# **Abbreviations and glossary**

## **Abbreviations**

| AADT            | Annual Average Daily Traffic (vehicles per day)                               |
|-----------------|---|
| ADMS            | Atmospheric Dispersion Modelling System                                       |
| AQMA            | Air Quality Management Area   |
| Aric            | Atmospheric Research Information Centre                                       |
| ARTEMIS         | Assessment and Reliability of Transport Emission Models and Inventory Systems |
| ATC             | Automatic Traffic Counts  |
| AURN            | Automatic Urban and Rural (air quality monitoring) Network                    |
| BAM             | Beta Attenuation Monitor  |
| BAT             | Best Available Techniques   |
| CCGT            | Combine cycle gas turbines  |
| ССТУ            | Closed Circuit Television   |
| CEN             | European Committee for Standardisation  |
| CLRTAP          | Convention on Long-Range Transboundary Air Pollution                          |
| CNG             | Compressed Natural Gas  |
| CO              | carbon monoxide   |
| CO <sub>2</sub> | carbon dioxide  |
| COMEAP          | Committee on the Medical Effects of Air Pollutants                            |
| COPERT III      | Computer Programme to Calculate Emissions from Road Transport (version III)   |
| CORINAIR        | COoRdination d'INformation Environmentale                                     |
| COST            | European Cooperation in the field of Scientific and Technical Research        |
| CRTs            | Continuously Regenerating Particulate Traps                                   |
| CSTM3           | Central Scotland Transport Model  |
| CVS             | Constant volume sampler   |
| Defra           | Department for Environment, Food & Rural Affairs                              |
| DfT             | Department for Transport  |
| DMRB            | Design Manual for Roads and Bridges   |
| EA              | Environment Agency  |
| EFD (or EFDB)   | Emissions Factor Database   |
| EfW             | Energy from Waste   |

| EGR              | Exhaust Gas Recirculation  |
|------------------|--|
| EIA              | Environmental Impact Assessment  |
| EMEP             | Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe  |
| EP68             | Dti's Energy Paper 68  |
| EPEFE            | European Programme on Emissions, Fuels and Engine technologies   |
| EPER             | European Pollutant Emission Regsiter   |
| ERG              | Environmental Research Group at King's College London,<br>developers of the empirical modelling approach most widely used<br>in London                         |
| EU               | European Union   |
| EU15             | The 15 Member State countries of the European Union  |
| FIGE             | Forschungsinstitut Geräusche und Erschütterungen   |
| FTIR             | Fourier Transform Infra-red Spectroscopy   |
| GDP              | Gross Domestic Product   |
| GIS              | Geographical Information System  |
| GLA              | Greater London Authority   |
| GSS              | Guidance for estimating the air quality impact of Stationary Sources   |
| НС               | Hydrocarbons   |
| HDV              | Heavy Duty Vehicles – Road vehicles greater than 3.5 tonnes weight (GVW).  |
| HECA             | Home Energy Conservation Act 1995  |
| HGV              | Heavy Goods Vehicle – Road vehicle greater 7.5 tonnes (GVW).<br>Where GVW is the gross vehicle weight i.e the combined weight<br>of the vehicle and the goods. |
| HGVa             | Heavy Goods Vehicle – articulated  |
| HGVr             | Heavy Goods Vehicle – rigid  |
| HONO             | Nitrous acid   |
| HNO <sub>3</sub> | Nitric acid  |
| HRTM             | Heathrow Road Traffic Model  |
| ICAO             | International Civil Aviation Organisation  |
| IIASA            | International Institute for Applied Systems Analysis   |
| IPC              | Integrated Pollution Control   |
| IPCC             | Intergovernmental Panel on Climate Change  |
| IPPC             | Integrated Pollution Prevention and Control  |
| ISO              | International Standards Organisation   |
| LAEI             | London Atmospheric Emissions Inventory   |

| LGV                     | Light Goods Vehicles – goods vehicles less than 3.5 tonnes in weight                                    |
|-------------------------|---|
| LAQN                    | London Air Quality Network  |
| LEZ                     | Low emission zone. A specific type of 'Clear Zone'.   |
| LRC                     | London Research Centre  |
| LTO                     | Landing and take-off  |
| LTS                     | London Transport Study  |
| mg m <sup>-3</sup>      | milligrams per cubic metre of air   |
| µg m⁻³                  | micrograms per cubic metre of air   |
| NAEI                    | National Atmospheric Emissions Inventory  |
| NAMAS                   | National Accreditation of Measurement and Sampling  |
| NECD                    | National Emissions Ceilings Directive   |
| netcen                  | National environmental technology centre, part of AEA<br>Technology plc                                 |
| NMVOC                   | Non-methane volatile organic compound   |
| NO                      | Nitrogen monoxide, also termed nitric oxide   |
| NO <sub>2</sub>         | Nitrogen dioxide  |
| NO <sub>x</sub>         | Nitrogen oxides (NO + NO <sub>2</sub> )   |
| NRTF                    | National Road Traffic Forecasts   |
| NWS                     | National Waste Strategy (Scotland)  |
| <b>O</b> <sub>2</sub>   | Oxygen  |
| <b>O</b> <sub>3</sub>   | Ozone   |
| OS                      | Ordnance Survey   |
| ох                      | Oxidant potential. A sum of $\rm O_3$ and $\rm NO_2$  |
| PAN                     | Peroxyacetyl nitrate  |
| PI                      | Pollution Inventory   |
| <b>PM</b> <sub>10</sub> | Particulate matter with an (equivalent aerodynamic) diameter of ten microns (10 $\mu\text{m})$ or less  |
| PM <sub>2.5</sub>       | Particulate matter with an (equivalent aerodynamic) diameter of 2.5 microns (2.5 $\mu\text{m})$ or less |
| ppb                     | parts per billion (1,000,000,000)   |
| ppm                     | parts per million   |
| QA/QC                   | Quality Assurance and Quality Control   |
| RO <sub>2</sub>         | organic peroxy radicals   |
| SCR                     | Selective Catalytic Reduction   |
| SEPA                    | Scottish Environment Protection Agency  |
| SO <sub>2</sub>         | sulphur dioxide   |

| TEMPRO | Trip End Model PROjections of growth in travel demand, and the underlying car ownership and planning data projections |
|--------|---|
| ТЕОМ   | Tapered Element Oscillating Microbalance  |
| TRAMAQ | DfT funded, Traffic management and air quality research programme. http://www.roads.dft.gov.uk/roadnetwork/tramaq/    |
| TRL    | Transport Research Laboratory   |
| TÜV    | German Accreditation Organisation   |
| UKAS   | United Kingdom Accreditation Service  |
| ULSD   | Ultra-Low Sulphur Diesel  |
| ULSP   | Ultra-Low Sulphur Petrol  |
| UNECE  | United Nations Economic Commission for Europe   |
| USA    | Updating and Screening Assessment   |
| USEPA  | United States Environmental Protection Agency   |
| VOC    | Volatile organic compound   |
| WASP   | Workplace Analysis Scheme for Proficiency   |
| WDF    | Waste Derived Fuel (or Refuse Derived Fuel)   |

## Glossary

| Accuracy                        | A measure of the closeness of the agreement between the result<br>of a measurement and the true value (see also Uncertainty and<br>Precision).  |
|---------------------------------|---|
| Air quality objective           | Policy targets generally expressed as a maximum ambient<br>concentration to be achieved, either without exception or with a<br>permitted number of exceedences within a specified timescale<br>(see also air quality standard).   |
| Air quality standard            | The concentration of a pollutant, and associated averaging period,<br>which is without significant effect on human health at a population<br>level.   |
| Ambient air                     | Outdoor air in the troposphere, excluding workplace air   |
| Annual mean                     | The average of the concentrations measured for each pollutant<br>for one year. In the case of the air quality objectives this is for a<br>calendar year.  |
| AQMA                            | Air Quality Management Area, an area which a local authority has designated for action, based upon predicted exceedences of Air Quality Objectives.   |
| Area source                     | Emission sources that are too diffuse to identify individually (for example residential properties)   |
| Atmospheric<br>boundary layer   | The lowest 100 to 3000 m of the atmosphere. That part of the troposphere that is directly influenced by the presence of the earth's surface, and responds to surface forcing with a time scale of about an hour or less. The forcing includes frictional drag, evaporation and transpiration, heat transfer, pollutant emission, and terrain induced flow modification. |
| Atmospheric<br>dispersion model | A mathematical, often computer-based method for calculating<br>pollutant concentrations from emissions data and specified<br>meteorological conditions. Models vary from screening models<br>to detailed, 'new-generation' types.   |
| AURN                            | Automatic Urban and Rural Network of air pollution measurement<br>sites, managed by contractors on behalf of Defra and the devolved<br>administrations.   |
| Baseline                        | Concentration of a pollutant (usually used referring to ozone) at a location unaffected by local or regional sources.   |
| Blending height                 | Height over the ground at which the ground inhomogeneity is not<br>perceived, over which the various internal boundary layers merge<br>into a layer having a horizontally homogeneous structure.  |
| Calibration (modelling)         | The process of multiplying the output of a model by a fixed correction factor to give, on average, a 1:1 relationship with measured data.   |
| Calibration (monitoring)        | The process of reducing the uncertainty of monitoring data by<br>controlled tests on the analyser, normally traceable to internationally<br>accepted measurements standards.  |

