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AIR QUALITY MONITORING FOR FLUORIDES: I. ESTABLISHMENT AND QUALITY ASSURANCE

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The brickfields in the Marston Vale of Bedfordshire and surrounding areas account for almost half of the UK brick production. Consequently the region contributes to significant emission of fluorides to atmosphere. Previous data left much uncertainty about the accuracy of the results and whether they gave a true picture of air quality. The setting up of a spatially extensive programme for atmospheric fluorides is described, together with the quality assurance procedures essential for producing reliable data. A brief indication of air quality data is presented.

KEY WORDS: Fluoride, brickworks, quality assurance, monitoring.

INTRODUCTION

The biological effects of fluoride have long been recognised, with problems in agriculture being found worldwide as a result of coal combustion and emissions from the fertiliser, aluminium melting and ceramic industries. Fluoride is used as a generic term that refers to the fluoride ion and to combined forms of the element fluorine, but whatever the form of fluoride, it is regarded as probably the most phytotoxic of the common pollutants. Susceptible species of plants can be injured at atmospheric concentrations many times lower than those of other major pollutants. One characteristic feature of fluoride is the accumulation in plants and subsequent ingestion can cause disease in herbivores.

Estimates of fluoride emissions to atmosphere in the United Kingdom for 1978 are summarised below:

Whereas the emissions of fluoride from brick making are less than 10% of those

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Fluoride Emissions (UK) for 1978¹

<i>Process</i>	<i>Production or usage</i>	<i>Emission (tonne)</i>
Coal burning	120×10^6 tonne coal	12 000
Iron and steel	20×10^6 tonne steel	1 300
	11.4×10^6 tonne pig iron	
Fletton brick	2.6×10^9 bricks	1 100
Primary aluminium	0.35×10^6 tonne Al	1 000

from coal burning, the brick kilns tend to be concentrated in certain areas and so the emission sources are not widely dispersed as is the case for coal burning. Moreover, the common location of the kilns in rural areas is of particular significance as far as effects on vegetation and livestock are concerned.

Notwithstanding their considerable environmental effects, fluorides have probably received less study than other air pollutants. Certainly, the available data leave a number of important questions unanswered, not the least being what concentrations actually exist in the atmosphere.

The Bedfordshire brickfields have declined in activity over the years, but the largest brickworks in Europe remains at Stewartby. Some 30 years ago it was stated that, so far as could be ascertained, there was no public health hazard from the fluorine emissions.² Continuing concern heightened by a proposal to extend the brickworks resulted in a comprehensive review in 1980.¹ Among the principal recommendations resulting from this review was the suggestion that a more spatially extensive programme of air quality monitoring for fluoride be established, with aims to provide more reliable data than were available hitherto, and to include a study of seasonal variations as well as an examination of any links with herbage contamination.

The establishment of the programme and the extensive quality assurance procedures are described in this paper. Subsequent papers will describe the results of the programme, which was supported by funding through and under the auspices of the Fletton Brickworks Liaison Committee. Warren Spring Laboratory participated in the programme by acting as technical assessors in respect of site selection, measurement methodology and in data analysis.

QUALITY ASSURANCE

World Health Organisation guidelines³ identify a quality assurance component as essential to any monitoring programme. Such a component indicates whether acceptable data are produced and establishes comparability of data among agencies. The application of the well-developed discipline of quality assurance to air pollution monitoring has been outlined by Apling.⁴ In this context the definition of quality assurance is cited as all activities and functions concerned with the attainment of quality, which in turn is defined as the totality of features

and characteristics of a product or service that bear on its ability to satisfy a given need. For the work described in the present paper, the need was to produce authoritative data for fluorides in the atmosphere of the Marston Vale of Bedfordshire. In this respect, the basic elements addressed for the purpose of quality assurance were:

- i) site location and character;
- ii) analytical method for fluoride;
- iii) sampling procedure;
- iv) performance of sampling equipment;
- v) comparison of sampling methodology.

SITE LOCATION AND CHARACTER

The research programme set out to investigate air quality in the Marston Vale by sampling the atmosphere at 10 sites selected according to the following criteria:

- i) the current activity at Stewartby and the siting of any new brickworks;
- ii) concentration on the south west/north east transept;
- iii) inclusion of a site near an established sulphur dioxide monitoring station;
- iv) where possible, the co-ordination of sites with the herbage sampling programme carried out previously and to be repeated as part of the overall present exercise;
- v) location of sites on the basis of simple dispersion theory subject to practical limitations of site availability and security;
- vi) one master site to include various sampling methods.

