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Elemental composition of fog interstitial particle size fractions and hydrophobic fractions related to fog droplet nucleation scavenging

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ABSTRACT

The cloud nucleation scavenging process was studied during a joint campaign of the EUROTRAC sub-project Ground-based Cloud Experiment. It was found that the particle size has a strong influence on the partitioning of particles between the cloud droplet and the interstitial aerosol reservoirs. A new aerosol sampling unit, the relative humidity processing system, was employed for the extraction of particles with a low growth-ability with respect to increased relative humidity. The system supplied tracer elements on the particle growth-ability. These elements could be used to identify a factor related to particle hygroscopic properties, which was in effect as a selector of cloud condensation nuclei.

1. Introduction

A large number of different sources, natural as well as anthropogenic, emit particles and gaseous particle precursors to the atmosphere. Depending on the source type, the particles are found in different size intervals. While particles from sources such as soil erosion and sea-spray are preferentially found as supermicrometer particles forming a coarse particle size mode, high-temperature processes, such as combustion, produce particles down to below nanometer diameter. These nuclei mode particles coagulate rapidly, and together with gas-to-particle transformation mechanisms, an accumulation mode consisting of approximately 0.05–2 μm particles is formed (Whitby, 1978). These particles are characterised by low deposition rates with respect to diffusion as well as sedimentation. It is a well known fact that the particle chemical composition vary with the size. The interaction between the coarse mode and the finer modes is relatively weak, which means that the mass transfer from the finer particles is not sufficient to significantly change the coarse mode chemical composition. A chemical composition difference between these modes is generally found in the atmospheric aerosol, see, e.g., Lannefors et al. (1983). The coagulation and gas-to-particle conversion processes tend to mix material from different sources. The mixing state is of great importance for the modelling of the accumulation mode behaviour in terms of chemical reaction paths and atmospheric life times. Martinsson et al. (1984) observed a size-dependent elemental composition within the accumulation mode in long-distance transported aerosol from continental Europe in rural areas of southern Sweden, Covert and Heintzenberg (1984) found a high degree of external mixture between elemental carbon and sulphur in an urban aerosol and Svenningsson et al. (1992) found an external mixture in the accumulation mode size range studied (<0.2 μm)

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in the interstitial aerosol during fog events (this campaign).

Particles are the sites for the formation of cloud and fog droplets. The supersaturation required to form an activated droplet is basically related to the Kelvin effect and the water activity, i.e., the particle size and the chemical composition. The complexity of the chemical composition factor depends on the degree of internal/external mixture of the aerosol particles. A large particle may contain no, or a very small fraction of water soluble material but still form an activated droplet. The number of coarse mode particles are generally low, implying that the number of cloud condensation nuclei from this mode is low. However, the mass of each nucleus is high. The external mixture between the coarse mode and the accumulation mode therefore has implications for the bulk chemical composition of the particles that act as cloud condensation nuclei. The mixing state of the accumulation mode may affect scavenging related to a certain particle size. An increased amount of water insoluble material, increases the supersaturation required for activation for a certain particle size (Hänel, 1976), and surfactants present may form a lipophilic film (Gill et al., 1983) which may delay or inhibit the onset of activation (Niessner et al., 1990).

In this work the factors controlling the formation of fog droplets are investigated by comparing the elemental composition of fog droplet residual particles with particles that did not form droplets, i.e., interstitial aerosol particles. The interstitial aerosol particles were size fractioned and sized particles with a low growth-ability were extracted using a technique by Martinsson et al., 1992. The different fractions were analysed for elemental composition in order to examine the influence from particle size and particle hygroscopic properties on the partitioning of particles between the droplet and interstitial aerosol reservoirs.

2. Aerosol collection and analysis methods

This experiment was undertaken in the fall of 1989 in northern Italy at a site located outside San Pietro Capofiume in the Po Valley as part of a joint campaign within the EUROTRAC subproject Ground-based Cloud Experiment (GCE) programme. The sampling site, which is located in the largest industrial and agricultural area of Italy, is described by Fuzzi et al., 1992.

2.1. *Aerosol collection technique*

The sampling equipment is shown in Fig. 1. Two different kinds of impactors were used as sampling inlets. Cloud Virtual Impactors (CVI, Ogren et al., 1985; Noone et al., 1988) were used to collect droplets larger than 5 μm. Droplets from the ambient air were impacted into a dry, particle-free carrier air stream. In this air stream the volatile components of the droplets are vaporised (mainly water), and dry residual particles were formed. Aerosol filters were used to collect residual particles for chemical analysis on a one-hour basis during fog events.

