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# Measurements of the size dependence of the concentration of non-volatile material in fog droplets

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ABSTRACT

Measurements of the size dependence of the mass concentration of non-volatile material dissolved and suspended in fog droplets were obtained with three complementary approaches, covering a size range from ca. 1–50 $\mu$m diameter: a counterflow virtual impactor, an eight-stage aerosol impactor, and a two-stage fogwater impactor. Concentrations were observed to decrease with size over the entire range, contrary to expectations of increasing concentrations at larger sizes. It is possible that the larger droplets had solute concentrations that increased with increasing size, but that the increase was too weak for the measurements to resolve. Future studies should consider the hypothesis that the droplets were coated with a surface-active substance that hindered their uptake of water.

## 1. Introduction

Chemical reactions in cloud droplets are known to be strongly dependent on the pH of the aqueous phase, which is controlled by the chemical composition of the droplets. Both field observations (Noone et al., 1988a; Munger et al., 1989; Ogren et al., 1989; Schell and Georgii, 1989) and model calculations (Flossmann et al., 1985; Seidl, 1989; Twohy et al., 1989; Ayers and Larson, 1990; Hegg and Larson, 1990; Pandis et al., 1990; Bower et al., 1991) of the chemistry of clouds indicate that droplet composition is dependent on the size of the droplets.

We hypothesize that condensational growth is the dominant factor determining the size dependence of the chemical composition and concentration of species dissolved and suspended (hereafter called "solute") in cloud droplets. This process results in solute concentrations in small particles/droplets that decrease with increasing size, while solute concentrations in larger droplets increase with size. In order to test this hypothesis, we obtained measurements of the size dependence of solute concentrations over a range of droplet sizes where major differences were expected.

## 2. Experimental approach

Measurements were carried out in Italy during November, 1989 as part of the Po Valley Fog Experiment 1989. A comprehensive description of the field campaign and the methods used is presented in Fuzzi et al. (1992). For the present analysis, three independent measurements of the

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size-dependence of fog droplet solute mass concentrations are used.

Dual counterflow virtual impactor (CVI) systems (Ogren et al., 1985) were deployed to sample fog droplets larger than a selectable size (cut diameter, $D_{50}$). One system was operated at a constant $D_{50}$ of about 5 $\mu$m, while the value of $D_{50}$ for the other system was varied systematically between 5 and 20 $\mu$m to allow study of selected subsets of the total droplet population. The sampled droplets in each system were evaporated, and the number size distribution of the residual (dry) aerosol particles was determined with an optical particle counter (OPC). The mass concentration of the particles in the diameter range 0.11–1.0 $\mu$m was determined from the measured number size distribution assuming spherical particles with a density of 2 g cm$^{-3}$. The amount of evaporated water vapor, corresponding to the liquid water content (LWC) of the sampled droplets, was determined with a dual-beam Lyman-alpha hygrometer (Zuber and Witt, 1987). By systematically varying the cut size of the CVI and evaluating the resulting changes in the residual particle size distribution and LWC, it is possible to calculate the mass concentration of non-volatile material dissolved or suspended in the droplets (Ogren et al., 1989). For brevity, we will use the word "solute" to denote non-volatile material dissolved or suspended in the droplets.

An eight-stage aerosol impactor (Fuzzi et al., 1992) collected samples of aerosol particles, at ambient relative humidity, with a time resolution of three hours. For the present work, the mass of dry particles on the impactor stages covering the (wet) size ranges 1–2, 2–4, 4–8, and 8–16 $\mu$m are used, together with the size distribution of fog droplets determined with a PMS Forward Scattering Spectrometer Probe (FSSP 100), to calculate the mass concentration of non-volatile material dissolved or suspended in the droplets. This mass concentration should be directly comparable to the mass concentration determined with the CVI. Additionally, chemical measurements are available from the 1–4 $\mu$m and 4–16 $\mu$m size ranges (Fuzzi et al., 1992).

A two-stage fogwater impactor (Schell and Georgii, 1989) was used to obtain samples of droplets with diameters in the ranges 2–4 $\mu$m and $>4$ $\mu$m. These samples were analyzed by ion chromatography for major ions.

## 3. Results

The utility of the CVI data for evaluating the size dependence of solute concentrations turned out to be limited by two factors: the hygrometer on CVI #2 was inoperative, and the fog LWC and droplet number concentration often changed substantially over the 30 minutes needed for a CVI scan of 4 or 5 different $D_{50}$-settings. Consequently, only the data from one CVI are used, and the difference between consecutive measurements at different cut sizes is very difficult to evaluate.

