Real time monitoring and environmental fate of oxides of nitrogen in the construction industry

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The UK Workplace Exposure Limits of nitrogen monoxide (nitric oxide, NO) and nitrogen dioxide (NO₂) are currently under review. In the meantime, both NO and NO₂ were subject to a CHAN (Chemical Hazard Awareness Notice) of 1 ppm (8-hr time-weighted average, TWA), significantly lower than the previous occupational exposure standards. Note that all CHANs have now been suspended (from December 2006).

Exposure to these oxides of nitrogen commonly arises in the construction industry from diesel engine exhaust emissions and from the use of explosives. This project addresses (a) the effectiveness of real-time monitors, particularly personal monitors, at these concentration levels and (b) the environmental fate of NO and NO₂ in the construction environment by laboratory and field experiments.

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EXECUTIVE SUMMARY

The UK Workplace Exposure Limits of nitric oxide (NO) and nitrogen dioxide (NO₂) are currently under review. In the meantime, both NO and NO₂ were subjected to a CHAN (Chemical Hazard Awareness Notice) of 1 ppm (8-hr time-weighted average, TWA), significantly lower than the previous occupational exposure standards. Note that all CHANs have now been suspended (from December 2006). Exposure to these oxides of nitrogen commonly arises in the construction industry from diesel engine exhaust emissions and from the use of explosives. This project addresses (a) the effectiveness of real-time monitors at these concentration levels and (b) the environmental fate of NO and NO₂ in the construction environment.

Objectives

1. To identify and evaluate real-time NO and NO₂ monitors capable of measuring around the (previous) CHAN limit of 1 ppm (8-hr TWA) for NO and NO₂, and robust enough for use in the construction sector, particularly tunnelling.
2. To review the environmental fate of nitric oxide (NO) and nitrogen dioxide (NO₂), the dispersion and ventilation of nitrogen oxides (NOx) resulting from the emission of diesel exhaust into the workplace and how this might affect industry monitoring.
3. To generate knowledge which can help develop control guidance for HSE and the industry for NOx.

Main Findings

Instrumentation (laboratory and field experiments)
Personal monitoring for NO is feasible at a datalogging resolution of 0.1 ppm with the Rae Systems MultiRae, although this instrument does not display at this resolution - its display resolution is only 1 ppm due to truncating of the decimal place. The cross sensitivity of the NO sensor to NO₂ is ~7 - 24%.

Personal monitoring for NO is feasible at a display and datalogging resolution of 0.5 ppm with the Drager PAC III.

The Crowcon Triple Plus (incorporating both City Technology and Alphasense NO sensors) was not able to measure sub-ppm NO concentrations with sufficient accuracy.

Personal monitoring for NO₂ is feasible with sufficient resolution (0.1 ppm) with most current instrumentation, including those investigated here.

The 2B Technologies NO Monitor has the resolution (<0.1 ppm) and low cross sensitivity to NO₂ (~2%) required to monitor sub-ppm concentrations of NO. However, it is not a portable monitor and has not been designed for rugged use.

The Teledyne-API M200A NOₓ Analyser has the resolution (<0.1 ppm) and low cross sensitivity (~1 - 3%) required to monitor sub-ppm concentrations of NO, NO₂ and NOₓ. It is useful as a fixed, reference instrument but the location and/or the sampling system would need to be carefully considered in view of its fragility.

Long-path optical instruments for NO (and NO₂) are increasingly being used and developed, putatively having sufficient resolution and stability for fixed monitoring in tunnels.
Environmental fate of NO (laboratory and field experiments)

Using the glass vessel to study NO oxidation kinetics, qualitative agreement was found between the experimental oxidation rate and that predicted by the model: the higher the initial NO concentration, the faster the NO decay rate.

The laboratory experiments showed that the conversion of NO is fairly rapid for high concentrations (order of 100 ppm) but this is not the case in relation to the timescale required to reduce the concentration to 1 ppm. Experiments and modelling of the kinetics of the thermal oxidation indicate that the timescale to reduce to a concentration of NO of 1 ppm is of the order of 50-100 hours, which is well in excess of the timescales associated with the dispersion of NOx via mechanical ventilation. The field tests in the gallery confirmed that NO levels around 1 ppm were persistent over this timescale.

In the glass vessel experiments, the NO concentration reduced at a slower rate than the model predicted, while the NO2 concentration began to increase following the trend of the mathematically modelled values for a short time, before reducing along the same trend as the NO concentration. Other factors such as adsorption on the walls of the vessel and the small but significant generation of NO from the NO2 electrochemical sensor, both of which it would be possible to correct for, may account for these discrepancies.

The dilution of the diesel fume within 0.5 m of the source to approximately 1% of the NO concentration at the source prevented any effective method of comparing the environmental fate of NO and NO2 as a function of time and distance with a relatively unreactive species (CO) in the exhaust gas.

Ventilation & modelling (literature reviews)

Formerly, ventilation systems were designed to dilute CO. The airflows required to dilute CO also ensured the dilution of other pollutants, in particular NOx.

Cuts in CO emissions from vehicles have not been matched by a decrease in NOx levels. NO2 concentrations must be taken into account when calculating ventilation flow rates.

Airflow rates necessary to dilute NO2 can be calculated from the emission factors for NOx for different vehicle types, the mix of traffic and the traffic flow rate. Tunnel gradient may also need to be taken into account.

Travel times through tunnels are usually short and relatively high concentrations of pollutants may be acceptable for short term exposures.

Tunnels with bi-directional traffic flows are generally regarded as the most difficult to ventilate. Ventilation might be improved if the traffic flows can be partitioned.

High longitudinal air velocities can cause a variety of problems and an upper limit of 10 – 12 m/s is usually recommended.

A review of the literature shows that the emphasis has been on the modelling of the photochemical (atmospheric) conversion of NO in the presence of O3, and that only a couple of studies have dealt with other oxidation pathways for NO.

Recommendations

1. NO will be persistent in tunnels at concentrations around a few ppm and will therefore require measurement, in addition to NO2, for personal protection. Some portable NO
monitors are available, although not as many as is desirable, for NO\textsubscript{2}; therefore this is currently feasible. Although NO:NO\textsubscript{2} ratios can be established generally in tunnels from fixed monitors, the ratio may vary from location to location and therefore may not be reliably used to estimate personal exposure the concentration of one gas from the measurement of the other. As, typically, NO is 10\% of the NO\textsubscript{x} concentration, more error will be generated in trying to estimate NO from NO\textsubscript{2} (i.e. the reverse calculation to that usually performed in tunnels – estimation of NO\textsubscript{2} from NO).

2. Gas detection manufacturers should be re-engaged (directly or via CoGDEM) to develop personal NO sensors/instruments capable of monitoring with display and datalogging resolution of 0.5 ppm or ideally 0.1 ppm resolution, with sufficient stability in a tunnel environment to measure accurately around the recommended level.

3. Fixed installations for NO and NO\textsubscript{2} play an important role in warning of build-up of NO\textsubscript{x}. They are increasingly being used to warn and help control NO and NO\textsubscript{2} levels. Again, they should have a resolution of better than 0.1 ppm and sufficient stability to monitor around and below the 1 ppm level. Long-path optical monitors show promise in this area and the industry should be encouraged to evaluate and use them.

4. The glass vessel used in the measurement of NO reactivity provides a controlled environment to investigate factors influencing NO decay. The reactivity of NO in actual diesel exhaust should be studied using this system to provide further information on NO reactivity in actual exhaust mixtures. It will conveniently allow the influence on the NO reaction rate of such factors as NO concentration, O\textsubscript{2} concentration, temperature, diesel type, UV radiation levels, volatile organic compounds in the exhaust, water vapour concentration, O\textsubscript{3} concentration, total pressure, to be studied. However, the variability in the rate of oxidation of NO between runs needs to be better understood and reduced, if possible, in order to quantify the effect of the above-mentioned factors.

5. A further series of experiments in the Buxton gallery at higher NO concentrations should be performed to further investigate NO levels and its decay, and comparison with measurements of ‘unreactive’ CO and/or CO\textsubscript{2}, as the measurements carried out in this report were inconclusive.

6. It was not possible to visit and install suitable monitors in an actual tunnel during this project. However, it would be useful to datalog readings over an extended period, e.g. of the order of a month, using the MultiRae, Drager and 2BT monitors to investigate their suitability and performance in the intended environment. It would also enable background and personal levels of NO\textsubscript{x} to be measured.

7. The usefulness of modelling fluid flow and NO\textsubscript{x} concentrations in tunnels should be further investigated. This will be simplified as the oxidation of NO to NO\textsubscript{2} can be neglected in the calculations.
1 INTRODUCTION

The UK Workplace Exposure Limits (WELs) for nitric oxide (NO, also known as nitrogen monoxide) and nitrogen dioxide (NO₂) are currently under review. In the meantime, both nitric oxide and nitrogen dioxide were subject to a CHAN (Chemical Hazard Awareness Notice) of 1 ppm 8-hr Time Weighted Average (TWA) (HSE, 2003a, 2003b), which was in existence during the period of this study. However, note that all CHANs have recently been suspended (since December 2006). Moreover, guidance on NO levels has been issued (in August 2006) by the British Tunnelling Society, jointly with HSE, (BTS, 2006). Exposure to these oxides of nitrogen (NOx) commonly arises from diesel engine exhaust emissions and from the use of explosives. Both types can occur in the construction industry, particularly when tunnelling (see Section 5 Ventilation). The physico-chemical properties and health effects of NO are summarised in the Appendix (Section 8.1).

Real-time monitors are required by the construction industry as they can provide a simple means of checking that controls (e.g. ventilation, vehicle maintenance) are adequate. For example, guidance on tunnel sensor limits in the Design Manual for Roads and Bridges (Highways Agency, 1999) for road users within a tunnel is based on the HSE EH40/2002 values of 35 ppm and 5 ppm for the 15-min short-term limit values for nitric oxide and nitrogen dioxide respectively (HSE, 2002). The tunnel sensors activate mechanical ventilation, if provided, in stages before the pollutants reach various limiting values. Both portable (personal or hand-held) or fixed monitors which alarm at a preset level, eg 1 ppm can be used to minimise exposure risk. Such monitors should alarm reliably at these low levels in the often harsh construction environment. Although the CHAN limit is 1 ppm 8-hour TWA, setting the control level at an ‘instantaneous’ value is preferable as:

- diesel plant generating the NOx tends to be working at least 8 hours per day therefore controlling to a 1 ppm ceiling would afford better protection; and
- it is simpler to understand and implement than a time weighted average system.

Real-time monitors, ie portable (personal or hand-held) or fixed instruments, for nitric oxide and nitrogen dioxide are available but whether they are suitable for monitoring accurately and on a routine basis at 1 ppm and down to a fraction of this level, particularly for nitric oxide, with the required level of ruggedness, is under discussion. European standards (BS EN 45544 series) exist for the performance testing and guidance for use of real-time instruments for measurement of toxic gases and vapours in the workplace (BSI, 2000). It is believed, however, that no instruments for NO or NO₂ have yet been tested to this standard (only those for carbon monoxide). Furthermore, the standard test gas concentration used for NO is based on the pre-CHAN levels, ie 25 ppm; the equivalent for NO₂ is 3 ppm.

The measurement and control strategy for NO and NO₂ will depend to an extent on the relative amounts of each. However, this might be complicated by the environmental fate of NO and NO₂. The kinetics of oxidation of NO to NO₂, while understood from laboratory experiments on pure gases, are not as clear when considered in the field where there are additional factors to consider, eg the emission source (diesel exhaust and explosives, principally) which is a mixture of various gases and particulate matter; environmental factors (temperature, humidity, light, other pollutants such as ozone); and dispersion (natural and forced ventilation). Modelling may however assist in determining the environmental fate of nitric oxide and nitrogen monoxide in tunnels.

Guidance is therefore required to develop an appropriate monitoring strategy, particularly for personal exposure, based on (a) the type of gas monitors suitable for the application; and (b) the
environmental fate of NO and NO₂ when emitted from the exhaust (and explosives), and its subsequent dispersion and reaction in the workplace atmosphere.

The original aims of this project were:

1. To identify and evaluate real-time NO and NO₂ monitors capable of measuring around the CHAN advisory limit of 1 ppm for NO and NO₂ and robust enough for use in the construction sector, particularly tunnelling.
2. To review the environmental fate of nitric oxide (NO) and nitrogen dioxide (NO₂), the dispersion and ventilation of nitrogen oxides (NOx) resulting from the emission of diesel exhaust into the workplace and how this might affect industry monitoring.
3. To generate knowledge which can help develop control guidance for HSE and the industry for NOx

This report focuses on instrument evaluation in the laboratory and the field, and measurements of NO oxidation in the laboratory. The fieldwork comprises tests on instruments using diesel exhaust emissions in HSL’s surface gallery (dust tunnel). Additionally, reviews were carried out on ventilation and dispersion in tunnels, particularly relating to NO.
2 EVALUATION OF REAL-TIME INSTRUMENTS FOR NO AND NO₂ MONITORING

This phase of the investigation was designed to test the performance and suitability of existing instruments, particularly portable ones, which may be capable of monitoring the NO and NO₂ down to the concentrations required, i.e. ~0.1 ppm or 10% of the CHAN. See Appendix (Section 8.2) for the principle of operation and the specifications of the existing types of NO and NO₂ monitors, both portable and fixed.

2.1 NO AND NO₂ REAL-TIME MONITORS SELECTED FOR EVALUATION

Research into existing instruments shown in Appendix (Section 8.2) which may be capable of monitoring the NO and NO₂ down to the concentrations required in this investigation led to the selection of the instruments listed in Table 2.1, photographs of which can be seen in Figure 2.1.
The instruments responses and cross sensitivities were characterised by exposure to relevant concentrations of NO and NO₂, after being zeroed in clean air and calibrated at the maximum concentration of the relevant range immediately prior to commencement of each set of tests. The responses on the instrument display and the recorded datalogs were analysed (averages were taken at each setting where the signals showed significant variation). The NO and NO₂ concentrations were achieved using Alpha Volumetric, Spectra Seal, Size AV cylinders with certificates of Analysis, listed in the Appendix (Section 8.3), clean laboratory air and calibrated Mass Flow Controllers (MFCs) for the relevant ranges.

### 2.2 MULTIRAE NO & NO₂ MONITOR CHARACTERISATION

Five MultiRAE monitors were used in this investigation, serial numbers 500871 (denoted black), 502465 (blue), 502816 (orange), 502967 (red) and 502966 (yellow), each installed with an NO and an NO₂ sensor. The same sensors were used in the same instrument throughout this investigation. See Appendix (Section 8.4.1) for sensor data sheets and brief explanation of sensor operation.

Inspection of the display panels on each of these instruments showed a resolution of 0.1 ppm for the NO₂ readings but only 1 ppm for the NO readings. Inspection of the logged data, however, showed both NO₂ and NO concentrations to be recorded to 0.1 ppm. Enquiries to RAE Systems revealed no reason for this and no information on the accuracy of the sub-ppm readings.

The sensors were characterised over 2 ranges of exposure to NO and NO₂, 0 - 1 ppm (in 0.1 ppm steps) and 0 - 5 ppm (in 1 ppm steps), after being zeroed in clean air and calibrated at the maximum concentration of the relevant range of each gas immediately prior to commencement of each set of tests.

#### 2.2.1 MultiRAE response & cross sensitivity to NO

Exposing the instrument to NO allowed the response of the NO sensor and the cross sensitivity of the NO₂ sensor to NO to be determined simultaneously. Fig. 2.2 (0 – 1 ppm) and Fig. 2.3 (0 – 5 ppm) show the response of the NO sensors and the sensitivity of the NO₂ sensors in each of the MultiRAE monitors upon exposure to the various concentrations of NO.

---

Table 2.1: Specifications of real-time monitors selected for evaluation

<table>
<thead>
<tr>
<th>Instrument Manufacturer</th>
<th>Model</th>
<th>Portable</th>
<th>Sensors</th>
<th>Sensor Type</th>
<th>Range</th>
<th>Display Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B Technologies</td>
<td>NO Monitor</td>
<td>No</td>
<td>NO</td>
<td>ultraviolet absorption</td>
<td>0 – 2 ppm</td>
<td>0.001 ppm</td>
</tr>
<tr>
<td>RAEPOL.com</td>
<td>M200A NO₂</td>
<td>No</td>
<td>NO, NO₂</td>
<td>chemiluminescence</td>
<td>0 – 20 ppm</td>
<td>0.001 ppm</td>
</tr>
<tr>
<td>Crowcon.com</td>
<td>Triple Plus +</td>
<td>Yes</td>
<td>NO</td>
<td>electrochemical</td>
<td>0 – 35 ppm</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>RAESystems.com</td>
<td>MultiRAE Plus</td>
<td>Yes</td>
<td>NO</td>
<td>electrochemical</td>
<td>0 - 250 ppm (1000 ppm max overload)</td>
<td>1.0 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO₂</td>
<td>electrochemical</td>
<td>0 - 20 ppm (150 ppm max overload)</td>
<td>0.1 ppm</td>
</tr>
</tbody>
</table>

4
Figure 2.2: Response of the NO and NO₂ sensors in the MultiRAEs to NO between 0 – 1 ppm

Equations 2.1a to 2.1e show the response parameters for each instrument when used in the 0 to 1 ppm NO range.

\[
\begin{align*}
\text{Black RAE NO Reading (ppm)} &= 0.92 \times \text{NO Concentration (ppm)} \quad (2.1a) \\
\text{Blue RAE NO Reading (ppm)} &= 1.02 \times \text{NO Concentration (ppm)} \quad (2.1b) \\
\text{Orange RAE NO Reading (ppm)} &= 0.82 \times \text{NO Concentration (ppm)} \quad (2.1c) \\
\text{Red RAE NO Reading (ppm)} &= (0.97 \times \text{NO Concentration}) + 0.30 \text{ (ppm)} \quad (2.1d) \\
\text{Yellow RAE NO Reading (ppm)} &= 0.81 \times \text{NO Concentration (ppm)} \quad (2.1e)
\end{align*}
\]

Figure 2.3: Response of the NO and NO₂ sensors in the MultiRAEs to NO between 0 – 5 ppm
Equations 2.1f to 2.1j show the response parameters for each instrument when used in the 0 to 5 ppm NO range.

\[ \begin{align*}
\text{Black RAE NO Reading (ppm)} &= 1.03 \times \text{NO Concentration (ppm)} \quad (2.1f) \\
\text{Blue RAE NO Reading (ppm)} &= 1.00 \times \text{NO Concentration (ppm)} \quad (2.1g) \\
\text{Orange RAE NO Reading (ppm)} &= 1.04 \times \text{NO Concentration (ppm)} \quad (2.1h) \\
\text{Red RAE NO Reading (ppm)} &= (0.94 \times \text{NO Concentration}) + 0.34 \quad (2.1i) \\
\text{Yellow RAE NO Reading (ppm)} &= 1.02 \times \text{NO Concentration (ppm)} \quad (2.1j)
\end{align*} \]

The logged concentration detected in real time fluctuated by \( \pm 0.2 \) ppm about the average. The concentration shown on instrument display showed only the integer value of NO, the decimal place being truncated.

All of the NO sensors are just within acceptable uncertainty, showing \( \pm 0.2 \) ppm of the set concentrations, except for the NO sensor in the Red MultiRAE, which displays an offset of \( \pm 0.3 \) ppm at lower concentrations, becoming comparable to the other sensor readings as the concentration increases. This suggested that the instrument did not zero properly at the outset of the procedure.

The sensitivity of all of the NO\(_2\) sensors shows no dependence on the NO exposure level, and is an acceptable background level of less than 0.1 ppm (<10% of full scale) for all but the red MultiRAE, which remains around 0.5 ppm (10% - 50% of full scale).

Further investigation showed the offset to be corrected and the NO characteristic and NO\(_2\) cross sensitivity acceptable when the red MultiRAE was re-zeroed before use in later parts of this investigation.