For particles less than 5 μm an interstitial inlet was used, which consists of an impactor that removes large particles from the air stream. Aerosol filters were used to collect interstitial aerosol particles in pairs with the filters for droplet residual particles. A relative humidity processing system was operated on the interstitial aerosol. It consists of a cascade impactor (a Battelle impactor (Mitchell and Pilcher, 1959) was used during this campaign) which collected the particle size fractions <0.25, 0.25–0.5, 0.5–1, 1–2, 2–4 and >4 μm (stages IV–I) after the aerosol had passed a diffusion drier. In a second line particles with a low growth-ability ("hydrophobic" particles) are collected in sized fractions. This was obtained by passing the aerosol through a humidifier that rose the relative humidity to approximately 97%. The aerosol was then divided into three lines, and

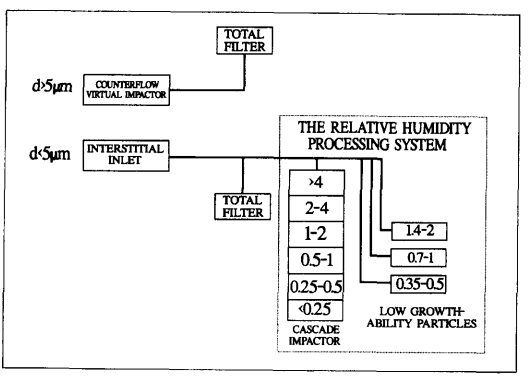

Fig. 1. Overview of the sampling equipment. Filters were used for taking bulk samples and the relative humidity processing system for collecting particle size distributions and fractions consisting of particles with a low growth-ability in the interstitial aerosol. The numbers indicate the particle sizes collected (μm).

single stage impactors, one in each line, with cut-off diameters of 0.5, 1 and 2 μm were used to remove particles larger than the respective size at the high relative humidity. The high-humidity impactors were followed by diffusion driers, which reduced the size of particles with a high growth-ability ("hygroscopic" particles), thus leaving a size fraction consisting only of low-growth-ability particles. These particles were collected by single stage impactors with cut-off diameters of 0.35, 0.7 and 1.4 μm, respectively. To summarise: in the relative humidity processing system an interstitial particle size-distribution was collected and particles with a low growth-ability were collected in the size fractions: 0.35–0.5, 0.7–1 and 1.4–2 μm. The relative humidity processing system is described in detail by Martinsson et al., 1992.

2.2. *Collected samples, analysis and data selection*

The Po Valley campaign covered totally five different fog events. The aerosol filters for the collection of the total interstitial and cloud droplet residual particle samples were operated during all the fog events. The interstitial aerosol size-distribution and the low growth-ability fractions, collected with the relative humidity processing system, resulted in six samples each consisting of totally nine fractions, see Table 1. Three of the samples were taken during the second fog event and are denoted sample 2a, 2b and 2c (in chronological order). During fog events three and five, one sample from each occasion was taken (sample 3 and 5), and finally, one sample was taken during clear weather conditions (sample "clear") between fog events two and three.

The bulk cloud interstitial and cloud residual particle samples were collected on Nuclepore filters. In the relative humidity processing system, the impaction plates were coated with thin, paraffin greased polystyrene films which were removed from the plates prior to analysis. The final stage of the cascade impactor consisted of a Nuclepore filter. The samples were analysed for elemental composition using Particle-Induced X-ray Emission (Johansson and Campbell, 1988).

Table 1. *The samples taken with the relative humidity processing system*

Sample	Start (date, time)	Sampling time (h)	Weather condition
2a	12 Nov. 1989 at 21^{00}	6^{00}	fog
2b	13 Nov. 1989 at 03^{40}	5^{50}	fog
2c	13 Nov. 1989 at 11^{00}	6^{00}	fog
C	14 Nov. 1989 at 10^{45}	5^{05}	clear
3	14 Nov. 1989 at 18^{40}	5^{40}	fog
5	17 Nov. 1989 at 00^{20}	2^{40}	fog

The analysis resulted in the detection of about 15 elements. However, some of the elements only appeared occasionally at levels above the limit of detection, especially in the size-resolved samples. Those elements with a large fraction of missing data were excluded prior to the evaluation work. In total nine elements are included in the data evaluation. They are; phosphorous (P), sulphur (S), potassium (K), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn) and lead (Pb). The particle size fractions above 1 μm are generally low-loaded, which means that data is missing for several elements. These stages are evaluated in section 3.1, but not in the elemental composition evaluations of sections 3.2 and 3.3. One sample, the 0.25–0.5 μm fraction of the cascade impactor for sampling event 2b, contained extremely high amounts of Fe and Ni. Statistical evaluation shows that the sample has an elemental composition that is extremely different from every other sample. It is therefore strongly suspected that the sample from that impactor stage was contaminated.

