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**A Pilot Study of Formaldehyde
Monitoring in Ambient Air**

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Centre for Optical and Environmental Metrology
National Physical Laboratory

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1. INTRODUCTION

This report describes a pilot study on aldehyde monitoring in ambient air at a number of locations in the UK. The pilot study was carried out by the National Physical Laboratory (NPL) on behalf of the Department of the Environment, Transport and the Regions (DETR) during the period January - March 2000.

Aldehydes form an homologous series of oxygenated organic compounds found in both the natural and man made environment. They are important contaminants in ambient air through their rôle in atmospheric chemical processes. Major anthropogenic emissions in ambient air originate from motor vehicles and stationary combustion of fossil fuel in coal burning for domestic heating. Vehicle engines not fitted with catalytic converters are the most important anthropogenic source. In comparative terms emission from the combustion of diesel fuel is greater than that from petrol. Other sources include the use of formaldehyde in industry as a chemical reagent and in the production of formaldehyde resins and foams.

Some aldehydes are of special concern because of their potential impact on air pollution and human health; in this context formaldehyde is the most widely studied aldehyde species. The predominant health effects are eye, skin and respiratory irritation, and at particularly high levels they are associated with neurophysiological and behavioural effects.

There is also epidemiological evidence of associations between relatively high occupational exposure to formaldehyde and nasopharyngeal and sinonasal cancers. However, based on the limited data that are available it is classed in the USA as an A2 suspected human carcinogen, whilst the International Agency for Research on Cancer (IARC) class formaldehyde in group 2A as a probable human carcinogen (IARC, 1995). Although formaldehyde in ambient air is not a regulated compound it has been classed by the European Union as a category 3 carcinogen which requires labeling with the risk phrase 'risk of irreversible effects' (EEC, 1993).

According to the World Health Organisation Air Quality Guidelines (WHO, 1987), human responses start with an odour threshold of about $60 \mu\text{g m}^{-3}$ and a threshold of irritation of about $100 \mu\text{g m}^{-3}$. The Institute of Environment and Health (IEH, 1996) recommended that an ambient maximum concentration of $100 \mu\text{g m}^{-3}$ averaged over 30 minutes would protect most people against transient sensory effects due to formaldehyde in indoor environments although some people may be sensitive at, or below, this level.

Many countries have set a formaldehyde standard for occupational exposure and WHO have set the air quality guideline value of 0.1 mg m^{-3} ($100 \mu\text{g m}^{-3}$), as a 30 minute average for indoor air in non-industrial buildings, to avoid the complaints of sensitive people (WHO, 1987).

There are few data available on background concentrations of formaldehyde in ambient air but a recent unpublished review suggested that such data as are available indicate an average annual level of about $1.5 \mu\text{g m}^{-3}$. This value ranges between 0.71 and $2.59 \mu\text{g m}^{-3}$ for the ten months in which measurements were made, with the highest being observed in the summer months.

In urban environments, outdoor ambient air concentrations are more variable and depend on local meteorology, irradiation intensity and traffic density. Annual averages are usually between 1 and 20 $\mu\text{g}\text{m}^{-3}$. However, in certain circumstances, such as short term peaks in traffic flow or severe temperature inversions, concentrations can approach the WHO air quality guideline value of 100 $\mu\text{g}\text{m}^{-3}$ (WHO 1987).

Measurements at all locations suggested seasonal and diurnal variations in formaldehyde concentrations reflecting changes both in meteorological conditions and in photochemical production sources. These variations were not apparent in other aldehyde species.

2. OBJECTIVES

Given the concerns over the adverse health effects of aldehydes, the UK Department of Health intend to review the effects of aldehydes as part of an ongoing review of pollutants. In addition, given the lack of comprehensive data on aldehyde concentrations in outdoor environments in the UK, the study reported here aims to inform this review. The aim of the short term pilot study (Phase 1) reported here is to determine the optimal methodologies for measuring aldehyde concentrations in ambient air and analyse parameters for a larger (Phase 2) study should a larger study be thought necessary. The objectives of this pilot study are therefore:

- To determine the most appropriate measurement techniques and strategies for measuring aldehyde concentrations in ambient air as part of a larger study and ;
- To determine, through measurements at selected UK sites, the most important parameters (eg. site location, time resolution, measurement timescales) to be considered in planning the Phase 2 measurements.

3. MEASUREMENT TECHNIQUES AND MEASUREMENT SCHEDULE

Three techniques were used for the aldehyde measurements reported here: a continuous fluorescence based technique; pumped samplers using the derivatisation of 2,4 dinitrophenyl hydrazine (DNPH); and diffusive 'badge' samplers using DNPH. These techniques are described below. In this report, concentrations are given in dimensions mass.volume⁻³, normally $\mu\text{g}\text{m}^{-3}$ or mgm^{-3} , referenced to atmospheric pressure and a temperature of 25°C.

3.1 THE CONTINUOUS FORMALDEHYDE ANALYSER

3.1.1 Measurement principle

The monitoring instrument used to measure the formaldehyde concentration at each site was the AL4021 Formaldehyde Analyser manufactured by Aerolaser, Germany. The detection principle

used by this analyser is based on the liquid phase reaction of formaldehyde with acetylacetone (2,4-pentadione) and an amine, such as NH_3 . This reaction, known as the Hantzsch reaction, produces α - α' -dimethyl- β - β' -diacetyl-pyridine which can be excited at 253 and 400 nm and the resulting fluorescence detected at 510 nm. The intensity of the fluorescence is proportional to the concentration of formaldehyde present in the initial sample. The Hantzsch reaction is shown in Figure 1.

The use of the Hantzsch reaction increases the sensitivity to formaldehyde by a factor of 400 over the current fluorescent formaldehyde analysers which employ direct excitation of the formaldehyde. The Hantzsch reaction has to be carried out in the liquid phase and, therefore, vapour phase formaldehyde must be transferred into the liquid phase before the reaction process begins. This transfer is achieved in the instrument in a stripping coil, where the sampled air and a stripping solution are brought together at defined flow rates and contact surfaces. The vapour phase formaldehyde readily dissolves into the stripping solution. The resultant air and liquid streams are separated and the solution is analysed by detecting the fluorescence from the formaldehyde derivative. The formaldehyde in air concentration is then calculated from the concentration in solution and the ratio of sampled air flow to stripping solution flow.

3.1.2 Reagent solutions and their preparation

Two solutions are used in the measurement process: the stripping solution and the Hantzsch reagent solution. The stripping solution is pH-buffered formaldehyde free water and can be stored at room temperature. The Hantzsch reagent solution contains acetylacetone and ammonia dissolved in formaldehyde free water, and has to be stored between 4 and 10 °C. The typical amounts of stripping solution and Hantzsch reagent solution used per day of continuous operation are 0.83 and 0.33 litres respectively.

The solutions are not supplied with the formaldehyde analyser, and must be prepared by the user. Once prepared, the solutions can be used for up to one month if properly stored at the correct temperatures.

3.1.3 Calibration

A two stage calibration process is performed when the analyser is used to make measurements of formaldehyde in the vapour phase. The first stage involves the introduction of a liquid sample of formaldehyde of a known concentration into the analyser. The liquid standard is used to derive the permeation rate of a permeation source of formaldehyde situated within the analyser. Once the permeation rate of this internal source has been determined it is used to provide an internal formaldehyde in air calibration standard at $14.1 \mu\text{g m}^{-3}$ (11.5 ppb). The gaseous phase formaldehyde standard is used together with a zero air sample (ambient air through internal scrubber) to perform an automated daily calibration of the analyser.

