



Spatial variability of wet deposition in a rural upland area of England

D.W. Raper,^a D.S. Lee,^b J.W.S. Longhurst^a

^a*ARIC, Department of Environmental and Geographical Sciences, Manchester Metropolitan University, Manchester M1 5GD, UK*

^b*AEA Technology, National Environmental Technology Centre, Culham Laboratory, Oxfordshire OX14 3DB, UK*

Abstract

A network of 10 bulk precipitation collectors was established in an upland region of northern England to examine the small-scale variability of precipitation composition in a rural area. Significant spatial variability was shown for non sea-salt sulphate, calcium and hydrogen ion concentrations. Although nitrate concentrations did not show significant variability, a coherent gradient across the study area was observed. The large variability of calcium ion concentration across the area was related to limestone quarrying, which is prevalent in the south of the study area. Calcareous wind-blown soil may have also made a minor contribution to the abundance of calcium in the rainwater samples. It is likely, however, that a large fraction of the calcium was dry deposited to the funnels of the collectors in the form of particles. The network was not designed to study orographic enhancement of deposition, but it is suggested that this mechanism, along with wind-drift of scavenged cap-cloud droplets, cannot explain the spatial variation in ion concentrations. It is speculated that the variability in non sea-salt sulphate concentrations may also be partially explained by reaction of CaCO_3 particles deposited to the funnels of the collectors with SO_2 .

Introduction

The wet deposition of inorganic pollutants as a result of emissions of sulphur dioxide (SO_2), nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and ammonia (NH_3) is a process which is monitored on large scales across Europe, North America and many other regions where industrial emissions impact upon terrestrial and aquatic ecosystems (for example [1], [2], [3]). In the United Kingdom, the composition of rain water is currently monitored at 32 sites across the UK in order to characterise regional variation [4]. Quantification of wet and dry deposition is vital for the calculation of 'critical loads' [5], [6] and the validation of long-range transport models used in the formulation of policy for negotiation of emissions reductions at an international level.

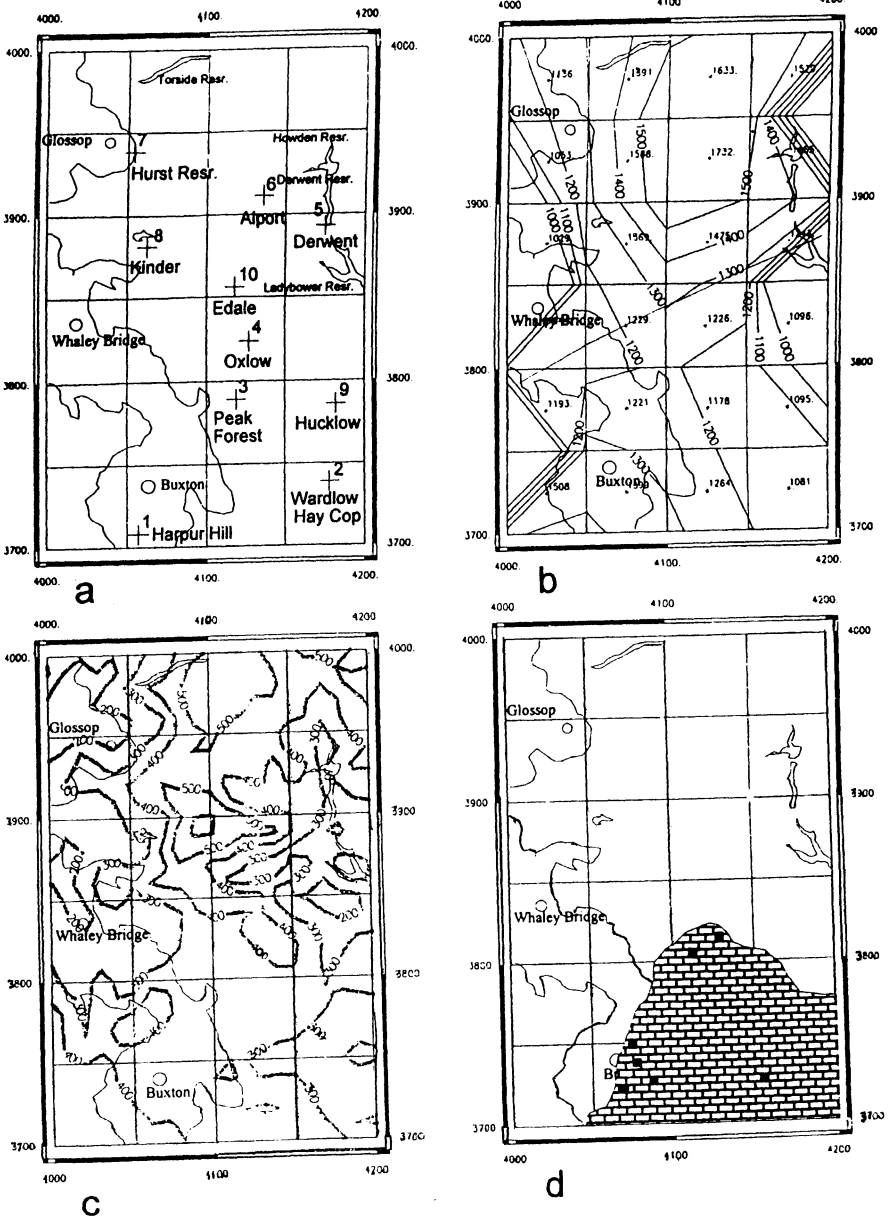
An assumption in the design of networks for the monitoring of precipitation composition is that the spacing between the sites at which measurements are made is small enough to characterise regional variations in composition, and that the interpolation of these measurements is a valid model. This is usually necessary for reasons of cost and practicality.

