it does not resuspend material already collected. The standard deposit gauge described above has no directional characteristics and if information on the directional deposition flux is required then the British Standard Directional Deposit Gauge(2) may be used. This measures the lateral flux through four vertical slots to collectors arranged on a vertical support. This method is useful but is subject to a limitation in that its results are in no way comparable to those derived from the horizontal, non-directional collector.

6.6 TRENDS IN UK EMISSIONS AND CONCENTRATIONS

6.6.1 Emissions

UK Government statistical digests(3) provide a source of information on trends in smoke emissions covering a period of over three decades. Smoke being defined here as 'suspended particulate of < 15 µm diameter arising from the incomplete combustion of fuel'.

The term 'smoke' refers to primary particles irrespective of their darkness. However, because measurements of airborne smoke depend upon the blackening of a filter paper, the term 'black smoke' (or 'dark smoke') was introduced to allow for the different soiling capacities of smoke particles from different sources. Dark smoke is the product of multiplication of the mass or concentration of smoke by a soiling factor. Table 6.8 contains emission factors used in the UK for smoke, together with soiling factors and the resultant dark smoke emission factors. It will be seen that the scale is normalised to coal, which has a soiling factor of 1.0, and that emissions from gas oil and diesel combustion are darker, per unit mass, than coal smoke.

Figure 6.7 shows recent trends in black smoke emissions for each emission source. It can be seen that emissions fell by almost 100 thousand tonnes between 1980 and 1984, rising again in 1986 following the end of a period of industrial action by miners. Since 1986 emissions have fallen steadily to 453,000 tonnes in 1990. Emissions from domestic sources reduced by 50% between 1980 and 1990, and as a percentage of total emissions fell from 56% to 33%. Over the same period emissions from road transport almost doubled, rising from 21% of total emissions to 46%. Thus, in 1989 for the first time, emissions from road vehicles exceeded those from domestic sources and this trend is likely to be maintained.

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(1) British Standards Institution (1969) **Methods for the Measurement of Air Pollution: Deposit Gauges** BS1747 Part 1 BSI, UK.
(2) British Standards Institution (1972) **Directional Dust Gauges** BS1747 Part 5 BSI, UK.
(3) Department of Environment (1992) **Digest of Environmental Protection and Water Statistics 1991, No 14**, HMSO, UK.

Table 6.8. Smoke Emission Factors and Relative Soiling Factors for Fuel Types Predominantly Used Within the UK

Fuel type	Smoke emission factor (% by mass)	Approx soiling factor relative to coal	Dark smoke emission factor (% by mass)
Coal: domestic	3.5	1.0	3.5
Coal: industrial	0.25	1.0	0.25
Coal: power station	0.025	1.0	0.025
Solid smokeless domestic	0.56	1.0	0.56
Solid smokeless industrial	0.023	1.0	0.023
Gas oil	0.025	1.55	0.039
Fuel oil	0.10	0.43	0.043
Motor spirit	0.15	0.43	0.065
Diesel fuel	0.60	3.0	1.8

Figure 6.7 Black Smoke Emissions, by Source, for the UK (1980-1990)

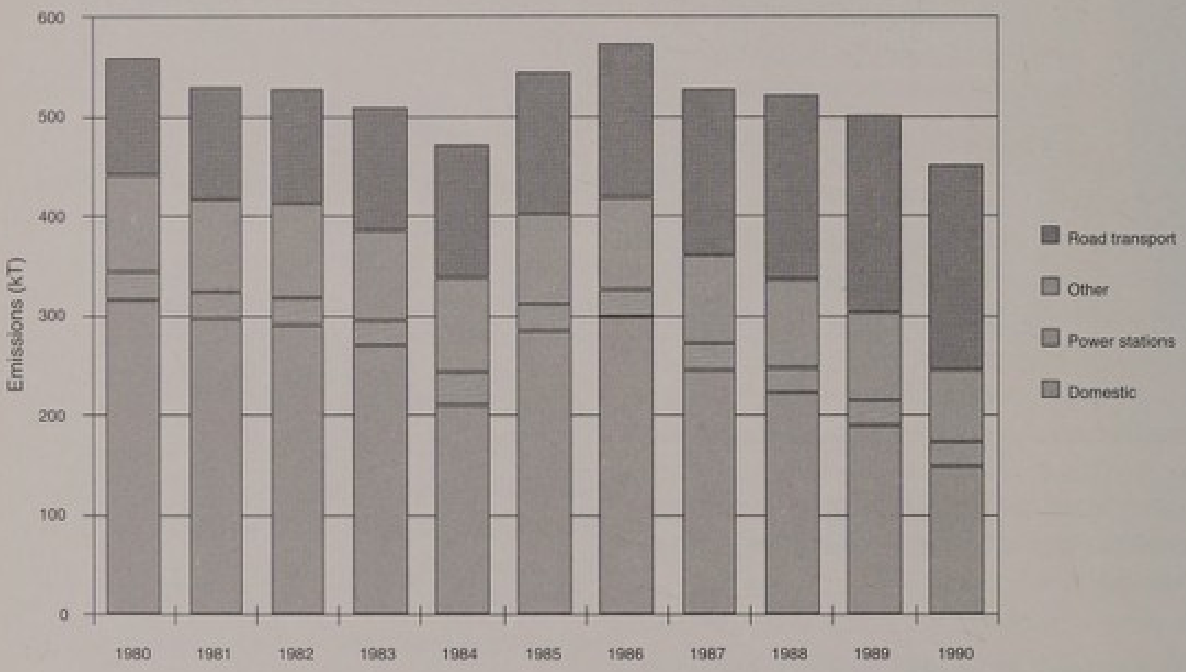

Figure 6.8 Black Smoke Emissions, by Fuel Type, for the UK (1980-1990)

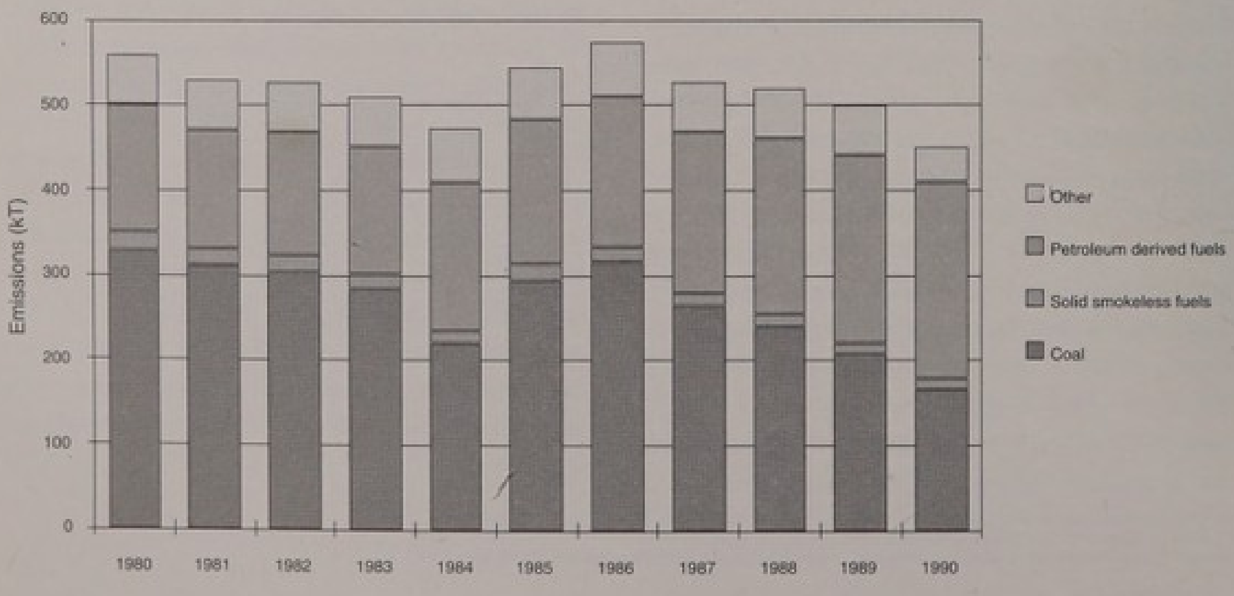

Figure 6.9 Mean Urban Concentrations of Black Smoke in the UK (1962-1990)

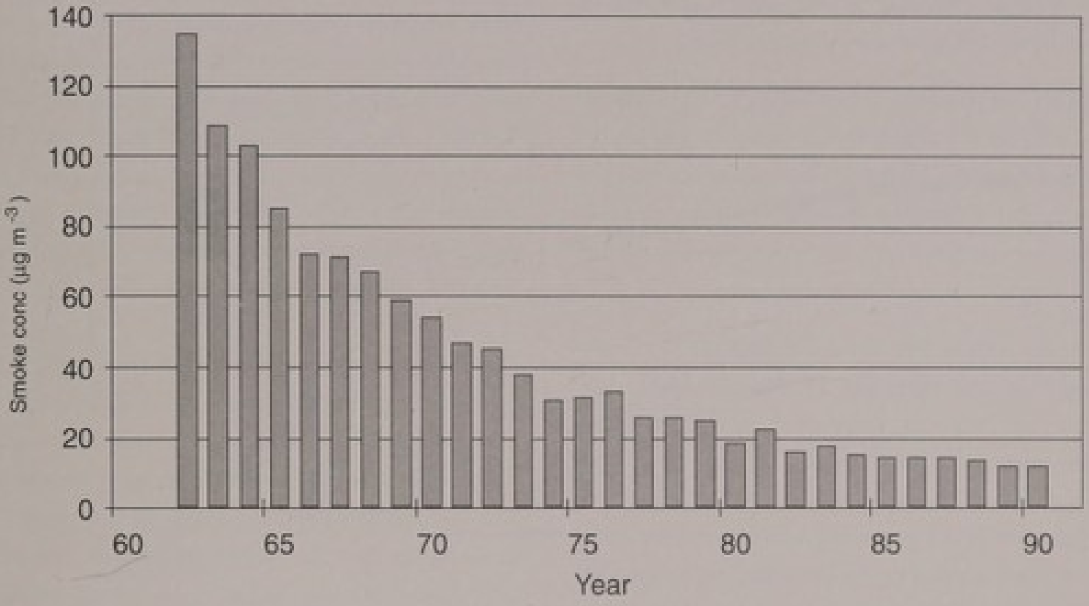

Figure 6.10 Annual Mean Concentrations of Suspended Particles at Four Sites in London (1986-1989)[1]

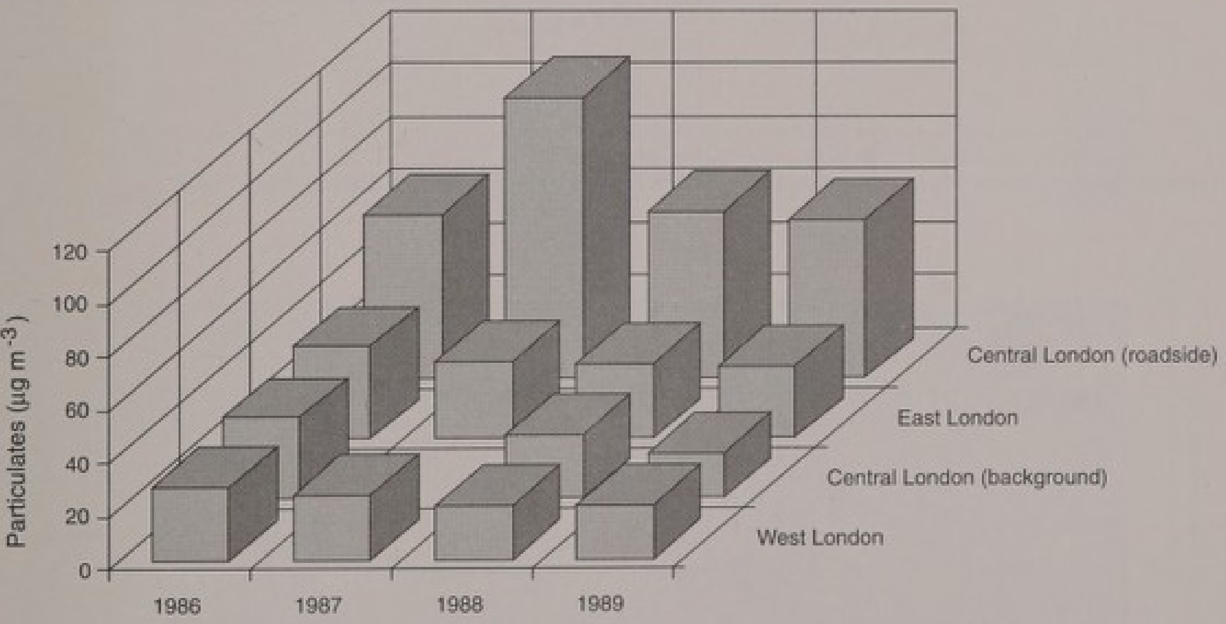

Figure 6.8 shows trends in emissions by fuel type where related changes have taken place, with a substantial reduction in coal consumption and an almost doubling of emissions from diesel combustion. As would be expected, emissions from diesel combustion now exceed those from coal combustion. Figure 6.9 shows how the trends in emissions are mirrored in urban ground level concentrations.

6.6.2 Urban Monitoring Networks

The national survey of smoke and sulphur dioxide began in 1961 but has been re-organised and updated in order to take account of decreases in urban concentrations of these pollutants and to ensure that the UK's responsibilities in respect of EC Directive 80/779/EEC are discharged.

Currently three networks monitor particulate levels as follows.

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(1) London Scientific Services (1989) **London Air Pollution Monitoring Network Fourth Report** Rendel Science and Environment, London, UK.

- *Basic Urban Monitoring Network of 76 sites (1990), reduced from 175 sites in 1986, and operated to assess urban exposure and evaluate trends.*
- *EC Directive Network of 166 sites (1990), reduced from 330 sites in 1986, operated in those areas where exceedences of the Directive limit values are thought possible. The 50% reduction in the size of this network in only four years has been made in recognition of the continuing decreases in emissions noted earlier.*
- *Enhanced Urban Network of 6 sites (1992) to be extended to approximately 24 sites by 2000, and operated in order to extend the range of pollutant measurements to include* PM_{10}.

These three networks together represent one of the most extensive urban monitoring programmes in Europe and form a large data set on which to base future policy decisions.

6.6.3 London Particulate Survey

Over the years 1986-1989, London Scientific Services measured concentrations of airborne particulates at four sites in London. Sampling was carried out using the Warren Spring M-type sampler and the particle mass determined gravimetrically. As described above this air sampler has a 50% size cut-off generally larger than 10 µm and hence the measurements will be greater than for a PM_{10} sampler at the same site.

The results are summarised as annual averages in Figure 6.10. The apparent downward trend at the non-roadside sites is probably real, as other pollutants measured at these sites show little temporal change over the period. The concentrations at the roadside site are about 2.5 to 3 times higher than the background station indicating the importance of road traffic as a source of airborne particles. Both exhaust emissions and dust raised by passing traffic are expected to be important.

Figure 6.11 Hourly Mean PM_{10} Concentrations from the London and Birmingham EUN Sites (Mar-Nov 1992)

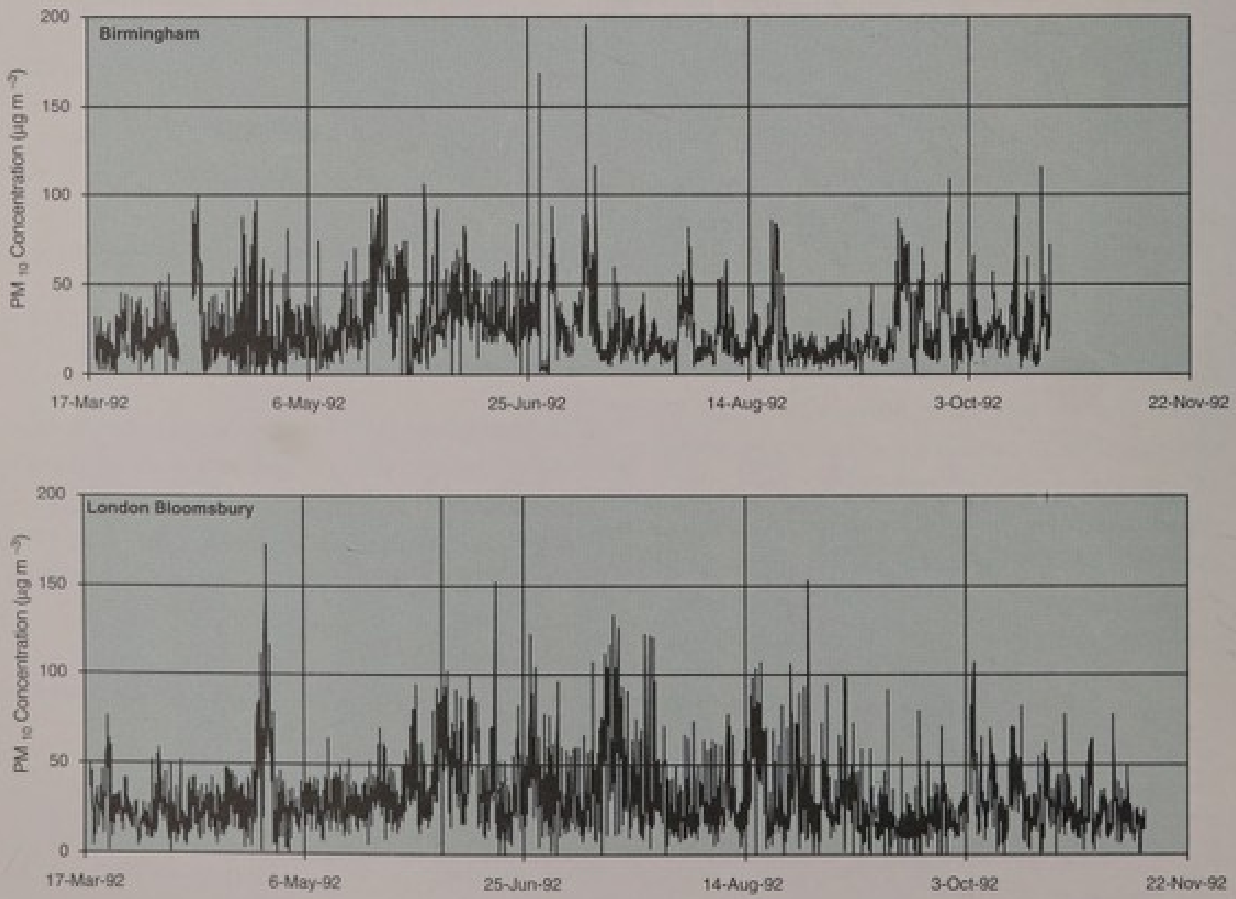

Figure 6.12 Frequency Distributions of Hourly Mean PM$_{10}$ Concentrations at London, Birmingham, Cardiff and Newcastle EUN Sites (1992)

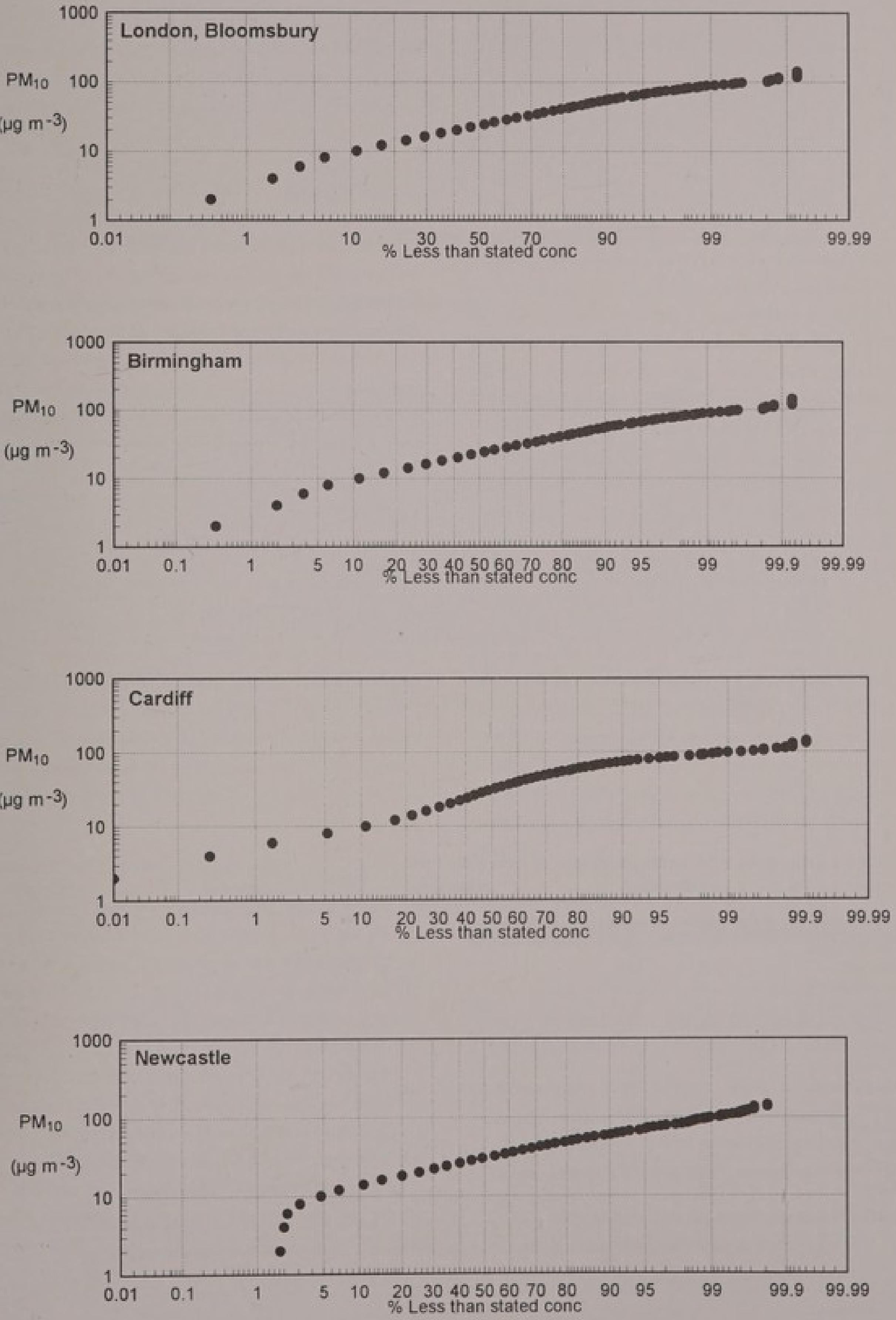

Figure 6.13 Diurnal Variation in Hourly Mean Concentrations of PM_{10} and CO at the London EUN Site (1992)

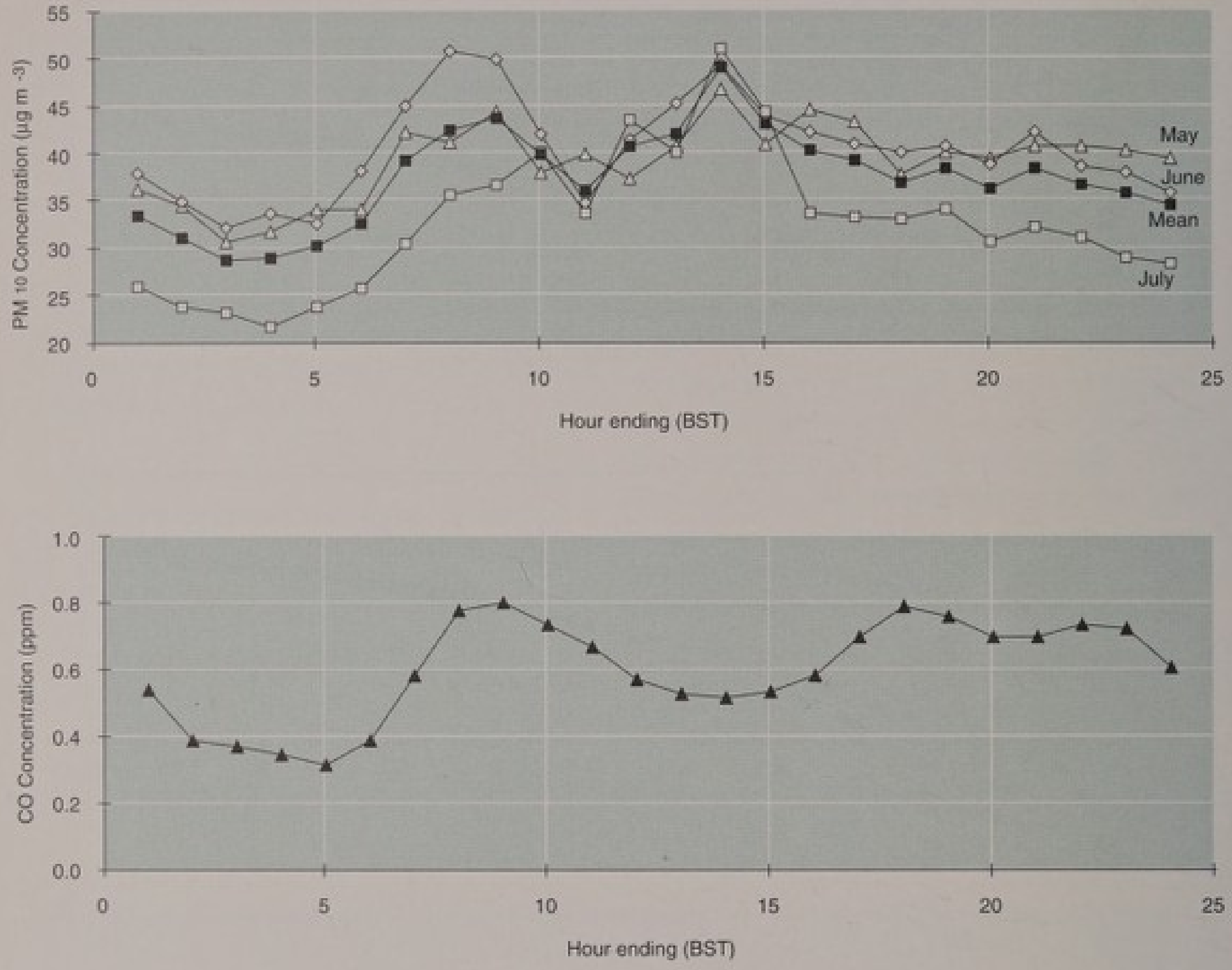

Table 6.9. Exceedence of EC Smoke Directive at UK Sites, 1987 - 1991

Station	1987/1988		1988/1989		1989/1990		1990/1991	
Crewe		1x4						
Mexborough		1x4						
Seaham	220	1x4						
Sunderland	370							
Hetton le Hole	265	1x4	224		296	1x6		
Houghton le Spring	263	1x7						
Featherstone	215	1x4						
Ashington		1x4						
New Ollerton				1x5				
Belfast 39		1x4						
Belfast 42					217		236	1x4
Belfast 12							244	1x4
Belfast 11							227	1x4
Newry					355	1x11		

Notes: Values are smoke (µg m^{-3}) in British units

1x4, 1x7 etc denotes the number of occasions > 213 µg m^{-3} x number of consecutive days per occasion.

Smoke is defined as suspended matter collected in accordance with BS1747 part 2.

6.6.4 Enhanced Urban Network Data for PM_{10} - The First Year

Hourly PM_{10} data recorded over the period March to July 1992 in London and Birmingham are shown in Figure 6.11. Levels generally range between 10 µg m^{-3} and 45 µg m^{-3} with short-term peaks extending to over 60 µg m^{-3}. The moving average (London site) is fairly stable at approximately 30 µg m^{-3}.

The difference between the results obtained from the two sites is small, and there is in fact slight visible correlation, suggesting that common external factors, eg meteorology, are acting. In general the Birmingham levels are slightly lower than those recorded in London. This difference is more clearly evident in a comparison of the cumulative frequency distribution (Figure 6.12). Such distributions are shown for London, Birmingham, Cardiff and Newcastle stations, based on hourly data for a period of 6 months.

Table 6.9

	Mean	95%ile	98%ile
London	34.3	74	90
Birmingham	28.2	70	80
Cardiff	36.4	86	96
Newcastle	32.2	70	86

Since there are no UK air quality guidelines for long-term PM_{10} levels, these results must be compared to the current USEPA standard or WHO 24-hour 'thoracic particle' guideline. All fall below the USEPA annual mean guideline of 50 µg m^{-3}, and the WHO thoracic particle guideline of 70 µg m^{-3}.

6.6.5 Diurnal Variation in PM_{10} Levels

Hourly data for PM_{10} averaged by month reveal the diurnal pattern in PM_{10} at the London site (Figure 6.13). This bears some similarity to the traffic-dominated pattern for CO (Figure 6.13), but clearly traffic is not the only source of PM_{10}. Examination of the time series graph suggests some correlation between these two variables, and this is apparent on a scatter plot of PM_{10} against CO levels. A linear regression on this data produces a correlation coefficient value of approximately 0.3, indicating only a weak correlation suggesting that road traffic (the major source of the CO) may play a minor role in the generation of airborne particulate matter in urban air.

There can be a large variation in PM_{10} levels from one day to the next and, since the variation in road traffic activity is small, this variation is most likely to be due to the influence of meteorological factors, in particular, windspeed and rainfall. Periods of high windspeed, but low rainfall are likely to enhance the tendency of deposited material to be resuspended, and to mask any lesser influences on airborne particulate levels such as production by high-level sources.

6.6.6 Exceedences of the EC Directive Limit

As described previously, limit values for sulphur dioxide and smoke are set by EC Directive 80/779/EEC. The 166 site EC Directive network monitors compliance within the U.K. with this Directive, and the data show that breaches of the limit value have fallen from 13 in 1983/84 to only three in 1990/91. The reductions are due to a combination of the effects of legislation, principally the Clean Air Acts of 1956 and 1968 and to structural changes in the economy. Smoke Control Orders made under the legislation are continuing to be made, with a 14% increase between 1980 and 1990. During this period the number of premises affected has risen by 18% and the area covered by 27%.

The above EC Directive prescribes mandatory limit values for ground level concentrations of smoke (and sulphur dioxide) to be met throughout the EC from 1.4.83. However, in the UK derogations were sought for 29 areas, allowing up to 1.4.93 to meet the limit values. The number of derogation areas was reduced to 22 in 1989. Exceedences of the Directive are listed in Table 6.10.

6.7 SUMMARY AND KEY ISSUES

- *The pollution by black smoke which afflicted UK cities in the 1950's and 1960's has been largely supplanted by other forms of particulate pollution.*
- *Urban monitoring of black smoke in the UK air involves a Basic Urban network of 76 sites and an EC Directive network of 166 sites. Both emissions and urban concentrations of black smoke have fallen in recent years.*

- *Recent developments in measurement technology allow automated hourly gravimetric measurements of airborne particles of less than 10 micrometres (termed PM_{10}).*
- *Measurements of PM_{10} at UK urban sites started only in 1992 and the concentrations have so far been below the USEPA annual standard, and the WHO 24-hour guideline.*
- *Particulate elemental carbon comprises only a minor proportion of the mass of suspended particles, but plays a disproportionate role in visibility reduction. Diesel vehicles are responsible for almost 90% of UK emissions.*
- *Particulate matter is a mixture of both primary (emitted directly) and secondary (formed in the atmosphere) components. The precise composition is variable both spatially and temporally.*
- *Sources of PM_{10} in UK urban air are not quantitatively known. Weak correlations with carbon monoxide and higher levels at roadsides suggest a contribution from motor vehicles, both in the form of direct emissions and resuspension of deposited dusts.*

6.8 RESEARCH RECOMMENDATIONS

- *In the light of recent North American studies showing correlations of PM_{10} concentration with morbidity and mortality, there is a need for quantitative information on the sources of PM_{10} in urban air and on the composition of the particles collected.*
- *Knowledge of the size distribution and chemical composition of UK urban atmospheric particulates is sorely needed.*
- *Spatially-resolved measurements of PM_{10} are required within urban areas.*
- *The role of particulate elemental carbon in soiling and corrosion of buildings requires further evaluation.*

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7 Oxidants

7.1 INTRODUCTION

Historically, oxidants were one of the earliest air pollutants investigated in urban centres throughout Europe. During the nineteenth century, ozone (O_3) was monitored using indicator papers based on the Schönbein test. Unfortunately, this technique is not quantitative and it is not possible to reconstruct these old datasets on to the same basis as current ozone observations. Nevertheless, these old studies did identify that the atmosphere possessed an inherent oxidising capacity and did initiate an interest in ozone research which has continued over the last century.

Ozone is not the only oxidant which has been identified in the UK. Both PAN (peroxyacetyl nitrate) and hydrogen peroxide have been monitored systematically at a small number of rural locations. However, there have been no recent systematic measurements of either of these oxidants in urban areas, and hence no further mention is made of them in this Chapter.

The distribution of ozone in urban areas is complex. Although the basic principles which govern this distribution are comparatively straightforward, their interplay is not. This chapter concentrates on a discussion of the basic principles, introduces the air quality data for urban areas in the United Kingdom and lists the main scientific issues which remain to be resolved. The special nature of ozone pollution means that this Chapter does not have the same structure as the other Chapters in this report. In reviewing the subject of ozone and photochemical oxidants in general, the text that follows draws heavily from the three reports of the UK Photochemical Oxidants Review Group.(1)(2)(3)

7.2 OZONE PHOTOCHEMISTRY

There are no direct and significant emission sources of ozone in urban atmospheres and almost all the ozone formed in the atmosphere was generated there by the recombination of molecular and atomic oxygen. In this respect, ozone is a secondary pollutant as opposed to a primary pollutant (eg sulphur dioxide, carbon monoxide) that is emitted directly into the atmosphere.

Most atmospheric ozone is formed in the stratosphere at altitudes between 12 and 40 km (the 'ozone layer'), and at this altitude the oxygen atoms are produced photochemically by the photodissociation of molecular oxygen with deep ultraviolet radiation:

$$(1)\ O_2 + h\nu\ (\lambda = <242\ \text{nm}) \rightarrow O + O$$

$$(2)\ O + O_2 + M \rightarrow O_3 + M$$

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

Some of this ozone is transported down through the troposphere during certain atmospheric conditions and into the boundary layer where it is finally removed at the surface of the earth.

At lower altitudes, only radiation with a wavelength greater than 290 nm is present and the only significant source of atomic oxygen is the photodissociation of nitrogen dioxide.

$$(3)\ NO_2 + h\nu\ (\lambda = 290 - 430\ \text{nm}) \rightarrow NO + O$$

$$(2)\ O + O_2 + M \rightarrow O_3 + M$$

In unpolluted air, almost all of the ozone molecules so formed react quickly with nitric oxide to reform nitrogen dioxide, re-establishing the balance between oxidising and reducing gases which is inevitably present in the sunlit atmosphere:

$$(4)\ NO + O_3 \Leftrightarrow NO_2 + O_2$$

These chemical reactions are known collectively as the photostationary state system.

If nitric oxide is oxidised to nitrogen dioxide by other species, the system is perturbed and net production of ozone results. This occurs by reaction with peroxy radicals RO_2 where R is a hydrogen atom or an organic radical, either naturally-occurring or man-made. In unpolluted air, net ozone production is driven by the oxidation of methane and carbon monoxide. In polluted

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(1) United Kingdom Photochemical Oxidants Review Group (1987) **Ozone in the United Kingdom; an Interim Report** AEA Technology, Harwell, Oxon, UK.
(2) United Kingdom Photochemical Oxidants Review Group (1990) **Second Report; Oxides of Nitrogen in the United Kingdom** AEA Technology, Harwell, Oxon, UK.
(3) United Kingdom Photochemical Oxidants Review Group (1993) **The Third Report** — in press.

air, the amount of ozone formed will depend upon the concentrations of organic radicals and nitrogen oxides resulting from human activity. The long-term effect of both processes has been the establishment of a rural ozone background concentration of 20 - 50 ppb over Europe and the United Kingdom.

During a photochemical episode, these reactions can be considerably enhanced downwind of large conurbations resulting in episodic elevations of ozone concentrations. Photochemical episodes are usually associated with anticyclonic weather systems during summer which result in hot, clear and still days. The resulting ozone 'plume' can travel many hundreds of kilometres whilst these ideal conditions persist, often crossing international boundaries(1). Although these elevated concentrations are usually present in rural areas, changes in the chemistry of the incident air mass has implications for urban air quality. These aspects are considered in Section 7.3 below.

7.3 BEHAVIOUR OF OZONE AT GROUND LEVEL IN URBAN AREAS

7.3.1 General Issues

The reactions of the photostationary state system dominate the behaviour of ozone in urban areas, and it is usual therefore to consider all three pollutants (NO, NO_2 and ozone) as a chemical family. The oxidising species, ozone and nitrogen dioxide, are inextricably linked and in many urban situations it is often simpler and preferable to consider NO_2 and O_3 and deal in total oxidant terms, O_x. The photostationary state leaves O_x unchanged (equivalent in this context to no net production of ozone) and this may aid interpretation of urban air quality data in some circumstances.

The time scales of the reactions in the photostationary state system are extremely rapid in urban areas under daylight conditions. The mean lifetimes of both nitrogen dioxide and ozone are in the order of minutes. NO_2 molecules survive only about two minutes before being photolysed to ozone and the ozone molecules survive a similar period before reacting with a molecule of nitric oxide to form NO_2. During the night, nitrogen dioxide photolysis ceases and almost all the ozone molecules in urban areas are removed by reaction with nitric oxide leading to the formation of nitrogen dioxide, with ozone concentrations usually falling to very low values.

7.3.2 Ozone Trajectory Modelling

The behaviour of ozone in urban areas is best understood by following the life cycle of the molecule in an air parcel as it travels across an urban area. This is called trajectory modelling. Initially, it is assumed that the air parcel starts in an upwind rural area, close to ground level and within the atmospheric boundary layer. Typically, such air parcels will contain 20-50 ppb of ozone, derived from ozone production within the troposphere or stratosphere, and driven by the oxidation of methane and carbon monoxide. NO_x levels will be in the order of 1-3 ppb, with NO_2 levels about double NO levels.

As the air parcel moves over the suburban fringe of an urban or industrial area, it will pick up nitric oxide close to ground level from motor traffic sources as it passes over busy roads. Rapid vertical dispersion will reduce ground level NO concentrations downwind, oxidation by ozone will occur and NO_2 concentrations will rise above the rural baseline values. The sum of $NO_2 + O_3 = O_x$ usually remains unchanged at ground level, increasing only if primary NO_2 emissions are significant.