The liquid formaldehyde standard was prepared from a 0.01 M stock solution of formaldehyde. The uncertainty assigned to the stock solution was 1.3% (at the 95% confidence level). The formaldehyde stock solution and liquid standard are not supplied by the instrument manufacturer, and must be prepared by the user.

In addition to the above procedure, the analyser was calibrated using mixtures generated by the NPL's primary standard facility for formaldehyde in the range $36.8 \mu\text{g m}^{-3}$ to 2.4 mg m^{-3} (30 ppb to 2 ppm) ($\pm 3\%$). The formaldehyde mixtures are prepared by dynamic blending of a balance gas with formaldehyde released from a permeation tube. The permeation rate of the tube is determined during the measurement by continuous weighing using a calibrated microbalance, and the flow rate of the balance gas is measured using a high accuracy flow meter. Both measurements are traceable to standards of mass. Quality assurance checks include purity analysis of the permeation and balance gas, and the comparison of the instrumentation with the NPL primary standard facility for the production of SO_2 , which is based upon a similar continuous weighing system. The formaldehyde analyser was calibrated using the formaldehyde primary standard facility and the derived calibration factor used to produce the presented concentrations.

3.1.4 Uncertainty in formaldehyde measurement

The overall uncertainty in the formaldehyde measurements made with the AL4021 formaldehyde analyser is $\pm 8\%$ at the 95% confidence interval for averaging periods of 30 seconds measuring typical ambient concentrations.

3.1.5 Operational procedures

The formaldehyde analyser was installed in the NPL mobile laboratory at five of the six monitoring sites, and installed in the AURN site managed by SEIPH at Marylebone Road, London for the other site. The analyser was controlled and the data recorded using a PC with the appropriate software supplied by the manufacturer. The data from the analyser was also recorded by a data logger, which provided a back up system in the event of the PC failing. The analyser was operated with an averaging period of 30 seconds. Backup data recorded by the logger was measured every 30 seconds but stored as 5 minute averages.

3.2 PUMPED DNPH CARTRIDGES AND DIFFUSIVE BADGE SAMPLERS.

3.2.1 Introduction

The most widely used technique for the measurement of aldehydes in ambient air utilises a measurement principle based on the derivatisation of 2,4 dinitrophenylhydrazine (DNPH). Typically a cartridge substrate material (for pumped sampling) or a filter (for badge sampling) is impregnated with DNPH and ambient air is sampled actively by pumping through the cartridge or passively through diffusion. The aldehydes present in the air sampled react with DNPH to form stable

aldehyde hydrazone derivatives which are retained on the sampling substrate. These derivatives can be recovered later and analysed by high performance liquid chromatography (HPLC) to produce estimates of the total mass of each aldehyde sampled. From measurements of the sampling time and the flow rate through the sampling cartridge, or estimates of the diffusive uptake coefficient, the total volume of air sampled can be estimated and the resulting mean concentrations of the aldehydes sampled can be estimated. Both active and passive samplers were used during this pilot study. Sampling during this study was carried out for periods of 30 minutes using commercial cartridges (Supelco) and calibrated constant flow pumps (Dupont) operating at flow rates of 1.5 lmin^{-1} . The diffusive badges were operated to give two one week long average measurements at each site.

The aldehydes that can be measured using the DNPH cartridges are listed in Tables 2, 4, 5, 6, 7 and 8. The concentration of each aldehyde present has been listed when it is above the detection limit of the technique.

3.2.2 Validation and Uncertainty

Pumped and diffusive samplers have been widely used over the last fifteen years for the measurement of aldehydes in ambient outdoor air, in indoor air and in workplace exposure monitoring.

The sampling of formaldehyde in air is described in a draft ISO standard (ISO 16000, 1998). The scope of the standard covers concentrations in the range $10 \mu\text{gm}^{-3}$ - 1 mgm^{-3} with a relative measurement uncertainty of $\pm 15\%$. However, limited data is included in the standard to substantiate the stated measurement uncertainty.

In order to gain a better understanding of the performance of the DNPH samplers a review was carried out of previous published measurement studies. Publications in this area cover both validation studies aimed at establishing the performance of DNPH samplers and research studies, some of which give an estimated measurement uncertainty. In using DNPH samplers measurement error can arise from a number of sources. The main sources are :

- Sampling errors - for example leaks in the sampling line or absorption effects in the sampling line
- Sample breakthrough
- Incomplete recovery of the DNPH derivatives
- Cartridge-to-cartridge variability in the background ('blank') concentrations
- Calibration errors - for example errors introduced in the calibration of the HPLC analyser , or errors introduced in the calibration of the sample pumps.

Most validation studies to date have focused on establishing the performance of tubes in conducting measurements close to the occupational exposure limit, 2.4 mgm^{-3} (2 ppm) in the UK. For example Goelen et al (1997) report the results of an EU interlaboratory intercomparison exercise involving twenty six laboratories, twenty of which employed pumped DNPH samplers for measurements of formaldehyde. Sixty per cent of laboratories reported overall measurement uncertainties of less than 30%. However, the concentration levels sampled were in the range $0.4 - 1.5 \text{ mgm}^{-3}$ ($0.35 - 1.5$

ppm) and sampling times were in the range 2 - 4 hours. These concentrations are 200 - 500 times greater than those found in ambient outdoor air and the measurement times are 4 -8 times longer than the measurement times required in this study. The authors identify incomplete recovery of the hydrazone derivatives (estimated to be 89% - 95%) and inaccurate liquid phase calibration standards for the HPLC analyses as likely contributors to the observed measurement bias. Of all reported analyses, 18% exhibited measurement bias in excess of 25%. The authors also note the large biases (as large as 50%) evident in the measurements of acrolein and identify instability of the acrolein derivative as the primary cause of this bias. They conclude DNPH based techniques are not appropriate for measurements of acrolein in ambient air.

Berry et al (1996) report the results of another EU intercomparison of GMD 570 series passive badge samplers (the type used in this study) carried out in 1993. Formaldehyde measurements obtained by diffusive samplers were compared with 'reference' values obtained using pumped DNPH cartridges. As this exercise was aimed at evaluating the performance of diffusive samplers in measuring formaldehyde concentrations typical of indoor air environments the concentration levels to which the badges were exposed were in the range 0.23 - 1.42 mgm⁻³. Badge exposure times were in the range 2.5 - 3.0 hours. Taking the results of the twenty one participating laboratories the mean derived concentration showed a bias of -12% relative to the reference value and showed a scatter of ±33%.

Kleindienst et al (1988) describe an intercomparison of a range of methods for the determination of formaldehyde in ambient air, including pumped DNPH samplers operated in accordance with US EPA guidelines. The analytical precision is estimated to be 10% and the mean bias is 20% in the concentration range 2.1 - 126.5 µgm⁻³ (1.7 - 103 ppb). Measurement periods were in the range 14 - 36 hours.

Muller et al (1997) describe the use of a modified DNPH method for the determination of aldehyde concentrations at two locations in Germany over a period of 2.5 years. Overall measurement uncertainties for all aldehydes and ketones measured were estimated to be ±15% at the 0.6 µgm⁻³ (0.5 ppb) level. Sampling times were 3 hours and sample volumes of 540 litres were obtained for each analysis.