The dried cloud interstitial particles were collected with Battelle impactors. The sampling substrate was coated with a thin layer of paraffin in order to reduce particle bounce-off. This effect causes wall losses and particle re-entrainment with subsequent deposition of the particles at lower stages. It can be suspected that the steps taken to prevent bounce-off were not sufficient, since the impactor was operated under very dry conditions. Therefore the data should be treated with some caution.

3. Results

3.1. *Elemental concentrations and size-distributions*

The upper particle size limit was defined by the 5 μm cut-off of the interstitial inlet which was

operated in a high-relative-humidity environment. After the inlet, the aerosol water content was evaporated by a diffusion drier which reduced the relative humidity to below 10%. The total elemental concentrations in the cascade impactor under these conditions are presented in Table 2. The mass median aerodynamic diameter (MMAD) of the six samples and nine elements can also be found in Table 2. For the clear weather sample, three different groups of elements can be identified: A low-MMAD group consisting of P, S, K, Ni and Pb. Elements Fe and Zn are found to have a high MMAD, while Mn and Cu are at an intermediate level. The MMAD:s during fog are significantly reduced for all elements, and the group of elements with a low MMAD are always found to have an MMAD below 0.25 μm.

Fig. 2 shows the size-distribution for three elements, representing the three above mentioned MMAD groups, during clear weather and fog. The mean distribution is presented for the fog samples. All the distributions are normalised to the final stage of the impactor, i.e., particles less than 0.25 μm where the effect of scavenging is smallest according to Table 2, in order to facilitate comparisons with respect to distribution differences. When comparing the size-distributions of the clear weather sample, it is found that the major differences between the three different groups of elements appear above 0.5 μm when normalising to the size fraction below 0.25 μm. The six elements not presented in Fig. 2 show the same behaviour when comparing different MMAD groups. From Fig. 2 it is also clear that the fog samples show a lower amount relative to the finest-particle-stage at all higher impactor stages, which indicates that these particle sizes are more efficiently scavenged by the cloud nucleation process than the particles below 0.25 μm. Again the trends are the same for the six elements not presented in Fig. 2. The effect is particularly strong for particle sizes above 1 μm. For e.g., Zn the ratios between fog and clear weather size distribution, when normalised to the finest-particle stage, are: (1), 0.36, 0.23, 0.04 and 0.04 for particle size fractions (<0.25), 0.25–0.5, 0.5–1, 1–2 and 2–4 μm, thus indicating that the particles with a size of above 1 μm are the most efficiently scavenged. It is evident that all the 9 elements are present on scavenged particles, but their relative importance cannot be determined with this evaluation technique.

3.2. *The elemental composition of low-growth-ability particle fractions*

Particles of a certain size which contain a low amount of soluble matter, require a high super-

Table 2. *Total elemental concentrations and mass median aerodynamic diameters (MMAD) for particles below 5 μm, which, during fog conditions, is denoted interstitial aerosol; the aerosol inlet was operated at ambient relative humidity; the aerosol was dried before it reached the cascade impactor*

	Elemental concentration (ng/m^3)								
Sample	P	S	K	Mn	Fe	Ni	Cu	Zn	Pb
2a	333	2450	243	11.7	59.8	5.41	5.64	59.8	101
2b*	346	2270	177	14.0	*	*	4.30	48.0	80.3
2c	276	2360	307	57.9	109	6.20	6.48	113	122
3	266	3130	615	69.5	247	10.7	12.7	110	188
5	769	6280	1040	58.1	320	16.2	13.0	132	376
C	527	5250	504	43.8	271	13.6	18.6	235	211
	Mass median aerodynamic diameter (μm)								
2a	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
2b*	<0.25	<0.25	<0.25	0.36	*	*	0.31	0.36	<0.25
2c	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
3	<0.25	<0.25	<0.25	0.31	0.35	<0.25	<0.25	0.32	<0.25
5	<0.25	<0.25	<0.25	0.34	0.38	<0.25	0.33	0.26	<0.25
C	0.31	0.36	0.34	0.45	0.63	0.26	0.46	0.63	0.36

* Affected by contamination at impactor stage V (0.25–0.5 μm)

