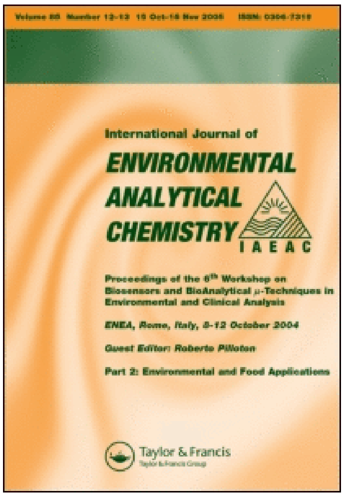

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Air Quality Monitoring for Fluorides II. Spatial and Temporal Distributions Around a Brickworks

E. R. Clark[a][b]; P. C. Robins[a][c]; J. G. Irwin[d]; R. S. Barratt[e]
[a] Aston University, Birmingham, UK [b] Department of Chemical Engineering and Applied Chemistry, [c] Operations and Information Management Division, Management Centre, [d] Warren Spring Laboratory, Department of Trade and Industry, Stevenage, UK [e] Environmental Engineering Subject Group, The Open University, Walton Hall, Milton Keynes, UK

To cite this Article Clark, E. R. , Robins, P. C. , Irwin, J. G. and Barratt, R. S.(1991) 'Air Quality Monitoring for Fluorides II. Spatial and Temporal Distributions Around a Brickworks', International Journal of Environmental Analytical Chemistry, 44: 2, 87 — 101
To link to this Article: DOI: 10.1080/03067319108027539
URL: http://dx.doi.org/10.1080/03067319108027539

Intern. J. Environ. Anal. Chem., Vol. 44, pp. 87–101
Reprints available directly from the publisher
Photocopying permitted by license only

AIR QUALITY MONITORING FOR FLUORIDES II. SPATIAL AND TEMPORAL DISTRIBUTIONS AROUND A BRICKWORKS

E. R. CLARK* and P. C. ROBINS†

Aston University, Aston Triangle, Birmingham, B4 7ET, UK

J. G. IRWIN

Warren Spring Laboratory, Department of Trade and Industry, Stevenage, SG1 2BX, UK

R. S. BARRATT‡

Environmental Engineering Subject Group, The Open University, Walton Hall, Milton Keynes, UK

(*Received 8 August 1990*)

The results of a spatially extensive monitoring programme for gaseous fluorides are described for the area surrounding a major brickworks. Monthly mean concentrations of atmospheric fluoride ranged from $0.04\,\mu g/m^3$ to $0.86\,\mu g/m^3$ through the two-year programme of air sampling. Daily and seasonal variations are analysed together with spatial distributions in the region.

KEY WORDS: Air, fluoride, brickworks, monitoring.

INTRODUCTION

Perhaps one of the most intractable air pollution control problems concerns the brickworks on the belt of Lower Oxford Clay, which extends from Peterborough, through Bedfordshire to the Bletchley area of Buckinghamshire in the United Kingdom. This layer of Jurassic shale is believed to be unique to the United Kingdom and provides the raw material for a large proportion of the national brick production, specifically known as Fletton bricks. Traditionally, Flettons are made in continuous, annular kilns with many chambers in which the bricks are stacked, and the fire is moved around the chambers of the kiln over a period of several days. The clay has the advantage not only of being available in large amounts, but also of containing a sufficiently high content of organic matter (5–6% carbon) which supplies some 70% of the energy needed to fire the kilns.

---

*Department of Chemical Engineering and Applied Chemistry.

†Operations and Information Management Division, Management Centre.

‡To whom correspondence should be sent.

Unfortunately the process also leads to destructive distillation of some organic matter resulting in the production of malodorous compounds which in the relatively low-temperature and oxygen-deficient atmosphere of the kiln do not burn to odourless combustion products. Hence the characteristic brickworks odour of the district. Contribution to the odour comes from sulphur compounds in the clay, while other constituents are fluorine compounds, the fluorine content being approx. 500 mg/kg.

Despite many attempts to develop satisfactory gas cleaning systems for the kilns, no economic or practicable method has yet been found. Consequently the combustion products are discharged to atmosphere untreated. The emissions are not always well dispersed owing to the relatively low buoyancy of the plumes, and so the odours are readily detected. This draws attention to the emissions, although concern is more associated with the accompanying fluorides in view of the potential risk to vegetation and human or animal health. Fluoride is one of the most phytotoxic pollutants with acute and chronic effects on vegetation. Accumulation in herbage may cause a high intake by grazing livestock with consequent symptoms of fluorosis. The significance of fluorides to human health is currently under critical review in the USA.