In summary, a review of previous validation and research activities shows that measurement uncertainties of 15% - 33% have been achieved for the measurement of aldehydes in air. However, most of these estimates have been obtained for sampling regimes in which concentrations, sample flow rates and/or sampling times have been much greater than those in this study. On the basis of these figures it might be argued that 15 - 33% represents the best initial estimate of the uncertainties which might be expected for samples obtained in ambient outdoor air for sampling times of 30 minutes.

However, in the long term it is expected that many of the sources of measurement bias could be eliminated through validation studies addressing appropriate sampling/concentration regimes. In this case it is expected that the minimum detection limits, and overall measurement uncertainties, will be determined from the measured variability in the analysed masses of DNPH derivatives on blank sample cartridges or badges. In order to estimate the best achievable detection sensitivities a mean scatter value for the mass of derivatives recovered from batches of blank samples has been

determined and are shown in Table 1. The equivalent concentration for sampling flow rates of 1.5 lmin^{-1} and 10 lmin^{-1} over a period of 30 minutes (giving sample volumes of 45 l and 300 l respectively) are also indicated in Table 1. Flow rates of 1.5 lmin^{-1} were used throughout this pilot study.

In conclusion, in the longer term it should be possible to achieve detection sensitivities, and overall measurement uncertainties, as indicated in Table 1, through a combination of higher sample flow rates and targeted validation studies.

3.3 AUXILIARY DATA

The NPL mobile laboratory was equipped with a range of continuous analysers for the measurement of CO, SO₂, NO, NO₂ and PM10. In addition local wind speed data were obtained using a rotary anemometer on a 3 metre meteorological mast. The continuous analysers were calibrated at the beginning of each set of site measurements using NPL secondary standard calibration gases to give overall measurement uncertainties in the range 5% - 10% (at 95% confidence interval). Temperature data were obtained using calibrated temperature sensors.

3.4 MEASUREMENT SCHEDULE.

Following installation of the monitoring equipment in the mobile laboratory during the period 5th - 19th January measurements were carried out at six UK sites chosen to be representative of typical roadside, urban, suburban, rural, industrial and coal burning areas. Measurements were carried out for periods of 4 - 7 days at each site and the schedule for these measurements is given below.

- Teddington (suburban site) 19th January - 26th January 2000
- Marylebone Road (roadside site) 26th January - 3rd February 2000
- Southampton (urban site) 7th February - 14th February 2000
- Rochester (rural site) 21st February - 25th February 2000
- Industrial site 28th February - 7th March 2000
- Rotherham (coal burning site) 8th March - 16th March 2000

4. MEASUREMENTS

4.1 TEDDINGTON - SUBURBAN SITE

The NPL site at Teddington was chosen as a first field measurement site, in order that the automated operation of the continuous analyser and the modem communication link to the mobile laboratory could be checked without the risk of significant amounts of data being lost. The location of the mobile laboratory within the NPL site is shown in Figure 2. The mobile laboratory was located approximately 150 metres away from a busy road (Queens Road, traffic flow between 16:00 - 18:00 is typically 1200 cars per hour). The location is representative of a typical suburban site and the mobile laboratory was sited within 100 metres of the DETR AURN site at Teddington.

Following initial checks, calibration of the instrumentation and installation in mobile laboratory during the period 5th-19th January, measurements began at 15:35 on 19th January and continued until 10:00 on 26th January.

The time series of formaldehyde concentration measurements during this time, expressed in μgm^{-3} (referenced to 25 °C), is shown in Figure 3. Time series of NO_x/NO , NO_2 , O_3 , SO_2 , CO and PM_{10} are shown in Figures 4 - 9 respectively. The RMS difference between measurements obtained by the mobile laboratory and those obtained from the Teddington AURN site were 1.5 ppb, 8.0 ppb and 4.0 ppb for SO_2 , NO and NO_2 respectively. The concentrations of formaldehyde vary between absolute minimum and maximum values of $0.25 \mu\text{gm}^{-3}$ and $9.1 \mu\text{gm}^{-3}$ (0.2 and 7.4 ppb) respectively with an overall mean value of $3.2 \mu\text{gm}^{-3}$ (2.6 ppb). The formaldehyde concentrations show a clear diurnal cycle (see Figure 10) which is correlated with expected local traffic flow patterns. This cycle shows low concentrations between 03:00-05:00 (mean $0.8 \mu\text{gm}^{-3}$ (0.7 ppb)) and high concentrations forming a broad plateau between 10:00-22:00 (mean values $3.0 \mu\text{gm}^{-3}$ (2.4 ppb)).

The day-to-day variability in the concentrations observed during the mid afternoon plateau appears to be related to the wind speeds observed during this time. For example, the highest mid afternoon concentrations are observed on 20th, 24th and 25th January when the mean wind speeds (see Figure 11) are 0.6 , 1.8 and 0.6 ms^{-1} respectively. Conversely, the lowest mid afternoon concentrations are found on 22nd and 23rd January when the mean wind speeds are 6.2 and 4.5 ms^{-1} respectively.

From the wind rose data (see Figure 12) there appears to be no obvious correlation between wind direction and the concentrations observed. This is to be expected as the NPL site is surrounded on all sides by traffic sources of comparable strength.

A correlation analysis was carried out using the measurements of CO, NO and NO_2 from the co-located analysers in the mobile laboratory. The results are shown in Figure 13. These analyses reveal a weak correlation between formaldehyde concentrations and both CO and NO concentrations, and a stronger correlation between formaldehyde and NO_2 . The coefficients are R^2 values are given below:

$$\begin{aligned}
 [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 0.087 [\text{CO}]_{\text{ppm}} + 1.099 \quad (\text{R}^2 = 0.22) \\
 [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 0.010 [\text{NO}]_{\text{ppb}} + 1.780 \quad (\text{R}^2 = 0.11) \\
 [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 0.119 [\text{NO}_2]_{\text{ppb}} - 0.728 \quad (\text{R}^2 = 0.63)
 \end{aligned}$$

The good correlation with NO_2 indicates primary emissions from traffic as the major source. The significant difference in R^2 values for NO compared with NO_2 reflects the relatively large distance (150m) from the major source.

The frequency distribution of concentrations in the range 0 - 10 μgm^{-3} (0 - 8.1 ppb) are shown in Figure 14 as a series of histogram plots for 5 minute, 15 minute, 30 minute and 60 minute averaging periods.

During the measurements at Teddington a small scale validation exercise was carried out in order to establish the performance of the pumped diffusion tubes. This information was then used to determine the sampling strategy for the measurement campaigns to follow. Nine tubes were used in this exercise: three were used as blanks, two tubes were used to obtain measurements during the period 12:00-12:30 on Monday 24th January without using an ozone pre-scrubber and a further four were used to sample during the same period using an ozone scrubber, in order to eliminate the interference effect noted by Arnts et al (1989). Sample volumes of approximately 45 litres were obtained during the sample period. The results are summarised in Table 2. The two tubes used to obtain samples without the use of an ozone scrubber produced results of 3.5 and 7.9 μgm^{-3} (2.9 and 6.4 ppb). The four tubes which sampled through ozone scrubbers yielded formaldehyde concentrations of 0.84, 3.13, 3.34 and 3.15 μm^{-3} (0.7, 2.5, 2.7 and 2.6 ppb). Neglecting the 0.84 μgm^{-3} measurement as an outlier, the other values show reasonable consistency (within 0.2 μgm^{-3}) but are low relative to the values obtained by the continuous analyser by 17% to 24%. Given these results it was decided that for the Marylebone Road (roadside) and Southampton (urban) field measurements fourteen tubes should be used: three tubes for each of the four designated measurement periods and two blanks.

