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1 Introduction

1.1 This report presents the results of the 1993 London-Wide Nitrogen Dioxide (NO_2) Diffusion Tube Survey, conducted between January 1993 and December 1993. This survey has been on-going since 1986 and forms part of the London-Wide Environmental Programme (LWEP).

1.2 The LWEP is sponsored by participating London Boroughs; the following 19 Boroughs contributed to the NO_2 Diffusion Tube survey in 1993:

London Borough of Barking & Dagenham
London Borough of Barnet
London Borough of Bexley
London Borough of Brent
London Borough of Camden
Corporation of London
London Borough of Croydon
London Borough of Ealing
London Borough of Greenwich
London Borough of Hammersmith & Fulham
London Borough of Harrow
London Borough of Hillingdon
London Borough of Hounslow
Royal Borough of Kensington & Chelsea
Royal Borough of Kingston-upon-Thames
London Borough of Richmond
London Borough of Sutton
London Borough of Tower Hamlets
City of Westminster

1.3 The primary aims of this diffusion tube survey are to identify locations where people may be exposed to high NO_2 concentrations, to identify long term NO_2 concentration trends and to update the NO_2 diffusion tube survey database which has been on-going since 1986. The results provide valuable information to assist in the selection of potential sites for chemiluminescence monitors which are required to check compliance with EC air quality standards for NO_2.

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1.4 The London-wide nitrogen dioxide diffusion tube survey underwent two major changes during 1993 in order that a number of sites could be incorporated into the Department of the Environment national NO_2 diffusion tube survey, which is co-ordinated by Warren Spring Laboratory.

To accommodate this, a large number of new sites were introduced, with many of these categorised as background or intermediate sites; only 45% of the sites are now roadside sites compared to 86% in 1986. The second major change is that the diffusion tube exposure periods have been extended from two weeks, to four and five week periods in accordance with the WSL protocols for the national survey.

Although we were initially assured by Warren Spring Laboratory that NO_2 tube performance would not be affected by the extended exposure period, some comparative studies between tubes exposed over four, one-weekly and monthly periods suggest that concentrations may be reduced by between 10 and 19% for tubes exposed over one month. Such effects may need to be taken into account for assessment of trends in data, until such time as a precise relationship is defined.

1.5 In 1993, each participating Borough maintained between four and twelve monitoring sites, making a total of 161 sites across Greater London. Annual average NO_2 concentrations have been estimated for 143 of the sites which collected at least 26 weeks data; however, the measured levels for sites at which sampling was conducted for a shorter period are also reported, though the figures cannot be approximated to an annual mean for comparison with the results of previous years for these sites. As traffic is the major source of NO_2 in London, nearly half of the sites (72 out of the 161) are at roadside locations. The remainder are at locations where industry is considered to be a potential source (two sites, one near a power station and the other on an industrial estate), a car park (Brent Cross shopping centre), or at intermediate/background locations (86 sites), in order to give an indication of concentrations distant from the influence of local sources.

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2 Sources of Nitrogen Oxides (NO_x)

2.1 The most important nitrogen oxides present in urban locations are nitric oxide (NO), which is relatively innocuous as a primary pollutant as it has no known local adverse effects, and nitrogen dioxide (NO_2) which can cause adverse respiratory effects in sensitive individuals, eg asthmatics, at high concentrations. NO_2 is formed both directly by combustion of fossil fuels and from the oxidation of NO.

2.2 The NO_x emitted in largest quantities is NO. The proportion of NO which is converted to NO_2 depends on the ozone (O_3) concentration. Close to busy road junctions or street canyons, the supply of O_3 may be rapidly exhausted and a large proportion of the NO remains unoxidised.

2.3 Road transport is the main source of NO_x in London, and in the UK as a whole. Estimates made on a national scale indicate that 51% of NO_x emissions from ground based sources come from road transport[1]. Rail transport is estimated to contribute just 1.5%. Estimates for the UK are in line with those for other countries. In OECD countries for example, 47% of NO_x emissions are estimated to come from road vehicles, in about equal amounts from cars and heavy goods vehicles (HGV).