The above assumption gives rise to the practice of calculating deposition fields from interpolated measurements of rainfall amount made on a much finer scale (e.g. approximately 4000 sites in the UK) from larger scale measurements of precipitation



386 Air Pollution Monitoring, Simulation and Control

Figure 1. Location of sites (a), rainfall in mm on 5km grid (b), altitude in m from 1 km grid (c) and extent of limestone and locations of quarries (d)





Air Pollution Monitoring, Simulation and Control 387

composition which is thought to vary on a scale of tens to hundreds of kilometres in rural areas where topography does not influence wet deposition processes. Small-scale variability of precipitation composition has been shown in an urban area [7] but has not been subject to much investigation in rural areas, particularly in the UK.

Dry deposition, however, may vary on a relatively fine scale, according to meteorology and characteristics of the surface type, e.g. grassland, water, forest etc. For dry deposition fluxes of some gases in the UK, such as SO_2 , NO_2 and HNO_3 , it is possible to formulate complex process models using land-use and meteorological data which allow the quantification of fluxes on a scale as fine as 1 by 1 km. However, it is usually considered that the scale of the measurements of gaseous concentrations limit these calculations to a 20 km grid system in the UK [8]. Cloud- and fog-water deposition also varies on a fine scale, according to the extent to which it is formed, and can be treated in the same way as large particle deposition [9].

One process which has been demonstrated to modify wet deposition on a fine scale in upland environments is the 'seeder-feeder' process [10] whereby seeding precipitation scavenges cap-cloud, which frequently has large concentrations of ions, so that enhanced deposition at altitude occurs [11]. This process is now incorporated into mapping the deposition of inorganic ions in the UK by a simple parameterisation process [12].

Methods

Ten bulk deposition collectors were sited in the Peak District, at the southern end of the Pennine range of hills in central northern England according to the same siting criteria as those utilised in the UK Secondary Precipitation Composition Network [1]. The major land-uses of the study area are agriculture, forestry, mineral extraction and water collection. The area is flanked by the cities of Manchester to the west and Sheffield to the east. The precipitation composition network and features of rainfall, topography and locations of open-cast quarries are shown in Fig. 1. The altitude of the sites ranged from 280 - 435 m and cap cloud was observed at 4 sites (Harpur Hill (380 m), Wardlow Hay Cop (350 m), Oxlow House (435 m) and Hucklow (390 m). Samples were collected on a weekly basis over a period of 12 months in 1987.

The precipitation collectors were the same in design as those used in the UK Secondary Precipitation Composition Network, and are described by [13]. Essentially, they consist of an open polyethylene funnel connected to a polypropylene collection bottle at a height of 1.75 m above the ground. British Standard rain gauges were collocated with these collectors at all but one of the sites. Analytical protocols have been given in detail by [14].