The Bedfordshire brickfields have declined in activity over the years, but one of the largest brickworks in Europe remains at Stewartby. Thirty years ago it was stated that so far as could be ascertained there was no public health hazard from the fluorine emissions.[1] Continuing concern heightened by a proposal to extend the brickworks resulted in a comprehensive review in 1980.[2] Among the principal recommendations resulting from this review was the suggestion that a spatially extensive programme of air quality monitoring for fluoride be established to include observation of seasonal effects and to provide more reliable data than were available hitherto. The establishment of the monitoring network and the quality assurance procedures have been described in a previous paper.[3] The present communication presents a summary of the air quality data for ambient fluorides and examines relationships between source and certain meteorological parameters. A subsequent paper will relate the air quality to the fluoride content of herbage in the area.

METHODS OF INVESTIGATION

Between October 1984 and October 1986 regular measurements of mean daily fluoride concentrations were made in the region surrounding the brickworks in the Marston Vale of Bedfordshire.

Air was sampled at nine sites concentrated along the SW/NE axis through the brickworks and along the predominant wind direction. An additional site, designated site 3, was located approximately 16 km NW of the works and was intended to provide background data. The relative locations of the sites around the brickworks are shown in Figure 1. At each site samples were obtained continuously over 24 h sampling periods by drawing air through circular cellulose pads impregnated with sodium carbonate and glycerol. The resulting samples were

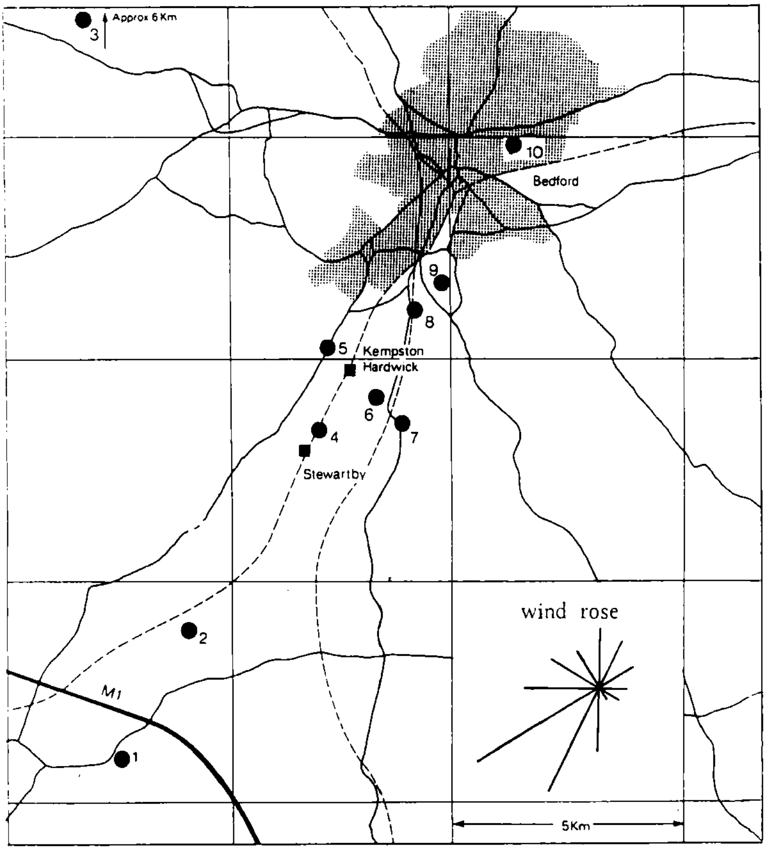

Figure 1 Location and identification numbers of air sampling stations in the Marston Vale of Bedfordshire. ■ Denotes location of brickworks.

analysed using a fluoride-selective electrode. Full details of the equipment, methods and validation together with the criteria and calculations involved in selecting these locations have been reported previously.[3] An overall data capture of 97% demonstrated the soundness of the technology used.

RESULTS AND DISCUSSION

Mean, median and percentile concentrations of airborne fluoride at each site for the two year period are presented in Table 1. Comparing these values with the locations shown in Figure 1, it can be seen that the relative values at the sites are as would be expected. Thus the background site (site 3) had the lowest values, closely followed by concentrations at the two sites to the South West of the brickworks (sites 1 and 2). The sites to the North East of the source showed the highest values, although at site 10 the levels can be seen to be approaching the

Table 1 Summary data of fluoride concentrations for the 2-year programme at all sampling stations

Site	*No. of readings*	*Overall mean conc. ($\mu g/m^3$)*	*Median*	*75%*	*90%*	*95%*
1	663	0.13	0.12	0.14	0.21	0.21
2	726	0.18	0.13	0.16	0.21	0.25
3	686	0.07	0.09	0.10	0.11	0.11
4	717	0.40	0.26	0.45	0.70	0.85
5	713	0.24	0.17	0.22	0.40	0.60
6	717	0.48	0.26	0.55	1.05	1.30
7	720	0.25	0.18	0.26	0.40	0.55
8	709	0.29	0.18	0.31	0.51	0.65
9	721	0.26	0.18	0.31	0.50	0.60
10	725	0.18	0.17	0.21	0.26	0.30

