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THE GREAT DUN FELL CLOUD EXPERIMENT 1993: AN OVERVIEW

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Abstract—The 1993 Ground-based Cloud Experiment on Great Dun Fell used a wide range of measurements of trace gases, aerosol particles and cloud droplets at five sites to study their sources and sinks especially those in cloud. These measurements have been interpreted using a variety of models. The

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conclusions add to our knowledge of air pollution, acidification of the atmosphere and the ground, eutrophication and climate change. The experiment is designed to use the hill cap cloud as a flow-through reactor, and was conducted in varying levels of pollution typical of much of the rural temperate continental northern hemisphere in spring-time. © 1997 Elsevier Science Ltd.

Key word index: Aerosol, cloud, trace gas, acid deposition, global warming, air quality, ammonia, oxides of nitrogen, sulphur dioxide, atmospheric chemistry, organic molecules, transition metals, Henry's law, air flow, entrainment, lagrangian, field experiment, measurement, instrumentation, modelling, environmental science and technology, quality assurance, closure.

1. INTRODUCTION

The Ground-Based Cloud Experiment (GCE) is one of 14 subprojects within the EUROTRAC project (Borrell *et al.*, 1993, 1994). EUROTRAC is the largest of a dozen or more Environmental Science and Technology projects within the EUREKA initiative on technological collaboration within Europe. The acronym EUROTRAC stands for European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe. This paper gives an outline of the methods and results of the measurement campaign which was performed by GCE on Great Dun Fell (GDF) in April–May 1993. This was the third campaign performed by GCE, previous experiments having been performed in radiation fog in the Po Valley (Fuzzi *et al.*, 1992) and in polluted, continental cloud at the summit of Kleiner Feldberg, Taunus (Wobrock *et al.*, 1994). Since these experiments, GCE has been enlarged by the addition of research groups from Eastern Europe and elsewhere. A list of participating groups in the 1993 experiment on GDF is shown in Table 1.

The aims of the 1993 GCE campaign are to investigate:

(i) the chemistry of oxides of nitrogen and sulphur as an airstream flows through cloud, especially the conversion of gas-phase species to aerosol.
(ii) the modification of the aerosol particle size spectrum as an airstream flows through cloud, including the enhancement of cloud condensation nuclei by aqueous-phase cloud chemistry and the production or loss of small particles.
(iii) the budget of ammonia and ammonium as an airstream flows through cloud.
(iv) the importance of organic compounds as sinks of oxides of nitrogen, including the atmospheric chemistry of nitrated phenols.
(v) the partitioning of material between cloud droplets and the interstitial air, including the partitioning of soluble material between large and small cloud droplets.
(vi) the loading of material dissolved in cloud-water as a function of height above the base of the cloud.

Table 1. Research groups which participated in the Great Dun Fell 1993 experiment and modelling (in alphabetical order of abbreviation)

Abbreviation	Full name	Location	Country
ECN	Netherlands Energy Research Foundation	Petten	The Netherlands
FISBAT	Istituto per lo studio dei fenomeni fisici e chimici della bassa ad alta atmosfera	Bologna	Italy
HUS	Universität Hohenheim	Stuttgart	Germany
IEP	Institut für Experimentalphysik, Universität Wien	Vienna	Austria
IC	Imperial College	London	United Kingdom
IFU	Fraunhofer Institute for Environmental Research, Air Chemistry Group	Berlin	Germany
ITA	Fraunhofer Institute for Toxicology and Aerosol Research	Hannover	Germany
KIL	National Institute of Chemistry	Ljubljana	Slovenia
Lund	Lund University	Lund	Sweden
MISU	Stockholm University Meteorology Department	Stockholm	Sweden
MOH	Meteorologisches Observatorium Hamburg	Hamburg	Germany
MPI	Max-Planck Institut für Chemie	Mainz	Germany
UMIST	University of Manchester Institute of Science and Technology	Manchester	United Kingdom
ZUF	Zentrum Umweltforschung, Universität Frankfurt	Frankfurt	Germany
AEA[a]	Atomic Energy Authority	Harwell	United Kingdom
EAWAG[a]	Swiss Federal Institute for Environmental Research and Technology	Dübendorf	Switzerland
IFT[a]	Institute for Tropospheric Research	Leipzig	Germany
ITE[a]	Institute for Terrestrial Ecology	Edinburgh	United Kingdom
LAMP[a]	Laboratoire de Météorologie Physique	Clermont-Ferrand	France
UB[a]	University of Birmingham	Birmingham	United Kingdom

[a] Guest participant, formally not part of GCE.

2. FIELD SITE AND DESIGN OF EXPERIMENT

Great Dun Fell is the second highest point on the Pennine Hills, which run along the centre of Northern England (Fig. 1). The Pennines in the vicinity of GDF form a two-dimensional ridge, orientated north-west to south-east, perpendicular to the prevailing south-westerly winds. Air approaching the ridge is forced to rise up over it, cooling by adiabatic expansion and forming orographic cloud in the boundary layer. This cloud is in contact with the ground at the summit on at least 220 d yr^{-1}. Such a providential combination of hill shape and occurrence of cloud has led to the selection of Great Dun Fell as a natural laboratory for the study of air flow over hills, cloud physics, air and cloud chemistry and cloud droplet deposition over the past 25 yr (Corbin *et al.*, 1977; Gallagher *et al.*, 1988a, b; Choularton *et al.*, 1986; Chandler *et al.*, 1988; Radojevič *et al.*, 1990; Gay 1991; Fowler *et al.*, 1988). It is therefore one of the best characterized field sites of its type in the world. Over the past decade, the Great Dun Fell cap cloud has been used as a natural flow-through reactor to study what determines the physical and chemical properties of cloud and how an air mass is altered by passage through the cloud. The two-dimensional shape of the ridge makes it possible for ground-based instrumentation to sample similar parcels of air before, during and after their transit through the cloud, even from measurement sites which are not directly in a straight line. The proper functioning of this flow-through reactor cloud experimental design is demonstrated in Colvile *et al.* (1997). Figure 2 shows the sites where measurements were made during the 1993 experiment. In a south-westerly wind, the air is sampled in the Eden Valley before it enters the cloud and in Teesdale after cloud processing. Upwind sites Wharley Croft (WC, 206 m a.s.l.) and Fell Gate (FG, 430 m a.s.l.) in the prevailing southwesterly winds serve similar purposes but offer different facilities, Wharley Croft being an old farmhouse with mains electricity, running water, etc. while Fell Gate is more exposed and closer to GDF but relies on a diesel generator to supply electrical power to portable buildings. At the downwind site, Moor House (MH, 550 m a.s.l.), a generator supplies power to a remote farmhouse. The distance from Wharley Croft to Moor House is 9 km, giving a total transit time of some 15 min at a typical wind speed of 10 m s^{-1}. At GDF Summit (Su, 850 m a.s.l.), accommodation and mains electric power are provided in a permanent laboratory and supplemented by caravans and a generator. Of all the five sites, this site is most often in cloud, being at the highest altitude on top of the Pennine ridge. Mine Road (MR, 670 m a.s.l.), between Fellgate and GDF Summit, is often close to the base of the cloud, and relies on a generator to provide power to instrumented caravans.

