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SOURCE IDENTIFICATION DURING THE GREAT DUN FELL CLOUD EXPERIMENT 1993

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Abstract—A characterisation of the sources influencing the site for the final field campaign of the EUROTRAC subproject GCE (Ground-based Cloud Experiment) at Great Dun Fell, Cumbria, Great Britain in April–May 1993 is presented. The sources were characterised mainly by means of aerosol filter and cascade impactor data, single particle analysis, gas data, data on aromatic organic compounds, cloud water ionic composition, measurements of aerosol size distributions and hygroscopic properties and various meteorological information. Receptor models applied on the aerosol filter and impactor data sets separately revealed two major source types being a marine sea spray source and a long-range transported anthropogenic pollution source. The results of the receptor models were largely consistent with the other observations used in the source identification. Periods of considerable anthropogenic pollution as well as almost pure marine air masses were clearly identified during the course of the experiment. © 1997 Elsevier Science Ltd.

Key word index: Source identification, receptor modelling, ground-based cloud experiment.

1. INTRODUCTION

The final field campaign of the EUROTRAC subproject GCE (Ground-based Cloud Experiment) was carried out in April–May 1993 at Great Dun Fell (GDF), Cumbria, Great Britain. The purpose of GCE is to elucidate the interaction between clouds and fogs and various gaseous and particulate pollutants. An

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overview of the GDF experiment is described by Choularton *et al.* (1997).

The aim of the present paper is to identify the sources of pollution and characterise the air masses which affected the GDF field sites during the experiment. This source identification is meant to facilitate the interpretation of the process-oriented studies performed during the experiment. A statistical analysis of two aerosol data sets could essentially reveal only two major source types, sea spray and long-range transported anthropogenic pollution. A range of other measurements performed during the experiment contributed complementary information and considerably strengthened the interpretation regarding the effective sources and their origin.

2. TOOLS

The data used in the source identification and characterisation were mainly three-dimensional air mass back trajectories obtained from the German Weather Service, synoptic weather maps, mesoscale air flow and cloud field modelling (Wobrock *et al.*, 1997; Colvile *et al.*, 1997), wind speed and direction at GDF Summit (847 m.a.s.l.), receptor modelling applied on aerosol filter samples taken at Fell Gate (430 m.a.s.l.) and GDF Summit as well as cascade impactor samples from Wharley Croft (206 m a.s.l.; Laj *et al.*, 1997), aerosol size distributions and hygroscopic properties measured at Fell Gate (Wiedensohler *et al.*, 1997; Svenningsson *et al.*, 1997), single particle analysis of aerosol samples taken at Fell Gate and GDF Summit (Gieray *et al.*, 1997), NO_x($NO + NO_2$) and SO_2 gas data mainly from Wharley Croft, Mine Road (670 m a.s.l) and Moor House (550 m a.s.l.; Laj *et al.*, 1997; Cape *et al.*, 1997), aromatic compounds in both gas and liquid phase at Fell Gate and GDF Summit (Lüttke *et al.*, 1997) and finally cloud water ionic composition at GDF Summit and Mine Road (Schell *et al.*, 1997; Pahl *et al.*, 1997).

Effectively, all measurements which contained information regarding the sources influencing the GDF sites during the experiment were considered. Here, experimental details will only be given for the aerosol filter measurements performed at Fell Gate and GDF Summit since information regarding the other measurements can be found in the references given above. The paper is essentially divided into two parts, one describing the modelling performed on the two aerosol data sets and the other in which measurements relevant to the source identification are summarised and put in relation to the receptor modelling results.

2.1. *Aerosol filter samples*

Samples of the fine fraction ambient aerosol were taken at Fell Gate and GDF Summit at intermittent occasions from 28 April to 12 May 1993. The aerosol was sampled through the interstitial inlets, consisting of slit impactors having a 2 μm wet aerodynamic diameter cut-off at Fell Gate and 5 μm at GDF Summit. These inlets were designed to sample primarily the aerosol particles which had not been activated into cloud droplets. Sampling duration varied, but each filter was typically exposed for 2 h. Two parallel sets of filters were collected at each sampling occasion, both on 25 mm diameter, 0.4 μm pore size, Nuclepore™ polycarbonate membrane filters. The filters dedicated for Particle Induced X-ray Emission analysis (PIXE; Johansson *et al.*, 1995) and soot analysis were masked to give an exposed filter diameter of 8 mm, which also restricted the flow rate to maximum 5 $\ell\,min^{-1}$. The filter samples taken in parallel made use of the full filter area (flow rate 12 $\ell\,min^{-1}$) and were analysed for major ions by ion chromatography (IC). The PIXE analyses were performed at the department of Nuclear Physics in Lund while the IC analyses were undertaken by the Department of Physics at the University of Manchester. Soot was quantified with a light attenuation method (Heintzenberg, 1988) at the Department of Meteorology in Stockholm prior to the PIXE analysis.

