Observations of aerosols and droplets in California stratus

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ABSTRACT

A program of aerosol and cloud droplet measurements in stratus clouds was carried out during the summer of 1968 in the hills south of San Francisco. Size distributions were determined with a Royco light-scattering particle counter, a condensation nuclei counter, and a settling tunnel. Two six-stage cascade impactors were used to collect samples for sulfur-compound and chloride analysis. The size distribution data showed a mode in the submicron size range. Secondary modes occurred at radii of about 6 to 8 μ in developed clouds and at somewhat smaller sizes during periods of cloud dissipation. The aerosol below the cloud did not show the secondary mode at the larger sizes. The location of the secondary mode is consistent with some of the distributions calculated from theory, but the observed concentrations of about 1 droplet per cc per μ of radius at the secondary mode are substantially less than calculated. One possible reason involves the mixed chemical composition of the nuclei; another is the high cooling rates used for the calculations. The observations show organic material to be present and a nonuniformity in the distribution of sulfur compounds and chlorides over the droplet spectrum. The average ratio of sulfur to chloride varies from about 4 for $r = 0.2$ μ to about 0.4 for $r = 2$ μ to about 1.3 for $r = 4$ μ. The results of some other studies of fog and stratus droplets are also reviewed briefly.

Introduction

During the summer of 1968, a series of measurements of droplet parameters and nuclei chemistry were made in stratus clouds found in the hills south of San Francisco. Stratus clouds occur frequently during the summer here, and suitable sampling locations are reasonably accessible. The combination of upwelling in the coastal waters and the inversion associated with the Pacific high pressure area causes the frequent summertime occurrence of stratus in the marine air just below the inversion. The winds are almost invariably from the westerly quadrand during the summer so the stratus is advected to the hills, over a narrow coastal area that is generally free of pollution sources. The degree to which the stratus penetrates depends largely on the heating of the hills and of the interior lands.

One of the decided advantages of ground sampling is that it is possible to remain in the cloud for longer periods than is generally feasible for aircraft sampling. The other problems that are avoided by ground sampling include limitations in size and weight of the instrumentation and in the design of inlet tubing that will not discriminate against certain droplet sizes. On the other hand, ground-based sampling sacrifices the ability to move into the heart of the cloud and, to some extent, freedom from urban pollution sources.

Sampling instrumentation and procedures

The objectives of the program were to obtain cloud drop size distributions and measurements of variations in chemical constituents with droplet size. The sizes of interest ranged from submicron to tens of microns. Three different instruments were used to cover different parts of this range. The largest droplets with radii from about 8 to about 40 μ were measured with a "settling tunnel". This device is 122 cm long. Air is drawn through the 15.3-cm wide by 0.7-cm high entrance at a rate of 56.6 l min^{-1}; the linear speed is 88 cm sec^{-1}. Droplets fall to the bottom of the tunnel as the air progresses through the length of the device. The droplets mark magnesium oxide coated microscope slides (see May, 1950, for a description of the method

of preparation) set flush with the bottom surface of the tunnel. If the flow is laminar and the droplets are uniformly dispersed upon entry into the tunnel, the droplet size distribution can be calculated from the number of droplet marks per unit area at different distances from the tunnel entrance. For droplets that follow Stoke's law the relevant equation is:

$$f(r_m) = \frac{9\mu}{2Tg\varrho r_m^2} \frac{dN}{dr_m} \tag{1}$$

where:

$f(r_m)$ is average number of droplets of radius r_m per unit volume and per unit interval of radius,
r_m is the maximum radius of the droplets deposited at some given distance from the tunnel entrance,
μ is the viscosity of the air,
T is length of the sampling period,
g is acceleration of gravity,
ϱ is droplet density,
N is the number of droplets per unit area deposited at the distance corresponding to r_m.

The maximum deposited radius, r_m, is related to distance from the tunnel entrance, L, by

$$r_m = \sqrt{\frac{9\mu v h}{2g\varrho L}} \tag{2}$$

where:
v is the linear speed of the air through the tunnel,
h is the height of the tunnel.

The derivation of this equation is closely related to that for determining the size distrbutions from deposition rates at the bottom of a closed chamber (see, e.g., Cadle, 1955, pp. 204–8). Size distributions were calculated from Eqs. (1) and (2) using finite differences between the numbers of droplets per square millimeter deposited at different distances from the tunnel entrance. The distances generally used were 2.5, 5, 10, 20, 41, 81, and 102 cm. Photomicrographs were made of the droplet marks in the magnesium oxide at these distances and then the marks were counted.

For low wind speeds, settling tunnel sampling was nearly isokinetic. However, wind speed was often greater than 5 m sec^{-1}, so we might expect some biasing of the sample. Green & Lane (1957) give data that indicate that the concentrations of the largest droplets measured may be as much as 50 percent too high for the sampling arrangement used. For the smaller sizes measured, the effect would be smaller, around 10 percent. The decline in actual droplet frequency may be somewhat more rapid with increasing size than our data indicate.

