Monitoring Methodologies and Results

3

3.1 MEASUREMENT OF NITROGEN DIOXIDE WITH PASSIVE DIFFUSION SAMPLERS

Passive diffusion tube samplers have been used to monitor atmospheric NO_2 concentrations at numerous sites throughout the UK and elsewhere for over a decade. The performance of the NO_2 diffusion tube was investigated by First Phase local authority groups in Ribble Valley, Aberdeen and London. In particular, the effect of the length of the exposure period (two or four weeks) was examined as was the comparison of diffusion tube and chemiluminescence analyser measurements. As diffusion tubes will be widely used for review and assessment of nitrogen dioxide for the purposes of the Environment Act (1995), these performance investigations are of particular interest.

3.1.1 Ribble Valley: measurements at a rural site influenced by industrial emissions

Diffusion tubes were exposed in triplicate in the village of Chatburn, Lancashire, alongside the inlet of a chemiluminescence analyser over the period May to October 1997. Individual exposure periods were one month long and analysis was carried out by Lancashire County Laboratory. While there was variability between the triplicate diffusion tubes, the means of the three triplicate values were similar to the monthly mean concentration determined by the automatic analyser. The mean concentrations over the six months measured by the two techniques were identical to the nearest ppb. Data are summarised in Table 3.1. The Chatburn results demonstrate the reliability of nitrogen dioxide diffusion tubes and the value of using triplicate tubes rather than a single tube.

3.1.2 Kerbside Sites: London Marylebone Road and Camden Kerbside

Diffusion tubes were exposed in triplicate at the automatic urban network (AUN) site on Marylebone road (February to May 1997) and also at the Camden Kerbside site (June to August 1997). Exposure periods at both locations were 2 weeks long. Again, variability in the triplicate diffusion tube concentration was evident by between –27% and +17% of the mean (Figure 3.1) but at these sites the concentrations determined by diffusion tubes were usually less than those determined by chemiluminescence. The variation ranged from +5% to –49% (Figure 3.2).

Diffusion tubes were also exposed for monthly periods at both of the London sites to enable comparisons with fortnightly exposures and the continuous analyser. In this case, concentrations of NO_2 measured by exposure of diffusion tubes over differing periods were different. Exposure of 2 weeks underestimated NO_2 on average by 25% relative to the automatic analyser, whereas exposure of 4

TABLE 3.1. MONTHLY MEAN CONCENTRATION OF NITROGEN DIOXIDE MEASURED BY 3 DIFFUSION TUBE SAMPLERS AND A CONTINUOUS ANALYSER (PPB).

Month	*hours of exposure*	*Tube 1*	*Tube 2*	*Tube 3*	*Mean of Tubes*	*continuous analyser*
May	740	7	4	10	7	7
June	699	8	<4	<4	5	7
July	741	7	10	9	9	8
August	744	8	6	7	7	9
September	720	11	8	5	8	9
October	720	10	12	7	10	7
Average		8	7	7	8	8

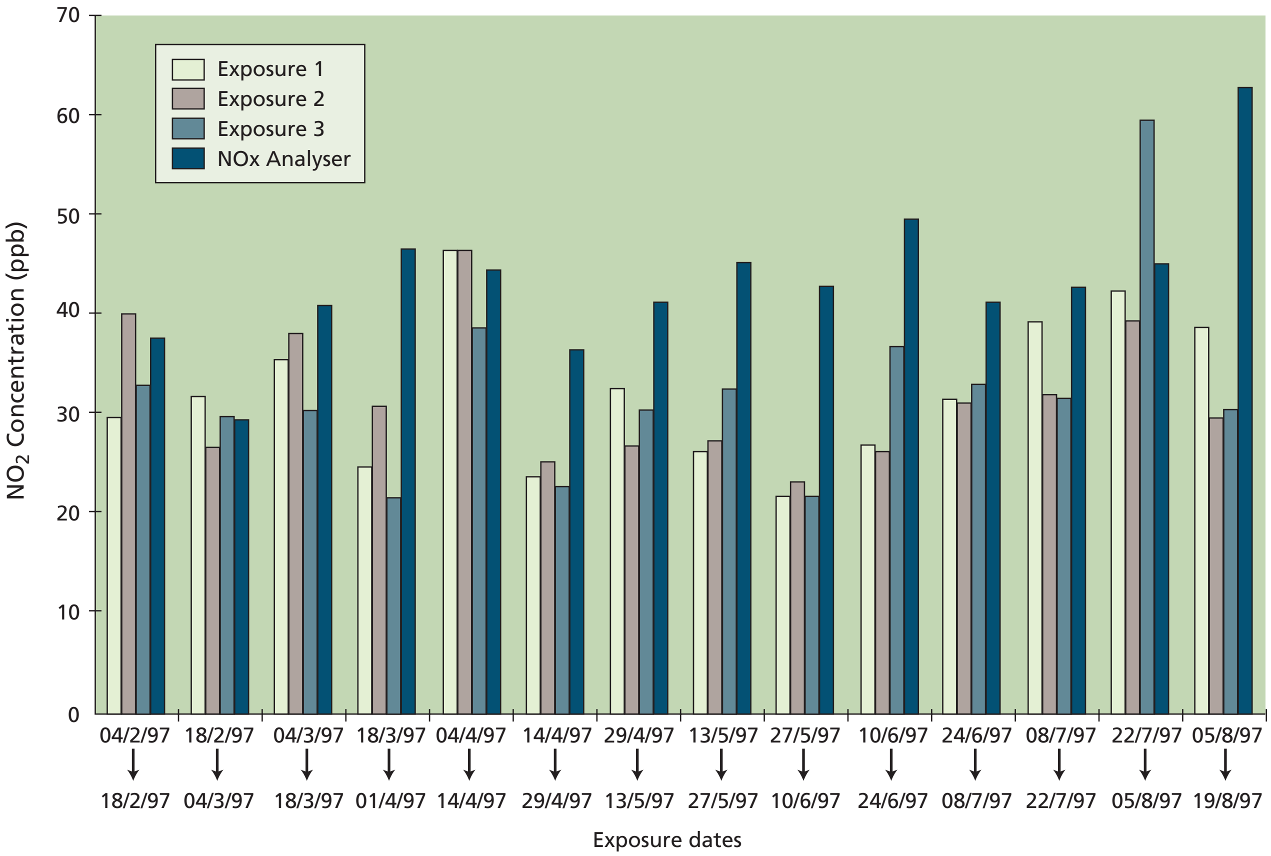

Figure 3.1 Nitrogen dioxide diffusion tube data compared to those from an automatic analyser at Camden Kerbside (4/2/97–27/5/97) and Marylebone Road (27/5/97–19/8/97) (ppb).

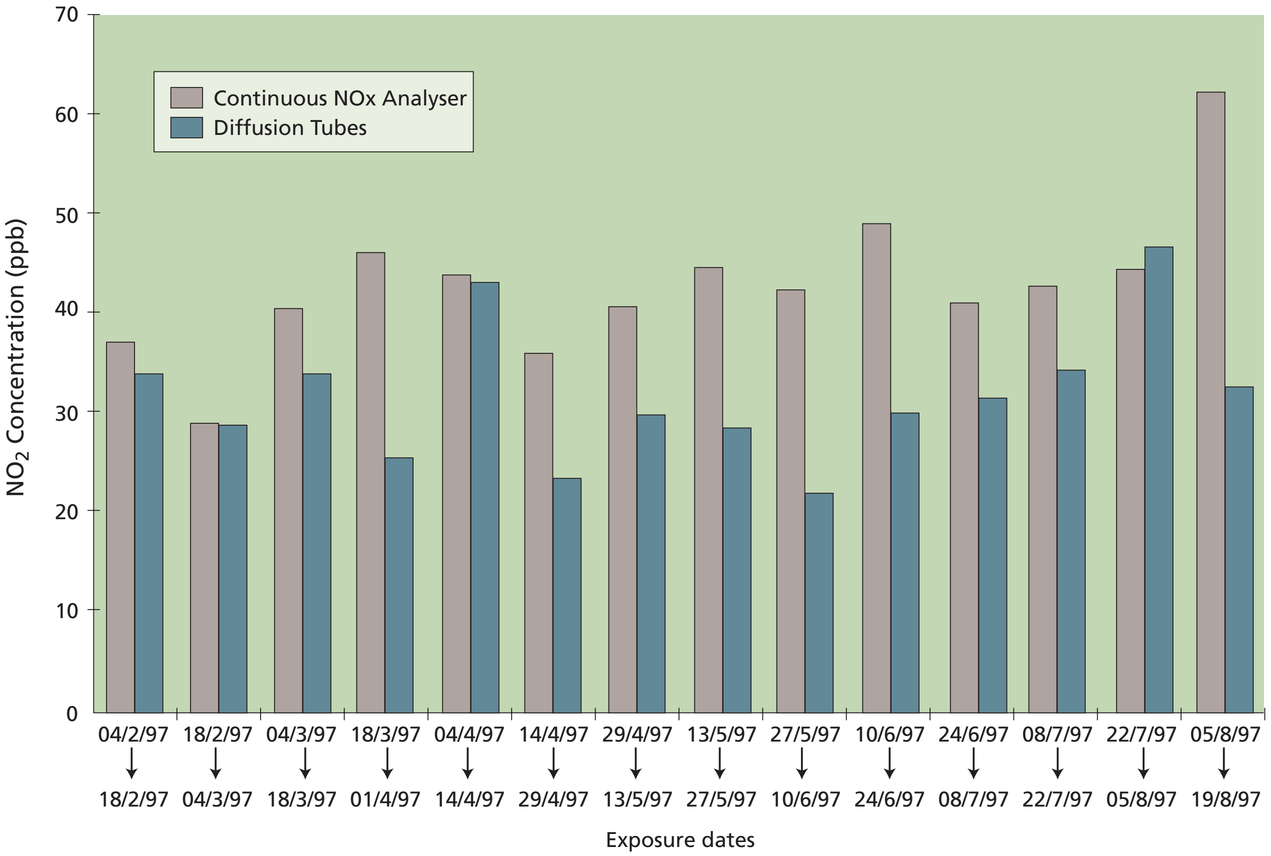

Figure 3.2 Nitrogen dioxide diffusion tube data compared to those from an automatic analyser at Camden Kerbside (4/2/97–27/5/97) and Marylebone Road (27/5/97–19/8/97) (ppb).

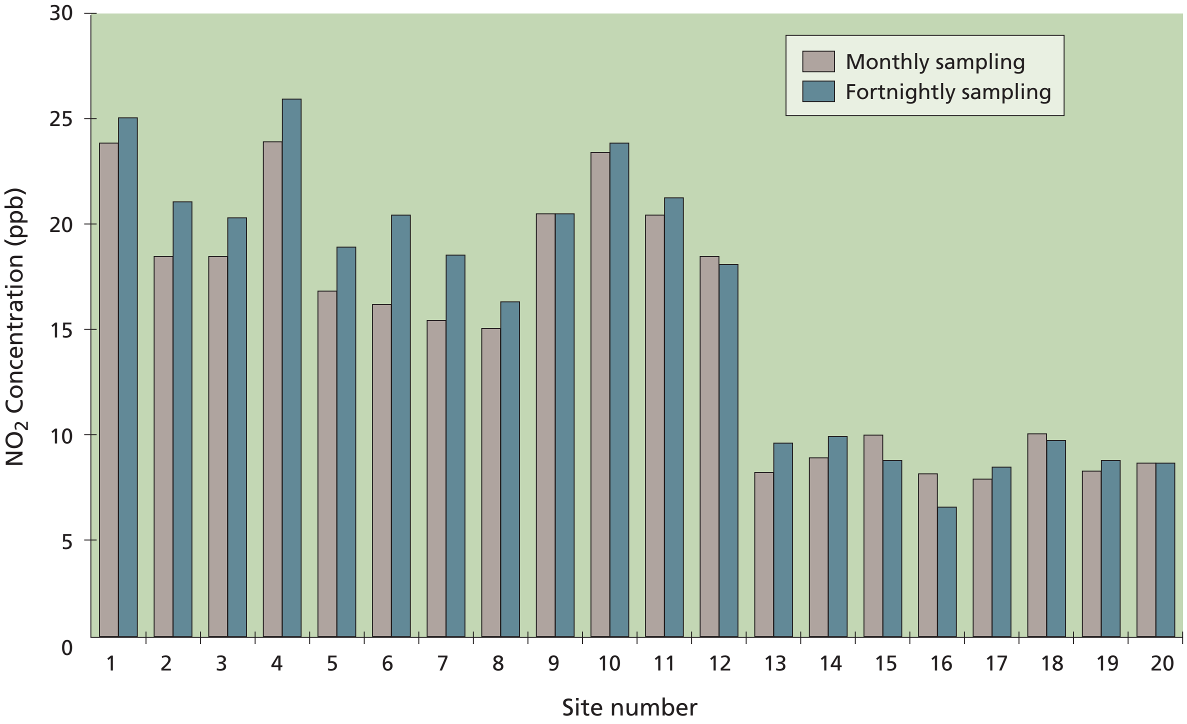

Figure 3.3 Nitrogen Dioxide Diffusion Tube Data (Six Monthly Averages) Measured at 20 Sites in Aberdeen (ppb).

weeks on average underestimated NO_2 relative to the automatic analyser by 40%. The difference between the exposure periods suggests that some loss of the NO_2 absorbed by the sampler was occurring at these sites, perhaps through photolysis.

Differences between the apparent performance of diffusion tubes between sites and laboratories, even those with many years' experience in this sort of work, are common. It is important that users demand appropriate validation of the measurement from the supplier laboratory. The Monitoring Guidance recommends that second stage review and assessment screening measurements using passive samplers should be considered as having an overall uncertainty of +/– 30%.

3.1.3 Aberdeen

Aberdeen City Council established a nitrogen dioxide diffusion tube survey within the city centre area. A total of twenty sites were selected for exposure of tubes, 12 of which were near-road and 8 at urban background locations. The near-road sites were approximately 3 m high on building frontages facing Union Street, the main street in the city where an automatic monitoring station is located, and also along the roads adjoining Union Street. The urban background sites were approximately 1 km from Union Street. Tubes were exposed in triplicate for 2 week and 4 week periods over the 6 month monitoring period, December 1996 to May 1997.

The aims of this study were:

- *assess the variability in concentrations of the triplicate measurements,*
- *assess the variability between 2 week and 4 week monitoring periods,*
- *compare the concentrations at the different locations on Union Street and the urban background sites,*
- *assess the variability in concentrations over the 6 month period, and*
- *compare the diffusion tube measurements with those from the continuous monitoring station. This could not be done, however, as tubes mounted alongside the monitoring station at the kerbside were lost to vandalism.*

The average percentage variation in the triplicate tubes over all sites for a 2 week exposure period was 20% and for a 4 week exposure period 16%. The measured average concentrations of NO_2 were very similar for two-weekly and four-weekly sampling intervals (Figure 3.3).