In accordance with the above criteria, provisional sites were selected on the basis of simple dispersion theory.

The wind directions for the region are represented by the wind rose shown in Figure 1. This wind rose is for data from Bedford in 1985, but does not differ significantly from data for the periods 1960–69 and 1971–78 on which the theoretical predictions were based. These data demonstrated the need to concentrate on the SW/NE transept which accounts for winds for nearly 50% of the time. The Stewartby works is the major focus of the monitoring programme, but at the time of planning the locations there was a proposal to develop the former Coronation site. This acts as the secondary focus which is represented by C on the map. The annual average wind speed is 4.2 m/s. The sites of maximum ground level concentration for given wind speeds and atmospheric stability can be predicted simply by the method of Turner.⁵ On this basis and using data from an assessment of the region in the Department of the Environment Report¹ the radii of maximal ground level concentrations were predicted and are presented in Table 1 and on Figure 1. This also shows the final sites and their relationship to other criteria points. Site 3 was established as a remote background site, while sites 2 and 4 also maintained established sulphur dioxide monitoring stations, the latter serving as a master site for comparison of sampling methods.

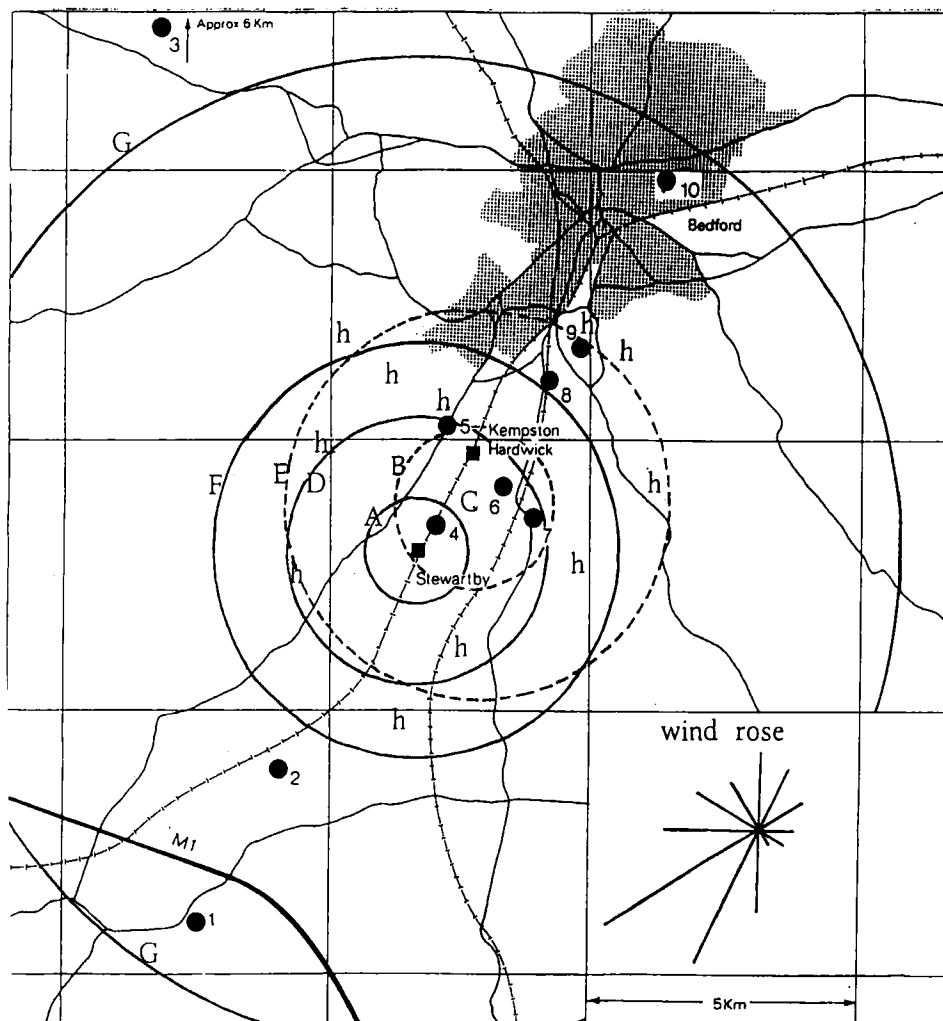


Figure 1 Sketch map of the Marston Vale, Bedfordshire, relating air sampling sites to brickworks and former herbage sampling sites. Key: ●, with numbers 1 to 10 denote air sampler locations; ■, brickworks; h, former herbage sampling sites; C, location of former Coronation works and possible future brickworks site.