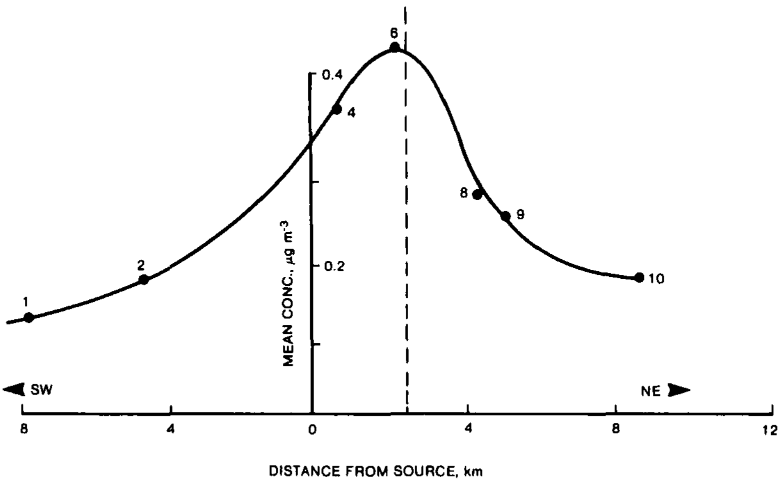

Figure 2 Distribution of overall mean fluoride concentrations along the SW-NE-axis. Site identification numbers are indicated and the broken line shows the predicted location of maximum ground level concentration.

lower levels found at sites 1 and 2. These cursory observations on the data relate to one objective of the survey, namely to take account of the prevailing wind direction, i.e. the SW/NE axis. The spatial variation along this axis is also represented in Figure 2, which shows the two-year mean concentrations at sites on the axis plotted as a function of their distance downwind and upwind from the Stewartby works. This figure demonstrates typical behaviour of ground-level concentrations as the distance from an elevated source increases. Of particular note is the observation that site 6, the site with the highest mean, is on the prevailing wind axis and close to the calculated radius of maximum ground level concentration which was used to guide the location of monitoring stations. While

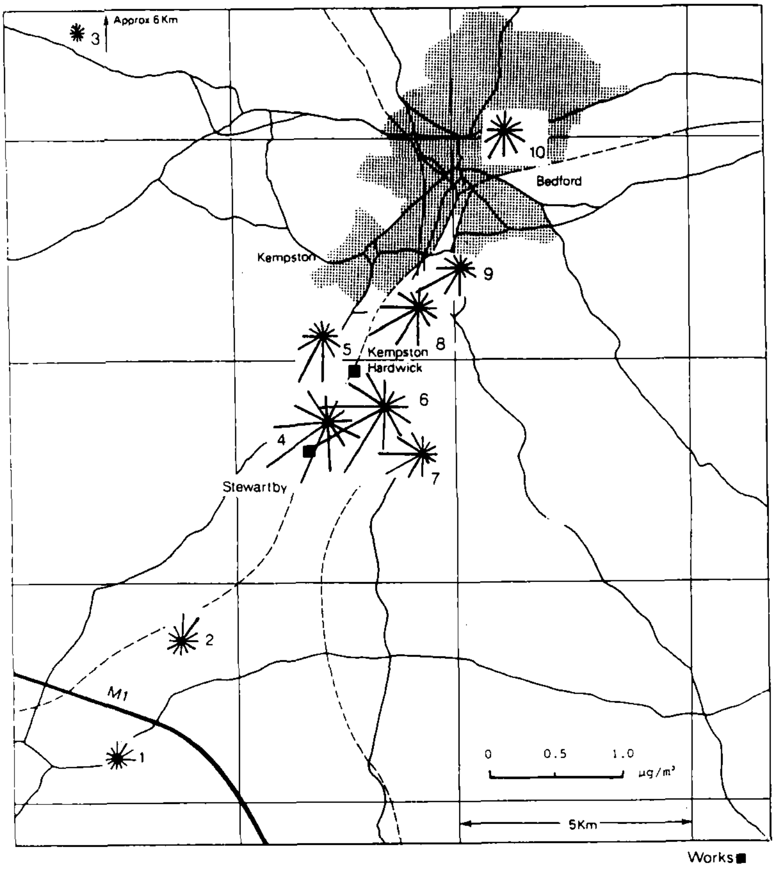

Figure 3 Pollution roses for sites in the Marston Vale.

sites 2 and 8 and sites 1 and 10 are respectively at similar distances from the brickworks, the differences between the average values at the sites as shown in Table 1 and Figure 2 almost certainly reflect the differing distribution of wind directions. Figure 1 shows that sites 5 and 7 were on a similar radius from the works as site 6, but exhibit lower fluoride concentrations. Once again, this is attributed to the frequency of wind directions.