As a result of our failure to obtain simultaneous CVI measurements of two size fractions, along with the natural variability of the fog, the CVI results can only be evaluated as the solute mass concentration of a broad range of droplets. The upper size limit of droplets sampled by the CVI is a function of the wind speed. A time series of observed wind speeds, presented in Wobrock et al. (1992), shows that winds were generally below 4 m s$^{-1}$ at 10 m above ground level, and even lower near the height of the CVI inlet. Wind tunnel experiments at a wind speed of 2.8 m s$^{-1}$ indicate that 17 $\mu$m diameter droplets are sampled with 90% efficiency, and that the sampling efficiency is 50% for 30 $\mu$m diameter droplets (Noone et al., 1992a).

Fortunately, the independent measurements of the number concentration of residual aerosol particles in the CVI (which we assume corresponds directly to the number concentration of fog droplets) and of the liquid water content of the fog droplets (determined with the Lyman-alpha hygrometer) provide a measure of the mean size of the droplets. The diameter of mean mass (DMM) of the sampled droplets is defined as

$$\mathrm{DMM} = \sqrt[3]{\frac{6}{\pi}\frac{\mathrm{LWC}}{\rho N}},$$

where $N$ is the number concentration of fog droplets and $\rho$ is the density of water. Fig. 1 illustrates how DMM varies at the cut size of the CVI is changed. The internal consistency of the approach is apparent, as the value of DMM is almost always larger than $D_{50}$. In interpreting data using DMM as the size parameter, it is important to recognize that observations with low DMM could only be obtained when the total droplet size distribution had a low DMM, as there was no

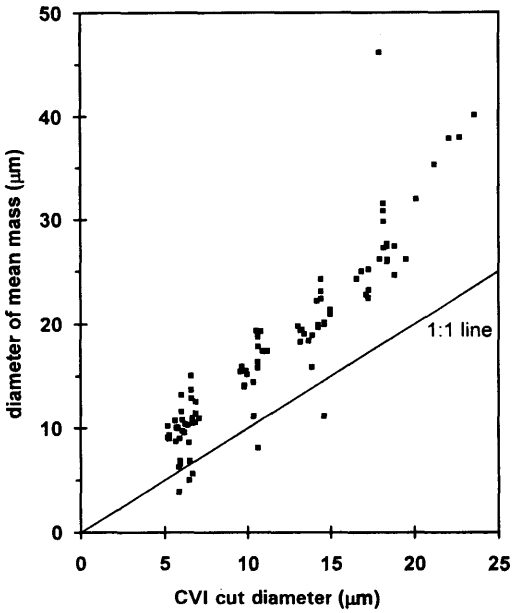


*Fig. 1.* Change in diameter of mean mass of fog droplets with CVI cut diameter.

control over the upper size cut for the CVI. In contrast, observations with large DMM could be obtained with any droplet size distribution where large droplets were present, as the smaller droplets could be excluded with a large $D_{50}$-setting of the CVI.

Fig. 2 shows the average solute mass concentration for all droplets sampled by the CVI (determined from the residual aerosol mass concentration measured with the OPC and the liquid water content measured with the Lyman-alpha hygrometer) versus the diameter of mean mass of the sampled droplets. Each observation is a 3-min mean value. These results were obtained on 11–13 November, during the second fog event, as the CVI was not operated in the scanning mode (systematically varying $D_{50}$) during the other events. Solute concentrations are observed to decrease with size over the entire range of mean droplet sizes encountered. In order to show the results at larger DMM-values more clearly, the figure does not include a few observations at low DMM that had average solute concentrations in the range 300–1000 mg/l$^{-1}$.

Similar results were obtained with the aerosol impactors (Fig. 3) during the first four fog events

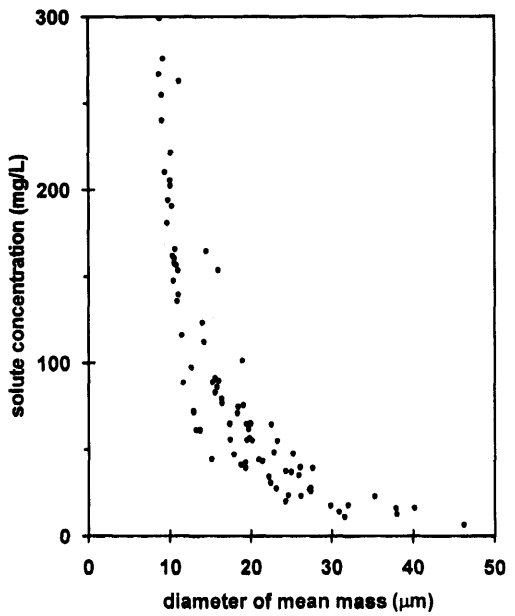


*Fig. 2.* Size dependence of fogwater solute concentration observed with CVI.

