Phase partitioning for different aerosol species in fog

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ABSTRACT

Simultaneous measurements of several non-volatile species in unscavenged aerosol particles and in fog droplets have revealed differences in partitioning for different chemical species. The average scavenged fraction of sulphate was 18 % and the corresponding fraction of elemental carbon was only 6 %. This suggests that the aerosol was externally mixed, and that the chemical mixture of the aerosol as a function of size is important in the context of nucleation scavenging. The measurements obtained could not distinguish between the two primary hypotheses for explaining the observed differences, (a) that the particles had the same size distribution and their chemical composition was the controlling factor, and (b) that the elemental carbon was associated with smaller particles than the sulphate, so that the difference in scavenging efficiency was controlled by the size distribution of the particles.

1. Introduction

Knowledge of the partitioning of various chemical species in the atmospheric aerosol between droplets and the interstitial air in cloud or fog is necessary for understanding how chemical transformations are influenced by clouds and fogs, and also how the lifetime of the aerosol species is thereby affected.

Partitioning of sulphate and nitrate has been studied with the goal of achieving an estimate of the efficiency of nucleation scavenging and the amount of material produced by chemical reactions in the cloud droplets, particularly in the context of acid rain formation. A range of values has been measured (e.g., Hegg et al., 1984; Hegg and Hobbs, 1986; ten Brink et al., 1987) suggesting

that the efficiency will depend on several factors. Some factors that can influence the nucleation scavenging efficiency have been modelled by Jensen and Charlson (1984) who showed that the nucleation scavenging efficiency decreases with decreasing updraft velocity and decreases with increasing submicrometer aerosol mass.

The efficiency with which other compounds, e.g., elemental carbon (EC) and trace metals, are incorporated into cloud droplets is also of importance. EC can have an enhanced effect on the cloud radiative properties when present in cloud droplets rather than in the interstitial air (Ackerman and Baker, 1977; Chylek et al., 1984). Another consequence of the presence of EC and trace metals in cloud droplets is their ability to act as a catalysts in the oxidation of sulphite to sulphate (Benner et al., 1982; Weschler et al., 1986).

The incorporation of carbon into water droplets has been studied by Benner et al. (1989). They found that a high fraction of carbon was incorporated when the concentration of black carbon was $< 5 \mu g/m^3$ and that the incorporation decreased at higher concentrations. The super-

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saturation used in their system was however not well known. Hansen and Novakov (1989) studied the incorporation of aerosol black carbon into advection fogs. They found that the fraction incorporated varied with the total black carbon concentration and the density of the fog. Dlugi (1989) has found from field measurement that soot particles were activated to a lower extent than other particles during fog formation.

Given that various chemical compounds have different affinities for water one could postulate that a differentiation in scavenging could occur for different chemical species in the atmospheric aerosol. Different compounds, e.g., sulphate and EC, may not act as condensation nuclei for cloud droplets to the same extent. Covert and Heintzenberg (1984) studied the hygroscopic growth of particles at 90% RH. They found a difference in hygroscopic growth for sulphur and EC where sulphur containing particles grow to a larger extent than EC containing particles.

The question we want to address with this paper is: can we see a difference in partitioning for different chemical compounds? In trying to answer this question we will first describe measurements of the partitioning between fog droplets and interstitial air for different chemical compounds. We will focus on two compounds with different affinities for water, sulphate and EC, and perform a statistical analysis on the data to see if a difference in scavenging can be observed. Size-segregated measurements of the aerosol particles with regard to their mass and water-soluble fraction will be used in trying to characterize the aerosol. Finally, possible explanations for a difference in scavenging are discussed.