Circles denote predicted locations of maximal ground level locations as follows:

- A: Stability C, radius 0.95 km based on Stewartby;
- B: Stability C, D(ii), radius 1.6 km based on Coronation;
- D: Stability D, radius 2.5 km based on Stewartby;
- E: Stability C, D(iii), radius 4 km based on Coronation;
- F: Stability E, radius 4 km based on Stewartby;
- G: Stability F, radius 9 km based on Stewartby.

The wind rose represents data from Bedford for 1985.

Table 1 Radii of maximal ground level concentrations

Pollution sources: Stewartby works—19 chimneys, each 61 m high, effective height 80 m, closely grouped				
Pasquill stability categories	C/D(ii)	C/D(iii)	E*	F*
Frequency	23 %	44 %	12 %	
Mean wind speed (m/s)	4.4	7.8	2.8	
Radius of max. conc. (km)	0.95	2.6	4.0	9.0
Under the same conditions the radii for maximal ground level concentrations from the proposed Coronation works are calculated as follows:				
Radius of max. conc. (km)	1.6	4.0	10.2	
These are based on a stack height of 121.9 m with an allowance for plume rise				

*Stabilities E and F are common in autumn with winds from NE, E and SE.

ANALYTICAL METHOD FOR FLUORIDE

Routine measurements of fluoride concentrations on filter pad samples were made using an ion-selective electrode meter (Orion 407A) with a fluoride-specific electrode (Orion 94-09) and single-junction reference electrode. Reagents used in the determination were prepared as follows.

Total Ionic Strength Adjustment Buffer (TISAB)

Glacial acetic acid (57 cm³, Analar grade) was added to deionised water (500 cm³) in a polythene beaker, followed by sodium chloride (58 g, Analar grade), the mixture being stirred until the solid dissolved. Sodium hydroxide solution was added to adjust the solution to pH 5.0 to pH 5.5, and the volume was made up to 1000 cm³ with deionised water.

Standard Fluoride Solutions

Each day a fresh standard fluoride solution containing 50 mg F/l was prepared by dilution from BDH 1000 ppm Fluoride standard. Working standards were prepared from this solution to give nominal standards of 2.0, 1.0, 0.5 and 0.25 ppm F. In this context, "nominal" means that, for example, 1 ppm F diluted by an equal volume of TISAB gives a solution in the beaker of 0.5 ppm F, although the reading is set at 1 ppm F on the logarithmic scale of the meter.

A sample pad for analysis was transferred to a polythene beaker (50 cm³) and deionised water (12.5 cm³) containing 0.25 ppm F added, followed by TISAB (12.5 cm³). The standard addition of fluoride was found to be necessary to enable more reliable measurements of low levels of fluoride as described later. The covered filters were allowed to steep for no less than 1 hour and were then pulped using polypropylene spatulas.

The electrode system was left in contact with standard fluoride solution of

0.25 ppm overnight. Immediately before measuring fluoride content of samples, freshly prepared fluoride standards were used to calibrate the ion selective electrode system. Standardisation was re-checked after measurement of each group of six or seven samples. The electrodes were immersed in the analyte liquid to a depth of 1 cm and this liquid was stirred continually using a plastic stirring bar and magnetic stirrer. The time required for a stable reading of F concentration varied.

Concentrations within a narrow range of each other (± 0.05 ppm) gave stable readings very quickly, but wider variations required periods of 10 min or more for stabilisation. In such circumstances more frequent calibration checks were made and it was important to ensure that continual stirring of the solution did not raise the temperature of the sample solution. Sometimes it was necessary to switch off the stirrer to avoid a temperature rise, although an insulating sheet between the beaker and stirrer may have reduced the problem.

The concentration of the atmospheric fluoride in the sampled atmosphere was calculated using the equation:

$$\text{concentration } (\mu\text{g}/\text{m}^3) = \frac{25[0.5(\text{meter reading} - 0.125)]}{\text{volume of air sampled } (\text{m}^3)}$$

ANALYTICAL RELIABILITY

The analytical procedure was evaluated by halving sample pads and comparing results from two laboratories. Exchanges of sample solutions were also made to identify possible sources of discrepancy.