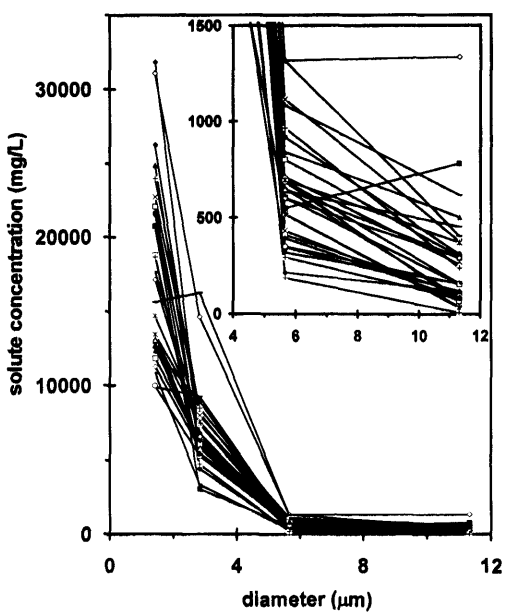


*Fig. 3.* Size dependence of wet aerosol solute concentration determined with 8-stage impactor and FSSP.

(10–16 November). Here, the size plotted is the aerodynamic, geometric mean diameter of the impactor stage, and there is both an upper and a lower size bound for each observation. Only those impactor samples where the fog liquid water content was greater than 10 mg $m^{-3}$ are included in the figure. Quantitative comparison of the CVI results with the aerosol impactor data is complicated by the different measures of droplet size employed by the two techniques. The impactor results represent the solute concentrations in a specific size range, whereas the CVI results represent the average solute concentration in a population of droplets with the indicated mean size. Nevertheless, both approaches show the same trend of decreasing concentrations with increasing droplet size, and the observed concentrations are of the same order of magnitude.

The results of the chemical analyses of the samples obtained with the eight-stage aerosol impactor, illustrated in Fig. 4 for $NH_4^+$; show a strong decrease of solute concentrations with droplet diameter. A similar decrease was observed for $NO_3^-$ and $SO_4^{2-}$. After determining the aerosol mass of each aluminium foil, the foils from adjoining stages were grouped together and extracted with deionized water for subsequent chemical analysis (Fuzzi et al., 1992). Therefore chemical results are available in a four size range subdivision (0.06–0.25, 0.25–1, 1–4, 4–16 $\mu$m diameter). The upper two size ranges were taken to calculate size dependent solute concentrations by using the FSSP data as described above. The plotted droplet diameter represents the geometric mean of the two collection stages.

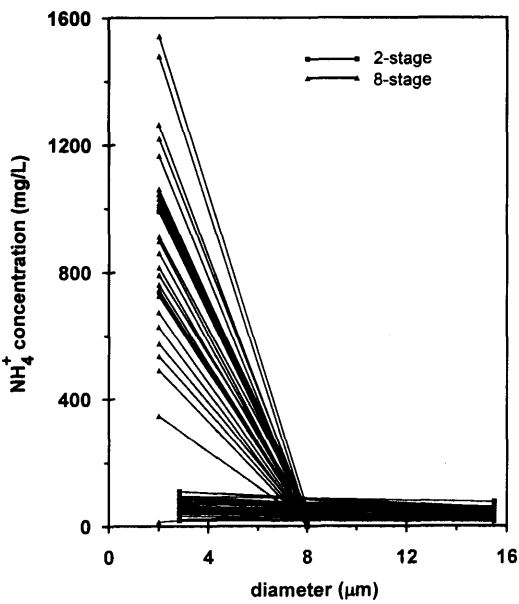


*Fig. 4.* Size dependence of ammonium concentration determined with 8-stage aerosol impactor and 2-stage fogwater collector.

Fig. 4 also shows the results of the $NH_4^+$ concentrations of the droplets collected with the two-stage fogwater collector during the first four fog events. The samples were taken from the droplet size ranges 2–4 $\mu$m and >4 $\mu$m with a time resolution of 1–2 h, depending on the amount of water collected by the second stage (small droplet range). The indicated droplet diameter represents the geometric mean of the collection stage; an upper size of 80 $\mu$m was arbitrarily assumed for the first stage. Most of the water collected by the second stage (up to 80%, based on a comparison of the water available in this size range with the collected water mass) derives from droplets larger than 4 $\mu$m diameter, which passed the first stage without impaction due to its non step-like collection efficiency curve. Accordingly, the ratio of the solute concentrations is the small and large size classes is up to a factor of 5 too low.

A comparison of the mean concentrations for each size fraction of the aerosol impactor shows that solute concentrations decrease with droplet size by roughly a factor of 27, 33 and 36 for $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ respectively. The same analysis for the two-stage fogwater collector shows factors of 4 ($SO_4^{2-}$, $NO_3^-$) and 2 ($NH_4^+$). The remarkable difference between these two results can be explained mainly by the different size ranges which are covered by the two methods and the already mentioned "contamination" of the samples of the lower size range by bigger droplets that passed the first stage.