2. Experimental approach

The experiment was part of the first field campaign held by the EUROTRAC sub-project Ground-based Cloud Experiment (GCE). The campaign took place in November 1989 in the Po Valley near San Pietro Capofiume, Italy. A detailed description of the site and an overview of the campaign itself are presented in Fuzzi et al. (1992). The idea behind our sampling strategy was to separate the fog droplets from the interstitial aerosol and collect the two fractions on filters. Due to the technical approach used the dividing

line between these two parts of the aerosol was assumed to be 5 μm in diameter. Two kinds of sampling inlets were used to separate the fog droplets from the interstitial air. The "interstitial" inlet used an annular-slit impactor to remove particles and droplets larger than 5 μm in diameter. Once separated from the fog, the particles were pulled through a tube to a distribution plenum inside the sampling container. Because the temperature in the container usually was 10–20°C above ambient, the particles will have been dried somewhat before being sampled. The other inlet used a counterflow virtual impactor (CVI) (Ogren et al., 1985; Noone et al., 1988) to sample only particles and droplets larger than 5 μm in diameter. Once the fog droplets are extracted from the ambient air they are surrounded by a dry, particle-free carrier air stream. The fog droplets will evaporate and the water and volatile species in the droplets are driven into the gas phase. Upon evaporation, each fog droplet is assumed to release a single (residual) particle that contains the non-volatile material that was dissolved or suspended in the fog droplet. Thus, both inlets separate the aerosol particles and fog droplets in their wet condition but finally the particles were collected on filters as dry. The interstitial inlet was located ca. 6 m above the ground and the CVI inlet ca. 4 m above the ground on top of a sampling container. More details of the inlets are described in Noone et al. (1992a).

Cascade impactors (described below) sampled and size segregated mainly the interstitial part of the aerosol particles as a function of their ambient wet size. The impactors were used in trying to characterize the chemical composition of the aerosol particles as a function of size. The impactors were situated at a distance of ca. 100 m from the other two sampling inlets.

2.1. Filter samples

During periods without fog the interstitial samples were taken on a three-hour basis and during fog periods samples from both the interstitial and CVI inlets were generally taken on an hourly basis. Nuclepore polycarbonate membrane filters (25 mm diameter, 0.4 μm pore size) were used (to collect samples) in both inlets. The sample was concentrated onto a spot of 8 mm in diameter by using a mask in the filter holder.

The following analyses were performed on the filters in the given order: particulate mass by gravimetric measurements with a Mettler (ME30) microbalance, EC using a light absorption technique, trace elements using Particle Induced X-ray Emission (PIXE), and finally sulphate by extracting the filter in water and subsequent analysis with ion chromatography (IC).

The lowest detectable mass on the microbalance was 1 μg. Ten repeated weighings of the same filter gave a precision of 1 μg. On each measuring occasion a reference filter was used to verify the accuracy of the balance and each sample filter was weighed once. Since the balance was situated indoors a typical value for the RH while weighing would be about 30%. An electrostatic charge neutralizer was used in the sample chamber during the weighing procedure.

2.1.1. EC from a light absorption technique. A photometer based on the integrating plate method (IPM, Lin et al., 1973) was used to estimate the amount of EC in the samples (Heintzenberg, 1988). The instrument measures the attenuation of a light beam as it passes through the sample. By both measuring at the sample spot and on a blank spot on the same filter the attenuation caused by the absorbing material in the sample can be determined. By assuming that all the absorbing material in the sample is EC and by using Monarch 71 (M71) soot (Cabot. Corp.) as a reference (specific light absorption 9.68 $m^2 g^{-1}$) the amount of light absorbing material in the sample can be reported as an equivalent mass of EC.

The detection limit for EC was 0,04 μg based on blank filter measurements. The detection limit expressed as a mass concentration in ambient air will vary from filter to filter due to the inherent enrichment in the CVI system. To get a rough estimate, a typical value of the detection limit for filters sampled in the CVI would be 0.01–0.03 μg EC m^{-3} and 0.06–0.24 μg EC m^{-3} for filters sampled in the interstitial inlet.

2.1.2. Trace metals from PIXE analysis. The amount of the elements P, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, Se, Br, and Pb sampled on the filter was determined using PIXE. PIXE is generally non-destructive under the conditions used. Volatile species like nitrate, organic material may however be lost. They are however not discussed in the results. A test on parallel filter samples with

regard to their sulphate content obtained with IC before and after PIXE analysis showed an average difference of $+/-10\%$ which is within the experimental error. In this paper only results dealing with the partitioning of the different elements between fog droplets and interstitial air will be discussed. A more extensive statistical analysis of the PIXE results is given in Noone et al. (1992b).

