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TRACERS AND DISPERSION OF GASEOUS POLLUTANTS IN AN URBAN AREA

Birmingham Tracer Experiments

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Abstract

The transport and dispersion of pollutants in the urban environment are important processes due to their potential impact on city inhabitants. The physical processes governing flow and dispersion at neighborhood scales are not well understood. Furthermore, it is not clear whether a traditional approach using averaged characteristics such as the roughness length is sufficient to predict the concentration field at these scales. For this purpose, three field experiments were designed within the UK Urban Regeneration and the Environment (URGENT) program, sponsored by the Natural Environment Research Council (NERC) as a result of a collaborative effort between the University of Bristol, the University of Cambridge and Cambridge Environment Research Consultants (CERC).

The experiments were performed in the city of Birmingham using a finite duration release of perfluoromethylcyclohexane (PMCH) and perfluoromethylcyclopentane (PMCP). The combination of low background concentration of PMCH and PMCP, their non-depositing and non-reacting characteristics, as well as the ability of measuring very low concentration values with a newly developed gas chromatography technique allowed the realisation of nearly ideal fluid dynamic experiments in real urban environments. The present report documents these experiments from the experimental technique and experimental arrangement to results. Meteorological data, necessary to interpret the measurements, are also documented.

1.0 Introduction and Experimental Goals

The transport and dispersion of pollutants, within and from a large urban area, are important processes due to their potential environmental impact on city inhabitants. The release of atmospheric tracers is a powerful technique to simulate the dispersion of pollutants and enables direct measurements of concentrations along the trajectory of a plume. Suitable tracers are inert, non-toxic, non-depositing, with low atmospheric background concentrations, long atmospheric lifetimes and limited commercial use. Perfluorocarbons (PFCs), especially perfluorocycloalkanes, fall into this category and have been successfully used to directly measure the atmospheric concentrations along a trajectory path (Lovelock and Ferber, 1982; Dietz, 1986; D'Ottavio *et al.*, 1986; Largomarsino, 1996). Indeed, these tracers allow the realisation of nearly ideal fluid dynamic experiments in real urban environments.

A novel technique that is able to selectively detect and quantify perfluorocycloalkane tracers with a dynamic range of 10^{-5} to $10 \mu\text{g m}^{-3}$ has been developed at the University of Bristol. The new approach utilises advances in adsorbent enrichment techniques coupled with bench-top capillary gas chromatography and negative ion-chemical ionisation mass spectrometry (GC-NICI-MS). In a pioneering effort Begley *et al.* (1988) demonstrated that GC-NICI-MS could provide a uniquely selective analytical method for PFCs due to the formation of stable molecular anions. The relatively high molecular weights of the PFCs coupled with their low vapour pressures provides a novel and characteristic combination of early chromatographic elution with a high mass ion which is very unlikely to be compromised by the co-elution of interfering species.

This technique was applied to three field experiments in Birmingham, UK, designed and performed during 1999 and 2000 as part of a collaboration between the University of Bristol, University of Cambridge (Department of Engineering and DAMTP) and Cambridge Environmental Research Consultants (CERC). The main goals of these field experiments were to test this new technique as well as provide the scientific community with a data set for dispersion over spatial scales between 1km and 10 km. These data sets could be used to improve the understanding of the

physical processes on these scales as well as in the evaluation of pollution dispersion models.

2.0 Instrumentation and Technique

The following chapter reports on the instrumentation developed to perform the tracer experiments. A detailed description of the release and sampling systems are reported.

2.1 Tracer Release Apparatus and Release Sequence

The tracer release apparatus consisted of an insulated stainless steel chimney of height 4.5 m and top section diameter of 255 mm (Figure 2.1), through which hot air flowed at a rate of $6.16 \times 10^{-3} \text{ m}^3\text{s}^{-1}$ at $\sim 125^\circ\text{C}$. Into this hot air stream the tracer species were pumped, using high pressure liquid chromatography pumps (HPLC), at a rate of 0.1–4 gs^{-1} , via a nozzle of angle 40° (Delevan Spray Technologies, UK). The nozzle allowed a uniform distribution and very fine atomisation of the tracer, thus ensuring rapid vaporisation within the chimney. The amount of tracer released was directly measured by continuously logging the weight loss of the tracer reservoir on to a PC.



Figure 2.1: Tracer Release Apparatus.

To reduce the risk of either a premature release or post release taking place the following protocol was used:

- i. All tracer species were sealed and transported at $-18\text{ }^{\circ}\text{C}$ in a cold box with freezer blocks to minimise the risk of evaporation prior to the experiment.
- ii. The release apparatus was set up at least one hour prior to commencement of the experiment.
- iii. The HPLCs and related tubing were flushed out with a surrogate tracer, nonafluorobutylmethyl ether (HFE 7100, F2 Chemicals, UK.), of similar density and properties of the actual tracer species perfluoromethylcyclohexane (PMCH) and perfluoromethylcyclopentane (PMCP) used. This surrogate tracer is undetectable by the analytical system, thus does not interfere with the actual release data acquired.
- iv. The release temperature was allowed to stabilise to $\sim 125^{\circ}\text{C}$ at least an hour before the release.
- v. The weight loss of the surrogate tracer and the actual tracer species were monitored throughout the pre-release, release and post-release periods.
- vi. At the end of the release, the system was flushed with the surrogate tracer to make sure the entire tracer had been released.
- vii. The entire system was left in place for at least one hour after the release to avoid any possibility of an accidental post-release taking place whilst the apparatus was being dismantled.

2.1.1 Tracer Characteristics and Background Values

Table 2.1 gives the properties and background concentrations of the perfluorocarbons and other commonly used tracers. As can be seen from the table, PMCH and PMCP, the tracers used for this work have very low background concentrations.

Table 2.1: Properties of Perfluorocarbon and other tracers

Compound Name	Abbreviated Name	Molecular Formula	B Pt/ °C	Molecular Weight	Density / kg/l at 25 °C	Background Concentrations in $\mu\text{g m}^{-3}$ (fl/L)
Perfluorodimethyl-cyclobutane	PDCB	C6F12	45	300	1.67	
Perfluoromethyl-Cyclopentane	PMCP	C6F12	48	300	1.707	5.64×10^{-5} ($4.6 \pm 0.3^*$)
Perfluoromethyl-Cyclohexane	PMCH	C7F14	76	350	1.788	6.58×10^{-5} ($4.6 \pm 0.8^*$)
Perfluoro- <i>o</i> -dimethyl-Cyclohexane	PDCH	C8F16	102	400	1.828	1.57×10^{-5} ($0.96 \pm 0.33^*$)
Perfluoro- <i>m</i> -dimethyl-Cyclohexane	PDCH	C8F16	102	400	1.828	15.21×10^{-5} (trans) ($9.3 \pm 0.8^*$) 1.43×10^{-5} (cis) (8.8 ± 0.8)
Perfluoro- <i>p</i> -dimethyl-Cyclohexane	PDCH	C8F16	102	400	1.828	9.98×10^{-5} (cis/trans) ($6.1 \pm 0.8^*$)
Perfluoro-Trimethyl-Cyclohexane	PTCH	C9F18	128	450	1.888	
Perfluorodecalin	PD	C10F18	141	462		
Telomar 6		SF5(CF2)3 Cl		312		
Sulphur Hexafluoride		SF6	-63.8 sub- limes	146	Gas 6.602g/l	0.227 ($3.8 \times 10^3 \&$)

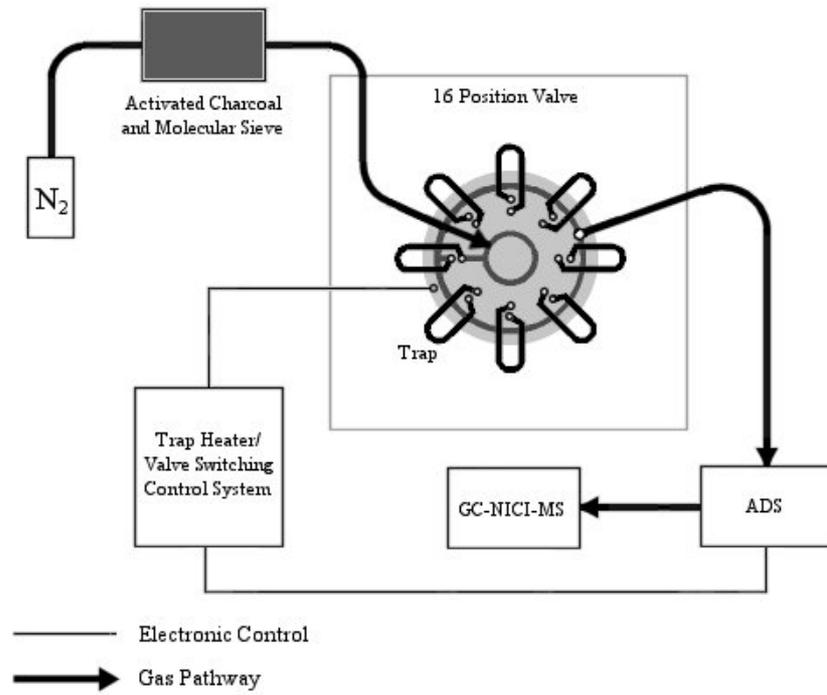
(*Straume *et al.*,1998; &Maiss *et al.*, 1998)

2.2 Trap Samplers

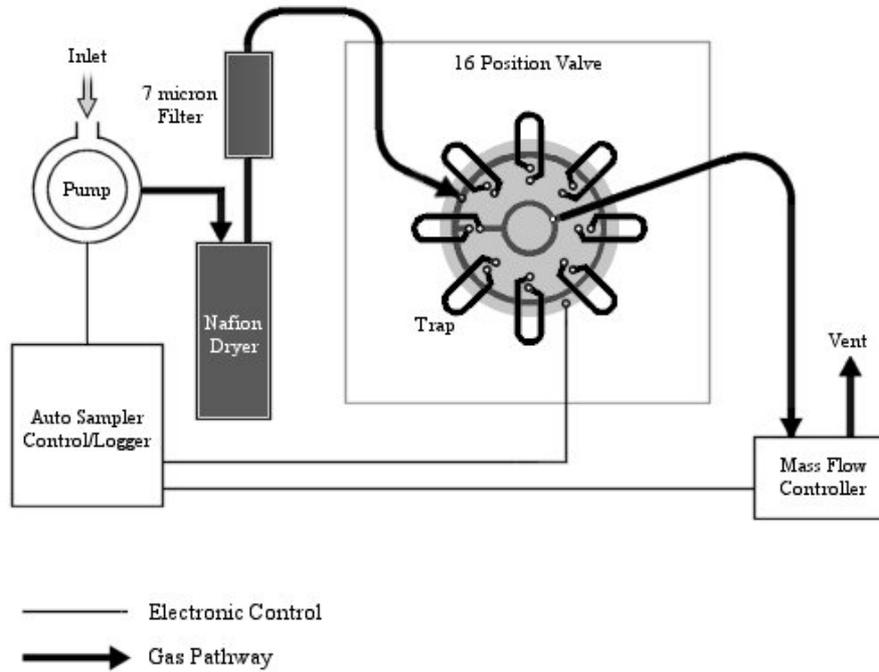
Two designs of automatic sequential samplers were constructed for this work. The first, illustrated in Figures 2.2, consisted of a 16-position multiport valve (Valco Instruments Co. Inc., Houston), fitted with 15 stainless steel adsorption traps (0.159 cm o.d, by 0.127 cm i.d), containing 150 mg Carboxen 564 (Sigma-Aldrich, Bellefonte, PA). Each trap was conditioned in the laboratory by heating to ~ 350 °C (29.6 Watts) for an hour under a constant flow of 100 ml min^{-1} nitrogen (5.0 grade, Air Products Ltd, UK) prior to use. The multiport valve system was then incorporated into a robust stand-alone metal sampling box system, Figure 2.3. Air was sampled sequentially via the valve through each trap at a predetermined flow rate controlled by a mass flow controller (Unit Instruments Ltd, Ireland). The box was then sealed and

taken to the laboratory for analysis. The system was fully automated during the sample acquisition and the volume of air and ambient temperature automatically logged for each trap (CGL Technology Ltd., UK). In the laboratory, each trap was resistively heated in turn to ~ 300 °C for 10 minutes (26.25 Watts) under a constant flow of 10 ml min^{-1} of nitrogen (5.0 grade, Air Products). The desorbed tracer was re-focused onto the micro-trap within the Adsorption-Desorption System (ADS) described in Section 3.1 and subsequently transferred by rapid thermal desorption to the GC-MS.

The sample averaging times used in this work for the trap samplers were 15 and 20 minutes, whereby 3 litres of air would be sampled. No air was sampled onto the first trap and this acted as a blank reference. In a field campaign situation, the second trap would start sampling before the PFC tracer was released, thus the background concentration of PFCs could be ascertained.



(a)



(b)

Figure 2.2: Schematic of Macro-Trap Sampler. (a) Field sampling mode.

(b) Laboratory analysis mode.

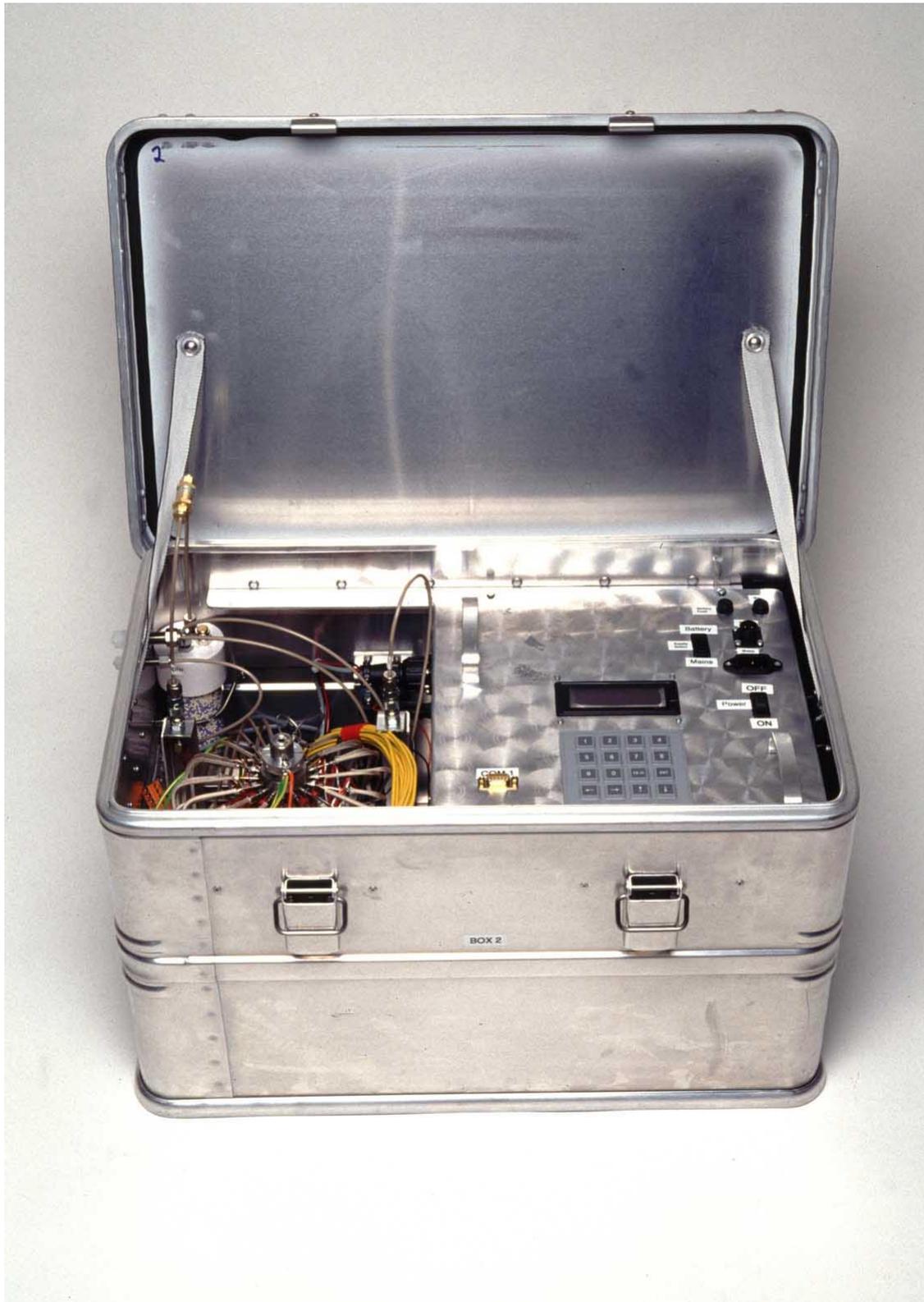


Figure 2.3: Trap Box with Macro Traps

2.3 Bag Samplers

The second sampling system consisted of a 10-port multiple base fitted with small solenoid valves (Pneumax, Italy), onto which a series of either 5-L or 10-L Tedlar bags (SKC Ltd, UK) were attached (see Figure 2.4). The air sample was pumped into each bag in turn by electrical actuation of the appropriate solenoid, which before and after the sampling was maintained in the normally closed position. The sampling time and position was pre-programmed using a custom designed built-in microprocessor (PIC16C64, Microchip Technology Inc., USA) system (Kauri Ltd, UK and T. Makepeace, University of Bristol, UK). The filled bags, isolated by their stainless steel valve fittings, were then returned to the laboratory to be analysed. Tests have indicated that the tracer concentrations remain constant in the bags for more than ten months.

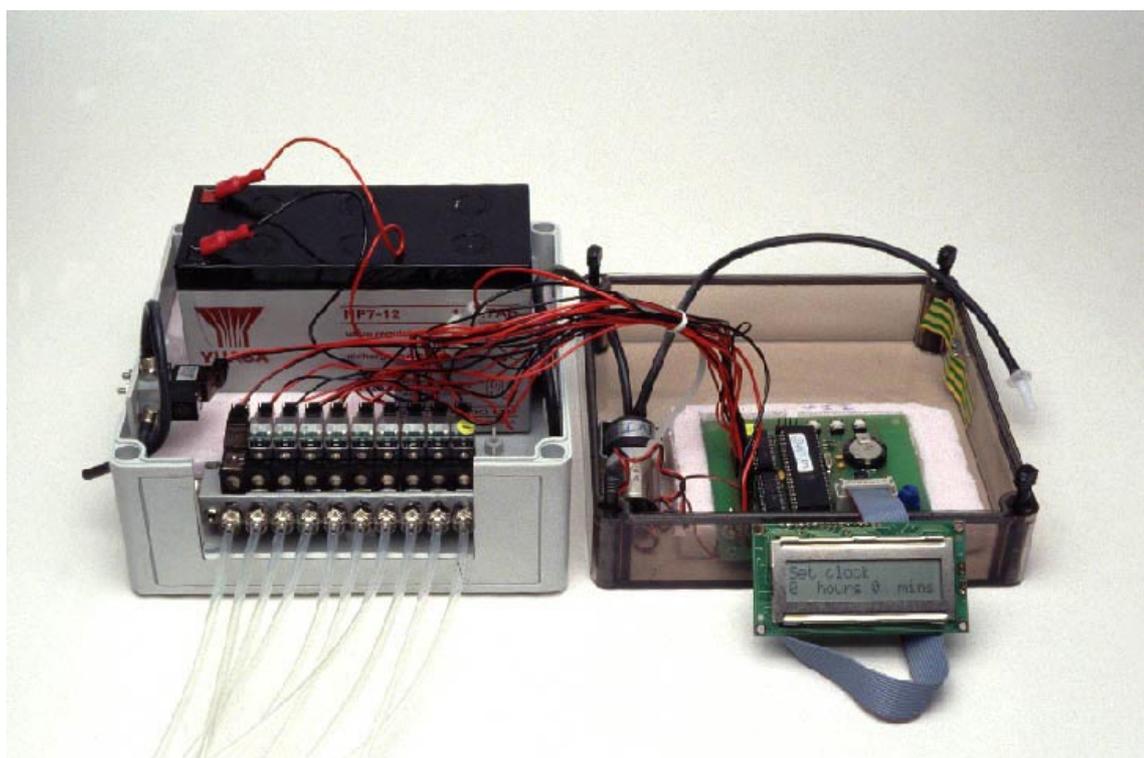


Figure 2.4: Automatic Bag Sampler; in this view the sample box has been opened to show the internal components.

The sampling average times were varied from 3 minutes, 6 minutes and up to 15 minutes, depending on the objectives of the tracer release experiment. At least 3 litres of air had to be taken so that background concentrations and above of tracer species could be easily quantified. In all field experiments a bag sample was taken 30 minutes before the start of the release to ascertain the background concentrations.

2.3.1 Bag and Trap Sampler Intercomparison

Inter-comparisons of the trap and bag samplers were carried out during an urban tracer release experiment in Birmingham, UK, as shown in Figure 2.5. The two systems were co-sited and samples of the same volume and duration were taken in parallel. When the trap and bag sample concentrations were plotted to give a straight-line graph through the origin, a least squares fit of $R^2 = 0.9919$ and a slope of 1.01 was obtained, indicative of close agreement between the two independent sampling systems.

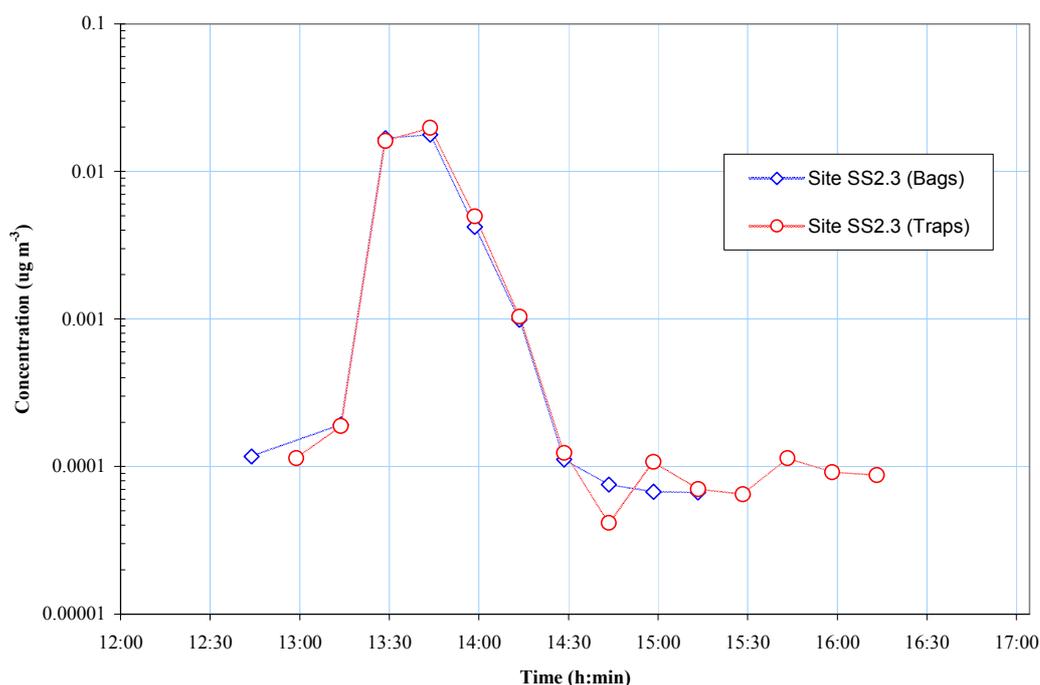


Figure 2.5: Comparison of perfluoromethylcyclohexane mixing ratio sampled by the macro-traps and bags at the same site, in parallel.

3.0 Analytical System

3.1 System Description

The analytical instrumentation consisted of a gas chromatograph (model 6890, Agilent Technologies Ltd., USA) with a mass selective detector (model 5973, Agilent Technologies Ltd., USA), which can operate in either electron impact (EI) or chemical ionisation (CI) mode, Figure 3.1. For tracer experiments using PFCs, the mass spectrometer was operated in the negative ion-chemical ionisation (NICI) MS mode, a highly selective and sensitive technique due to the efficient formation of stable cyclic molecular anions.

An adsorption-desorption system (ADS) was constructed, based on the design described in Simmonds *et al.* (1995) and Bassford *et al.* (1998) and modified to accept atmospheric samples collected by the two field-sampling systems. Samples returned from the field campaigns are sequentially sampled into the ADS, and quantitatively adsorbed onto a small micro-trap, which is maintained at a temperature of $-50\text{ }^{\circ}\text{C}$ and filled with 4mg Carboxen 1000 and 6mg Carboxen 1003, 45-50 Mesh (Supelco, Bellefonte, USA). Under these conditions the PFCs from several litres of air can be quantitatively re-focused onto the micro-trap well within the theoretical breakthrough volumes (BTV) of the species. To ensure that the micro-trap was clean prior to sampling, it was subjected to four thermal clean up cycles at $255\text{ }^{\circ}\text{C}$ under a constant flow of helium before each sample was introduced. The trap is thermally desorbed at $255\text{ }^{\circ}\text{C}$ in approximately four seconds onto the capillary GC column, which is sufficient to desorb completely the PFCs of interest. The very low volume of the micro-trap coupled with the rapid thermal desorption ensures that the enriched sample is transferred to the capillary column with negligible band broadening.



Figure 3.1: Analytical System, ADS-GC-NICI-MS.

3.2 Chromatography

The chromatographic resolution of all possible isomers of the PFCs is a challenging analytical problem. After evaluating a number of capillary columns, a gas-liquid wall-coated open tubular (WCOT) CP-Sil 5 CB methyl silicone column (0.32 mm x 100 m, 5 μm film thickness, Varian Inc, The Netherlands) was selected as the best compromise between resolution and analysis time. The GC oven temperature was maintained isothermally at 30°C for 22 minutes, then increased to 150°C at 20°C min⁻¹, where it remained for a further 10 minutes. Helium (GC+ grade, Air Products Ltd, UK) was used as the carrier gas at a flow rate of 1 ml min⁻¹. Methane was employed (grade 4.5, Air products Ltd, UK) as the reagent gas for the MS, with the source temperature maintained at 150°C and pressure regulated at 2.1×10^{-4} Torr with the methane reagent gas. The combination of the column and suitable temperature programme allowed the separation of the majority of the PFCs and their isomers, as shown in Figure 3.2. Four of the six possible perfluorodimethylcyclohexanes (PDCH) are resolved with co-elution of the meta/para-cis and meta/para-trans

isomers. For the tracer dispersion studies the preferred tracers were PMCP and PMCH since they are well resolved from all other PFCs.

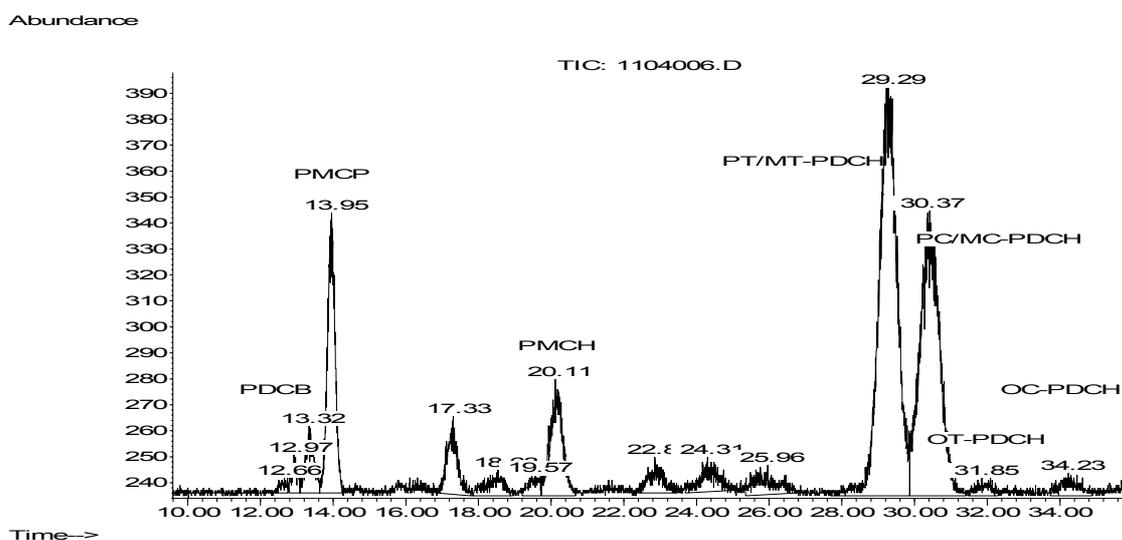


Figure 3.2: NICI-SIM chromatogram of 3-L Birmingham (UK) background air, with m/z : 300, 350, 400, 450. (PDCB: perfluorodimethylcyclobutane, PMCP: perfluoromethylcyclopentane, PMCH: perfluoromethylcyclohexane, PDCH: perfluorodimethylcyclohexane).