Air leaving the rear of the settling tunnel entered two Andersen cascade impactors (Andersen, 1958) through ports in the bottom of the tunnel. These six-stage samplers fractionated the remaining aerosol according to particle size so that differences in chemical composition could be studied as a function of particle or droplet radius. Because the tunnel removed some of the particles of sizes collected by the Andersen samplers, the collections on each stage had to be corrected for the tunnel losses in order to obtain accurate estimates of the concentrations found in the original aerosol.

For cascade impactor data reduction, the tunnel was considered as another stage preceding the first stage of the impactor. The tunnel's cutoff radius was taken to be 4.6 μ, the radius at which the tunnel is 50 percent efficient. The Andersen sampler calibrations used are from Flesh *et al.* (1967). The effective cutoff radii for the stages were taken to be the 50 percent collection radii as discussed by Ludwig (1968). The material not collected by the Andersen samplers was caught on glass fiber filters at the impactor outlets. A pump pulled air through the tunnel, the impactors, and the filters.

A Royco particle counter, Model PC 200A (Royco Instruments, Menlo Park, Calif.), was used to determine the size distribution of particles, including droplets with radii between 0.34 and 6.9 μ. This instrument determines particle size from the amount of white light scattered at an angle of 90 degrees to the incident beam. There are shortcomings to such techniques (Whitby & Vomela, 1967; Hodkinson & Greenfield, 1965). First, the resolution of the instrument is not as good as the fifteen available size classes would indicate (Preining, 1968), but this is not considered to be a serious drawback for the use described here, where averages were sometimes taken over several hours during periods of changing concentration and where the other instruments used in the program had comparable resolution. In addition, Whitby & Vomela (1967) have found the

Royco counter to be sensitive to surface irregularities and shape variations, particularly for the larger sizes. However, in cloud studies the larger sizes are almost certain to be droplets and therefore regular in shape and surface.

The particle size indicated by the Royco counter depends to some extent on the particle's index of refraction (Hodkinson & Greenfield, 1965). The size categories assigned the channels by the manufacturer are approriate to a refractive index of 1.6. For measurements made in clouds and at high humidites, a refractive index of 1.33 (equal to that of water) would seem to be a better choice. Using the Hodkinson–Greenfield curves, and the assumption that 0.5 μ is the average wavelength of the white light used in the instrument, the channel intervals have been corrected to values corresponding to a refractive index of 1.33.

The inlet to the Royco is vertical, about 20 cm high and 2 mm inside diameter. About halfway between the inlet and the optical counting cell, there is a small chamber into which clean air can be introduced to dilute aerosols of high concentration. No dilution was necessary during this program. The flow rate through the instrument was 300 cm^3 min^{-1}. The number of particles in each channel was not determined simultaneously for all channels, but each channel was monitored for one minute out of fifteen.

The fragility of fog droplets is well known. The possibility of evaporation or condensation during passage through the Royco instrument could be a serious problem. To minimize such effects the top of the instrument was removed to allow amibient air to circulate freely about the inlet tube so that it would remain at very nearly the environmental temperature. As was noted above, the sampled air was undiluted, so that no humidity change was introduced via this route. In the absence of independent size measurements the data themselves provide good evidence that there were no substantial changes in droplet size during passage through the instrument. The data from three different instruments, the Royco, the settling tunnel, and the condensation nuclei counter, fit together with very little discontinuity. There is slight evidence to suggest some aerodynamic loss of the largest droplets at the Royco inlet. Otherwise, the settling tunnel data appear to be quite reasonable extrapolations of the Royco data to larger sizes, and the condensation nuclei counts to smaller

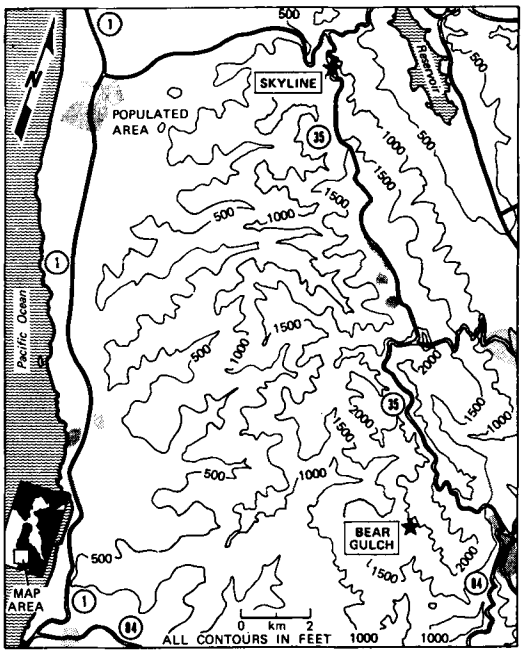

Fig. 1. Sampling sites.

sizes. The representativeness of the data is further supported by its general consistency with theoretical calculations and measurements by other investigators.