## 4. Discussion

A detailed discussion of inhomogeneities in cloud droplet composition has been presented in Ogren and Charlson (1992). A conceptual picture of the expected behavior of solute concentration with droplet size, along with the factors controlling that behavior, is shown in Fig. 5. This is the

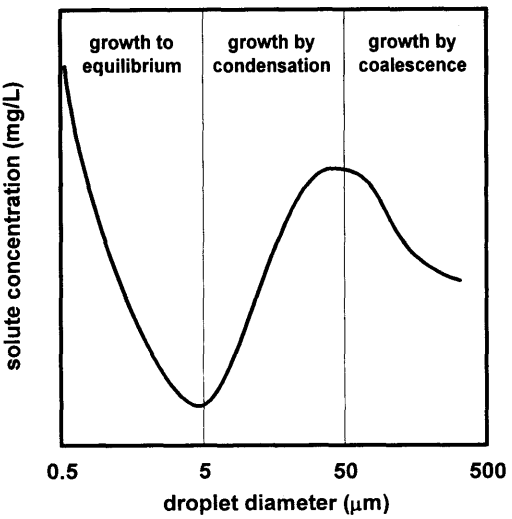


*Fig. 5.* Conceptual model of the dependence of droplet solute concentration on size. Note that the radius scale is approximate, and will vary from cloud to cloud.

behavior expected for an air parcel cooling adiabatically and with larger droplets, formed by coalescence at higher levels, falling through the parcel. Condensational growth of the droplets results in an $r^{-1}$ growth law ($dr/dt \propto r^{-1}$), causing the smallest droplets to react quickly to changes in supersaturation. These droplets rapidly grow to their equilibrium size at the prevailing relative humidity, and thus follow the $r^{-1}$ growth law for only a limited period of time. Droplets in this "equilibrium growth" category have increasing solute concentrations with decreasing size, deriving from the fact that decreasing drop size causes a droplet of pure water to have an increasing equilibrium vapor pressure; thus, at equilibrium, smaller droplets require a greater vapor pressure depression, and hence a higher solute molarity. Larger droplets require longer to reach their equilibrium size, and will not reach equilibrium if the supersaturation in the cloud remains above their equilibrium supersaturations. These larger droplets, after following the $r^{-1}$ condensational growth law long enough to counteract their initial size-dependence of solute concentration in the "equilibrium growth" category, will have solute concentrations that increase with increasing size, because the relative rate of dilution $(1/r)\, dr/dt$ varies with droplet size as $r^{-2}$. However, the rate of condensational growth slows down at large drop sizes (again due to the $r^{-1}$-growth law), and at some point coalescence results from the collection of small (dilute) droplets by larger (more concentrated) droplets, we expect that solute concentrations must again decrease with droplet size in the coalescence-growth regime. Previous observations in relatively clean stratocumulus clouds by Ogren et al. (1989) confirmed one aspect of this conceptual model, as droplet solute concentrations were observed to increase by a factor of three as droplet diameter increased from 10 to 18 $\mu$m.

The behavior observed in the Po Valley is seen to differ markedly from the expected behavior. The behavior at small sizes is as expected, but at no point do solute concentrations begin to increase with size. Several explanations for the observed dependence of solute mass concentration on droplet size are possible:

1. The large droplets were not present, due to sedimentation.
2. The CVI did not collect the large droplets, due to inlet losses.
3. Large particles, which contributed the residual mass associated with larger droplets, were not included in the integrated size distributions from the OPC.
4. The droplets were not activated, due to

   (a) the presence of large amounts of insoluble material in the aerosol, or

   (b) frequent periods of subsaturated conditions, or

   (c) the presence of a surface-active coating on the droplets, altering their surface tension.

5. The actual size-dependence was too weak to be resolved by the CVI.

Other processes that could conceivably affect the size-dependence of droplet solute concentrations include entrainment, which mixes unactivated particles and subsaturated air into the fog from above, and coagulation between interstitial particles and fog droplets. However, entrainment cannot explain the observed size-dependence of solute concentrations in droplets above 10–15 $\mu$m, because producing those droplets requires extended growth times. As discussed above, the $r^{-1}$ dependence of the condensational growth rate produces solute concentrations that increase with

increasing size. Moreover, entrainment of substantial amounts of aerosol mass into the fog would most likely lead to frequent periods of subsaturated conditions in the fog, which is inconsistent with the observations (see discussion below). The contribution of coagulation between interstitial particles and fog droplets to the solute mass in the fog droplets was evaluated by Noone et al. (1992b), who concluded that the amount of mass transferred to the droplets via coagulation was negligible.