Eventually, the air parcel will reach the urban centre and by then, the consumption of ozone by motor vehicle-derived NO will outstrip the rate of its supply by downwards transport. When this condition as reached, ground level ozone concentrations will approach zero, NO_2 concentration will approach the upwind O_x level and much of the NO_x at ground level will be present as NO and any primary NO_2 emitted. This condition will prevail during daylight in most busy canyon streets carrying large traffic flows. The relative distribution of NO, NO_2 and O_3 concentrations at other urban locations during daylight will be somewhere between the extremes represented by:

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(1) Stedman JR & Williams ML (1992) **A Trajectory Model of the Relationship Between Ozone and Precursor Emissions** Atmospheric Environment **26A**, 1272-1281.

* upwind rural distribution

O_3 = 20 - 50ppb

NO = 1 ppb

NO_2 = 2 x NO

* canyon street distribution

O_3 = zero

NO_2 = upwind O_3 (20 - 50 ppb) + primary NO_2

NO = up to 1 ppm

During the night, ozone concentrations will decrease monotonically towards the centre of urban areas because reaction with nitric oxide acts as a complete sink for ozone.

7.3.3 Vertical Distribution in Urban Areas

There have been few studies of the vertical distribution of ozone above urban areas. The first report of the Photochemical Oxidants Review Group reviewed two studies in London which showed a well mixed daytime atmosphere with no gradient, but a depletion of ozone at night time below inversions at around 200-300m.

Ground level concentrations in busy canyon streets may well be close to zero. Concentrations increase rapidly with height, reaching the rural ozone background level at some point above even the busiest of streets. Ozone lifetimes are of the order of seconds in these highly polluted conditions so vertical dispersion is usually the major determinant of nitric oxide and ozone vertical profiles. Under conditions of good mixing, ozone concentrations reach their upwind rural values within a hundred metres of street level in most urban areas.

7.3.4 Influence of Meteorology

From the above descriptions, it is clear that windspeed exerts the dominant influence of all the meteorological parameters on urban ozone levels. As wind speed increases, air parcels move in more quickly across suburban areas into the central districts and dilute NO_x concentrations. Vertical dispersion is often assisted by the turbulence generated by the increased surface roughness generated by buildings. It is often the case then that urban ozone concentrations increase with windspeed due to the lower resulting NO_x levels, the more ready supply of ozone downwards and the enhanced upwards mixing of NO.

7.3.5 Behaviour During Photochemical Episodes

Photochemical episodes invariably occur in summer with high levels of solar radiation, clear skies and high temperatures. Convection usually dominates as the driving mechanism for vertical dispersion since winds are light and frictional terms less important. During photochemical episodes, changes in the distribution of NO, NO_2 and ozone are apparent in the air parcel entering the urban environment. Upwind rural ozone concentrations are significantly higher and may well be in the range 75 - 125 ppb. Depending on the importance of local ozone formation versus long range transport, upwind NO_x levels may be significantly higher, up to 10 ppb in excess of background. Under these conditions, ground level urban ozone concentrations rarely decrease to zero even in busy canyon streets. This is because the vertical convective dispersion of NO and ozone can be efficient and in any case the availability of ozone in the incident air mass is much greater.

During photochemical episodes, therefore, ozone is often present throughout most urban areas. Generally, ground level concentrations distribution will show increases towards the suburban areas and decreases towards the more polluted central areas. In parks and open spaces, ozone concentrations will approach suburban levels which are typically a few ppb lower than upwind rural ground level concentrations.

For very large conurbations, such as the London area, net ozone production occurs during photochemical episodes. Under these conditions, downwind O_x values can be higher than upwind inflow O_x values. This net ozone production is driven by hydrocarbon oxidation through the photochemical reactions outlined in Section 7.2. Urban hydrocarbon emissions particularly from motor traffic contain highly reactive hydrocarbons. Over the time scales of an hour or so, these reactive hydrocarbons are oxidised by hydroxyl radicals, formed by ultraviolet photolysis of ozone, generating peroxy radicals. These peroxy radicals react with NO to form NO_2 and hence drive the photostationary state system in favour of net ozone production. Under suitable wind conditions, the excess ozone will be transported away from the city resulting in episodic elevations in ozone concentrations in rural areas.

Taking a cross-section along the wind direction through a large conurbation during a photochemical episode, it is possible to construct an idealized behaviour for ozone. In upwind rural areas, ozone levels are elevated due to prior ozone formation. Ground level ozone concentrations decrease slightly into the suburban areas and more steeply into central districts. Ozone concentrations rise once again passing into the downwind suburban areas. Once into the downwind rural areas, ozone concentrations continue rising and at some point, reach upwind rural levels. Further downwind, ozone concentrations continue increasing, eventually producing an ozone plume due to the conurbation. For London, the excess ozone in the plume may be up to 70 ppb over background and may be apparent 30-80km downwind of central London.

There is some evidence from mobile monitoring of ozone(1) that within large cities such as London, ozone concentrations exhibit horizontal microscale variations during photochemical episodes. Figure 7.1 shows the results of two mobile ozone monitoring transects across London during the summers of 1983 and 1984. The upper trace was taken travelling on major roads, whilst the lower trace was taken travelling on relatively minor roads. The data imply that the processess leading to the elevation of ozone towards rural concentrations may well occur over much smaller spatial scales. Whilst this implication is consistent with the local scale chemical processes known to occur in urban areas in the vertical plane (Section 7.3.3), temporally coincidental transects need to be carried out to confirm this variability. It is important that this issue is addressed, since the existence of microscale horizontal variations in ozone will have implications for the siting of continuous urban ozone monitors.

7.4 AIR QUALITY STANDARDS AND GUIDELINES FOR OZONE

The concentrations of ozone at which no effects are observed as regards animals and plants is only a little greater than the long-term background concentrations. This means that even limited episodic excursions above background levels will exceed short-term health guidelines and standards. These are listed in Table 7.1.

7.5 MEASURED CONCENTRATIONS OF URBAN OZONE

7.5.1 Monitoring of Urban Ozone Concentrations

The United Kingdom Photochemical Oxidants Review Group has reviewed the techniques used to measure ozone concentrations. The Group identified two main types of data collection:

- *fixed monitoring sites operated continuously;*
- *mobile monitoring or remote sensing data obtained on a campaign basis.*

The data from mobile measurements are referred to in Section 7.3.5. Fixed, continuous and remote sensing monitoring are reviewed below.

7.5.2 Urban Ozone Concentration Data

Much of the urban ozone concentration data available up to and including 1986 and 1990 has also been reviewed by the Photochemical Oxidants Review Group. Data for oxides of nitrogen are contained elsewhere in this report, and in the second report of the Group.

The Enhanced Urban Monitoring Initiative (EUMI), which commenced in early 1992 and includes the Enhanced Urban Network (EUN), has provided additional urban ozone monitoring data. Consequently, there are three main sources of urban ozone monitoring data to review.

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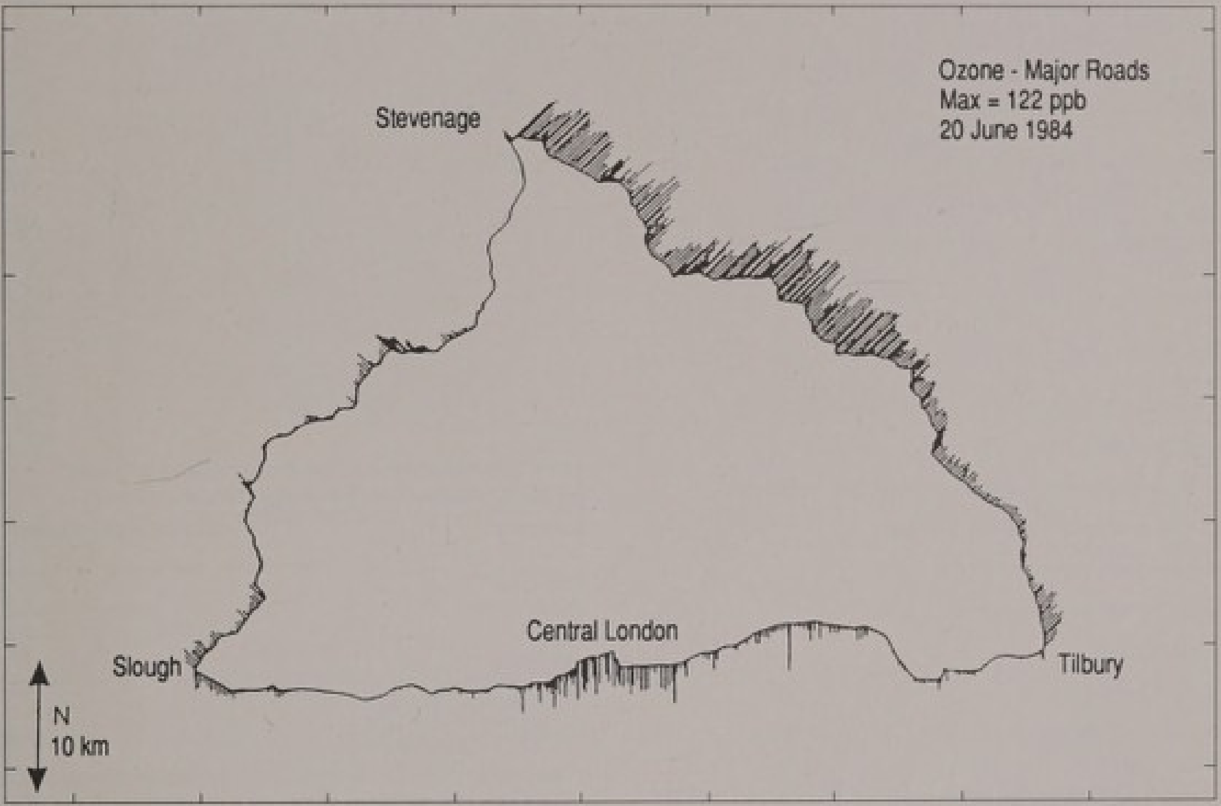
(1) Commission of the European Communities Directorate-General XII for Science, Research and Development: COST 613/2 (1992) **Report Series on Air Pollution Epidemiology: Report Number 1** (EUR 14345 EN)- Exposure Assessment.

Figure 7.1 Mobile Laboratory Measurements on Major and Minor Roads Through London During Two Ozone Episodes (7 July 1983)



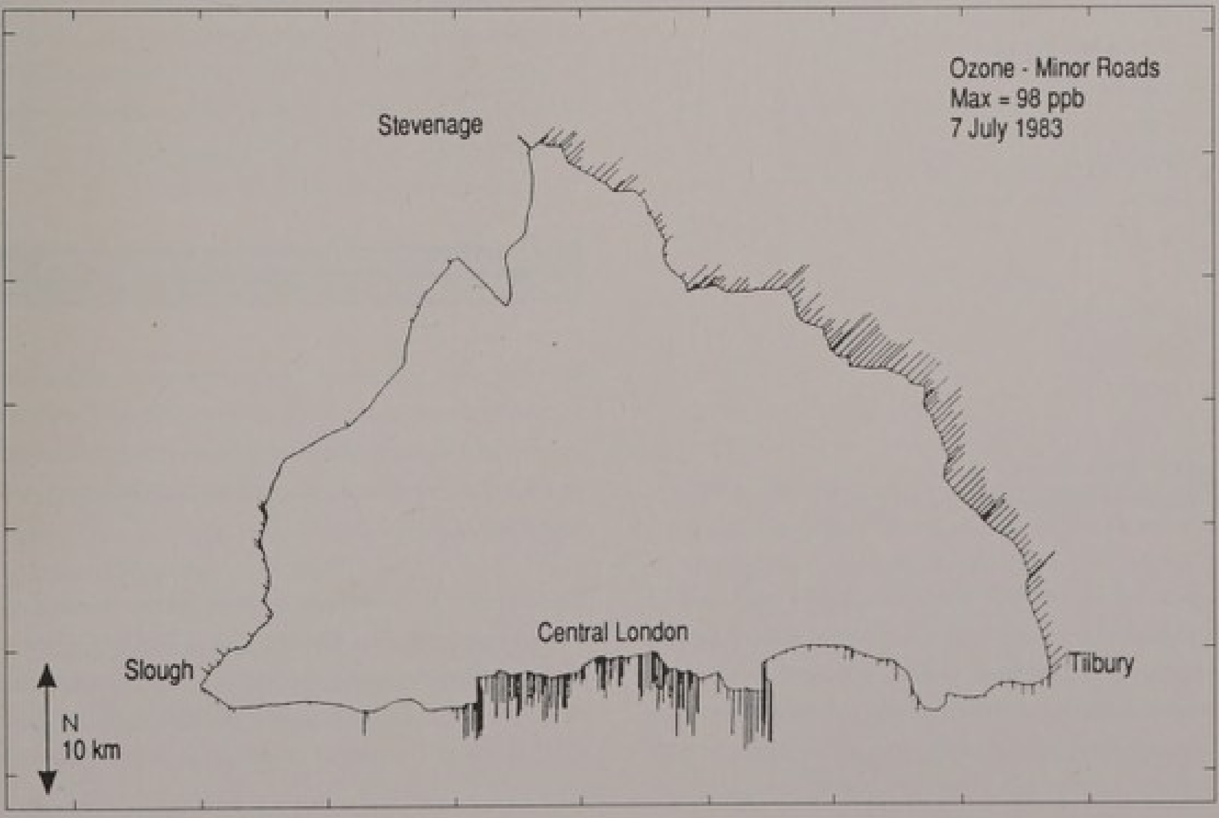


Table 7.1a: Air Quality Standards and Guidelines for Ozone (ppb)

Organisation/ Type	Growing Season Mean[a]	24-hour	8-hour	1-hour
World Health Organization				
-Health	-	-	50-60	76-100
-Vegetation	30	33	-	100
UN ECE[b]				
-Vegetation	25	-	30	75
European Commision O_3 Directive (Proposed)				
-Health	-	-	55[c]	-
-Vegetation	-	33	-	100
-Public[d]	-	-	-	90
-Public[e]	-	-	-	180
Department of the Environment				
-Health[f]	-	-	50	

[a] April - September

[b] United Nations Economic Commission for Europe

[c] non-overlapping moving average

[d] public information threshold

[e] public warning threshold

[f] provisional

Table 7.1b Department of the Environment Air Quality Bands for Ozone (Hourly Average Concentrations)

Category	Concentrations (ppb)
Very good	< 50
Good	50-89
Poor	90-179
Very Poor	≥ 180

Pre-1990 Continuous Ozone Monitoring Data

Urban ozone concentration data are available from the United Kingdom Photochemical Oxidants Review Group's database for the following monitoring sites:

- *Glasgow*
- *County Hall, London*
- *East Kilbride*
- *Central London*
- *Stevenage*
- *Cromwell Road, London*
- *Chigwell*
- *Kew*
- *Hainault*
- *Teddington*
- *Harrow*
- *Cardiff*
- *Islington*
- *National Westminster Tower, London*

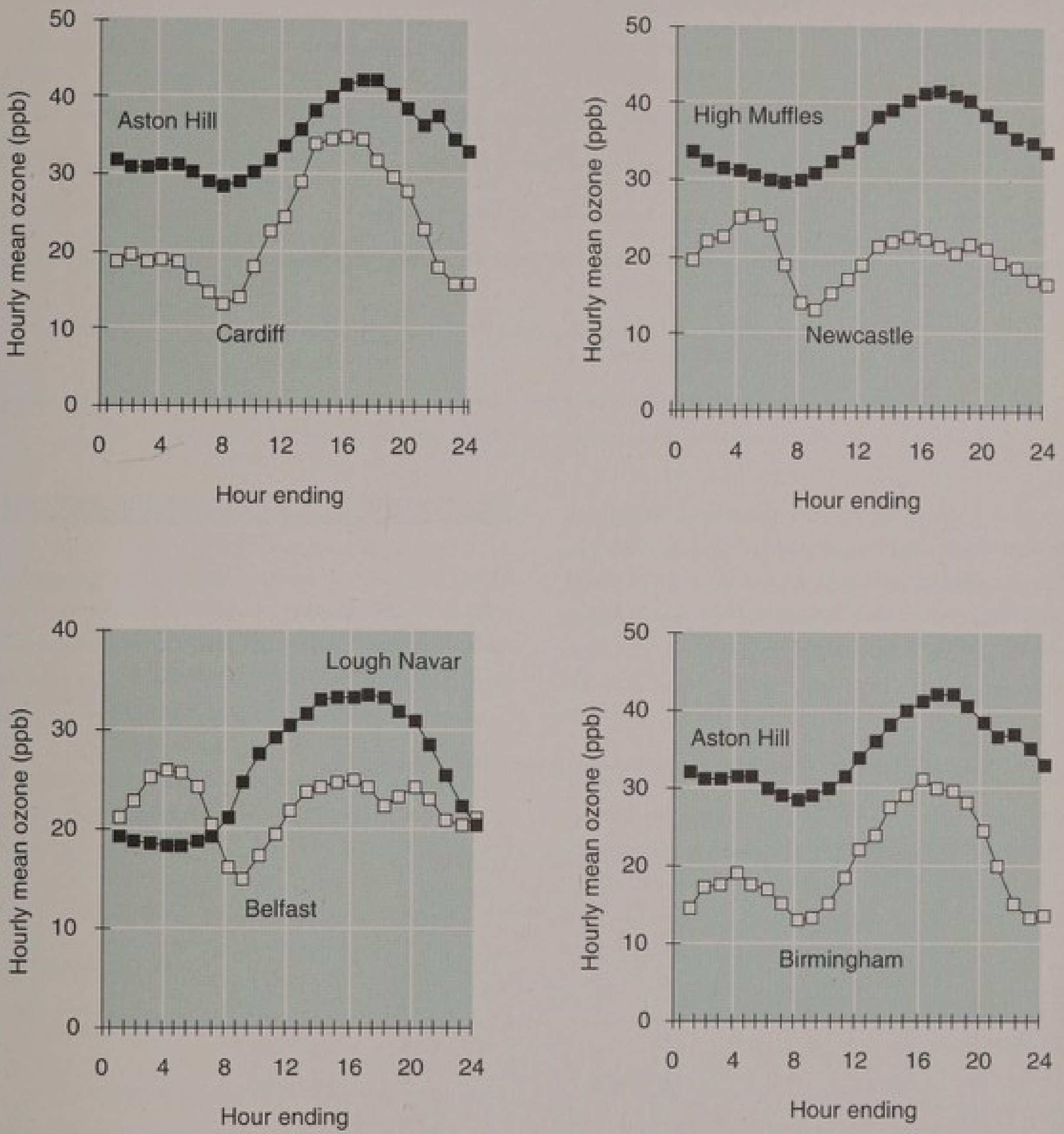
Annual mean and 98th percentile hourly mean ozone concentrations at urban sites are lower than at nearby suburban and rural sites. Generalisations become more difficult when it comes to episode statistics or extreme concentrations. It is usual for numbers of hours of peak ozone concentrations above thresholds and peak concentrations to be lower in urban areas than in comparable rural areas. However in some years there are examples in the database when this is manifestly not the case. There are occasions when maximum ozone concentrations observed anywhere in the UK during a particular episode have been reported at the London Victoria site, in particular. This may be an artefact of a sparse database containing inadequate suburban ozone monitoring data.

7.6 ENHANCED URBAN MONITORING NETWORK DATA FOR OZONE

In 1992, the Enhanced Urban Network added six telemetered ozone sites to complement the single urban site in Victoria, central London. These sites are described in Table 7.2. Summary 1992 data from this network are presented in Table 7.3.

The novelty of co-ordinated urban ozone monitoring means that unlike the Photochemical Oxidant Review Group's rural database, no single urban database has been compiled. The urban data for May, June and July 1992 illustrate features of urban ozone distribution and

Figure 7.2 Mean Diurnal and Urban Ozone Concentrations at Four EUN Sites (1 May-31 July 1992)



formation. Figure 7.2 shows 4 diurnal plots taken from urban stations and their closest comparable rural location. These plots show that:

- *Annual mean and 98th percentile hourly mean concentrations are lower at urban sites compared with nearby suburban and rural sites.*
- *Urban sites show a reduction in ozone concentrations in mid-morning. This is caused by NO mediated ozone destruction caused by elevated emissions during the morning rush hour.*

Table 7.2 Current UK Urban Ozone Monitoring Network Data Summary

Site name	Description	Grid Reference.
London, Bloomsbury	Urban parkland (Russell Square) 33m from major road	TQ 302 820
London, Bridge Place	Second floor office overlooking backstreet near Victoria Station (close to previous site, London Victoria)	TQ 289 788
Cardiff	Pedestrianised street (Frederick Street) 190m from major road	ST 184 765
Belfast	Pedestrianised street (Lombard Street) 25m from major road	n/a
Leeds	Open area (Queen Square Court) 30m from major road	SE 941 339
Newcastle	Elevated pedestrian walkway (Princess Square) over lorry delivery area 40m from major road	NZ 205 646
Birmingham	Pedestrianised area (Centenary Square) 80m from major road; 10m from small car park	SP 064 868
Edinburgh	Urban parkland (East Princess Street Gardens) 35m from major road	NT 254 738

Note: Sites in Bristol, Liverpool, Southampton, Kingston-upon-Hull and Leicester are planned for 1993 to 1994.

Figure 7.3 shows diurnal data from the London sites compared to a suburban site and two nearby rural sites. The mesoscale variations in ozone concentrations occurring between the urban atmospheric chemistry in London and Stevenage are particularly clear.

7.7 TRENDS IN URBAN OZONE CONCENTRATIONS

Figure 7.4 show long-term time series of monthly maximum and monthly mean ozone concentrations taken from the London Victoria site, which has been operational since 1972. The seasonal variations in

Figure 7.3 Diurnal Variation of Hourly Mean Ozone Concentrations (1 May-31 July 1992)

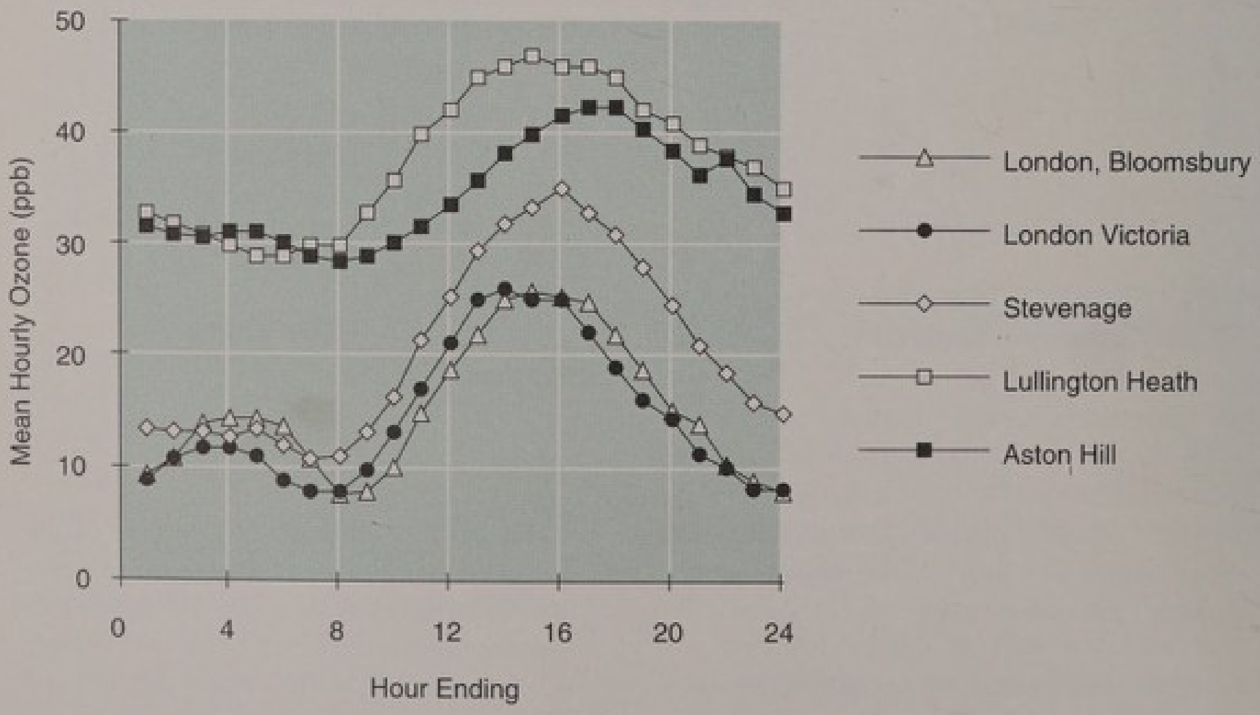


Table 7.3: UK 1992 Urban Ozone Data Summary (ppb)

Site	Start Date	Peak Hour	Peak 8-Hour	Number of hours exceeding EC Directive public information thresholds		Percentiles of 1-hour means		
				90-179ppb	≥180ppb	99	98	50
London, Bloomsbury	23/1/92	73	64	0	0	51.8	41.4	8.6
London, Bridge Place	1/7/90	76	52	0	0	49.0	41.0	10.0
Newcastle	23/2/92	68	51	0	0	43.5	40.3	16.6
Belfast	8/3/92	71	55	0	0	45.9	42.2	20.7
Birmingham	18/3/92	81	69	0	0	60.2	50.0	16.6
Cardiff	2/5/92	99	93	11	0	74.9	63.7	13.4
Edinburgh	23/9/92	22	18	0	0	19.3	17.7	6.1

episodic ozone concentration are visible as a year-by-year fluctuation in maxima mainly as a result of meteorological variations.

The third report of the Photochemical Oxidants Review Group has analysed the UK ozone database statistically in an attempt to compensate for variations such as this. The group reached the general conclusion that the weighted monthly mean at London Victoria decreased in recent years under the influence of increased NO_x emissions.

As highlighted in Chapter 10, a decline in urban NO emissions accompanying the introduction of catalytic converters will lead to an increase in central urban ozone concentrations, due to a reduction in local destruction of ozone.

7.8 OUTSTANDING SCIENTIFIC ISSUES

Current air quality policy for ozone rests on the premise that ozone is largely a rural pollutant. The evidence for this policy stance, such as we have, is summarised above. This evidence is underpinned by our understanding of the complex interplay with NO_x and the timescales of hydrocarbon oxidation which leads to photochemical ozone production.

Until the Enhanced Urban Network, monitoring in urban locations has been discontinuous, unco-ordinated and difficult to evaluate. The EUN sites are carefully located and will provide the continuous, co-ordinated and systematic urban ozone data required to provide a more complete picture of ozone concentrations at central urban sites.

The results of ozone monitoring during 1992 at the EUN sites has proved to be a valuable extension to the UK database. By careful choice of sites, reproducible and consistent urban ozone monitoring can be achieved. The main scientific conclusions from urban monitoring to date can be summarised as follows.

- *Ozone levels, as expected, are lower in urban areas compared with rural regional scale background values.*
- *There is limited evidence for microscale elevations in ozone concentration across urban areas.*

Expanding upon the last point, there remains an absence of cogent evidence for the occurrence of net ozone production within urban areas. Clearly, ground level ozone distributions in urban areas are complex and any 'hot spots' could have been missed. However, all of the spatial detail so far observed has been driven by ozone destruction and spatial detail in urban areas driven by net ozone production has not been observed. The 'London Ozone Study(1)' provided evidence of net ozone

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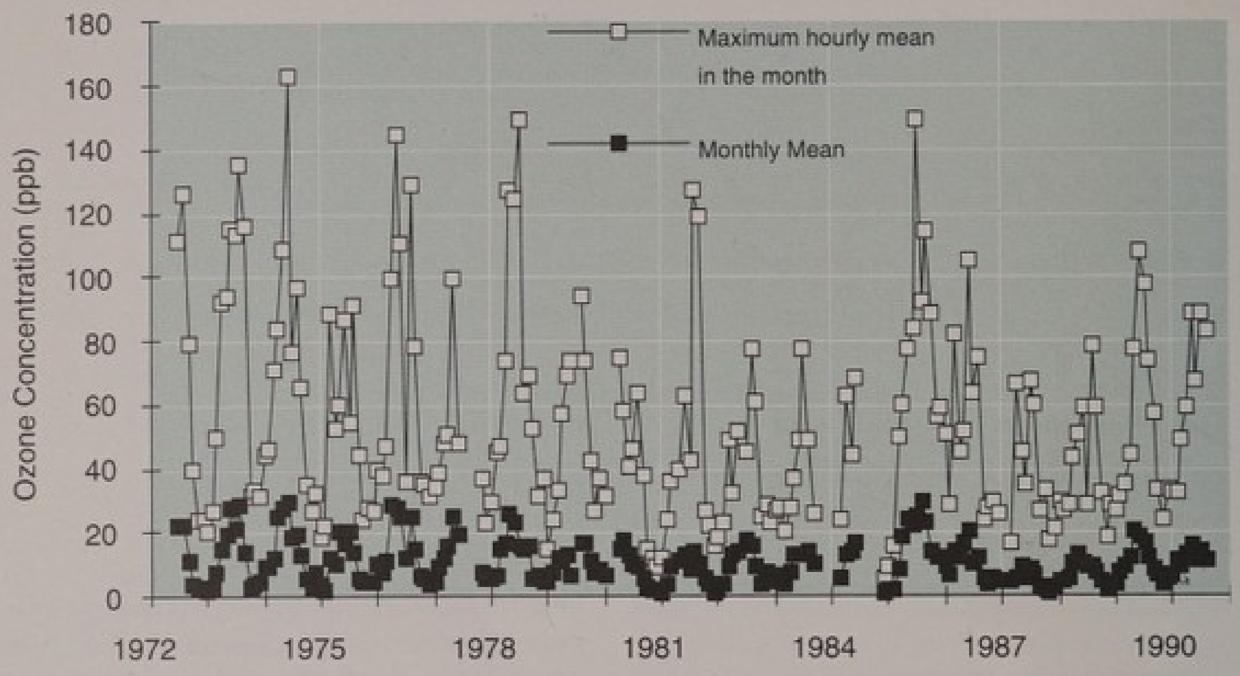
(1) Varey RH, Ball DJ, Crane AJ, Laxen DPH, Sandalls J (1988) **Ozone Formation in the London Plume** Atmospheric Environment **22**, 1335-1246.

Figure 7.4 Monthly Mean and Maximum Monthly Ozone (ppb) Concentrations Recorded at London Victoria (1972-1990)



production on the 10-80 km scale. This is in the mesoscale and ozone formation on this spatial resolution is well understood.

It may well be that ozone monitoring with fixed sites, no matter how carefully sited as in the EUN, is not the most efficient way to identify whether or not ozone hot spots do exist in urban areas. Mobile monitoring provides an alternative strategy but this is limited to the ground level in situations accessible to a vehicle. Local NO_x levels are often highest in these locations and hence they are not necessarily those where ozone hot-spots could be readily detected.

Remote sensing methods for ozone monitoring have been described in the First Report of the Photochemical Oxidants Review Group. These methods have great potential for the elucidation of the dynamics of ozone in urban areas. If the spatial resolution of LIDAR type systems can be improved, then they may have some value in the detection of any local ozone 'hot spots'. Long path ozone measurements by differential optical absorption spectroscopy (DOAS) because of their huge spatial averaging, are probably unsuitable in this context.

Diffusion tubes for ozone have been reported in the literature. If they are sensitive enough, cheap enough and can be deployed in large enough numbers, they could conceivably provide a dramatically improved understanding of average urban ozone concentrations but not of peaks.

7.9 FUTURE DEVELOPMENTS

The importance of co-ordinated urban ozone monitoring, both continuous and campaign, is likely to be central to the appraisal of planned urban pollution abatement strategies. According to some predictions, one deleterious effect of the introduction of the three-way catalyst would be to reduce ambient concentrations of NO_x and hydrocarbons, which depending upon the level of photochemical activity in a particular urban area, may well increase urban ozone concentrations towards upwind rural background. This possibility has implications both in terms of the development and validation of urban photochemical dispersion modelling as well as in relation to public exposure.

It is necessary to develop further photochemical oxidation models with greater spatial resolution.

7.10 SUMMARY AND KEY ISSUES

- *Ozone is a secondary pollutant that is not emitted directly but is formed by a complex series of photochemical reactions in the atmosphere. These reactions can either occur naturally, or, in the lower atmosphere (the troposphere) involve precursor pollutants such as nitrogen oxides and hydrocarbons.*
- *These reactions, together with the occasional intrusion of ozone from the stratosphere produce a background of tropospheric ozone.*
- *This background can be enhanced during photochemical episodes. These episodes usually occur during hot, clear, still weather, conditions which are ideal for the photochemical reactions to occur. During such episodes, ozone concentrations frequently exceed international health standards both in urban and rural areas.*
- *During photochemical episodes, pollutant emissions from large conurbations can generate a net increase in ozone as the plume travels downwind of the city. This excess ozone can be transported to rural areas often across many hundreds of kilometres.*
- *Ozone concentrations tend to be lower in urban areas because emissions of nitric oxide from motor traffic depress the photostationary state concentrations.*
- *There is evidence that increased emissions of nitrogen oxides from motor traffic have induced a downward trend in urban ozone concentrations over the last decade.*
- *Ozone monitoring in urban areas has, until recently, been limited to a handful of sites. The Enhanced Urban Network has added 6 more sites with a further 6 in 1993/94. These will form the basis of a comprehensive urban ozone database. Other techniques, such as remote sensing or mobile monitoring, are also used.*

7.11 RESEARCH RECOMMENDATIONS

- *There are considerable gaps in our knowledge of the atmospheric chemistry of ozone in urban areas, especially in relation to changes in the emission and distribution of ozone precursor pollutants.*
- *The coverage of urban ozone monitoring from carefully located, fixed sites needs to be increased and should include suburban sites. This network needs to be complemented by studies on the microscale horizontal distribution of ozone in urban environments, using LIDAR and, when proven, ozone diffusion tubes.*

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United Kingdom Photochemical Oxidants Review Group (1993) **The Third Report** (in press).

Varey RH, Ball DJ, Crane AJ, Laxen DPH, Sandalls J (1988) **Ozone Formation in the London Plume** Atmospheric Environment **22,** 1335-1246.

8 Metals

8.1 INTRODUCTION

Metals in varying concentrations are a ubiquitous component of the lower atmosphere mainly occurring in association with particulate matter. Their widespread occurrence reflects their sources:

- *natural, such as windblown soils, volcanic dust, sea salt aerosols;*
- *anthropogenic, from such activities as fossil fuel combustion, metal industries and waste incineration.*

For some metals the amounts mobilised to the global atmosphere by human activities can rival and even exceed natural sources. In industrialised countries, and urban areas especially, anthropogenic sources make the predominant contribution to measured concentrations of most atmospheric trace metals(1).

At sufficiently high concentrations in the atmosphere metals can be damaging to human health(2). Effects can result directly through inhalation as well as indirectly due to wet or dry deposition of metals to the ground and subsequent entry into drinking water and the food chain. This chapter, however, is concerned only with direct exposure to airborne metals.

A wide range of adverse effects have been reported(3) including damage to the cardiovascular and pulmonary systems, skin disease and effects on the nervous system. Certain forms of some metals have been identified by the International Agency for Research on Cancer (IARC) as being carcinogenic, notably arsenic, chromium and nickel.

The species reviewed in this chapter include all those regarded as having an impact on the environment and covers those with EC and WHO air quality standards and guidelines.

This chapter also reviews key measurement programmes undertaken in the UK and places their results in context in terms of:

- *compliance with standards and guidelines;*
- *spatial variations;*
- *temporal trends.*

8.2 SOURCES

8.2.1 General

Metals occur in the atmosphere mainly in particulate form originating from the mixing of finely divided materials from various sources. Both natural and anthropogenic sources contribute to atmospheric trace metal loads. The relative strength of each contribution varies from metal to metal as well as spatially and temporally. Natural sources mainly comprise wind blown soil material, volcanogenic emissions, sea salt aerosols and vegetation combustion products. The principal anthropogenic sources are fossil fuel combustion, ferrous and non-ferrous metallurgical industries, vehicle emissions, waste incineration and the cement and fertiliser industries. On a global scale(4)(5) natural emissions are as large as those from anthropogenic sources for many species and for some they are considerably larger. However, in industrialised countries, and in urban areas particularly, anthropogenic sources dominate.

When discussing sources some other points are worth making:

- *natural trace metal sources tend to act as 'area sources' while anthropogenic sources tend to act more as 'point sources';*
- *resuspension of deposited material to the atmosphere readily takes place in the urban environment due to such features as paved surfaces.*

8.2.2 Anthropogenic Sources

In the major anthropogenic sources materials are volatilised at high temperature and recondense on particulate matter before emission to the atmosphere. The exception is mercury which for the most part is

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(1) Demuynk M, Rahn KA, Janssens M and Dams R (1976) **Chemical Analysis of Airborne Particulate Matter During a Period of Unusually High Pollution** Atmospheric Environment **10** 21-26.

(2) Di Ferrante E (1978) **Trace Metals Exposures and Health Effects** Proceedings of the Research Seminar held at the University of Surrey, Guildford, United Kingdom, 10-13 July 1978.

(3) World Health Organization Regional Office for Europe **Air Quality Guidelines for Europe (1987)** European Series Number 23, World Health Organization, Copenhagen.

(4) Nriagu JO (1989) **Natural Versus Anthropogenic Emissions of Trace Elements to the Atmosphere: in Control and Fate of Atmospheric Metals.** Kluwer Academic Publishers.

(5) Nriagu JO and Pacyna JM (1988) **Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace Metals** Nature **333,** 134-139.

emitted as a vapour and remains in the atmosphere, principally in elemental form(1). The form of metals in particulate matter is varied and sometimes complex. They may occur as elemental metal, in inorganic form such as oxides and chlorides and in organic form such as methyl compounds. They are also present in different valency states with corresponding different reactivity and toxicity. Some species are readily soluble and others are not(2). In many cases concentrations are at the limits of detection and most methods of particulate analysis measure only the metal concentration and do not differentiate between the forms in which the metals are present. Consequently, our understanding of the speciation of metals in the atmosphere is incomplete.

A key feature of trace metal behaviour in atmospheric particles is the variation in concentrations (for some metals) with particle size. For metals of pollutant interest this behaviour is intrinsically related to their generation. Volatile materials, especially those (such as cadmium, lead and zinc) which form oxides with boiling points at or below1500°C(3), are vaporised during high temperature combustion processes. The volatile metals then condense onto the surfaces of ambient particles. This process is generally size dependent since smaller particle condensation nuclei have a larger surface area/ volume ratio. Surface analysis studies (see for example Farmer and Linton)(4) have verified that certain metals are concentrated on particle surfaces during high temperature combustion. Two important points follow from this behaviour.