One unexpected benefit of using NICI was that the more abundant chlorofluorocarbons (CFCs) and other halocarbons present in the background atmosphere were not detected. Although individual CFCs may have a high electron affinity, some are more likely to undergo dissociative electron attachment under the NICI conditions used, rather than form stable molecular anions (Knighton, 1996). This considerably simplifies the overall analysis by removing the need for high temperature catalytic scrubbers and/or pre-clean-up procedures inherent when using electron capture detectors (ECDs) (Lagomarsino, 1996; Nodop *et al.*, 1998)

3.3 Sensitivity of the System

In Section 2.1.1, Table 2.1 lists some of the key properties of the candidate tracers and their background atmospheric mixing ratios determined during the ETEX project (Straume *et al.*, 1998). An analytical sensitivity in the fl L^{-1} range is clearly a prime requisite for the detection of these compounds. Studies of the sensitivity of the GC/MS system in NICI-SIM mode have been carried out by direct injection of a dilute PFC standard (nominally ppt range) via a 100 μl stainless steel loop. It was found that 10.6 fg [ca. $7.9 \times 10^{-13} \text{ cm}^3 \text{ (v/v)}$], 9.5 fg [ca. $7.1 \times 10^{-13} \text{ cm}^3 \text{ (v/v)}$], and 18.2 fg [$1.2 \times 10^{-12} \text{ cm}^3 \text{ (v/v)}$], of PDCB, PMCP and PMCH respectively, could be detected with a signal to noise ratio of 3:1 when in SIM-mode with selected ions m/z 300 and 350. To detect atmospheric background concentrations of PFCs at the fl L^{-1} level with high precision therefore requires a sample volume of several litres. The European background atmospheric concentration of the preferred tracer PMCH has been reported to be $4.6 \pm 0.8 \text{ fl L}^{-1}$ (Straume *et al.*, 1998), which is easily detected using the pre-concentration techniques described, coupled with the enhanced sensitivity of the NICI-SIM mode.

3.4 Calibration

A gravimetrically prepared standard gas mixture with a stated accuracy of $\pm 1\%$ was purchased from Linde Gases Ltd, UK. The primary standard contained 20.1 ppm PMCP, 19.9 ppm PDCB, 20.0 ppm PMCH and high ppm levels of CCl_3F (CFC-11, 2300 ppm) and CCl_2F_2 (CFC-12, 5000ppm). The primary standard was diluted volumetrically into an ultra clean 36-L electropolished stainless steel cylinder, using high purity zero air (5.5 grade, Air Products Ltd, UK) as the diluent gas. Dilutions were performed in an all stainless steel dilution apparatus based on a design developed by the Scripps Institution of Oceanography (SIO) for the preparation of standards for the Advanced Atmospheric Gases Experiment (AGAGE) (Simmonds *et al.*, 1998; Prinn *et al.*, 2000). The single step dilution of the primary standard presumes a linear relationship between all species and assigns a concentration to each PFC relative to the two CFCs in the mixture for which SIO maintains absolute calibration standards. The concentration of the two CFCs can be measured directly using GC-MS in electron impact (EI) mode, however EI is unable to detect the PFCs

in the low levels, hence the necessity of presuming a linear relationship between all species. As a second test the Bristol standard was inter-compared with a perfluorocarbon standard provided by the Environmental Measurements Laboratory (DOE, NY). The agreement between the two standards was excellent with a ratio of PCMP = 1.064, and PMCH = 0.992. The Bristol standard was higher in the case of PMCP, but fractionally lower for PMCH. For all tracer measurements, the secondary standard was analysed either side of the air sample to minimise any discrepancies due to a drift or change in performance of the analytical instrumentation.

3.5 Standard Performance

With continuous use the response of the NICI-MS to the PFCs was found to gradually decrease with time, which could be corrected by either routinely re-tuning the MS or cleaning the ion source. To overcome any short term instrumental drift, an analysis sequence of standard-sample-standard, with the concentration of the tracer determined from the ratio of the peak area of the sample to the average peak areas of the two bracketing standards was used. A “standard ratio” was also calculated by dividing each standard by the mean of its bracketing standards (Bassford *et al.*, 1998). The ratio should give a number close to unity and is an excellent indicator of the reproducibility of the method. The percentage RSDs for the precision (n=40) of PDCB, PMCP and PMCH were $\pm 2.58\%$, $\pm 1.86\%$, $\pm 1.68\%$, respectively.

The system was found to be linear over five orders of magnitude with respect to the PFCs. A broad linearity range is needed for tracer experiments, particularly when any sampling points are close to the release point. Significantly, the GC-MS system does not suffer from the much smaller linear dynamic range, which is a characteristic of the more commonly used ECD.

4.0 Tracer Release Experiment

The experimental arrangement of a full-scale dispersion experiment has several constraints. First, it has to be as simple as possible from the dispersion point of view. Secondly, the meteorological conditions during the experiment must be well documented. Finally, the experimental arrangement depends on the intrinsic limitations of the technique in terms of the maximum and minimum measurable concentrations, the number of available receptors, number of samplers (i.e. bags or traps) for each receptor (site) as well as the minimum averaging time for each sampler.

Three full-scale experiments were designed and realised in the city of Birmingham, UK. Birmingham is the second largest city in the UK with a population of approximately 1 million. It covers an area of 400 km², with the city centre itself extending over an area of about 9 km², with a mean building height of between 20 and 30 m.

The novel technique described in the previous chapters (Cooke *et al.*, 2000) was applied for the first time to the study of dispersion mechanisms in an urban environment.

Figure 4.1 shows the area over which the three experiments took place. It indicates the relative position of the release sites, measuring sites in the main arc (in the city centre) and the secondary measuring sites on the outskirts of Birmingham. R1, R2 and R3 indicate the release sites for the first, the second and the third experiment, respectively. S1.*n*, S2.*n* and S3.*n* indicate the measuring sites in the main arc for the first, the second and the third experiment, respectively. SS1.*n*, SS 2.*n* and SS 3.*n* indicate the secondary sites for the first, the second and the third experiment, respectively.

Table 4.1, Table 4.2 and Table 4.3, at the end of this chapter, give the co-ordinates and other details of the release sites and measuring sites for the three experiments.

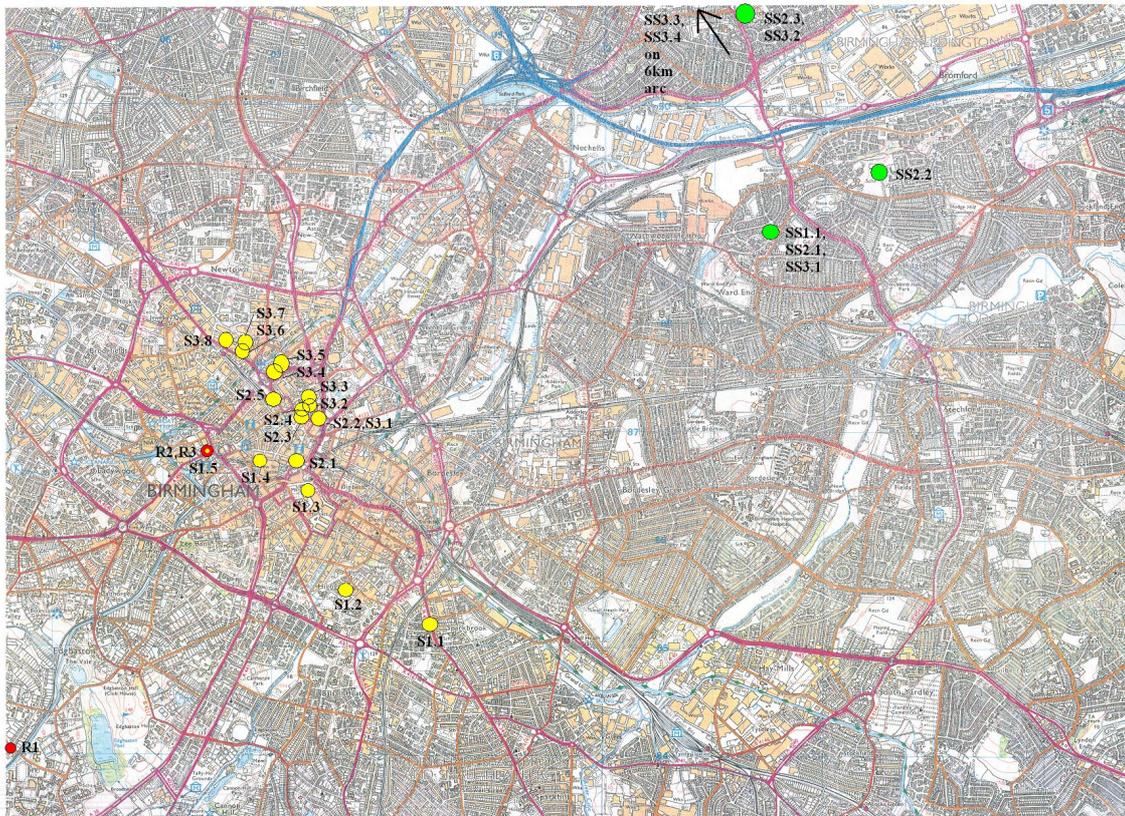


Figure 4.1: Overall area and experimental configuration for the three experiments.

4.1 First Experiment: Birmingham, UK, 1st July 1999

4.1.1 Preliminary Study

For the first experiment the distance between the release point and the main arc of the receptors (bag samplers) was chosen to be 3-4 km which ensured a balance between a scientifically interesting experiment and the testing of the novel technique for detecting very low concentrations. This scale of 3-4 km is intermediate between the city scale (~ 20 km) and street canyon scale (~ 100 m) and can be regarded for the city of Birmingham as roughly a neighbourhood scale.

The spatial and temporal experimental arrangement was determined using simple analytical models and the ADMS3 (CERC, 2000) operational dispersion model.

The available wind roses (Birmingham City Council) show that in the July period, the dominant wind direction is south-west. Consequently the configuration of the experiment was chosen for south-westerly wind within a range of 215° and 250°. Near neutral atmospheric stability and a wind speed of about 4-5 m/s satisfied the requirements for the simplest meteorological conditions for the experiment.

4.1.2 Overall Experimental Area Description

Pritchatts Road (a site at the University of Birmingham) was chosen as the release point as the terrain is fairly flat along the expected plume path and meteorological data were available at this site. The average building height is about 6-9 m which correspond to 2-3 storey buildings.

The size of the plume was estimated using ADMS3 and an analytical Gaussian plume model (Hanna *et al.*, 1982). The plume width, estimated on the basis of σ_y , for neutral atmospheric stability was ~ 600 m.

The optimum spacing between the samplers was deduced to be about 500 m. Five samplers were then placed in an arc at approximately 3.5 km from the release point with a cross-wind spacing of about 500 m. They are referred to as Sites S1.1, S1.2, S1.3, S1.4 and S1.5 (Figure 4.2). A secondary receptor Site SS1.1 (trap sampler, Cooke *et al.*, 2000) was placed on the outskirts of Birmingham at about 8.5 km from the release source. It was expected that measurements at a distance comparable with the city scale would be easily interpreted through standard plume dispersion models. A detailed description of the sites can be found in Table 4.1.

The release rate was selected in order to make the most of the dynamic range of the analytical instrumentation. The release time was adjusted in order to record the total temporal evolution of the puff, the averaging time of the receptors being set at their minimum value at the time of the experiment.

A release of perfluoromethylcyclohexane (PMCH) took place on 1st July 1999, from a heated chimney at 4.5m height described in Section 2.1. The release apparatus was situated at the University of Birmingham, Pritchatts Road and the effective release rate was 4 gs⁻¹ over a 40-minute period (see Figure 6.1). Due to some problems with the pump in the release arrangement, the “top hat” conditions were only approximately obtained. Figure 6.2 shows the total mass of tracer released as a function of the time.

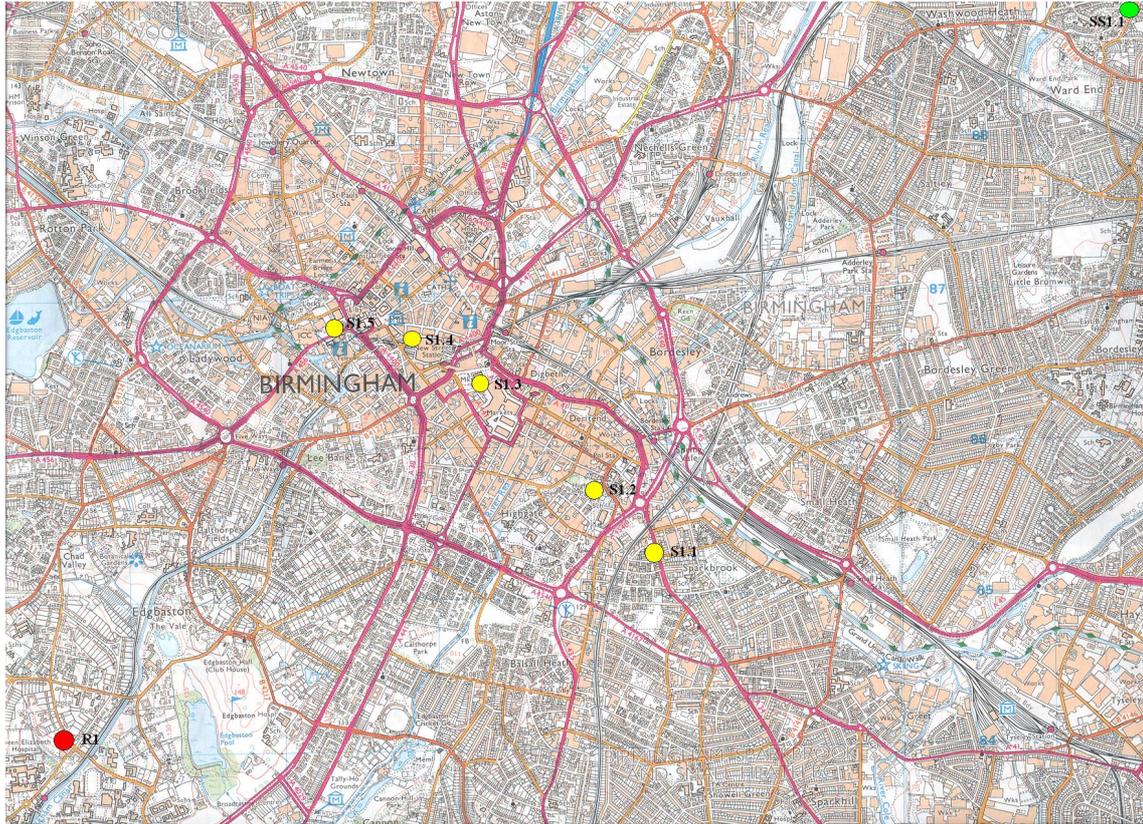


Figure 4.2: First experiment: Birmingham, UK, 1st July 1999. Tracer release and sampling sites.

4.2 Second Experiment: Birmingham, UK, 1st February 2000

The second experiment took place on the 1st February 2000. It was decided on the basis of the results obtained in the previous experiment to perform it in an area where the plume depth is more comparable with the building heights. It was then decided to perform the experiment in a region with higher buildings and place the receptors at a smaller distance from the source than in the first experiment. The distance between source and receptors was ~ 1 km. The cross-wind spacing between receptors was then determined by using simple analytical models to be around 300 m, with an averaging time for the samplers in the main arc of 3 minutes. This better time resolution was expected to give more data during the rise and the decay which, at this distance from the source, was estimated to be faster. Three secondary receptors were placed at about 6 km from the release position (see Figure 4.3). The release rate was then reduced to 0.23 gs^{-1} and the duration of the release was 35 minutes.

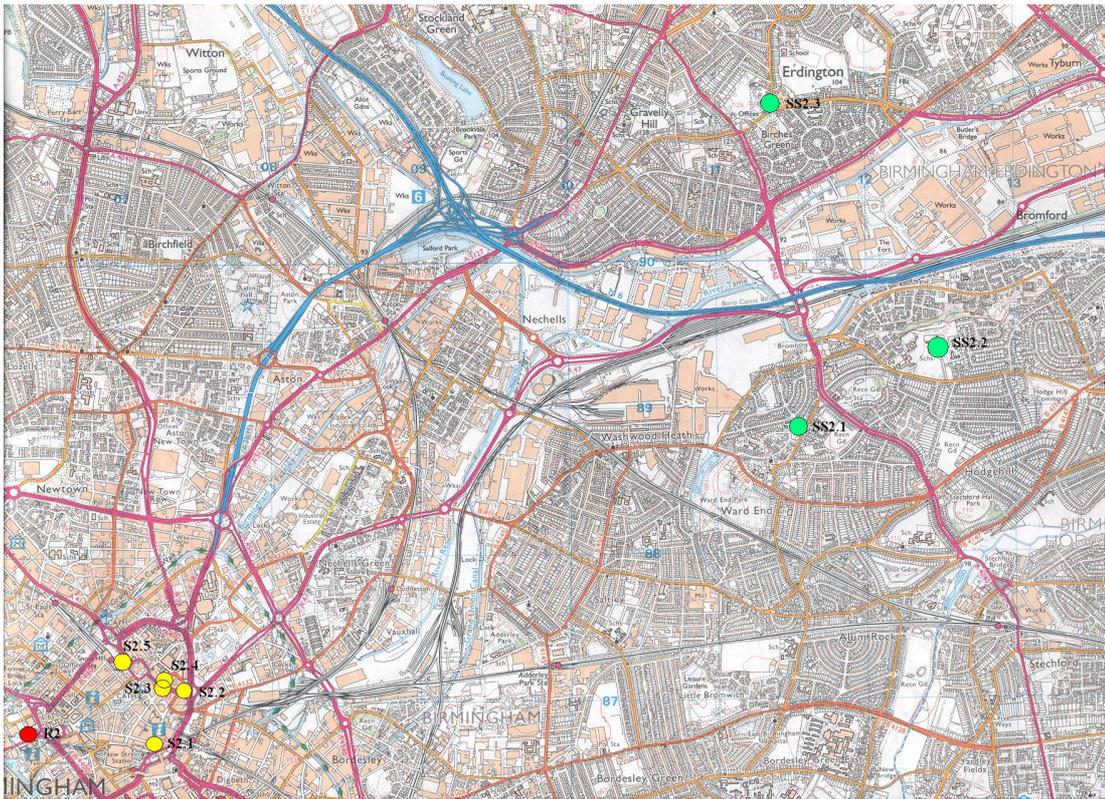


Figure 4.3: Second experiment: tracer release and sampling sites. Birmingham, UK, 1st February 2000.

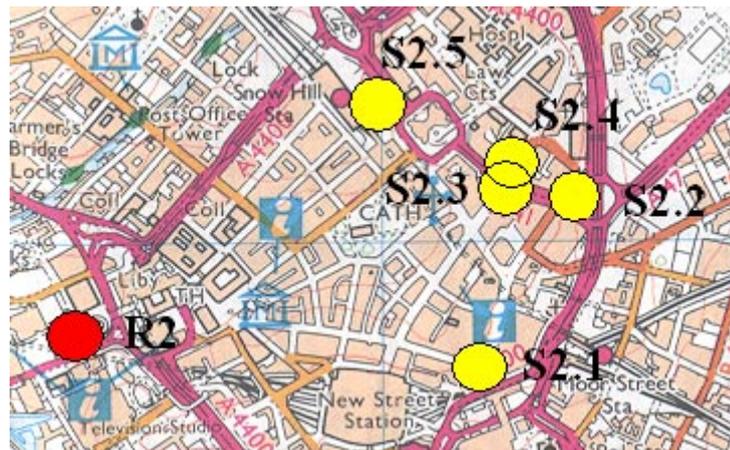


Figure 4.4: Second experiment: tracer release and sampling sites on main arc. Birmingham, UK, 1st February 2000.

4.3 Third Experiment: Birmingham, UK, 2nd August 2000

The third experiment performed on the 2nd August 2000, was mainly designed on the basis of the second one. The second experiment showed some interesting features but did not give conclusive results for the sites in the main arc (see results shown in chapter 6). This was because the plume was partially missed and it turned out that the most important receptor failed. For the second experiment, measurements taken at site SS3.3 gave some interesting indications. The first was that the measurements obtained by both a trap sampler and bag sampler are consistent. The second is that the measurements are of the same order of magnitude as estimated by analytical models. These results also gave an estimate of the extremes of the plume paths. At a distance of 1 km, the plume is not very wide (~150 m estimated by simple analytical models, with stability class D), the accuracy of the meteorological conditions and in particular wind direction, is a critical factor for the success of the experiment.

Based on the observations above it was decided to reduce the cross-wind spacing between the receptors. As a second tracer (PMCP) was also available, it was used in this experiment in conjunction with the first tracer (PMCH). The secondary tracer release was delayed by half the sampling period (averaging time). The sampling period was 6 minutes. The primary tracer, PMCH, was released on 2nd August at 13:00 while the secondary tracer, PMCP, was released at 13:03. The motivation for this was to obtain the same time resolution over a longer measuring period without using more sampling bags.

The release rate was 0.22 gs^{-1} for PMCH and 0.18 gs^{-1} for PMCP.

Table 4.3 summarises the characteristics and positions of the sites. Figures 4.5 and 4.6 show the map of the experiment and the positions of the sites.

Table 4.1: Site characteristics: Birmingham, 1st July 1999

SITE NUMBER	LOCATION	DISTANCE FROM RELEASE (km)	MEASUREMENT HEIGHT (m)	OS-CO-ORDINATES	LONGITUDE/LATITUDE	BEARING (°) FROM RELEASE SITE (R1)
R1	Pritchatts Road, Birmingham University		4.5 (Release height)	404500/284100	52,27',20"N/ 1,56',00"W	
S 1.1	Auckland Rd./ Stratford Rd	4.05	1.9	408400/285320	52,27',55"N/ 1,52',40"W	251
S 1.2	Highgate Park	3.8	1.9	408000/285720	52,28',10"N/ 1,52',55"W	246
S 1.3	Moat Lane Multi-storey Car Park <i>ROOF</i>	3.6	40	407300/286450	52,28',35"N/ 1,53',30"W	230
S 1.4	The Pallasades	3.5		406850/286750	52,28',43"N/ 1,54',00"W	222
S 1.5	City Centre Cabin	3.2	3 and 1.6	406350/286800	52,28',45"N/ 1,54',25"W	216
SS 1.1	Birmingham East, Ward End J&I School, B8	8.38	3	411500/288850	52,29',50"N/ 1,49',50"W	235

Table 4.2: Site characteristics: Birmingham, 1st February 2000

SITE NUMBER	LOCATION	DISTANCE FROM RELEASE (km)	MEASUREMENT HEIGHT (m)	OS-CO-ORDINATES	LONGITUDE/LATITUDE	BEARING (°) FROM RELEASE SITE (R2)
R 2	Centenary Square		4.5 (Release Height)	406350/286800	52,28',45"N/ 1,54',25"W	
S 2.1	Rotunda	0.88	2.1	407200/286750	52,28',43"N/ 1,53',40"W	273
S 2.2	Dale End	1.05	2.1	407350/287050	52,28',50"N/ 1,53',30"W	254
S 2.3	Old Square	0.95	2.1	407250/287150	52,28',55"N/ 1,53',35"W	250
S 2.4	Priory House <i>ROOF</i>	1.00	30	407250/287200	52,28',57"N/ 1,53',35"W	247
S 2.5	Snow Hill	0.83	2.1	407000/287300	52,29',00"N/ 1,53',50"W	232
SS 2.1	Ward End School	5.5	3	411500/288850	52,29',50"N/ 1,49',50"W	249
SS 2.2	Tame Valley	6.63	3	412600/289450	52,30',10"N/ 1,47',50"W	247
SS 2.3	Spring Lane, Erdington	6.6	3	411500/291125	52,31',05"N/ 1,49',50"W	229

Table 4.3: Site characteristics: Birmingham, 2nd August 2000

SITE NUMBER	LOCATION	DISTANCE FROM RELEASE (km)	MEASUREMENT HEIGHT (m)	OS-CO-ORDINATES	LONGITUDE/LATITUDE	BEARING (°) FROM RELEASE SITE (R3)
R 3	Centenary Square		4.5 (Release Height)	406350/286800	52,28°,55"N/ 1,54',25"W	
S 3.1	Dale End, Queens Way	1	1.8	407350/287050	52,28°,50"N/ 1,53',30"W	254
S 3.2	Birmingham Children's Hospital, Steelhouse Lane	1	1.8	407250/287350	52,29°,00"N/ 1,53',35"W	241
S 3.3	Birmingham Children's Hospital, <i>ROOF</i>	1	~20	407250/287375	52,29°,02"N/ 1,53',35"W	238
S 3.4	Salvation Army	1	2	407000/287525	52,29°,10"N/ 1,53',50"W	219
S 3.5	Salvation Army, <i>ROOF</i>	1	~20	407000/287550	52,29°,11"N/ 1,53',50"W	222
S 3.6	SND Electrical Wholesalers, Constitution Hill	1	2	406675/287700	52,29°,15"N/ 1,54',07"W	202
S 3.7	SND Electrical Wholesalers, <i>ROOF</i>	1	11	406700/287700	52,29°,15"N/ 1,54',05"W	204
S 3.8	Fashionmark, Howard Street	1	2	406500/287800	52,29°,20"N/ 1,54',15"W	192
SS 3.1	Ward End School	5.5	3	411500/288850	52,29°,50"N/ 1,49',50"W	249
SS 3.2	Spring Lane, Erdington	6.6	3	411500/291125	52,31°,05"N/ 1,49',50"W	229
SS 3.3	Stockland Green School	6.0	10	409400/291600	52,31°,20"N/ 1,51',40"W	214
SS 3.4	College High School	6.5	10	408600/292700	52,31°,55"N/ 1,52',20"W	200

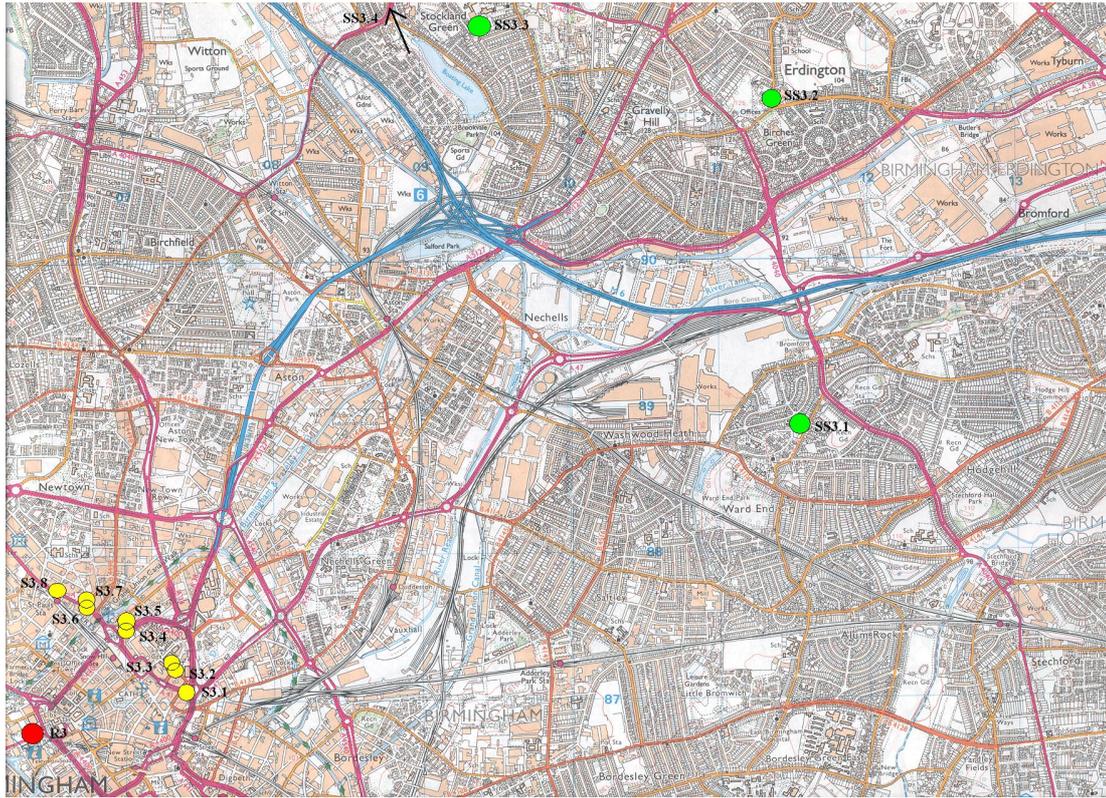


Figure 4.5: Third experiment: tracer release and sampling sites. Birmingham, UK, 2nd August 2000.