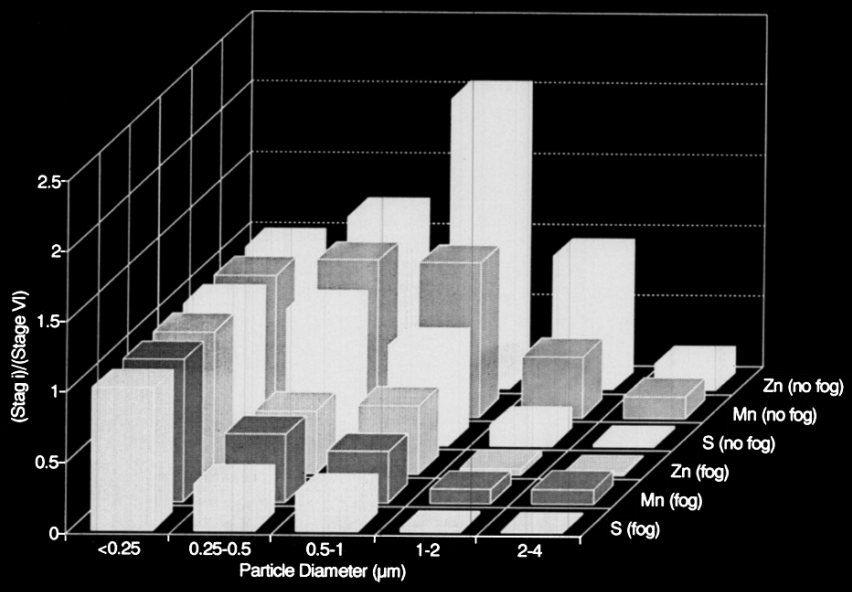

Fig. 2. Elemental particle size distributions for three elements, which belong to three different groups of elements with respect to MMAD. The distributions are normalised so that the size fraction <0.25 μm is set to 1 for all elements. Size distributions are presented both for clear weather conditions and fog. For the fog samples the mean particle size-distribution is given. The particles were sized under dry conditions.

saturation for activation. With increasing particle size the fraction soluble matter required for activation is decreased. The situation is illustrated in Fig. 3, assuming two externally mixed, distinct types of accumulation mode particles with different hygroscopic properties. The presence of a coarse mode is indicated. The coarse mode particles can be expected to appear in the cloud droplet reservoir to a large extent due to the size effect, which is also in agreement with our findings, see Fig. 2.

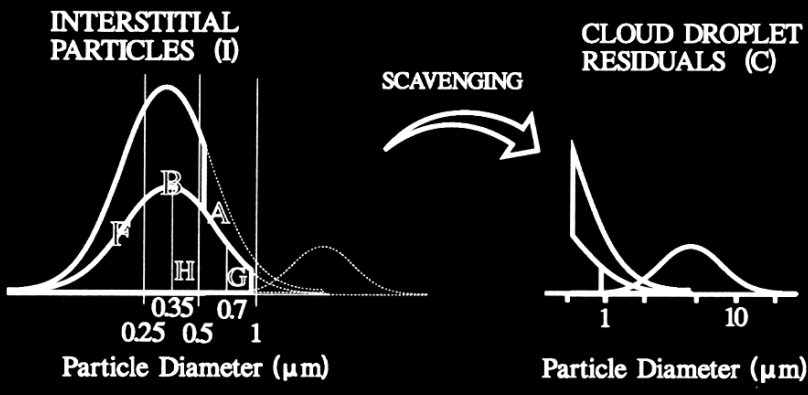

Fig. 3. Conceptual illustration of the cloud scavenging process related to growth-ability of the accumulation mode particles. The bottom fraction in the left side of the figure symbolises particles with a low growth-ability, while the overlaying fraction symbolises particles with a high growth-ability. The presence of a coarse mode is indicated. It is expected to be scavenged to a high degree. The horizontal axes express dry particle/residue diameter. The vertical axis is given as a mass distribution rather than a number distribution, although the relative mass of the accumulation and the coarse mode is somewhat arbitrarily chosen. More details are given in the text. The letters indicate the samples taken. I and C are the bulk samples of interstitial particles and droplet residuals, respectively. F, B and A are the different size fractions from the cascade impactor, while G and H are samples of low-growth-ability particles.

When dealing with chemical composition, the mass distribution rather than the particle number distribution is of importance, i.e., Fig. 3 should not be confused with the number distribution of the cloud condensation nuclei. The following sections are devoted to the identification of the factors controlling the scavenging, based on chemical information from the different reservoirs. The letters C, I, A, B, F, G and H in Fig. 3 denote sample type, and are used for identification in the figures below.