It is unlikely that sedimentation of large droplets could be sufficient to account for the missing increase of droplet solute concentrations with size. Examination of Fig. 2 shows that diameters of mean mass greater than 20 $\mu$m were observed on quite a few occasions. Such droplets are large enough that they should have been activated, and thus have increasing concentrations with increasing size.

The hypothesis that the CVI did not sample the larger droplets can be tested by comparing the diameter of mean droplet mass calculated from the CVI instrumentation with the same parameter calculated from the FSSP, for all droplets larger than the cut size of the CVI. If the CVI undersampled the larger droplets, then the FSSP would show larger diameters of mean mass than derived from the CVI. This comparison is illustrated in Fig. 6, which shows that it is possible that the CVI undersampled the larger droplets on some, but not all, occasions. Our interpretation of this result is that undersampling of the larger droplets was not a major problem and would be insufficient to account for the observed decrease in droplet solute concentration with increasing droplet size for larger droplets.

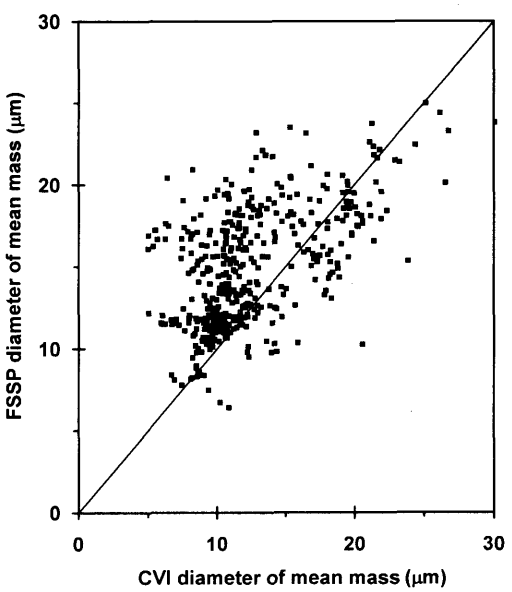


*Fig. 6.* Comparison of CVI and FSSP determinations of diameter of mean mass of fog droplets.

The aerosol size distributions used in the calculations underlying Fig. 2 covered the diameter range 0.1–1 $\mu$m. The upper diameter limit of the OPC used on the CVI inlet was 7.5 $\mu$m, but the data above 1 $\mu$m were not used because our calibration of the instrument only went up to 1 $\mu$m. By excluding the supermicrometer particles, we underestimated the solute mass concentration, an effect that would presumably be most important for the larger droplet sizes. Little effect on the calculated DMM would be expected, however, because the number concentration of residual particles is dominated by the submicrometer fraction. In order to evaluate the potential importance of the supermicrometer particles, we recalculated the droplet solute concentrations using the entire 0.1–7.5 $\mu$m diameter range covered by the OPC, on the basis of the size calibration provided by the manufacturer. The result of this calculation yielded a size-dependence of solute concentration that showed the same trend as in Fig. 2, although the solute concentrations were approximately double. Thus, although the exclusion of the supermicrometer particles causes erroneously low values in the calculated solute concentration, there was no trend of this error with DMM.

Based on the observed chemical composition of the aerosol particles (Fuzzi et al., 1992), we can construct a simple model of the composition of the particles and calculate the size at which a particle would activate. In this simple model, the aerosol particles are 50% insoluble material, 25% ammonium nitrate, and 25% ammonium sulfate (by mass). The resulting size at which a particle activates corresponds to the maximum in the Köhler curve for the particle, which relates the equilibrium vapor pressure of water vapor above the solution droplet to the size and composition of the particle:

$$\frac{e_a}{e_s} = S - 1 = 1 + \frac{A}{a} - \frac{B}{a^3 - r_u^3},$$

where $e_a$ is the equilibrium vapor pressure of water above a solution droplet of radius $a$ having an insoluble core of radius $r_u$, $e_s$ is the saturation vapor pressure above the droplet, $S$ is the supersaturation, and $A$ and $B$ are constants determined by temperature, the surface tension of the droplet, and by the chemical composition of the droplet (Pruppacher and Klett, 1978). The values of $A$ and $B$ for droplets where the surface tension is that of pure water are given by

$$A = \frac{3.3 \times 10^{-5}}{T} \quad \text{and} \quad B = \frac{4.3\, \nu m}{M}$$

where $T$ is the temperature, $\nu$ is the van't Hoff constant for the solute molecule, $m$ is the mass of solute, $M$ is the molecular weight of the solute, and the constant terms are given in cgs units. For our simple model of the aerosol, $B$ can be expressed as

$$B = 4.3\left(\frac{\nu_n m_n}{M_n} + \frac{\nu_s m_s}{M_s}\right),$$

where the subscripts $_n$ and $_s$ denote the values for ammonium nitrate and ammonium sulfate.