The Eden Valley is mostly dairy farmland enclosed by dry stone walls, with occasional trees and small villages and towns connected by minor roads. Great Dun Fell is open rough grassland grazed by sheep and wild ponies. Teesdale is extremely sparsely populated with very few roads. The major local sources of pollution were therefore our own generators. By fitting a 50 m long extension to the exhaust via a venturi, the times when generator exhaust was sampled, either at the same site or at the next, were reduced to periods when the wind direction was marginally suitable for the flow-through reactor field experiment to work or the wind speed too low for air to blow over the hill. All other major sources of pollution are more than 80 km away and include Liverpool and Manchester to the

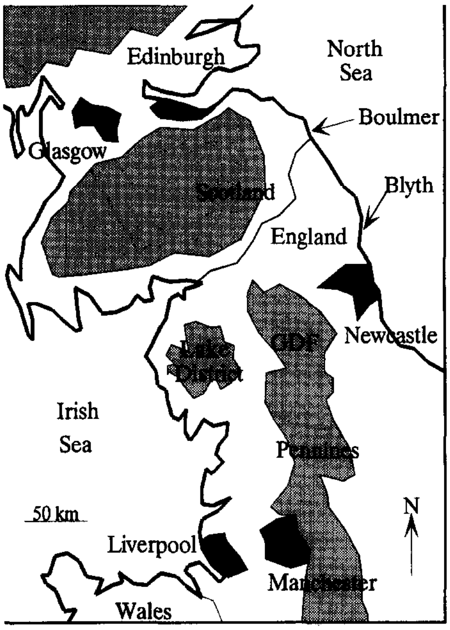

Fig. 1. Location of Great Dun Fell in Northern England.

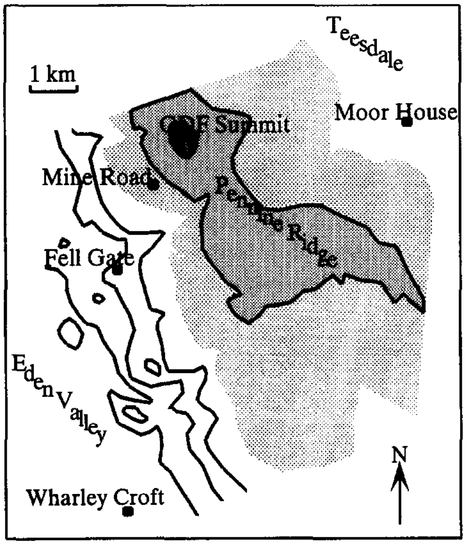

Fig. 2. Location of measurement sites on Great Dun Fell.

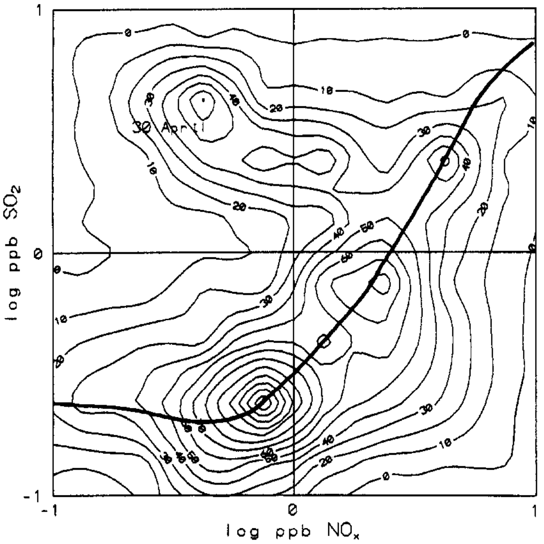

Fig. 3. Contour lines of point density on a scatter-plot of NO_x mixing ratio against SO_2 mixing ratio at Mineroad for all periods when both instruments were operational during the five-week experiment. Measurements are half-hour averages of smoothed data, excluding periods of contamination by local generator exhaust. The labels on the contours are percentage occurrence per log NO_x mixing ratio per log SO_2 mixing ratio, i.e. if a surface plot were used instead of contours, the total volume under the surface would be 100.

southwest and Newcastle to the northeast (see Fig. 1). Air which has passed over these sources typically arrives at GDF in a plume tens of kilometres wide containing as much as 20 ppb each (see Appendix) of SO_2 and NO_x and a total aerosol mass loading as high as 40 $\mu g\, m^{-3}$. This aerosol includes acidic sulphates and nitrates as well as non-ionic material and variable amounts of material of maritime origin (Swietlicki *et al.*, 1997). Air which has travelled over southeast England or Continental Europe is typically more homogeneous and contains up to half as much pollution. In comparison, air which has come off the North Atlantic from the tropics or from Greenland, or down the North Sea from the Arctic, at its cleanest, contains less than 0.1 ppb of SO_2 and NO_x and as little as 3 $\mu g\, m^{-1}$ of aerosol material mostly of maritime origin. Air from Continental Europe or North America which has travelled to GDF via a long passage over the sea sometimes contains low levels of trace gases but a higher aerosol loading. Pollution levels at GDF thus include conditions representative of the boundary layer in most temperate populated regions of the northern hemisphere.

Figure 3 shows the gas-phase mixing ratios of NO_x and SO_2, including the correlation between the two. It shows that there is a positive correlation between these two gases, but with much scatter, and a cluster of outliers from one day's measurements. The NO_x mixing ratio was close to 1 ppb for much of the time, while the SO_2 mixing ratio varied from the instrument detection limit to several ppb. The high frequency of occurrence of SO_2 mixing ratios below 0.3 ppb compared with that of NO_x mixing ratios is to be expected from the widely distributed nature of sources of SO_2 plus the efficient consumption of SO_2 by oxidation in cloud. A similar argument can explain the SO_2 episode on 30 April. Figure 4 shows that the total number of aerosol particles per unit volume of air (down to 3 nm dry diameter) was even more variable than the SO_2 mixing ratio, with 5% of 15-min average measurements being separated from each other by more than a factor of 100 in particle number. This is indicative of the source and sink processes which control the number of aerosol particles being even more variable in time and space than those for SO_2.