2.2. *Receptor modelling*

Source/receptor models are a group of mathematical and statistical models which aim at establishing the relationship between the concentrations of various pollutants measured at a site, the receptor, and the sources causing the pollution (Henry *et al.*, 1984; Hopke, 1985). More specifically, receptor models aim at (1) determining the number of sources affecting the receptor site, (2) estimating the characteristic chemical composition of these sources (the source profiles) and finally (3) determine the impact of the various identified sources on the levels of pollutants observed at the receptor site. All but the very simplest of receptor models are multivariate, i.e. they make use of the concurrent observation of a number of pollutants at the receptor site. The model used here to study the aerosol filter and cascade impactor data sets is the so-called Absolute Principal Component Analysis (APCA) (Keiding *et al.*, 1986; Maenhaut and Cafmeyer, 1987; Swietlicki *et al.*, 1997). Receptor models, including APCA, are based on the assumption that the original receptor site concentrations of the measured pollutants can be adequately explained by a linear combination of contributions from various relevant sources with fixed composition such that

$$x_{ij} = \sum_{k=1}^{p} a_{ik} f_{kj} \qquad (1)$$

where x_{ij} is the measured ambient concentration of the pollutant $i (i = 1, \ldots, m)$ during sampling occasion $j (j = 1, \ldots, n)$. A number of $p (p < m)$ relevant sources are considered significant. The vector $(a_{1k}, a_{2k}, \ldots, a_{mk})$, containing the mass fractions a_{ik} of pollutant i in source k, is called the source profile for source k and is often given in ppm, ng mg^{-1} or similar

fractions. Here, it is given in ng m^{-3} as an estimate of the mean contribution of pollutant i from source k taken over the measurement period. These fixed source profiles are not necessarily identical with those measured at the sources themselves, but incorporate transformations taking place during transport to the receptor. f_{kj} is the mass contributed by source k during sampling occasion j. Since the aerosol mass was not measured for the data sets under consideration, only normalised source contributions can be given here, having unit variance.

3. RECEPTOR MODELLING RESULTS

Receptor models were only calculated for the aerosol filter and impactor data sets separately. Even though such models can be used to analyse essentially any type of ambient pollutant data, the basic model requirement that all measurements must be performed on the same time basis was not fulfilled for the entire set of measurements considered here.

3.1. *Aerosol filter samples*

Due to the short sampling time (typically 2 h), the PIXE analysis of the aerosol filter samples collected at Fell Gate and GDF Summit only gave reliable data for some major aerosol components. These were soot, sulphur, iron, copper and zinc. The short sampling time also posed a problem for the IC analysis of the major ions. Thus, only the ions NH_4^+, SO_4^{2-}, Na^+, Mg^{2+} and Ca^{2+} were selected for receptor modelling. Three samples showing extreme values in Cu and Zn were taken out of the data set since they caused the receptor model to be unstable.

Table 1 shows the Varimax rotated principal component (PC) solution. The so-called PC loadings given in the table are the correlation coefficients between the pollutant in question and the various hypothetical sources and range from -1 to $+1$. PC loadings close to $+1$ indicate that the specific pollutant is highly characteristic to the given source. The communalities also given in Table 1 reveal the fraction of pollutant variance accounted for by the model and should be as close to one (1) as possible. PC loadings with a magnitude less than one standard deviation of the communalities (Heidam, 1982) were considered insignificant and set to zero. The structure of the PC loading matrix is the basis for the interpretation of the underlying physical/chemical nature of the hypothetical sources.

Three sources were considered relevant for an adequate model reproduction of the receptor site data. These were interpreted as being (1) an anthropogenic source type describing a continental influence following long-range transport (denoted "LRT"); (2) a natural marine source type (denoted "Sea") and finally (3) a local anthropogenic and probably automotive source type (denoted "Local"). The "Local" source type only affected the Fell Gate site significantly.

The ability of the receptor model to reproduce the measured mean concentrations of the various pollutants is shown in Fig. 1. A summed source contribution lower than 100% indicates that the absolute receptor model underestimates the concentrations of the pollutant in question and vice versa. The ability of the receptor model to reproduce the measured concentrations is lower than is usually the case (see e.g. Swietlicki *et al.*, 1996), which is manifested in the large deviation of the summed model source contributions from 100%. A possible explanation for this is the short sampling time which affected the quality of the data set and caused a number of important tracer pollutants to fall below or close to the detection limit. Nevertheless, some general observations can be made. The "LRT" source type accounts for most of the soot, elemental S, SO_4^{2-}, NH_4^+ and elemental Zn. The "Sea" source type explains the main portion of the ions Na^+, Mg^{2+} and Ca^{2+}, while the "Local" source

Table 1. Varimax rotated PC solution, measured arithmetic mean concentrations and standard deviations for the interstitial aerosol filter samples collected at Fell Gate and GDF Summit (Comm. = communality)

	Varimax rotated PC solution				Measured conc. (ng m^{-3})	
Pollutant	LRT	Sea	Local	Comm.	Mean	S.D.
Soot	0.93	—	0.09	0.87	313	190
S	0.86	0.30	0.10	0.85	949	587
SO_4^{2-}	0.92	0.12	0.07	0.86	1770	1740
NH_4^+	0.94	0.09	—	0.90	739	739
Fe	0.34	0.25	0.76	0.76	28.0	21.0
Cu	—	0.17	0.85	0.76	1.46	2.18
Zn	0.77	—	0.35	0.71	2.87	3.84
Na^+	0.12	0.91	—	0.84	646	534
Mg^{2+}	0.11	0.94	0.18	0.93	47.0	46.9
Ca^{2+}	0.08	0.80	0.36	0.79	192	223

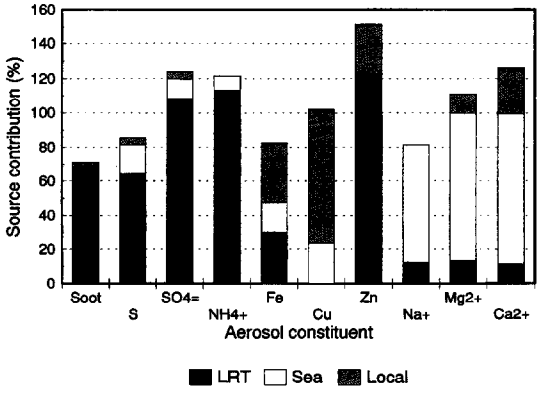

Fig. 1. The ability of the APCA receptor model to reproduce the measured mean concentrations for the filter samples collected at Fell Gate and GDF Summit.