The first samples to be received from the initial operating sites were divided into two equal portions. One half of each filter was analysed for the trapped gaseous fluoride content at Warren Spring Laboratory (laboratory 2), while the other half was analysed at Aston University (laboratory 1). Data for which matched pairs were available showed differing arithmetic means with those from Aston being higher. This was also shown in the frequency distributions of the respective sample populations. However, the data were related with a correlation coefficient of 0.575.

It was clear from the discrepancies that many measurements were being made at or near the limit of detection for the ion selective electrode procedure, and in a nonlinear range of the calibration curve. Routine measurements required standard additions to counteract these problems.

The results of subsequent comparative measurements are presented in Figure 2. For the analyses by ion selective electrode, an addition of $3.125 \mu\text{g}$ was made to the solution for extraction of each half pad as described in the analytical method section. The improvement in agreement was considerable, with scatter being reduced to the extent that the correlation coefficient improved to 0.95. Two further quality assurance checks were made. In the first of these an analytical check on the standard solutions was made by comparing nominal (made up) concentrations for routine use at Aston with measured concentrations made at Warren Spring Laboratory. The differences were small as is demonstrated by the data in Table 2.

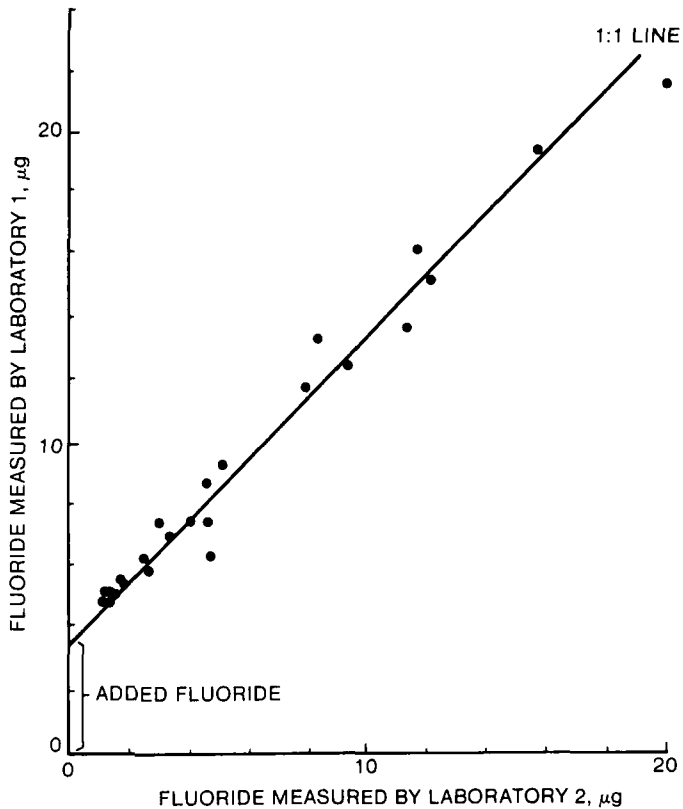


Figure 2 Comparison of analytical results for halved filter pads from site 4 over the period 1.11.84–24.11.84.

Table 2 Inter-laboratory comparison of nominal and measured concentrations

Standard	Fluoride concentration (ppm F ⁻)		
	Nominal	Measured	Difference
A	1.25	1.24	-0.01
B	0.25	0.24	-0.01
C	0.05	0.047	-0.003
D	0.15	0.137	-0.003
E	0.15	0.138	-0.012
F	2.5	2.45	-0.05
G	0.4	0.37	-0.03
H	0.075	0.097	+0.022
I	0.25	0.23	-0.02

Table 3 Results of repeated measurements of standard solutions

Fluoride concentration (ppm F ⁻)			Number of observations
Standard	Measured	95% Confidence	
2.0	1.99	±0.136	20
1.0	0.98	±0.059	20
0.75	0.73	±0.039	20
0.5	0.49	±0.028	20
0.25	0.26	±0.018	20
0.1	0.11	±0.012	20

A further test examined the variability in the measurement process. Between 15 December 1984 and 2 February 1985 repeated measurements were made of six standard solutions covering the measurement range. This was done at intervals during routine measurements of the air quality survey. The results are summarised in Table 3. The mean values were all within 0.02 ppm F⁻ of the nominal value and confirm that the measurement process was being carried out consistently.

