



VERTICAL GRADIENTS OF DISSOLVED CHEMICAL CONSTITUENTS IN EVAPORATING CLOUDS

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Abstract—Vertical gradients in cloud-water composition were investigated during the Ground-based Cloud Experiment at Great Dun Fell (GDF) 1993. The cloud-water measurements were performed at two heights above the cloud base. The observed changes in cloud-water concentration were not only induced by dilution or concentration due to an increasing or decreasing liquid water content (LWC), but also by loss or uptake of chemical compounds, and, under appropriate meteorological conditions (downslope flow), by evaporation of small droplets between the two heights. The observed vertical gradients were found to be ion-specific. Higher amounts of total dissolved material were measured at greater distances above the cloud base, e.g. SO_4^{2-} during most of the time of the monitored cloud events. Thus, vertical gradients may be important for deposition calculations of trace substances onto vegetation via cloud-water interception. In any case, the cloud base is a very important parameter relevant for the cloud chemical studies, because it is of importance for data interpretation. © 1997 Elsevier Science Ltd.

Key word index: Cloud-water measurements, vertical gradients, ionic concentration, droplet spectra, Great Dun Fell, Ground-based Cloud Experiment.

1. INTRODUCTION

Clouds develop in supersaturated air by condensation of water vapour onto aerosol particles. In the newly formed droplets, soluble gases can dissolve and react to form new products. Supersaturation, condensation and the mixing ratios of trace substances vary with height above the cloud base, causing vertical gradients of trace substance concentrations in the cloud droplets. Vertical movements of air parcels, turbulent mixing and entrainment of dry air into the cloud are additional processes modifying the vertical gradients.

While it is obvious that vertical gradients exist, less information is available on the magnitude of such

gradients. Junge (1963) expected a simple dilution, inversely proportional to the increasing liquid water content (LWC) with height above the cloud base. Mohnen and Vong (1993) reported measurements at two heights above the cloud base at Whiteface Mountain confirming higher trace substance concentration of dissolved species close to the cloud base. From their measurements they concluded that height above the cloud base is an important factor which influences cloud-water acidity and will be a source of variability in both liquid water content and cloud chemistry. More quantitative information on vertical gradients, however, is necessary to improve our understanding and estimation of pollutant transfer via cloud-water deposition onto vegetation in subalpine forests, where mountains are immersed in clouds and vegetation on slopes is exposed to vertical gradients in chemical cloud-water composition. The importance of the cloud-water deposition process for forest decline at high elevation, in addition to dry and wet deposition, has been reported earlier (Lovett, 1984; Krugmann

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and Winkler, 1989; Pahl *et al.*, 1994; Saxena *et al.*, 1989; Vong *et al.*, 1991).

Several investigations have shown that the amount of cloud water deposited onto forests increases with height, due to increasing LWC, wind speed, and the shift of the droplet spectrum to larger droplets (Lin and Saxena, 1991; Lovett and Kinsman, 1990; Pahl and Winkler, 1993). The decreasing concentration of chemical compounds dissolved in cloud water, caused particularly by an increasing LWC, may compensate for the increasing cloud-water deposition with greater elevation and may result in a maximum of ion deposition via cloud water below the summit (Lovett and Kinsman, 1990). Observed vertical gradients in cloud-water composition can be caused by simple accumulation of water with the ongoing condensation process (Fowler *et al.*, 1988; Junge, 1963). In this case we do not expect that the decreasing concentration of trace compounds in droplets with height will lead to significant differences in deposition as a function of elevation, since the total amount of trace substances does not alter in the condensed phase.

It should be kept in mind that the concentration of a trace substance in cloud water does not depend only on the LWC but may also be influenced by uptake or loss of chemical compounds, and interaction of the airflow with complex terrain. Processes like chemical reactions of gases with or inside droplets, uptake or activation of aerosol particles can alter vertical gradients in the cloud-water composition to such a degree that they result in vertical gradients in pollutant deposition onto vegetation via cloud-water interception. The influence of vertical gradients in cloud-water composition on the total amount of trace substances deposited in upland areas has not yet been evaluated. The purpose of this study was to investigate the magnitude of vertical gradients in chemical composition near the cloud base and the processes which influence them.

Measurements usually show a high variability of the liquid water content as well as of the various trace substance concentrations in cloud water (Facchini *et al.*, 1992; Mohnen *et al.*, 1990). This variability is caused by meteorological conditions and differences in the trace substance concentrations in different air masses. It is not possible to predict vertical gradients from simple theoretical considerations. During the field experiment carried out at Great Dun Fell (GDF) in April/May 1993 investigations of cloud-water composition were made simultaneously at two heights above the cloud base. From these observations it was possible to derive vertical gradients of the chemical compounds dissolved in the cloud droplets depending on the height above the cloud base, and to investigate processes affecting these vertical gradients.

2. MEASURING SITE AND INSTRUMENTATION

The area chosen for this experiment, as part of the Ground-based Cloud Experiment (GCE), includes a ridge oriented

northwest-southwest in the northern Pennine hills of U.K., where orographic clouds frequently occur. The summit of the specific hill selected for measurements (Great Dun Fell, GDF) is in cloud for some part of more than 200 days every year (Gallagher *et al.*, 1988). An extended description of the measuring sites and instrumentation is given by Choularton *et al.* (1997).

At Great Dun Fell, two of the five measuring sites were suitable for the investigation of gradients in cloud-water composition. The site close to the cloud base called "Mine Road" (670 m a.s.l.) is situated on the western slope of the approximately two-dimensional ridge. The site on top of Great Dun Fell called "GDF summit" has an elevation of 850 m a.s.l. Therefore, the difference in elevation above the cloud base between Mine Road and the GDF Summit is 180 m while the horizontal distance is about 500 m (Colville, 1994). During the experiment the air flow was mostly down-slope and both sites were located in the same air mass. Therefore, and because of the short horizontal distance between the two sites, the measurements performed at these ground-based sites represent the in cloud situation at different heights above the cloud base.

It should be emphasized that these ground-based measurements are not considered to be representative for vertical gradients in clouds of the free atmosphere. They were designed and are relevant for the investigation of the deposition of cloud droplets to forest canopies on mountain slopes by cloud-water impaction.

For the investigation and determination of the vertical gradients in cloud water we used the following.

- Active cloud-water collectors at both, the GDF Summit and Mine Road sites. A detailed description of the sampling instrument is given by Winkler (1992) and of its performance by Schell *et al.* (1992); weighing of the samples and comparison with the liquid water content of the PVM (see below) gave collection efficiencies between 70 and 80% (Pahl and Winkler, 1995).
- Active two-stage cloud-water collector (Schell *et al.*, 1997).
- Data for the chemical composition of the cloud water according to Laj *et al.* (1997), who also discussed the analytical quality.
- Measurements of the liquid water content (LWC) with two PVM-100 (Gerber, 1984). The data were averaged for the periods during which cloud water was collected (typically 1 h).
- Measured droplet size spectra as discussed by Colville *et al.* (1997).
- Description of the meteorological situation by Colville *et al.* (1997), and 72 h back trajectories provided by the German Weather Service (Swietlicki *et al.*, 1997).