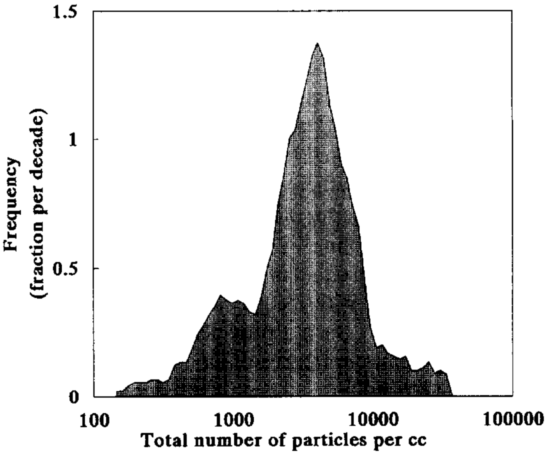

Fig. 4. Frequency distribution of total number of aerosol particles below cloud during the experiment.

A period five weeks in length is chosen for most Great Dun Fell experiments. Longer periods are prohibitively exhausting for people and equipment alike while shorter periods run the risk of being dominated by unsuitable weather conditions. Cloud occurs most frequently in winter, but November to March must be avoided as sub-zero temperatures at altitude render the sites inaccessible and the super-cooled cloud difficult to study. During the period selected in spring 1993, conditions were perfect, with cloud and southwesterly winds, during the initial week when most instrumentation was still in the process of being set up. There followed a cloud-free period. Cloud returned for the final week of the experiment, but with persistent northeasterly winds. Fortunately, the experiment works well with the upwind and downwind sites reversed. A greater problem was the unexpected frequency of occurrence of cloud at ground level at Moor House, which will be discussed in Colvile *et al.* (1997).

3. MEASUREMENTS MADE

Figure 5 shows a cross-section through Great Dun Fell and an outline of how the instrumentation was deployed.

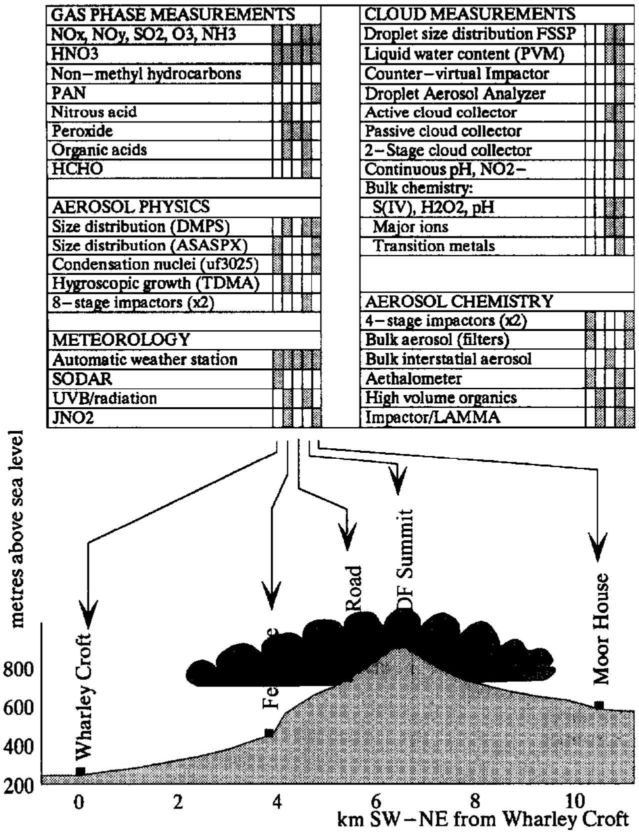

Fig. 5. Plan in cross-section of the Great Dun Fell experiment.

The northeasterly wind (right to left) should be reversed for the one day when measurements were made in a southwesterly wind. The trace-gas chemistry of the air and the aerosol particles suspended in it were characterized before and after the air passed through the cloud. Inside the cloud, samples of cloud water were collected and analysed by various techniques to measure the levels of trace substances dissolved and suspended in the droplets. The microphysical properties of the cloud were also measured and certain gas and aerosol measurements were repeated in the cloud for comparison with the measurements below cloud. To aid the interpretation of the measurements, meteorological measurements were made at each site.

Previous multiple-site experiments on Great Dun Fell have featured carefully selected measurements targeted at studying a particular process. Previous GCE campaigns have featured a wider range of measurements to study different inter-related processes simultaneously, but primarily at a single site. The combination of the two methodologies, with a wide range of measurements made at five sites, has resulted in the 1993 experiment being probably the most intensive ground-based characterization of a cloud ever performed. The measurement techniques and their deployment are described below.

3.1. *Gas measurements*

Specifications of the trace-gas measurements made are shown in Table 2. For gases such as NO_x and O_3, which are sparingly soluble and react slowly on the time-scales which parcels of air spend in transit through the cap cloud, measurements made at any one of the five sites may be used to find what mixing ratio was entering the cloud and passing through it. Many of these measurements, however, were duplicated at more than one site. This allows the flow of air over the hill and mixing processes in the cloud to be studied using the mixing ratios of these species as conserved quantities (Colvile *et al.*, 1997). Mixing ratios of rapidly consumed gases, such as H_2O_2, may vary over short distances. Measurements of these species were therefore made at the point of interest. Duplication of these measurements at different sites then allows the consumption and replenishment of these species to be observed (Laj *et al.*, 1997b). Gases such as HNO_3, HCOH, HCOOH and CH_3COOH which dissolve readily in cloud-water, were measured in cloudy air to study their phase partitioning (Laj *et al.*, 1997b). Finally, gases such as NH_3, which can be consumed or liberated during cloud processing, were measured on both sides of GDF, to allow the mixing ratio as air leaves the cloud to be compared with that which entered the cloud (Wells *et al.*, 1997; Cape *et al.*, 1997). For all these applications, fast response is important (seconds to minutes), and lack of interferents is perhaps less important. The air at GDF is often very clean, so low detection limits are desirable. Furthermore, operating conditions of high humidity at remote sites are more easily tolerated by small gas analysers than by sophisticated optical techniques. Most trace gases were therefore measured using commercial instruments: NO by chemiluminescence, SO_2 by pulsed fluorescence, and O_3 by UV absorption; NO_2 was reduced by UV photolysis or catalytically over Molybdenum for detection as NO. Instruments for the following were constructed by participants in the experiment: measurement of NH_3 and HNO_3 by annular wet denuder (batch samples for HNO_3; batch samples and continuous sampling for NH_3), reduction of NO_y by CO over Au for detection as NO, chemiluminescence instruments for HCHO, peroxides and SO_2. Phenols and