The mean concentrations at the various sites along Union Street were found to vary from 15 to 25 ppb (sites 1-12 on Figure 3.3). It may be surprising that concentrations should vary so much along a single road but differences were thought to be related to varying traffic flows and speeds. Highest concentrations occurred at sites where significantly more heavy goods vehicles were permitted. Also, at sites in street canyons concentrations tended to be higher, presumably as a result of poorer dispersion.

Unsurprisingly, concentrations were found to be lower at the urban background sites (sites 13 to 20 on Figure 3.3), although period to period fluctuation patterns were very similar for both site types. The six-monthly average concentrations at all urban background sites were below the air quality objective for the annual mean concentration of 21 ppb while the average concentrations at a number of the roadside sites were above this level.

3.1.4 Conclusions

Passive samplers for NO_2 provide a useful screening tool. This was clearly demonstrated in Aberdeen where diffusion tube measurements indicated that an annual mean concentration of 21 ppb was widely exceeded along Union Street but not at background locations. Use of these data to forecast likely concentrations in 2005 is difficult since nitrogen dioxide concentrations will not decline linearly with nitrogen oxide emissions, but it is unlikely that the 21 ppb annual mean objective for 2005 will continue to be exceeded in this city if urban nitrogen oxide emissions halve as expected.

Co-located passive and automatic samplers at Ribble Valley and in London highlighted the possible inaccuracies of diffusion tubes and the difficulty of using a measurement method that cannot be calibrated against accredited standard gas mixtures. The diffusion tube method alone is not suitable where there is a need for a measurement accuracy better than 30%, as required for detailed third stage reviews. If a network of diffusion tubes were used along with an automatic monitor, the diffusion tubes could be calibrated by reference to the monitor and the data would provide more detailed information of the spatial variation of NO_2 concentrations than a single monitor measurement. There was evidence of a small difference between two and four week tube exposure which was similarly found in a validation study undertaken by Stanger and NETCEN (1997).

3.2 MEASUREMENT OF PM_{10}

PM_{10} is not a distinct chemical species, but is a fraction of airborne particles, the nature of which is defined by the method of measurement. Within Europe, non-gravimetric real-time measurements are the most widely used system and the use of gravimetric samplers is less widespread. However, the WRAC (a gravimetric sampler) has been adopted as the reference standard for PM_{10} measurement. The size of the WRAC instruments make it unsuitable for use in the field. Two gravimetric transfer standards have been proposed, the US Hi-Vol sampler and the Kleinfiltergerat - neither of which are commonly used for routine urban PM_{10} measurement in Europe.

In the UK, the majority of the PM_{10} monitors in the national networks are real-time TEOM instruments, though one Beta gauge instrument is also now included in the UK Automatic Urban Network. The use of real-time instruments allows the dissemination of hourly information to the public on PM_{10} and assists in source apportionment studies. There is also a large body of data on “black smoke”. As part of the First Phase studies, several groups investigated the relationship between measurements of particles carried out by the instruments most commonly used in the UK and gravimetric samplers. The specific measurement methods used were:

- ***Tapered element oscillating microbalance (TEOM).*** *This instrument continuously records the resonant vibration frequency of a tapered cylindrical element to measure the mass of the sampling filter. Instruments are calibrated using pre-weighed filters and pre-calibrated flow meters.*
- ***Partisol,*** *model 2000. This is a low volume sampler for the collection of filter samples. These must then be weighed to measure the particulate loading. Very accurate weighing and consistent conditioning (temperature and humidity) of the filters are required.*
- ***Cassella,*** *APM 950, this instrument combines ‘real-time’ optical measurements of particle concentration by light scattering with the collection of particles on a filter for subsequent gravimetric analysis. Hourly light scattering data and weekly gravimetric data can be derived.*
- ***Black Smoke.*** *Daily filter samples are collected using an 8-port bubbler for subsequent estimation of black smoke concentration by reflectance measurement. This is the method used within the national Smoke and Sulphur Dioxide monitoring networks.*

The black smoke instrument is not fitted with a PM_{10} head but probably collects particles up to about 4 µm in diameter.

3.2.1 Comparison of Partisol and TEOM methods

Scatter plots of daily average concentrations of PM_{10} measured by these two methods are shown in Figures 3.4 to 3.7 and the linear regression statistics are summarised in Table 3.2. While measurements were found to be well correlated at all sites, the Partisol instruments were found to give higher values, particularly on the days with the highest concentrations. There are also indications at some sites that the Partisol measurements are lower on days with particularly low concentrations. The higher values recorded by the gravimetric method can be, at least partly, explained by the heating of the TEOM samples to 50°C, causing some loss of volatile components of the airborne particles.

TABLE 3.2. REGRESSION EQUATIONS FOR PARTISOL AND TEOM.

Authority	Linear Regression Equation	Correlation coefficient r^2
Ribble Valley	Partisol = 1.15 x TEOM – 0.05	0.85
South Yorkshire	Partisol = 1.3 x TEOM	0.8
Cornwall	Partisol = 1.55 x TEOM – 6.1	0.89
London Kerbside	Partisol = 1.2 x TEOM – 3.1	0.85
Belfast	Partisol = 1.3 x TEOM + 4.9	0.47

Those Authorities carrying out particle sampling method studies included Ribble Valley, the South Yorkshire Authorities, Cornwall, the London Authorities and Belfast. Ribble Valley carried out its comparison at Chatburn near Clitheroe, a rural community site for which air quality is influenced by major industrial installations in Clitheroe. Partisol data were collected on alternate days for the period from April to September 1997 and the TEOM instrument operated continuously. Figure 3.4 compares the coincident daily average data points. The daily average PM_{10} concentration measured by the TEOM for these days varied from around 5 $\mu g\ m^{-3}$ to 45 $\mu g\ m^{-3}$. The daily average concentrations measured by the Partisol were between 0% and 30% larger than those measured by the TEOM for daily average concentrations above 30 $\mu g\ m^{-3}$.

The Authorities in South Yorkshire compared daily measurements at Brampton near Rotherham for the three month period from March to May 1997.

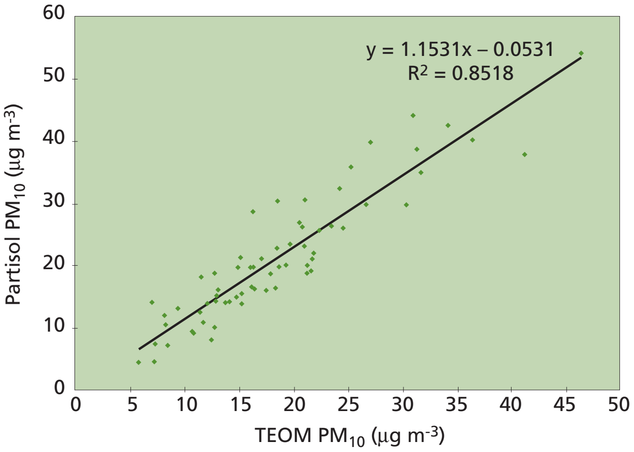

Figure 3.4 Comparison of daily PM_{10} concentrations ($\mu g\ m^{-3}$) measured by TEOM and Partisol instruments at Ribble Valley, April to September, 1997.

Data are shown in Figure 3.5. These data include five days with daily average concentrations above 50 $\mu g\ m^{-3}$ but the Partisol data are again mostly within 30% of the TEOM data.

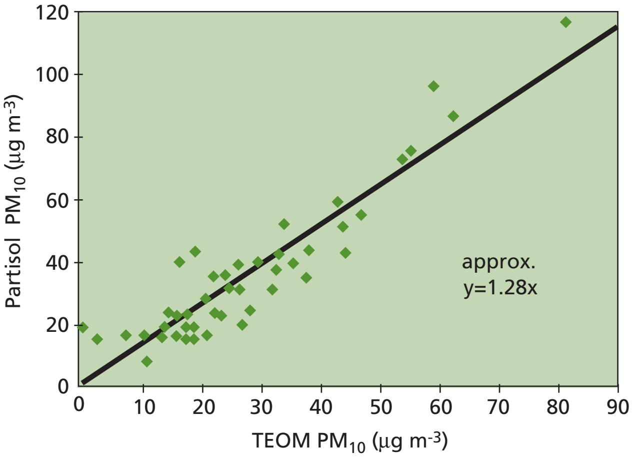

Figure 3.5 Comparison of daily PM_{10} concentrations ($\mu g\ m^{-3}$) measured by TEOM and Partisol instruments at Rotherham, March to May, 1997.

The authorities in Cornwall compared alternate day daily measurements at St Dennis near to China Clay workings at St Austell. Data are shown in Figure 3.6. The daily averages measured by the TEOM were generally smaller than at the other Authorities' sites. The TEOM:Partisol ratio was smaller at St. Dennis than at the other three sites. For those days on which daily average concentrations were in the range 25 $\mu g\ m^{-3}$ to 40 $\mu g\ m^{-3}$, the Partisol:TEOM ratio varied from 1.2 to 1.5.

These data did not best fit a linear regression but rather a curvilinear relationship was preferable. Attempts to fit a linear regression suggest a

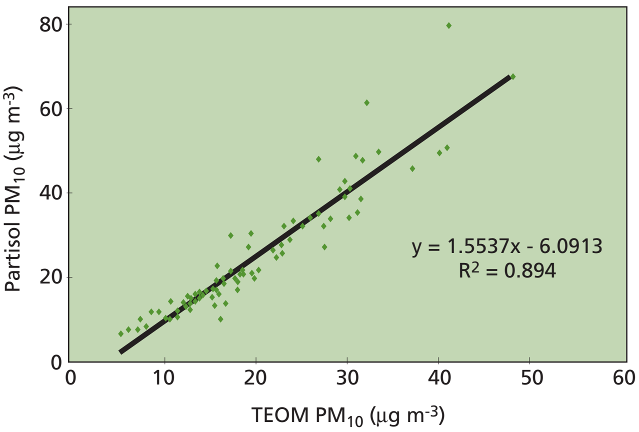

Figure 3.6 Comparison of daily PM_{10} concentrations (µg m^{-3}) measured by TEOM and Partisol instruments at Cornwall, April to October, 1997.

substantial intercept which is not borne out be examination of the data. Thus, both the slope and the intercepts suggested by linear regression of these data are very misleading. At a Partisol measured concentration of 50 µg m^{-3} the TEOM is reading about 38 µg m^{-3}, indicating Partisol results about 32% higher than the TEOM which is broadly consistent with the relationship found in South Yorkshire. Thus, at concentrations around the air quality standard, the extent of under-reading by the TEOM relative to the Partisol indicated by the data in Table 3.2 is around 15 - 30%. Further long term studies have been established by the Governments to provide a rigorous analysis of the relationship between concentrations of these two sampler types. It is useful to bear in mind that the UK air quality standard for PM_{10} of 50 µg m^{-3} as maximum 24 hour running average was recommended by the Expert Group on Air Quality Standards using, amongst other information, the results of an epidemiological study which used data from a TEOM instrument (EPAQS, 1995). There is therefore consistency between the monitoring method and the current standard, and hence any underestimation of PM_{10} by the TEOM relative to other sampling methods does not imply a relaxation in the protection of public health.

A comparison at the kerbside London Marylebone Road site was carried out by the London authorities. Data are shown in Figure 3.7. At this kerbside site, there were no days for which the daily mean concentration was smaller than 20 µg m^{-3} and many daily averages were above 50 µg m^{-3}. The results of the two methods were well correlated. The Partisol values were again generally higher than those from the TEOM, by between 0% and 30%.

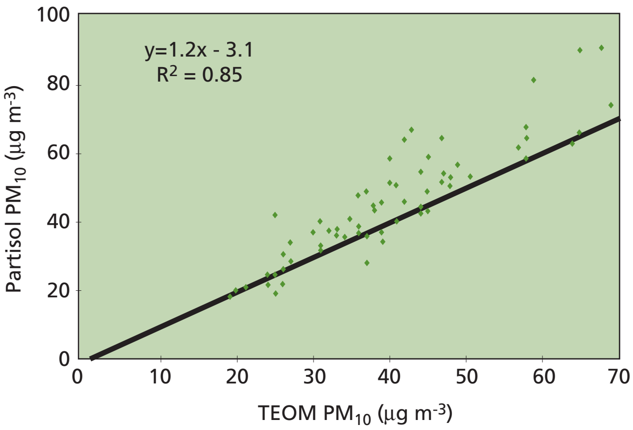

Figure 3.7 Comparison of daily PM_{10} concentrations (µg m^{-3}) measured by TEOM and Partisol instruments at London Marylebone Road, June to August, 1997.

Belfast City Council undertook monitoring from January to mid-April 1997. Over this period the mean concentrations were 34.2 µg m^{-3} for the Partisol and 22.8 µg m^{-3} for the TEOM. The relationship between the daily mean concentrations measured by the two methods are shown in Figure 3.8. However, the correlation was not as robust (r^2 = 0.47) and there were a number of days when Partisol measurements were around three times that from the TEOM.

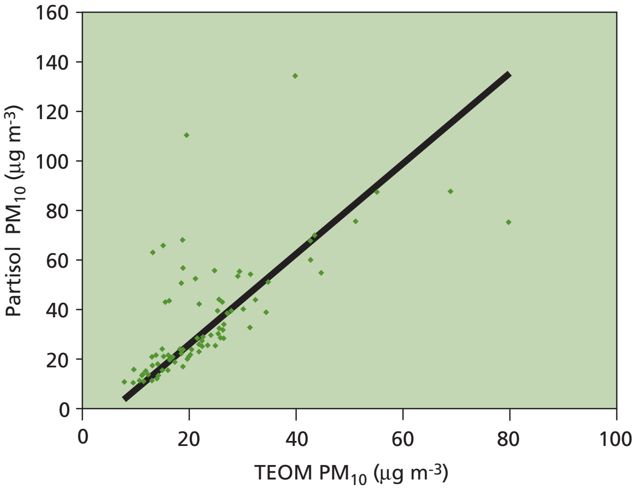

Figure 3.8 Comparison of daily PM_{10} concentrations (µg m^{-3}) measured by TEOM and Partisol instruments in Belfast, January to April, 1997.

