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NIGHT-TIME FORMATION AND OCCURRENCE OF NEW PARTICLES ASSOCIATED WITH OROGRAPHIC CLOUDS

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Abstract—The formation and occurrence of new ultrafine aerosol particles were studied in association with an orographic cloud during a field experiment at Great Dun Fell (GDF), Northern England. Three size spectrometers to measure submicrometer aerosol particles were located upwind, on top, and downwind of GDF Summit to investigate changes in the aerosol size distribution. During two nighttime cloud periods, ultrafine particles were observed downwind of the hill while no particles were detected upwind of the hill. During one cloud event, there was some evidence of entrainment. In this case, the occurrence of ultrafine particles may have been due to entrainment from aloft or by homogenous nucleation downwind of the hill. During the other cloud event, the formation of an ultrafine particle mode (nucleation mode) occurred probably after the cloud passage. There was no evidence of entrainment during this time period.

Multicomponent homogeneous nucleation models were used to simulate the formation of new particle downwind of an orographic cloud. Possible homogeneous nucleation processes for this could be the formation of sulphuric acid or ammonium chloride due to outgassing of hydrochloric acid. It was not possible, however, to simulate formation rates of new particles as observed downwind the hill using a model for the binary or ternary homogeneous nucleation process of ammonia and hydrochloric acid. During the first event with high sulphur dioxide concentrations, the formation of new particle via binary homogeneous nucleation of sulphuric acid and water could be only predicted using a high nighttime hydroxyl radical concentration. No formation of sulphuric acid particle could be simulated during the second event with low sulphur dioxide concentrations. © 1997 Elsevier Science Ltd.

Key word index: Nighttime nucleation, cloud-induced particle formation, ultrafine aerosol.

INTRODUCTION

It is important to understand the formation of new aerosol particles in the atmosphere by natural and anthropogenic emissions of precursor gases. A change in total number concentration of atmospheric aerosol particles could lead to an increased number of available cloud condensation nuclei. This parameter controls the indirect radiative forcing of the climate by aerosols, i.e. through their effect on cloud properties (Twomey, 1977).

It is believed that particles smaller than 10 nm in diameter are generated by homogeneous nucleation processes from precursor gases. In remote marine areas and the free troposphere, sulphuric acid (H_2SO_4), formed by oxidation of sulphur dioxide (SO_2) in the presence of hydroxyl (OH) radicals, may produce these ultrafine particles (Raes *et al.*, 1992; Easter and Peters, 1994). The homogeneous nucleation process is strongly dependent on factors such as temperature, the partial pressure of condensable material, the partial pressure of water vapour (H_2O), and the surface area of pre-existing particles (Seinfeld, 1986; Jaecker-Voirol and Mirabel, 1989). Existing

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theories, however, predict nucleation rates that differ by orders of magnitude (Girshick *et al.*, 1990).

New particle formation in polluted areas is probably more complex than under remote atmospheric conditions. A host of gas precursors, such as volatile organic compounds, hydrochloric acid (HCl), nitric acid (HNO_3) and ammonia (NH_3), may also contribute to homogeneous nucleation processes besides sulphuric acid. Besides the binary homogeneous nucleation process described earlier, ternary homogeneous nucleation processes such as H_2SO_4–H_2O–NH_3, HCl–H_2O–NH_3 and HNO_3–H_2O–NH_3 may occur in the atmosphere. Modelling results from Coffmann and Hegg (1995) show that ternary homogeneous nucleation could be a viable explanation for particle production in the marine boundary layer.

There are also measurements suggesting that ultrafine particle production is associated with clouds, especially in or just above the cloud top. It is assumed that such layers with high particle concentrations (Hegg *et al.*, 1990) or a separate ultrafine particle mode (Hoppel *et al.*, 1994) are the result of *in situ* photochemical particle production by H_2SO_4. Another possible process, which may occur near evaporating clouds, is the particle formation by homogeneous nucleation of HCl–NH_3 or HCl–H_2O–NH_3. Evaporating cloud droplets might release HCl locally so that this species is able to nucleate homogeneously in association with ammonia and water. These homogeneous nucleation processes, however, have never been observed in the atmosphere and it is uncertain under what conditions these nucleation processes may occur. In contrast to the particle production by H_2SO_4, particle formation of ammonium chloride is also possible in the absence of OH radicals. This means that new ultrafine particles can also be formed during nighttime.

The third field campaign within the ground-based cloud experiments (GCE), a subproject of EUROTRAC, was held from 22 April to 12 May in 1993 at Great Dun Fell, a hill site in Northern England (Colvile *et al.*, 1997 (a)). To study the modification of the aerosol size distribution as air is processed by passage through a hill cap cloud, a quasi-Lagrangian experiment was arranged. Aerosol size spectrometers were placed at measuring sites upwind, at the summit, and downwind the hill: Fell Gate (430 m a.s.l., usually below cloud), GDF Summit (847 m a.s.l., usually in cloud), and Moor House (550 m a.s.l., usually below cloud), respectively.* Note, in this natural flow reactor, it is not possible to follow the same air parcel. It is assumed that the aerosol size distribution of the air mass is horizontally, homogeneously distributed, and experiences a similar modification during the cloud passage. Aerosol modifications of interest in this experiment include the formation of new atmospheric particles, the loss of aerosol particles in clouds, the scavenging ratio of particles to cloud droplets (particle size distribution in cloud to out of cloud), and the production of new aerosol mass by aqueous-phase chemical reaction (e.g. sulphate production by oxidation of SO_2 in cloud droplets)

The aim of this paper is to study the occurrence and the formation of new, ultrafine particles associated with orographic clouds. Two intensively measured cloud periods are studied in detail, during which air flow was connected from Moor House to Fell Gate passing through GDF Summit (Colvile *et al.*, 1997 (b)). In the early morning before sunrise, on 9 and 10 May 1993, ultrafine particles were observed at Fell Gate while a negligible number of particles were detected at Moor House in the ultrafine size range below 15 nm in diameter.

INSTRUMENTATION

Spectrometers to measure the submicrometer particle-size distribution called differential mobility particle sizer (DMPS) were place upwind, on top, and downwind of the hill to measure modifications of the particle size distribution. At Fell Gate and GDF Summit, Twin-DMPS-systems were set-up to measure particle-size distributions in the diameter range 3–600 nm. A Twin-DMPS consists of two differential mobility analyzers (DMA) to measure a wider size range than otherwise a single DMPS could do. Because of the limited number of particle counters that were available, one ultrafine condensation particle counter (UCPC, model TSI 3025) was shared by two DMAs: (a) an Ultrafine DMA (UDMA) (Hauke-type VIE-06 with an effective centre rod length of 11 cm; size range 3–20 nm) and (b) a DMA (Hauke-type VIE-06 with an effective centre rod length of 28 cm; size range 20–600 nm). The UDMA was operated with an aerosol/sheath air flow ratio of $2\,\ell\,min^{-1}/20\,\ell\,min^{-1}$, while the DMA operated on a flow ratio of $1.5\,\ell\,min^{-1}/7.5\,\ell\,min^{-1}$. The DMPS set-up at Moor House consisted of one DMA (special Hauke version for outdoor applications; size range 7–600 nm) and a UCPC. The DMA was operated with an aerosol/sheath air flow ratio of $2.4\,\ell\,min^{-1}/24\,\ell\,min^{-1}$. The mobility distribution was inverted to the size distribution using the bipolar charge distribution formula by Wiedensohler (1988).