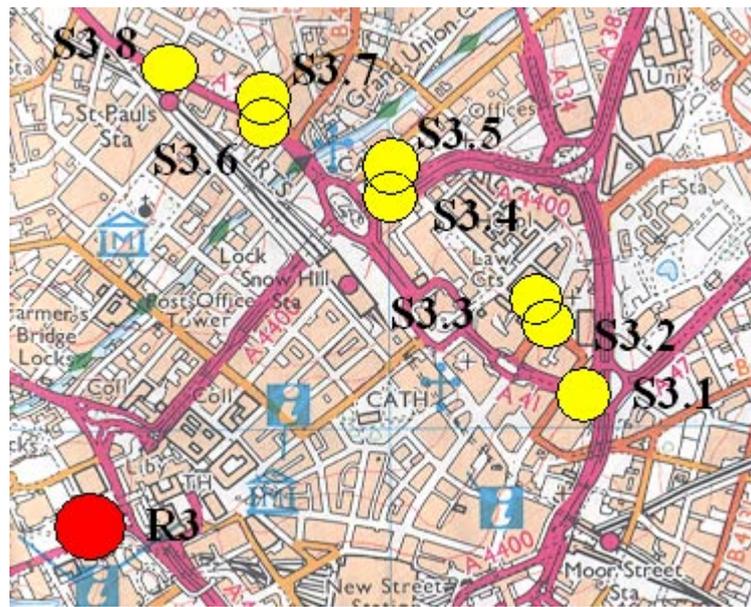


Figure 4.6: Third experiment: tracer release and sampling sites on main arc. Birmingham, UK, 2nd August 2000.

5.0 Meteorological Measurements

5.1 PUMA Campaign

Meteorological measurements were provided by the PUMA (Pollution of the Urban Midlands Atmosphere) consortium as part of the UK's Urban Regeneration and the Environment (URGENT) programme, sponsored by the Natural Environment Research Council (NERC). The URGENT/PUMA campaigns coincided with the tracer release experiments in Birmingham. The measurements were taken at various sites within the Birmingham urban area. Figure 5.1 show the location of the PUMA sites. Measurements were averaged over 15 minutes. Table 5.1 shows an example of a typical meteorological file.

Station ID	Julian Day	Time	Temp	Hum max	Hum min	Wind Speed	Wind Direction	Battery Voltage
475	215	00:15	16.84	79.3	76.9	2.547	209.5	12.7

Table 5.1: PUMA meteorological file description

5.1.1 PUMA Data Availability

For the first tracer experiment meteorological PUMA data were available from only two sites: Prichatts Road and Frankley Reservoir. Measurements were taken at 12 m and 10 m above ground level, respectively.

For the second tracer experiment meteorological PUMA data were available from 7 sites: Barr Beacon, Frankley Reservoir, Halfpenny Green, Kidderminster, Solihull Sixth Form College, Tamworth Farm and Turner's Hill. All measurements were taken at 10 m above ground level

For the third tracer experiment meteorological PUMA data were available from 5 sites: Brockhill, Frankley Reservoir, Kidderminster, Solihull Sixth Form College, and Turner's Hill. Again, all measurements were taken at 10 m above ground level.

Table 5.2 summarises PUMA data availability and show site details and co-ordinates.

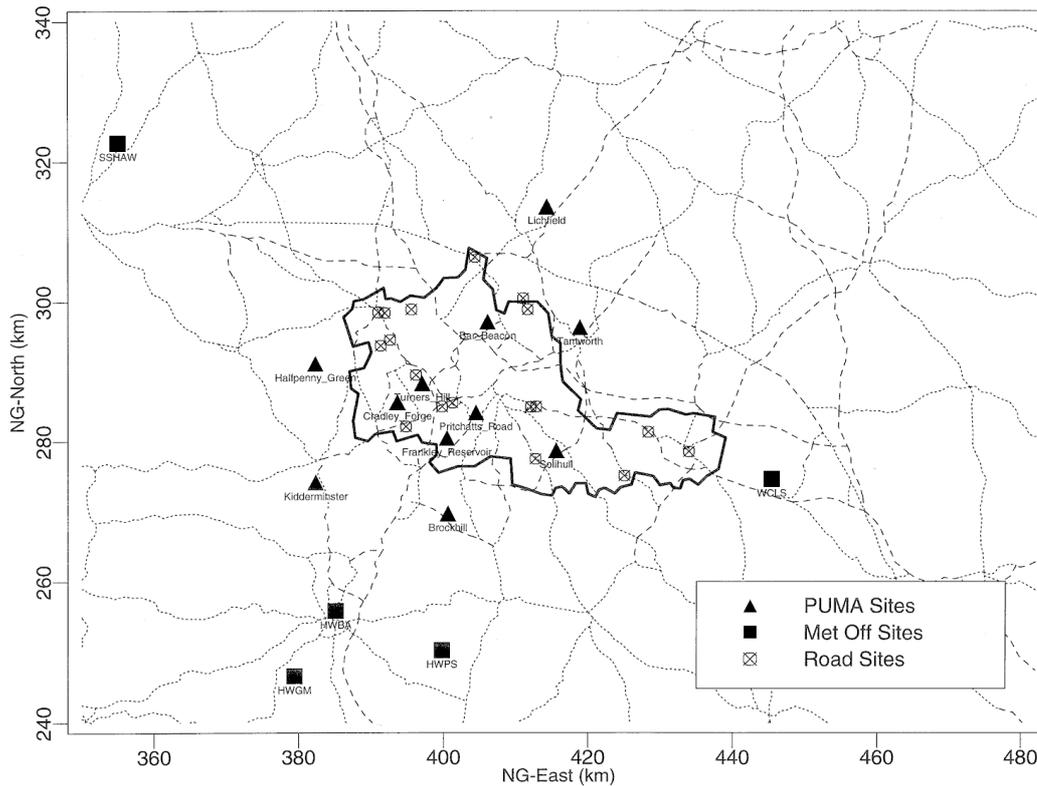


Figure 5.1: Overall map of meteorological sites.

5.2 Additional Meteorological Data

As well as data provided by the PUMA campaigns, other meteorological measurements were taken to support the tracer experiments.

For the second and third tracer experiments additional wind speed and wind direction data were measured using a standard Porten anemometer and wind vane positioned on a 6m high mast erected at the release site. The measurements suffered from interference from building and street canyon effects. However the measurements give a good indication of actual conditions experienced within the city. It must be noted that the data from the third experiment was unavailable at the time of writing this report, as it had not been processed. For further details please contact Mr. T. Makepeace, University of Bristol.

For the third experiment other data was obtained using a cup anemometer and wind vane positioned at the top of the 140 m BT tower (Figure 5.2). The tower is about 570 m from the release site, the layout of which is shown in Figure 5.3. It was

logistically impossible to get complete clearance from obstructions on the platform, however the meteorological instrumentation was set up at a height of 4 m above the platform, so that the least amount of interference would be encountered under south-westerly wind conditions. Hence the data obtained is only indicative of actual conditions at the time of the experiment, and should be treated with caution.

Meteorological data was also made available by the Met. Office (Bracknell) for the third experiment for 15 m, 30 m and 45 m at an urban site in Birmingham (Table 5.3).

During the second and third tracer experiment, qualitative information about wind direction was available from the release of helium filled domestic balloons domestic balloons from the release site. The approximate weight of a balloon was 1.46 g (+/-0.25 g) and were filled to an approximate lift of 2 g. They were observed for 60-90 seconds after the release and their trajectory sketched on a map.

For all the campaigns, qualitative observations were made at the sampling points and are given in Appendix B.

For the second experiment an estimate of the boundary layer height was available from a remote sensing LIDAR instrument run by the University of Cambridge as part of PUMA. A detailed description of which can be found in Appendix C.

Table 5.3 summarises additional data availability, site details and co-ordinates.

Table 5.2: PUMA meteorological sites.

(All data was kindly provided by Dr. G. McGregor, University of Birmingham)

Location	Ordinance Survey co-ordinates	Latitude/ Longitude	Height of Measurements (m)	DATA AVAILABLE		
				1 st July, 1999	1 st Feb, 2000	2 nd Aug., 2000
Tamworth/ Middleton House Farm	418870/ 296350	52,31'50"N 1,43'20"W	10	No	Yes	No
Barr Beacon/ South Staffs Water	406100/ 297150	52,34'20"N 1,54'30"W	10	No	Yes, but data unreliable	No
Frankley Reservoir/ Severn Trent Water	400650/ 280400	52,25'00"N 1,59'50"W	10	Yes	Yes	Yes
Turners Hill/ Sandwell/ Midland Quarry	397020/ 288310	52,29'30"N 2,2'40"W	10	No	Yes	Yes
Brockhill/ Bromsgrove/ Severn Trent	400250/ 270160	52,19'40"N 1,59'50"W	10	No	No	Yes
Lichfield/ Fradley Park	414300/ 313950	52,43'20"N 1,47'20"W	10	No	No	No
Solihull Sixth Form College	415600/ 278700	52,24'20"N 1,46'20"W	10	No	Yes	Yes
Kidderminster Sewerage Works	382360/ 274125	52,21'50"N 2,15'30"W	10	No	Yes	Yes
Halfpenny Green Airport	382300/ 291125	52,31'00"N 2,15'30"W	10	No	Yes	No
Birmingham University, Pritchatts Road	404500/ 284100	52,27'20"N 1,56'00"W	12	Yes	No	No

Table 5.3: Additional meteorological sites.

Description/ Location	Data Source	Ordnance Survey co-ordinates	Latitude/Lo ngitude	Height of Measurements (m)	DATA AVAILABLE		
					1 st July, 1999	1 st Feb, 2000	2 nd Aug., 2000
Release site met. data, Centenary Square	T. Makepeace, University of Bristol	406350/ 286800	52,28',45"N/ 1,54',25"W	6	No	Yes	Yes, but not processed at the time of the report
Met. Data, BT. Tower	T. Makepeace, University of Bristol	406500/ 287350	52,29',00"N/ 1,54',15"W	140	No	No	Yes
Met. Data, Dunlop Site	N. Ellis, Met Office.	412600/ 290600	52, 30', 45"/ 1, 48' 50"	15 30 45	No	No	Yes
Balloon Release Data, Centenary Square	T. Makepeace, University of Bristol	406350/ 286800	52,28',45"N/ 1,54',25"W	Not Applicable	No	Yes	Yes
Boundary Layer height measurement with LIDAR, Pritchatts Road	E.Norton University of Cambridge	404500/ 284100	52,27',20"N/ 1,56',00"W	Not Applicable	No	Yes	No
Qualitative Observations at sampling sites		Positions given in Tables 4.1, 4.2, 4.3		Ground and Roof based	Yes	Yes	Yes



Figure 5.2: British Telecom (BT) Tower, Birmingham, UK.

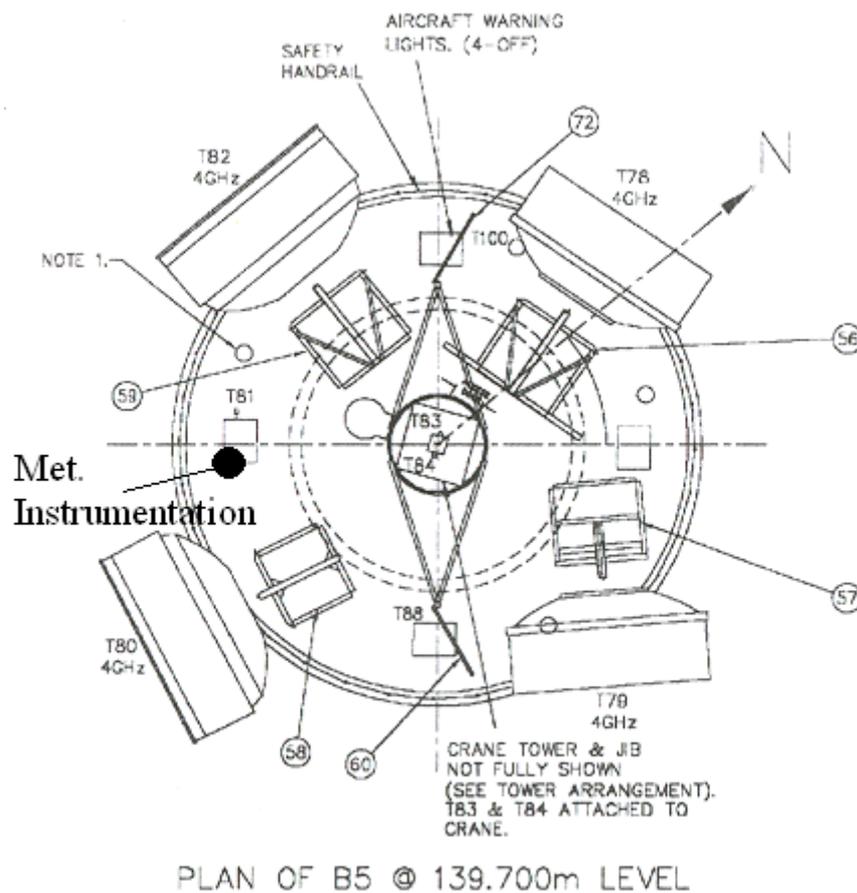


Figure 5.3: British Telecom Tower (BT), Birmingham, UK, general top platform arrangement.

6.0 Summary of Results

6.1 First Experiment: 1st July 1999

6.1.1 Tracer Release

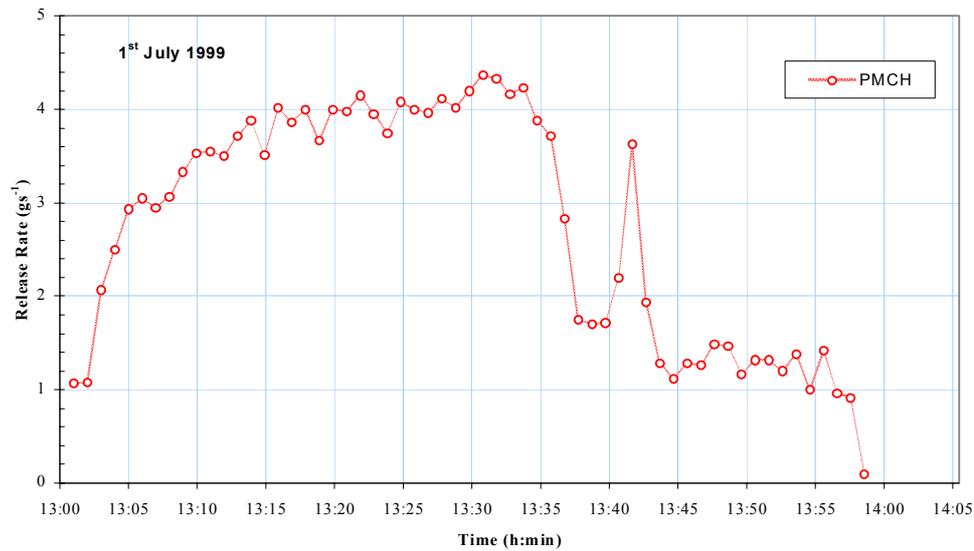


Figure 6.1: Tracer release rate.

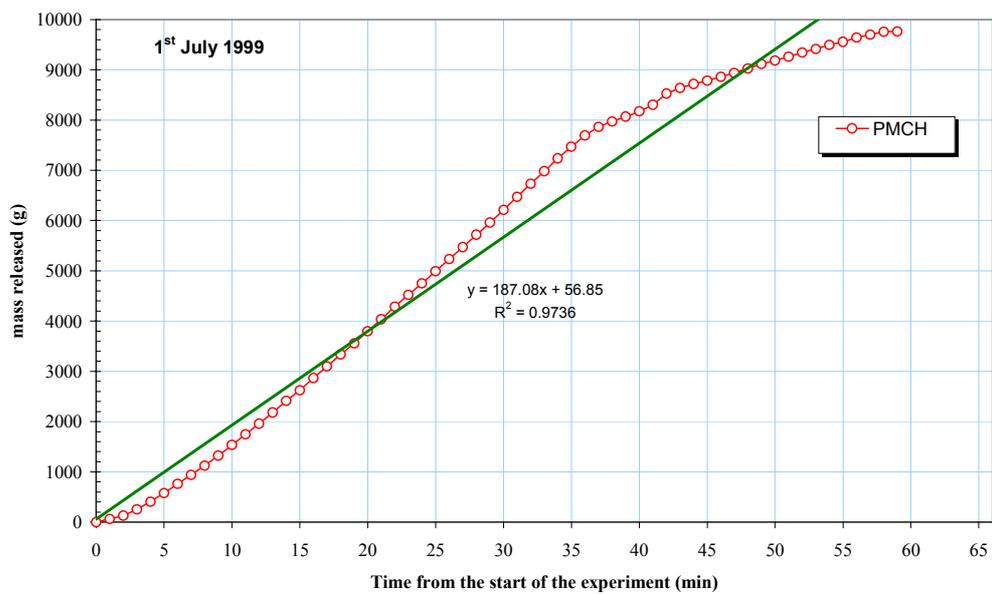


Figure 6.2: Tracer total mass released during the experiment.

6.1.2 Concentration Measurements at the Main Sites

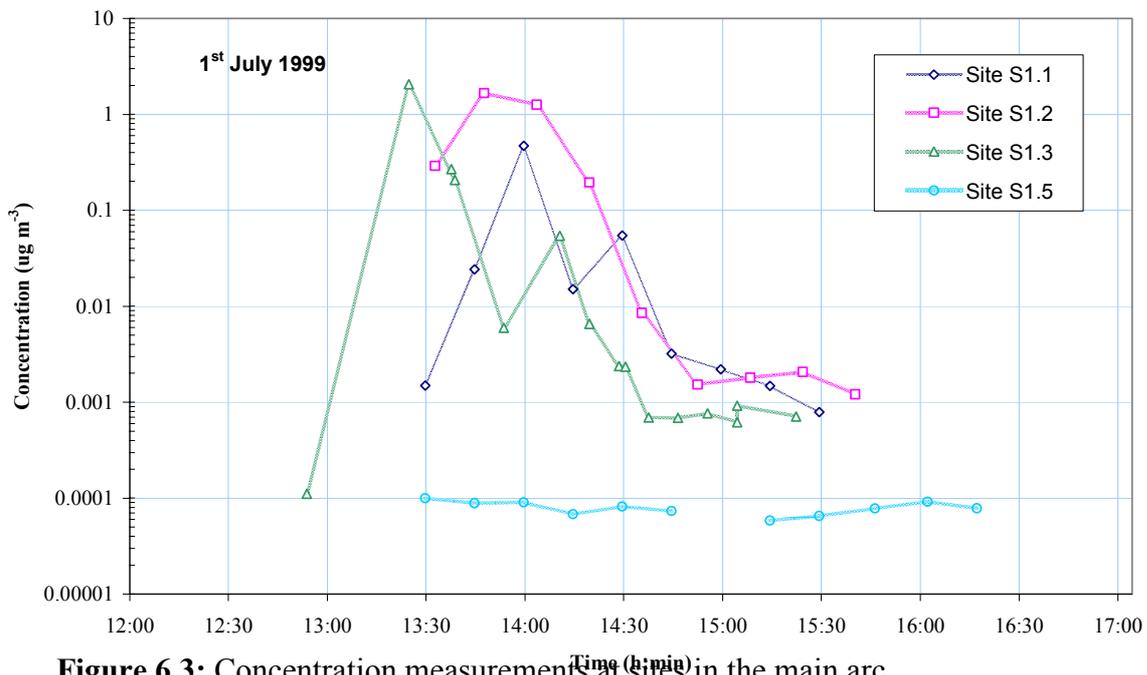


Figure 6.3: Concentration measurements at sites in the main arc.

6.1.3 Concentration Measurements at the Secondary Site

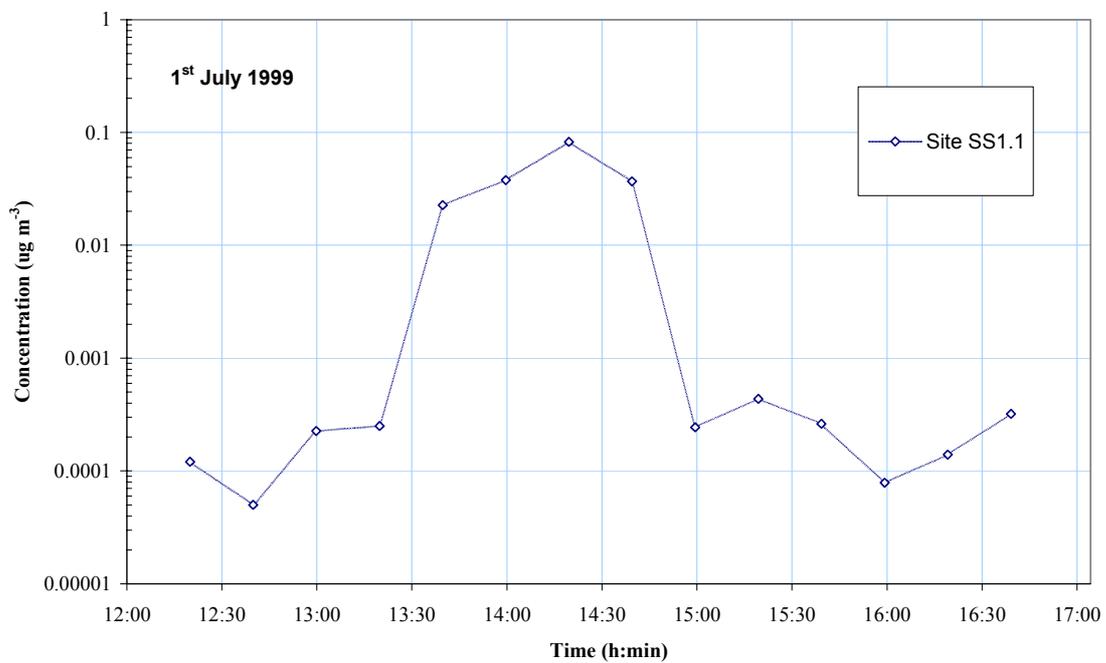


Figure 6.4: Concentration measurements at the secondary site.

6.1.4 Meteorological Measurements

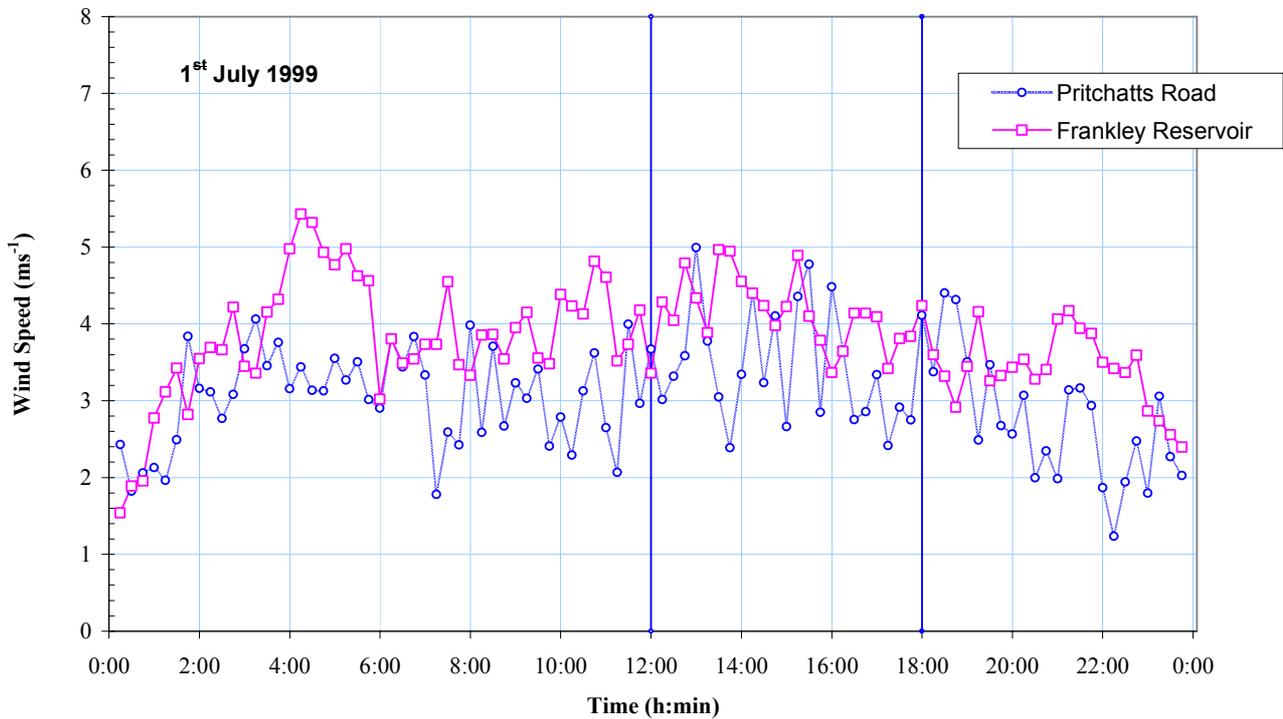


Figure 6.5: Wind speed measurements from the available PUMA sites.

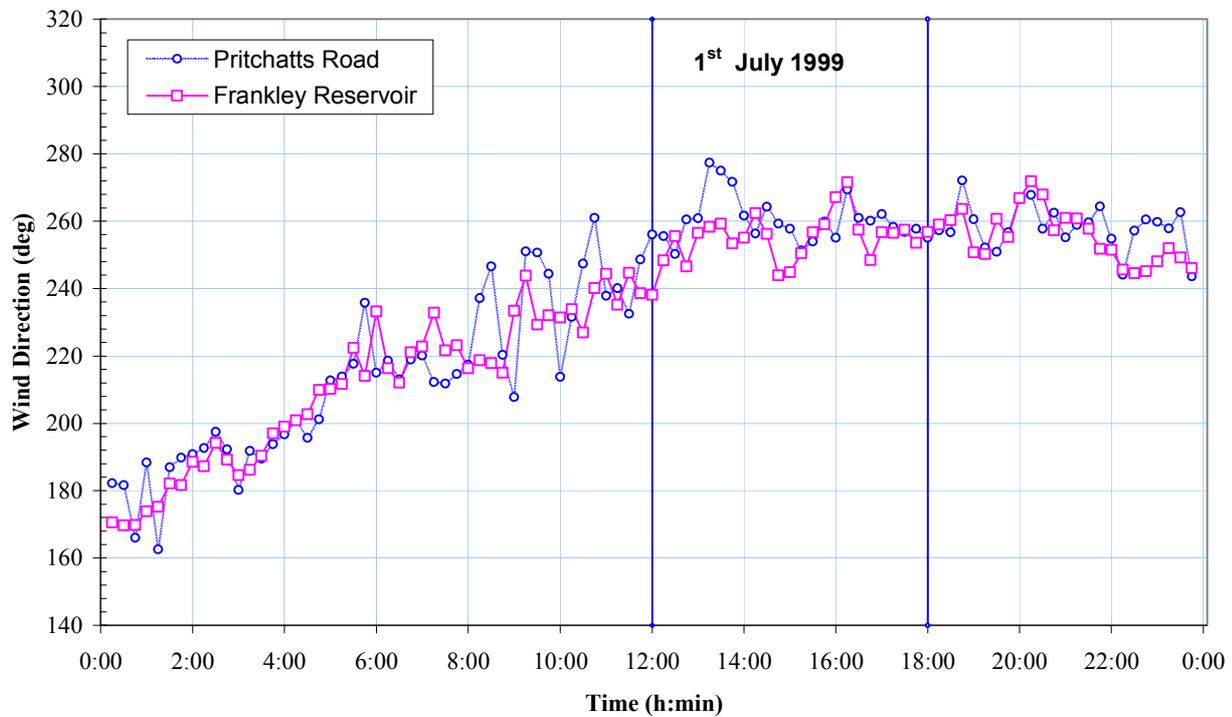


Figure 6.6: Wind direction measurement from the available PUMA sites.

6.2 Second Experiment

6.2.1 Tracer Release

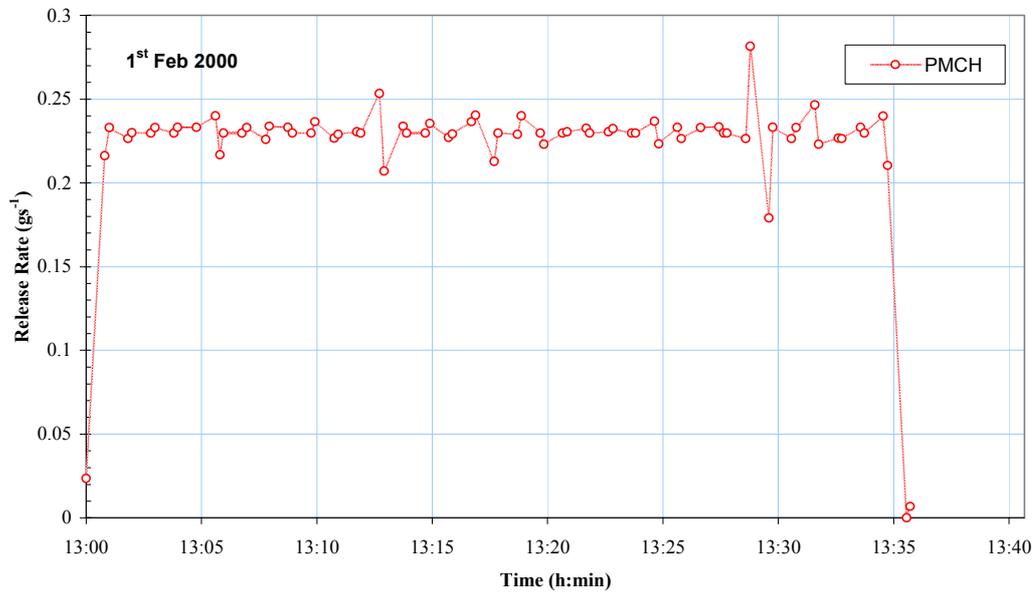


Figure 6.7: Tracer release rate.