Table 2. Varimax rotated PC solution for the cascade impactor aerosol samples collected at Wharley Croft (Comm. = communality)

Pollutant		Varimax rotated PC solution			Measured conc. ($ng\,m^{-3}$)	
		Sea	LRT	Comm.	Mean	S.D.
Na^+	(0–2)	0.85	0.08	0.73	396	393
Mg^{2+}	(0–2)	0.88	0.18	0.81	31.0	41.5
Cl	(0–2)	0.83	—	0.69	261	554
Na^+	(3)	0.91	0.14	0.85	376	369
Mg^{2+}	(3)	0.92	0.16	0.88	52.8	52.0
Cl	(3)	0.95	—	0.91	385	707
K	(0–2)	0.42	0.68	0.63	72.1	53.7
Ca^{2+}	(0–2)	0.13	0.74	0.56	68.0	113
K	(3)	0.71	0.22	0.56	20.6	18.0
Ca^{2+}	(3)	0.30	0.65	0.51	91.0	88.4
NH_4^+	(0–2)	—	0.78	0.63	1800	1290
SO_4^{2-}	(0–2)	—	0.80	0.64	5230	3990
NO_3^-	(0–2)	—	0.80	0.65	952	1540
NH_4^+	(3)	—	0.88	0.77	66.6	65.3
SO_4^{2-}	(3)	0.42	0.77	0.76	257	202
NO_3^-	(3)	0.25	0.79	0.69	485	502

Note: Numbers (0–2) and (3) indicate impactor stages collecting particles with aerodynamic diameters $d_{ae} < 1.4\ \mu m$ (stages 0–2) and $1.4\ \mu m < d_{ae} < 5\ \mu m$ (stage 3). Also given are the measured arithmetic mean concentrations and standard deviations (S.D.).

type adds significantly to the measured concentrations tions of elemental Fe, Cu and to some extent also Zn.

3.2. *Cascade impactor samples*

This data set was described in Laj *et al.* (1997). Before the receptor model was applied on the Wharley Croft cascade impactor data set, the three last impactor stages (0–2) were summed to give the ambient concentrations for aerodynamic particle diameters (d_{ae}) $< 1.4\ \mu m$. The upper stage (3) collected particles with $1.4\ \mu m < d_{ae} < 5\ \mu m$. The data set consisted of the ions NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Mg^{2+}, Cl^-, K^+ and Ca^{2+}.

Table 2 shows the Varimax rotated PC solution for the Wharley Croft cascade impactor data set. Two source types were selected as being relevant, one "LRT" source type and one "Sea" source type. The low communalities for several ions, especially Ca^{2+} (stages 0–2), Ca^{2+} (stage 3) and K (stage 3), reveal that the two-source model cannot adequately account for the variance of these ions. The absolute receptor model can partly be validated by comparing the sea source profile (not given here) with an average sea water composition as that given by Stumm and Morgan (1981). Figure 2 shows the enrichment factors to Na, $(EF(Na)_x)$, for the "Sea" source profile. The enrichment factors are defined as $EF(Na)_x = (c_x/c_{Na})_{air}/(c_x/c_{Na})_{sea}$, where c_{Na} and c_x are the concentrations of Na and element x in air and sea water. These enrichment factors are in general close to 1, which is an indication that the sea spray source profile calculated

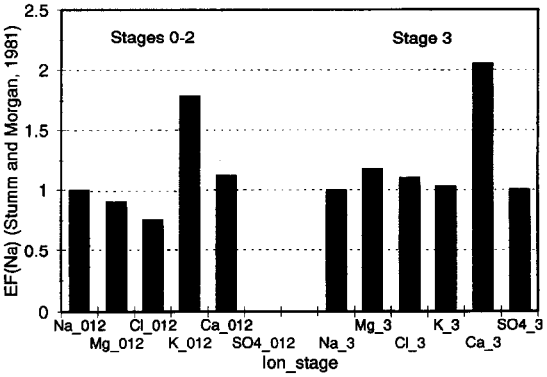

Fig. 2. Enrichment factors to Na, EF(Na), for the "Sea" source profile for the cascade impactor samples collected at WharleyCroft. The average sea water composition of Stumm and Morgan (1981) was used as reference. The numbers after the underscore denote the impactor stages used (stages 0, 1 and 2 were summed).