**2.2.2 MultiRAE response & cross sensitivity to NO\(_2\)**

Exposing the instrument to NO\(_2\) allowed the response of the NO\(_2\) sensor and the cross sensitivity of the NO sensor to NO\(_2\) to be determined simultaneously. Fig. 2.4 (0 – 1 ppm) and Fig. 2.5 (0 – 5 ppm) show the response of the NO\(_2\) sensors and the sensitivity of the NO sensors in each of the MultiRAE Monitors upon exposure to the various concentrations of NO\(_2\).
Equations 2.2a to 2.2e show the response parameters for each instrument when used in the 0 to 1 ppm NO₂ range.

\[
\text{Black RAE NO}_2 \text{ Reading (ppm)} = 0.86 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.2a)
\]
\[
\text{Blue RAE NO}_2 \text{ Reading (ppm)} = 0.94 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.2b)
\]
\[
\text{Orange RAE NO}_2 \text{ Reading (ppm)} = 1.01 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.2c)
\]
\[
\text{Red RAE NO}_2 \text{ Reading (ppm)} = 0.98 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.2d)
\]
\[
\text{Yellow RAE NO}_2 \text{ Reading (ppm)} = 1.06 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.2e)
\]
Equations 2.2f to 2.2j show the response parameters for each instrument when used in the 0 to 5 ppm NO$_2$ range.

\[
\text{Black RAE NO}_2 \text{ Reading (ppm)} = 1.01 \times \text{NO}_2 \text{ Concentration (ppm)} \quad (2.2f)
\]
\[
\text{Blue RAE NO}_2 \text{ Reading (ppm)} = 1.08 \times \text{NO}_2 \text{ Concentration (ppm)} \quad (2.2g)
\]
\[
\text{Orange RAE NO}_2 \text{ Reading (ppm)} = 1.07 \times \text{NO}_2 \text{ Concentration (ppm)} \quad (2.2h)
\]
\[
\text{Red RAE NO}_2 \text{ Reading (ppm)} = 1.00 \times \text{NO}_2 \text{ Concentration (ppm)} \quad (2.2i)
\]
\[
\text{Yellow RAE NO}_2 \text{ Reading (ppm)} = 1.04 \times \text{NO}_2 \text{ Concentration (ppm)} \quad (2.2j)
\]

The logged concentration detected in real time again fluctuated by ~!0.2 ppm about the average. The concentration shown on instrument display fluctuated by ~!0.1 ppm about the average logged value.

All of the NO$_2$ sensors are just within acceptable resolution, showing ! 0.2 ppm of the set concentrations.

The sensitivity of all of the NO sensors shows some dependence on the NO$_2$ exposure level, ranging between 7% to 24% of the NO$_2$ set concentration, mainly for exposures above 1 ppm NO$_2$.

The characteristics of the MultiRAEs for both NO and NO$_2$ can be seen to be linear over the full range of concentrations of NO and NO$_2$, and the resolution (~0.2 ppm) just within the tolerances required for use in further tests in this investigation.

2.3 CROWCON TRIPLE PLUS + NO & NO$_2$ MONITOR CHARACTERISATION

Alphasense and City Technology each sent 2 samples of NO and NO$_2$ sensors to HSL for characterisation at concentrations around and below 1 ppm. The sensors were installed by Crowcon into modified versions of their existing Triple Plus instruments, to facilitate signal processing and datalogging of the sensor outputs. The Alphasense sensors were installed in Crowcon Triple Plus instruments, serial numbers 2560023691 (denoted instrument C1) and 2560023692 (C2), and the City sensors were installed in Crowcon Triple Plus instruments, serial numbers 2560023693 (C3) and 2560023694 (C4). See Appendix (Section 8.4.1) for sensor data sheets and brief explanations of sensor operation.

Initial inspection of the display panels on each these instruments showed a resolution of 0.1 ppm for the NO readings, but only 1 ppm for the NO$_2$ readings. Enquiries to Crowcon revealed the option of changing the resolution for NO$_2$ to 0.1 ppm via the dedicated software provided. None of the instruments would calibrate using the original multi-sensor calibration mask supplied. After consultation with Crowcon a single sensor mask, used in factory calibrations was despatched, which allowed successful calibration of all but one of the sensors. Throughout the calibration procedure the gas was fed into the calibration mask at the recommended flow rate of 500 ml/min via an external pump.

The sensors were characterised over 2 ranges of exposure of NO and NO$_2$, 0 - 1 ppm (in 0.1 ppm steps) and 0 - 5 ppm (in 1 ppm steps).

2.3.1 Crowcon Triple Plus response & cross sensitivity to NO

Figures 2.6 (0 – 1 ppm) and 2.7 (0 – 5 ppm) show the response of the NO sensor in each Crowcon Triple Plus instrument upon exposure to the various concentrations of NO.
Equations 2.3a to 2.3d show the response parameters for each instrument when used in the 0 to 5 ppm NO range.

\[ C1 \text{ Instrument NO Reading (ppm)} = 1.13 \times \text{NO Concentration (ppm)} \]  
\[ C2 \text{ Instrument NO Reading (ppm)} = (0.97 \times \text{NO Concentration}) + 0.51 \text{ (ppm)} \]  
\[ C3 \text{ Instrument NO Reading (ppm)} = 1.09 \times \text{NO Concentration (ppm)} \]  
\[ C4 \text{ Instrument NO Reading (ppm)} = 0.97 \times \text{NO Concentration (ppm)} \]

The logged concentration detected in real time generally fluctuated by ~ 0.5 ppm about the average in both ranges.

The NO characteristics of the Crowcon Triple Plus can be seen to be linear over the 0 to 5 ppm range, but the accuracy over the 0 to 1 ppm range is outside the tolerances required for use in further tests in this study.

Further tests in clean air showed the zero level of the Alphasense NO sensor could drift by ~1 ppm; and the zero level of the City NO sensors could drift by ~0.5 ppm.
2.3.2 Crowcon Triple Plus response & cross sensitivity to NO₂

Figures 2.8 (0 – 1 ppm) and 2.9 (0 – 5 ppm) show the response of 3 of 4 the NO₂ sensors C1, C3 and C4 (both of the City sensors and one of the Alphasense sensors), upon exposure to the concentrations of NO₂. The other Alphasense sensor, C2, would not calibrate to 5 ppm NO₂ and could therefore not be characterised.

![Figure 2.8: Response of the NO₂ sensors in the Crowcon Triple Plus to NO between 0 – 1 ppm](image)

Equations 2.4a to 2.4c show the response parameters for each instrument when used in the 0 to 1 ppm NO₂ range.

\[
\begin{align*}
C1 \text{ Instrument NO}_2 \text{ Reading (ppm)} &= 0.86 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.4a) \\
C3 \text{ Instrument NO}_2 \text{ Reading (ppm)} &= 0.86 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.4b) \\
C4 \text{ Instrument NO}_2 \text{ Reading (ppm)} &= 0.86 \times \text{ NO}_2 \text{ Concentration (ppm)} \quad (2.4c)
\end{align*}
\]
Equations 2.4d to 2.4f show the response parameters for each instrument when used in the 0 to 5 ppm NO\textsubscript{2} range.

\begin{align*}
C1 \text{ Instrument } NO\textsubscript{2} \text{ Reading (ppm)} &= 0.98 \times NO\textsubscript{2} \text{ Concentration (ppm)} \quad (2.4d) \\
C3 \text{ Instrument } NO\textsubscript{2} \text{ Reading (ppm)} &= 1.01 \times NO\textsubscript{2} \text{ Concentration (ppm)} \quad (2.4e) \\
C4 \text{ Instrument } NO\textsubscript{2} \text{ Reading (ppm)} &= 1.00 \times NO\textsubscript{2} \text{ Concentration (ppm)} \quad (2.4f)
\end{align*}

The signal noise was found to be generally within the display resolution, and on the few instances where significant noise was present, the signal variation was within ±0.1 ppm of the average.

The NO\textsubscript{2} characteristic of the Crowcon Triple Plus can be seen to be to be linear over the full range, and the resolution (0.1 ppm) within the tolerances required for use in further tests in this investigation.

Further tests in clean air showed the zero level of the Alphasense NO\textsubscript{2} sensor was consistent within ±0.1 ppm; and the zero level of the City NO\textsubscript{2} sensors could drift by ±0.5 ppm.

The NO\textsubscript{2} readings observed on the instrument display panel and the datalogger readings are identical for this instrument in both the 0 – 1 ppm and 0 – 5 ppm ranges, the instrument display panel reading being virtually constant at each setting.

### 2.4 2B TECHNOLOGIES NO MONITOR CHARACTERISATION

The 2B Technologies NO Monitor was characterised over a range of NO concentrations from 0 to 2 ppm in steps of 0.1 ppm and NO\textsubscript{2} concentrations from 0 to 4.5 ppm. See Appendix (Section 8.4.2) for instrument data sheet and brief explanation of sensor operation. This instrument is calibrated by entering the slope and intercept of a straight-line graph, constructed from the averaged readings taken at each setting, into the instrument configuration.
2.4.1 2B Technologies NO Monitor response to NO

Figure 2.10 shows the response to NO and the sensitivity to NO₂ of the 2B Technologies NO Monitor.

![Graph showing response to NO and NO₂](image)

**Figure 2.10: Response of the 2B Technologies NO Monitor to NO and NO₂**

Equation 2.5a shows the calibration factor determined from these readings.

\[
\text{Instrument NO Reading (ppm)} = 0.94 \times \text{NO Concentration (ppm)} \quad (2.5a)
\]

Equation 2.5b shows the effect of NO₂ on the NO sensor to be negligible (~2%) over the range.

\[
\text{Instrument NO Reading (ppm)} = 0.02 \times \text{NO₂ Concentration (ppm)} \quad (2.5b)
\]

In both cases the logged concentration detected in real time fluctuated by ~ 0.02 ppm about the average.

The readings observed on the instrument display panel and the data log readings were found to be identical for this instrument.

The NO characteristic of the 2B Technologies NO Monitor can be seen to be linear over the full range of concentrations of NO, and the resolution is well within the tolerances required (~0.1 ppm) for use in further tests in this investigation.

2.5 API M200A NOₓ ANALYSER CHARACTERISATION

As the Teledyne-API M200A NOₓ Analyser is used in UK air quality network measurements, this instrument was used as the reference analyser as stated in the Appendix (Section 8.2). It measures NO, NO₂ and their sum - NOₓ.

The operational characteristics of the M200A NOₓ Analyser require that the instrument is only calibrated to NO, as the NO₂ detection facility uses the same sensor to determine NO₂ concentrations. See Appendix (Section 8.4.3) for instrument data sheet and brief explanation of sensor operation.
2.5.1  M200A NO\textsubscript{x} Analyser response & cross sensitivity to NO

The M200A NO\textsubscript{x} Analyser was characterised for NO over a range of concentrations from 0 - 5 ppm.

Figure 2.11 shows the response of the M200A NO\textsubscript{x} Analyser upon exposure to the various concentrations of NO during the NO sensing period, and the sensitivity of the instrument to NO during the NO\textsubscript{2} sensing period, as the instrument runs through its sensing cycle.

![Graph showing response of M200A NO\textsubscript{x} Analyser to NO](image)

Equation 2.6a shows the response parameters of the instrument over the range of concentrations of NO during the NO sensing mode. Equation 2.6b shows the sensitivity of the instrument to NO during the NO\textsubscript{2} sensing period to be negligible (~3%) over the range

\[ \text{Instrument NO Reading (ppm)} = 0.99 \times \text{NO Concentration (ppm)} \]  
\[ \text{Instrument NO\textsubscript{2} Reading (ppm)} = 0.03 \times \text{NO Concentration (ppm)} \]  

2.5.2  M200A NO\textsubscript{x} Analyser response & Cross Sensitivity to NO\textsubscript{2}

The M200A NO\textsubscript{x} Analyser was also characterised for NO\textsubscript{2} over a range of concentrations from 0 – 4.5 ppm. Figure 2.12 shows the response of the M200A NO\textsubscript{x} Analyser upon exposure to the various concentrations of NO\textsubscript{2} during the NO\textsubscript{2} sensing period, and the sensitivity of the instrument to NO\textsubscript{2} during the NO sensing period, as the instrument runs through its sensing cycle.
Equation 2.7a shows the response parameters of the instrument over the range of concentrations of NO₂ during the NO₂ sensing mode. Equation 2.7b shows the sensitivity of the instrument to NO₂ during the NO sensing period to be negligible (~1%) over the range

\[
\text{Instrument NO}_2 \text{ Reading (ppm)} = 1.00 \times \text{Set NO Concentration (ppm)} \quad (2.7a)
\]

\[
\text{Instrument NO Reading (ppm)} = 0.01 \times \text{Set NO}_2 \text{ Concentration (ppm)} \quad (2.7b)
\]

Throughout the exposure to both NO and NO₂ the signal noise was found to be generally within the display resolution, and on the few instances where significant noise was present, the signal variation was within ±0.1 ppm of the average

The readings observed on the instrument display panel and the data log readings were found to be identical for this instrument.

The characteristic of the M200A NO₃ Analyser can be seen to be linear over the full range of concentrations of NO and NO₂, and the resolution well within the tolerances required for use in further tests in this investigation.
This phase of the investigation was designed to investigate the environmental fate of NO via oxidation to NO$_2$ by oxygen (O$_2$) in the air, under laboratory conditions.

These investigations were performed in a purposely-designed air-tight and vacuum-tight glass vessel with an internal volume of 12 L (QVF Process Systems Ltd.), a photograph of which is shown in Figure 3.1 and a schematic of which can be seen in Figure 3.2.

Due to its performance in the previous part of the investigation and its compact portable design, one of the MultiRAEs (black) was selected as the instrument to measure the concentrations of...
NO and NO₂ inside the vessel during the following tests. The instrument was calibrated to the relevant concentrations of NO and NO₂ before each stage of these tests. A fan was placed inside the vessel in all of the following tests to aid mixing of the NO, NO₂, N₂ and air fed into the vessel.

The gas concentrations used in the following tests were achieved using Alpha Volumetric, Spectra Seal, Size AV cylinders with certificates of Analysis listed in the Appendix (Section 8.3), laboratory air supply, laboratory N₂ supply, and calibrated Mass Flow Controllers (MFCs) of the relevant ranges. The more complex configuration of the MFCs throughout this section of the investigation resulted in a less precise mixture of the gases than would normally be expected in a simpler configuration, hence concentrations of NO and NO₂ detected in the vessel may differ slightly from the nominal set values. This will not affect the validity of the relative changes in concentration observed in this section.

3.1 FACTORS INFLUENCING NO AND NO₂ CONCENTRATIONS IN VESSEL

Electrochemical sensors are effectively fuel cells which results in the conversion of a small fraction of the target sample, by oxidation (NO) or reduction (NO₂), into different chemical compounds and thus consume that fraction of the sample (unlike physical sensors e.g. infra-red which do not). One of the products of the chemical reaction of the NO₂ sensor is NO, as shown in the Appendix (Section 8.4.1). The NO concentration is therefore reduced due to the operation of the NO sensor, while the NO concentration is increased and the NO₂ concentration reduced due to the operation of the NO₂ sensor.

The NO cylinders used in this part of investigation include small concentrations of NO₂ as shown in Appendix (Section 8.3), the 25.4 ppm cylinder (diluted to 10 ppm NO in N₂) includes 0.1 ppm NO₂, the 1040 ppm cylinder (diluted to 50 ppm NO in N₂ and 100 ppm NO in N₂) includes 3 ppm NO₂.

NO and, particularly, NO₂ are also known to adsorb onto surfaces which may reduce the concentrations of each in the vessel.

In the closed system utilised in this part of the investigation it is therefore necessary to investigate the extent of these effects on the NO and NO₂ concentrations in the vessel, before the actual investigation into NO oxidation.

3.1.1 Changes in NO Concentration due to operation of NO sensor

The black MultiRAE was placed inside the vessel and a nominal concentration of 5 ppm (actual concentration measured at 5.8 ppm) of NO in pure nitrogen (N₂) was made to flow through the vessel (with the valves open) until all of the air was replaced, (O₂ concentration seen to drop to 0% on instrument display and NO concentration constant). The valves were then closed and the NO, NO₂ and O₂ concentrations logged over time and shown in Figure 3.3. The inset shows the reduction of NO with time after the valves were closed.
Figure 3.3: Conversion of NO in vessel (nominal concentration 5 ppm NO in N₂)

The NO concentration had been observed at a steady 5 ppm on the instrument display for ~30 minutes before the valves were closed, but, as stated in the previous section, only integer values are displayed, hence the increase in NO concentration from 5.0 ppm to 5.3 ppm before closing the valves was not evident, however, all of the air must have been replaced by this mixture as the concentration O₂ can be seen to have reduced to 0%. The increase in NO concentration from 5.3 ppm to 5.8 ppm after closing the valves suggests that the NO and N₂ were not uniformly mixed in the cylinder at the time of sealing.

The NO concentration in the vessel can be seen to have reduced from a maximum level of 5.8 ppm by 0.8 ppm (~14%) to 5 ppm in approximately 12 hours. This reduction may be due in part to the following effects:

1. the NO and N₂ mixture in the vessel becoming more homogeneous
2. adsorption of the NO onto the instrument and vessel surfaces
3. oxidation of NO by the chemical reaction in the sensor itself (see Appendix, Section 8.4.1)

As the detected level of NO₂ was found to be 0.0 – 0.1 ppm throughout the duration of the test then oxidation by trace O₂ (in any air which may not have been fully purged from the vessel) is unlikely.

The rate of reduction in NO concentration slowly reduces with time suggesting that any adsorption of the NO onto the instrument and vessel surfaces and the oxidation of NO by the chemical reaction of the sensor itself are not major factors.

3.1.2 Changes in NO₂ and NO Concentration due to operation of NO₂ sensor

The black MultiRAE was placed inside the vessel and a nominal concentration of 5 ppm (actual concentration measured at 4.9 ppm) of NO₂ in air was made to flow through the vessel (with the valves open) until the NO₂ concentration on the instrument display remained constant. The valves were then closed and the NO₂, NO and O₂ concentrations logged over time and shown in
Figure 3.4. The inset shows the reduction of NO and NO₂ with time after the valves were closed. The O₂ concentration remained at 20.9% throughout this test.

The NO concentration in the vessel can be seen to increase to 2 ppm as the NO₂ concentration increases to 4.9 ppm during the introduction of the NO₂/air mixture. As there was no NO in the mixture or the vessel, this may be due to the reaction of the NO₂ sensor converting NO₂ to NO during the sensing process, (for every molecule of NO₂ reduced, one molecule of NO is produced). As all sensors in the instrument are located in a confined area and fed via the same pumped route, the NO sensor could be exposed to a significant fraction of this converted NO.

The NO₂ concentration in the vessel can be seen to have reduced from a maximum level of 4.9 ppm by 4.4 ppm (~90%) to 0.5 ppm in approximately 12 hours, and by a further 0.3 ppm (6%) to 0.2 ppm in a total of ~20 hours. This reduction may be due in part to the following effects:

1. the NO₂ and air mixture in the vessel becoming more homogeneous
2. adsorption of the NO₂ onto the instrument and vessel surfaces
3. reduction of NO₂ by the chemical reaction in the sensor itself

The NO concentration in the vessel can be seen to have reduced from a maximum level of 1.9 ppm by 1.4 ppm (~90%) to 0.5 ppm in approximately 12 hours, and by a further 0.1 ppm (5%) to 0.4 ppm in a total of ~20 hours. This reduction may be due in part to the following effects:

1. the NO and air mixture in the vessel becoming more homogeneous
2. adsorption of the NO onto the instrument and vessel surfaces
3. conversion of NO to NO₂ by oxidation with O₂ in the air. The resolution of the O₂ sensor of 0.1% (1000 ppm) is insufficient to show any resulting reduction in O₂ in the vessel due to this effect.

The fact that rate of reduction in NO₂ and NO concentration reduces with time and seems to be tending towards a constant value suggests that the adsorption of the NO₂ and NO to the instrument and vessel surfaces is reaching equilibrium.
This experiment was performed again using a nominal concentration of 40 ppm NO\(_2\) in air to observe the effect of a higher concentration on the reduction rate and repeated to confirm the repeatability of the setup. Figure 3.5 shows the change in NO\(_2\) concentration after the vessel had been filled with 40 ppm NO\(_2\) in air and the valves closed. The inset shows the corresponding changes in NO concentration due to generation by the NO\(_2\) sensor (by reduction of NO\(_2\)).

![Figure 3.5: Conversion of NO\(_2\) in vessel (nominal concentration 40 ppm NO\(_2\) in air)](image)

The fractional changes in NO\(_2\) concentration using the nominal concentration of 40 ppm and 5 ppm are comparable. The NO\(_2\) concentration in the vessel can be seen to have reduced by ~90% in approximately 12 hours, and by a further ~6% in a total of ~20 hours. However, the fractional changes in NO concentration using the nominal concentration of 40 ppm and 5 ppm are not comparable.