To remove activated cloud droplets from the aerosol, the DMPS systems were run on interstitial inlets with a calculated cut-off size of 5 μm. This was especially necessary for the size distribution measurements of cloud interstitial particles on Summit.

OBSERVATIONS

In time intervals of 15 min, submicron particle size distributions were taken at the three measuring sites

* Moor House is the upwind station and Fell Gate is the downwind station during easterly or northeasterly winds. During westerly or southwesterly winds, the reverse order is valid.

Table 1. Submicron aerosol modes identified during the GCE field campaign at Great Dun Fell, 1993

Name of the particle mode	Description of the particle mode	Approximate size range of the geometric mean diameter (nm)
Ultrafine (nucleation)	Separate mode of newly formed particles	5–15
New Aitken	Aged ultrafine particles, separate mode or shoulder of the Aitken mode	15–35
Aitken	Precursor mode of the accumulation mode	35–100
Accumulation	Aged Aitken mode (probably due to cloud processing)	100–350

from 1 to 12 May. In order to simplify the entire data set, the particle size distributions were parameterised by log-normal distributions. A maximum of four aerosol modes (Table 1) were found in the submicrometer size range. The following procedure was used to fit the distributions.

At first, the measurements were fitted using the commercially available program DistFit®. This fit program, however, gives sometimes unrealistic physical results such as aerosol modes with large geometric standard deviation (up to 6.0) or aerosol modes that have their geometric mean diameter very close to each other. Therefore, all size distribution fits were visually checked afterwards, and if necessary, improved to fulfil the following physical constraints:

(1) a maximum geometric standard deviation of 1.8 for atmospheric aerosol modes (submicrometer aerosol modes derived from gas-to-particle conversion and coagulation are generally small in standard deviation),

(2) at most one aerosol mode in the size range 35–100 nm (as Aitken mode),

(3) at most one aerosol mode in the size range >100 nm (accumulation mode),

(4) a significant shoulder of the Aitken mode to smaller particle sizes or a separate peak in the size range 15–35 nm is defined as "new Aitken" mode,

(5) at most one aerosol mode in the size range <15 nm (ultrafine mode),

(6) the modes were fitted in logarithmic scale to match the concentration of the measured size distribution over 2 orders of magnitude.

Due to measurement limitations (the measured mobility bins might not catch the peak of the aerosol mode), small deviations of maximum $\pm 5\%$ from the geometric mean diameter of the mode are possible. This statistical error is minimised by averaging size distributions over a certain time period. Furthermore, the modal concentration may have an uncertainty of up to $\pm 10\%$ for Aitken and accumulation mode particles. This error is systematic and mainly caused by uncertainties in the sheath air flow of $\pm 1\%$ and cannot be eliminated by averaging size distributions. Consequently, the difference in number concentration of the Aitken or accumulation mode between two measuring sites can be up to 20% in the worst case. The present knowledge is that the particle transmission efficiency of UDMAs and DMAs drops drastically for particles smaller than 20 nm. The particle-size-dependent transmission function differs for different DMA-types as well as for different flow rates (Fissan *et al.*, 1996). Unfortunately, the transmission functions were not determined for the DMAs used in the experiment. Thus, number concentration of the ultrafine particle modes might be a factor two to five higher than that calculated and presented in this paper.

On GDF Summit, a UCPC was used to read continuously the total number concentration. This total number agreed within 10% to the number derived from the DMPS measurements when no ultrafine mode was present.

Time series of the different aerosol modes observed at the measuring sites can be used to find indications of processes that modify the aerosol size distribution during a cloud passage. By comparing the time series of the aerosol modes at Moor House and Fell Gate, formation of new ultrafine particles (homogeneous nucleation) and growth of accumulation and Aitken mode particles (e.g. sulphate production) might be found. The growth of the accumulation and Aitken mode particles due to aqueous-phase chemical reactions is discussed in Bower *et al.* (1997). The nucleation scavenging efficiency of aerosol particles to become cloud droplets can be found by taking the difference between the submicron size distribution upwind of Great Dun Fell and the size distribution of interstitial particles at GDF Summit (Svenningson *et al.*, 1997). Furthermore, time series of the accumulation and Aitken mode parameters (geometric mean diameter and number concentration) can help to identify changes in air mass and possible source regions of the atmospheric aerosol.

The experiment was designed for westerly winds with relatively clean marine air. The cloud events investigated here, however, occurred with northeasterly air flows. The flow of the air mass was connected between Moor House and Fell Gate passing the summit of GDF during the time periods 9 May, 00.00–06.00 h and 10 May, 00.00–06.00 h (Colvile *et al.*, 1997 (b)). Temperature differences between the sites, wind velocities, O_3 and NO_2 gas concentrations, and the shape of the aerosol size distributions indicate that the same air mass was measured at the different measuring sites during this time period.

During the time period from 9 to 10 May, two time periods of 6 h, during which time a cloud was present at GDF Summit, could be identified when an ultrafine particle mode was measured at Fell Gate while no ultrafine particles or a negligible number were detected at Moor House. These time periods are intensively investigated in the following paragraphs.

Case study 1: 9 *May*, 00.00 *h*–06.00 *h*

Studies of back trajectories showed the following meteorological situations: From the evening of 8 May through the morning of 9 May, 06.00 h, air masses originating from the Atlantic Ocean arrived at Great Dun Fell. Swietlicki *et al.* (1997) found by e.g. back-trajectory and chemical source–receptor analysis that the air mass was strongly polluted by emissions from the coal-fired power plant in Blyth, Scotland, during this time period. This is supported by SO_2 gas-phase concentrations of 2–4 ppbv measured at Mine Road (670 m a.s.l.), a measuring site located between GDF Summit and Fell Gate close to the cloud base. After 06.00 h, the air masses reaching GDF switched from Atlantic to continental origin. This pattern is seen by studying time series of the geometric mean diameter and number concentration. The time series of the different aerosol modes on 9 May 1993 are shown in Figs 1 and 2. The number concentrations of the ultrafine, new Aitken, Aitken and accumulation mode are plotted in Fig. 1a–d, respectively. The geometric mean diameters of the four modes are shown in Fig. 2a–d. The open squares, shaded triangles and solid circles represent measurements at Fell Gate, Moor House and GDF Summit, respectively (these markers will also be used in the time series presented later). During