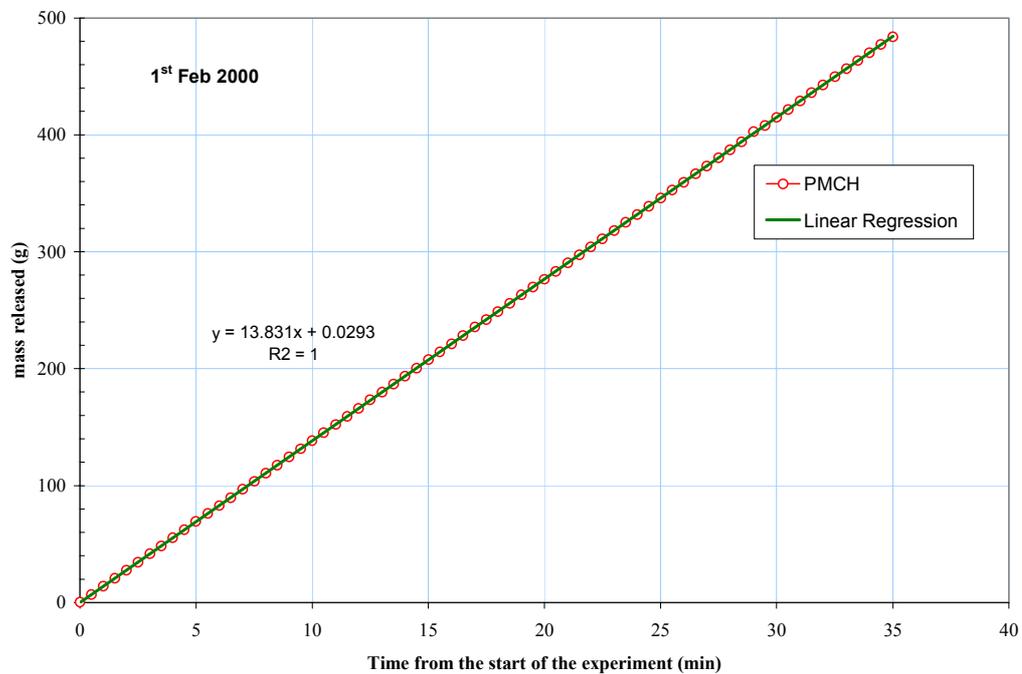


Figure 6.8: Tracer total mass released during the experiment.

6.2.2 Concentration Measurements at the Main Sites

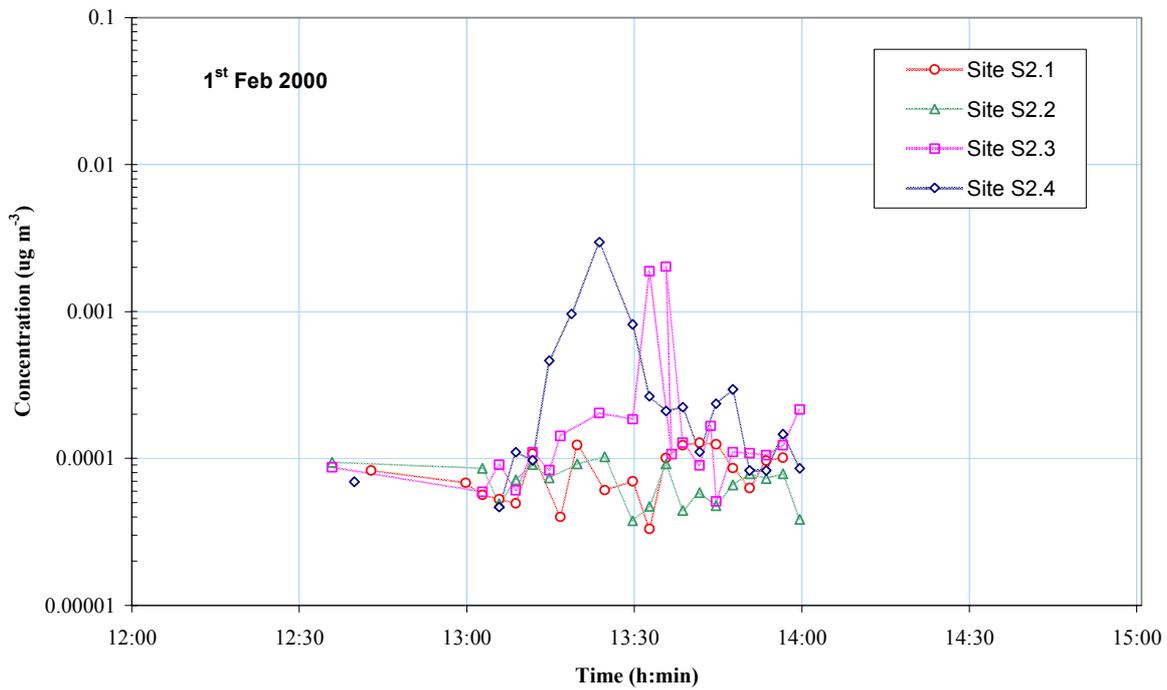


Figure 6.9: Concentration measurements at sites in the main arc.

6.2.3 Concentration Measurements at the Secondary Site

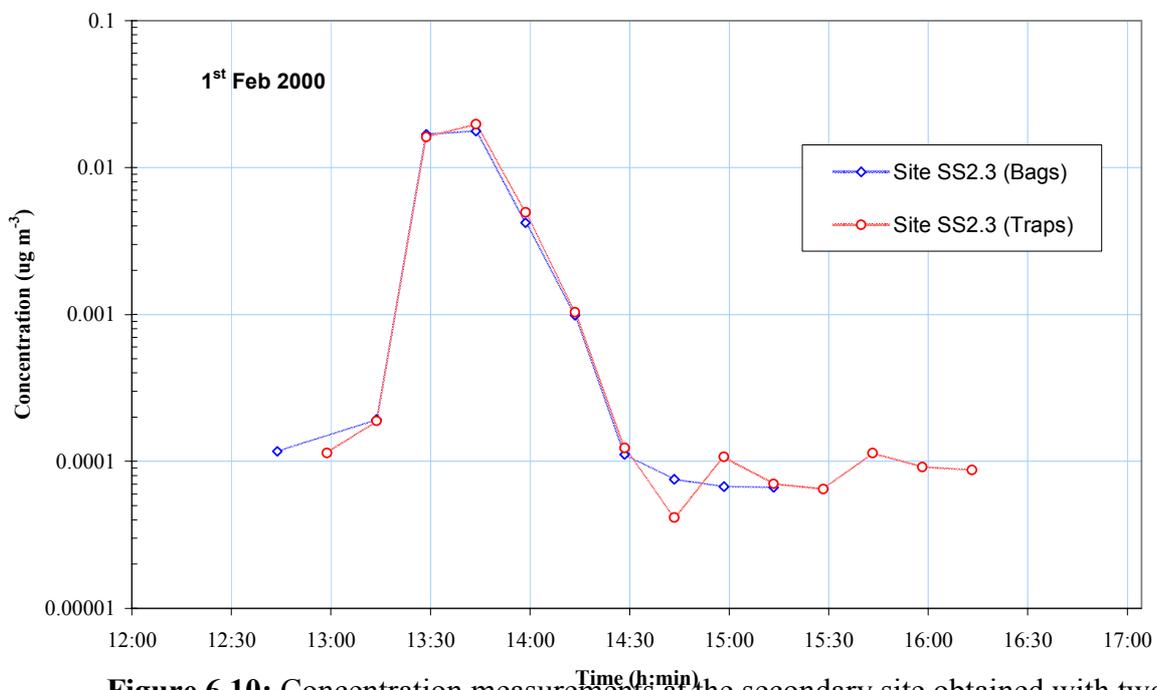


Figure 6.10: Concentration measurements at the secondary site obtained with two different instruments.

6.2.4 Meteorological Measurements

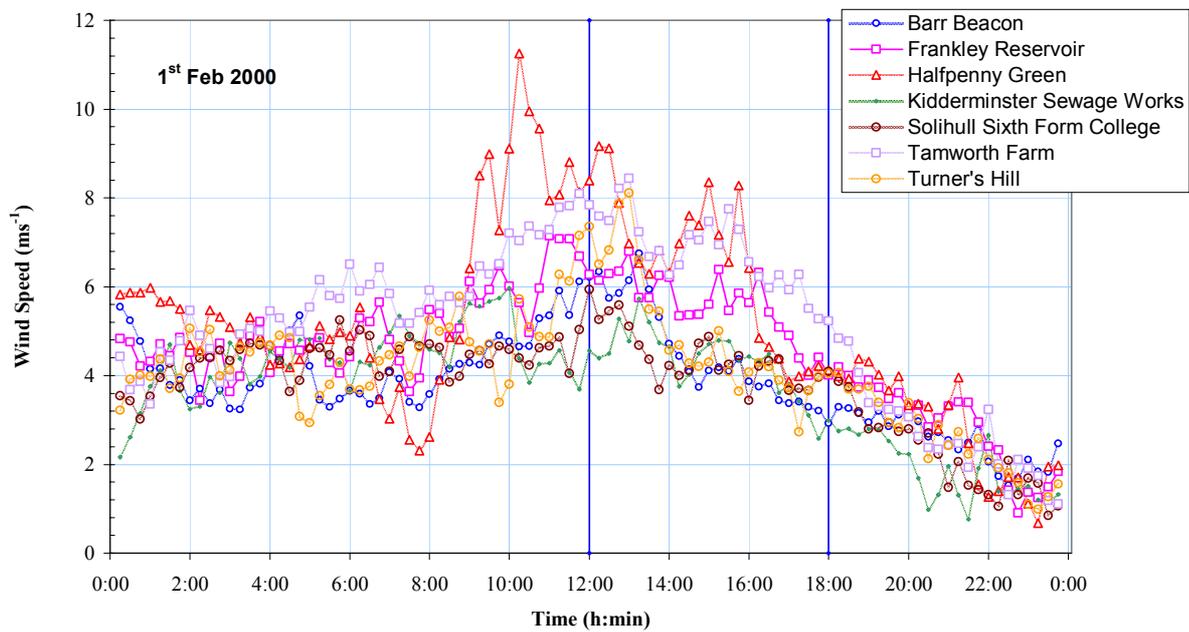


Figure 6.11: Wind speed measurements from the available PUMA sites.

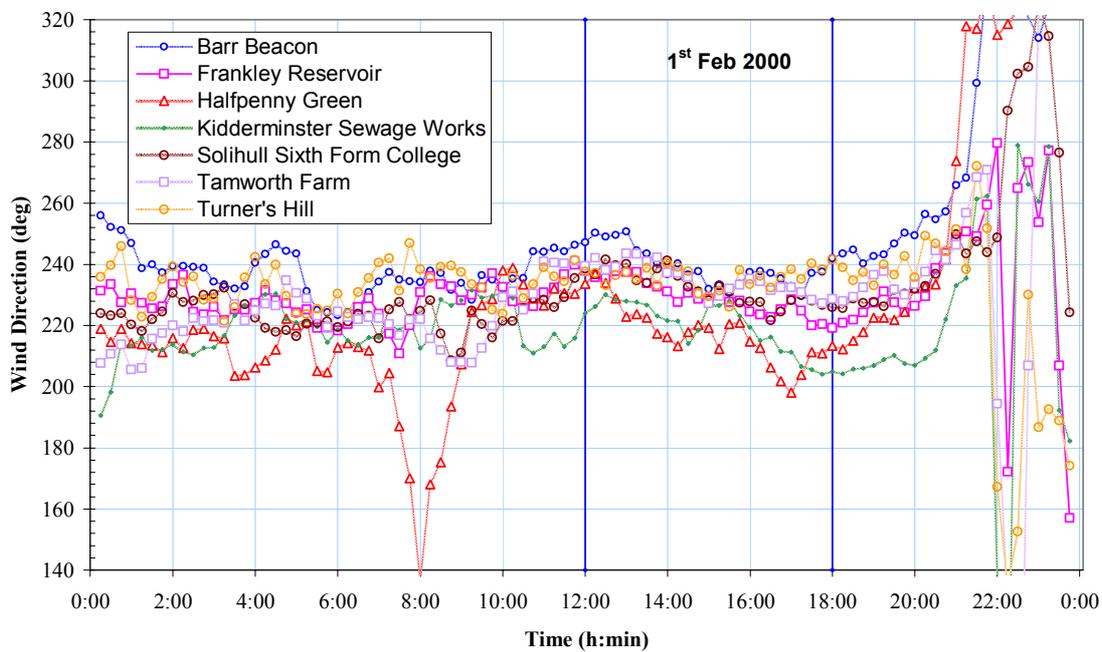


Figure 6.12: Wind direction measurements from the available PUMA sites.

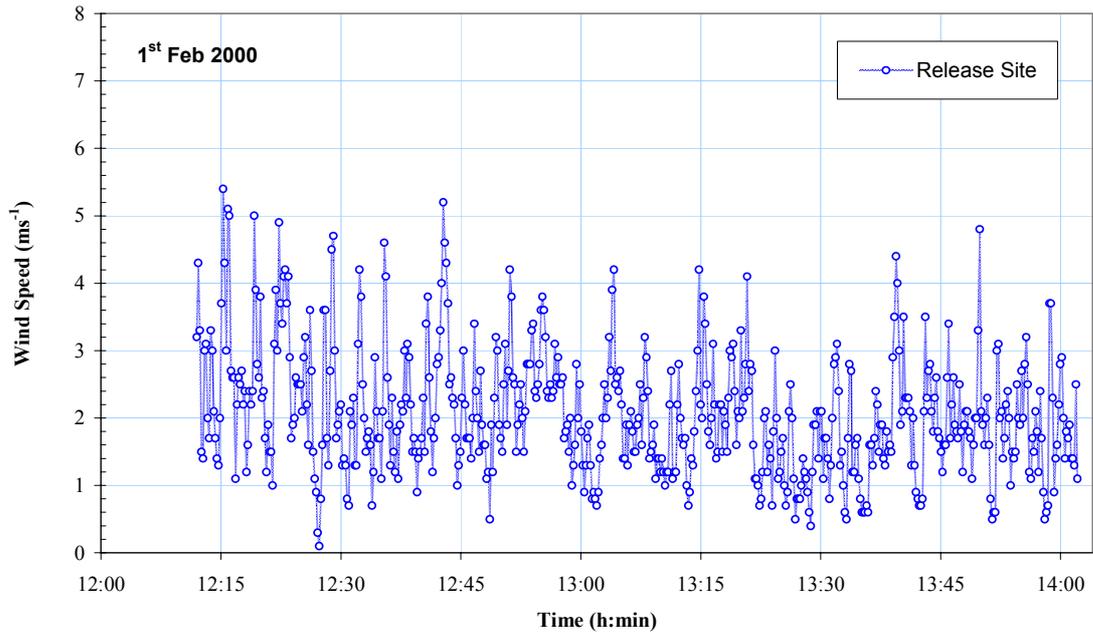


Figure 6.13: Additional meteorological data: wind speed measurements from the release site.

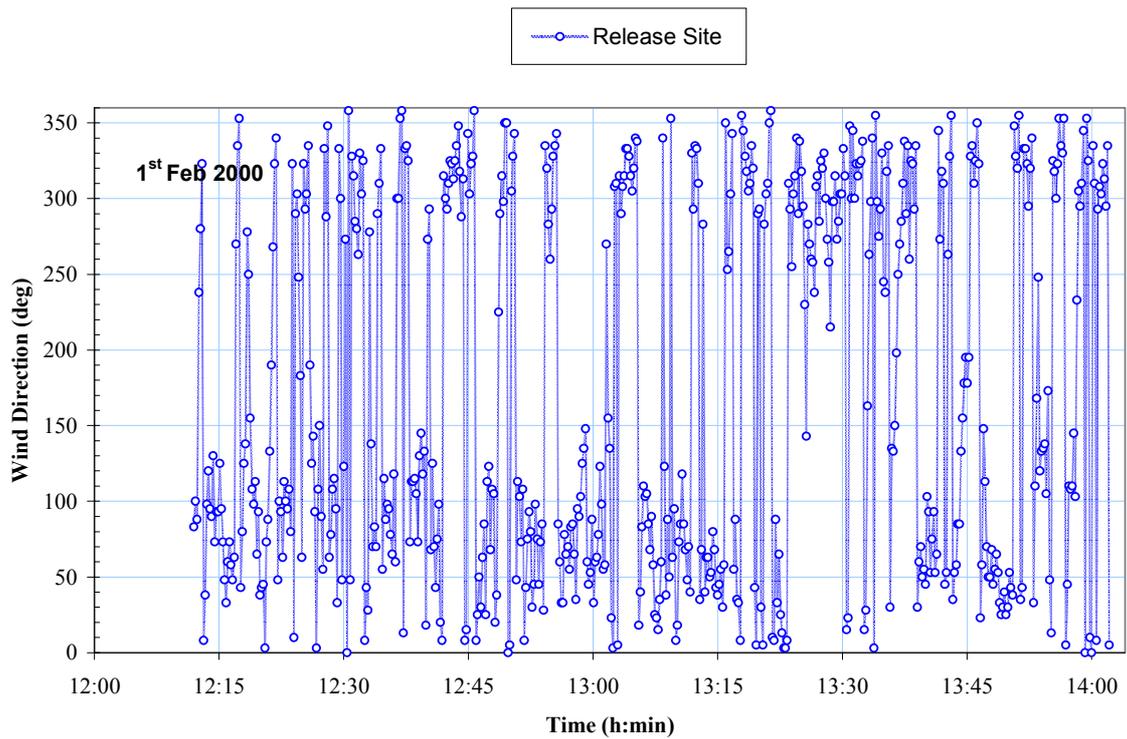


Figure 6.14: Additional meteorological data: wind direction measurements from the release site.

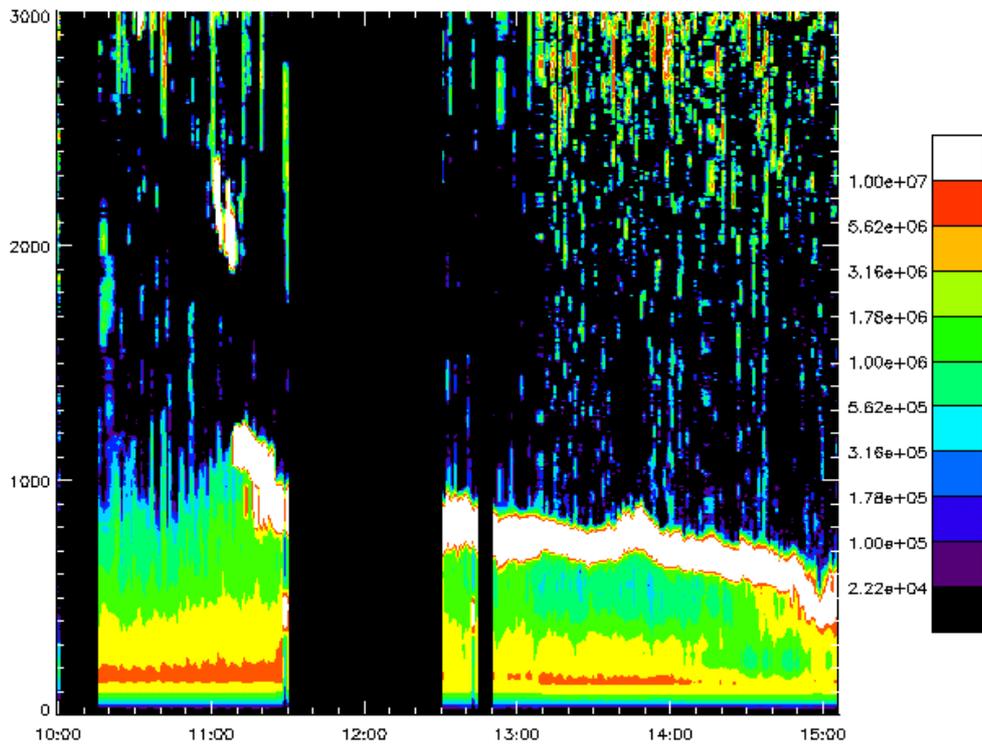


Figure 6.15: Pictorial representation of boundary layer height obtained by the LIDAR. The black area is when no data was collected (due to rain) and white area is cloud, which is indicative of boundary layer height.

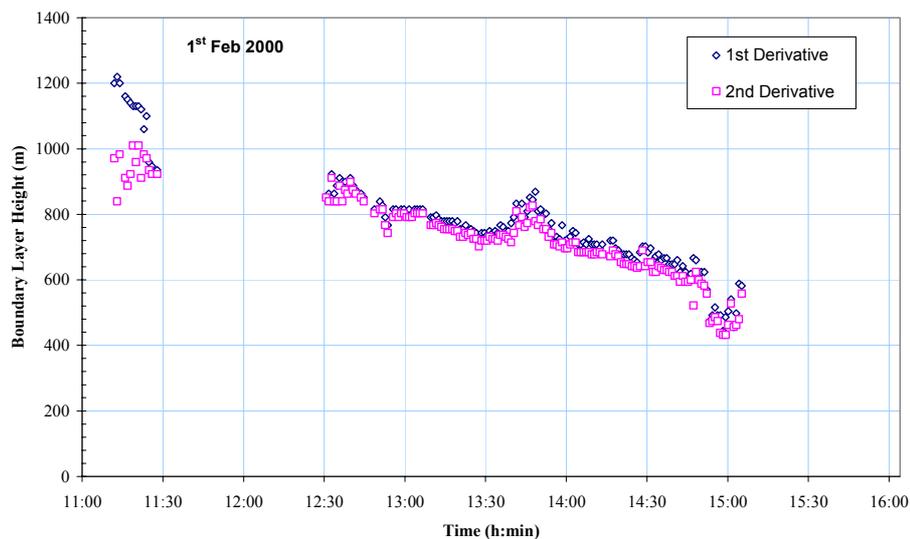


Figure 6.16: Boundary layer height from the LIDAR. The 1st derivative is representative of the top of the mixed layer (i.e. the base of the transition zone). The 2nd derivative is representative of the interface between the mixed layer and the free troposphere.

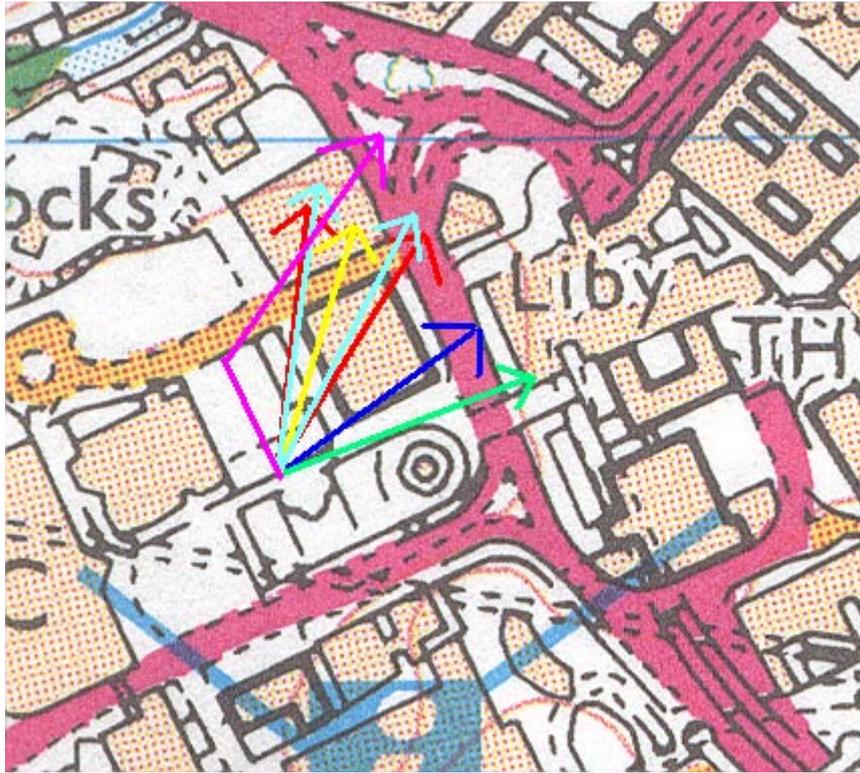


Figure 6.17: Sketch of the balloon trajectories. The balloons were releases on the 1st February at 12:45 (red line), 13:00 (dark blue line), 13:15 (green line), 13:30 (yellow line), 13:45 (light blue line) and at 14:00 (dark pink line).

6.3 Third Experiment

6.3.1 Tracer Release

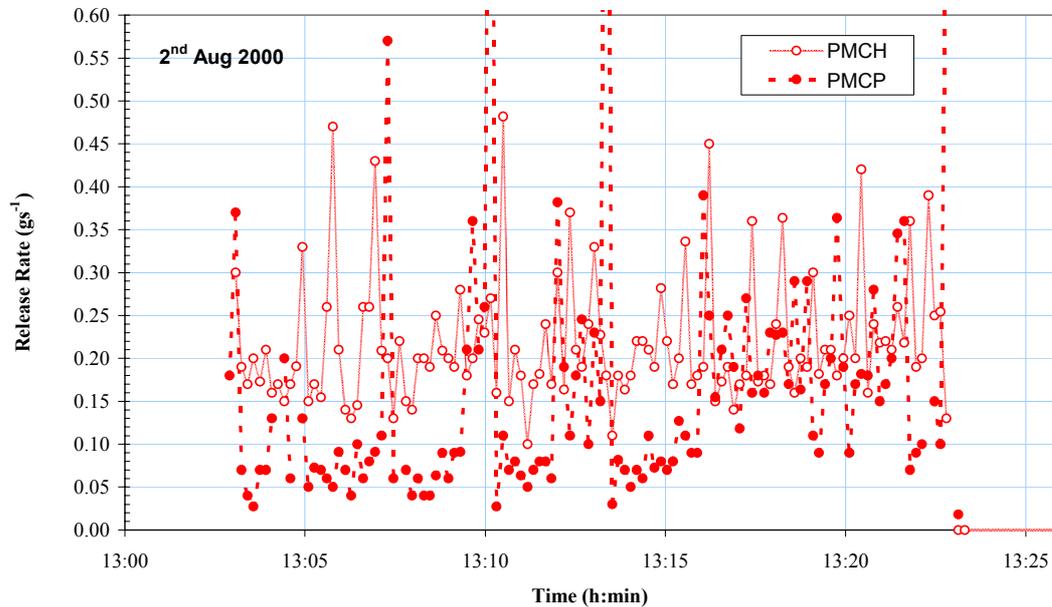


Figure 6.18: Tracer release rate (NB Due to rain prior to the release, the weigh balances were placed inside a van, and were consequently disturbed whenever personnel entered the van to check the equipment. This resulted in an incorrect reading of the actual release and consequently the time at which these disturbances occurred have not been included in the overall release rate).

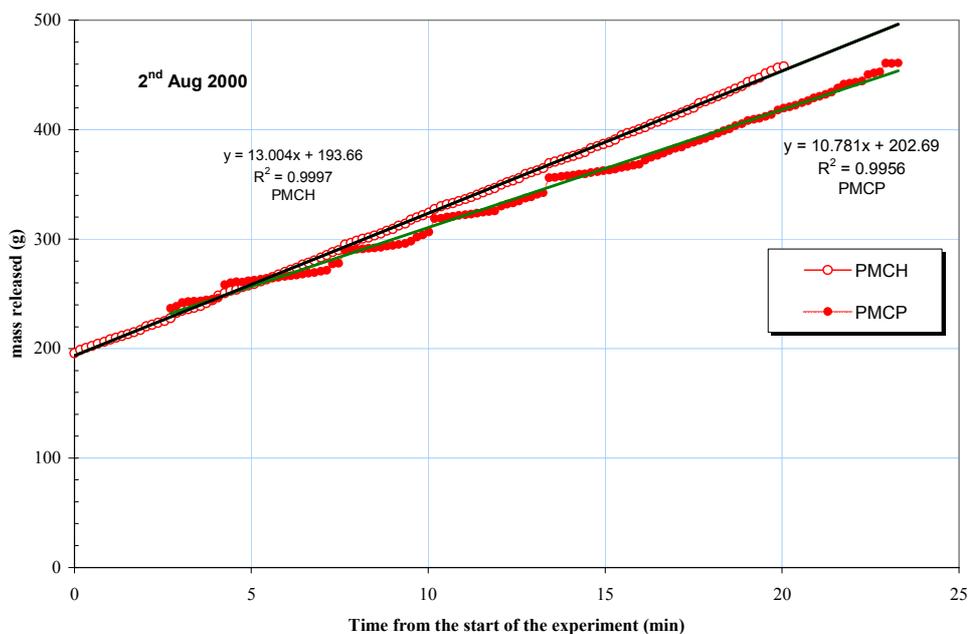


Figure 6.19: Total mass released during the experiment for the two tracers.