### 3.2 CONVERSION RATE MEASUREMENTS

#### 3.2.1 Theory

The derivation of the rate equations for oxidation of NO by O\(_2\) to NO\(_2\) is given in the Appendix (Section 8.5).

The time \(t\) taken for a certain fraction \(f\) of a given concentration of NO \((NO_i)\) to react with a given concentration O\(_2\) \((O_j)\) to become NO\(_2\) is described by Equation 3.1 (Tsukahara et al, 1999).

\[
 t = \frac{1}{2k(O_j)(NO_i)} \times \frac{f}{1 - f} \quad (3.1)
\]

where:  
- \(k\) = reaction rate constant = \(\frac{7300 \times 10^{-12}}{RT}\) (L\(^2\).mol\(^{-2}\).s\(^{-1}\))  
- \(R\) = ideal gas constant = 0.0821 (L.atm/mol.K)

![Table 3.1: Instrument Reading](image)
\[ T = \text{absolute ambient temperature (K)} \]

This equation can be manipulated to give Equation 3.2, the fraction \( f \) of a given concentration of NO \((NO_l)\) which will have reacted with a given concentration of O_2 \((O_l)\) to become NO_2 as a function of time \( t \),

\[
f = \frac{t [2k(O_l)(NO_l)]}{t [2k(O_l)(NO_i)] + 1} \tag{3.2}
\]

The concentration of NO as a function of time can therefore be modelled using Equation 3.3

\[
NO_{\text{converted}} = (1 - f) NO_l \tag{3.3}
\]

The reduction in the concentration of NO, and thus the increase in concentration of NO_2, as a function of time can be modelled using Equation 3.4

\[
NO_2_{\text{converted}} = f(NO_l) \tag{3.4}
\]

### 3.2.2 Experimental

The black MultiRAE was placed inside the vessel and a nominal concentrations of 10, 50 and 100 ppm of NO (in N_2) and 20.9% O_2 were made to flow through the vessel (with the valves open) until the NO concentration on the instrument display remained constant. The valves were then closed and the NO, NO_2 and O_2 concentrations logged over time. This procedure was performed at each of the concentrations, with and without the NO_2 sensor in the instrument to observe the effects of the NO_2 sensor operation on the NO concentrations in the vessel. As there were no significant effects evident (any effects of the NO_2 sensor operation on the NO concentration are less than the repeatability levels of the experimental set up), the procedure was performed twice more at each of three concentrations of NO with the NO_2 sensor in the instrument to observe NO_2 levels in the vessel and check the repeatability of the set up.

The change in concentration of NO and NO_2 with time determined experimentally with and without the NO_2 sensor in the instrument, and the ideal change modelled using Equations 3.3 and 3.4 (using the actual initial concentrations of NO not the nominal concentrations) are shown in Figures 3.6 to 3.8.
Figure 3.6: Change in concentration of NO and NO₂ with time, and the change modelled using Equations 3.3 and 3.4 using nominal concentration of 10 ppm NO

Figure 3.7: Change in concentration of NO and NO₂ with time, and the change modelled using Equations 3.3 and 3.4 using nominal concentration of 50 ppm NO

Figure 3.8: Change in concentration of NO and NO₂ with time, and the change modelled using Equations 3.3 and 3.4 using nominal concentration of 100 ppm NO
The reduction rate of NO determined experimentally is less than the modelled rate in all cases investigated except the second test for NO$_i$ = 10 ppm, which follows the modelled rate closely.

The three sets of experimentally determined results at each initial nominal NO concentration are reasonably consistent (except the second test for NO$_i$ = 10 ppm) allowing for the differences in the actual initial NO concentrations.

Results obtained in Section 3.1 suggest that the reduction rate of NO determined experimentally would be greater than the modelled rate due to the added reduction due to effects other than NO to NO$_2$ conversion.

Some NO to NO$_2$ conversion was detected in the vessel even as it was being filled with the respective NO$_i$ concentrations resulting in the NO$_2$ concentration being greater than 0 ppm (~0.5 ppm for NO$_i$ = 10 ppm, ~7 ppm for NO$_i$ = 50 ppm, ~20 ppm for NO$_i$ = 100 ppm) at the time that the valves were closed. This cannot accurately be allowed for in the modelled reduction rates. The existence of this NO$_2$ concentration at the outset of each observation may also have caused some reduction in the rate of NO to NO$_2$ conversion throughout each of the tests, although the kinetics (as discussed in the Appendix, Section 8.5) do not indicate a dependence of the NO oxidation rate on NO$_2$ concentration.

The rate of increase in NO$_2$ concentration tends to follow that of the modelled rate to some degree for around 30 minutes in all cases investigated, at which point the reduction due to effects observed in Section 3.1 become apparent. The maximum NO$_2$ concentrations reached increase with initial NO concentration (~3 ppm for NO$_i$ = 10 ppm, ~22 ppm for NO$_i$ = 50 ppm, ~42 ppm for NO$_i$ = 100 ppm).
4 TUNNEL TESTS

This phase of the investigation was designed to test the operational suitability of the instruments selected in Section 2 under site conditions, and to measure the environmental fate of NO and NO\textsubscript{2} as a function of time and distance from a suitable diesel source.

4.1 EXPERIMENTAL

4.1.1 Tunnel

The 366 m surface gallery at HSL, Buxton was chosen as a suitable location in which these tests could be performed in surroundings which are close to those in a real tunnel. The dimensions of the gallery are:

\[
\begin{align*}
\text{length (L)} & : 366 \text{ m} \\
\text{diameter (d)} & : \sim 2.55 \text{ m (cross section of gallery not totally circular)} \\
\text{cross sectional area (csa)} & : 5.6 \text{ m}^2
\end{align*}
\]

Integral controllable large fans (experimentally determined air speed partially controllable from \~0.5 m/s to \sim 2 m/s) allowed the air speed in the tunnel to simulate the air speed of the ventilation in a real tunnel situation. For an air speed of 1 m/s through the tunnel the flow rate of air would be 336 L/min.

4.1.2 Diesel Fume Source

The diesel generator (adjustable in speed and load settings) situated in close proximity to the gallery was used as the diesel source. The generator is a four stroke diesel engine with a compression ratio of 21:1, and a capacity of \~7 L. The four cylinders, each of \~1.74 L capacity, will generate a total of \~6.64 L of exhaust fume for every two revolutions (4 strokes) of the engine. See Appendix (Section 8.6) for calculation.

The fuel used was standard gas oil.

Garage exhaust ducting was purchased from PAR (Manchester) Ltd. (60 m of 127 mm diameter PGEX 1) to route the diesel exhaust fume from the generator into the gallery. The ducting is rated to 150° C and is stated as not being reactive to diesel fume.

4.1.3 Instrumentation

The 2B Technologies NO Monitor, the M200A NO\textsubscript{x} Analyser, and the five MultiRAE monitors selected in Section 2 were used in this phase of the investigation. To distinguish between decrease in NO concentration due to dispersion into the tunnel atmosphere and oxidation to NO\textsubscript{2}, the CO concentration (which does not react in the conditions in the gallery) was also monitored as a function of time and distance from the diesel source. The CO sensors were 3 Zellweger Impact instruments, serial numbers 10513955 (denoted red), 10513956 (blue) and 513579 (black).
4.2 PROCEDURE

The exhaust fume was routed from the diesel generator into the gallery via 60 m of exhaust ducting, the opening of the ducting being positioned diametrically central to the gallery, and 3 m in front of the tunnel’s integral fans, to reduce the effects of the initial turbulence in the air. The generator was allowed to ‘warm up’ for ~1 hour before the diesel fume was fed into the gallery. The air speed in the gallery was set to ~1.2 m/s (403.2 l/min) using the integral fans and monitored along the utilised length of the gallery using anemometers throughout all three tests. The fans were left on for ~15 minutes after the diesel fume supply was removed to allow the gallery to be purged before any personnel (wearing personal monitors) entered to retrieve the instruments.

Initial intentions to monitor the NO\textsubscript{x} and CO concentration changes along the length of the 60 m ducting before the diesel entered the gallery were aborted after the temperature of the fume inside the ducting was found to be greater than the upper operational temperature limit of the MultiRAE sensors (45°C).

Three tests were performed to investigate the operational suitability of the instruments under site conditions, and to measure the environmental fate of NO and NO\textsubscript{x} as a function of time and distance from the diesel source. All instruments were calibrated before each test, calibration checked after each test, and the relevant correction factors for each test determined.

The lowest setting of the diesel generator of ~920 rpm was used in the first two tests to observe the changes in NO, NO\textsubscript{x} and CO along the gallery at that setting, and to test the repeatability of the experimental set up. In the second of these tests the red MultiRAE was positioned directly in front of the ducting outlet to observe the level of the NO\textsubscript{x} concentration before contact with the air in the gallery. The moisture in the fume, however, caused the instrument to malfunction after ~15 minutes, and this position was therefore not monitored in further tests. The third test, at a generator speed setting of ~1500 rpm, allowed the effect of increased initial NO concentration to be observed and compared to those at the previous lower setting.

The locations of the sensing instruments in the gallery are shown in Figure 4.1, and the sensors positioned in each location in each test are listed in Table 4.1. The instruments were positioned to sample the fume concentration at a height of ~1.25 m and as close as possible to the diametric centre of the tunnel.

![Diagram of tunnel layout and sensor locations](image)

**Figure 4.1: Locations of sensors and position of ducting outlet in gallery**
Table 4.1: Instruments located at each sensor position in gallery in each test

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Instrument Positioned at Sensor Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Black MultiRAE</td>
</tr>
<tr>
<td>2</td>
<td>Red MultiRAE</td>
</tr>
<tr>
<td>3</td>
<td>Black MultiRAE</td>
</tr>
</tbody>
</table>

The M200A NO\textsubscript{x} Analyser and the 2B Technologies NO Monitor were positioned in sensor locations 4 and 5 respectively, where the concentration levels were expected to be lowest, to make the best use of their better accuracy and resolution. The black MultiRAE at sensor position 1a in the second test malfunctioned and recorded no useable data. The 2B Technologies NO Monitor at sensor position 5 in the third test recorded no data due to a problem with the data logging facility of the instrument.

4.3 RESULTS

Averages of the data at each generator setting and each location were calculated and the variations of the actual data about the average levels were taken as the uncertainty in the instrument data. Figures 4.2 to 4.5 show the concentrations of the relevant gases detected on the instruments (after application of the relevant correction factors) as a function of distance along the gallery from the opening of the exhaust ducting.
Figure 4.2: Concentration of NO at sensor locations 1a to 5 at generator speeds of ~920 rpm (Tests 1 & 2) and ~1500 rpm (Test 3). (Inset: Includes sensor location 1)

Figure 4.3: Concentration of NO₂ at sensor locations 1a to 5 at generator speeds of ~920 rpm (Tests 1 & 2) and ~1500 rpm (Test 3). (Inset: Includes sensor location 1)

Figure 4.4: Concentration of NOₓ at sensor locations 1a to 5 at generator speeds of ~920 rpm (Tests 1 & 2) and ~1500 rpm (Test 3). (Inset: Includes sensor location 1)
The NOx concentrations stated at each location are the sum of the NO and NO2 concentrations detected at that location (performed externally for MultiRAEs and internally for the M200A NOx Analyser).

As the results of the first 2 tests at the same generator speed of ~920 rpm are almost identical for each instrument at sensor locations 2 to 5 along the gallery, suggesting good repeatability of the set up, it is reasonable to assume that the concentrations of NO, NO2 and NOx at position 1a would also have been comparable, thus the concentrations of NO, NO2 and NOx detected in test 1 at this position have been assumed in test 2 and included in Figures 4.2 to 4.4.

The instruments all showed ~0.0 ppm of NO and NO2 after the diesel fume had been turned off and the gallery flushed with air from the fans.

The concentrations of NO, NO2 and NOx detected at sensor location 1 before the instrument malfunctioned (directly in front of the ducting outlet) are 148 ! 42 ppm, 43 ! 3 ppm and 191 ! 45 ppm respectively and are within the expected levels for standard gas oil at idling speed of 153 ppm, 48 ppm and 201 ppm shown in Appendix (Section 8.7) (Dabill et al, 2004) respectively.

The concentrations of NO, NO2 and NOx in test 3 are higher at each sensor location than in tests 1 and 2, but as only 2 different generator settings were investigated no correlation between generator setting and NO NO2 and NOx reduction was possible.

Assuming ideal mixing, the flow rate of the air from the integral fans of 403 x10^3 L/min should dilute the initial concentrations of the constituent gases of the diesel fume from the outlet of the ducting of 3154 L/min (tests 1 and 2, 950 rpm) and 4980 L/min (test 3. 1500 rpm) by 99.2% to 0.8% and by 98.8% to 1.2% of the initial concentration levels respectively. This agrees closely with the reductions in initial concentration levels of NO of 99.7% (148 ppm to 2.1 ppm), NO2 of 99% (43 ppm to 1.3 ppm) and NOx of 99% (191 ppm to 3.4 ppm) observed in test 2 between sensor location 1 (the outlet of the ducting) and sensor location 1a. The changes in concentrations are minimal at further increases in distance from the duct outlet, but do generally tend to reduce in all 3 tests.

The concentrations of CO detected at sensor location 1a (0.5 m) in the first 2 tests at the same generator speed of ~920 RPM (shown in Figure 4.5) are not comparable, and are higher than the concentration detected at the higher exhaust setting in test 3. None of these levels are

---

**Figure 4.5: Concentration of CO at sensor locations 1a to 5 at generator speeds of ~920 rpm (Tests 1 & 2) and ~1500 rpm (Test 3).**
comparable to documented levels for standard gas oil at idling speed of 187 ppm [6]. Inspection of the data logged on the instrument at this location shows the pump to be working intermittently, which may have caused erroneous readings. These readings must therefore be treated as suspect. The close proximity of the instrument to the duct outlet (0.5 m) and the integral fans (3.5 m) may have exposed it to higher levels of moisture and dust than it can operate in effectively. The zero level readings of the CO sensors positioned further along the gallery suggest that they may also be experiencing problems due to the atmospheric conditions in the gallery.
5 VENTILATION REVIEW

5.1 BACKGROUND

As a result of an agreement made between HSE and the Tunnelling Industry, the HSE issued an interim guidance note on occupational exposure to NO in a tunnel environment (HSE, 2006). This states that: “With the withdrawal of the EH40 OES for NO of 25 ppm … the COSHH Regulations become the controlling legislation for occupational exposure to NO. Therefore ALARP principles should be applied throughout scheme planning, design, construction, operation and maintenance phases to minimise risk of ill health from occupational exposure to NO”. This document also states that, although emphysema has been found in laboratory animals exposed to NO, it is not known if this occurs in humans exposed to NO.

A CHAN of 1 ppm (8-hr TWA) was set for NO. However, as the ratio for NO/NO\textsubscript{2} found in road tunnels is approximately 10:1, the effective limit for NO\textsubscript{2} is 0.1 ppm i.e. a reduction by a factor of 30. This reduction in the limit for NO\textsubscript{2} has caused considerable concern in the tunnelling industry that it will be difficult, if not impossible, to meet this requirement in some road tunnels with the existing infrastructure and traffic flows.

The problem of NO\textsubscript{x} emissions is complicated by the fact that oxidation of NO into NO\textsubscript{2} takes place. Some conversion takes place rapidly but is dependent on the NO concentration. The rate of NO conversion depends on many factors including oxygen and ozone levels, temperature, sunlight, humidity and the presence of other gases and particulates.

For those at work in road tunnels, the more common hazards include carbon monoxide, oxides of nitrogen, benzene, particulates and dust. Exposure to oxides of nitrogen commonly arises from diesel engine exhaust emissions and the use of explosives; these sources are found in the construction and operation of road tunnels. Road tunnel ventilation control systems have classically been designed on the dilution of CO to acceptable levels. For example, El-Fadel and Hashisho (2001) state that “Compliance with CO standards will typically ensure proper air quality inside a tunnel” and “Usually, the ventilation requirement is based on reducing carbon monoxide concentrations to safe levels, because this will typically ensure the dilution of other pollutants present in the tunnel atmosphere”. Airflows required for the dilution of CO were supposed to guarantee the dilution of other pollutants, including NO\textsubscript{2}. However recent regulations to reduce vehicle exhaust emissions have lead to a significant decrease in the amount of CO in exhaust gases. Measurements of vehicle emission factors (EFs) (the emitted mass of a compound per mile or kilometre) in the Tauern tunnel in Austria in 1988 and 1997 showed a decrease in the levels of CO and total VOCs by a factor of approximately 10 for light duty vehicles, LDVs (Schmid, 2001). Due to this decrease, control of ventilation based on CO measurements is no longer sufficient. (This decrease in emissions from LDVs was also found during eight measurements campaigns in the Gubrist tunnel between 1990 and 2002 by Steinemann and Zumsteg (2003).)

The problem is further complicated by the lack of industrial instruments that can reliably measure NO\textsubscript{2} at low-level concentrations. Although there are laboratory instruments that will measure NO\textsubscript{2} accurately, their costs, complexity and environmental needs would not make their use in a ventilation control system a practical proposition. Jacques and Possoz (2000) point out that accurate measurement of NO\textsubscript{2} concentrations in the range 0 – 0.5 ppm implies sophisticated techniques and that the equipment required is expensive and requires frequent maintenance as well as calibration checks.
5.2 TUNNEL VENTILATION

The minimum length of structure to be termed a tunnel appears to be in the range of 80 – 200 m (Day, 2005) although the EU Directive on minimum safety requirements for tunnels in the trans-European road network (EU, 2004) only applies to tunnels longer than 500 m. UK guidelines (BD78/99, 1999) defines a road tunnel as “a subsurface highway structure enclosed for a length of 150 m or more”.

The principle aims of a road tunnel ventilation system are:

- To supply sufficient fresh air to all parts of the tunnel to provide tunnel users with a hazard free environment i.e. vehicle exhaust pollutants are kept within prescribed limits whilst the comfort of users is kept at an acceptable level.
- To respond quickly and reliably to emergency situations e.g. equipment failure, accidents or fire in the tunnel.
- To discharge fume from the tunnel in such a way as to minimise its impact on the local community *.
- To keep air volume flow rates as low as possible in order to reduce plant and running costs.

Note that the last requirement may be in conflict with the previous three aims. In an emergency situation the ventilation objectives are quite different to those under normal operating conditions, and economic considerations are no longer the prime concern.

* For instance, the Massachusetts air pollution control regulations (El-Fadel and Hashisho, 2001) require that “prior to the construction of a major roadway tunnel ventilation system …. (it) must be certified that when operated it will not cause or exacerbate a violation of …. (the) 1-hour nitrogen dioxide policy level (0.17 ppm applicable to the second highest 1-hour concentration each year), when compared with the non-build alternative”.

5.2.1 Ventilation system types

El-Fadel and Hashisho (2001) state that “Decisions about the appropriate ventilation type to be installed is mainly based on the length of the tunnel, its configuration, and the cost of the ventilation system”. The types of ventilation systems in road tunnels can be natural, mechanical or a combination of both types. Mechanical ventilation systems can be in a variety of configurations and several factors need to be considered when selecting a system. The resulting system should be aerodynamically sound and satisfy the aims set out above. In addition to the natural and/or mechanical ventilation, the movement of vehicles can in itself induce an airflow through a tunnel. This is known as the “piston effect”. Naturally and mechanically ventilated tunnels with one-way traffic rely partly on traffic movement for ventilation.

The EU Directive does not require a mechanical ventilation system for tunnels shorter than 1000 m. However BD78/99 states that “in many short one-way tunnels, up to 300 m in length, the “piston effect” of vehicle-induced air flow will provide satisfactory natural ventilation for normal environmental needs ….. For tunnels between 300 to 400 m in length, mechanical ventilation plant will need to be considered with respect to fire control ….. Mechanical ventilation is required for all longer (400 m and above) tunnels and for 200 m and above tunnels on steep gradients or those subject to frequent congestion ….” Similar guidance is not given for tunnels with bi-directional traffic except that “for shorter tunnels, with two-way traffic, longitudinal ventilation could be from portal to portal ….”

In the United States, the National Fire Protection Association Standard NFPA 502 states that if a tunnel is longer than 244 metres (800 feet), emergency ventilation is required.
It is important for tunnels to be as aerodynamically efficient as possible. For a given size of tunnel, the piston effect can be maximised by making the tunnel interior aerodynamically smooth e.g. smooth interior surface, avoid sudden changes in cross-section.