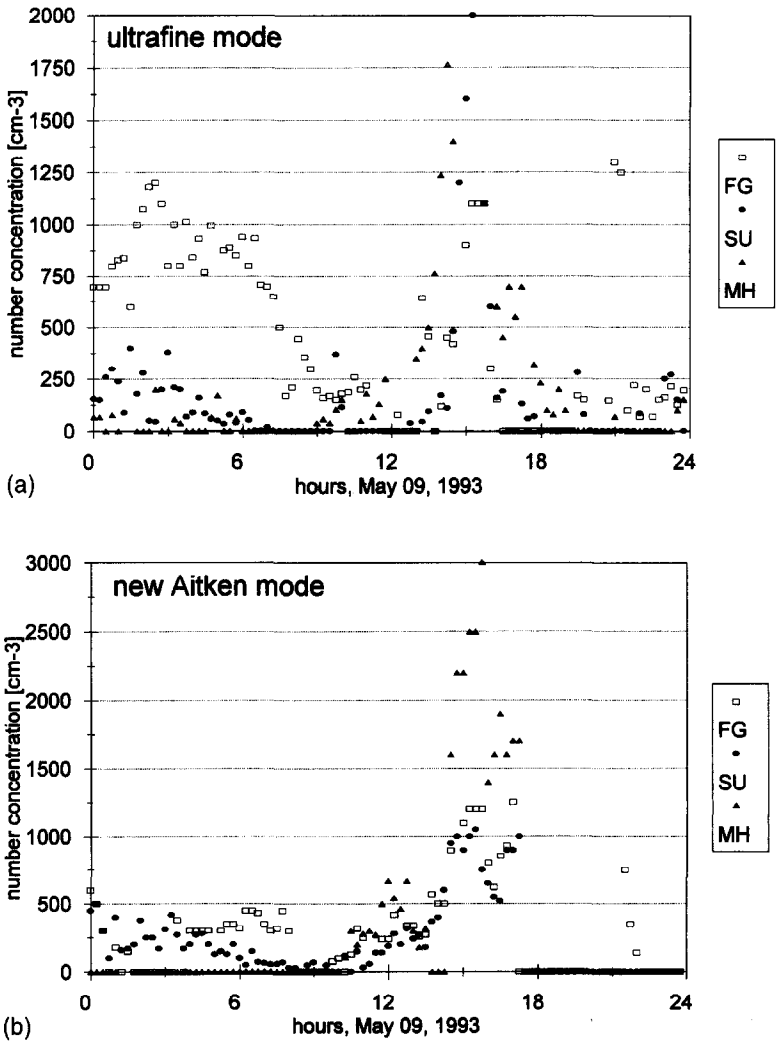

Fig. 1. Time series of the number concentrations of the ultrafine particle mode (a), the new Aitken mode (b), Aitken mode (c) and accumulation mode (d) from 9 May 1993. Cloud was present when the number concentration of the accumulation mode at Summit is very low (or zero) compared to the number concentration observed at Moor House or Fell Gate.

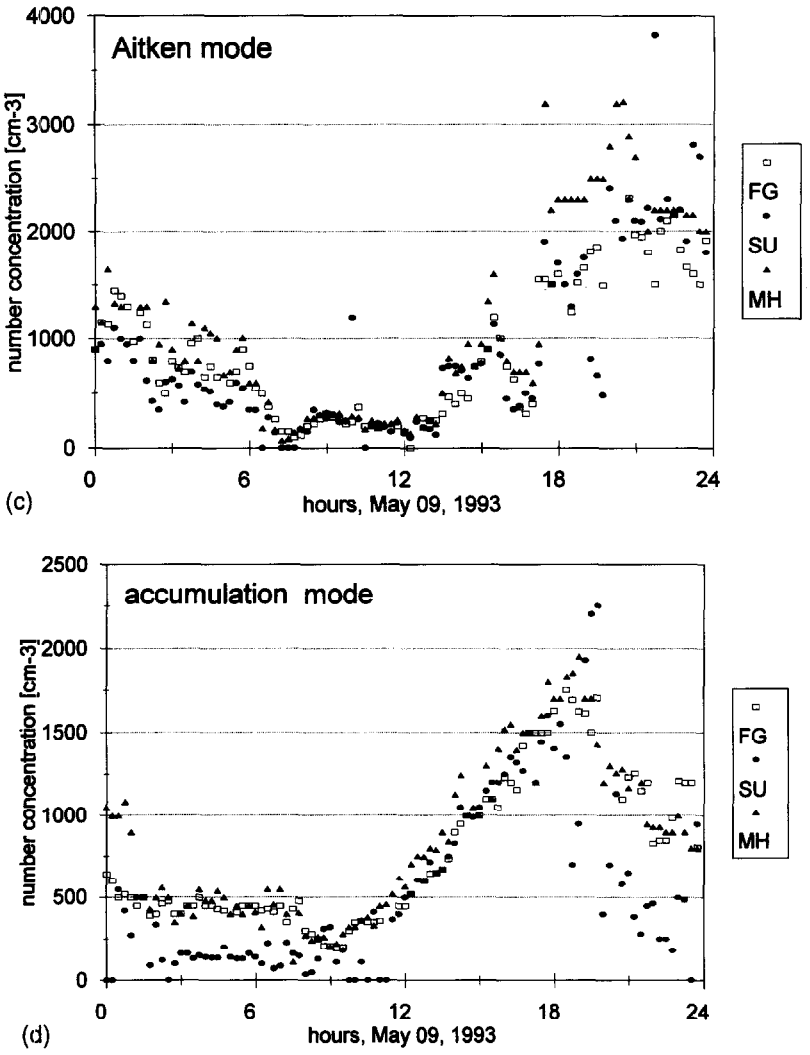

Fig. 1. (*Continued*).

these time periods when the modal diameter of the accumulation mode at GDF Summit is much smaller than those measured at Fell Gate and Moor House measurements, a cap cloud was present on GDF Summit. In this case, the below cloud accumulation mode had been partly or completely activated to cloud droplets.

The mean diameter of the accumulation mode at Fell Gate and Moor House was relatively large (250–300 nm) and increased slightly from 00.00 to 06.00 h, while the number concentration remained relatively stable (400–500 cm^{-3}). The large mean diameter of the accumulation mode, and the relatively high number of particles in the Aitken (about 2000 cm^{-3}) and accumulation mode range (compared to remote marine number concentrations) confirm Swietlicki's conclusions that the air mass was polluted.

The submicron size distributions observed at the three measuring sites are shown in Fig. 3. The open squares, solid dots, and shaded triangles represent the averaged measured size distributions taken at the sites Fell Gate, GDF Summit and Moor House, respectively. The solid line, the dashed line, and the dotted line show in comparison the log-normal fit of the averaged measurements. At Moor House, the size spectrum has the typical bimodal shape of a marine aerosol consisting of an Aitken and accumulation mode as shown before e.g. by Hoppel *et al.* (1994). The shape of the size distribution observed at GDF Summit changed compared to the distribution observed at Moor House. A large fraction of accumulation mode particles were activated to cloud droplets. The accumulation mode measured at Fell Gate agreed well with the accumulation mode observed at Moor House. This gives us the confidence that the same air mass was investigated before and after cloud passage. However, Colvile *et al.* (1997 (b)) shows that there were indications for entrainment during the time