In order to investigate vertical changes of trace substance concentration in cloud water and to compare measurements of different altitudes, it is useful to convert the liquid-phase concentration into air-equivalent units. Therefore, the following expression is applied:

$$[X](\text{neq m}^{-3}) = [X](\mu\text{eq l}^{-1}) \text{LWC}(\text{l m}^{-3}) \quad (1)$$

where $[X]$ is the concentration of a given chemical species in cloud water and LWC the averaged LWC during the sampling period (the LWC was taken from the PVM measurements). This weighted concentration simplifies the investigation of the vertical gradients, because the dissolved trace substance concentration expressed in air-equivalent units is independent of the amount of condensed water in which the species is dissolved. In the case of pure dilution occurring between Mine Road and GDF Summit, due to higher LWC at the GDF Summit, equal air-equivalent concentrations at both sites would be observed. Only losses or uptake of aerosol and gas-phase reactions occurring between the two sites can cause gradients in weighted concentrations.

In terms of quantifying the deposition of trace substances onto vegetation as a function of height above the cloud base, any alteration of the total dissolved material will have a great impact (Pahl, 1996).

3. CASE STUDIES

Most measurements were made during discrete periods of several hours in length. Three events were chosen for the investigation of vertical gradients in cloud-water composition (Table 1). During the selected events a "connected flow" was detected by several indicators, i.e. the air sampled at the five measuring sites below and inside cloud on the up-wind side of the ridge as well as on the down-wind side was indeed from the same air parcel (see Colville *et al.*, 1997). In the following case studies the vertical gradients for various trace constituents dissolved in cloud droplets are studied, taking into account the local as well as the large-scale meteorological situation, the air mass origin and the air flow over the hill.

3.1. Morning of 9 May

In this event northeasterly wind was observed at all measuring sites. The air flow between the two sites above the cloud base, GDF Summit and Mine Road was downslope resulting in partial evaporation of droplets during transport from the GDF Summit to the Mine Road. The trace substance composition in the cloud water with relatively high concentrations of NO_3^- and SO_4^{2-} of 49 and 186 neq m^{-3} , respectively, indicated a continentally influenced air mass. Additionally, the sea-salt concentration was quite low, which confirmed mainly the continental character of the air mass.

At the beginning of the event, higher concentrations of H^+ , NH_4^+ , NO_3^- and SO_4^{2-} expressed in air equivalent units were measured at the GDF Summit as compared to the Mine Road (Fig. 1). Accordingly, there must have been a loss of dissolved material to the interstitial air within the cloud during the transport from the top to the cloud base which can only be explained by complete evaporation of a droplet fraction or escape of gas. Another possible contribution could originate from deposition of large droplets between the two sites; however, as was calculated by Colville (1994), this influence is of negligible importance and can thus be ruled out in our case.

The opposite behaviour was found by dissolved compounds originating from sea-salt aerosol, e.g. Na^+ which does not show any distinct vertical gradi-

ent during the event (Fig. 1). The different behaviour of Na^+ and SO_4^{2-} appears to be caused in their different distribution across the droplet spectrum. The sea-salt aerosol was preferentially dissolved in the larger droplets while non-sea-salt SO_4^{2-} was found in the smaller droplets (Gieray *et al.*, 1997). The non-sea-salt (nss) SO_4^{2-} is calculated applying the equivalence ratio of SO_4^{2-} to Na^+ of 0.119 in sea salt (Friedlander, 1973).

For investigating the influence of droplet size on the evolution of vertical gradients in dissolved trace substances, a two-stage fog water collector sited at the GDF Summit was used (Schell *et al.*, 1997). During the first 5 h the LWC was distributed between the smaller ($6 < d < 11 \mu\text{m}$) and larger ($d > 11 \mu\text{m}$) fraction of the droplets. The strongest vertical gradients in H^+ and nss SO_4^{2-} occurred especially during periods when high concentrations were found in the fraction of small droplets (Fig. 2).

The distinct vertical gradients for the major ions (Fig. 1) became negligible towards the end of this event. After 6 a.m. BST the concentrations as well as the extent of the vertical gradients for H^+ , NO_3^- and nss SO_4^{2-} decreased significantly while the LWC remained high. This development was caused by advection of a less polluted air mass after that time (Swietlicki *et al.*, 1997). In this second part of the event the main amount of water was shifted to the larger droplets and led to a significant decrease of trace substances dissolved in the small droplet fraction (Fig. 2). Since small droplets evaporate more rapidly than larger ones (Huret *et al.*, 1994) we expect the smallest droplets to evaporate completely during transport from the GDF Summit to cloud base (close to Mine Road). This effect could be confirmed by FSSP measurements (compare Figs 4b and 6b). Thus, the chemical constituents dissolved in this small drop size fraction at GDF Summit, like H^+ , NO_3^- and nss SO_4^{2-} , were turned to the interstitial gas or aerosol phase at Mine Road while the total amount of these ions in the liquid phase decreased during transport from GDF Summit to Mine Road.

Trace substances preferentially dissolved in the partially shrinking larger droplets, such as Na^+ , remained in the liquid phase as seen from the nearly unchanged Na^+ concentration (air equivalent units) at Mine Road.

3.2. Night of 9–10 May

The second case study was characterized by a maritime air mass. The backward trajectories indicated

Table 1. List of periods investigated for cloud-water composition in two heights above cloud base

Case	Date	Time	No. of samples (GDF Summit)	No. of samples (Mine Road)
1	09.05	00:00–12:00	12	10
2	09.05–10.05	20:00–07:00	11	11
3	10.05	18:00–24:00	6	4