| Concentration                | The amount of a (polluting) substance in a volume (of air), typically expressed as a mass of pollutant per unit volume of air at standard conditions of temperature and pressure (eg micrograms per cubic metre, $\mu$ g m <sup>-3</sup> ) or as the ratio of the number of molecules of the pollutant to the total number of molecules in the volume of air (for example, parts per billion, ppb).                  |
|------------------------------|--|
| Conservative                 | Tending to over-predict the impact rather than under-predict.  |
| Convective boundary<br>layer | The atmospheric boundary layer under strong insolation, which causes positive buoyancy and the generation of turbulence (as opposed to the stable boundary layer).   |
| Correlation coefficient      | The fraction of the variability in one set of data that is proportional to the value of some other set of data.  |
| Diffusion equation           | Mathematical expression relating the rate of change of concentration<br>in time to the rate of change of concentration over distance.  |
| Data capture                 | The percentage of all the possible measurements for a given period that were validly measured.   |
| Emission                     | The amount of a (polluting) substance emitted in a certain amount<br>of time, typically expressed as a mass of pollutant per unit time<br>(for example, grams per second, or tonnes per year for a single<br>source). May also be expressed per unit length of a road (for<br>example, g s <sup>-1</sup> m <sup>-1</sup> ), or per unit area of an urban area (for example,<br>t a <sup>-1</sup> km <sup>-2</sup> ). |
| Emissions inventory          | A quantification and compilation of emission sources by geography<br>and time, usually including data covering one or several years.   |
| Euro I                       | Europe-wide vehicle standard that required vehicles manufactured<br>after 1992 to achieve set emissions limits. For petrol cars this was<br>achieved by the fitting of three way catalysts.  |
| Euro II, III, IV & V         | Europe-wide vehicle standards that are progressively stricter, for years 1996, 2000, 2006 and 2008 respectively.   |
| Exceedence                   | A period of time where the concentration of a pollutant is greater than the appropriate air quality objective.   |
| Free radical                 | A molecule with an unpaired electron. Most free radicals are highly reactive. NO and $NO_2$ are examples of free radicals that are comparatively stable.   |
| Inertial sublayer            | The remaining part of the urban surface layer above the roughness sublayer where surface layer scaling (Monin-Obukhov similarity) applies.   |
| Internal boundary layer      | The atmospheric layer that develops after a change in ground roughness or surface temperature. Its height increases with the distance from the change.   |
| Line source                  | A long, narrow source of emissions such as a road, railway line or shipping lane.  |
| Maximum hourly<br>average    | The highest hourly reading of air pollution obtained during the time period under study.   |

| Metadata                   | Information about a dataset which provides the data analyst with an<br>essential description of the data capture process. For example, the<br>instrument used, temporal resolution, monitoring site details, quality<br>control process applied, etc.  |
|----------------------------|--|
| mg m <sup>-3</sup>         | Milligrams per cubic metre of air. A unit for describing the concentration of air pollutants in the atmosphere, as a mass of pollutant per unit volume of air. This unit is one thousand times larger than the $\mu$ g m <sup>-3</sup> unit listed below. Valid comparisons of concentrations given in mg m <sup>-3</sup> usually require the volume of air to be corrected to a common temperature and pressure.  |
| Microgram (µg)             | One millionth of a gram.   |
| μg m <sup>-3</sup>         | Micrograms per cubic metre of air. A unit for describing the concentration of air pollutants in the atmosphere, as a mass of pollutant per unit volume of air. A concentration of 1 µg m <sup>-3</sup> means that one cubic metre of air contains one microgram of pollutant. Valid comparisons of concentrations given in µg m <sup>-3</sup> usually require the volume of air to be corrected to a common temperature and pressure.  |
| Micrometre (µm)            | One millionth of a metre, also referred to as a micron.  |
| Minor roads                | Non A roads or motorways.  |
| Mixed layer                | The major part of the convective boundary layer. Within the mixing<br>layer the vertical profiles of most meteorological variables are<br>roughly constant with height due to the intensive vertical mixing.<br>The mixing height is the height of the layer next to the ground over<br>which pollutants or any constituents emitted within this layer or<br>entrained into it become vertically dispersed by convection<br>or mechanical turbulence within a time scale of approximately<br>30 minutes. |
| Model adjustment           | Following model verification, the process by which modelled results are amended. This corrects for systematic error.   |
| Multiple regression        | A method of statistical analysis that identifies empirically how a<br>variable of interest (for example, pollutant concentration) depends<br>on the value of several determinants (for example, emissions, wind<br>speed, altitude).   |
| nm                         | Nanometre 10 <sup>-9</sup> metres.   |
| Oxidation                  | The increase in the proportion of oxygen in a molecule.  |
| Percentile                 | A value that is the rank at a particular point in a collection of data.<br>For instance, a 98th percentile of values for a year is the value that<br>98% of all the data in the year fall below, or equal.   |
| Photochemical<br>processes | Chemical reactions which occur following the absorption of light by a molecule.  |
| Photolysis                 | The decomposition of molecules following the absorption of light.  |
| PM <sub>10</sub>           | Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter and which transmits particles of below this size.   |

| PM <sub>2.5</sub>         | Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter and which transmits particles of below this size.  |
|---------------------------|--|
| Point source              | A stationary location or fixed facility from which pollutants are discharged or emitted, this may include a number of stacks or a large plant.   |
| ррb                       | Parts per billion. The concentration of a pollutant in air in terms of molar ratio. A concentration of 1 ppb means that for every billion (10 <sup>9</sup> ) molecules in a volume of air, there is one molecule of the specified pollutant present. For practical purposes in ambient air, the molar ratio and volume ratio (the volume occupied by the pollutant gas within a given volume of air) are identical.  |
| ppm                       | Parts per million. The concentration of a pollutant in air in terms of molar ratio. A concentration of 1 ppm means that for every million (10 <sup>6</sup> ) molecules in a volume of air, there is one molecule of the specified pollutant present. For practical purposes in ambient air, the molar ratio and volume ratio (the volume occupied by the pollutant gas within a given volume of air) are identical.  |
| Precautionary approach    | In air quality modelling, erring on the side of predicting<br>concentrations higher than those that actually occur or will occur,<br>when there are known to be significant uncertainties in the model.  |
| Precision                 | A measure of the closeness of the agreement between the results<br>of successive measurements where the true value remains constant<br>(see also Accuracy and Uncertainty).  |
| Ratification (monitoring) | Involves a critical review of all information relating to a data set, in<br>order to amend or reject the data. When the data have been ratified<br>they represent the final data to be used (see also Validation).   |
| Regression                | See multiple regression.   |
| Road link                 | A length of road, usually in a traffic model or emissions inventory,<br>which has the same flow of traffic along its length. Usually, a link<br>is the road from one junction to the next.   |
| Roughness                 | A length-scale describing how a bumpy surface influences the development of turbulence in a flow of air above that surface.  |
| Roughness sublayer        | The lowest part of the urban surface layer, where the strong influence of the buildings and roughness elements and turbulence is three-dimensional.  |
| Running mean              | A mean – or series of means – calculated for overlapping time<br>periods, and is used in the calculation of several of the national air<br>quality objectives. For instance, an 8-hour running mean is<br>calculated every hour, and averages the values for eight hours.<br>The period of averaging is stepped forward by one hour for each<br>value, so running mean values are given for the periods $00:00 –$<br>07:59, 01:00 – 08:59 etc. By contrast a non-overlapping mean is<br>calculated for consecutive time periods, giving values for the<br>periods $00:00 – 07:59, 08:00 – 15:59$ and so on. There are,<br>therefore, 24 possible 8-hour means in a day (calculated from<br>hourly data) and 3 non-overlapping means. |