All rain-water in the UK contains sulphate derived from sea-spray, the contribution of which has been calculated by assuming that all the sodium in rain-water is derived from the sea, and that the ratio of sodium to sulphate is the same in sea-water as it is in rain-water. The term 'non sea-salt' has been used in preference to 'non-marine', as some sulphate in rain-water will originate from dimethylsulphonisopropionate emissions from plankton, which cannot be discriminated on the basis of a sodium correction factor. Kriging was used for mapping of concentrations and deposition [15].

388 Air Pollution Monitoring, Simulation and Control

Results and discussion

Precipitation-weighted mean annual concentrations of the ions and annual deposition are given in Table 1. Precipitation weighted mean annual non sea-salt sulphate concentrations ranged between approximately 64 and 87 $\mu\text{eq l}^{-1}$. Nitrate concentrations ranged between 26 and 36 $\mu\text{eq l}^{-1}$. However, the ions which showed most variation were calcium (18 to 67 $\mu\text{eq l}^{-1}$) and hydrogen (15 to 47 $\mu\text{eq l}^{-1}$). The statistical significance of this variability was tested using a one-way analysis of variance test on log transformed data. The *F* ratios, given in Table 2 show that sulphate, non sea-salt sulphate, calcium and hydrogen ions came from different populations, which is taken to indicate statistically significant spatial variability. Concentration data are plotted as contour plots in Figs 2a-d and deposition in Figs 3a-d using the long-term (1941—1970) 5 km rainfall field and interpolated measurements of rainfall composition.

Table 1 Precipitation-weighted mean annual concentrations, year and site specific deposition and rainfall

		Concentrations									
		(ueq l ⁻¹)									
		H ⁺	SO ₄ ²⁻	nss SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	mm
1	Harpur Hill	36.3	92.3	84.3	35.8	76.6	50.7	10.6	1.9	38	880.6
2	Wardlow Hay Cop	35	89.2	80.6	37.9	79.2	67.5	12.3	2.2	41.9	895.5
		35		92	36	85	58	15	2	52	889
3	Peak Forest	15.1	88.9	79.7	32.1	82.3	67.7	12.8	2.9	49.6	973.6
4	Oxlow House	35.3	99.2	87.1	38.2	85.9	53.9	11.9	2	41.9	934
5	Derwent Reservoir	46.1	78.5	69.2	33.3	83.4	28.4	13.4	1.9	48.5	988
6	Alport	42.1	73.7	63.9	30.6	90.9	24.9	14.7	3.4	55.8	1,264.1
7	Hurst Reservoir	47.7	76.6	66.7	26.5	92.1	18.8	13.1	1.8	48.8	1,068.6
8	Kinder Reservoir	44.3	74.4	67.1	30.1	87.6	20.8	14.2	2	52	932.8
9	Hucklow	34.6	88.7	78.1	36.9	83.6	61.2	13	2.5	44.1	810
10	Edale	41.9	84.2	74.4	34.9	85.9	27.3	12.3	3.7	44.1	828.9
		Annual deposition									
		kg ha ⁻¹ yr ⁻¹									
		H	SO ₄ S	nss SO ₄ S	NO ₃ N	Cl	Ca	Mg	K	Na	
1	Harpur Hill	0.32	13	11.9	4.4	23.6	8.9	1.1	0.6	7.7	
2	Wardlow Hay Cop	0.31	12.8	11.5	4.7	24.8	12.1	1.3	0.8	8.6	
3	Peak Forest	0.15	13.8	12.4	4.4	28.1	13.2	1.5	1.1	11.1	
4	Oxlow House	0.33	14.8	13	5	28.1	10.1	1.3	0.7	9	
5	Derwent Reservoir	0.46	12.4	10.9	4.6	28.8	5.6	1.6	0.7	11	
6	Alport	0.53	14.9	12.9	5.4	40.2	6.3	2.2	1.7	16.2	
7	Hurst Reservoir	0.51	13.1	11.4	4	34.4	1	1.7	0.8	12	
8	Kinder Reservoir	0.41	11.1	10	3.9	28.6	3.9	1.6	0.7	11.2	
9	Hucklow	0.28	11.5	10.1	4.2	23.7	9.9	1.3	0.8	8.2	
10	Edale	0.35	11.2	9.9	4	24.9	4.5	1.2	1.2	8.4	

*Results from UK national network for 1987

Air Pollution Monitoring, Simulation and Control 389

Non sea-salt sulphate and calcium ion concentrations show a distinct south to north gradient, with lowest concentrations being found in the north. Concentrations of acidity show a gradient in the opposite direction, with much higher concentrations of acidity to the north of the area. Nitrate also shows a north-south gradient with a slight easterly bias, although the results of the F ratio indicate that it is not statistically significant. A Student's t -test indicates that the populations from the sites which show the largest and smallest mean annual concentrations, Wardlow Hay Cop and Hurst Reservoir, respectively, show no significant difference. However, the contour plot shows a discernible gradient, even though the F ratio is not significant.

