

The Effects of Desert Particles Coated with Sulfate on Rain Formation in the Eastern Mediterranean

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ABSTRACT

Measurements of aerosol composition in the eastern Mediterranean reveal that sulfate is found in most aerosol particles. Some of the large particles contain mixtures of chemicals such as sulfate and sea salt. The most striking observation is the discovery that mineral dust particles often get coated with sulfate and other soluble materials. The amount of soluble material on these particles is found to be related to their surface area, suggesting that the deposition process could be surface dependent. The mechanism by which sulfate is found on some of the mineral dust particles is believed to originate from evaporating cloud drops, which were originally nucleated on sulfate cloud condensation nuclei (CCN) and subsequently collected dry interstitial mineral dust particles. The presence of soluble material on mineral dust particles, converts the latter into effective giant CCN. This is further corroborated by the fact that the few large drops near the bases of convective clouds near the coast of Israel sometimes contain both dust and sulfate. Calculations show that the presence of such large CCN could be instrumental in producing large drops (20–40 μm), which would accelerate precipitation development through drop growth by collection. Ice crystal concentration in these types of clouds was found to be much higher than expected based on previously reported measurements of ice nuclei. These high concentrations are believed to be produced by one or more of the ice multiplication processes such as the Hallett–Mossop mechanism and/or the enhanced nucleation of ice under supersaturation conditions. Both ice multiplication mechanisms are possible when large drops are formed. These findings point out that many of the rain clouds in this region have mixed characteristics (between maritime and continental).

Since cloud seeding with ice nuclei attempts to increase ice crystal content in the clouds in order to enhance rain, the use of such seeding techniques in these clouds seems to be fruitless since any additional ice would not enhance rain or may even reduce it.

1. Introduction

The composition and concentration of aerosol particles in the atmosphere affect cloud growth and rain development in a number of ways. When the concentrations of cloud condensation nuclei (CCN) are high, clouds of continental character develop (e.g., Pruppacher and Klett 1979). In these clouds, water drops with narrow size spectra (maximum size smaller than 20 μm) and high concentrations (more than about 600 cm^{-3}) are formed. Such composition limits cloud drop growth by collection and inhibits the production of large drizzle drops. Rain normally falls from such clouds when they manage to develop to high altitudes where the temperature is far below the freezing level

and where ice production through ice nucleation becomes effective (Gagin 1975).

In contrast, conditions in which the atmosphere consists of relatively low concentrations of soluble aerosol particles result in the development of maritime-type clouds whose drop concentrations are low ($<200 \text{ cm}^{-3}$) and in which the size spectra are wide (often drops larger than 40- μm radius are found). These clouds rapidly develop large drops through the collection process, and rain can form even when the clouds contain no ice (e.g., Pruppacher and Klett 1979; Rogers and Yau 1989). Of course, in tropical regions or in other humid environments, latent heat release by condensation during hydrometers' growth and strong inflow by larger-scale circulation can drive the clouds to heights at which the temperature is low enough for ice to form. Measurements in such clouds indicate that the concentrations of ice particles far exceed those expected to form by nucleation on the observed ice nuclei (e.g., Mossop and Ono 1969; Hobbs 1969; Mossop and Hallett 1974; Hobbs 1974; Hallett et al. 1978; Rangno and Hobbs 1990). Some have argued that the high concentrations of ice crystals result from secondary ice

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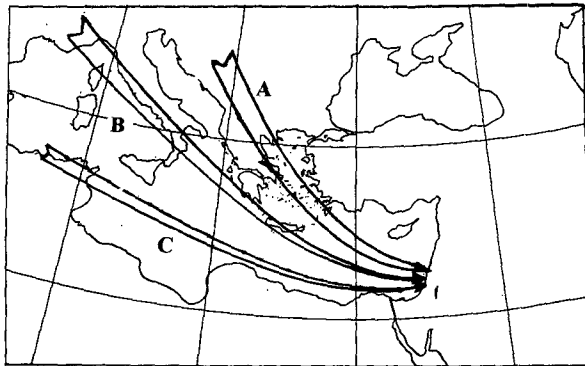


FIG. 1. Typical air mass trajectories that produce rain clouds in the eastern Mediterranean.

processes (e.g., Hallett et al. 1978), while others have suggested that primary ice formation processes could be counted upon to explain the discrepancy (Rangno and Hobbs 1990).