2.1.3. Sulphate from IC analysis. The sample was extracted by first wetting the sample spot with a drop of ethanol and then adding 5 ml of deionized (Milli-Q) water. The extracts were warmed in a microwave oven and then put in a ultrasonic bath for 5 min. The samples were analysed using a DIONEX 4000i ion chromatograph (guard columns: AGA4 and NG1 Guard; separator column: Fast Sep Anion-1; suppressor: Anion Micro Membrane Suppressor; detector: conductivity meter; eluent: 2 mM Na_2CO_3/0.15 mM $NaHCO_3$; flow rate: 2 ml/min). The concentrations were obtained from a calibration curve of standards. The average blank value was 0.33 μeq/l and was subtracted from the samples. The samples were at minimum a factor of 10 above the blank value and on average even more.

2.2. Impactor samples

In the first period of the campaign, eight-stage, low-pressure cascade impactors (Hanke company, Gmünden, Austria, Model LPI 30/0.06/2; Berner et al., 1979) were used for collecting the aerosol. These impactors have a flow rate of 30 L min^{-1} and the particle size ranges covered were 0.06–0.125, 0.125–0.25, 0.25–0.50, 0.50–1.0, 1.0–2.0, 2.0–4.0, 4.0–8.0, and 8.0–16 μm diameter. From 15:00 on 16 November, four-stage, high-volume impactors (Hanke company, Gmünden, Austria, Model LPI 80/0.15/3.2/BF) were used instead. These impactors, which are equipped with a backup filter, have the working range 0–0.15, 0.15–0.48, 0.48–1.6, and 1.6–5.0 μm diameter and a flow rate of 75 litres min^{-1}.

The mass on each impactor stage was determined with a Mettler (ME3) microbalance by weighing the substrates before and after sampling and then the impactor stages were extracted with deionized water for chemical analysis. In the eight-stage impactor, substrates from adjacent stages were combined in pairs before extraction to obtain sufficient sample for the chemical analyses.

The major anions (SO_4^{2-}, NO_3^-, and Cl^-) were determined by the same method used for the IC analysis on the filters (see Subsection 2.1.3.). The cations Na^+, K^+, Ca^{2+} and Mg^{2+} were determined by using Atomic Absorption and NH_4^+ was determined using IC. Detection limits for the different ions and more information of the chemical analyses are given in Fuzzi et al. (1992).

3. Results

3.1. Filter/Impactor comparison

The interstitial mass and sulphate concentrations obtained from the filter samples and the impactor samples are shown in Figs. 1 and 2. The mass and sulphate concentrations from the impactors were calculated by summing the stages below the cut size of the interstitial inlet. For the eight-stage impactor, only data from stages below 4 μm were used. The mass lost due to the interval between 4 and 5 μm is, however, only a small fraction of the total. For the four-stage impactor, all of the stages were summed.

As can be seen in Fig. 1 the mass concentration is on average 85 μg m^{-3}. The mass concentration obtained with the filters was always lower, which can be interpreted as a loss of volatile species such

as nitrate and ammonium from the particles (White and Macias, 1987). Subtracting the nitrate and ammonium mass concentrations from the total mass concentration on the impactors gives better agreement between the impactor and filter sampling systems. The sulphate concentration in Fig. 2 shows good agreement between the two different sampling systems. The average difference is 2 μg m^{-3}. Sulphate concentrations obtained with the impactor from midnight to 06:00 the 12 November differ markedly from the concentration obtained from the filter samples. No reasonable explanation for this has been found.

3.2. Scavenging of sulphate and EC

The total concentrations of sulphate and EC in the aerosol (obtained from the filters) are shown in Figs. 3 and 4, respectively. They have been obtained by summing the concentration measured with the interstitial inlet and the concentration measured with the CVI inlet. The fog periods are marked with boxes. These figures give an idea of how the concentrations varied and of their relative magnitudes. The average mass fraction of the interstitial total mass concentration (obtained from the impactor) is 10% for sulphate and for EC only 4%.

