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**Monitoring Concentrations and Dry Deposition
of Sulphur Dioxide in The United Kingdom**

**Outline of the Contract Report to the
Department of the Environment**

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Introduction

The operation of UK rural monitoring network for SO₂ has continued for a further 3 years. NETCEN have continued to operate the UK network of rural SO₂ monitoring stations including 32 bubbler sites (providing daily SO₂ concentrations) and 5 continuous (hourly average) SO₂ monitoring stations using UVF methods. Monthly and annual SO₂ concentration fields have been provided by NETCEN for use in the ITE process-based SO₂ dry deposition model for the UK which provides inputs for the major land classes within each 20 x 20 km grid square of the UK.

The SO₂ dry deposition monitoring station for long-term validation of the dry deposition model over an agricultural landscape in Nottinghamshire has continued to provide continuous flux measurements. These data have been supplemented by data for an additional dry deposition monitoring station set up in 1994 under the EU LIFE programme at Auchencorth Moss near the ITE Edinburgh Research Station.

The estimates of dry (and wet) deposition from models can be validated using catchment hydrochemical budget for a range of UK sites. These include Beacon Hill in the East Midlands and Plynlimon and Llyn Brianne in central Wales.

Dry deposition inputs of SO₂ have been provided to the critical loads mapping centre and to the user community.

The reduction in SO₂ emissions over the past 10 years have been reflected in the SO₂ concentrations and deposition measurements. However the decline is non-linear, i.e. SO₂ concentrations and dry deposition in areas close to emission sources have shown a large decline in the rainfall concentration and wet deposition of S in areas remote from sources.

Objectives

- To provide monthly and annual SO₂ concentration and dry deposition estimates at 10 km by 10 km scale.
- To make continuous measurements of SO₂ dry deposition at a monitoring station in Nottinghamshire. As well as providing long term dry deposition measurements, this site will provide valuable information of the effects of the FGD equipment recently installed at Ratcliffe power station (6 km N of our monitoring station).
- To validate dry and wet deposition model estimates against catchment hydrochemical budgets for a range of UK sites. (Beacon Hill East Midlands, Plynlimon and Llyn Brianne in Central Wales.)
- To develop dry deposition estimates over large areas of Northern Europe based on monitoring networks in The Netherlands, Germany the UK, Denmark and Sweden in collaboration with the RIVM (Bilthoven) and IVL (Gothenburg).
- To compile and examine all existing rural UK SO₂ concentration measurements for the period 1970 to 1994 for evidence of changes in rural (and sub-urban) concentrations. In addition, these data, with existing rural and urban measurements and maps will be used to advise the Department of the Environment on the optimum density of monitoring stations.

Results

SO₂ concentrations and maps

Annual maps for SO₂ concentrations have been provided by NETCEN as part of this contract for the years 1994 and 1995. These have been used to model UK dry deposition at 20 km x 20 km resolution. The underlying methodology for concentrations and deposition is described in the recent CLAG fluxes subgroup report. The maps produced are averaged over the years 1992 to 1994 to reduce the influence of inter-year differences in meteorology and yet produce an up-to-date summary of the deposition climate.

The current network of approximately 40 sites with SO₂ monitors provides a concentration field using kriging methods. Such a network is not adequate to provide 10 km x 10 km resolution. Even with 20 km x 20 km resolution each monitor represents 600,000 ha of land area. The magnitude of variability in fine scale SO₂ concentration (e.g. 1 km x 1 km) is probably similar to those for SO₂ since both gases are deposited at terrestrial surfaces at smaller rates and both show pronounced chemical variations. Much of the systematic variability in SO₂ concentration could probably be simulated but the underpinning mechanistic studies and modelling have not been done.

Smith *et al.* (1995) estimated the fine scale variability in SO₂ deposition at some representative UK sites for illustrative purposes only. These estimates showed that in the polluted regions (e.g. E. Midlands) that local fine scale variability in deposition was mainly caused by variability in ambient SO₂ concentrations.

Dry deposition measurements

Two sites have been developed to monitor SO₂ deposition in the UK. The first at Sutton Bonington has operated almost continuously since spring 1993. Ambient SO₂ concentrations, even in this polluted region of the UK are small, typically 3 ppb SO₂ and have declined substantially since the mid 1980s.