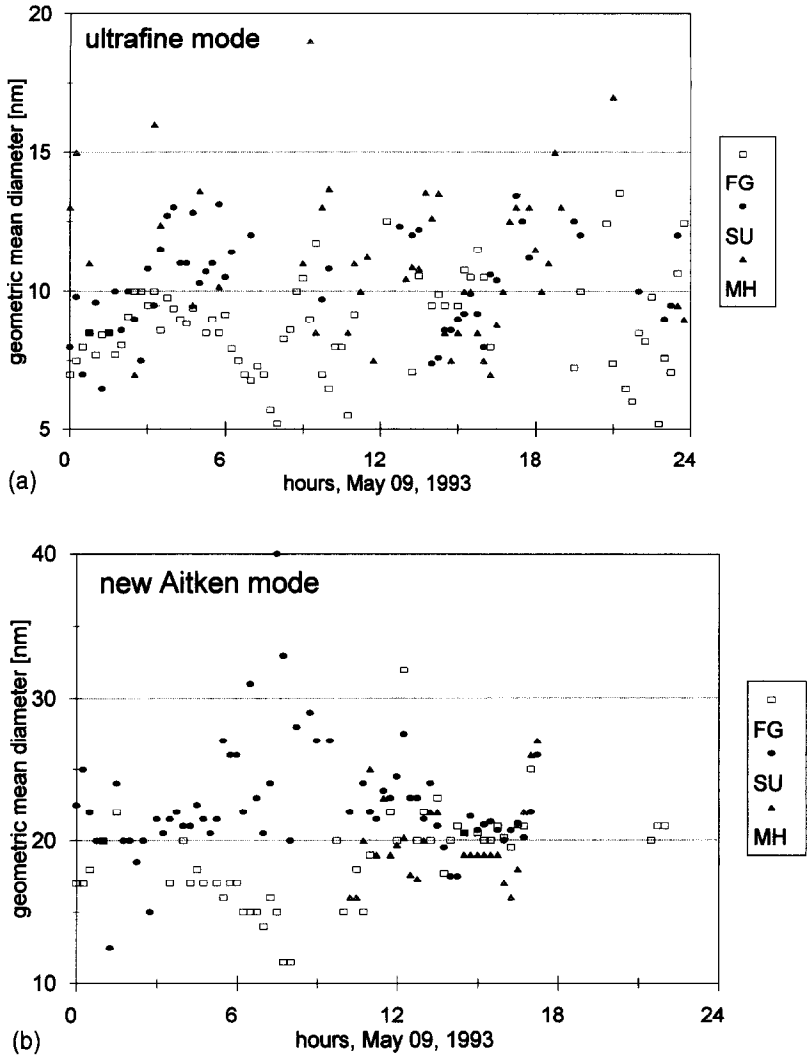

Fig. 2. Time series of the geometric mean diameters of the ultrafine particle mode (a), the new Aitken mode (b), Aitken mode (c) and accumulation mode (d) from 9 May 1993. Cloud was present when the geometric mean diameter of the accumulation mode observed at Summit is much smaller (or not given) than the mean geometric diameter at Moor House or Fellgate.

period investigated here. The most compelling feature here was the faster than adiabatic decrease in liquid water content between Summit and Mine Road (measuring site downwind of the hill between Summit and Fell Gate). The Aitken mode is normally least influenced by in-cloud processes. Thus, it would reflect most clearly the effect of entrainment events that may change the mean geometric diameter and number concentration. In this case, entrainment can be confirmed by the change of the number concentration of the Aitken mode from Moor House to Fell Gate if the air mixed from aloft had a lower particle number concentration. Compared to the Moor House measurements, the number concentration of the Aitken mode diameter at Fell Gate was in average 30% lower. The geometric mean diameter, however, of the Aitken mode did not change significantly. Furthermore, the similarity of the accumulation mode upwind and downwind of the hill also does not indicate entrainment unless sulphate production would compensate the dilution. Unfortunately, during this time period no impactor measurements upwind and downwind of the hill were performed that could give information about sulphate production.

At Fell Gate, however, the observed number concentrations of ultrafine particles were in the range of 700–1200 cm^{-3} while almost no ultrafine particles were measured at Moor House. The geometric mean diameter of the ultrafine mode varied between 7–10 nm. These small geometric mean diameters imply that the ultrafine particles were probably produced between Blyth (Scotland) and Fell Gate. The covariance between the mean diameter and the number concentration is 0.6 (range 0–1). In other words, as

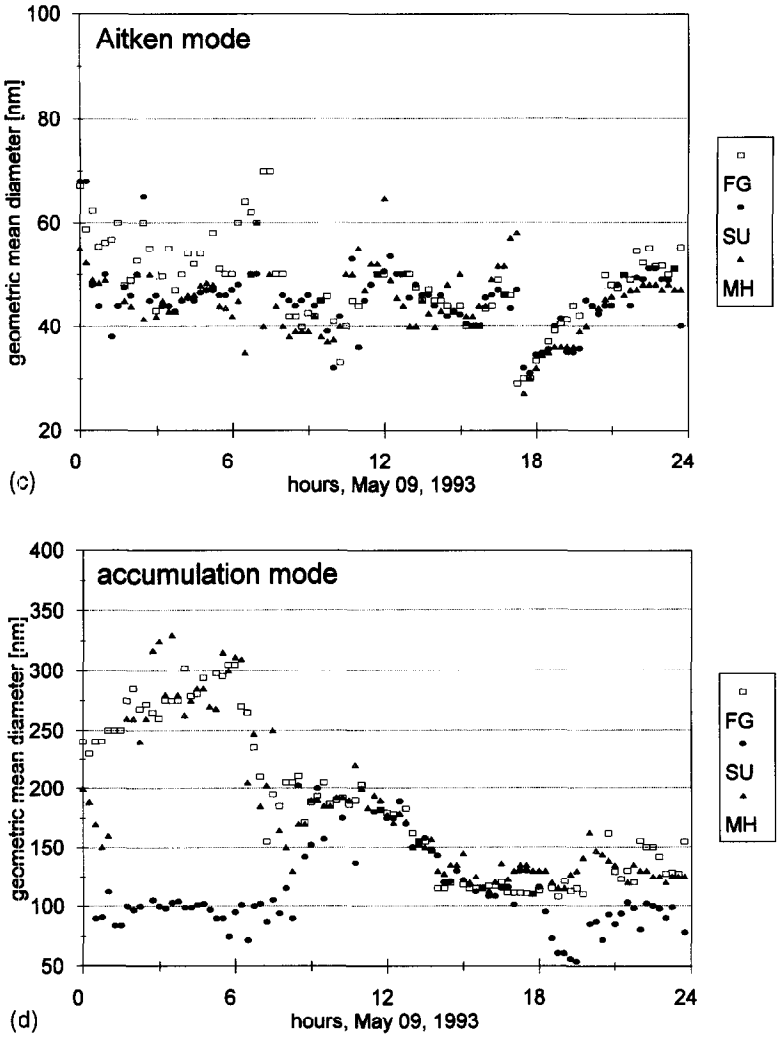

Fig. 2. (*Continued*).

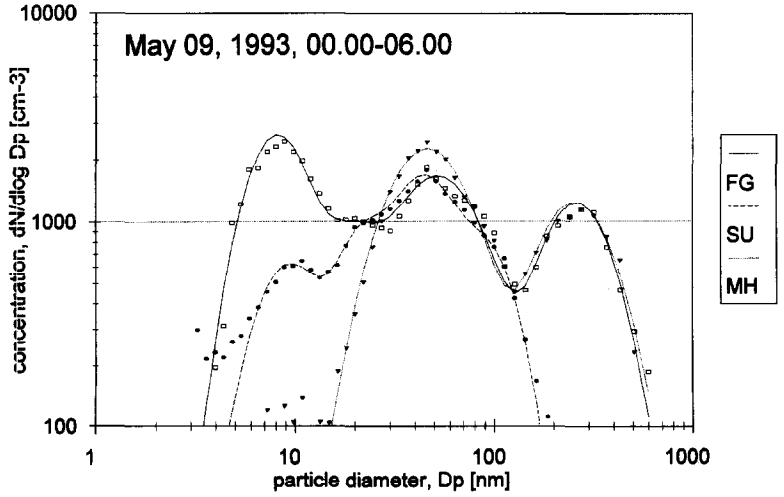

Fig. 3. Averaged particle size distributions observed at Moor House (upwind of the hill), on Summit (in cloud on top of the hill) and at Fell Gate (after cloud passage downwind of the hill) in the morning of 9 May 1993, 00.00–06.00 h.