SAMPLING PROCEDURE

Kirk and Lester⁶ note that sampling for airborne fluorides is complicated by the very low concentrations of these compounds generally present in ambient atmospheres. Typical concentrations in a range <0.1 to <10 µg/m³ are quoted. A further complication is the possible occurrence of fluoride in gaseous, particulate, and aerosol forms, or as gaseous fluoride absorbed on dust. As gaseous fluoride is generally most toxic to vegetation, a collection system must be able to separate gaseous and particulate forms; sampling for total fluoride is of limited value. One procedure for separating, collecting and concentrating particulate and gaseous fluoride is to use a pre-filter followed by an alkali-treated pad. A cellulose nitrate membrane filter acts as the preliminary stage to collect particulate. This is followed by an alkali treated filter pad, which retains the gaseous fluoride. This procedure has been used previously⁷ and is similar in principle to others widely used for the determination of atmospheric fluoride.^{8,9}

Filters were contained in plastic holders which were inserted as sets of eight under a weather hood: a plastic cylinder approximately 30 cm diameter and 30 cm long which was open at the bottom. So far as was practicable, the height of hoods was approx. 1.8 m above ground level for all sites, and the equipment was no closer than 2 m from buildings and other obstructions. Air was sampled through one filter for 24 h with an upward flow. At midnight each day an automatic valve (AGL) switched the flow to the next filter. Suction pumps (Class B, IEC, Charles Austen Pumps) provided the air flow which gave air volumes samples ranging from 15 to 35 m³/day at different sites, although variation was little at a given site. The volume of air sampled was assessed from readings of a dry gas meter in the

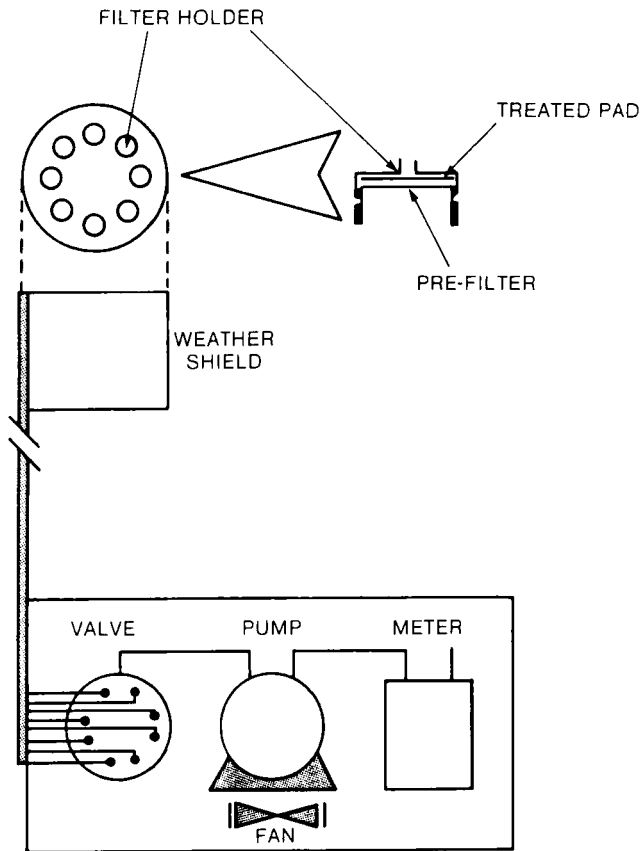


Figure 3 Air sampling equipment.

flow line and which was read during the weekly visits to each site in order to collect and replace the filters. These weekly visits made by personnel from collaborating local authorities included site checks on sampling line integrity and noting any unusual features as well as replacing filters. Figure 3 represents the sampling apparatus. In terms of the physical reliability of the sampling equipment, there were initial problems through overheating within the pump and meter cabinets at certain exposed sites during hot summer days. However, the overall reliability of the sampling system and the conscientious work of local authority staff who changed filters and checked the sites combined to give an excellent degree of data capture of about 97% for over 7000 air samples.

Performance of the Sampling Equipment

Tests were made to establish the reliability of a single treated pad for trapping gaseous fluoride by replacing pad holders containing a single treated pad with

Table 4 The assessment of the degree of breakthrough of fluoride on two treated filter pads placed in series