The resulting size where the particles activate, termed the critical size, is shown in Fig. 7, along with the supersaturation required to activate the particles (the critical supersaturation). CVI measurements of the size distribution of the nonvolatile material in the droplets show that very few particles in the diameter range 0.1–0.3 $\mu$m were scavenged by the fog (Noone et al., 1992b). Thus, droplets associated with dry aerosol particles smaller than 0.3 $\mu$m are likely to be unactivated, which from Fig. 7 is seen to correspond to droplet diameters below 4 $\mu$m. This helps to explain the results observed with the aerosol impactor, as only the two largest impactor stages (4–8 and 8–16 $\mu$m) could be expected to have sampled droplets in the "condensational growth" regime of Fig. 5.

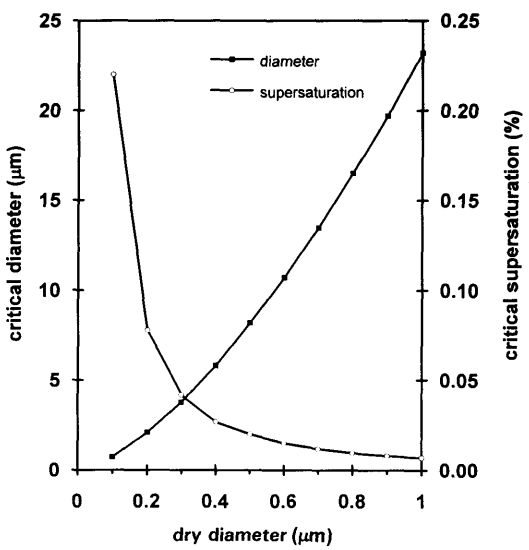


*Fig. 7.* Calculated critical size and supersaturation of the Po Valley aerosol.

Fig. 7 can also be used to deduce the magnitude of the peak supersaturation reached in the fog, given that particles below 0.3 $\mu$m diameter were essentially unscavenged by the fog. For the simple model of aerosol composition used here, which assumes that all the particles have the same composition, it would appear that supersaturations were generally below 0.04%.

Gerber (1981) observed extended periods of subsaturated conditions ($\sim$10 min) in a radiation fog, interspersed between periods of relatively high (up to 0.4%) supersaturation. Under such conditions, the smaller activated droplets would deactivate, and the size-dependence of droplet solute concentrations could display a monotonically decreasing trend with increasing droplet size. The larger cloud condensation nuclei (CCN) have very long response times for changes in relative humidity (Table 1), and would not be expected to follow such a time-history of supersaturation.

Table 1. *Equilibrium sizes and pseudo first-order response time for growth of particles composed 50% (by mass) of ammonium sulfate and 50% insoluble material*

| Dry diameter ($\mu$m) | Equilibrium diameter ($\mu$m) $S = 0\%$ | Equilibrium diameter ($\mu$m) $S = 0.005\%$ | Response time (s) |
|---|---|---|---|
| 0.3 | 1.1 | 1.2 | 30 |
| 0.5 | 4.4 | 5.3 | 200 |
| 0.7 | 6.6 | 9.2 | 800 |
| 1.0 | 12.3 | 18.1 | 4000 |

The tabulated response time is how long it takes the particle to grow from its equilibrium size $D_0$ at $S = 0\%$ to $D_0 + (D_{0.005} - D_0)(1 - e^{-1})$, where $D_{0.005}$ is the equilibrium size at $S = 0.005\%$, in response to a step change in $S$ from 0% to 0.005%.

The hypothesis that deactivation of the smaller droplets during periods of subsaturation was responsible for the lack of a minimum in the solute concentration versus droplet size curve can be tested using a simple model of droplet growth. The objective of these model calculations is not to simulate the actual fogs studied, but rather to explore the consequences for the size-dependence of droplet solute concentrations of different supersaturation time histories. The model calculates the growth of a given droplet (or aerosol particle) over a fixed droplet size grid by integrating forward in time the equation

$$\frac{\partial f(r)}{\partial t} = \frac{\partial}{\partial r}\left(\frac{\mathrm{d}r}{\mathrm{d}t} f(r)\right)$$

for cloud condensation nuclei of a given size and composition, using a prescribed time history of the relative humidity. The number density distribution function for drops and particles, $f(r)$, is initially zero everywhere except for one category where $f(r)\,\mathrm{d}r = 1$ (Wobrock et al., 1986), and $\mathrm{d}r/\mathrm{d}t$ is the droplet growth velocity (Pruppacher and Klett, 1978, eqs. (13–28)). The size grid has a log normal spacing, as suggested by Berry and Reinhardt (1974), with a mass doubling every fourth bin. The calculations were performed for a temperature of 5°C, and assumed that the particles were 25% ammonium sulfate, 25% ammonium nitrate and 50% insoluble material (by mass). At the start of the calculation, the particles were assumed to be in equilibrium at an ambient RH of 95%. The accommodation coefficient for water was taken to be 1.0.