- *It is generally the smaller particles produced during high temperature combustion processes which are most likely to pass through emissions controls and escape to the atmosphere, their small size allowing maximum transport from the source.*
- *These surface adsorbed metals can be readily bio-available be it through contact with lung tissues (small size will also allow maximum lung deposition) or dissolved in water supplies.*

8.2.3 UK Source Inventories

There is at present no systematic and regularly maintained source inventory for heavy metals in the UK such as those prepared for nitrogen oxides and sulphur dioxide. However, estimates of atmospheric emissions in the UK have been analysed by Warren Spring Laboratory (WSL),(5). They use data published by Pacyna(6), Pacyna and Munch(7), Hutton and Symon (8) and the UK submission to the Secretariat of the Working Group on the Atmospheric Input of Pollutants to the North Sea (ATMOS 1990)(9). Data from the Coleman analysis are summarised in Table 8.1 which has been compiled by taking the mean of the values available in the three inventories. The allocation of some species to different industrial sectors is not given in all three inventories, as noted in the Table 8.1; this applies most notably for chromium, copper and nickel for which the only data available are those from ATMOS.

The difficulty in producing accurate estimates of the emissions of heavy metals is illustrated by the considerable differences in the three inventories, an example of which is shown in Table 8.2 for cadmium. A detailed discussion of the accuracy of the estimates and the basis of the calculations is given in Coleman et al (9).

Emissions of **arsenic** are mainly from the combustion of fuels and the smelting of metals, particularly in the production of copper and nickel. In air it is present mainly as inorganic arsenic in particulate form.

Beryllium, cobalt, molybdenum and **antimony** arise predominantly from the combustion of coal and vanadium from the burning of residual and fuel oils.

Nickel also arises mainly from the burning of coal and oil and occurs principally as soluble nickel sulphate in fly ash though some is in the form of insoluble oxides.

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(1) Lindqvist O and Rodhe, H (1985) **Atmospheric Mercury: A Review** Tellus **37B** 136-159, UK.

(2) Lum KR, Betteridge JS and Macdonald RR (1982) **The Potential Availability of P, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Urban Particulate Matter** Environmental Technology Letters **3** 57-62, UK.

(3) Kaakinen JW, Jorden RM, Lawasani MH and West RE (1975) **Trace Element Behaviour in a Coal Fired Power Plant** Environmental Science and Technology **9** 862-869, UK.

(4) Farmer MB and Linton RW (1984) **Correlative Surface Analysis Studies of Environmental Particles** Environmental Science and Technology **18**,319-326, UK.

(5) Coleman P, Eggleston S, Marlow I and McInnes G, (1991) **Atmospheric Inputs to the North Sea Feasibility Study Phase One - Emission Inventory** WSL Report CR3411(AP/PA), Warren Spring Laboratory, Stevenage, UK.

(6) Pacyna JM and Munch J (1988) **Atmospheric Emissions of Arsenic, Cadmium, Mercury and Zinc in Europe in 1982** Norwegian Institute for Air Research Report 17/88, Norway.

(7) Demuynk M, Rahn KA, Janssens M and Dams R (1976) **Chemical Analysis of Airborne Particulate Matter During a Period of Unusually High Pollution** Atmospheric Environment **10,** 21-26.

(8) Hutton M and Symon C (1986) **The Quantities of Cadmium, Lead, Mercury and Arsenic Entering the UK Environment From Human Activities** The Science of the Total Environment **57,** 129-50, UK.

(9) ATMOS (1990) **Atmospheric Emissions from Industrial Sectors; Eighth meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters**, Paper 8/5/1-F, Bilthoven.

Table 8.1 UK Emissions of Heavy Metals (reference years 1979, 82, 83) (Tonnes/annum)(1)(2)(3)(4)(5)

	As		Cd		Cr		Cu		Pb		Hg		Ni		Zn	Total	
	T	%	T	%	T	%	T	%	T	%	T	%	T	%	T	%	T
Non-ferrous metals	82	34	19	40	-	-	147	25	630	7	2	5	10	1	1620	47	2510
Fossil fuel combustion	130	54	12	26	222	20	246	42	150	2	16	43	864	96	230	7	1870
Iron/steel production	9	4	4	9	870	77	97	17	490	6	2	5	19	2	480	14	1971
Cement production	8	3	1	2	26	2	-	-	30	0.3	3	8	-	-	140	4	208
Waste incineration	1	0.4	11	23	16	1	88	15	170	2	5	14	2	0.2	970	28	1263
Petrol consumption	-	-	-	-	-	-	-	-	6800	83	-	-	-	-	-	-	6800
Chlor-alkali production	-	-	-	-	-	-	-	-	-	-	9	24	-	-	-	-	9
Miscellaneous	9	4	0.5	-	-	-	2	0.3	12	0.1	0.5	-	2	0.2	2	0.1	28
Total	239		47.5		1134		580		8772		37.5	.	897		3442		14659

Table 8.2 UK Emissions of Cadmium(2)(4)(5)

Units: Tonne/annum	Pacyna	Hutton/Symon	ATMOS
Non-ferrous metals	5.5	3.7	49
Fossil fuel combustion	16	1.9	18
Iron and steel	2.6	2.3	5.9
Cement production	0.5	1.0	0.6
Waste incineration	5.2	5.2	22
Industrial application	0.3	no data	0.8
Total	31	14	97

The largest single source of **cadmium** is the smelting of non-ferrous metals, principally copper, nickel and zinc. Fossil fuel combustion also produces a significant proportion as also does waste incineration. A smaller proportion arises from the production of iron and steel.

Chromium and **manganese** enter the atmosphere mainly from processes involved in the production of iron and steel with a smaller proportion from the combustion of fossil fuels, mainly coal. In some areas both chromium and manganese in the atmosphere are dominated by wind blown dust inputs from natural sources but this is not regarded as a significant source of these metals in the urban atmosphere. Chromium occurs most commonly in the trivalent form which is insoluble and not highly toxic. However, the hexavalent form is often soluble and very toxic and carcinogenic and consequently has to be considered separately in legislation for public exposure. Manganese occurs almost entirely as an oxide and has not been found to be carcinogenic.

Copper and **zinc** come mainly from smelting processes with smaller but not insignificant emissions arising from the burning of fossil fuels. Tyre wear is also a source of zinc. The ATMOS data quoted in Coleman et al(1) suggest that for the UK the proportion of copper in the atmosphere arising from the combustion of fossil fuels is rather higher than in Europe as a whole.

The dominant source of **lead** is petrol combustion. The reference years for the data in Table 8.1 are 1979, 1982 and 1983. In January 1986 the permitted lead content of petrol was reduced from 0.40 to 0.15 g l^{-1} and there has been the subsequent progressive introduction of lead free petrol. As a result lead emissions have reduced

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(1) Coleman P, Eggleston S, Marlow I and McInnes G, (1991) **Atmospheric Inputs to the North Sea Feasibility Study Phase One - Emission Inventory** WSL Report CR3411(AP/PA), Warren Spring Laboratory, Stevenage, UK.

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(5) ATMOS (1990) **Atmospheric Emissions from Industrial Sectors; Eighth meeting of the Working Group on the Atmospheric Input of Pollutants to Convention Waters**, Paper 8/5/1-F, Bilthoven.

Table 8.3 UK Annual Lead Emissions 1984-90, kT(1)

Year	Vehicle emissions	Total emissions
1984	7.2	8.2
1985	6.5	7.5
1986	2.9	3.9
1987	3.0	4.0
1988	3.1	4.1
1989	2.6	3.6
1990	2.2	3.2

substantially and it has been estimated(1)(2) that between 1984 and 1990 annual vehicle emissions in the UK decreased from 7.2 kT to 2.2 kT as shown in Table 8.3. On the assumption that emissions from other sources have remained constant during that period this still leaves petrol combustion as the major source but with the production of ferrous and non-ferrous metals, fossil fuel combustion and waste incineration producing significant proportions of the present total.

Unlike the other heavy metals **mercury** occurs in the atmosphere predominantly as a vapour. There is some uncertainty over its speciation although it is generally accepted that more than 80% is in elemental form(3) with a small proportion appearing as soluble methyl mercury compounds. Elemental mercury can also be oxidised in the atmosphere to soluble forms which can be deposited at the ground by wet or dry processes. The main sources of mercury in the atmosphere are fossil fuel combustion, chlor-alkali processes and waste combustion.

8.3 ATMOSPHERIC TRACE METAL MEASUREMENTS IN THE UK

8.3.1 General

There are several sources of information on metals in the UK atmosphere in both urban and rural areas. These sources comprise the following:

- *long-term measurements of a range of metals by Warren Spring Laboratory and AEA Technology, Harwell at urban and non-urban sites*
- *metal specific studies (eg Hg and Pb) at various sites by Warren Spring Laboratory*
- *various ad hoc studies by local authorities/ government agencies, research establishments and industry.*

The first category, appropriately augmented by the second, gives the best overall picture especially as regards temporal trends. The latter type of study is still useful, however, especially since they tend, in a number of instances, to focus on 'hot spots' where exceedence of guidelines and standards could potentially occur.

8.3.2 Long-Term Programmes

Warren Spring Laboratory Multi-element Survey

Warren Spring Laboratory operate the Multi-element Survey on behalf of the Department of the Environment. The programme began in 1976 with measurements at 20 monitoring sites in a range of UK urban locations. After two years the programme was reduced to cover five stations which had produced relatively high concentrations of the 16 elements monitored during the first two years.

The objective of the Multi-element Survey is to provide data on concentrations and trends of a range of trace elements at the five urban locations. A description of each of these sites is given in Table 8.4.

The outputs of the Warren Spring Laboratory measurement programme comprise a series of Summary Reports for each year's results. The most recent report(4) analyses trends between 1976/77 and 1988/89 as well as summarising the most recent year's data (see for example Tables 8.5 and 8.6).

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(1) Coleman P, Eggleston S, Marlow I and McInnes G, (1991) **Atmospheric Inputs to the North Sea Feasibility Study Phase One - Emission Inventory** WSL Report CR3411(AP/PA), Warren Spring Laboratory, Stevenage, UK.

(2) McInnes G (1987) **The Impact of the Reduction in the Lead Content of Petrol on Airborne Lead Concentrations in the United Kingdom from January 1986** WSL Report LR633(AP)M, Warren Spring Laboratory, Stevenage, UK.

(3) Lindqvist O and Rodhe, H (1985) **Atmospheric Mercury: A Review** Tellus **37B,** 136-159.

(4) McInnes G (1990) **Multi-element Survey: Summary and Trend Analysis 1976/7-1988/9** WSL Report LR771(AP)M, Warren Spring Laboratory, Stevenage, UK.

Table 8.4 Summary of Long-term Monitoring Sites

	Period of Operation	Site Characteristics
WSL Urban(a)		
Motherwell	All from 1976	Civic Centre, 500m south of Ravenscraig Steel Works
London Brent		Industrial/residential, 50m from the busy North Circular Road
London VB Road(b)		City centre, commercial area close to Victoria Railway Station
Leeds(c)		City centre, commercial/residential
Glasgow		East of city centre in an area with several non-ferrous metal works
AEA Technology,Urban		
Trafford-A	1978-89	Residential
Trafford-F	1971-89	Residential
Manchester-R	1975-89	Residential
Manchester-B	1975-88	Industrial/Residential
London-B	1975-89	Residential
London-L	1976-82	Residential
Walsall	1976-89	Industrial
AEA, Technology Rural		
Chilton, Oxfordshire	From 1972	Rural
Styrrup, Nottinghamshire	From 1972	Rural but close to collieries
Trebanos, Wales	From 1972	Rural, on outer limit of industrial area
Wraymires, Cumbria	From 1970	Rural

(a) From November 1983 responsibility for operating all but the Central London site was transferred to Northern Environmental Consultants Ltd (now ERL North). As, Ti and V ceased to be measured at these sites. Different analytical procedures were used by WSL and NECL; however, detailed intercomparison studies showed reasonable agreement between the two.

(b) Site location changed in 1990.

(c) Two sites (2058 and 2059) operated in Leeds between 1976 and 1978; 2058 only from 1978-1981 and 2059 only from 1981 onwards.

AEA Technology, Harwell

As a part of their survey of atmospheric trace elements in the UK, AEA Technology, Harwell have maintained monitoring stations at several UK locations for a number of years (Table 8.4) from the mid-70s to 1989. The work was funded in the main by local authorities.

It is also worth noting that AEA Technology operated a programme of rural (or non-urban) monitoring sites over a similar time period in a study funded by the DOE.

Outputs of the AEA Technology measurement programmes take the form of annually published reports of a year's summarised data(1)(2).

8.3.3 Mercury and Lead Measurements

Mercury

Due to the nature of its atmospheric behaviour (ie it is present predominantly as a vapour rather than in particulate form), Hg requires a different sampling strategy to other routinely monitored trace metals. In a study(3) over the years 1975-1979, Warren Spring Laboratory monitored atmospheric mercury concentrations at a variety of sites. Warren Spring Laboratory focused their study on areas which might be expected to display heavy contamination (eg chlor-alkali works, sewage works, etc) through to urban and remote rural areas less likely to show any serious pollution.

Lead

Reflecting concern over health implications as well as EC and UK Government initiatives, Pb is the most widely studied and monitored of atmospheric trace

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(1) Cawse PA (1981) **A Survey of Atmospheric Trace Elements in the UK: Results for 1979 UK AEA Research Establishment** Report AERE-R 9886. AEA Technology, Harwell, Oxon, UK.

(2) Lee DS, Fox AA, Garland JA, **A Statistical Analysis of Atmospheric Trace Element Concentrations in Urban Areas of the United Kingdom** (1992) AEA-EE-0285. AEA Technology, Harwell, UK.

(3) Turner AC, Barrett CF, Carroll JD, McInnes G, Kraggs M and Richardson J (1983) **Airborne Mercury Concentrations in the UK** WSL Report LR441(AP)M, Warren Spring Laboratory, Stevenage, UK.

Table 8.5 WSL Multi-element Survey Annual Average Concentrations(a) (ng m^{-3}); Mean of Five Sites and Overall Percentage Reduction, April 1976 - March 1989

Element	76/77	77/78	78/79	79/80	80/81	81/82	82/83	83/84	84/85	85/86	86/87	87/88	88/89	5 Yr mean 1985-89	%age reduction 1976-89
Arsenic(b)	6.5	7.1	6.1	-	-	7.0	12	-	-	-	-	-	-	-	-
Beryllium	0.30	0.25	0.25	-	-	0.34	0.24	-	-	-	-	-	-	-	-
Cadmium	7.1	4.9	4.4	4.5	2.7	2.5	1.7	2.8	2.6	2.4	1.5	3.2	3.5	2.6	51
Cobalt	1.8	1.9	1.3	-	-	1.5	1.2	-	-	-	-	-	-	-	-
Chromium	18	19	9.5	-	-	16	12	16	5.6	6.4	7.8	7.1	6.9	6.8	62
Copper	54	42	38	28	26	23	21	20	22	24	47	35	18	29	67
Iron	1670	1420	1070	1000	1000	1000	960	990	790	930	830	860	920	870	45
Manganese	64	58	40	29	26	30	28	33	29	29	26	28	24	27	63
Molybdenum(b)	4.6	3.4	3.2	-	-	3.1	1.9	-	-	-	-	-	-	-	-
Nickel	22	22	20	-	-	14	12	12	12	12	8.9	11	14	12	36
Lead	820	610	650	620	480	500	430	380	370	350	220	200	190	270	77
Antimony(b)	9.0	9.7	8.9	-	-	5.9	4.0	-	-	-	-	-	-	-	-
Titanium(b)	74	62	68	-	-	20	15	-	-	-	-	-	-	-	-
Vanadium(c)	50	33	48	22	20	24	23	19	32	14	14	14	10	17	80
Zinc	860	820	440	270	200	200	120	110	100	130	120	160	170	140	80

(a) Year ending March

(b) Concentrations at or below limits of WSL detection. Results to be treated with caution

(c) Results from Central London site only

metals. As well as featuring in the long-term programmes described in Section 8.3.2, a number of individual studies of Pb have also been undertaken in the UK(1)(2)(3)(4). The principal monitoring networks can be summarised as follows.

- *Following decisions to reduce and eventually eliminate Pb in petrol DOE commissioned Warren Spring Laboratory to set up a series of monitoring sites. These comprised seven initial locations (2 rural, 2 suburban, 3 kerbside) to which an eighth was added as part of DOE's Blood Lead Programme.*
- *A kerbside site at Cromwell Road has been operated continuously (1988 excepted) by Warren Spring Laboratory since 1979 as part of the DOE Continuous Monitoring Survey.*
- *London Scientific Services (formerly the Scientific Services Branch of the Greater London Council) has operated a number of monitoring stations in London to assess the effects of reductions of Pb in petrol. One site at County Hall has operated since 1977.*

Pb has also been monitored in Warren Spring Laboratory's Multi-element Survey and AEA Technology's surveys described earlier.

8.3.4 Ad Hoc Studies

Numerous ad hoc studies of atmospheric trace metals have been carried out in recent years. Typically, these have focused on a specific industry or area to assess its contribution to ambient concentrations of atmospheric trace metals. Some of the more important ones are summarised below.

- *Warren Spring Laboratory were commissioned, by the Industrial Air Pollution Inspectorate of the Health and Safety Executive (now Her Majesty's Inspectorate of Pollution), in the early to mid-1980s to carry out monitoring surveys in the vicinity of a series of ferrous and non-ferrous metal works.*
- *In recent years, prospective developers (eg of waste incinerators) have commissioned environmental baseline surveys of atmospheric trace metals at*

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(1) McInnes G (1991) **Airborne Lead Concentrations in the United Kingdom** 1985-1989 WSL Report LR814(AP), Warren Spring Laboratory, Stevenage, UK.

(2) Carroll JD and McInnes G (1988) **Multi-element and Sulphate-in-particulate Surveys: Summary of Eighth Year's Results** (1983/84) WSL Report LR655(AP)M, Warren Spring Laboratory, Stevenage, UK.

(3) Hickman AJ (1989) **Measurement of Particulate Lead on the M4 Motorway at Harlington, Middlesex (5th Report)** Research Report 184, Transport and Road Research Laboratory, Department of Transport, UK.

(4) Schwar MJR and Ball DJ (1983) **Thirty Years on: A Review of Air Pollution in London** Greater London Council, UK.

Table 8.6 Urban and Rural Concentrations of Metals in Particulate Matter (ng m^{-3})

	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Fe	Sb	Ti	V	Zn	Sn
WSL Urban (1977-90)																
Motherwell	-	-	2.9	-	16	31	69	-	23	260	2100	-	-	-	260	-
London-B	-	-	2.2	-	8.5	22	16	-	11	690	600	-	-	-	91	-
London-VBR	-	-	3.8	-	11	26	21	-	13	530	1000	-	-	25	140	140
Leeds	-	-	2.4	-	12	28	43	-	13	350	760	-	-	-	130	-
Glasgow	-	-	5.6	-	9.6	45	20	-	13	380	670	-	-	-	780	-
Mean	7.7(a)	0.28	3.4	1.5(a)	11	30	34	3.2(a)	15	440	1000	7.5(a)	4.8(a)	25(b)	280	
AEA Technology Urban (1970-89)																
Trafford-A	4.7	-	3.6	-	17.2	-	-	-	17.2	267	737	-	-	15.4	113	
Trafford-F	7.1	-	4.8	-	6.0	-	-	-	9.8	427	737	-	-	20.9	115	-
Manchester-R	6.5	-	5.8	-	5.8	-	-	-	13.2	341	667	-	-	32.2	134	-
Manchester-B	7.6	-	6.5	-	8.1	-	-	-	13.2	380	1013	-	-	26.7	339	-
London-B	6.1	-	9.2	-	4.4	-	-	-	11.9	670	938	-	-	26.5	126	-
London-L	7.2	-	4.9	-	4.9	-	-	-	14.5	529	1031	-	-	31.3	177	-
Walsall	93.9	-	28.3	-	24.9	-	-	-	31.2	1316	1687	-	-	21.2	2634	-
Mean(c)	6.5	-	5.8	-	7.7	-	-	-	13	440	850	-	-	26	170	-
Irish Sea (1982)(d)	-	-	0.26	0.13	1.6	2.4	6.5	0.19	2.4	30	226	-	26	5.9	15	
AEA Technology Rural (1972-81)																
Chilton	3.6	-	<2.5	0.34	2.9	18	15	<0.9	6.5	120	280	2.2	22	11	98	-
Styrrup	15	-	<5	0.59	12	32	43	<1.2	9.3	240	670	5.1	40	15	230	-
Trebanos	6.5	-	4.2	9.6	11	29	15	<1.0	91	140	370	2.7	28	12	130	-
Wraymires	2.7	-	<2.5	0.25	2.2	17	11	<0.6	4.5	67	240	1.7	20	7.6	59	-
Mean	7.0	-	<3.5	0.39(e)	7.0	24	21	<0.9	6.8(e)	140	390	2.9	28	11	130	-

(a) Data for 1976/77, 77/78, 78/79, 81/82 and 82/83 only. Concentrations at or below detection limits, to be treated with caution (McInnes, 1990)

(b) Measurements at London, Vauxhall Bridge Road only

(c) Walsall not included in mean

(d) Data from Murphy (1985)(2) summarising samples collected over two weeks in 1982.

(e) Trebanos not included in mean

specific locations as part of the Environmental Assessment and Integrated Pollution Control procedures.

A number of University research establishments have also studied various aspects of atmospheric trace metal behaviour over the years(1)(2).

8.3.5 Measurement Methods

In contrast with the monitoring of many other atmospheric pollutants (eg CO, SO_2) metals measurement is a two stage process whereby samples are collected and then at a later date analysed in the laboratory.

A variety of sampling and analytical techniques have been used to measure trace metal concentrations in air. It is worth noting that for the major long- term programmes (eg the Warren Spring Laboratory Multi-element Survey) detailed intercomparison studies have been undertaken where techniques differ.

Two important features generally common to measurement methods in the UK over the last 15 to 20 years are as follows:

- *total atmospheric particulate samples are collected and analysed with no distinction between particle sizes;*
- *typically one sample might span a week, thus temporal resolution tends to be less than for many other pollutant measurements and 'peak' short-term incidents pass unrecorded.*

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(1) Lin FJ (1988) **The Solid State Speciation and Solubility of Elements in Marine Aerosols** PhD Thesis, University of Liverpool, UK.
(2) Murphy KJ (1985) **The Trace Metal Content of the Atlantic Aerosol** PhD Thesis, University of Liverpool, UK.

8.4 COMPLIANCE WITH STANDARDS AND GUIDELINES

8.4.1 Introduction

Air quality standards and guidelines for a series of metals are given in Table 8.7. The only metal for which there is EC air quality legislation is Pb with a limit value of 2 µg m^{-3} as an annual average. The US EPA ambient air quality standard for lead is 1.5 µg m^{-3} as a quarterly average. There are WHO air quality guidelines for Cd, Mn, Pb, and V. In addition, using the criteria of the International Agency for Research on Cancer (IARC), WHO have identified As, Cr and Ni as being carcinogenic and give no safe threshold for atmospheric concentrations.

The Health and Safety Executive quote Long-term Occupational Exposure Limits (OEL) for each metal listed. An OEL is based on exposure for eight hours per day, 5 days per week. The HSE OEL values are sometimes, for example by HMIP, reduced by a factor of 40 to allow for exposures in excess of a working week and for elderly or ill persons being exposed.

It is worth noting that although most metals are not covered by legislation as regards their atmospheric concentrations, emissions of such metals (eg Cr, Mn, Cu, Ni, As, Sn, Cd, Sb, V, Co and Hg) from certain types of industrial and commercial sources are regulated by HMIP and local authorities.

8.4.2 Lead

As previously stated, lead is the best studied (both spatially and temporally) of the atmospheric trace metals. A comparison between annual average concentrations recorded at monitoring stations and the various guideline and limit values yields the following general conclusions.

- *The Warren Spring Laboratory Multi-element Survey did not record any exceedences of the EC limit value. However, the lower limit of the WHO guideline was exceeded at Brent in each year up to 1985/6 and occasionally at Leeds, Central London and Glasgow prior to 1986. Subsequent to the reduction of lead in petrol (in 1986) no exceedences of the WHO guideline have been reported.*

Table 8.7 EC Limit, WHO Guidelines and HSE Occupational Exposure Limits (µg m^{-3}) for Heavy Metals

Metal	EC Limit	WHO Guideline	OEL/40
Arsenic (As)	-	nsf(a)	2.5(b)
Beryllium (Be)	-	-	0.05(c)
Cadmium (Cd)	-	0.001-0.005 rural(d) 0.01-0.02 urban(d)	1.25(b)
Cobalt (Co)	-	-	2.5(c)
Chromium (Cr)	-	nsf(a)	1.25(e)
Copper (Cu)	-	-	5(e)(f)
Manganese (Mn)	-	1	25(e)(f)
Nickel (Ni)	-	nsl(a)	2.5(b)(g)
Lead (Pb)	2	0.5-1.0	3.75(e)
Iron (Fe)	-	-	25(e)
Antimony (Sb)	-	-	12.5(e)
Titanium (Ti)	-	-	125(e)
Vanadium (V)	-	1 (24-hour average)	1.25(e)(h)
Zinc (Zn)	-	-	25(e)(i)
Tin (Sn)	-	1	50(e)
Mercury (Hg)	-	-	1.25(e)

(a) No safe limit - carcinogen; WHO have assigned a unit lifetime risk for a concentration of 1 µg m^{-3}. These are As: 4x10^{-3}; Cr(VI) 4x10^{-2} and Ni: 4x10^{-4}.

(b) Maximum Exposure Limit

(c) Occupational Exposure Standard under review

(d) The WHO rural guideline for cadmium is lower than the urban due to the possibility of it entering the food chain

(e) Occupational Exposure Standard

(f) Fume

(g) Soluble salts

(h) Divanadium pentoxide fume and respirable dust

(i) Zinc chloride fume

- *The Warren Spring Laboratory 'Lead in Petrol' survey recorded only one exceedence of the EC limit value (Manchester, 1985). Cardiff exceeded the WHO upper guideline value in 1985 and both Cardiff and Manchester exceeded the lower WHO guideline values in the years up to 1989, albeit with concentrations steadily falling each year.*

- *Warren Spring Laboratory's continuous monitoring site at Cromwell Road registered exceedences of the upper WHO guideline (1985) and lower guideline (1986 and 1987). The EC limit was not exceeded.*

- *Pre-1980 studies by the GLC showed various exceedences, at building facade and kerbside locations, of the EC limit and WHO guidelines. However, given the experiences elsewhere it is extremely unlikely that such exceedences would have been sustained into the mid and late 1980s.*

The picture for lead has been dramatically influenced by the reduction of lead in petrol and this is discussed further in Section 8.5.2.

8.4.3 Other Metals

Of the remaining metals covered by the Warren Spring Laboratory Multi-element Survey, Cr, Cu, Fe, Mn, Ni and Zn did not approach OEL/40 or WHO guideline values at any time. Cd exceeded the lower WHO guideline value in Glasgow in the first two years of the survey and approached it at Vauxhall Bridge Road site in 1988/89. No exceedences of the OEL/40 have been recorded.

Since vanadium is only routinely monitored at one site on a weekly basis comparisons with the WHO 24hr average guideline are difficult. However, results indicate that exceedence of this guideline value is possible.

Data for mercury are sparse for recent years. Warren Spring Laboratory's extensive survey in the late 1970's did not record any exceedences of the WHO guideline or OEL/40 values. However, one site, near a chlor-alkali plant in Runcorn, approached the WHO guideline.

8.4.4 Summary

Although data are sparse in some instances, long-term monitoring programmes show relatively few exceedences of limit and guideline values and then primarily in the case of lead only, for which metal marked improvements have occurred since the mid-1980s. The more recent exceedences (for Pb) recorded in Manchester and Cardiff during the 'Lead in Petrol Survey' were for kerbside locations where particularly high concentrations might be expected anyway.

8.5 SPATIAL AND TEMPORAL DISTRIBUTIONS

8.5.1 Spatial Distributions

Due to the small number of monitoring stations for atmospheric trace metals it is difficult to make anything more than very general statements regarding their distributions on a national basis and across individual towns and cities.

Data from various sources previously mentioned in this chapter are summarised in Table 8.6. They include, for comparative purposes, data from AEA Technology, Harwell rural studies and atmospheric concentrations measured over the Irish Sea. Several features are apparent.

- *The recorded concentrations (averaged over several years to exclude temporal variations) clearly illustrate the relationship between atmospheric metal loading and source proximity/strength.*
- *Lead behaves differently from the other metals. Although it may exhibit some dependence on point industrial sources this is almost completely masked by inputs from petrol combustion. Thus the highest lead levels are measured in areas of dense traffic movement and heavy road use.*
- *For virtually all the remaining metals, the highest concentrations are recorded for monitoring sites in areas which combine heavy industry (eg Motherwell, Glasgow) with dense urbanisation.*
- *This behaviour is also reflected in the AEA Technology, Harwell 'rural' data set. Two of the sampling sites, although rural, are close to industrial activity and tend to exhibit higher metal concentrations than the other two.*
- *The set of offshore samples from above the Irish Sea indicate that even the 'rural' sampling sites are quite strongly influenced by pollutant inputs. It is worth noting that the Irish Sea concentrations cannot be regarded as 'pristine background' levels since that area is polluted. The Warren Spring Laboratory 'Lead in Petrol' Survey and site specific studies of ferrous and non-ferrous metal works*(1) *also illustrate some key points on atmospheric metal distributions.*
- *Site specific studies of metal works using directional samplers (ie samplers which operated only when the wind was blowing from the selected source, allowing comparison with background levels) allowed a clear identification of such activities as a source of elevated atmospheric metal concentrations. Clear relationships were apparent between proximity to the source and levels recorded.*

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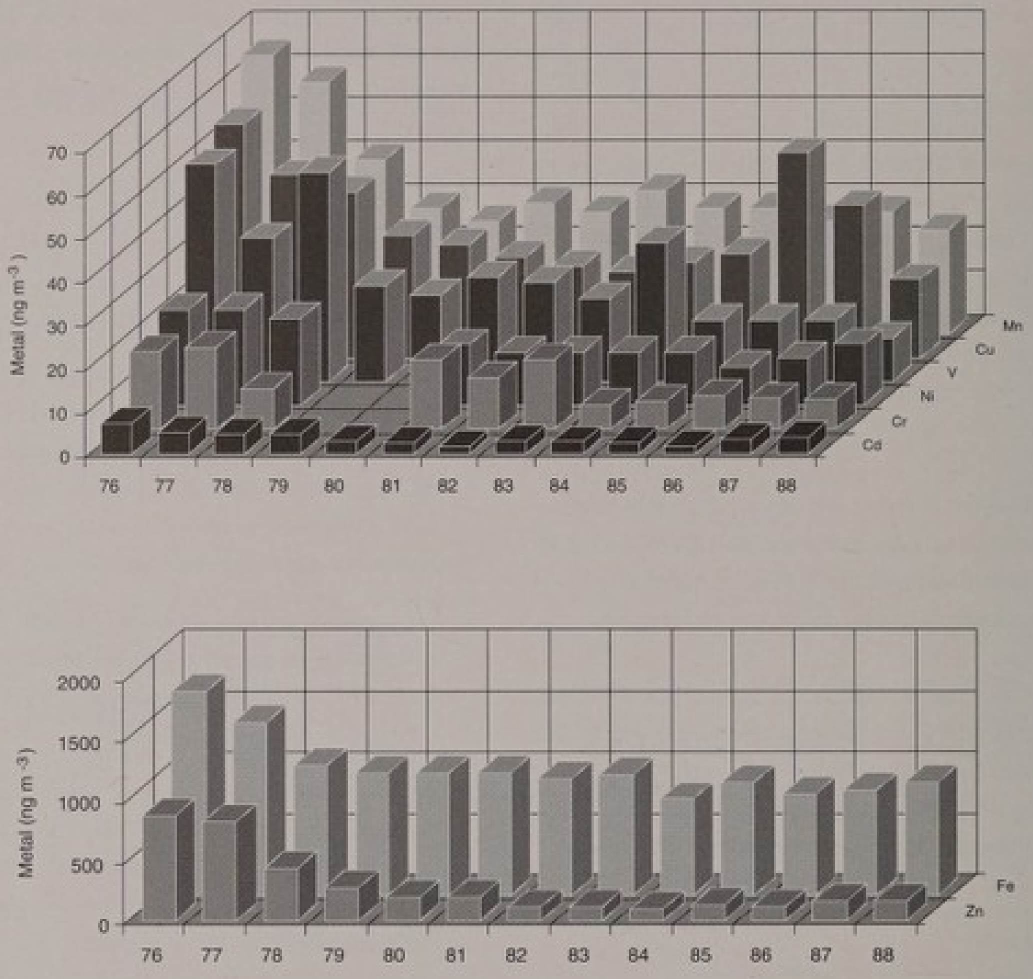
(1) Davis BJ and Clayton P (1985) **Assessment of Particle and Heavy Metal Concentrations in the Atmosphere Around the Commonwealth Smelting Ltd Works at Avonmouth** WSL Report LR553(AP)M, Warren Spring Laboratory, Stevenage, UK.

Figure 8.1 Annual Mean Concentrations (ng m^{-3}) of Various Metals (1976-1988)



- *The Warren Spring Laboratory 'Lead in Petrol' Survey sampled at a range of sites from rural, through urban to 'kerbside' locations. Kerbside concentrations were typically double or triple those measured in the general urban environment indicating a fairly rapid fall-off in concentrations with distance from the immediate source.*

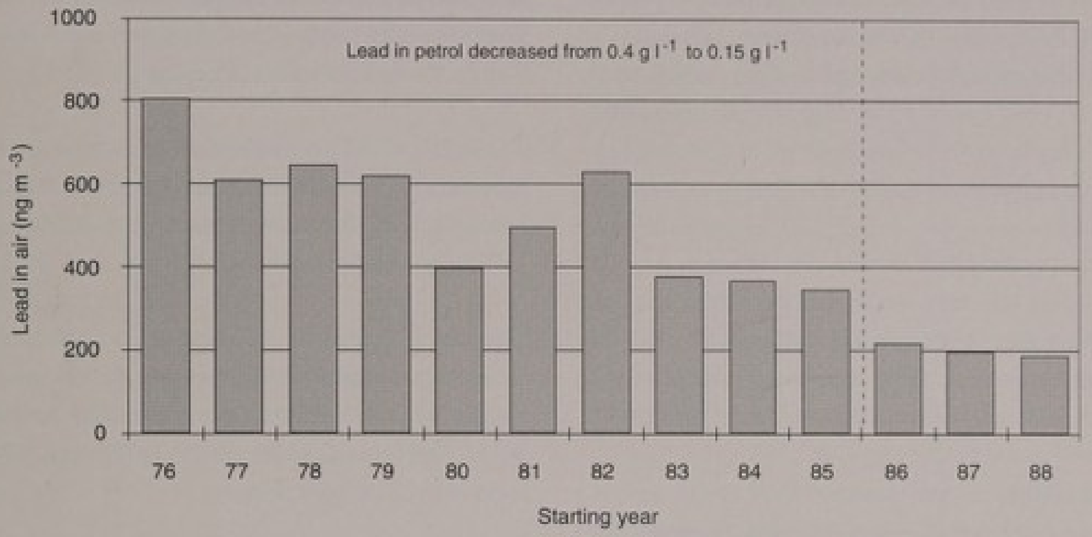
To summarise, preparation of an atmospheric metal concentration distribution map of the UK is not a readily feasible undertaking based on present data. However, data collected to date show quite clearly that when measured values are smoothed out to allow for meteorological fluctuations the general pattern to emerge is a straightforward relationship between metal loadings and source strength/proximity. Measured rural levels indicate that there is an annual average threshold, or 'background' below which levels will not drop (except in the remoter parts of the UK) and superimposed on this are higher concentrations around urban and industrial areas. Within urban and industrial areas higher concentrations again will be recorded in closer proximity to discrete sources.

8.5.2 Temporal Variations

Long-term temporal variations in atmospheric metal concentrations are clearly illustrated by the Warren Spring Laboratory 'Multi-element Survey' data which span the years 1977 to 1989, supplemented by the 'Lead in Petrol Survey' data for lead. The trends for the metals (Cd, Cr, Cu, Fe, Mn, Ni, V and Zn) for which data are most complete are shown in Figure 8.1. The trend for Pb is shown separately in Figure 8.2.

Setting aside minor inter-site variations the key trend to emerge, for metals other than lead, is one of a steady year by year fall between 1977 and the early to mid 1980's

Figure 8.2 Annual Mean Concentrations (ng m^{-3}) of Lead in Air (1976-1988)



followed by a levelling out. At this stage it is difficult to determine whether the overall decline in metal levels is due to improvements in control technology/working practices or whether it is linked to the decline of the manufacturing industry in the UK. Certainly, lower levels were noted in Glasgow after the shut-down of a number of local metal works in the early 1980s(1). It is also worthy of note that monitoring at AEA Technology, Harwell's rural sites between 1972 and 1979 also showed significant downward trends for most metals(2).

Lead, however, is a quite different matter. Figure 8.2 shows annual average lead levels over the years from a number of sampling programmes. Overall, lead concentrations, averaged over the five Warren Spring Laboratory 'Multi-element Survey' sites, for example, have reduced by 77% over the years 1976/7-1988/9. Such reductions reflect initiatives on the reduction of the lead content of petrol. This is clearly illustrated in one instance by the sharp drop in measured concentrations following the reduction in the maximum lead content of petrol (from 0.4 to 0.15 g l^{-1}) in January 1986; note the difference between 1985 and 1986 levels.

8.6 SUMMARY AND KEY ISSUES

A review of atmospheric trace metal concentrations in the urban UK, in the context of various air quality limits and guidelines, as well as spatial distributions and temporal trends in concentrations, allows several key conclusions to be made.

- *The results from a number of long-term monitoring programmes show that exceedences of applicable guidelines and limits have rarely occurred.*
- *In the early years of monitoring programmes exceedence of the EC limit for annual average lead concentrations occurred at a few sites. Such exceedences were not sustained into the latter part of the 1980's after the reduction of lead content in petrol.*
- *Annual average trace metal concentrations show a clear dependence on proximity to source and source strengths. Away from urban areas all metal levels tend to decline. Within urban areas lead concentrations tend to be higher, especially in proximity to areas of heavy traffic. Other metal levels reflect their inputs from such activities as ferrous and non-ferrous metal refining.*
- *Most of the metals (other than lead) showed a steady decline in annual average concentrations in the early years of the surveys. In the early-mid 1980's this decline tended to level out with little or no discernible trend upward or downward to date.*

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(1) McInnes G (1990) **Multi-element Survey: Summary and Trend Analysis 1976/7-1988/9** WSL Report LR771(AP)M, Warren Spring Laboratory, Stevenage, UK.