| Surface layer            | The lowest 10% of the atmospheric boundary layer. Frictional drag,<br>heat conduction and evaporation from the surface causes<br>substantial changes with height of the mean wind speed,<br>temperature and humidity. However, the turbulent fluxes are<br>relatively constant with height in the surface layer; hence the<br>surface layer is also known as the constant flux layer.   |
|--------------------------|---|
| ТЕОМ                     | Tapered element oscillating microbalance. Equipment used for measuring fine particulate matter such as PM <sub>10</sub> .   |
| True value               | The value of a concentration, for example, which is entirely<br>consistent with the definition of the units in which it is given.<br>This is the value that would be obtained by a perfect measurement.   |
| Uncertainty              | A measure, associated with the result of a measurement, that<br>characterizes the range of values within which the true value is<br>expected to lie. Uncertainty is usually expressed as the range within<br>which the true value is expected to lie with a 95% probability, where<br>standard statistical and other procedures have been used to<br>evaluate this figure. Uncertainty is more clearly defined than the<br>closely related parameter <i>accuracy</i> , and has replaced it on recent<br>European legislation. |
| Urban boundary layer     | The atmospheric boundary layer over an urban area. Its structure,<br>at least in its lowest layers, is modified by the high drag and<br>sensible heat fluxes of the urban area, especially their strong in<br>homogeneity.  |
| Validation (modelling)   | Refers to the general comparison of modelled results against monitoring data carried out by the model developers.   |
| Validation (monitoring)  | Screening monitoring data by visual examination to check for spurious and unusual measurements (see also Ratification).   |
| Verification (modelling) | Comparison of modelled results versus any local monitoring data at relevant locations.  |

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## Appendix 1

# **Technical annex to Chapter 2**

## **Emission controls and abatement technologies**

- Section 2.5 gave a brief description of three of the main techniques used to control NO<sub>x</sub> emissions from stationary and mobile combustion sources. These were low-NO<sub>x</sub> burners for stationary combustion sources and Exhaust Gas Recirculation and Three-Way Catalyst technology for motor vehicles. However, there are a number of other technologies already available or under development that are showing promise for NO<sub>x</sub> emission abatement.
- 2. In this Annexe, more fundamental and design characteristics of the three technologies discussed in Section 2.5 are provided and a description is made of several other important methods for controlling NO<sub>x</sub> emissions, at present not widely used in the UK. This is not meant to be an exhaustive list of all methods either available now or under development.

#### Emission abatement for stationary combustion sources

#### Low-NO<sub>x</sub> burners

- 3. Low-NO<sub>x</sub> burners work on the principle of staged combustion in which the fuel and air are mixed in the burner in stages to create regions of different temperature and fuel/air ratio in the flame. Fuel-rich regions allow the conversion of NO and its precursors to N<sub>2</sub>
- **4.** For pulverised coal combustion, there are two main types of low-NO<sub>x</sub> burner designs which both involve the use of staged combustion to achieve the desired effect. These are air-staged and fuel-staged burners, shown schematically in Figure A1, or variants of these.



**Figure A1.1** Low-NO, burner concepts for pulverised coal flames.

5. In air-staged burners, the first stage of combustion occurs in a slightly fuel-rich zone, at the optimum fuel/air stoichiometric ratio (1.1–1.3) for conversion of fuel-nitrogen to N<sub>2</sub>. A second stage of combustion is operated fuel-lean by addition of secondary air in such a way as to complete fuel burnout, with careful temperature control to minimise the formation of thermal-NO in this zone. There are various designs of air-staged burners which differ in the way the two combustion zones are created. The aerodynamics of the fuel-air mixing are key design factors

controlling the effectiveness of air-staged burners, ensuring the optimum residence time and temperatures in each stage.

- 6. In fuel-staged burners, NO is allowed to be formed in the primary combustion zone, but fuel is injected downstream to create a secondary fuel-rich or 'reburn' zone where the NO is reduced to N<sub>2</sub>. Further air is added downstream to complete combustion of the excess fuel in a tertiary combustion zone, again with careful control of temperature to minimise thermal-NO formation.
- 7. Understanding how NO is converted to  $N_2$  in low-NO<sub>x</sub> burners requires an understanding of the full cycle of nitrogen chemistry in combustion systems, from formation of NO from  $N_2$  and fuel-bound nitrogen in the first instance. The main steps in the chemical mechanism involved in the formation and removal of NO in combustion is shown in Figure A2.

Figure A1.2 Chemical mechanism for formation and removal of NO in combustion.



8. The key reactions responsible for conversion of NO to N<sub>2</sub> in the fuel-rich zones of both types of low-NO<sub>x</sub> burners are those between NO and small hydrocarbon and nitrogen-containing radicals (CH, CH<sub>2</sub>, NH, NH<sub>2</sub> and NCO) which are present under these conditions. The reaction sequence is complex, but the main steps are shown in Figure A2. Among the key reactions are:

 $CH_2 + NO \rightleftharpoons HCNO + H$   $NH_2 + NO \rightleftharpoons N_2 + H_2O$  $NH_2 + NO \rightleftharpoons N_2 + H + OH$ 

- 9. A chemical cycle exists (Figure A2) interconverting NO with species like HCN and other reduced nitrogen species. While these compounds have the potential to continuously regenerate NO, the key point is that each time the chemistry passes through one loop, some of the nitrogen is taken out of the loop as N<sub>2</sub>.
- 10. The effectiveness of these methods for reducing  $NO_x$  emissions depends on a number of factors including burner design, operation and coal type.  $NO_x$  reductions of between 30 and 60% have been achieved.

#### Selective catalytic reduction

11. Selective catalytic reduction (SCR) is a well developed and widely used aftertreatment methods for reducing NO<sub>x</sub> emissions in the flue gas of a stationary combustor. The process involves the reduction of NO (and NO<sub>2</sub>) to N<sub>2</sub> with approximately stoichiometric amounts of ammonia (NH<sub>3</sub>) over a catalyst bed. The overall reaction is:

$$4NO + 4NH_3 + O_2 \rightleftharpoons 4N_2 + 6H_2O$$

- 12. The catalyst effectively reduces the temperature at which this reaction occurs to  $350-400^{\circ}$ C, but this is still sufficiently high for it to be necessary to install the SCR reactor near the boiler if the flue gas is not to be reheated. This can cause problems if the flue gas is laden with SO<sub>2</sub> and particulate; SO<sub>2</sub> can poison the catalyst and particulates cause clogging.
- 13. A range of different catalyst materials can be used. Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) supported on titanium dioxide (TiO<sub>3</sub>) are one of the most effective and widely used materials as they have a high resistance to SO<sub>2</sub>. Other substances exhibiting catalytic activity are oxides of iron and copper and the metals platinum, palladium, rhodium and ruthenium.
- 14. SCR can achieve 80–90% efficiency in  $NO_x$  reduction.

#### Selective non-catalytic reduction

- **15.** The selective non-catalytic reduction process (SNCR), also known as the thermal-deNO<sub>x</sub> process, reduces NO by addition of  $NH_3$  in the flue gas without the use of a catalyst.  $NH_3$  is injected in the high temperature region of the boiler to reduce NO to N<sub>2</sub> thermally by the same overall reaction as occurs in SCR, shown above. The presence of excess oxygen is required and a residence time of 0.1 to 0.4 seconds.
- **16.** A feature of this process is that it is only effective over a narrow temperature window between 1050–1350°C. This can be a problem if the flue gas temperature changes with load. However, the position and width of the temperature window is affected by additives, for example, hydrogen and hydrogen peroxide shift the temperature window down to 900–1220°C.
- **17.** The reaction mechanism is a homogeneous gas-phase one, the key step being one of the reactions important in low-NO<sub>x</sub> burner mechanisms:

 $NH_2 + NO \rightleftharpoons N_2 + H_2O$  $NH_2 + NO \rightleftharpoons N_2 + H + OH$ 

- **18.** The supply of sufficient NH<sub>2</sub> radicals to sustain this reaction and competition with reactions of NH<sub>2</sub> with oxidising radicals leading to the formation of NO explains the existence of the temperature window.
- **19.** The efficiency of  $NO_x$  removal by SNCR is ~60%.
- **20.** A variation of the SNCR thermal deNO<sub>x</sub> process involves injecting solid cyanuric acid (HOCN)<sub>3</sub> into the flue gas. Upon heating, this compound decomposes to gaseous isocyanic acid (HNCO) which itself thermally decomposes to radicals engaging in a sequence of reactions removing NO similar to those in the thermal-deNO<sub>x</sub> mechanism. This method is effective over a broader temperature window than the thermal deNO<sub>x</sub> process involving NH<sub>3</sub>, typically 430–1130°C. Very high efficiencies of NO<sub>x</sub> reduction can be achieved (>90%) and this method has been applied to smaller-scale boilers. Urea can also be used as an SNCR reagent.