3.2.2 Comparison of Black Smoke and TEOM methods

Table 3.3 summarises the comparisons between black smoke and TEOM measurements. These sites: Edlington near Doncaster, Brampton, near Rotherham and Belfast are in areas likely to be

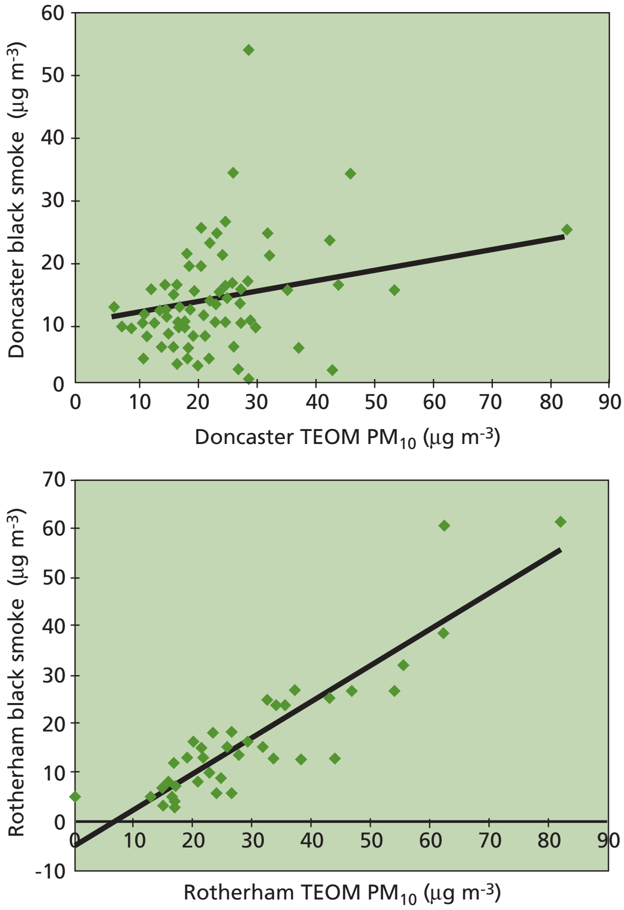

Figure 3.9 Comparison of daily PM_{10} concentrations measured by TEOM and black smoke concentrations at Doncaster and Rotherham, March to May, 1997 (µg m^{-3}).

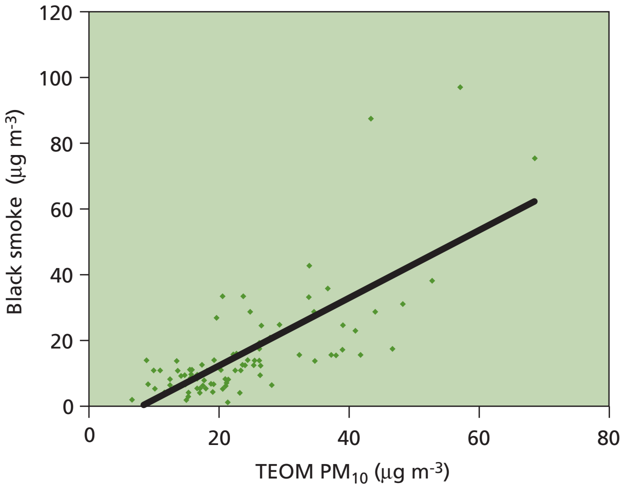

Figure 3.10 Comparison of daily PM_{10} concentrations (µg m^{-3}) measured by TEOM and black smoke concentrations at Belfast, January to April, 1997.

influenced by domestic solid fuel use. The black smoke values are lower than those recorded by the TEOM and are not well correlated. PM_{10} comprises a range of particulate material. Carbon-containing soot and smoke will stain filter paper black. Sulphate-containing “secondary” particles are colourless and will not contribute to the opacity of the smoke stain. Smoke measured as the stain on a filter paper is not, therefore, the same measurement as a particle mass measurement but is likely to be a good measure of carbon-based particles. Black smoke concentrations are therefore expected to be smaller than PM_{10}.

Measurements for the period March to May 1997 in South Yorkshire are shown in Figure 3.9 and measurements for January to mid-April 1997 in Belfast are shown in Figure 3.10.

TABLE 3.3 SUMMARY OF OBSERVED RELATIONSHIPS BETWEEN TEOM MEASUREMENTS OF PM_{10} AND BLACK SMOKE IN SOUTH YORKSHIRE

Authority	Linear Regression Equation	Correlation coefficient r^2
S. Yorkshire, Doncaster	Poor correlation	
S. Yorkshire, Rotherham	Black smoke = 0.75 x TEOM – 8	0.8
Belfast	Black smoke = 1.03 x TEOM – 8	0.5

3.2.3 Comparison of Black Smoke and Partisol methods

The authorities in South Yorkshire and Belfast also compared Partisol and black smoke measurements at Goldthorpe, Barnsley; Brampton, Rotherham and Belfast. The results of these comparisons are shown in Figure 3.11 and Figure 3.12 and are consistent with the results of the other intercomparisons presented here. The regression analyses (Table 3.4) show that while the correlation between these daily measurements was good, the black smoke measurements provide much lower absolute concentration values.

TABLE 3.4. SUMMARY OF OBSERVED RELATIONSHIPS BETWEEN PARTISOL (298K) MEASUREMENTS OF PM_{10} AND BLACK SMOKE IN SOUTH YORKSHIRE

Authority	Linear Regression Equation	Correlation coefficient r^2
S. Yorkshire, Rotherham	Black smoke = 0.57 x Partisol – 4	0.8
S. Yorkshire, Barnsley	Black smoke = 0.38 x Partisol – 1	0.8
Belfast	Black smoke = 0.4 x Partisol + 0.4	0.5

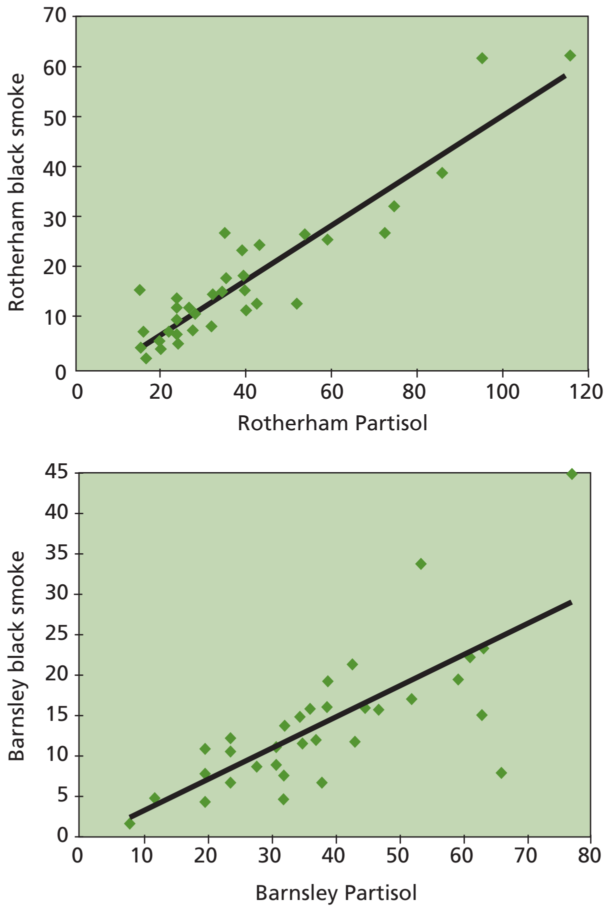

Figure 3.11 Comparison of daily PM_{10} measured by a Partisol and black smoke concentrations at Rotherham and Barnsley (μg m^{-3}).

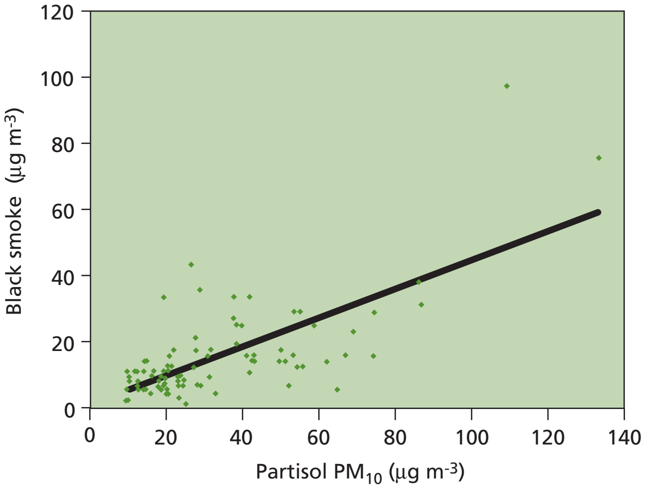

Figure 3.12 Comparison of daily PM_{10} measured by a Partisol and black smoke concentrations at Belfast (μg m^{-3}).

3.3 MEASUREMENT OF SULPHUR DIOXIDE

Some of the First Phase local authority groups, for example South Yorkshire, were asked to examine monitoring methods for sulphur dioxide by using a continuous UVF analyser and a bubbler. Sulphur dioxide is measured in the Automatic Urban Network with analysers using an ultra-violet fluorescence method. In these instruments, ultraviolet radiation excites SO_2 molecules causing them to fluoresce. The fluorescence is measured using a photo multiplier tube placed at right angles to the direction of the UV lamp. This light level is proportional to the concentration of the SO_2 present.

SO_2 and black smoke concentrations have been measured using 8-port bubblers by many local authorities over the last several decades. In these instruments air is pumped through a filter paper which collects the particles and then is passed through a dilute solution of hydrogen peroxide. SO_2 is converted to sulphuric acid which is determined by titration with a dilute alkali. The concentration of SO_2 in the atmosphere is then calculated from the titration result and the air flow volume.

3.3.1 South Yorkshire

Sulphur dioxide was measured using both techniques for four months between February and May 1997 at three sites, one in each of the Barnsley, Doncaster and Rotherham areas. Automatic measurements were logged as 15 minute averages, while the 8-port system yielded data as daily averages. To enable comparison of monitoring techniques, the 15 minute data were combined to provide daily averages.

The data from the three sites were inconsistent. At the Barnsley site there was a moderate correlation between the UVF instrument and the 8-port bubbler (correlation coefficient, $r^2=0.7$) but the 8-port bubbler measurements were on average twice as high as those from the UVF analyser (Figure 3.13). At the Doncaster site there was no significant correlation between the 8-port and the UVF instrument (Figure 3.14). At the Rotherham site there was a weak to moderate correlation ($r^2=0.5$). The average concentrations recorded by the two instruments were similar, although the measurements from the 8-port bubbler were generally higher than those recorded from the UVF instrument when low concentrations were recorded by both instruments (Figure 3.15).

This relatively poor agreement is not unusual when UVF analysers and bubblers are compared. In work at NETCEN (Downing and Campbell, 1992), bubbler instruments were found to underestimate

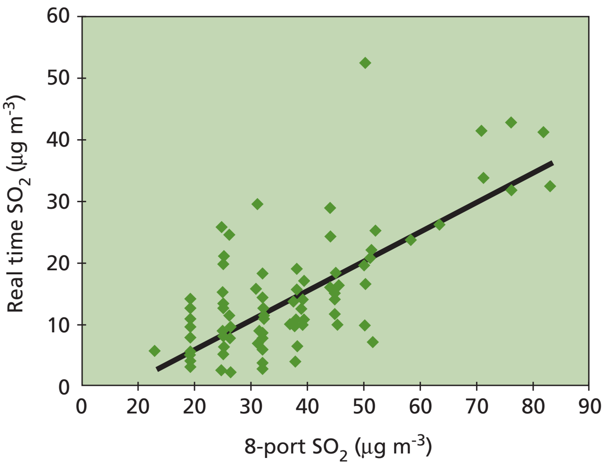

Figure 3.13 Comparison between daily average SO_2 concentrations measured by an 8-port bubbler and UVF instruments at Barnsley (µg m^{-3}).

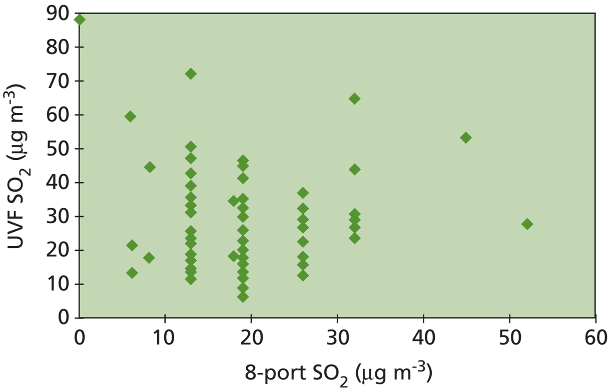

Figure 3.14 Comparison between SO_2 concentrations measured by an 8-port bubbler and UVF instruments at Doncaster (µg m^{-3}).

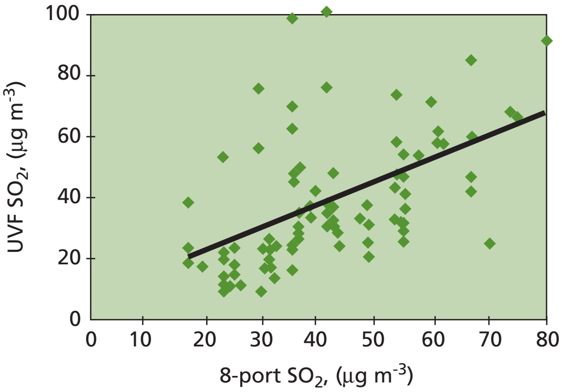

Figure 3.15 Comparison between SO_2 concentrations measured by an 8-port bubbler and UVF instruments at Rotherham (µg m^{-3}).

by around 10% to 20% relative to UVF, using calibration standard gas. In that study, bubbler solutions were analysed by a sulphate-specific method that is more sensitive and less subject to interference than the acid-base titration. In the South Yorkshire study, the Rotherham observations accord more with previous experience than do the observations at Barnsley and Doncaster.

3.4 IDENTIFICATION OF LOCAL SOURCES OF PM_{10}

Atmospheric particulates at a particular location will comprise of particles from a range of sources. Secondary particles, such as sulphates and nitrates are formed by relatively slow oxidation processes in the atmosphere and concentrations likely to be fairly uniform across a local authority area (QUARG, 1996). Particles are emitted by road vehicles, particularly heavy duty diesel vehicles and the area impacting from such particles can be expected to vary with distance from roads and local traffic movements. The ambient concentrations of particles due to emissions from local industrial and/or other sources have not, however, been examined in detail in the past. Several authorities undertook measurements of PM_{10} concentrations in areas where it was thought likely that local particle sources, other than road transport, would be significant. The influence of industrial emissions on a range of pollutant measurements is discussed in section 3.6. Some key results from the monitoring of PM_{10} concentrations near sources of concern because of their potential impact on ambient concentrations of particles are discussed here.