Table 2 also gives a breakdown of the other carbonyls measured above the limit of detection. Formaldehyde, acetaldehyde and acetone are the most abundant, accounting for 76% of the total mass of carbonyls measured by the DNPH cartridge method, in roughly equal proportion. The remaining 24% comprises propionaldehyde, butyraldehyde and benzaldehyde. The breakdowns of aldehydes measured using the DNPH cartridge method at all measurement sites are shown in Figure 15.

Weekly average measurements were also obtained by passive 'badge' type diffusive samplers. Two badges were used during each of two weeks of measurements. During the week of 24th-31st January the badges gave a value of 2.6 μgm^{-3} (2.1 ppb) compared with an average value of 3.2 μgm^{-3} (2.6 ppb) for the period 19th-26th January obtained by the continuous analyser. During the week of 3rd - 10th February the average concentration measured by the badge samplers was 1.8 μgm^{-3} (1.5 ppb).

4.2 MARYLEBONE ROAD - ROADSIDE SITE

The Marylebone Road site in Central London (see Figure 16) was chosen as an example of a city centre roadside site. The site is the busiest thoroughfare on the network and is a fundamental reference point for the urban environment. The NPL continuous analyser was integrated into the existing air quality monitoring facility operated by South East Institute for Public Health (SEIPH) during Wednesday 26th January. Measurements commenced at 17:30 on 26th January and continued until 08:30 on 3rd February. The formaldehyde concentration time series, together with simultaneous co-located measurements of CO, NO and NO₂ are shown in Figures 17 - 19.

The formaldehyde data vary between an absolute minimum concentration of 2.0 μgm^{-3} (1.6 ppb) and an absolute maximum of 33.6 μgm^{-3} (27.4 ppb), with an overall mean value of 13.4 μgm^{-3} (10.9 ppb). The data displays a diurnal cycle (see Figure 20) which is quantitatively similar to that observed at Teddington with a low at 04:00-05:00 (mean concentration 5.4 μgm^{-3} (4.4 ppb)) followed by high concentrations during a broad plateau between 08:00-20:00 (mean concentration 16.7 μgm^{-3} (13.6 ppb)). This diurnal pattern is qualitatively related to patterns in traffic flow data which is shown in Figure 21. Due to a failure of the SEIPH anemometer on 26th February no wind speed data are available for the Marylebone Road measurements but it is expected that the day-to-day variability is governed by mean wind speeds. The strong correlations between formaldehyde and CO, NO and NO₂ evident in Figures 17, 18 and 19 were investigated further in a series of correlation analyses. Correlation analyses were carried out for formaldehyde concentrations versus CO, NO and NO₂ concentrations for averaging periods for 15, 30 and 60 minutes. The resulting correlation plots are shown in Figures 22, 23 and 24 and the results summarised in Table 3.

As can be seen from Figures 22 and 23 good correlation is observed for CO and NO, with R^2 values ranging from 0.77-0.85. The R^2 values improve only slightly in going from correlations obtained for 15 minute averaging times to those obtained for 60 minute averaging times. For NO₂ the correlation is less good (see Figure 24) with an R^2 value of 0.48 for 15 minutes averaged data and an R^2 value of 0.72 for 60 minutes averaged data.

Ferrari et al (1998) analysed and compared formaldehyde concentrations obtained at a roadside site in Grenoble, France with simultaneous and co-located measurements of toluene. Benzene and toluene data, obtained from continuous GC analysers operated as part of the UK hydrocarbon monitoring network at the Marylebone Road site, were used in a similar way during the Marylebone Road measurement programme. The correlation plots are shown in Figure 25. The R^2 values for benzene and toluene (0.28 and 0.28 respectively) are significantly lower than those obtained for CO, NO and NO₂. The coefficients for toluene also differ from those obtained by Ferrari et al. The gradient term is a factor of twenty times smaller in this study than that observed by Ferrari et al, and the offset term is a factor of two smaller. Therefore, projections based on measured toluene concentrations and the coefficients determined by Ferrari et al. would overestimate the concentrations of formaldehyde at roadside sites by around a factor of twenty.

The overall frequency distribution of formaldehyde concentration is shown in Figure 26. From the limited dataset available here (obtained over seven days) it appears unlikely that concentrations of formaldehyde would frequently exceed 40 μgm^{-3} (32.6 ppb). The concentrations of formaldehyde

observed during this study are significantly lower than values projected from the empirical correlations of Ferrari et al together with an estimate of typical toluene concentrations at Marylebone Road.

Following the measurement strategy outlined previously in Section 3.2 three pumped DNPH cartridge samples were obtained during each of four periods throughout the day on 28th January; 09:20-09:50; 12:00-12:30; 14:00-14:30 and 16:00-16:30. The results are summarised in Table 4. The scatter in the results obtained, within each batch of three samples during a given period, was small (1.0%, 4.6%, 1.6% and 0.3% respectively). However, the concentrations obtained were 22%-39% lower than those observed using the continuous analyser.

The partitioning of the measured carbonyls is also given in Table 4. Formaldehyde, acetaldehyde and acetone account for 77% of the carbonyls measured. The remaining 23% is made up of propionaldehyde, benzaldehyde, valeraldehyde and hexaldehyde.

The badges for Week 1 (26th January - 3rd February) yield mean formaldehyde concentrations of 10.8 and 9.7 μgm^{-3} (8.8 and 7.9 ppb), representing differences of 19% and 28% relative to the mean concentration observed by the continuous analyser over the same period. During Week 2 (3rd February - 9th February) the badges yielded mean formaldehyde concentrations of 8.4 and 8.8 μgm^{-3} (6.8 and 7.2 ppb).

4.3 SOUTHAMPTON - URBAN SITE

The existing UK AURN air quality monitoring site at Southampton was chosen as a representative UK urban site. The location of the site is given in Figure 27. The NPL mobile laboratory was transported to the site on 7th February and measurements commenced at 17:00 on that day. Continuous measurements were obtained for the following seven days and measurements were stopped on 14th February.

The time series of formaldehyde measurements is shown in Figure 28. The measurements vary between an absolute minimum concentration of 0.1 μgm^{-3} (0.08 ppb) to an absolute maximum of 20.9 μgm^{-3} (17.0 ppb). The overall mean concentration during the period 7th - 14th February was 2.3 μgm^{-3} (1.9 ppb). Continuous measurements of NO_x/NO , NO_2 , O_3 , SO_2 , CO and PM_{10} from the co-located analysers in the mobile laboratory, over the same period, are shown in Figures 29 - 34 respectively.

The diurnal cycle is shown in Figure 35 and shows qualitatively similar behaviour to that observed at both Teddington and Marylebone Road. Minimum concentrations are observed during the period 04:00-05:00 (mean values of 1.0 μgm^{-3} (0.8 ppb)) and maximum values observed during a broad plateau spanning 07:00-21:00 with identifiable peaks at morning rush hour (08:00-09:00, mean value 3.0 μgm^{-3} (2.4 ppb)) and evening rush hour (17:00-18:00, mean value 3.3 μgm^{-3} (2.7 ppb)).