Table 2. Trace-gas measurements made on Great Dun Fell in 1993. (Operators names may be found in Table 1)

Site	Gas	Instrument	Reference	DL[e] (ppb)	Error	TR[f] (s)	Operator[g]
WC	SO_2	Thermo Environmental 43S		0.1	± 1%	60	ITE
MR	SO_2	Thermo Environmental 43S		0.1	± 1%		IFU
Su	SO_2	ZUF CFCl analyzer		0.06	± 5%	180	ZUF
Su	SO_2	Thermo Environmental 43S		0.1	± 1%	120	ZUF
MH	SO_2	Thermo Environmental 43S		0.6	± 1%		AEA
WC	NO	Ecophysics CLD 770 al		0.01	± 1%	60	ITE
WC	NO_2	Ecophysics PLC 760 converter			± 5%	60	ITE
MR	NO	Ecophysics CLD 770 al		0.01	± 1%		IFU
MR	NO_2	Ecophysics PLC 760 converter			± 5%		IFU
MH	NO, NO_2	Thermo Environmental 42S		0.5	0.5 ppb		AEA
WC	NO_y	Au converter on Thermo Environmental 42S NO detector		0.5	0.5 ppb	60	ITE
MR	HNO_3	Wet annular denuder		0.08	± 5%	2400	ECN
WC	HNO_3	Denuder with filters				21,600	UB
WCMR SuMH	NH_3	Wet annular denuder		0.3	± 5%	2400	ECN, AEA
MR	NH_3	Continuous wet denuder					ITE
WC	O_3	Thermo Environmental 49		2	1.0 ppb	60	ITE
MR	O_3	Environics Series 300		1	1.0 ppb		IFU
Su	O_3	Monitor Labs		1	1.0 ppb	900	UMIST
Su	HCHO	FISBAT fluorometric monitor	[a]	0.2	± 5%		FISBAT
Su	H_2O_2	ZUF CFCl analyzer	[b]	0.1	± 20%	240	ZUF
Su	peroxides	FISBAT fluorometric monitor	[c]	0.05	± 5%		FISBAT
MR	peroxides	Aerolaser AL1002		0.05	± 5%		IFU
FGSu	H_3CCO_2H	Scrubber	[d]	0.3	± 12%	7200	MPI
FGSu	HCO_2H	Scrubber	[d]	0.15	± 12%	7200	MPI
FG	Aromatic hydrocarbons	Adsorption onto Tenax				14,400	ITA
Su	Phenols, nitrophenols	Scrubber behind cloudwater collector				14,400	ITA

[a] Lazrus *et al.* (1988).
[b] Beltz *et al.* (1987).
[c] Lazrus *et al.* (1986).
[d] Cofer.
[e] DL = detection limit.
[f] TR = time resolution or integration time used (may be slower than instrumental capability).
[g] See Table 1.

nitrophenols were determined in aqueous solution in the laboratory after scrubbing from the air, while benzene, methyl benzene (toluene) and *ortho-*, *meta-* and *para*-dimethyl benzene (xylene) were adsorbed onto a solid substrate and thermally desorbed in the laboratory for analysis by gas chromatography and mass spectroscopy. A commercial chemiluminescence peroxide instrument was also used. Some of the chemiluminescence instruments detecting soluble gases in cloud were switched to measure the dissolved species in sampled cloud water as well as the gas in the interstitial air.

3.2. *Aerosol and cloud droplet measurements*

Instrumentation for counting and sizing aerosol particles and cloud droplets may be divided into two groups: laser scattering instruments and electrostatic mobility techniques. A combination of both types of measurements was used, because each has its advantages and limitations. The mobility techniques lack the weaknesses suffered by the optical techniques in deriving particle size from the intensity of a pulse of scattered light. The optical methods, however, offer orders of magnitude greater particle size and time resolution. The lower particle size limit of a mobility instrument is determined by the sensitivity of the condensation particle counter used, which can be good down to particles as small as 3 nm diameter. Mobility instruments are limited to maximum particle diameters of less than 1 μm. Optical methods can size larger particles, but cannot extend below about 0.2 μm diameter because of the wavelength of the light used. All diameters are dry size, which is what these instruments measure on account of the elevated temperatures inside them.

Specifications of aerosol measurements are included in Table 3. Optical particle counters (OPC) and differential mobility particle sizers (DMPS) were deployed below cloud on both sides of the hill. Comparison of measurements upwind of the cloud with those downwind thus allows modification of the aerosol size spectrum by cloud processing to be observed (Wiedensohler *et al.*, 1997; Bower *et al.*, 1997). In cloud, further DMPSs were deployed, but with inlets which excluded material of ambient diameter greater than 5 μm. This allows comparison between below-cloud and in-cloud sites to show which particles had grown to form cloud droplets (Svenningsson *et al*, 1997). The cloud droplets were also counted as a function of their wet size by forward scattering spectrometer probes (FSSPs). These are conceptually similar to OPCs, but require different physical and electronic configuration and different laser mode to handle larger particle sizes.

In addition to the above, two sites were selected for measurement of the ability of aerosol particles to grow and form cloud droplets, one site for aerosol particles below

Table 3. Aerosol particle and cloud droplet measurement and sampling techniques used on Great Dun Fell in 1993

Sites	Instrument	Manufacturer	Particle diameters (nm)	Number of size bins	Time resolution (s)	Operator
WCMH	OPC	PMS ASASP-X	Dry 100–3000	32	1.0	UMIST
FGMR SuMH	DMPS	Lund	Dry 3–600	17	900.0	Lund
MR	FSSP	PMS	Wet 1–64	64	600.0	ECN
Su	FSSP	PMS	Wet 1–64	64	600.0	ZUF
Su	FSSP	PMS	Wet 2–32	16	0.1	UMIST
FG	TDMA	Lund	Dry 50–265	5	3600.0	Lund
Su	DAA	Lund	Wet 1–50 Dry 50–73	14 7	3600.0	Lund
FGMR SuMH	Mini–impactor	HUS	Wet 0–8000	5	3600.0	HUS
WCMH	Impactor	Berner	Wet 0–5000	4	10,800.0	IEP
WCMH	Filter	Rotheroe–Mitchell	All	1	3600.0	AEA
Su	Filter	Lund	Wet 0–5000	1	43,200.0	Lund
WC	Aethalometer	Magee Scientific	All	1	3600.0	KIL
Su	Aethalometer	Magee Scientific	Wet 0–5000	1	900.0	KIL
MRSu	Passive string CWC	UMIST, IFU	All?	1	900.0	UMIST, IFU
Su	Activated string CWC	EAWAG	All?	1	3600.0	EAWAG
MRSu	Active CWC	MOH	Wet > 5000	1	3600.0	UMIST
MRSu	Active CWC	Berner	Wet > 5000	1	3600.0	UMIST
MRSu	Active CWC	Enviscope	Wet > 2000	1	3600.0	ZUF
Su	Active CWC	ZUF[a]	Wet > 5000	2	3600.0	ZUF
Su	Active CWC	ITA	Wet > 4000	1	3600.0	ITA
Su	CVI	MISU	Wet > 5000	1	NA	Lund