The scavenged fraction of sulphate and EC, that is the mass fraction of the species found in the fog
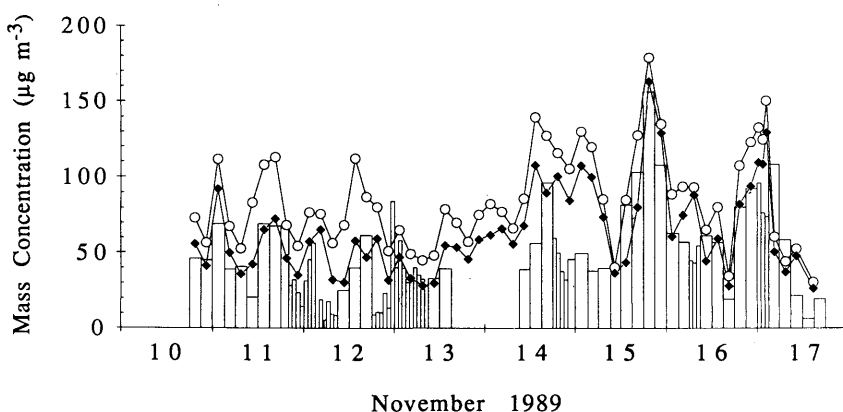

Fig. 1. Interstitial mass concentration determined from filters and impactors. Bars correspond to the concentration obtained with filters. Impactor samples are given versus the middle of the 3-h sampling period. The symbol —○— represents the total mass concentration and the symbol —◆— represents the total mass concentration, minus the nitrate and ammonium concentrations.
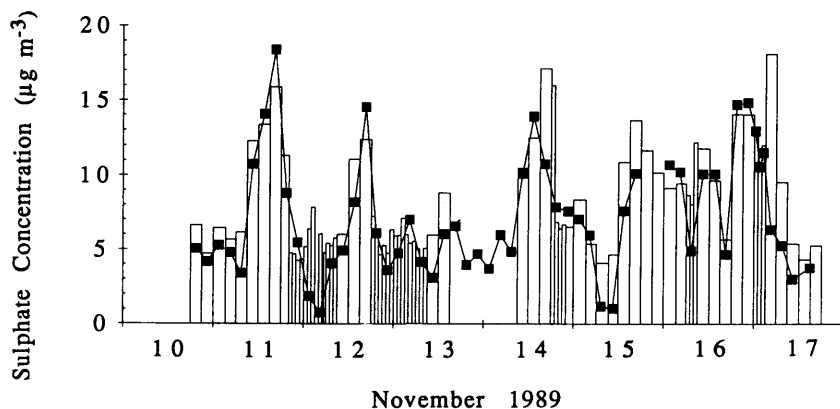
Fig. 2. Interstitial sulphate concentration obtained with filters and impactors. Bars correspond to the concentration obtained with filters. Concentrations obtained from impactors are given versus the middle of the 3-h sampling period.

droplets due to processes transferring material to the droplet phase from the particle and gas phases, is in Figs. 5 and 6 given by

$$\text{scav. frac.} = \frac{X_{\text{fog}}}{X_{\text{interstitial}} + X_{\text{fog}}},$$

where X is either the sulphate concentration or EC concentration with units of $\mu g\ m^{-3}$. X_{fog} refers to the ambient concentration of X in the residual particles that are obtained when the fog droplets evaporate in the CVI. $X_{\text{interstitial}}$ refers to the ambient concentration of X in the interstitial

particles. Three samples at the start of fog periods were obtained. As can be seen by comparison of Figs. 5 and 6, the scavenged fraction of sulphate is always higher than the scavenged fraction of EC. The average scavenged fraction of sulphate was 18% and the average scavenged fraction of EC was 6%.

A paired *t*-test was performed on the sulphate and EC fraction scavenged. When only considering the three initial periods of fog a difference in scavenging was observed, significant at the 92% confidence limit. Taking all of the periods in fog into account where parallel samples were taken
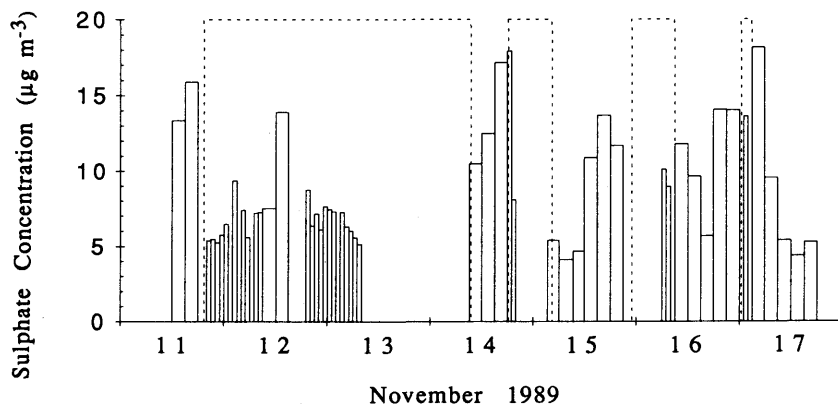