As with the Teddington data the day-to-day variability in the peak concentrations of formaldehyde can be explained in terms of mean wind speed. For example, the highest formaldehyde

concentrations are found on 9th February (09:00), 11th February (07:00-09:30) and 13th February (18:00-22:00) and for all of these periods the wind speed was less than 1.0 ms⁻¹ (see Figure 36). Conversely, the lowest formaldehyde concentrations during peak traffic flow times are found on 8th February and 10th February when wind speeds were greater than 2.0 ms⁻¹.

The formaldehyde concentration show weak correlations with CO , NO and NO₂ . Correlation plots for all three compounds for the 15 minute average data are shown in Figure 37. The correlations do not improve significantly in going from 15 minute averaged data to 60 minute averaged data. The resulting empirical relationships for the 15 minute averaged data are given below:

$$\begin{aligned} [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 2.56 [\text{CO}]_{\text{ppm}} - 0.20 & (\text{R}^2 = 0.60) \\ [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 0.030 [\text{NO}]_{\text{ppb}} + 1.42 & (\text{R}^2 = 0.58) \\ [\text{H}_2\text{CO}]_{\mu\text{gm}^{-3}} &= 0.14 [\text{NO}_2]_{\text{ppb}} - 0.442 & (\text{R}^2 = 0.66) \end{aligned}$$

The frequency distribution of formaldehyde measurements are shown in Figure 38.

Three pumped DPH cartridge samples were obtained during each of four periods throughout the day on 14th February: 09:00-09:30, 11:00-11:30, 13:00-13:30 and 15:00-15:30. The results are summarised in Table 5. The scatter in the formaldehyde concentration value, within each batch of three samplers during each period, was 0.2%, 8.7%, 25.3% and 11.1% respectively. These retrieved concentration values were low relative to the values obtained by the continuous analyser by 12-48%.

The partitioning of the measured carbonyls is also shown in Table 5. Formaldehyde, acetaldehyde and acetone account for 82% of the measured carbonyls. The remaining 18% comprises benzaldehyde and hexaldehyde.

The passive badge samplers for week 1 (7th - 14th February) gave formaldehyde concentrations of 4.1 and 6.1 μgm^{-3} (3.3 and 5.0 ppb) compared with a mean concentration of 2.3 μgm^{-3} (1.9 ppb) obtained by the continuous analyser.

During week 2 (14th -21st February) the badges gave formaldehyde concentrations of 4.9 and 4.4 μgm^{-3} (4.0 and 3.6 ppb).

4.4 ROCHESTER - RURAL SITE

The existing UK AURN air quality monitoring site at Stoke, Rochester was chosen as a representative rural site. The location of the site is given in Figure 39. The NPL mobile laboratory was transported to the site on 21st February and measurements commenced at 14:45 on that day. Continuous measurements were obtained for the following four days and were stopped on 25th February.

The time series of formaldehyde measurements is shown in Figure 40. The measurements vary between an absolute minimum concentration of $0.2 \mu\text{gm}^{-3}$ (0.16 ppb) to an absolute maximum of $4.0 \mu\text{gm}^{-3}$ (3.3 ppb). The overall mean concentration during the period 21st - 25th February was $1.2 \mu\text{gm}^{-3}$ (1.0 ppb). Simultaneous measurements of other pollutant species were made (see Figures 41- 46 for simultaneous measurements of NO_x/NO , NO_2 , O_3 , SO_2 , CO and PM_{10}), but do not show strong correlations with formaldehyde.

The diurnal cycle is shown in Figure 47 and possesses no significant features. Minimum concentrations are observed at 01:00 (mean value of $0.8 \mu\text{gm}^{-3}$ (0.7 ppb)) and maximum values are observed during a broad plateau spanning 08:00 - 23:00 (mean value of $1.3 \mu\text{gm}^{-3}$ (1.1 ppb)). The diurnal cycle is consistent with a rural site, where there are no strong local sources of formaldehyde.

As with previous sites the variability of formaldehyde can be explained in terms of mean wind speed. For example, the highest concentrations of formaldehyde can be found during 21st February (20:00) - 22nd February (23:00) when the wind speed was less than 3.5ms^{-1} (see Figure 48). Conversely, lower formaldehyde concentrations were observed during 23rd February (18:00) - 25th February (23:00) when the wind speed was greater than 4.0ms^{-1} .

The frequency distribution of formaldehyde measurements is shown in Figure 49.

Four pumped DNPH cartridge samples were obtained during the day on 25th February at: 09:00-09:30, 11:00-11:30, 13:06-13:36 and 15:00-15:30. The results are summarised in Table 6. The retrieved concentration values were low relative to the values obtained by the continuous analyser by a mean of 46.8%.

The partitioning of the measured aldehydes is shown in Table 6. Formaldehyde, acetaldehyde and acetone account for 65% of the measured carbonyls. The remaining 35% comprises of propionaldehyde, hexaldehyde, benzaldehyde and valeraldehyde.

The passive badges for week 1 (21st - 25th February) gave formaldehyde concentrations of $3.5 \mu\text{gm}^{-3}$ and $2.2 \mu\text{gm}^{-3}$ (2.9 and 1.8 ppb) compared with a mean of $1.2 \mu\text{gm}^{-3}$ (1.0 ppb) obtained by the continuous analyser. During week 2 (25th February - 1st March) the badges both gave a concentration of $2.8 \mu\text{gm}^{-3}$ (2.3 ppb).

4.5 INDUSTRIAL SITE NEAR HULL

The industrial site was chosen as it uses formaldehyde extensively in the production of chemicals for the tanning industry. The site currently possesses a licence for the fourth largest authorised release of formaldehyde in the UK (3774 kg in 1998). The site was recommended for this study by an industrial contact who has been involved in stack measurements of formaldehyde initiated by the company to test the effectiveness of a number of abatement measures. The same contact has also carried out dispersion modeling studies of the ambient formaldehyde levels in the local area.

The location of the site, and the position of the NPL mobile laboratory within the site, are shown in Figure 50. Measurements commenced at 17:25 on 28th February and continued until 19:30 on 3rd

March. Simultaneous measurements of other pollutants were recorded during this time, but are not detailed here as there was little correlation between them and the formaldehyde measurements.

The formaldehyde time series data is shown in Figure 51. Simultaneous measurements of NO_x /NO, NO₂, O₃, SO₂, CO and PM₁₀ are shown in Figures 52 -57. The measured formaldehyde concentrations varied between an absolute minimum of 0.15 µgm⁻³ (0.12 ppb) and an absolute maximum of 45.0 µgm⁻³ (36.6 ppb), with a mean value of 4.4 µgm⁻³ (3.6 ppb) during the measurement period. The diurnal cycle is shown in Figure 58. The diurnal cycle shows maximum concentrations between 03:00 - 04:00 (mean concentration 12.8 µgm⁻³ (10.4 ppb)) and minimum concentrations between 15:00 - 17:00 (mean concentration 1.9 µgm⁻³ (1.5 ppb)). The peak evident in the diurnal cycle plot may be due to a batch process beginning at approximately 02:00 or a favourable wind direction at this time. The wind direction was 225 degrees during the measurements at 03:00 - 04:00. The high concentrations begin to fall at 05:00 and concentrations of formaldehyde are at a minimum by 15:00.

The wind rose data for formaldehyde is shown in Figure 59. The wind rose shows that the formaldehyde measured is emitted from a source at 170° - 210°, which corresponds to the position of the industrial site. The wind rose data gives confidence in the assumption that the dominant source of formaldehyde is the industrial site.