In this section, the elemental composition of the particles with a low growth-ability with respect to an increased relative humidity are sought, i.e., particles that have a chemical composition that might inhibit the formation of cloud droplets by nucleation scavenging although particles of an equal size but with a different chemical composition are scavenged. In order to obtain a measure on the tendency of the elements to appear in hydrophobic particles, the ratio of the amount of each element to sulphur was formed for each fraction. Then these ratios were compared between hydrophobic and total interstitial aerosol particles of similar sizes, e.g., the hydrophobic fraction between 0.7 to 1 μm was compared with the interstitial aerosol size fraction 0.5–1 μm. Thus, the following expression of the "hydrophobic ratio" was used:

$$R_i = \frac{\left(\frac{m(E_i)}{m(S)}\right)_H}{\left(\frac{m(E_i)}{m(S)}\right)_T},$$

where m is the mass obtained from the analysis, E_i is element i and subscripts $_H$ and $_T$ denote interstitial hydrophobic fraction and total interstitial fraction. A value of R_i larger than 1 means that element E_i appear in the hydrophobic fraction to higher degree than S. The hygroscopic ratios are presented in Fig. 4. The choice of S as the reference element is based on the hypothesis that hygroscopic particles have a high S content. It can be seen in Fig. 4 that no element systematically show a more hygroscopic behaviour than S. Thus the choice of S as the indicator of hygroscopic particles seems justified. When comparing the hydrophobic ratios of Fig. 4 for different elements, it is striking that Mn always appear to a higher extent in hydrophobic particles. Also Fe and perhaps P appear to be more oriented towards hydrophobic particles.

3.3. Factors controlling the scavenging due to droplet nucleation

In order to examine the factors controlling in the scavenging process, the data set was evaluated by the multivariate statistical methods SIMCA (Wold and Sjöström, 1977) and discriminant-PLS (Vong et al., 1988). A comprehensive presentation of these techniques applied to atmospheric aerosol long-range transport receptor modelling can be found in Swietlicki (1989).

SIMCA may be used to investigate the degree of similarity or dissimilarity between groups of measurements. As a first step in this investigation, the elemental composition of the interstitial aerosol is compared with that of cloud droplet residual particles. In the SIMCA data analysis these two types of measurements form the groups. The main variance of each group is investigated by principal component analysis, thus forming a model of each group with a lower dimensionality than the original data. The original data span nine dimensions, since nine elements (variables) were included in the evaluation. The normalisation technique (Hansson et al., 1984) used prior to the statistical analysis reduces the dimension of the so called measurement space to eight. The low-dimensional models are used as a reference of position in the measurement space. Depending of the dimensionality, these position references can thus be a point, a line, a plane, etc. In this case the interstitial model is one-dimensional and the residual particle model span two dimensions. When a measurement resembles the main features of the data that were used to form a model, that measurement point is found close to that model in the measurement space, and by calculating the distance between each measurement to the models, the distribution of the data points with respect to the models can be obtained. Fig. 5a is a plot of such distances. The horizontal axis shows the distance from the measurement points to the model of the cloud droplet residual particles, and the vertical axis shows the distance from the measurements to the model of the cloud interstitial aerosol particles. It can be seen that none of the measurements of the composition of the droplet residuals (C) are found to fit the model of the interstitial particles (I) with a probability of more than 5%, and about a