The wind rose for the area, as compiled from Meteorological Office data from Bedford for the period January–December 1985, is shown in Figure 1. On this basis the sites to the NE of the brickworks would be expected to have higher fluoride levels than those to the SW, as indeed was observed. A more direct assessment of the effect of wind direction was made for the period for which appropriate meteorological data were available, namely January–December 1986. The measured fluoride concentrations for this period were partitioned according to wind direction in 30° sectors, and mean values for each sector calculated. The resulting pollution roses are presented in Figure 3. This demonstrates quite clearly that the greatest concentrations at each site occur when the wind blows from the brickworks. By comparison, when the wind blows from other directions, most sites experience uniformly low concentrations of approx. $0.14\,\mu g\,m^{-3}$. One exception to this is site 3 which shows no pronounced variation with wind direction, and justifies its choice as a background site. It was noted that most sites showed higher concentrations than at this site irrespective of wind direction. This may in part be attributed to emissions from the urban areas around the works.

Site 6 also deserves comment. It may be noted that concentrations much greater than background levels occur over a wide range of wind directions, especially when site 6 is compared with sites 5 and 7 which are at similar distances from the works. This behaviour may reflect particular meteorological conditions at the site. An influence from a smaller brickworks at Kempston Hardwick is another possibility, although the absence of any similar discernible effect at site 5 makes this explanation unlikely.

A comparison can also be made of the pollution roses for sites 1 and 10 and sites 2 and 8, which are respectively at similar distances from the brickworks but in opposite directions. This comparison identified concentration differences which may be attributed to differences in atmospheric mixing properties associated with different wind directions. While average concentrations are expected to reflect the frequency that the wind is in the direction of the works, mean values calculated for those occasions when the wind blew from the works should be similar if similar dispersion processes operated. The analyses found no such agreement. This issue could only be fully addressed by a modelling study, which was outside the scope of the programme.

The measured concentrations of fluoride around a brickworks will also be influenced by variations in source strength. Brick production provides an indicator of the source strength, but variations in emissions over the production cycle of several days and the availability of production data only as monthly totals makes it difficult to establish a direct relationship. Figure 4 represents the monthly concentrations, as an average of those at all sites except the background site, as a function of monthly brick production. No clearer relationship was identifiable when individual site means or means for groups of sites (e.g. sites 5, 6, 7) most likely to be influenced by the source were plotted against brick production. Logarithmic-transformed mean concentrations produced worse correlations against brick production. It is apparent that while brick production as an indicator of source strength varied by a factor of two during the programme, the variations were irregular. In view of the highly significant influence of meteorological parameters, the absence of a major excursion in the emissions makes it difficult to evaluate a relationship between emissions and ambient concentrations beyond the broad observation that atmospheric fluoride concentrations tend to be higher when production is higher. A modelling study may be more appropriate to further investigate the relationship.

Daily Variations

An indication of the daily variation of fluoride concentrations is shown by the percentile concentrations reported in Table 1 while Figure 5 presents the site data

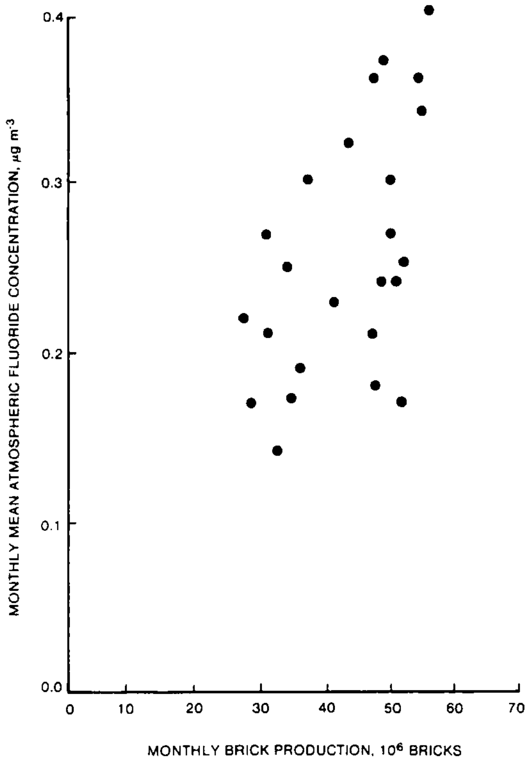

Figure 4 Monthly mean fluoride concentrations plotted as a function of monthly brick production.

as percentiles in diagrammatic form. This figure suggests quite strongly the separation between sites 1, 2 and 3 and the remaining sites, i.e. a demarcation between background and sites to windward of the source, and those predominantly influenced by it.

Frequency distributions for the sites are presented in Figure 6. These distributions all exhibit skewness characteristic of air pollution data which usually conform well to the log-normal distribution. The probability distributions represented in Figure 7 indicate that the data for sites such as 2 and 3 follow this log-normal distribution rather better than sites such as 4 and 6, which exhibit departure from linearity. Another characteristic of the log-normal model of air quality data is the so-called "arrowhead" display linking averaging time with concentrations. This is illustrated for sites 1 and 6 in Figure 8.