[a] Schell *et al.* (1997).

cloud and the other for cloud droplets. These measurements were made using electrostatic mobility techniques. It is important to consider the fact that only a fraction of each aerosol particle is composed of ionic material such as sea salt or ammonium sulphate. The tandem differential mobility analyser (TDMA) measures what fraction of each particle is ionic by comparing its dry size with that at a relative humidity of 90% (Svenningsson *et al.*, 1997). The droplet aerosol analyser (DAA) counts and sizes cloud droplets using the amount of charge per particle, then counts and sizes also the residue left when the droplet is evaporated to dryness (Cederfelt *et al.*, 1997). It therefore produces a three dimensional data-set. 1993 was the first time this new instrument had been deployed in an intensive field experiment.

3.3. *Sampling and chemical analyses of cloud water and aerosol*

Sampling methods for cloud water and aerosol are listed in Table 3. Bulk samples of cloud water were collected using active and passive collectors (CWCs) (Mohnen *et al.*, 1989; Schell *et al.*, 1992). Active collectors, using the impactor principle, have sampling characteristics which are better defined than those of passive string collectors. Passive collectors, however, provide larger volumes of water in a shorter time. Most samples were divided into several aliquots for different analyses. These aliquots were analysed immediately in the field for conductivity, pH (glass combination electrode), organic acids (ion chromatography), NH_4^+, S(IV) and H_2O_2 (same instruments as gas-phase measurements). Aliquots were refrigerated and transported to UMIST for analysis for major ions by ion chromatography, refrigerated and transported to KIL for analysis for transition metals, or frozen and transported to FISBAT for analysis for carbonyl compounds by HPLC. Some cloud water collectors were reserved for specific analyses: The large sample volume of a passive collector made it possible to analyse cloud water continuously for pH, NH_4^+ and NO_2^-. This pH measurement was made at constant high ionic strength by adding KCl to the cloud water. Two active collectors with six slit inlets each were operated in parallel to provide sufficient water hourly for analysis for phenols and nitrophenols (Lüttke *et al.*, 1997) — these cloud-water collectors were fitted with scrubbers to sample gas-phase phenols and nitrophenols as well, as described in Section 3.1. Active strand string collectors (Jacob *et al.*, 1985) were specially constructed to provide samples for transition metal analysis atomic absorption spectroscopy. A typical level of analytical error in all these techniques is ± 10%.

Aerosol samples were collected below cloud on either side of the hill by cascade impactors and on filters. Four-stage impactors with teflon foils and automated Whatman-41 paper filter samplers with isokinetic inlets collected samples which were extracted into water in a sonic bath then analysed for major ions by ion chromatography. This enabled the total contribution of ions to the aerosol to be determined along with its particle size dependence, and changes therein due to cloud processing to be studied (Laj *et al.*, 1997a). To identify changes in size distribution, the four-stage impactor inlet at Moor House was warmed by 3°C to account for the difference in altitude, relative humidity and swelling of hygroscopic particles between Wharley Croft and Moor House. Samples from the mini cascade impactors were reserved for laser microprobe mass analysis to identify the atomic and molecular composition of single particles. The filters exposed in cloud were on the same 5 μm inlet as the DMPS, so they collected aerosol material that did not form cloud droplets, for analysis for major ions by ion chromatography, soot by light absorption and elements by particle induced X-ray emission. The dominant analytical error in most of these techniques is caused by the variability of blank values which must be subtracted, so varies from ± 10% for the most abundant species to ± 25% or worse close to the detection limit.

3.4. *Meterological and thermodynamic measurements*

The most important thermodynamic parameters to be measured for a multiple-site experiment such as the GCE 1993 campaign, are liquid and vapour water mixing ratios. To this end, aspirated wet and dry bulb platinum resistance psychrometers at sites 1 and 5, a hair hygrometer at site 3 and a capacitance hygrometer at site 4 were deployed. Most importantly, cloud liquid water content (LWC) was measured at sites 3 and 4 using Gerber Particulate Volume Monitors (PVM-100 and PVM-300, Gerber, 1991). The difference in LWC between the two sites was used to study the evolution of the cloud (Colvile *et al.*, 1997) while the absolute value at either site was used to estimate the height of the base of the cloud (Colvile *et al.*, 1997) and to calculate masses of dissolved material per unit volume of cloudy air from measurements of aqueous concentration in cloud-water (Laj *et al.*, 1997a). Combining all the liquid and vapour water measurements allows a water budget to be constructed across the hill, as an aid to identifying airflow types and mixing processes (Colvile *et al.*, 1997).

To aid the interpretation of all the other measurements, automatic weather stations were deployed at all sites, measuring wind speed and direction, wet and dry-bulb screen temperatures, rainfall, and solar and net radiation. Finally, an ultrasonic anemometer was deployed at GDF Summit to aid the study of high-frequency structure in the turbulence and cloud microphysics. The wind speed, cloud liquid water content and cloud droplet size spectrum measurements were all made within 1 m of the passive cloud-water collector. This enables the collection efficiency of the CWC and the sample volume of the FSSP to be monitored using the other measurements.

3.5. *Self-consistency of data-set*

When such a large number of measurements are made simultaneously as were during the GCE 1993 campaign, it is inevitable that some apparent inconsistencies will emerge. By understanding the causes of differences between similar measurements, it is possible to increase our knowledge of the instrumentation and maximize the amount of information obtained from the experiment.