Fig. 3. Total sulphate concentration, calculated as the sum of sulphate concentrations determined with the interstitial and CVI inlets. Periods with fog are indicated by dashed lines.
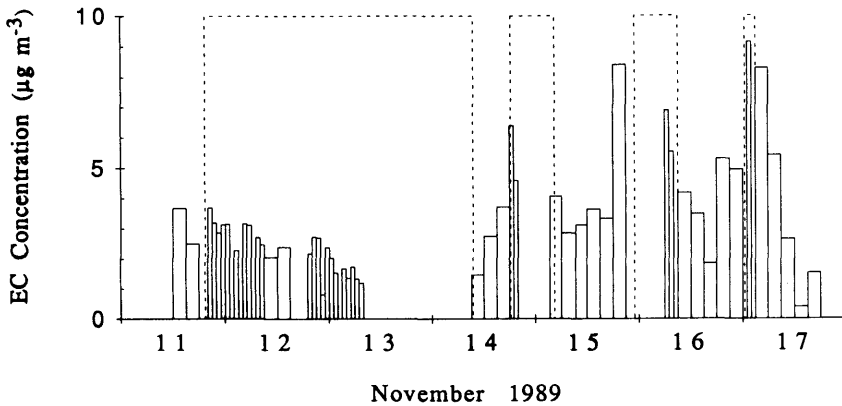
Fig. 4. Total EC concentration, calculated as the sum of EC concentrations determined with the interstitial and CVI inlets. Periods with fog are indicated by dashed lines.

with the two inlets a difference in scavenging was observed, significant to a 99.99 % confidence limit. This result confirms that a difference in scavenging was observed.

Processes responsible for scavenging are nucleation scavenging, coagulation, Brownian diffusion, and incorporation of gases with subsequent transformation. To be able to explain the difference in scavenging we have to ascertain which one of these processes is the dominant one.

Ideally, when studying the effect of nucleation scavenging one would like to compare the aerosol before and just after a radiation fog formation. For this comparison to be valid, one should be sampl-

ing in the same air mass. Wobrock et al. (1992) characterized the different fog episodes and found that the radiation fog was not the dominant type observed. Most of the fog episods was either due to advection of fog layers developed elsewhere or due to advection of moisture and cold air. A direct comparison of the aerosol before fog start and the aerosol in newly formed fog is therefore difficult given the long sampling periods that had to be used and the large variation of the aerosol.

If nucleation scavenging is thought to be dominant, other processes such as coagulation and Brownian diffusion affecting the partitioning should be insignificant. This question was
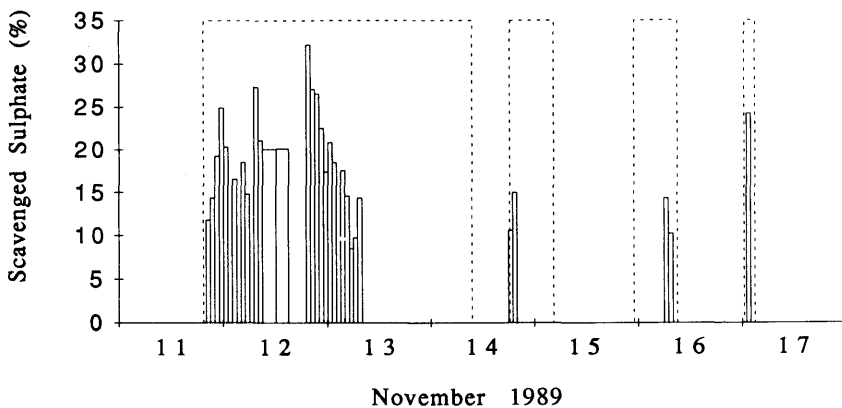