Deposition shows broadly similar contour plots to concentration for calcium and acidity. The pattern of deposition of non sea-salt sulphate is not so similar to concentrations, the pattern being modified by rainfall amount, which is a strong controlling factor on deposition.

Table 2 One-way analysis of variance of concentrations of ions in precipitation and precipitation amount

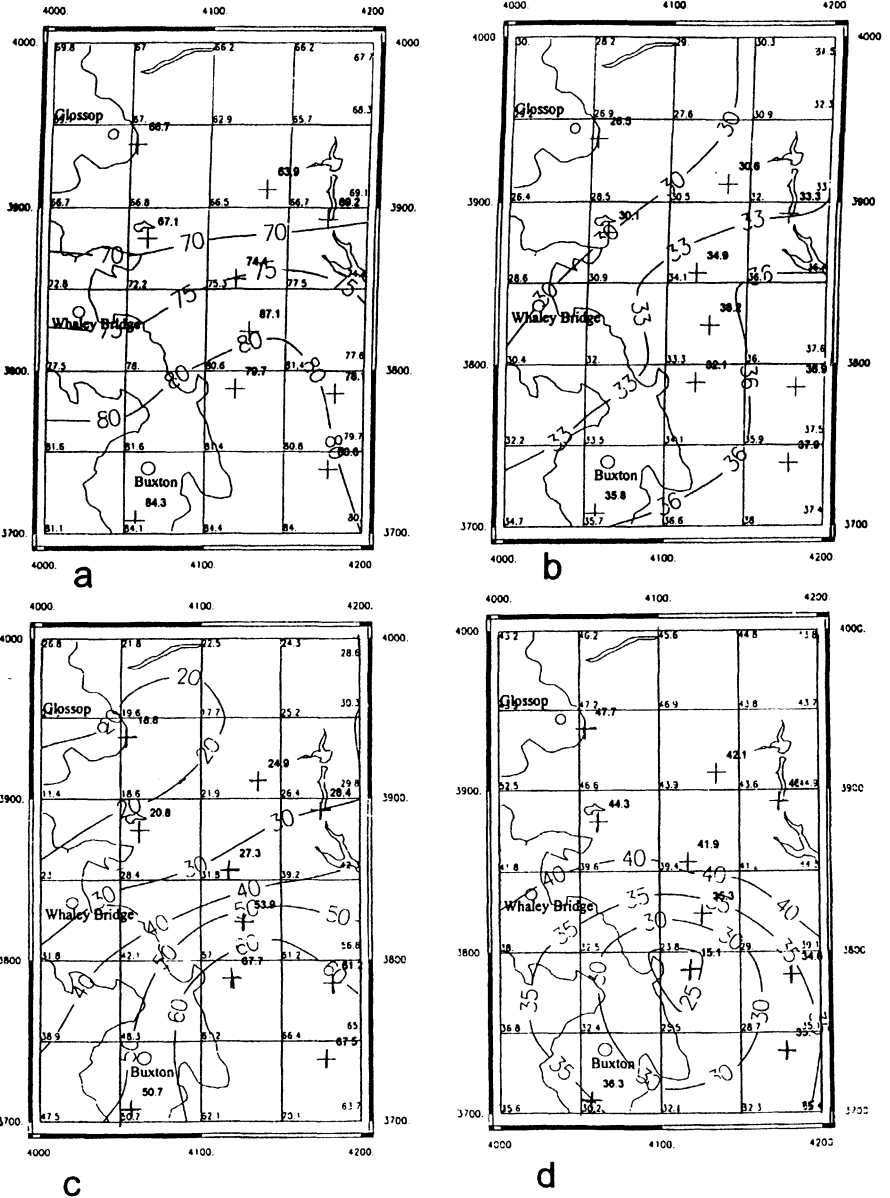
	F Statistic	p	Between groups degrees of freedom	Within groups degrees of freedom
H ⁺	9.79	<0.001	9	546
SO ₄ ²⁻	3.06	0.014	9	541
nss SO ₄ ²⁻	3.42	0.004	9	508
NO ₃ ⁻	0.99	0.447	9	541
Cl ⁻	0.32	0.968	9	540
Ca ²⁺	15.67	<0.001	9	512
Mg ²⁺	0.22	0.991	9	514
K ⁺	0.92	0.508	9	504
Na ⁺	0.45	0.981	9	512
mm	140	0.182	9	606