5.2.1.1 Natural ventilation

Natural ventilation is used in tunnels less than about 300 m in length where pollutants are not expected to accumulate. Natural ventilation through a road tunnel is made up of the piston effect induced by moving vehicles together with the draught due to pressure differences arising from metrological conditions such as wind forces and temperature differences. When these forces are greater than the drag due to the roughness of the tunnel surface and to the vehicles within the tunnel, air movement will occur. Because of the uncertainty of natural ventilation (especially because of weather conditions), natural ventilation cannot be relied upon completely to prevent the build-up of fumes within a tunnel. Also, in the event of a fire, there will be no control of smoke etc. from the fire. However, for short tunnels it is more than adequate to dilute vehicle emissions and give an acceptable air quality during normal operating conditions. In unusual traffic conditions (e.g. congestion) ceiling-mounted jet fans, blowing in the same direction as the traffic flow, would be required (Berner and Day, 1991).

Note: a) that the air exchange rate will increase with vehicle speed thereby resulting in a decrease in pollutant levels and b) that in tunnels with two way traffic, that flows induced by the opposing vehicle movement will tend to cancel each other, even to the extent that the piston effect can be negligible. Opposing traffic flows should therefore be separated.

5.2.1.2 Mechanical ventilation

There are several different types of mechanical ventilation, the traditional ones being longitudinal, transverse and semi-transverse ventilation.

Longitudinal ventilation

The simplest system is longitudinal ventilation of which there are a number of variants. It is typically used for tunnels less than about 600 m in length (Chang and Rudy, 1990). Large axial fans move the air along the tunnel assisted by jet (impulse) fans installed at intervals along the roof of the tunnel. These fans enhance the natural airflow through the tunnel. Longitudinal ventilation has economic advantages when used in unidirectional tunnels because of the vehicle-induced flow. The major constraints on longitudinal ventilation systems are the excessive air volumes and velocities. As with natural ventilation, the degree of pollution increases with distance along the tunnel and is greatest at the discharge position. Longer tunnels can be split into separate ventilation sections with discharge and inlet shafts at each junction. This will reduce the build-up of pollutant concentration along the tunnel and will also keep the frictional pressure losses (which increase with tunnel length) to a manageable level. Longitudinal ventilation is not only the simplest form of mechanical ventilation but also has (relatively) low capital and running costs.

Transverse ventilation

In transverse (cross) ventilation systems, fresh air is introduced and extracted uniformly along the length of the tunnel via separated distribution and collection ducts. The system can be classified as lateral, upward or downward transverse. In the lateral type, air is supplied on one side of the tunnel and extracted on the opposite side. In the upward type, air is supplied at a low level and extracted at a high one; in the downward type, the converse is the case. A transverse ventilation system has the advantage that, as air is supplied and extracted along the length of the tunnel, contaminant levels do not build up along the tunnel. It is thus suitable for long tunnels.
(longer than about 1500 m). It also offers the advantage that, in the event of a fire, “fumes can be extracted from the traffic area with an intensive suction system up to several hundred metres from the fire, especially if the extraction vents are such that the hot fumes trigger an opening mechanism which enlarges them. It is thus clear that the extraction vents must be in the roof of the tunnel” (Anon. 1980). Note that the latter “requirement” is not general as it is only satisfied by upward ventilation, but this is quite a common arrangement.

**Semi-transverse ventilation**

In the fully transverse system, fresh air is supplied through ports commonly located throughout the tunnel at floor level whilst the vitiated air is extracted at similarly spaced ports at ceiling level. In the semi-transverse system, air is either supplied or extracted along the length of the tunnel. In the supply case, clean air is introduce on one side, at the roof or at the floor of the tunnel over its entire length whilst vitiated air is exhausted through the tunnel itself or through a small number of portals. Pollutant concentrations will reach maximum values at the exit ports. In the extract case, the converse airflow is used. Whilst more expensive than longitudinal ventilation, it is less costly than the fully transverse system. In general the semi-transverse system is used in tunnels less than 1500 m in length. This type of system is used, for example, in the L.-H.-La Fontaine road tunnel in Montreal (Kashef et al, 2005). The tunnel consists of two tubes separated by a central section with galleries which are used to supply air along the tunnel length through side openings at high and low levels. These galleries can also be used as evacuation routes. Air is extracted at 4 local points in each tube.

**Discharge from tunnels**

The discharge of polluted air extracted from tunnels has an air quality impact on surrounding developments and must be carefully assessed. Kwa (2004) address this aspect of tunnel design in the Kallang/Paya Lebar Expressway due to open in Singapore in 2007. A simple computer model of the dispersion of pollutant from a road tunnel portal has been developed by Oettl et al (2002). (See also reference to Massachusetts air pollution control regulations in Section 5.2.)

### 5.2.2 Tunnels under construction

Jenny (1982) gives the supply of fresh air during the construction of tunnels as “not less than 200 cfm/employee and the velocity should be at least 30 feet per minute where conditions can produce harmful dusts or gases”.

Large amounts of dust and fume are liberated during the construction phase of underground tunnels. Oxides of nitrogen are produced by diesel-powered machinery as well as during blasting. Personal exposure data have been reported in only a few studies and several authors have stressed the need for more information on exposure levels related to job tasks. Bakke et al (2001) reported maximum peak values of NO₂ levels for a 2-minute averaging period of 0.1 to 20 ppm for drill and blast crews. The high peaks were due to workers passing through blasting fumes during the transportation of blasted rock out of the tunnel.

The Guidelines for Tunnel Safety published for the ITA/AITES 1991 London Congress (Lock, 1991) states that the quantity of air supplied or exhausted from a tunnel face shall be such that the average flow in the full cross-section of the tunnel or shaft shall exceed 10 m³/min but be not more than 45 m³/min at all times. Minimum quantities of air for personnel to be 3 m³/min/man, 1 m³/min/kW for the electric machines and 6 m³/min/kW for diesel machines.
5.3 AIR QUALITY

Early tunnels such as the Rotherhide and Blackwall tunnels under the Thames were built for the horse and cart or mixed traffic which had only a small percentage of vehicles driven by internal combustion engines. Subsequently removal of smoke/fume became a main factor governing ventilation design. Following the standards adopted for the Clyde Tunnel in 1963 (Jones, 1981), the general British practice was that the CO concentration should not exceed 250 ppm. With a mix of petrol and diesel engines, visibility is usually unacceptable at this level and, in normal running, it is rare for the CO concentration to exceed about 100 – 150 ppm (Jones, 1981). Jones further noted that the HSE recommended an exposure limit of 50 ppm for CO and that “much higher levels are acceptable for the shorter periods (cf. 8 hour day) needed to drive through a tunnel”.

5.3.1 Tunnels

Although the exposure time inside tunnels is typically short, this can be outweighed by elevated concentration levels of the pollutants. However this may not always be the case especially in urban tunnels at peak traffic times when not only can the transit time be considerably lengthened, but also vehicle emission rates may rise. The concentration of pollutants in tunnels depends on several factors: tunnel characteristics (e.g. gradients, ventilation type, air quantity), vehicle related factors (e.g. vehicle mix, engine type, age) operating conditions (e.g. traffic speed, stop/go, temperature, tunnel maintenance). CO emissions can increase or decrease by 40 – 50% on up/down gradients (Pierson et al (1983), Sagebiel et al (1996)); higher emission are associated with heavy vehicles such as buses and trucks (Faiz et al, 1996); diesel engines can emit high concentrations of NOx; deceleration/acceleration of traffic under stop/start conditions can cause a 5 – 10 fold change in emission rates (Faiz et al, 1996); emission factors decrease with vehicle speed up to a certain speed and then increase again.

Non-uniformities are found in concentration measurements along and across tunnels. Rotzer and Riesing (1985) found that SF6 concentrations became uniform across a tunnel at 106 hydraulic diameters whilst at 53 diameters it varied by a factor of more than 2 at an airspeed of 6.5 m/s.

5.3.2 Roads

A report on the WHO web site (www.euro.who.int) states that the hourly average NO2 concentrations near very busy roads often exceeds 940 µg/m³ (0.5 ppm). “Maximum hourly concentrations in the United Kingdom are generally of the order of 470 – 750 µg/m³ (0.25 – 0.4 ppm)” (AGMAAPE, 1993)

5.4 NOX IN TUNNELS

PIARC (2000) says: “Results of studies where people have been exposed to NO2 have demonstrated that this gas can effect healthy people as well as sensitive people. But sensitivity levels are very different. For healthy people effects have been noted for levels higher than 4,000 µg/m³; no effects have been observed for levels under 2,000 µg/m³. For sensitive people, effects have been observed for concentrations exceeding 190 µg/m³. Noting this difference, it is important to appreciate the effects of NO2 on sensitive people”. People most sensitive to NO2 are those who suffer from asthma. Asthma is a global problem which is increasing world-wide. (Note: for NO2 1 ppp = 1,880 µg/m³).

Marsault (in PIARC, 2000) notes that NO2 accounts for a very low percentage of NOx in tunnels (less than 10%) and that direct measurement is difficult to perform in tunnels. Continuous reading of NO could allow NO2 concentrations to be deduced by applying a coefficient determined from the NO2/NOx ratios measured in tunnels. A 10% NO2/NOx ratio can be
considered an upper value and consequently a safe value for the design of ventilation systems according to NO\textsubscript{x} emission levels. Comparison of results from measurements of NO\textsubscript{2} made in various tunnels is difficult as the experimental conditions and presentation of results differ significantly from one study to another. Marsault excludes results from a number of studies on various grounds: old results and basic data missing, results given in NO\textsubscript{x} only, data gathered over a very limited time period and not enough data available on the site and the measurement conditions. Table 5.1 summarises these data.

<table>
<thead>
<tr>
<th>Experimental Site</th>
<th>Maximum concentration (ppb)</th>
<th>Average concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonderledstunnel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1\textsuperscript{st} test 1993</td>
<td>273</td>
<td>103</td>
</tr>
<tr>
<td>2\textsuperscript{nd} test 1996</td>
<td>256</td>
<td>80</td>
</tr>
<tr>
<td>Tingstadstunnel</td>
<td>413</td>
<td>52</td>
</tr>
<tr>
<td>Gnistangstunnel</td>
<td>708</td>
<td>47</td>
</tr>
<tr>
<td>Ambroise Pare Tunnel</td>
<td>181 (153)</td>
<td>63</td>
</tr>
<tr>
<td>Saint-Cloud Tunnel</td>
<td>452 (365)</td>
<td>81</td>
</tr>
<tr>
<td>Croix-Rousse Tunnel</td>
<td>590 (562)</td>
<td>290</td>
</tr>
<tr>
<td>Mont-Blanc Tunnel</td>
<td>1280 (1070)</td>
<td>500</td>
</tr>
</tbody>
</table>

The maximum levels are given in mean values over 10 – 15 minutes during a number of hours (shown in parenthesis). The Croix-Rousse Tunnel and the Mont-Blanc Tunnel are both two-way tunnels and have the highest average concentration levels. The Saint-Cloud Tunnel has two four-lane tubes with longitudinal ventilation. The Ambroise Pare Tunnel has two three-lane tubes with semi-transverse ventilation.

In a paper on the influence of decreasing vehicle exhaust emissions on the standards for ventilation systems for urban road tunnels, Meyeroltmanns (1991) notes that soot and CO are decisive factors for dimensioning and operating future road ventilation systems but states that “Nitrogen oxides (NO, NO\textsubscript{x}) are then relevant only if the present maximum values (German TLV value for NO\textsubscript{x}; American TLV value or PIARC recommendation for NO) were to be considerable reduced (e.g., in the case of NO, to below 10 ppm)”. He further notes that “because nitrogen oxide emissions do not drop to the same extent as CO and soot emissions, a slight increase in the amount of NO\textsubscript{x} in the tunnel air is expected in the next few years”. He continues: “because considerably more fresh air is required to dilute CO and soot than simply to dilute NO\textsubscript{x}, the NO\textsubscript{x} concentrations clearly will remain below the current levels”. Values quoted by Meyeroltmanns include CO: 100 ppm (practice n existing tunnels), NO\textsubscript{x}: 3 ppm (TLV/Switzerland) and 5ppm (TLV/Germany) and NO: 5 ppm/10 ppm (recommendation of SUVA for tunnelling with diesel machines) and 25 ppm (PIARC recommendation, 1995).

Colberg et al (2005) present a statistical analysis of measurements of NO\textsubscript{x}, CO and total VOCs made between spring 2001 and autumn 2002 in 3 road tunnels: the Lundby tunnel (Sweden), the Plabutsch tunnel (Austria) and the Gubrist tunnel (Switzerland). Lundby and Gubrist had passive ventilation with one-way traffic whilst Plabutsch had a cross-ventilation system with a single lane of traffic in each direction. In the case of NO\textsubscript{x}, the results show a large effect of tunnel gradient on the EFs of heavy duty vehicles (HDVs) but a less pronounced effect for LDVs. Large differences were found in the values of NO\textsubscript{x} measured in the 3 tunnels (up to a factor of 10 for HDVs and 3 for LDVs) with the lowest values on the down gradient of the Lundby tunnel. EFs on weekdays were approximately 15 % higher than at weekends, probably due to the different compositions of the traffic. For weekdays, typical values of NO\textsubscript{x} EFs for LDVs would be 0.34 g/km and 10.5 g/km for HDVs. In the Lundby tunnel this varied from 1.12 to 11.2 g/km between the down slope and the slight incline.
5.5 AIR QUANTITIES

A number of factors affect the airflow through a tunnel. The amount of air moved depends not only on fans but also on such variables as traffic speed, traffic composition and density. There can also be considerable non-uniformities across the tunnel cross-section in the airflow pattern and contaminant concentrations. In the Cassiar tunnel, Vancouver, for a typical air speed of 7 m/s and a hydraulic diameter of 9.3 m, the centreline velocity was 113% of the average velocity whilst at 0.9 m from the wall the velocity was 90% of the average (Rogak et al, 1998).

On the acceptability of airflow velocities, Pera (1988) states that “in longitudinal ventilation …. Air flow is confined by the cross-section area and a limiting acceptable air flow. Indeed, if the air velocity exceeds about 10 m/s, it becomes difficult to open the doors. Dust, papers, water drops are raised and blown up. Pedestrians can hardly walk along with an air flow over 14 m/s. Workers require an air velocity under 5 – 6 m/s. So, usually, the air velocity is restricted to 7 m/s.” A maximum velocity of “about 10 m/s” in a longitudinal system was also given by Pursall (1976). Jafari and Moghaddam (2000) quoting PIARC (1995) say “longitudinal air velocity is limited to 10 – 12 m/s in a tunnel”.

Bendelius(1974) looked at the ventilation systems in three categories of vehicle road tunnel: mountain, sub aqueous and urban. One system in each category was explored. The Lowry Hill Tunnel, an urban tunnel in downtown Minneapolis, designed in the mid-60s and opened in 1971, is approximately 450 m long and has a semi-transverse system, selected because of the tunnel’s short length and the anticipated heavy traffic flow. The air quantities selected were 230 m³/s for the northbound tunnel and 278 m³/s for the southbound based on a CO level of 200 ppm. Air was supplied through a duct, which did not run the full length of the tunnel, to a series of ceiling slots. The fans were operated automatically by a system using the output of 6 CO analysers. Four fans operated in pairs based on signals received from their respective analysers.

The Trans-Koolau Tunnel in Hawaii is a mountain tunnel consisting of two three-lane bores. The fully transverse ventilation has six supply and six exhaust fans in the inbound tunnel and four supply and four exhaust fans in the outbound tunnel. The ventilation system supplies fresh air to the ventilation zone and the piston action of the vehicles disperses the pollutants longitudinally. Air quantities were computed using a maximum environmental limit of 200 ppm of CO under the most severe traffic conditions with all fans operating. The proposed design ventilation rates were 440 m³/s for the outbound tunnel and 944 m³/s for the inbound. The proposed rate for the inbound tunnel should maintain a CO level of 150 ppm within the tunnel or 175 ppm with partially stalled traffic.

The sub-aqueous tunnel at Hampton Roads in Virginia was being built as a parallel facility to an existing tunnel. The planned longitudinal ventilation of 800 m³/s was based on allowing a CO level of no more than 190 ppm. A continuous CO sampling, analysis and recording system was to be installed with an alarm level to be set at 300 ppm.

The Chesapeake Bay Bridge-Tunnel has two underwater tunnels each slightly less than 6000 feet in length. The transverse ventilation system id designed to provide 225 cfm per lineal foot of tunnel at maximum operation of the fans which change the air in the tunnel every 1.7 minutes. There is no longitudinal draft caused by the system, “this being advantageous in case of fire in the tunnel” (Egilsrud, 1964). In the Chesapeake Bay tunnel, the design called for no more than 300 ppm of CO. A continuous sampling CO recorder was provided for each ventilation section, the sample being taken from the exhaust duct air 1000 feet down the tunnel from the portal.
The 7864 m long single-tube Karawanken tunnel between Austria and Yugoslavia was originally planned in 1978 with a fully transverse ventilation system. In 1985, when construction started, the system was reconsidered (Díaz, 1988). In the intervening period there had been a substantial lowering of exhaust emissions and this trend was expected to continue and even increase. A study indicated that a combined longitudinal and transverse system without shafts would cut costs considerably. The original transverse system planned for the whole tunnel length was to provide fresh air at 100 m³/s/km and an exhaust rate of 80 m³/s/km. At full load this would amount to 786 m³/s of fresh air and 629 m³/s exhaust air. An alternative ventilation system was required to meet a number of conditions including: transverse ventilation should be designed for a fresh air rate of 80 m³/s/km; longitudinal air velocities in the bi-directional traffic space should not exceed 8 m/s (This limited the maximum air quantity to 400 m³/s). The redesigned tunnel had no ventilation shafts and had transverse ventilation sections each 3,332 m in length at the north and south ends of the tunnel with a 1,200 m long central section with longitudinal ventilation. If the tunnel were only longitudinally ventilated at a throughput of 600 m³/s, the longitudinal velocity would exceed 12 m/s and a power requirement in excess of 6,000 kW. For fully transverse flow, 315 m³/s of fresh air and the same amount of exhaust air would require a power consumption in excess of 8,000 kW. A combination of systems together with some semi-transverse ventilation was used to optimise cost saving.

The Gotthard Tunnel in Switzerland is 16.3 km long and has a transverse ventilation system with equal amounts of supply and exhaust air. A maximum amount of 2,800 m³/s of fresh air could be supplied and the amount of air is constantly adjusted to the concentration of CO, “the CO concentration being the decisive waste gas component of the tunnel air” (Anon. 1980). “The CO concentration must never exceed 150 ppm.”

Ventilation velocities are not quotes by Coberg but, in an investigation of heat release from HDV fires in tunnels, Ingason and Lonnermark (2005) used initial longitudinal ventilation velocities in the range 2.8 to 3.2 m/s. Similar earlier tests had used initial velocities of 5 to 6 m/s (EUREKA 499) and a natural ventilation velocity of 0.5 m/s. Lemaire et al (2002) reports tests carried out with natural ventilation of 0.5 m/s and forced ventilation of 1 to 2 m/s, 4 to 6 m/s and 6 m/s. BD 78/99/ states that “most vehicle fires will generate that can be controlled by a velocity of between 3 and 5 m/s …”. Day (2005) shows the development of longitudinal flow in a tunnel from the thermal buoyancy forces due to a 30 MW fire in a tunnel with a gradient of 8.5%. The air velocity through the tunnel reached 3 m/s after 3 minutes and rose to almost 8 m/s. A pass/fail criterion for ventilation velocity could be the “critical” velocity. This is defined in NFRA 502 as the “the minimum steady-state velocity of the ventilation airflow moving towards a fire, in a tunnel, that is necessary to prevent backlayering. Backlayering is the movement of smoke or hot gases against the ventilating airflow. Appendix C of NFRA 502 gives a guideline for the calculation of critical velocity in road tunnels.

Airflow velocities are usually measured at, or close to, the tunnel walls. The airflow meter is therefore strongly influenced by the movement of traffic. Azuma et al (2000) measured airflow velocities across the section of a vehicle tunnel using ultra sonic anemometers and compared them with data from near-wall-mounted instruments. Measurements were made in the Hou-ou Tunnel in Japan, a two-way longitudinally ventilated tunnel about 3100 m in length. There was excellent correspondence between the two methods of measurement. Over a 10 hour period airflow velocities varied between +5 m/s and -4 m/s.