Fig. 5. Fraction of sulphate mass scavenged by the fog. The average scavenged fraction is 18 %. (Dashed lines indicate fog periods.)
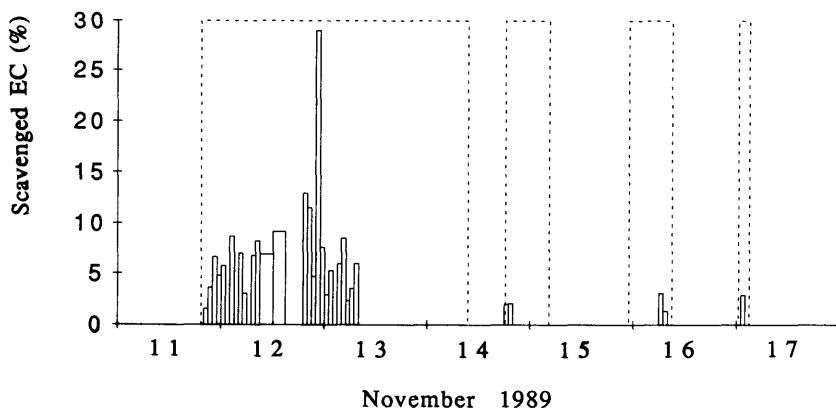
Fig. 6. Fraction of EC mass scavenged by the fog. The average scavenged fraction is 6 %. (Dashed lines indicate fog periods.) The single value that is much higher than the rest is probably due to an underestimate of the EC mass on the interstitial filter.

addressed in Noone et al. (1992a) and it was concluded that contribution from coagulation and Brownian diffusion was negligible and that the mass of aerosol scavenged could be interpreted as primarily an effect of nucleation.

One process that could be important for the scavenging of sulphate is that production of sulphate due to uptake of sulphur dioxide and subsequent oxidation in the fog droplets is occurring. This question has been addressed in Facchini et al. (1992), who draw the conclusion that a very little, if any, sulphate was produced during the fog periods, due to very low SO_2 concentrations in the ambient air.

Finally, no differences in losses during sampling should exist. The question of losses during sampling of the aerosol with the CVI inlet is discussed in Noone et al. (1992a). It is pointed out that on some occasions there was a gap between the interstitial inlet cut size and the cut size of the CVI. Residual particles associated with droplets in this size interval were not sampled. It seems unlikely that more of the EC mass compared to sulphate mass would be associated with droplets in this size range and thereby give rise to a sampling artifact.

Based on the discussion above we believe that the major process responsible for the scavenging is nucleation.

3.3. Result from PIXE analysis

The average scavenged fraction of different species obtained from the PIXE analysis is given in

Table 1, calculated in the same manner as in Subsection 3.2. The average scavenged fraction of EC is also included as a comparison. The average fraction of sulphur scavenged is the same as that obtained for sulphate from IC analysis. As can be seen in Table 1, there is a range of scavenging fractions for different species. This may be explained by a difference in composition for those particles more efficiently scavenged compared to those less

Table 1. *Average scavenged fraction of aerosol species; the average scavenged fraction of aerosol species measured with PIXE and the average scavenged fraction of EC; the calculation of the fraction is explained in the text*

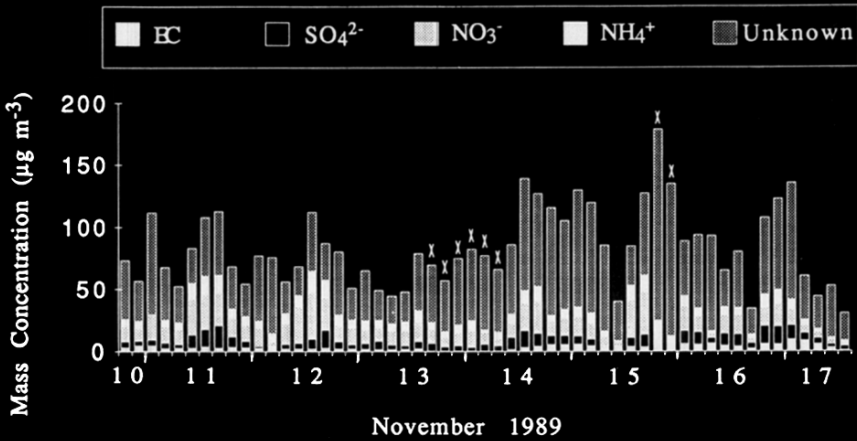| Element	Average scavenged fraction
P	0.14
S	0.18
Cl	0.19
K	0.09
Ca	0.36
Cr	0.14
Mn	0.16
Fe	0.22
Ni	0.10
Cu	0.22
Zn	0.25
Se	0.08
Br	0.09
Pb	0.11
EC	0.06