2.4 A study of emissions of NO_x in greater London in 1983/84 demonstrated that transportation was the major source, contributing about 75% to the total emissions, compared to 51% at a national level. Transport is clearly a more important source of NO_x in Greater London than in the UK as a whole. Petrol-driven vehicles account for 73% of these transport emissions, diesel-engines 24% and aviation fuel 3%. Emissions from rail transport were not included in this particular study.

[1] 1991 Digest of environmental Protection and Water Statistics, No. 14, HMSO

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3 Air Quality Standards For NO_2

3.1 Air quality criteria are designed to protect human health and the environment. The European Community (EC) air quality standards specified in the relevant Directives have been incorporated into UK legislation by Statutory Instrument. EC air quality standards have been formulated for NO_2, sulphur dioxide (SO_2) and smoke, and lead (Pb) in air, and consist of Limit and Guide Values.

3.2 **EC Limit Values:** These are set to protect human health and the environment. They are binding on member states. If the standards are exceeded the member states are obliged to institute measures to reduce concentrations to meet the standards.

3.3 **EC Guide Values:** These are long-term precautions and are designed to improve the protection to human health and the environment. They are not mandatory.

3.4 Air Quality standards for NO_2, both Limit and Guide Values, are specified in EC Directive 85/203/EEC and are summarised in Table 19.

3.5 In addition to the EC Limit and Guide Values, the World Health Organisation (WHO) has set guidelines for NO_2 with regard to the 'lowest observed effect' level on asthmatics, and allow for a further margin of safety. The WHO guideline for NO_2 is a one-hourly concentration of 400 $\mu g/m^3$; this guideline is not mandatory.

4 Sampling Technique and Data Analysis

4.1 Diffusion tubes are passive devices comprising inverted perspex cylinders which sample NO_2 by absorption on to chemically coated discs. The tubes are 71 mm long by 12 mm internal diameter and are sealed at one end with a polythene cap containing two stainless steel mesh discs coated with triethanolamine. The other end is sealed with a removable cap when not in use. On exposure, ambient NO_2 diffuses up the tube and is absorbed by the triethanolamine.

4.2 All tubes were prepared and analysed by TBV Science. Quality Assurance in the form of contamination, blank and precision checks were performed on each manufactured batch of test tubes and were found to be satisfactory on all occasions. TBV Science also participates in the Warren Spring Laboratory intercomparison scheme for nitrogen dioxide tubes.

4.3 Each tube was exposed for a period of four or five weeks by the Environmental Health Officer of each participating Borough. The tubes were positioned approximately two metres above ground, on lamp posts, window sills, etc, at locations selected by the Borough, in accordance with the siting criteria.

4.4 Data handling and analysis was performed by TBV Science using a specially designed software package. Site by site reports were produced on a monthly basis for each Borough, together with statistical summaries of the year's data.

4.5 While diffusion tubes may have many advantages (eg, low-cost for spatial distribution mapping and investigation of long-term trends), one shortcoming is that they normally need to be exposed for at least one week, and it is not possible to carry out direct short-term measurements such as the hourly mean values required by the EC Directive for NO_2 or for comparison against the WHO guideline.

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4.6 It has been shown from TBV Science's database of monitoring data, and also WSL measurements in urban areas, that there is a reasonably consistent relationship between long-term averages of NO_2 and the 98th and 50th percentiles. For example, the annual mean has been found to be a good predictor (with an uncertainty of ± 10%) of the 98th and 50th percentiles of hourly values, the relationships being:

98th percentile	=	2.38 x annual mean
50th percentile	=	0.93 x annual mean

The diffusion tube results can thus provide an approximate guide to NO_2 levels in relation to the EC Limit and Guide Values.