3.4.1 High Peak: PM_{10} in the vicinity of quarry activities

The High Peak authorities investigated the influence of mineral processing activities on local PM_{10} concentrations. Four monitoring sites were established, three within 400 m of the boundaries of large limestone quarries in the Buxton area, and a background site which was more than 5 km from the nearest mineral process. The locations of the monitoring sites and mineral processing activities are shown in Figure 3.16. The instruments used were Casella APM950 which combines real time optical measurements with gravimetric collection of dust on a filter. A TEOM was also located at the Tunstead site. Measurements were carried out between December 1996 and September 1997 and hourly and running 24-hour average PM_{10} concentrations were calculated and compared with city centre PM_{10} monitoring results from the AUN sites in Sheffield and Manchester. Weekly concentrations of a variety of elements from the particles collected were also measured by scanning electron microscopy.

Exceedances of the national air quality standard

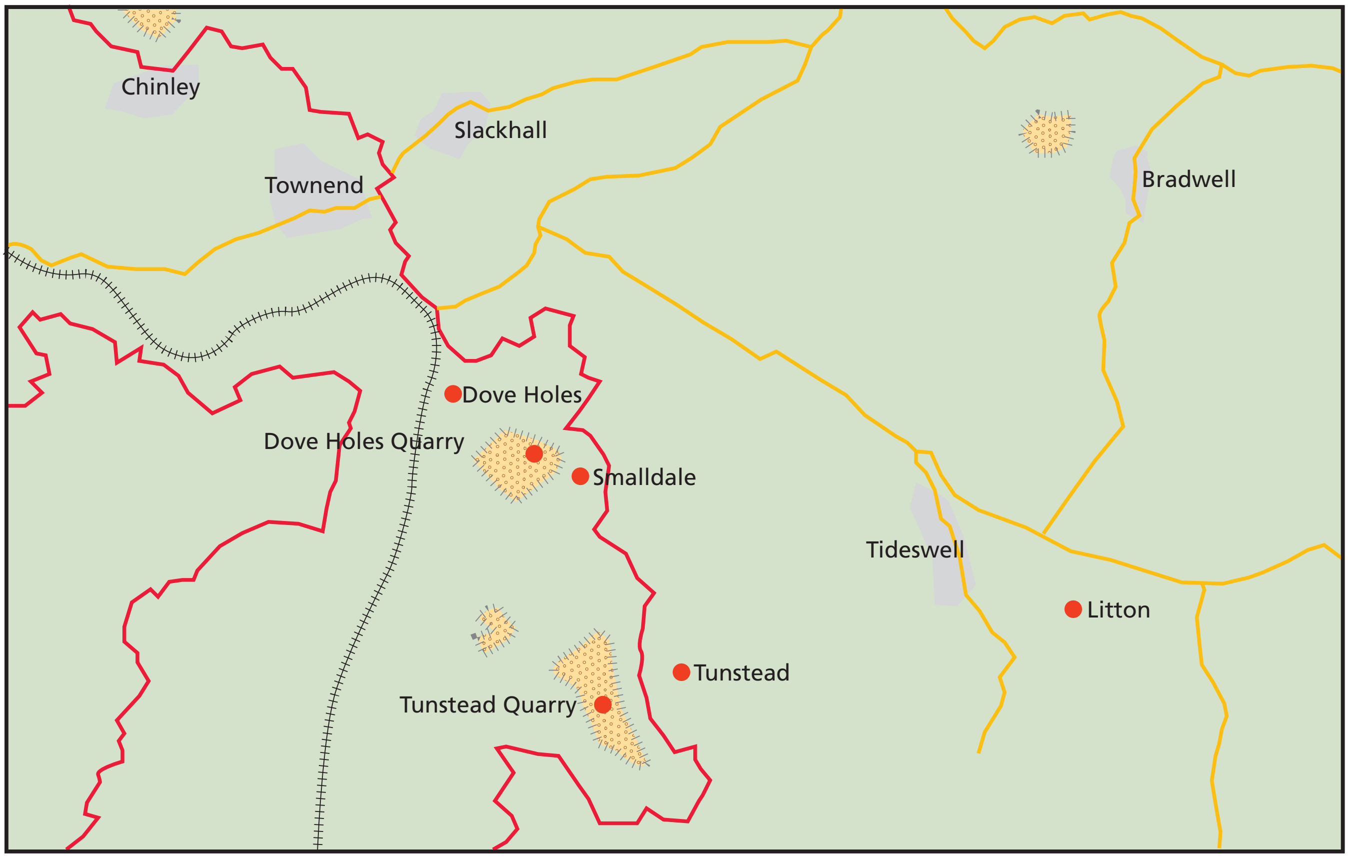

Figure 3.16 Sketch map showing monitoring sites in the High Peak study.

24 hour running mean threshold of 50 µg m^{-3} were recorded at all of the monitoring sites in this study, with the background site at Litton showing the smallest number of exceedance days. Exceedances of the air quality standard threshold during the winter at these sites generally occurred at more than one site and coincided with high concentrations at the Sheffield and/or Manchester AUN sites. These exceedances were associated with cold, still conditions, with the likelihood of temperature inversions. The sulphur concentrations in the particles associated with this type of episode were generally more significant than calcium, indicating that sources other than quarries made a significant contribution.

Summer-time exceedances were different, with calcium more dominant, indicating the importance of local quarry sources and/or lime or cement processes. Exceedances were almost always due to calm overnight conditions. Quarry crushing and screening processes do not operate at night but lime and cement processes continue. When wind speeds increased in the morning, PM_{10} concentrations decreased. These exceedances also often coincided with increased concentration at the Sheffield and Manchester AUN sites. Two episode periods at the Tunstead site that were clearly strongly influenced by the local mineral process emissions are illustrated in Figure 3.17. Concentrations at this site were significantly elevated above those measured at the AUN sites on the 11th and 12th of August and again on the 10th and 11th of September. The scanning electron microscopy analysis results for the weekly filter samples collected over these periods clearly indicate the importance of calcium (Figure 3.18).

3.4.2 Cornwall: PM_{10} in the vicinity of china clay workings

The authorities participating in the Cornwall Air Quality Forum made measurements of PM_{10} concentrations at sites within the St Austell china clay area in order to provide new information on the likely impact of mineral extraction activities on local air quality. Partisol instruments were used at three sites but in addition a TEOM was placed alongside the Partisol at the St Dennis site. Monitoring continued at the sites shown in Figure 3.19 from April to October 1997. Figure 3.20 shows a comparison of the daily PM_{10} concentrations at these sites. The large mineral extraction related particles causing visible nuisances in the area will

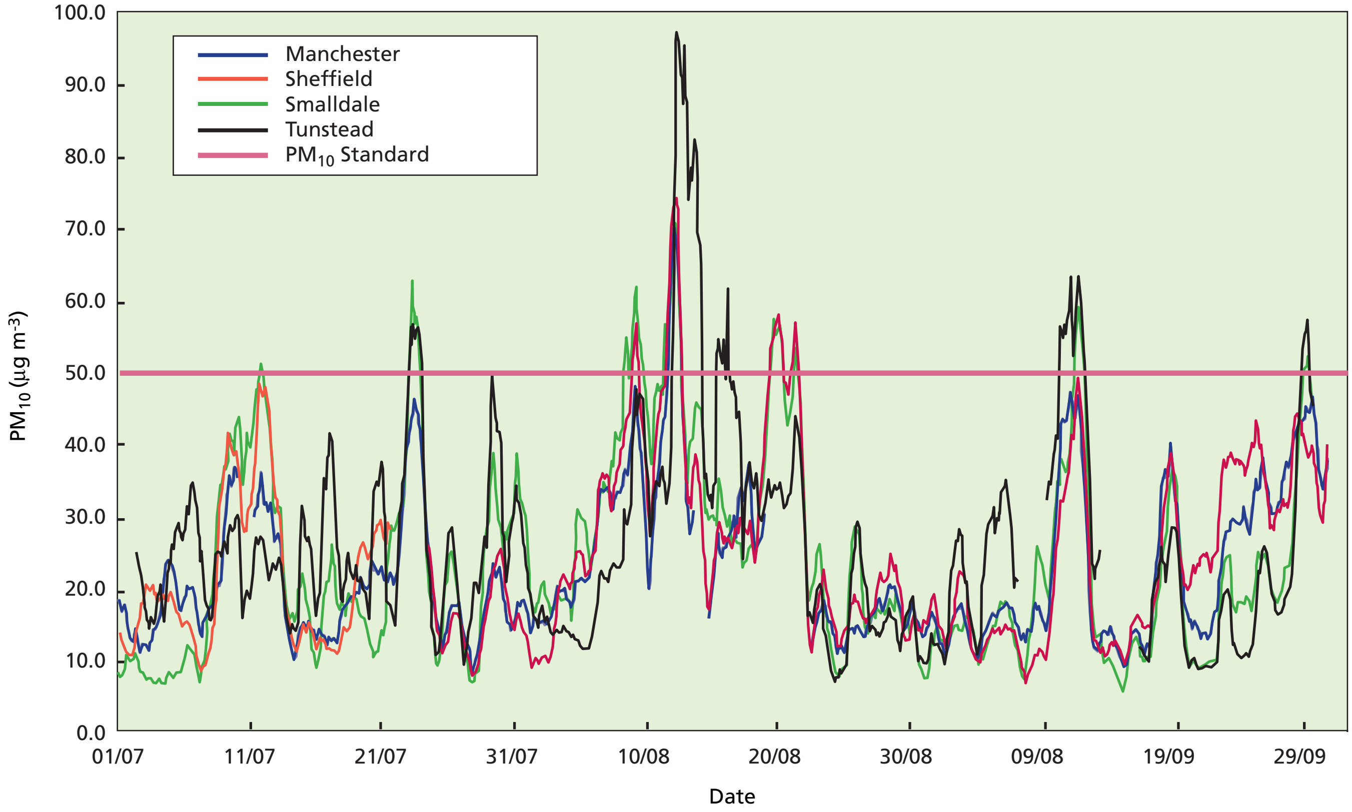

Figure 3.17 Running 24 hour average PM_{10} concentrations at Smalldale and Tunstead (gravimetric measurements) and at the Manchester and Sheffield AUN sites (TEOM measurements), July to September, 1997, (µg m^{-3}).

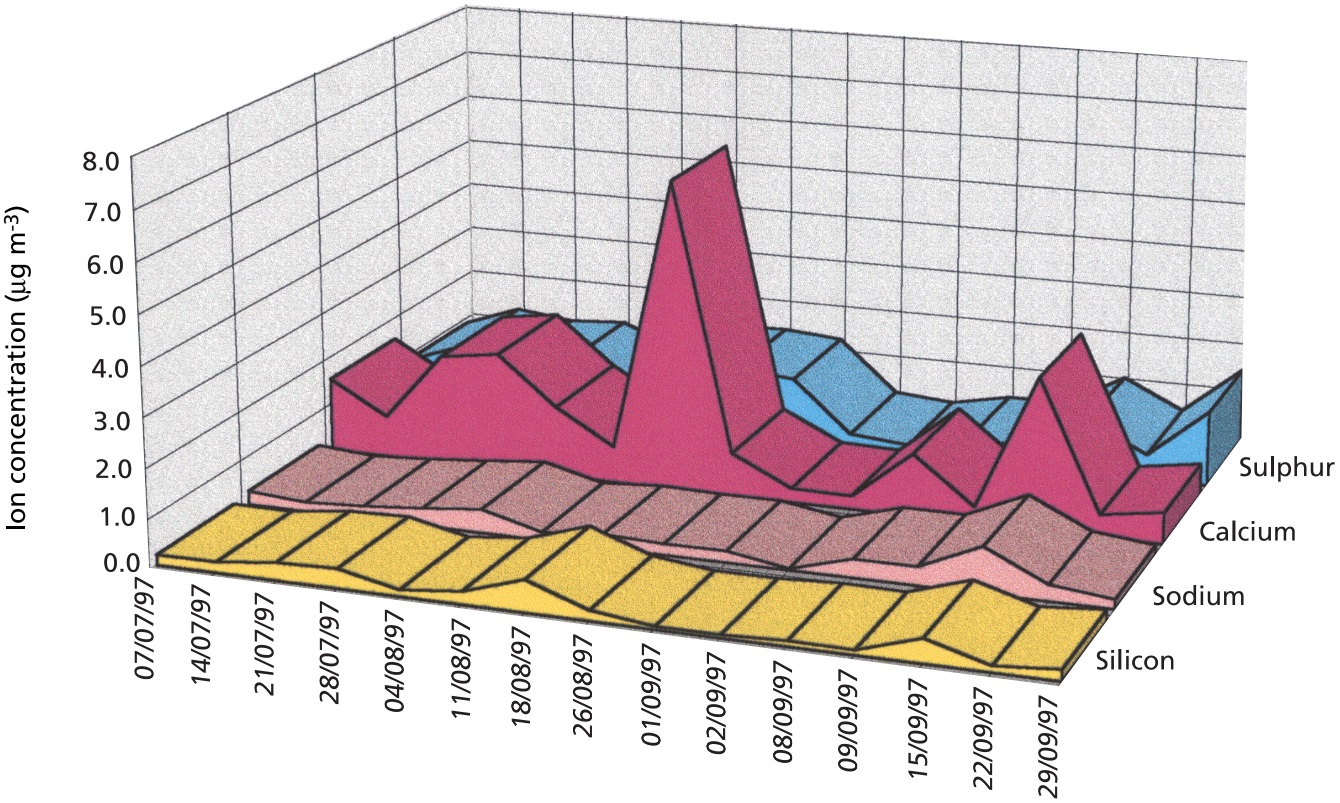

Figure 3.18 Chemical composition of PM_{10} measured at Tunstead, High Peak, July to September, 1997, (µg m^{-3}).