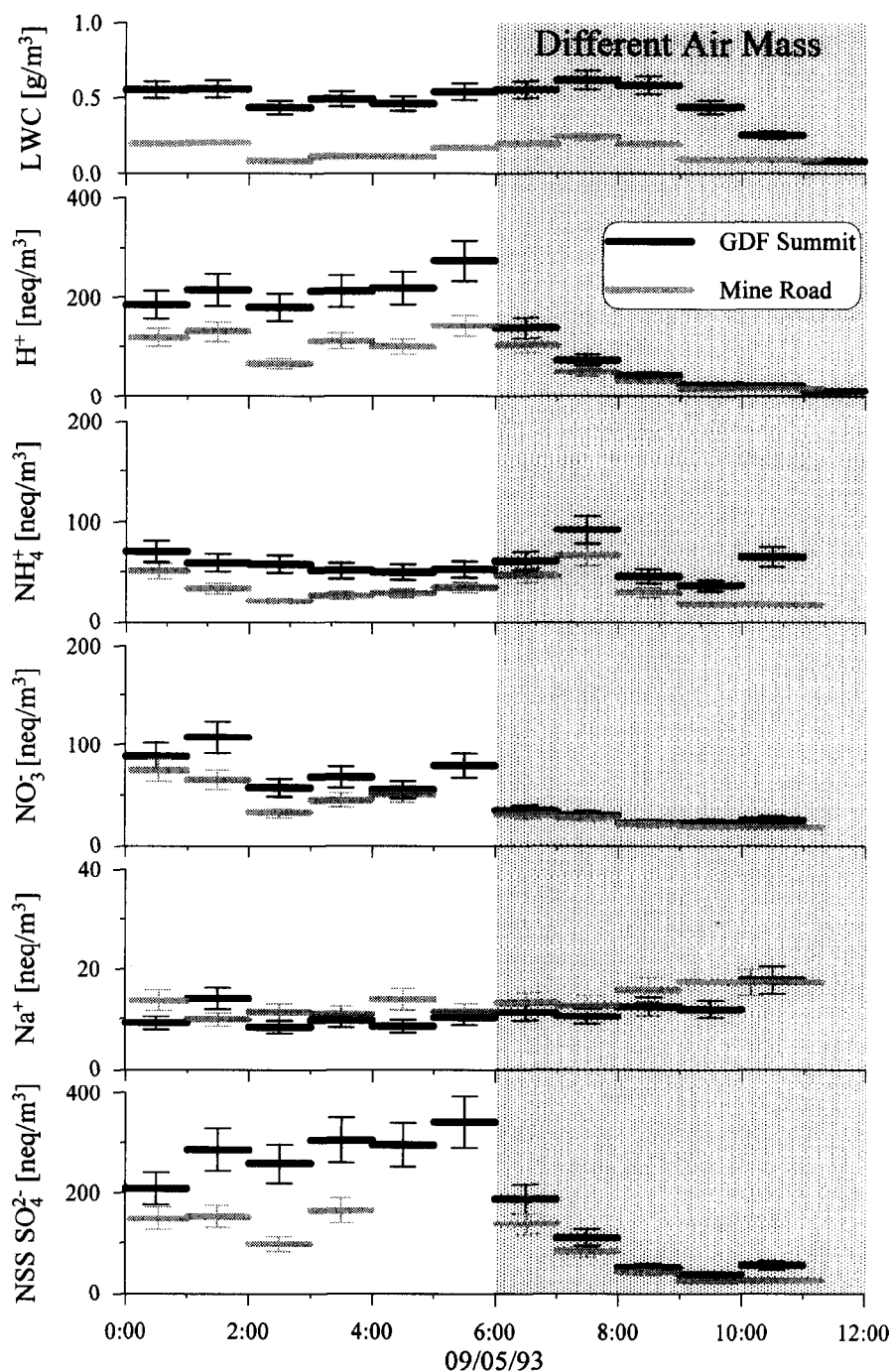


Fig. 1. Comparison of liquid water content (LWC) and cloud-water composition measured at two heights above the cloud base. Concentrations of dissolved H^+ and major ions show higher air-equivalent concentrations at the higher level above the cloud base (GDF Summit) than close to the cloud base (Mine Road).

a stably stratified situation. The lowest layer of air came from the North Sea south of the Shetland Islands. The higher levels (850 h Pa) were of continental origin starting over Russia, but due to the stability only little mixing of both air masses could be expected. This meteorological situation did not change during the whole event (Swietlicki *et al.*, 1997).

Low concentrations of NO_3^- and SO_4^{2-} in the liquid phase, 30 and 60 neq m^{-3} , respectively, indicated minor industrial influence on the air mass while it passed cities at the east coast of Britain. The wind at GDF was mainly northeast and the Mine Road was again on the downwind side of the ridge. The LWC was high with 0.67 g m^{-3} , on average, at

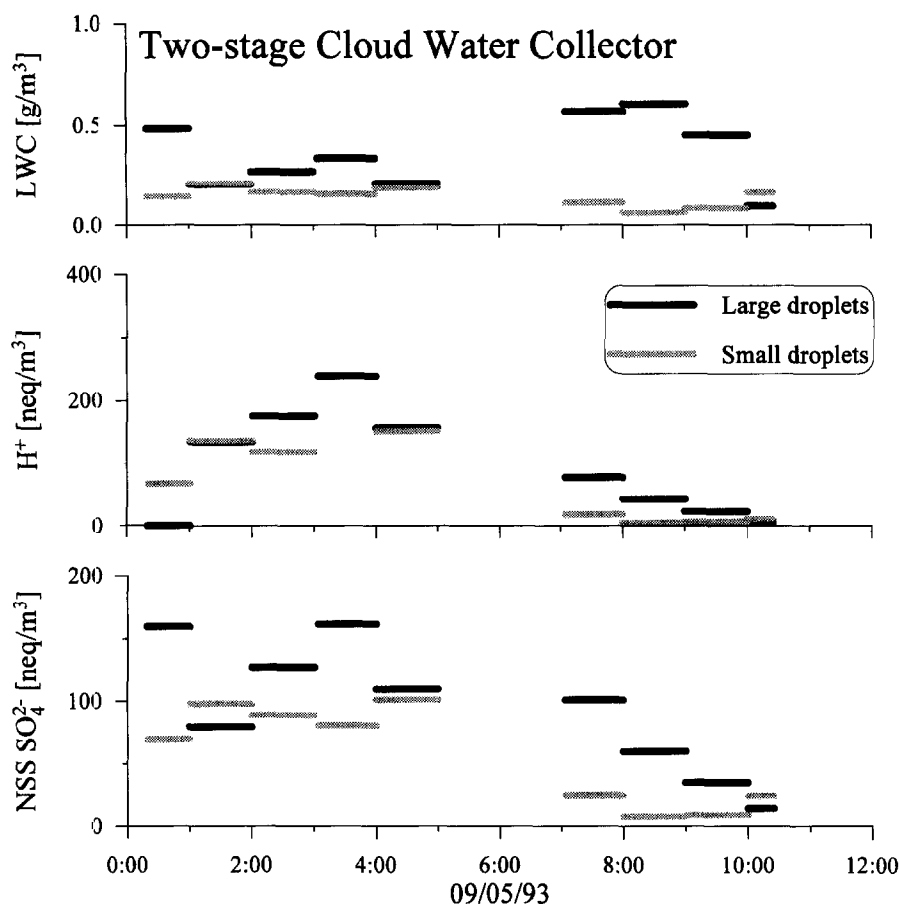


Fig. 2. Size-dependent distribution of LWC and air-equivalent concentration of dissolved H^+ and SO_4^{2-} in cloud water at the GDF Summit for small ($5 < d < 11 \mu\text{m}$) and large droplet size ($d > 11 \mu\text{m}$) measured with a two-stage cloud-water impactor.

the GDF Summit and 0.28 g m^{-3} at Mine Road and the variation remained small. The difference in the LWC between GDF Summit and Mine Road was slightly above the adiabatic gradient which is a piece of evidence for slight entrainment of dry air into the investigated cloud (Colvile *et al.*, 1997).

During this long event with a duration of 11 h no significant gradients in the H^+ , NH_4^+ , NO_3^- and nss SO_4^{2-} air-equivalent concentrations between GDF Summit and Mine Road were observed (Fig. 3). The concentration ratios between GDF Summit and Mine Road remained close to unity throughout the period. Also, substances derived from the sea-salt aerosol, like Na^+ and Mg^{2+} , did not show any significant gradients between the two sites. This indicates that the LWC at the Mine Road was still high enough to keep the condensation nuclei incorporated in the cloud droplets, i.e. droplets became smaller but did not evaporate when arriving at Mine Road site. This interpretation is corroborated by the FSSP measurements. The measured droplet spectrum was unimodal at the GDF Summit as well as at the Mine

Road. The volume median diameter (VMD) in the upper part of the cloud was higher at an average of $15.8 \mu\text{m}$ at the GDF Summit, while close to cloud base the VMD had decreased to $12.5 \mu\text{m}$ at the Mine Road (Fig. 4a). Thus, the droplets shrunk in size but did not evaporate completely, as confirmed by the total number of droplets larger than $5 \mu\text{m}$ diameter, which did not change during the transport from GDF Summit to Mine Road (Fig. 4b).