The frequency distribution of formaldehyde concentration measurements is shown in Figure 60. From this limited data set (recorded over 5 days) it appears unlikely that the formaldehyde concentration would frequently exceed 45 µgm⁻³ (36.6 ppb). Further measurements over a longer time period would be needed to verify this and to observe the effects of a wider range of meteorological conditions. Measurements at other industrial sites (such as manufacturers of fibreboard, particle board and foam) over longer time periods are needed to form more reliable statistics on the aldehyde concentrations in the vicinity of a 'typical' industrial site.

The correlation between formaldehyde and other gaseous pollutants (NO_x, CO and SO₂) was investigated. Correlation analyses for formaldehyde versus NO, NO₂, CO and SO₂ gave R² values of 0.0005, 0.0314, 0.1472 and 0.2616 respectively. The poor correlation between formaldehyde and other gaseous pollutants, as shown by the low R² values, indicates that the industrial site is the source of the measured formaldehyde. A very weak correlation is seen between formaldehyde and SO₂, because SO₂ is also emitted by the industrial site.

Four pumped DNPH samples were obtained during the day on 29th February at: 09:00 - 09:30, 11:00 - 11:30, 13:00 - 13:30 and 15:00 - 15:30. The results are summarised in Table 7. The retrieved concentration values were low relative to the measurements made by the continuous analyser by an average of 53%. The partitioning of the measured carbonyls is shown in Figure 15. Propionaldehyde, acetylaldehyde, acetone and formaldehyde account for 82% of the measured carbonyls. The remaining 18% comprises butyraldehyde and hexaldehyde.

The passive badges for week 1 (29th February - 7th March) both gave formaldehyde concentrations of 2.3 µgm⁻³ (1.9 ppb), compared with a mean of 2.4 µgm⁻³ (2.0 ppb) obtained by the continuous analyser. The passive badges for week 2 (7/3/00 - 14/3/00) gave concentrations of 2.9 µgm⁻³ and 2.1 µgm⁻³ (2.4 and 1.7 ppb).

As part of a plume tracking exercise measurements were obtained with the continuous analyser at three different sites around the town were obtained during the day on 7th March. The site positions are shown in Figure 61. The mean concentrations of formaldehyde at site 1, site 2 and site 3 were $1.4 \mu\text{gm}^{-3}$, $0.8 \mu\text{gm}^{-3}$ and $1.7 \mu\text{gm}^{-3}$ (1.1, 0.7 and 1.4 ppb) respectively. The average measurement time at each site was 1 hour 50 minutes.

4.6 ROTHERHAM - COAL BURNING SITE

The local authority air quality monitoring site at Brampton, Rotherham was chosen as a representative coal burning site. The location of the site is given in Figure 62. Measurements commenced at 15:20 on 8th March and ended at 09:00 on 16th March. The data recorded by the local authority site has not been ratified and is therefore not available for comparison with the NPL data set.

The time series of formaldehyde measurements is shown in Figure 63. The measurements vary between an absolute minimum concentration of $0.1 \mu\text{gm}^{-3}$ (0.08 ppb) and an absolute maximum concentration of $2.5 \mu\text{gm}^{-3}$ (2.0 ppb). The overall mean concentration during the period 8th - 16th March was $0.6 \mu\text{gm}^{-3}$ (0.5 ppb). Simultaneous measurements of NO_x/NO , NO_2 , O_3 , SO_2 , CO and PM_{10} are shown in Figures 64 - 69 respectively.

The diurnal cycle is given in Figure 70. It shows minimum values at 03:00 (mean concentration $0.2 \mu\text{gm}^{-3}$ (0.16 ppb)) and then a steady rise from 04:00 to maximum values during a plateau between 17:00 - 21:00 (mean concentration $0.8 \mu\text{gm}^{-3}$ (0.7 ppb)). A decrease in formaldehyde concentration is then observed between 22:00 - 03:00. The observed diurnal cycle is consistent with the production of formaldehyde from domestic coal burning, which will peak in mid-to-late evening.

Although simultaneous measurements of other gaseous pollutants were made, there was no strong correlation between them and formaldehyde. A histogram showing the frequency distribution of measured formaldehyde concentrations is given in Figure 71.

Four pumped DNPH samples were obtained during the day on the 9th March at: 09:15 - 09:45, 11:15 - 11:45, 13:15 - 13:45 and 15:15 - 15:45. The results are summarised in Table 8. The retrieved concentrations were low by a factor of 2.9.

The passive badge samplers for week 1 (9th - 16th March) gave formaldehyde concentrations of $1.9 \mu\text{gm}^{-3}$ and $1.7 \mu\text{gm}^{-3}$ (1.5 and 1.4 ppb) compared with a mean of $0.6 \mu\text{gm}^{-3}$ (0.5 ppb) obtained using the continuous analyser. The passive badge samplers for week 2 (16th - 23rd March) gave formaldehyde concentrations of $2.9 \mu\text{gm}^{-3}$ and $2.8 \mu\text{gm}^{-3}$ (2.4 and 2.3 ppb).

5. CONCLUSIONS

5.1 SITE DATASETS

- Measurements of formaldehyde and higher aldehyde concentrations in ambient air were obtained at six UK sites during the period 20th January - 16th March 2000. These sites were selected to represent typical rural, suburban, urban, roadside, industrial and coal burning areas. Continuous datasets on formaldehyde were obtained at each site for between 4 -7 days, with 60 hours of data lost during 40 days of continuous measurements, representing a mean data capture rate of 94%. During the same period measurements of formaldehyde and higher aldehyde concentrations were obtained using pumped DNPH samplers at least four times at each of these sites, in order to capture the main features of the diurnal cycle. Measurements were also obtained for two weeks at each site using passive diffusive samplers to give (two) week long average concentration measurements. The pumped tube data has been used to determine a speciated breakdown of the aldehydes measured at each site.
- The highest average, and peak, concentrations of formaldehyde were found at the roadside site (Marylebone Road) and at an industrial site near Hull engaged in the manufacture of process chemicals for leather treatment. The average concentrations, obtained by the continuous analyser, at these sites were 13.4 (7 day mean) and 4.4 μgm^{-3} (4 day mean) (10.9 and 3.6 ppb) respectively. Peak concentrations at these sites reached 33.6 and 45.0 μgm^{-3} (27.4 and 36.6 ppb) respectively for periods of 15 and 5 minutes respectively. Maximum 30 minute average concentrations at these times were 31.2 and 12.4 μgm^{-3} (25.4 and 10.1 ppb) respectively.
- At the roadside site (Marylebone Road) diurnal variations in the concentrations of formaldehyde are strongly linked with traffic flow. Average concentrations increased from background levels of approximately 5 μgm^{-3} (4.1 ppb) at around 07:00 before reaching a broad plateau at concentrations of approximately 17 μgm^{-3} (13.8 ppb) between 09:00 and 18:00 before returning to near background levels at 23:00. The suburban (Teddington) and urban (Southampton) data show qualitatively similar diurnal patterns to that observed at the roadside site indicating vehicle emissions as the main source of formaldehyde, as expected.
- The day-to-day variability at the Teddington and Southampton sites appears to be influenced by average wind speed which determines the rate at which the formaldehyde emitted from vehicles is diluted. Although wind data were not available for the Marylebone Road data set, it is expected that average concentrations would be anti-correlated with mean wind speed.
- Mean measured concentrations of formaldehyde at Marylebone Road were lower, by a factor of 4, as compared to those predicted in a recent unpublished report (Stealey, private communication) on the basis of the formaldehyde/toluene empirical correlation studies of Ferrari et al (1998). Using ratified toluene and benzene data from the UK Hydrocarbon site at Marylebone Road a weak positive correlation was found between formaldehyde and these compounds, giving empirical relationships of the form :

$$[\text{HCHO}]_{\mu\text{gm}^{-3}} = 0.49[\text{toluene}]_{\text{ppb}} + 7.2 \quad (R^2 = 0.28)$$

$$[\text{HCHO}]_{\mu\text{gm}^{-3}} = 1.8[\text{benzene}]_{\text{ppb}} + 7.2 \quad (R^2 = 0.28)$$