Figure 1

MTHMED.XLS Chart 5

Monthly median SO2 concentrations Sutton Bonington 1993-1996

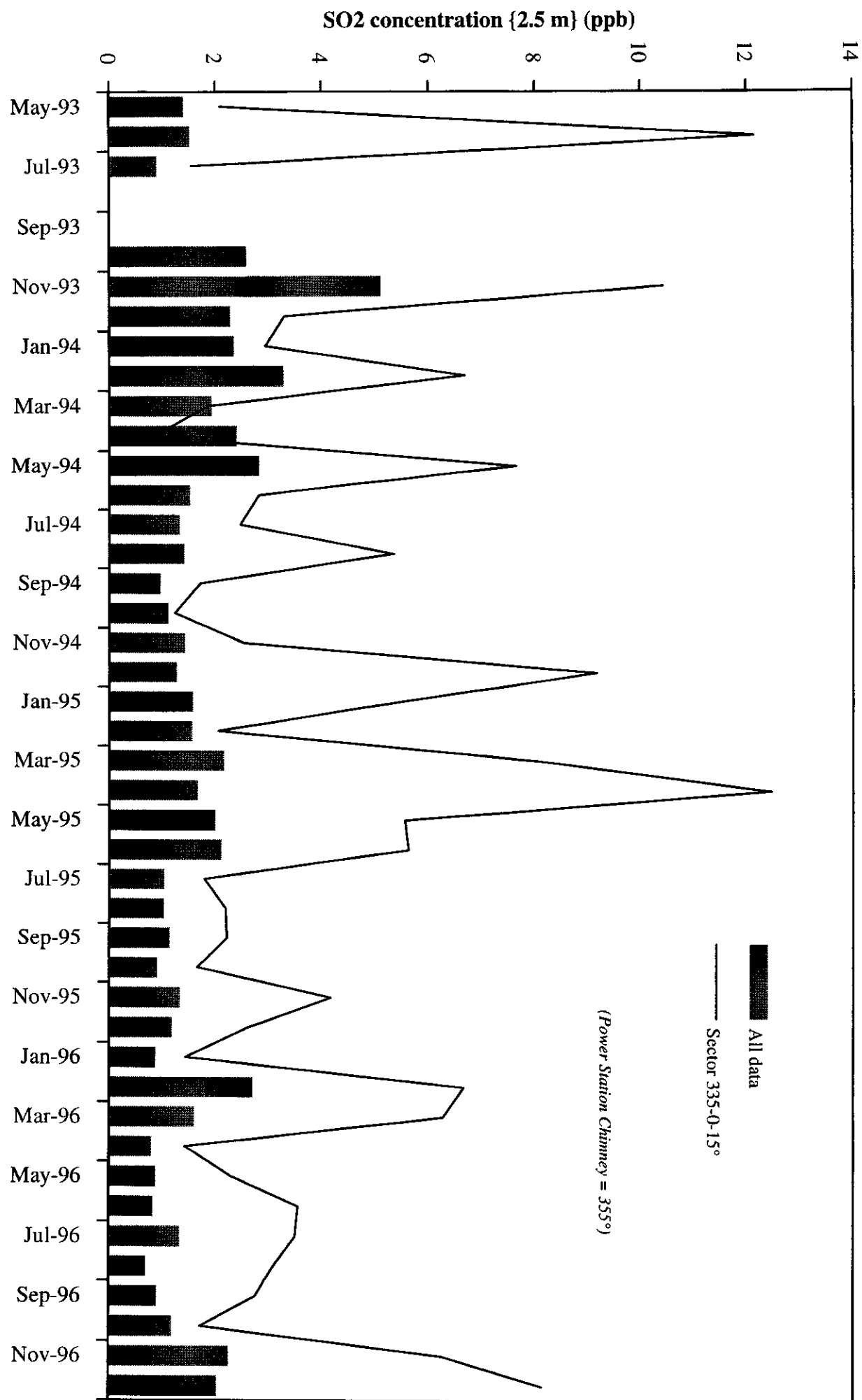


Figure 2

Wind direction dependence of SO₂ concentration {2.5m} (ppb) at Sutton Bonington 1993-96 (averages)