For ventilation calculations, it is necessary to decide upon a permissible level for a particular pollutant (say NO₂). The known (or expected) traffic flow rate, the mix of vehicles (from which emission rates can be estimated) and the gradients in the tunnel are required. In some instances altitude may be a factor. The total volume flow rate of air can then be calculated and, from the length of the tunnel, the air quantity per unit length of tunnel can be found. The figure will be of
the order of 0.3 m³/s/m. Pursall (1976), for example, points out that “it is advisable with one-way traffic to vary the ventilation rate on gradients by reducing the maximum ventilation rate to say 0.232 m³/s/m on down-gradients and increasing it to 0.387 m³/s/m on up-gradients”.

5.6 THE TYNE VEHICLE TUNNEL

The Tyne vehicle tunnel is a single tube for vehicles opened in 1967 and is one of a group of 3 tunnels that allow passage under the river Tyne. The design capacity of the tunnel was 24,000 vehicles/day but in 2004 the actual usage had risen to 38,000 vehicles/day. The tunnel has a bi-directional traffic flow (and therefore no piston effect from the traffic flow) and the ventilation system is bi-directional semi-transverse. It is ventilated by fan shafts at the north and south ends of the tunnel. Additional fans (jet fans) were installed in the 1990’s to remove smoke and fume more efficiently in the event of a fire.

Difficulties may arise if the limits of 1 ppm for both NO and NO₂ are proscribed. While the level of 1 ppm for NO₂ could be met, the use of shaft fans at maximum speed could reduce the NO level to below 4 ppm. However the speed control system is not designed to be continuously rated.

5.7 SIMULATION

In the mid 1960’s, Kennedy (1965, 1966) and Helly (1965) developed models of a tunnel ventilation system for the Port of New York Authority. The tunnel was divided into a number of uniform sections and a mass balance applied to each section. The models were used, not only to determine pollution profiles and the dynamics of the system, but also to assist in the choice of best points for the positioning of gas analysers.

Bring et al (1997) describe a computer program for use on a PC to study airflows in tunnels and pollution concentrations due to emissions from vehicles. Results from simulations include air pressures, flow rates and pollution concentrations along the tunnel. The program was validated against older programs and results also compared with measurements made in the Soderledstunneln, a busy road tunnel in central Stockholm.

Chung, Chung and Chen (2004) modelled the turbulent flow and dispersion of CO and NOₓ in a road tunnel and solved the problem numerically using the finite volume method. The effects of fan ventilation, roughness and the piston effect of the moving vehicles on the airflow and the pollutant dilution were examined. The piston effect alone was predicted to supply 25 – 34% dilution of pollutants in the tunnel. The numerical results showed that the cross-sectional concentrations of pollutants were non-uniformly distributed.

Katolicky and Jicha (2005) used a Eulerian-Lagrangian model to simulate cars inside a tunnel and the impact on operational ventilation. The airflow was solved using the commercial CFD code StarCD. The model was validated using experimental data from Chen et al (1998) from a small-scale tunnel. The model showed that the flow rate of air depended on traffic flow rate, speed of traffic and tunnel length; the effect of traffic flow rate approached a limiting value whilst the speed of vehicles had a stronger effect on the airflow rate.

Further discussion of mathematical models which could be applied to the prediction of the distribution of NO throughout a tunnel can be found in Section 6.
5.8 CONCLUSIONS

Formerly, ventilation systems were designed to dilute CO. The airflows required to dilute CO also ensured the dilution of other pollutants, in particular NOx.

Cuts in CO emissions from vehicles have not been matched by a decrease in NOx levels. NO2 concentrations must be taken into account when calculating ventilation flow rates.

NO2 concentrations can be derived from NO measurements using the ratio NO2/ NO = 0.1. However, this may only be suitable for fixed monitors and may not be appropriate for personal monitors.

Air flow rates necessary to dilute NO2 can be calculated from the emission factors for NOx for different vehicle types, the mix of traffic and the traffic flow rate. Tunnel gradient may also need to be taken into account.

Travel times through tunnels are usually short and relatively high concentrations of pollutants may be acceptable for short term exposures.

Tunnels with bi-directional traffic flows are generally regarded as the most difficult to ventilate. Ventilation might be improved if the traffic flows can be partitioned.

High longitudinal air velocities can cause a variety of problems and an upper limit of 10 – 12 m/s is usually recommended.
6 MATHEMATICAL MODELLING REVIEW

6.1 INTRODUCTION

Modelling can provide very useful insight into the flow. In the idealised situation, modelling can be used to simulate the flow and provide information about regions where NO$_x$ may accumulate. It can provide guidance for changes in the ventilation strategy and or where sensors may be located to monitor the levels of NO$_x$ within the tunnel.

There are models of different levels of complexity from the simple empirical correlations, via zone models to CFD models. The different types of models will be discussed in greater detail below.

6.2 SIMPLE MODELS

6.2.1 Empirical correlations

Empirical correlations are simple to use, and often requires the input of a small numbers of variables that are either tabulated or known in some other way. Some of the important features of the empirical models are:

- Based on experimental data
- Quick and easy to use
- Limited range of applicability – dictated by the available experimental data
- Tend not to take into account geometrical complexity

It is important to bear in mind the limitations of a correlation that is due to the (limited) range of experiments against which the constants have been calibrated. One cannot say anything about the performance or accuracy of a correlation when it is being used outside its range of applicability. Real–life scenarios tend to involve very complex geometries and the correlations tend to ignore interaction between the fluid flow and obstacles or buildings in the geometry. There may be situations where this is not a problem, though more often than not, these complex interactions are very important. These simple models can be used for quick calculations and be used in conjunction with a more accurate tool, where the correlation may be used as a screening tool.

6.2.2 Integral and zone models

This class of models is made up of two different types of models. The integral models solve a set of ordinary differential equations, where the mass, momentum, energy and species mass fractions are conserved. The zone models may be coded in simple spreadsheet type software, where the important quantities are exchanged between the different zones.

Some of the features of this class of models are:

- Based on experimental data, against which constants are calibrated
- Solves a set of conservations equations (as ordinary differential equations) for mass, momentum, energy, turbulence quantities and species concentrations, for each zone;
- Can provide valuable information about the flow
- Models retain some flow physics
- Quick and easy to use – runtimes longer than for empirical correlations, but still $O(< 600s)$
- Limited range of applicability – dictated by the available experimental data
- Tend to ignore geometrical complexities
- Plug flow reactor model
• Continuously stirred tank reactor

These tools are simple, yet can be used in an effective manner, either as a screening tool to be used in conjunction with a CFD model or in their own right. The models have a limited range of applicability, due to the constants being calibrated against experiments. It is important to try to assess whether the models adequately represent the geometry and describes the flow physics in sufficient detail. It would also be necessary to somehow automate the analysis of the results in order to identify interesting scenarios, which may require investigation with a CFD model, if the model is used a screening tool.

6.3 CFD MODELS

CFD provides the most realistic representation of the physical and chemical processes. The basis of CFD is to obtain a solution to the Navier-Stokes equations, the set of highly non-linear and strongly coupled partial differential equations (PDEs) that govern the fluid flow. It would appear that there is not on unique solution to the problem. In addition one would also solve transport equations, involving accumulation, convection, diffusion and source terms, for energy, turbulence quantities, see below, species mass fractions, etc. The CFD solution provides a wealth of information about the flow, i.e. velocities, temperature, and species concentrations.

A scenario would be described in a so-called geometry in the CFD model, which would contain objects and walls. In theory, the geometry can highly complex, though in reality there is an upper limit to how much detail can be retained. The large mesh and the subsequent long computational run times are two important factors that impose the restriction on the level of detail. The geometry is than sub-divided into a large number of smaller computational cells called the mesh or grid. One is solving a set of algebraic equations and not the PDEs; the process of transforming the PDEs to algebraic equations is called discretisation, which may both spatially and temporally. The better the mesh resolution, e.g. finer mesh or larger number of cells, leads to a more accurate solution. The PDEs are solved for each of these cells. One talks of discretisation methods of various order of accuracy. The discretisation is based on a Taylor series expansion of the equations and the order of a method depends on the highest order of terms that are retained. The discretisation of the equations introduces a truncation error, or numerical diffusion, through the process of discarding higher order terms in the expansion. The convection terms, i.e. the first derivatives, are particularly troublesome. The effect of numerical diffusion is to smear out sharp gradients. One should use the most accurate discretisation scheme possible in order to reduce the influence of numerical diffusion.

It is also necessary to provide some information about the conditions on the various boundaries. The so-called boundary conditions are seldom well characterised, especially in atmospheric flows, where wind speed and direction can change significantly with time. The initial flow field must also be specified somehow and the information about the flow conditions is usually scant or non-existent. This may not be a trouble in some flows and is also dependent on the type of model employed, but one cannot a priori say whether it will have an effect on the solution.

It can be very time consuming to set up a CFD model, especially for complex geometries. It might not be practical to include all the finer details so engineering judgment as to what features must retained and what can be neglected will be required. The computer run times can be very long, especially if the flow is transient.

CFD is a knowledge-based technique, which places great demand on the user’s understanding of the problem. The user must be well versed in a number of subject areas, i.e. fluid mechanics, physics, chemistry, numerical analysis, computer science, etc.
6.3.1 Turbulence Models

While many of the physical processes are reasonably well understood, the models still are inadequate for many flows. One issue of particular importance is that of turbulence. Turbulence modelling is a very active field, yet the development and deployment of the models is not rapid. There are many different types of turbulence models of varying complexity. The most commonly used types of models are:

- Reynolds Averaged Navier-Stokes (RANS) models
- Eddy viscosity models, i.e. a variant of the $k$-$\varepsilon$ model or $k$-$\omega$ model
- Algebraic Reynolds Stress Transport Models
- Reynolds Stress Transport Models
- Large Eddy Simulation (LES) with some sub-grid scale model
- Detached Eddy Simulation (DES) combining an eddy viscosity model and LES to draw upon the best features of each of the models
- Direct Numerical Simulation (DNS) does not require modelling of any of the physical processes

RANS model is the most common approach to model turbulent flows. Traditionally one would perhaps think of $k$-$\varepsilon$ and $k$-$\omega$ models, which are two-equation models ($k$ and $\varepsilon$ or $\omega$), but there are also zero-equation and one-equation models. The zero- and one-equation models have their use for certain specific types of problems, i.e. where one might be able to identify a representative length scale or eddy viscosity, but are not generally applicable to complex flows.

The ubiquitous $k$-$\varepsilon$ model is available in many variants, where the model and its constants have been tweaked slightly to better be able to model certain phenomena. The model is generally not well suited to flow with curvature or swirl. The model has also been extended to account for non-linear effect (Speziale et al, 1987). The non-linear $k$-$\varepsilon$ model is not as robust as the linear version and is quite complex. The advent of faster, cheaper computers has made other types of models affordable and have essentially superseded the non-linear approach.

Algebraic Reynolds Stress Transport Models (ARSMs) were made popular by Rodi (1980). Algebraic correlations were used to calculate the Reynolds stresses. The ARSMs fell out of favour for a decade, after which there was a renewed interest for this type of model in the field of Aerodynamics. The original ARSMs were numerical unstable and did not offer any significant advantage over the more complex Reynolds Stress Transport Models. ARSMs has not as yet found widespread use outside the fields of hydraulics and aerodynamics.

Reynolds Stress Transport Models (RSTMs) have undergone development over the last 30-odd years, i.e. papers by Hanjalic and Launder (1972, 1976) and Launder, Reece and Rodi (1975) marked the beginning of this field. The RSTMs tend to be numerically unstable, require finer mesh resolution than the two-equation turbulence models and involve solving more PDEs. It has also been found that it might be necessary to model the third-order moments for certain types of flows, which further increase the computational effort and the uncertainties, Craft et al. (2003). There is also a lack of experimental data for some of the quantities that are introduced during the derivation of the transport equations of the Reynolds stresses, which means that there uncertainty in the values to assign to these constants. The scalar transport equations introduce velocity-scalar fluctuations, analogous to the Reynolds stresses. It has been assumed that the velocity-scalar fluctuations can be treated just like the Reynolds stresses, though this is by no means certain. The Reynolds stress and scalar transport models have the potential to model the underlying physical processes in a more realistic fashion than is possible with two-equation.
models. However, the disadvantages with the RSTMs, as outlined above has precluded the use of RSTMs for routine calculations.

LES is finding increasing use for atmospheric and other types of flows. The technique is also suitable for flows that are transitional, e.g. somewhere between laminar and turbulent. LES is computer intensive and fine meshes are required, but the information that the technique provides information that RANS models are not able to provide. LES is particularly suited to dispersion-type flows as it can provide realistic information about concentration fluctuations, which is of importance when considering toxic gases. The average concentrations provided by the RANS models are not adequate. There are also problems in the near-wall region where the assumption of large eddies break down. There are a number of different sub-grid scale models. The sub-grid scale models introduce a parameter, \( C_s \), which can either be a constant or be calculated in real-time. Pope (2004) has highlighted a number of problems with the LES technique, one of which is that the model constant \( C_s \) is not a constant(!), as it will vary depending on the mesh resolution; hence it is not possible to obtain a grid independent solution with one unique value for \( C_s \). One must specify a realistic initial flow field, including velocity fluctuations and species concentration fluctuations. One disadvantage with LES is that it is necessary to simulate steady-state flows for a long time, i.e. multiples of some characteristic eddy turnover time, before one can begin to sample the flow statistics. Moreover, it is also necessary to carry to the sampling for a sufficiently long time for the statistics to be truly representative and accurate. For transient flows, it could be argued that strictly one should carry out a number of simulations of the same problem, but with slightly different initial conditions. The results from these simulations could then be used to calculate an ensemble average. It is not clear how many simulations would be required to give a realistic ensemble average. Multiple transient calculations are rarely performed due to the computational effort involved; Jones et al. (2006) performed eight transient simulations of the same problem, but with different initial flow field, which the authors concluded was sufficient number. The user can specify the cut-off frequency for the LES model. This determines how much of the eddies are modelled with sub-grid scale model and how much of the energy spectrum is not modelled. It is not a trivial task to work out exactly how much of the eddy structures are modelled, which means that it is difficult to assess the quality of the simulation.

DES is hybrid turbulence model, which combines the best features of a RANS model, sometimes even a zero-equation or one-equation model suffices, and a LES model. The RANS model is used in the near-wall regions, where the assumption of large eddies does not hold. The LES model is then used everywhere else in the domain. DES initially found use in aerodynamic flows and has yet to find widespread use in other types of flows. The advantage with DES over LES is that the simulations are much less computer intensive, by at least a factor of two. The switchover point between the different models may cause problems. Furthermore, DES also shares the problem with the sub-grid scale modelling with the LES technique. Some of the DES formulations use a RANS model to resolve the entire boundary layer and the benefit of using an LES model is less obvious. There is also a crop of other DES models, where the RANS model is only applied in the near-wall region, e.g. for \( y^+ \leq 100 \). The latter DES implementations have yet to find widespread use in flows other than aerodynamic flows.

It is possible to simulate fluid flows without having to resort to any models at all – Direct Numerical Simulation (DNS). It is necessary to resolve all relevant length and time scales when using DNS, either of which can involve six or more orders of magnitude. Therefore, DNS is not a viable option for real-life scenarios due to the huge computational cost associated with this technique. DNS will not be used routinely for modelling of atmospheric flows. It is envisaged that DNS will be used to do numerical experiments, which will lead to improvements of turbulence models.
An interesting development is the coupling of simple models, i.e. zone models, with CFD models. This is particularly desirable for transient simulations that are required to run for a long time (in real-time), i.e. dispersion flows. Coupling of zone and CFD models is still in its infancy, but shows great promise.

6.3.2 Quality and accuracy of CFD simulations

Many experimentalists are sceptical about the results provided by mathematical models. The question of quality and trust in the accuracy of the CFD simulations is of utmost importance. The responsibility of ensuring the quality and trust in the CFD solutions is achieved is shared by the code developer and the user performing the calculations.

Three important issues are:
- Verification – responsibility of the code developer
- Validation – shared responsibility between the code developer and the user
- Sensitivity analysis of the solution

Verification is the process of ensuring that the correct equations are solved. This is almost universally the case with most commercial CFD codes and zone models. The verification can only really be carried out by the code developer, who is the only one who knows exactly what terms have been included in the equations.

Validation is the process by which the accuracy of the simulation is assessed through comparison of the calculated values of key parameters to available experimental data. The code developers will want to carry out some validation of their code themselves. However, due to the versatility of the CFD technique it is not possible for the code developer to validate all physical sub-models against experiments for all scenarios that the code is likely to be used. Therefore some of the validation will by necessity be performed by the individual users of the code. Hence the onus is on the user to ensure that the code has been validated against relevant experiments. It should be clearly stated if the code has not been validated against experiments. The lack of validation does not mean that the simulations are worthless, just that one should be careful and not draw far-reaching conclusions from the simulations. It is important to bear in mind that the validation is a necessary but not sufficient method to ensure the quality of the simulations is acceptable.

In an ideal world, the sensitivity of the CFD solution to computational cell size, size of time step, and choice of discretisation scheme (especially for the convective terms in the transport equation) should be performed. The solution can change significantly depending on any or all of these parameters as well as the specification of the initial flow field. The latter can be very difficult to ascertain in real scenarios, especially if it involves the atmosphere, as it is very changeable and is not known in great detail. However, in practice these issues are not addressed in full if at all. The effort involved in investigating the sensitivity can be very large. It is likely that, say, grid independence may become a requirement in the future. A number of learned journals already operate a policy of rejecting papers submitted for publication if a grid dependency has not been carried out. Roache (1998) has expanded on the issue of validation and verification. There are also a number of Best Practice Guidance documents, from ERCOFAC, Wintergerste and Casey (2000) and various NAFEMS documents, which can guide the user in the selection of tools and parameter settings. The fact remains that advanced mathematical modelling, e.g. CFD, is a knowledge-based discipline and the user has to have thorough understanding of a diverse range of topics, including fluid mechanics, combustion, numerical mathematics, etc.
It is also become more important to document the experience and training of the user of CFD, which is in recognition of the variability, or user dependence, that has been detected in various modelling exercises.

6.3.3 Sources of errors

There are a number of sources of errors and uncertainties associated with the use of mathematical models. Some of these sources of errors are not directly related to verification, validation or sensitivity analysis.

The errors have been categorised according the source:

There are a number of sources of errors and uncertainties associated with the use of mathematical models:

- Numerical errors
  - Discretisation errors
  - Iteration errors
  - Convergence errors
- Model errors
  - Inadequacies in the model, i.e. due to incomplete understanding of the physical processes
  - Use of the wrong or inappropriate model
  - Unjustifiable simplifications
- User errors
  - Poor mesh quality or poor representation of the geometry
  - Lack of understanding of the underlying physics
  - Selection of parameter settings
  - Choice of boundary conditions
  - Post-processing
- Uncertainties in the scenario
  - Lack of knowledge of initial conditions, i.e. the ambient wind speed and direction, turbulence levels and temperature field
  - Lack of detailed information on the geometry
- Software errors
  - Incorrect algorithms
  - Coding errors
  - Memory leakage or undefined variables

6.4 DISPERSION MODELLING

There are a considerable number of papers and books describing atmospheric dispersion of pollutants, i.e. Hanna, Briggs and Hosker (1982).

Dispersion of a chemical species can be modelled in a number of ways. The chemical species can be treated as a passive scalar if it does not undergo chemical reaction or in some other way interacts with the fluid flow. The ambient flow field can be calculated beforehand and the simulation of the dispersion can then be performed as a post processing exercise. It is not possible to carry out the dispersion as a post processing stage if the release of the chemical species has significant momentum so that it influences the ambient flow field. The calculation of the ambient flow field and the dispersion must be coupled if the chemical species undergoes chemical reaction. Real-life situations involving NOx emissions might be transient, e.g. will vary with time.

Important factors needed to be taken into account, in no particular order, are:
• Geometrical complexity
  o Machinery (stationary and/or moving)
  o Tunnel sections branching off the main roadway
• Effect of release direction and height
• Mass flow rate or velocity of the release
• External conditions, i.e. wind speed and direction, atmospheric stability
• Turbulence enhancing dispersion
• Effect of fans/ventilation, flow rate, location
• Temperature of the exhaust gases
• Temperature of the air in the tunnel
• Surface roughness and temperature of tunnel walls
• Location of hot surfaces/machinery
• Can we afford to model all equipment explicitly or do we need to resort to regions of porous media?