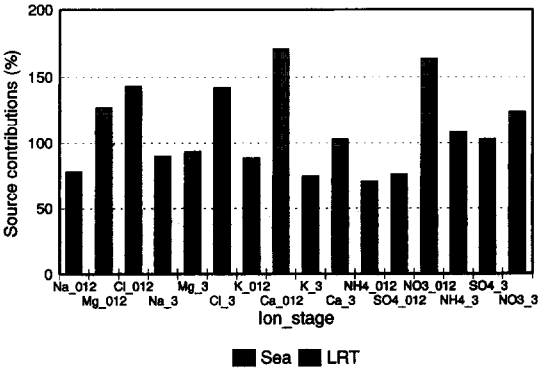

Fig. 3. The ability of the APCA receptor model to reproduce the measured mean concentrations for the cascade impactor samples collected at Wharley Croft. The numbers after the underscore denote the impactor stages used (stages 0, 1 and 2 were summed).

by the receptor model is quite similar to an average sea water composition. When comparing the PC loadings for Ca in Tables 1 and 2, it is obvious that a larger fraction of the observed Ca concentrations is attributed to the "LRT" source type for the impactor data set compared with the filter data set. This is caused by three impactor samples with high fine and coarse mode Ca concentrations collected on the evening of 29 May during a cloud-free pollution episode (see also Fig. 4). No filter samples were collected at that time. As seen in the enrichment factors (Fig. 2), the sea source profile estimated by the APCA model for the impactor data set seems to be largely correct for fine mode Ca (stages 0–2) and only slightly overestimated for coarse mode Ca (stage 3).

The source contributions estimated by the absolute receptor model are given in Fig. 3 in per cent of the measured pollutant mean. It is interesting to note that some nitrate is attributed to the stage 3 "Sea" source type, which suggests an interaction between gaseous

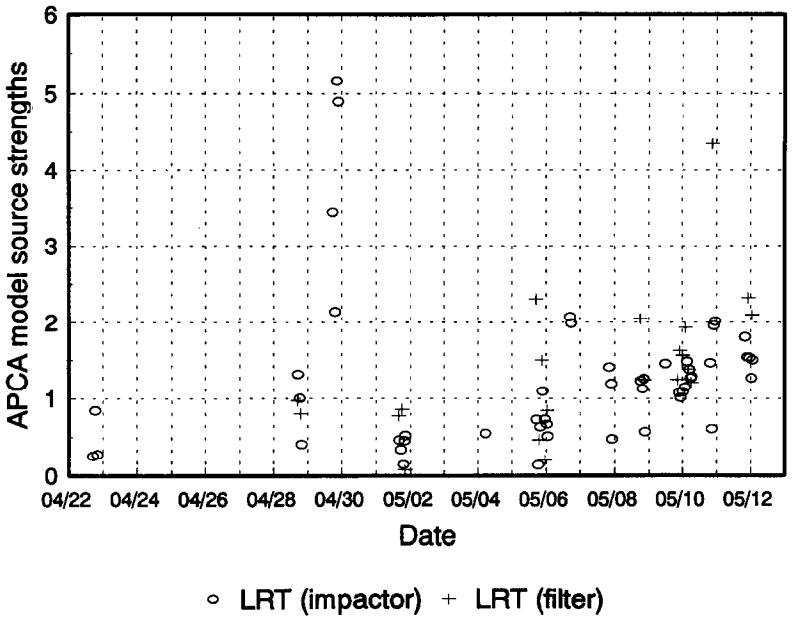

Fig. 4. Normalised APCA model "LRT" source contributions for the Wharley Croft cascade impactor aerosol samples and the Fell Gate filter samples.

nitric acid and sea salt particles and subsequent gas-to-particle transformation of nitrate species during long-range transport according to $NaCl + HNO_3 \rightarrow HCl(g) + NaNO_3$ (Hara *et al.*, 1989).

3.3. *Influence of the marine and continental sources over time*

The APCA receptor model calculates the sample-to-sample contribution of each identified source type. Since the aerosol mass was not measured on the same samples, the source contributions (absolute PC scores) can only be given in a normalised form, in a way that the source contributions from each given source type has unit variance taken over the measurement period.

Figure 4 shows the normalised "LRT" source contributions given by the APCA models when applied on the (Wharley Croft) cascade impactor aerosol samples and the (Fell Gate) filter samples separately. Source contributions for GDF Summit are not shown since they are clearly affected by in-cloud nucleation scavenging (Gieray *et al.*, 1997). The corresponding "Sea" source contribution time series is given in Fig. 5. The two APCA models follow the same general pattern, showing periods with distinct high and low source contributions.

4. CLASSIFICATION OF CLOUD EVENTS

This section presents an effort to synthesise all available data from the GDF experiment 1993 which are relevant to the source identification and also to put the results from the receptor model described above into a broader perspective. The results are summarised in Table 3. Meteorological conditions during the various cloud events will be discussed only when relevant to the source identification. For more information, see Colvile *et al.* (1997) and Wobrock *et al.* (1997). All hours given are British summer-time (BST = UTC + 1 h). The time periods selected for special study are those classified as cloud events in Colvile *et al.* (1997).

4.1. *Evening of 22 April*

The evening of 22 April was the only occasion during the campaign when cloud was present at GDF Summit while winds came from the southwest (Colvile *et al.*, 1997).

Impactor aerosol samples taken at Wharley Croft show a rather modest contribution from sea spray (Fig. 5) and long-range transported continental pollutants (Fig. 4). Nevertheless, the air reaching GDF had picked up fresh anthropogenic pollution as it passed over the densely populated Liverpool–Manchester area. Levels of SO_2 at GDF Summit rose sharply after 20:00 from 2 ppb to peak at 11 ppb shortly before 21:00 as the path of the ground-level trajectories moved slowly eastwards across the Midlands. The large coal-fired power station at Fiddler's Ferry close to Liverpool and Manchester might be a main contributor to the observed levels of SO_2 at GDF during this period. In cloud water samples taken at GDF Summit between 20:00–22:00 (Schell *et al.*, 1997), Cl^- was found in large excess of Na^+, compared to the sea water Cl/Na ratio. The excess Cl^- indeed suggests an influence from coal combustion. Measurements of aromatic compounds