6.3.2 Concentration Measurements at the Main Sites

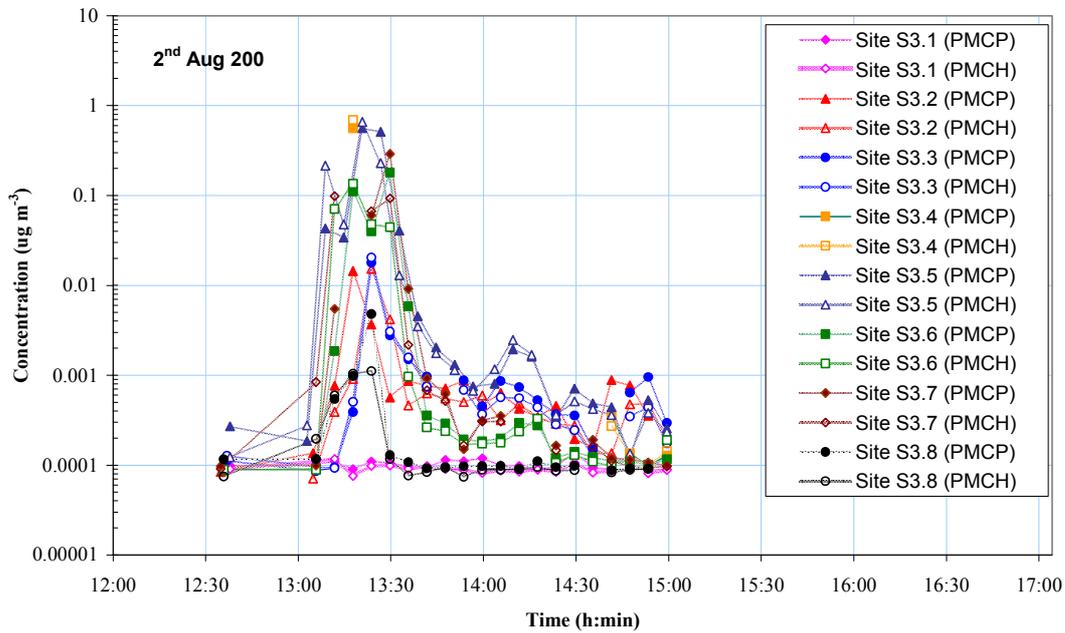


Figure 6.20: Concentration measurements at the sites in the main arc for both PMCH and PMCP.

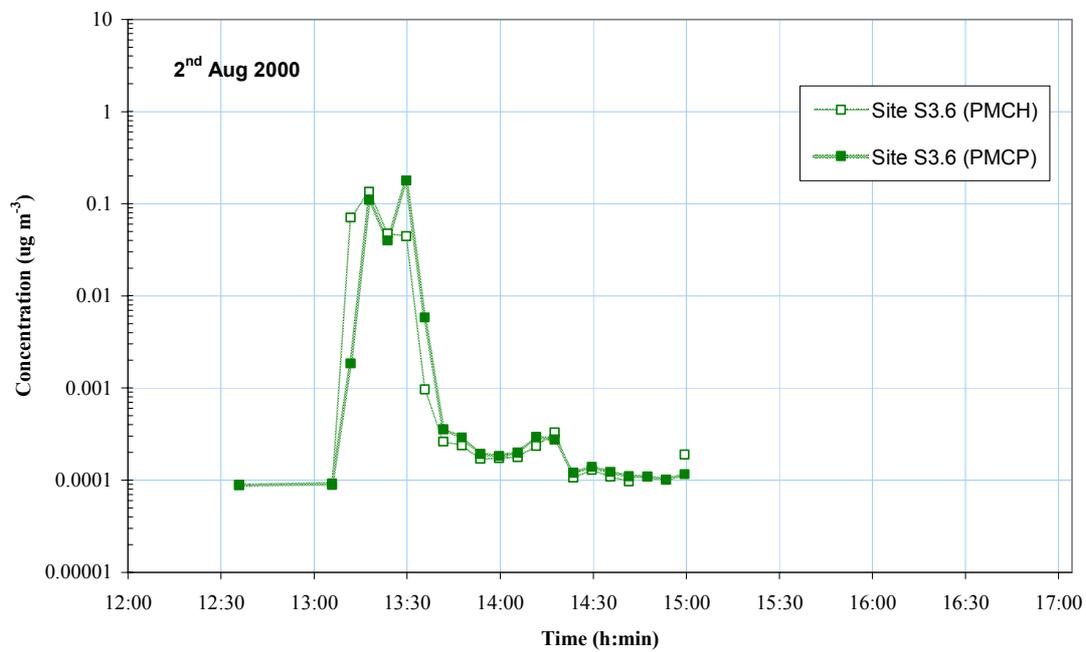


Figure 6.21: Example of concentration of PMCH and PMCP measured at one site in the main arc.

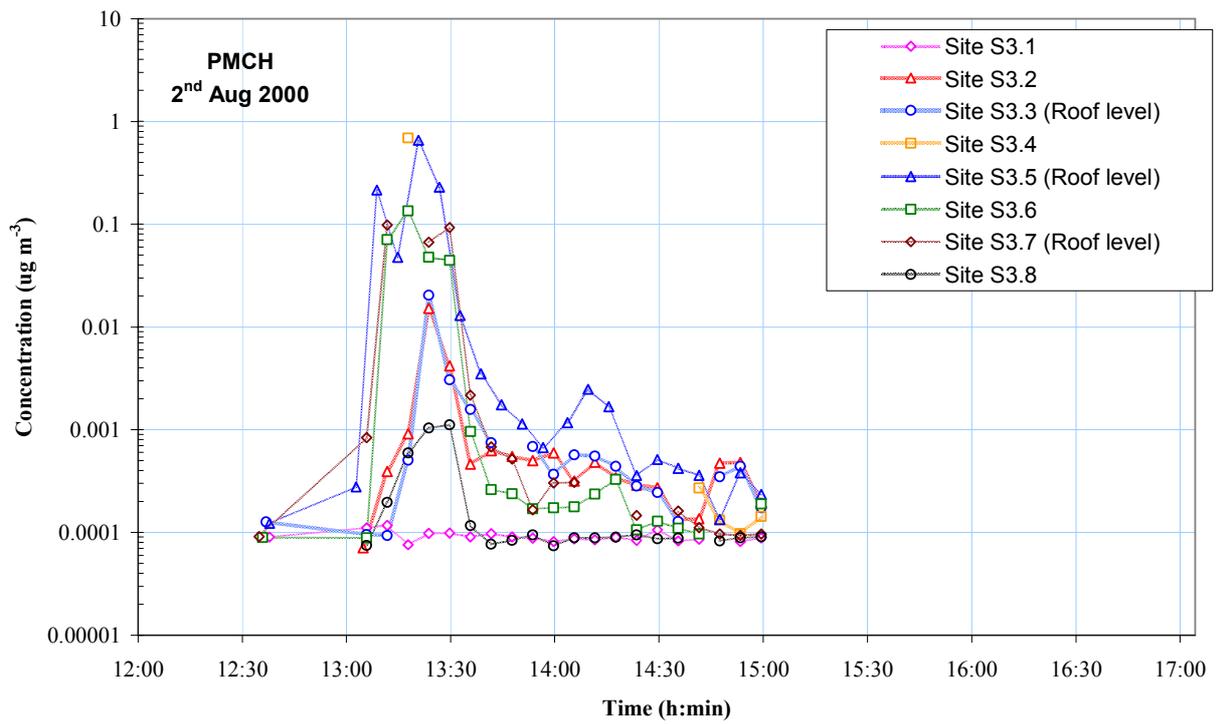


Figure 6.22: Concentration measurements of PMCH at sites in the main arc.

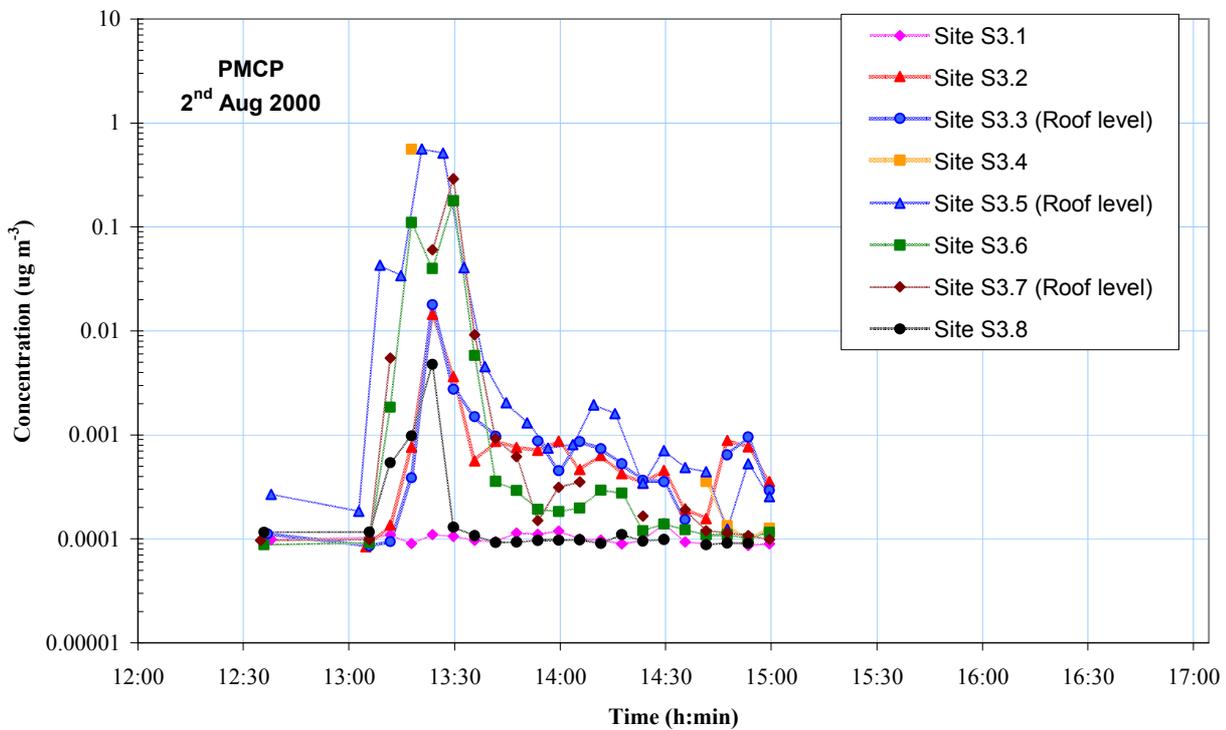


Figure 6.23: Concentration measurements of PMCP at sites in the main arc.

6.3.3 Concentration Measurements at the Secondary Sites

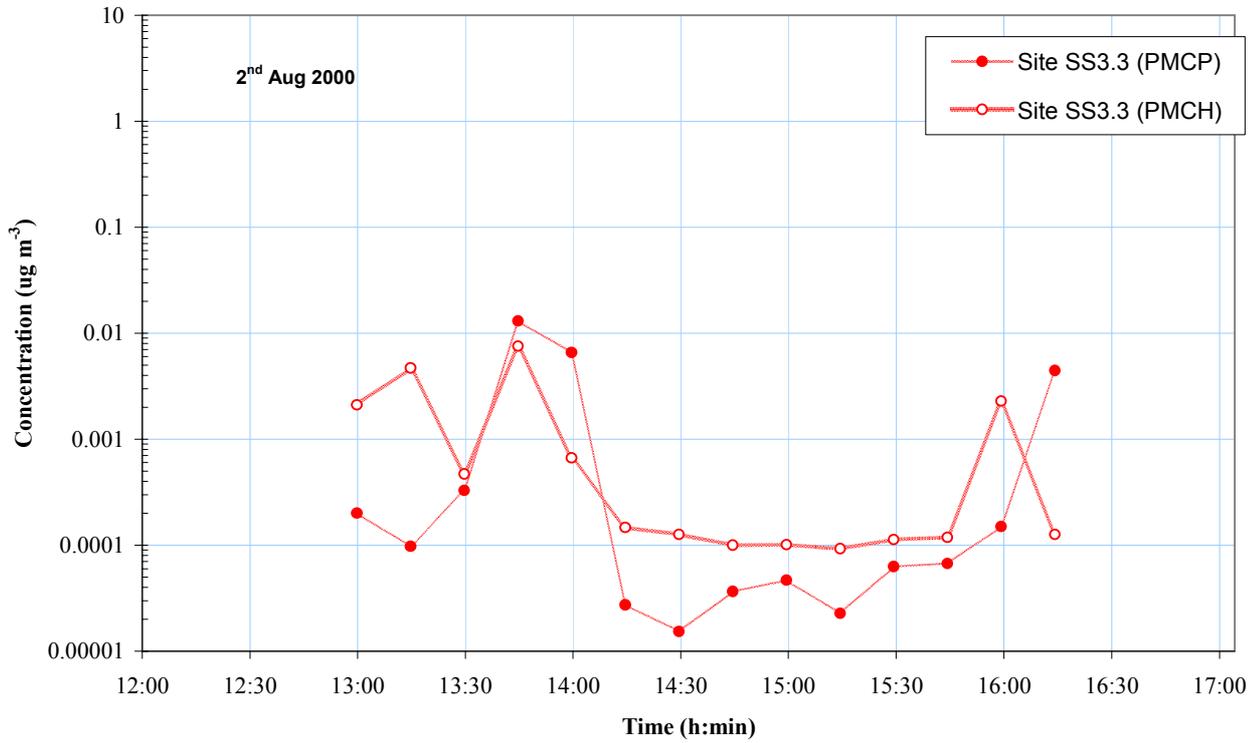


Figure 6.24: Concentration measurements of both PMCH and PMCP at one of the secondary sites.

6.3.4 Meteorological Measurements

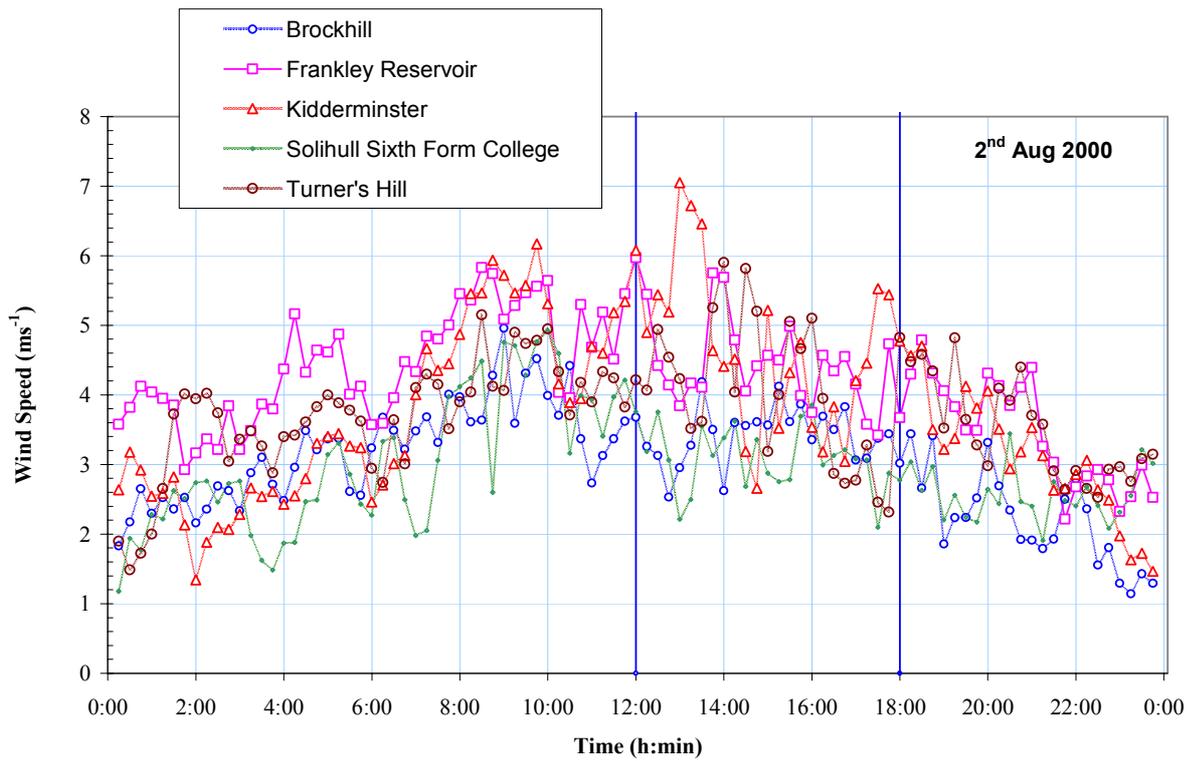


Figure 6.25: Wind speed measurements from the available PUMA sites.

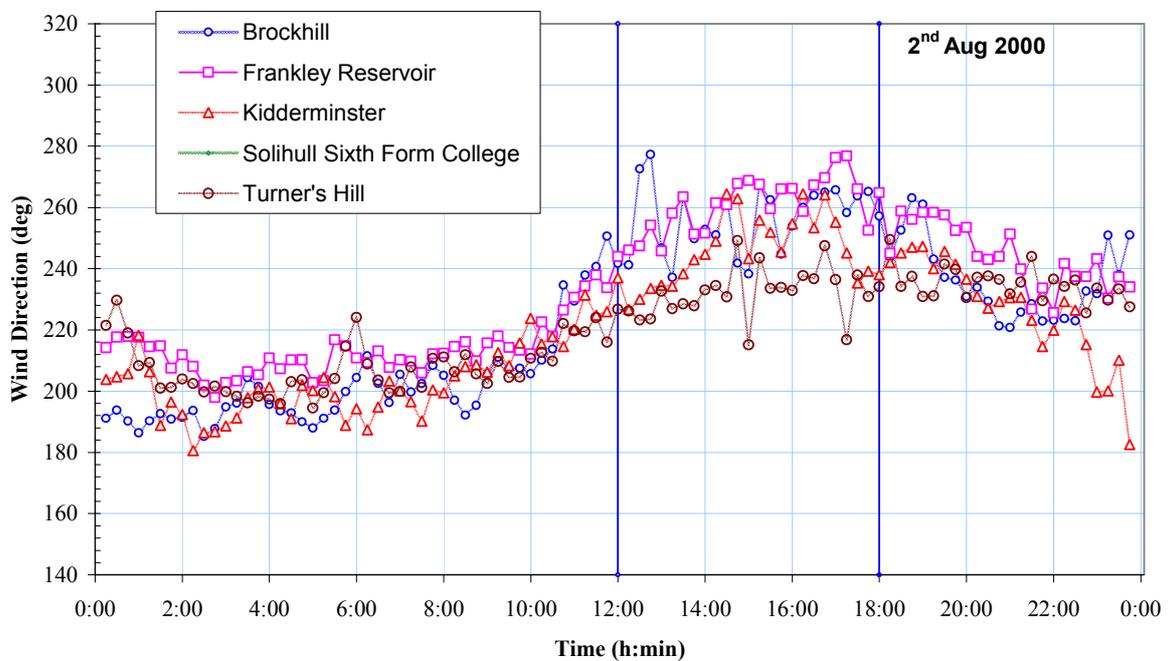


Figure 6.26: Wind direction measurements from the available PUMA sites.

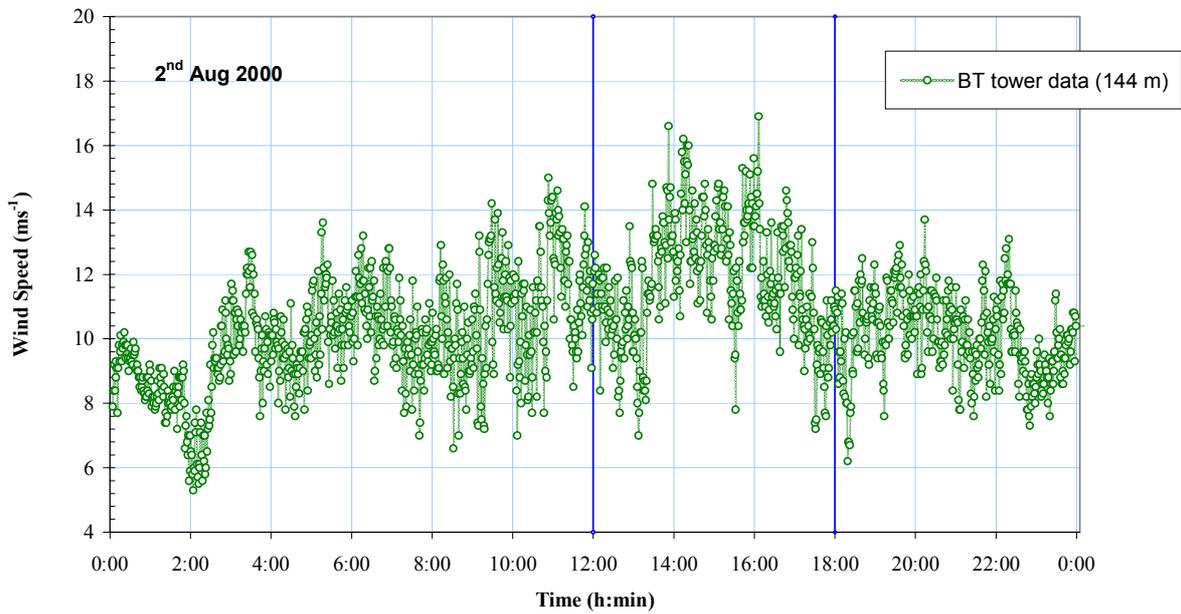


Figure 6.27: Additional meteorological data. Wind speed time series from the British Telecom (BT) tower.

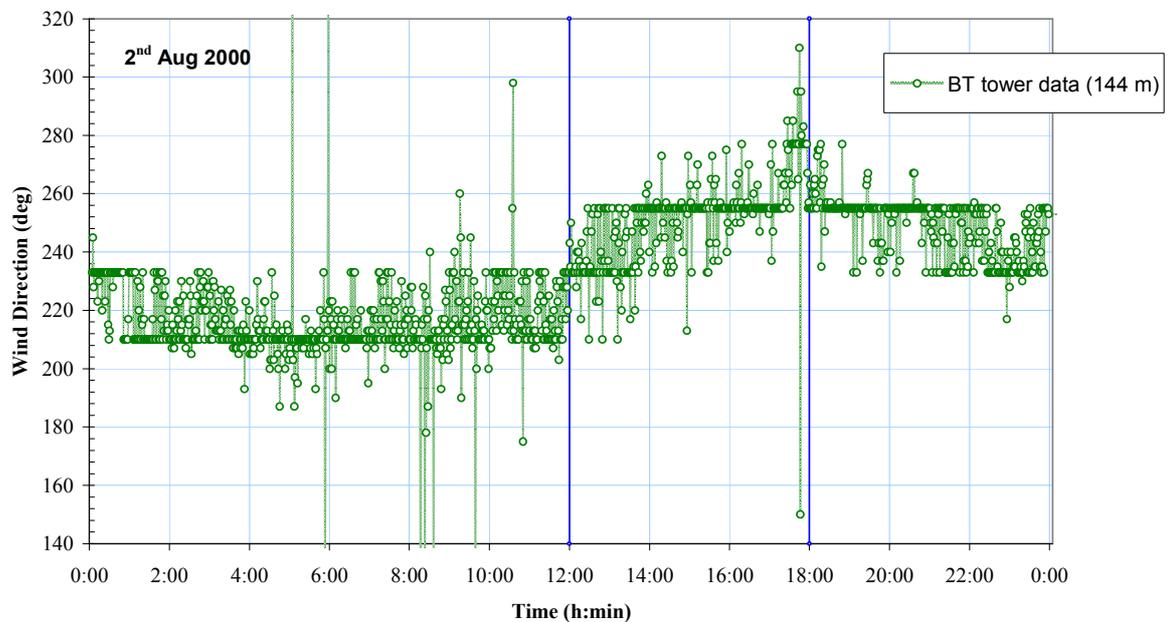


Figure 6.28: Additional meteorological data. Wind direction time series from the British Telecom (BT) tower.

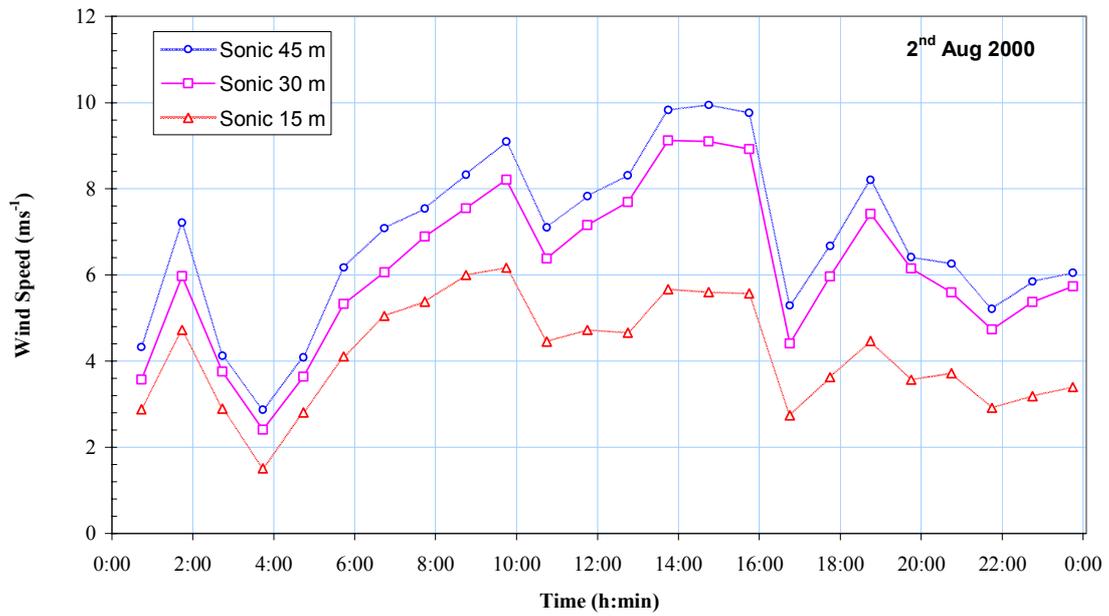


Figure 6.29: Additional meteorological data. Wind speed measurements from the Met. Office tower.

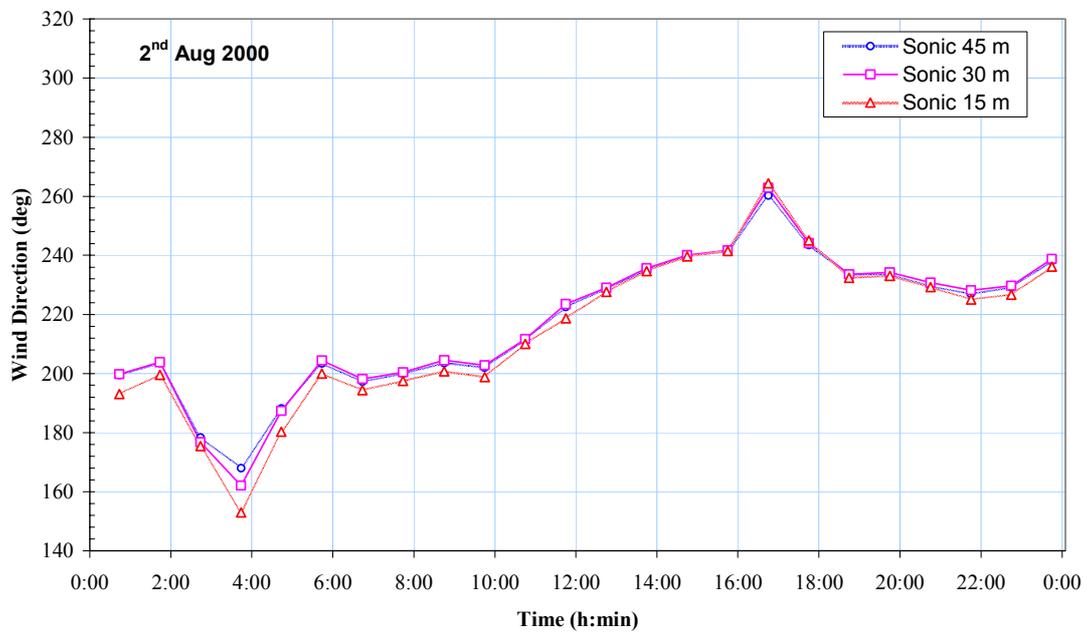


Figure 6.30: Additional meteorological data. Wind direction measurements from the Met. Office tower.