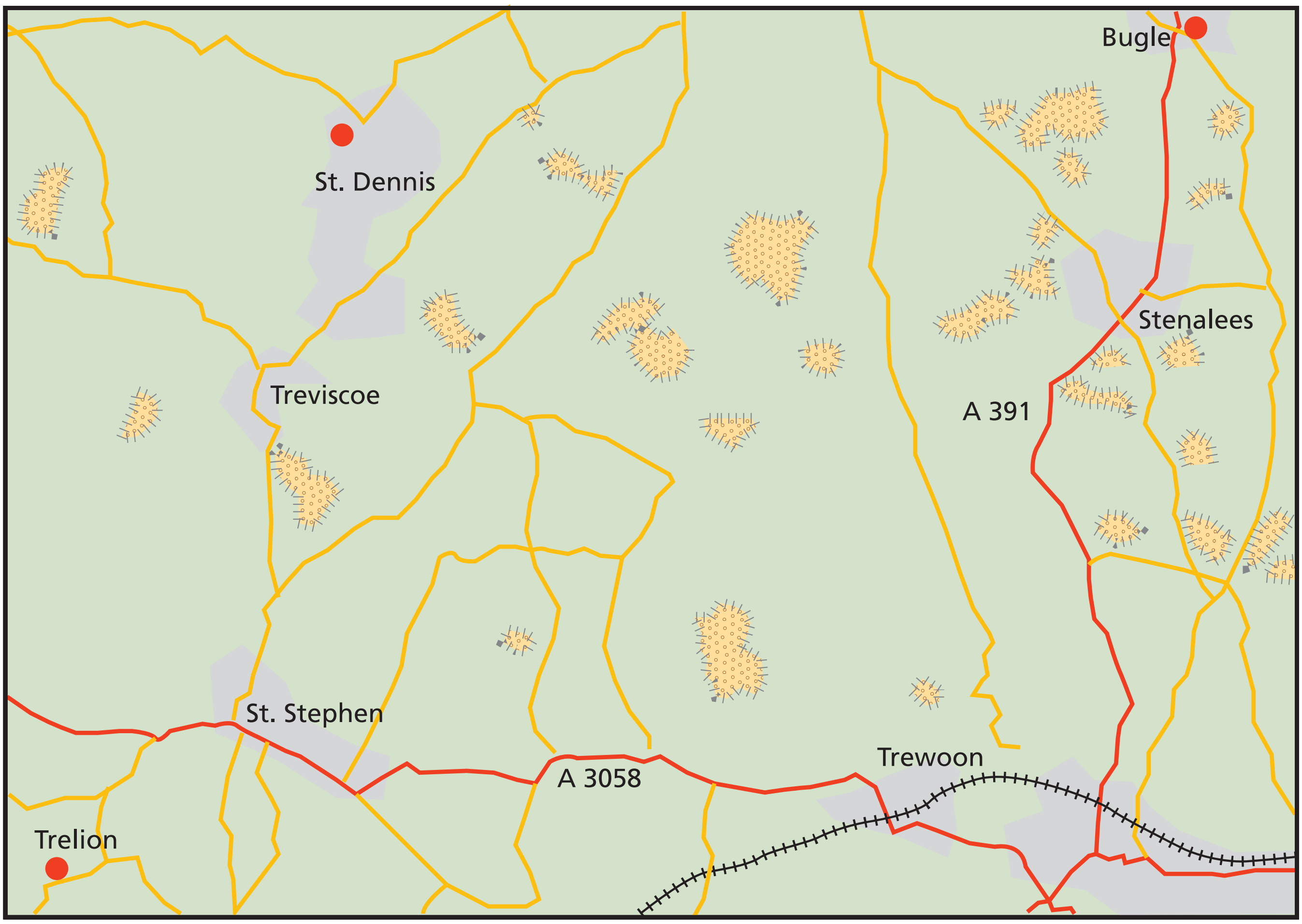

Figure 3.19 Sketch map showing monitoring sites in the Cornwall study.

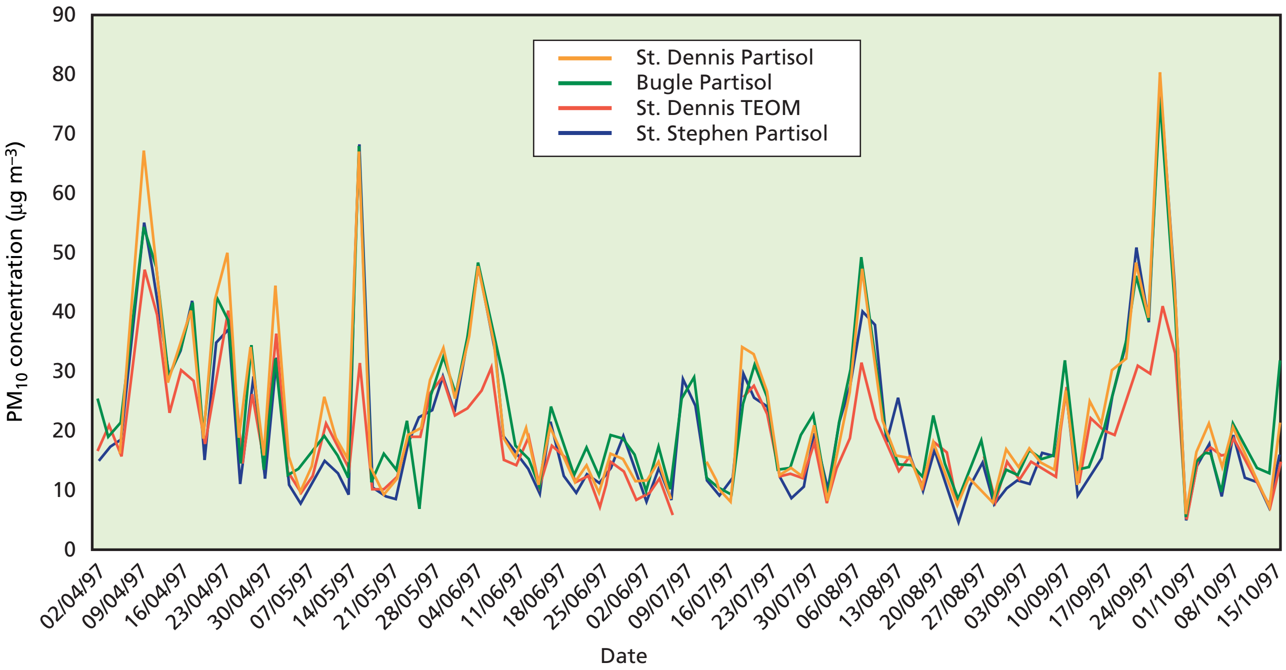

Figure 3.20 Daily PM_{10} concentrations at St. Dennis, Bugle and St. Stephen measured by Partisol instruments and at St. Dennis measured by a TEOM instrument, April to October, 1997 (µg m^{-3}).

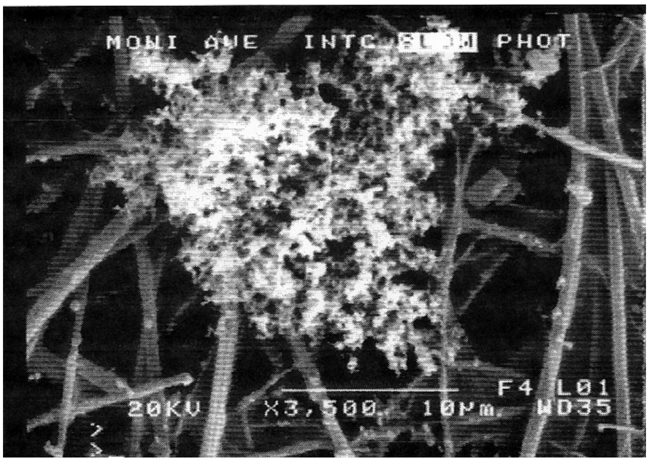

Figure 3.21a SEM analysis from Cornwall

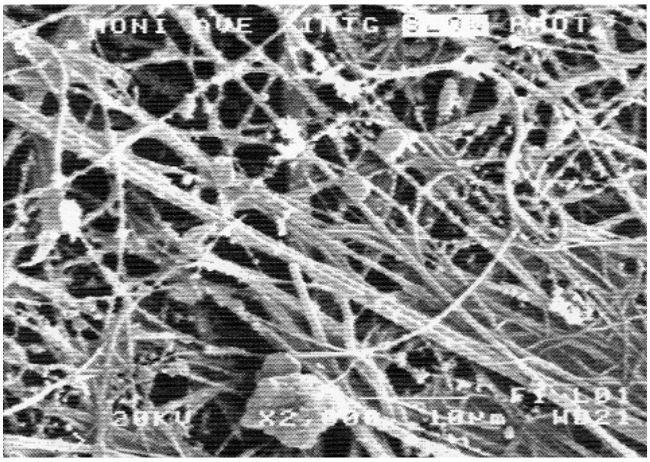

Figure 3.21b SEM analysis from Cornwall

not have contributed to the measured PM_{10} concentrations due to their large size. Tentative conclusions from scanning electron microscopy and X-ray fluorescence studies on a small number of the filter samples collected indicated the possible presence of fine particles (less than 2.5 µm in diameter) from the mineral extraction activities. Figure 3.21 shows two SEM pictures from the same filter. The first shows a large agglomeration, which has tentatively been identified as combustion material, while the second includes a number of small particles, which are thought to be kaolinite.

While there were no exceedances of the 24 hour average threshold of 50 µg m^{-3} within the dataset from the TEOM instrument at St Dennis, PM_{10} daily concentrations were over 50 µg m^{-3} on a number of occasions at the three sites using Partisols.

3.4.3 Chesterfield area: PM_{10} in the vicinity of a range of sources

The authorities in the Chesterfield area carried out a campaign of PM_{10} monitoring using Partisol samplers at a total of six sites. The locations of these sites were chosen in order to investigate the variations in particle concentrations across a transect of about 8 km between Chesterfield and Bolsover (Figure 3.22) in the vicinity of open cast coal mines, the M1 motorway and a solid fuel processing plant. The sites are listed in Table 3.5 along with the number of days with measured daily mean PM_{10} larger than 50 µg m^{-3} and the mean value for the period. Samples were collected on alternate days from November 1996 to October 1997.

Both the period mean concentrations and the number of days on which the average concentration was larger than 50 µg m^{-3} were very similar at all sites except Arkwright where the slightly sheltered position of the monitor may have influenced the results. Apart from this, the variation in concentrations from day to day was very consistent across these sites and indeed similar to that observed at the Sheffield Centre AUN site (Figure 3.23). This indicates that particle concentrations are strongly influenced by regional scale meteorological conditions and emissions. Measured

TABLE 3.5. MEASUREMENTS OF PM_{10} IN NORTH DERBYSHIRE USING PARTISOL SAMPLERS, NOVEMBER 1996 TO OCTOBER 1997

Site Number and Name	Location	Period mean (µg m^{-3})	Days with average concentration >= 50 µg m^{-3}	Number of measurement days
1.Hasland	Urban background	26	22	157
2.Arkwright	close to opencast mine	18	12	125
3.Longcourse	close to opencast mine	28	23	153
4.Duckmanton	close to M1	26	20	137
5.Shuttlewood	close to solid fuel plant	28	19	116
6.Castle	Urban housing	26	22	130

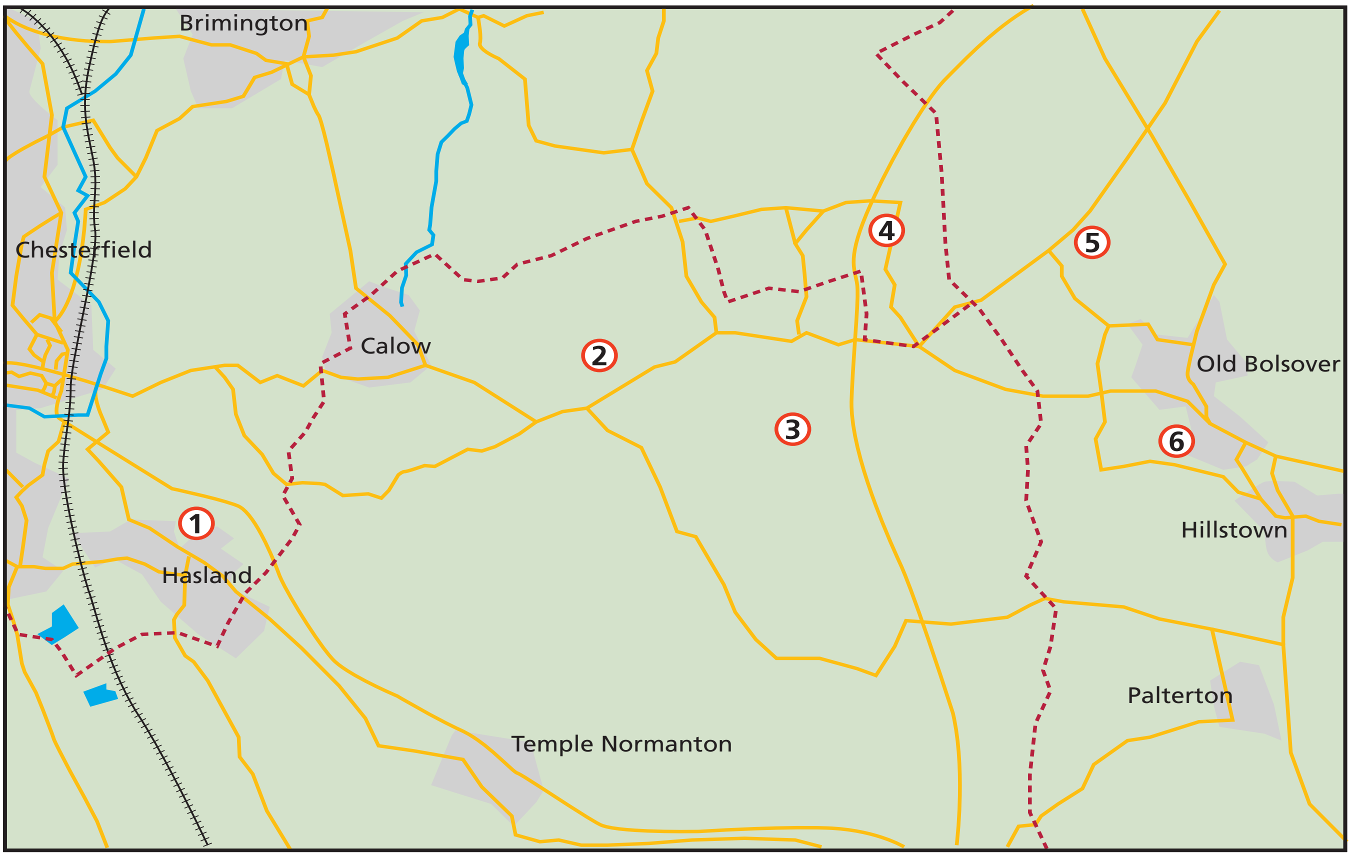

Figure 3.22 Sketch map showing monitoring sites in the Chesterfield area. The sites are listed in Table 3.5