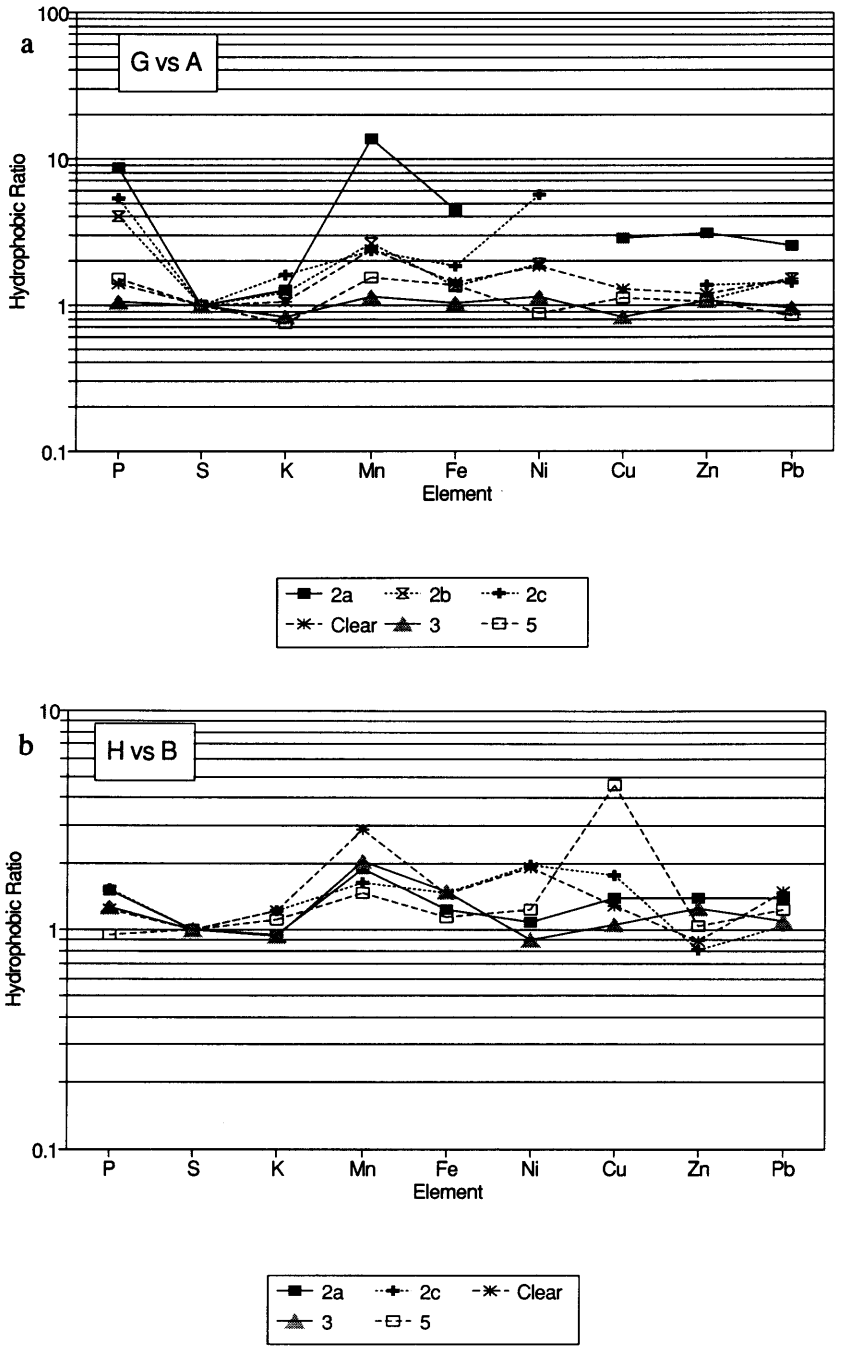

Fig. 4. The hydrophobic ratio (R_i, see the text) related to sulphur for different elements. An R_i larger than 1 indicates that the element is present on particles with a low growth-ability to a higher extent than sulphur. (a) The hydrophobic fraction for 0.7–1 μm particles compared with the 0.5–1 μm fraction from the cascade impactor. (b) The 0.35–0.5 μm hydrophobic versus the 0.25–0.5 μm cascade impactor fraction.

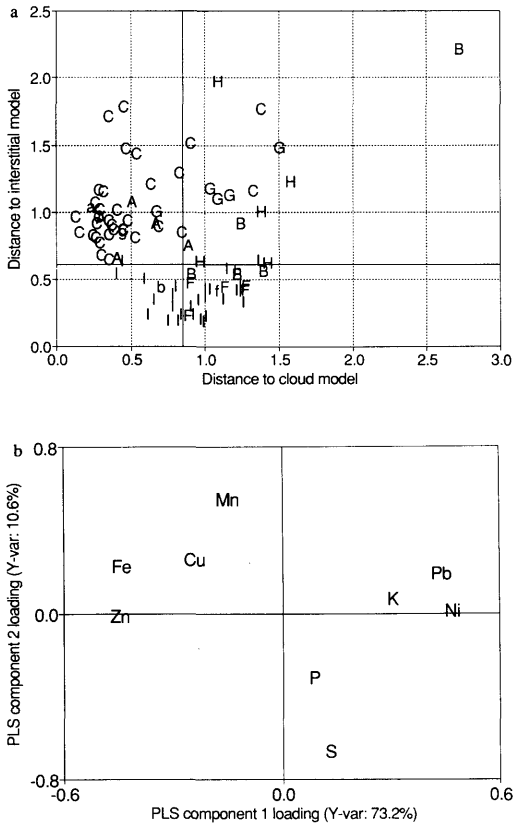

Fig. 5. (a) The distance of the samples from principal component models, as obtained with SIMCA. The horizontal axis shows the distance to the model of the bulk samples of droplet residuals, while the vertical axis shows the distance to the model of bulk interstitial aerosol samples. The full lines are the 5% probability levels for a measurement of belonging to the respective groups of data (C and I). (b) The two main components, as obtained with PLS, responsible for the discrimination with respect to elemental composition between the two groups of samples mentioned under a. An orientation towards the positive directions implies enrichment of the element in the bulk interstitial aerosol samples, and vice versa.