The study shows that calcium ion plays an important role in precipitation composition in the study area, particularly with respect to the acidity of the samples. In the south of the study area, there are a number of open limestone quarries which are of national importance in terms of output (see Fig. 1d). These workings represent a major source of wind-blown particles to the atmosphere from blasting and suspension of particles from the exposed rock. These particles are likely to range in size from the very large, which will deposit by gravitational settling from blasting, to those < 100µm which may be suspended by wind [16]. However, it is likely that the particles which are available for suspension are < 20 µm. Unfortunately no measurements of particle composition and size fractionation are available from the area but the composition of calcium particles will be predominantly CaCO₃. Thus, the associated solution anion with the calcium source, hydrogen-carbonate, will partially neutralise the acidity of the rain-water samples. The question of the location of this neutralisation is then raised. The most likely explanation is that a large fraction of the particles are dry deposited to the funnels of the collectors, which are open all the time, and are swept in by precipitation events and result in partial neutralisation of the samples. If these calcium particles were neutralising acidity in the free atmosphere, then they would need to be



390 Air Pollution Monitoring, Simulation and Control

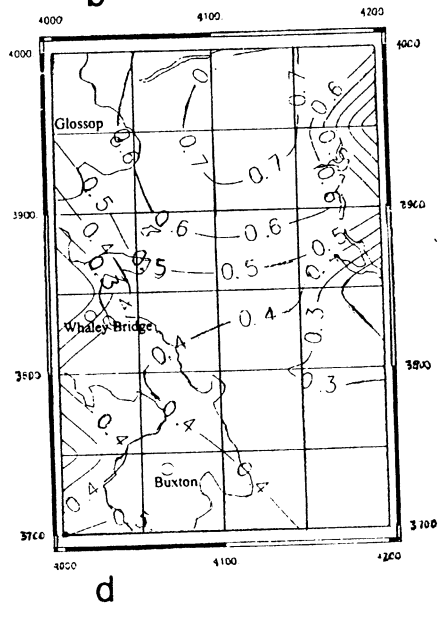
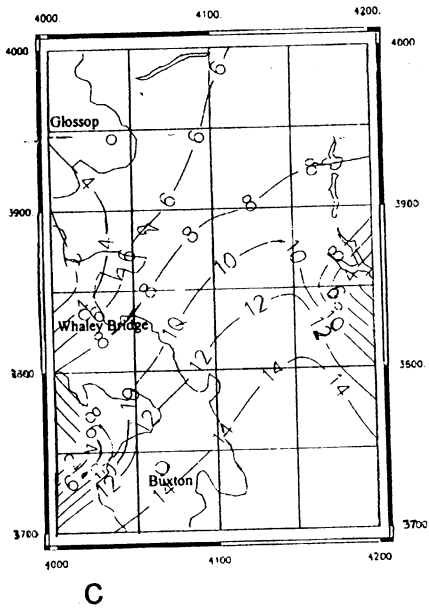
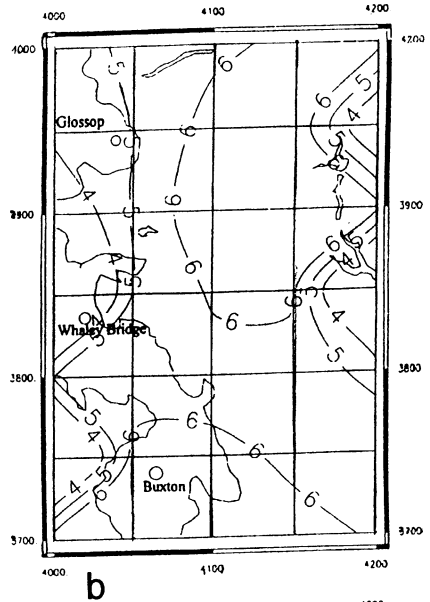
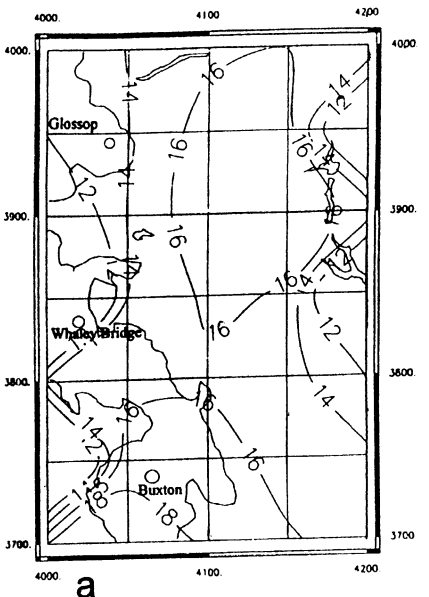
Figure 2. Concentrations of non-sea- salt sulphate (a), nitrate (b), calcium (c) and hydrogen (d) ions in precipitation (ueq^l⁻¹)