6.5 MODELLING CHEMICAL REACTIONS

The formation of NOX during the combustion is rapid, and takes place at high temperature. The oxidation of NO to NO2 on the other hand is slow, of the order of seconds.

The thrust of the modelling efforts into the fate of NOX centres on the conversion of NOX through either reactions with O3 or photochemical conversion. Table 8.10 in Appendix (Section 8.5) lists a large number of chemical reactions that are important in the atmospheric chemistry, Seinfeld and Pandis (1998). Thermal oxidation of NO by oxygen is not included. It is expected that the level of ozone in the tunnel is going to be low and this will not be a major reaction path. The photochemical conversion of NOX in the tunnel can also be discounted as the artificial light will not be of the right wavelength and there is no direct sunlight into the tunnel.

Calculations using the chemical kinetics scheme proposed by Tsukahara et al. (1999) have been carried out as part of the present project; Table 6.1 lists the reactions that were considered. Calculations of the decay in NO concentration with time using rate constants from Tsukahara et al. (1999) show that the initial rate of decay is fairly rapid, see Figure 8.2 Appendix (Section 8.5). However, the threshold level of 1 ppm is only reached after 50 hours, for initial NO concentrations exceeding 10 ppm. This timescale is significantly longer than the expected residence time, which is based on the ventilation flow velocity, typically of the order 1 m s\(^{-1}\), and the length of the tunnel. Hence the thermal oxidation of NO within the tunnel can be neglected. The level of O3 is expected to be low in the tunnel, so the conversion rate should be negligibly low.

Important factors to be considered are:
• Temperature of exhaust gas – how rapidly does it cool down?
• Five transport equations for NO, NO\(_2\), NO\(_3\), (NO)\(_2\) and O\(_2\) and one constraint for N\(_2\)?
• Laminar flamelets (unsteady) or Eddy BreakUp type – neither approach is applicable to modelling what is essentially an isothermal process
• Temperature of the air in the tunnel
• Residence time of species within the tunnel – will depend on the ventilation arrangement
• Are there stagnant regions, i.e. tunnels branching off from the main roadway
Table 6.1: Important thermal oxidation reactions of NOx, Tsukahara et al. (1999)

\[
\begin{align*}
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
\text{NO} + \text{NO} & \rightarrow (\text{NO})_2 \\
(\text{NO})_2 + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
\text{NO} + \text{O}_2 & \rightarrow \text{NO}_3 \\
\text{NO}_3 & \rightarrow \text{NO} + 2\text{NO}_2,
\end{align*}
\]

(R.1) (R.2) (R.3) (R.4) (R.5)

6.5.1 Introduction to reactive flow modelling

There are a number of approaches that can be used to model reacting flows:
- Detailed and reduced chemical kinetics modelling – generally applicable
- Laminar flamelets with prescribed Probability Density Function – applicable mainly to combusting flows
- Transported Probability Density Function modelling – applicable mainly to combusting flows

6.5.2 Detailed and reduced chemical kinetics modelling

It may be desirable to model the detailed kinetics, though this is usually only of interest if the kinetics is likely to affect the fluid flow, i.e. flame extinction. The computational overhead is modest for simple reaction systems, but quickly becomes computationally intractable for large systems involving a large number of chemical species and a large number of reactions, such as hydrocarbon combustion. In the latter case it may be possible to reduce the number of species through sensitivity analysis, a thorough understanding of the chemical kinetics or the use of linear algebra, which relies solely on mathematics.

A transport equation, e.g. a partial differential equation, for each of the important chemical species is required. The source term in the transport equation will contain the Arrhenius-type reaction rate expressions so that formation and destruction of any particular species can be calculated. This results in a system of highly non-linear and strongly coupled partial differential equations. The system of equations is likely to encompass many orders of magnitude of timescales, which lead to a so-called stiff system. Stiff systems can be numerically sensitive and might give rise to poor convergence.

6.5.3 Laminar flamelets with prescribed Probability Density Function

Usage of a prescribed Probability Density Function (p-PDF) is associated with non-premixed turbulent combustion, i.e. Bilger (1980) and Vervisch and Veynante (2002). A similar approach has also been applied to premixed combustion, i.e. Bray and Moss (1977), Bray (1980), and Bray, Moss and Libby (1985), but has not found widespread use.

The technique with a lookup table and p-PDF could easily be used for modelling the NOx chemistry, but is unlikely to be used.

The prescribed PDF gets its name from the fact that the shape of the PDF is determined from turbulence quantities, which provide a turbulent time scale, and the mixture fraction and its variance. Jones (1980) showed that the exact shape of the PDF does not have a significant effect on the predictions. The most commonly used shape is the so-called β-PDF, which can readily be expressed in terms of a series of exponential terms.
6.5.4 Transported Probability Density function

A more sophisticated approach, and computationally expensive, is to solve a transport equation for the PDF, hence the name transported PDF or t-PDF. Pope has been a champion of this technique, i.e. Pope (1995). It is one of two ways by which detailed chemical kinetics can be incorporated into CFD calculations. The technique is based on the introduction of a number of particles at each node or computational cell, which are then convected by the mean flow, diffused by gradients, interacting with other particles in a random fashion, e.g. through a Monte Carlo simulation, and undergoing combustion/chemical reaction. Unfortunately, a large number of particles is required to get an accurate solution, which leads to long computational run times. Pope has shown that one could avoid a great deal of modelling, especially of the turbulence quantities, by constructing a joint-PDF, consisting of mass, momentum, turbulence quantities and species mass fractions, but this approach is not used routinely due to the computational overhead.

The computational cost could be reduced somewhat if a reduced chemical kinetics scheme is used instead of a detailed one. One of the main disadvantages with the reduced kinetics scheme is that the system of chemical reactions becomes increasingly stiff, in the numerical sense, which can impede convergence or make the solution unstable.

The t-PDF approach lends itself to non-premixed combustion, but there is no reason why it could not be used for premixed combustion or chemically reacting flows, other than combusting ones. Though the approach is not the best way to model thermal oxidation of NOx.

6.6 OTHER TYPES OF MODELS

6.6.1 Statistical approaches

It may prove that it would be advantageous to use statistical models, utilising Bayesian statistics instead of the more traditional methods, i.e. CFD.

Carvel et al. (2001) have used a Bayesian statistical approach to model the effects of ventilation on pool fires in tunnels. The application of the statistical methods along the lines of Carvel et al. (2001) is appears not to be as flexible as CFD. It is not known if a similar approach has been used to model reactive (non-combusting) flows.

6.6.2 Integration of models

CFD provides a wealth of information about the flow field. However, it is a modelling technique, which may not be feasible for simulating long transients in long tunnels. (This is not entirely true, as there are tools, which are very quick to run (relatively speaking) that would allow long tunnel simulations to be performed). There are encouraging signs that integral models and CFD models can be used in conjunction, thus alleviating the problem of long computer run times.

Monte Carlo (MC) simulations are finding increasing use for modelling dispersion of pollutants in the atmosphere. The principle behind Monte Carlo simulations is that fictitious particles with appropriate properties are released in the flow. The particles are then tracked and their fate recorded. The MC approach can be used both with simple models and with CFD models.

If it is assumed that the pollutant is inert and small enough not to influence the flow behaviour, the species can then be treated as a passive scalar, which effectively means that it will be convected by the flow and experience molecular and turbulent diffusion. The calculation can be
performed as a post-processing exercise, since the species does not react or otherwise interact with the flow.

6.7 EXAMPLES OF MODELLING THERMAL OXIDATION OF NO\textsubscript{x}

Modic (2003) proposed a non-dimensional critical number for determining the conditions at the exit of road tunnels, which is used to give guidance on the ventilation requirements. Modic (2003) also developed a mathematical tool to calculate the conditions, which was calibrated against available experimental data. This mathematical tool does not consider thermal oxidation reactions involving NO\textsubscript{x}.

It appears that modelling of the fate of NO\textsubscript{x} in tunnels is rarely if ever undertaken, while modelling of the atmospheric chemistry is a very active field, e.g. due to the current emphasis on climate change modelling.

Lindqvist et al. (1982) discussed conversion of NO\textsubscript{x} due to low-temperature oxidation in polluted air. Lindqvist et al. (1982) were only interested in the chemical kinetics and did not consider the interaction between the fluid flow, i.e. dispersion of NO\textsubscript{x}, and the chemical reactions. The presence of ozone and incident solar radiation provide two important reaction pathways for conversion of NO\textsubscript{x} in the atmosphere. However, the level of ozone in the tunnel is likely to be low and there is no direct sunlight in tunnels, so these reaction pathways can be assumed to make a negligible contribution to the NO\textsubscript{x} conversion. Furthermore, in tunnels, the ratio of timescale of the chemical reactions to the typical ventilation flow timescale, based on a typical ventilation velocity and the length of the tunnel, is sufficiently small that the thermal oxidation of NO\textsubscript{x} can be considered to be negligible. This argument does not take into account the layout of the tunnel, which may include side tunnels where the ventilation is poor, yet the timescale of the conversion is such that this is almost certainly an acceptable assumption.

6.8 CONCLUSIONS

Mathematical tools can be used to answer what-if questions without the need to resort to experiments. This does not mean that fluid flow modelling should be seen as a replacement for experiments; the two techniques are complementary.

There are a number of different models of varying complexity. The simpler models, empirical correlations, are based solely on experimental data and thus have limited range of applicability. Zone models are also based on empirical correlations so share the restriction of a limited range of applicability, but have a more realistic representation of the flow physics. These two types of models are quick and easy to use, but do not take into account geometrically complex scenarios. CFD models offer the best representation of the flow physics, but the simulations are computer intensive, might require a long time to set up the problem, and require that the user is experienced and has a thorough understanding of physics, chemistry, numerical analysis, etc. Some of the physical sub-models implemented in CFD codes are also based on empirical correlations so will also have limited range of applicability. Some physical processes, i.e. transition from laminar to turbulent flow, are poorly understood and hence the models cannot be expected to give accurate answers if the correct terms are not included in the models.

It is vitally important that one ensures that the quality of the CFD results is adequate and the results are realistic. The CFD modeller ideally should carry out a sensitivity analysis to ascertain how sensitive the solution is to mesh resolution, choice of mesh type (structured v. unstructured), choice of time step size, and choice of spatial and temporal discretisation schemes, etc. However, pressure of tight deadlines, tight budgets and computationally expensive calculations frequently preclude an in-depth sensitivity analysis. The solution could also be greatly influenced by the initial and boundary conditions specified. In real-life situations, there
is likely to be great uncertainty in what the initial and boundary conditions are. There are statistical techniques that are applied to CFD simulations, but the application of these techniques is still in its infancy.

It is not clear cut which is the best tool to use. This will be problem dependent and also dependent on what level of accuracy is required. CFD models provide the most realistic representation of the physical and chemical processes and provide a wealth of information about the flow. The CFD technique is also more costly to use, in terms of computer resources and the length of time it takes to set-up and run a simulation. Zone models and empirical correlations are much quicker to use and can provide all the information one requires. Alternatively, the simpler models can be used as a screening tool and a smaller number of interesting cases can be selected for a more detailed investigation with a CFD tool.

The choice of which turbulence model to use when calculating a fluid flow is not clear-cut, i.e. it is problem dependent. Currently the LES technique probably places too great a demand on the computer resources to be used routinely. However, the LES technique is rapidly finding more widespread use as the computers are getting faster and cheaper. The most commonly used turbulence models are variants of the k-ε and k-ω models. The capabilities and weaknesses of these models are quite well understood and documented, so that one has a rough idea of the accuracy that can be expected.

No examples of modelling thermal oxidation of NOx in tunnels have been found in the open literature, which is in sharp contrast to the conversion of NOx in the atmosphere, which is a very active field. Two main reaction pathways in the atmosphere involve reactions with ozone and photochemical conversion due to absorption of photons of the right wavelength by the molecules. These reaction pathways are not likely to be of great importance in a tunnel, where the ozone level is expected to be low and there is no direct sunlight. Calculations of the conversion of NOx performed as part of the current study show that the timescale for the NOx concentration to get down to 1 ppm, for a high initial concentration (10 ppm or higher), is of the order of 50 hours or longer, while the timescale of the flow, based on the length of the tunnel and a typical ventilation velocity, is of the order of a few minutes. The thermal oxidation processes of NOx can therefore be neglected and the dispersion of NOx is the main mechanism, which determines the NOx concentration in the tunnel.
7 OVERALL CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

7.1.1 Instrumentation

Personal monitoring for NO is feasible at a datalogging resolution of 0.1 ppm with the Rae Systems MultiRae, although this instrument does not display at this resolution - its display resolution is only 1 ppm due to truncating of the decimal place. The cross sensitivity of the NO sensor to NO₂ is ~7 - 24% which is acceptable.

The Crowcon Triple Plus (incorporating both City Technology and Alphasense NO sensors) was not able to measure sub-ppm NO concentrations with sufficient accuracy.

Personal monitoring for NO₂ is feasible with sufficient resolution (0.1 ppm) with most current instrumentation, including all those investigated here.

The instrument Drager PAC III which was briefly investigated in an earlier study (Simpson and Hardwick, 2003) may also be suitable in tunnels if a resolution of 0.5 ppm is acceptable. Some response characteristics of the instrument are shown in Table 7.1 below and those for the sensor used in this instrument are listed in the Appendix (Table 8.6, Section 8.4).

Table 7.1: Measured responses of Drager PAC III to NO and NO₂

<table>
<thead>
<tr>
<th>Test gas concentration (ppm)</th>
<th>Test gas</th>
<th>Drager PAC III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NO sensor (ppm)</td>
</tr>
<tr>
<td>NO 25 ppm NO/N₂</td>
<td>±0.3</td>
<td>25.5</td>
</tr>
<tr>
<td>0.98 ppm NO/N₂</td>
<td>± 0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>NO₂ 36.6 ppm NO₂/air</td>
<td>± 1.8</td>
<td>2</td>
</tr>
<tr>
<td>5.46 ppm NO₂/air</td>
<td>± 0.27</td>
<td>0</td>
</tr>
<tr>
<td>0.83 ppm NO₂/air</td>
<td>± 0.04</td>
<td>0</td>
</tr>
</tbody>
</table>

It will not, however, be able to measure concentrations below 0.5 ppm NO with sufficient accuracy. The cross-sensitivity of the NO sensor to NO₂ is only significant at the high level of 36 ppm. Similarly cross-sensitivity of the NO₂ sensor to NO is only significant at the highest NO concentration.

The 2B Technologies NO Monitor has the resolution (<0.1 ppm) and low cross sensitivity to NO₂ (~2%) required to monitor sub-ppm concentrations of NO. However, it is not a portable monitor and has not been designed for rugged use.

The Teledyne-API M200A NOₓ Analyser has the resolution (<0.1 ppm) and low cross sensitivity (~1 - 3%) required to monitor sub-ppm concentrations of NO, NO₂ and NOₓ. It is useful as a fixed, reference instrument but the location and the sampling system would need to be carefully considered in view of its fragility.

Long-path optical instruments for NO (and NO₂) are increasingly being used and developed, putatively having sufficient resolution and stability for tunnel monitoring.
7.1.2 Environmental fate of NO (laboratory and field experiments)

Using the glass vessel to study NO oxidation kinetics, qualitative agreement was found between the experimental oxidation rate and that predicted by the model: the higher the initial NO concentration, the faster the NO decay rate.

The laboratory experiments showed that the conversion of NO is fairly rapid for high concentrations (order of 100 ppm) but this is not the case in relation to the timescale required to reduce the concentration to 1 ppm. Experiments and modelling of the kinetics of the thermal oxidation indicate that the timescale to reduce to a concentration of NO of 1 ppm is of the order of 50-100 hours, which is well in excess of the timescales associated with the dispersion of NOx via mechanical ventilation. The field tests in the gallery confirmed that NO levels around 1 ppm were persistent over this timescale.

In the glass vessel experiments, the NO concentration reduced at a slower rate than the model predicted, while the NO₂ concentration began to increase following the trend of the mathematically modelled values for a short time before reducing along the same trend as the NO concentration. Other factors such as adsorption on the walls of the vessel and the small but significant generation of NO from the NO₂ sensor, both of which it would be possible to correct for, may account for the discrepancy.

The dilution of the diesel fume within 0.5 m of the source to approximately 1% of the NO concentration at the source prevented any effective method of comparing the environmental fate of NO and NO₂ as a function of time and distance with a relatively unreactive species (CO) in the exhaust gas.

7.1.3 Ventilation & modelling

Cuts in CO emissions from vehicles have not been matched by a decrease in NOx levels. NO₂ concentrations must be taken into account when calculating ventilation flow rates.

Airflow rates necessary to dilute NO₂ can be calculated from the emission factors for NOx for different vehicle types, the mix of traffic and the traffic flow rate. Tunnel gradient may also need to be taken into account.

Tunnels with bi-directional traffic flows are generally regarded as the most difficult to ventilate. Ventilation might be improved if the traffic flows can be partitioned.

A review of the literature shows that the emphasis has been on the modelling of the photochemical (atmospheric) conversion of NO in the presence of O₃, and that only a couple of studies have dealt with other oxidation pathways for NO.

Modelling the fluid flow in tunnels may provide useful guidance on the ventilation requirements. Thermal oxidation of NO can be neglected in the model and dispersion of NOx is the main mechanism that determines the NOx concentration in the tunnel.

7.2 RECOMMENDATIONS

NO will be persistent in tunnels at concentrations around a few ppm and will therefore require measurement, in addition to NO₂, for personal protection. Some portable NO monitors are available, although not as many as is desirable, for NO; therefore this is currently feasible. Although NO:NO₂ ratios can be established generally in tunnels from fixed monitors, the ratio may vary from location to location and therefore may not be reliably used to estimate personal
exposure the concentration of one gas from the measurement of the other. As, typically, NO is 10% of the NOx concentration, more error will be generated in trying to estimate NO from NO2 (i.e. the reverse calculation to that usually performed in tunnels – estimation of NO2 from NO).

Gas detection manufacturers should be re-engaged (directly or via their trade association CoGDEM) to develop personal NO sensors/instruments capable of monitoring with display and datalogging resolution of 0.5 ppm or ideally 0.1 ppm resolution, and with sufficient stability in a tunnel environment to measure accurately around the recommended level.

Fixed installations for NO and NO2 play an important role in warning of build-up of NOx. They are and should be used to warn and help control NO and NO2 levels. Again they should have a resolution of better than 0.1 ppm and sufficient stability to monitor around and below the 1 ppm level. Long-path optical monitors show promise in this area and their application to tunnelling should be encouraged and evaluated.

The glass vessel used in the measurement of NO reactivity provides a controlled environment to investigate factors influencing NO decay. The reactivity of NO in actual diesel exhaust should provide further information on NO reactivity in actual exhaust mixtures. It will conveniently allow the influence on the NO reaction rate of such factors as NO concentration, O2 concentration, temperature, diesel type, UV radiation levels, volatile organic compounds in the exhaust, water vapour concentration, O3 concentration, total pressure, to be studied. However, the variability in the rate of oxidation of NO between runs needs to be better understood and reduced, if possible, in order to quantify the effect of the above-mentioned factors.

A series of further experiments in the Buxton gallery at higher NO concentrations should be performed to further investigate NO decay and compare with CO and/or CO2 measurements, as the measurements carried out in this report were inconclusive.

It was not possible to visit and install suitable monitors in an actual tunnel during this project. However, it would be informative to datalog readings over an extended period, eg of the order of a month, using the MultiRae, Drager and 2BT monitors to investigate their suitability and performance in the intended environment. It would also enable background and personal levels of NOx to be measured, providing the level of diesel engine activity was sufficiently high.

The usefulness of modelling fluid flow and NOx concentrations in tunnels should be further investigated. This will be simplified as the oxidation of NO to NO2 can be neglected in the calculations.
8 APPENDICES

8.1 PROPERTIES OF NO

8.1.1 Physico-chemical properties

NO is a colourless and odourless gas that is only slightly soluble in water. It is a by-product of combustion processes, arising from high temperature oxidation of molecular nitrogen from the combustion air, and from oxidation of nitrogen present in certain fuels such as coal and heavy oil. The ratio of NO to NO\textsubscript{2} in oxides of nitrogen (NO\textsubscript{x}) emitted from combustion sources is generally between 9:1 and 19:1.