Estimates of small particle concentrations were obtained with a General Electric small particle detector (type CN). This is a condensation nuclei counter of the photoelectric type in which the attenuation of a light beam by the cloud formed on adiabatic expansion is related to the numbers of particles present. The calibration is based on the work of Nolan & Pollak (1946). Junge (1966) has compared values obtained from the G.E. counter used on this program with those obtained from an absolute counter of the Scholz type and used the comparisons to correct the G.E. counter calibration. The values given here are based on Junge's correction curve.

The two locations shown on the map in Fig. 1 served as the sites for the measurements reported here. The general area is about 40 km south-southeast of San Francisco. The Royco particle counter and the entrance to the settling tunnel were operated at the back door of a compact van. The van was parked on the upwind side of the road at the Skyline site with the back doors open and facing into the wind.

The equipment was powered by a 2500-watt generator located about 30 m from the truck. About the only major source of pollution upwind was a highway about 3/4 km to the west and at an elevation about 170 m lower than the Skyline sampling site. There was usually moderate traffic on this upwind road and light traffic on the road where the van was parked. Occasionally condensation nuclei counts in the early morning indicated that pollution from the Bay Area may have gone to sea on an evening land breeze and then returned as the wind reverted to westerly.

Operations at Bear Gulch were similar to those at Skyline except that the truck had to be parked on the downwind side of the road. This should have introduced very little error, as the traffic was limited to an occasional vehicle traveling to or from one of the four or five ranches. Southwest of the site there was also some construction which contributed to traffic past the site. One or two vehicles per hour was the average traffic flow. Other than this very light traffic, there were virtually no pollution sources upwind of the Bear Gulch location.

Generally, sample collection began between 0830 and 0930 Pacific Standard Time and continued until after there was no longer fog at the site. Thus, the results may include some periods of dissipating cloud as well as the periods of complete cloudiness. During the cloudy periods there were often times when the clouds lifted or otherwise became thin. Inasmuch as the instruments required long sampling periods or long averaging intervals as compared to the frequency of the changes in cloud density, it was not possible to resolve these short-period fluctuations. Long sampling times were necessary in order for the cascade impactors to collect large enough samples for chemical analysis.

The sample extraction and analytical methods for sulfur and chloride compounds were essentially the same as those described by Junge (1966). The chloride analysis made use of a titration cell (Coulson & Cavanagh, 1960) in which the chloride ions are titrated with coulometrically generated silver ions. The method does not distinguish Cl^- from Br^- or I^-. Generally, the ratio of bromide to chloride or iodide to chloride in the atmosphere is small (e.g., Duce *et al.*, 1965), so these halides have been treated as though they were all chloride.

A titration apparatus similar to that used for the chloride analysis was used for the sulfur analysis. First, the sulfates (and some other sulfur compounds present) are reduced to hydrogen sulfide in a microcombustion furnace. The hydrogen sulfide is then determined by iodimetric microcoulometric titration. Volatile organic sulfur-containing substances should be steam distilled from the sample during extraction. Sulfites may be converted to sulfates during preparation of the sample, so the results may include all or part of the sulfites.

The sulfur and chloride determinations were both made with the samples from one of the cascade impactors. The second impactor was used for determinations of organic aerosol material. Although substantial amounts of organic material were collected, problems have been encountered in both the detailed analysis and interpretation of these samples. Therefore, the organic data have not been included in the discussion.

In addition to the droplet measurements, meteorological measurements were made of temperature, humidity, and wind.

Results

The size distribution data from the Royco particle counter have been treated in two different ways: they were grouped to coincide with the chemical data collection periods, and they were grouped in categories qualitatively reflecting the nature of the cloud. This second group of categories includes mid-cloud, lower edge of cloud, below cloud, and dissipating cloud. There is considerable overlap in the data because of the long collection times. It was considered desirable to have the settling tunnel and the Royco sampling periods cover approximately the same time periods. The data categories by cloud type have been analyzed as conventional frequency distributions with the number of particles per cubic centimeter per micron of radius interval determined as a function of particle radius.

The data grouped for comparison with chemical results were converted to mass distributions. It was assumed that the droplets had a specific gravity of 1. The data obtained with the cascade impactors naturally yield mass distributions. Fig. 2 shows the mass distributions of sulfur and chloride and the ratio of sulfur concentration to chloride concentration as a function of droplet radius. The curves show

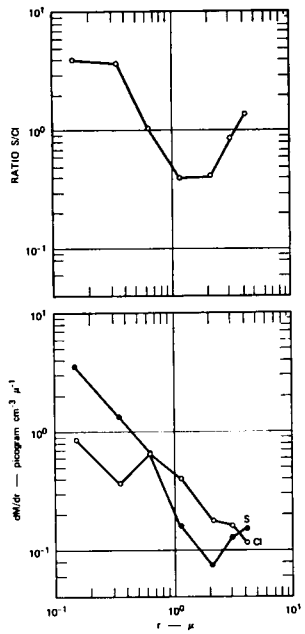

Fig. 2. Average sulfur and chloride mass distributions and sulfur-to-chloride ratio as a function of drop radius.