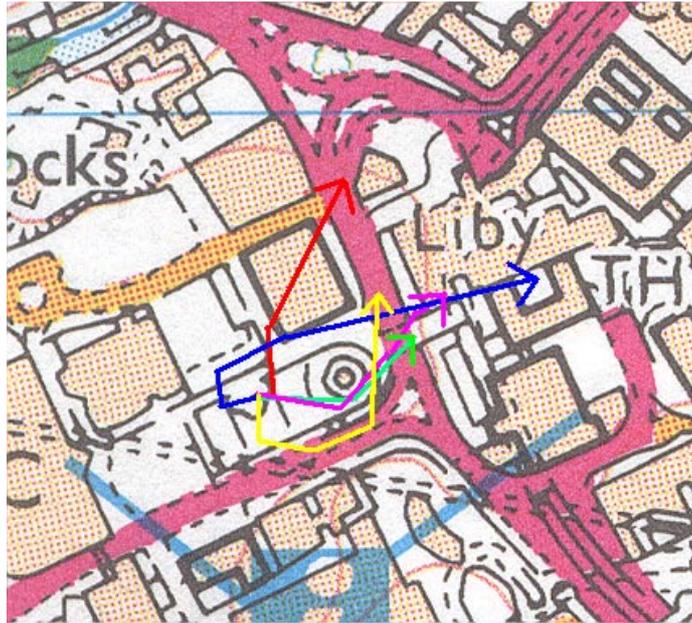


Figure 6.31: Sketch of the balloon trajectories. The balloons were released on the 2nd August at 12:06 (red line), 12:16 (green line), 12:25 (dark pink line), 12:36 (dark blue line) and 12:50 (yellow line).

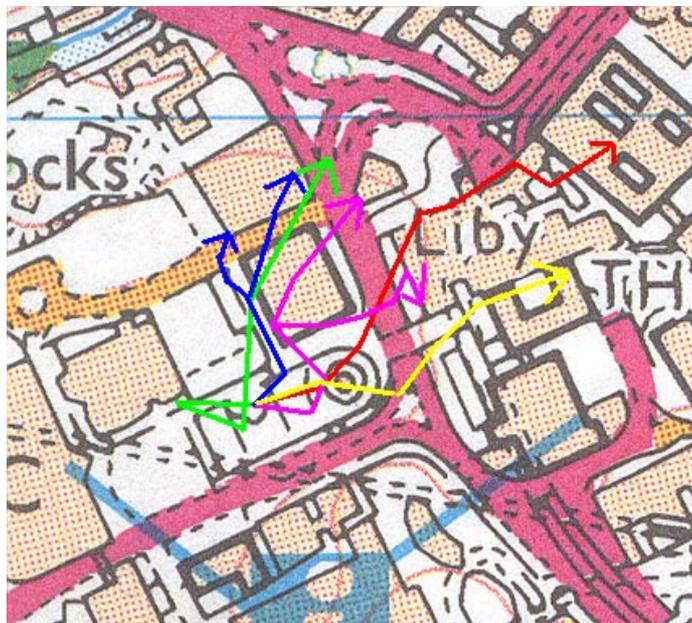


Figure 6.32: Sketch of the balloon trajectories. The balloons were released on the 2nd August at 13:00 (red line), 13:10 (green line), 13:15 (dark pink line), 13:23 (dark blue line) and 13:29 (yellow line).

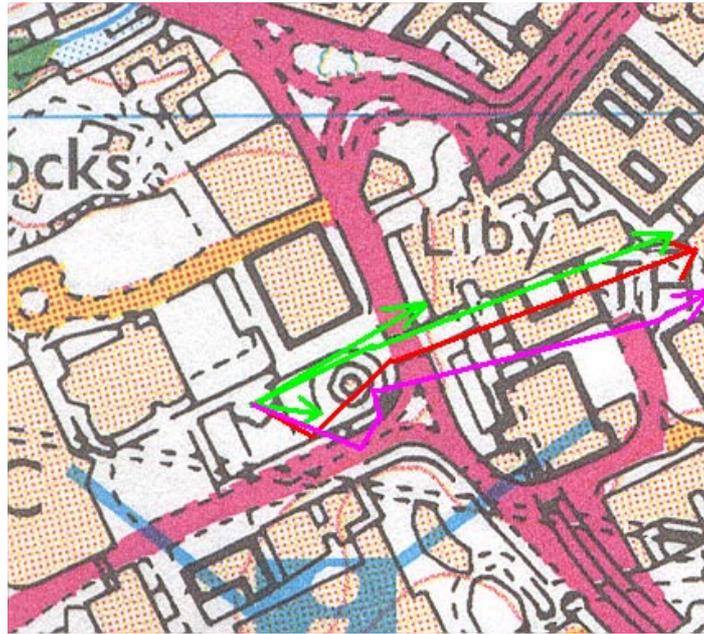


Figure 6.33: Sketch of the balloon trajectories. The balloons were released on the 2nd August at 13:55 (red line), 14:09 (green line) and 14:23 (dark pink line).

7.0 Comparison of Measured and Modelled Data

In this chapter we show a comparison between measurements and some simple analytical models. A comparison between data and a time dependent finite duration release model ADMS3 is also briefly discussed.

7.1 First Experiment

7.1.1 Maximum Concentration

The maximum concentration measured during the first experiment for the main arc was $C = 2.16 \mu\text{gm}^{-3}$, recorded at site S1.3 and $C = 0.08 \mu\text{gm}^{-3}$ for the secondary receptor SS1.1. Some simple steady state models were used in order to determine whether these maximum values were broadly consistent with expectations. The simplest way to do that is by expressing the concentration C via a Gaussian plume model for a continuous source of strength Q and uniform wind speed U (Pasquill 1961, 1974). In order to calculate C , for our case, an emission rate $Q = 4\text{gs}^{-1}$ was used. That is we used the strength of the source equal to that of the tracer release rate.

Many parameterisations of σ_y and σ_z are available in literature. The formulas proposed by Briggs for urban conditions (Hanna *et al.*, 1982) give the following values: for neutral conditions, (Pasquill stability class D): $\sigma_y = 361\text{m}$ and $\sigma_z = 342\text{m}$. These values give a concentration estimate of $C = 3 \mu\text{gm}^{-3}$. For near-neutral conditions (Pasquill stability class C), $\sigma_y = 497\text{m}$ and $\sigma_z = 700\text{m}$. These values give a concentration estimate of $C = 1 \mu\text{gm}^{-3}$.

Similarly for a downwind distance from the source of 9 km, Briggs formulas give: $\sigma_y = 671\text{m}$, $\sigma_z = 655\text{m}$ for Pasquill stability class D. These values give a concentration estimate of $C = 0.09 \mu\text{gm}^{-3}$. For Pasquill stability class C, $\sigma_y = 923\text{m}$, $\sigma_z = 1800\text{m}$ which give $C = 0.15 \mu\text{gm}^{-3}$.

The estimation of the concentration was done for the two different stability classes C and D in order to determine some boundary values for the expected concentrations.

Since standard deviations of wind direction were available from Pritchatts Road it was possible to calculate the diffusion parameters using those values in the following way (Hanna *et al.* 1982):

$$\sigma_y = \sigma_\theta x f_y \quad (7.1)$$

$$\sigma_z = \sigma_e x f_z \quad (7.2)$$

where σ_θ and σ_e are the measured standard deviations of wind direction and elevation respectively and f_y and f_z are the following universal functions:

$$f_y = (1 + 0.031x^{0.46})^{-1} \quad (7.3)$$

$$f_z = (1 + 0.4(\frac{x}{uT_z})^{0.5})^{-1} \quad (7.4)$$

Since σ_e was not available from the meteorological measurements, it can be calculated as $\sigma_e = \frac{2}{3}\sigma_\theta$ (Hanna *et al.*, 1982). With this parameterisation and assuming that $f_z = f_y$ (not strictly true for urban conditions) and taking $\sigma_\theta = 0.35$ rad (obtained from Pritchatts Road meteorological measurements) the Equations (7.1) and (7.2) become:

$$\sigma_y = 0.35x(1 + 0.031x^{0.46})^{-1} \quad (7.5)$$

$$\sigma_z = 0.23x(1 + 0.031x^{0.46})^{-1} \quad (7.6)$$

The equations above give: $\sigma_y = 527$ m, $\sigma_z = 351$ m and $C = 2 \mu \text{ gm}^{-3}$ for 3.5 km and $\sigma_z = 690$ m $C = 0.35 \mu \text{ gm}^{-3}$ the 9 km measurements.

The above estimated concentration values are reported in Table 7.1.

Table 7.1: Measured and modelled maximum concentrations.

Distance from release <i>km</i>	Measured concentration $\mu \text{ gm}^{-3}$	Briggs curves Class C $\mu \text{ gm}^{-3}$	Briggs curves class D $\mu \text{ gm}^{-3}$	$\sigma_y \sigma_z$ method $\mu \text{ gm}^{-3}$
3.5	2.16 (Site S1.3)	1.	3	2
9	0.08 (Site SS1.1)	0.09	0.15	0.38

The table above shows that at 3.5 km distance from the release source the agreement between the predicted and measured values are good, the measured data being well within the interval 1-3 $\mu \text{ gm}^{-3}$ estimated by the models. At the distance of 9 km the models slightly over predict the measured data. Many factors could be responsible for this discrepancy, but it could be attributed to the wind direction not remaining constant. However, this comparison should be regarded as a first order comparison to show the consistency of the measured data.

7.1.2 Discussion and Conclusions on the First Experiment

The analysis of the experimental concentration history for the main arc receptors as reported in Figure 7.1 shows that the concentration evolution curve is sharply asymmetrical. The starting time if the increase in concentration corresponds to the advection time: $t = 3500/3.5 \sim 17$ minutes, the release starting at about $t = 5$ minutes. The concentration rise is very sharp over a short duration of 1-2 minutes. It is expected to have an elevated plateau of duration comparable to that of the release duration and this is approximately shown by the measurements. The measurements also show a slow exponential-like decay, which takes about 50 minutes and has a well-defined time constant. This time constant has been estimated to be 7 minutes (Britten *et al.*, 2000). Figure 7.1 shows also a comparison of the measurements with ADMS3 model predictions. The model runs were done using its finite duration release model option and a roughness length $z_0 = 1\text{m}$.

The first part of the concentration history is well predicted by the ADMS3 dispersion model. The maximum value of the concentration is predicted within a factor of two by ADMS3.

The good agreement between the measurements and the model predictions support the experimental techniques and procedures. However, a long-lived plateau at low

concentration is observed, but is not predicted by the model. This low concentration plateau which is about one order of magnitude higher than the background values could have very important applications, such as the modelling of industrial accidents.

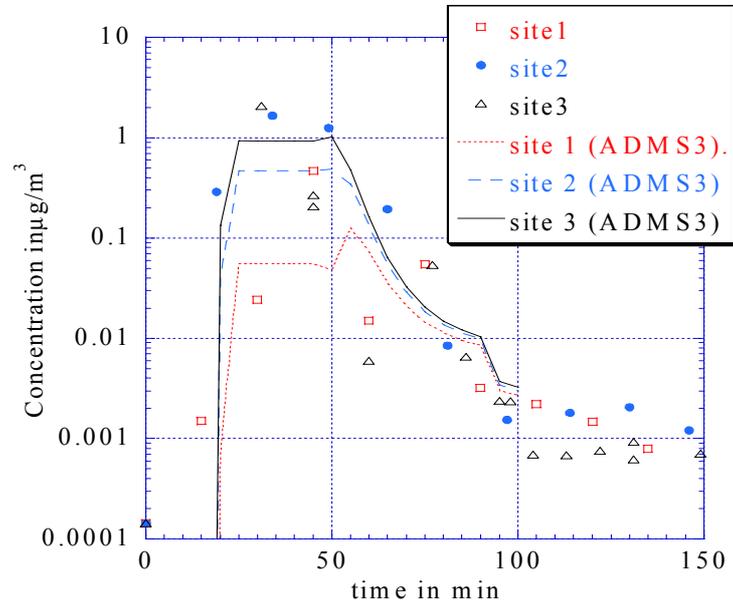


Figure 7.1: Comparison of the measured concentration and ADMS3 predictions at sites S1.1 (site 1), S1.2 (site 2) and S1.3.

7.2 Second Experiment

7.2.1 Maximum Concentration

The maximum concentration measured during the second experiment for the main arc was $C = 0.003 \mu \text{ gm}^{-3}$, recorded at site S2.4 at roof level and $C = 0.017 \mu \text{ gm}^{-3}$ (as measured by bags) for the secondary receptor SS2.3. By analogy with the analysis discussed in section 7.1.1 we compared these maximum concentrations with those calculated using the Gaussian plume model and Briggs equations for σ_y and σ_z . The formulas proposed by Briggs for urban conditions give the following values: for neutral conditions, (Pasquill stability class D): $\sigma_y = 135 \text{ m}$ and $\sigma_z = 123 \text{ m}$. Using an emission rate $Q = 0.23 \text{ gs}^{-1}$ and wind speed of 5 ms^{-1} , these σ -values give a concentration estimate of $C = 0.9 \mu \text{ gm}^{-3}$. For near-neutral conditions (Pasquill stability class C), $\sigma_y = 186 \text{ m}$ and $\sigma_z = 200 \text{ m}$. These values give a concentration estimate of $C = 0.4 \mu \text{ gm}^{-3}$.

Similarly for a downwind distance from the source of 6.6 km, Briggs formulas give: $\sigma_y = 572$ m, $\sigma_z = 535$ m for Pasquill stability class D. These values give a concentration estimate of $C = 0.05 \mu\text{gm}^{-3}$. For Pasquill stability classes C, $\sigma_y = 761$ m, $\sigma_z = 1320$ m which give $C = 0.015 \mu\text{gm}^{-3}$.

As before the estimation of the concentration was done for the two different stability class C and D in order to determine some boundary values of the expected concentration.

The above estimated concentration values are reported in Table 7.2.

Table 7.2: Measured and modelled maximum concentrations.

Distance From release <i>km</i>	Measured concentration μgm^{-3}	Briggs curves class C μgm^{-3}	Briggs curves class D μgm^{-3}
1	0.003 (Site S2.4)	0.4	0.9
6.6	0.017 (Site SS2.3)	0.015	0.05

It is clear from Table 7.2 that we missed the plume. Site S2.4 has a bearing of 247°. According to results obtained with the analytical model, the site was about 30° off the centreline of the plume. By adopting Pasquill stability class D, the 6.6 km site is about 10° off the centreline of the plume. This broadly confirms that model results are consistent with measurements for a wind direction of 220°. This value is in the range of wind directions measured at the PUMA stations (see Figure 6.12).

7.3 Third Experiment

7.3.1 Maximum Concentration

The maximum concentration measured during the third experiment for the main arc was $C = 0.69 \mu\text{gm}^{-3}$, recorded at site S3.5 at roof level and $C = 0.008 \mu\text{gm}^{-3}$ for the secondary receptor SS3.3 which is at 6 km from the release site.

Again by analogy with the analysis discussed in sections 7.1.1 and 7.2.1 we compared these maximum concentrations with those calculated using the Gaussian plume model and Briggs equations for σ_y and σ_z .

Using an emission rate $Q = 0.22 \text{ gs}^{-1}$ (PMCH), a wind speed of 4 ms^{-1} and σ -values calculated in section 7.1.1, ^{for the 1 km site} we obtain a concentration estimate of $C = 1 \mu \text{ gm}^{-3}$ for Pasquill stability class C and $C = 0.5 \mu \text{ gm}^{-3}$ ^{for Pasquill stability class D.}

Similarly, for the site at 6 km, Briggs formulas give: $\sigma_y = 716 \text{ m}$, $\sigma_z = 1200 \text{ m}$ for Pasquill stability class D. These values give a concentration estimate of $C = 0.02 \mu \text{ gm}^{-3}$. For Pasquill stability class C, $\sigma_y = 520 \text{ m}$, $\sigma_z = 502 \text{ m}$ which give $C = 0.07 \mu \text{ gm}^{-3}$.

As before the estimation of the concentration was done for the two different stability classes C and D in order to determine some boundary values of the expected concentration.

The above estimated concentration values are reported in Table 7.3.

Table 7.3: Measured and modelled maximum concentrations.

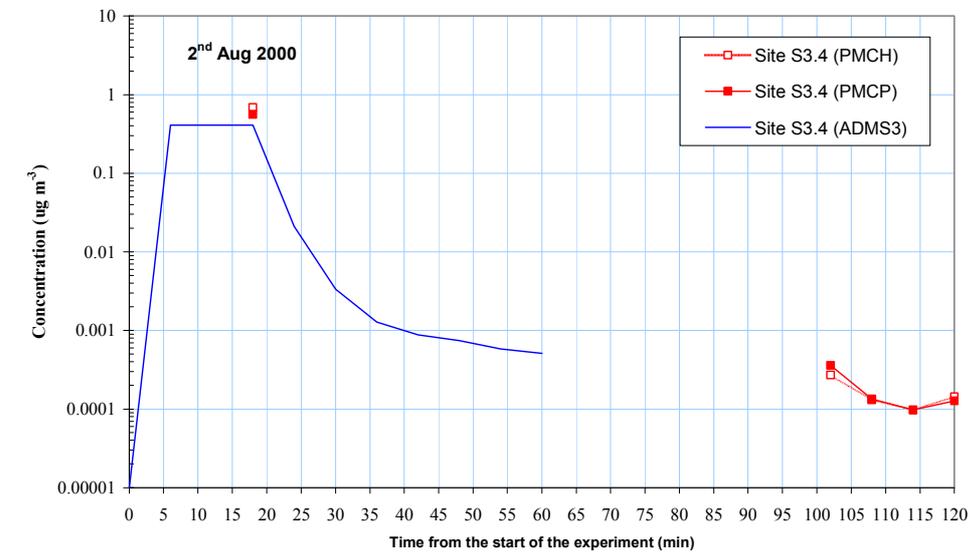
Distance from release <i>km</i>	Measured concentration $\mu \text{ gm}^{-3}$	Briggs curves class C $\mu \text{ gm}^{-3}$	Briggs curves Class D $\mu \text{ gm}^{-3}$
1	0.69 (SiteS3.4)	0.5	1
6.6	0.008 (SiteSS2.3)	0.02	0.07

Table 7.3 above shows that at 1 km distance from the release source the agreement between the predicted and measured values is good, the measured data being well within the interval $0.5\text{-}1 \mu \text{ gm}^{-3}$ estimated by the models. At the distance of 6 km the models over predict the measured data.

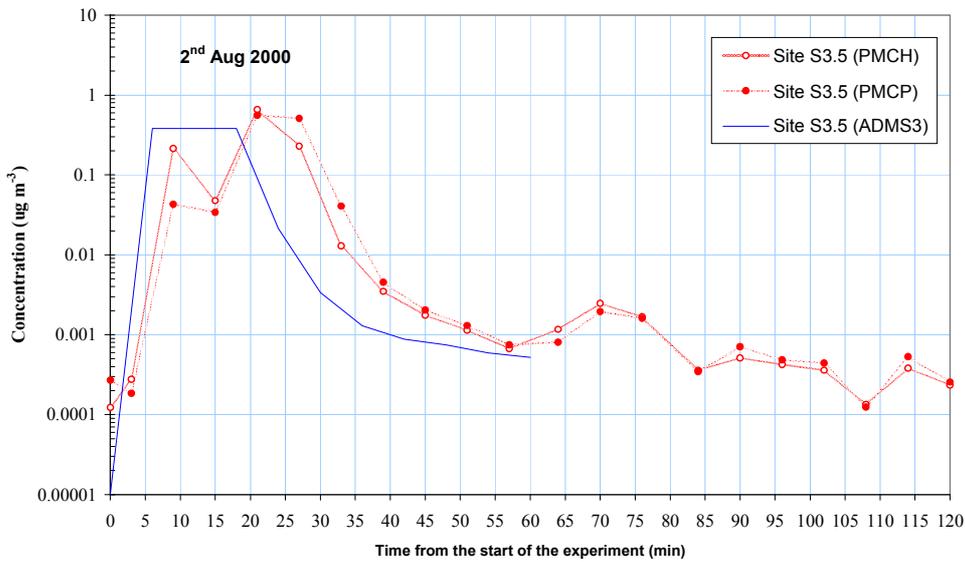
7.3.2 Comparison with ADMS3 Model Predictions

Concentration measurements for the main arc sites were compared with ADMS3 model predictions. We observed in the previous section that the maximum concentration in the main arc occurred at site S3.4 that is consistent with a wind direction of 219° . This wind direction is about 20° less than measured at the PUMA stations. However, we used 219° for the model runs. ADMS3 was used in its finite duration release (puff model) option. A roughness length of 1 m was used. Figure 7.2 (a,b,c) shows a comparison between model predictions and measured data. The first

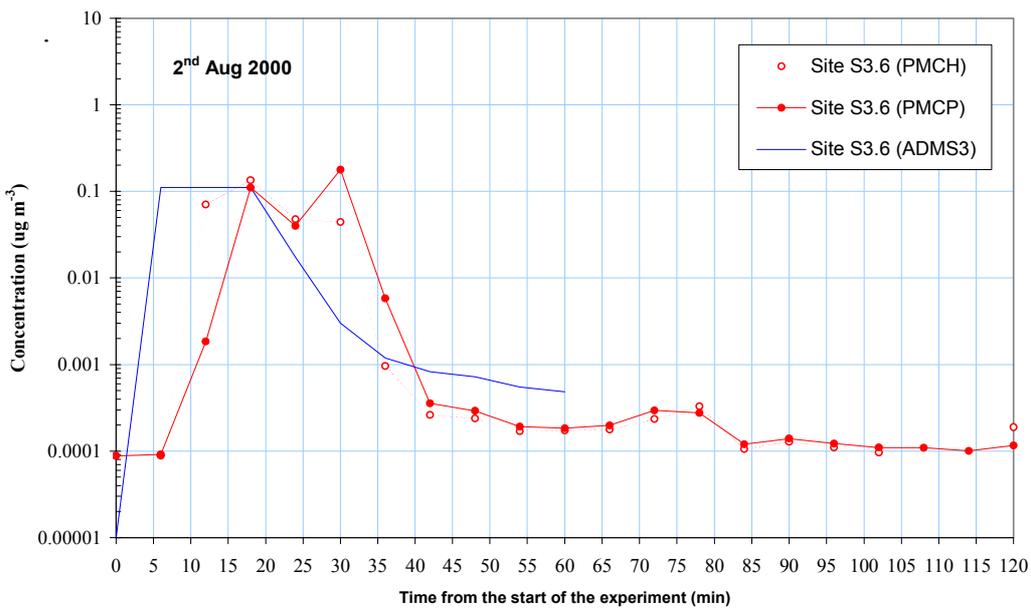
observation is that the maximum value is well reproduced by the model. However, the maximum is predicted much earlier than the measured values. The reasons for this will be investigated and studied in a future work.



(a)



(b)



(c)

Figure 7.2: Comparison of the measured concentration and ADMS3 predictions at Site S3.4 (a), Site S3.5 (b) and Site S3.6 (c).

8.0 Conclusions

A new technique utilising advances in sampling modes and capillary gas chromatography and negative ion-chemical ionisation mass spectrometry (GC-NICI-MS) has been developed at the University of Bristol. It allows a dynamic range of perfluorocarbon tracer concentration measurements of about five orders of magnitude.

Three tracer release field experiments have been carried out successfully over Birmingham City centre. These have provided a series of valuable data sets for testing various atmospheric dispersion models. It is expected that the complete analysis of the concentration data will give insight in the dispersion mechanisms at the neighbourhood scale. This analysis is ongoing as part of future work.

9.0 References

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7. Cooke, K.M.; Simmonds, P.G.; Nickless, G.; Caton, F.; Di Sabatino, S.; Britter, R., **2000**, Tracers and Dispersion of Gaseous Pollutants, *Proceedings of the URGENT annual meeting – Cardiff 2000*, in press

APPENDIX A: Tabular Data Summary for Tracer Release

Table A.1: Birmingham, 1st July 1999

SAMPLE START	SAMPLE FINISH	SAMPLE TIME min	BAG/ TRAP n°	SITE n°	PDCB Conc ppt	PMCP Conc ppt	PMCH Conc ppt	PDCB Conc µg m ⁻³	PMCP Conc µg m ⁻³	PMCH Conc µg m ⁻³
S1.1										
13:00	13:15	15	UR041	S1.1	BDL	BDL	BDL	BDL	BDL	BDL
13:15	13:30	15	UR042	S1.1	BDL	BDL	1.22E-01	BDL	BDL	1.75E-03
13:30	13:45	15	UR043	S1.1	BDL	1.90E-02	1.87E+00	BDL	2.34E-04	2.67E-02
13:45	14:00	15	UR044	S1.1	2.35E-02	3.71E-02	3.47E+01	2.88E-04	4.55E-04	4.96E-01
14:00	14:15	15	UR045	S1.1	BDL	2.77E-02	1.11E+00	BDL	3.40E-04	1.58E-02
14:15	14:30	15	UR046	S1.1	2.49E-02	1.75E-02	3.78E+00	3.06E-04	2.15E-04	5.42E-02
14:30	14:45	15	UR047	S1.1	BDL	1.57E-02	2.23E-01	BDL	1.93E-04	3.19E-03
14:45	15:00	15	UR048	S1.1	BDL	2.22E-02	1.60E-01	BDL	2.72E-04	2.29E-03
15:00	15:15	15	UR049	S1.1	BDL	2.08E-02	1.44E-01	BDL	2.55E-04	2.07E-03
15:15	15:30	15	UR050	S1.1	BDL	BDL	7.26E-02	BDL	BDL	1.04E-03
S1.2										
13:00	13:15	15	UR031	S1.2	BDL	BDL	BDL	BDL	BDL	BDL
13:19	13:33	14	UR032	S1.2	1.94E-02	2.97E-02	2.13E+01	2.38E-04	3.65E-04	3.05E-01
13:34	13:48	14	UR033	S1.2	BDL	1.33E-01	1.21E+02		1.63E-03	1.74E+00
13:49	14:04	15	UR034	S1.2	BDL	9.02E-02	9.14E+01		1.11E-03	1.31E+00
14:05	14:20	15	UR035	S1.2	2.68E-02	1.82E-02	1.43E+01	3.28E-04	2.23E-04	2.05E-01
14:21	14:36	15	UR036	S1.2	BDL	BDL	6.75E-01	BDL	BDL	9.67E-03
14:37	14:53	16	UR037	S1.2	BDL	1.86E-02	1.70E-01	BDL	2.28E-04	2.44E-03
14:54	15:09	15	UR038	S1.2	BDL	BDL	1.47E-01	BDL	BDL	2.11E-03
15:10	15:25	15	UR039	S1.2	BDL	BDL	1.71E-01	BDL	BDL	2.45E-03
15:26	15:41	15	UR040	S1.2	BDL	BDL	9.85E-02	BDL	BDL	1.41E-03
S1.3										
12:45	12:54	9	UR051	S1.3	3.29E-03	6.91E-03	7.98E-03	4.03E-05	8.47E-05	1.14E-04
13:16	13:25	9	UR022	S1.3	BDL	1.61E-01	1.51E+02	BDL	1.98E-03	2.16E+00
13:30	13:39	9	UR023	S1.3	2.69E-02	5.11E-02	1.52E+01	3.30E-04	6.27E-04	2.17E-01
13:30	13:38	8	UR052	S1.3	BDL	2.52E-02	1.85E+01	BDL	3.09E-04	2.64E-01
13:45	13:54	9	UR024	S1.3	2.24E-02	1.59E-02	4.39E-01	2.75E-04	1.95E-04	6.28E-03
14:02	14:11	9	UR025	S1.3	BDL	BDL	3.97E+00	BDL	BDL	5.68E-02
14:11	14:20	9	UR026	S1.3	BDL	BDL	4.45E-01	BDL	BDL	6.38E-03
14:20	14:29	9	UR027	S1.3	BDL	BDL	1.73E-01	BDL	BDL	2.48E-03
14:23	14:31	8	UR053	S1.3	2.42E-02	4.98E-02	1.83E-01	2.96E-04	6.11E-04	2.63E-03
14:29	14:38	9	UR028	S1.3	BDL	BDL	7.06E-02	BDL	BDL	1.01E-03
14:38	14:47	9	UR029	S1.3	BDL	BDL	6.78E-02	BDL	BDL	9.71E-04
14:47	14:56	9	UR030	S1.3	BDL	BDL	6.22E-02	BDL	BDL	8.90E-04
14:56	15:05	9	UR021	S1.3	BDL	BDL	4.88E-02	BDL	BDL	6.98E-04
14:56	15:05	9	UR054	S1.3	BDL	1.84E-02	9.47E-02	BDL	2.25E-04	1.36E-03
15:14	15:23	5	UR056	S1.3	BDL	BDL	5.95E-02	BDL	BDL	8.51E-04
S1.5										
13:15	13:30	15	UR002	S 1.5	2.11E-02	7.63E-03	7.58E-03	2.59E-04	9.37E-05	1.09E-04
13:30	13:45	15	UR003	S 1.5	2.79E-02	8.25E-03	7.13E-03	3.42E-04	1.01E-04	1.02E-04