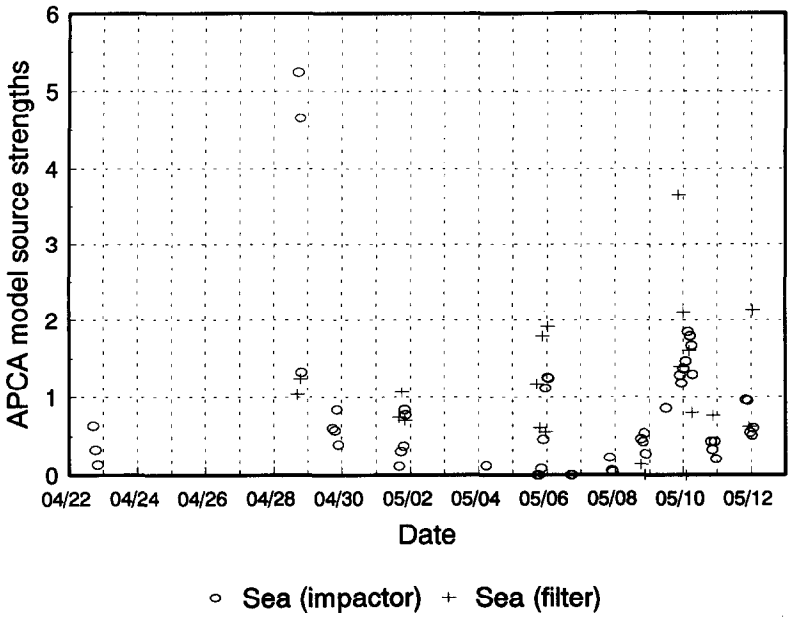

Fig. 5. Normalised APCA model "Sea" source contributions for the Wharley Croft cascade impactor aerosol samples and the Fell Gate filter samples.

at GDF Summit and Fell Gate on 22 April 16:05–20:35 also showed a mixture between an aged and a freshly polluted air mass (Lüttke *et al.*, 1997).

4.2. *Night of* 25–26 *April*

Not very many measurements were made during this event which prevents a more detailed analysis of the sources influencing the GDF sites. The air mass reaching GDF from the east was relatively clean with SO_2 and NO_x levels around 1 ppb or less.

4.3. *Night of* 27–28 *April*

As for the previous event, only a limited set of measurements are available for the night between 27–28 April. The observed levels of SO_2 at GDF were stable and low ($\sim$1 ppb) from late evening on 27 April to early morning on 29 April. However, concentrations of NO_x were much more variable and were as high as 11 ppb shortly before noon on 27 April and then decreased to around 1 ppb during the following night. Winds shifted from southwesterly to northeasterly at 17:00 on 27 April.

Impactor and filter aerosol samples taken during the evening of 28 April (16:00–21:00) showed a moderate influence from long-range transported pollution (Fig. 4) and a high to very high sea spray contribution (Fig. 5), during which winds at Fell Gate were northeasterly and around 15 m s^{-1} in strength. On 28 April between 17:20 and 20:05, the lowest benzene and toluene concentrations during the whole campaign were observed (Lüttke *et al.*, 1997).

4.4. *Evening of* 2 *May*

Aerosol samples were taken only during the evening of 1 May and showed low contributions from both sea spray and anthropogenic long-range transported pollution. This followed a two-day period of atmospheric stability, sunny weather and high pollution levels (SO_2 at GDF Summit peaked at 34 ppb in the early morning hours of 30 April). The pollution episode was clearly manifested in the high "LRT" source contributions given by the impactor data set APCA model on 29 May (Fig. 4).

According to the air mass back trajectories, the air approached GDF from northwest on the evening of 2 May. This air had levels of SO_2 and NO_x around 1–2 ppb.

4.5. 5–6 *May*

The general weather pattern during this period was governed by a high pressure moving eastwards from Northern Ireland towards the North Sea passing immediately north of GDF (Colvile *et al.*, 1997). The 3D air mass back trajectories, both at ground and higher levels, showed that the air masses (up to 96 h back in time) originated from over the Northern Atlantic. Local winds came steadily from the northeast and the North Sea.

The cloud at GDF was part of a continuous cloud deck stretching upstream over the hilly landscape east of GDF to the North Sea and the air masses actually crossing over GDF Summit at this occasion experienced little mixing from above (Wobrock *et al.*, 1997;

Table 3. Summary of the air mass characterisation during the cloud events of the Great Dun Fell Cloud Experiment 1993

Period (1993)	Marine influence	Continental influence	Source regions (trajectories)
Evening of 22 April	Low	Low	Atlantic, Liverpool–Manchester
Night of 25–26 April	—	—	—
Night of 27–28 April	High	Moderate	Marine air mass from North Sea with some anthropogenic influence
2 May	(Low)	(Low)	North Sea
5 May until 20:00	Low	Moderate	Polluted air from Glasgow–Edinburgh superimposed on an Atlantic air mass
5–6 May	Moderate	Moderate	Marine air mass from North Sea with some anthropogenic influence
Evening 05/08–05/09 06:00	(Low–moderate)	(Moderate)	In plume from Blyth coal-burning power station
05/09 06:00–midday 05/09	Moderate	Moderate	Marine air mass of Atlantic and North Sea origin with some anthropogenic influence
Evening 05/09–morning 05/10	High	Moderate	Marine air mass polluted by anthropogenic sources in Eastern Europe
Morning 05/10–evening 05/10	(Low)	(Moderate)	Anthropogenic pollution from sources in Eastern Europe
Evening 05/10–midday 05/11	Low	High	Anthropogenic pollution from sources in Eastern Europe, especially the "Black triangle"
Midday 05/11–morning 05/12	Moderate–high	Fairly high	Marine air mass polluted by anthropogenic sources in Eastern Europe

Colvile *et al.*, 1997). Based on the air mass trajectories and pollutant loading, two periods, before and after 20:00 on 5 May, are clearly separable.