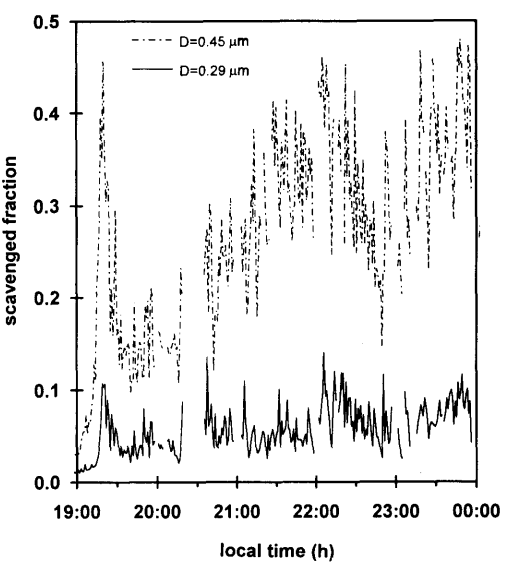


*Fig. 8.* Fraction of 0.29 and 0.45 particles scavenged by the fog droplets on November 11, 1989. Only observations from CVI #2, with $D_{50}$-values in the range 5–7 μm diameter, are included.

The model results demonstrate that it is possible to obtain droplet solute concentrations that decrease monotonically with increasing size most of the time. The time history of supersaturation used to obtain this result was subsaturated 90% of the time, which short bursts of supersaturation up to 0.08% every 17 min. However, measurements made in the fog put strong constraints on the supersaturation time history, and the above time history of supersaturation is incompatible with those constraints.

Observations constraining the time history of supersaturation in the fog include:

(a) the low fraction of 0.3 μm particles that were scavenged by the fog. Fig. 8 shows this fraction for 0.29 and 0.45 μm particles, determined from the OPC's sampling from the interstitial and CVI inlets (Noone et al., 1992b); each observation represents an average over one minute; the low scavenging efficiency for 0.29 μm diameter particles is not consistent with peak supersaturations above ca. 0.04% (Fig. 7);

(b) the frequent scavenging of a sizeable fraction of the 0.45 μm diameter particles (Fig. 8). These particles have a response time of about 3 minutes, and would be expected to deactivate if the air was subsaturated for longer periods;

(c) the observed solute concentrations (Fig. 2 and 3) are too dilute to allow for extended periods of subsaturation, and require that the air stays supersaturated much of the time in order that the droplets grow enough to produce solute concentrations of order $10^2$ mg $\cdot l^{-1}$ for droplet diameters of 10–20 μm.

A supersaturation time history that produces results consistent with the above constraints is shown in Fig. 9. The resulting droplet sizes and solute concentrations are shown in Figs. 9 and 10 for dry CCN diameters of 0.3, 0.5, 0.7, and 1.0 μm. Dry particles smaller than ca. 0.3 μm diameter are not activated, while the 0.5 μm diameter particles remain activated about 40% of the time. Solute

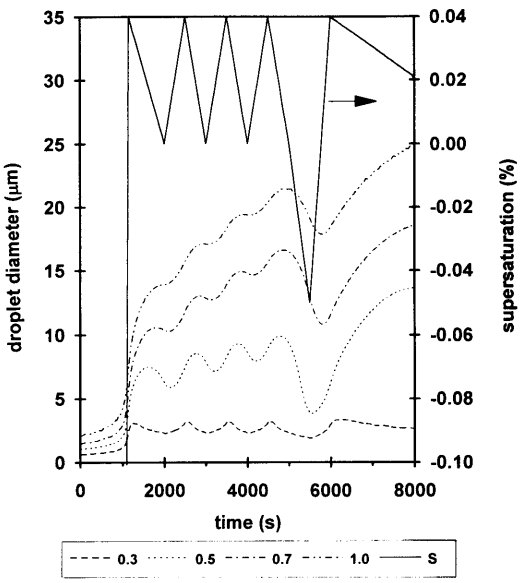


*Fig. 9.* Prescribed supersaturation (S) and calculated evolution of droplet diameter for four categories of CCN. The labels indicate the dry diameter ($\mu$m) of the CCN.