(2) Cawse PA (1981) **A Survey of Atmospheric Trace Elements in the UK: Results for 1979 UK AEA Research Establishment** Report AERE-R 9886. AEA Technology, Harwell, Oxon, UK.

- *The picture is quite different for lead. Lead has shown a more or less steady decline (in excess of 75% over the thirteen years of Warren Spring Laboratory's survey for example). The effect of the reduction of lead in petrol from 0.4 to 0.15 g* l^{-1} *in January 1986 was clearly reflected by a drop in atmospheric concentrations.*

It is apparent from this review that although a good understanding has been obtained of the overall level of atmospheric trace metals present in the urban UK, and their long-term trends, there are still some areas where there are gaps in our knowledge and understanding of atmospheric trace metal behaviour.

8.7 RESEARCH RECOMMENDATIONS

The main thrust of future studies should centre on continued monitoring at a small number of stations to determine long-term trends in atmospheric trace metal concentrations. Various subsidiary studies could be incorporated into the main programme to aid our understanding of atmospheric metal behaviour. Possible areas of study could include:

- *establishing short-term fluctuations (see eg Demuynk et al, 1976);*
- *size fractionation studies (see eg Davidson and Osborn, 1987);*
- *surface analysis or chemical leaching tests to determine the environmental availability of atmospheric metals (see eg Harrison, 1987).*

The sampling strategy for vanadium may need to be reviewed since the applicable air quality standard for this metal is based on a 24-hour average.

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9 Organic Compounds

9.1 INTRODUCTION

The majority of organic compounds emitted to the atmosphere are contained within a class known as volatile organic compounds (VOCs). Methane is an important component of VOCs, but its environmental impact derives principally from its contribution to global warming and to the production of ozone in the background troposphere. Regional effects derive from non-methane VOCs (NMVOCs). Most VOCs are non-toxic or are present at levels well below guideline values. Others, such as benzene and 1,3-butadiene, are carcinogens. The major environmental impact of VOCs, however, lies in their potential for generating the secondary pollutant, ozone, via photochemical oxidation.

VOCs comprise a wide range of chemical compounds including hydrocarbons (alkanes, alkenes, aromatics), oxygenates (alcohols, aldehydes, ketones, acids, ethers) and halogen containing species. They are generated from a variety of sources, with transport related emissions as a major contributor. Thus cities have significant vehicular sources of VOCs and concentrations are generally higher there than in rural areas.

The photochemical oxidation of VOCs is a slow process, and their transport results in the generation of ozone at considerable distances from the source of its precursors. In addition, enhanced NO concentrations in urban areas cause significant reactive loss of ozone whose concentration is, in consequence, higher in rural than in heavily trafficked urban areas. Urban VOC levels, whilst not in themselves health- threatening in the most part, need to be established because of their involvement in ozone formation. Sources must be identified and legislation formulated to reduce emissions of the more effective ozone generators, along with emissions of toxic compounds.

Toxic organic micropollutants (TOMPS) are a further important class of atmospheric pollutants. They include polycyclic aromatic compounds (PAC) which contain polycyclic aromatic hydrocarbons (PAH) as a sub-set. Urban emissions of PAC are primarily transport- related although there are some contributions from stationary combustion. The lighter PAH are present mainly in the vapour phase while the heavier species are carried on particles. Polychlorinated biphenyls (PCBs), largely deriving from the decommissioning of industrial plant, and dioxins, generated by combustion of chlorine containing compounds, are other important toxic pollutants.

Compared with other pollutants, the monitoring of speciated organic compounds in urban regions of the UK is in its infancy and long time-series databases are not available. This chapter, therefore, concentrates on reviewing the current situation with little attempt at data analysis or source reconciliation. The Department of the Environment's programmes for monitoring both VOCs and TOMPS should, in the coming years, provide an excellent basis for such an analysis.

9.2 VOLATILE ORGANIC COMPOUNDS

9.2.1 Nature and Sources

(i) Sources of NMVOCs

Volatile organic compounds are emitted by a wide variety of sources. The best estimates of total emissions are contained in emissions inventories; for the UK, these are prepared by the Warren Spring Laboratory as part of the National Atmospheric Emissions Inventory. The inventory is based on literature reviews, consultation with experts such as the current trade associations, and monitoring eg by sampling and analysis of exhaust gases. A summary of best emission estimates of NMVOCs is given in Table 9.1. Each overall source is subdivided into detailed sources and Table 9.2 provides a further breakdown for solvents, which represent 35% of the total stationary NMVOC emissions (Table 9.1).

The estimates in Tables 9.1 and 9.2 refer to total UK emissions; they are not partitioned between urban and non-urban sources. A useful sub-division for stationary sources is between domestic and industrial emissions. The primary domestic emissions are paint, 77 kta^{-1}, consumer products, 190 kT yr^{-1}, adhesives, 4 kT yr^{-1} and combustion 45 kT yr^{-1} giving a total domestic NMVOC emission of 316 kT yr^{-1}, which represents 14% of the national total for stationary emissions. The major sources for overall emissions, both of which are particularly significant in urban areas, are transport (30%) and solvent use (24%).

Table 9.1 Best Emission Estimates for NMVOCs(1) from Stationary Sources

	emission/kT yr^{-1}	Percentage of overall total
(i) Stationary sources		
Solvent use	787	24.2
Oil Industry	451	13.9
Chemical Industry	445	13.7
Stationary Combustion	51	1.6
Food Industry	373	11.5
Iron and Steel	12	0.4
Waste Disposal	56	1.7
Agriculture	98	3.0
Miscellaneous	5	0.2
Sub Total	2275	70.2
(ii) Mobile sources		
Petrol exhaust	652	20.0
Diesel exhaust	175	5.4
Petrol evaporation	143	4.4
Sub Total	970	29.8
Overall Total	3245	100.0

Emissions inventories are valuable in the development of abatement strategies. The UN ECE Convention on Transboundary Air Pollution requires a 30% reduction from 1988 levels in total VOC emissions, with sector-dependent compliance dates in the late 1990's. Some sectors, eg parts of the painting and printing industries, are controlled under the 1990 Environmental Protection Act. Road transport emissions are not controlled under the Act, but EEC directives 91/441/EEC (cars) and 91/542/EEC (heavy duty vehicles) have been issued which will regulate emissions. A variety of abatement strategies are being developed. For the paint sector, for example, these include product reformulation, improved application techniques and the use of carbon adsorption, bioscrubbers and biofilters. Petrol exhaust emissions will be reduced by equipping cars with three way catalysts. Significant emissions from petrol evaporation will be controlled by improvements in fuel supply systems and by reducing petrol volatility. Reduction levels of 41- 45% in petrol exhaust and evaporative emissions are envisaged by 1999, the target figure depending on the growth of road transport.

(ii) Speciated NMVOC Emission.

The environmental impact of NMVOCs varies considerably from compound to compound. Some are carcinogens (eg benzene and 1,3-butadiene). All VOCs are precursors of ozone through photochemical oxidation, but their photochemical ozone creation potentials (POCP) vary widely (see Section 9.2.2). Current legislation is aimed at limiting total NMVOC emissions but there is a powerful case for the formulation of future legislation in species specific terms. Indeed in formulating strategies for reducing NMVOCs, the Department of the Environment is already incorporating POCP assessments. Table 9.3 provides the most recent emissions inventory update of speciated NMVOCs. The most prevalent compounds for the sectors included in Table 9.3 are the butanes, which are emitted principally from petrol, solvents and petrol refining and distribution, and toluene which is mainly produced from petrol exhausts and from solvents. The higher volatility of the butanes accounts for the substantial evaporative, refining and distribution losses. POCP values for these compounds are n-butane 41.4, i-butane 31.5, and toluene 56.3 (see Section 9.2.2), and they represent significant sources of ozone.

Table 9.2 Breakdown of Solvent NMVOCs Emission Sources

	Emission/kT yr^{-1}
Painting industry	278.0
Printing industry	41.4
Metal cleaning	46.4
Dry cleaning	13.0
Adhesives	58.0
Oil extraction	10.0
Leather industry	3.0
Pharmaceuticals	40.0
Consumer products	190.0
Agrochemicals	37.4
Other	70.0
Total	**787.2**

A comparison of Tables 9.1 and 9.3 shows significant differences in overall emission estimates and in estimates for certain sectors. These discrepancies reflect developments in our understanding of sources of VOCs. Table 9.3 gives the speciated breakdown which corresponds to the overall sector-specific emission figures published in the 1991 Digest of Environmental Protection and Water Statistics (No. 14), while Table 9.1 refers to Warren Spring Laboratory's latest best estimates, which have incorporated significant revisions in certain sectors. Speciated emissions have not yet been calculated for these latest estimates. These same considerations account for the difference between Table 9.1 and Tables 2.1 and 2.2.

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(1) Marlowe IT (1992) **Interim Report — Emissions of Volatile Organic Compounds in the United Kingdom: A Review of Emission Factors by Species and Process** WSL Report LR882(PA), Warren Spring Laboratory, Stevenage, UK.

Table 9.3 Speciated VOCs Emission Inventory (1991)

Emissions (T)	Petrol Exhaust	Diesel Exhaust	Petrol Evaporation	Stationary Combustion	Solvents	Pro-cesses	Petrol Refn/Distn	Gas Leaks	Ind/Resid Waste	Species Sub-total	Species Sub-total
ethane	6,074	875	0	6,516	0	0	0	22,049	1,408	36,922	1.86
propane	1,374	0	0	3,506	0	0	0	5,512	1,408	11,800	0.59
n-butane	22,988	7,000	28,586	1,422	34,522	0	45,560	1,587	0	141,666	7.14
i-butane	10,517	3,500	14,986	3,200	34,522	0	25,125	1,279	0	93,129	4.69
n-pentane	10,704	4,900	10,325	5,206	1,561	0	11,685	573	0	44,953	2.27
i-pentane	31,382	7,350	14,515	852	1,561	0	18,318	706	0	74,682	3.76
n-hexane	10,226	1,750	2,889	349	12,534	0	1,662	278	0	29,686	1.50
2-methylpentane	12,377	3,675	4,319	349	1,561	0	3,095	186	0	25,561	1.29
3-methylpentane	8,611	1,925	2,874	349	1,561	0	1,930	115	0	17,363	0.88
2,2-dimethylbutane	1,615	700	858	349	1,561	0	777	0	0	5,859	0.30
2,3-dimethylbutane	3,230	700	1,058	349	1,561	0	804	62	0	7,763	0.39
n-heptane	4,407	0	1,005	171	1,561	0	224	145	0	7,513	0.38
2-methylhexane	8,265	0	1,321	171	1,561	0	402	68	0	11,788	0.59
3-methylhexane	6,614	0	1,333	171	1,561	0	382	76	0	10,136	0.51
n-octane	4,037	0	386	171	1,561	0	28	68	0	6,251	0.32
methylheptanes	32,298	0	964	171	1,561	0	99	75	0	35,167	1.77
n-nonane	438	0	0	171	22,807	0	0	43	0	23,459	1.18
methyloctanes	3,704	0	0	168	22,807	0	0	12	0	26,692	1.35
n-decane	869	0	0	0	22,807	0	0	17	0	23,694	1.19
methylnonanes	1,960	0	0	0	22,807	0	0	2	0	24,769	1.25
n-undecane	3,920	0	0	0	22,807	0	0	0	0	26,727	1.35
n-duodecane	3,920	0	0	0	3,121	0	0	0	0	7,041	0.35
ethylene	51,010	19,250	0	8,666	0	0	0	0	0	78,925	3.98
propylene	25,395	5,950	0	4,526	0	0	0	0	0	35,871	1.81
1-butene	4,268	875	2,131	20	0	0	3,484	0	0	10,778	0.54
2-butene	10,989	0	3,647	20	0	0	5,789	0	0	20,445	1.03
2-pentene	5,449	0	3,361	109	0	0	4,583	0	0	13,501	0.68
1-pentene	4,087	1,225	701	109	0	0	858	0	0	6,979	0.35
2-methyl-1-butene	1,060	0	958	109	0	0	603	0	0	2,731	0.14
3-methyl-1-butene	1,060	875	958	109	0	0	603	0	0	3,606	0.18
2-methyl-2-butene	1,060	875	1,873	109	0	0	2,023	0	0	5,941	0.30
2-methyl-1-propene	4,937	0	0	20	0	0	0	0	0	4,958	0.25
acetylene	30,711	5,600	0	531	0	0	0	0	0	36,841	1.86
benzene	39,251	4,550	3,346	943	0	0	1,367	377	0	49,835	2.51
toluene	88,015	1,400	8,094	152	52,797	0	1,166	105	0	151,729	7.65
o-xylene	30,584	1,400	2,274	38	23,235	0	80	9	0	57,619	2.90
m-xylene	38,927	1,400	2,688	38	23,235	0	255	9	0	66,552	3.35
p-xylene	38,926	1,400	2,688	38	23,235	0	121	9	0	66,417	3.35
ethylbenzene	25,493	1,400	1,888	38	0	0	121	1	0	28,940	1.46
n-propylbenzene	3,002	875	586	38	6,394	0	11	0	0	10,906	0.55
i-propylbenzene	1,498	875	172	38	6,394	0	3	0	0	8,980	0.45
1,2,3-trimethylbenzene	4,019	875	443	38	6,394	0	4	0	0	11,773	0.59
1,2,4-trimethylbenzene	17,141	875	2,288	38	6,394	0	27	4	0	26,767	1.35
1,3,5-trimethylbenzene	5,356	875	558	38	6,394	0	8	0	0	13,229	0.67
o-ethyltoluene	4,506	875	529	38	6,394	0	8	0	0	12,350	0.62
methyltoluene	7,507	875	915	38	6,394	0	16	0	0	15,745	0.79
p-ethyltoluene	7,507	875	915	38	6,394	0	16	0	0	15,745	0.79
formaldehyde	5,590	10,325	0	984	0	0	0	0	92	16,992	0.86
acetaldehyde	1,245	1,750	0	217	0	0	0	0	0	3,212	0.16
propionaldeheye	1,633	1,750	0	217	0	0	0	0	0	3,600	0.18
butyraldehyde	265	1,750	0	217	0	0	0	0	0	2,232	0.11
i-butyraldehyde	0	1,750	0	217	0	0	0	0	0	1,967	0.10
valderaldehyde	136	0	0	217	0	0	0	0	0	352	0.02
benzaldehyde	1,344	0	0	217	0	0	0	0	0	1,560	0.08
acetone	499	3,500	0	217	14,966	0	0	0	0	19,182	0.97
methylethylketone	0	0	0	217	0	0	0	0	0	217	0.01
methyl-i-butylketone	0	0	0	217	7,448	0	0	0	0	7,665	0.39
methanol	0	0	0	217	0	0	0	0	0	217	0.01
ethanol	0	0	0	217	13,099	0	0	0	0	13,316	0.67
methyl acetate	0	0	0	0	0	0	0	0	0	0	0.00
ethyl acetate	0	0	0	0	15,728	0	0	0	0	15,728	0.79
isopropyl acetate	0	0	0	0	0	0	0	0	0	0	
n-butyl acetate	0	0	0	0	9,518	0	0	0	0	9,518	0.48
s-butyl acetate	0	0	0	0	9,518	0	0	0	0	9,518	0.48
dichloromethane	0	0	0	0	8,738	0	0	0	0	8,738	0.44
1,1,1-trichloroethane	0	0	0	0	24,522	0	0	0	0	24,522	1.24
tetrachloroethylene	0	0	0	0	17,275	0	0	0	0	17,275	0.87
trichloroethylene	0	0	0	0	23,730	0	0	0	0	23,730	1.20
methylcyclohexane	0	0	0	0	4,514	0	0	0	0	4,514	0.23
styrene	0	0	0	0	7,894	0	0	0	0	7,894	0.40
n-butanol	0	0	0	0	31,355	0	0	0	0	31,355	1.58
diacetone alcohol	0	0	0	0	19,078	0	0	0	0	19,078	0.96
formic acid	0	0	0	0	0	0	0	0	46	46	0.00
acetic acid	0	0	0	0	0	0	0	0	46	46	0.00
methylchloride	0	0	0	852	0	0	0	0	0	852	0.04
CFCs	0	0	0	0	5,215	0	0	0	0	5,215	0.26
Unknown	0	68,600	16,569	12,263	33,614	0	2,760	632	0	134,439	6.78
propan-2-ol	0	0	0	0	8,969	0	0	0	0	8,969	0.45
2-methylpropanol	0	0	0	0	22,070	0	0	0	0	22,070	1.11
butan-2-ol	0	0	0	0	19,034	0	0	0	0	19,034	0.96
butanone	0	0	0	0	16,586	0	0	0	0	16,586	0.84
2-methylpentan-4-one	0	0	0	0	22,987	0	0	0	0	22,987	1.16
cyclohexanone	0	0	0	0	11,919	0	0	0	0	11,919	0.60
cyclohexanol	0	0	0	0	4,514	0	0	0	0	4,514	0.23
butylglycol	0	0	0	0	18,729	0	0	0	0	18,729	0.94
methoxypropanol	0	0	0	0	4,962	0	0	0	0	4,962	0.25
3,5-dimethylethylbenzene	0	0	0	0	10,730	0	0	0	0	10,730	0.54
3,5-diethyltoluene	0	0	0	0	10,730	0	0	0	0	10,730	0.54
Total	**652,000**	**175,000**	**143,000**	**56,000**	**787,000**	**0**	**133,995**	**34,000**	**3,000**	**1,983,995**	**100.00**

(iii) Methane

Sources and best emission estimates for methane are listed in Table 9.4. Once again, these values are national totals and are not readily disaggregated into urban and rural sources. Not all potential sources are incorporated in the current inventory; for example there is no estimate for animal waste. Methane is non-toxic and has a very low POCP value. Its major significance is as a greenhouse gas although in the background troposphere it is the primary determinant of hydroxyl radical and ozone concentrations.

(iv) Natural NMVOCs

A wide variety of NMVOCs are produced by plants. The most important compounds are isoprene, which is primarily emitted by deciduous trees, and monoterpenes which are primarily emitted by conifers. Other sources, eg bracken and gorse, also contribute although our understanding of biogenic NMVOC emission sources is far from complete. The National Atmospheric Emissions Inventory estimate of biogenic NMVOC emissions is 80 kT yr^{-1}; despite the difficulties of making this estimate, it has been suggested that the figure is unlikely to lie outside the 50 - 100 kT yr^{-1} range. These natural sources provide only a minor contribution to total VOCs and are of little significance in urban areas. This situation contrasts markedly with that in the USA, where tree cover is much higher and natural VOC emissions are substantial, even in urban areas.

Table 9.4 Best Emission Estimates for Methane[1]

	Methane emission/kT yr^{-1}	% of total
Oil industry (offshore flaring and venting)	20.0	4.5
Chemical industry	4.4	0.1
Stationary combustion:		
domestic	52.7	1.1
industrial, power generation	8.8	0.2
Iron and steel industry	0.5	0.1
Waste disposal:		
landfill	1980.0	40.6
other	61.8	1.2
Agriculture (animal respiration)	1204.4	24.7
Gas leakage	350.0	7.2
Coal Mines	990	20.3
Total	**4872.6**	**100.0**

9.2.2 Effects on Health and Oxidant Formation

(i) Non-carcinogenic Effects

Exposure to organic chemicals at concentrations higher than usually encountered in urban areas may be associated with a wide range of effects. Guideline values for health effects, other than cancer, are based upon expert evaluation of the toxicological information available on compounds, usually in isolation. Possible additive or synergistic effects are difficult to take into account and are usually ignored. An attempt to accommodate likely variations in individual susceptibility is made by the use of 'uncertainty' factors (also known as safety or protection factors) in moving from the No Observed Adverse Effect Level (NOAEL) or the Lowest Observed Effect Level (LOEL) to the recommended guideline. Uncertainty factors are also applied when extrapolation from animal data is unavoidable. For example, in the WHO Air Quality Guidelines for Europe 100 ppm of toluene was identified as the Lowest Observed Adverse Effect Level in man. A factor of 50 (24-hour averaging time) was then applied and a guideline of 2 ppm recommended. The use of a factor of 50 was justified on the grounds of: "the data on negative effects in humans, the lack of evidence of a chronic effect and the minimally adverse nature of the observed effects at the Lowest Observed Effect Level". 2 ppm is well in excess of typical urban concentrations.

Malodorous compounds affect the quality of life and guideline values have been developed for a range of compounds, based on detection and nuisance thresholds. For many compounds, these values lie below the toxic guideline values. For toluene, for example, the guideline value is 270 ppb, based on the detection threshold.

(ii) Carcinogenic Effects

Carcinogens may be divided into those thought to act via a direct effect upon the genetic material of the cell (genotoxic carcinogens) and those thought to act by

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(1) Marlowe IT (1992) **Interim Report — Emissions of Volatile Organic Compounds in the United Kingdom: A Review of Emission Factors by Species and Process** WSL Report LR882(PA), Warren Spring Laboratory, Stevenage, UK.

other means (non-genotoxic carcinogens). For the former it is generally accepted that no threshold can be defined and thus there can be no definition of an absolutely safe level of exposure. For non-genotoxic carcinogens, where the mechanism of action is well understood, it may be possible to define a level of exposure below which no effects would be expected. If, however, the mechanism of effect is not well understood then the default option of assuming "no safe level" is generally adopted.

Compounds such as benzene and benzo(a)pyrene are genotoxic carcinogens. Chlorinated hydrocarbons as a group include both genotoxic and non-genotoxic carcinogens. Certain hormones and compounds capable of inducing enzymes, eg phenobarbitone, are among the large and diverse group of non-genotoxic carcinogens.

The perceived impossibility of defining a safe level of exposure for genotoxic carcinogens has led some workers to adopt a risk estimation approach. Working from such human data and animal-based data as are available, attempts have been made to calculate the risks associated with exposure to a given level of the carcinogen in question. This approach was adopted by WHO in the preparation of the WHO Air Quality Guidelines for Europe in 1987. Alternatively the approach may be used to calculate a level of exposure thought to be likely to be associated with a given excess risk of developing some defined disease. Such approaches are sometimes referred to as examples of (Quantitative Risk Assessment (QRA)).

The approach suffers from a number of defects or difficulties of methodology. Inevitably one assumption has to be made: that one can extrapolate satisfactorily from data related to high level exposures and predict effects at low levels of exposure. The outcome of such extrapolation depends upon the shape of the dose response curve. This is far from clearly understood and may or may not conform to a straight line. A second assumption, often inevitable, is that one may extrapolate satisfactorily from animal studies to man. This is also much less firmly based than would be desirable.

In addition to these difficulties is the danger that the results of a quantitative risk assessment may be adopted uncritically and interpreted as an accurate and precise estimate of risk.

In the UK the Department of Health Committee on Carcinogenicity has adopted a cautious approach to QRA holding that if Quantitative Risk Assessments are well founded they should be taken into account in assessing the likely risk attendant upon a given exposure to a carcinogen. QRA is seen then as a part of a risk assessment.

The Expert Panel on Air Quality Standards has accepted the advice of the Committee on Carcinogenicity and has decided not to adopt Quantitative Risk Assessment as a standard means of setting air quality standards for the UK. Quantitative Risk Assessment exercises will of course be taken into account in the setting of standards for carcinogens.

(iii) Secondary Effects

The principal environmental impact of most NMVOCs is the generation of photochemical smog. Ozone is an important constituent of such smogs and its health effects are discussed in Chapter 7. The sequence of reactions which leads to ozone generation is initiated by the photolysis of ozone itself to generate electronically excited oxygen atoms, O*:

$$O_3 + h\nu \rightarrow O^* + O_2$$

Most O* are collisionally deactivated to form ground state oxygen atoms; a small fraction reacts with water vapour to form hydroxyl radicals:

$$O^* + H_2O \rightarrow 2OH$$

The principal reactive sink for a hydrocarbon, RH, is reaction with OH to form a radical R which initiates the sequence of oxidation reactions:

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

$$R + O_2 \rightarrow RO_2$$

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

The NO_2 is photolysed to regenerate NO and to produce ground state oxygen atoms which in turn form ozone:-

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$

Table 9.5 POCP Values and Rate Constants for Reaction with OH for Representative VOCs

VOCs	POCP(1)	k(a) (cm^3 $molecule^{-1}$ s^{-1})	Lifetime(b) (hours)	Distance scale(c) (km)
methane	0.7	5.5×10^{-15}	59400	1.07×10^{6}
ethane	4.0	2.8×10^{-13}	1240	22300
ethylene	100.0	2.6×10^{-12}	134	2410
n-butane	41.4	2.1×10^{-12}	165	2970
benzene	18.9	1.3×10^{-12}	267	4810
toluene	56.3	6.4×10^{-12}	54	972

(a) Data from; Kinetics Data Centre, University of Leeds

(b) 1/e lifetime with [OH] = 8×10^{5} molecules cm^{-3}

(c) Distances travelled with wind speed of 5 m s^{-1} in 1/e lifetime

Thus, even for this simple reaction scheme, each ozone molecule consumed by photolysis generates two ozone molecules via the oxidation of two RH molecules. The chain is, however, continued by the further oxidation reaction of the alkoxy radical. This series of reactions can generate more ozone, the yield depending on the nature of the alkoxy radical, RO. The potential of a VOC to generate ozone is quantified via its photochemical ozone creation potential (POCP) determined using atmospheric trajectory calculations which incorporate detailed chemistry. Representative POCP values, based on a value of 100 for ethylene, are given in Table 9.5. The values correlate approximately with the rate constant, k, for initial OH attack on the VOCs, which determines the timescale of the transformation, and the molecular weight of the VOCs, which is a crude indicator of the ozone yield per VOCs molecule reacted. Unsaturated compounds, eg alkenes and aromatics, have high POCP values.

The table also shows the atmospheric lifetime of each VOCs for a typical OH concentration, assuming that no other removal mechanism applies and the distances travelled in this time. The photochemical oxidation sequence has additional consequences, such as the generation of lachrymators (eg peroxyacetyl nitrate (PAN) and aerosol.

The classic example of photochemical smog formation is Los Angeles where high vehicle emissions are coupled with a local meteorology which confines the air within the Los Angeles basin so that the smog is generated in the large urban region responsible for the primary VOC emissions. In the UK, the polluted air mass can be transported over large distances (> 100 km) during the timescale of photochemical reactions. Thus photochemically generated ozone levels are generally higher in rural than in urban regions although transport from other cities can lead to significant ozone levels in a given urban area (see Chapter 7).

9.2.3 Analytical Techniques

(i) Gas Chromatography

Gas chromatography is the most flexible and unambiguous technique for analysing volatile organic compounds. An air sample is drawn through an adsorption tube at a fixed flowrate and for a pre-set time. The tube is then heated and the organic compounds adsorbed on the tube packing are driven onto a cooled concentrator. Once the transfer is complete, the concentrator is heated and the compounds are carried on to a capillary column in a flow of helium gas. Analysis is generally by flame ionisation or electron capture. The technique is sensitive, precise and species specific. Monitoring can either be in batch mode, with remote air sampling, or quasi-continuously, with a sampling period of typically 30 minutes in every hour.

In June 1992 the Air Quality Division of the Department of Environment appointed AEA Technology, Harwell as the Central Management and Co-ordination Unit for the UK Hydrocarbon Monitoring Network. This network will utilise automatic gas chromatographic equipment to collect and measure 26 hydrocarbon species. Data will be collected for each hour of the day continuously. The network will consist of 12 sites located in major cities. AEA Technology, Harwell are currently establishing sites in London, Birmingham, Belfast, Edinburgh and Cardiff which are due to come into operation during

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(1) Derwent RG and Jenkin ME (1991) **Hydrocarbons and the Long Range Transport of Ozone and PAH Across Europe** Atmospheric Environment **25A**, 1661-1678.

Table 9.6 Annual Average Hydrocarbon Concentrations (ppb); Rural and Urban Sites Overall Means

Compound/Site	Harwell	Middlesbrough	Great Dun Fell	West Beckham	Teddington
Time period	86-90	92	89-91	89-91	88-91
No of samples	486	534	166	186	19
1 Ethane	3.948	8.304	2.097	2.804	2.547
2 Ethylene	2.232	5.948	0.986	1.546	1.993
3 Propane	1.763	6.913	0.857	1.313	5.607
4 Propene	0.429	5.913	0.162	0.270	2.422
5 i-Butane	2.041	5.705	0.335	0.722	2.128
6 n-Butane	3.511	6.826	0.708	1.637	3.281
7 Acetylene	2.433	5.513	0.779	1.396	2.175
8 i-Pentane	1.726	4.073	0.315	0.855	1.652
9 n-Pentane	0.739	2.025	0.192	0.443	0.883
10 2-Methyl Pentane	0.610	0.695	-	-	0.588
11 3-Methyl Pentane	0.493	0.771	-	-	0.870
12 n-Hexane	0.917	0.793	0.098	0.144	5.780
13 Benzene	0.814	1.914	0.343	0.725	1.982
14 Toluene	1.495	2.584	0.501	0.999	1.431
15 Ethyl Benzene	0.366	0.533	0.129	0.244	1.544
16 (m+p)-Xylene	0.773	2.123	0.277	0.537	5.983
17 o-Xylene	0.377	0.879	0.115	0.242	1.349

Notes: Harwell operated by AEA Technology (April 1986–August 1990). Middlesbrough operated by AEA Technology (January June 1992). Great Dun Fell operated by University of East Anglia. West Beckham Operated by University of East Anglia. Teddington operated by National Physical Laboratory.

January 1993. Two sites will be established within London at Bloomsbury and Greenwich. Instrumentation of the type to be utilised for the network has been operated already for some time by Imperial College (Exhibition Road, London) and AEA Technology, Harwell (Middlesbrough).

(ii) Optical Techniques

The long path absorption technique (DOAS — Differential Optical Absorption Spectroscopy), described in Chapter 2, can also be used to monitor some hydrocarbons. Aromatic compounds, in particular benzene and toluene, have been analysed in this way using OPSIS instruments; both compounds are prevalent in urban areas and they have absorption bands in the 250-300 nm region, where the xenon lamp has a reasonable output and atmospheric attenuation is not too severe. Great care needs to be taken in interpreting DOAS spectra to check light levels and attenuations. The major problem is the difficulty of making proper allowance for overlapping absorptions eg from ozone and SO_2. The procedure is more reliable for benzene, which has a characteristic structured absorption. The toluene spectrum is largely unstructured and greater care has to be exercised in spectrum deconvolution. The technique provides average concentrations over several hundred metres with short reporting periods (eg 1-hour or less) and is finding increasing use by local authorities. The major difficulty is that of spectrum deconvolution; the technique needs more detailed testing and the development of reliable protocols.

9.2.4. Urban Concentrations

(i) Chromatography

The majority of systematic UK measurements of volatile organic compounds refer to rural locations (AEA Technology, Harwell) and Great Dun Fell and West Beckham (University of East Anglia)). The longest systematic data set for urban air is the National Physical Laboratory's compilation for Teddington which runs from October 1987. Yearly averages for 17 hydrocarbons (C_2 - C_8) are given in Table 9.7. Table 9.6 compares the overall average values for Teddington with those for the rural sites and with recent measurements for the Middlesbrough site. Table 9.8 lists yearly averages for Harwell over the period 1986-1990 and provides an interesting comparison with Table 9.6. The species concentrations measured at the Middlesbrough site, averaged over the period January to June 1992, are shown in Figure. 9.1.

All of the sites show high ethane levels, which can be at least partly ascribed to the high tropospheric background concentration for this compound of 2ppb. For the other compounds a comparison with UK emissions shows a reasonably satisfactory correlation except for ethylene, acetylene and propane. A preliminary source

Table 9.7 Hydrocarbon Measurements at The National Physical Laboratory, Teddington Annual Mean Concentrations (ppb)

Compound	1988	1989	1990	1991	Overall
No of samples	4	6	6	3	19
1 Ethane	1.733	2.788	1.943	4.087	2.547
2 Ethylene	0.923	2.228	1.148	4.283	1.993
3 Propane	1.537	3.602	9.465	5.970	5.607
4 Propene	3.927	2.602	1.423	2.557	2.422
5 i-Butane	0.673	2.208	1.833	4.010	2.128
6 n-Butane	1.327	3.123	2.530	7.053	3.281
7 Acetylene	0.890	2.112	1.230	5.477	2.175
8 i-Pentane	0.553	1.510	1.245	3.850	1.652
9 n-Pentane	0.573	0.900	0.582	17.63	0.883
10 2-Methyl Pentane	-	0.300	0.300	0.780	0.588
11 3-Methyl Pentane	-	-	-	0.870	0.870
12 n-Hexane	-	0.340	-	0.657	0.578
13 Benzene	0.435	0.947	0.902	7.247	1.982
14 Toluene	0.340	1.512	0.865	4.210	1.431
15 Ethyl Benzene	0.603	3.053	0.622	1.310	1.544
16 (m+p)-Xylene	2.030	10.000	2.650	5.513	5.983
17 o-Xylene	0.720	1.497	0.470	3.443	1.349

Table 9.8 Hydrocarbon Measurements Made at Harwell 1986-1990 (ppb)

Time period	1986(a)	1987	1988	1989	1990(b)	Overall
No of samples	102	130	90	105	59	486
1 Ethane	3.227	5.534	3.900	3.465	3.092	3.948
2 Ethylene	1.318	3.256	1.753	2.476	1.490	2.232
3 Propane	1.314	2.283	1.591	1.725	1.851	1.763
4 Propene	0.084	0.490	0.410	0.599	0.392	0.429
5 Acetylene	1.663	3.620	2.089	2.317	3.447	2.433
6 i-Butane	1.289	2.476	1.300	2.017	0.889	2.041
7 n-Butane	2.124	3.867	2.328	3.907	1.605	3.511
8 2-Methyl-Butane	0.998	1.999	1.215	1.992	0.691	1.726
9 n-Pentane	0.501	0.843	0.519	0.883	0.701	0.739
10 2-Methyl Pentane	0.346	0.735	0.658	0.755	0.180	0.610
11 3-Methyl Pentane	0.304	0.598	0.639	0.482	-	0.493
12 n-Hexane	0.382	0.991	1.525	1.263	0.169	0.917
13 Benzene	0.625	1.138	0.662	0.732	0.773	0.814
14 Toluene	1.171	2.206	1.107	1.432	0.965	1.495
15 Ethyl Benzene	0.334	0.507	0.380	0.269	0.243	0.366
16 (m+p)-Xylene	0.550	1.100	0.750	0.682	0.440	0.773
17 o-Xylene	0.372	0.564	0.306	0.297	0.173	0.377

(a) Data for the April to December period only (January to March is usually when concentrations are highest)

(b) Data ends August 1990

reconciliation,(1) carried out on the basis of the rural measurements (Table 9.9), demonstrates the high contribution from transport sources, even in rural areas. The zero solvent figure is an artifact of the range of analysed species which does not include solvent VOCs.

Figure 9.2 shows the average diurnal variations for 18 hydrocarbons at the Exhibition Road Site (Imperial College). Most of the hydrocarbons included in Figure 9.2 shows similar diurnal patterns which correlate well with the patterns of the vehicle derived pollutants CO and NO_x. As would be expected, vehicle emissions dominate the hydrocarbon spectrum for this roadside Central London site. Ethane and propane show different patterns. Ethane contains a contribution from the tropospheric background (2 ppb). The additional source is probably natural gas leakage, with the temporal variation in the measured values being explained by greater daytime dispersion. Data for ethane and benzene have also been recorded at Middlesbrough (Figure 9.3). The ethane levels are higher at Middlesbrough, but show a similar daytime reduction. The benzene datasets are very similar; both show double daytime peaks which appear to be related to rush hour traffic.

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(1) United Kingdom Photochemical Oxidants Review Group (1993) **The Third Report** (in press).

Figure 9.1 Hydrocarbon Concentrations in Middlesbrough (Jan-June 1992) (DOE Hydrocarbon Network Site)

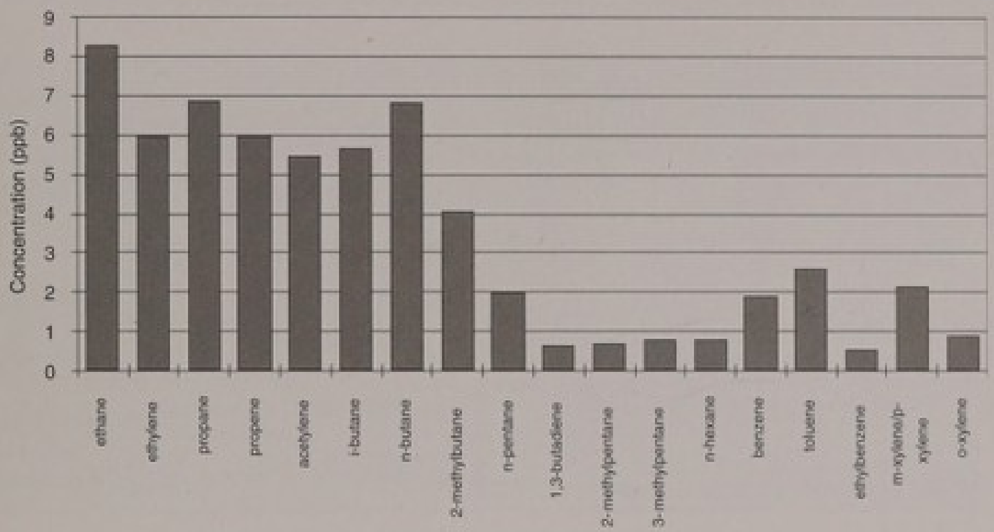

Table 9.9 Preliminary Source Reconciliation for Rural Hydrocarbon Sites

	% Contribution to Average Concentrations				
Site	**Petrol Vehicle Exhaust**	**Evap/ Distrib.**	**Solvents**	**Gas Leakage**	**Stationary Combustion**
Harwell (86-87)	25.5	42.2	0	16.5	15.8
Great Dun Fell	39.7	6.7	0	32.6	21.1
West Beckham	38.9	19.0	0	24.6	17.6

The Imperial College group obtained an interesting set of Chrompack data during the December 1991 pollution episode.(1) Table 9.10 compares concentrations before and during the episode for a representative set of hydrocarbons and demonstrates clearly the substantial episodic increase.

(ii) OPSIS Measurements

There are increasing numbers of datasets for benzene and for toluene obtained by local authorities using the long path absorption (OPSIS) technique. Figure 9.4 shows the daily averages for August 1992 for Westminster as an example. The averages were obtained from hourly measurements made by the City of Westminster's Environmental Services Department. Together, the OPSIS measurements provide a potentially very powerful resource. The Westminster toluene data show a marked diurnal pattern, similar to that found at Exhibition Road, with the highest concentrations occurring at times of peak traffic flow. Benzene spikes were attributed to petrol deliveries because they correlated with delivery times and wind directions. High levels of both benzene and toluene were recorded during a period of roadworks with a consequential change in engine activity and performance.