Fig. 7. Variation in interstitial aerosol particle composition. Each bar corresponds to a 3-h period, and the top of the bar is equal to the total concentration. Only the major water soluble ions are included from chemical analyses on the impactor samples. Bars indicated with an X are periods when data are missing for one or more of the included species.

efficiently scavenged. It should also be noticed that the trace metals Fe, Mn, and Cu are as efficiently scavenged as sulphur while EC is scavenged to a lesser degree.

3.4. Aerosol composition from impactor data

The interstitial aerosol composition obtained from the impactors plus the EC concentration from the filter samples is shown in Fig. 7. Not all of the measured ions are shown. The major part

of the measured water-soluble ions consisted of NH_4^+, NO_3^-, and SO_4^{2-}. The remaining measured water soluble ions (Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}) when summed together were on average only 10% of the total mass and are therefore not included in the figure. As can be seen in Fig. 7, a major part of the aerosol mass was not determined. Fig. 8 shows the fraction each species contributes to the total mass. Taking all of the measured ions into account, only about 40–50% of the mass concentration can be explained. The plausible
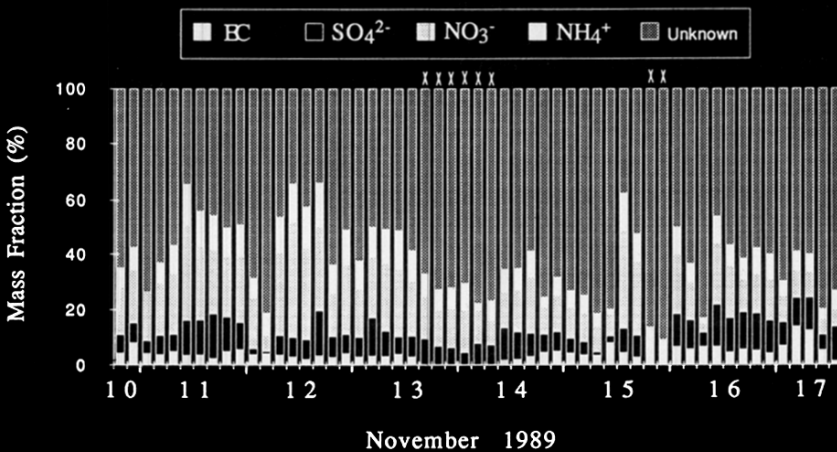

Fig. 8. Variation in the relative contribution of the indicated species to the interstitial aerosol particle mass, based on information from Fig. 7.

explanation for this unknown mass is that it consists of water, oxygen in oxides, oxides of silicon, and organic material.

The variation of the measured water soluble fraction with size of the aerosol did not reveal any striking information. The measured water soluble fraction was more or less constant with size. This was the case both before and after fog formation which prevented us from drawing any conclusions regarding changes in the relative composition of soluble versus insoluble fraction with size.

4. Discussion

The ability of a particle to act as a cloud condensation nucleus (CCN) and thereby be scavenged by nucleation is, according to Köhler theory, dependent on its size, composition, and the supersaturation reached in the cloud. Another important consideration is that the time for the particle to grow by condensation to its critical radius corresponding to its critical supersaturation given by the Köhler equation must be sufficiently short compared to the time spent by the particle in an environment with a supersaturation sufficient to activate it.

Theoretical calculations, (Pruppacher and Klett, 1980), have shown that the critical supersaturation needed for activation of an aerosol particle will depend on the amount of soluble material in the particle. It can vary by an order of magnitude for a particle of a given size that is 100% soluble compared to a particle of the same size which is insoluble but still wettable. If we assume that for a given dry size, the particles will have different amounts of soluble material, then at a given supersaturation, only those particles with a sufficient amount of soluble material corresponding to a critical supersaturation below the ambient supersaturation will be activated.