NO is a free radical that will react with a wide range of molecules and it is readily oxidised to NO\textsubscript{2}. NO may be oxidized to NO\textsubscript{2} by atmospheric oxygen but at low NO concentrations this reaction is slow and is important only when concentrations of NO > 1 ppm (Boström, 1993); see also Appendix (Section 8.5) for further discussion. At lower concentrations NO can react with ozone to form NO\textsubscript{3} and molecular oxygen. NO can also react with other radical species present in photochemical smogs. In the absence of ozone arising from photochemical reactions, the conversion of NO to NO\textsubscript{2} in tunnel environments is much slower than in ambient air.

NO may also combine with NO\textsubscript{2} and water to form nitrous acid. In sunlight, atmospheric concentrations of HNO\textsubscript{2} are limited by the photolysis of HNO\textsubscript{2} to produce NO and hydroxyl radical, but higher concentrations can develop in indoor air. Nitrous acid is a weak reducing agent and is oxidized to nitrate only by strong chemical oxidants and by nitrifying bacteria.

8.1.2 Health effects

Pending the outcome of the current review of the UK Workplace Exposure Limits of nitrogen monoxide (NO) and nitrogen dioxide (NO\textsubscript{2}), both NO and NO\textsubscript{2} were subject to a CHAN (Chemical Hazard Alert Notice) of 1 ppm. A CHAN is guidance issued by the Health and Safety Executive the following of which, although not compulsory, is normally sufficient to ensure compliance with the law. Note that as from December 2006, CHANs have been suspended. The limits are 8-hour Time Weighted Average (TWA) values. Since the implementation of the COSHH Regulations in 1989, nitrogen monoxide and nitrogen dioxide have had Occupational Exposure Standards (OESs) of 25 ppm and 3 ppm for 8-hour TWAs respectively and 35 ppm and 5 ppm for short–term exposure limits respectively.

The Health and Safety Commission’s Working Group on the Assessment of Toxic Chemicals (WATCH) reviewed the evidence on the health effects of these substances and concluded that the OESs may not have been adequate to protect occupational health. The Health and Safety Commission decided therefore to withdraw them from EH40 as from April 2003. Studies in laboratory animals have shown that long-term exposure to low concentrations of nitrogen dioxide (less than 1 ppm) can cause lung damage in the form of emphysema. On the basis of available evidence WATCH concluded that, to protect workers against the possible development of emphysema, the 8-hour TWA exposure to NO\textsubscript{2} should not exceed 1 ppm. However the studies had also shown that the long-term exposure to low level concentrations of NO (in the region of 1 ppm) could also cause lung damage. WATCH therefore concluded that the long-term TWA exposure to NO should also not exceed 1 ppm.

Further information on the health effects of NO (and NO\textsubscript{2}) can be found in various reviews (WHO, 1997; SCOEL, 2003).
### 8.2 PRINCIPLES OF OPERATION AND SPECIFICATIONS OF NO AND NO₂ MONITORS.

Table 8.1 Principles of operation and the specifications of the more prevalent types of real-time instrument for NO and NO₂ (Walsh et al, 2005)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Instrument operating principle</th>
<th>Measurement range¹</th>
<th>Limit of detection</th>
<th>Precision</th>
<th>Response time $t_{50}$ (to 90%) (s)</th>
<th>Potential interferents</th>
<th>Types of instrument</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>electrochemical</td>
<td>0-250 ppm</td>
<td>&lt;1 ppm approx.</td>
<td>±2 ppm or 10% of reading</td>
<td>&lt;20</td>
<td>H₂S, NO₂, HCl, SO₂,</td>
<td>Personal, hand-held,</td>
<td>Electrochemical cell lifetime is 1-2 years. Most common method for occupational hygiene measurements.</td>
</tr>
<tr>
<td></td>
<td>chemiluminescence</td>
<td>0-50 ppb to 0-20 ppm</td>
<td>&lt;5 ppb</td>
<td>±2.5 ppb (accuracy ± 10% reading)</td>
<td>&lt;60 (t₉₀)</td>
<td>No major effects.</td>
<td>Transportable, fixed</td>
<td>Used in UK air quality network measurements. Based on reaction with ozone. Very accurate.</td>
</tr>
<tr>
<td></td>
<td>ultraviolet absorption photometry</td>
<td>0-100 ppm and greater for point monitors.</td>
<td>0.2 - 5 ppb for point monitors.</td>
<td>50 for point monitors.</td>
<td>Certain hydrocarbons.</td>
<td>Fixed</td>
<td>Open-path systems used for traffic tunnel and environmental monitoring. Used for process control, in situ stack gas analysis.</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>electrochemical</td>
<td>0-10 ppm</td>
<td>0.2 - 1 ppm</td>
<td>±0.3 ppm or 10% of reading</td>
<td>15-60</td>
<td>H₂S, SO₂ and possibly CO. These gases can have a negative effect of the response.</td>
<td>Personal, portable, transportable, fixed</td>
<td>Sensor lifetime 2 years. Used in variety of instruments because of low cost, low power, small size.</td>
</tr>
<tr>
<td></td>
<td>chemiluminescence</td>
<td>0-50 ppb to 0-20 ppm</td>
<td>&lt;5 ppb</td>
<td>3.5 ppb³</td>
<td>&lt;60</td>
<td>None but correction needed for NO.</td>
<td>Transportable, fixed</td>
<td>NO₂ converted to NO for measurement. Used in UK air quality network measurements.</td>
</tr>
<tr>
<td></td>
<td>ultraviolet-visible absorption photometry</td>
<td>0-50 ppm for point monitors; 0-1000 ppm for long-path monitors but depends on path length.</td>
<td>0.1 - 5 ppb for long-path monitors but depends on path length.</td>
<td>&lt;30</td>
<td>Possibly organic compounds</td>
<td>Fixed; flue gas analyser</td>
<td>Long path monitor used for air quality measurements.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>colorimetry (chemical cassette type)</td>
<td>0.4-50 ppm; 2-9999 ppb</td>
<td>depends on cassette, e.g. 2 ppb for high sensitivity; 0.3 ppb others.</td>
<td>longer response than other methods, e.g. &gt; 60 s</td>
<td>None usually (depending on reagent on cassette)</td>
<td>Transportable, fixed</td>
<td>Limited shelf life for cassettes.</td>
<td></td>
</tr>
</tbody>
</table>

¹Values are typical and are taken from a range of commercial instruments. There are obviously differences in some characteristics between different models therefore the values above should not be taken to apply to all models of a particular operating principle. Values should be taken as best case values as they are measured under ideal laboratory conditions. Operation in the field may impose greater constraints on the performance of the instruments. ² Usually a range of concentrations can be configured. The most appropriate for measurement of NO in the workplace are given. ³ This parameter is not usually shown in manufacturer's literature. However, an estimate can sometimes be made based on other data provided. ⁴ Data from "Air Pollution in the UK: 1997", AEAT-5303, AEA Technology Environment, February 2000.
Table 8.2: Specifications of some types of fixed real-time monitors using ultraviolet-visible absorption photometry (not selected for use in this investigation)

<table>
<thead>
<tr>
<th>Instrument</th>
<th>NO</th>
<th>NO₂</th>
<th>Measuring Path Length</th>
<th>Response Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vicotec 320 NO &amp; NO₂ Measuring Device</td>
<td>Range 0–45 ppm</td>
<td>Resolution/Min Detection Limit 100 ppb</td>
<td>Zero Drift ±0.5% of range per month</td>
<td>Range 0–3 ppm</td>
</tr>
<tr>
<td><a href="http://www.sick-maihak.com">www.sick-maihak.com</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opsis Long Path Air Quality Monitoring System</td>
<td>Range 0–8 ppm</td>
<td>Resolution/Min Detection Limit 3 ppb</td>
<td>Zero Drift ±2.4 ppb per month</td>
<td>Range 0–5 ppm</td>
</tr>
<tr>
<td><a href="http://www.opsis.se">www.opsis.se</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nova NO Monitor</td>
<td>Range 0–100 ppm</td>
<td>Resolution/Min Detection Limit 0.1 ppm</td>
<td>Zero Drift &lt;1 ppm</td>
<td>-</td>
</tr>
<tr>
<td><a href="http://www.tunnelsensors.com">www.tunnelsensors.com</a></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### SPECIFICATIONS OF GAS CYLINDERS USED AS NO AND NO₂ SOURCES

Table 8.3: Specifications of Gas Bottles used as NO and NO₂ Sources

#### NO

<table>
<thead>
<tr>
<th>Nominal Concentration</th>
<th>Certified Concentration</th>
<th>Balance Gas</th>
<th>Total NOₓ *</th>
<th>Accuracy</th>
<th>Cylinder Size</th>
<th>Cylinder No</th>
<th>Bottle ID No</th>
<th>Product Code</th>
<th>Certification Date</th>
<th>Use By Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td>0.98 ppm</td>
<td>N₂</td>
<td>1.02 ppm</td>
<td>1%</td>
<td>AV 10L</td>
<td>108319</td>
<td>1236</td>
<td>15087-AV-V</td>
<td>02/03/05</td>
<td>02/03/10</td>
</tr>
<tr>
<td>5 ppm</td>
<td>4.98 ppm</td>
<td>N₂</td>
<td>5.18 ppm</td>
<td>5%</td>
<td>AV 10L</td>
<td>162497</td>
<td>1951</td>
<td>152517-AV-S</td>
<td>13/03/06</td>
<td>13/03/11</td>
</tr>
<tr>
<td>25 ppm</td>
<td>25.4 ppm</td>
<td>N₂</td>
<td>25.5 ppm</td>
<td>5%</td>
<td>AV 10L</td>
<td>162953</td>
<td>1806</td>
<td>149414-AV-S</td>
<td>18/12/05</td>
<td>18/12/10</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>1040 ppm</td>
<td>N₂</td>
<td>1043 ppm</td>
<td>1%</td>
<td>AV 10L</td>
<td>164204</td>
<td>517</td>
<td>294516-AV-V</td>
<td>10/06/04</td>
<td>10/06/09</td>
</tr>
</tbody>
</table>

#### NO₂

<table>
<thead>
<tr>
<th>Nominal Concentration</th>
<th>Certified Concentration</th>
<th>Balance Gas</th>
<th>Accuracy</th>
<th>Cylinder Size</th>
<th>Cylinder No</th>
<th>Bottle ID No</th>
<th>Product Code</th>
<th>Certification Date</th>
<th>Use By Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td>0.830 ppm</td>
<td>Air</td>
<td>5%</td>
<td>AV 10L</td>
<td>108654</td>
<td>1237</td>
<td>152639-AV-S</td>
<td>18/04/05</td>
<td>18/04/10</td>
</tr>
<tr>
<td>5 ppm</td>
<td>5.46 ppm</td>
<td>Air</td>
<td>5%</td>
<td>AV 10L</td>
<td>164085</td>
<td>515</td>
<td>149732-AV-S</td>
<td>15/07/04</td>
<td>15/07/09</td>
</tr>
<tr>
<td>5 ppm</td>
<td>5.2 ppm</td>
<td>Air</td>
<td>5%</td>
<td>AV 10L</td>
<td>132985</td>
<td>2173</td>
<td>149732-AV-S</td>
<td>10/08/06</td>
<td>10/08/11</td>
</tr>
<tr>
<td>40 ppm</td>
<td>37.0 ppm</td>
<td>Air</td>
<td>5%</td>
<td>AV 10L</td>
<td>108555</td>
<td>1464</td>
<td>149096-AV-S</td>
<td>20/07/05</td>
<td>20/07/10</td>
</tr>
</tbody>
</table>

*Total NOₓ is NO + NO₂
8.4 PRINCIPLES OF OPERATION AND SPECIFICATIONS OF THE NO AND NO₂ REAL-TIME MONITORS SELECTED FOR EVALUATION

8.4.1 NO and NO₂ electrochemical sensors

8.4.1.1 MultiRAE NO and NO₂ electrochemical sensor data sheets

Table 8.4: MultiRAE NO electrochemical sensor data sheet (RAE, 2006)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conc.</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>300 ppm</td>
<td>0 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>5 ppm</td>
<td>0 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>25 ppm</td>
<td>2 - 9 ppm</td>
</tr>
<tr>
<td>ClO₂</td>
<td>1 ppm</td>
<td>-0.2 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>50 ppm</td>
<td>0 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>5 ppm</td>
<td>about 0.5 ppm</td>
</tr>
</tbody>
</table>

Table 8.5: MultiRAE NO₂ electrochemical sensor data sheet (RAE, 2006)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conc.</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>25 ppm</td>
<td>2.2 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>50 ppm</td>
<td>-0.2 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>300 ppm</td>
<td>-0.2 ppm</td>
</tr>
<tr>
<td>H₂S</td>
<td>25 ppm</td>
<td>-2.2 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>5 ppm</td>
<td>0 ppm</td>
</tr>
<tr>
<td>ClO₂</td>
<td>1 ppm</td>
<td>-1 ppm</td>
</tr>
<tr>
<td>ClO₃</td>
<td>1 ppm</td>
<td>-2 ppm</td>
</tr>
</tbody>
</table>

* Causes a transient drop upon exposure to this compound.
### Alphasense, Citicel and Drager NO and NO<sub>2</sub> electrochemical sensor data

Table 8.6: Electrochemical NO parameters (typical values for sensors for portable instruments) (Walsh et al, 2005)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alphasense NO2-A1</th>
<th>Alphasense NO2-B1</th>
<th>CTL 7 NT</th>
<th>CTL 4NT</th>
<th>Sensoric NO 3E 100</th>
<th>Drager XS EC NO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time t&lt;sub&gt;90&lt;/sub&gt; (s)</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;30</td>
<td>&lt;15</td>
<td>&lt;20</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Resolution (ppm)</td>
<td>&lt;0.2</td>
<td>&lt;0.15</td>
<td>0.5</td>
<td>0.5</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Range (full scale) (ppm)</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>100</td>
<td>100 or 500</td>
<td>200</td>
</tr>
<tr>
<td>Operating life (month)</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>36</td>
<td>24</td>
<td>&gt;18</td>
</tr>
<tr>
<td>% Sensitivity @ -20°C, normalised to 22°C</td>
<td>83 to 93</td>
<td>87 to 95</td>
<td>65 to 85</td>
<td>82 to 85</td>
<td>&lt;0.2% value/°C</td>
<td></td>
</tr>
<tr>
<td>Temperature coefficient (sensitivity)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature coefficient (zero)</td>
<td>3 to 1</td>
<td>6 to 10</td>
<td>5.5 to 8</td>
<td>7 to 13</td>
<td>&lt;0.01 ppm/°C</td>
<td></td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt; sensitivity (% measured gas)</td>
<td>&lt;2</td>
<td>&lt;4</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>&lt;5</td>
</tr>
<tr>
<td>CO sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt; sensitivity (% measured gas)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>35</td>
<td>&lt;5</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; sensitivity (% measured gas)</td>
<td>nd**</td>
<td>nd</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S sensitivity (% measured gas)</td>
<td>&lt;15</td>
<td>&lt;5</td>
<td>0</td>
<td>0</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>-30 to 50</td>
<td>-30 to 50</td>
<td>-20 to 50</td>
<td>-20 to 50</td>
<td>-15 to 40</td>
<td>-40 to 50</td>
</tr>
<tr>
<td>Pressure range (kPa)</td>
<td>80 to 120</td>
<td>80 to 120</td>
<td>90 to 110</td>
<td>90 to 110</td>
<td>70 to 130</td>
<td></td>
</tr>
<tr>
<td>Humidity range (%rh)</td>
<td>15 to 90</td>
<td>15-90</td>
<td>15 to 90</td>
<td>15 to 90</td>
<td>20 to 90</td>
<td>10 to 90</td>
</tr>
</tbody>
</table>

* with replaceable selective filter.
** nd – not detected
Table 8.7: Electrochemical \( \text{NO}_2 \) (sensors for portable instruments) (Walsh et al, 2005)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alphasense NO2-A1</th>
<th>Alphasense NO2-B1</th>
<th>CTL 7 NDH</th>
<th>CTL 4ND</th>
<th>Sensoric NO2 3E 50</th>
<th>Drager XS EC NO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time ( t_{90} ) (s)</td>
<td>&lt;40 (10R)</td>
<td>&lt;40 (33R)</td>
<td>&lt;40</td>
<td>&lt;25</td>
<td>&lt;30</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Resolution (ppm)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Range (full scale) (ppm)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Operating life (month)</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>&gt;24</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Temperature coefficient (sensitivity)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% sensitivity @ 50°C, normalised to 20°C</td>
<td>101 to 110</td>
<td>78 to 93</td>
<td>100 to 103</td>
<td>97 to 105</td>
<td>0.5% K</td>
<td>&lt;5% value</td>
</tr>
<tr>
<td>Temperature coefficient (zero) @ 50°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zero @ 50°C, normalised to zero offset at 20°C (equivalent ppm)</td>
<td>0 to -0.4</td>
<td>&lt;0.1 to -0.25</td>
<td>-0.3 to -0.6</td>
<td>0 to -0.3</td>
<td>&lt;1 ppm</td>
<td>&lt;0.5 ppm</td>
</tr>
<tr>
<td>SO(_2) sensitivity (% measured gas)</td>
<td>&lt;2.5</td>
<td>&lt;2</td>
<td>&lt;-1</td>
<td>0</td>
<td>25</td>
<td>&lt;100</td>
</tr>
<tr>
<td>NO sensitivity (% measured gas)</td>
<td>&lt;0.5</td>
<td>&lt;+0.5</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>CO sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.5</td>
<td>0</td>
<td>0</td>
<td>nd</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Cl(_2) sensitivity (% measured gas)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H(_2) sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0</td>
<td>nd*</td>
<td>0</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>C(_2)H(_4) sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0</td>
<td>nd</td>
<td>nd</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>H(_2)S sensitivity (% measured gas)</td>
<td>&lt;-40</td>
<td>-100</td>
<td>&lt;-10</td>
<td>-8</td>
<td>nd</td>
<td>&lt;500</td>
</tr>
<tr>
<td>NH(_3) sensitivity (% measured gas)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0 to -10</td>
<td>nd</td>
<td>-0.1</td>
<td>nd</td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>-20 to 50</td>
<td>-30 to 50</td>
<td>-20 to 50</td>
<td>-20 to 50</td>
<td>-20 to 40</td>
<td>-40 to 50</td>
</tr>
<tr>
<td>Pressure range (kPa)</td>
<td>80 to 120</td>
<td>80 to 120</td>
<td>90 to 110</td>
<td>90 to 110</td>
<td>70 to 130</td>
<td></td>
</tr>
<tr>
<td>Humidity range (%rh)</td>
<td>15 to 90</td>
<td>15 to 90</td>
<td>15 to 90</td>
<td>15 to 90</td>
<td>10 to 95</td>
<td>10 to 90</td>
</tr>
</tbody>
</table>

* nd – not detected
8.4.1.3 **Principle of electrochemical sensor operation**

The basic form of electrochemical sensor has a sensing electrode and a counter electrode separated by a thin layer of electrolyte and connected externally by a low resistance circuit [9]. Gas is oxidised (as in the NO sensor) or reduced (as in the NO₂ sensor) on contact with the sensing electrode causing the potential at that electrode to change and a measurable current, proportional to the concentration of gas, to flow through the external circuit to the counter electrode.

The reaction mechanisms of the NO and NO₂ sensors can be represented in the standard chemical equations 8.1 and 8.2 below (City Technology, 1999).

\[
\text{NO} + 2\text{H}_2\text{O} \rightarrow \text{HNO}_3 + 3\text{H}^+ + 3\text{e}^- \quad 8.1
\]

\[
\text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O} \quad 8.2
\]

8.4.2 **2B Technologies NO Monitor**

8.4.2.1 **2B Technologies NO Monitor data sheet**

<table>
<thead>
<tr>
<th>Power Requirements</th>
<th>11-14 V DC, nominally 0.9 A at 12 V, 11 watt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>3.5” x 8.3” x 11.6”</td>
</tr>
<tr>
<td>Weight</td>
<td>6.4 lbs (2.9 kg)</td>
</tr>
<tr>
<td>Precision (10-s measurements)</td>
<td>higher of 2.5 ppb or 2%</td>
</tr>
<tr>
<td>Accuracy</td>
<td>higher of 1 ppb or 1%</td>
</tr>
<tr>
<td>Data Transmission</td>
<td>4800 baud, 8 bits, no parity, 1 stop bit</td>
</tr>
</tbody>
</table>

8.4.2.2 **Principle of 2B Technologies NO Monitor operation**

The principle of operation is based on the quantitative reaction of NO with ozone (O₃) as described in Equation 8.3 (2B Technologies, 2005).