A correlation matrix for all data at all sites is shown in Table 2 This reflects the expected lack of or low degree of correlation between sites upwind and downwind of the source. By comparison, sites 6, 7, 8 and 9 show strong correlations. It is also noticeable that sites 1 and 3 correlate, suggesting the absence of a significant influence from the brickworks at site 1.

The apparent similarities and differences between sites can be analysed more closely using non-parametric or distribution-free statistics. Such tests are appropri-

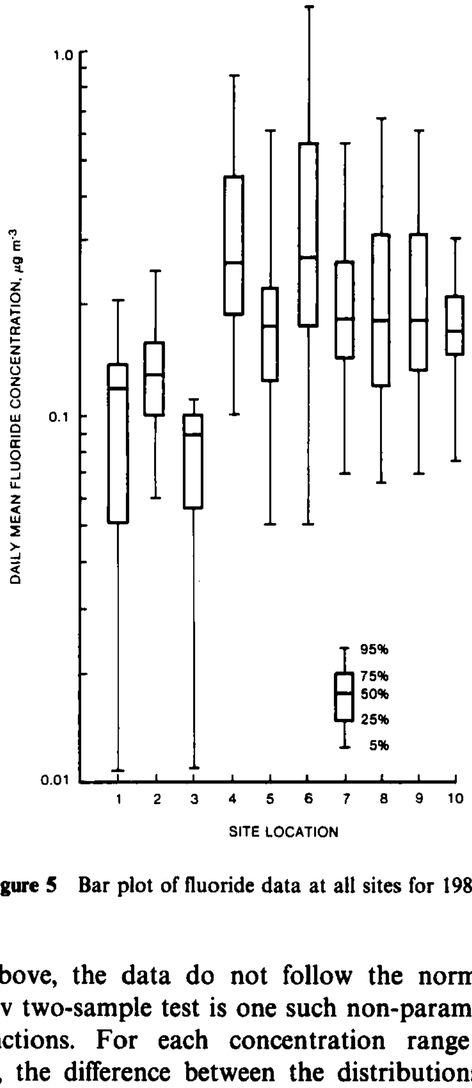

Figure 5 Bar plot of fluoride data at all sites for 1985.

ate for, as shown above, the data do not follow the normal distribution. The Kolmogorov–Smirnov two-sample test is one such non-parametric test for examining distribution functions. For each concentration range in the cumulative distribution function, the difference between the distributions for data from two sites is calculated. The absolute value of the differences so obtained are compared with one another and the greatest absolute value is chosen as the test statistic for the two sided version of the test. This test statistic is then compared with a theoretical test statistic for a particular probability. If the theoretical statistic is exceeded, the null hypothesis (that the distributions are the same at all concentration ranges) is rejected at the given probability. Table 3 presents the application of the test to sites in the present study. This demonstrates that there is no significant difference between the data distributions for sites 5 and 7, 8 and 9, and 4 and 6, whereas all of the other paired comparisons show significant differences at the 0.01 level. In particular it is noted that sites 1 and 3 are from different distributions, despite the apparent grouping together indicated in Figure 5. No doubt the distribution for site 3 represents the background, while that for site 1