Similarly interesting results have been recorded in Widnes — Runcorn made by the Environmental Health Department of Halton Borough Council. The average figures for benzene for Runcorn for 1991 show no dependence on wind direction, with an average value of ~ 2 ppb. In Widnes, by contrast, the benzene concentration increased to ~ 5 ppb, from a value slightly below 2ppb, for winds in the S-SW direction. The data suggest a specific benzene source for Runcorn. These examples illustrate the potential value of the OPSIS measurements and emphasise the urgency of the validation of this technique and the development of protocols.

9.2.5 Policy Implications

The monitoring of urban hydrocarbons in the UK is in its infancy and long runs of reliable data, covering a wide range of VOCs, are not yet available. The correlation between measured hydrocarbon concentrations and the concentrations of CO and NO_x clearly demonstrate the

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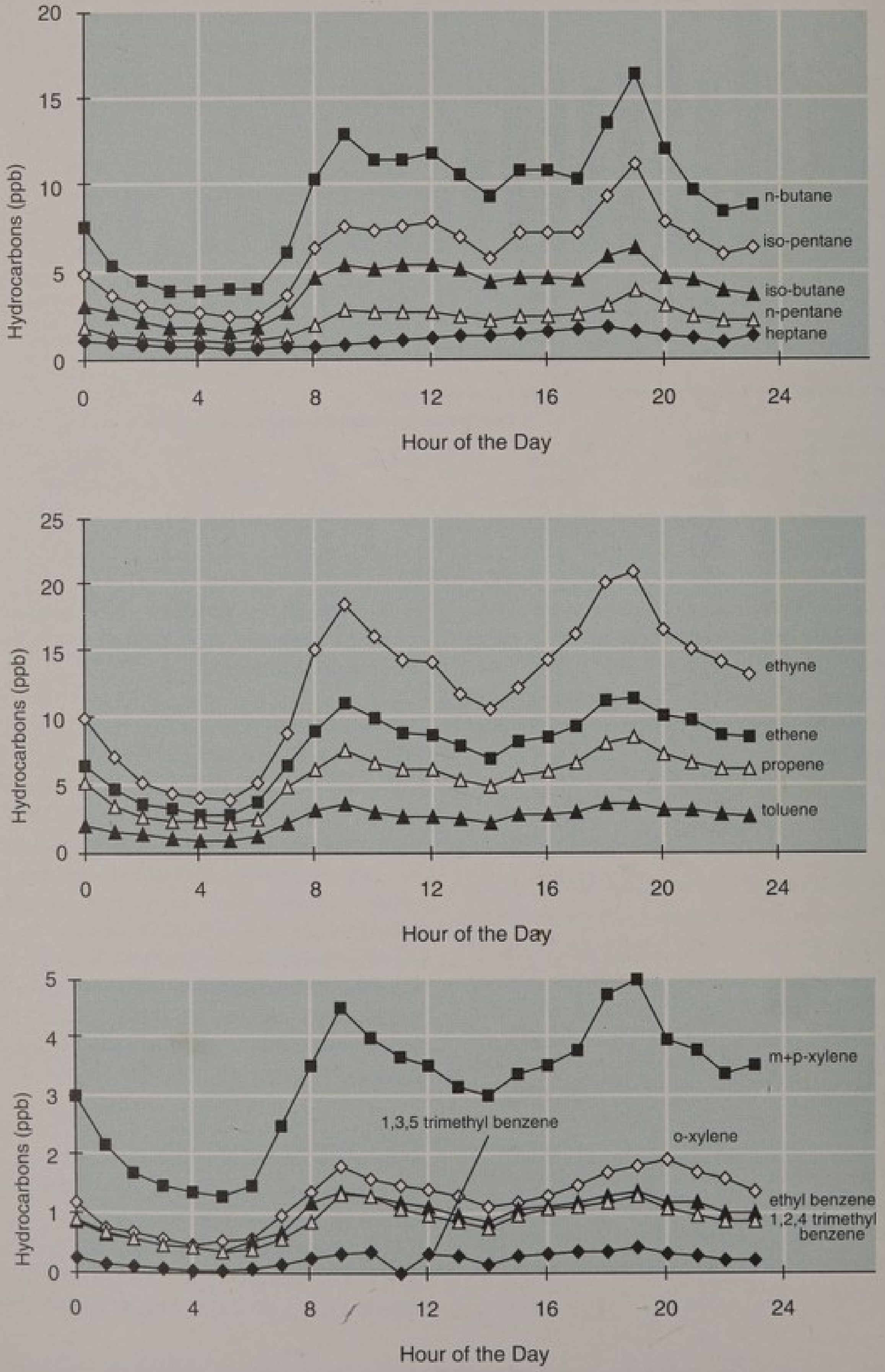
(1) Field RA, Philips JL, Goldstone ME, Lester JN and Perry R (1992) **Indoor/Outdoor Interactions During an Air Pollution Event in Central London** Environmental Technology **13**, 391-408.

Figure 9.2 Diurnal Variation of Hourly Mean Hydrocarbon Concentrations in Exhibition Road, London (DOE Hydrocarbon Network Site)



Continued

Figure 9.2 Diurnal Variation of Hourly Mean Hydrocarbon Concentrations in Exhibition Road, London (DOE Hydrocarbon Network Site) (Continued)

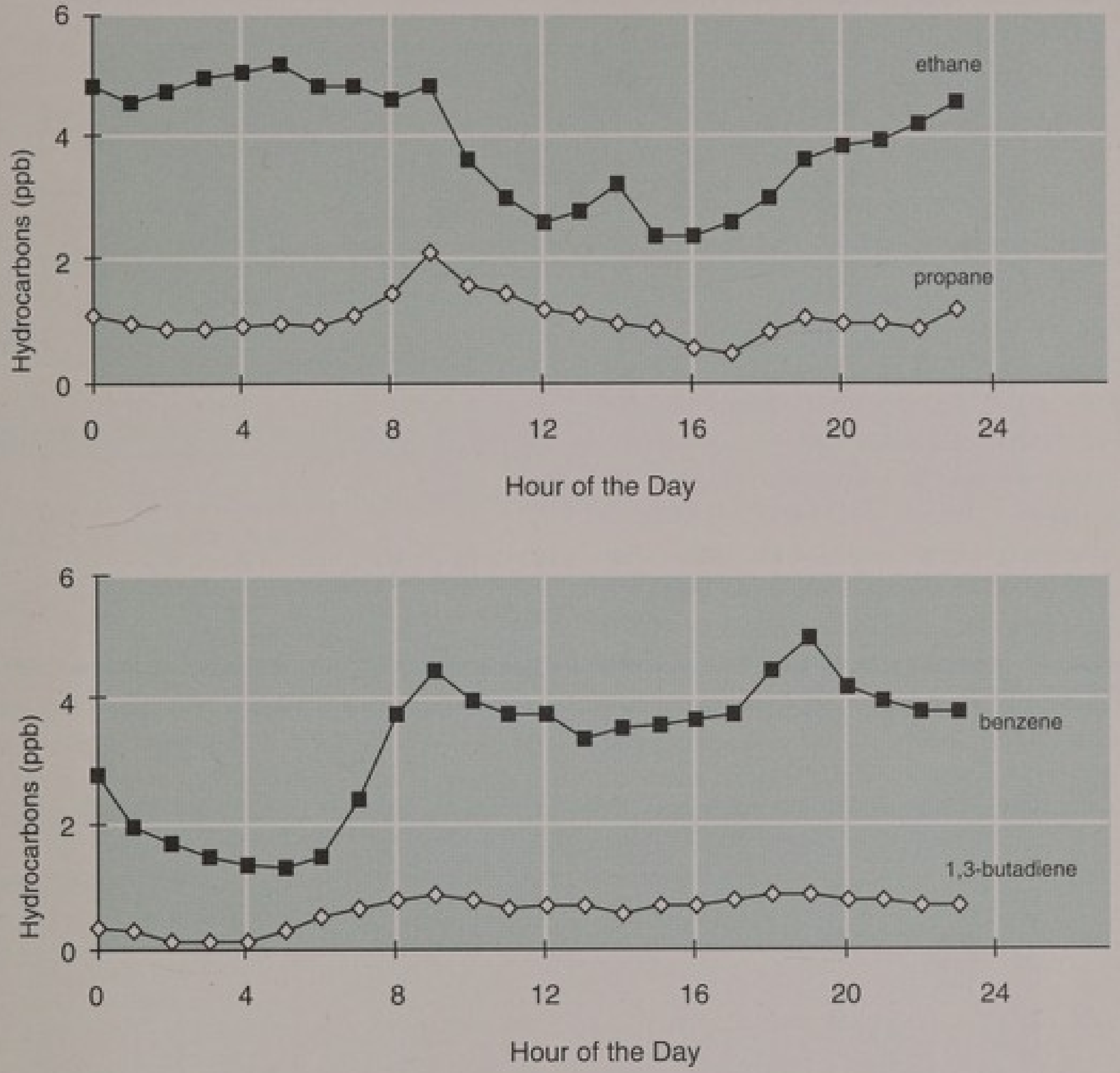


Table 9.10 Hydrocarbon Concentrations at Exhibition Road Before and During the December 1991 Pollution Episode (ppb)

Compound	Concentration before episode(a)	Concentration during episode(b)
Ethane	51.9	126.9
Ethylene	76.9	307.8
Acetylene	79.2	306.0
n-Butane	45.6	165.2
1,3-Butadiene	2.7	10.6
Benzene	18.0	118.2
Toluene	30.0	63.7

(a) Mean values, 0000 hrs, 9.12.91 - 1600 hrs, 11.12.91

(b) Mean values, 1600 hrs, 11.12.91 - 2300 hrs, 15.12.91

significance of road transport as a source of hydrocarbons, including the carcinogenic species benzene and 1,3-butadiene. However, emissions inventories argue that a wide range of other activities lead to VOC emissions, with solvent use as a major contributor.

Legislation has centred on limiting emissions of total hydrocarbons. The toxicity of some species and the wide variation in photochemical ozone creation potentials together argue the need for species specific limitations on VOC emissions. Fuel formulations, for example,

Figure 9.3 Mean Diurnal Variation of Hourly Ethane and Benzene Concentrations in Middlesbrough (Jan-June 1992) (DOE Hydrocarbon Network Site)

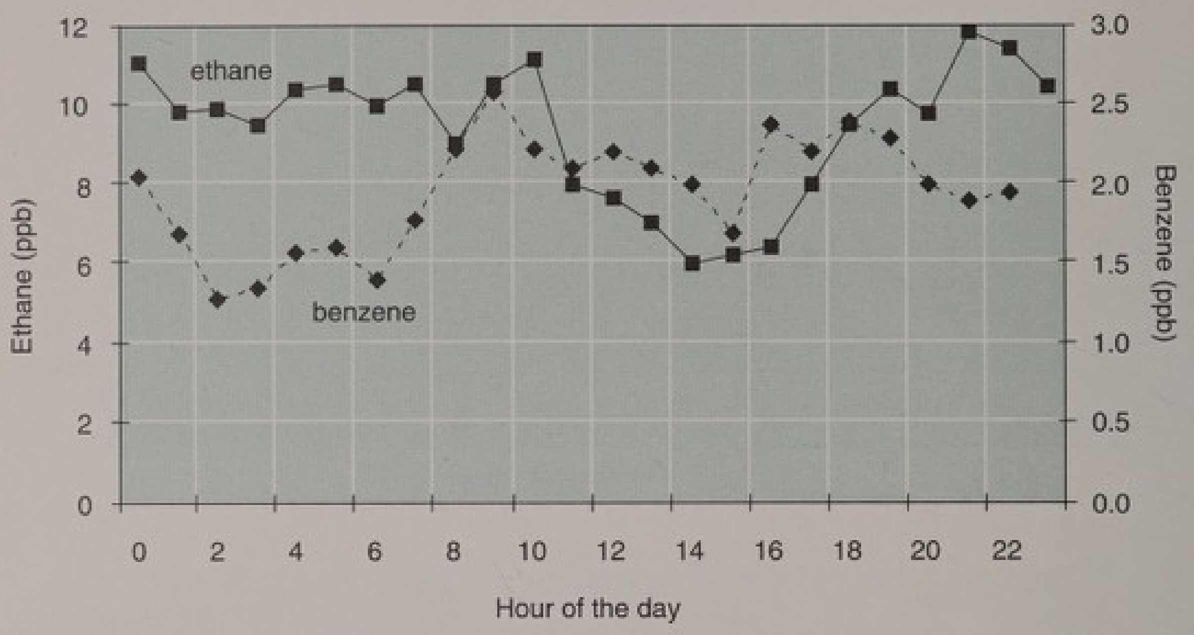
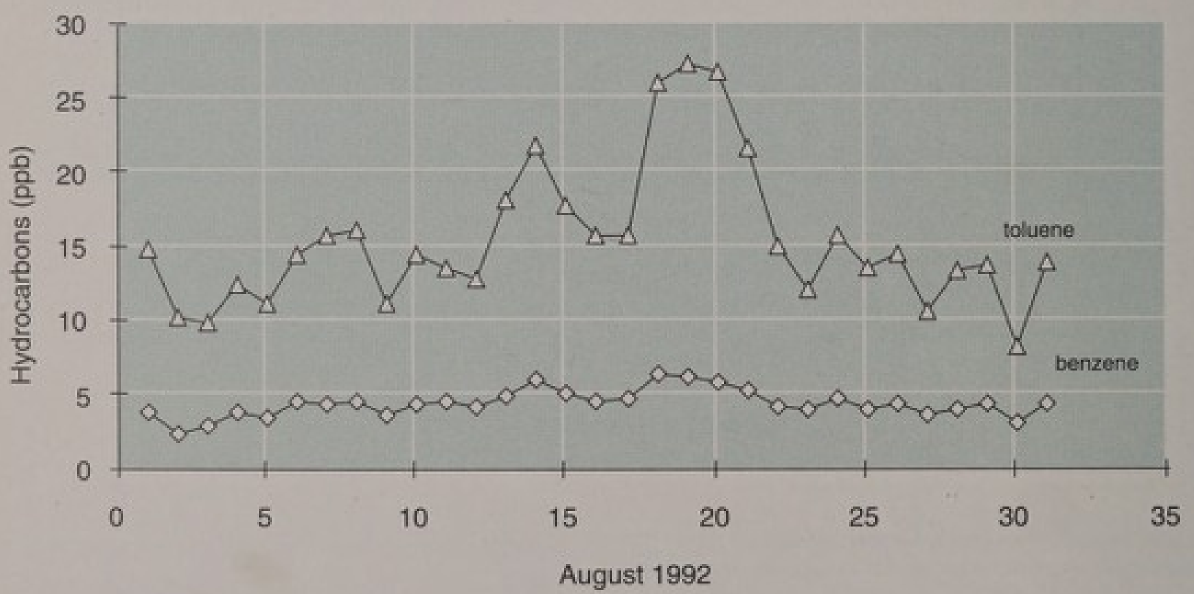


Figure 9.4 Diurnal Variation of Hourly Mean Toluene and Benzene Concentrations in the City of Westminster (August 1992) OPSIS Measurements



need to be influenced through legislation to take account of the environmental impact of particular hydrocarbon species. Benzene has received particular attention, because of its carcinogenic properties. Table 9.3 shows that petrol engine emissions are a major source of benzene. Lead free petrol contains higher concentrations of unsaturated hydrocarbons to increase the octane number and in some countries higher concentrations of benzene have been employed. In the UK, however, there is no evidence for an increase in either benzene or other aromatic hydrocarbon content of petrol over the period 1980-1990. UK fuels have been reformulated by increasing the content of alkenes and butanes. These compounds have high POCP values and consequently a detrimental environmental impact especially in summer. The Second Review of the White Paper proposes summer fuel specifications of reduced volatility. Other industry sectors have started to tackle this type of problem, for example by the development of solvents such as glycol ethers.

Developments in technology also have a role in reducing the environmental impact of VOCs. Three way catalysts will lead to improvements, with measurements at Warren Spring Laboratory showing reductions in benzene of 94% under optimal conditions. However, the overall performance of catalysts and their behaviour under a range of engine and catalyst conditions is not fully understood.

9.3 TOXIC ORGANIC MICROPOLLUTANTS (TOMPS)

9.3.2 Polycyclic Aromatic Compounds

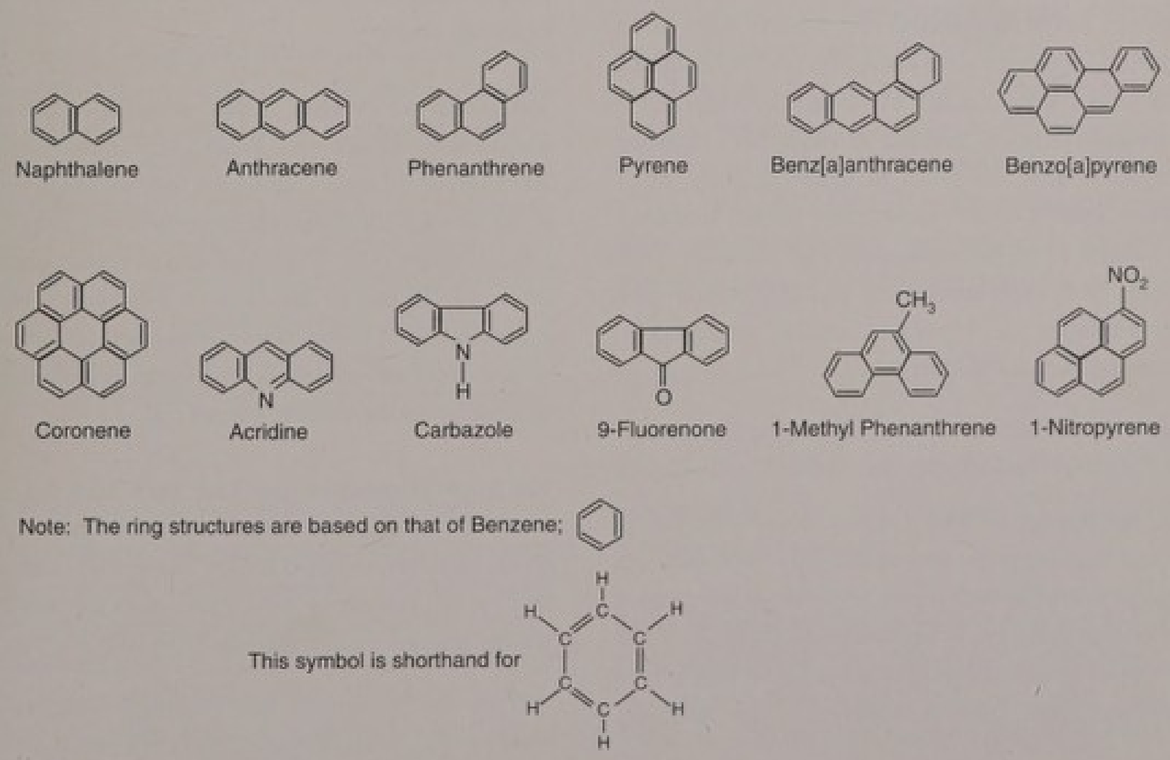
(i) Nature

Polycyclic aromatic hydrocarbons (PAH) are the parent homocyclic class of condensed, multinumbered benzenoid-ring compounds. Representative examples are given in Figure 9.5. The broader class of polycyclic aromatic compounds (PAC) incorporate a range of substituent groups and/or heteroatoms, N, O, S, in the ring structure. The compounds are emitted in low concentrations in the vapour phase and on particulates and are particularly important in diesel emissions. The primary toxicity of the compounds derives from their carcinogenic properties.

(ii) Sources and Chemical Origin

Estimates of atmospheric emissions of PAH by source type for Sweden and the UK are given in Table 9.11. The major sources in these countries are stationary and sensitive to the type of plant and fuel. In urban areas, however, mobile sources are likely to be the major contributors to PAH emissions. Recent analysis of diesel exhaust particulates showed that the major PAH components are naphthalene, fluorene, phenanthrene and their alkyl derivatives, while carbazole and dibenzothiophene are the major N- and S- containing PAC.⁽¹⁾ Firm evidence was provided that the bulk of the particulate PAC (including PAH) derives from unburned fuel, with some high molecular weight (5-ring) PAH being formed in-cylinder, presumably from lower molecular weight PAH.⁽²⁾ The ratio PAH particulate emission/PAH content in the fuel increased markedly at

Figure 9.5 Chemical Structure of Some Polycyclic Aromatic Compounds



Note: The ring structures are based on that of Benzene;

This symbol is shorthand for

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(1) Williams PT, Bartle KD and Andrews GD, **The Relationship Between Polycyclic Aromatic Compounds in Diesel Fuels and Exhaust Particulates** Fuel, 1986, **65**, 1150.
(2) Williams PT, Abbass MK and Andrews GE, **Diesel Particulate Emissions: The Role of Unburnt Fuel, Combustion and Flame** Combustion and Flame, 1989, **75** 1-24.

Table 9.11 PAH (Borneff)(a) Emissions to Air from Diffuse Sources in European Countries 1985 (T yr^{-1})

	Sweden	UK
Anthracite	-	29.4
Bituminous Coal	5.8	91.0
Wood	325.0	2.5
Gasoline	3.2	17.1
Motor Diesel Oil	1.6	7.9
Coke production	3.6	27.8
Total	**339.0**	**176.0**

(a) Borneff PAHs: fluoranthene, benzo (b+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene

low air/fuel ratios (AFR). A contribution from the lubricating oil was ascribed to the accumulation of unburned fuel PAC in the oil. AFR was also established as a significant determinant of PAH emissions from spark-ignition vehicles, and cold-starts were found to increase emissions substantially.

(iii) Health

Some PACs are potent carcinogens and/or mutagens. Initial interest centred on PAH but it has been demonstrated that such compounds account for only a part of the mutagenic activity of the ambient mixture and nitro-compounds are particularly biologically active. In addition to their production in diesel, nitro-PAC can also be formed by reaction in the atmosphere, either in the gas phase or in particulates. For example, 2-nitrofluoranthene and 2-nitropyrene have been detected in ambient air, but not in direct emission studies. PAH have been found on crops in significant concentrations so, in addition to inhalation , ingestion provides a route for PACs to enter the body. DNA adducts, formed following enzymatic oxidation of PAC, are thought to be the initiators of cell mutation. Such adducts have been detected in cultured human cells derived from the bronchus, colon, oesophagus, pancreatic duct and bladder.

(iv) Urban Concentrations

PAC are present as both gaseous compounds and in association with particulate matter, and techniques are required to monitor both phases. Particulates are sampled by filtration using low or high volume techniques, while the vapour phase is sampled by adsorption using filtered air, eg on Tenax. Soxhlet extraction is then generally performed with analysis by high performance liquid chromatography (HPLC), gas chromatography (GC) or liquid chromatography/gas chromatography (LC/GC). Long sampling periods are usually required (1-7 days) and the extraction and analysis procedures are lengthy, so that reporting is less frequent than is the case for VOCs. In addition, chemical transformation of PAH on filters, eg by ozonolysis, is possible and must be properly recognised if accurate PAH loadings are to be determined. The analysis of PAH is included in the TOMPS (Toxic Organic Micropollutants) programme recently established by the Warren Spring Laboratory for the Department of the Environment. Sites have been established in Westminster, Manchester, Cardiff and Stevenage to monitor PAH, polychlorinated biphenyls (PCBs) and dioxins(1).

The most complete set of PAH measurements has been made in South Kensington.(2) Annual averages for 1985/6 and 1987 for 18 PAH are given in Table 9.12 and compared with more limited measurements in Folkestone and Ashford, a rural location. Similar particulate concentrations were detected at a City Centre site in Birmingham over the period 1976/8. Table 9.12 also shows results for 17 PAH obtained at a height of 15m at Birmingham University at a distance of ~ 300m from a major road and preliminary results from the Manchester TOMPS site which is a rooftop site located in the city centre.

The results are broadly similar although quantitative comparisons are not very good. There is considerable variability in the results from week to week and from site to site which is illustrated in Figure 9.6 for the total PAH concentrations. The South Kensington results showed large variations in the yearly averaged species concentrations. Further quality assessment and intersite comparisons are needed before it can be established whether or not these variations are real.

The South Kensington data have been analysed on a seasonal basis although such an analysis is questionable given the results reported above. The overall emissions showed an increase in wintertime, with the summer/winter species ratios varying from 0.3 to 0.9. As

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(1) Clayton P, Davis BJ, Jones K and Jones P (1992) **Toxic Organic Micropollutants in Urban Air** WSL Report LR904(PA), Warren Spring Laboratory, Stevenage, UK.
(2) Baek SO, Goldstone ME, Kirk PWW, Lester JN and Perry R (1991) **Phase Distribution and Particle Size Dependency of PAH in the Urban Atmosphere** Chemosphere, **22** 503.

Table 9.12 Average PAH Concentrations (ng m^{-3}) for South Kensington, Birmingham, Manchester and Folkestone and Ashford

PAH	South Kensington[(a)]		Birmingham[(b)]		Manchester[(c)]		Folkestone and Ashford
	Particulate	Vapour	Particulate	Vapour	Particulate	Vapour	Particulate
Naphthalene	-	-	0.21	13.0	-	-	-
Acenapthylene	-	-	0.61	14.8	-	-	-
Fluorene	-	-	1.1	12.6	0.5	26.0	-
Acenaphthene	-	-	1.6	11.9	ND	1.2	-
Phenanthrene	0.11	5.01	1.1	23.0	0.4	56.7	0.02
Anthracene	0.18	2.66	0.4	4.1	0.05	4.7	0.03
Fluoranthene	0.81	2.65	1.2	11.2	0.63	16.2	0.21
Pyrene	0.79	3.00	2.4	35.6	0.8	10.7	0.21
Benzo[c]phenanthrene	0.85	1.98	-	-	-	-	0.18
Cyclo[c,d]pyrene	2.61	1.47	-	-	-	-	0.28
Benzo[a]anthracene	0.79	0.62	1.5	4.1	1.0	0.5	0.28
Chrysene	1.22	0.40	2.2	4.3	1.8	1.6	0.16
Benzo[b]fluoranthene	0.98	0.24	-	-	-	-	0.32
Benzo[e]pyrene	2.00	0.31	-	-	-	-	0.55
Benzo[b]fluoranthene	1.61	0.17	2.0	0.19	2.4	ND	0.52
Benzo[k]fluoranthene	0.68	0.07	1.1	0.08	2.4	0.03	0.21
Benzo[a]pyrene	1.44	0.19	0.73	0.08	1.6	ND	0.43
Dibenzo[a,h]anthracene	0.12	ND	0.79	0.04	-	-	0.05
Benzo[g,h,i]perylene	3.30	0.01	1.9	0.06	3.1	0.02	1.16
Indeno[1,2,3,c,d]pyrene	1.57	ND	2.0	ND	-	-	0.54
Anthanthrene	0.63	ND	-	-	-	-	0.02
Coronene	1.67	ND	1.0	ND	1.4	ND	0.21

(a) annual average;

(b) average of 27 daily samples, February 1992;

(c) results for week 7, Manchester TOMPS site.

expected, the vapour/particulate partition ratio increased in the summer because of the dependence on temperature.

The Imperial College group investigated the particle size dependence of the particulate PAH using a cascade impactor.(1) Such an analysis is of significance given the particle size dependence of respirable material (Chapter 6): particles of less than 2.5 µm aerodynamic diameter are able to access the alveolar region of the lung. The ambient aerosol showed a bimodal distribution but the PAH, by contrast, exhibited unimodal mass distributions with peaks located in the 0.4 - 1.1 µm range. Thus the bulk of the PAH appears to be carried on respirable particles.

While the systematic study of atmospheric PAH is in its infancy, studies of archived herbage samples have been shown to provide a reliable monitor of historic vapour phase concentrations of both PAH and PCBs. Jones et al(2) analysed archived soil and plant samples from the Rothamsted Experimental Station using Soxhlet extraction and gas chromatography. PAH are not taken up by plant roots and the plant uptake can be interpreted, at least qualitatively, as a measure of the atmospheric concentration. Over the period 1965-1989, the total PAH concentrations in the plant samples declined by 60%; the decline was most marked for the lighter species, such as phenanthrene, which exist mainly in the vapour phase. The soil samples, by contrast, showed an increase in PAH concentrations indicating that loss rates from the soil are lower than input rates. The decrease in vapour phase concentration can, presumably, be ascribed to changes in stationary combustion practice.

(v) Transport

Analyses of soil and sediments show that PAH is widely distributed throughout the world, with higher concentrations close to urban areas, but a remarkably constant species spectrum.

These observations provide strong evidence for long-range transport of PAH. 1µm particles, which are the main carriers of the heavier PAH, can have a range of well over 1000 km. This transport distance and that for

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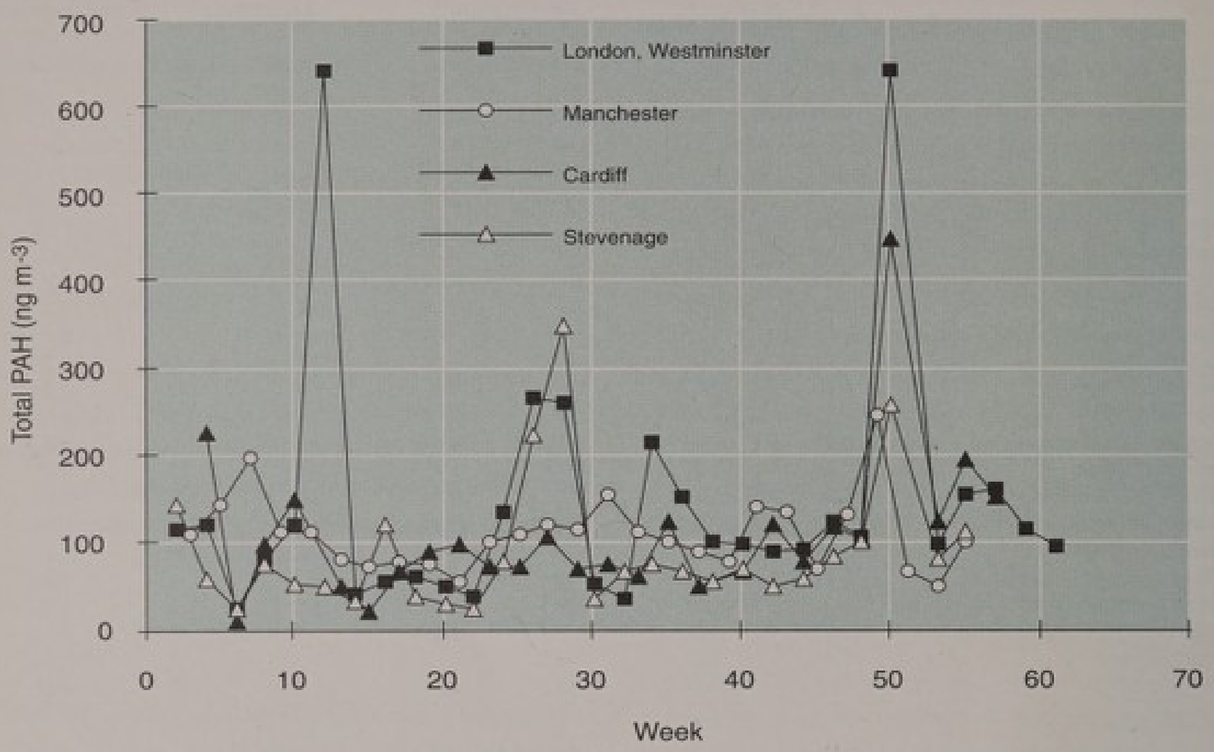
(1) Baek SO, Goldstone ME, Kirk PWW, Lester JN and Perry R (1992) **Concentrations of Particulate and Gaseous PAH in London Following a Reduction in the Lead Content of Petrol in the UK** Science of the Total Environment **111**, 169-199.

(2) Jones KC, Sanders G, Wild SR, Burnett V and Johnston AE (1992) **Evidence for a Decline of PCBs and PAHs in Rural Vegetation and Air in The UK.** Nature **1992** 356-137.

Figure 9.6 Total PAH Concentrations in Air at Four TOMPS Sites (ng m^{-3}) During 1991



the vapour phase fraction is limited by chemical reaction. The most significant rate processes include reaction with OH and ozone and photolysis; the effects of adsorption on particles are not well characterised. As discussed above, the atmospheric formation of nitro-PAH is of importance because of the possible carcinogenic properties of such compounds.

9.3.2. Polychlorinated Biphenyls (PCBs) and Dioxins

PCBs were first manufactured in 1929 but their use in 'open' systems has been severely limited since the 1970s. In addition, there is evidence for formation of PCBs in combustion processes. Plant herbage samples show high levels between 1965 and 1970 which then fall dramatically, with the late 1980s average corresponding to only 2% of the 1965-1969 average. The analysis showed a change in the congener spectrum, with di-tetra chlorinated species declining more rapidly than the pentachlorinated congeners. This trend presumably reflects the greater persistence of the heavier PCBs. The data suggest that present atmospheric levels arise from a recycling of older PCBs, between air, soil and water bodies with a possible contribution from landfill sources.

Table 9.13 contains average concentrations for PCBs at the four TOMPS monitoring sites. The product spectrum is dominated by the more volatile congeners, with lower chlorine content (congeners 28, 52 and 101), and these compounds were also found to dominate the PCB content of deposited particulate material.

Dioxins include polychlorinated dibenzo-p-dioxins and furans. They are formed primarily from the combustion of chlorine containing compounds and have been particularly implicated in the incineration of municipal solid waste. Other potential sources include vehicle emissions, domestic and industrial coal combustion and power generation. Monitoring dioxins is difficult and time-consuming and relies on gas chromatography coupled with mass spectrometry. Table 9.13 includes average concentrations for the four monitoring sites.

Table 9.13 Average Concentrations of PCBs and Dioxins at the Four TOMPS Sites

Site	PCBs/ng m^{-3}	Dioxin/pg TEQ m^{-3}
Manchester	434	0.67
Cardiff	485	0.21
London	1382	0.24
Stevenage	402	0.21

The WHO Regional Office for Europe recommends a tolerable daily intake (TDI) of 10 pg TEQ (Toxic Equivalent) per kg body weight per day. Ambient concentrations typically produce intake levels significantly below the TDI.

9.3.3 PCBs and Dioxins in London

Average total PCB concentrations measured at a roof top site in Marsham Street, London (part of the TOMPS network) are just under 1.5 ng m^{-3} over the first complete year of monitoring data (see Figure 9.7). The lighter chlorine-substituted PCBs dominate over the heavier, with PCBs 28 and 52 by far the largest contributors by mass. PCBs appear to be predominantly in the gas phase rather than attached to suspended particulate matter.

Total PCB deposition has averaged about 600 ng m^{-3} day^{-1} over this same first year of monitoring (see Figure 9.8) and again PCBs 28 and 52 dominate, accounting for over 70% of both deposition and air concentrations, alike.

Air concentrations of PCBs 28 and 52 peaked during the summer months of July, August and September of 1991 and were lowest in December, January and February of 1991/92 (see Figure 9.9). This is stark contrast to almost all other primary pollutants in London. This strongly suggests that their main source is unlikely to be primary emission which generates highest concentrations in wintertime. It could well point to an evaporative source which would be favoured by the warmer summertime conditions.

Average total dioxin concentrations at the same TOMPS site and over the same year averaged about 5pg m^{-3} (1pg = 10^{-12} g). The largest single dioxin congener, OCDD, contributed about one half of the total mass, as shown in Figure 9.10. For dioxins, the congener contributions increase on a by mass basis with increasing chlorine substitution.

Total dioxin deposition averaged about 3.5 ng m^{-3} day^{-1} and again the dioxin congener OCDD made the largest by mass contribution to deposition (see Figure 9.11)

As shown in Figure 9.11, air concentrations of dioxins peak in the wintertime as they should if primary emission were their major source. Interestingly enough, the ratio of the dioxin deposition rate to their air concentration implies a rather large apparent deposition velocity. This would be consistent with the observations that the bulk of the airborne dioxin material is attached to rather large particles. These are particles largely associated with resuspension, a source term associated with the windier and wetter winter conditions.

The dioxin or furan congener which contributes the greatest toxic load of all the dibenzo-p-dioxins or dibenzofuran congeners detected is apparently 23478 pentachlorodibenzofuran. This congener is present at about the 50-300 fg m^{-3} (1fg = 10^{-15} g) level, that is at about 2% of the total dioxin concentration. Again, as with the other dioxins and furans the air concentration of 23478 PCDF shows a winter maximum and a summer minimum.