Date	Fluoride concentration ($\mu\text{g}/\text{m}^3$)		Date	Fluoride concentration ($\mu\text{g}/\text{m}^3$)	
	First pad	Second pad		First pad	Second pad
6.3.85	0.046	0.034	25.3.85	0.127	0.020
7.3.85	0.137	0.034	26.3.85	0.161	0.015
8.3.85	0.193	0.011	27.3.85	0.207	0.030
9.3.85	0.273	0.046	28.3.85	0.456	0.024
10.3.85	0.273	0.046	29.3.85	0.859	0.034
11.3.85	0.023	0.000	30.3.85	1.037	0.024
12.3.85	0.046	0.000	31.3.85	0.634	0.024
13.3.85	0.134	0.029	1.4.85	0.859	0.041
14.3.85	0.058	0.023	2.4.85	0.592	0.012
15.3.85	0.157	0.041	3.4.85	0.427	0.024
16.3.85	0.134	0.029	4.4.85	0.373	0.024
17.3.85	0.110	0.012	5.4.85	0.184	0.036
18.3.85	0.192	0.023	6.4.85	0.326	0.018
19.3.85	0.058	0.029	7.4.85	0.124	0.018
20.3.85	0.093	0.029	8.4.85	0.610	0.083
21.3.85	0.103	0.024	9.4.85	0.681	0.041
22.3.85	0.093	0.034	10.4.85	0.552	0.024
23.3.85	0.200	0.034			
24.3.85	0.391	0.039			

holders containing two pads in series. The preparation and analysis of these pads followed the normal procedure.

A comparison of the fluoride found on the primary and secondary pads showed that there was negligible passage of gaseous fluoride through the first pad, and this is demonstrated by the data in Table 4. Of the 36 comparisons made between the capture on the two pads, only one showed any significant breakthrough, perhaps the result of leakage past the first filter. In all other cases the fluoride content in the backing filter contained much less than $0.05 \mu\text{g}/\text{m}^3$, which corresponded to the level of fluoride in an unexposed pad. There was no indication that the fluoride content of the second pad was related to the measured content of the first.

A Comparison of Sampling Methodology

Airborne fluoride concentrations have been measured in the Marston Vale of Bedfordshire for many years by means of a bubbler system. This established bubbler sampling involves collection of the sample over a period of 2 or 3 days, and so in order to compare results obtained by the two methods it was necessary to calculate means from the daily filter pad values. As sample changeover times did not coincide for the two systems, some partitioning of pad values was necessary, with the result that some variability may be introduced in the comparison.

The results are presented graphically in Figure 4. While the points were generally grouped around the 1:1 line, there were occasions when the bubbler

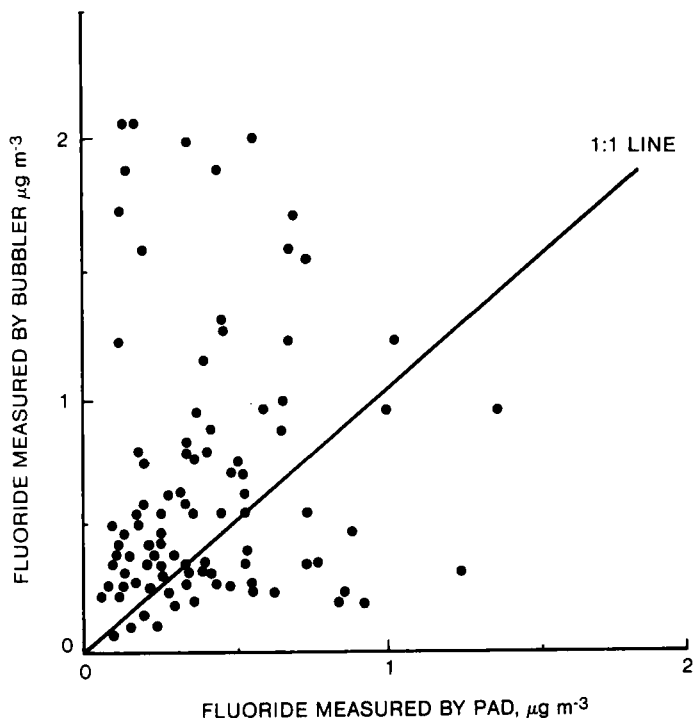


Figure 4 Comparison of measurements made between October 1984 and April 1985 by bubbler and filter pad methods at site 4.

samples indicated substantially higher concentrations than the pad samples. These points were not matched by similar extreme differences where pad samples were found to be much greater than bubbler values. Particulate fluoride may account for some of the differences, but to explore the problem further, a truly matched comparison was established.