3.3. Evening of 10 May

During this event the air-equivalent concentrations of H^+ , NH_4^+ , NO_3^- and SO_4^{2-} in the liquid phase were relatively high, with maximum values of 90 neq m^{-3} NO_3^- and 270 neq m^{-3} SO_4^{2-} . The concentrations were of comparable magnitude to those on the morning of 9 May. Any maritime influence on the cloud-water composition was small, as was shown by low sea-salt concentrations. Three-dimensional back-trajectories over 72 h indicate that during the whole event the air mass which arrived at GDF started from a higher level over Russia and slid under the maritime

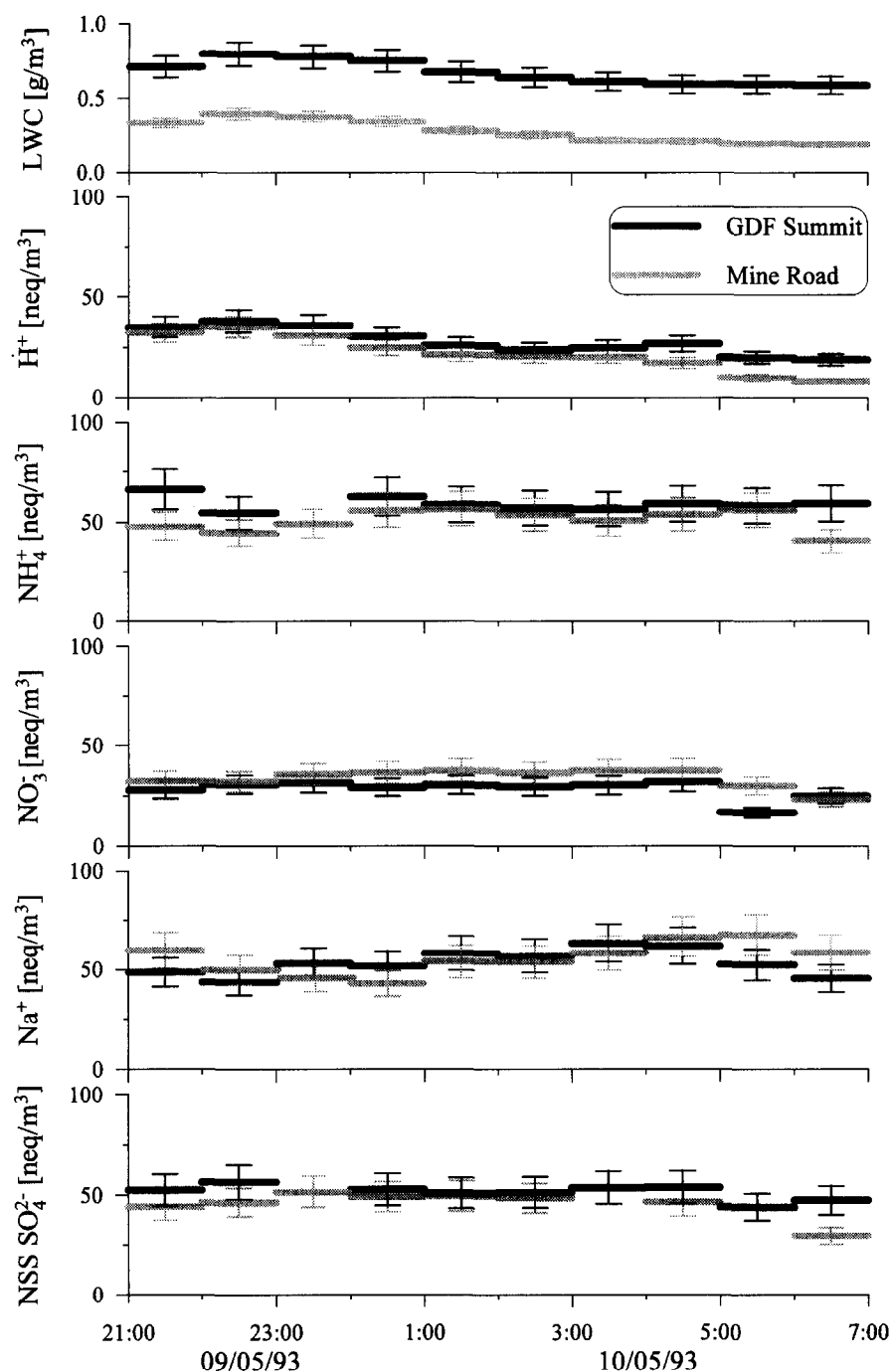


Fig. 3. Comparison of LWC and cloud-water composition measured at two heights above the cloud base. Concentrations of dissolved H^+ and major ions show similar air-equivalent concentrations at the higher level above the cloud base (GDF Summit) than close to the cloud base (Mine Road).

air mass from north of Great Britain (Swietlicki *et al.*, 1997). In this case some turbulent mixing of both air masses may have occurred and the reduced maritime influence on the evening of 10 May compared to that during the night of 9–10 May (second case study) can be explained. The wind direction at the GDF Summit was northeast to eastnortheast with down-

wind flow from the GDF Summit to the cloud base site at Mine Road.

This event started with very high LWC and showed a maximum hourly average of 0.90 g m^{-3} at the GDF Summit and 0.41 g m^{-3} at the Mine Road from 8 to 9 p.m. The measured LWC at the Mine Road was up to 33% lower than the expected adiabatic LWC

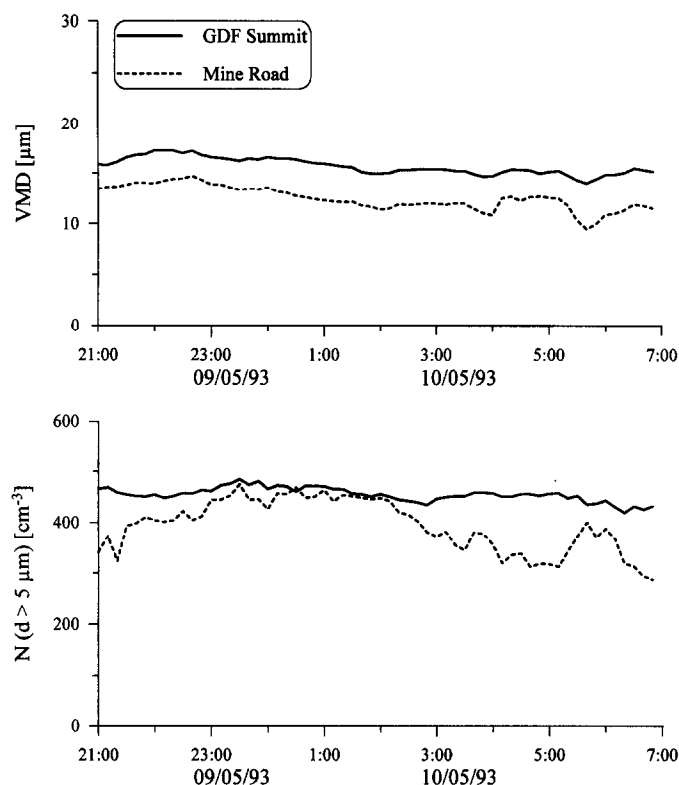


Fig. 4. Comparison of the cloud droplet volume median diameter and number concentration of droplets larger than $5 \mu\text{m}$ diameter measured at two heights above the cloud base with a Forward Scattering Spectrometer Probe (FSSP).