dM/dr, the change in the mass of material with radius less than r, as a function of r. This can be related to $dM/d \log_{10} r$, a representation often used in the literature (e.g., Junge, 1963) by:

$$\frac{dM}{d \log_{10} r} = \frac{r}{\log_{10} e} \frac{dM}{dr} \qquad (3)$$

The curves are for the totals of all the samples collected. For most of the points this represents the sampling of 65.4 m³ of air. This volume was collected during 18 separate sampling periods, all in the late spring or summer of 1968. The points at $r = 3.1$ μ are based on 52.2 m³ because one of the individual samples was contaminated. Two sulfur-compound samples were lost due to a failure of the analytical equipment, so the sulfur points for the radii 1.15 and 0.63 μ are also based on 52.2 m³ samples. It was arbitrarily assumed that the material collected by the filters represented particles with radii from 0.05 μ to the cutoff radius of the impactor's final stage, 0.25 μ. The mass distributions plotted at 0.15 μ were based on the filter data and such an assumption.

The individual collections show many of the same features as the averages in Fig. 2, but as is to be expected, they exhibit considerable scatter; Fig. 3 shows the five collections used to compile the averages. In these graphs the dashed segments indicate points missing, either because of contamination or equipment failure, and the arrows indicate that collections were less than the 0.2 μ gm needed for analysis. The mass distributions of sulfur-containing compounds show minima at radii of about 2 μ both in the individual distributions and in the average. In general, there is less chloride mass contained in the larger sizes than in the smaller. The average shows a slight minimum at a radius of about 0.35 μ, as do several of the individual cases.

The ratio of sulfur to chloride ranges from about 4 for the small sizes to about 0.4 for radii between 1 and 2 μ and back to greater than 1 for droplets with radii greater than about 3.5 μ. All these ratios are much greater than the value of 4.72×10^{-2} found in sea water (Sverdrup *et al.*, 1942). It appears that sea spray is not the

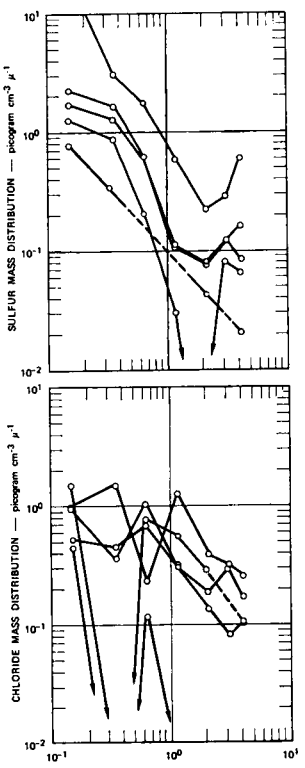

Fig. 3. Sulfur and chloride mass distributions, individual collections.

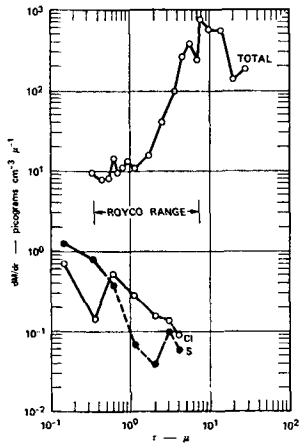

Fig. 4. Total mass distribution compared with sulfur and chloride mass distributions.

dominant aerosol at these sites even though they are within a few kilometers of the ocean.

Although the impactor separates the chloride and sulfur compounds into fractions according to particle size, these compounds are probably mixed with other materials in the cloud. The larger droplets contain substantial amounts of water with the sulfur and chloride compounds present as nuclei. If the chloride and sulfur compounds were collected as the nuclei of droplets rather than as solid particles, then we can conclude that the chloride and sulfur compounds found on the first stages of the impactor are those which constituted nuclei for the larger droplets. These were the nuclei that were large enough or hygroscopic enough to induce droplet growth, i.e., active nuclei. The material found on the last stages and the filter would be made up of those particles that have not grown very much—inactive nuclei.

For three of the cascade impactor collections, data were also available from the Royco counter. The Royco and settling tunnel size distributions converted to a mass basis, are shown in Fig. 4, as are the mass distributions for chloride and sulfur. Unfortunately, it was from this chloride and sulfur group that some impactor samples were lost because of instrument malfunction. The distributions are shown as dashed lines where they are the average of only two collections (25.5 m^3 of air) instead of three (37.7 m^3). As is to be expected, the sulfur and chloride distributions show the same general features seen before. Also as expected, the chlorides and the sulfur compounds are much smaller fractions of the total material for the larger sizes. For 4 μ radius drops the sulfur constitutes about 4 parts in 10^4 and the chloride about 6 parts in 10^4. For 0.3 μ radius the corresponding fractions are about 1 in ten and 2 parts in a hundred. The concentrations found here are not likely to be found in every droplet. It is more likely that some droplets will have formed on the chloride nuclei, some on sulfur compounds, and some on mixtures of these and other compounds. During their lifetime, the droplets may also sweep out additional aerosols.