- The datasets from the high time resolution continuous analyser were well suited to correlation analyses. Good correlation was found at Marylebone Road between formaldehyde and NO, CO and NO₂. The CO and NO_x/NO measurements were obtained from co-located, calibrated continuous analysers managed by SEIPH as part of the DETR Automated Urban and Rural Network. Correlation analyses were performed on data binned in 15 minute, 30 minute and 60 minute time bins. The correlation showed only slight improvement in R² values in going from 15 minute to 60 minute averages. The resulting analyses for the 60 minute time averages give :

$$[\text{HCHO}]_{\mu\text{gm}^{-3}} = 3.92[\text{CO}]_{\text{ppm}} + 1.9 \quad (R^2 = 0.80)$$

$$[\text{HCHO}]_{\mu\text{gm}^{-3}} = 0.036[\text{NO}]_{\text{ppb}} + 4.9 \quad (R^2 = 0.85)$$

$$[\text{HCHO}]_{\mu\text{gm}^{-3}} = 0.26[\text{NO}_2]_{\text{ppb}} - 0.81 \quad (R^2 = 0.72)$$

- High concentrations of formaldehyde were measured at the fenceline of an industrial plant engaged in the production of process chemicals for leather treatment. Measurements obtained over 4 days just inside the fenceline of the plant gave peak values of between 30 - 45 μgm⁻³ (24.4 - 36.6 ppb) over a period of 30 minutes, superimposed on broader elevated values of around 20 μgm⁻³ (16.3 ppb) lasting over 4 hours. The incidence of these elevated concentrations was linked to the operation of a number of spray driers operated at the plant. The plant is located close to a residential area and thus it might be assumed that these concentrations are typical of the concentrations to which the local residents are exposed. However, with such a limited dataset it is difficult to assess how frequently such concentration peaks occur. During a 1 day plume tracking exercise efforts were made to measure concentrations several hundred metres downwind of the plant; measured concentrations were in the range 0.8 - 1.7 μgm⁻³ (0.7 - 1.4 ppb).
- From the measurements obtained at Rotherham, chosen to be representative of a coal burning area, peak concentrations were 2.5 μgm⁻³ (2.0 ppb). On the basis of the short term dataset obtained here it appears unlikely the health thresholds of 100 μgm⁻³ would be exceeded frequently. However, a longer term study, aimed at assessing the effects of prolonged local temperature inversion, would provide more reliable statistics on the likelihood of exceedances.
- Measurements at Rochester, Kent (the representative rural site) gave concentrations between 0.2 and 4.0 μgm⁻³ (0.16 and 3.3 ppb). In the absence of a strong local source of aldehydes it appears unlikely that health thresholds would be exceeded in rural locations.

5.2 MEASUREMENT TECHNIQUES

- The continuous formaldehyde analyser (Aerolaser model AL4021) performed reliably throughout the six field campaigns with only 60 hours lost from 40 days of continuous data for reasons that are avoidable in future (eg reagents freezing). Automated operation, using a modem/mobile phone communications link, has been demonstrated. The detection sensitivity of the analyser is $0.06 \mu\text{gm}^{-3}$ (0.05 ppb) and the time resolution is 30 seconds.
- Initial validation measurements at NPL using the pumped DNPH cartridges, aimed at assessing the repeatability of DNPH cartridge measurements for formaldehyde monitoring highlighted the potentially large scatter in the measured results. As a result a strategy was adopted whereby three tubes were used for each measurement at Marylebone Road and Southampton (14 tubes in total were used for the Marylebone Road and Southampton measurements comprising 4 sets of 3 tubes + 2 blank tubes). Repeatability of the tube measurements, assessed from triplicate co-located simultaneous measurements, is in the range 0.2% - 25% for concentrations in the range $1.2 - 16.1 \mu\text{gm}^{-3}$ (1.0 - 13.1 ppb) for 30 minute sample times. These repeatability values are close to those expected from a review of previous validation studies which were aimed at assessing the performance of DNPH samplers in measuring higher concentrations relevant to workplace monitoring. In addition the formaldehyde concentration measurements obtained using the pumped DNPH samplers showed a bias of - (24 - 42) % relative to the concentrations measured by the continuous analyser. The bias was larger for measurements made at the other sites; however, with fewer data (four measurements per site) it is more difficult to assess the significance of these biases.
- The repeatability of the measurements of higher aldehyde concentrations was assessed by examining the scatter in the masses of the corresponding DNPH derivatives from blank cartridges. This gave estimated detection sensitivities for all aldehydes measured in the range $0.2 - 2.4 \mu\text{gm}^{-3}$ (0.16 - 2.0 ppb) for 45 litre sample volumes and detection sensitivities in the range $0.03 - 0.36 \mu\text{gm}^{-3}$ (0.02 - 0.29 ppb) for sample volumes of 300 litres.
- The projected detection sensitivity of $\pm 1 \mu\text{gm}^{-3}$ (± 0.8 ppb) for formaldehyde has been achieved in the measurements reported here. However, the unexpectedly low concentrations observed make this level of detection sensitivity a significant contribution to the relatively large measurement uncertainties. However the DNPH cartridge sampling technique is intrinsically very sensitive and measurements with overall measurement uncertainties (for formaldehyde) of less than $\pm 15\%$ could be achieved by using higher sample flow rates during the 30 minute sampling period and by adopting more appropriate calibration procedures appropriate for sampling at low ambient concentration levels.
- It appears that DNPH pumped tubes are not an appropriate technique for the measurement of acrolein in ambient air due to the instability of the corresponding acrolein DNPH derivative.
- The passive diffusive samplers or 'badges' gave results which, at Marylebone Road, showed a bias of +24% relative to the measurements obtained by the continuous analyser. At the other

sites the bias was +17%, -112%, -57%, +4% and -192% for Teddington, Southampton, Rochester, the Industrial site near Hull and Rotherham.

- In order to understand fully the relative costs of both techniques (continuous analyser versus pumped DNPH samplers) for measuring **formaldehyde** it is necessary to consider the required data capture rate, the measurement uncertainties sought (which impacts on the number of pumped tubes per measurement), and the overall timescale of a monitoring programme. In broad terms longer measurement periods, high data capture and high accuracy favour the use of a continuous analyser. As an example, once per week measurements using 4 tubes (3 samples and 1 blank) gives a cost break even point at around nineteen months. However, for measurements of higher aldehydes DNPH samplers probably offer the most cost effective measurement solution.

6. RECOMMENDATIONS

The recommendations resulting from this pilot study address two distinct but related issues: firstly those relating to the choice of measurement techniques and strategy and secondly those relating to site selection and measurement timescales. The recommendations in both areas are given below.