which indicated entrainment of dry air from above the cloud (Colville *et al.*, 1997). The development of the dissolved major ions as well as H^+ and Na^+ at both sites is presented in Fig. 5. Strong vertical gradients in the air-equivalent concentrations, especially for NH_4^+ , NO_3^- and nss SO_4^{2-} were observed, while components originating from the sea salt (e.g. Na^+) did not show any significant vertical gradients. The amount of NH_4^+ in the liquid phase was about 110% higher at the GDF Summit than at Mine Road, while NO_3^- and SO_4^{2-} were higher by 63 and 93%, respectively. These gradients cannot be explained by uptake of trace gases with subsequent liquid-phase reactions because of the expected longer lifetime of the droplets at the Mine Road. Such a process could only explain an inverse vertical gradient, with higher concentrations at Mine Road.

The observed vertical gradients of NO_3^- and SO_4^{2-} are inversely correlated to the development in the LWC at the GDF Summit. The vertical gradients increased while the LWC at both sites decreased. A similar explanation of the observed gradients as in case 1 (morning of 9 May) can be given here, namely, that different size fractions of aerosol particles are incorporated into the cloud droplets of various size. On the way down to the cloud base the smaller droplets evaporate more rapidly. Obviously, the smallest evaporating droplets dried and released aero-

sol particles such as $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 on the way down to the Mine Road. The NH_4^+ concentration plotted for both sites (Fig. 5) confirms this assumption. The NH_4^+ concentration remains nearly constant at the GDF Summit while at the Mine Road the concentration decreased by about a factor of 0.5 with decreasing LWC.

The vertical gradients of nss SO_4^{2-} and NH_4^+ were steeper than that of NO_3^- , perhaps because of a droplet size-dependent distribution of those compounds: nss SO_4^{2-} has primarily been incorporated in smaller droplets while NO_3^- is not expected to have shown a pronounced size dependence. Uptake of NO_3^- into the droplets from the gas phase (HNO_3) should have caused higher concentrations (expressed in air-equivalent units) in the larger droplets because of the high solubility which would permit droplets of all sizes to achieve equilibrium according to Henry's law. Due to the greater volume of the large droplets they contribute more to the total amount of NO_3^- in the liquid phase than the smaller ones. SO_2 is less soluble than HNO_3 and it can be expected that only smaller droplets are able to reach equilibrium, especially when the lifetime of the droplets is short due to a higher cloud base at the upwind side of the ridge.

During this cloud event the measurements of the two-stage cloud water collector could not give any additional information to confirm this hypothesis,

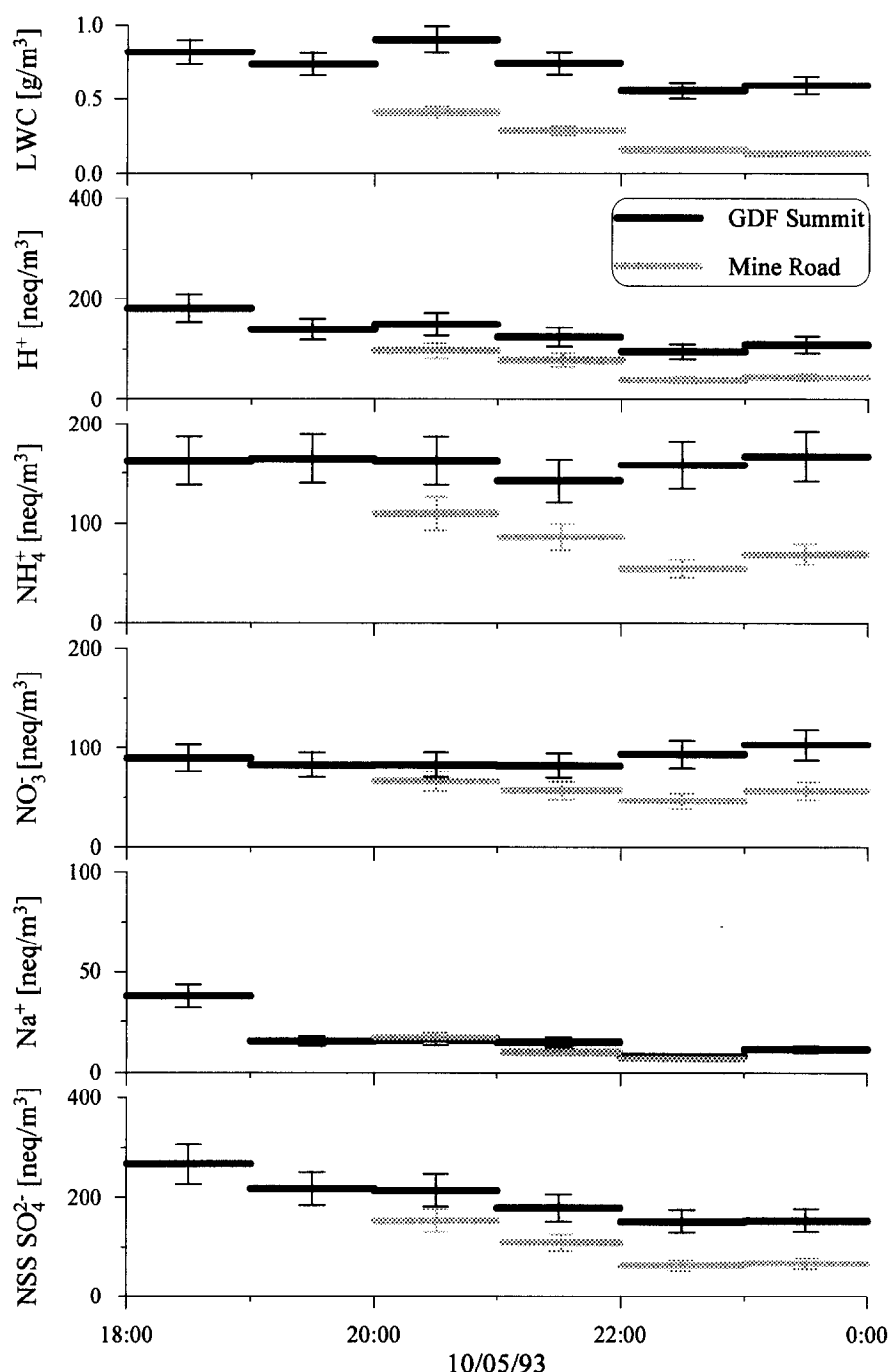


Fig. 5. Comparison of liquid water content (LWC) and cloud-water composition at two heights above the cloud base. Concentrations of dissolved H^+ and major ions show higher air-equivalent concentrations at the higher level above the cloud base (GDF Summit) than close to the cloud base (Mine Road).