Figure 9.7 Average PCB Distribution in Air in London (1991)

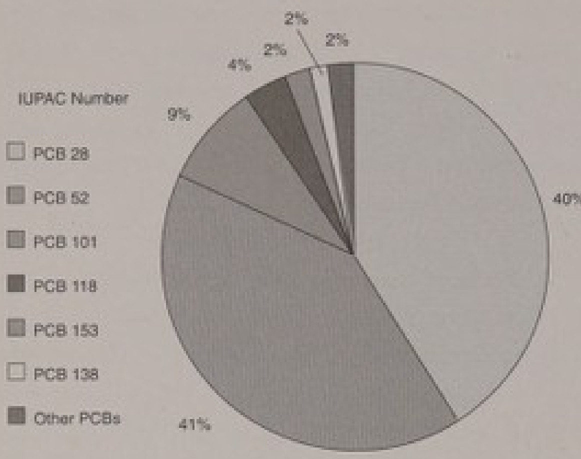


Figure 9.8 Average PCB Distribution of Deposited Particulate Material in London (1991)

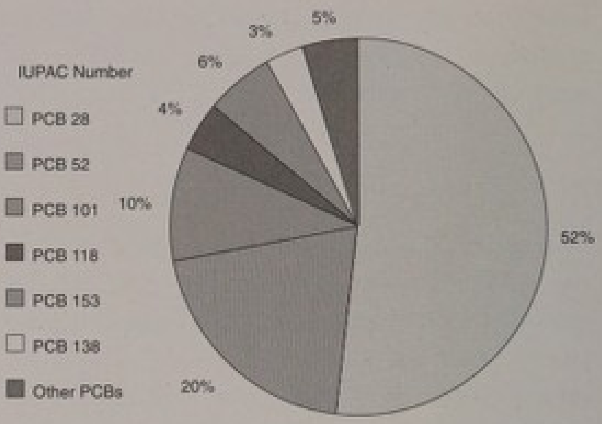


Figure 9.9 Air Concentration (pg m⁻³) of Selected PCBs in London (1991/2)

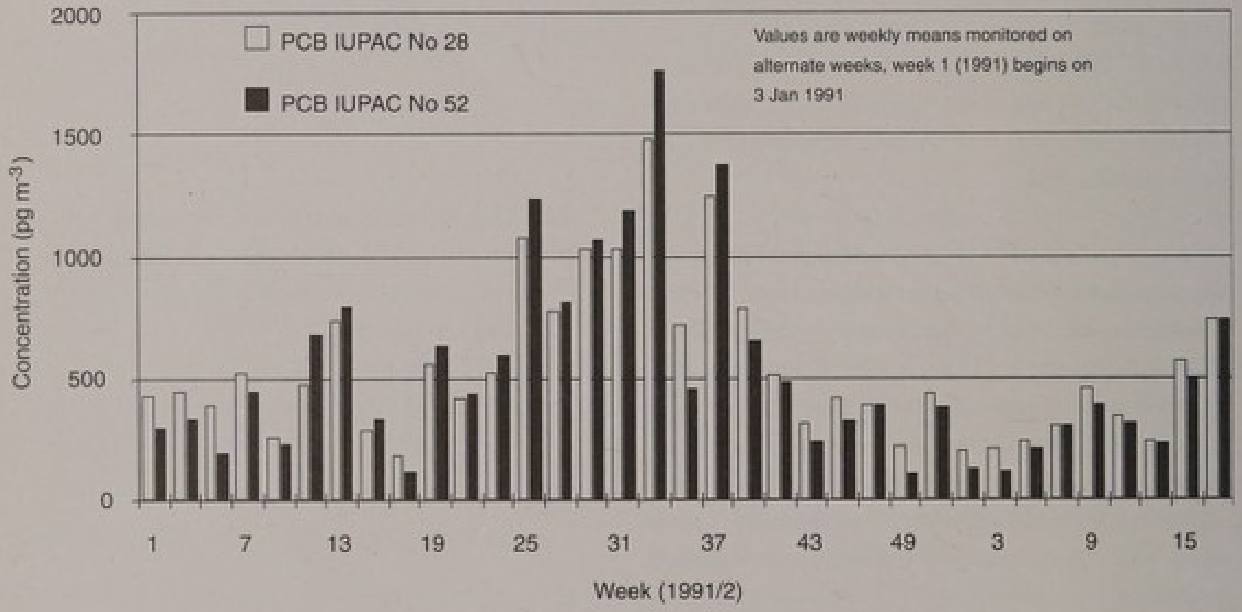


Figure 9.10 Average Dioxin Distribution in Air in London (1991)

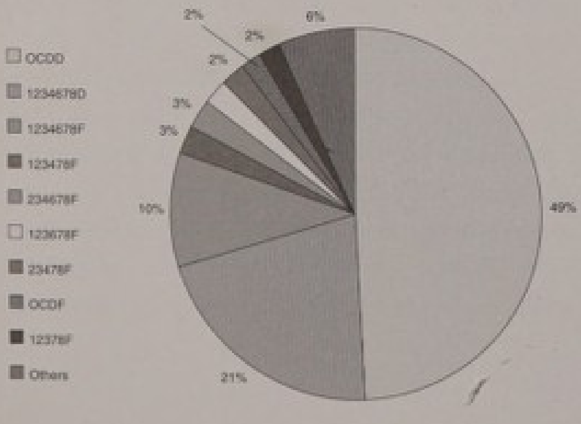


Figure 9.11 Average Dioxin Distribution of Deposited Particulate Material in London (1991)

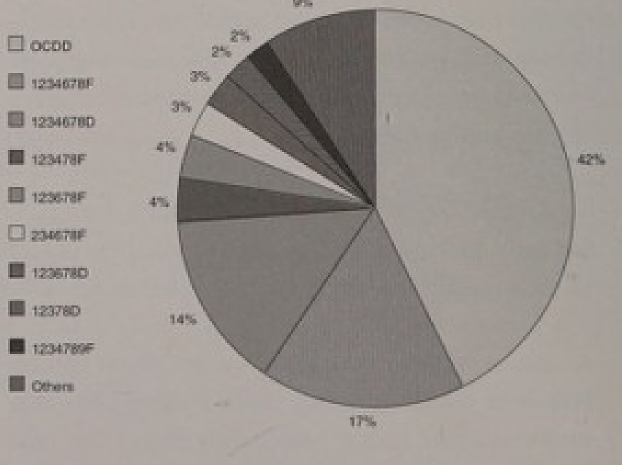
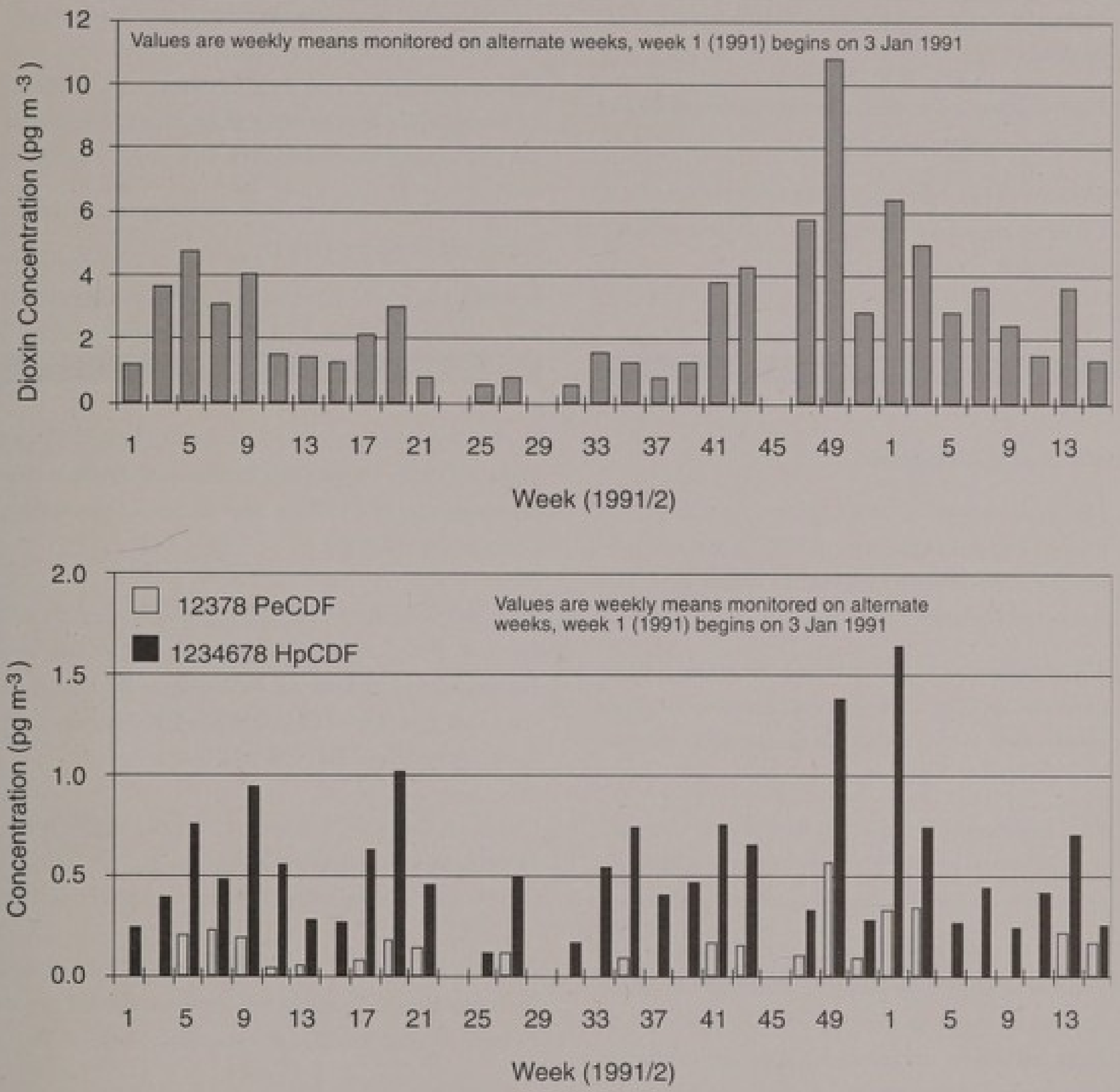


Figure 9.12 Air Concentrations (pg m^{-3}) of Dioxins and PCDFs in London (1991-1992)



9.4 SUMMARY AND KEY ISSUES

Volatile Organic Compounds (VOCs)

- *Vehicle emissions are a primary urban source of non-methane VOCs, although significant emissions derive from other sources, especially solvents.*
- *Direct effects of VOCs include both carcinogenic and non-carcinogenic health impacts and odour. VOCs are also involved in the production of photochemical smog.*
- *The primary and secondary impacts of VOCs are species specific and the speciation of VOC emissions must be recognised in future legislation.*
- *Consistent monitoring of VOCs is in its infancy. Long time series of urban concentrations are not yet available and source reconciliation has not been fully developed. The DOE Hydrocarbon Network will provide much needed information, primarily for vehicle emissions.*

Toxic Organic Micropollutants (TOMPS)

- *TOMPS include polycyclic aromatic hydrocarbons, (PAH) and compounds (PAC), polychlorinated biphenyls (PCB) and dioxins. All are formed in combustion. Diesel emissions are the primary source of urban PAH. Dioxins are formed by the combustion of chlorine-containing compounds; sources include* *vehicles and incineration. An important source of PCBs is their discontinued manufacture for industrial purposes.*

- *The compounds are present in the vapour phase and on particles. Many are carcinogenic.*
- *Monitoring has been very limited but the new DOE TOMPS programme is beginning to provide valuable information.*

9.5 RESEARCH RECOMMENDATIONS

Volatile Organic Compounds

- *The development of strict analysis protocols for optical detection techniques (eg OPSIS) and of remote sensing techniques (eg LIDAR) to obtain time- and space-resolved concentrations.*
- *The development of low cost, specific techniques for analysis such as diffusion tubes and solid state sensors and their deployment in spatial grids over extended urban areas.*
- *The validation of emissions inventories, the development of robust source apportionment techniques and their deployment on new datasets.*
- *The development of techniques for handling and visualising the large datasets generated in future campaigns (large species spectrum correlating with large emissions inventory, spatial and temporal dimensions, meteorological data, geographical information on local point and extended sources, atmospheric chemistry).*
- *Guidelines for the use of volatile organic compounds, based on photochemical ozone creation potentials and toxicity guidelines.*

Toxic Organic Micropollutants

- *The establishment of longer running data sets is needed with, where possible, correlation with meteorological conditions and potential local sources.*
- *Monitoring is required for a range of emissions sources for the construction of reliable emissions inventories and the apportionment of sources.*
- *The atmospheric chemistry of TOMPS is poorly understood, especially on particles. It is significant, especially for PAH, because of the formation of potentially carcinogenic PAC, such as nitrocompounds. The atmospheric monitoring of such compounds is also needed.*
- *More work is needed on the development of source reconciliation for TOMPS.*

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Williams PT, Abbass MK, Andrews GE, Bartle KD **Diesel Particulate Emissions: The Role of Unleaded Fuel** Combustion and Fuel **75,** 1-24.

10 Future Trends

10.1 INTRODUCTION

This chapter of the report addresses the issue of future trends in air pollution emissions in the UK and their consequences for urban air quality. In most of the urban areas of the UK, and in all the largest ones, road traffic emissions probably make the dominant contribution to ground level concentrations of most pollutants. The exceptions are in those relatively few towns, generally of fairly small size, where coal and smokeless fuel consumption in the domestic sector is still significant. These areas form a special case and will not be discussed further in this section.

An assessment of future trends in urban air quality will therefore depend very strongly on trends in road traffic emissions. These in turn will depend primarily on two factors, namely the effect of regulations on the technology determining emissions of individual vehicles and the total use of vehicles in and around the urban area in question. Other factors will also play a role such as changing levels of congestion, periodic emissions testing etc

In assessing the effect of regulations on individual vehicle emissions it is essential to take into account the actual technology used in meeting the regulation and its emission performance over the range of operating conditions experienced in practice.

Very few forecasts of traffic activity in individual urban areas are available, and much of the discussion below deals with forecasts at a national level. Consequently extrapolations of national trends to trends in specific urban centres will not always be straightforward, and the discussion below should be read with this in mind.

10.2 VEHICLES

10.2.1 Regulatory Background

The discussion in this section will deal primarily with forthcoming regulations on motor vehicle emissions. There are other commitments to national emission targets which the UK has made, notably the SO_2 and NO_x and VOC Protocols of the UNECE Convention on Long Range Transboundary Air Pollution, but with the exception of the VOC Protocol, the non- vehicular source reductions required to meet the emissions targets will have a relatively small effect on urban air quality.

The most recently agreed EEC Directive governing emissions from light duty vehicles is 91/441/EEC and the limits in this Directive are compared with the preceding limits (83/351/EEC also known as ECE Regulation 15-04) in Table 10.1. There is also a limit on evaporative emissions of 2 g of hydrocarbons per SHED test in 91/441/EEC. Also shown in Table 10.1 are extensions to the 91/441/EEC limits which have been proposed to the EC by the Motor Vehicles Emissions Group (MVEG). It should be noted that these latter are suggestions only at this stage. The EC is scheduled to produce an official Proposal by the end of 1992.

le 10.1 EC Directive Limits for Light Duty Vehicles

ective	Reference Weight		Dates		Type Approval				Conformity of Production				
	Min kg	Max kg	Type Approval	Entry into Service	CO g/km	$HC+NO_x$ g/km	Partic. g/km	Idle CO%	CO g/km	$HC+NO_x$ g/km	Partic. g/km	Idle CO%	Comments
351/EEC	0	1020	1 Oct 82	1 Oct 85	14.31	4.69		3.5	17.28	5.87		4.5	EC Urban cycle
351/EEC	1021	1250	1 Oct 82	1 Oct 85	16.54	5.06		3.5	19.74	6.32		4.5	EC Urban cycle
351/EEC	1251	1470	1 Oct 82	1 Oct 85	18.76	5.43		3.5	22.46	6.79		4.5	EC Urban cycle
351/EEC	1471	1700	1 Oct 82	1 Oct 85	20.73	5.80		3.5	24.93	7.26		4.5	EC Urban cycle
351/EEC	1701	1930	1 Oct 82	1 Oct 85	22.95	6.17		3.5	27.64	7.72		4.5	EC Urban cycle
351/EEC	1931	2150	1 Oct 82	1 Oct 85	24.93	6.4		3.5	29.86	8.17		4.5	EC Urban cycle
351/EEC	2151	3500	1 Oct 82	1 Oct 85	27.15	6.91		3.5	32.58	8.64		4.5	EC Urban cycle
441/EEC	0	3500	1 Jul 92	31 Dec 92	2.72	0.97	0.14	3.5	3.16	1.13	0.18	4.5	
???/EEC	0	3500	1 Jan 96		2.2	0.5	0.08		Gasoline vehicle				St.2 proposal by 31 Dec 1992
					1.0	0.7	0.08		IDI Diesel				
					1.0	0.9	0.1		DI Diesel				

Table 10.2 Emission Limits for Heavy Goods Vehicles (g/kWh)

Directive	Dates	Type Approval				Conformity of Production			
		CO	HC	NO_x	Partic.	CO	HC	NO_x	Partic.
88/77/EEC	1 Oct 1990	11.2	2.4	14.4	-	12.3	2.6	15.8	-
91/542/EEC	1 July 1992	4.5	1.1	8.0	0.36[a]	4.9	1.23	9.0	0.4[b]
	1 Oct 1995	4.0	1.1	7.0	0.15	4.0	1.1	7.0	0.15

(a) If engine <85 kW then value is 0.51 g/kWh

(b) If engine <85 kW then value is 0.68 g/kWh

It is clear that the 91/441/EEC limits represent considerable reductions in emissions compared with the Reg 15-04 limits. To meet the limits, gasoline vehicles will need to use three-way catalyst technology. Diesel cars will also have to be capable of meeting these light-duty vehicle limits and accordingly, for the first time, a gravimetric particulate emission limit of 0.14 g km^{-1} is included. In order to meet the increased stringency of the MVEG-proposed limits, it is likely that improvements to catalyst light-off performance, and hence cold start emissions, will be required.

An EEC Directive limiting Heavy Duty Vehicle emissions was also agreed in 1991 (91/542/EEC) and the emission limits are shown in Table 10.2. They take effect from 1 July 1992 and 1 October 1995, and can be compared with the limits existing before July 1992 also shown in Table 10.2.

Taken together these increasingly stringent limits will lead to very significant reductions in emissions from individual vehicles. The next section discusses how these regulations and technology changes will influence future emissions in combination with traffic demand forecasts.

10.2.2 Future of UK Emissions

The discussion in this section is taken from recent detailed calculations and a report by Eggleston (1), to which the reader is referred for a full description. That report considers future developments in emissions from all major sources including the electricity supply industry, road transport and others.

The forecasts used current emission control legislation as described above for motor vehicles and incorporated the requirements of the EC Large Combustion Plant Directive. The work also used official UK Government forecasts of relevant activities. Energy use projections were those produced by the (then) Department of Energy in Energy Paper Number 58, 1990. Forecasts of road traffic growth were those published in 1991 by the Department of Transport (Transport Statistics Great Britain 1991).

The implications of the regulatory background and usage forecasts in terms of technologies used by road traffic have also been taken into account.

Of more importance in the context of urban air quality, the assumptions regarding vehicle technologies, their use and performance are summarised below.

- *Catalysts - All new passenger cars will be fitted with closed loop three-way catalysts from 31 Dec 1992. Some vehicles are already fitted with catalysts. These are assumed to fail at a rate of 5% a year. After cars are 3 years old failed catalysts will be detected at the annual MoT test and repaired with a 95% success rate. Catalysts will degrade with use. In the absence of any better data it is assumed that the degradation just meets US federal requirements and is linear with mileage. Failed catalyst cars are assumed to emit at Reg 15/04 rates.*
- *Cold Starts - These are estimated in the same manner as for the National Atmospheric Emission Inventory. Driver behaviour is assumed not to change in the future so the fraction of short journeys remains unchanged. This is a significant source of emissions especially into the future when emission from warm vehicles will be substantially reduced.*
- *Vehicle Age - Vehicle age profiles have been derived from the DTp Statistics for each vehicle type. These are assumed to remain constant into the future. While this may be a reasonable estimate over the longer term, short term deviations may occur. For example if a recession in the future causes owners to delay*

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(1) Eggleston, H.S. (1992) **Pollution from the Atmosphere: Future Emissions From the UK**. WSL Report LR888(AP), Warren Spring Laboratory, Stevenage, UK.

replacing old vehicles the introduction of new technologies will be delayed leading to under-estimates of future emissions.

- *Goods Vehicle Emissions Control - This will be introduced in two stages as currently proposed.*

Emission factors for the study were taken from measurements made at the Warren Spring Laboratory or from the COPERT Working Group(1).

Forecast emissions from road traffic to 2010 are shown in Figures 10.1 to 10.4, for NO_x, CO, VOC and particulates.

In Figure 10.1 to 10.4, the rapid increase in NO_x emissions from road traffic is clearly shown, arising mainly from an increase in vehicle activity but also from an increase in NO_x emissions of Reg 15-04 cars compared with earlier homologations. The reductions brought about by catalysts in future years are clearly apparent, to the extent that by 2010 HGVs are estimated to emit roughly the same amount of NO_x as gasoline vehicles on a national basis.

Figures 10.2 and 10.3 show the large decreases in CO and VOC emissions brought about by catalyst technology. These reductions are larger in proportional terms than for NO_x because of the small contribution of HGVs to CO and VOC emissions. In the case of VOCs, evaporative emission controls will also lead to a reduction in evaporative emissions.

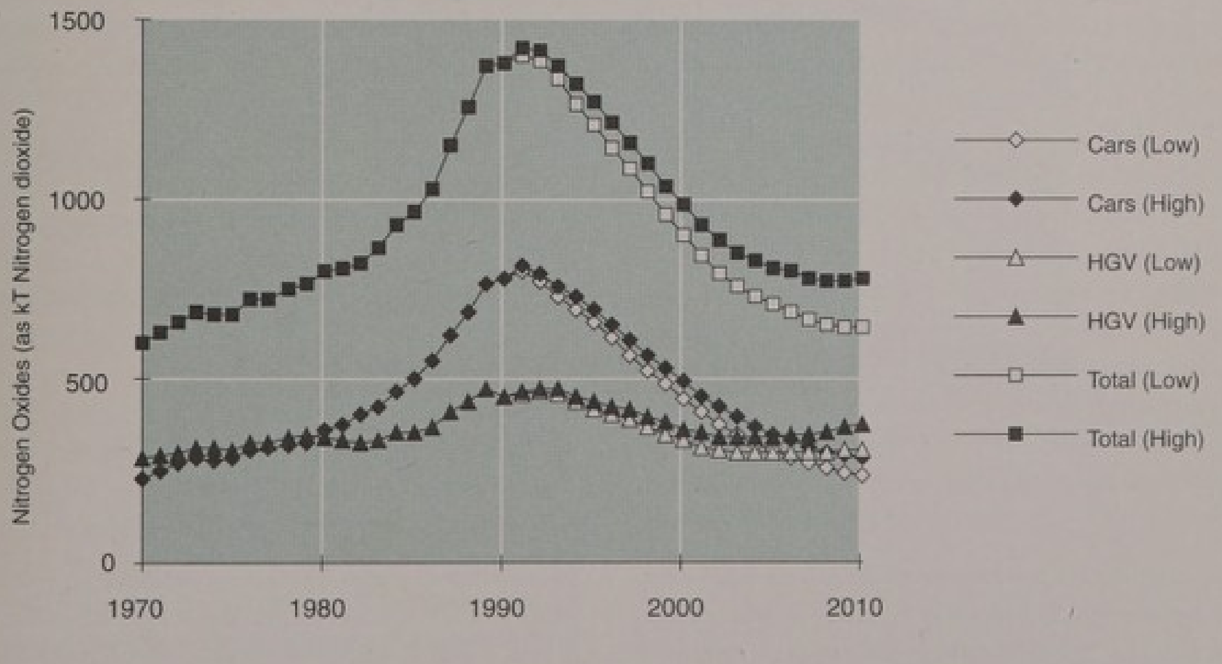
Particulate emissions, (Figure 10.4), currently arise mainly from the use of diesel fuel and are forecast to reduce due to the new limit on particulate emissions. However with the traffic growth forecasts used, emissions begin to increase again after 2005.

As discussed in Section 10.1 however, the forecasts discussed here deal with national figures and the future air quality in any particular urban area will be determined by changes in local traffic activity (and other sources where this is relevant). This is addressed in the following section.

10.2.3 Future Emission Trends and Urban Air Quality

Although the national forecasts discussed in the previous section give a very valuable background against which urban air quality trends might be considered, there are

Figure 10.1 UK Road Transport Emissions of NO_x (1970-2010)



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(1) Eggleston HS, Gaudioso D, Goriben N, Joumard R, Rijkeboer RC, Samaras Z and Zierock K-H. (1991) **CORINAIR Working Group on Emission Factors for Calculating 1990 Emissions from Road Traffic Volume Commission of The European Communities.** Final Report Contract B4-3045 (91) 10PH.

Figure 10.2 UK Road Transport Emissions of CO (1970-2010)

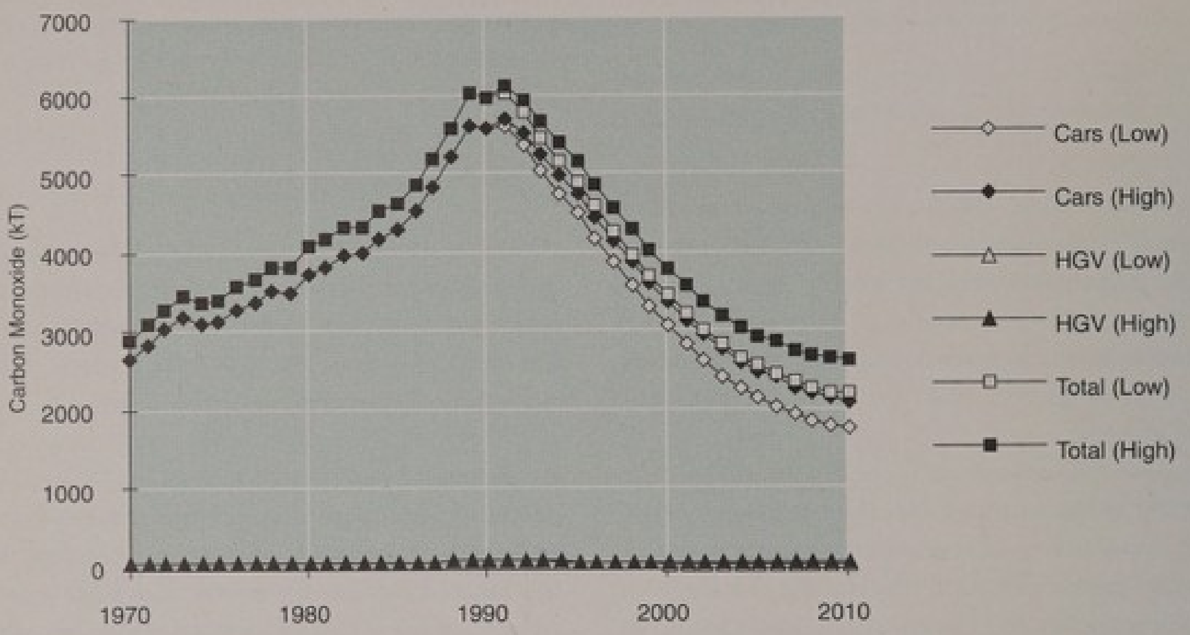
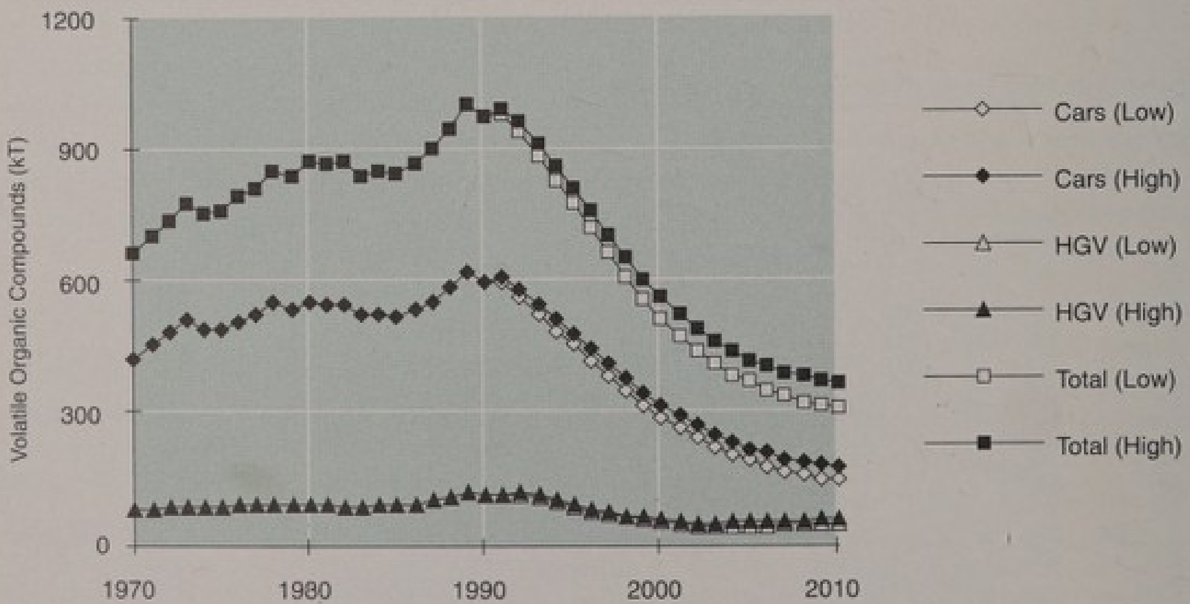
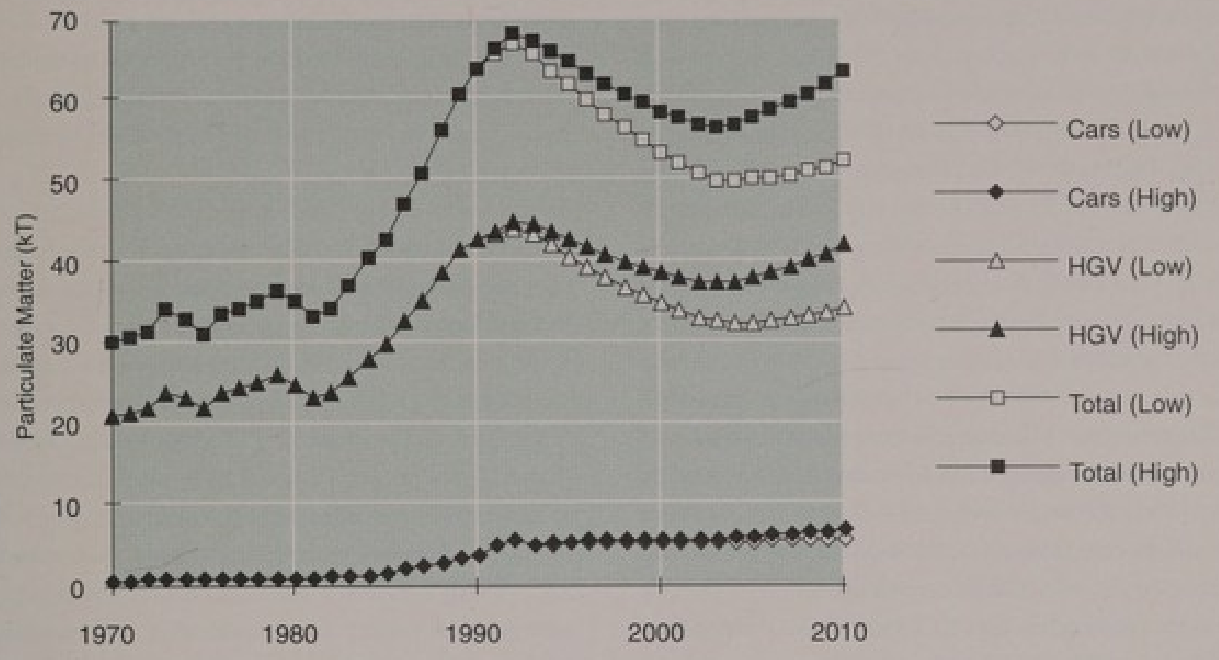


Figure 10.3 UK Road Transport Emissions of VOC (1970-2010)



several important areas where differences will occur. Most importantly perhaps is the extent to which traffic activity in terms of vehicle-kilometres driven, will increase in urban areas compared with national demand forecasts. For several reasons, such as congestion, saturation, and policies encouraging public transport use, the tendency is likely to be such that in large urban areas at least, if growth does differ from the national trend then

Figure 10.4 UK Road Transport Emissions of Particulate Matter (1970-2010)



it would tend to slower increases. In recent years for example growth in motorway use has been greater than that on other roads.

The other important local issue to consider is the gasoline/ diesel or light duty/heavy duty vehicle use mix in individual urban areas which also may differ from the national totals.

Consequently, as has already been noted, assessments of future air quality trends in an urban area should ideally use information specific to the town or city in question. To date only one published study is readily available, and this deals with present and future NO_x concentrations in London⁽¹⁾.

This study, which was carried out two years earlier than the forecasts described in the previous section, was designed to assess the likely future concentrations of NO_x and NO_2 in London. The future year in question was 2000. Rather than use the national traffic growth forecasts, in the London study a 1% per annum increase in road traffic activity was assumed. NO_x concentrations were calculated using a Gaussian plume model and a 1 x 1 km emission inventory. The results showed decreases in annual mean NO_x concentrations from 1983/4 to 2000 of typically 20%. The decrease in NO_2 concentrations however is likely to be less than this and in Central London was estimated to fall by only about 5% compared with the 1983/4 Figure. This estimate was based on empirical relationships between NO_x and NO_2 concentrations measured in Central London.

Since this study was carried out, the later forecasting study has shown that, nationally at least, a minimum in NO_x emissions is reached in 2010, so that NO_x concentrations in London may continue to decrease beyond 2000. The forecasting of NO_x and other pollutants in London is being updated by Warren Spring Laboratory on behalf of DOE using more recent information on vehicle emissions performance and regulation than was available to the earlier modelling study of NO_x in London.

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(1) Munday PK, Timmis R and Walker CA (1989) **A Dispersion Modelling Study of Present Air Quality and Future NO_x Concentrations in Greater London** WSL Report LR731(AP) Warren Spring Laboratory, Stevenage, UK.

For pollutants such as CO and VOCs, although no detailed calculations have yet been carried out for urban areas, it is likely that substantial improvements in urban air quality will occur at least to 2010. The national forecasts referred to above estimate reductions of 56-62% in CO emissions and 61-67% in VOC emissions from 1992 to 2010. One feature of the urban situation which may tend to reduce the size of the decrease in emissions is the performance of catalyst vehicles under cold start conditions before the catalyst attains its operating temperature. There is some uncertainty about how important this will be in practice, and as has already been noted, the stringency of the recently proposed EC Directive may well lead to improvements in cold start performance. Equally it should be noted that urban traffic activity in the larger cities, may well grow at slower rates than the national forecasts. Taking all these qualifications on board, it is therefore clear that substantial improvements in urban CO and VOC concentrations should occur over the next two decades.

In terms of individual hydrocarbons, measurements to date suggest that emissions of many species will reduce substantially with catalyst technology. Emissions of benzene and 1,3-butadiene have been measured from three TWC vehicles(1). Over cold start EC urban cycle, average benzene emissions over the three vehicles were 50 mg km^{-1}, 75% less than for the current non-catalyst vehicles tested in the same work. However when the catalyst operating temperature was reached, the average benzene emission was 5 mg km^{-1} or less across the whole speed range up to 90 kph. This represents a better than 90% reduction in benzene emissions compared with current technology vehicles. Emissions at 113 kph were higher than at other speeds but were still 90% less than current vehicles.

Average emissions of 1,3-butadiene on cold start EC cycle tests for non-catalyst cars were 35 mg km^{-1} with values in the range of about 10-20 mg km^{-1} over the full speed range. In TWC cars, 1,3-butadiene was below the detection limit of the measurements. It is therefore likely that TWC technology will lead to percentage reductions for 1,3-butadiene of a similar size to those of benzene, amounting to 90% or more in warm engine conditions.

Future trends in urban particulate concentrations are less clear. At a national level the current emissions forecasts show a relatively small decrease of the order of 17-26% from 1992 to about 2003-2004 when national emissions are estimated to increase again, with the high growth emissions reaching within ~7% of 1992 values by about 2010.

The important point for urban air quality is that unless local urban vehicle activity grows much slower than the national forecasts, urban particulate concentrations are unlikely to improve by the substantial amounts forecast for pollutants such as CO and VOCs. Reductions in particulates of the order of 15-25% (rounding to the nearest 5) may occur up to about 2005, when, depending on traffic activity changes in the urban areas in question, increases may occur, approaching 1992 levels by about 2010 in a high growth scenario. In this context the term particulates would cover not only gravimetric concentrations of PM_{10}, but such species as PAHs etc associated with diesel particles.

10.3 NON-VEHICULAR SOURCES AND IMPACTS

Whilst it is clear that developments in relation to vehicle emissions will have the single largest impact on ground level concentrations of most urban air pollutants, other sources will also have some effect. Many of the pollutants discussed in this report originate from combustion processes and urban areas contain a wide variety of these. Non-combustion sources consist largely of evaporative emissions of volatile organic compounds, which arise from domestic and commercial activity as well as industry.

Future trends in urban air quality are therefore partly dependent on developments relating to emissions from stationary sources. Developments are likely to come about either as a result of legislation and regulation or changes in lifestyles of people in urban areas.

The 1990 Environmental Protection Act introduced a new framework for regulation and control of industrial emissions, with a timetable for improvement of existing processes. By 1996, most of the industry in England, Wales and Scotland will either be regulated by Her

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(1) Bailey JC, Flain RM and Parkes S (1992) **Emissions of Benzene and 1,3-Butadiene from Light Duty Vehicles Under Normal UK Driving Conditions** (submitted for publication)

Majesty's Inspectorate of Pollution (HMIP) (HM Industrial Pollution Inspectorate in Scotland) or the local authority, in terms of pollutants emitted into the atmosphere. Furthermore, the emission limits laid down in the legislation are considerably more stringent than has been the case prior to 1990.

Provided that both HMIP and individual local authorities are able effectively to register and inspect the industrial processes for which they are responsible, there should be a significant reduction in emissions. The extent to which urban air quality improves in individual towns and cities will obviously depend upon the industrial activity and its influence in each case.

Not only have emission limits applicable to many of the industries become much more stringent since the old 'Best Practicable Means' notes issued by HMIP but a wider range of pollutants and processes have been included. For example, much greater attention is now paid to emissions of NO_x and volatile organic compounds. In most cases there is also a requirement for monitoring of emissions, so not only will it be demonstrable that emissions will be below the specified emission limits, but also a better database can be established of industrial emissions.

In addition to the reduction of emissions from existing industrial sources, the introduction of new plant will also influence urban air quality. The electricity supply industry is an obvious example of a possible shift in the distribution of sources in urban areas. In the 1960s the trend was very much towards constructing large power stations away from urban areas, in contrast to the earlier philosophy of siting power stations in cities. Examples of the latter approach to the siting of power stations in the 1920s are familiar to us today; Battersea power station remains a prominent landmark alongside the Thames. It was the creation of the Central Electricity Generating Board for the generation of electricity and the National Grid for its transmission which encouraged the construction of power stations in rural areas. This was undoubtedly a significant factor in improving urban air quality, (although leaving other less desirable impacts on a regional scale).

The 1989 Electricity Act profoundly changed the nature of electricity generation and distribution in England and Wales. As a result of this and the new freedom to use natural gas as a fuel to generate electricity it seems unlikely that new power stations will be of the large, coal-fired type. Furthermore, the new market in electricity allows significant consumers to generate their own supply. So, for example, large hospitals or transport companies might consider it worthwhile to generate electricity in urban locations on the scale of 1-10 MW. Another possibility is the emergence of 'combined heat and power' (CHP) facilities in the UK. Whilst these are common in other countries, they have never become established in the UK, partly because the structure of the electricity supply industry has never made them economic on a widespread basis. Isolated examples can be found of the supply of process heat to specific industries, but the idea of CHP for district heating has never taken root here. The possibility of establishing a city-wide scheme in Leicester was actively pursued from 1985 to 1989, but was eventually abandoned. A proposal at Elswick in Newcastle for a district heating scheme has received outline planning permission in 1992, but it is not yet certain to proceed.