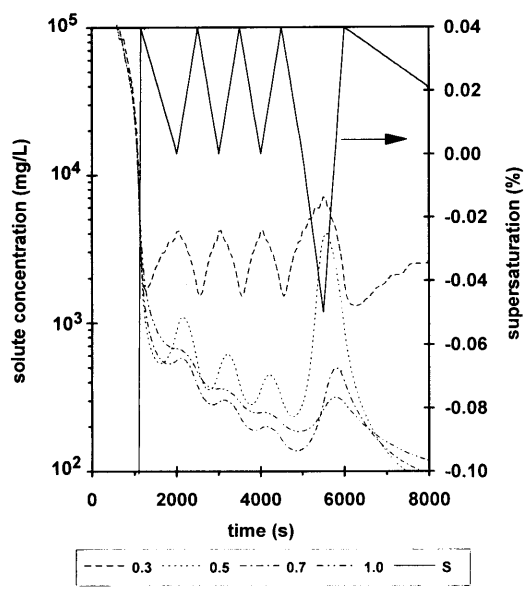


*Fig. 10.* Prescribed supersaturation (S) and calculated evolution of droplet solute concentration for four categories of CCN. The labels indicate the dry diameter ($\mu$m) of the CCN.

concentrations for 10–20 $\mu$m diameter droplets are of order $10^2$ mg $l^{-1}$. The smallest activated droplets can have lower or higher solute concentrations than larger droplets, depending on the particular relative humidity at the moment. Most of the time, the largest droplets have larger solute concentrations than intermediate sizes, and the small unactivated droplets have the highest solute concentrations of all.

The model results show that, in principle, it is possible to obtain droplet solute concentrations that decrease monotonically with increasing droplet size. However, if the prescribed supersaturation time history is constrained by the observed scavenging efficiencies and solute concentrations, a minimum in the solute concentration versus droplet size curve is expected somewhere in the 10–20 $\mu$m diameter range. Thus, we reject the hypothesis that the observed size dependence of droplet solute concentration was due to the occurrence of frequent periods of subsaturation in the fog.

Another hypothesis is that the droplets were coated with a surface-active compound that changed the surface tension of the droplets and hindered their uptake of water. Such coatings have been observed in both marine and pollution aerosols, as reviewed by Gill et al. (1983). Giddings and Baker (1977) showed that a monolayer of surfactant on a growing droplet will increase the critical size, reduce the critical supersaturation, and decrease the quasi-steady-state growth rate of the droplets; the latter was claimed to be the predominant effect. We do not have data pertaining to the surface properties of the droplets, and so are unable to reject or confirm this hypothesis.

Finally, we consider the hypothesis that the expected size-dependence of solute concentration was present, but that the dependence was too weak to be resolved by the CVI. In the relatively clean stratocumulus clouds over Sweden studied by Ogren et al. (1989), most of the scavenged aerosol mass was in the dry particle diameter range 0.1–1.0 $\mu$m diameter (Heintzenberg et al., 1989). Particles in this size range have masses spanning a factor of 1000 (mass $\propto r^3$). Assuming that the main mass of water was associated with droplets spanning a factor of two in size (ca. 10 in mass), then the droplet solute concentrations might have been expected to increase by a factor of ca. 100 with a factor of two increase in droplet size. The

observed solute concentrations increased by only a factor of three as droplet size increased by a factor of two, a difference that was primarily attributed by Ogren et al. (1989) and Twohy et al. (1989) to averaging the solute concentration over a finite range of droplet sizes, and to the non-ideal transmission curve of the CVI.

In the Po Valley, most of the scavenged mass came from particles larger than 0.3 $\mu$m diameter (Noone et al., 1992b), which, combined with the upper diameter limit of calibrated OPC data of 1.0 $\mu$m, yields particle masses varying by a factor of ca. 30. Droplet mass size distributions typically were dominated by droplets spanning a factor of 2–3 in size (Fuzzi et al., 1992), corresponding to a factor of 10–30 in mass. Thus, the measured droplet solute concentrations might only be expected to increase by a factor of 1–3, which, in light of the observations in Sweden, may very well be below the resolving power of the CVI.

## 5. Conclusion

We are unable to explain the size dependence of the mass concentration of non-volatile material dissolved and suspended in droplets observed in fogs during the Po Valley Fog Experiment 1989. Previous observations, as well as theoretical and model results, indicate that there should be a minimum in the solute concentration versus droplet size curve somewhere around 10–20 $\mu$m diameter. Instead, solute concentrations were observed to decrease monotonically with droplet size. It is possible that the true size-dependence of solute concentration was too weak for the CVI to resolve, although future studies should consider the hypothesis that the droplets were coated with a surface-active substance that hindered their uptake of water. Future experiments will need to include measurements of supersaturation and of the surface properties of the droplets (surface tension, chemical composition of the surface layer) in order to test this hypothesis.

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