because the droplet spectra were shifted to very large droplets. A VMD of $19 \mu\text{m}$ on average and the fact that only a small part of the total LWC was found in the small size bin (e.g. $\text{LWC} < 0.1 \text{ g m}^{-3}$ for drop sizes $5 < d < 11 \mu\text{m}$) while a LWC difference of 0.45 g m^{-3} , on average, between GDF Summit and Mine Road was observed and can be interpreted as

pieces of evidence that also a fraction of droplets with diameters above $11 \mu\text{m}$ are expected to evaporate during transport from GDF Summit to the cloud base. However, the main reason for the specific vertical gradients of nss SO_4^{2-} and NO_3^- is assumed to be caused by partial evaporation of the smallest droplets due to entrainment of dry air between Summit and

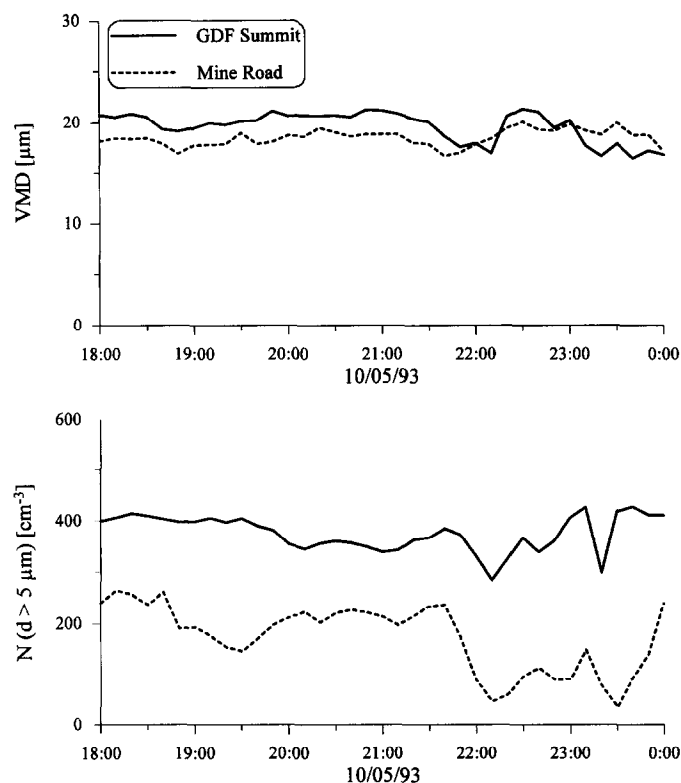


Fig. 6. Comparison of the cloud droplet volume median diameter and number concentration of droplets larger than $5\text{ }\mu\text{m}$ measured at two heights above the cloud base with a Forward Scattering Spectrometer Probe (FSSP).

Mine Road station. This is confirmed by a comparison of droplet spectra at the two sites. While the VMD did not change significantly (Fig. 6a) the number of droplets with a diameter above $5\text{ }\mu\text{m}$ (lower cut-off of cloud-water collectors) decreased from 360 cm^{-3} at the GDF Summit to 150 cm^{-3} at the Mine Road (Fig. 6b).

4. INTERPRETATION OF THE OBSERVATIONS

The observations obtained during the GDF experiment brought the unexpected result that the various ions exhibit different gradients as a function of height above the cloud base. Those ions which mainly occur in the coarse aerosol fraction like Na^+ (sea salt) are activated as condensation nuclei at the very beginning of the cloud formation. Thus, these ions also form large cloud droplets as the air rises more and more above the cloud base. Since the number of coarse aerosol particles is limited, they are completely activated at a very early stage of cloud formation. When the air continues to lift upwards over the hill, the supersaturation depending on the slope of the hill and on the uplift velocity reaches such high values that at higher levels above the cloud base more and more smaller aerosol particles become activated. This is confirmed by the modelled supersaturation profile for easterly flow which showed a second maximum close

to the GDF Summit (Bower *et al.*, personal communication). Since the small particles consist mainly of $(\text{NH}_4)_2\text{SO}_4$, the SO_4^{2-} concentration in the condensed phase rises with height above the cloud base. These small condensation nuclei form only small droplets. Thus, we expect a large droplet fraction containing a certain amount of ions originating from coarse particles and a small droplet fraction which develops at higher levels above the cloud base and incorporates aerosol particles of different chemical composition. This process, which transforms different aerosol particle sizes into different drop sizes, is disturbed when soluble gases such as, e.g. SO_2 , NH_3 or HNO_3 are also available. Once droplets are formed, these gases try to equilibrate according to Henry's law. However, no special droplet size is preferred but the gases dissolve in any droplet size. Whether Henry's law equilibrium can be achieved will depend on how quickly the droplets grow to their final size, or whether the droplet growth continues because supersaturation is still present. The gas transfer to the liquid phase must be proportional to the droplet surface area, i.e. very small droplets and those droplets which contribute mostly to the surface are expected to equilibrate faster while the droplets with the largest volume equilibrate later.

Here a complicated equilibration process starts, depending on the development of supersaturation, the development of the drop size distribution, diffusion

coefficients, the amount of trace gases and their Henry coefficients, and so on (Schwartz, 1986). When the first droplets are formed, they take up soluble gases. The highly soluble gases, especially HNO_3 , will nearly completely transfer to the liquid phase where upon the gas phase depletes. As supersaturation remains high and new condensation nuclei are activated, these new droplets can only equilibrate to a lower gas-phase concentration while the droplet fraction which was formed earlier and contained most of the HNO_3 grows to larger drops. Less-soluble gases like SO_2 do not deplete so rapidly and thus smaller droplets which develop late are exposed to gas-phase concentrations similar to those near the cloud base. However, large drops which contribute more to the volume than to the overall drop surface can reach equilibrium for highly soluble gases and thus their contribution to the dissolved material per m^3 air will be high. It is through processes such as these that certain ions are not uniformly distributed across the drop size spectrum.

It must be emphasized that such processes are a result of the airflow over complex terrain, and will not be generally applicable for a cloud in the free troposphere. The interpretation given above is complicated further when uptake of trace gases with subsequent liquid-phase reaction occurs, as for example SO_2 with subsequent oxidation by O_3 or H_2O_2 and neutralization by NH_3 . This process needs some time which can also lead to formation of vertical gradients. However, since this SO_4^{2-} should remain in the cloud water when the air was flowing from the GDF Summit to the cloud base station, both sites should exhibit similar SO_4^{2-} concentrations in the condensed phase or the lower station should even show higher concentrations, because more time was available for a liquid-phase production due to the air flow downhill during the events studied. Although liquid-phase production of SO_4^{2-} took place (Laj *et al.*, 1997), we have evidence that the height dependence of the activation of aerosol particles in the accumulation mode gave the main contribution to the gradients which were observed. It can be concluded that trace substances mainly incorporated in larger droplets which do not evaporate so rapidly exhibit smaller or no gradients between two heights above the cloud base, while trace substances mainly dissolved in the smaller droplets show distinct vertical gradients with the lower concentration close to the cloud base. This process will be intensified by entrainment and homogeneous mixing.

5. CONCLUSION

Vertical gradients can be expressed in terms of concentration per litre of cloud water or in terms of chemical compounds in the condensed phase per m^3 of air. While the first type depends on the condensation process above the cloud base, the second type

allows the study of processes independent of dilution by condensation.