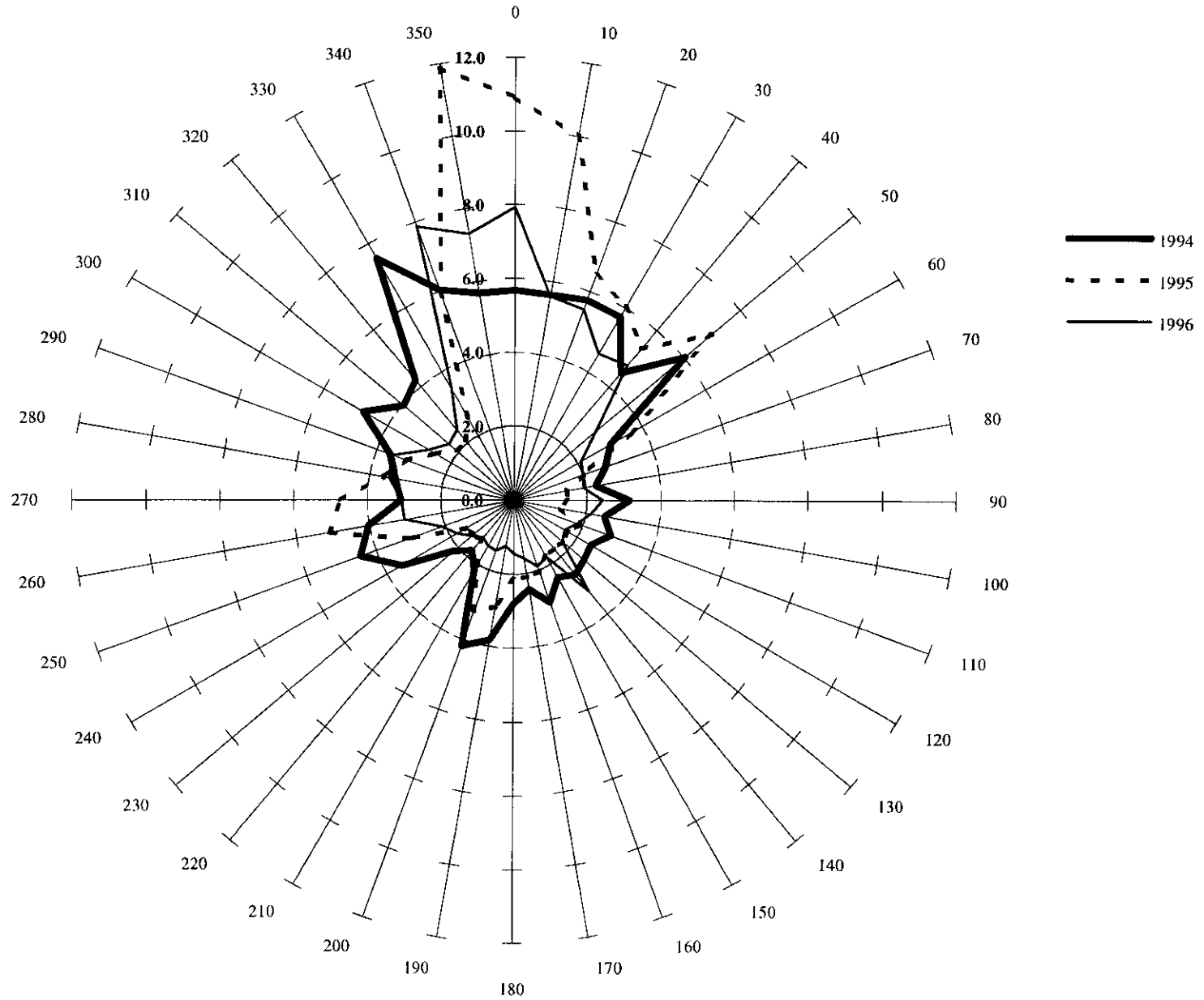


Figure 3

Frequency distributions of wind direction at Sutton Bonington 1993-96

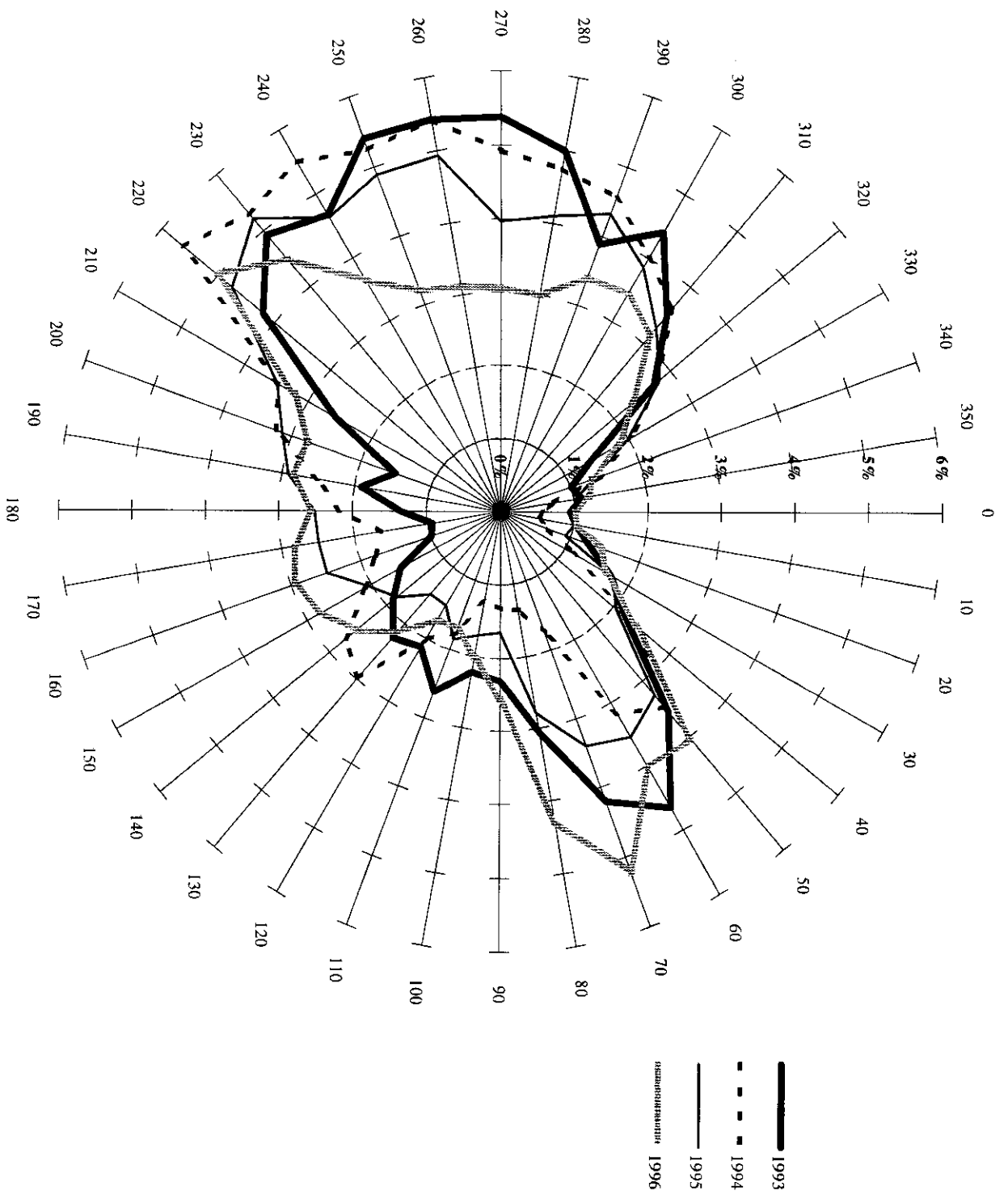
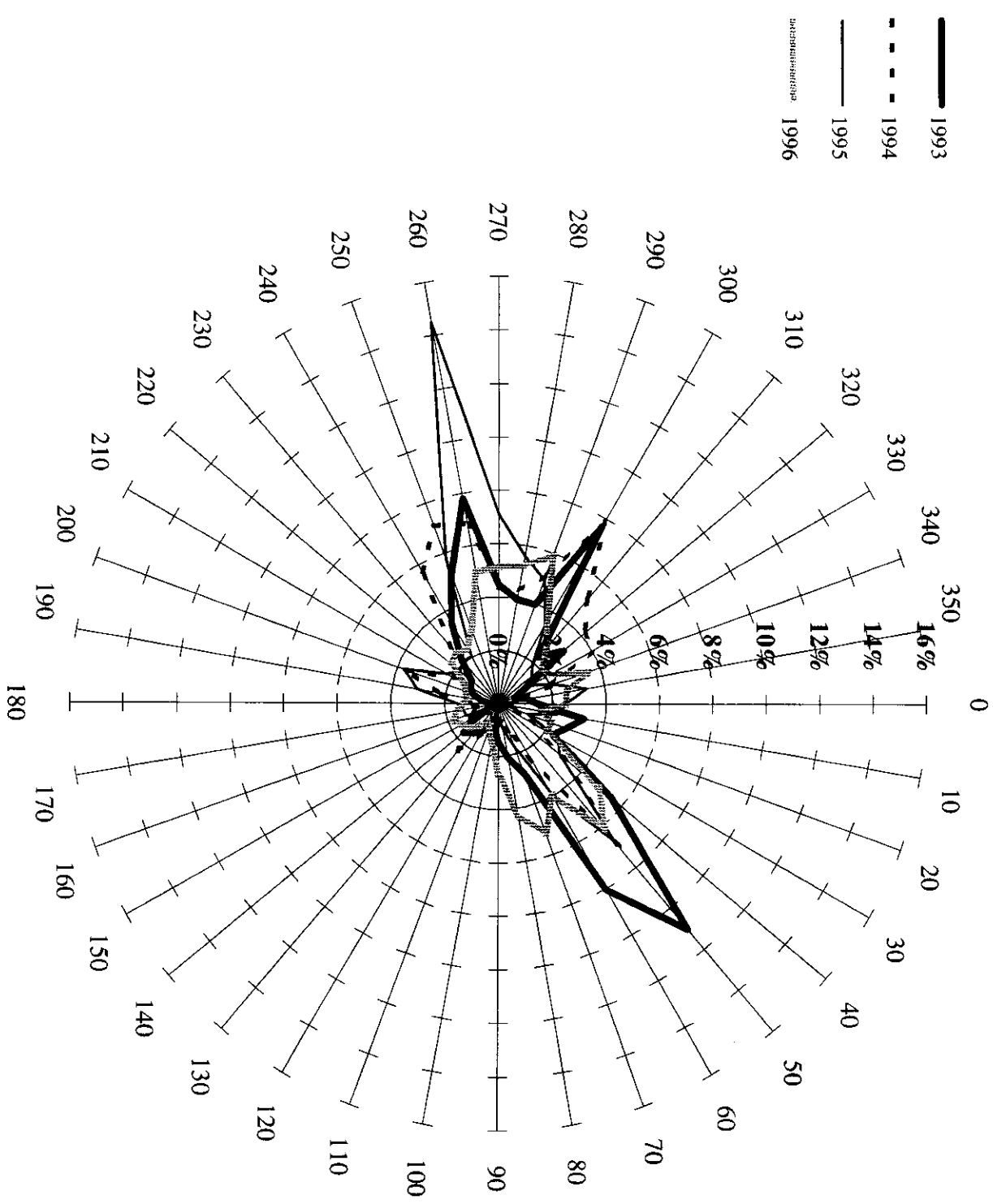