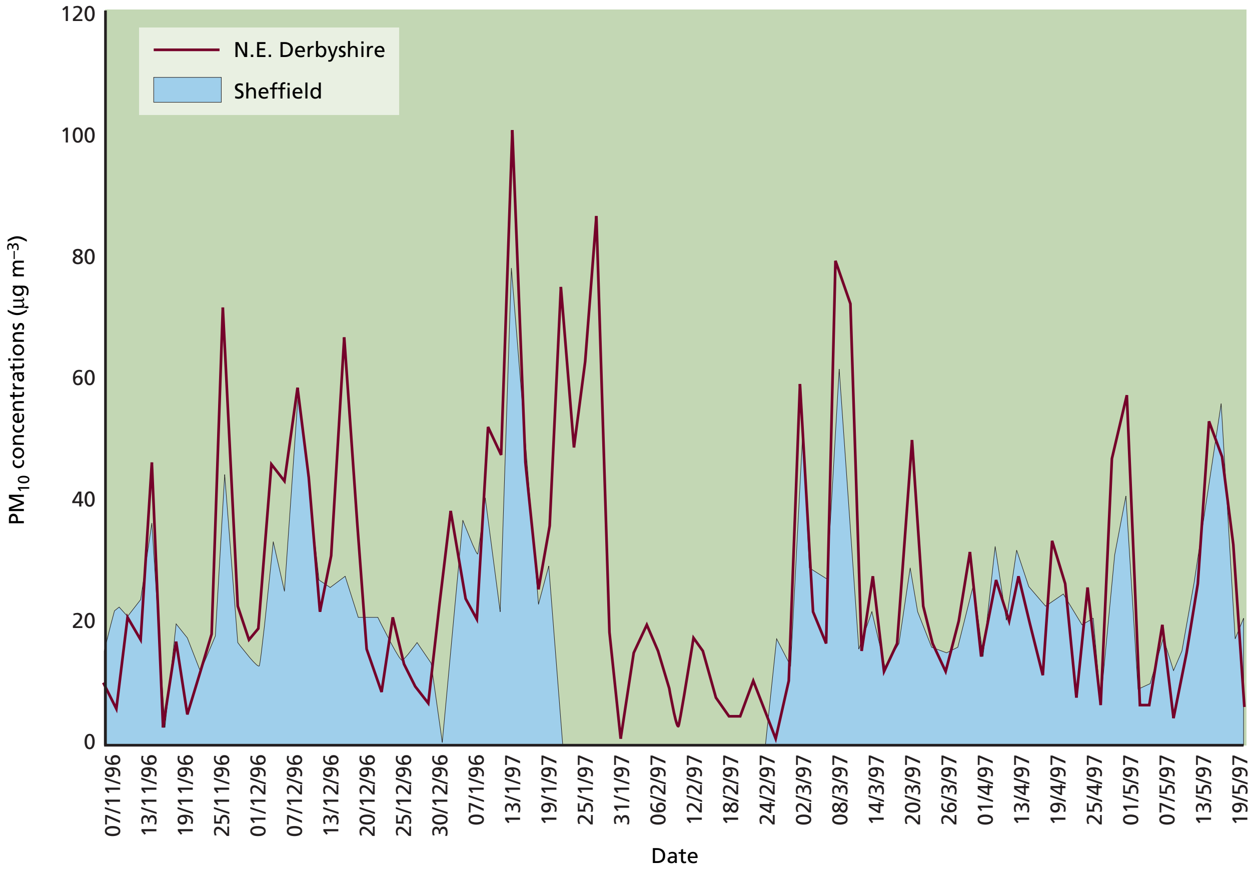

Figure 3.23 Daily average PM_{10} concentrations from the six monitoring sites in N.E. Derbyshire and in Sheffield ($\mu g\ m^{-3}$).

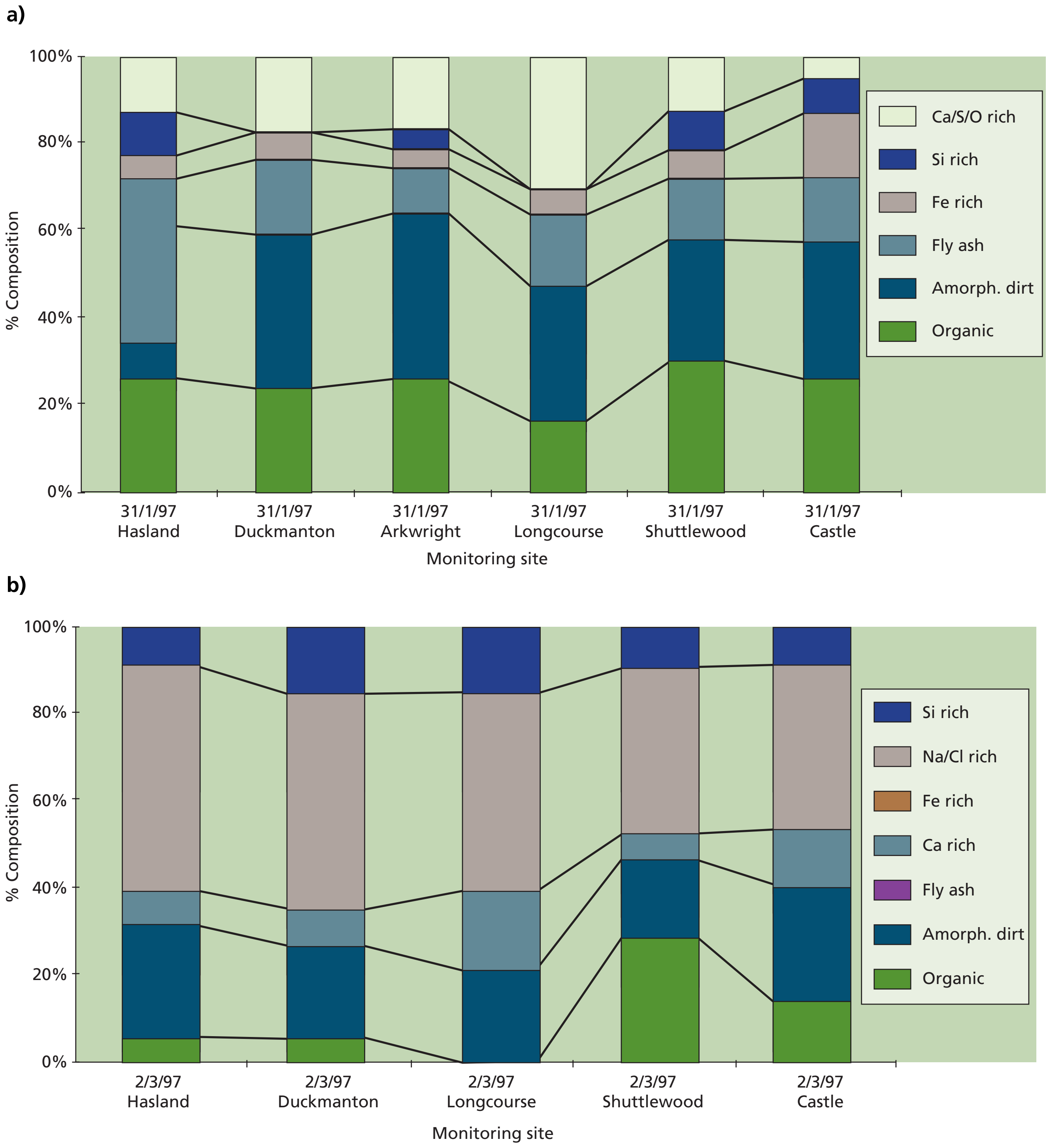

Figure 3.24 Chemical composition of PM10 measured in N.E. Derbyshire on a) 31 January 1997 and b) 2 March 1997.

concentrations were generally larger than at the Sheffield city centre site but it should be noted that the Sheffield concentrations were measured with a TEOM instrument and that Partisol values are generally higher than those monitored using TEOM instruments (see section 3.2).

The chemical composition of the particles collected on selected filters at these sites was characterised by scanning electron microscopy and some example results are shown in Figure 3.24. These analyses have shown that the chemical composition of the samples at the different sites on the same day were generally similar but that there was a significant variation from day to day, particularly in the relative contributions from organic and sea salt derived particles. Portions of several filters were also analysed for a range of organic species by pyrolysis and subsequent GCMS analysis. Qualitative results indicated the proportions of the different organic species were quite variable from day to day.

3.5 INDUSTRIAL SOURCE IMPACTS

3.5.1 Sulphur Dioxide in the Avonmouth Area

Avonmouth is an industrial area to the west of Bristol where there are a number of Part A processes which are potential sources of sulphur dioxide. An air quality impact study of the area is therefore a good model for future studies in industrial areas. The Avon study included both a modelling- and monitoring-based assessment of the industrial impacts. The locations of the main sources are shown in Figure 3.25 and the emissions estimates are summarised in Table 3.6. The largest sources are Britannia Zinc and Sevalco, although these sources are fitted with 93 m and 46 m chimneys respectively.

TABLE 3.6. EMISSIONS FROM INDUSTRIAL PROCESSES IN THE AVONMOUTH AREA

Site	easting, northing	Annual SO_2 emissions (tonnes)	Stack height (m)
Blagden Packaging	3519,1784	3.1	2
Britannia Zinc	3527,1796	3720	93
Chemical Recoveries	3520,1800	1.4	26
Sevalco	3536,1818	871	46
Zeneca	3545,1834	0.001	2 and 12
Park Hill	3534,1768	1.4	?

A mobile laboratory was located about 1 km east of Britannia Zinc. The instrumentation in the mobile lab was similar to that at national monitoring network sites measuring NOx, SO_2, CO and PM_{10}. Meteorological data were also collected. The latter are desirable for all monitoring studies but are a necessity for the analysis of data from stack impact studies. Figure 3.26 shows the measurements of 15 minute average SO_2 and wind direction during August 1996. As can be seen, there are occasional episodes of elevated SO_2 well above the national air quality standard threshold for 15 minute average concentrations of 100 ppb when the wind is from the west, consistent with Britannia Zinc being the source. However, consultation with Britannia Zinc indicated that some of the episodes observed occurred when there were no plant operations taking place that could have been sources of SO_2, indicating that other sources were responsible for at least some of the episodes. These episodes of SO_2 were high, with maximum 15 minute averages being approximately 550 ppb. At the national monitoring site in Bristol Centre the maximum 15 minute

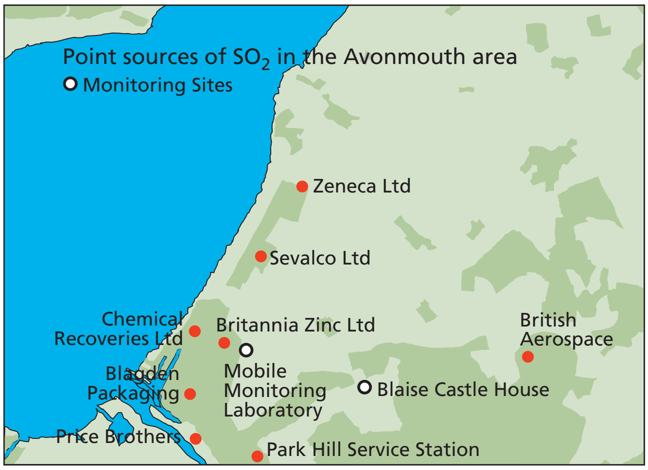

Figure 3.25 Industrial sources in the Avonmouth Area and the locations of monitoring sites

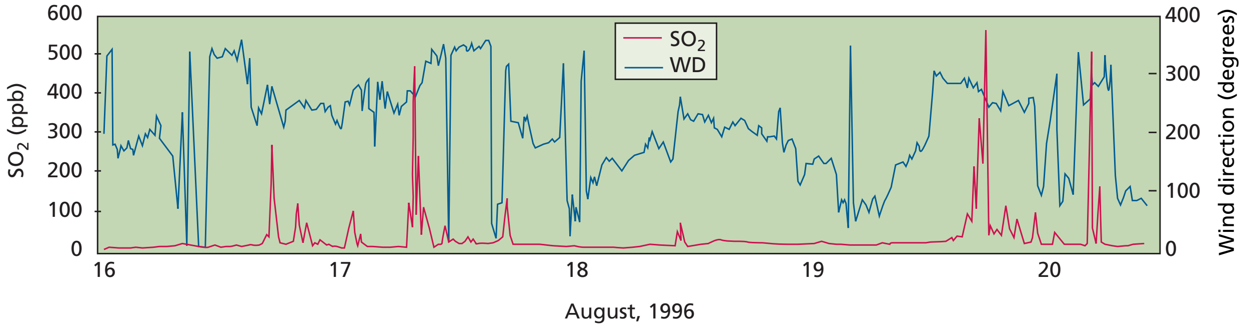

Figure 3.26 Measurements of 15 minute average concentrations of sulphur dioxide and wind direction 1 km east of Britannia Zinc, Avonmouth, August 1996.

averages of SO_2 over this period was only 26 ppb.

3.5.2 Comparison of pollution levels at two locations near British Steel Port Talbot Works.

Two automatic monitoring stations were installed to the north-east of the British Steel works at Port Talbot (see map, Figure 3.27). PM_{10}, CO, SO_2 and NOx were measured continuously. Monitoring at Groeswen Hospital took place between 4th January and 30th July 1997 and at Prince Street from 1st January to 10th April. Wind speed and direction data were collected at Groeswen Hospital.

The measurements at the two sites were surprisingly dissimilar for two sites within 1 km of each other. Groeswen is closer to the M4 so traffic-related pollutant concentrations would be expected to be larger while Prince Street is closer to the British Steel plant so concentrations of pollutants released at low-level on the site would be expected to be larger there.

Hourly mean concentrations of NO_2 at the two sites were well correlated with slightly larger concentrations at Groeswen Hospital. Hourly mean concentrations of SO_2 were also generally larger at Groeswen Hospital than at Prince Street. Hourly mean PM_{10} concentrations at the two sites were correlated with co-incident hourly peaks but concentrations at Prince Street were larger. Hourly mean concentrations above 100 µg m^{-3} were frequently observed at this site, with a 98th percentile of hourly averages of 119 µg m^{-3}. For comparison, at AUN sites, the annual 98th percentiles are typically in the range 70 µg m^{-3} to 90 µg m^{-3}. The 98th percentile at Groeswen was 98 µg m^{-3}.