4.5.1. *Afternoon of 5 May.* The ground-level trajectories (1000 hPa), passing GDF on the afternoon and early evening of 5 May (16:00–20:00), originated from the Northern Atlantic passing southwest of Iceland. The trajectory tail then swept across southern and central Scotland towards the North Sea for GDF arrival times between 16:00–18:00 on 5 May. In doing so, they passed over some densely populated regions of Scotland, most notably the Glasgow–Edinburgh area. Local winds at GDF Summit were northeasterly at 11 $m s^{-1}$. Wind speeds at lower levels were much lower owing to the close proximity to the centre of the high pressure.

SO_2 concentrations ($\sim$0.5 ppb) were lower than expected for air masses passing over Glasgow–Edinburgh. However, SO_2 was scavenged in the extensive cloud cover upstream of GDF. Depletion of SO_2 across the hill from GDF Summit to Mine Road was indeed observed on 5 May between 19:00–21:00 (Laj *et al.*, 1997). The S(IV) oxidation exhausted hydrogen peroxide as long as GDF was in the plume of Glasgow–Edinburgh. Levels of H_2O_2 increased rapidly from 20:00 on 5 May, when cleaner marine air masses were brought to GDF.

Single particle analysis showed that sulphate mixed with carbonaceous material made up a substantial fraction of the aerosol particles for the 16:15–17:15 sampling period of 5 May (Gieray *et al.*, 1997). In fact, sulphate was found in almost all cloud droplet residuals. A marine influence is indicated by the presence of particles with significant amounts of MSA internally mixed with sulphate.

Observations of aromatic organic compounds during 16:00–20:50 on 5 May gave further evidence that the air mass sampled at GDF was moderately anthropogenically polluted and had undergone transformation during transport (Lüttke *et al.*, 1997).

The cascade impactor receptor model corroborates the other observations and shows a low marine impact (Fig. 5) and a moderate "LRT" influence (Fig. 4).

4.5.2. *Night between 5 and 6 May.* As the lower level trajectories turned away from Glasgow–Edinburgh on 5 May at 20:00, the character of the air mass reaching GDF changed drastically from being clearly anthropogenically influenced and sulphate-rich to a considerably purer marine air mass. The cascade impactor data showed increasing concentrations of Na and Cl in the aerosol after 20:00, and the marine impact according to the receptor model increased correspondingly from low to moderate (Fig. 5).

Measurements of the hygroscopic properties of the submicrometer aerosol (Svenningsson *et al.*, 1997) showed a steady increase in hygroscopic growth from 20:00 on 5 May until 08:00 on 6 May. The diameter growth factor of individual particles when taken from a dry state to 90% relative humidity changed from 1.4 to 1.65 for 165 and 265 nm particles and somewhat

less for 110 nm particles. This could be caused by a higher soluble fraction as the marine influence increases or a higher mass fraction of NaCl. Pure NaCl has a considerably higher growth factor than e.g. pure ammonium sulphate.

Single particle analysis (Gieray *et al.*, 1997) also clearly recognised the period between 21:00 on 5 May and 01:00 on 6 May as being basically a marine air mass, with some anthropogenic influence. The majority of the particles analysed were classified as aged sea salt. The observed ammonium sulphate particles contained tracer elements for combustion processes like V and Ni (residual oil combustion) and carbonaceous materials.

No sulphate production across GDF could be observed after 01:00 on 6 May (Laj *et al.*, 1997).

The receptor models showed a varying but mostly moderate continental influence all through the period (Fig. 4). The "LRT" aerosol component is normally associated with aged air masses (in the order of one to several days). It can therefore be hypothesised that the moderate continental influence observed during this period is partly due to sources in the U.S. and Canada. However, the available air mass back trajectories do not reach back in time long enough to validate this assumption.

At around noon on 6 May, the impact from the Newcastle region became evident. The levels of aromatic organic compounds observed during 16:05–19:30 on 6 May all indicate an influence from car traffic within the nearest few hours of atmospheric transport (Lüttke *et al.*, 1997).

4.6. *Evening of* 8 *May to morning* 12 *May*

The same overall weather pattern lasted for the whole period between 5 and 13 May, i.e. a high pressure was situated north of GDF and minor low pressures were found over continental Europe. Nevertheless, the movement of these pressure systems caused the weather conditions at GDF to change (Colvile *et al.*, 1997). Like on the previous days, local winds came from the north-east off the North Sea. At GDF Summit, the wind speed freshened from 10 m s^{-1} on the evening of 8 May to 18 m s^{-1} in the early morning hours of 10 May. Wind speeds dropped somewhat on the evening of 10 May (10 m s^{-1}) only to increase again during the evening of 11 May (17–19 m s^{-1}). This clearly affected the intensity of sea spray aerosols measured at GDF.

4.6.1. *Evening* 05/08–*midday* 05/09. During the night between 8 and 9 May and the early morning hours of 9 May, both the ground-level and the higher level air mass back trajectories made a wide loop over the open sea around Ireland and Great Britain before reaching GDF from the northeast. Around midday on 9 May, the air masses reaching GDF switched from Atlantic to European as the high pressure north of Great Britain developed into a high pressure ridge stretching as far as Norway. Considerable mixing between air at different levels was modelled to occur around GDF (Wobrock *et al.*, 1997).