Daily bubbler samples were collected simultaneously at the same site (site 4) as filter pad samples were obtained. The bubbler system was provided by Warren Spring Laboratory and used PTFE tubing and polyethylene bubblers to minimise losses of fluoride to surfaces. Air was sampled at a nominal $2 \text{ m}^3/\text{day}$ (actual range $1.96\text{--}2.04 \text{ m}^3/\text{day}$) through two bubblers in series, each containing an absorbing solution of sodium carbonate (0.05 M , 75 ml). The system is described in more detail by Irwin,¹⁰ and the major differences from that operated previously was in the sampling period of 1 day, rather than 2 or 3 days. The results of this comparison are presented in Figure 5. Scatter about the 1:1 line is again evident, but the pad samples were now rather higher than those from the bubbler. The mean values from the filter pad and bubbler were $0.75 \mu\text{g}/\text{m}^3$ and $0.62 \mu\text{g}/\text{m}^3$, respectively. A comparison of all three measurement systems is plotted in Figure 6, which shows no consistent discrepancies between the methods.

The reasons for the differences could not be established, but differences in

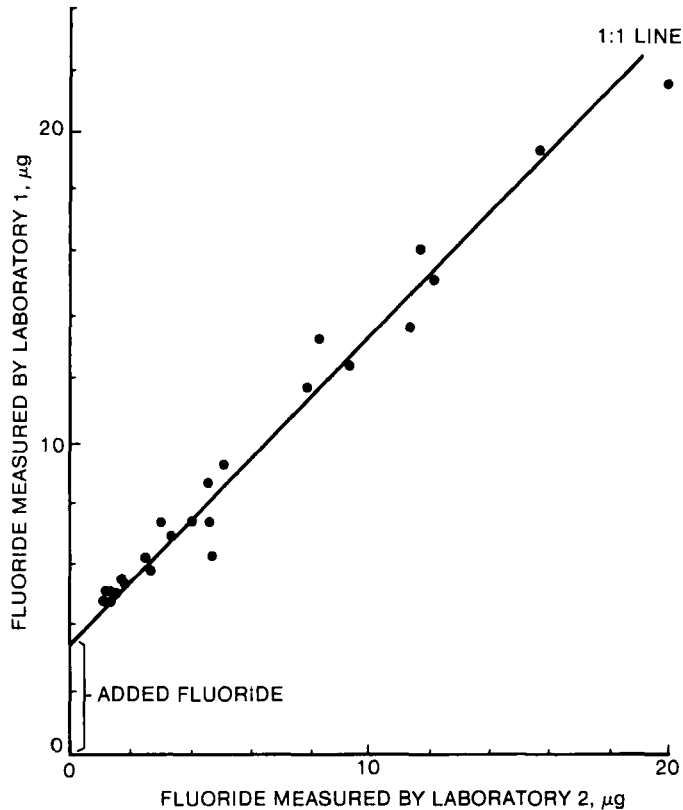


Figure 5 Comparison of measurements made between 28.6.85 and 20.7.85 by WSL bubbler and filter pad methods at site 4.

changeover times, losses to the tubing of bubbler systems and effects of particulate matter may all have contributed. For practical purposes, however, it was noted that the filter pad method gave the higher concentrations, and agreement over longer term periods was better than on a daily basis.

Particulate Fluoride

When considering possible effects the chemical form of fluoride in the environment is important. Gaseous fluorides are reactive and in addition to presenting a serious phytotoxic problem they present difficulties in measurement. The problem may initially be considered one of resolving gaseous from particulate forms of fluoride that may be present in the atmosphere, but more may be involved. The gaseous fluorides may react with other components of the atmosphere and thereby render them less harmful in the short term but certainly more difficult to analyse, especially if strong complexes with metals are involved. Obviously the nature of