During the GDF-experiment three case studies in evaporating clouds under different conditions have been conducted. The flow in each case was downhill so that the air flow at the cloud base site was out of the cloud. In the first case, the liquid water content was low so that the smallest droplets had already evaporated above the cloud base site. In the second case, the liquid water content was high and all droplets had become smaller but no size fraction evaporated between the sites. In the third case, the liquid water content was highest but due to entrainment of dry air from above the cloud between the two sites, again the smallest droplets evaporated completely during transport.

Since the cloud-water composition was not uniform across the drop spectrum, vertical gradients above the cloud base were different for various ions in the case of selective evaporation of small drops at some distance above the cloud base. Those ions incorporated in large drops do not exhibit significant vertical gradients in terms of equivalent units per m^3 of air while those ions in small droplets develop large vertical gradients. The principal development of vertical gradients is summarized in Fig. 7. The behaviour of SO_4^{2-} and Na^+ is presented for two cases: the solid curve represents the situation where all SO_4^{2-} and Na^+ remain in the liquid phase. The concentration per litre of cloud water increases inversely with the LWC, and in this case the air-equivalent concentration per m^3 air remains constant with height. The dashed line represents the observed case for SO_4^{2-} , where small droplets containing most of the SO_4^{2-} evaporate between the sites. One would expect that in the opposite than the observed case, i.e. when the air enters the cloud base, new small droplets would have formed in between the two sites producing similar but not necessarily the same vertical gradients of dissolved ions. The concentration in $\mu\text{eq l}^{-1}$ increases only slightly towards the cloud base, and here the air-equivalent concentration per m^3 of air decreases strongly with decreasing height. It should be kept in mind that liquid-phase production of SO_4^{2-} in cloud water had raised the concentration at the cloud base at the point marked as "observed" concentration.

The observed gradients of Na^+ deviated much less from the solid curve which is valid when all Na^+ remains in the liquid phase, giving the same expected concentration increase ($\mu\text{eq l}^{-1}$) towards the cloud base as for SO_4^{2-} (constant air equivalent concentration per m^3 of air). Since Na^+ also is partly found in small drops which evaporated above Mine Road, their Na^+ content is lost from the liquid to the interstitial phase resulting in the "observed" concentration. The air-equivalent concentration decreases only slightly towards the cloud base.

The observed vertical gradients showed large variations and individual extent for the specific ions. Thus, the results cannot be generalized for cloud base

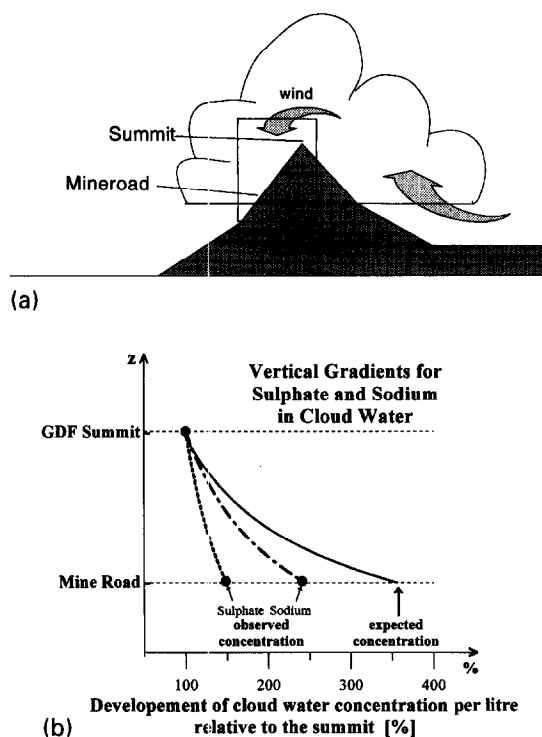


Fig. 7. Sketch showing the development of vertical gradients for different chemical constituents in cloud water during transport from GDF Summit to Mine Road near the cloud base. The solid curve describes the expected case in which all material is dissolved in cloud drops at GDF Summit remains in the liquid phase. The expected increase in concentration is caused by the decreasing LWC, and will be valid for all chemical constituents. The development of the observed sodium concentration (dashed-dotted curve) deviates much less to the expected than the observed non-sea-salt sulphate concentration (dashed curve), because sodium is mainly dissolved in large drops which become smaller during transport to cloud base but which do not evaporate completely as the small sulphate containing droplets will do.

situations, especially in newly developing clouds, although similar gradients may form under certain conditions. In any case vertical gradients are also influenced by interaction of the air flow with complex terrain because the supersaturation history and thermodynamic equilibration is strongly depending on the location of first condensation and the distance to the measuring site.

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REFERENCES

- Bower, K. N., Choulaton, T. W., Gallagher, M. W., Colvile, R. N., Wells, M., Beswick, K. M., Wiedensohler, A., Hansson, H.-C., Svenningsson, B., Swietlicki, E., Wendisch, M., Berner, A., Kruisz, C., Laj, P., Facchini, M. C., Fuzzi, S., Bizjak, M., Dollard, G., Jones, B., Acker, K., Wiprecht, W., Preiss, M., Sutton, M. A., Hargreaves, K. J., Storeton-West, R. L., Cape, J. N. and Arends, B. G. (1997) Observation and modelling of the processing of aerosol by a hill cap cloud. *Atmospheric Environment* **31**, 2527–2543.
- Choulaton, T. W., Colvile, R. N., Bower, K. N., Gallagher, M. W., Wells, M., Beswick, K. M., Arends, B. G., Möls, J. J., Kos, G. P. A., Fuzzi, S., Lind, J. A., Orsi, G., Facchini, M. C., Laj, P., Gieray, R., Wieser, P., Engelhardt, T., Berner, A., Kruisz, C., Möller, D., Acker, K., Wiprecht, W., Lüttke, J., Levens, K., Bizjak, M., Hansson, H.-C., Cederfelt, S.-I., Frank, G., Menten, B., Martinsson, B., Orsini, D., Svenningsson, B., Swietlicki, E., Wiedensohler, A., Noone, K. J. and Pahl, S. (1997) The Great Dun Fell Cloud Experiment 1993: an overview. *Atmospheric Environment* **31**, 2393–2405.
- Colvile, R. N. (1994) Field study and computer modelling of oxides of nitrogen, aerosols and acidity in hill cap clouds. Ph.D. thesis. University of Manchester Institute of Science and Technology: Atmospheric Physics Research Group – Department of Pure & Applied Physics.
- Colvile, R. N., Bower, K. N., Choulaton, T. W., Gallagher, M. W., Wobrock, W., Hargreaves, K. J., Storeton-West, R. L., Cape, J. N., Jones, B., Wiedensohler, A., Hansson, H.-C., Wendisch, M., Acker, K., Wiprecht, W., Pahl, S., Winkler, P., Berner, A. and Kruisz, C. (1997) Meteorology of the Great Dun Fell Cloud Experiment 1993. *Atmospheric Environment* **31**, 2407–2420.
- Facchini, M. C., Fuzzi, S., Kessel, M., Wobrock, W., Jaeschke, W., Arends, B. G., Möls, J. J., Berner, A., Solly, I., Kruisz, G., Reischl, G., Pahl, S., Hallberg, A., Ogren, J. A., Fierlinger-Oberlininger, H., Marzorati, A. and Schell, D. (1992) The chemistry of sulfur and nitrogen species in a fog system. A multiphase approach. *Tellus* **44B**, 505–521.
- Fowler, D., Cape, J. N., Leith, I. D., Choulaton, T. W., Gay, M. J. and Jones, A. (1988) The influence of altitude on rainfall composition at Great Dun Fell. *Atmospheric Environment* **22**, 1355–1362.
- Friedlander, S. K. (1973) Chemical elements balances and identification of air pollution sources. *Envir. Sci. Technol.* **7**, 235–240.
- Gallagher, M. W., Choulaton, T. W. and Hill, M. K. (1988) Some observations of airflow over a large hill of moderate slope. *Boundary-Layer Met.* **42**, 229–250.
- Gerber, H. (1984) Liquid water content of fogs and hazes from visible scattering. *J. Clim. Appl. Met.* **23**, 1247–1252.
- Gieray, R., Wieser, P., Engelhardt, T., Swietlicki, E., Hansson, H.-C., Menten, B., Orsini, D., Martinsson, B., Svenningsson, B., Noone, K. and Heintzenberg, J. (1997) Phase partitioning of aerosol constituents in cloud based on single-particle and bulk analysis. *Atmospheric Environment* **31**, 2491–2502.
- Huret, N., Chaumerliac, N. and Isaka, H. (1994) Influence of different microphysical schemes on the prediction of dissolution of nonreactive gases by cloud droplets and raindrops. *J. appl. Met.* **33**, 1096–1109.
- Junge, C. (1963) *Air Chemistry and Radioactivity*. Academic Press, New York.