There are two major sources upwind of GDF at Blyth and the city of Newcastle for the winds prevailing during this time period. The coal-burning power station at Blyth (55°7′N; 1°30′W) north of Newcastle emits more than 40 thousand tonnes of SO_2 per year (Buckland, 1994) and is the only major power station in the northeasterly direction from GDF. A co-located smelter emits some additional 9 thousand tonnes of SO_2 per year. It is evident from the mesoscale dispersion model of Wobrock *et al.* (1997) that GDF was highly influenced by Blyth at the 800 m level on the morning of 9 May. Most of the plume from Newcastle was deflected southwards when it hit the Pennine ridge since it travelled at a lower altitude than the Blyth plume.

As evidenced by the SO_2 concentrations, GDF entered the Blyth plume on 8 May at 22:00 and moved out of the plume again on 9 May between 06:00 and 07:00. During this time period, SO_2 measured at the GDF Summit first increased from 1 ppb to 10 ppb and then dropped again to less than 1 ppb. The excess Cl in cloud water (Cl in excess of the sea water Cl/Na ratio) covaried with GDF Summit SO_2, corroborating an influence from coal-burning. Concentrations of NO_x covaried closely with those of SO_2, and reached 6 ppb around midnight between 8/9 May again indicating a freshly polluted air mass.

The influence from Blyth was clearly seen also in the cloud water samples collected at GDF Summit (Schell *et al.*, 1997; Pahl *et al.*, 1997) and Mine Road (Pahl *et al.*, 1997). A depletion of SO_2 across the ridge from GDF Summit to Mine Road was clearly observed on 9 May during 00:00–06:00 (Laj *et al.*, 1997) indicating that S(IV) oxidation took place within the cloud.

The submicrometer aerosol size distribution (Wiedensohler *et al.*, 1997) also changed considerably during the period of influence from the Blyth coal-burning power station. Most striking is the linear increase in the accumulation mode mean geometric diameter measured at Fell Gate from 150 nm on 8 May at 18:00 to a very high value of 300 nm on 9 May at 06:00, while at the same time, the accumulation mode number concentration stayed remarkably constant around 400 cm^{-3}. This means that the mass in the accumulation mode increased roughly by a factor of 8 during this period. The Aitken mode mean geometric diameter decreased slightly from almost 65 to 50 nm, while the number concentration of the Aitken mode dropped substantially and linearly from ca 1400 cm^{-3} on 8 May at 20:00 to 500 cm^{-3} on 9 May at 06:00. It can be hypothesised that the largest and more hygroscopic of the Aitken mode particles were activated in the upstream cloud deck gaining sufficient mass through aqueous phase S(IV) oxidation to grow into the accumulation mode following evaporation (Hoppel *et al.*, 1994). The accumulation mode particles increased their soluble fraction somewhat

during the morning of 9 May while no corresponding change was observed for the Aitken mode particles (Svenningsson *et al.*, 1997).

The impactor sampling was discontinued at 22:00 and the filter sampling at 22:20 on 8 May since no cloud was present at GDF Summit after about 17:00. This unfortunately meant that no cascade impactor or filter aerosol samples were taken during the period when GDF was in the plume from Blyth, and the plume influence on the aerosol could therefore only be seen indirectly through the cloud water composition. For the time periods immediately before and after the Blyth plume influence, both impactor and filter aerosol data showed a varying but mostly moderate continental influence (Fig. 4).

On the evening of 8 May, wind speeds over the North Sea (around 10 $m\,s^{-1}$ at GDF Summit) were not strong enough to result in more than a moderate marine influence on the aerosol. At noon on 9 May, the winds at GDF Summit had freshened to 14 $m\,s^{-1}$ and continued to increase further, causing also the sea spray aerosol contribution to increase. The receptor model for the impactor samples showed a moderate sea spray contribution around noon (Fig. 5). A similar pattern was seen in the GDF Summit and Mine Road cloud water samples (Schell *et al.*, 1997; Pahl *et al.*, 1997).

4.6.2. *Evening* 05/09–*morning* 05/10. At 18:00 on 9 May, the switch from an Atlantic to a European flow pattern was fully developed, bringing air masses at the 850 hPa level across from Ukraine, northern Poland, the southern Baltic Sea, Denmark and the North Sea to GDF. The ground-level trajectories originated from over the North Sea between Scotland and Norway. The mesoscale dispersion model run for 10 May 00:00 showed the strongest lee-side downdrafts of all three runs (Wobrock *et al.*, 1997). It is therefore likely that mixing of air from various levels took place at GDF.

From late evening on 9 May to early morning on 10 May the winds were strong both at GDF Summit (17–19 $m\,s^{-1}$) and over the North Sea causing the sea spray contribution to peak around midnight between 9 and 10 May and reach its highest value during the entire 8–12 May period, as seen in both the impactor and filter data receptor models (Fig. 5).

The classification of the air masses as being of clearly marine character was verified by both the cloud water composition and the single particle analysis. Na^+ and Cl^- represented more than 50% of the conductivity of the cloud water collected at GDF Summit for the period 22:00 on 9 May to 07:00 on 10 May (Schell *et al.*, 1997). At Mine Road, cloud water concentrations of H^+, NH^+, NO_3^- and nss-SO_4^{2-} remained low and fairly constant from 21:00 on 9 May to 07:00 on 10 May (Pahl *et al.*, 1997). According to the impactor and filter data receptor models, the influence from continental sources during this time period were moderate or slightly higher than moderate (Fig. 4).