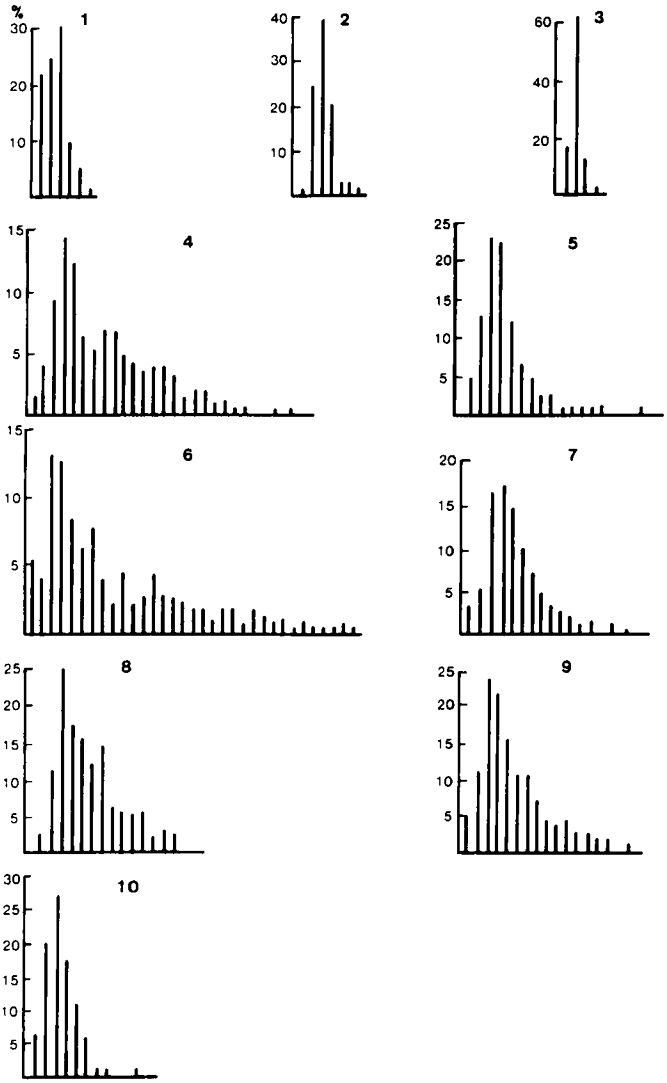

Figure 6 Frequency distributions of fluoride concentrations at each site. Each bar represents an increment of 0.05 $\mu g/m^3$.

had the relatively small influence of the brickworks superimposed. Further significant differences are apparent between sites and 1 and 10 and 2 and 8, despite the sites being at respectively similar distances from the source. In both cases the dominant effect of the prevailing wind is implicated.

Seasonal Variations

The monthly arithmetic mean values for each site (Table 4) showed that in general

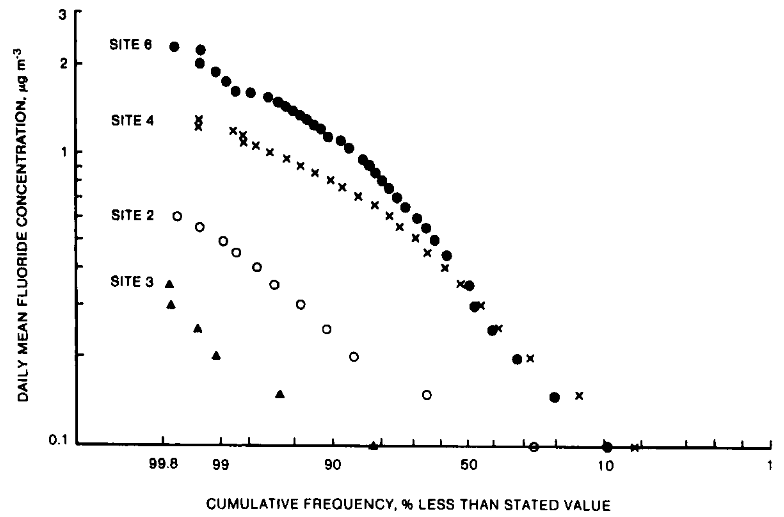

Figure 7 Cumulative probability distribution curves for fluoride concentrations.

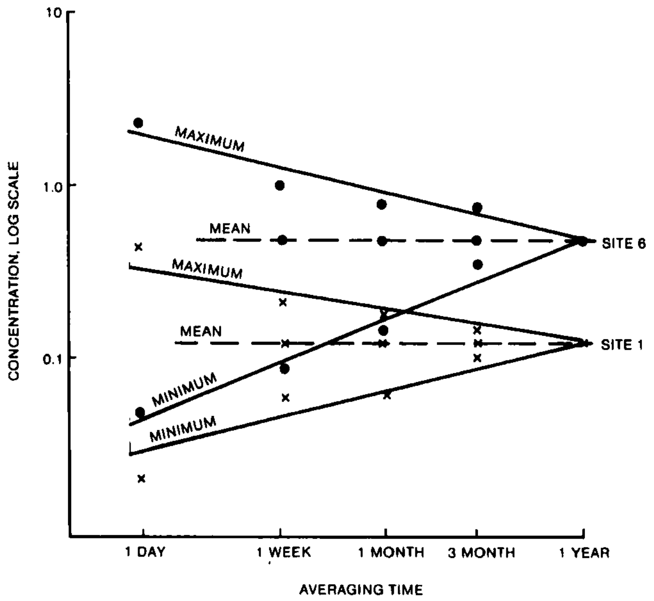

Figure 8 Averaging time model for fluoride air quality data at sites 1 and 6 for 1985.

Table 2 Correlation matrix for all data at all sites

	1	2	3	4	5	6	7	8	1
1	1								
2	0.02	1							
3	0.28	−0.04	1						
4	0.09	−0.02	0.02	1					
5	−0.12	0.23	0.07	0.03	1				
6	−0.16	−0.05	−0.15	0.21	0.002	1			
7	−0.04	0.003	−0.05	0.20	−0.005	0.44	1		
8	−0.19	−0.02	−0.06	0.19	0.14	0.58	0.31	1	
9	−0.16	−0.07	−0.07	0.19	0.13	0.53	0.32	0.75	1
10	−0.17	−0.05	0.02	0.07	0.13	0.16	0.10	0.48	0.51