The above results show that the aerosol material and the droplet nuclei may be of mixed composition. Other studies (Goetz, 1965; Blanchard, 1968) have shown that even in a relatively clean atmosphere of recent maritime origin, the cloud nuclei present may include substantial amounts of organic material, as preliminary analyses have shown in our samples. The winds during all the sampling were from the westerly quadrant and the circulation associated with the Pacific high pressure area suggests a long trajectory over the ocean. On a few occasions some of the sampled air may have been carried to sea the night before during a period of land breeze. It is clear that the aerosol population is considerably more complex than what would be deduced from the composition of the dissolved salts in seawater.

Before presenting the particle size spectra for the different types of cloud, two apparent artifacts in the Royco particle counter data should be noted. First is the apparent loss of some of the larger droplets. This has already been mentioned, and evidence of such loss can be seen in Fig. 4, where the total distribution dips at a radius of 6.9 μ, the upper channel of the particle counter. Similar features are to be found in several of the size distributions to be presented. The other artifact occurs at the channel marked by the points at 0.63 μ radius. The 90° scattering at refractive indices of 1.6 and 1.33 is such that this channel is supposed to resolve a very narrow range of radii. For physical, optical, and electronic reasons, the resolution of the instrument is not as good as the theory predicts (Preining, 1968). Thus, when the theory is used to calculate the size distribution (as has been done for all cases presented here) this channel tends to give unrealistically high results. The adjacent channels

may show values somewhat too low as a result of the same mechanism. The artifact does not seriously affect the major features of the distributions.

As has already been noted, the total size distributions were obtained with three different instruments. The parts of the distributions for radii greater than 7 μ come from settling tunnel data. For radii from 0.34 to 7 μ the distributions are based on Royco particle counts. Below 0.34 μ condensation nuclei counts were used. The Royco and the settling tunnel data generally agree quite well with each other, particularly when the probable low counts of large particles with the Royco are considered. The condensation nuclei counts are consistent with the other data, but certain assumptions are necessary to combine them with the other size distribution data.

To obtain a rough idea of the nature of the size distributions for small radii, the condensation nuclei counts have been assumed to be constituted entirely of particles with radii between 0.01 and 0.1 μ and to be uniformly distributed over the interval. The Royco size distributions have then been extrapolated to 0.1 μ radius. This treatment of the data is similar to that used by Junge (1966). It is intended only to approximate the gross features of the distributon. The portions of the size distributons shown in Figs. 5 and 6 that are based on the condensation nuclei counts are represented by dashed lines. The representation is in terms of dN/dr, where N is the number per cm³ of particles with radii less than r. This is related to $dN/d\log_{10}r$ by the same relationship presented between dM/dr and $dM/d\log_{10}r$.

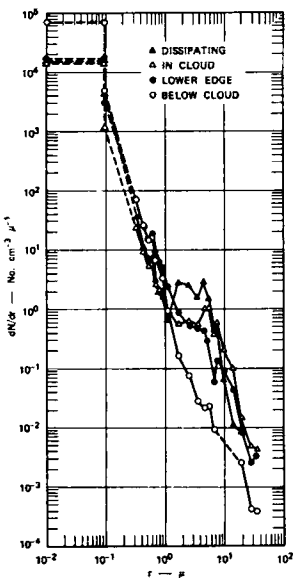

Fig. 5. Average size distributions.

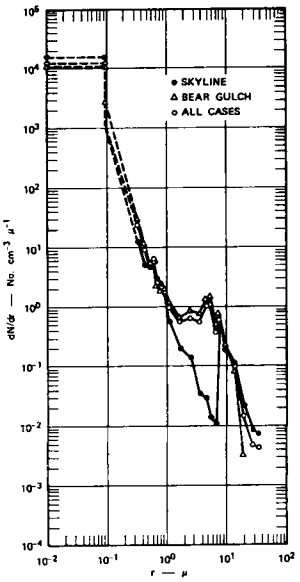

Fig. 6. Average size distributions in the cloud.

Fig. 5 shows the average size distribution based on data collected under several different types of cloud condition. The curve marked "below cloud" shows the size spectrum in the marine air below the stratus at the Skyline site. Data were collected for a total of about 5½ hours on five different days. A paucity of large droplets prevented the determination of the size distribution in the interval from 7 to 20 μ, marked by the dashed segment in the figure. The settling tunnel is more sensitive for the larger droplets, so their frequency could be determined. The droplet frequency is approximately proportional to $r^{-3.3}$ over the interval $0.3\ \mu \leq r \leq 4\ \mu$. The distribution over this size range is quite similar to that found on the coast of Oregon by Junge (1966) which suggests that these results may be representative of the eastern Pacific maritime aerosol. At the larger sizes ($r > 4\ \mu$) there were more droplets found than would have been expected from extrapolation of the power law size distribution. Consideration of probable losses at the larger sizes

counted by the Royco would accentuate the effect.