third of the bulk interstitial particle composition measurements (I) fit the model of the droplet residuals. Thus, there are statistically significant dissimilarities with respect to elemental composition between these two groups of data. The data from the relative humidity processing system are included in Fig. 5a as a test set, i.e., they do not refer to a principal component model of their own, but to the models of the droplet residuals (C) and the bulk interstitial aerosol (I). Starting with the data from the cascade impactor, it can be seen that the smallest particles (<0.25 μm; F) have a chemical composition that closely resembles the composition of the total interstitial aerosol. The next particle size fraction (B), between 0.25 and 0.5 μm, slightly deviates from the total interstitial model. (One of the data points from this particle size interval show a very strong difference in elemental composition compared with every other measurement. It is the contamination sample, see section 2.2.) Both these two size fractions have in common that their elemental composition differ significantly from the composition of the cloud droplet residuals. The next size fraction, 0.5–1 μm (A), deviates significantly from the total interstitial particle composition, while a certain degree of similarity is found when compared with the droplet residuals. From Fig. 5a it is evident that the elemental composition of the droplet residuals differs from that of the bulk interstitial particle samples. It is also clear that the elemental composition of the interstitial particles is size-dependent. The hydrophobic fractions (G and H) show dissimilarities in elemental composition compared with the bulk interstitial aerosol samples as well as with the bulk droplet residual samples.

In order to investigate which elements are responsible for the separation found, discriminant-PLS was applied. This technique can be viewed upon as multiple linear regression with inherent noise reduction. In this analysis, an extra variable was introduced which expresses group belonging. Then the measured variables are used to explain the variance of the added variable in a PLS regression model. The two most important components in respect of discrimination, when comparing the droplet residuals with the total interstitial aerosol, are shown in Fig. 5b. When comparing the first PLS component with the MMAD (Table 2) it is evident that those elements with a low MMAD (P, S, K, Ni and Pb) are preferably found in the interstitial aerosol, while the medium-to-high-MMAD elements (Mn, Fe, Cu and Zn) dominate the cloud residual composition. Hence, the particle size governs the first PLS component when comparing bulk samples of the residuals and the interstitial particles. The second PLS component of Fig. 5b highlights S and Mn. In the section above, these

elements were found to be the best indicators of high and low growth-ability particles, respectively. It can be seen that the second PLS component orients S towards the cloud droplet residuals, while Mn is oriented towards the interstitial aerosol particles. This second component thus strongly indicates the presence of a chemical composition factor affecting the scavenging process, which can be attributed to an external mixture of the accumulation mode aerosol.

4. Discussion

The results of the investigation show that the particle size is a major factor controlling the partitioning between the fog droplet and the interstitial aerosol reservoirs, when bulk samples are compared. Average elemental scavenging ratios for the fog events were determined during this campaign. The scavenging ratios were based on the bulk interstitial and the bulk cloud droplet residual particle samples, which also constitute a part of the present data set. Thus the pattern found should also appear in the scavenging efficiency. In order find out whether that is the case, the scavenging ratios were compared with the MMAD:s of the sample taken during clear weather condition, i.e., when the size distribution was not affected by fog droplet formation. Although this single clear weather sample does not represent the whole campaign, the basic orientation of the elements with respect to size mode is stable, see, e.g., Lannefors et al. (1983) and Martinsson et al. (1984) who measured elemental particle size-distributions under ambient relative humidity conditions and without a size-selective aerosol inlet like the interstitial inlet. The result of the comparison is presented in Fig. 6 (Calcium (Ca) could be included in Fig. 6, since it was over the detection limit at all the stages of the cascade impactor in the clear weather sample. The overall fraction missing data was to high, 20%, for the inclusion in the statistical evaluation.) It can be seen that there is a very strong correlation between the particle size and the fraction scavenged.

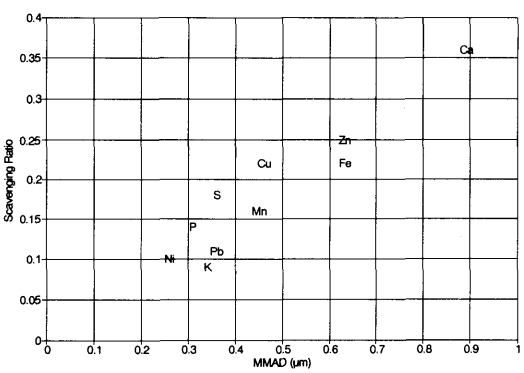

Fig. 6. Elemental average bulk sample scavinging ratios (Hallberg et al., 1992) compared with mass median aerodynamic diameters measured during clear weather conditions.