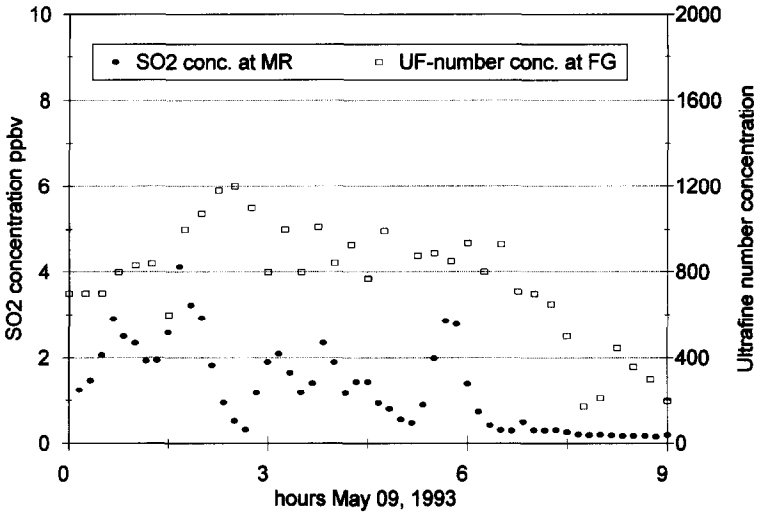

Fig. 4. SO_2 concentration observed at Mine Road and ultrafine number concentration measured at Fell Gate on 9 May, 00.00–09.00 h.

Table 2. Mean mode diameters, number concentrations and the relative standard deviation $dN/d\log D_P$ for the mean mode diameters of the size distribution at the three measuring sites measured on 9 May, during 00.00–06.00 h

	Mean diameter (nm)	Number concentration (cm^{-3})	Relative deviation of $dN/d\log D_P$ (%)
Fell Gate			
Ultrafine mode	8.2	950	30
New Aitken	19.5	250	20
Aitken	53.0	830	32
Accumulation	265.0	500	13
Summit			
Ultrafine mode	9.5	250	40
New Aitken	22.0	220	33
Aitken	45.0	600	38
Accumulation	95.0	220	43
Moor House			
Ultrafine mode	—	—	—
New Aitken	—	—	—
Aitken	47.0	1100	26
Accumulation	260.0	550	15

more particles were formed (a measure of the gaseous precursor concentration) the growth process accelerated. Furthermore, there seems to be a correlation between the occurrence of new particles at Fell Gate and SO_2 concentration measured at Mine Road (Fig. 4). The occurrence of ultrafine particles might have been caused by entrainment from aloft or due to homogeneous nucleation of H_2SO_4 and H_2O downwind of GDF. These two scenarios are based on the assumption that there was no horizontal gradient of ultrafine particle concentration in the same air mass. The occurrence of an ultrafine mode at Summit in cloud, however, supports the entrainment from aloft. To our understanding, ultrafine particles can neither be formed nor survive in cloud due to the large surface area of the cloud droplets.

The mean mode diameters, number concentrations, and the relative standard deviation $dN/\log D_P$ for the mean mode diameters of the size distribution at the three measuring sites are given in Table 2. The variability of the number concentration of the Aitken mode especially at GDF Summit supports the indications for entrainment.

In conclusion, a polluted air mass with high SO_2 concentrations was observed on 9 May, 00.00–06.00 h. Liquid water content measurements at

Summit and Mine Road indicated entrainment downwind of GDF Summit. However, the aerosol measurements cannot fully confirm this entrainment event. Ultrafine particles occurred downwind of the hill. The origin of these new particles, however, cannot be entirely explained by the observations.

Case study 2: 10 *May*, 00.00–06.00 *h*

During this cloud event, the meteorological situation was different. Because Great Dun Fell was close to the inversion between the marine and continental air, it is important to identify the air mass to interpret the measurements. Back trajectories indicate that marine air from the North Sea was overlaid with more continental air from East and Central Europe. Fortunately, single-particle analysis for aerosol particles larger than 200 nm by laser microprobe mass spectroscopy (LAMMS) was performed during this measuring period. The LAMMS results (Gieray *et al.*, 1997) show that a marine air mass passed Great Dun Fell in the night from 9 to 10 May. The results can be confirmed by the mode parameters of the Aitken and accumulation modes at Moor House and Fell Gate. The time series of the different aerosol modes on 10 May 1993 are shown in Figs 5 and 6. Again, the number concentrations of the ultrafine, new Aitken, Aitken, and accumulation mode are plotted in Fig. 5a–d, respectively. The geometric mean diameters of the four modes are shown in Fig. 6a–d. The accumulation mode mean geometric diameter observed upwind of GDF at Moor House was approximately 150 nm. After the cloud passage at Fell Gate,

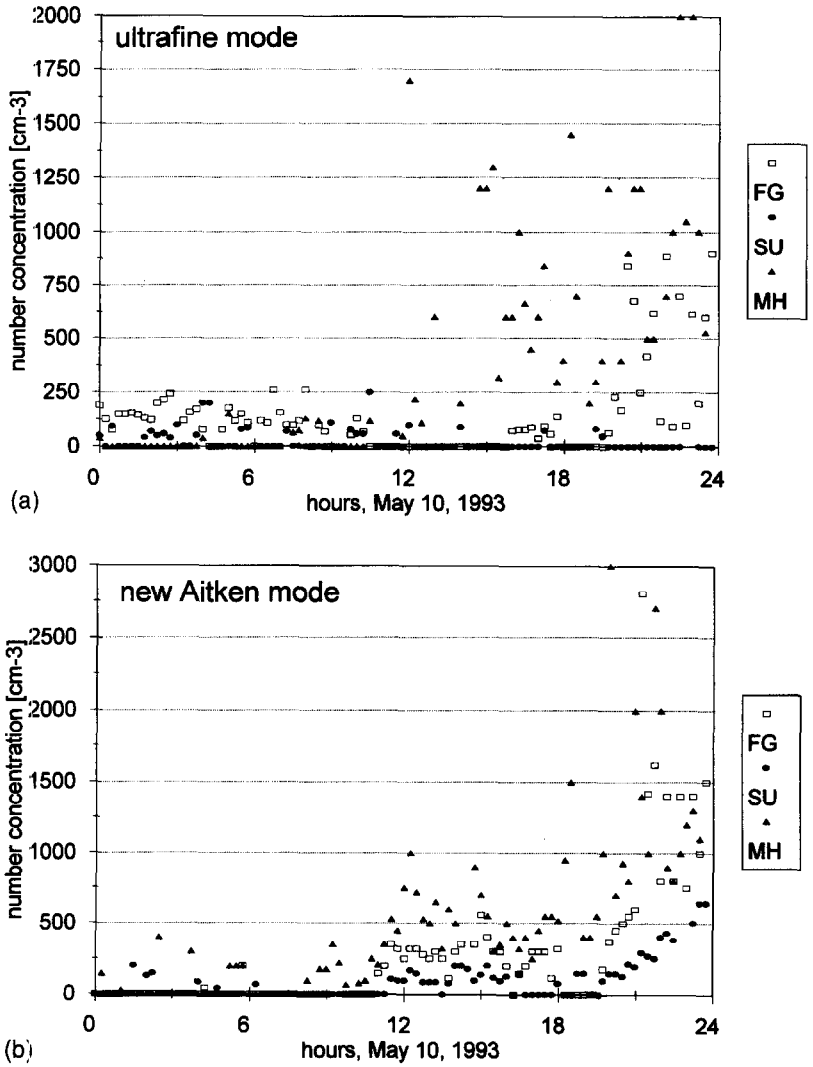

Fig. 5. Time series of the number concentrations of the ultrafine particle mode (a), the new Aitken mode (b), Aitken mode (c) and accumulation mode (d) from 10 May 1993. Cloud was present when the number concentration of the accumulation mode at Summit is very low (or zero) compared to the number concentration observed at Moor House or Fell Gate.