The curve marked "lower edge" in Fig. 5 shows the average size distribution observed at the bottom edge of the cloud. Samples were collected on five separate days, four at the skyline site, one at the Bear Gulch site. The six-hour total sampling time included about two hours at the Bear Gulch site.

For radii between about 0.3 and 2 μ, the average size distribution at the lower edge of the cloud is approximated by a power law with an exponent of about -2.8. Over this interval the size distribution is quite similar to that found below the cloud. Outside this radius interval there are fewer small particles and more large droplets. This change is to be expected, of course, as we move into the cloud.

The curve in Fig. 5 marked "in cloud" shows the average size distributions in the cloud for all the measurements made at the two different locations. Fig. 6 shows this curve and the averages for each of the two individual sites. The Skyline average represents a total of about three hours observation on two separate days. The Bear Gulch average is based on about $7\frac{1}{2}$ hours observation on five separate days.

The three curves shown in Fig. 6 are similar for radii less than 1 μ and greater than 7 μ. Between these two radii there is considerable difference between the Bear Gulch average and the Skyline average distribution. At present there is not sufficient data to determine whether there is some fundamental difference between the geography at the two locations which would cause the observed size distribution differences. Both locations have distributions that can be approximated by a power law distribution with an exponent of about -3 in the region $0.3\ \mu \leqslant r \leqslant 1\ \mu$. Both show secondary maxima in their frequency distributions, Bear Gulch at about 6 μ and Skyline at about 8 μ. The major difference between the two is that the Skyline distribution shows a very pronounced minimum at a radius of about 5 μ (allowing for the probable loss of droplets of the sizes counted by the uppermost Royco channels), while the Bear Gulch distribution has a shallow minimum between about 2 and 3 μ.

The average size distribution for the last cloud-type category is shown by the curve marked "dissipating" in Fig. 5. The data for this average were collected at the Bear Gulch site on three separate days for a total of about five hours of observation. The dissipation was generally caused by the stratus mixing with drier air above the marine layer as the air flowed upward over the coastal mountains. This effect was also accompanied by a general daytime heating. Relative humidities observed during these observation periods ranged from 81 to 99 %, but were generally above 90 %.

For radii less than 1 μ, the size distribution observed during cloud dissipation is very nearly the same as that found within the stratus at the same site, Bear Gulch. For $1\ \mu \leqslant r \leqslant 6\ \mu$, there were more particles observed during the dissipation phase than were found in the cloud. For the larger sizes the situation is reversed. The secondary maximum found during dissipation is at a smaller radius and is broader than was found in the developed cloud.

Discussion

Although condensation processes involving a spectrum of nuclei are enormously complex, several authors have treated the subject theoretically with reasonable rigor. The work of Neiburger and Chien (1960) provides an interesting basis for the interpretation of the data presented here. They have calculated droplet spectra on the basis of cloud cooling rates of 6°C/hr, which is greater than generally found during marine stratus formation. Their calculations are based on reasonably realistic nuclei size distributions. They include the feedbacks between condensation and supersaturation and use accurate representations of the microphysical processes, including solution and curvature effects as well as the transfer of heat and water vapor. Besides cooling rate, the principal point at which Neiburger and Chien's calculations may be unrealistic is in their choice of initial nuclei. The size distribution was chosen carefully to correspond with observations, but the composition was taken to be entirely sodium chloride. The data discussed earlier in this paper, and data from many other sources (see, e.g., Junge, 1963), make it clear that NaCl is only a fraction of the total aerosol material.

Figs. 7 and 8 show the results of the Neiburger–Chien calculations. In both figures the calculations were based on the 6°C hour^{-1} cooling rate, starting from 288°K and 75 % RH. The difference between the two is in the assumed initial

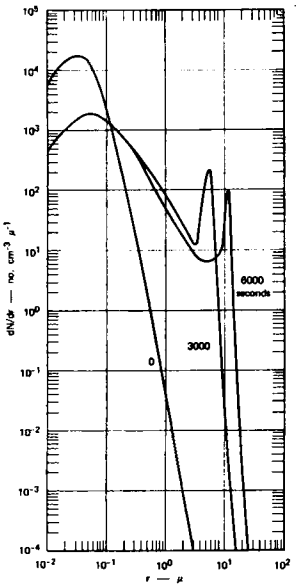

Fig. 7. Neiburger–Chien (1960) calculated size distributions, Stratus Case A.

nuclei distributions: case A (Fig. 7) has fewer of the larger nuclei than case B (Fig. 8). The two nuclei distributions result in droplet spectra that are quite similar. Both cases result in spectra with secondary maxima at a radius of about 5 μ after 3000 sec and about 12 μ after 6000 sec. These secondary modes are somewhat less pronounced for the case with the fewer large nuclei. Mason (1960) has pointed out that all the droplets in a stratus cloud do not have the same growth history; mixing with air outside the cloud causes the removal of droplets and the introduction of fresh nuclei. Thus, according to Mason, the cloud consists of droplets that have been growing for a wide variety of time periods, rather than all having equal growth periods as in the Neiburger–Chien calculations. The assumption of a variety of growth periods leads to a much broader secondary mode in the size distribution. It also tends to stabilize the size distribution so that the peak does not continue its rapid shift to larger sizes with time. Mason's assumptions lead to a broad secondary peak at a radius of about 3 μ. The distribution appears to change only slightly with time after 3000 sec.