Under conditions of low wind speeds (less than about 13 m s^{-1}) good agreement was found between the active and passive cloud-water collectors. At higher wind speeds, however, the concentrations of dissolved material in samples from the passive collectors was found to be larger than that in samples from the active collectors. This phenomenon was accompanied by a rapid drop in the passive collection efficiency as a function of wind speed. At worst, the concentration difference between samples from the two types of collector was a factor of three, and was larger for NaCl than for $(NH_4)_2SO_4$. It is difficult to explain in detail how such a large difference might arise, but it has been observed that updraughts in turbulent flow can cause cloud water to collect for long periods of time on the vertical strings of a passive collector when it is windy, without running down into the sample bottle below. It is likely that this problem with the passive collectors is the cause of the discrepancy between the two types of collector. Furthermore, loadings calculated from LWC and cloud-water composition using the active collectors agree better with the masses of the same ions collected below cloud by the filters and impactors than if the passive collectors are used. Only the active collectors have therefore been used when there is a discrepancy of more than 15% between them and the passive collectors, the passive collectors under such circumstances providing only an approximate measure of concentrations of different species in the cloud water relative to each other.

Of all the analyses performed on the cloud-water samples, pH is arguably the most difficult. Combination electrodes do not perform well in samples of low ionic strength which may vary greatly from the buffers which are used for calibration. The quality of the complete analysis of each sample was checked by calculating the total charge concentration of the sample and the expected conductivity. The total charge should be within experimental error of zero and the calculated conductivity should be within experimental error of the measured conductivity. For many samples, there was an apparent excess of positive charge and the theoretical conductivity was higher than the measured conductivity. This problem was worst for samples with a high pH, for which the pH electrode had been slow to give a stable reading. Replacing the hydrogen ion activity (concentration with correction for the effects of higher ionic strength in some samples) with an activity required to give charge neutrality with all the other analyses produced a calculated conductivity experimentally equal to the measured one, and also gave better agreement with the continuous pH measurement which was performed at high ionic strength (Cape *et al.*, 1997). The pH was therefore recalculated from the hydrogen ion activity which gave charge neutrality.

The total mass of soluble aerosol material per unit mass of air may be calculated either from the Rotheroe–Mitchell filter measurements or from the Berner four-stage impactors. This calculation is complicated by the fact that these two instruments have different sampling characteristics (Laj *et al.*, 1997a). Each Berner Impactors was fitted with a 5 μm inlet but may be assumed to sample 100% of the aerosol smaller than that wet diameter. Each filter sampler was fitted with an isokinetic inlet, but rely on Whatman-41 paper to intercept the aerosol. The collection efficiency of Whatman-41 is a minimum for particles of wet diameter about 0.2 μm (Hinds, 1982). The Berner Impactors and OPCs show that this is about the size of the mass mode for non-sea-salt sulphate aerosol, while nitrate and sodium chloride have larger diameters. The Berner Impactors may therefore be used to correct the filter measurements for $< 100\%$ efficiency of sampling non sea-salt sulphate and associated ions. Conversely, the filter measurements may be used to quantify the effect of the 5 μm inlet on the Berner Impactors, especially at Moor House when the base of the cloud was low on that side of the hill so the aerosol particles were large. Similar corrections may be made, making use of other measurements made at the same site or elsewhere on the hill, to account for the tendency of filters to collect HNO_3 vapour and other sticky gases and the possibility that teflon impactor foils may lose some volatile material between exposure and analysis. The size of the corrections depends on conditions and on chemical species, and varies from 10 to 30%. The filter measurements have a time resolution of 60 min, while each set of impactor foils was exposed for 180 min but with a new set put out on a second impactor at each site every 90 min. Using corrections as described above and interpolation between impactor measurements, an hourly data-set for total aerosol loading has been produced. On a couple of occasions when the differences between the two measurements were too large to be explained, an average has been taken and the data interpreted taking the uncertainty into consideration.

During the interpretation of this aerosol data-set, the following errors have been taken into account: each sampling method, filter or impactor, is subject to analytical error of about ± 10% as described in Section 3.3. This analytical error refers to the amount of material which was collected on a filter or on a set of impactor stages. It does not take into account the sampling characteristics of each method. For the hourly data-set of total atmospheric aerosol loading, an error may be estimated which also takes into account the uncertainties in the sampling characteristics. This error varies from ± 10 to ± 30%, depending on species, conditions and site. It is often systematic in nature, affecting a whole time series of data at one site for one case study in the same way while possibly having the opposite sign at another site at the same time. When attempting to find changes in the atmospheric loading of an ion from one site to another, it is therefore necessary to design a methodology which can identify statistically significant differences in time and space. This is done (Laj *et al.*, this issue, a; Wells *et al.*, 1997; Cape *et al.*, 1997) by studying ratios between different ions which are sampled with similar efficiency, especially between an ion such as SO_4^{2-} which is expected to vary in space and one such as Na^+ which is known to be conserved during passage through cloud (Laj *et al.*, 1997).

The final example of a significant discrepancy being observed between instruments which might be expected to measure the same thing is the aerosol particle size spectrum. Between 0.1 and 0.3 μm dry diameter, there is good agreement between the OPCs and the DMPSs, although differences between the two are sometimes as large as 40%, presumably due to variability of sample flows which are not mass-flow controlled or due to variations in detection efficiency. Above 0.3 μm diameter, however, there are some large differences between the two instruments. At worst, the OPCs detect almost an order of magnitude fewer particles than the DMPSs. The discrepancy is less serious when the total number of particles is small. The DMPSs produce a size spectrum which can easily be fitted to a sum of three or four log-normal distributions, as might be expected from natural variability in size-dependent particle production mechanisms. The OPC spectra, however, often have a marked cliff at 0.3 μm, which is not expected. This may be an optical or an electronic problem. It is not known whether it is a feature of the individual OPCs used, or the particular conditions and aerosol properties prevailing during the experiment. The result is that the DMPSs have been assumed to produce the best measure of the spectral shape, and the OPCs have been used merely to provide a semi-quantitative measure of rapid variability and spectral shape between 0.6 and 3 μm diameter, or total spectral shape at times when no DMPS was working. In order to improve on the coarse particle size resolution of the DMPSs, log-normal distributions have therefore been fitted to the measured points and used to provide interpolations. Not only individual spectra, but also time series of parameters describing the log-normal distributions may then conveniently be compared across the hill in order to study aerosol modification by cloud processing.

The removal of apparent inconsistencies such as these is part of the quality assurance process which must be performed before any analysis is made of the data-set of such an integrated experiment. This process continues during the construction of input for a model, where exact values within the limits of experimental error are chosen in such a way as to produce a data-set which is entirely self-consistent. The range of models applied to the 1993 experiment on Great Dun Fell is described below.