6.1 MEASUREMENT TECHNIQUES AND MEASUREMENT STRATEGY

The main elements of a Phase 2 monitoring programme could be :

- **The development and validation of a modified DNPH measurement technique**, aimed at achieving a target measurement uncertainty of less than $\pm 15\%$ (at 95% confidence interval) for 30 minute sampling periods for selected aldehydes. These aldehydes could comprise the most commonly measured aldehydes from this study: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and benzaldehyde. As discussed in Section 3.2, the main modifications to the measurement technique would involve the use of higher sampling flow rates (to give larger sample volumes) and the development on an improved HPLC calibration technique. Validation would be achieved using gravimetrically prepared standard gas mixtures, thereby ensuring absolute accuracy to specified levels.
- **The development of a prototype automated sampling system for DNPH samplers.** This facility would involve automated sampling of air through DNPH cartridges to give measurements of formaldehyde and higher aldehyde concentrations using the modified sampling method outlined above. This would enable medium time resolution data to be obtained without incurring large manpower costs. An automated sampling manifold could be designed to allow (multiple) daily cartridge samples to be obtained over a period of 2-3 weeks. Cartridges could then be collected by a local site operator at 2- 3 week intervals coincident with scheduled site visits and sent to a central analytical laboratory for subsequent analysis.
- **Deployment of the Aerolaser continuous formaldehyde analysers at selected sites.** The correlation studies described here offer the possibility of developing and validating empirical predictive models for aldehydes based on co-located measurements of CO and NO_x/NO for sites where vehicle emissions are the dominant source of aldehydes. These studies would be most cost effective if high accuracy, high time resolution formaldehyde analysers are used. Studies of the small spatial scale variability of formaldehyde would be best achieved using this technique.
- **Evaluation of the performance and cost effectiveness of an on-line HPLC for continuous measurements** of formaldehyde and higher aldehyde concentrations as part of an existing monitoring site. The use of on-line HPLC for continuous automated measurements of formaldehyde and acetaldehyde has been demonstrated by Komazaki et al (1999). A time resolution of 1 hour has been achieved using this approach and detection limits of 0.06 $\mu\text{g m}^{-3}$ and

0.19 μgm^{-3} (0.05 and 0.15 ppb) have been demonstrated. A study could be carried out to assess the feasibility of this technique for long term measurements.

- **Auxiliary data** will play an important part in the interpretation of any data obtained as part of a phase 2 study. As highlighted in this pilot study the most important auxiliary data to be obtained is :
 - ⇒ Co-located high time resolution measurements of CO, NO and NO₂ in situations where vehicle emissions are likely to be the main source, in order that correlations can be validated over a wide range of meteorological and seasonal conditions.
 - ⇒ Local wind speed data, in order that the inverse relation between average wind speed and average aldehyde concentrations highlighted in this study can be put on a more quantitative basis.
 - ⇒ Pressure and temperature data, in order that local inversion conditions can be identified and the effects on aldehyde concentrations better understood

6.2 SITE SELECTION AND MEASUREMENT TIMESCALES

Based on the measurements obtained during this pilot study a number of monitoring activities can be proposed which could form the basis of a Phase 2 study. These are described in outline below.

- **Longer term measurements at selected urban and roadside sites.**

The measurements reported here give an initial indication of the range of concentrations of aldehydes at a range of UK locations. As expected, vehicles and direct industrial emissions appear to be the most significant sources which are most likely to cause local exceedances of health thresholds (100 μgm^{-3} , averaged over 30 mins). However, a longer term study, covering at least 1 year in order to capture seasonal variability, would be required to build confidence in the statistics of such exceedances. Obvious locations for monitoring sites would be roadside sites at urban street canyon sites. The measurement strategy could employ modified pumped DNPH samplers, as outlined above, and/or a continuous analyser for formaldehyde as demonstrated in this study.

- **Measurements in coal burning areas.**

It is not clear from the limited measurements reported here that ambient levels of formaldehyde in coal burning areas are likely to exceed health thresholds. Further measurements would answer this more definitively. A monitoring campaign could be organised during the period October - March when inversion conditions are most likely to cause high aldehyde concentrations

- **Measurements at selected industrial sites.**

Industries which have not been addressed in this pilot study (eg producers of urea formaldehyde resins, fibreboard and particleboard manufacturers, foam manufacturers) could cause localised exposure to high concentrations of formaldehyde and possibly higher aldehydes. A representative set of industrial sites could be investigated, employing a mobile laboratory in the same way as has been demonstrated during this pilot study. For example, measurements could be obtained at ten selected sites for a period of 1 month at each site, over a total period of 1 year. A continuous analyser is best suited to this type of measurement where exceedances may be transient. An automated DNPH tube sampling system could be designed which is triggered by high formaldehyde concentrations measured by a continuous analyser in order to measure higher aldehydes in a cost effective way.

- **Measurements to validate correlation analyses**

Based on the correlation studies reported here for sites where vehicles are the dominant source (at suburban, urban and roadside sites) measurements of CO and NO appear to give a good estimate of formaldehyde concentrations. For these measurements to offer a reliable and consistent proxy estimate for formaldehyde concentrations there is a requirement to demonstrate the validity of these correlations under a wider range of conditions (eg in different seasons, in different meteorological conditions, in different locations relative to the source). This could only be done cost effectively using continuous analyser data.

- **Measurements to study the small scale variability of formaldehyde concentrations**

In order to assess the likelihood of health effects of transient high exposures to formaldehyde a study of the small scale variability in formaldehyde concentrations may be required. For example measurements at the kerbside could be compared to measurements obtained at shop fronts. This could only be done using a continuous analyser.

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(for 5, 15, 30 and 60 minute averaging periods , top - bottom)

10. LIST OF ABBREVIATIONS

AURN	-	Automated Urban and Rural Network
DETR	-	Department of Environment, Transport and the Regions
DNPH	-	2, 4- dinitrophenylhydrazine
HPLC	-	High Performance Liquid Chromatography
IARC	-	International Agency for Research on Cancer
IEH	-	Institute for Environmental Health
ISO	-	International Organization for Standardization
NPL	-	National Physical Laboratory (UK)
ppb	-	parts per billion
SEIPH	-	South East Institute for Public Health
US EPA	-	United States Environmental Protection Agency
WHO	-	World Health Organization

11. APPENDIX A - PPB TO mgm^{-3} CONVERSION

The concentration measurements presented in this report have been expressed in both μgm^{-3} (at a pressure of 1013.25 mbar and temperature of 25°C) and ppb units. The equation used to perform the conversion from ppb to μgm^{-3} , at a standard pressure of 1013.25 mbar, is shown below:

$$\text{mgm}^{-3} = (\text{ppb value}) \times \left(\frac{30.03}{22.41} \right) \times \left(\frac{273.15}{T} \right)$$

where 30.03 g is the molar mass of formaldehyde, 22.41 l is the volume occupied by a mole of gas at standard temperature and pressure, 273.15 K is standard temperature and T represents the temperature at which the measurements were made in degrees Kelvin.

The table below shows the implementation of the above expression for a series of concentrations measured at a temperature of 25°C (298.15 K).

Concentration in ppb	Concentration in mgm^{-3}
0.1	0.12
0.5	0.61
1	1.23
2	2.46
3	3.68
4	4.91
5	6.14
6	7.37
7	8.59
8	9.82
9	11.05
10	12.28