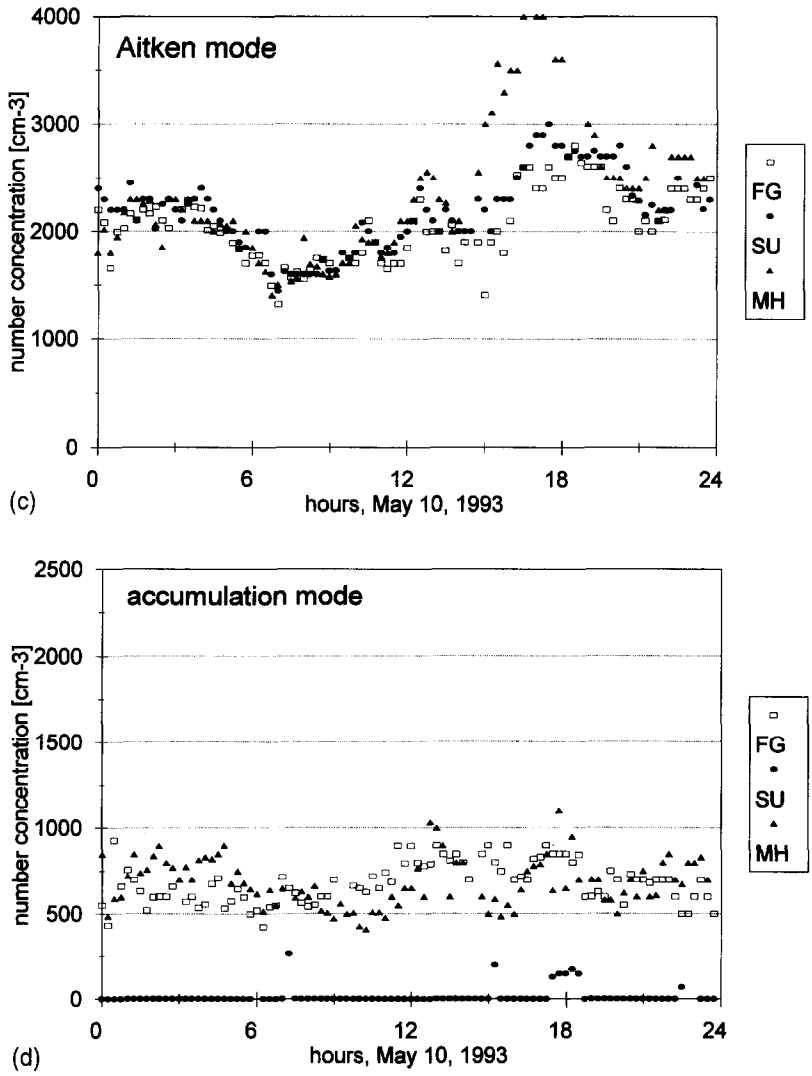

Fig. 5. *(Continued).*

the mean geometric diameter shifted on average slightly towards larger sizes. The shift in size might be explained by sulphate production due to cloud processes. Impactor and filter measurements, however, show only very little sulphate production (Laj *et al.*, 1997). Bower *et al.* (1997) predicted with their model a sulphate production of 0.25 $\mu g\,m^{-3}$. Although the geometric mean diameters of the Aitken and accumulation modes observed during this time period are typical for marine aerosols, the number concentrations are higher than that common to remote marine size distributions. This implies that the marine air mass was probably slightly polluted due to mixing processes with the overlaying continental air mass. Also the SO_2 concentration measured during this time period indicates a slight anthropogenic influence. The SO_2 concentrations were less than 0.5 ppbv, and thus, up to one order of magnitude lower than those observed the night before.

Colvile *et al.* (1997 (b)) found only very little indications for entrainment during the time period 00.00–06.00 h on 10 May 1993. This can be confirmed by the number concentration of the Aitken mode. The Aitken number concentration agreed on average very well for all measuring sites (within 5% deviation). This is a remarkable agreement and strongly supports our assumption that the Aitken mode is the least influenced aerosol mode by in-cloud processes. The number concentration of the accumulation mode, however, was decreased by about 20%. This deviation cannot be fully explained by our measurements. Large instrumental uncertainties are unlikely because of the good agreement between the the Aitken modes at the different measuring sites during the same time period. It can be concluded that there was no indication for mixing from aloft. Furthermore, it can be assumed that the same air mass was probably investigated at all measuring sites.

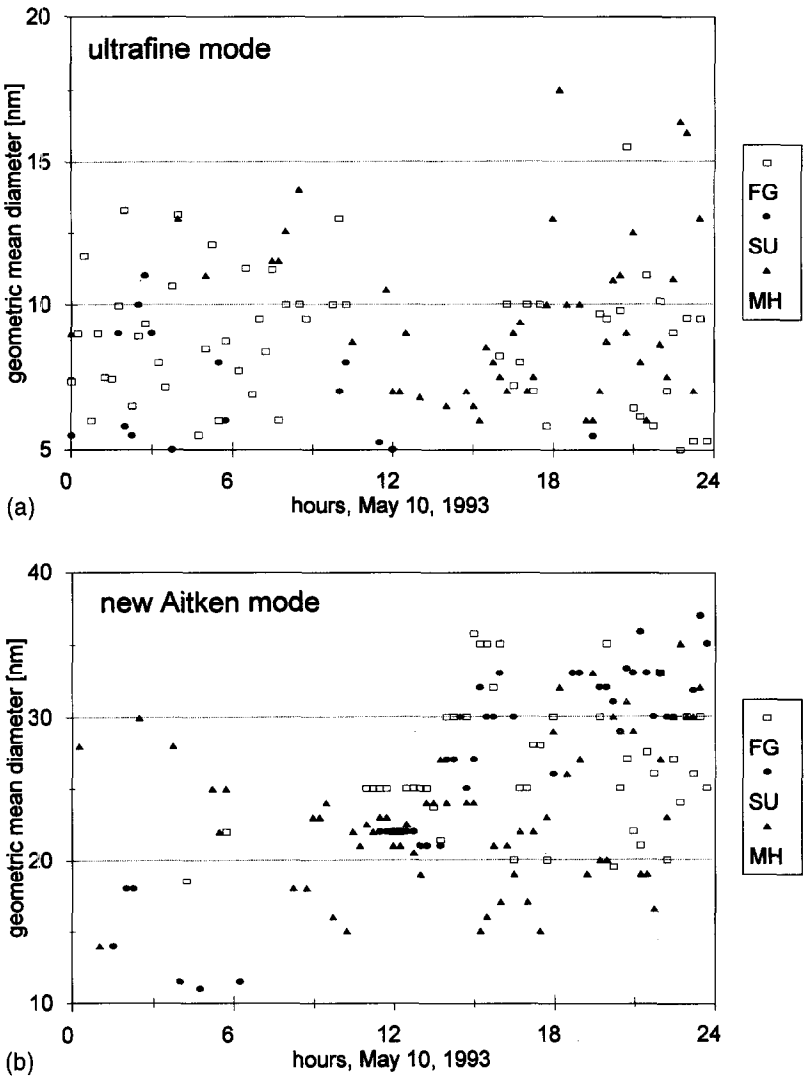

Fig. 6. Time series of the geometric mean diameters of the ultrafine particle mode (a), the new Aitken mode (b), Aitken mode (c) and accumulation mode (d) from 10 May 1993. Cloud was present when the geometric mean diameter of the accumulation mode observed at Summit is much smaller (or not given) than the mean geometric diameter at Moor House or Fellgate.