Figure 4

Contributions of the 36 (10°) wind direction sectors to the SO₂ advection fluxes over Sutton Bonington 1993-96



The data for Sutton Bonington are illustrated in Figure 1 which includes the monthly median concentrations for the 4 years as a time series. Also included on the Figure is a sub-set of the data for the sector which winds from a northerly point (335° to 15°) in which the Ratcliffe Power Station stack is located at a distance of 5 km.

The concentrations with Ratcliffe Power Station upwind are larger, typically 5 to 12 ppb when averaged over the month.

The large variability in concentrations with wind direction is illustrated in Figure 2 which shows that the largest concentrations occur with northerly winds and that the three years 1994, 1995 and 1996 are very similar. It is important however to show the frequency distribution of the wind direction (Figure 3), which shows the dominance of westerlies and that the northerly winds are uncommon (1% to 2% of the time only). Taking wind direction and SO_2 concentration together the advected flow of SO_2 over the monitoring station may be readily calculated. The analysis (Figure 4) shows that westerly and easterly winds dominate the SO_2 concentrations at the site with northerlies providing only 3% of the SO_2 .

The concentrations and fluxes were monitored continuously and achieved 95% and 50% data capture respectively. While the monitoring equipment operates reliably and is frequently calibrated and subject to zero checks, the meteorological conditions and state of the field crops reduce the scope for satisfactory flux measurement. Nevertheless the 50% data capture covers almost the full range of atmospheric and surface conditions and allows testing and development of the model. A summary of the flux measurements is provided as Fig. 5 which shows an average deposition velocity of 5 mm s^{-1} , above 40% of V_{max} . The canopy resistance averages 126 s m^{-1} .

A time series of the data on fluxes shows over the 4-year period, quite small variations in deposition velocity relative to the shorter term variations (Figure 6).

The monthly averaged fluxes of SO_2 show a clear diurnal cycle with daytime maxima at typically 100 to $150 \text{ ng SO}_2 \text{ m}^{-2} \text{ s}^{-1}$ and nocturnal values of 20 to $30 \text{ ng SO}_2 \text{ m}^{-2} \text{ s}^{-1}$ (Figure 7).

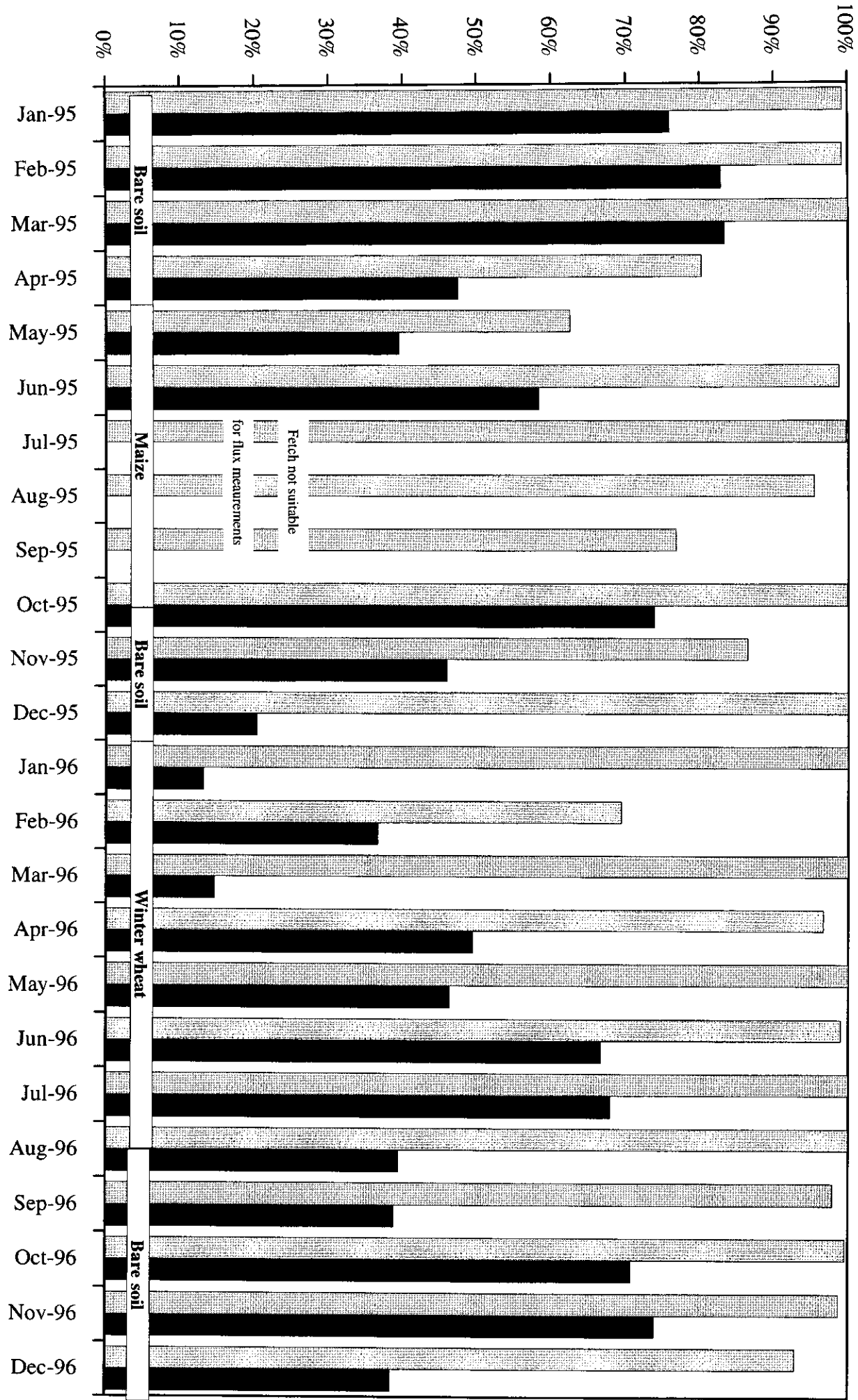
FIG. 5 ; Summary table of measured SO2 fluxes over agricultural land at Sutton Bonington for the period Jan-95 to Dec-96