It is evident that Mn is enriched in particles with a low growth-ability. Contrary to S, which was found preferably in particles with a high growth-ability, Mn is a minor constituent of the total aerosol mass. This means that Mn itself cannot be responsible for the behaviour of these particles at high relative humidity, but rather be a tracer of the presence of other aerosol components that probably were emitted from the same source. Fe, which according to the hydrophobic ratios in Fig. 4 was the second strongest indicator of low-growth-ability particles, is often emitted from the same source as Mn, e.g., soil erosion and steel industries. The two element were found to have different MMAD:s, which could be caused by the presence of two or more sources emitting particles of different sizes. This forms a possible source pattern, but more information on the composition of the particles is needed. Hallberg et al., 1992 analysed the bulk samples from droplet residuals and interstitial particles with respect to major ions and elemental carbon. They could only account for 40–50% of the total interstitial aerosol mass, where elemental carbon on average only constituted 4%, while the remainder of the mass determined was water soluble (NH_4, SO_4 and NO_3 ions). Svenningsson et al., 1992 estimated the fraction of water insoluble mass to about 50% for the whole accumulation mode. This indicates that a large fraction of the interstitial aerosol mass, unaccounted for by analysis, consists of water insoluble compounds. Bearing in mind that Mn and Fe constitute less than 0.1% of the total interstitial aerosol mass, thus also a small fraction of the water insoluble fraction, it is found that more information on the composition of this fraction is needed before a source pattern can be revealed.

The data presented here show that the particle

size is of great importance for scavenging due to droplet nucleation. A second factor, depending on varying chemical composition of particles with similar sizes, could be found by the aid of tracer elements, which were extracted using the relative humidity processing system. These findings points towards that a more detailed knowledge about the chemical composition than the simplifying approach of an internal mixture, is needed when modelling the scavenging process. They also imply that the chemical composition of cloud droplets may vary considerably, not only because of the diffusional growth-rate-effect (Jensen and Charlson, 1984), but also due to a varying composition of the condensation nuclei, which may affect the modelling of liquid phase chemical reactions. The subject of the effect of the chemical composition and mixing state of the aerosol particles on the scavenging process due to cloud droplet nucleation need to be studied further. An obvious improvement would be achieved with a size-selective collection of cloud droplet residuals combined with a broader analysis of chemical composition.

5. Conclusions

The factors controlling the fog droplet nucleation process have been studied by comparing the elemental composition of cloud interstitial particle size fractions and hydrophobic fractions with fog droplet residuals. It was found that the mass median aerodynamic diameters were element dependent and that the elemental composition varied with particle size between the coarse mode and the accumulation mode and within the accumulation mode. The formation of fog significantly reduced the mass median aerodynamic diameter of dried, interstitial aerosol particles. The particulate matter load reduction could be traced down to the particle size interval 0.25–0.5 μm, and becomes stronger in the coarse mode. The interstitial aerosol was found to contain a fraction of low-growth-ability particles which displayed an elemental composition which was different from that of similarly sized fractions of the total interstitial aerosol. Sulphur (S) preferably appeared in particles with a high growth-ability, while manganese (Mn) was enriched in low-growth-ability particles. When comparing bulk interstitial aerosol samples with bulk cloud droplet residual samples, a difference in elemental composition was found. The primary pattern of these differences correlated strongly with the elemental size distributions, i.e., elements which are more oriented towards the larger (when dry) particles were found to be present in higher concentrations in the droplet residuals and vice versa. A strong correlation between elemental scavenging ratios and elemental mass median aerodynamic diameters supports these findings. A second factor was found, which could be identified as the influence of particle hygroscopic properties on the selection of cloud condensation nuclei.

In conclusion: the particle size was found to be of primary importance for the ability to act as a cloud condensation nucleus when considering the particle mass scavenged during fog. Coarse mode oriented elements like calcium and iron were found to be present in the droplet residual samples to high degree, although they can be expected to appear in water-insoluble, erosion-related particles in the coarse mode. Strong evidence was found of an external mixture in the accumulation mode which also affected the scavenging. For the conditions prevailing during this campaign, S and Mn were the strongest indicators of high and low growth-ability particles, respectively. While S is well known to be present in water soluble sulphates in large amounts, Mn can only be regarded as a tracer of hydrophobic particulate matter. Since a large fraction of the total aerosol mass was not analysed, the causes of the behaviour of Mn in view of source profiles could not be determined.

It can also be concluded that the prerequisites for the identification of the factors controlling cloud droplet nucleation can be improved by employing an experimental technique where both the interstitial aerosol particles and the cloud droplet residuals are sampled size-resolved in conjunction with a broadening of the chemical analysis.

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