The averaged size distributions for Fell Gate, GDF Summit and Moor House are plotted in Fig. 7. Again, these curves are derived by log-normal fits of the average measured size distribution for the 6 h time period investigated. Once again, the shape of the number size distribution at Moor House is bimodal. The accumulation mode particles seem to be largely activated to cloud droplets at GDF Summit. At Fell Gate, the bimodal input distribution changed to a trimodal size distribution with a separate ultrafine mode. (Note that this ultrafine mode is an average of many individual size distributions and the ultrafine modes actually observed have a much smaller geometric standard deviation than the average one.) The number concentration in the ultrafine particle mode observed at Fell Gate ranged between 100 and 250 cm^{-3} while almost no particles were observed at Moor House or GDF Summit (Fig. 5a). The mean mode diameters, number concentrations, and the relative standard deviation $dN/d\log D_p$ for the mean mode diameters of the size distribution at the three measuring sites are given in Table 3.

MODELLING OF NEW PARTICLE FORMATION

Two possible chemical mechanisms were considered to model the occurrence of ultrafine particles. The first mechanism involves the formation of sulphuric acid aerosol from the biomolecular homogeneous nucleation of sulphuric acid and water vapour. The sulphuric acid is formed from the oxidation of SO_2 by the OH radical. To simulate the formation of sulphuric acid particles, we used the model of Kulmala *et al.* (1995a). This model provides the simulation of new particle formation via SO_2 oxidation. As compact

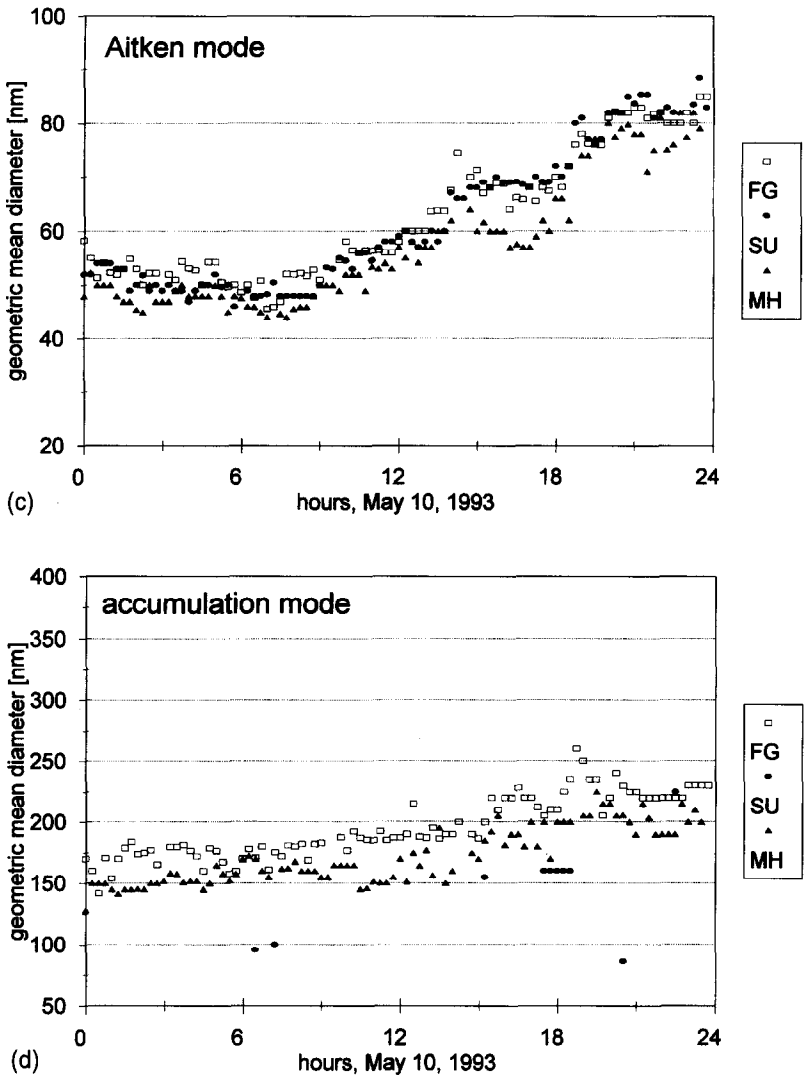

Fig. 6. (*Continued*).

result, an analytical expression is given for atmospheric conditions. The formation of new particles is limited by the sulphuric acid concentration and number of preexisting particles. For homogeneous nucleation, the ratio F_{exp}/F_{theor} should be near unity. The following equation was used to estimate possible binary homogeneous nucleation:

$$F_{exp} = \frac{[OH][SO_2]}{BN} = \frac{[OH][SO_2]}{\sum_i [D_{Pi}^2/(0.2\ \mu m)^2] N_i}$$

with BN as measure for vapour depletion to preexisting particles, D_P as particle diameter, and N as number concentration, and

$$F_{theor} = 10^{(13 + \Delta T/20\,K + \Delta rH/40\%)}$$

with, $\Delta T = T - 253.15$, $\Delta rH = 90\% - rH$.

For both case studies, no OH-measurements were performed. In our simulations, we used, therefore, estimated OH concentrations in the range 10^4–10^6 molecules cm^{-3}. SO_2 concentrations were continuously measured downwind of the hill near cloud base. Temperature and relative humidity were varied in the range 4–6°C and 97–99%, respectively. The probability of new particle formation depends strongly on the depletion of vapour to preexisting particles. In this model, the "dry" number size distribution at Moor House was taken to determine the factor BN. The influence of an ambient (wet) number size distribution cannot be described by this nucleation model.

We found a little probability for binary homogeneous nucleation via the H_2SO_4–H_2O route for Case study 1 on 9 May if we assume a relatively high OH concentration of 10^6 (Table 4). Only OH concentrations in the range 10^6–10^7 molecules cm^{-3} would give a larger probability of homogeneous nucleation. These high nighttime OH concentrations, however,

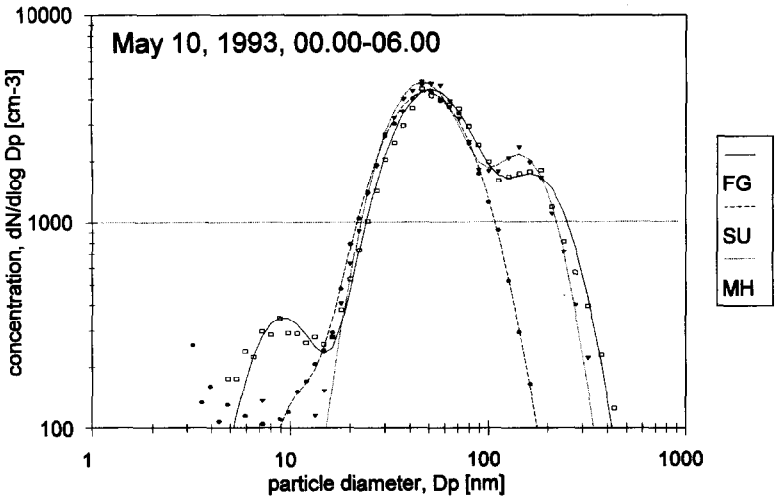

Fig. 7. Averaged particle size distributions observed at Moor House (upwind of the hill), on Summit (in cloud on top of the hill), and at Fell Gate (after cloud passage downwind of the hill) in the morning of 10 May 1993, 00.00–06.00 h.