If CHP was to become economically attractive, then a switch from larger non-urban power stations to smaller CHP installations in populated areas would have some significance for atmospheric emissions. Clearly, it is important for the generating facility to be close to the users of the process heat and it is this factor which determines the location. Certainly, there would be strong support for CHP from some quarters, since it has potential benefits in respect of CO_2 emissions and is arguably a much more thermally efficient use of fuel. In the near future, such schemes would most likely use natural gas as a fuel and the impact on urban air quality would be minimal. In any eventuality, the emissions from such plant would be tightly controlled and if such a shift in the siting of generating capacity were to occur, there would not necessarily be a reduction in urban air quality as a result.

Another consequence of the way in which the CEGB was divided into private generating companies, with Nuclear Electric remaining in the public sector, was the creation of the Non-Fossil Fuel Obligation (NFFO). This allows certain approved projects to sell electricity at a significant premium above the prevailing 'pool' price. As a result, some 'refuse-to-energy' plants have been proposed and in some cases granted planning permission in urban areas. Such plants are, in effect, municipal waste incinerators which produce electricity as a by-product, but the sale of the electricity at an attractive price makes the schemes viable economically. However, the NFFO tariff is due to expire in 1997 and it is not clear at this stage whether municipal waste incineration will remain as attractive as it is currently. In the long-term, much will depend on the availability of landfill and the consequent effect on the prices of various routes of waste disposal. The siting of large waste incinerators is a controversial topic and their impact on air quality is usually put forward as one of the principal objections. Inevitably, developers of such projects prefer to site them in or near to urban areas where the waste is generated. Incinerators of various kinds, (sewage sludge, hazardous waste, clinical waste as well as municipal waste) are likely to be increasingly required in the near future as waste disposal by the more traditional means becomes unacceptable or illegal. Any incinerator will release to atmosphere a much wider range of pollutants than typical combustion processes, as a result of their feedstocks. For example, small quantities of heavy metals and organic compounds will be emitted. However, their impact on local air quality is likely to be slight, since emission limits are very stringent and stack heights will be sufficient to ensure adequate dispersion of the pollutants. New incinerators will be vastly superior to the older municipal waste and clinical waste incinerators in terms of their emissions. Any of the existing incinerators which do not meet the new standards set by the Environmental Protection Act will not obtain authorisations to continue operation.

One very significant factor in the sharp reduction in smoke and SO_2 concentrations in most UK towns and cities has been the switch from coal to natural gas as a means of space heating. Oil has its sulphur content regulated and contents have been progressively reduced. The scope for further reductions of sulphur dioxide and particulate emissions is therefore limited in this respect will in the foreseeable future, given the available supplies of natural gas. As can be seen from Chapter 4, however, there are still parts of the UK which either have not or cannot make this fuel switch. Belfast was cited as the prime example of this and the air quality in winter would undoubtedly benefit should a natural gas pipeline to the province be constructed.

Evaporative emissions from a wide variety of sources account for much of the volatile organic compounds in the urban atmosphere. These arise from industrial, commercial and domestic activities and any reduction in emissions is likely to come about by a variety of means. Industry is being asked to reduce VOCs in order to reduce the formation of ozone and the instrument for achieving this is the Environmental Protection Act. In many cases industry is reacting well to new emission limits and changing processes in order to comply or investing in control technology. The use of paints with a reduced solvent content for vehicle respraying is a good example of this.

In other countries, specific compounds have been targeted for combative measures to reduce emissions. In California, the filling stations are required to have special nozzles which trap and recycle petrol vapours which would otherwise escape to atmosphere. Such a measure would have the effect of locally reducing benzene concentrations as well as assisting in a minor way to limiting precursor emissions to the formation of photochemical oxidants. As yet, there appears to be no move to introduce similar measures in the UK, although the Second Update to the 1991 White Paper 'This Common Inheritance' did include a commitment to reducing the summer volatility of petrol.

Furthermore, the European Commission are considering a draft Directive aimed at reducing by 90% over a ten year period, the volatile organic compounds which escape into the atmosphere whenever petrol is handling at storage depots or filling stations.

It is possible that domestic emissions of VOCs could decline as a result of greater consumer awareness as has been the case for chlorofluorocarbons (CFCs). Paradoxically, of course, CFCs have sometimes been replaced as aerosol propellants by hydrocarbons. Water based paints have increased in popularity for use in and around the home and if this trend is continued then emissions of certain VOC species will decline. If consumers are made aware of the environmental implications of particular products, the evidence seems to be that their purchasing habits can be modified. It must be the case that future urban air quality depends on the lifestyles and behaviour of the populace of urban areas.

In summary, it seems likely that urban air quality will not deteriorate further as a result of non-vehicular emissions. Provided that the Environmental Protection Act legislation is properly enforced by HMIP and local authorities air quality should improve in those urban areas which are currently influenced by industrial emissions. Further scope for improvement of smoke and SO_2 concentrations as a result of domestic coal burning is limited to a few areas only.

10.4 OZONE

Ozone is a secondary pollutant which makes the prediction of future trends in its concentrations even more difficult than for the primary pollutants. The precursor emissions are oxides of nitrogen and volatile organic compounds. Both of these are forecast to decline in the next ten years, largely as a result of reduced vehicle emissions following the introduction of catalytic converters. However, this does not automatically imply a reduction in concentrations of ozone, especially in urban locations.

The mechanisms for ozone formation are complex and far from completely understood. For example, the ozone creating potential of some volatile organic compounds has been estimated but this process cannot be done for the entire range of VOCs emitted.

At present, the ozone concentrations in UK towns and cities are thought to be suppressed, especially in city centres and near to high traffic flows which are sources of nitric oxide (NO). Hence, in the current situation the emphasis is not so much on ozone formation but ozone destruction. In a future scenario in which emissions of NO_x and VOCs were reduced the outcome for urban ozone concentrations is very hard to determine. If the introduction of catalytic converters on vehicles results in a significant reduction in the amount of NO emitted, it is conceivable that ozone concentrations in urban areas could rise. There is some evidence to suggest that at present concentrations in suburban areas and parks may be more similar to those in rural areas. It is likely that any rise in urban ozone concentrations would be characterised by a spreading of the zones where ozone is not currently being destroyed by NO. Therefore, it would be a rise in concentrations averaged over the whole urban area which would result, rather than a rise in the magnitude of concentrations at specific locations where they may already be significant.

10.5 SUMMARY AND KEY ISSUES

- *Future urban air quality will be largely determined by the future pattern of motor vehicle emissions.*
- *Current and forthcoming EC legislation will result in considerable reductions in emissions on a per-vehicle basis from petrol engined and light duty diesel vehicles. Similar legislation will also reduce emissions from heavy duty vehicles.*
- *Taken together, the increasingly stringent limits have been estimated to lead to major reductions in national emissions of NO_x, CO and VOCs from road transport of 53%, 66% and 68% respectively from 1990 to 2010. UK particulate emissions from road transport are estimated to decrease by only 18% over the same period.*
- *By 2010, HGV emissions of NO_x are estimated to be more than half the total UK road transport NO_x emissions (compared with about 40% at present). The proportion of road traffic particulate emissions arising from HGVs is estimated to remain at about 65% over the period 1990-2010.*
- *Only one study of future urban air quality in the UK has been carried out. This study which assessed NO_x concentrations in London in 2000 was carried out four years ago, since which time emissions inventories, air quality information and assessment techniques have improved. The study estimated decreases in annual average NO_x concentrations of 20% in London from 1983/4 to 2000. Decreases in NO_2 concentrations were estimated at only about 5%.*

10.6 RESEARCH RECOMMENDATIONS

- *Forecasts of national emissions should be updated regularly as new information becomes available and as new or proposed legislation emerges.*
- *An updated forecasting study of urban air quality in London and other major UK cities should be carried out as a matter of urgency.*

- *Such forecasts should draw on the results of the NO/NO_2/NO_x mechanistic modelling study being carried out by AEA Technology Harwell and on the measurements from the Enhanced Urban Network.*

REFERENCES

Bailey JC, Flain RM and Parkes S (1992) **Emissions of Benzene and 1,3-Butadiene from Light Duty Vehicles Under Normal UK Driving Conditions**. To be submitted for publication.

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Eggleston HS, Gaudioso D, Goriben N, Joumard R, Rijkeboer RC, Samaras Z and Zierock, K-H (1991) **CORINAIR Working Group on Emission Factors for Calculating 1990 Emissions from Road Traffic Volume Commission of The European Communities**, Final Report Contract B4-3045 (91) 10PH.

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A Terms of Reference and Membership

TERMS OF REFERENCE

1. The UK Review Group on Urban Air Quality is a working group of experts established by the Department of the Environment to review current knowledge on urban air quality and to make recommendations to the Secretary of State for the Environment.

2. The initial objective of the Group is to prepare a review of urban air quality and how it is assessed in the United Kingdom especially in relation to public exposure, and how this information is passed on to the public. To this end the Group will consider:

   i) the pollutants measured,

   ii) the extent of monitoring networks,

   iii) the consistency of data,

   iv) the types and location of monitoring equipment and

   v) any other relevant material.

3. The longer term objectives of the Group will be to:

   i) perform a rolling review of the subject in the light of scientific and technological developments,

   ii) consider, in the light of national and international guidelines and advice, the need to add or subtract sites from the networks and the need for additional networks for different pollutants and

   iii) to consider arrangements for the public availability of data.

4. The Group will identify areas of uncertainty and recommend where further research is needed.

5. The Group will make recommendations for changes to relevant monitoring networks and public information systems.

6. The Group will act as an informal forum for the discussion of research plans and results.

7. The Group will act as a point of liaison with relevant international bodies.

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B Towns and Cities Selected by the DOE for Priority Monitoring

Urban Areas	Population
Inner London (North) Inner London (Central) Inner London (West A)	4090851
Birmingham	1024118
Glasgow	765030
Liverpool	544861
Sheffield	477257
Leeds	452841
Manchester	448604
Bristol	420234
Edinburgh	420169
Leicester	328835
Kingston upon Hull	325485
Coventry	322573
Belfast	314000
Bradford	295048
Nottingham	277203
Stoke-on-Trent	275168
Cardiff	266267
Wolverhampton	265631
Plymouth	242560
Derby	220681
Southampton	214802
Newcastle on Tyne	203591

C Regulations Relevant to UK Urban Air Quality, 1956-1992(1)

Year	**Legislation/Regulation** - Impact on Urban Air Quality
1956	**Clean Air Act** - Introduced Smoke Control Areas and grants for conversion to smokeless fuels. Controlled chimney heights. Prohibited emission of dark smoke from chimneys with some exceptions.
1968	**Clean Air Act** - Extended the Smoke Control provisions. Extended the prohibition of dark smoke emissions.
1970	**EC Directive 70/220/EEC** - relating to measures to be taken against air pollution by gases from positive ignition engines of motor vehicles. Limited emissions of carbon monoxide and hydrocarbons from petrol cars. Introduced into European legislation the requirements of UN Economic Commission for Europe (ECE) Regulation 15. Came into force in 1971.
1971	**The Performance of Diesel Engines for Road Vehicles BSI AU 141a** - Controlled black smoke from heavy duty vehicles.
1972	**EC Directive 72/306/EEC** - measures to be taken against emissions of pollutant from diesel engines for use in motor vehicles. Limited black smoke emissions from heavy duty vehicles. Essentially extended UK BSI AU 141 requirements throughout the EC.
1974	**Control of Pollution Act** - Allowed for the regulation of the composition of motor fuels; and limited sulphur in fuel oil.
1974	**EC Directive 74/290/EEC** - Amending 1970 directive relating to measures to be taken against air pollution by gases from positive ignition engines of motor vehicles. Reduced limit values for carbon monoxide and hydrocarbons emissions from petrol cars in line with UN ECE Regulation 15.01. Came into force in 1975.
1975	**EC Directive 75/441/EEC** - Established a common procedure for the exchange of information between the surveillance and monitoring networks based on data relating to sulphur dioxide and smoke. Set up a procedure for exchanging air quality information between Member States.
1975	**EC Directive 75/716/EEC** - Relating to the approximation of the laws of Member states on the sulphur content of certain liquid fuels. Defined two types of gas oil (diesel and heating oil). Introduced in two stages sulphur limits for these fuels.
1977	**EC Directive 77/102/EEC** - Amended 1970 directive relating to measures to be taken against air pollution by gases from positive ignition engines of motor vehicles Reduced limit values for carbon monoxide and hydrocarbons. Introduced limits for nitrogen oxides emissions from petrol cars in line with UN ECE Regulation 15.02. Came into force in 1977.
1978	**EC Directive 78/665/EEC** - Amended 1970 Directive relating to measures to be taken against air pollution by gases from positive ignition engines of motor vehicles. Reduced limit values for carbon monoxide, hydrocarbons, and nitrogen oxides emissions from petrol cars in line with UN ECE Regulation 15.03. Came into force in 1979.
1978	**EC Directive 78/611/EEC** - Concerning the lead content of petrol. Limited the maximum permissible lead content of petrol at 0.4 g l^{-1}. Came into force in 1981.
1980	**EC Directive 80/779/EEC** - Air quality limit values and guide values for sulphur dioxide and suspended particulates.
1981	**The Motor Fuel (Lead Content of Petrol Regulation)** - Limited the maximum amount of lead in petrol to 0.4 g l^{-1}.
1982	**EC Directive 82/459/EEC** - Repealed Directive 75/441/EEC and established a reciprocal exchange of information and data from networks and individual stations measuring air pollution within Member States. Set up a procedure for exchanging air quality information.
1982	**EC Directive 82/884/EEC** - Limit value for lead in the air.
1983	**EC Directive 83/351/EEC** - Amended 1970 directive relating to measures to be taken against air pollution by gases from engines of motor vehicles. Reduced limit values for carbon monoxide, hydrocarbons and nitrogen oxides emissions from petrol cars in line with UN ECE Regulation 15.04. Introduced limits for diesel engines for first time. Due to come into force in 1984 but was never introduced into British legislation.
1984	**Directive 84/360/EEC** - A framework directive on combating air pollution from industrial plants. The introduction of a common framework for reducing air pollution from industrial plants in the Community. Came into force in 1987.
1985	**EC Directive 85/203/EEC** - Air quality standards for nitrogen dioxide.
1985	**EC Directive 85/210/EEC** - The approximation of Member State legislation on lead content of petrol, and the introduction of lead-free petrol. Allowed for the introduction of unleaded petrol. Limited the benzene concentration of petrol to 5 % by volume.
1985	**The Motor Fuel (Lead Content of Petrol Regulation)** - Limited the maximum amount of lead in petrol to 0.15 g l^{-1}. Came into force in December 1985.
1987	**EC Directive 87/217/EEC** - Prevention and reduction of environmental pollution by asbestos. Controlled the pollution of air, water and land by asbestos from all significant point sources.

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(1) Adapted from; '**National Society for Clean Air and Environmental Protection (1992) Pollution Handbook**' NSCA, Brighton, UK.

1987	**EC Directive 87/219/EEC** - Amended Directive 75/716/EEC. Limited sulphur content of all gas oil to 0.3 % by weight.
1987	**EC Directive 88/76/EEC** - Amended 1970 directive relating to measures to be taken against air pollution by gases from engines of motor vehicles. Sets stringent emission standards for carbon monoxide, hydrocarbon and nitrogen oxides together and nitrogen oxides from large cars (>2 litres), with less stringent requirements from medium and small cars.
1987	**EC Directive 88/77/EEC** - The approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous pollutants from diesel engines for use in vehicles. Controlled emissions of gaseous pollutants from heavy duty vehicles.
1988	**EC Directive 88/609/EEC Directive** - Limited emissions of certain pollutants into the air from large combustion plants. Limited emissions of sulphur dioxide, nitrogen oxides and particulates from power stations and other large combustion plant.
1988	**EC Directive 88/436/EEC** - Amendment of 1970 Directive relating to measures to be taken against air pollution by gases from engines of motor vehicles. Controlled particulate emissions from diesel cars.
1989	**EC Directive 89/369/EEC** - Directive on air pollution from new municipal waste incinerators. Set emission limits on new waste incinerators.
1989	**EC Directive 89/429/EEC** - Directive on air pollution from existing municipal waste incinerators. Set limits on emissions from existing waste incinerators.
1989	**EC Directive 89/427/EEC** - Limit values and guide values of air quality for sulphur dioxide and suspended particulates. Harmonised measurement methods.
1989	**EC Directive 89/458/EEC** - Amendment of 1970 Directive relating to measures to be taken against air pollution by gases from engines of motor vehicles. Introduced limits for emissions of carbon monoxide and hydrocarbons and nitrogen oxides from small cars (<1.4 litres). Mandatory for the first time.
1989	**The Air Quality Standards Regulations 1989** - Statutory Instrument No 317. Formally brought into UK legislation the limit and guide values for sulphur dioxide and suspended particulates, lead in air and nitrogen dioxide set by EC Directives.
1990	**The Motor Fuel (Sulphur Content of Gas Oil) (Amendment) Regulations** - Brought into UK legislation the requirements of EC Directive 87/219/EEC that limits the sulphur content of diesel fuel to 0.3% by weight.
1990	**The Oil Fuel (Sulphur Content of Gas) Regulations** - Brought into UK legislation the requirements of EC Directive 87/219/EEC that limits the sulphur content of gas oil to 0.3% by weight.
1990	**Environmental Protection Act** - Brings many smaller emission sources under air pollution control by local authorities for the first time.
1991	**EC Directive 91/441/EEC ('The Consolidated Directive')** - Amendment of 1970 Directive relating to measures to be taken against air pollution by gases from engines of motor vehicles. Introduced mandatory emission requirements that effectively require the fitting of closed loop three way catalysts to all new petrol cars from 1993 and new limit values for diesel cars.
1991	**EC Directive 91/542/EEC** - Amendment of Directive 88/77/EEC on the approximation of the laws of the Member states relating to the measures to be taken against the emission of gaseous pollutants from diesel engines for use in vehicles. Introduced a two stage reduction in emission from heavy duty diesel vehicles (to come into effect in 1992 and 1995). Introduced emission controls for particulates for the first time.
1991	**The Road Vehicles (Construction and Use)(Amendment) - Regulations 1991** Set standards for in-service emissions of carbon monoxide and hydrocarbons to be included in the MOT test for petrol cars and light goods vehicles.
1992	Agreed EC Directive but unpublished at the time of writing this report Amends Directive 87/219/EEC. Limits sulphur content of diesel to 0.05% by weight.
1992	**EC Directive 92/72/EEC** - Air Pollution by Ozone. Establishes a harmonised procedure for monitoring, exchange of information, and informing and warning the public on ozone pollution.

D Description of the Locations of Automated Monitoring Networks in Urban Areas of the UK

NO_2 Directive Sites

Site Name	Grid Reference	Pollutants Measured	Site Description
London, Earls Court	TQ 251788	NO_x, CO	Urban
Glasgow	NS 595653	NO_x, CO	Urban
Manchester	SJ 839979	NO_x, CO	Urban
Walsall	SO 995985	NO_x	Urban
Billingham	NZ 470237	NO_x	Industrial
Sheffield	SK 403905	NO_x, CO	Urban
London, Bridge Place	TQ 289788	SO_2, NO_x, CO, O_3	Urban

SO_2 Directive Sites

Site Name	Grid Reference	Pollutants Measured	Site Description
Belfast, East	J 357740	SO_2, Smoke	Urban (Residential)
Rugeley	SK 043173	SO_2, Smoke	Municipal building on edge of small town
Barnsley	SE 348094	SO_2, Smoke	Municipal Building on edge of coal mining town

Enhanced Urban Network Sites

Site Name	Grid Reference	Pollutants Measured	Site Description
Belfast	Not available	NO_2, SO_2, CO, O_3, PM_{10}	Pedestrianised street (Lombard Street) 25m from major road
Edinburgh	NT 254738	NO_2, SO_2, CO, O_3, PM_{10}	Urban parkland (East Princess Street Gardens), 35m from major road
Cardiff	ST 184765	NO_2, SO_2, CO, O_3, PM_{10}	Pedestrianised street (Frederick Street) 190 from major road
London Bloomsbury	TQ 302820	NO_2, SO_2, CO, O_3, PM_{10}	Urban park (Russell Square), 35m from kerbside
Birmingham	SP 064868	NO_2, SO_2, CO, O_3, PM_{10}	Pedestrianised area (Centenary Square),10m from major road; 10m from small car park
Bristol	ST 299343	NO_2, SO_2, CO, O_3, PM_{10}	Pedestrianised walkway (Lower Castle Street to Bond Street) ,43m from major road.
Leeds	SE 941329	NO_2, SO_2, CO, O_3, PM_{10}	Open area (Queen Square Court) 30m from major road
Liverpool	to be decided	NO_2, SO_2, CO, O_3, PM_{10}	
Newcastle	NZ 205646	NO_2, SO_2, CO, O_3, PM_{10}	Pedestrian area 40m from road
Leicester	to be decided	NO_2, SO_2, CO, O_3, PM_{10}	
Southampton	to be decided	NO_2, SO_2, CO, O_3, PM_{10}	
Kingston upon Hull	to be decided	NO_2, SO_2, CO, O_3, PM_{10}	

UK Carbon Monoxide Monitoring Sites

Site Name	Grid Ref	Site Description
Stevenage	TL 237225	On edge of town, near light industrial site. 100m E of A1(M), flat topography
London, Earls Court(1)	TL 251788	Located in a municipal depot in a partially residential area bounded on all sides by major roads, 90m from Warwick Road
Glasgow(1)	NS 595653	Central city near-kerbside location (8m from road). Partially residential area, but with large traffic volumes in surrounding areas
Manchester(1)	SJ 839979	City centre but elevated location. 20m from nearest road, 150m from large thoroughfare (St Peter's Square)
Sheffield(1)	SK 403905	Near community centre in a mixed residential / industrial area 200 m from the M1
London, Bridge Place(1)	TQ 289788	Second floor office overlooking back-street near Victoria Station
London Bloomsbury(2)	TQ 302820	Urban parkland (Russell Square) 33m from major road
Cardiff(2)	ST 184765	Pedestrianised street (Frederick Street) 190m from major road
Belfast(2)	Not available	Pedestrianised street (Frederick Street) 25m from major road
Birmingham(2)	SP 064868	Pedestrianised street (Centenary Square) 80m from major road; 10m from small car park
Newcastle(2)	NZ 250646	Elevated pedestrian walkway (Princess Square) over lorry delivery area; 40m from major road
West London	TQ 091744	Residential near Heathrow airport
Central London (kerbside)	TQ 306797	County Hall, roof-top site 30m above ground
Central London (kerbside)	TQ 307797	County Hall, roadside
East London	TQ 501794	East London residential/industrial area
Edinburgh(2)	NT 254738	Urban parkland (East Princess Street Gardens) 35 m from major road
Bristol(2)	ST 299313	Pedestrian zone
Leeds(2)	SE 941329	30 m from kerbside
Liverpool(2)	To be decided	
Leicester(2)	To be decided	
Southampton(2)	To be decided	
Kingston upon Hull(2)	To be decided	

(1) NO$_2$ directive sites

(2) Enhanced Urban Network sites

Urban Ozone Monitoring Sites

Site Name	Grid Reference	Description
London, Victoria	TQ 292791	Urban 20 m high 100m from major road
Stevenage	TL 237225	Suburban, edge of industrial site
London, Bloomsbury(1)	TQ 302820	Urban parkland (Russell Square) 33m from major road
London, Bridge Place	TQ 289788	Second floor office overlooking back-street near Victoria Station
Cardiff(1)	ST 184765	Pedestrianised street (Frederick Street) 190m from major road
Belfast(1)	n/a	Pedestrian street (Lombard Street) 25m from major road
Newcastle(1)	NZ 205646	Elevated pedestrian walkway (Princess Square) over lorry delivery area; 40m from major road
Birmingham(1)	SP 064868	Pedestrianised area (Centenary Square) 80m from major road; 10m from major road
Edinburgh(1)	NT 254738	Urban parkland (East Princess Street Gardens) 35m from major road

(1) Enhanced Urban Network site

Toxic Organic Micro Pollutants

Site Name	Grid Reference	Pollutants Measured	Site Description
London, Marsham Street	TQ 300775	Dioxins, PAHs, PCBs	Urban
Cardiff	ST 190770	Dioxins, PAHs, PCBs	Urban
Manchester	SJ 830985	Dioxins, PAHs, PCBs	Urban
Stevenage	TL 235230	Dioxins, PAHs, PCBs	Urban

Hydrocarbons Network

Site Location	Grid Reference	Pollutant Measured	Site Description
Belfast	to be confirmed	Range of aliphatic and aromatic hydrocarbons	Urban
Birmingham	to be confirmed	Range of aliphatic and aromatic hydrocarbons	Urban
Edinburgh	NT 257730	Range of aliphatic and aromatic hydrocarbons	Urban
Middlesbrough	NZ 505194	Range of aliphatic and aromatic hydrocarbons	Urban
London, Greenwich	TQ 440 747	Range of aliphatic and aromatic hydrocarbons	Urban
London, Gordon Square	TQ 299822	Range of aliphatic and aromatic hydrocarbons	Kerbside
Cardiff	to be confirmed	Range of aliphatic and aromatic hydrocarbons	Urban

Figure D1 Geographical Distribution of Smoke and SO_2 Monitoring Sites

E Urban Ozone and Carbon Monoxide Concentrations

Table E1 Urban Ozone Concentrations 1972-1990 from Photochemical Oxidant Review Group Database (ppb)

Site	Year	Annual Mean	1-hour 98th %ile	1-hour Max	8-hour 98th %ile	8-hour Max
Canvey Island	1977	33	97	179	88	123
	1978	23	68	147	65	114
	1979	17	53	93	47	77
	1980	14	40	77	35	57
London, Victoria	1972	11	67	126	53	94
	1973	13	73	135	66	98
	1974	15	57	163	51	100
	1975	9	46	91	43	79
	1976	15	65	144	56	99
	1977	13	45	99	41	64
	1978	13	56	149	48	92
	1979	11	42	94	37	54
	1980	9	37	75	33	58
	1981	7	32	127	30	82
	1982	8	33	77	29	46
	1983	10	34	77	31	41
	1984	11	41	68	36	53
	1985	16	59	149	55	105
	1986	10	47	105	41	70
	1987	5	28	67	26	43
	1988	7	29	78	25	36
	1989	10	46	108	43	69
	1990	12	42	88	35	63
Chigwell	1979	19	63	128	59	78
	1982	25	70	119	61	81
	1983	16	62	114	53	89
	1984	23	76	160	78	106
	1985	29	67	88	61	75
County Hall, London	1975	20	74	171	64	114
	1976	27	100	212	96	148
	1978	8	38	103	29	54
	1979	19	66	153	57	94
	1980	18	54	116	53	62
	1981	15	51	112	44	72
	1982	12	48	91	45	55
	1983	25	78	99	63	78
	1984	25	67	88	60	74
	1985	28	65	98	58	73
	1986	15	71	130	57	88
	1989	19	76	124	64	93
London, Cromwell Road	1973	7	31	100	31	64
	1974	5	21	45	17	26
Glasgow	1983	19	53	104	48	72
	1984	15	47	82	42	64
	1985	8	25	108	24	86
	1986	12	34	57	31	39
Hainault	1975	22	90	126	79	97
	1976	38	123	175	113	139
Islington	1976	10	63	117	54	82
	1977	10	45	127	41	94
	1978	8	46	98	39	66
Kew	1979	17	58	156	51	110
Lincoln	1986	17	44	61	41	45
	1987	17	47	80	46	65
	1988	16	40	95	38	61
National Westminster Tower, London	1983	19	68	107	57	81
St Bartholomew's, London	1976	59	150	183	136	138
Teddington	1975	22	92	140	80	98
	1976	41	130	211	113	160
	1978	25	91	157	77	99
	1982	20	69	123	54	84
	1983	34	85	137	74	100
	1984	22	72	117	64	82
	1985	24	67	104	58	72
	1987	14	48	118	48	89
	1988	21	71	123	66	82
York	1986	14	28	36	26	30
	1987	15	38	76	37	57
	1988	12	33	49	32	43
	1989	9	29	59	30	58
	1990	11	27	64	27	49

Table E2 Carbon Monoxide Calendar Year Statistics

Site	Year	Annual mean (ppm)	50th %ile (ppm)	84th %ile (ppm)	90th %ile (ppm)	98th %ile (ppm)	Max. 1-hour (ppm)	Max. 8-hour (ppm)	Standard geometric deviation	Data capture (%)
STE	78	-	-	-	-	-	-	-	-	9
STE	79	-	-	-	-	-	-	-	-	23
STE	80	0.4	0.3	0.7	0.9	1.7	6.5	2.2	2.2	95
STE	81	0.4	0.3	0.7	1.0	2.0	5.5	2.2	2.3	90
STE	82	0.6	0.4	0.9	1.2	2.4	18.0	4.1	2.2	76
STE	83	0.4	0.3	0.6	0.7	1.3	6.9	1.3	2.0	33
STE	84	-	-	-	-	-	-	-	-	22
STE	85	-	-	-	-	-	-	-	-	0
STE	86	-	-	-	-	-	-	-	-	0
STE	87	-	-	-	-	-	-	-	-	0
STE	88	-	-	-	-	-	-	-	-	0
STE	89	0.6	0.4	1.0	1.4	2.8	5.5	3.3	2.5	49
STE	90	0.7	0.6	1.1	1.3	2.2	6.4	2.1	2.0	79
STE	91	0.7	0.5	1.0	1.3	2.9	7.4	4.5	2.0	99
LV	72	1.9	1.3	3.4	4.9	7.7	14.8	9.7	2.7	47
LV	73	2.8	2.6	4.5	5.1	6.8	13.6	7.4	2.2	86
LV	74	3.4	3.0	5.1	5.7	7.7	13.9	8.2	1.8	71
LV	75	2.8	2.5	4.1	4.9	7.7	21.4	11.1	1.9	55
LV	76	3.4	3.2	5.1	5.8	8.2	14.0	10.6	1.9	40
LV	77	2.7	2.3	4.1	4.9	7.0	36.8	9.2	1.9	29
LV	78	2.2	1.9	3.3	3.9	5.9	13.4	8.3	1.9	53
LV	79	3.1	3.1	4.3	4.8	6.7	15.7	11.2	1.9	83
LV	80	1.0	0.8	1.5	1.9	3.4	7.3	4.3	2.2	92
LV	81	1.1	0.9	1.8	2.2	4.0	13.6	9.8	2.3	84
LV	82	0.9	0.7	1.4	1.7	2.9	4.5	2.9	2.2	84
LV	83	0.8	0.6	1.2	1.5	3.3	9.2	5.4	2.3	53
LV	84	0.8	0.7	1.3	1.7	2.9	11.5	7.0	2.3	78
LV	85	0.7	0.6	1.2	1.5	2.8	7.9	4.9	2.3	68
LV	86	0.7	0.6	1.1	1.3	2.4	5.6	2.2	2.1	49
LV	87	-	-	-	-	-	-	-	-	19
LV	88	1.1	0.8	1.7	2.2	4.9	15.1	6.0	2.3	82
LV	89	1.3	1.0	1.9	2.4	5.5	20.9	16.2	2.4	77
LV	90	0.9	0.8	1.4	1.7	2.6	10.7	3.0	2.2	57
CRD	73	6.1	5.1	10.4	12.2	17.9	34.6	19.8	2.5	72
CRD	74	4.6	4.0	7.2	8.3	12.3	32.5	14.7	2.0	70
CRD	75	5.9	4.9	9.3	11.0	17.9	53.8	22.1	2.1	76
CRD	76	6.9	5.5	11.2	13.6	22.3	42.2	25.4	2.1	77
CRD	77	5.1	4.0	9.0	11.1	18.0	36.2	21.4	3.3	75
CRD	78	6.1	5.4	9.6	11.2	16.7	34.4	24.7	2.3	38
CRD	79	4.7	3.9	7.5	8.9	13.5	40.0	13.6	2.2	32
CRD	80	-	-	-	-	-	-	-	-	17
CRD	81	-	-	-	-	-	-	-	-	0
CRD	82	3.1	2.4	5.6	6.7	9.9	13.6	11.2	2.7	62
CRD	83	2.4	1.7	4.4	5.5	9.0	18.2	12.8	3.0	88
CRD	84	2.5	2.0	4.4	5.5	8.2	13.4	10.2	2.7	59
CRD	85	-	-	-	-	-	-	-	-	0
CRD	86	-	-	-	-	-	-	-	-	0
CRD	87	-	-	-	-	-	-	-	-	0
CRD	88	-	-	-	-	-	-	-	-	0
CRD	89	3.6	3.0	5.8	7.0	10.4	24.8	18.1	2.4	66
CRD	90	2.9	2.5	4.7	5.6	8.2	18.4	11.2	2.4	95
CRD	91	3.3	2.9	5.1	5.9	9.1	16.7	11.4	2.0	99
CAR	73	8.2	6.6	14.5	17.7	27.0	49.5	27.1	2.6	36
CAR	74	5.7	4.2	10.0	12.3	20.2	43.0	25.2	2.6	94
CAR	75	6.2	4.4	10.8	13.3	22.2	50.3	26.9	2.4	78
CAR	76	2.7	2.5	4.0	4.6	6.3	17.6	7.6	1.7	44
GLAS	73	3.8	2.7	6.6	8.2	14.2	22.1	20.1	2.5	46
GLAS	74	3.8	3.0	6.6	7.8	11.2	23.0	15.2	2.3	69
GLAS	75	4.3	3.4	6.9	8.4	12.6	25.8	17.3	2.0	68
GLAS	76	5.6	4.4	9.2	11.3	18.7	34.7	29.1	2.3	61
GLAS	77	4.5	3.8	7.3	8.7	14.4	26.7	19.2	2.4	59
GLAS	78	4.1	3.1	7.0	8.6	13.5	26.6	17.5	2.3	85
GLAS	79	3.8	2.9	6.4	8.0	13.1	30.5	24.9	2.4	84
GLAS	80	3.5	2.9	5.9	7.1	11.3	27.4	16.0	2.6	64
GLAS	81	3.8	2.9	6.1	7.8	13.3	21.5	13.9	2.1	37
GLAS	82	2.8	2.2	4.3	5.4	8.8	21.3	12.2	1.9	67

Continued

Table E2 Carbon Monoxide Calendar Year Statistics (Continued)

Site	Year	Annual mean (ppm)	50th %ile (ppm)	84th %ile (ppm)	90th %ile (ppm)	98th %ile (ppm)	Max. 1-hour (ppm)	Max. 8-hour (ppm)	Standard geometric deviation	Data capture (%)
BHAM	74	5.5	5.3	8.0	9.1	12.0	21.7	13.6	1.9	51
BHAM	75	5.9	5.1	9.7	11.0	17.1	31.5	21.9	2.1	72
BHAM	76	6.4	5.1	10.4	12.6	20.4	37.1	26.4	2.2	81
BHAM	77	5.9	5.2	9.6	10.9	14.4	29.8	15.2	2.0	79
BHAM	78	-	-	-	-	-	-	-	-	4
CAMB	74	-	-	-	-	-	-	-	-	15
CAMB	75	5.0	4.5	8.2	9.2	13.1	28.2	16.7	2.1	88
CAMB	76	5.3	4.5	8.2	9.7	15.3	91.5	29.2	2.1	65
CAMB	77	5.6	4.7	9.4	11.1	16.0	28.9	18.4	2.3	65
CAMB	78	-	-	-	-	-	-	-	-	14
HARR	79	0.9	0.5	1.6	2.3	4.1	6.3	4.1	2.8	36
HARR	80	0.6	0.3	1.0	1.3	3.1	6.4	4.2	2.5	69
CAN	77	-	-	-	-	-	-	-	-	17
CAN	78	0.9	0.7	1.4	1.8	3.8	9.5	5.5	2.1	33
CAN	79	0.7	0.7	1.0	1.1	1.7	5.9	2.6	1.5	58
CAN	80	-	-	-	-	-	-	-	-	1
LEC	89	-	-	-	-	-	-	-	-	16
LEC	90	1.5	1.2	2.2	2.7	4.4	13.2	8.8	2.0	79
LEC	91	1.7	1.4	2.5	2.9	5.4	18.0	13.2	2.0	91
GLA	89	1.6	1.0	2.7	3.7	7.6	19.2	11.6	3.1	43
GLA	90	1.1	0.7	1.8	2.3	5.1	17.0	7.8	2.8	87
GLA	91	1.4	1.0	2.0	2.5	5.0	16.3	12.1	2.0	97
MAN	91	0.9	0.7	1.5	1.8	3.2	8.6	3.6	2.1	36
SHE	91	0.9	0.6	1.3	1.7	4.1	8.3	5.7	2.1	40
BRI	90	1.3	1.0	2.0	2.3	4.5	11.7	6.2	2.1	36
BRI	91	1.4	1.1	2.0	2.4	4.4	13.9	9.8	1.9	99
LW	86	1.1						-		
LW	87	2.0						18.5		
LW	88	2.1						17.2		
LW	89	1.4						13.0		
CLB	86	1.0						-		
CLB	87	1.7						10.5		
CLB	88	1.3						9.7		
CLB	89	1.5						15.2		
CLK	86	3.6						-		
CLK	87	3.6						14.3		
CLK	88	3.9						14.2		
CLK	89	3.8						16.6		
EL	86	1.9						-		
EL	87	2.2						6.1		
EL	88	2.5						11.4		
EL	89	1.6						7.4		

Data displayed for data captures ≥ 25%

Site abbreviations

STE	Stevenage
LV	London, Victoria
CRD	London, Cromwell Road
CAR	Cardiff (kerbside)
GLAS	Glasgow, Hope Street
BHAM	Birmingham (kerbside)
CAMB	Cambridge
HARR	Harrow
CAN	Canvey
LEC	London, Earls Court
GLA	Glasgow
MAN	Manchester
SHE	Sheffield
BRI	London, Bridge Place
LW	West London
CLB	Central London (background)
CLR	Central London (kerbside)
EL	East London

F The Key Urban Pollutants

POLLUTANT	SOURCES
SULPHUR DIOXIDE (SO_2)	Fuel combustion for domestic heating, power stations, industrial boilers and chemical processes, waste incinerators, diesel vehicles.
NITROGEN OXIDES (NO_x)	Transport (road, rail, passenger and commercial) fuel combustion for domestic heating, power stations, industrial boilers and chemical processes, waste incinerators.
PARTICULATE MATTER	Fuel combustion for domestic heating, power stations, industrial boilers and most industrial processes, transport, waste incinerators.
ORGANIC COMPOUNDS	Transport, oil based fuel combustion sources, chemical processes, solvent use, waste incinerators. Specific pollutants considered here include: • *Benzene - petrol combustion products, evaporation from petrol pumps and fuel tanks.* • *Polynuclear aromatic hydrocarbons (PAH). Fuel combustion.* • *Volatile organic compounds (VOCs). A range of VOCs are involved in ozone and PAN (peroxyacetyl nitrate) formation; main sources include: transport and solvents (esp use of paints in industrial and domestic sectors).*
TRACE METALS	Metal production and finishing operations, products manufacture, fuel combustion and waste incinerators, chemical processes, transport. Specific pollutants considered here include: • *Lead (Pb). Use of lead additives in petrol* • *Cadmium (Cd). Fuel combustion, metal production processes, waste incinerators.*
CARBON MONOXIDE (CO)	Motor vehicles and combustion processes
OZONE (O_3)	Secondary pollutant from primary emissions of NO_2 and VOCs

NITROGEN OXIDES (NO_x)

1. Description

NO_x is a collective term used to refer to two species of oxides of nitrogen: nitric oxide (NO) and nitrogen dioxide (NO_2). (Other oxides of nitrogen exist, but are not included in the definition of NO_x). These two oxides are grouped together because most anthropogenic NO_2 derives from emissions of NO. NO_2 is generally regarded as being more important from the point of view of human health. Consequently, data on health risks, ambient concentrations and standards and guidelines are expressed in terms of NO_2 rather than NO_x.