A disadvantage of these techniques is that fairly significant concentrations of  $N_2O$  can be formed as a by-product.

#### Emission abatement for mobile combustion sources

#### Exhaust gas recirculation

- 21. Exhaust Gas Recirculation (EGR) controls NO<sub>x</sub> formed in internal combustion engines by recycling a fraction of the exhaust gases through a control valve from the exhaust to the engine where it acts as a diluent, thereby reducing the peak flame temperature and hence the rate of NO formation in the burned gases through the thermal-NO mechanism. Increasing the amount of gas recirculated reduces the rate of NO formation. However, it also reduces the combustion rate making stable combustion more difficult to achieve. Nevertheless, substantial reductions in NO<sub>x</sub> emissions (60–80%) can be achieved with 15–25% EGR, about the maximum amount of EGR the engine will tolerate under normal conditions.
- **22.** Reductions in NO<sub>x</sub> emissions from EGR can be accompanied by modest increases in CO and hydrocarbon emissions, depending on engine conditions. In diesel engines, EGR can, under certain conditions increase particulate (PM) emissions, but this problem can be resolved by careful engine design.

#### Three-way catalysts for petrol vehicles

- **23.** As discussed in Section 2.5.2, three-way catalysts have been fitted on all new petrol cars and vans sold in Europe since 1992. A single catalyst bed can reduce NO and oxidise CO and HC if the fuel/air ratio is maintained close to stoichiometric (i.e. neither fuel or oxygen are in excess).
- 24. There is a narrow range of fuel/air ratios close to the stoichiometric condition in which high conversion efficiencies of all three pollutants are achieved, so an oxygen sensor in the exhaust is used to detect whether the engine is operating on the fuel rich or lean side of stoichiometric and to adjust the fuel system accordingly. In reality, the fuel/air ratio fluctuates around the optimum level, but all three pollutants can still be removed with high efficiency if the appropriate catalyst material is used. Commercial three-way catalyst units use various combinations of the metals platinum (Pt), palladium (Pd) and rhodium (Rd) as the active catalyst materials on various substrates. The reactions on the catalyst surface removing NO are:

 $2NO + 2CO \rightleftharpoons N_2 + 2CO_2$  $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$ 

25. Catalysts are only effective when the temperature is above 250–300°C. This is known as the catalyst light-off temperature. When the vehicle is started with the engine cold, it takes a certain time for the catalyst to warm up to its optimum temperature by the exhaust gases. During this time, emissions are higher than they are when the catalyst is at its optimum temperature. This contributes to the excess emissions during the cold start period of a trip. Recent developments in three-way catalyst technology have concentrated on reducing the time it takes for catalysts to reach the light-off temperature, thus reducing the excess cold start emissions. This has been achieved by modifying the composition of the active catalyst material and changing the thermal capacity of the substrate. For example, higher palladium content reduces the light-off temperature. It has also been achieved by physically moving the catalyst unit closer to the engine or using supplementary heating.

- **26.** Three-way catalysts are susceptible to poisoning by sulphur present in the fuel, significantly reducing its efficiency and durability. This has been the motivation for reducing the sulphur content of fuels from levels of above 300 ppm in petrol in the early 1990s to below 50 ppm today in the UK, levels that meet the European Fuel Directive limits for 2005. This is ultra-low sulphur petrol grade. However, even at this level, the performance of the catalyst can be compromised and consideration is currently being given to implementing directives and policies which set a ceiling of 10 ppm on the sulphur content of fuels so-called sulphur-free fuels.
- 27. Reduced catalyst light-off time together with improved catalyst materials, engine design and cleaner fuels are together likely to be the means by which petrol vehicles will meet the stringent Euro IV standards.

#### DeNO<sub>x</sub> systems for diesel vehicles using selective catalytic reduction

28. Selective catalytic reduction systems have potential for reducing emissions of NO<sub>x</sub> in exhausts of heavy duty diesel vehicles. These work in much the same way as SCR systems for stationary combustion except they use urea instead of NH<sub>3</sub> as the active reagent. A 32% solution of urea in water is stored on the vehicle and injected into the exhaust upstream of the SCR catalyst. Urea is a safe and relatively inexpensive reagent which when heated liberates NH<sub>3</sub>, initiating the SCR deNO<sub>x</sub> process on the catalyst surface at 250–500°C:

$$(NH_2)_2CO + H_2O \rightleftharpoons 2NH_3 + CO_2$$
  
4NO + 4NH<sub>3</sub> + O<sub>2</sub>  $\rightleftharpoons$  4N<sub>2</sub> + 6H<sub>2</sub>O

- **29.** On-board diagnostics with  $NO_x$  or  $NH_3$  sensors linked to a dynamic urea injection control system are required to optimise the performance of the SCR system. An oxidation catalyst downstream of the SCR catalyst may be used to eliminate the possibility of  $NH_3$  slip.
- **30.** This is still an emerging technology for mobile applications, but tests show it can achieve 80% reduction in NO<sub>x</sub> emissions from heavy duty diesel vehicles, allowing them to meet the 2008 Euro IV standards. It requires ultra-low sulphur diesel (<50 ppm) to be used, but the technology is reasonably sulphur-tolerant. An infrastructure for the supply of urea-water solution is a prerequisite for widespread application.
- **31.** SCR systems based on urea combined with Continuously Regenerating Trap (CRT) technology have been developed to simultaneously reduce both PM and NO<sub>x</sub> emissions from heavy duty diesel exhausts.

#### DeNO<sub>x</sub> systems using NO<sub>x</sub> traps

**32.** NO<sub>x</sub> traps are another exhaust aftertreatment technology which have potential for reducing NO<sub>x</sub> emissions from diesel and other lean-burn vehicles. However, they are believed to be more appropriate for light duty diesel vehicles, rather than heavy duty vehicles. The system works by adsorbing NO<sub>x</sub> on a catalyst surface in the exhaust during lean cycles at temperatures between  $250-450^{\circ}$ C. Desorption occurs during periodic, short rich 'spikes' in the exhaust when the NO<sub>x</sub> is reduced to N<sub>2</sub> in the rich environment and the catalyst trap regenerated. Using sophisticated engine management systems, engine cycles must be adjusted so that periodic rich excursions will regenerate the trap, burning off NO<sub>x</sub> at 650°C without producing significant amounts of particulates.

**33.** The adsorbing material is highly susceptible to sulphur poisoning. To be effective  $NO_x$  traps require very low levels of sulphur in the fuel, even below 15 ppm. This is still an emerging technology for mobile applications, but tests show that  $NO_x$  emission reductions as high as 80% can be achieved with this technology and with the prospect of very low sulphur fuels coming on the market,  $NO_x$  traps will have potential for meeting Euro IV standards.

#### Alternative fuels

- **34.** A number of alternative fuels for road vehicles have been developed for addressing a range of different environmental and energy supply issues. Vehicles running on compressed natural gas (CNG) and liquefied petroleum gas (LPG) show potential benefits in reducing emissions compared with conventional fuels. However, while many laboratory tests show improvements in terms of NO<sub>x</sub> emissions when vehicles are run on LPG or CNG fuels, tests carried out on vehicles while 'on-road' show the benefits are often less obvious. This may in part be due to the limited amount of 'on-road' data available for vehicles running on these fuels, making it difficult to allow thorough comparisons with conventional fuels. Much of the available data are associated with relatively small pilot studies using 'specially maintained' vehicles. More thorough testing is clearly required.
- **35.** Other advanced vehicle technologies will undoubtedly show NO<sub>x</sub> emission benefits. Hybrid electric and fuel cell powered vehicles will substantially reduce or eliminate NO<sub>x</sub> emissions from vehicles at point of use.

#### Off-road mobile machinery

- **36.** As well as road vehicles, emissions have recently become regulated for off-road vehicles and mobile machinery which run on diesel engines between 18 and 560 kW power. These cover a range of different machinery which may run on gas oil or road diesel used in industry (for example, forklifts, compressors), construction (for example, cranes, bulldozers), agriculture (for example, tractors, combines) and airport support vehicles. Directives 97/68/EC and 2000/25/EC set limits of NO<sub>x</sub> and other pollutant emissions according to engine rating introduced in two stages between 1998 and 2003.
- **37.** Many of the abatement methods discussed above for road vehicles will be applicable to offroad machinery, provided the quality of the fuel used is adequate, for example, ultra-low sulphur grade diesel may be necessary for some technologies.