It is obvious that there are both similarities and differences between the observations and the theoretical calculations. The most pronounced difference is between the observed and calculated concentrations for the large droplets. The model concentrations calculated by Neiburger and Chien and by Mason are from tens to hundreds of particles per cubic centimeter per micron of radius. The observations show only a few percent of this number. For the larger sizes, e.g., radii around 20 μ, the calculations and observations are in much better agreement.

One of the reasons for the discrepancy between the Neiburger–Chien calculations and the observations may be the cooling rate used in the calculations. Six degrees centigrade per hour is a much more rapid cooling rate than is usually found during the radiative cooling accompanying the stratus formation. The more rapid cooling should result in the activation of more nuclei with consequent greater numbers of droplets formed. Some size distribution differences might also result.

Another possible reason for the smaller number of droplets is probably the fact that the number of nuclei available for droplet formation is substantially less than the number used in the calculations. Where the calculations assumed the entire initial nuclei population to consist of hygroscopic sodium chloride, observations indicate that a substantial fraction of the material is not salt. For radii less than about 1 μ, the

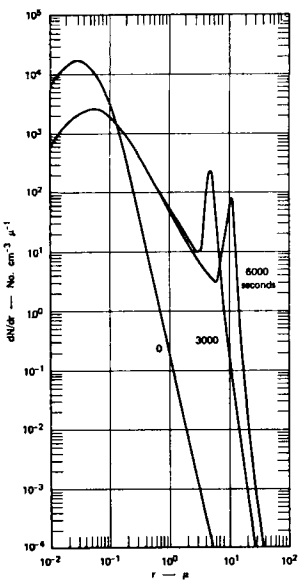

Fig. 8. Neiburger–Chien (1960) calculated size distributions, Stratus Case B.

observed size distributions agree quite closely with the initial nuclei size distributions used by Neiburger and Chien, although the observations were taken after cloud formation rather than before. It appears that many of the nuclei do not participate as actively in the cloud formation process as the calculations show. This, of course, is consistent with the chemical data.

Intuitively, we might expect that, if fewer nuclei are activated to droplet growth, those that are might grow to larger size. The data provide some support for this notion, in a relative sense at least. For 6000 seconds the Neiburger–Chien calculations show five orders of magnitude difference between the modal radius (about 12 μ) concentration and the 20 μ radius concentration for the stratus case type A and about $3\frac{1}{2}$ orders of magnitude for stratus case B. The observations show differences of about 2 orders of magnitude. The absolute observed concentrations at 20 μ are somewhat greater than those calculated for stratus A and somewhat less for stratus B.

The droplet size at which the secondary mode in the frequency distribution has been observed is in reasonably good agreement with the calculations. For developed clouds the observations show modes around 6 to 8 μ radius. The Neiburger-Chien calculations show the mode shifting from about 5 μ to about 12 μ between 3000 and 6000 sec after development begins. The Mason calculations show the mode at about 2 to 3 μ. The observations taken in dissipating clouds show the mode to be at smaller sizes. The mixing of cloud and noncloud air during the dissipation phase may more nearly match the assumptions that Mason used in developing his model.

Some other observations of droplet size distributions in stratus are available in the literature, but they do not generally include measurements at submicron sizes. Neiburger & Chien (1960) present three examples collected from a blimp, but they do not give the details of how the samples were collected and analyzed. They observed modes around radii of 4 or 5 μ and modal concentrations of about 50 to 150 droplets $cm^{-3}\mu^{-1}$.

Pedersen & Todsen (1960) used a cascade impactor to obtain droplet distributions over periods of 10 sec or less in stratus outside Oslo at an elevation of 500 m. The average of ten observations taken at wind speeds less than 4 kt has a mode at a radius of about 3.5 μ with a concentration of about 6 droplets $cm^{-3}\mu^{-1}$. For eight cases at wind speeds greater than 4 kt, the mode came at about 2.5 μ and about 30 droplets $cm^{-3}\mu^{-1}$.

Eldridge (1961) observed fogs with a particle counter based on the same principle as the Royco, but designed to be more suitable for sampling large droplets. He used 20-second sampling periods. His data do not show evidence of a secondary mode, but the drop-size classes are rather coarse in the 2 to 10 μ interval where such a mode might be expected. He sized droplets from 0.5 to 32 μ over intervals of 0.5–1 μ, 1–2 μ, 2–4 μ, etc. This may not have provided sufficient size resolution to detect a secondary mode unless it was quite pronounced. The average concentration of droplets in the 4–8 μ class was about 130 cm^{-3}. This is an average of about 33 $cm^{-3}\mu^{-1}$ over the interval.