13:45	14:00	15	UR004	S 1.5	1.93E-02	4.89E-03	4.43E-03	2.36E-04	6.00E-05	6.34E-05
14:00	14:15	15	UR005	S 1.5	1.93E-02	6.22E-03	5.17E-03	2.37E-04	7.63E-05	7.41E-05
14:15	14:30	15	UR006	S 1.5	2.78E-02	8.53E-03	6.39E-03	3.41E-04	1.05E-04	9.15E-05
14:30	14:45	15	UR007	S 1.5	2.53E-02	7.91E-03	6.09E-03	3.11E-04	9.70E-05	8.72E-05
14:45	15:00	15	UR008	S 1.5	2.26E-02	7.75E-03	5.22E-03	2.77E-04	9.51E-05	7.48E-05
15:00	15:15	15	UR009	S 1.5	2.26E-02	7.75E-03	5.22E-03	2.77E-04	9.51E-05	7.48E-05
15:15	15:30	15	UR010	S 1.5	2.51E-02	8.05E-03	6.15E-03	3.08E-04	9.87E-05	8.80E-05
15:32	15:47	15	UR001	S 1.5	2.69E-02	8.30E-03	6.09E-03	3.30E-04	1.02E-04	8.71E-05
15:48	16:03	15	UR018	S 1.5	1.01E-02	1.05E-02	6.56E-03	1.24E-04	1.29E-04	9.39E-05
16:03	16:18	15	UR019	S 1.5	2.47E-02	1.22E-02	9.79E-03	3.03E-04	1.50E-04	1.40E-04
13:45	13:50	5	UR020	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
13:52	13:57	5	UR011	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
13:58	14:03	5	UR012	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
14:03	14:08	5	UR013	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
14:08	14:14	6	UR014	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
14:23	14:33	10	UR015	S 1.5	BDL	BDL	BDL	BDL	BDL	BDL
14:34	14:46	12	UR016	S 1.5	1.16E-02	7.43E-03	5.50E-03	1.43E-04	9.12E-05	7.88E-05
14:46	14:56	10	UR017	S 1.5	8.56E-03	3.97E-03	5.47E-03	1.05E-04	4.88E-05	7.84E-05
SS1.1										
12:00	12:20	20	Trap203	SS1.1			8.44E-03			1.21E-04
12:20	12:40	20	Trap204	SS1.1			3.51E-03			5.02E-05
12:40	13:00	20	Trap205	SS1.1			1.58E-02			2.27E-04
13:00	13:20	20	Trap206	SS1.1			1.74E-02			2.50E-04
13:20	13:40	20	Trap207	SS1.1			1.58E+00			2.27E-02
13:40	14:00	20	Trap208	SS1.1			2.64E+00			3.78E-02
14:00	14:20	20	Trap209	SS1.1			5.76E+00			8.24E-02
14:20	14:40	20	Trap210	SS1.1			2.57E+00			3.69E-02
14:40	15:00	20	Trap211	SS1.1			1.70E-02			2.44E-04
15:00	15:20	20	Trap212	SS1.1			3.04E-02			4.35E-04
15:20	15:40	20	Trap213	SS1.1			1.83E-02			2.62E-04
15:40	16:00	20	Trap214	SS1.1			5.50E-03			7.88E-05
16:00	16:20	20	Trap215	SS1.1			9.77E-03			1.40E-04
16:20	16:40	20	Trap216	SS1.1			2.25E-02			3.22E-04

(BDL = Below Detection Limit)

Table A.2: Birmingham, 1st February 2000

SAMPLE START	SAMPLE FINISH	SAMPLE TIME	BAG/ TRAP n ^o	SITE n ^o	PDCB Conc ppt	PMCP Conc ppt	PMCH Conc ppt	PDCB Conc µg m ⁻³	PMCP Conc µg m ⁻³	PMCH Conc µg m ⁻³
S2.1										
12:43	12:51	6.5	UR009	S2.1	6.77E-03	6.51E-03	5.79E-03	8.31E-05	7.98E-05	8.29E-05
13:00	13:03	3	UR121	S2.1	3.70E-03	7.40E-03	4.77E-03	4.54E-05	9.08E-05	6.83E-05
13:03	13:06	3	UR122	S2.1	4.01E-03	7.90E-03	3.95E-03	4.92E-05	9.70E-05	5.65E-05
13:06	13:09	3	UR123	S2.1	8.30E-03	6.35E-03	3.68E-03	1.02E-04	7.79E-05	5.27E-05
13:09	13:12	3	UR124	S2.1	6.49E-03	7.54E-03	3.46E-03	7.96E-05	9.25E-05	4.96E-05
13:12	13:15	3	UR125	S2.1	BDL	7.65E-03	7.52E-03	BDL	9.38E-05	1.08E-04
13:17	13:20	3	UR001	S2.1	BDL	6.66E-03	2.79E-03	BDL	8.17E-05	3.99E-05
13:20	13:25	5	UR145	S2.1	BDL	6.90E-03	8.63E-03	BDL	8.47E-05	1.24E-04
13:25	13:30	5	UR008	S2.1	BDL	6.06E-03	4.25E-03	BDL	7.44E-05	6.08E-05
13:30	13:33	3	UR002	S2.1	2.64E-03	5.94E-03	4.88E-03	3.24E-05	7.29E-05	6.99E-05
13:33	13:36	3	UR003	S2.1	BDL	5.07E-03	2.32E-03	BDL	6.22E-05	3.32E-05
13:36	13:39	3	UR004	S2.1	BDL	6.36E-03	7.04E-03	BDL	7.80E-05	1.01E-04
13:39	13:42	3	UR006	S2.1	3.11E-03	6.38E-03	8.58E-03	3.81E-05	7.82E-05	1.23E-04
13:42	13:45	3	UR007	S2.1	BDL	7.02E-03	8.91E-03	BDL	8.61E-05	1.28E-04
13:45	13:48	3	UR126	S2.1	3.99E-03	7.50E-03	8.73E-03	4.90E-05	9.20E-05	1.25E-04
13:48	13:51	3	UR127	S2.1	2.84E-03	7.99E-03	6.00E-03	3.49E-05	9.80E-05	8.58E-05
13:51	13:54	3	UR128	S2.1	BDL	8.51E-03	4.40E-03	BDL	1.04E-04	6.30E-05
13:54	13:57	3	UR129	S2.1	5.19E-03	3.28E-03	6.76E-03	6.37E-05	4.03E-05	9.67E-05
13:57	14:00	3	UR130	S2.1	7.29E-03	7.34E-03	7.16E-03	8.95E-05	9.01E-05	1.02E-04
S2.2										
12:30	12:36	6	UR143	S2.2	BDL	6.25E-03	6.58E-03	BDL	7.67E-05	9.42E-05
13:00	13:03	3	UR111	S2.2	BDL	7.83E-03	5.98E-03	BDL	9.61E-05	8.56E-05
13:03	13:06	3	UR112	S2.2	2.91E-03	7.50E-03	3.44E-03	3.57E-05	9.20E-05	4.92E-05
13:06	13:09	3	UR113	S2.2	BDL	7.84E-03	5.01E-03	BDL	9.62E-05	7.17E-05
13:09	13:12	3	UR114	S2.2	4.09E-03	7.34E-03	6.33E-03	5.02E-05	9.01E-05	9.06E-05
13:12	13:15	3	UR115	S2.2	BDL	BDL	5.16E-03	BDL	BDL	7.38E-05
13:16	13:20	4	UR018	S2.2	BDL	6.63E-03	6.41E-03	BDL	8.14E-05	9.17E-05
13:20	13:25	5	UR019	S2.2	BDL	7.50E-03	7.17E-03	BDL	9.20E-05	1.03E-04
13:25	13:30	5	UR020	S2.2	2.57E-03	7.22E-03	2.63E-03	3.15E-05	8.86E-05	3.77E-05
13:30	13:33	3	UR116	S2.2	BDL	7.58E-03	3.29E-03	BDL	9.31E-05	4.71E-05
13:33	13:36	3	UR117	S2.2	BDL	2.74E-03	6.41E-03	BDL	3.36E-05	9.17E-05
13:36	13:39	3	UR118	S2.2	BDL	BDL	3.09E-03	BDL	BDL	4.43E-05
13:39	13:42	3	UR119	S2.2	BDL	7.75E-03	4.10E-03	BDL	9.51E-05	5.87E-05
13:42	13:45	3	UR120	S2.2	3.42E-03	8.02E-02	3.32E-03	4.20E-05	9.84E-04	4.76E-05
13:45	13:48	3	UR021	S2.2	BDL	5.91E-03	4.61E-03	BDL	7.25E-05	6.59E-05
13:48	13:51	3	UR024	S2.2	BDL	6.50E-03	5.51E-03	BDL	7.98E-05	7.88E-05
13:51	13:54	3	UR025	S2.2	BDL	6.64E-03	5.10E-03	BDL	8.15E-05	7.30E-05
13:54	13:57	3	UR026	S2.2	BDL	6.12E-03	5.50E-03	BDL	7.51E-05	7.87E-05
13:57	14:00	3	UR027	S2.2	3.24E-03	6.06E-03	2.69E-03	3.97E-05	7.44E-05	3.85E-05
S2.3										
12:30	12:36	6	UR141	S2.3	BDL	6.84E-03	6.08E-03	BDL	8.40E-05	8.71E-05
13:00	13:03	3	UR146	S2.3	5.01E-03	7.77E-03	4.13E-03	6.15E-05	9.54E-05	5.92E-05
13:03	13:06	3	UR147	S2.3	BDL	8.00E-03	6.32E-03	BDL	9.81E-05	9.05E-05

13:06	13:09	3	UR148	S2.3	BDL	7.48E-03	4.24E-03	BDL	9.18E-05	6.07E-05
13:09	13:12	3	UR149	S2.3	BDL	7.17E-03	7.67E-03	BDL	8.80E-05	1.10E-04
13:12	13:15	3	UR150	S2.3	BDL	6.75E-03	5.83E-03	BDL	8.29E-05	8.34E-05
13:15	13:17	2	UR048	S2.3	BDL	7.20E-03	9.93E-03	BDL	8.84E-05	1.42E-04
13:18	13:24	6	UR047	S2.3	BDL	6.32E-03	1.42E-02	BDL	7.76E-05	2.04E-04
13:25	13:30	5	UR046	S2.3	BDL	6.17E-03	1.29E-02	BDL	7.57E-05	1.85E-04
13:30	13:33	3	UR034	S2.3	BDL	7.13E-03	1.31E-01	BDL	8.75E-05	1.88E-03
13:31	13:37	6	UR042	S2.3	BDL	5.48E-03	7.46E-03	BDL	6.72E-05	1.07E-04
13:33	13:36	3	UR033	S2.3	BDL	6.60E-03	1.41E-01	BDL	8.10E-05	2.02E-03
13:36	13:39	3	UR031	S2.3	2.90E-03	7.38E-03	8.93E-03	3.56E-05	9.05E-05	1.28E-04
13:39	13:42	3	UR049	S2.3	BDL	5.89E-03	6.27E-03	BDL	7.23E-05	8.98E-05
13:40	13:44	3	UR045	S2.3	BDL	6.01E-03	1.16E-02	BDL	7.38E-05	1.66E-04
13:42	13:45	3	UR041	S2.3	BDL	6.81E-03	3.56E-03	BDL	8.36E-05	5.10E-05
13:45	13:48	3	UR054	S2.3	BDL	7.20E-03	7.70E-03	BDL	8.83E-05	1.10E-04
13:48	13:51	3	UR056	S2.3	BDL	7.58E-03	7.59E-03	BDL	9.31E-05	1.09E-04
13:51	13:54	3	UR053	S2.3	BDL	8.54E-03	7.35E-03	BDL	1.05E-04	1.05E-04
13:54	13:57	3	UR051	S2.3	BDL	7.12E-03	8.59E-03	BDL	8.73E-05	1.23E-04
13:57	14:00	3	UR035	S2.3	2.88E-03	9.09E-03	1.50E-02	3.53E-05	1.12E-04	2.15E-04
S2.4										
12:30	12:40	10	UR144	S2.4	BDL	7.79E-03	4.85E-03	BDL	9.56E-05	6.94E-05
13:00	13:03	3	UR131	S2.4	LOST					
13:03	13:06	3	UR132	S2.4	BDL	BDL	3.26E-03	BDL	BDL	4.67E-05
13:06	13:09	3	UR133	S2.4	4.35E-03	8.56E-03	7.70E-03	5.34E-05	1.05E-04	1.10E-04
13:09	13:12	3	UR134	S2.4	5.14E-03	4.03E-03	6.59E-03	6.31E-05	4.95E-05	9.44E-05
13:12	13:15	3	UR135	S2.4	BDL	BDL	3.23E-02	BDL	BDL	4.63E-04
13:15	13:19	3	UR010	S2.4	BDL	7.12E-03	6.28E-02	BDL	8.74E-05	8.99E-04
13:20	13:24	4	UR011	S2.4	BDL	3.27E-03	2.05E-01	BDL	4.01E-05	2.94E-03
13:25	13:30	5	UR012	S2.4	BDL	5.72E-03	5.72E-02	BDL	7.02E-05	8.19E-04
13:30	13:33	3	UR136	S2.4	BDL	7.23E-03	1.85E-02	BDL	8.87E-05	2.64E-04
13:33	13:36	3	UR137	S2.4	BDL	6.80E-03	1.47E-02	BDL	8.35E-05	2.10E-04
13:36	13:39	3	UR138	S2.4	BDL	7.57E-03	1.56E-02	BDL	9.28E-05	2.23E-04
13:39	13:42	3	UR139	S2.4	BDL	7.53E-03	7.74E-03	BDL	9.24E-05	1.11E-04
13:42	13:45	3	UR140	S2.4	BDL	7.98E-03	1.65E-02	BDL	9.80E-05	2.36E-04
13:45	13:48	3	UR013	S2.4	BDL	5.94E-03	2.06E-02	BDL	7.29E-05	2.95E-04
13:45	13:48	3	UR050	S2.4	BDL	8.06E-03	2.23E-02	BDL	9.88E-05	3.19E-04
13:48	13:51	3	UR014	S2.4	BDL	8.46E-03	5.78E-03	BDL	1.04E-04	8.28E-05
13:51	13:54	3	UR015	S2.4	BDL	9.91E-03	5.78E-03	BDL	1.22E-04	8.27E-05
13:54	13:57	3	UR016	S2.4	BDL	5.26E-03	1.02E-02	BDL	6.46E-05	1.46E-04
13:57	14:00	3	UR017	S2.4	BDL	8.01E-03	5.99E-03	BDL	9.83E-05	8.58E-05
S2.5										
12:30	12:37	7	UR142	S2.5	2.46E-03	6.54E-03	9.40E-03	3.01E-05	8.03E-05	1.35E-04
13:00	13:03	3	UR110	S2.5	BDL	BDL	BDL	BDL	BDL	BDL
13:03	13:06	3	UR109	S2.5	BDL	BDL	BDL	BDL	BDL	BDL
13:06	13:09	3	UR108	S2.5	BDL	BDL	BDL	BDL	BDL	BDL
13:09	13:12	3	UR107	S2.5	BDL	BDL	BDL	BDL	BDL	BDL
13:12	13:15	3	UR106	S2.5	BDL	BDL	BDL	BDL	BDL	BDL
13:15	13:20	5	LOST							
13:20	13:25	5	LOST							
13:25	13:27	2	UR029	S2.5	BDL	6.80E-03	3.27E-01	BDL	8.34E-05	4.68E-03
13:30	13:33	3	UR101	S2.5	BDL	BDL	BDL	BDL	BDL	BDL

13:33	13:36	3	UR102	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:36	13:39	3	UR103	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:39	13:42	3	UR104	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:42	13:45	3	UR105	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:42		?	UR037	S2.5	BDL	6.73E-03	4.63E-01	BDL	8.25E-05	6.62E-03	
13:45	13:48	3	UR039	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:48	13:51	3	UR028	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:51	13:54	3	UR070	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:54	13:57	3	UR040	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13:57	14:00	3	UR038	S2.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SS2.3											
12:30	12:44	14	UR151	SS2.3	3.76E-03	8.36E-03	8.17E-03	4.62E-05	1.03E-04	1.17E-04	
12:59	13:14	15	UR152	SS2.3	2.95E-03	8.05E-03	1.34E-02	3.62E-05	9.87E-05	1.92E-04	
13:14	13:29	15	UR153	SS2.3	1.91E-03	9.67E-03	1.17E+00	2.35E-05	1.19E-04	1.68E-02	
13:29	13:44	15	UR154	SS2.3	BDL	BDL	1.24E+00	BDL	BDL	1.77E-02	
13:44	13:59	15	UR155	SS2.3	5.50E-03	7.97E-03	2.95E-01	6.75E-05	9.78E-05	4.22E-03	
13:59	14:14	15	UR156	SS2.3	4.16E-03	7.90E-03	6.90E-02	5.10E-05	9.70E-05	9.88E-04	
14:14	14:29	15	UR157	SS2.3	3.84E-03	8.18E-03	7.79E-03	4.71E-05	1.00E-04	1.12E-04	
14:29	14:44	15	UR158	SS2.3	2.86E-03	7.99E-03	5.27E-03	3.50E-05	9.80E-05	7.54E-05	
14:44	14:59	15	UR159	SS2.3	3.49E-03	8.63E-03	4.71E-03	4.28E-05	1.06E-04	6.74E-05	
14:59	15:14	15	UR160	SS2.3	3.04E-03	8.56E-03	4.65E-03	3.73E-05	1.05E-04	6.65E-05	
SS2.3											
12:44	12:59	15	Trap203	SS2.3			7.97E-03			1.14E-04	
12:59	13:14	15	Trap204	SS2.3			1.32E-02			1.89E-04	
13:14	13:29	15	Trap205	SS2.3			1.12E+00			1.61E-02	
13:29	13:44	15	Trap206	SS2.3			1.38E+00			1.98E-02	
13:44	13:59	15	Trap207	SS2.3			3.46E-01			4.96E-03	
13:59	14:14	15	Trap208	SS2.3			7.25E-02			1.04E-03	
14:14	14:29	15	Trap209	SS2.3			8.64E-03			1.24E-04	
14:29	14:44	15	Trap210	SS2.3			2.90E-03			4.15E-05	
14:44	14:59	15	Trap211	SS2.3			7.51E-03			1.08E-04	
14:59	15:14	15	Trap212	SS2.3			4.92E-03			7.04E-05	
15:14	15:29	15	Trap213	SS2.3			4.53E-03			6.48E-05	
15:29	15:44	15	Trap214	SS2.3			7.95E-03			1.14E-04	
15:44	15:59	15	Trap215	SS2.3			6.41E-03			9.17E-05	
15:59	16:14	15	Trap216	SS2.3			6.11E-03			8.74E-05	

(BDL: Below Detection Limit)

Table A.3: Birmingham, 2nd August 2000

SAMPLE START	SAMPLE FINISH	SAMPLE TIME	BAG/TRAP	SITE	PDCB Conc ppt	PMCP Conc ppt	PMCH Conc ppt	PDCB Conc $\mu\text{g m}^{-3}$	PMCP Conc $\mu\text{g m}^{-3}$	PMCH Conc $\mu\text{g m}^{-3}$
S3.1										
12:32	12:38	6	UR208	S3.1	4.50E-03	8.02E-03	6.31E-03	5.52E-05	9.85E-05	9.03E-05
13:00	13:06	6	UR 109	S3.1	6.48E-03	8.38E-03	7.73E-03	7.95E-05	1.03E-04	1.11E-04
13:06	13:12	6	UR 110	S3.1	4.79E-03	8.91E-03	8.18E-03	5.87E-05	1.09E-04	1.17E-04
13:12	13:18	6	UR 111	S3.1	4.35E-03	7.35E-03	5.30E-03	5.34E-05	9.02E-05	7.58E-05
13:18	13:24	6	UR 112	S3.1	5.15E-03	8.94E-03	6.84E-03	6.32E-05	1.10E-04	9.79E-05
13:24	13:30	6	UR 113	S3.1	4.60E-03	8.62E-03	6.91E-03	5.65E-05	1.06E-04	9.89E-05
13:30	13:36	6	UR 114	S3.1	3.23E-03	7.88E-03	6.34E-03	3.96E-05	9.67E-05	9.08E-05
13:36	13:42	6	UR 115	S3.1	2.73E-03	7.68E-03	6.80E-03	3.35E-05	9.42E-05	9.73E-05
13:42	13:48	6	UR 116	S3.1	4.76E-03	9.31E-03	6.34E-03	5.84E-05	1.14E-04	9.08E-05
13:48	13:54	6	UR 117	S3.1	3.96E-03	9.04E-03	6.13E-03	4.86E-05	1.11E-04	8.78E-05
13:54	14:00	6	UR 118	S3.1	3.95E-03	9.70E-03	5.71E-03	4.85E-05	1.19E-04	8.17E-05
14:00	14:06	6	UR 006	S3.1	5.04E-03	8.12E-03	6.04E-03	6.18E-05	9.97E-05	8.65E-05
14:06	14:12	6	UR 007	S3.1	4.72E-03	7.97E-03	5.92E-03	5.79E-05	9.78E-05	8.47E-05
14:12	14:18	6	UR 008	S3.1	2.38E-03	7.29E-03	6.25E-03	2.92E-05	8.95E-05	8.95E-05
14:18	14:24	6	UR 009	S3.1	5.04E-03	7.83E-03	5.85E-03	6.18E-05	9.60E-05	8.37E-05
14:24	14:30	6	UR 010	S3.1	5.40E-03	1.15E-02	7.39E-03	6.63E-05	1.41E-04	1.06E-04
14:30	14:36	6	UR 111	S3.1	4.08E-03	7.60E-03	5.77E-03	5.01E-05	9.33E-05	8.27E-05
14:36	14:42	6	UR 053	S3.1	2.76E-03	7.34E-03	5.98E-03	3.39E-05	9.00E-05	8.56E-05
14:42	14:48	6	UR 054	S3.1	LOST					
14:48	14:54	6	UR 056	S3.1	3.98E-03	7.06E-03	5.69E-03	4.88E-05	8.66E-05	8.14E-05
14:54	15:00	6	UR 058	S3.1	5.02E-03	7.32E-03	6.16E-03	6.16E-05	8.98E-05	8.82E-05
S3.2										
12:31	12:35	4	UR201	S3.2	LOST					
13:00	13:05	5	UR 209	S3.2	4.38E-03	6.82E-03	4.95E-03	5.37E-05	8.37E-05	7.08E-05
13:06	13:12	6	UR 210	S3.2	1.67E-03	1.11E-02	2.74E-02	2.05E-05	1.36E-04	3.93E-04
13:12	13:18	6	UR 211	S3.2	4.45E-03	6.21E-02	6.37E-02	5.46E-05	7.62E-04	9.12E-04
13:18	13:24	6	UR 212	S3.2	1.39E-02	1.18E+00	1.06E+00	1.70E-04	1.45E-02	1.52E-02
13:24	13:30	6	UR 213	S3.2	3.52E-03	2.98E-01	2.92E-01	4.32E-05	3.65E-03	4.18E-03
13:30	13:36	6	UR 214	S3.2	1.32E-02	4.59E-02	3.23E-02	1.62E-04	5.63E-04	4.63E-04
13:36	13:42	6	UR 215	S3.2	3.81E-03	7.05E-02	4.36E-02	4.68E-05	8.65E-04	6.24E-04
13:42	13:48	6	UR 216	S3.2	5.97E-03	6.19E-02	3.83E-02	7.33E-05	7.59E-04	5.49E-04
13:48	13:54	6	UR 217	S3.2	5.15E-03	5.80E-02	3.50E-02	6.32E-05	7.12E-04	5.01E-04
13:54	14:00	6	UR 218	S3.2	1.91E-02	7.11E-02	4.16E-02	2.35E-04	8.72E-04	5.95E-04
14:00	14:06	6	UR 119	S3.2	7.12E-03	3.79E-02	2.21E-02	8.73E-05	4.65E-04	3.16E-04
14:06	14:12	6	UR 120	S3.2	4.80E-03	5.19E-02	3.38E-02	5.89E-05	6.37E-04	4.83E-04
14:12	14:18	6	UR 121	S3.2	4.40E-03	3.46E-02	2.37E-02	5.40E-05	4.25E-04	3.40E-04
14:18	14:24	6	UR 122	S3.2	1.39E-02	2.79E-02	2.02E-02	1.70E-04	3.42E-04	2.89E-04
14:24	14:30	6	UR 123	S3.2	4.39E-03	3.71E-02	1.91E-02	5.38E-05	4.55E-04	2.73E-04
14:30	14:36	6	UR 124	S3.2	1.69E-02	1.59E-02	9.33E-03	2.08E-04	1.95E-04	1.33E-04
14:36	14:42	6	UR 012	S3.2	4.89E-03	1.28E-02	9.49E-03	6.00E-05	1.57E-04	1.36E-04
14:42	14:48	6	UR 013	S3.2	4.87E-03	7.19E-02	3.30E-02	5.98E-05	8.83E-04	4.73E-04
14:48	14:54	6	UR 014	S3.2	4.61E-03	6.25E-02	3.36E-02	5.65E-05	7.67E-04	4.80E-04
14:54	15:00	6	UR 015	S3.2	1.38E-02	2.90E-02	1.35E-02	1.69E-04	3.56E-04	1.94E-04

S3.3											
12:32	12:37	6	UR205	S3.3	4.69E-03	9.14E-03	8.85E-03	5.75E-05	1.12E-04	1.27E-04	
13:00	13:06	6	UR 249	S3.3	2.45E-03	6.99E-03	6.66E-03	3.01E-05	8.57E-05	9.53E-05	
13:06	13:12	6	UR 250	S3.3	3.59E-03	7.68E-03	6.51E-03	4.40E-05	9.42E-05	9.32E-05	
13:12	13:18	6	UR 251	S3.3	BDL	3.16E-02	3.52E-02	BDL	3.87E-04	5.04E-04	
13:18	13:24	6	UR 252	S3.3	2.20E-03	1.46E+00	1.42E+00	2.70E-05	1.79E-02	2.03E-02	
13:24	13:30	6	UR 253	S3.3	2.62E-03	2.25E-01	2.14E-01	3.22E-05	2.76E-03	3.06E-03	
13:30	13:36	6	UR 254	S3.3	BDL	1.22E-01	1.10E-01	BDL	1.50E-03	1.58E-03	
13:36	13:42	6	UR 255	S3.3	3.44E-03	7.90E-02	5.24E-02	4.22E-05	9.70E-04	7.51E-04	
13:42	13:48	6	UR 256	S3.3	LOST						
13:48	13:54	6	UR 257	S3.3	3.84E-03	7.15E-02	4.78E-02	4.71E-05	8.77E-04	6.84E-04	
13:54	14:00	6	UR 258	S3.3	3.46E-03	3.69E-02	2.56E-02	4.24E-05	4.53E-04	3.67E-04	
14:00	14:06	6	UR 143	S3.3	3.28E-03	7.03E-02	3.96E-02	4.02E-05	8.62E-04	5.67E-04	
14:06	14:12	6	UR 144	S3.3	3.98E-03	6.01E-02	3.87E-02	4.89E-05	7.38E-04	5.54E-04	
14:12	14:18	6	UR 145	S3.3	3.15E-03	4.29E-02	3.07E-02	3.87E-05	5.27E-04	4.39E-04	
14:18	14:24	6	UR 146	S3.3	3.56E-03	2.99E-02	1.97E-02	4.36E-05	3.67E-04	2.82E-04	
14:24	14:30	6	UR 147	S3.3	4.16E-03	2.90E-02	1.70E-02	5.11E-05	3.56E-04	2.44E-04	
14:30	14:36	6	UR 148	S3.3	4.12E-03	1.25E-02	8.91E-03	5.05E-05	1.53E-04	1.28E-04	
14:36	14:42	6	UR 036	S3.3	LOST						
14:42	14:48	6	UR 037	S3.3	3.72E-03	5.24E-02	2.42E-02	4.56E-05	6.43E-04	3.47E-04	
14:48	14:54	6	UR 038	S3.3	3.97E-03	7.79E-02	3.09E-02	4.87E-05	9.56E-04	4.42E-04	
14:54	15:00	6	UR 039	S3.3	2.78E-03	2.39E-02	1.22E-02	3.41E-05	2.94E-04	1.74E-04	
S3.4											
12:30	12:37	7	UR202	S3.4	LOST						
13:00	13:06	6	UR 219	S3.4	LOST						
13:06	13:12	6	UR 220	S3.4	LOST						
13:12	13:18	6	UR 221	S3.4	1.69E-02	4.53E+01	4.82E+01	2.07E-04	5.56E-01	6.90E-01	
13:18	13:24	6	UR 222	S3.4	LOST						
13:24	13:30	6	UR 223	S3.4	LOST						
13:30	13:36	6	UR 224	S3.4	LOST						
13:36	13:42	6	UR 225	S3.4	LOST						
13:42	13:48	6	UR 226	S3.4	LOST						
13:48	13:54	6	UR 227	S3.4	LOST						
13:54	13:48	4	UR 228	S3.4	LOST						
14:00	14:05	5	UR 125	S3.4	LOST						
14:06	14:11	5	UR 126	S3.4	LOST						
14:12	14:17	5	UR 127	S3.4	LOST						
14:18	14:23	5	UR 128	S3.4	LOST						
14:24	14:29	5	UR 129	S3.4	LOST						
14:30	14:35	5	UR 130	S3.4	LOST						
14:36	14:42	6	UR 016	S3.4	2.85E-03	2.91E-02	1.89E-02	3.50E-05	3.58E-04	2.71E-04	
14:42	14:48	6	UR 017	S3.4	2.94E-03	1.10E-02	9.15E-03	3.60E-05	1.35E-04	1.31E-04	
14:48	14:54	6	UR 018	S3.4	3.01E-03	7.97E-03	6.80E-03	3.69E-05	9.79E-05	9.74E-05	
14:54	15:00	6	UR 019	S3.4	2.90E-03	1.04E-02	1.00E-02	3.55E-05	1.27E-04	1.44E-04	
S3.5											
12:35	12:38	3	UR204	S3.5	2.73E-03	2.19E-02	8.58E-03	3.35E-05	2.69E-04	1.23E-04	
13:00	13:03	3	UR 239	S3.5	9.57E-03	1.51E-02	1.93E-02	1.17E-04	1.85E-04	2.77E-04	
13:06	13:09	3	UR 240	S3.5	4.66E-03	3.49E+00	1.50E+01	5.72E-05	4.28E-02	2.14E-01	
13:12	13:15	3	UR 241	S3.5	4.05E-03	2.77E+00	3.33E+00	4.97E-05	3.40E-02	4.76E-02	
13:18	13:21	3	UR 242	S3.5	2.00E-02	4.56E+01	4.58E+01	2.45E-04	5.59E-01	6.56E-01	