## ${\rm UK}~{\rm NO}_{\rm x}$ emission projections for road transport

38. Section 2.12.1 discussed the NAEI emission projections for road transport. Tables A1 and A2 in this Annexe provide figures for UK and urban UK road transport emissions of NO<sub>x</sub> by vehicle type. These are based on the new vehicle emission factors discussed in Section 2.7.2.1 and the figures are projections from 2000 and consistent with the plots in Figure 2.13.

|        |                      |                            |                         |                         | ^                       |                        |                        |                        |                        |                        |
|--------|----------------------|----------------------------|-------------------------|-------------------------|-------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| k      | tonnes               |                            | 1990                    | 1995                    | 2000                    | 2005                   | 2010                   | 2015                   | 2020                   | 2025                   |
| C      | Cars                 | Petrol<br>DERV<br>All Cars | 752.5<br>7.1<br>759.6   | 579.6<br>19.0<br>598.7  | 383.1<br>31.1<br>414.2  | 223.9<br>42.8<br>266.7 | 146.1<br>37.5<br>183.7 | 114.1<br>35.7<br>149.8 | 114.3<br>35.3<br>149.6 | 118.3<br>36.5<br>154.8 |
| L      | .GV                  | Petrol<br>DERV<br>All LGV  | 52.8<br>20.4<br>73.2    | 36.7<br>36.0<br>72.7    | 16.3<br>51.0<br>67.3    | 4.7<br>53.4<br>58.1    | 2.1<br>37.7<br>39.8    | 1.7<br>31.5<br>33.3    | 1.8<br>32.1<br>33.9    | 2.0<br>35.2<br>37.2    |
| F      | IGV                  | Artic<br>Rigid<br>ALL HGV  | 194.9<br>187.8<br>382.7 | 188.9<br>138.9<br>327.7 | 205.9<br>107.7<br>313.6 | 160.6<br>83.0<br>243.6 | 108.1<br>54.8<br>162.9 | 76.2<br>36.0<br>112.2  | 74.3<br>30.4<br>104.6  | 81.7<br>31.1<br>112.8  |
| E<br>N | Buses<br>Aotorcycles |                            | 69.6<br>0.8             | 63.0<br>0.7             | 48.3<br>0.9             | 40.7<br>1.0            | 30.7<br>1.1            | 21.9<br>1.2            | 17.4<br>1.2            | 15.8<br>1.3            |
| A<br>A | NI DERV<br>NI Petrol |                            | 479.8<br>806.2          | 445.8<br>617.1          | 444.0<br>400.3          | 380.5<br>229.6         | 268.8<br>149.3         | 201.3<br>117.0         | 189.5<br>117.4         | 200.3<br>121.6         |
| A      | Il Vehicles          | 3                          | 1286.0                  | 1062.8                  | 844.3                   | 610.0                  | 418.1                  | 318.3                  | 306.8                  | 321.9                  |

Table A1.1 UK road transport emissions of NO<sub>x</sub>.

| Table A1.2 Urban UK road transport emissions of No | Э <sub>х</sub> . |
|--|------------------|
|--|------------------|

| ktonnes     |            | 1990  | 1995  | 2000  | 2005  | 2010  | 2015  | 2020  | 2025  |
|-------------|------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cars        | Petrol     | 270.0 | 222.6 | 165.5 | 116.3 | 74.6  | 53.8  | 52.9  | 54.7  |
|             | DERV       | 3.3   | 9.0   | 13.3  | 18.1  | 15.2  | 14.3  | 14.1  | 14.5  |
|             | All Cars   | 273.3 | 231.6 | 178.8 | 134.4 | 89.8  | 68.1  | 67.0  | 69.2  |
| LGV         | Petrol     | 20.1  | 13.8  | 6.4   | 2.4   | 1.2   | 1.0   | 1.0   | 1.1   |
|             | DERV       | 9.1   | 15.7  | 20.7  | 21.3  | 14.9  | 12.2  | 12.2  | 13.2  |
|             | All LGV    | 29.2  | 29.5  | 27.0  | 23.7  | 16.1  | 13.2  | 13.3  | 14.3  |
| HGV         | Artic      | 24.2  | 21.4  | 18.3  | 14.4  | 10.7  | 7.4   | 7.0   | 7.5   |
|             | Rigid      | 58.5  | 45.4  | 30.3  | 27.2  | 17.9  | 11.9  | 10.1  | 10.4  |
|             | ALL HGV    | 82.7  | 66.8  | 48.6  | 41.6  | 28.6  | 19.3  | 17.1  | 18.0  |
| Buses       | S          | 41.6  | 45.3  | 34.6  | 30.8  | 22.3  | 15.9  | 12.6  | 11.5  |
| Motorcycle  |            | 0.3   | 0.3   | 0.3   | 0.3   | 0.4   | 0.4   | 0.4   | 0.5   |
| All DERV    | All DERV   |       | 136.8 | 117.2 | 111.9 | 80.9  | 61.7  | 56.1  | 57.2  |
| All Petrol  | All Petrol |       | 236.6 | 172.2 | 119.0 | 76.2  | 55.2  | 54.4  | 56.3  |
| All Vehicle | es         | 427.2 | 373.4 | 289.4 | 230.9 | 157.1 | 116.9 | 110.5 | 113.5 |

## Appendix 2

# Factors affecting diffusion tube performance

- 1. This appendix presents a review of the possible factors affecting the performance of nitrogen dioxide diffusion tubes. Although diffusion tubes are, and are likely to remain, important for general assessment of NO<sub>2</sub> air quality, this AQEG report utilises data obtained almost exclusively from chemiluminescence analysers, rather than diffusion tubes, for its analyses of NO<sub>2</sub> in the UK. Therefore this report is not the appropriate place for an exhaustive review of the literature.
- 2. The following factors are reviewed together with potential explanatory mechanisms for their effects on diffusion tube performance:
  - the laboratory preparing and analysing the tubes;
  - the exposure interval weekly, 2-weekly or monthly;
  - the time of year;
  - the exposure setting sheltered or exposed;
  - the exposure location roadside or background;
  - the tube preparation method; and
  - the exposure concentration and  $NO_{2}/NO_{x}$  ratio.

It is important to recognise that the effect of one factor on a diffusion tube measurement may act to obscure or offset the effects of other factors acting on the same measurement. This complicates attempts at comparing data from different studies, and of interpretation of results.

### **Role of laboratory**

3. Early studies involving monthly exposure at a number of sites around the UK of tubes prepared with 50% TEA-in-acetone found an average diffusion tube bias of +26%, although this varied from site to site (Campbell et al., 1994). Bush et al. (2001a) carried out a more extensive validation study over a full year in 1996/97 using tubes also prepared and analysed by Harwell Laboratory using 50% TEA-in-acetone. This study identified an overall positive diffusion tube bias of +8% for monthly exposure. Heal et al. (1999), using tubes prepared and analysed in their own laboratory with 50% TEA-in-acetone, found an average over-estimation of +1% for tubes exposed monthly over a 4 month summer period in Edinburgh. However it is not a universal picture that diffusion tubes over-estimate concentrations. For a number of years AEA Technology carried out an annual one-month intercomparison exercise using tubes prepared and analysed by a wide range of UK laboratories. Tubes were exposed at an urban background site (Walsall) alongside an automatic monitor. These exercises have shown that diffusion tubes exposed monthly can both under- and over-estimate concentrations by up to  $\pm 30\%$  or more. The indications were of a consistency in the performance of a particular laboratory from year to year. A more recent study by Laxen & Wilson (2002) has examined data from collocation studies carried out by 23 local authorities, giving 44 site-years worth of data. This has confirmed that diffusion tubes both over- and under-estimate concentrations and that the most significant factor affecting tube performance is the laboratory preparing and analysing the tubes. The reasons for the differences between the laboratories are currently not understood. No criticism of the laboratories should be implied as there is no carefully defined procedure to follow. In practical terms, what matters is that laboratories are consistent in their

performance. This may allow a diffusion tube bias to be determined and applied to the results from that laboratory.