Air Pollution Monitoring, Simulation and Control 391

Figure 3. Deposition of non-sea-salt sulphate (a), nitrate (b), calcium (c) and hydrogen (d) in precipitation ($\text{kg ha}^{-1}\text{yr}^{-1}$)





392 Air Pollution Monitoring, Simulation and Control

very small, perhaps $< 1\mu\text{m}$, and could thus be incorporated into cloud droplets and subsequently rained out. However, this mechanism would necessitate a larger scale effect than the local effect observed. It is also possible that particles in the size range 2-10 μm are scavenged below cloud by falling raindrops and that this is the location of neutralisation. However, in a comparison of a precipitation composition from a wet-only and bulk collector in an urban centre, it was found that approximately 50% of the calcium ion was dry deposited to the bulk collector [17]. Whilst the source of the calcium is different in these two environments, the chemical form (CaCO_3) is thought to be the same [7]. It is therefore suggested that partial neutralisation of the samples resulted from the dry deposition of alkaline particles to the funnels. Unfortunately, no wet-only collector was operated in the study to quantify the neutralisation artefact. An additional explanation to the abundance of calcium ion in precipitation is that soil particles may also be suspended into the atmosphere. However, given the extent and magnitude of the quarrying activities, this is a less likely explanation.

Non sea-salt sulphate ion shows a larger variation across the study area than might be reasonably expected from atmospheric oxidation mechanisms of SO_2 to sulphate, with subsequent wet deposition. Some of the variability may be the result of orographic enhancement of deposition, either directly or by wind-drift effects. An additional explanation is that SO_2 may react with CaCO_3 particles deposited to the collector funnels. An oxidation rate of 20% per hour for this reaction in the atmosphere has been demonstrated by [18]. Sulphur dioxide concentrations in this region are relatively high for a rural area of the UK, ranging between approximately 10 to 20 $\mu\text{g m}^{-3}$, probably influenced by the Trent Valley power stations to the east of the study area. It is possible that particle deposition of CaCO_3 to surfaces may enhance sulphur deposition. A similar phenomenon of covariance of sulphate and calcium concentrations has been observed in a study of urban precipitation composition, where the source of CaCO_3 was thought to be eroded building materials [7]. However, in both urban and rural environments, the conclusion can only be speculative and requires further work to elucidate the possibility and magnitude of this effect.

Although nitrate ion concentrations do not show significant spatial variability, as tested by a one-way analysis of variance, it has been argued that there is a non-random gradient across the network. The cause of this gradient is difficult to explain, but it is apparent that orographic enhancement cannot explain the spatial pattern.

Summary and conclusions

From a study of wet deposition using 10 bulk collectors in an rural upland area of England, 20 by 30 km in extent, significant spatial variability of non sea-salt sulphate, hydrogen, calcium ions in precipitation were found. Nitrate concentrations did not show significant spatial variability but a coherent gradient across the study area of approximately 26 to 38 $\mu\text{eq l}^{-1}$ was observed.

Limestone quarries in the south of the study area were a large source of CaCO_3 particles which were thought to represent a large dry deposition artefact to collectors in the south of the area. As Wardlow Hay Cop is a national network site, mapping procedures across the UK will substantially overestimate concentration fields and thus deposition fields of calcium in this region, and beyond. The pattern of hydrogen ion in precipitation across the study area mirrored that of calcium and the dissolution of the



CaCO₃ particles dry deposited to the funnels thus represent a sampling artefact, underestimating hydrogen ion in precipitation, and therefore deposition of acidity.