Table 3 Kolmogorov–Smirnov two group test summary; data for 1985

Sites compared	*Test statistic*	*Critical level*	
		at 0.05 level	*at 0.01 level*
1 and 3	0.3205	0.1007	0.1240
1 and 10	0.5188	0.1013	0.1251
2 and 3	0.5412	0.1013	0.1251
2 and 8	0.3280	0.1062	0.1312
3 and 10	0.7297	0.1012	0.1251
4 and 6	0.1257	0.1279	0.1580
5 and 7	0.0972	0.1025	0.1266
6 and 5	0.1769	0.1162	0.1435
8 and 9	0.0629	0.1079	0.1332

Table 4 Monthly mean atmospheric concentrations at each site. (Concentration $\mu g/m^3$)

Site	*Mean monthly mean*	*Range*	*Date of maximum*	*Date of minimum*
1	0.13	0.0 –0.27	May 1986	Feb. 1985
2	0.17	0.09–0.86[a]	Oct. 1986	May 1986
3	0.07	0.04–0.11	July 1985	July/Aug. 1986
4	0.39	0.14–0.78	July 1985	Feb. 1986
5	0.24	0.10–0.65	Nov. 1985	Feb. 1986
6	0.43	0.16–0.85	Oct. 1984	Feb. 1986
7	0.25	0.12–0.37	Oct. 1984/Sept. 1985	Feb. 1986
8	0.27	0.12–0.47	Oct. 1984	Feb. 1986/Sept. 1980
9	0.25	0.11–0.39	Aug. 1985	May 1985
10	0.17	0.10−0.26	Mar. 1986/Sept. 1986	Apr. 1986

[a] An anomalously high monthly mean of 0.86 $\mu g/m^3$ was due to 5 unusually high daily values. Unusual activity near the site or contamination of the sample between collection and analysis are possible explanations. The mean and range excluding these values are 0.14 $\mu g/m^3$ and 0.09–0.2 $\mu g/m^3$ with the new maximum occurring in May 1985.

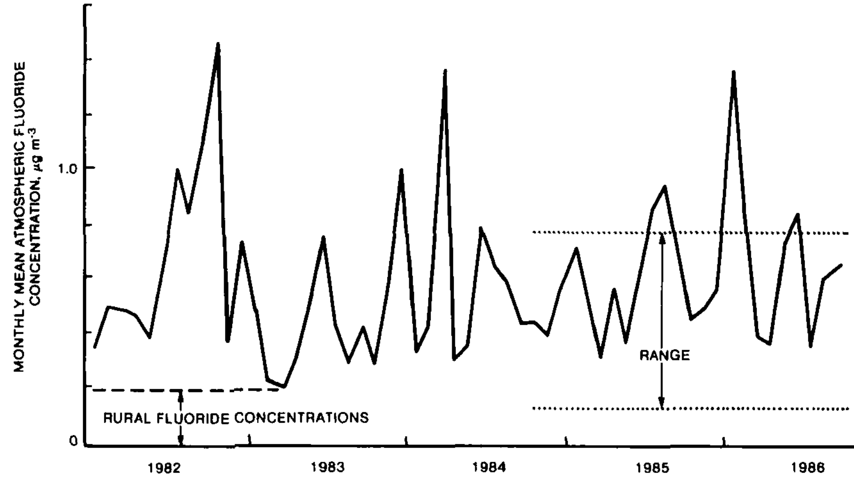

Figure 9 Monthly mean fluoride concentrations measured in bubbler samples from site 4 since 1982. The range of concentrations at site 4 in the present survey is shown for comparison.

the differences between sites were relatively small compared with ranges at individual sites. The greatest variations occurred at site 6 with a spread of almost 0.7 µg/m^3 between the highest range of 0.16 µg/m^3 and 0.85 µg/m^3; by comparison the least variation was at site 3 with a range from 0.04 to 0.11 µg/m^3. No marked seasonal pattern was found although the minimum value occurred in February at half of the sites (sites 1, 4, 5, 6, 7 and 8) which will be noticed as predominantly those showing the highest concentrations. By comparison, half of the sites (2, 5, 6, 7 and 8) showed maxima in the autumn.

It is believed that the scale of daily variation in concentrations was greater than any seasonal trend that may be present, and consequently a much larger monitoring programme would be needed to detect any meaningful pattern. Bubbler measurements made at site 4 since 1982 and described in a previous publication[3] provide a long observation period at one site, but no marked seasonal pattern is evident as can be seen from Figure 9.

POLLUTION CONTOURS

A map of the distributions of annual mean atmospheric concentrations was drawn by calculating concentrations for locations at a range of compass bearings where data were not obtained directly. These calculations produced a circle of mean concentrations around the brickworks based on each of the ten monitoring sites. The data were obtained by modifying the measured pollution rose for each site to take account of the different proportion of time that the wind blew from the works at the appropriate compass bearing. The resulting value was adjusted by a factor to account for the windspeed/stability differences mentioned previously. The mean concentrations for sites at similar distances from the works were combined at an

Figure 10 Contour map of airborne fluoride concentrations calculated by interpolation from sampling station data.

average distance, while values at intermediate distances were obtained by interpolation. The results of this analysis are shown in Figure 10 as as contour map. The predominantly SW-NE distribution of sampling stations limits adequate definition of concentrations to the NW and SE of the area. In general, however, independent mapping by the participating laboratories in this study confirmed the pattern presented. This spatial pattern is very much as expected in the original establishment of the networks, and earlier modelling studies such as that reported by the Department of the Environment[2] are in accord with the present data. A particularly important feature of the present study, however, is that it is the first time that measured atmospheric fluoride concentrations have been reported for a large part of the Marston Vale.