4. APPLICATION OF MODELS

Modelling of Great Dun Fell and the surrounding area at various scales is an important part of this integrated experiment.

The largest scale model used is the Europa Modell of the German Weather Service, which has been used to study the paths along which air travelled during the days prior to its arrival at Great Dun Fell (Colvile *et al.*, 1997; Swietlicki *et al.*, 1997).

On a smaller scale, the non-hydrostatic cloud model of T. Clark (e.g. Clark, 1977; Clark and Hall, 1991) has been used to investigate the cloud formation over the northern Pennines in northeasterly winds (Wobrock *et al.*, 1997). An interactive grid nesting also allowed the airflow pattern and the influence of distant sources of pollution to be investigated on different scales.

The most detailed and extensive modelling of the experiment has been performed using several versions of the UMIST lagrangian cloud parcel model of the hill cap cloud (Bower *et al.*, this issue; Wells *et al.*, 1997). The kinematic basis for this model is provided by a three-dimensional air flow model, Flowstar (Carruthers and Hunt, 1990). The cloud model includes droplet and aerosol size-dependent microphysics, kinetics of phase transfer of water vapour and soluble gases, and rates of reaction of chemical species in the gas and aqueous phase (Bower *et al.*, 1991; Sander *et al.*, 1995). When such detailed models are used, it is usually necessary to provide estimates or parameterizations of several important inputs. For such an intensive field experiment as the GCE 1993 campaign, however, this is not the case. The only difficulty is producing a completely self-consistent set of model inputs for each period of time which the model is required to represent. Such a closure requirement is a stringent test of the quality of field measurements. For the Great Dun Fell 1993 experiment, it has been possible to meet such a requirement, and the system is over-constrained with more measurements made than the model requires. The application of the model is therefore a test of the model's performance. The results of this model may be compared with a related study using the model of Flossmann *et al.* (1985) on a streamline produced by the Clark model instead of Flowstar (Hallberg *et al.*, 1997). The different air flow models are intercompared in Wobrock *et al.* (1997). The significant differences between the UMIST and Flossmann models are that the Flossmann model has much simpler chemistry than the UMIST model, but has more complex cloud microphysics. It redistributes the cloud material between the droplet size bins each time-step, the droplet diameters of the bins remaining constant, while the UMIST model simply allows the droplet size of each bin to grow. This permits processes such as coalescence to be included in the Flossmann model, and thus to confirm that such processes are unimportant in the Great Dun Fell hill cap cloud. Simplified spectral microphysics models of cloud droplet growth only are also used by Martinsson *et al.* (1997) and Schell *et al.* (1997a).

Three further models have been used to study individual processes occurring on Great Dun Fell and in parcels of air upwind: (i) Swietlicki *et al.* (1997) use an Absolute Principal Component Analysis source-receptor model to identify groups of aerosol constituents which are found in fixed proportions to each other, and hence to assign relative strengths to different sources for each aerosol sample; (ii) Sutton *et al.* (1997) use a resistance model to study the deposition of ammonia to the hill surface; (iii) Svenningsson *et al.* (1997) use a model of high ionic strength solution droplets to calculate the hygroscopic growth of aerosol particles as a function of their active volume fraction. This uses some similar theory to the representation of the effects of high ionic strength on phase partitioning of soluble gases in evaporating droplets employed by Wells *et al.* (1997).

5. SUMMARY OF RESULTS

5.1. *Cloud dynamics and microphysics*

It has been shown that the flow of air over Great Dun Fell and development of the microphysics of the hill cap cloud can be described within a dynamical framework given by two very different flow models (Wobrock *et al.*, 1997). For most of the duration of the case studies considered it has been shown that the flow is well connected between the five sites used in the experiment and that the use of the hill cap cloud as a natural flow through reactor to study the evolution of the properties of the atmosphere due to cloud processing is well justified (Colvile *et al.*, 1997). During some periods of the experiment the cloud observed near the ground was strongly affected by the entrainment of air from the free troposphere above the cap cloud. On other occasions the effect of entrainment was minimal or confined to regions above that in which measurements were made (Colvile *et al.*, 1997).

On many occasions, with the wind blowing from the northeast, a very broad droplet size distribution was observed at GDF Summit. This can be attributed to the activation of droplets at more than one altitude above the base of the cloud due to a complex supersaturation history. During some periods, the cloud-droplet microphysics and chemistry were strongly affected additionally by entrainment of dry air from above, which resulted in bimodal droplet size distributions at GDF Summit (Colvile *et al.*, 1997). This is consistent with results from the droplet aerosol analyser at GDF Summit, which showed that droplets had a wide range of lifetimes on many occasions. Measurements were made of the size-distribution and hygroscopic properties of the aerosol particles. The numbers of particles which would be expected to have acted as cloud condensation nuclei agreed well with the observations and the modelled water vapour supersaturation peaks in the cloud agreed with those predicted from the observations of which particles were nucleation scavenged (Hallberg *et al.*, 1997; Svenningsson *et al.*, 1997; Martinsson *et al.*, 1997).

Particle-induced X-ray emission analysis and laser microprobe mass spectroscopy have been used to study the composition of the aerosol particles including the non-hygroscopic fraction by Gieray *et al.* (1997). This work investigates what chemical compounds control the nucleation scavenging of individual particles, including the greater scavenging efficiency of sulphur compared with carbon.

5.2. *Cloud chemistry*

It has been shown by Pahl *et al.* (1997) that the variation in the chemical composition of the cloud water between sites within the cloud is determined not only by the dilution of material entering the cloud droplets through nucleation scavenging and by the take-up of soluble gases, but also on the droplet-size dependence of rates of growth and evaporation. In addition, measurements of the size-resolved droplet chemistry (Schell *et al.*, 1997a), have shown that the partitioning of species between large and small droplets deviates from the predictions of a droplet growth model which assumes a constant updraught. These ideas have been developed further by Laj *et al.* (1997a, b), who have shown that production of SO_4^{2-} through oxidation of SO_2 by H_2O_2 occurred in the cloud water and that this was sometimes enhanced by the entrainment of H_2O_2. The oxidation of S(IV) by O_3 occurred as well, but is generally less important in these clouds in May where H_2O_2 is abundant. Evidence of H_2O_2 production following HCOOH formation was also found. Chemical transformations involving SO_2, HCOOH, NO_x and H_2O_2 were observed not only in the presence of cloud but also occurring on haze particles in the absence of a cap cloud.