### Role of exposure interval

4. Bush et al. (2001a) cite unpublished evidence from the 1990s that tubes exposed for four week periods produced lower concentrations than those exposed for one week, especially during summer months. The study by Heal et al. (1999) during a 4 month summer period in Edinburgh also found tubes exposed for four-weeks to give much lower concentrations than those exposed for one-week intervals in parallel (ratios to a chemiluminescence analyser of 1.01 and 1.26, for four and one week exposures, respectively). In a separate study over 11 months, Heal et al. (2000) found average ratios between diffusion tube and chemiluminescence analyser of 1.06, 1.15 and 1.24 for exposure intervals of 4 weeks, 2 weeks and 1 week, respectively. On the other hand, the national collocation study carried out by Bush et al. (2001a) over a full year found only a very small enhancement for 2-week exposures compared with 4-week exposures. The recent examination of collocation studies by Laxen & Wilson (2002) found indicative evidence of a significant effect of exposure interval, but this was not based on results for tubes supplied and analysed by the same laboratory, so must be treated with some caution. Overall, the evidence points to the exposure interval affecting performance, with concentrations being lower for longer exposure intervals. Heal et al. (2000) postulated some, as yet unidentified, exposure-interval dependent loss of nitrite at the adsorbent to explain the decrease in effective uptake of NO<sub>2</sub> with exposure interval. They argued that this loss factor, acting in the opposite direction to a positive bias on diffusion tube performance from within-tube chemistry (see section on Mechanisms), explained the effective closer agreement between their diffusion tube measurements and continuous analyser as exposure interval was increased.

#### Role of time of year

5. Heal et al. (1999) have argued on a theoretical basis, that chemistry taking place within the diffusion tubes (see section on Mechanisms), means that they will over-estimate by a greater amount in the summer at a polluted site, but that there should be little or no overestimation, and consequently no seasonal effect in such a bias, at a low pollution site. A similar theoretical study by Bush et al. (2001b) also predicted that tubes would over-estimate by a greater amount in summer than winter, although they concluded this would occur at all types of site, not just polluted sites. Kirby et al. (2001) report results of a 12-month survey using 10% TEAin-water tubes at a site in Cambridge that showed greater over-estimate in summer than winter, +18% cf. +13%. In a separate study, also in Cambridge, they reported a summer (March-August) over-estimate of +7% and a winter (December-March) under-estimate of -6%. Tubes were exposed for 2-week intervals in both cases. Bush et al. (2001a) on the other hand reported no seasonal difference for 50% TEA-in-acetone tubes exposed monthly at 17 sites across the UK. Laxen & Wilson (2002) have analysed data for tubes prepared by a single laboratory using two different methods, 50% TEA-in-acetone and 50% TEA-in-water, and exposed alongside a chemiluminescence monitor for 1-month at a time over an annual period, at 5 and 6 different locations respectively. The results show no evidence of a seasonal pattern for tubes prepared with 50% TEA-in-acetone (Figure A1). In the case of tubes prepared by the same laboratory using 50% TEA-in-water there is evidence of higher diffusion tube/chemiluminesence ratios during the four months August, September, October and November (Figure A2). A similar pattern was found in the results for 10% TEA-in-water tubes prepared and analysed by a different laboratory, based on 12 site-years of data. In this case the diffusion tube/chemiluminesence ratios were higher in August, September and October (Laxen & Wilson, 2002). Heal et al. (2000) present diffusion tube and collocated

chemiluminesence data for an 11-month period for tubes prepared with 10% TEA-in-water exposed at a city centre site in Cambridge. The diffusion tube/chemiluminesence ratios were significantly higher in the period mid-September to mid-November (no data were available for August and December). There is thus evidence for a dependency upon time of year (but not a simple summer/winter split) for tubes prepared with TEA-in-water, but not for tubes prepared with 50% TEA-in-acetone. There is currently no explanation for this pattern associated with preparation method.

**Figure A2.1** Ratio of diffusion tube to chemiluminescence for tubes prepared and analysed by one laboratory using 50% TEA-in-acetone. Box and whisker plots for each month for 5 site-years of data. (Laxen & Wilson, 2002).



**Figure A2.2** Ratio of diffusion tube to chemiluminesence for tubes prepared and analysed by one laboratory using 50% TEA-in-water. Box and whisker plots for each month for 6 site-years of data. (Laxen & Wilson, 2002).



### **Role of exposure setting**

6. Bush *et al.* (2001a) found unsheltered tubes, exposed monthly for a full year at 17 locations around the UK, over-estimated concentrations by +10%, while tubes sheltered beneath an inverted bucket under-estimated concentrations by -10%. Kirby *et al.* (2001) found a similar behaviour, with unsheltered tubes at a location in Cambridge over-estimating by +16%, while the sheltered tube beneath an inverted bucket over-estimated by +3%. This is an artificial situation, as tubes are not routinely exposed in this way, but Campbell *et al.* (1994) report a study that suggests tubes in an exposed location on a roof top will over-estimate by up to +40% due to wind induced turbulence in the mouth of the diffusion tube, compared with tubes in a more sheltered location near to a wall (see below under Mechanisms).

### Role of exposure location – roadside/background

7. Heal et al. (1999), in a study using 50% TEA-in-acetone tubes exposed for one-week in Edinburgh, found that 2 roadside sites over-estimated by +50 and +37%, while an urban background site over-estimated by +13%. Kirby et al. (2001) report a +14% over-estimate for tubes exposed for 2-week intervals at an urban background (Norwich) site, but a lower (+4%) over-estimate at a roadside (Marylebone Road, London) site. The difference between the two studies may be associated with differences in concentrations of NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> at the various sites, with a resultant impact on the photochemical equilibrium within the tubes (see below under Mechanisms). The examination by Laxen & Wilson (2002) of results obtained by a number of local authorities found that the performance of tubes exposed for a month at a time at roadside sites fell within the range of the performance at background sites (comparison based on tubes supplied and analysed by the same laboratory and prepared in the same way). The evidence for a consistent difference between roadside and background monitoring location is therefore equivocal.

### Role of tube preparation method

8. The comparative study by Kirby *et al.* (2000) using 2-week exposure intervals over 5 months showed similar performances for tubes prepared using 50% TEA-in-acetone, 10% and 20% TEA-in-water, but tubes prepared with 50% TEA-in-water gave lower concentrations. AEA Technology (2002), in a study over one month (October), compared tubes prepared by three different laboratories using 50% TEA-in-acetone, 20% and 50% TEA-in-water. As with Kirby *et al.* (2000) 50% TEA-in-acetone tubes gave the highest concentrations, with 50% TEA-in-water tubes giving the lowest concentrations. However, unlike the Kirby *et al.* (2000) study, 20% TEA-in-water tubes gave intermediate values. In contrast, the data compiled by Laxen & Wilson (2002) for monthly exposure of tubes prepared by one laboratory using 50% TEA-in-water (six sites) and 50% TEA-in-acetone (5 sites), over a full year, showed no difference in the performance. The method of tube preparation does not therefore affect performance in a consistent way.

## Role of exposure concentration and NO<sub>2</sub>/NO<sub>x</sub> ratio

9. Atkins et al. (1986) found no dependency of the performance of 50% TEA-in-acetone tubes on NO<sub>2</sub> concentration when exposed weekly to concentrations over the range 10–110 µg m<sup>-3</sup>. In contrast, Kirby et al. (2001) found that the performance of 10% TEA-in-water tubes was strongly related to the total NO<sub>2</sub> concentration. Tubes exposed to 1-week or 2-week NO<sub>2</sub> concentrations (chemiluminescence) of around 55 µg m<sup>-3</sup> under-estimated by around 0 to -10%, while tubes exposed to concentrations of around 25-30 µg m<sup>-3</sup> over-estimated by around +30 to +45%. Heal et al. (1999) reported similar behaviour for 50% TEA-in-acetone tubes exposed

weekly to NO<sub>2</sub> concentrations in the range 30–65  $\mu$ g m<sup>-3</sup>. Laxen & Wilson (2002) found a more confusing picture for annual mean performance of tubes prepared in different ways and exposed for 1-week, 2-week or monthly time intervals (Figure A3). Some of the variability may follow from the relationships also observed between 1-week tube performance and NO<sub>2</sub>:NO<sub>x</sub>, NO:NO<sub>2</sub> and O<sub>3</sub>:NO<sub>2</sub> ratios and explained by a within-tube chemistry mechanism (Heal *et al.*, 1999, Heal *et al.*, 2000, Kirby *et al.*, 2001). If ambient concentrations of NO<sub>x</sub>, NO<sub>2</sub> and O<sub>3</sub> are affecting tube performance, then it will clearly be in a complex way.

**Figure A2.3** Diffusion tube bias vs annual mean concentration (automatic monitor). Data grouped by laboratory and tube preparation method. Lines are linear best-fit relationships: solid lines for 50% TEA in water, monthly exposure; small dashed line for 50% TEA in water, monthly exposure; and small/large dashed lines for 10% TEA in water, 1-week and 2-week exposure. (Laxen & Wilson, 2002).