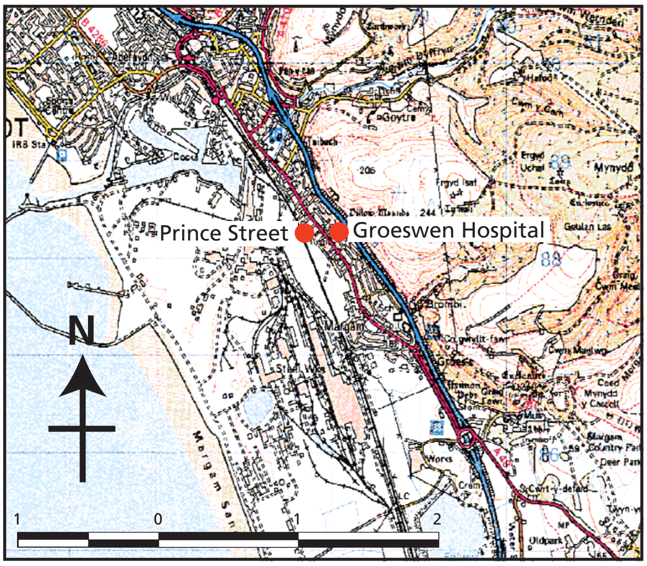

Figure 3.27 Locations of automatic monitoring sites, Port Talbot

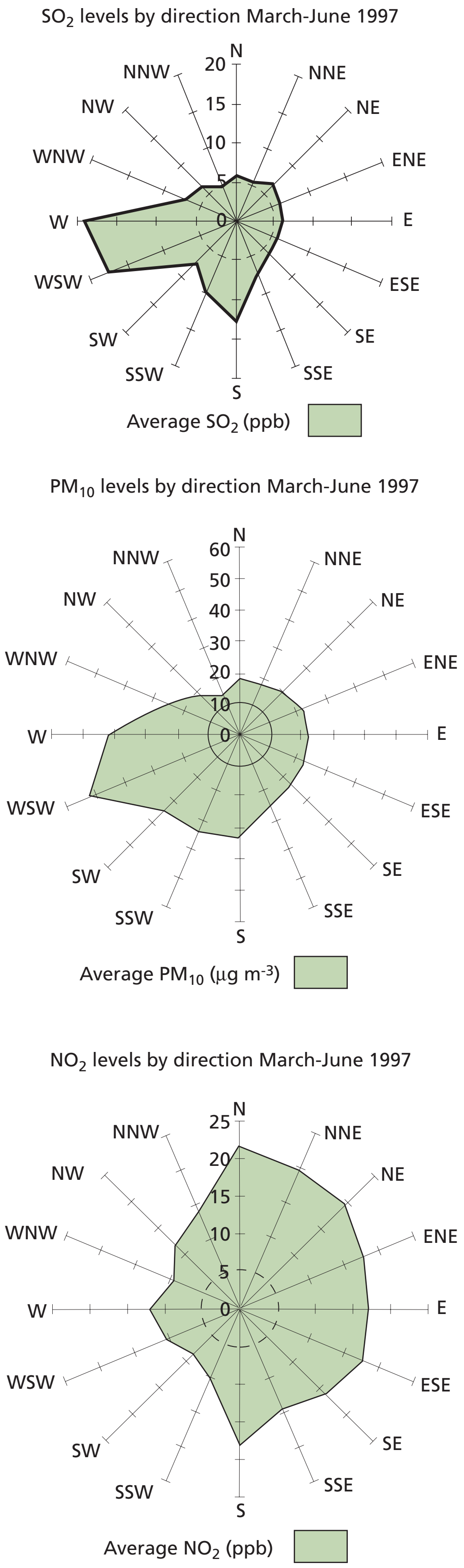

Figure 3.28 Dependence of mean concentrations of NO_2, SO_2 and PM_{10} with wind direction, Groeswen Hospital, March to June 1997.

Meteorological data were available for Groeswen Hospital for March to June only and "pollution roses" have been prepared from the measurements at this site over this period. The mean sulphur dioxide concentration when the wind direction was westerly or south-westerly was 18 to 19 ppb, compared to 5 to 6 ppb in northerly wind directions, indicating a significant contribution from industrial sources to the west. For PM_{10}, the mean concentration was also larger in westerly flow than northerly and easterly. The mean concentration associated with the west to south-westerly wind direction was 52 µg m^{-3} compared to 11 µg m^{-3} associated with the easterly direction. For NO_2, the largest mean concentrations were associated with northerly wind directions, the direction of the M4 motorway. The pollution roses are shown in Figure 3.28.

Table 3.7 summarises the maximum concentration that were observed. Although the monitoring period did not extend for a full year, appropriate statistics were calculated using the available data for comparison with the national air quality objectives for 2005 and these are also included in Table 3.7. Running 24 hour mean PM_{10} levels did exceed 50 µg m^{-3} and the 99th percentiles of running 24 hour averages were 103 µgm^{-3} at Prince Street and 69 µg m^{-3} at Groeswen. Although not considered in the First Phase report, it will clearly require considerable reductions in emissions to meet the air quality objective for 2005. The hour to hour variation and dependence on wind direction were evidence of an intermittent source from the industrial site to the west. Other pollutants measured in the study did not exceed the objective thresholds.

TABLE 3.7 MAXIMUM CONCENTRATIONS OBSERVED AT GROESWEN HOSPITAL AND PRINCE STREET, PORT TALBOT, JANUARY TO JUNE 1997.

	Groeswen Hospital	Prince Street
NO_2 maximum hour (ppb)	59	48
NO_2 hourly average (ppb)	15	14
SO_2 maximum hour (ppb)	75	43
SO_2 99.9th percentile 15 min (ppb)	81	31
SO_2 hourly average (ppb)	7	2
CO maximum hour (ppm)	no data	18.4
CO maximum 8 hour (ppm)	no data	4.0
CO hourly average (ppb)	no data	0.6
PM_{10} maximum hour (µg m^{-3})	186	317
PM_{10} 99th percentile 24 hour (µg m^{-3})	69	103
PM_{10} hourly average (µg m^{-3})	28	36

3.5.3 Measurements of Hydrocarbons in Port Talbot

A Perkin Elmer gas chromatography analyser was installed in a cabin in the grounds of Baglan Primary School and data were collected from 14th November 1996 until 31st July 1997. Data for benzene and butadiene were quality assured by the National Environmental Technology Centre. The monthly mean concentration of benzene varied from 0.4 ppb in June to 1.2 ppb in December. Hourly mean concentrations of butadiene rarely exceeded 1 ppb, the objective for the running annual mean. The industrial sources in the area do not appear to lead to any risk of exceedance of the air quality objectives for benzene or butadiene at this site. The variation in benzene concentrations over a wide area was studied with diffusion tubes (see Section 3.9.1). However, the reported values from diffusion tubes were around three times the values from the automatic monitor, calling into question the quality of the diffusion tube data (see Figure 3.29). If the diffusion tube overread at the automatic site applied everywhere, then 2 week average concentrations of benzene would not exceed 5 ppb.

3.6 MEASUREMENTS AROUND INDUSTRIAL SOURCES OF PM_{10} IN TYNE AND WEAR

Gravimetric (Partisol) PM_{10} samplers were installed around individual industrial processes in Tyne and Wear:

1. *Process 1 was an open cast and reclamation site. Two monitoring sites were used: "Sund 2" was the nearest residential property in the prevailing downwind direction; "Sund 1" was the nearest residential area on the opposite side of the site.*
2. *Process 2 was an oil platform construction and repair site using shotblasting to prepare surfaces for coating. Two monitoring sites were used: "NT1", a source of a recent complaint and "Mill", the nearest residential location.*
3. *Process 3 was a limestone quarry. One monitoring site was used, "Souter" the nearest residential location.*
4. *A control site was installed at the council offices in Washington Village*

A summary of exceedances of various thresholds for the 24 hour average PM_{10} concentrations is

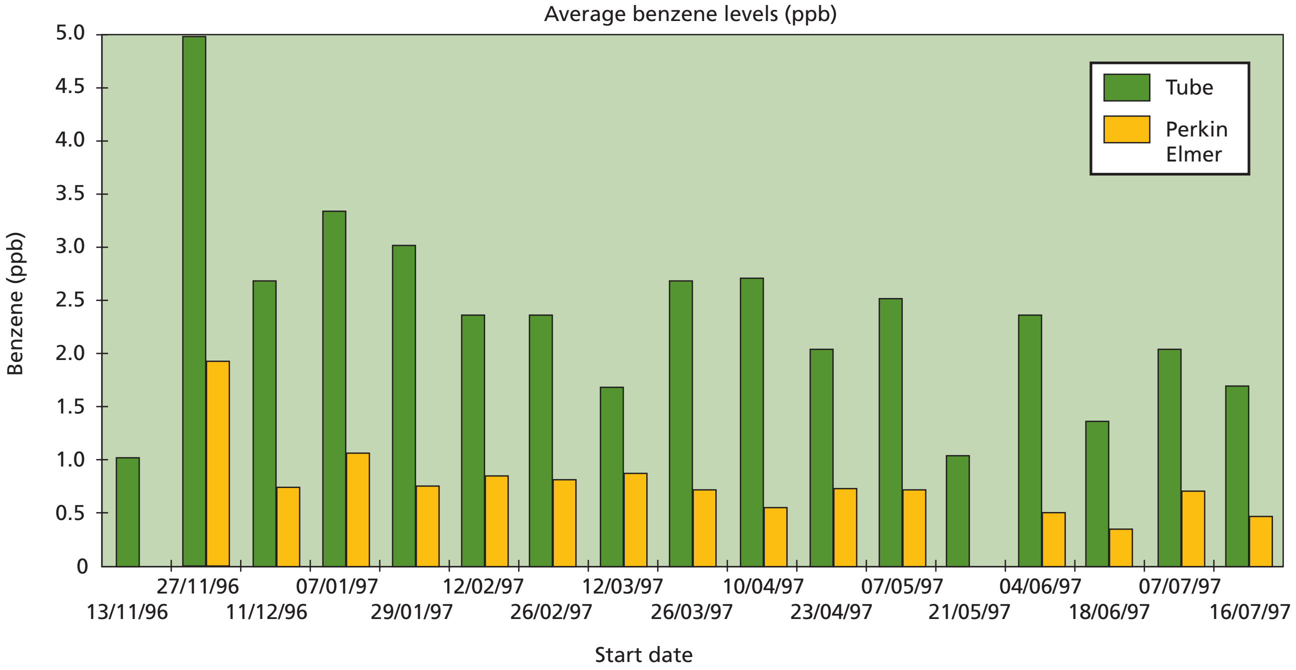

Figure 3.29 Comparison of diffusion tube and automatic measurement of benzene (2 week average concentrations), Baglan Primary School, Port Talbot.

given in Table 3.8. SEM-EDX (scanning electron microscopy – energy dispersive X-Ray) Spectroscopic analysis of some of the filters showed that industrial source particles were clearly present. For example, at the Sund 1 and Sund 2 sites, 10 to 30% of the particles by number were shale particles typical of those from the opencast coal overburden. At Mill, 45% by number of the particles in one sample were iron particles probably derived from shotblasting, although another sample from a day with a similar PM_{10} concentration was dominated by carbon, sulphate and biological particles.

TABLE 3.8. DISTRIBUTION OF THRESHOLD EXCEEDANCES FOR 24 HOUR AVERAGE PM_{10} CONCENTRATION IN TYNE AND WEAR, AND MEAN CONCENTRATION, MARCH TO SEPTEMBER 1997.

	Mill	Souter	NT1	Sund1	Sund2	Control
Number of exceedances						
50-99 µg m^{-3}	10	14	6	5	8	0
100-149 µg m^{-3}	1	1	0	0	2	0
150-199 µg m^{-3}	0	1	0	0	1	0
200-249 µg m^{-3}	0	0	0	1	0	0
250-299 µg m^{-3}	0	0	0	0	0	0
300-349 µg m^{-3}	0	0	0	0	0	0
above 350 µg m^{-3}	0	0	0	0	1	0
Mean µg m^{-3}	32	36	26	29	38	18

3.7 MEASUREMENTS OF LEAD CONCENTRATIONS AROUND PART B PROCESSES IN THE WEST MIDLANDS

Three processes were investigated: a ferrous foundry, a non-ferrous foundry and a lead crystal glassworks. Three Warren Spring Laboratory directional M-Type samplers were used around each process: one site "upwind", one "downwind" and a third close to the works to monitor fugitive emissions. Ground level concentrations were first modelled using simple Gaussian dispersion calculations (Turner, 1969). The distance for the sampler from the works to the point of maximum impact was estimated and the downwind sites were located as close as possible to this point.

Each process was monitored for a three month period. The directional M-Type was set up to sample through the directional filter whenever:

- *the wind speed exceeded 0.5 m sec^{-1},*
- *the wind was blowing from a 50 degree sector centred on the works and*
- *the wind remained within the sector for more than 10 seconds.*

3.7.1 Ferrous foundry

The works produced grey iron castings in a pair of cold blast cupolas rated at 10 tonnes hour^{-1} melting capacity from scrap iron and process returns with each cupola fitted with a wet arrestor. Casts were prepared in sand moulds using a cold resin binder. Mechanical shot blasting took place with dressing operations involving hand grinders and chipping hammers.

Process data were as follows:

Estimated stack height	35 m
Stack diameter	1.22 m
Stack gas temperature	517 K
Efflux velocity	7.1 m sec^{-1}
Emission rate	0.52 g sec^{-1}

The location of maximum ground level impact and thus the optimum monitoring site was calculated to be between 750m and 900m downwind of the stack. The lead concentration was estimated to be 2.44 µg m^{-3}. As always, practical siting considerations prevented the use of the ideal site and the sampler was located 510 m to the NE of the foundry. The "upwind" site was located 440 m to the SW of the foundry. (see map, Figure 3.30). At the "downwind" site the calculated mean concentration was 2.44 µg m^{-3} for wind blowing from the works at a speed at the top of the stack of 20 m sec^{-1}.

The results of the first eleven weeks sampling period, from 14 January 1997 to 2 April 1997 are summarised in Table 3.9. The measured average concentration by the directional filter at the downwind site of 2 µg m^{-3} is reasonably close to the modelled estimate of 1.4 µg m^{-3}. Note that the non-directional filter value is higher than would be expected from typical urban background sources (i.e. leaded petrol-fuelled vehicle emissions) and indicates that emissions from the works or other non-vehicle emissions are contributing to the "background" measurement.

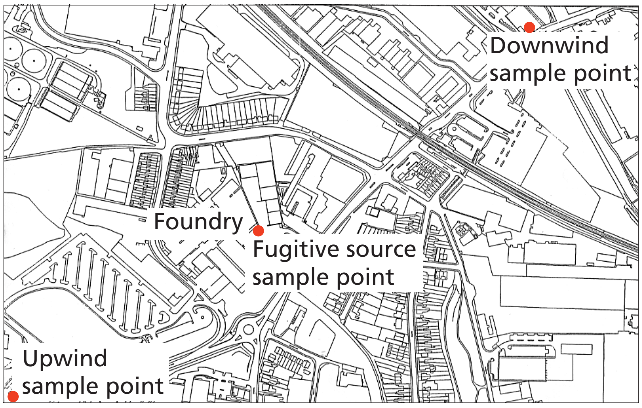

Figure 3.30 Map showing location of monitoring points around a ferrous metal foundry in Sandwell, West Midlands.

The equation for calculating the overall mean from

$$C_t = C_b + x\,\frac{C_d - C_b}{100}$$

the directional and background filter results is: where C_b is the measured background concentration, C_d is the directional concentration and x is the percentage of time for which the sampler was sampling through the directional filter (Barnett, Clayton and Davis, 1987). In this case x was 21% so C_t = 0.9 µg m^{-3}. The calculated average concentrations at the upwind and "fugitive" sites were 0.2 µg m^{-3} and 0.9 µg m^{-3} respectively. Monitoring at the "fugitive" site took place at the foundry about 50 m from foundry operations.