Sutton Bonington	<i>N fluxes</i>	<i>% data capture</i>	<i>N concentr.</i>	<i>% data capture</i>	<i>RaH(1m) (s m-)</i>	<i>Rb SO2 (s m-1)</i>	<i>Flux SO2 (ng m-2 s-1)</i>	<i>SO2(1m) (ug m-3)</i>	<i>Vd mm s-1</i>	<i>Vmax mm s-1</i>	<i>Rc s m-1</i>
Jan-95	1130	76%	1478	99%	53.4	16.9	-41.37	3.73	11.1	14.2	20
Feb-95	1114	83%	1334	99%	48.0	16.4	-36.53	3.87	9.4	15.5	41
Mar-95	1240	83%	1488	100%	52.2	15.8	-31.39	5.50	5.7	14.7	107
Apr-95	683	47%	1155	80%	70.4	19.5	-32.21	3.84	8.4	11.1	29
May-95	586	39%	929	62%	60.7	22.9	-45.81	4.86	9.4	12.0	22
Jun-95	840	58%	1423	99%	47.4	25.2	-34.98	5.27	6.6	13.8	78
Jul-95	#N/A	#N/A	1484	100%	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Aug-95	#N/A	#N/A	1420	95%	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Sep-95	#N/A	#N/A	1105	77%	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Oct-95	1098	74%	1487	100%	63.9	24.3	-8.21	2.38	3.5	11.3	202
Nov-95	661	46%	1244	86%	72.3	21.7	-13.08	3.26	4.0	10.6	155
Dec-95	303	20%	1488	100%	59.7	25.7	-6.62	2.92	2.3	11.7	356
Jan-96	196	13%	1488	100%	29.6	20.3	-5.33	2.27	2.3	20.1	377
Feb-96	510	37%	965	69%	54.8	18.9	-26.73	6.64	4.0	13.6	175
Mar-96	218	15%	1488	100%	49.6	23.7	-15.44	4.04	3.8	13.6	188
Apr-96	712	49%	1392	97%	63.4	23.5	-2.56	2.09	1.2	11.5	728
May-96	689	46%	1488	100%	37.9	23.4	-6.86	2.19	3.1	16.3	258
Jun-96	959	67%	1426	99%	44.8	33.5	-5.85	2.11	2.8	12.8	283
Jul-96	1010	68%	1488	100%	41.6	29.2	-20.90	3.54	5.9	14.1	99
Aug-96	586	39%	1488	100%	46.9	30.1	-5.03	2.19	2.3	13.0	359
Sep-96	559	39%	1410	98%	53.8	23.6	-6.68	2.34	2.8	12.9	273
Oct-96	1051	71%	1482	100%	60.6	18.7	-17.10	2.87	6.0	12.6	88
Nov-96	1063	74%	1422	99%	59.1	19.1	-28.74	5.60	5.1	12.8	117
Dec-96	571	38%	1381	93%	58.3	26.4	-3.74	5.31	0.7	11.8	1334
Total	15779	45%	32953	94%	59.1	19.7	-16.43	3.36	4.9	12.7	126