May (1961) collected fog samples with a two-stage impactor for periods up to about a minute. The size range covered by his data was from radii of about 0.5 μ to about 50 μ. He says that a minority of his distributions were bimodal with peaks around $r = 1$ μ and around $r = 10$ μ. His complete data are not presented, so that it is not possible to determine the frequencies at the mode, but his total concentrations ranged from about one to a thousand drops per cubic centimeter.

Webb (1956) measured droplet distributions in fog by a photographic technique where about 1 cm^3 of air constituted the sample. He presents four samples of fog distributions with modes varying from a radius of about 5 μ to about 13 μ and modal concentrations from about 5 $cm^{-3}\mu^{-1}$ to greater than 100.

The above recital of results from other studies is not complete, but serves to illustrate the fact that bimodal distributions are not uncommon, but are not universally observed though theory says they should be expected. When a second mode occurs it seems to be most commonly found at a radius between about 3 and 12 μ. The droplet frequencies observed in the hills south of San Francisco are generally smaller than those cited above, but this may reflect the longer sampling periods, during which the cloud had a chance to display its full range of inhomogeneities. The short-period samples typical of the other studies may have been selectively collected during the periods when the cloud was thickest.

The data have shown that there is great variability in stratus droplet size distribution and concentration. Some examples reported in the literature have shown a bimodal distribution. Other observations do not show the second mode. The difference could well reflect differences in the nuclei population that initiates the cloud growth. Certainly the data collected during this study show that the sulfur compounds and chlorides are not found in equal proportion over the entire range of particle and droplet sizes. Others have found much variety in the chemical composition of fog water from time to time and place to place (e.g., Miyake, 1948; Houghton, 1955; Mrose, 1966; Okita, 1968), but have not studied changes with droplet size.

The distribution of sulfate with particle size parallels the droplet size distribution, greater amounts of sulfate being found at the larger and smaller sizes and a minimum between. It appears that the activity of the sulfates as droplet nuclei is largely a size-dependent property. The small sulfate particles are inactive and grow little. The larger particles are active and grow to larger droplets, leaving a minimum in the spectrum between the growing droplets and the inactivated particles. The distribution of the chlorides does not show a minimum between active and inactive nuclei. Although the sodium chloride found in sea salt should form quite active nuclei at the larger sizes, the evidence shows that there is relatively little chloride associated with the larger droplets. Robbins *et al.* (1959) have proposed an atmospheric reaction that could account for this dearth of chloride in the larger droplets. They suggested that HNO_3 vapor is formed from NO_2 by hydrolysis. The HNO_3 then is absorbed quickly by the solution droplets and reacts with NaCl to release HCl vapor. The process is more efficient with the more dilute droplets. The more dilute droplets are the larger ones, so the reaction would preferentially remove chlorides from the larger droplets. The reaction reaches equilibrium in a matter of minutes so there should be sufficient time between stratus formation and sample collection for the larger droplet chlorides to be lost as HCl. This reaction would increase nitrate concentrations with droplet size, and future studies should investigate the amounts of this anion as a function of droplet size.

The results of this program emphsize the importance to cloud formation of the total numbers of available nuclei and their constituent materials. These factors must certainly be important to the size spectrum that develops in a cloud and may well account for differences in observed size distributions and differences between observation and theory.

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НАБЛЮДЕНИЯ АЭРОЗОЛЕЙ И КАПЕЛЬ В СЛОИСТЫХ ОБЛАКАХ В КАЛИФОРНИИ

В течение лета 1968 г. в холмистой местности к югу от Сан-Франциско проводилась программа измерений аэрозоля и облачных капель в слоистых облаках. Распределение по размерам определялось с помощью счетчика частиц Ройко, использующего принцип рассеяния света, счетчика ядер конденсации и заборной трубы. Два шестикаскадных датчика использовались для сбора проб для анализа на серные и хлоридные компоненты. Данные о распределении по размерам указывают на существование субмикронной фракции. Вторичные моды встречаются с радиусами от приблизительно 6 до 8 мкм в развивающихся облаках, а несколько меньшего размера частицы — в периоды рассеяния облаков, аэрозоль ниже облаков не имеет вторичной моды для больших размеров. Положение этой вторичной моды согласуется некоторыми теоретически рассчитанными распределениями, однако, наблюдавшиеся концентрации порядка 1 капли на см³ на 1 мкм радиуса в этой моде существенно меньше рассчитанных. Одна из возможных причин заключается в смешанном химическом составе ядер, другая — в высоких скоростях охлаждения, используемых для расчетов. Наблюдения указывают на присутствие органического материала и на неоднородность в распределении серных компонент и хлоридов в спектре капель по размерам. Среднее отношение серы к хлоридам меняется от, приблизительно, 4 для $r = 0{,}2$ мкм до 0,4 для $r = 2$ мкм и до 1,3 для $r = 4$ мкм. Сделан также краткий обзор некоторых других исследований туманов и капель в слоистых облаках.