The network was not designed to examine orographic enhancement, but this effect, in combination with wind drift of scavenged cap cloud droplets cannot explain all the spatial variation of ions in precipitation. The ions did not show similar spatial variability, which might have been expected if variability was the result of orographic enhancement.

References

- [1] RGAR *Acid deposition in the United Kingdom*. Third report of the United Kingdom Review Group on Acid Rain. Warren Spring Laboratory, Stevenage, Herts. UK, 1990.
- [2] Tuovinen J. P., Barrett K. and Styve H. *Transboundary Acidifying Pollution in Europe: Calculated Fields and Budgets 1985-93*. Meteorological Synthesising Centre West, Norwegian Meteorological Institute, Norway, 1994.
- [3] Sisterson D. L., Bowersox V. C., Meyers T. P., Olsen A. R. and Vong R. J. Deposition monitoring: methods and results. NAPAP Report 6. *Acidic deposition: State of Science and Technology Volume 1, Emissions, Atmospheric Processes and Deposition*. National Acid Precipitation Assessment Program, Washington D.C, 1990.
- [4] Campbell G. W., Stedman J. R., Downing C. E. H., Vincent K. J., Hasler, S. E. and Davies M. *Acid deposition in the United Kingdom: data report 1993*. AEA Technology AEA/CS/16419029. Culham, Oxon., UK, 1994.
- [5] Bull K. R. The critical loads/levels approach to gaseous pollutant emission control. *Environ. Pollut.* **69**, 105—123, 1991.
- [6] Bull K. R. An introduction to critical loads. *Environ. Pollut.* **77**, 173—176, 1992.
- [7] Lee D. S. The spatial variability of urban precipitation chemistry and deposition; statistical associations between constituents and potential removal processes of precursor species. *Atmospheric Environment* **27B**, 321—327, 1993.
- [8] CLAG *Critical Loads of Acidity in the United Kingdom*. Critical Loads Advisory Group Summary Report. Institute of Terrestrial Ecology, Edinburgh, UK, 1994.
- [9] Dollard G. J. and Unsworth M. H. Field measurements of turbulent fluxes of wind-driven fog drops to a grass surface. *Atmospheric Environment* **17**, 775—780, 1983.
- [10] Bergeron T. On the low-level redistribution of atmospheric water caused by orography. *Supp. Proc. Int. Conf. Cloud Phys.* Tokyo, May 1965, 96—100, 1965.
- [11] Fowler D., Cape J. N., Leith I. D., Choularton T. W., Gay M. J. and Jones A. The influence of altitude on rainfall composition. *Atmospheric Environment* **22**, 1355—1362, 1988.
- [12] Dore A. J., Choularton T. W. and Fowler D. An improved wet deposition map of the United Kingdom incorporating the seeder-feeder effect over mountainous terrain. *Atmospheric Environment* **26A**, 1375—1381, 1992.
- [13] Devenish M. *The United Kingdom precipitation monitoring networks*. Report LR 584(AP) M, Warren Spring Laboratory, Stevenage, Herts. UK, 1986.
- [14] Raper D. W., Longhurst J. W. S. and Gunn J. *Evidence for significant small scale variation in acid deposition, a study from the Derbyshire High Peak District*. In 'Acid Deposition: Sources, Effects and Controls' (ed. J.W.S. Longhurst). British Library, London and Technical Communications, Letchworth, 1989.
- [15] Webster R., Campbell G. W. and Irwin J. G. Spatial analysis and mapping the annual mean concentrations of acidity and major ions in precipitation over the United Kingdom in 1986. *Environ. Mon. Assess.* **16**, 1—17, 1991,



394 Air Pollution Monitoring, Simulation and Control

- [16] Nicholson K. W. A review of particle resuspension. *Atmospheric Environment* **12**, 2639—2651, 1988.
- [17] Lee D. S. and Longhurst J. W. S. A comparison between wet and bulk deposition at an urban site in the U.K. *Water, Air, Soil Pollut.* **64**, 635—348, 1992.
- [18] Buttler T. J. Composition of particles dry deposited to an inert surface at Ithaca, New York. *Atmospheric Environment* **22**, 895—900, 1988.