13:24	13:27	3	UR 243	S3.5	1.78E-02	4.16E+01	1.60E+01	2.18E-04	5.11E-01	2.29E-01
13:30	13:33	3	UR 244	S3.5	4.22E-03	3.31E+00	9.01E-01	5.18E-05	4.07E-02	1.29E-02
13:36	13:39	3	UR 245	S3.5	3.63E-03	3.70E-01	2.44E-01	4.46E-05	4.54E-03	3.50E-03
13:42	13:45	3.5	UR 246	S3.5	4.80E-03	1.66E-01	1.22E-01	5.89E-05	2.04E-03	1.75E-03
13:48	13:51	3	UR 247	S3.5	3.67E-03	1.06E-01	7.96E-02	4.50E-05	1.30E-03	1.14E-03
13:54	13:57	3	UR 248	S3.5	3.86E-03	6.09E-02	4.70E-02	4.74E-05	7.47E-04	6.72E-04
14:00	14:04	4	UR 137	S3.5	4.50E-03	6.57E-02	8.15E-02	5.52E-05	8.06E-04	1.17E-03
14:06	14:10	4	UR 138	S3.5	3.63E-03	1.59E-01	1.73E-01	4.45E-05	1.95E-03	2.47E-03
14:12	14:16	4	UR 139	S3.5	3.82E-03	1.31E-01	1.17E-01	4.68E-05	1.60E-03	1.68E-03
14:18	14:24	6?	UR 140	S3.5	BDL	2.80E-02	2.51E-02	BDL	3.44E-04	3.59E-04
14:24	14:30	6	UR 141	S3.5	4.31E-03	5.77E-02	3.58E-02	5.29E-05	7.08E-04	5.12E-04
14:30	14:36	6	UR 142	S3.5	4.16E-03	3.96E-02	2.95E-02	5.10E-05	4.85E-04	4.22E-04
14:36	14:42	6	UR 028	S3.5	4.50E-03	3.60E-02	2.51E-02	5.52E-05	4.41E-04	3.59E-04
14:42	14:48	6	UR 029	S3.5	2.69E-03	1.01E-02	9.38E-03	3.31E-05	1.24E-04	1.34E-04
14:48	14:54	6	UR 030	S3.5	3.72E-03	4.31E-02	2.66E-02	4.56E-05	5.29E-04	3.81E-04
14:54	15:00	6	UR 031	S3.5	4.38E-03	2.08E-02	1.64E-02	5.37E-05	2.56E-04	2.34E-04
S3.6										
12:30	12:35	5	UR207	S3.6	1.70E-03	7.94E-03	6.35E-03	2.08E-05	9.74E-05	9.09E-05
13:00	13:06	6	UR 269	S3.6	2.49E-03	8.05E-03	5.86E-02	3.06E-05	9.88E-05	8.38E-04
13:06	13:12	6	UR 270	S3.6	3.17E-03	4.45E-01	6.85E+00	3.89E-05	5.46E-03	9.80E-02
13:12	13:18	6	UR 101	S3.6	LOST					
13:18	13:24	6	UR 102	S3.6	4.61E-03	4.90E+00	4.67E+00	5.65E-05	6.01E-02	6.69E-02
13:24	13:30	6	UR 103	S3.6	1.09E-02	2.37E+01	6.49E+00	1.34E-04	2.91E-01	9.29E-02
13:30	13:36	6	UR 104	S3.6	2.87E-03	7.46E-01	1.52E-01	3.52E-05	9.16E-03	2.17E-03
13:36	13:42	6	UR 105	S3.6	2.14E-03	7.55E-02	4.75E-02	2.62E-05	9.27E-04	6.80E-04
13:42	13:48	6	UR 106	S3.6	2.10E-03	5.03E-02	3.62E-02	2.58E-05	6.18E-04	5.18E-04
13:48	13:54	6	UR 107	S3.6	2.02E-02	1.22E-02	1.16E-02	2.48E-04	1.50E-04	1.66E-04
13:54	14:00	6	UR 108	S3.6	1.89E-02	2.55E-02	2.12E-02	2.32E-04	3.13E-04	3.04E-04
14:00	14:06	6	UR 154	S3.6	5.54E-03	2.89E-02	2.14E-02	6.80E-05	3.54E-04	3.07E-04
14:06	14:12	6	UR 155	S3.6	LOST					
14:12	14:18	6	UR 001	S3.6	LOST					
14:18	14:24	6	UR 002	S3.6	2.63E-03	1.35E-02	1.02E-02	3.23E-05	1.66E-04	1.46E-04
14:24	14:30	6	UR 003	S3.6	LOST					
14:30	14:36	6	UR 005	S3.6	3.92E-03	1.55E-02	1.13E-02	4.81E-05	1.91E-04	1.62E-04
14:36	14:42	6	UR 048	S3.6	2.38E-03	9.79E-03	7.80E-03	2.92E-05	1.20E-04	1.12E-04
14:42	14:48	6	UR 049	S3.6	3.16E-03	9.33E-03	6.71E-03	3.88E-05	1.15E-04	9.61E-05
14:48	14:54	6	UR 050	S3.6	2.58E-03	8.77E-03	6.57E-03	3.17E-05	1.08E-04	9.40E-05
14:54	15:00	6	UR 051	S3.6	2.45E-03	8.02E-03	6.72E-03	3.01E-05	9.85E-05	9.62E-05
S3.7										
12:30	12:36	6	UR206	S3.7	2.27E-03	7.17E-03	6.22E-03	2.78E-05	8.79E-05	8.90E-05
13:00	13:06	5.55	UR 259	S3.7	2.71E-03	7.48E-03	6.18E-03	3.33E-05	9.17E-05	8.85E-05
13:06	13:12	5.55	UR 260	S3.7	3.02E-03	1.51E-01	4.94E+00	3.71E-05	1.85E-03	7.07E-02
13:12	13:18	5.55	UR 261	S3.7	5.31E-03	9.00E+00	9.41E+00	6.52E-05	1.10E-01	1.35E-01
13:18	13:24	5.55	UR 262	S3.7	2.81E-03	3.25E+00	3.32E+00	3.44E-05	3.99E-02	4.75E-02
13:24	13:30	5.59	UR 263	S3.7	5.94E-03	1.46E+01	3.10E+00	7.29E-05	1.79E-01	4.44E-02
13:30	13:36	6.02	UR 264	S3.7	2.63E-03	4.75E-01	6.72E-02	3.23E-05	5.82E-03	9.62E-04
13:36	13:42	6	UR 265	S3.7	3.57E-03	2.90E-02	1.83E-02	4.38E-05	3.56E-04	2.62E-04
13:42	13:48	5.58	UR 266	S3.7	1.10E-03	2.37E-02	1.67E-02	1.35E-05	2.91E-04	2.38E-04
13:48	13:54	6.04	UR 267	S3.7	3.25E-03	1.57E-02	1.19E-02	3.98E-05	1.92E-04	1.70E-04
13:54	14:00	5.55	UR 268	S3.7	3.08E-03	1.49E-02	1.21E-02	3.78E-05	1.83E-04	1.73E-04

14:00	14:06	6.02	UR 149	S3.7	2.97E-03	1.61E-02	1.24E-02	3.65E-05	1.98E-04	1.78E-04
14:06	14:12	5.54	UR 150	S3.7	6.23E-03	2.40E-02	1.64E-02	7.64E-05	2.95E-04	2.35E-04
14:12	14:18	5.58	UR 151	S3.7	4.91E-03	2.25E-02	2.30E-02	6.02E-05	2.76E-04	3.29E-04
14:18	14:24	6	UR 152	S3.7	3.63E-03	9.79E-03	7.41E-03	4.46E-05	1.20E-04	1.06E-04
14:24	14:30	5.55	UR 153	S3.7	2.46E-03	1.14E-02	8.96E-03	3.02E-05	1.39E-04	1.28E-04
14:30	14:36	5.55	UR 004	S3.7	3.25E-03	1.00E-02	7.66E-03	3.99E-05	1.23E-04	1.10E-04
14:38	14:42	3.58	UR 040	S3.7	1.88E-03	8.95E-03	6.75E-03	2.31E-05	1.10E-04	9.67E-05
14:42	14:48	5.55	UR 041	S3.7	3.25E-03	8.92E-03	CON	3.99E-05	1.10E-04	CON
14:48	14:54	5.5	UR 042	S3.7	3.15E-03	8.22E-03	CON	3.87E-05	1.01E-04	CON
14:54	15:00	5.5	UR 047	S3.7	3.18E-03	9.46E-03	1.32E-02	3.91E-05	1.16E-04	1.89E-04
S3.8										
12:30	12:36	6	UR203	S3.8	LOST					
13:00	13:06	6	UR 229	S3.8	5.98E-03	9.46E-03	5.22E-03	7.34E-05	1.16E-04	7.47E-05
13:06	13:12	6	UR 230	S3.8	7.23E-03	9.51E-03	1.37E-02	8.87E-05	1.17E-04	1.96E-04
13:12	13:18	6	UR 231	S3.8	6.55E-03	4.42E-02	4.15E-02	8.04E-05	5.42E-04	5.95E-04
13:18	13:24	6	UR 232	S3.8	8.07E-03	7.95E-02	7.23E-02	9.91E-05	9.76E-04	1.04E-03
13:24	13:30	6	UR 233	S3.8	4.60E-03	3.89E-01	7.76E-02	5.65E-05	4.77E-03	1.11E-03
13:30	13:36	6	UR 234	S3.8	6.09E-03	1.05E-02	8.15E-03	7.47E-05	1.29E-04	1.17E-04
13:36	13:42	6	UR 235	S3.8	3.72E-03	8.78E-03	5.35E-03	4.56E-05	1.08E-04	7.66E-05
13:42	13:48	6	UR 236	S3.8	3.10E-03	7.54E-03	5.84E-03	3.81E-05	9.25E-05	8.36E-05
13:48	13:54	6	UR 237	S3.8	2.88E-03	7.60E-03	6.62E-03	3.53E-05	9.32E-05	9.47E-05
13:54	14:00	6	UR 238	S3.8	7.75E-03	7.89E-03	5.18E-03	9.51E-05	9.68E-05	7.41E-05
14:00	14:06	6	UR 131	S3.8	4.16E-03	7.94E-03	6.19E-03	5.11E-05	9.74E-05	8.86E-05
14:06	14:12	6	UR 132	S3.8	5.32E-03	7.99E-03	6.19E-03	6.52E-05	9.81E-05	8.86E-05
14:12	14:18	6	UR 133	S3.8	3.91E-03	7.39E-03	6.26E-03	4.79E-05	9.07E-05	8.96E-05
14:18	14:24	6	UR 134	S3.8	5.45E-03	8.99E-03	6.63E-03	6.69E-05	1.10E-04	9.49E-05
14:24	14:30	6	UR 135	S3.8	2.71E-03	7.75E-03	6.05E-03	3.32E-05	9.51E-05	8.66E-05
14:30	14:36	6	UR 136	S3.8	5.79E-03	8.02E-03	6.14E-03	7.10E-05	9.84E-05	8.79E-05
14:36	14:42	6	UR 021	S3.8	LOST					
14:42	14:48	6	UR 024	S3.8	3.06E-03	7.16E-03	5.77E-03	3.76E-05	8.79E-05	8.26E-05
14:48	14:54	6	UR 026	S3.8	2.95E-03	7.43E-03	6.20E-03	3.62E-05	9.12E-05	8.88E-05
14:54	15:00	6	UR 027	S3.8	5.97E-03	7.41E-03	6.33E-03	7.32E-05	9.09E-05	9.06E-05
Ss3.3										
12:45	13:00	15	Trap 403	SS3.3	3.16E-02	1.63E-02	1.48E-01	3.88E-04	2.00E-04	2.11E-03
13:00	13:15	15	Trap 404	SS3.3	6.30E-02	7.93E-03	3.28E-01	7.73E-04	9.73E-05	4.70E-03
13:15	13:30	15	Trap 405	SS3.3	1.57E-02	2.67E-02	3.28E-02	1.92E-04	3.28E-04	4.70E-04
13:30	13:45	15	Trap 406	SS3.3	1.40E-01	1.06E+00	5.27E-01	1.72E-03	1.30E-02	7.54E-03
13:45	14:00	15	Trap 407	SS3.3	1.12E-01	5.38E-01	4.65E-02	1.37E-03	6.60E-03	6.65E-04
14:00	14:15	15	Trap 408	SS3.3	1.11E-02	2.22E-03	1.02E-02	1.36E-04	2.73E-05	1.46E-04
14:15	14:30	15	Trap 409	SS3.3	BDL	1.25E-03	8.83E-03	BDL	1.53E-05	1.26E-04
14:30	14:45	15	Trap 410	SS3.3	1.34E-02	2.98E-03	6.98E-03	1.64E-04	3.65E-05	1.00E-04
14:45	15:00	15	Trap 411	SS3.3	1.78E-02	3.81E-03	7.05E-03	2.18E-04	4.67E-05	1.01E-04
15:00	15:15	15	Trap 412	SS3.3	7.69E-03	1.86E-03	6.46E-03	9.43E-05	2.28E-05	9.25E-05
15:15	15:30	15	Trap 413	SS3.3	4.13E-02	5.12E-03	7.88E-03	5.07E-04	6.28E-05	1.13E-04
15:30	15:45	15	Trap 414	SS3.3	3.43E-02	5.47E-03	8.27E-03	4.21E-04	6.71E-05	1.18E-04
15:45	16:00	15	Trap 415	SS3.3	1.86E-02	1.22E-02	1.59E-01	2.28E-04	1.49E-04	2.28E-03
16:00	16:15	15	Trap 416	SS3.3	1.32E-01	3.62E-01	8.84E-03	1.62E-03	4.44E-03	1.27E-04

(BDL = Below Detection Limit; CON = contaminated)

APPENDIX B: Qualitative Meteorological Observations at Sampling Sites

This appendix describes in a tabular form some qualitative observations of weather conditions made at the sampling sites by people involved in the measurements during the three tracer experiments.

Table B.1: Birmingham, 1st July, 1999

TIME	S1.1	S1.2	S1.3	S1.4	S1.5
13:00	Overcast, humid, medium wind SW-W	Overcast, mild breeze, started spotting with rain after 10 mins	Cloudy/Overcast/windy	No observations made at this site	Cloudy/Overcast
13:15		Overcast, no rain	Cloudy/Overcast		Cloudy/Overcast
13:30	Wind speed dropped at 13:40	Overcast, no rain	Cloudy/Overcast		Cloudy/Overcast
13:45		Overcast, no rain	Cloudy/Overcast		Cloudy/Overcast
14:00	Wind speed picked up	Overcast, no rain	Cloudy/Overcast		Cloudy/Overcast
14:15		Overcast (warm); wind eased possible change in direction	Brighter weather, much reduced wind speed		Cloudy/Overcast
14:30	Wind slowed down again	Overcast, wind up again			Cloudy/Overcast
14:45		Overcast, SW wind			Cloudy/Overcast
15:00	Wind low-medium	Overcast, no rain			Cloudy/Overcast
15:15		Overcast, no rain			Cloudy/Overcast

Table B.2: Birmingham, 1st February 2000

TIME	S 2.1	S2.2	S2.3	S2.4	S2.5	TIME	SS2.3
12:30	40° NE wd	220° SW wd, B=6	260° W wd Overcast	220° SW wd Cloudy, B=5	100° E wd, wind speed and direction very variable	12:30	Mild, B=3
13:00	No wind at start, after one min 280° W wd	220° SW wd, B=3-4, dropped to B=2, after 2 mins	240° SW wd 0.5 ms ⁻¹	210° SW wd	80° E wd	12:59	Mild, B=3
13:03	120° SE wd	230° SW wd B=3	260° W wd 2 ms ⁻¹	240° SW wd		13:14	Mild, B=3-4
13:06	100° E wd	220° SW wd B=3	270° W wd 0.4 ms ⁻¹	225° SW wd		13:29	Mild, B=3-4
13:09		260° W wd B=4	230° SW wd 1-1.4 ms ⁻¹	240° SW wd		13:44	Mild, B=1-2
13:12		180° S wd B=2-3 low	250° SW wd 2.4 ms ⁻¹	215° SW wd		13:59	Mild, gusty
13:16		B=4	240° SW wd 1.5 ms ⁻¹	220° SW wd		14:14	Mild, B=3-4 gusty
13:20	No wind	260° W wd		240° SW wd B=3-4		14:29	Mild, B=3-4, gusty
13:25		220° SW wd B=2-3	1.5 ms ⁻¹	250° SW wd B=3	140° SE wd, very variable	14:44	Mild, B=3-4 gusty slight rain
13:30		SW-W wd, B=3-4 gusty		200° S wd B=3, gusty		14:59	Mild, B=3-4, gusty slight rain
13:33		260 W-SW wd, B=4, gusty		220° SW wd			
13:36		220° SW wd, B=3-4, gusty	270° W wd 0.7 ms ⁻¹	225° SW wd			
13:39		220° SW wd B=3-4-5 gusty	310° NW wd 1.8-1.2 ms ⁻¹	225° SW wd			
13:42		230° SW wd B=3	240° SW wd 0.7 ms ⁻¹	200° SW wd			
13:45		220° S-SW wd B=2-3	220° SW wd 0.9 ms ⁻¹	200° SW wd			
13:48		200° S-SW wd B=2-3	270° W wd 1.0 ms ⁻¹	215° SW wd			
13:51		270° W wd B=2-1 or even lower	260° W wd, 1.3 ms ⁻¹	200° SW wd			
13:54		230° SW-S wd B=3-4, gusting to B=5 +	270° W wd 1.3 ms ⁻¹	180° S to 230° SW wd gusty			
13:57		230° SW wd B=2-3	240° SW wd 1.5 ms ⁻¹	210° SW wd			

(B=*n* refers to the Beaufort Wind Scale, (Met. Office, 1991) where 0=calm, 1=light air, 2=light breeze, 3=moderate breeze, 5=fresh breeze, 6=strong breeze, 7=near gale, 8=gale, 9=strong gale, 10=storm *etc* up to 12)

Table B.3: Birmingham, 2nd August, 2000

TIME	S3.1	S3.2	S3.3	S3.4	S3.5	S3.6	S3.7	S3.8
12:30	No observ. made	Low wind speed/ SW		Sunny windy	Windy but dry			Overcast but sunny
13:00		Intermittent sun/cloudy, rain stopped ~12pm, 230° SW wd	From 280° to 310° wd	Sunny wind	Windy but dry	Cloudy cc 7/8	Dry, blustery, warm, 70% blue sky	Overcast
13:06		Wind speed picked up, 230° SW wd	From 270° to 250°, not windy from 240° to 270°, strong wind	Sunny windy	Windy but dry	Cloudy	Dry, blustery, warm, 70% blue sky	Overcast sunny
13:12		Blustery, more cloud cover, 230° SW wd	From 230° to 250° wd	Sunny windy	Windy but dry	Cloudy	Sun gone! 10% blue sky	Overcast raining
13:18		Wind getting stronger, blustery, looks like rain, cloudier, 230° SW wd	Spots of rain between 13:21-13:23 getting windy- 230° strong wind at 13:20	Sunny windy	Windy with a little rain	Rained a few drops	Bit more sun, 20% blue, otherwise as before	Overcast
13:24		280° W wd patchy blue sky, windy, dark clouds forming	From 250° to 270° wd	Overcast windy	No more rain	Cloudy		Overcast
13:30		230° SW wd strong wind, blue sky overhead,	320° at 13:33 not much wind	Overcast windy	Very blustery	Cloudy		Overcast
13:36		230° SW wd windy, low cloud, brightening up,	130° at 13:40 310° at 13:41 windy, variable.	Overcast windy	Very windy	Cloudy	Spots of rain	Overcast
13:42		230° SW wd blustery, clouds cover getting thicker	From 260° to 280° at 14:45 varying readings at 14:45	Sunny windy	Very windy	Cloudy towards clearing up	Dry and sunny, 25% blue sky	Overcast
13:48		230° SW wd some sun, blustery, blue sky W, thick cloud E	270° W wd not very windy at 13:51	Sunny windy	Windy sunny patches	Cloudy cc 6/8,	50% blue sky	Overcast sunny
13:54		230° SW wd sun gone out some blue sky, sunny blue sky coming across	220° at 13:56, sunny, not much wind 300° at 13:57, 160° at 13:59, still sunny varying directions	Sunny windy	Windy sunny patches	Cloudy with patches of sun	Sunny, 90% blue Sky	Overcast Sunny

14:00		Change of wd From 100° to 80°, drop in speed	Sock not moving at all 14:00, sock not moving at 14:03, sunny, 220° at 14:05 again varying directions	Sunny windy	Windy sunny patches	Cloudy cc 4/8	nice	Sunny
14:06		From 330° to- 230° wd	310° at 14:09 sunny, not very windy, 240° at 14:11	Sunny windy	Windy and sunny	Almost clear cc 3/8		Sunny
14:12		230° SW wd	Not windy – sunny, not very windy. 240 at 14:11	Sunny windy	Windy and sunny	Cloudy cc 4/8		Sunny
14:18		Sunny, lots of blue sky, wind dropped, picked up again, small clouds, 230° SW wd	Varying wind direction. 210° at 14:20 sock not moving at 14:22 sunny	Sunny! Windy	Sunny and a tiny bit less windy, wind from same direction through- out	Cloudy cc 4/8	Very sunny warm 80% blue sky	Sunny
14:24		From 230° to- 265° wd intermittent breeze, blue sky E, cloudy from W	Wind picking up Sunny 120° at 14:24 130° at 14:26 – all directions since	Sunny Windy	As above	Cloudy cc 5/8		Sunny
14:30		230° SW wd intermittent sun, coming clouds, wind dropped towards the end	Sock not moving at 14:30, wind picking up 270° at 14:32 140° at 14:34	Sunny Windy	As above	Cloudy cc 5/8	Very sunny	Sunny
14:36		Wind dropped 230°, picked up 230°-265°	wind sock hardly moving at 14:37 –, 160° at 14:38, strong wind 120° at 14:39 strong wind	Sunny Windy	As above	Cloudy cc 4/8		Sunny
14:42		From 230° to 300° wd Strong wind arrived, blustery, blue sky, some cumulous clouds	14:42 wind dropped 14:47 wind dropped	Sunny windy	As above	Cloudy cc 4/8		Sunny

14:48		From 40° to 230° SW wd Blustery, blue sky,		Sunny windy	As above	Cloudy cc 4/8		Sunny
14:54		230° SW wd wind dropped, gusty, blustery, clouding over	Wind dropped, at 14:59, wind picked up 140° SE wd	Sunny windy	As above	Cloudy cc 4/8	Very warm	Sunny

APPENDIX C: Boundary Layer Ranging Instrument

This appendix describes the LIDAR system used for the estimation of the Atmospheric Boundary Layer Height. Measurements performed by the Centre for on the 1st February are reported in Chapter 6.0.

The following text has been kindly provided by E. G. Norton, I. M. Povey, C. Hill and R.L Jones from Atmospheric Science of the University of Cambridge.

C1 Measurements

Backscattered light from a laser is proportional to the aerosol content of the atmosphere and therefore can be used to probe the atmospheric boundary layer height. The ground based remote-sensing LIDAR at the University of Cambridge emits the second harmonic of a Q-switched Nd:YAG laser operating at 20 Hz vertically into the atmosphere. Backscattered light from the laser is collected using a 40 cm, f/4 Newtonian telescope which focuses the light through a 532 nm laser line filter and into a time gated photomultiplier tube. Averaged backscatter profiles are recorded with an altitude resolution of 1.5 m every minute on a computer controlled oscilloscope. Figure C1.1 shows a schematic diagram of the instrumental arrangement.

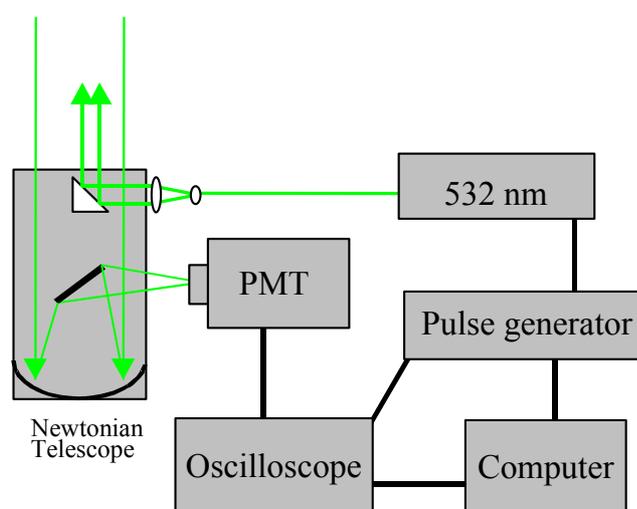


Figure C1.1 Arrangement of the LIDAR used for measuring the atmospheric boundary layer height.

C2 Analysis

The returned signal from the laser is proportional to the signal backscatter by particles and molecules in the atmosphere as shown in terms of the LIDAR equation C2.1

$$RS(\lambda, r) = \frac{C}{r^2} E_0 [\beta_m(\lambda, r) + \beta_p(\lambda, r)] T^2(\lambda, r) + RS_0 \quad \text{C2.1}$$

Where $\beta_p(\lambda, r)$ and $\beta_m(\lambda, r)$ are the particular and molecular backscattering coefficients respectively, C is a constant given for a particular LIDAR instrument, E_0 is the laser output energy, T^2 is the atmospheric transmission, r is the range between the laser source and scatter, λ is the wavelength and RS_0 is the background signal. Thus the range-squared-corrected signal (RSCS) is calculated for the averaged backscattered profiles from equation C2.2.

$$RSCS = (RS - RS_0)r^2 \quad \text{C2.2}$$

RSCS plotted as a time series for 01/02/00, is show in Figure 6.16. The lighter the colour the more intense the LIDAR backscatter signal. A cloud layer can be observed to appear over the site at Pritchats Road Birmingham after 11:00 am and to then persist throughout the rest of measurement period on 01/02/00. The RSCS was then analysed for boundary layer height using the inflection point method Menut *et al.* 1999. The inflection point method calculates either the first derivative or second derivative of averaged RSCS profiles with respect to the altitude. The minimum of the first derivative is taken to correspond to the altitude of the base of the transition zone (i.e. the top of the mixed layer) and the second derivative defines the middle of the transition zone (i.e. the interface between the mixed layer and the free troposphere).

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