Figure 6

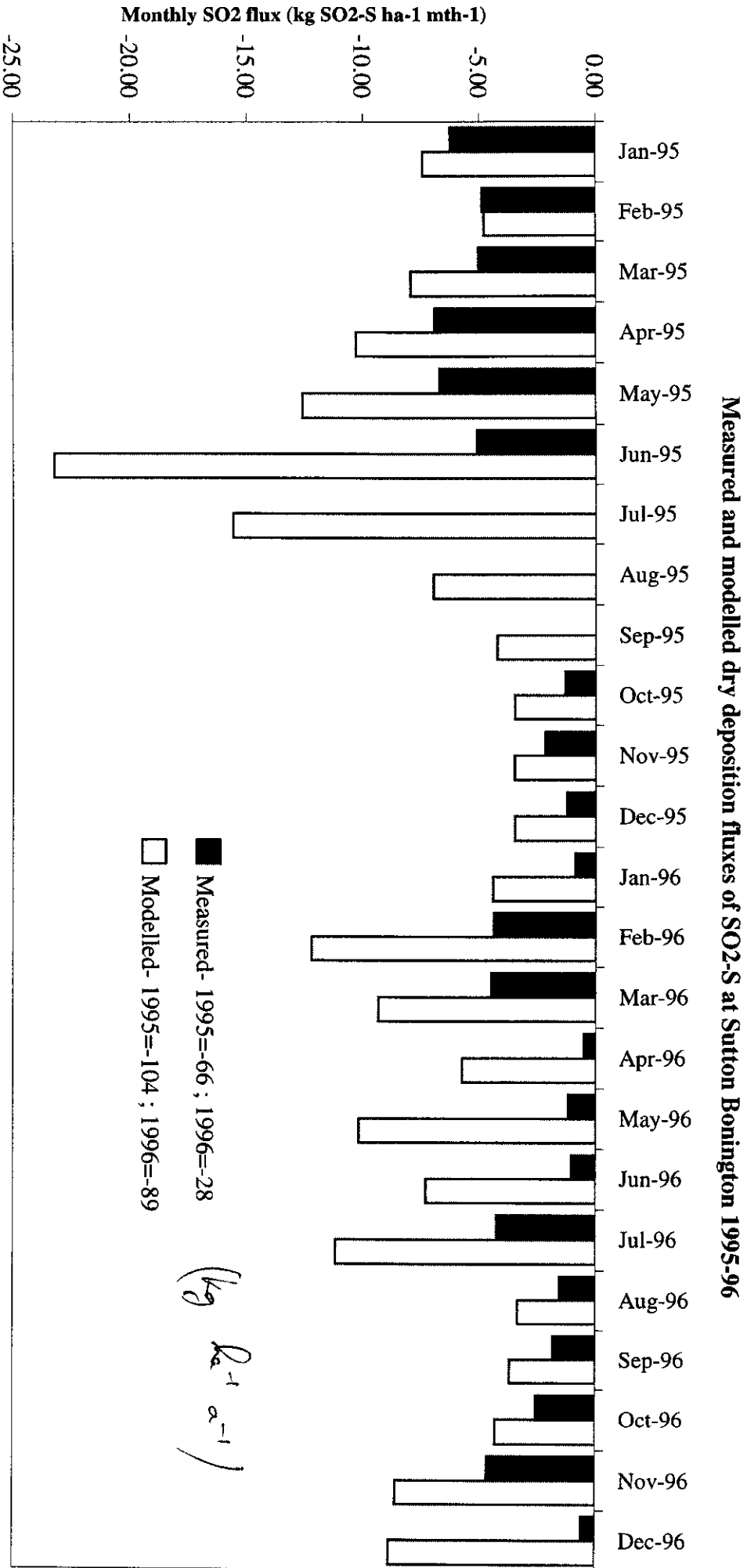
SMFL_9596.XLS Chart 9

Sutton Bonington data coverage 1995-1996



SO2 concentrations = 94%

SO2 fluxes = 45%



The data may be compared directly with the model used to calculate UK dry deposition. The comparison between measurement and model of monthly fluxes at Sutton Bonington shows (Figure 8) that the model over-estimates dry deposition, sometimes by a factor of 2 or more. The cause is the assumption of leaf surface uptake rates, simulated using a fixed canopy resistance component for dry and wet surfaces. The model can be modified to fit the data quite readily but more analysis of the data to understand the precise cause is necessary.

Auchencorth Moss

The site at an altitude of approximately 300 m contrasts with Sutton Bonington. The median concentration of SO₂ is 0.3 ppb and concentrations seldom exceed 10 ppb (0.2% time), (Figure 9 and Table 1). There are 3 distinct sources, the oil refinery at Grangemouth and Longannet Power Station some 60 km to the NW on a bearing of 310° (Figure 10) and the local urban areas of Edinburgh 25 km N and Penicuik to the east. The deposition velocity for SO₂ at Auchencorth moss is generally smaller than at Sutton Bonington and very much smaller than V_{max} (Figure 11). A summary of the data (Table 2) shows:

1. That despite being a windy upland site which is frequently wet with rain that deposition velocity is smaller than in the E. Midlands.
2. Mean deposition velocity is approx 3 mm s⁻¹ (*cf* 5 mm s⁻¹ at SB).
3. Aerodynamic resistances are smaller, as expected at the upland sites, 35 s m⁻¹ v 50 s m⁻¹ in agricultural lowlands of England.
4. Surface (or canopy) resistance at Auchencorth Moss is 300 to 600 s m⁻¹ about a factor of 2 larger than at SB.
5. The measured deposition SO₂ rate for uplands smaller than that used in the UK model.

	SO ₂			O ₃			NO			NO ₂			NH ₃		
N (1/2 hr)	17383	17382	17383	15794	15789	15790	17306	17300	17301	17066	17069	17058	11912	10462	12000
Average	1.00	0.92	0.86	26.38	25.34	24.58	0.35	0.34	0.35	3.11	3.04	2.98	1.59	1.39	1.14
Stdev	2.23	2.07	2.00	9.18	8.96	8.86	1.49	1.48	1.49	3.68	3.56	3.46	3.20	2.53	1.85
Median	0.34	0.32	0.30	26.81	25.78	25.06	0.09	0.09	0.09	1.83	1.81	1.79	0.73	0.68	0.57
Geomean	0.40	0.38	0.36	24.39	23.36	22.58	0.11	0.11	0.11	1.91	1.88	1.86	0.75	0.69	0.58
Geostdev	3.52	3.39	3.31	1.58	1.59	1.61	4.02	3.95	3.97	2.76	2.73	2.71	3.32	3.31	3.21

Table 1. Concentration data Auchencorth Moss January-December 1995. (in ppbv)