Trends and Standards

The data from the bubbler which had been in operation at site 4 since 1982 are shown in Figure 9, which also includes a band indicating the range of monthly means at this site as measured in the current programme. It is apparent that

Table 5 Typical ambient air quality standards for fluoride

Region	*Atmospheric fluoride concentration* ($\mu g/m^3$)		
	Daily mean	*Monthly mean*	*Annual mean*
Belgium	4[a]	–	2
West-Germany	10	–	5
Italy	20	–	–
Netherlands	10	–	–
Washington State, USA	–	8.4	–
Kentucky State, USA		0.82	
Hungary	20		
Maryland State, USA	0.02		

[a] Not to be exceeded on more than 8 days in one year, nor on 2 consecutive days.

concentrations at site 4 have shown no marked trend over the years. As the site is downwind of and close to the Stewartby brickworks it will clearly be influenced predominantly by this source. However, other brickworks formerly in the Marston Vale have closed and been demolished, and to detect any effects of this it is necessary to consider data from the other sites.

Previous measurements of fluoride concentrations in the Vale[2] have reported values ranging from 0.2 to 13.3 $\mu g/m^3$. The maximum monthly mean value in the present study was 0.86 $\mu g/m^3$ at site 2, closely followed by a value of 0.85 at site 6. These data broadly suggest a general reduction in fluoride levels. The plot of contour levels of annual mean concentrations is shown in Figure 10. By referring to this it will be seen that the 0.2 $\mu g/m^3$ contour includes Kempston and the southern suburbs of Bedford, much as the previous model study reported.[2] However, to the SW of the brickworks there are significant changes. The high concentrations near site 1 were neither measured nor calculated in the present study and this reflects the closure of a brickworks formerly near site 1. The 0.2 $\mu g/m^3$ contour is now calculated to occur within 1 km of the SW side of the works, instead of 11 km reported previously.[2] Likewise, on the NE side of the works the 0.5 $\mu g/m^3$ contour is calculated to be less than 1 km from the works instead of the previous 3 km distance. Overall, the results indicate that there has been a general decline in exposure to fluoride through the Vale, although the change to the NE side of the works is less marked. The levels measured remain rather higher than values reported from rural areas (Figure 9), but are considerably lower than values reported for other areas close to identified sources of fluoride. The concentrations are comparable to urban values reported elsewhere.[4]

In the context of compliance with air quality standards for fluoride, some values applicable in various countries are given in Table 5. All of the European standards were met in full over the two-year period, with only 2% of the daily measurements exceeding 2 $\mu g/m^3$. Only three of the 240 monthly mean concentrations equalled or exceeded the 0.82 $\mu g/m^3$ standard applicable in Kentucky State. The standard of Maryland State appears to be very much lower than data reported for UK sites.[4]

Biersteker *et al.*[5] estimate that a maximum daily fluoride concentration in air of 3 $\mu g/m^3$ around an aluminium works contributed to a maximum daily intake of 0.06 mg F/day. This is small compared with the average UK dietary intake of 1.8 mg F/day estimated many years ago[6] before fluoridation of water, but allowing for the high consumption of tea. Clearly, the contribution from the atmosphere in the Marston Vale to human intake is likely to be much lower than these levels.

Fluoride is, of course, a phytotoxic pollutant, and is also potentially significant in terms of its accumulation in herbage and subsequent intake by grazing livestock. The interrelationships between the presently reported atmospheric levels and those in herbage will be discussed in Part III of this series.

Acknowledgements

The authors gratefully acknowledge financial support for this programme from the Fletton Brickworks Liaison Committee. The analytical work of R. Duffy and site support by local authority staff are also recorded with thanks.

References

1. "96th Annual Report on Alkali Works for 1959," HMSO, London, 1960.
2. "Air Pollution in the Bedfordshire Brickfields." Report 6/80, Department of the Environment, London, 1980.
3. E. R. Clark, P. C. Robins, J. G. Irwin and R. S. Barratt, *Intern. J. Environ. Anal. Chem.* **39** (1990) 223–237.
4. A. J. Bennett and R. S. Barratt, *Roy. Soc. Health J.* **100** (1980) 86–89.
5. K. Biersteker, R. L. Zielhuis, O. Backer Dirks, P. Van Leeuwen and A. Van Ray, *Environ. Res.* **13** (1977) 129–134.
6. J. Longwell, *Roy. Soc. Health J.* **77** (1957) 361–370.