The night between 9/10 May showed the strongest marine influence of all events studied with single particle analysis (Gieray *et al.*, 1997). Nearly pure sea salt particles were found as droplet residues for the supermicrometer particle sizes, indicating that these particles were probably freshly generated over the windswept North Sea. The submicrometer particles were dominated by sulphate in an internal mixture with variable amounts of MSA. Some influence from anthropogenic sources such as combustion tracers (vanadium) could also be seen in the submicrometer ammonium sulphate particles.

4.6.3. *Morning* 05/10–*evening* 05/10. Late on 9 May, the path of the 850 hPa air mass back trajectories shifted slowly southwards across Poland and Ukraine. From the early morning hours on 10 May, the air masses reaching GDF had probably passed over the industrialised region around Donetsk in Ukraine. No aerosol samples were taken between 07:00 and 18:00 on this day, even though cloud remained at GDF Summit.

4.6.4. *Evening* 05/10–*midday* 05/11. As on the previous day, the air mass transport at the ground and 850 hPa levels showed quite different behaviour. While the ground-level trajectories originated from over the North Sea between Scotland and Norway and later extended to pass over Norway and the Norwegian Sea, the 850 hPa trajectories originated from Eastern Europe. From 16:00 on 10 May until roughly midday 11 May, the air on the 850 hPa level leaving Ukraine (passing south of Donetsk) passed over the highly polluted "Black triangle" on the borders between Germany, Czech Republic and Poland. Numerous coal-burning power plants and non-ferrous and ferrous smelters emitting large quantities of SO_2 and heavy metals are situated in this region (Pacyna, 1983). It is evident from the observations that mixing occurred between the lower and higher level air masses which resulted in polluted Eastern European air reaching the ground at GDF.

The period on 10 May between 19:00 and 23:00 proved to be the one with the largest influence from anthropogenic sources of all those studied by single particle analysis (Gieray *et al.*, 1997). Since the polluted air masses had also passed over the North Sea, it is not surprising that some large sea salt particles were also observed resulting in a low, but obvious marine contribution. However, ammonium sulphate particles dominated the supermicrometer size range also with about one third of the particles consisting partly of Al, Si, Ca, Fe and Ba probably originating from coal combustion. Tracers for residual oil combustion (V, Ni) were also found. Carbonaceous material was found in an internal mixture with sulphate, which implies that gas-to-particle conversion of sulphur species had occurred during atmospheric transport.

On the evening of 10 May, the filter aerosol samples taken at Fell Gate showed the highest impact of long-range transported, continental aerosol for the

whole campaign, while the impactor samples showed a high, but more variable "LRT" contribution (Fig. 4). The marine contribution to the collected aerosol according to the receptor model was rather low for both filter and impactor samples (Fig. 5).

Model calculations as well as measurements gave evidence of sulphate production during the evening of 10 May (Bower *et al.*, 1997; Laj *et al.*, 1997). The S(IV) oxidation was obviously facilitated by introduction of new reactants during the air mass mixing that occurred. In accordance with the other observations, the cloud water composition at GDF Summit and Mine Road had large conductivities almost entirely caused by H^+, NH_4^+, NO_3^- and nss-SO_4^{2-} (Schell *et al.*, 1997; Pahl *et al.*, 1997).

The influence from car traffic was evidenced by the fairly high levels of benzene and toluene on the evening of 10 May (Lüttke *et al.*, 1997).

4.6.5. *Midday* 05/11–*morning* 05/12. The air reaching GDF during the evening of 11 May and the night between 11 and 12 May originated from Ukraine (Donetsk), passing over Belorussia, Lithuania, the southern Baltic Sea, southern Sweden and the North Sea.

The influence from East European sources is manifested in a fairly high contribution of anthropogenic pollutants to the aerosol (Fig. 4). The marine influence on the aerosol was varying from moderate to high for GDF Summit wind speeds between 17 and 19 $m\,s^{-1}$ on the evening of 11 May (Fig. 5).

The most prominent feature observed in the single particle analysis was the strong internal mixture between natural sea spray components and MSA and the anthropogenic pollution products such as carbonaceous material, ammonium sulphate and elemental tracers for oil combustion (V, Ni). A further evidence of the strong internal mixture is that essentially only one mode of hygroscopic growth was present, at least for particles with dry sizes of 110 nm and larger (Svenningsson *et al.*, 1997). It therefore seems likely that the aerosol had undergone extensive modification during the long-range transport. The rather high concentrations of 2,4-dinitrophenol observed during 19:30–22:30 on 11 May is a further strong indication of an aged, polluted air mass (Lüttke *et al.*, 1997).

5. CONCLUSIONS

The sources of pollution which affected the field sites during the final field campaign of the EUROTRAC subproject GCE (Ground-based Cloud Experiment) at Great Dun Fell, Cumbria, Great Britain, in April–May 1993 were identified (Table 3). In this process, all measurements containing source information were considered. The separate receptor models for the two aerosol filter and cascade impactor data sets constitute the back-bone of the source identification to which all other observations were referred. A large degree of consistency was found between the various observations, which considerably strengthened the receptor model hypothesis concerning the source influence. The source identification analysis could possibly have been further improved had all the measurements been performed on the same time basis. If this were the case, then a single receptor model could have been applied to the data set, describing all relevant sources for which tracers were measured.

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