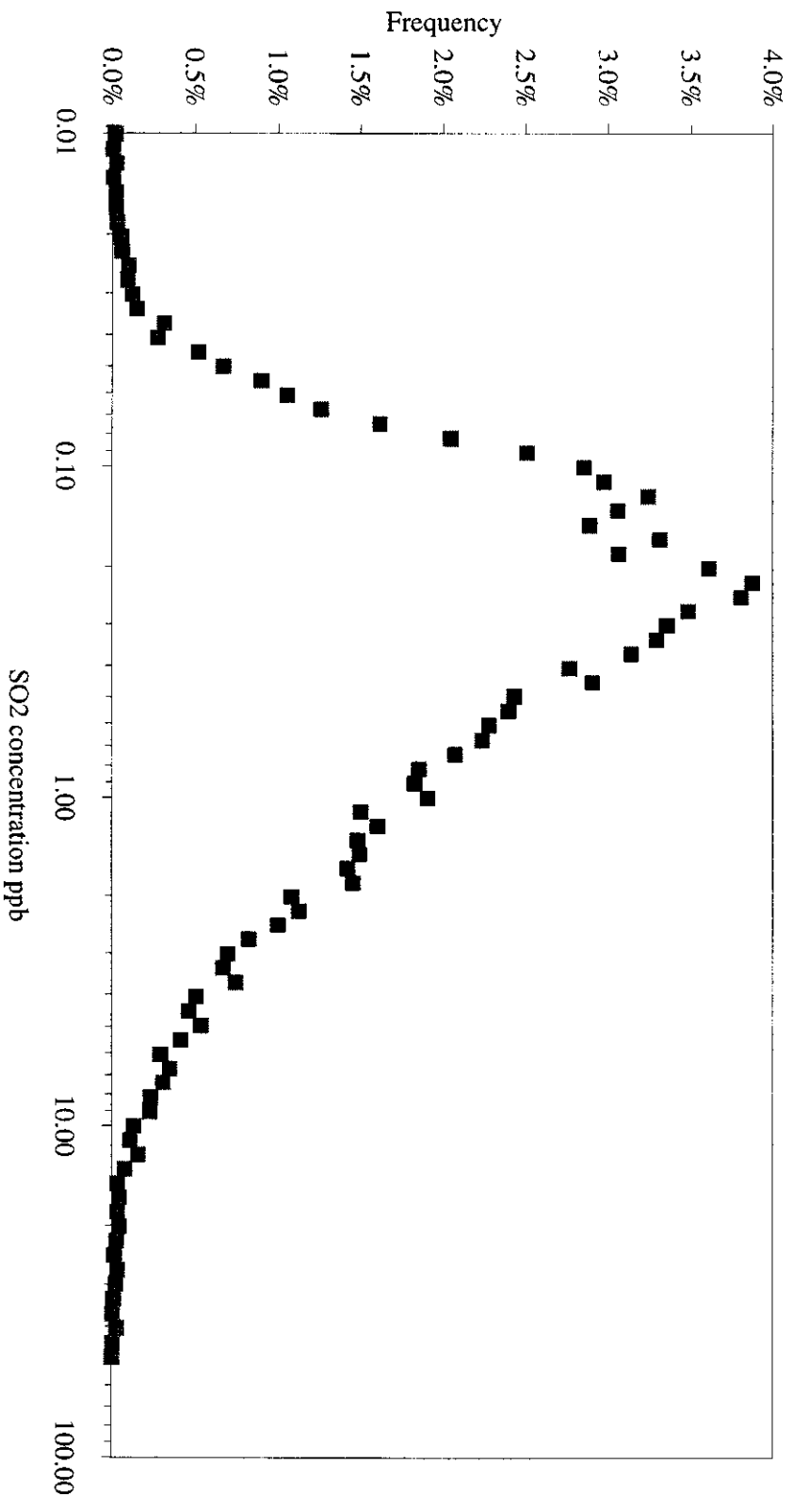


Figure 9. Frequency distribution of SO₂ concentration {Im.} Auchencorth Moss January-December 1995.

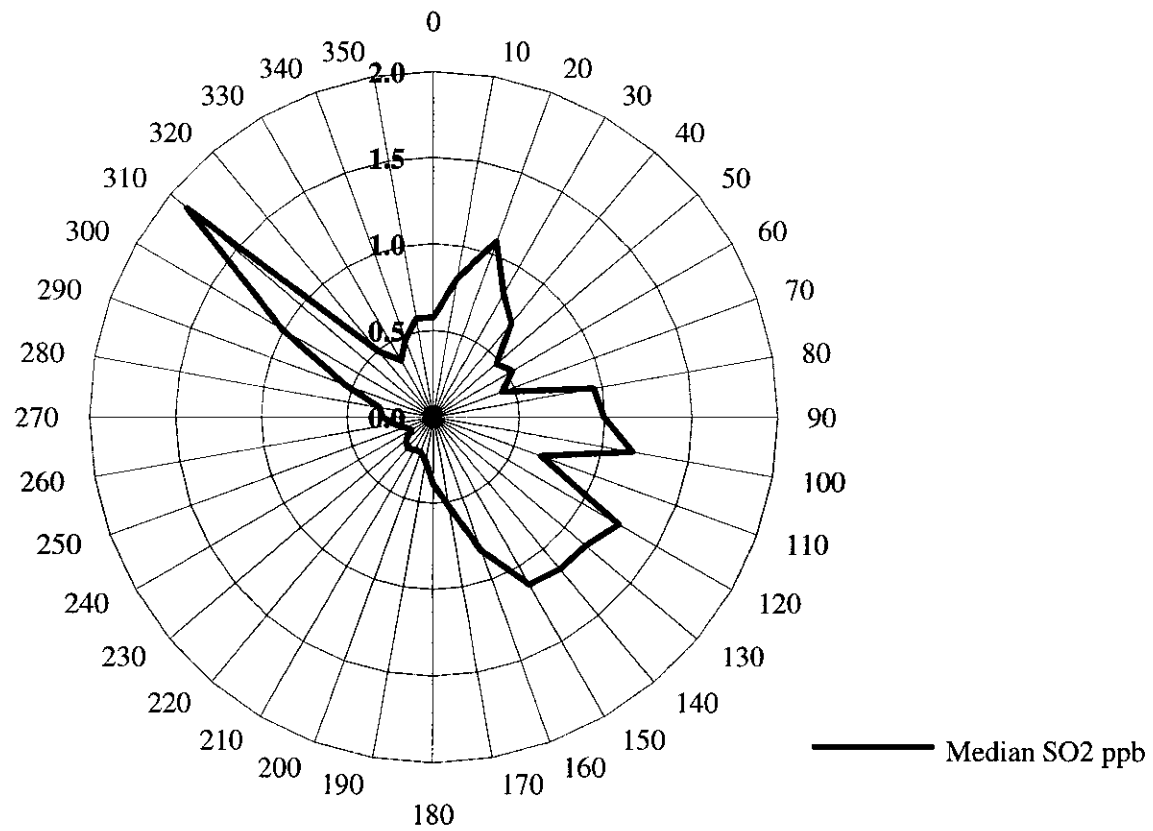
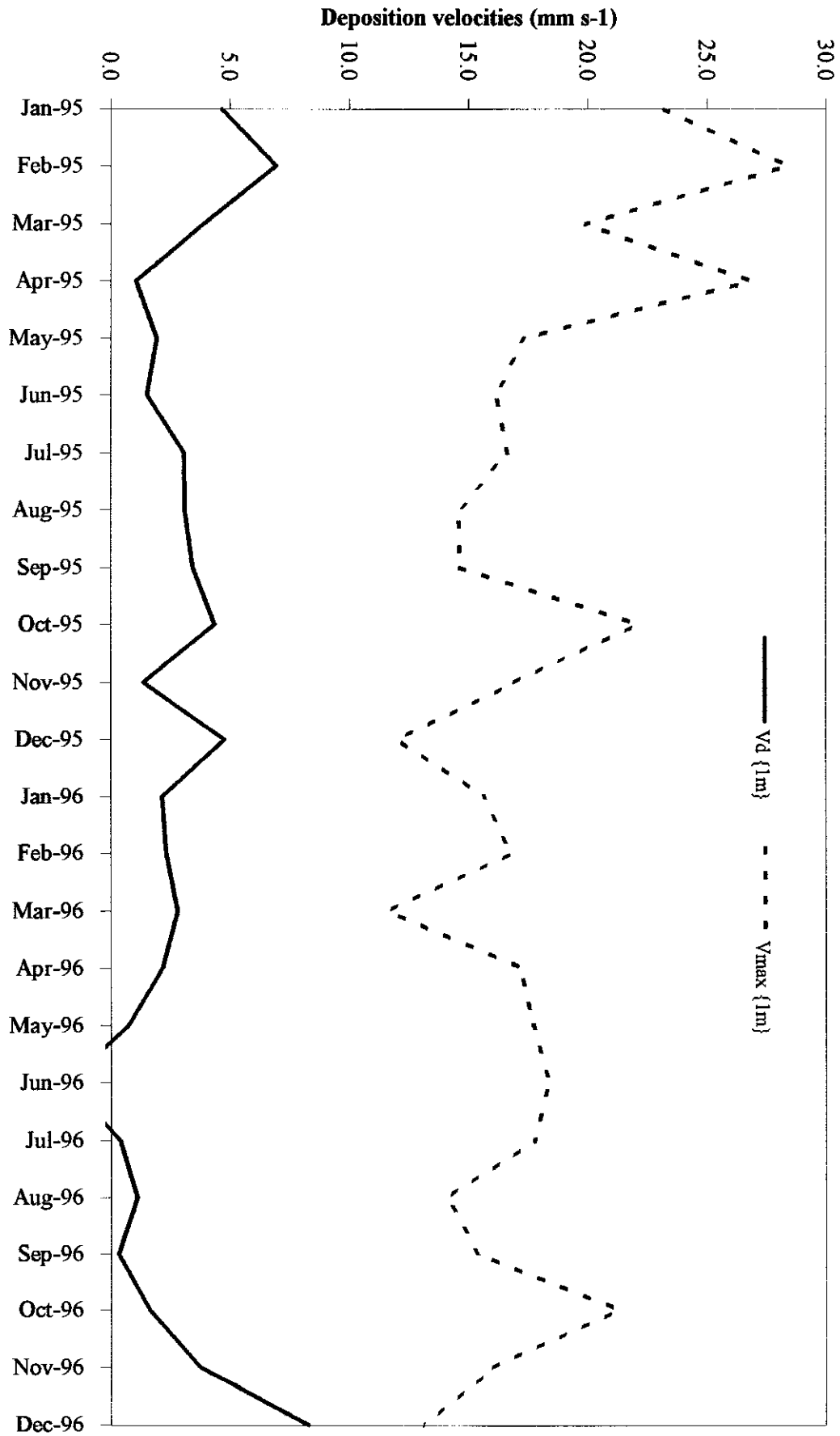