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + h\nu(\text{UV}) \quad (8.3)
\]

Inside the NO monitor a known constant small concentration of O₃ (3 – 5 ppm) is introduced into the sampled gas. The reduction in O₃ due to the above reaction is equal to the concentration of NO. The O₃ is detected by measuring the UV absorption at a wavelength of 254 nm.
8.4.3 API M200A NOx Analyser NO & NO2 Monitor

8.4.3.1 M200A NOx Analyser NO & NO2 Monitor data sheet

Table 8.9: M200A NOx Analyser NO & NO2 Monitor data sheet

<table>
<thead>
<tr>
<th>Description</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ranges</td>
<td>In 1 ppb increments from 50 ppb to 20,000 ppb</td>
</tr>
<tr>
<td>Range Mode</td>
<td>Single, Independent, AutoRange</td>
</tr>
<tr>
<td>Noise at Zero</td>
<td>0.2 ppb RMS</td>
</tr>
<tr>
<td>Noise at Span</td>
<td>&lt;0.5% of reading above 50 ppb</td>
</tr>
<tr>
<td>Lower Detectable Limit</td>
<td>0.4 ppb RMS</td>
</tr>
<tr>
<td>Zero Drift</td>
<td>&lt;0.5 ppb/24 hours</td>
</tr>
<tr>
<td>Zero Drift</td>
<td>1 ppb/7 days</td>
</tr>
<tr>
<td>Span Drift</td>
<td>&lt;0.5% FS/7 days</td>
</tr>
<tr>
<td>Lag Time</td>
<td>20 sec</td>
</tr>
<tr>
<td>Rise Time</td>
<td>95% in &lt;60 sec</td>
</tr>
<tr>
<td>Fall Time</td>
<td>95% in &lt;60 sec</td>
</tr>
<tr>
<td>Sample Flow Rate</td>
<td>500 cc/min. ± 10%</td>
</tr>
<tr>
<td>Linearity</td>
<td>1% of full scale</td>
</tr>
<tr>
<td>Precision</td>
<td>0.5% of reading</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>5-40°C</td>
</tr>
<tr>
<td>Temp Coefficient</td>
<td>&lt; 0.1% per °C</td>
</tr>
<tr>
<td>Humidity</td>
<td>0-95% RH non-condensing</td>
</tr>
<tr>
<td>Voltage Coefficient</td>
<td>&lt; 0.1% per V</td>
</tr>
<tr>
<td>Dimensions HxWxD</td>
<td>7&quot; x 17&quot; x 23.6&quot; (18cm x 43cm x 61cm)</td>
</tr>
<tr>
<td>Weight, Analyzer</td>
<td>43 lbs (20 kg) w/external pump</td>
</tr>
<tr>
<td>Weight, Analyzer</td>
<td>55 lbs (25 kg) w/internal pump</td>
</tr>
<tr>
<td>Weight, Ext Pump Pack</td>
<td>16 lbs (7 kg)</td>
</tr>
<tr>
<td>Weight, Internal Pump</td>
<td>5 lbs (2 kg)</td>
</tr>
<tr>
<td>Power, Analyzer</td>
<td>100 V ~ 50/60 Hz, 120V ~ 60 Hz, 220 V ~ 50 Hz, 240 V ~ 50 Hz, 125 watts</td>
</tr>
<tr>
<td>Power, Analyzer 3</td>
<td>230 V ~ 50 Hz, 2.5A peak</td>
</tr>
<tr>
<td>Power, Ext Pump</td>
<td>110 V ~ 60 Hz, 220V ~ 50 Hz, 240V ~ 50Hz, 295 watts</td>
</tr>
<tr>
<td>Power, Ext Pump 3</td>
<td>230 V ~ 50 Hz, 2.5A peak</td>
</tr>
<tr>
<td>Power, Int Pump</td>
<td>110 V/50/60 Hz, 60 watts</td>
</tr>
<tr>
<td>Environmental</td>
<td>Installation Category (Over-voltage Category) II Pollution Degree 2</td>
</tr>
<tr>
<td>Recorder Output 4</td>
<td>0-100 mV, 0-1, 5, 10v</td>
</tr>
<tr>
<td>Analog Resolution</td>
<td>1 part in 1024 of selected voltage or current range</td>
</tr>
<tr>
<td>Status Option</td>
<td>12 Status Outputs from opto-isolator</td>
</tr>
<tr>
<td>Measurement Units</td>
<td>ppb, ppm, ug/m³, mg/m³</td>
</tr>
</tbody>
</table>

1. As defined by USEPA.
2. Defined as twice the zero noise level.
3. At constant temperature and voltage.
4. Bi-polar
5. Electrical rating for CE Mark compliance.

8.4.3.2 Principle of M200A NOx Analyser NO & NO2 Monitor operation

The principle of operation is based on the measurement of the chemiluminescent emission of radiation following reaction of NO with O3 and is proportional to the NO concentration (API, 1999). The quantitative reaction of NO with O3 is as described in Equation 8.3. However, as the analysis is based on NO measurement, it is necessary to convert NO2 to NO. This conversion is performed internally by means of a molybdenum converter, a schematic diagram of which is shown in Figure 8.1, and externally by the use of an API Model 501 thermal converter placed in the sample stream.
Using Molybdenum Converter

Figure 8.1: Schematic diagram of M200A NOx Analyser NO & NO₂ Monitor Operation

To detect the NO concentration in a gas sample the selector valve will open the channel which routes the sample directly to the NO analyser (blue route in Figure 8.1) for ~5 seconds, where the NO is detected.

To detect the NO₂ concentration in a gas sample the selector valve opens the channel which routes the sample to the NO analyser via a molybdenum converter (red route in Figure 8.1) for ~5 seconds. The molybdenum converter reduces the NO₂ in the gas sample as described in Equation 8.4.

\[ 3\text{NO}_2 + Mo \rightarrow 3\text{NO} + MoO_3 \]  

(8.4)

The NO analyser detects the original NO in the sample and the converted NO as total NOₓ, and subtracts the NO detected on the NO cycle from this to yield the NO₂ concentration in the sample. The instrument cycles through the two

Using API Model 501 Thermal Converter

The API Model 501 Thermal Converter (API, 1995) allows the conversion of greater quantities of NO₂ (up to 250 ppm). The gas sample is directed through a hot stainless steel tube at 700°C, converting the NO₂ to NO catalytically as described in Equation 8.5.

\[ 2\text{NO}_2 + O_2 \rightarrow 2\text{NO} + 2O_2 \]  

(8.5)
8.5 ENVIRONMENTAL FATE OF NO

The reactions of NO upon emission from diesel exhaust, during welding and cutting processes or an explosive charge are additional factors to be considered when designing a monitoring strategy, which may then be used to initiate controls such as increasing ventilation and vehicle maintenance. In ambient air, the principal reactions of NO are with oxygen and ozone, both resulting in a reduction of the NO concentration with the concomitant formation of nitrogen dioxide (and, subsequently, nitrous and nitric acid by reaction of reactants and products with water vapour).

Thermal oxidation of NO with oxygen is much slower than with ozone and other reactions (see Table 8.10 in the Annex to this section). In a tunnel, therefore, where ozone levels are typically very low compared to NO levels (in contrast to the outdoor environment, (Leighton, 1961)), then the thermal oxidation reaction dominates. The basic reaction is:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]  \hspace{1cm} (8.6)

This proceeds as third-order reaction where the rate of NO reaction (equal to the rate of NO\textsubscript{2} production) is given by:

\[ \text{Rate} = 2k[\text{NO}]^2[\text{O}_2] \]  \hspace{1cm} (8.7)

where \(k\) is the rate constant (approximately \(7.10^3\) litre\textsuperscript{3}.mole\textsuperscript{2}.s\textsuperscript{-1}) and [NO] and [O\textsubscript{2}] are the NO and oxygen concentrations respectively\textsuperscript{2}. The reaction is therefore proportional to the square of the NO concentration if the oxygen concentration is assumed to be constant. When ppm units are used for NO or NO\textsubscript{2} and oxygen (in normal air the oxygen concentration is \(2.1\times10^5\) ppm) in Equation 8.7 above, then the rate constant is converted to:

\[ k_1 = k \frac{P}{RT} 10^{12} \]  \hspace{1cm} (8.8)

where \(P\) is the total atmospheric pressure in bar, \(R\) is the ideal gas constant (0.0821 litre.bar.mole\textsuperscript{-1}.K\textsuperscript{-1}) and \(T\) is the temperature (K). Consequently, at 298 K (25 °C)

\[ \text{Rate (ppm.s}^{-1}) = 4.92\times10^6[\text{NO/ppm}]^2 \]  \hspace{1cm} (8.9)

The fraction of NO reacting (or NO\textsubscript{2} being produced) as a function of time can be obtained by integrating Equation 8.9, which gives:

\[ t = \frac{(f(1-f))/(4.92\times10^6[\text{NO}]_0)} \]  \hspace{1cm} (8.10)

where \(t\) is the time (in seconds) at which a fraction \(f\) of NO, whose initial concentration (ppm) is \([\text{NO}]_0\), has become NO\textsubscript{2}, i.e. \(f = [\text{NO}_2]/[\text{NO}]_0\). Figure 8.2 shows the oxidation rate of NO for various initial concentrations. The time required for the conversion of a certain fraction of NO to NO\textsubscript{2} (e.g. the half-life, where \(f = 0.5\)) is inversely proportional to the initial NO concentration and the rate constant.
It can be seen that NO, once formed, persists at concentrations around the CHAN level of 1 ppm for significant periods (>24 hr).

The rate constant $k$ appears to be slightly negatively dependent on temperature (Tsukahara et al., 1999; Lindqvist et al., 1982). Around ambient temperature, the rate decreases by less than 1%/°C rise. Also, most studies (Tsukahara et al., 1999) agree that the rate constant is independent of variations in the total pressure, the absolute NO concentration or the NO:O$_2$ ratio (up to a thousand-fold variation).

The rate is directly proportional to the oxygen concentration (see Equation 8.7), although normally the oxygen concentration is not expected to deviate significantly from approximately 21%.

The above discussion relates, however, to ideal conditions with the minimum of impurities or additional factors. These have to be considered when modelling the environmental fate of NO in the workplace, e.g. in tunnels as they may affect the NO reaction rate, for example:

- presence of other gases, e.g. water vapour, oxidants other than oxygen;
- presence of aerosols and other surfaces;
- sunlight.

For water vapour, the majority of laboratory studies (Tsukahara et al., 1999) found that the rate constant is not affected by humidity (up to 90 %RH). Since water vapour reacts with NO$_2$ but not with NO, it is expected that the presence of water in NO/O$_2$ reaction systems will shift the equilibrium towards products such as oxyacids of nitrogen but will not change the rate at which NO is oxidised.

The influence of other factors is relatively unknown. A study has indicated (Lindqvist et al., 1982) that the presence of aerosols, at concentrations likely to be encountered in practice, does not
substantially influence the rate of oxidation of NO. Street surface materials (salt, snow, road dust) had a more significant influence, typically increasing the rate by 50% at –2 ºC. Sunlight appears not to affect the rate (Lindqvist et al., 1982).

Guidance by the Highways Agency (Highways Agency, 1999) on ventilation for tunnels for road users has been produced which assumes that the initial emission is solely NO and that this subsequently converts to NO₂ with a half-life of 1 week. Using Equation 8.10, this would be equivalent to an initial concentration of approximately 350 ppb NO.

Annex

Table 8.10 lists a number of important reactions involving NOₓ and other relevant chemical species, but not involving NO and molecular oxygen, taken from Seinfeld and Pandis (1998).

**Table 8.10 Important reactions involving NOₓ and other relevant chemical species, Seinfeld and Pandis (1998)**

\[
\begin{align*}
&\text{NO}_2 + h\nu (\lambda < 424 \text{ nm}) \rightarrow \text{NO} + \text{O}^- \quad (R.1) \\
&\text{O}^- + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (R.2) \\
&\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (R.3) \\
&\text{O}^- + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \quad (R.4) \\
&\text{O}^- + \text{NO}_2 + \text{M} \rightarrow \text{NO}_2 + \text{M} \quad (R.5) \\
&\text{NO} + \text{NO}_3 \rightarrow 2 \text{NO}_2 \quad (R.6) \\
&\text{O}^- + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} \quad (R.7) \\
&\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (R.8) \\
&\text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2 \quad (R.9) \\
&\text{O}_3 + h\nu \rightarrow \text{O}^{(1)}\text{O} + \text{O}_2 \quad (R.10) \\
&\text{O}^{(1)}\text{O} + \text{M} \rightarrow \text{O}^- + \text{M} \quad (R.11) \\
&\text{O}^{(1)}\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{OH}^- \quad (R.12) \\
&\text{CO} + \text{OH}^- \rightarrow \text{CO}_2 + \text{H}^- \quad (R.13) \\
&\text{H}^- + \text{O}_2 + \text{M} \rightarrow \text{HO}_2^- + \text{M} \quad (R.14) \\
&\text{CO} + \text{OH}^- \rightarrow \text{CO}_2 + \text{HO}_2^- \quad (R.15) \\
&\text{HO}_2^- + \text{NO} \rightarrow \text{NO}_2 + \text{OH}^- \quad (R.16) \\
&\text{OH}^- + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (R.17) \\
&\text{HCHO} + h\nu \rightarrow \text{H}^- + \text{HCO} \rightarrow \text{H}_2 + \text{CO} \quad (R18a) \\
&\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \quad (R.19) \\
&\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2^- + \text{CO} \quad (R.20) \\
&\text{HCHO} + h\nu \rightarrow 2\text{HO}_2^- + \text{CO} \rightarrow \text{H}_2 + \text{CO} \quad (R.21a) \\
&\text{HCHO} + \text{OH}^- \rightarrow \text{HO}_2^- + \text{CO} + \text{H}_2\text{O} \quad (R.22)
\end{align*}
\]
\[ O_3 + h\nu \Delta O_2 + O(1^D) \quad \text{(R.23)} \]
\[ O(1^D) + H_2O \Delta 2OH^- \quad \text{(R.24)} \]
\[ CH_4 + OH^- \Delta CH_3^- + H_2O \quad \text{(R.25)} \]
\[ CH_3^- + O_2 + M \Delta CH_3O_2^- + M \quad \text{(R.26)} \]
\[ CH_3O_2^- + NO \Delta CH_3O^- + NO_2 \quad \text{(R.27)} \]
\[ HO_2^- + NO \Delta NO_2 + OH^- \quad \text{(R.28)} \]
\[ CH_3O_2^- + NO_2 + M \Delta CH_3OOONO_2 + M \quad \text{(R.29)} \]
\[ CH_3O_2^- + HO_2^- \Delta CH_3OOH + O_2 \quad \text{(R.30)} \]
\[ CH_3OOH + h\nu \Delta CH_3OOH + O_2 \quad \text{(R.31)} \]
\[ CH_3OOH + OH^- \rightarrow H_2O + CH_3O_2^- \quad \text{(R.32a)} \]
\[ \quad \rightarrow H_2O + CH_3OOH^- \quad \text{(R.32b)} \]
\[ CH_3OOH + H_2O \Delta HCHO + OH^- \quad \text{(R.33)} \]
\[ CH_3O^- + O_2 \Delta HCHO + HO_2^- \quad \text{(R.34)} \]
\[ HO_2^- + HO_2^- \Delta H_2O_2 + O_2 \quad \text{(R.35)} \]
\[ H_2O_2 + OH^- \Delta H_2O + HO_2^- \quad \text{(R.36)} \]
\[ H_2O_2 + h\nu \Delta 2OH^- \quad \text{(R.37)} \]
\[ NO_2 + O_3 \Delta NO_3 + O_2 \quad \text{(R.38)} \]
\[ NO_3^- + h\nu (\lambda < 700 \text{ nm}) \Delta NO + O_2 \quad \text{(R.39)} \]
\[ NO_3^- + h\nu (\lambda < 580 \text{ nm}) \Delta NO_2 + O^- \quad \text{(R.40)} \]
\[ N_2O_5 + H_2O(s) \Delta 2HNO_3 \quad \text{(R.41)} \]
\[ HNO_3 + h\nu \Delta NO_2 + OH^- \quad \text{(R.42)} \]
8.6 CALCULATION OF VOLUME OF DIESEL FUME GENERATED FROM ENGINE

Capacity: 7 L
No of Cylinders: 4
Ignition Cycle: 4 stroke
Bore (b): 12.07 cm
Stroke(s): 15.24 cm
Compression Ratio (cr): 21:1
Each cylinder will have exhausted once in 2 revolutions of the engine

Volume of 1 cylinder (V₁):

\[ V₁ = \pi \left( \frac{b}{2} \right)^2 s = 1743.77 \text{ cc} \]

Volume of 1 cylinder exhausted (\(V_{E1}\)) per 2 revolutions at compression ration of 21:1:

\[ V_{E1} = \frac{20}{21} \times V₁ = 1660.73 \text{ cc} \]
\[ = 1.66 \text{ L} \]

Volume of all 4 cylinders exhausted (\(V_{E4}\)) per 2 revolutions:

\[ V_{E4} = V_{E1} \times 4 = 6.64 \text{ L} \]

∴ for 950 rpm: flow rate of fume

\[ = V_{E4} \times \frac{950}{2} \text{ L/min} \]
\[ = 6.64 \times \frac{950}{2} \text{ L/min} \]
\[ = 3154 \text{ L/min} \]

∴ for 1500 rpm: flow rate of fume

\[ = V_{E4} \times \frac{1500}{2} \text{ L/min} \]
\[ = 6.64 \times \frac{1500}{2} \text{ L/min} \]
\[ = 4980 \text{ L/min} \]
## 8.7 Concentrations of NO, NO2, NOx and CO in Diesel Exhaust Fume

Table 8.11: Concentrations of NO, NO2, NOx and CO in diesel exhaust fume (Dabill et al, 2004)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Engine Mode</th>
<th>Raw Exhaust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra Low Sulphur Diesel (ULSD)</td>
<td></td>
<td>Nitric Oxide (ppm)</td>
</tr>
<tr>
<td>Ultra Low Sulphur Diesel (ULSD)</td>
<td>Low Idle</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>Int. Speed / 50% load</td>
<td>514</td>
</tr>
<tr>
<td></td>
<td>Rated Speed / 50% load</td>
<td>501</td>
</tr>
<tr>
<td>Rapeseed Methyl Ester (RME)</td>
<td>Low Idle</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>Int. Speed / 50% load</td>
<td>542</td>
</tr>
<tr>
<td></td>
<td>Rated Speed / 50% load</td>
<td>525</td>
</tr>
<tr>
<td>Standard Gasoil</td>
<td>Low Idle</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>Int. Speed / 50% load</td>
<td>638</td>
</tr>
<tr>
<td></td>
<td>Rated Speed / 50% load</td>
<td>594</td>
</tr>
</tbody>
</table>
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**GLOSSARY**

NO$_2$  Collective term for NO and NO$_2$
NO  Nitric oxide, $M_w = 30.0061$ g mol$^{-1}$
NO$_2$  Nitrogen dioxide, $M_w = 46.0055$ g mol$^{-1}$
NO$_3$  Nitrogen trioxide, $M_w = 62.0049$ g mol$^{-1}$
N$_2$O$_5$  Dinitrogen pentoxide, $M_w = 108.0104$ g mol$^{-1}$
$E_a$  Activation energy, J K$^{-1}$
R  Universal gas constant, $R = 8.31472$ J mol$^{-1}$ K$^{-1}$
T  Temperature, K

$y^+$  Non-dimensionalised wall-normal distance, $y^+ = \frac{\mu^* y}{v} = \frac{y}{\sqrt{\frac{\mu}{\rho} \frac{\partial u}{\partial y}}}_{y=0}$

$h$  Planck’s constant, $h = 6.626068 \cdot 10^{-34}$ J s$^{-1}$
v  Frequency of light
Real time monitoring and environmental fate of oxides of nitrogen in the construction industry

The UK Workplace Exposure Limits of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are currently under review. In the meantime, both NO and NO\textsubscript{2} were subjected to a CHAN (Chemical Hazard Awareness Notice) of 1 ppm (8-hr time-weighted average, TWA), significantly lower than the previous occupational exposure standards. Note that all CHANs have now been suspended (from December 2006). Exposure to these oxides of nitrogen commonly arises in the construction industry from diesel engine exhaust emissions and from the use of explosives. This project addresses (a) the effectiveness of real-time monitors at these concentration levels and (b) the environmental fate of NO and NO\textsubscript{2} in the construction environment.

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