3.7.2 Lead Crystal Glassworks and Non-Ferrous Foundry

Three measurement sites were established in a similar fashion around a lead crystal glassworks and a non-ferrous foundry. The mean downwind concentration for the lead crytsal glassworks was 0.54 µg m^{-3}. Allowing for the percentage of time the wind would blow from the works at any single receptor location, an isolated works of this type would not exceed the 0.5 µg m^{-3} annual mean air quality objective. The downwind sampler for the non-ferrous foundry did not function properly, perhaps due to turbulence induced by nearby buildings such that the wind flow was never sufficiently unidirectional. The average concentration from the directional filter of the upwind sampler was 0.7 µg m^{-3}, again indicating that an isolated source of this type would not lead to exceedance of the objective.

TABLE 3.9. DIRECTIONAL MEASUREMENTS OF LEAD IN AIR AROUND A FERROUS FOUNDRY, JANUARY TO APRIL 1997 (µg m^{-3})

	minimum	*maximum*	*average*	*median*
"downwind" site				
Directional filter	0.4	3.9	2.0	1.6
Background filter	0.2	1.3	0.6	0.6
overall average	–	–	**0.9**	–
"upwind" site				
Directional filter	0	14.7	7.4	–
background filter	0	0.5	0.2	0.2
overall average	–	–	**0.2**	–
"fugitive" site				
Directional filter	0	1.9	0.6	–
Background filter	0.4	12.0	2.4	0.8
overall average	–	–	**0.8**	–

3.8 MEASUREMENTS OF LEAD AROUND A LEAD PROCESS IN WALLSEND, TYNE AND WEAR

The Tyne and Wear first phase group carried out a modelling and monitoring study of the impact of a Part A lead manufacturing process which produces lead oxides and is the only large lead source in the area. There were a number of release points on the site and the measured lead concentration in the emissions was typically 0.1 to 0.2 µg m^{-3}, corresponding to lead release rates in the range 0.1 to 1.5 µgsec^{-1}. The release height varied from 0 to 18m. Dispersion modelling work indicated that the maximum ambient annual average lead was 1.5 µg m^{-3} and that this occurred about a hundred metres from the factory. Predicted concentrations fell off rapidly with increasing distance.

Three monitoring sites were set up using the M-Type samplers as used by the West Midlands, but without directional capability. The “downwind” site to the north-east was placed around 500 m from the factory in a shopping centre, the nearest accessible site but outside the predicted high concentration zone. A second site was placed near to houses 150 m to the north of the factory and a control site was placed 1500 m to the north-west.

The measured weekly average lead concentrations are shown in Figure 3.31. The measured concentrations at the downwind site were little more than at the control site. Measured concentrations at the site closest to the factory were elevated but the average of 0.14 µg m^{-3} was below the air quality objective of 0.5 µg m^{-3}.

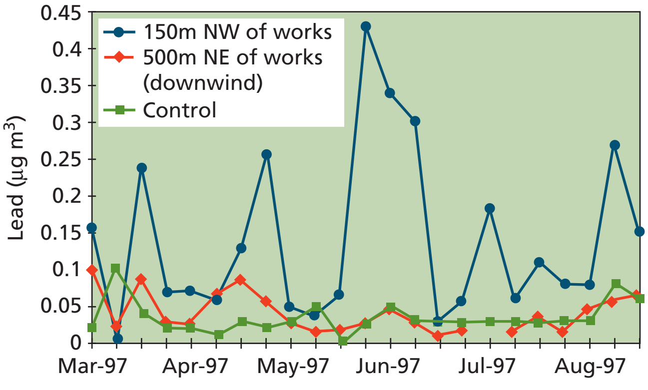

Figure 3.31 Weekly mean concentrations of lead around a lead oxide production process in Wallsend (µg/m³), March to August 1997.

3.9 SPATIAL DISTRIBUTIONS OF BENZENE FROM DIFFUSION TUBE SURVEYS

Diffusion tubes have been used by a number of first phase local authority groups to monitor ambient benzene concentrations. These tubes are 8.9 cm long with an outside diameter of 6 mm and Swagelok brass end fittings and PTFE ferrules to cap the tubes. Standard diffusion end fittings are used at one end when sampling. The tubes are packed with Chromosorb 106 60/80 mesh to a depth of 3 cm. Prior to use all tubes are conditioned by heating to 230°C for 8 hours whilst being purged with pure helium at 100 ml min^{-1}. After sampling, adsorbed hydrocarbons are thermally desorbed to a cold trap. The cold trap is then flash heated and the gases passed to a chromatography column with Flame Ionisation Detection. Since the hydrocarbons have to be thermally desorbed, the adsorbent packing must be chosen such that the gases are not irreversibly adsorbed. Some desorption and back diffusion occurs at ambient sampling temperatures and the overall uptake rate used in relating the amount of hydrocarbon found on the tube to the average ambient concentration must take account of this.

3.9.1 South Wales

A benzene/toluene/xylene (BTX) diffusion tube survey of 51 sites was carried out between November 1996 and July 1997 (see Figure 3.32). Tubes were exposed in pairs or triplicates and each sampler was exposed for a fortnight after which tubes were returned to Swansea University for analysis. Site locations included urban background and kerbside in Swansea, Neath and Port Talbot and several points close to British Steel Port Talbot, BP Baglan Bay and Mobil Llandarcy. Three samplers were located within industrial site boundaries. A single rural site was included to assess the regional background concentration.

The mean concentrations of benzene over the monitoring period were larger than 5 ppb at nine sites (uncorrected data). Seven of these sites were roadside, one was close to the coke works at BSC Port Talbot and the final site was located close to a petrol station. However, as discussed in Section 3.5.3, the measurements by diffusion tubes exposed next to an automatic hydrocarbons monitor were around a factor of three too large. If results from

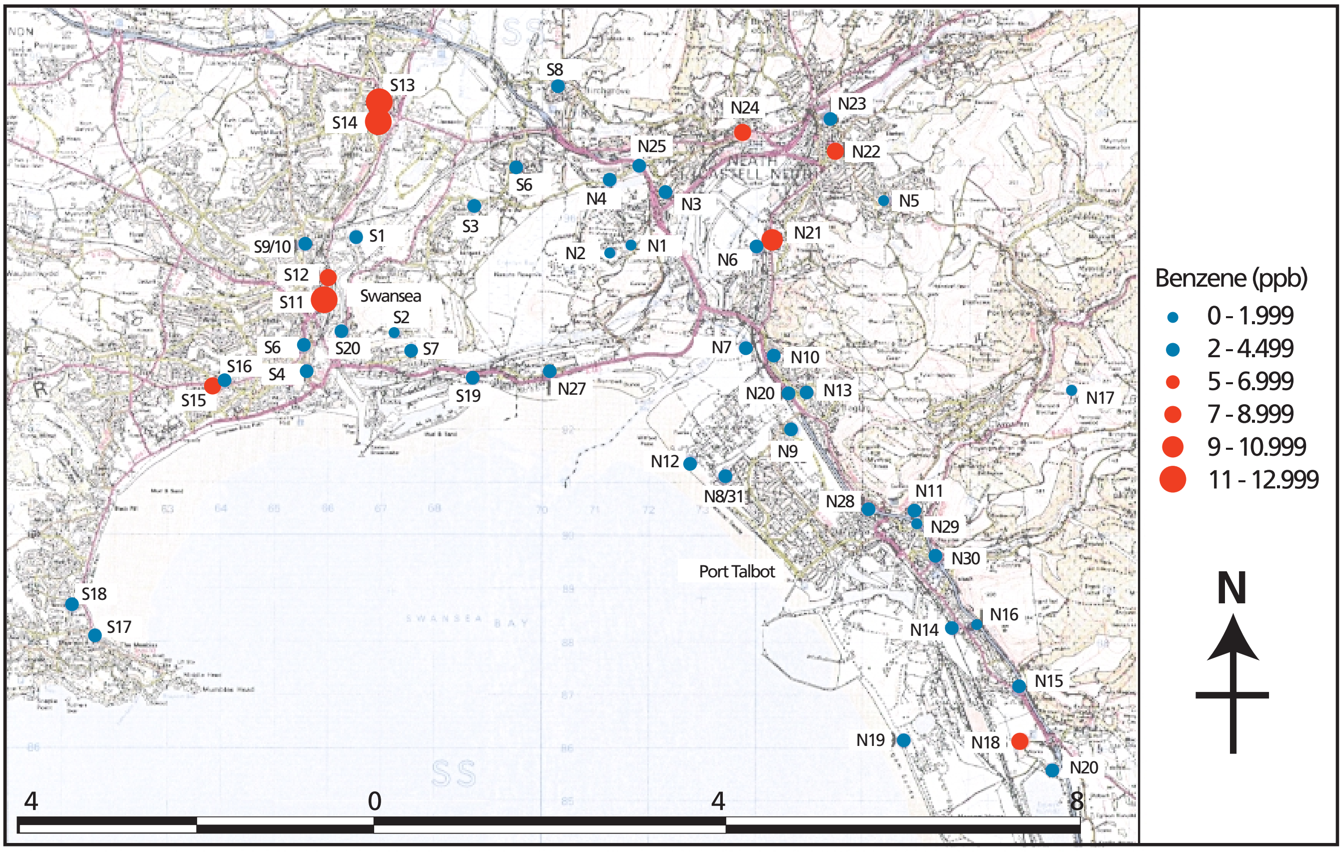

Figure 3.32 Concentrations of benzene at monitoring locations in the South Wales area (ppb) (uncorrected data).

all tubes were corrected by this factor, all monitoring period mean concentrations would have been less than the 5 ppb annual mean air quality objective threshold. Nevertheless, it is useful to consider the observed spatial patterns in the uncorrected benzene concentration. The largest concentrations were observed at kerbside sites. The average concentration of benzene recorded at the urban background sites was 3.6 ppb, at kerbside sites 3.75 ppb, at places of special interest (close to industrial plant) 2.5 ppb. The average concentration at the rural background site was 1 ppb. The benzene:toluene ratio was between 0.5 and 1.0 at most sites, as expected when vehicle emissions are the major source. Exceptions included two sites in Port Talbot (N18 benzene = 6 ppb and N19 benzene = 3 ppb in Figure 3.32) for which the British Steel Coke works appeared to be a source of benzene. Around BP Baglan Bay and Mobil Llandarcy the largest observed concentrations were at sites close to roads.

3.9.2 Tyne and Wear

Benzene concentrations were monitored at 30 sites throughout the Tyne and Wear First Phase Local Authority area. These were placed in six groups of five. Five of the groups were surrounding petrol stations or petrol storage/distribution facilities on either busy urban or semi-rural roads where tubes were placed within the petrol station grounds and within the front gardens of adjacent residential properties. The sixth group of tubes was placed away from petrol stations and major roads which acted as a control location. Monitoring was carried out from December 1996 to August 1997. Average concentrations over this period are given in Table 3.10. The concentrations at the site away from major sources of benzene showed the lowest mean concentration and none of the sites exhibited concentrations that were above the national air quality objective of 5 ppb.

TABLE 3.10 AVERAGE CONCENTRATIONS OF BENZENE MEASURED IN SIX LOCATIONS IN THE TYNE AND WEAR FIRST PHASE AREA.

Site Group	*Mean Concentration (ppb)*
1	1.7
2	1.4
3	1.9
4	1.5
5	1.6
control	0.9

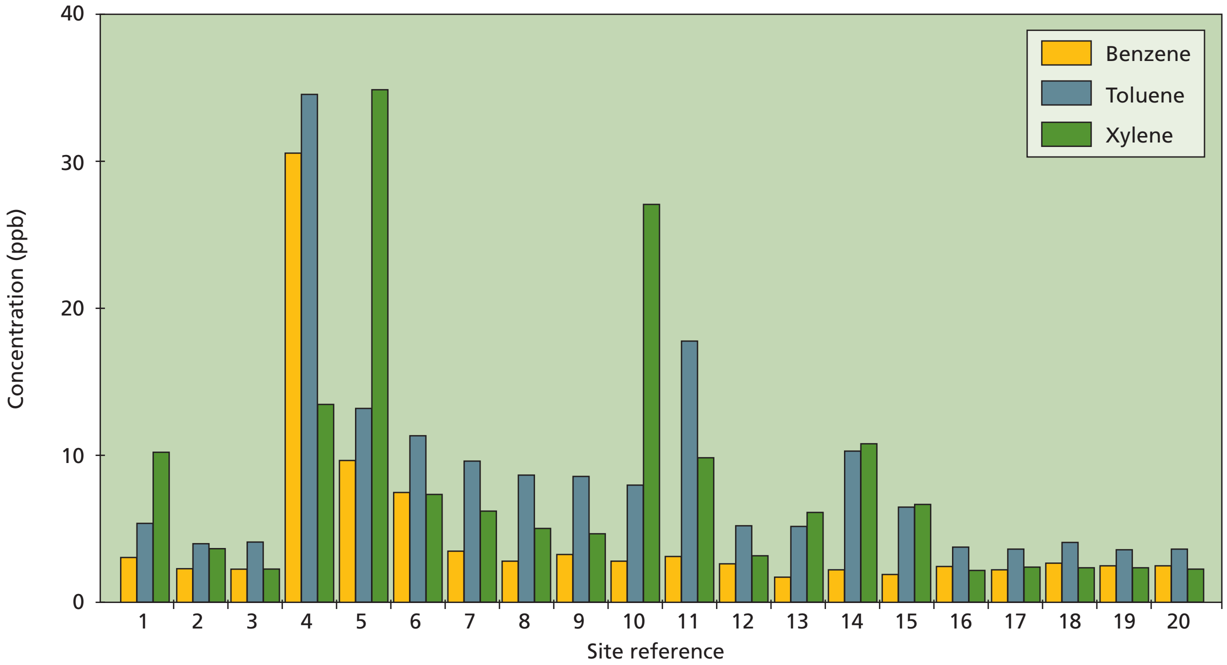

Figure 3.33 Average concentrations of benzene, toluene and xylene measured by BTX diffusion tubes at 20 sites in the Avonmouth area, August 1996 to September 1997.

3.9.3 Avon

BTX tubes were used to measure concentrations of benzene, toluene and xylene at 20 sites in Avon. Sixteen of these sites were in the vicinity of sources from petrochemical industry such as tank farms. Three sites (17-20) were in locations representative of the background. The study was generally successful but for the physical loss of a few tubes and the loss of one batch of results due to analytical equipment failure (a common problem with the thermal desorption method as there is no opportunity to repeat analyses). The average concentration during the monitoring period are illustrated in Figure 3.33 and show a strong contribution from evaporative sources at these sites. The average concentration of benzene was 7 ppb at one site, Site 4. This is particularly close to a tanker filling station and is in the prevailing wind direction from the facility. The average concentrations were smallest at the urban background sites. The sites closest to the tank farms were also characterised by unusual benzene:toluene and benzene:xylene ratios, a fact which has been confirmed by work on garage forecourts. All this work suggests that concentrations of hydrocarbons decline rapidly