The amount of aerosol scavenged through nucleation will then be a function of the supersaturation reached in the cloud or fog, the time for the particle to grow to its critical size, and also on the variation of chemical composition with size.

Model calculations by Jensen and Charlson (1984) showed that the fraction scavenged was low when the aerosol concentration was high as well as when a low driving force for the formation of liquid water was present. These effects are likely to be found in the Po Valley fog where it was observed that only a small fraction of the aerosol was scavenged (see Noone et al., 1992a). The influence of chemical composition on nucleation scavenging is probably of greater importance in a case with an overabundance of particles and in cases where the particles compete for a small amount of condensable water. For a clean-air aerosol under high updraft conditions, where all of the particles are likely to be activated, chemical composition is likely to be of secondary importance.

The information on the composition of the interstitial aerosol obtained from the impactors was, as discussed above, not sufficient to draw any conclusions regarding the variation of chemical composition with size of the aerosol. We can however hypothesize about the variation in chemical composition and discuss the possible outcome in terms of nucleation. Below are some hypothetical examples of aerosol composition.

(1) An externally mixed aerosol is one where particles of a given size can have different chemical compositions. This difference in composition may also be a function of particle size. As an example we can think of newly formed soot particles in an external mixture with ammonium sulphate particles. Soot particles are likely to be more hydrophobic than ammonium sulphate particles and thereby would require a higher supersaturation to be activated. So if the two types of particles have the same size distribution we would expect to activate more ammonium sulphate and a difference in scavenging between these two particle types would be obtained due to the chemical nature of the particles. However, a difference in the scavenged fraction of material for this type of aerosol does not necessarily need to be due to a chemical reason. If the mode of the soot particle distribution is at a smaller size compared to the mode of the ammonium sulphate distribution, then the difference in scavenging fraction may be due only to a difference in size. An externally mixed aerosol would probably be found close to the sources of the particles.

(2) An example of an *aged* externally mixed aerosol is one where the different types of particles have had a sufficient amount of time to coagulate with each other. It can, for instance, be an aerosol where soot particles and ammonium sulphate

particles have coagulated and thereby a change in composition with size could occur. They may as well have gone through one or several cloud cycles which could alter the original aerosol. We can then expect a range of variation in composition, all the way from the two different original compositions to any mixture of them. The effect of nucleation will then depend on the variation of the mixture with size and is therefore not simple to predict. A difference in nucleation scavenging where, for example, more ammonium sulphate is scavenged compared to soot would imply that particles larger than the size of the smallest particle activated would have a mixture with a larger fraction of ammonium sulphate than soot.

(3)   An internally mixed aerosol is one where every particle in the aerosol has the same composition, independent of size. All particles of a given size will be scavenged with the same efficiency which in itself depends on their common composition. While all particles of a given size nucleate in the same way, there remains a size dependency. A difference in the amount of the various species found in the fog droplets would be caused by a difference in the relative proportions of the species in the particles. Thus, relative mass fractions of different chemical species in the dry aerosol will be maintained in the droplets after the nucleation scavenging. In contrast to the other two hypothetical aerosols discussed above the *scavenged fraction* of the two compounds will however be the same.

From these 3 different examples above, we can conclude that the aerosol in our case was not internally mixed but externally mixed. Measurements presented in Svenningsson et al. (1992) support this conclusion. They studied the hygroscopic growth properties of aerosol particles less than 200 nm diameter and found that particles of the same dry size had two different growth factors at 85 % relative humidity. To answer fully the question of how the chemical composition varied with size and how this may have influenced the nucleation scavenging, one would like to have analysis of individual aerosol particles in the sub-μm range rather than a bulk analysis.

5. Conclusion

Simultaneous measurements of different chemical species in fog droplets and in interstitial particles confirmed our hypothesis that a difference in partitioning could be observed for sulphate and EC. Sulphate had an average scavenged fraction of 18 % and was always more scavenged than EC, which had an average scavenged fraction of 6 %. Some of the trace metals (Fe, Mn, and Cu) had scavenging efficiencies close to sulphate. Because of the differences in scavenging, we suspect that the aerosol was externally mixed.

6. Acknowledgements

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