5 Results of the 1993 Survey

5.1 The results from all 161 sites are summarised in Tables 1 to 18. Detailed results for the site in each participating Borough can be found in Appendix A.

5.2 Tables 1 to 18 categorise each site according to distance from a road. Sites are defined as 'roadside' if they are within 20 metres of a major road. An 'intermediate' location is one which is between 20 and 40 metres of a busy road or within 20 metres of a quiet road. A 'background site' is one which is beyond 40 metres of any road. In previous years, 'intermediate' sites had also been designated as 'background'. Data for both 1992 and 1993 NO_2 concentrations are given in these tables to enable easy year to year comparison.

5.3 Of the 161 sites in the 1993 survey, 72 were defined as 'roadside', 57 were 'background', 29 were 'intermediate' sites, and two were in the vicinity of industrial sources of NO_2 (a power station and an industrial estate). In addition, one monitoring site was within a supermarket car park.

5.4 Concentrations in Tables 1 to 18 are given as time-weighted averages. The data for the 143 sites which were in operation for at least 26 weeks, and the corresponding estimates of annual averages, 50th and 98th percentile values are shown for both 1992 and 1993. At roadside sites during 1993, annual average concentrations varied between 27 and 67 $\mu g/m^3$, with a mean of 42 $\mu g/m^3$. At intermediate sites, annual mean concentrations varied between 24 and 49 $\mu g/m^3$, with a mean of 34 $\mu g/m^3$. Background site NO_2 concentrations varied from 18 $\mu g/m^3$ to 48 $\mu g/m^3$, with a mean of 31 $\mu g/m^3$.

5.5 Compliance with EC Air Quality Standards

In 1993, 138 out of the 143 sites (97%) are estimated to have complied with the EC Guide Values. Of the intermediate/background sites, all sites complied with the EC Guide Values, whilst a total of 8% of roadside sites are estimated to have exceeded the EC Guide Values.

5.6 There are no sites which are estimated to have exceeded the EC Limit value during 1993.

6 Annual Trends in Nitrogen Dioxide Concentration

6.1 The variation in annual mean NO_2 concentrations for all of the background and roadside sites between 1986 and 1992, are shown in Figures 9 and 10 respectively, where the data have been averaged over sites in each of the two categories which have been in operation since 1986. These data suggest that NO_2 levels in 1993 were the lowest since monitoring began in 1986, and have decreased by 43% for roadside sites and by 38% for other sites since 1991.

6.2 The variation of annual mean concentrations at individual sites is shown in Figures 1 to 8. Seventeen sites have been in operation since 1986, thirteen of which are at roadside locations; a further two sites in Westminster have been in operation since 1988.

6.3 Of these sites, all showed lower concentrations in 1993 than in 1992 with an average reduction of about 24%. Though changes in meteorological conditions are likely to account for some of the year to year variation in mean concentrations, vehicle emission reductions, associated with the recent introduction of catalytic converters, are more likely to have contributed to the overall decrease in NO_2 levels.

6.4 However, it is considered that a factor associated with the change in period of tube exposure must also be taken into account for assessment of long-term trends in concentrations.

Since January 1993, the Department of the Environment has established a national NO_2 diffusion tube survey, which is currently being co-ordinated by Warren Spring Laboratory (WSL). The national survey was established on the basis of 12, monthly exchange periods (of either 4 or 5 weeks) and so that LWEP data could be incorporated, it was essential that the scheme changed from the original 2 week exposures in operation prior to 1993.

At this time, WSL suggested to us that such a change in the exposure period would not affect the results. However, discussions with other parties has now indicated otherwise, and there have been reports of a decrease in measured concentrations over a 4 week sampling period, of up to 19%.

Comparison of measured data from continuous monitoring sites also supports this theory. In contrast to the diffusion tube data, concentrations of NO_2 have only decreased by between 0% and 10% from 1992 to 1993 at the 4 networked sites in the London area.