Nitrogen dioxide (NO_2) is a reddish-brown gas. It is a strong oxidant and soluble in water.

2. Occurrence in Air

Annual mean concentrations in urban areas are generally in the range 10-45 ppb (20-90 $\mu g\ m^{-3}$). Levels vary significantly throughout the day, with peaks generally occurring twice daily as a consequence of "rush-hour" traffic. Maximum daily and one-hourly means can be as high as 200 ppb (400 $\mu g\ m^{-3}$) and 450 ppb (850 $\mu g\ m^{-3}$) respectively.

3. Major Sources

Globally, quantities of nitrogen oxides produced naturally (by bacterial and volcanic action and by lightning) far outweigh anthropogenic emissions. These give rise to low level background atmospheric concentrations. Anthropogenic emissions are mainly due to fossil fuel combustion from both stationary sources (heating, power generation) and transport (internal combustion engines).

In most cases, atmospheric nitrogen is oxidised to NO during combustion and then oxidised to NO_2 when emitted into the atmosphere. The former process is temperature dependent, with less "thermal" NO being produced in lower temperature combustion processes. (Nitrogenous compounds in coal, and to a lesser extent in oil, also make a contribution to the total quantity of NO emitted). A small percentage of NO_2 is also emitted from most combustion sources. The atmospheric oxidation of NO to NO_2 is caused by reaction with O_3 and other oxidants, such as HO_2. This occurs rapidly even when there are relatively low concentrations of NO and oxidants in the atmosphere.

Other atmospheric contributions come from non-combustion processes. (For example, nitric acid manufacture, welding processes and the use of explosives). Indoor sources of NO_2 include tobacco smoking and the use of gas fired appliances and oil stoves.

4. Atmospheric Behaviour

When NO is emitted into the atmosphere, most of it is rapidly oxidised to NO_2 by O_3 or other oxidants such as HO_2:

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

$$NO + HO_2 \rightarrow NO_2 + OH$$

In polluted atmospheres, other oxidation reactions take place involving hydrocarbons, aldehydes, CO and other compounds. NO also combines with OH radicals to produce nitrous acid (HNO_2).

Once formed, the atmospheric residence time of NO_2 is of the order of one day. It is then converted to nitric acid (HNO_3) by reaction with OH radicals. Most HNO_3 is then removed from the atmosphere by wet and dry deposition.

5. Human Health Effects

A variety of respiratory system effects have been reported to be associated with exposure to short-and long-term NO_2 concentrations less than 2000 ppb in humans and animals, including: (1) altered lung function and symptomatic effects observed in controlled human exposure studies and in community epidemiological studies, (2) increased prevalence of acute respiratory illness and symptoms observed in outdoor community epidemiological studies and in indoor community epidemiological studies comparing residents of gas and electric stove homes, and (3) lung tissue damage, development of emphysema-like lesions in the lung, and increased susceptibility to infection observed in animal toxicology studies. Certain human health effects may occur as a result of exposures to NO_2 concentrations at or approaching recorded ambient NO_2 levels.

Young children and asthmatics are the groups at greatest risk from ambient NO_2 exposures. Chronic bronchitics and individuals with emphysema or other chronic respiratory diseases may also be sensitive to NO_2 exposures.

6. Other Environmental Effects

Other environmental effects of NO_x compounds include increased acidic deposition and vegetation effects.

Visible injury to vegetation due to NO_2 alone occurs at levels which are above ambient concentrations generally occurring within the UK except around a few point sources. For long-term exposures, such as a growing season, the lowest concentration reported to depress growth is approximately 250 ppb (500 $\mu g\ m^{-3}$). Interactive effects with SO_2 may however be important.

SULPHUR DIOXIDE (SO_2)

1. Description

Sulphur dioxide (SO_2) is a colourless gas. It reacts on the surface of a variety of airborne solid particles, is soluble in water and can be oxidised within airborne water droplets.

2. Occurrence in Air

Annual mean concentrations in most major UK cities are now well below 35 ppb (100 $\mu g\ m^{-3}$), with typical mean values in the range 10-20 ppb (25-50 $\mu g\ m^{-3}$). Hourly peak values can be 400-750 ppb (1,000-2,000 $\mu g\ m^{-3}$) on infrequent occasions. Natural background levels are about 5 $\mu g\ m^{-3}$.

Acid aerosol (most of which is formed from SO_2) occurs in concentrations of the order of 0-20 $\mu g\ m^{-3}$ (measured as sulphuric acid) in North America and Europe.

3. Major Sources

The most important sources of emissions of SO_2 are fossil fuel combustion, smelting non-ferrous ores (mainly copper, lead, nickel and zinc), manufacture of sulphuric acid, conversion of wood pulp to paper, incineration of refuse, production of elemental sulphur. Coal burning is the single largest source of atmospheric SO_2, accounting for about 50% of annual global emissions in recent years, with oil burning accounting for a further 25-30% of emissions.

4. Atmospheric Behaviour

SO_2 is the principal pollutant associated with the problem of acid deposition, usually after having been oxidised to sulphuric acid. The most likely first step in a chain of reactions is oxidation of SO_2 by OH:

$$SO_2 + OH\ (+M) \rightarrow HSO_3\ (+M)$$

(Where M is a molecule of oxygen, nitrogen or other naturally occurring gas which carries off the excess energy, thereby preventing the immediate reversal of the reaction).

Oxidation reactions involving O_2, O_3 and the hydroperoxy radical (HO_2) are so slow as to be insignificant. Oxidation reactions with organic peroxy radicals (RO_2) can become significant in highly polluted atmospheres.

The subsequent reactions of the transient HSO_3 radical are still uncertain, although ultimately it is transformed to sulphuric acid (H_2SO_4). The most likely mechanism is thought to be:

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

This sulphuric acid is generally present as an acid aerosol, often associated with other pollutants in droplets or solid particles of a wide range of sizes.

SO_2 oxidation in water droplets by hydrogen peroxide and ozone is also an important mechanism.

The sulphuric acid is finally removed from the atmosphere by either wet or dry deposition.

4. Human Health Effects

Concentrations of more than 4,000 ppb (10,000 $\mu g\ m^{-3}$) SO_2 can give rise to severe effects in the form of bronchoconstriction, chemical bronchitis and chemical tracheitis. Concentrations of 1,000 ppb (2700 μgm^{-3}) give rise to immediate clinical symptoms with bronchospasm in asthmatics.

Epidemiological studies indicate the following effects after short term exposures to SO_2 and numerically similar concentrations of black smoke: possible small reversible decline in childrens lung function 100-150 ppb (250- 450 $\mu g\ m^{-3}$); aggravation of bronchitis (about 200 ppb); increased mortality (200-400 ppb).

Sulphuric acid and other sulphates also have human health effects. Respiratory effects have been reported for concentrations of 350-500 $\mu g\ m^{-3}$ sulphuric acid, with a lowest-demonstrated-effect level of 100 $\mu g\ m^{-3}$ for exercising adolescent asthmatics. The odour threshold for sulphuric acid is in the range of 750-3,000 $\mu g\ m^{-3}$.

High concentrations of SO_2 (>400 ppb) together with high concentrations of suspended particles are believed to have been responsible for high mortality levels during London smogs. (The December 1952 smog was associated with 4,000 excess deaths).

6. Other Environmental Effects

There is evidence that some species of plants are affected by SO_2 concentrations of the order of 20-40 ppb (50-100 $\mu g\ m^{-3}$). Various species of tree have exhibited effects at concentrations of less than 20 ppb (50 $\mu g\ m^{-3}$). However, interpretations these studies are complicated by the presence of other pollutants (O_3, NO_x, acid deposition and heavy metal soil contamination).

Acid deposition (to which sulphur compounds are the greatest contributors) can affect terrestrial ecosystems either directly, as above-ground effects or indirectly as a result of changes in soil characteristics.

SO_2 also has an important role to play in deterioration of stonework and metal corrosion.

CARBON MONOXIDE (CO)

1. Description

Carbon monoxide (CO) is a colourless, odourless, tasteless gas that is slightly lighter than air.

2. Occurrence in Air

Natural background levels of CO fall in the range 10 - 200 ppb. Levels in urban areas are highly variable, depending upon weather conditions and traffic density. 8-hour mean values are generally less than 10 ppm (12 mg m^{-3}) but can be as high as 50 ppm (60 mg m^{-3}).

3. Major Sources

CO is an intermediate product through which all carbon species must pass when combusted in oxygen. In the presence of an adequate supply of O_2, most CO produced during combustion is immediately oxidised to CO_2. However, this is not the case in spark ignition engines, especially under idling and deceleration conditions. Thus, the major source of atmospheric CO is the spark ignition combustion engine. Smaller contributions come from all other processes involving the combustion of organic matter (for example in power stations, industry, waste incineration). In the indoor environment, tobacco smoking can be a significant source of CO.

4. Atmospheric Behaviour

Once emitted to the atmosphere, CO is slowly oxidised to CO_2.

5. Human Health Effects

When CO is inhaled it enters the blood stream and may disrupt the supply of essential O_2 to the body's tissues. The health effects of CO result principally from its ability to displace O_2 from haemoglobin, forming carboxyhaemoglobin (COHb). (The normal function of haemoglobin is to transport O_2 from the lungs to all body tissues). The consequent reduced O_2 availability can give rise to a wide range of health effects (depending on how much the supply of oxygen to the body is impeded).

These health effects are usually related to blood levels of COHb (expressed as a percentage), which can in turn be related to exposure (as a function of exposure time as well as concentration). The "no-observed-effects" level is about 2% COHb which can be related to an 8 hour exposure (moderate activity) to 15-20 ppm.

Certain neurobehavioural effects can be expected at about 5% COHb (moderate activity for 8 hours in 35 ppm) that can be related to observable ambient concentrations. These include: impaired learning ability, reduced vigilance (ability to detect small changes in the subject's environment), decreased manual dexterity, impaired performance of complex tasks, and disturbed sleep activity.

However, of greater concern at more typical ambient CO concentrations are certain cardiovascular effects including aggravation of angina, in those individuals with impaired cardial blood supply, during exercise. This may occur at concentrations of carboxyhaemoglobin of between 2.9 and 4.5%.

Individuals most at risk from the effects of CO include those with existing cardiovascular or chronic respiratory problems, the elderly, young children and foetuses.

6. Other Environmental Effects

There are few if any, other significant environmental effects. Plants both produce and metabolize CO and are only harmed by prolonged exposure to very high levels. (The lowest levels of which significant effects on vegetation have been reported is 100 ppm for 3 to 35 days).

PARTICULATE MATTER

1. Description

Particulate matter is a complex mixture of organic and inorganic substances, present in the atmosphere as both liquids and solids. Coarse particles can be regarded as those with an aerodynamic diameter greater than 2.5 µm, and fine particles less than 2.5 µm. Coarse particles usually contain earth crustal materials and fugitive dust from roads and industries. Fine particles contain the secondarily formed aerosols, combustion particles and recondensed organic and metallic vapours. The acid component of particulate matter generally occurs as fine particles.

A wide range of terminology is applied to particulate matter, reflecting measuring methods (eg total suspended particulates), site of deposition in humans (eg inhalable, thoracic particles) or physical characteristics (eg PM_{10}, which refers to an aerodynamic diameter of less than 10 µm).

A further distinction that can be made is to classify particulate as either "primary" or "secondary", according to their origin. Primary particulates are those emitted directly to the atmosphere while secondary particulates are those formed by reactions involving other pollutants. In the urban context, most secondary particulate matter occurs as sulphates and nitrates formed in reactions involving SO_2 and NO_x.

2. Occurrence in Air

Reported concentrations vary according to the sampling technique. In urban areas typical annual mean values are 10-40 µg m^{-3} (black smoke method) or 50-150 µg m^{-3} (gravimetric method). Corresponding peak values are 100-250 µg m^{-3} (black smoke method) and 200-400 µg m^{-3} (gravimetric method). Background levels in rural areas range from 0-10 µg m^{-3} (black smoke method).

3. Major Sources

Particulate matter is emitted from a wide range of sources including power plants and industrial processes, vehicular traffic, domestic coal burning and industrial incinerators. Natural sources are less important. These include volcanoes and dust storms. Particulate matter can also be formed by the transformation of gaseous emissions such as oxides of sulphur and nitrogen, and VOCs.

4. Atmospheric Behaviour

Particulate matter is removed from the atmosphere by both wet and dry deposition.

5. Human Health Effects

Short term health effects of exposure to combined SO_2, and black smoke/particulates include increased mortality, morbidity and deficits in pulmonary function. Some of the 'lowest-observed effect' levels for short term exposure to particulate matter are: excess mortality - 500 µg m^{-3} (smoke and sulphur dioxide); increased acute respiratory morbidity (adults) - 250 µg m^{-3} (smoke and sulphur dioxide); decrements in lung function (children) - 180 µg m^{-3} (total suspended particulates)/ 110 µg m^{-3} (thoracic particles). Smoke levels of up to 6000 µg m^{-3} occurred in the 1952 London smog (see also SO_2).

In addition, exposure to air pollutants and especially particulates may give rise to feelings of discomfort, which may cause annoyance.

6. Other Environmental Effects

Other environmental effects include the soiling of exposed surfaces, impairment of visibility, potential modification of climate and contribution to acid deposition.

OZONE (O_3)

1. Description

Ozone (O_3) is the tri-atomic form of molecular oxygen. (Most atmospheric oxygen is in the di-atomic molecular form - O_2). It is one of the strongest oxidising agents, which makes it highly reactive.

2. Occurrence in Air

Background levels of O_3 in Europe are usually less than 15 ppb but can be as high as 60 ppb. Maximum hourly values may exceed 150 ppb in rural areas and 175 ppb in urban area.

3. Major Sources

Most of the O_3 in the troposphere (lower atmosphere) is formed indirectly by the action of sunlight on nitrogen dioxide - there are no direct emissions of O_3 to the atmosphere. About 10-15% of tropospheric O_3 is transported from the stratosphere where it is formed by the action of UV radiation on O_2. In addition to O_3, tropospheric photochemical reactions produce a number of oxidants including peroxyacetyl nitrate (PAN), nitric acid and hydrogen peroxide, as well as secondary aldehydes, formic acid, fine particulates and an array of short-lived radicals.

As a result of the various reactions that take place in the atmosphere, O_3 tends to build up downwind of urban centres (where most of NO_x is emitted from vehicles).

4. Atmospheric Behaviour

The O_3 producing reactions are:

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$

The reaction products, NO and O_3 can react to recreate O_2 and NO_2.

$$NO_2 + O_3 \rightarrow NO_2 + O_2$$

Thus the net result can be summarised as a reversible reaction:

$$NO_2 + O_2 \Leftrightarrow NO + O_3$$

The rate at which O_3 is produced is determined by a number of factors including the concentrations of each of the compounds and the intensity of sunlight. For this reason, O_3 episodes occur on hot days. The presence of other oxidants (eg HO_2) in the atmosphere contribute to the build up of O_3 by oxidising NO (produced during O_3 formation) to NO_2:

$$NO + HO_2 \rightarrow NO_2 + OH$$

The NO_2 is then available for further O_3 formation.

Short-lived VOCs, especially the chemically reactive hydrocarbons, contribute substantially to atmospheric photochemical reactions and thus to the formation of O_3. The lifetime of O_3 in polluted areas is about one day (and more in unpolluted areas). O_3 is removed from the atmosphere at approximately equal rates by dry deposition and chemical decomposition. One such reaction involves the OH radical:

$$NO_2 + OH \rightarrow HNO_3$$

The removal of NO_2 from the atmosphere disturbs the equilibrium position of the reversible reaction, $NO_2 + O_2 \Leftrightarrow NO + O_3$, such that the concentration of O_3 is decreased.

5. Human Health Effects

O_3 and other oxidants cause a range of acute effects including eye, nose and throat irritation, chest discomfort, cough and headache. These have been associated with hourly oxidant levels of about 100 ppb. Pulmonary function decrements in children and young adults have been reported at hourly average O_3 concentrations in the range 80-150 ppb. The non-ozone components of the photochemical mixture cause eye irritation at O_3 levels of about 100 ppb.

6. Other Environmental Effects

Other environmental effects include damage to materials (including as a result of prolonged exposure to low concentrations) and vegetation effects.

CADMIUM

1. Description

Cadmium is a soft, silver-white metal, with a relatively high vapour pressure.

2. Occurrence in Air

Yearly mean concentrations in rural areas range from <1-5 ng m^{-3}; in urban areas from 5-15 ng m^{-3}; in industrial areas from 15-50 ng m^{-3}. Short term values near metals processing industries can be as high as 5-11 μg m^{-3}.

3. Major Sources

The major sources of emissions of cadmium are oil and coal combustion, metal production (iron and steel, zinc, cadmium, copper, nickel), solid waste disposal, battery manufacture and cement production. Emissions from natural sources (eg volcanoes) are also significant. Tobacco smoking can make a significant contribution in the indoor environment. Tyre abrasion is also a source of cadmium.

4. Atmospheric Behaviour

Cadmium is mainly present in the atmosphere in particulate form. It is removed by either wet or dry deposition, and can thus enter the food chain. The residence time depends, amongst other things, upon particle size, the height of emission, and climatic conditions.

5. Human Health Effects

Human exposure to cadmium occurs by inhalation of airborne cadmium and ingestion of cadmium which has entered the food chain. Cadmium enters the food chain from natural sources and via the deposition of airborne cadmium.

Airborne cadmium is absorbed in the lungs and travels to the liver and to the kidneys. The health effects of cadmium occur because it competes with and displaces zinc in a number of zinc-containing metalloenzymes. The cadmium binds irreversibly with active sites, thereby destroying normal metabolism.

In terms of long term low level exposure, the kidney is regarded as the critical organ, with renal dysfunction expected as cadmium accumulates to levels of about 200 mg kg^{-1} wet weight. Acute and chronic respiratory effects (chemical pneumonitis) may be expected to result from exposure to 1 mg m^{-3} and 20 μg m^{-3} (for 20 years) respectively.

Other health effects of cadmium that have been identified in the literature include pulmonary and gastrointestinal effects (nausea, vomiting, diarrhoea, cardio-pulmonary depression) and damage to the liver.

6. Other Environmental Effects

Cadmium is generally toxic to both aquatic and terrestrial biota. For example, toxic effects have been found in aquatic organisms at level which can be observed in polluted environments. Cadmium toxicity is enhanced by the presence of other metals (eg zinc and copper) and is also affected by the hardness of water. For this reason, it has been difficult to establish definitive dose-response characteristics.

LEAD

1. Description

Lead is a bluish or silver-grey soft metal. In the context of air pollution, two of its most important compounds are tetraethyl and tetramethyl lead, which are used extensively as 'anti-knock' additives in petrol.

2. Occurrence in Air

In rural areas lead levels are now $<0.1\ \mu g\ m^{-3}$. UK urban values are now less than $1\ \mu g\ m^{-3}$.

Most of the lead in air occurs as fine, inorganic particles (eg PbBrCl). These particles are mainly submicron sized ($<10^{-6}$m). Although larger particles are also present. Some 10% or less occurs as organic (ie alkyl) lead which has escaped combustion.

3. Major Sources

Historically, the principal source of atmospheric lead has been the combustion of alkyl lead additives in motor fuels. However, the contribution from this source is decreasing in the UK as a result of controls on the lead content of fuels and the availability of lead free petrol. Other contributions come from: the production of metals (lead, copper, nickel, zinc, cadmium, iron and steel), thermal power plants and other coal combustion plants. Smaller contributions come from mining, cement production, refuse incineration and wood combustion. Lead based paints also contribute to lead in dust and hence in air by resuspension.

4. Atmospheric Behaviour

Particulate lead is removed from the atmosphere by wet or dry deposition. The residence time of lead containing particles in the atmosphere varies according to a number of factors such as particle size, wind currents, rainfall and emission height.

5. Human Health Effects

Human exposure to lead is through inhalation of airborne lead and ingestion of lead in foodstuffs and beverages. Whilst most airborne lead is of human origin, an appreciable proportion of that in food and water is of natural origin. Nevertheless both deposition of airborne lead, and lead from other man-made sources, eg pipes and solders, contribute to dietary intake. Blood lead concentrations are a good indicator of recent exposure to lead from all sources, and adverse health effects tend to increase in severity with increasing blood lead level.

US EPA standards are based upon the concept of a relationship between ambient air lead and blood lead concentrations, and presume that a blood lead level of $0.15\ \mu g\ ml^{-1}$ (mean value for children) can be achieved at an ambient air lead level of $1.5\ \mu g\ m^{-3}$.

The most sensitive body systems to the effects of lead are the haematopoietic system, the nervous system and the renal system. In addition, lead has been shown to affect the normal functions of the reproductive, endocrine, hepatic, cardiovascular, immunologic and gastrointestinal systems. The most sensitive group to lead poisoning is children. Studies indicate that children with high levels of lead in blood or accumulated in their teeth experience more behavioural problems, lower IQs and decreased ability to concentrate, although these findings are currently controversial.

6. Other Environmental Effects

Lead is generally toxic to both plants and animals, and although no serious effects are generally seen at current environmental levels, it is widely considered prudent to limit further dispersal of lead as far as possible.

VOLATILE ORGANIC COMPOUNDS (VOCS)

1. Description

VOCs (Volatile Organic Compounds) comprise a very wide range of individual substances, including hydrocarbons (alkanes, alkenes and aromatics), halocarbons (eg trichloroethylene) and oxygenates (alcohols, aldehydes and ketones). All are organic compounds of carbon and are of sufficient volatility to exist as vapour in the atmosphere.

2. Occurrence in the Air

Most measurements of total VOCs are in terms of their carbon content, without analysis as individual compounds. The major contributor to VOCs is normally methane which has a global background concentration of 1.6 ppm. Whilst most other individual compounds (eg benzene) are present in urban air at concentrations of a few ppb, or less, total VOCs amount to several hundred ppb in concentration in excess of the methane level.

3. Major Sources

These vary greatly for individual compounds. Hydrocarbons arise substantially from gasoline evaporation and incomplete combustion, and from leakage of natural gas from distribution systems. Oxygenates arise in vehicle exhaust and are also formed in atmospheric chemical reactions. Evaporation of solvents, used for example in paints, or industrial degreasing processes, causes release of hydrocarbons, oxygenates and halocarbons to the atmosphere.

4. Atmospheric Behaviour

Immense variations occur between compounds, with some being highly reactive and of short atmospheric lifetime, and others very long-lived. The short-lived compounds, especially the chemically reactive hydrocarbons, contribute substantially to atmospheric photochemical reactions and thus to formation of ozone and PAN. Less reactive substances are dispersed away from urban areas and decompose slowly in the non-urban atmosphere. Certain of the halocarbons (eg methyl chloroform) are so unreactive in the lower atmosphere that they enter into the stratosphere where they can contribute to ozone destruction.

5. Human Health Effects

No generalisations can be made, as health effects are compound-specific. A number of VOCs are proven or suspected carcinogens.

6. Other Environmental Effects

Many VOCs are of significance in relation to their environmental effects, particularly their contribution to secondary pollution formation and to stratospheric ozone depletion. VOCs also contribute indirectly to formation of atmospheric acidity. Ethylene, a major VOC component, is a plant hormone and can seriously inhibit the growth of plants.

BENZENE

1. Description

Benzene is a colourless, clear liquid with a boiling point of 80.1°C. It is fairly stable chemically, but highly volatile (that is, it readily evaporates).

2. Occurrence in the Air

Ambient concentrations of benzene are typically between 1 and 50 ppb. Levels close to major emission sources (for example, petrol stations) can be as high as several hundred ppb.

3. Major Sources

About 80% of anthropogenic emissions of benzene comes from petrol fuelled cars. This results from both the benzene content and partial combustion of petrol. A further 5% of emissions comes from the handling, distribution and storage of petrol, and about 1% comes from oil refining. Significant emissions also come from benzene producing and handling industries, involving such processes as the catalytic reforming of naphtha and the toluene hydrodealkylation. The burning of wood and other organic material also results in an appreciable release of benzene. Some emissions also come from the use of benzene as a laboratory reagent and in sample collection, preparation and extraction. Cigarette smoking may be a significant source of benzene for smokers, especially in the indoor environment. Another source in the indoor environment is the use of benzene in glues, adhesives and solvents.

4. Atmospheric Behaviour

Benzene is removed from the atmosphere by both wet deposition and chemical transformation in the atmosphere (principally by reaction with the hydroxyl radical OH). The half life for chemical transformation is about ten days. Deposition to the soil usually leads to degradation by bacterial action or re-evaporation (owing to benzene's high vapour pressure).

5. Human Health Effects

Benzene is known to have both carcinogenic and toxic effects. Epidemiological studies of workers exposed to high concentrations of benzene (> 20 ppm and probably > 100 ppm) for, on the whole, lengthy periods have demonstrated an increased risk of leukaemia.

Early manifestations of toxicity are anaemia, leucocyotopenia or thrombocytopenia (lack of white blood cells and platelets). Persistent exposure to toxic levels of benzene may cause injury to the bone marrow, resulting in pancytopenia. Exposure to high levels (>1,000 ppm) of benzene causes neurotoxic symptoms. No adverse effect on blood formation in humans has been confirmed following regular and repeated occupational exposure to benzene in air at concentrations below 25 - 30 ppm.

6. Other Environmental Effects

Benzene is generally toxic to biota, but there are no significant effects at ambient levels.

POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

1. Description

Polycyclic (or polynuclear) aromatic hydrocarbons (PAH) are a large group of organic compounds with two or more benzene rings. About 500 such compounds (including derivatives) have been detected in air. The best-known and most-measured of these is benzo[a]pyrene (BaP). The relative occurrence of individual compounds (the PAH profile) varies according to the source of the PAH.

2. Occurrence in Air

BaP concentrations in most cities are in the range 1-5 ng m^{-3}. (Values of the order of 100 ng m^{-3} were recorded in the 1960s when the use of open coal fires for domestic heating was more common). BaP concentrations of 40 ng m^{-3} have been found in areas close to coke oven plants, and occupational exposures can be in the range of 10-40 $\mu g\ m^{-3}$ (eg in aluminium smelting and coke production plants).

3. Major Sources

PAH are formed mainly as a result of pyrolytic (thermal degradation) processes, especially the incomplete combustion of organic matter. Major sources include motor vehicles and coke production, coal-fired heating, to a lesser extent, oil-fired heating and coal-fired power generation. (The contribution from coal-fired heating has decreased substantially as a result of smoke controls, especially in urban areas).

4. Atmospheric Behaviour

PAH are present in the atmosphere in gaseous form as well as adsorbed onto particulate matter. Smaller-molecule PAH tend to be predominantly in the gas phase, while larger-molecule PAH are more commonly bound to particulate matter. PAH are removed from the atmosphere by transformation (photochemical and thermal reactions involving OH radicals, O_2, O_3, and oxides of nitrogen and sulphur) and by wet and dry deposition.

5. Human Health Effects

There is some evidence that, in the past, people working as chimney sweeps and tar workers suffered from skin cancers caused by substantial dermal exposure to PAH. There is also evidence of an association between lung cancer and exposure to PAH in coke-oven workers, coal-gas workers and employees in aluminium production plants.

BaP is thought to be one of the most carcinogenic PAH. High levels of lung cancer have been observed in coke oven workers exposed to a BaP concentration of about 30 $\mu g\ m^{-3}$.

(Ambient levels in major urban areas are typically in the range 1-10 ng m^{-3}).

There are no known toxic effects other than carcinogenicity.

6. Other Environmental Effects

Laboratory tests involving exposure by skin painting, injection and inhalation have shown that PAH are toxic to animals, particularly small mammals.

G Units and Conversion Factors

In this report, the preferred unit for expressing concentrations of gases is parts per billion (ppb), or in some cases, parts per million (ppm). Occasionally, data have been given in microgrammes per cubic metre ($\mu g\ m^{-3}$) or milligrams per cubic metre ($mg\ m^{-3}$) where those data were originally published in that form.

The expression of air pollutant concentrations in more than one unit of measurement can cause confusion for those not professionally involved in the field. There are two main systems of unit in common use.

(i) Mass per unit volume: usually in $\mu g\ m^{-3}$. The mass of pollutants is expressed as a ratio to the volume of air. Since the volume of a given parcel of air is dependent upon the temperature and pressure at the time of sampling, the pollutant concentration expressed in these units is dependent also, and strictly speaking, the conditions at the time of sampling should be specified.

(ii) Volume mixing ratio; usually in ppm - parts per million (10^6), ppb - parts per billion (10^9) or ppt - parts per trillion (10^{12}). This unit expresses the concentration of a pollutant as a ratio of its volume if segregated pure, to the volume of the polluted air in which it is contained. Ideal gas behaviour is assumed and thus the concentration is not dependent upon temperature and pressure as these affect both the pollutant and the air to the same extent. As a consequence of the ideal gas laws, a gas present at a volume mixing ratios of 1 ppm is not only 1 cm^3 per 10^6 cm^3 of polluted air, it is also 1 molecule per 10^6 molecules and has a partial pressure of one millionth of the atmospheric pressure.

Some pollutants (eg sulphate, nitrate) are present as particles in the air and the concept of a volume mixing ratio of gases is obviously not applicable. Their concentrations are normally only expressed in $\mu g\ m^{-3}$.

Interconversion of the two sets of units can be achieved as follows:

$$\mu g\ m^{-3} = \text{ppb} \times \frac{\text{molecular weight}}{\text{molar volume (litres)}}$$

where,

$$\text{molar volume} = 22.41 \times \frac{T}{273} \times \frac{1013}{P} \text{ litres}$$

in which T = absolute temperature (K)
P = atmospheric pressure (mb)

Similarly,

$$\text{ppb} = \mu g\ m^{-3} \times \frac{\text{molar volume (litres)}}{\text{molecular weight}}$$

As mentioned above, mixing volume ratios (ppb, etc) are invariant with temperature and pressure, whilst $\mu g\ m^{-3}$ concentrations change with temperature and pressure. The magnitude of this change can be gauged from the variability of the molar volume (above). Generally, the molar volume is affected to the greatest degree by changes in temperature; a variation from 0°C to 27°C causes a change of 10% in molar volume, and thus the $\mu g\ m^{-3}$ concentrations. A rather extreme change in atmospheric pressure from 950 millibars to 1020 millibars gives a 7% change. Thus errors due to these factors can be significant, but are not massive.

For convenience, some commonly used factors are set out below. An atmospheric pressure of 1013mb has been assumed. The principal factors to consider are temperature and molecular weight.

Conversion Factors ($\mu g\ m^{-3} \rightarrow$ ppb)

Pollutant	Molecular weight	0°C	20°C	25°C
CO	28	0.800	0.859	0.873
NO_2	46	0.487	0.523	0.532
O_3	48	0.467	0.500	0.509
SO_2	64	0.350	0.376	0.382
C_6H_6	78	0.287	0.308	0.313

Conversion Factors (ppb $\rightarrow \mu g\ m^{-3}$)

Pollutant	Molecular weight	0°C	20°C	25°C
CO	28	1.250	1.165	1.145
NO_2	46	2.054	1.913	1.881
O_3	48	2.141	2.000	1.965
SO_2	64	2.857	2.704	2.617
C_6H_6	78	3.482	3.244	3.190

Abbreviations

λ	The greek symbol lambda, used to denote wavelength
$\mu g\ m^{-3}$	Micrograms per cubic metre - a unit of concentrations (1 millionth of a gram of pollutant per cubic metre of air)
μm	Micrometre (ie millionth of a metre)
AEA	As in *AEA Technology, Harwell.* The new name for the Atomic Energy Authority Research Establishment
AFR	Air Fuel Ratio
As	Arsenic
ATMOS	Working Group on the Atmospheric Inputs of Pollutants to the North Sea
Be	Beryllium
BSI	British Standards Institution
BST	British Summer Time
C_2-C_8	Hydrocarbons with 2-8 carbon atoms per molecule
CALINE 4	Californian Line Source Dispersion Model. Pollutant dispersion model for road network emission sources
Cd	Cadmium (a heavy metal)
CEGB	Central Electricity Generating Board
CFC	Cross Flow Correlation, a method for monitoring carbon monoxide concentrations
CFCs	Chlorofluorocarbons
CHP	Combined Heat and Power
CLL	Central London Laboratory
CMCU	Central Management and Coordination Unit
Co	Cobalt (a heavy metal)
CO	Carbon monoxide (see Annex F)
Cr	Chromium (a heavy metal)
Cu	Copper
DERV	Diesel fuel for road transport
DOAS	Differential Optical Absorption Spectroscopy
DOE	Department of the Environment
EC	European Community
EPAQS	Expert Panel on Air Quality Standards
EUMI	Enhanced Urban Monitoring Initiative
EUN	Enhanced Urban Network
Fe	Iron
GC/MS	Gas Chromatography/Mass Spectrometry
GC	Gas Chromatograph
GFC	Gas Filter Correlation, a method for monitoring carbon monoxide
GLC	Greater London Council
GMADS	Greater Manchester Acid Deposition Survey
H^+	Hydrogen ion
H_2SO_4	Sulphuric acid
HCl	Hydrogen chloride
Hg	Mercury (a heavy metal)
HMIP	Her Majesty's Inspectorate of Pollution
HNO_3	Nitric acid
HONO	Nitrous acid (or HNO_2)
HPLC	High Performance Liquid Chromatography
$h\upsilon$	Energy of a photon (used to represent sunlight in chemical reactions)
IARC	International Agency for Research on Cancer
ISC	Industrial Source Complex, plume dispersion model
ISO	International Standards Organisation
IUPAC	International Union of Pure and Applied Chemists
km	Kilometre
kT	Kilo tonnes (ie 1 thousand metric tonnes)
LC/GC	Liquid Chromatography/Gas Chromatography

LIDAR	A laser remote sensing technique which measures pollutant concentrations by backscatter of a laser beam
LSS	London Scientific Services (now Rendel Science & Environment)
m	Metre
$mg\ m^{-3}$	Milligrams per cubic metre - a unit of concentrations (ie 1 thousandth of a gram of pollutant per cubic metre of air)
Mn	Manganese
Mo	Molybdenum (a heavy metal)
MRC	Medical Research Council
MT	Mega tonne (ie 1 million metric tonnes)
MVEG	Motor Vehicles Emissions Group
MW	Mega Watts
N	Nitrogen atom
NDIR	Non-Dispersive Infra-Red, a method for monitoring carbon monoxide
NFFO	Non Fossil Fuel Obligation
NH_3	Ammonia
NH_4^+	Ammonium ion
NH_4Cl	Ammonium chloride
NH_4HSO_4	Ammonium bisulphate
NH_4NO_3	Ammonium nitrate
$(NH_4)_2SO_4$	Ammonium sulphate
$ng\ m^{-3}$	Nanograms per cubic metre (1ng = 10^{-9}g)
Ni	Nickel (a heavy metal)
nm	nanometer (ie thousand millionth of a metre, or 1 thousandth of a µm)
NMVOC	Non-methane volatile organic compounds
NO	Nitric oxide
NO_2	Nitrogen dioxide (see Annex F)
NO_3^-	Nitrate ion
NO_x	Oxides of nitrogen (ie NO and NO_2)
NPL	National Physical Laboratory
O	An oxygen atom
O^*	Electronically excited oxygen atom
O_2	An oxygen molecule
O_3	Ozone (see Annex F)
OEL	Occupational Exposure Limit
OES	Occupational Exposure Standard
OPSIS	Commercially available air pollution monitor which uses the Differential Optical Absorption Spectroscopy technique
O_x	Total oxidants
PAC	Polycyclic Aromatic Compounds
PAH	Polycyclic Aromatic Hydrocarbons (see Annex F)
PAN	Peroxyacetyl nitrate (see Annex F)
Pb	Lead (a heavy metal)
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo-p-furans
PEC	Particulate Elemental Carbon
PM_{10}	Particulate matter less than 10 µm aerodynamic diameter
POCP	Photochemical Ozone Creation Potential
PORG	Photochemical Oxidants Review Group
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
QA/QC	Quality Assurance/Quality Control
QRA	Quantitative Risk Assessment
QUARG	Quality of Urban Air Review Group
RO_2	Peroxy radicals where R is a hydrogen atom or organic radical
RSE	Rendel Science & Environment (formerly London Scientific Services)
S	Sulphur atom
Sb	Antimony

SHED	Sealed House Evaporative Determination
Sn	Tin
SO_2	Sulphur dioxide (see Annex F)
SO_4^{2-}	Sulphate ion
SPM	Suspended Particulate Matter
T	Metric tonne
TDI	Tolerable Daily Intake
TEOM	Tapered Element Oscillating Microbalance, (a type of instrument for measuring ambient particulate matter concentrations)
TEQ	Toxic Equivalent
Ti	Titanium
TOMPS	Toxic Organic Micro Pollutants
TSP	Total Suspended Particulate Matter
TWC	Three way catalyst
UEA	University of East Anglia
UK	United Kingdom
UN	United Nations
UNECE	United Nations Economic Commission for Europe
USEPA	United States Environmental Protection Agency
UVF	Ultra Violet Fluorescence (ie a technique for measuring sulphur dioxide concentrations)
V	Vanadium
VOCs	Volatile Organic Compounds (see Annex F)
WHO	World Health Organization
WSL	Warren Spring Laboratory
XRD	X-Ray powder diffraction
yr	year
Zn	Zinc (a heavy metal)

CHLORINE
FREE