## **Mechanisms**

- **10.** The two principal mechanisms proposed to account for overestimation by diffusion tubes are (i) a shortening of the diffusion length in the tube due to turbulence in the mouth of the tube brought about by higher windspeeds, and (ii) reaction within the tube between NO and O<sub>3</sub> that are not at photostationary equilibrium in the ambient air. Even when the ambient NO and O<sub>3</sub> are at photostationary equilibrium, additional NO<sub>2</sub> can be generated within the tube since the photolytic component of the NO-NO<sub>2</sub>-O<sub>3</sub> equilibrium is switched off within the tube. To date no convincing mechanism has been put forward to account for under-estimation of concentrations, although (as mentioned above in Role of Exposure Interval) Heal *et al.* (1999, 2000) postulate some form of light-dependent loss of the nitrite from the adsorbent.
- 11. The issue of a wind induced shortening of the diffusion length was first examined by Atkins et al. (1986). They postulated that there should be greater turbulence in the mouth of the tube at higher windspeeds, giving rise to a shorter diffusion length and hence higher 'apparent' concentrations. However they found no relationship between windspeed and tube performance, suggesting this mechanism is not significant. Campbell et al. (1994), on the other hand, concluded that over-estimation by diffusion tubes at some, but not all, sites in a UK-wide study in 1990/91, was likely to be due to wind-driven shortening of the diffusion length. They supported this with a study using tubes of different length in an exposed roof-top location and in a more sheltered location by a building wall. This showed that the sheltered

tubes experienced no reduction in diffusion length, while the exposed tubes showed a 2 cm reduction in diffusion length. For the standard 7.1 cm tube this would translate to a 40% increase in concentration. A similar study by Gair & Penkett (1995) also showed a constant shortening of the diffusion length, in their case 2.3 cm, for tubes of 4 to 14 cm length exposed on a roof. However, they found only a weak relationship between average windspeed over the exposure period and the shortening of the diffusion length. They concluded that for the standard diffusion tube the over-estimation would be 25% for their short period study at a rooftop location. Subsequent studies by Kirby *et al.* (2001) confirmed the findings of Atkins *et al.* (1986), finding no correlation between performance and windspeed. They did though find a reduced uptake for sheltered tubes, as did Bush *et al.* (2001a). The picture is thus somewhat confusing. There does seem to be evidence to support the view that turbulence in the mouth of the tube shortens the diffusion length, thus increasing the apparent concentration, but this effect is clearly not related to average windspeed over the sample period.

The potential for photolytic enhancement of concentrations was addressed when diffusion tubes 12. were first proposed. Atkins et al., (1986) used a chemical model to show that the reduced photolysis within the tube could lead to over-estimation of 11% during daylight hours in a low pollution area and 6% over-estimation in a polluted area. Taking account of no over-estimation during night-time the overall over-estimation would be substantially less. The mechanism postulated involves the photolytic breakdown of NO<sub>2</sub> being switched off within the tubes, as the acrylic walls do not transmit the necessary UV energy. This allows the NO within the tube to react with O<sub>3</sub> to create additional NO<sub>2</sub>, without the photolytic back reaction occurring. There is sufficient time for this reaction, as the transport time for the diffusing species within the diffusion tube is of the order of 2 minutes, which is similar to the NO +  $O_3$  reaction time (Heal & Cape, 1997). Clearly such an effect will be dependent on the ambient concentrations of NO and O<sub>3</sub>. Heal & Cape (1997) have carried out detailed modelling of the chemistry within tubes, and concluded that this would produce an overall over-estimate of NO2 concentrations by 14% in winter and 28% in summer at an urban location, and 8-9% at a rural location in both summer and winter. The over-estimation is greater than suggested by Atkins et al. (1986) and the low pollution - high pollution pattern is different. Bush et al. (2001b) have carried out further modelling, which shows the greatest over-estimation will occur when the annual mean NO, lies between 60-100 µg m<sup>-3</sup>. Their modelling suggests that the over-estimation would range from a maximum of around 7% in winter to 25% in summer. At high concentration, such as might be found close to busy roads (>200 µg m<sup>-3</sup> NO<sub>2</sub>), the over-estimation is predicted to be negligible, at <5%. Measurements at different times of year and at different types of location have been used by these authors to support the theoretical behaviour, but the full set of data analysed above do not support the chemistry mechanism fully. For instance, the apparent lack of seasonal pattern in the performance of tubes made up with 50% TEA-in-acetone is not consistent with the predictions of the chemistry model, neither is the odd behaviour of tubes made up with TEA-in-water, which produce higher concentrations in the months August to November, while the peak photolytic season, runs from May to August.

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## Appendix 3

# **Definition of site classes**

## Kerbside (U1)

A site sampling within 1 m of the edge of a busy road. Source influences: Local traffic Examples of objectives: Identifying vehicle pollution blackspots Assessing worst case scenarios Evaluating impacts of vehicle emission control technologies Determining impacts of traffic planning/calming schemes.

## Roadside (U2)

A site sampling between 1 m of the kerbside of a busy road and the back of the pavement. Typically this will be within 5 m of the road, but could be up to 15 m.

Source influences: Local traffic

Examples of objectives:

Assessing worst case population exposure

Evaluating impacts of vehicle emission controls

Determining impacts of traffic planning/calming schemes.

## Urban centre (U3)

A non-kerbside site, located in an area representative of typical population exposure in town or city centres (for example, pedestrian precincts and shopping areas). This is likely to be strongly influenced by vehicle emissions, as well as other general urban sources of pollution. Sampling at or near breathing-zone heights will be applicable.

Source influences: Vehicle, commercial, space heating Examples of objectives:

Identification of long-term urban trends.

## Urban background (U4)

An urban location distanced from sources and therefore broadly representative of city-wide background conditions, for example, elevated locations, parks and urban residential areas. Source influences: Vehicle, commercial, space heating Examples of objectives:

Trend analysis Urban planning Traffic and land-use planning.

## Urban industrial (U5)

An area where industrial sources make an important contribution to the total pollution burden. Source influences: Industrial, motor vehicles

Examples of objectives:

Assessing local impacts on health and amenity Process optimisation Source attribution/identification Providing model input data Model development/validation Local planning and plant authorisation.

## Suburban (SU)

A location type situated in a residential area on the outskirts of a town or city.

Source influences: Traffic, commercial, space heating, regional transport, urban plume downwind of a city

Examples of objectives

Traffic and land-use planning Investigating urban plumes.

# Rural (R1)

An open country location, in an area of low population density, distanced as far as possible from roads, populated and industrial areas.

Source influences: Regional long-range transport, urban plume

Examples of objectives

Ecosystem impact studies Assessing compliance with critical loads and levels for crops and vegetation Investigating regional and long-range transport Identification of  $O_3$  'hot spots'.

## Remote (R2)

A site in open country, located in an isolated rural area, experiencing regional background pollutant concentrations for much of the time.

Source influences: Regional/hemispheric background

Examples of objectives

Assessing 'unpolluted' global or hemispheric background conditions

Long-range transport studies

Long-term baseline trend analysis.

## Special (Sp)

A special source-oriented category covering monitoring studies undertaken in relation to specific emission sources such as power stations, petrol stations, car parks or airports.