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We have carefully checked our quality control procedures associated with tube preparation and analysis, and we are convinced that any measured decrease is not associated with the methodology.

We have discounted the possibility of saturation effects occuring, as there is no evidence of this from the data, and laboratory exposure trials have indicated that this should not be a problem over periods of up to 5 weeks. Other factors which could affect the tubes include degradation of the triethanolamine.

We are currently undertaking both laboratory and field experiments to investigate this problem and we will report the results as soon as possible. However, until further data are available, it is recommended that the 1993 results relating to trends in concentrations are treated with some caution.

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7 Discussion - The Impact of New Legislation on Vehicle Emissions in the UK

7.1 New European legislation agreed in 1991 aimed to reduce gaseous emissions for cars and goods vehicles by setting more stringent emission standards and checking exhaust emissions by means of road worthiness testing. The requirements and implementation dates for these new Directives and their implications for London's air quality are outlined below.

7.2 Cars

An amending EC Directive (91/441/EEC) published in August 1991 consolidated European legislation on vehicle emissions and sets more stringent emission standards. The new standards are mandatory and have applied to all new cars registered from 31 December 1992, and to new models from 31 July 1992. To meet the standards, petrol driven cars are fitted with three-way catalytic converters. A new EC Directive (93/59/EEC) will become effective from 1 October 1994. This directive removes the anomaly in EC Directive (91/441/EEC) which allows a car derived van to comply with less stringent emission limits than the equivalent car.

This directive applies to light vans and commercial vehicles below 3.5 tonnes. It imposes three emission standards, one for vehicles below 1250 kg, one for vehicles between 1251 and 1700 kg and one for vehicles in excess of 1700 kg.

7.3 Heavy Goods Vehicles

With respect to HGVs, Directive 91/542/EEC published in October 1991 tightened standards for gaseous emissions in two steps. The first stage reductions were planned for 1 July 1992 (new models) and 1 October 1993 (all new vehicles). The second stage is planned for 1 October 1995 (new models) and 1 October 1996 (all new vehicles) and matches the very stringent "US 1994" diesel standards.

7.4 Road Worthiness Testing

From 1 January 1993, all goods vehicles have required road worthiness testing, which includes checking of exhaust emissions (88/449/EEC). In addition, Directive 91/328/EEC, agreed in June 1991, introduced common worthiness tests for private cars from 1998. It will apply to all vehicles registered from 1994.

7.5 Impact on London's Air Quality

This European legislation will bring about a reduction in unit emissions of controlled pollutants (NO_X, carbon monoxide and hydrocarbons) from both cars and goods vehicles, but by how much is uncertain.

7.6 Under test conditions a controlled three-way catalyst at an operational temperature of 300°C will reduce NO_X emissions by 80-95%. However, in actual use in urban areas they are likely to be much less effective as they do not work when cold. However, manufacturers are currently looking to electrically heated catalytic converters to overcome this problem. Diesel engined cars have grown in popularity recently and now account for 20% of all new car registrations. Unfortunately due to the lean air fuel mixtures in diesel engines the fitting of three-way catalytic converters is not possible. Some diesel cars are equipped with oxidation catalysts which reduce carbon monoxide and VOCs but have no effect on oxides of nitrogen.

Diesel cars emit less NO_x than unrestricted petrol engines but their NO_x emissions are still approximately double those of catalyst equipped cars. The effectiveness of catalytic converters to reduce ambient NO_x emissions will be more limited if the popularity of diesel cars continues to increase. Reduction catalysts for diesel cars are being developed; however, they are still several years away from production.

The second report of the Quality of Urban Air Review Group (QUARG), *Diesel Vehicle Emissions and Urban Air Quality*, has considered the future impact of diesel vehicles in some detail. Their conclusions are that the increased market penetration of diesel cars will have a deleterious effect upon urban air quality, and will lead to a lengthening of the period before which wintertime NO_2 episodes are abolished.