Table 3. Mean mode diameters, number concentrations and the relative standard deviation $dN/d\log D_P$ for the mean mode diameters of the size distribution at the three measuring sites measured on 10 May, during 00.00–06.00 h

	Mean diameter (nm)	Number concentration (cm^{-3})	Relative deviation of $dN/d\log D_P$ (%)
Fell Gate			
Ultrafine mode	9.3	140	68
New Aitken	—	—	—
Aitken	52.0	2100	6
Accumulation	177.0	650	10
Summit			
Ultrafine mode	11.0	40	59
New Aitken	—	—	—
Aitken	49.0	2200	7
Accumulation	—	—	—
Moor House			
Ultrafine mode	—	—	—
New Aitken	—	—	—
Aitken	47.0	2100	8
Accumulation	150.0	750	12

may only occur in a highly polluted air mass (this is the case on 9 May). Peroxy radicals, precursors of OH radicals, can be formed, e.g. near the coast line, by nighttime reaction of NO_3 with organic compounds (Platt *et al.*, 1990). The production of OH by gas phase reactions of ozone with alkenes could be a possible route in a polluted air mass during nighttime (Atkinson *et al.*, 1995). On 10 May, the SO_2 concentration, however, was too low to predict any homogeneous nucleation via the H_2SO_4–H_2O route (Table 4).

The other mechanisms considered are the binary homogeneous nucleation of NH_3–HCl and the ternary homogeneous nucleation of NH_3–HCl–H_2O. The binary homogeneous nucleation process of ammonium chloride has been modelled by Kulmala *et al.* (1995b). This model is based on the description of Seinfeld (1986) modified by the self-consistent correction (SCC) to the classical theory (Girshick and Chia-Pin, 1990). Furthermore, the ternary formation of ammonium chloride aerosols has been modelled using the classical multicomponent homogeneous nucleation theory with some assumptions. The main assumption is that we consider critical clusters to have fixed composition. The fixed composition is determined to be the same composition as the bulk saturated solution. To perform the nucleation

Table 4. The ratio F_{exp}/F_{theor} representing the probability of binary homogeneous nucleation of H_2SO_4–H_2O using Kulmala's (1995) analytical expression

OH (mole cm^{-3})	SO_2 (ppbv)	BN (cm^3)	T (°C)	rH (%)	F_{exp}/F_{theor}
9 May, 00.00–06.00 h					
10^7	1.734	1192	4	99	4.10
10^6	1.734	1192	4	99	0.41
10^5	1.734	1192	4	99	0.041
10^4	1.734	1192	4	99	0.0041
10 May, 00.00–06.00 h					
10^6	0.157	714	4	99	0.06
10^5	0.157	714	4	99	0.006
10^4	0.157	714	4	99	0.0006

Note: The probabilities were calculated for atmospheric condition (temperature, relative humidity and preexisting aerosol) downwind of GDF. Higher temperatures and lower relative humidities resulted in lower nucleation propabilities. The given SO_2 concentration is the average during the investigated time period.

calculations, thermodynamical data obtained from Pio and Harrison (1987) and Hamer and Wu (1972) were used. The thermodynamical equilibrium values for the product of partial pressures of NH_3 and HCl ($p_{NH_3} \times p_{HCl}$) decreases significantly by increasing relative humidity (see also Pio and Harrison, 1987). The ternary nucleation model do not depend on preexisting particles.

Ammonia concentrations in the air were about 0.5 ppbv. The concentration of HCl gas was not measured, however, in the case of 10 May 1993, little sulphate production was observed in the cloud (Laj *et al.*, 1997) and some of the droplets formed on sea-salt aerosol. In these circumstances, HCl outgassing could occur. Comparing the in-cloud chloride concentrations with those measured in the aerosol downstream at the measuring site Wharleycroft (206 m a.s.l.), an HCl concentration of 0.5–1.0 ppbv may be estimated in the gas phase.

We used in our simulations an ammonia concentration of 0.5 ppbv, hydrochloric acid concentration in the range of 0.5–1.0 ppbv, temperatures in the range of 4–6°C, and relative humidities in the range of 97–99%. The size distribution of preexisting particles could not be included yet in the existing model as mentioned above.

New particle formation of ammonium chloride, however, could not be modelled using the binary homogeneous nucleation theory by Kulmala *et al.* (1995b). The simulation of the ternary homogeneous nucleation of HCl–NH_3–H_2O showed also no evidence of new particle formation for atmospheric conditions at GDF. Furthermore, the probability for the formation of ammomium chloride particles would be even lower by including the preexisting particle size distribution into the model. These results mean that either the particle formation of ammonium chloride is unlikely for atmospheric conditions, or the existing model does not describe this homogeneous nucleation process in the right way.

CONCLUSION

The nighttime formation and occurrence of new ultrafine aerosol particles was studied in association with orograhic clouds during the third field campaign within the EUROTRAC subproject ground-based cloud at GDF, Northern England. Three size spectrometers to measure submicrometer aerosol particles were located upwind, on top, and downwind of the hill to investigate changes in the aerosol size distribution.

During two nighttime cloud periods, ultrafine particles were observed downwind of the hill while no particles, or a negligible number, were detected upwind of the hill. During the early morning of 9 May 1993, it was found that ultrafine particles occurred when the SO_2 concentration was high. However, simulations of the binary homogeneous nucleation process of H_2SO_4–H_2O show that new particle formation for atmospheric conditions downwind of GDF can only be predicted with relatively high nighttime OH concentration of 10^6–10^7 molecules cm^{-3}. There are some indications that the ultrafine particle might be formed upwind of GDF and entrained due to the orographic cloud (discrepancy in cloud liquid content between Summit and Mine Road). However, the aerosol measurements cannot entirely confirm the entrainment hypothesis.

During the cloud event in the early morning of 10 May 1993, ultrafine particles occurred after the cloud passage. In this case, no evidences of entrainment were observed. The SO_2 concentration was too low during this time period to predict any new particle formation via the H_2SO_4 nucleation route for OH concentrations up to 10^6 molecules cm^{-3} and ambient temperatures and humidities. Another possible homogeneous nucleation process to explain the observations might be the formation of ammonium chloride due to ammonia and outgassing hydrochloric acid. A binary and ternary homogeneous nucleation model was used to simulate the formation of ammonium chloride particles using realistic concentrations of ammonia and hydrochloric acid. However, neither the binary nor the ternary homogeneous nucleation model could predict new particle formation for atmospheric conditions downwind of GDF.

It can be concluded that new particles were observed downwind of an orographic cloud. The observations, however, could not really be predicted by homogeneous nucleation models via the routes of H_2SO_4–H_2O, HCl–H_2O, or HCl–H_2O–NH_3. Orographic clouds might play a role in the nighttime occurrence and formation of new particles in the boundary layer. However, improved measurements and better homogeneous nucleation model are needed to explain the observation.

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