## Appendix 4

# Lists of sites exceeding threshold concentrations

**Table A4.1** Roadside and kerbside sites with measured annual mean NO<sub>2</sub> concentration in 2001 exceeding 40  $\mu$ g m<sup>-3</sup> and 'year factor' projection of concentration for 2005 and 2010 ( $\mu$ g m<sup>-3</sup>)

| Site name                        | Site type | 2001 | 2005 | 2010 |
|----------------------------------|-----------|------|------|------|
| Redbridge 2 – Ilford Broadway    | Roadside  | 120  | 107  | 88   |
| Kens and Chelsea – King's Rd     | Roadside  | 86   | 76   | 63   |
| London Marylebone Road           | Kerbside  | 84   | 75   | 62   |
| Kens and Chelsea – Knightsbridge | Kerbside  | 83   | 74   | 61   |
| London Cromwell Road 2           | Roadside  | 76   | 68   | 56   |
| Camden – Shaftesbury Avenue      | Roadside  | 75   | 67   | 55   |
| Glasgow Kerbside                 | Kerbside  | 71   | 63   | 52   |
| Hammersmith Broadway             | Roadside  | 70   | 62   | 51   |
| Bury Roadside                    | Roadside  | 69   | 62   | 51   |
| Tower Hamlets Roadside           | Roadside  | 69   | 62   | 51   |
| Croydon 5 – Norbury              | Roadside  | 69   | 61   | 50   |
| Islington – Holloway Road        | Roadside  | 67   | 60   | 49   |
| Camden Kerbside                  | Kerbside  | 66   | 59   | 48   |
| Brent – Ikea                     | Roadside  | 65   | 58   | 48   |
| Redbridge 3 – Fullwell Cross     | Roadside  | 65   | 58   | 48   |
| Southwark Roadside               | Roadside  | 65   | 58   | 48   |
| Dartford Roadside – St Clements  | Kerbside  | 62   | 55   | 45   |
| London Bromley                   | Roadside  | 61   | 54   | 45   |
| Haringey 3 – Bounds Green        | Roadside  | 61   | 54   | 44   |
| Oxford Centre                    | Roadside  | 60   | 54   | 44   |
| Salford M60                      | Roadside  | 58   | 52   | 43   |
| Lambeth – Christchurch Road      | Roadside  | 58   | 52   | 42   |
| Barnet – Tally Ho Corner         | Kerbside  | 58   | 51   | 42   |
| Bath Roadside                    | Roadside  | 57   | 51   | 42   |
| Bristol Old Market               | Roadside  | 57   | 51   | 42   |
| Croydon 4 – George Street        | Roadside  | 56   | 50   | 41   |
| Hounslow 4 – Chiswick High Rd    | Roadside  | 56   | 50   | 41   |

| Site name                              | Site type | 2001 | 2005 | 2010 |
|--|-----------|------|------|------|
| Greenwich 5 – Trafalgar Road           | Roadside  | 55   | 49   | 40   |
| Ealing 2 – Acton Town Hall             | Roadside  | 54   | 48   | 40   |
| Hounslow Roadside                      | Roadside  | 54   | 48   | 40   |
| London A3 Roadside                     | Roadside  | 54   | 48   | 40   |
| Newham Cam Road                        | Roadside  | 54   | 48   | 40   |
| Wandsworth 4 – High Street             | Roadside  | 53   | 47   | 39   |
| Richmond Mobile 6                      | Roadside  | 51   | 46   | 38   |
| Gravesham Roadside – A2                | Roadside  | 51   | 46   | 38   |
| Maidstone Roadside – Fairmeadow        | Kerbside  | 51   | 46   | 38   |
| Crystal Palace                         | Roadside  | 51   | 45   | 37   |
| Ealing Mobile – Southall               | Roadside  | 51   | 45   | 37   |
| A2 Falconwood                          | Roadside  | 51   | 45   | 37   |
| Enfield 4 – Derby Road, Upper Edmonton | Roadside  | 50   | 45   | 37   |
| Broxbourne Roadside                    | Roadside  | 50   | 44   | 37   |
| Tonbridge Roadside – Town Centre       | Roadside  | 49   | 44   | 36   |
| Haringey Roadside                      | Roadside  | 48   | 43   | 35   |
| Redbridge 4 – Gardner Close            | Roadside  | 48   | 43   | 35   |
| Cambridge Parker Street                | Roadside  | 47   | 42   | 34   |
| Cambridge Silver Street                | Roadside  | 46   | 41   | 34   |
| Watford Roadside                       | Roadside  | 46   | 41   | 33   |
| Richmond Mobile 5                      | Roadside  | 45   | 40   | 33   |
| Croydon 2 – Purley Way, 5 Ways         | Roadside  | 45   | 40   | 33   |
| Hillingdon – South Ruislip             | Roadside  | 45   | 40   | 33   |
| Stert St (Abingdon)                    | Roadside  | 45   | 40   | 33   |
| Richmond – Castlenau                   | Roadside  | 44   | 39   | 32   |
| M4                                     | Kerbside  | 44   | 39   | 32   |
| E. Herts Roadside (Sawbridgeworth)     | Roadside  | 44   | 39   | 32   |
| Sutton Roadside                        | Roadside  | 44   | 39   | 32   |
| Enfield 2 – Church Street              | Roadside  | 42   | 38   | 31   |
| Havering 3 – Romford                   | Roadside  | 42   | 37   | 31   |
| Exeter Roadside                        | Roadside  | 41   | 37   | 30   |

**Table A4.2** Background sites with measured annual mean  $NO_2$  concentration in 2001 exceeding 40 µg m<sup>-3</sup> and 'year factor' projection of concentration for 2005 and 2010 (µg m<sup>-3</sup>)

| Site name                       | Site type        | 2001 | 2005 | 2010 |
|---------------------------------|------------------|------|------|------|
| Brent – Harlesden               | Urban background | 76   | 69   | 59   |
| Corp. of London – Senator House | Urban background | 60   | 54   | 46   |
| London Southwark                | Urban centre     | 55   | 50   | 43   |
| Heathrow LHR2                   | Airport          | 54   | 49   | 42   |
| London Wandsworth               | Urban centre     | 53   | 48   | 41   |
| West London                     | Urban background | 52   | 47   | 40   |
| London Bloomsbury               | Urban centre     | 51   | 46   | 40   |
| Islington – Upper Street        | Urban background | 50   | 45   | 39   |
| London Hackney                  | Urban centre     | 48   | 44   | 37   |
| Manchester Town Hall            | Urban background | 47   | 43   | 37   |
| Tower Hamlets – Bethnal Green   | Urban background | 47   | 42   | 36   |
| London Hillingdon               | Suburban         | 46   | 42   | 36   |
| Glasgow City Chambers           | Urban background | 46   | 42   | 36   |
| Newham Tant Avenue              | Urban background | 46   | 42   | 36   |
| Sheffield Tinsley               | Urban industrial | 45   | 41   | 35   |
| Tower Hamlets 1 – Poplar        | Urban background | 45   | 41   | 35   |
| Bradford Centre                 | Urban centre     | 44   | 40   | 34   |
| Waltham Forest – Dawlish Road   | Urban background | 43   | 39   | 34   |
| Edinburgh Centre                | Urban centre     | 43   | 39   | 33   |
| London N. Kensington            | Urban background | 42   | 38   | 33   |
| Walsall Alumwell                | Urban background | 42   | 38   | 33   |
| Salford Eccles                  | Urban industrial | 42   | 38   | 33   |
| Hounslow 2 – Cranford           | Suburban         | 41   | 37   | 32   |
| Barnet – Finchley               | Urban background | 40   | 37   | 31   |
| Barnet – Strawberry Vale        | Urban background | 40   | 36   | 31   |

Table A4.3 Sites with more than 18 exceedences of 200  $\mu g$  m^-3 hourly mean  $NO_2$  concentration in 2001 (number of hours above 200  $\mu g$  m^-3)

| Site name                        | Site type        |     |  |
|----------------------------------|------------------|-----|--|
| Redbridge 2 – Ilford Broadway    | Roadside         | 826 |  |
| Bristol Old Market               | Roadside         | 98  |  |
| Kens and Chelsea – Knightsbridge | Kerbside         | 97  |  |
| Trafford                         | Urban background | 63  |  |
| London Marylebone Road           | Kerbside         | 60  |  |
| Glasgow Kerbside                 | Kerbside         | 54  |  |
| Stockport Cheadle                | Urban background | 45  |  |
| Stockport Bredbury               | Urban background | 34  |  |
| Dartford Roadside – St Clements  | Kerbside         | 25  |  |
| Brent – Ikea                     | Roadside         | 24  |  |
| Stockport                        | Urban background | 22  |  |
| Redbridge 3 – Fullwell Cross     | Roadside         | 19  |  |
| Brent – Harlesden                | Urban            | 19  |  |

Table A4.4 Sites with 3-hour mean  $NO_{\!_2}$  concentration greater than 400  $\mu g~m^{\text{-}3}$  in 2001

| Site name          | Site type        |
|--------------------|------------------|
| Stockport Bredbury | Urban background |

## Appendix 5

# **Respondents to the draft Nitrogen Dioxide in the United Kingdom Report**

Comments were gratefully received from the following organisations and/or individuals on the draft of this report, which was published in May 2003:

Air Monitors Ltd

Mr Robert Appleby

**BAA** Heathrow

British Airways

Dr Simon Watts

**Energy Saving Trust** 

Environment Agency

Greater London Authority

Highways Agency

Professor Stephen Holgate

Innogy plc

Johnson Matthey

Dr David Muir

Natural Environment Research Council (NERC)

nsca

Kirby Associates Limited

Scottish Environment Protection Agency

Welsh Air Quality Forum