- Krugmann, G. and Winkler, P. (1989) Abschätzung der feuchten Deposition durch Nebel auf Grund gemessener, chemischer und meteorologischer Parameter Bd. 1. Final Report BMFT-Project Grant No 07431018.
- Laj, P., Fuzzi, S., Facchini, M. C., Lind, J. A., Orsi, G., Preiss, M., Maser, R., Jaeschke, W., Seyffer, E., Arends, B. G., Möls, J. J., Acker, K., Wieprecht, W., Möller, D., Colville, R. N., Gallagher, M. W., Beswick, K. M., Hargreaves, K. J., Storeton-West, R. L. and Sutton, M. A. (1997a) Cloud processing of soluble gases. *Atmospheric Environment* **31**, 2589–2597.
- Laj, P., Fuzzi, S., Facchini, M. C., Orsi, G., Berner, A., Krusiz, C., Wobrock, W., Hallberg, A., Bower, K. N., Gallagher, M. W., Beswick, K. M., Colville, R. N., Choulaton, T. W., Nason, P. and Jones, B. (1997b) Experimental evidence for in-cloud production of aerosol sulphate. *Atmospheric Environment* **31**, 2503–2514.
- Lin, N.-H. and Saxena, V. K. (1991) Interannual variability in acidic deposition on the Mt. Mitchell area forest. *Atmospheric Environment* **25A**, 517–524.
- Lovett, G. M. (1984) Rates and mechanisms of cloud water deposition to a subalpine balsam fir forest. *Atmospheric Environment* **18**, 361–371.
- Lovett, G. M. and Kinsman, J. D. (1990) Atmospheric pollutant deposition to high-elevation ecosystems. *Atmospheric Environment* **24A**, 2767–2786.
- Mohnen, V. A. and Vong, R. J. (1993) A climatology of cloud chemistry for the eastern United States derived from the mountain cloud chemistry project. *Envir. Rev.* **1**, 257–272.
- Mohnen, V. A., Aneja, V., Bailey, B., Cowling, E., Goltz, S. M., Healey, J., Kadlec, J. A., Meagher, J., Mueller, S. F. and Sigmon, J. T. (1990) An assessment of atmospheric exposure and deposition to high elevation forests in the Eastern United States. MCCP Report CR 813934-03-0.
- Pahl, S. (1996) Feuchte Deposition auf Nadelwälder in den Hochlagen der Mittelgebirge. Berichte DWD No. 198, Offenbach.
- Pahl, S. and Winkler, P. (1993) Deposition von sauren und anderen Luftbeimengungen durch Nebel (GCE). Final Report. BMFT-Project Grant No 07EU7268.
- Pahl, S. and Winkler, P. (1995) Height dependence of trace substance deposition onto forests via clouds (in German). Final Report. BMFT-Project Grant No 07EU726A8.
- Pahl, S., Winkler, P., Schneider, T., Arends, B. G., Schell, D., Maser, R. and Wobrock, W. (1994) Deposition of trace substances via cloud interception on a coniferous forest at Kleiner Feldberg. *J. Atmos. Chem.* **19**, 231–252.
- Saxena, V. K., Stogner, R. E., Hendler, A. H., d. Felice, T. P., Yeh, R. J.-Y. and Lin, N.-H. (1989) Monitoring the chemical climate of the Mt. Mitchell State Park for evaluation of its impact on forest decline. *Tellus* **41B**, 92–109.
- Schell, D., Georgii, H.-W., Maser, R., Jaeschke, W., Arends, B. G., Kos, G. P. A., Winkler, P., Schneider, T., Berner, A. and Krusiz, C. (1992) Intercomparison of fogwater samplers. *Tellus* **44B**, 612–631.
- Schell, D., Wobrock, W., Maser, R., Preiss, M., Jaeschke, W., Georgii, H. W., Gallagher, M. W., Bower, K. N., Beswick, K. M., Pahl, S., Facchini, M. C., Fuzzi, S., Wiedensohler, A., Hansson, H.-C. and Wendisch, M. (1997a) The size-dependent chemical composition of cloud droplets. *Atmospheric Environment* **31**, 2561–2576.
- Schell, D., Maser, R., Wobrock, W., Jaeschke, W., Georgii, H. W., Kos, G. P. A., Arends, B. G., Beswick, K. M., Bower, K. N. and Gallagher, M. W. (1997b) A two-stage impactor for fog droplet collection: design and performance. *Atmospheric Environment* **31**, 2671–2679.
- Schwartz, S. E. (1986) Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds. In *Chemistry of Multiphase Atmospheric Systems* (edited by Jaeschke W.), Nato ASI series G: Ecological Sciences Vol. 6. Springer, Heidelberg.
- Swietlicki, E., Hansson, H.-C., Martinsson, B., Mentes, B., Orsini, D., Svenningsson, B., Wiedensohler, A., Wendisch, M., Pahl, S., Winkler, P., Colville, R. N., Gieray, R., Lüttke, J., Heintzenberg, J., Cape, J. N., Hargreaves, K. J., Storeton-West, R. L., Acker, K., Wieprecht, W., Berner, A., Krusiz, C., Facchini, M. C., Laj, P., Fuzzi, S., Jones, B. and Nason, P. (1997) Source identification during the Great Dun Fell Cloud Experiment 1993. *Atmospheric Environment* **31**, 2441–2451.
- Vong, R. J., Sigmon, J. T. and Mueller, S. F. (1991) Cloud water deposition to Appalachian forests. *Envir. Sci. Technol.* **25**, 1014–1021.
- Winkler, P. (1992) Design and calibration of a fog water collector. Instruments and observing methods. Bd. 49. Vienna: WMO/TD-No 462, 17–21.