Fig 10. Sector dependence of SO₂ {1m.} Auchencorth Moss Jan-Dec 1995.

Figure 11



Monthly median deposition velocities for SO₂ at Auchencorth Moss 1995-96

Table 2

Summary table for SO ₂ dry deposition at Sutton Bonington and Auchencorth Moss 1995-96								
		RaH(1m) (s m-1)	Rb SO ₂ (s m-1)	Flux SO ₂ (ng m-2 s-1)	SO ₂ (1m) (ug m-3)	Vd mm s-1	Vmax mm s-1	Rc s m-1
Sutton	1995	56.7	20.7	-24.63	3.75	6.6	12.9	75
Bonington	1996	48.4	23.3	-10.01	3.00	3.3	13.9	228
Auchencorth	1995	36.9	18.4	-2.24	0.77	2.9	18.1	290
Moss	1996	40.9	19.9	-1.26	0.78	1.6	16.4	558

Publications

- Downing, C.E.H., Vincent, K.J., Campbell, G.W., Fowler, D. & Smith, R.I. 1995. Trends in wet and dry deposition of sulphur in the United Kingdom. *Water, Air and Soil Pollution*, **85**, 659-664.
- Flechar, C.R. & Fowler, D. 1996. Long-term measurements of dry deposition fluxes of SO₂ and O₃ in the Baixo Vouga estuary, Portugal, and Madrid, Spain. Surface Resistance Emergency programme (SREMP). February 1996. Commission of the European Communities.
- Fowler, D., Leith, I.D., Smith, R.I., Choularton, T.W., Inglis, D. & Campbell, G. 1995. Atmospheric inputs of acidity, sulphur and nitrogen in the UK. In: *Acid rain and its impact: the critical loads debate*, edited by R.W. Battarbee, 17-26, London: Ensis.
- Fowler, D., Fletchard, C.R., Milford, C., Hargreaves, K.J., Storeton-West, R.L., Nemitz, E. & Sutton, M.A. 1996. Measurements of pollutant concentrations and deposition fluxes to moorland at Auchencorth Moss in southern Scotland, 1995. April 1996. 47pp. Commission of the European Communities.
- Fowler, D., Fletchard, C., Storeton-West, R.L., Sutton, M.A., Hargreaves, K.J. & Smith, R.I. 1995. Long term measurements of SO₂ deposition over vegetation and soil and comparison with models. In: *Acid rain research: do we have enough answers?* edited by G.J. Heij & J.W. Erisman, 9-19, Amsterdam: Elsevier.
- Fowler, D., Fletchard, C., Storeton-West, R.L., Smith, R.I., Coyle, M., Campbell, G., Stedman, J., Downing, C. & Vincent, K. 1995. Operation and data assessment of rural sulphur dioxide dry deposition monitoring network. 68pp. Department of the Environment.
- Fowler, D., Smith, R.I., Coyle, M., Sutton, M.A., Campbell, G., Downing, C. & Vincent, K. 1997. Rural air pollution in the UK. In: *Air Pollution in the United Kingdom*, edited by C.N. Hewitt & G. Davison. Cambridge: Royal Society of Chemistry (In press).
- Nisbet, T.R., Fowler, D. & Smith, R.I. 1995. Use of the critical loads approach to quantify the impact of afforestation on surface water acidification. In: *Acid rain and its impact: the critical loads debate*, edited by R.W. Battarbee, 116-118. London: Ensis.
- Nisbet, T.R., Fowler, D. & Smith, R.I. 1995. An investigation of the impact of afforestation on stream-water chemistry in the Loch Dee catchment, SW Scotland. *Environmental Pollution*, **90**, 111-120.

Reynolds, B., Fowler, D., Smith, R.I. & Hall, J.R. 1995. Hydrochemical budgets for major ions in five Welsh upland catchments. In: *European Network of Catchments Organised for Research on Ecosystems (ENCORE)*. May 1995. 22pp. Commission of the European Communities.

Smith, R.I., Fowler, D. & Bull, K.R. 1995. Quantifying the scale dependence in estimates of wet and dry deposition and the implications for critical load exceedances. In: *Acid rain research: do we have enough answers?* edited by G.J. Heij & J.W. Erisman, 175-186. Amsterdam: Elsevier.