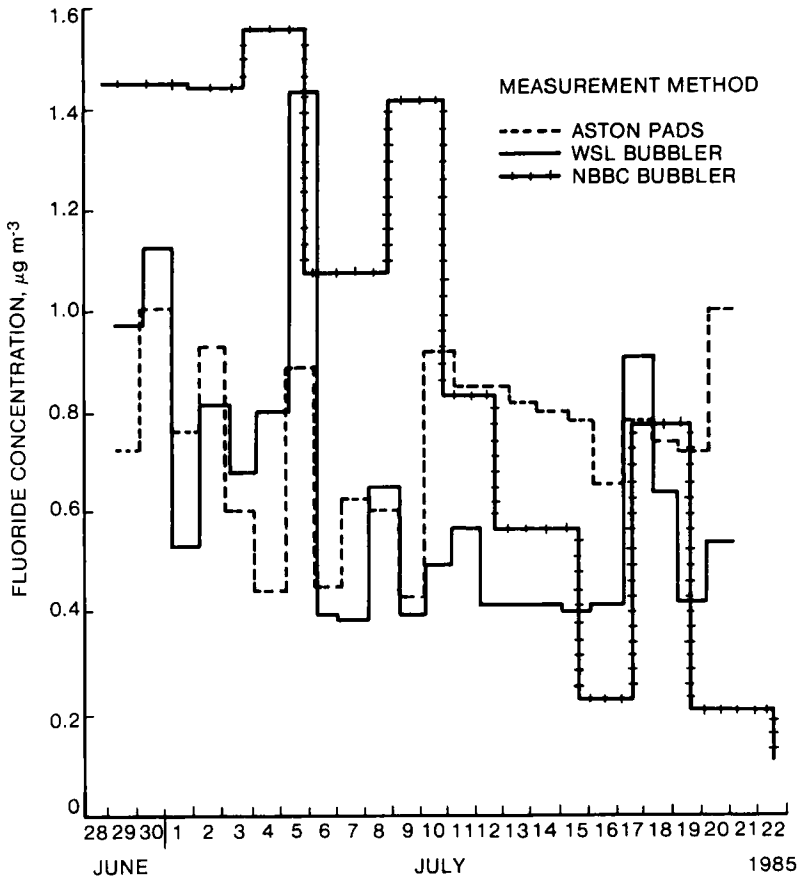


Figure 6 Comparison of three methods of measuring atmospheric fluoride concentrations at site 4. NBBC denotes North Bedfordshire Borough Council, WSL denotes Warren Spring Laboratory.

the atmospheric particulate varies with the sources in an area and so at some sites there may be more species for reaction with fluorides than at other sites.

In view of the differences between the sampling and analysis methods, the significance of the fluoride content of the particulate matter was examined on 2% of the micropore filters preceding the treated pads at the site exhibiting maximal pollution. Consistently negligible amounts of fluoride were found. Amounts ranged between not detected to 0.005 ppm, which represented 0–5.5% of a pad containing only 0.09 ppm F, which in turn corresponded to a calculated atmospheric concentration of about $0.16 \mu\text{g}/\text{m}^3$. Previous studies by London Brick Co. and the former Alkali Inspectorate had found that particulate matter accounted for about 5% of total fluoride emissions. While it is likely that hydrogen fluoride may be retained on all surfaces that are not acidic in reaction, there was no evidence of this occurring on the filters used in the present study. Clearly, in other areas the same behaviour may not be observed. Thus, for example, gaseous fluoride emissions

Table 5 Summary of airborne fluoride concentrations in the Marston Vale over the period October 1984 to September 1986

Site	No. of daily means	Concentration ($\mu\text{g}/\text{m}^3$)		
		Mean of daily means	Median of daily means	95 percentile
1	663	0.13	0.12	0.21
2	726	0.18	0.13	0.25
3	686	0.07	0.09	0.11
4	717	0.40	0.26	0.85
5	713	0.24	0.17	0.60
6	717	0.48	0.26	1.30
7	720	0.25	0.18	0.55
8	709	0.29	0.18	0.65
9	721	0.26	0.18	0.60
10	725	0.18	0.17	0.30

from or near aluminium works may undergo chemical reaction resulting in a greater proportion of fluoride in the particulate form.

OVERVIEW OF RESULTS

Air quality as indicated by daily average atmospheric fluoride concentrations were measured for a period of 2 years at the 10 sites in the Marston Vale. Mean concentrations over the whole period varied between $0.48 \mu\text{g}/\text{m}^3$ at the site 2.3 km from the major brickworks to $0.07 \mu\text{g}/\text{m}^3$ at the background site some 15.8 km distant. Table 5 summarises the air quality data over the 2 year period. The concentrations are generally lower than those typically reported around known fluoride sources and compare favourably with air quality standards for fluorides that apply in certain countries in the European Community. A detailed analysis of the results and discussion of the significance will be presented in a second paper.

CONCLUSION

The prime objective of the programme was to produce reliable data on air quality in the Marston Vale of Bedfordshire as influenced by fluorides from brick-making. Fundamental to meeting this objective was the establishment of a good sampling system supported by reliable analytical procedures. The system and procedures described in this paper resulted in a data capture of 97%. A technical assessment of the programme concluded that for the first time it was possible to draw a map of measured airborne fluorides in the area, and considerable confidence could be placed in the data. The air quality data themselves will be described in detail in a subsequent paper, but this work has demonstrated the important role of quality assurance procedures in the monitoring programme.

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