Sedlak *et al.* (1997) measured total and dissolved concentrations of Fe and Cu in the cloud water. They showed that reactions of these metals with photo-oxidants and S(IV) occur at significant rates in cloud droplets. The measured oxidation rates of dissolved Fe agreed with predictions based upon known rate constants for the redox reactions. During daylight hours, the reduction of dissolved Fe(III) by HO_2/O_2^- and Cu(I) or the photo-reduction of Fe(III)–oxalate complexes resulted in the establishment of a steady state, with respect to iron oxidation states, in which more than 50% of the dissolved Fe was presented as Fe(II). At night, Fe(II) was consumed by H_2O_2 and O_3.

The interaction of oxidised nitrogen species with clouds has been investigated by Cape *et al.* (1997). Loss of NO_x was seen to be accompanied by gains in HNO_2 and NO_3^-. HNO_3 contributed a significant fraction of the total atmospheric NO_3^-, even downwind of the cloud, as the cloud served to change the partitioning of oxidised nitrogen between NO_x and gaseous and particulate forms of NO_y. The concentrations of nitrophenols in the gas and aqueous phases were measured by Lüttke *et al.* (1997). Phenol was present at concentrations between 0.014 and 0.14 $\mu g\ m^{-3}$, and the total molar mixing ratio of nitrated phenols in the air, including particle-bound 4-nitrophenol, varied between 0.2 and 0.4 times the phenol mixing ratio. The partitioning of these species between the gas and aqueous phase showed marked deviations from the prediction of Henry's law (Lüttke and Levsen, 1997). Some suggestion of the formation of dinitrophenols in cloud by the nitration of phenol in water films in the presence of gaseous N_2O_5 and $ClNO_2$ was also found.

Ammonia was studied in detail as part of the 1993 project as the only basic trace gas in the atmosphere. The results of this study are contained in Wells *et al.* (1997). In general, it was found that the concentrations of NH_3 in the gas phase downwind of the cloud were high. These concentrations generally exceeded those predicted by a simple model of NH_3 fixing in cloud in association with the production of acidic species by aqueous-phase cloud chemistry and the solution of acidic gases. This is because the simple model treats the evaporating droplets as ideal solutions. Inclusion of the effects of high ionic strength increased the proportion of the NH_3 returned to the gas phase and results in good agreement between observations and predictions on many occasions. On some occasions, a net transfer of ammonium aerosol to ammonia gas on passage through the hill cap cloud was observed and modelled i.e. it was found that the gas-phase ammonia concentration leaving the cloud exceeded that entering the cloud. These findings imply that when ammonium sulphate aerosol is below its deliquescence point the solid aerosol can be transported in an ammonia deficient atmosphere long distances from its source region without any loss of reduced nitrogen. When this aerosol interacts with cloud then ammonia outgassing will occur and ammonia gas will be available for efficient dry deposition or the formation of new particles.

5.3. *Cloud–aerosol interactions*

It has been shown in Bower *et al.* (1997) that an aerosol size distribution is modified by passage through a cloud system due to S(IV) oxidation. If the effect is to be significant in the modification of the CCN activity spectrum, then chemical reactions in those droplets formed on the smallest aerosol particles are important as these are the particles which will have their critical supersaturation lowered significantly. In the hill cap cloud with a very low cloud base this is achieved most efficiently if entrainment introduces fresh oxidant through the top of the cloud, as only the larger particles are activated at cloud base before initial oxidant is all consumed.

If small particles are activated, the change in the aerosol size spectrum is detectable after a single cloud pass even if the amount of sulphate production is small. When a large amount of SO_2 is converted, the change in accumulation mode diameter is shown to be quantitatively consistent with model predictions of the effects of cloud processing. Multiple cloud passes, for example, in a turbulent stratocumulus capped boundary layer will be expected to produce a substantial increase in the accumulation mode diameter.

In addition, evidence has been found for the formation of new ultra-fine aerosol particles. This is reported in Wiedensohler *et al.* (1997). These were observed in substantial concentrations downwind of the hill cap cloud in two case studies. It was concluded that the formation mechanism in these two studies was different in the two cases. In the evening of 9 April there was strong evidence for entrainment of air from above cloud top. In the prevailing conditions, new particles in concentrations similar to those observed were predicted to be formed (via the nucleation of sulphuric acid) in a few hours within parcels of cloudy air detrained into the lower free troposphere. On this occasion, stratocumulus clouds extended far upwind of Great Dun Fell at the top of the boundary layer, so this mechanism followed by entrainment is a likely source of the particles observed. The case study on 10 April had very different conditions with no significant entrainment. It was concluded, therefore, that most of the ultra-fine particles observed downwind of the cap cloud were produced during the period between the airstream exiting from the cloud and reaching the observation point. The time available for this is approximately 3 min. Possible mechanisms for this include the nucleation of NH_4Cl aerosol from NH_3 and HCl gases which were both outgassed from the evaporating cloud droplets (Wells *et al.*, 1997). So far it has not been possible to model the production of the large concentration of small particles that were observed. Work is proceeding on investigating a tri-molecular nucleation process (Kulmala, personal communication) involving water vapour ammonia and HCl.

6. CONCLUSIONS

The results of the 1993 Ground-based Cloud Experiment on Great Dun Fell represent an increase in our understanding in all the areas represented by the aims of the campaign, from scavenging of aerosol and trace gases, through sulphur chemistry, oxidised and reduced nitrogen species, organic compounds and metals, to the processing of aerosol and trace gases by passage through cloud. These results are applicable to problems in atmospheric sciences from air pollution through acid deposition and eutrophication to climate change. In addition to meeting each specific aim, the whole of GCE has proved to be greater than the sum of its parts, as each individual study is set in the context of all the other studies within the experiment. The 1993 campaign therefore not only succeeds in answering questions today, but also serves as a springboard from which future investigations and collaborative groups are being formed. These include subprojects of the proposed successor to EUROTRAC and also parts of the ACE-2 North Atlantic Aerosol Characterization Experiment and other projects. The combined results of the three GCE campaigns at Po Valley, Kleiner Feldberg and Great Dun Fell will be evaluated in the EUROTRAC Final Report.

7. FUTURE WORK

Further detailed experiments are needed to investigate the mechanism of the new particle formation observed as the airstream exits from cloud. The aerosol processing needs to be studied with a wider range of air mass types and aerosol climates so that conditions in which a larger contribution of ions other than sulphate, for example nitrate may be examined. This technique of using a hill cap cloud as a natural flow through reactor can also be effectively used to study the interaction of the complex cocktail of pollutants, including organic compounds emitted by urban areas upstream of a range of hills.

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