The classification into maritime and continental clouds is, of course, an oversimplification of the real natural situation. Most cases fall somewhere in between these two extreme categories. Aerosols (CCN) having lower concentrations and a wide variety of sizes are often found, and their effect on cloud microstructure is more complex than has been described above.

Aerosols affecting cloud growth are generally soluble and of about 0.1–1.0 μm in diameter (e.g., Rogers and Yau 1989). Most are composed of sulfates or nitrates (e.g., Radke 1982; Leitch et al. 1982), even though other types of salts are sometimes present. These small particles are effective CCN because they rapidly reach their critical size under relatively low supersaturations. Even though larger soluble particles need lower supersaturation to reach their critical size, their effect on cloud growth is normally small because their number is relatively low and because the time required to reach their critical size is long.

In section 4 we present results of measurements of the chemical composition of individual aerosol particles in the eastern Mediterranean together with some in-cloud measurements of drop sizes and ice crystal concentrations. These two types of measurements, even though only preliminary, shed more light on the effects of aerosol composition and size on the formation of clouds and rain in this area and possibly in other semiarid regions around the world.

2. Clouds in the eastern Mediterranean

Based on measurements in isolated developing convective clouds over Israel, Gagin (1975) argued that rain clouds in this region are continental. His argument was based on the fact that the air masses reaching the eastern Mediterranean contain aerosols of anthropogenic origin from Europe. Since desert particles are not

effective CCN, the high concentrations of soluble aerosols from Europe make the clouds over Israel continental, with high drop concentrations (over 700 cm^{-3}) and narrow size spectra (the largest drop was $<20\ \mu\text{m}$). In addition, using an ice collecting and replicating system, low ice crystal concentrations were observed (around 1 L^{-1} at -20°C) and were found to correlate well with the concentrations of ice nuclei (IN). It was argued that the general agreement between the ice crystal concentrations and the IN activity spectrum was one more indication of the continental nature of the clouds. This was based on the findings of Hallett and Mossop (1974) that drops of sizes greater than $23\ \mu\text{m}$ at the temperature range of -5° to -8°C need to be present together with some graupel particles for ice multiplication to take place. Gagin's argument was that drops of this size are not found at that level in the clouds over Israel since their initial size spectra are very narrow, preventing them from rapidly growing by collection, as they ascend from cloud base (around 4° – 5°C).

It is worth noting that the continental nature of the clouds over Israel was one of the main physical explanations for the success of the Israeli cloud seeding experiments I and II (see Gagin and Neumann 1974, 1981).

More recently, however, Rangno (1988) has questioned the observations of low ice concentrations in the clouds over Israel and pointed out that in many cases ice concentrations of about 1 L^{-1} are present in clouds whose tops are warmer than -10°C . If IN activity is any indication of the presence of ice in clouds, ice crys-

TABLE 1. Calibration curves for various elements, using two different acceleration voltages in the electron microscope, as obtained by the method described in the appendix.

Element	Kilovolts	Calibration equations
S	15	$M_{\text{Na}} = 10^{-11.455}(N_{\text{Na}})^{0.777}$
	25	$M_{\text{Na}} = 10^{-10.998}(N_{\text{Na}})^{0.772}$
Na	15	$M_{\text{S}} = 10^{-11.069}(N_{\text{S}})^{0.761}$
	25	$M_{\text{S}} = 10^{-10.363}(N_{\text{S}})^{0.772}$
K	15	$M_{\text{K}} = 10^{-11.273}(N_{\text{K}})^{0.793}$
	25	$M_{\text{K}} = 10^{-10.770}(N_{\text{K}})^{0.773}$
Mg	15	$M_{\text{Mg}} = 10^{-11.042}(N_{\text{Mg}})^{0.782}$
	25	$M_{\text{Mg}} = 10^{-10.626}(N_{\text{Mg}})^{0.787}$
Ca	15	$M_{\text{Ca}} = 10^{-11.301}(N_{\text{Ca}})^{0.778}$
	25	$M_{\text{Ca}} = 10^{-10.912}(N_{\text{Ca}})^{0.757}$
Fe	15	$M_{\text{Fe}} = 10^{-10.890}(N_{\text{Fe}})^{0.769}$
	25	$M_{\text{Fe}} = 10^{-10.623}(N_{\text{Fe}})^{0.761}$
Cl	15	$M_{\text{Cl}} = 10^{-11.292}(N_{\text{Cl}})^{0.759}$
	25	$M_{\text{Cl}} = 10^{-10.812}(N_{\text{Cl}})^{0.773}$
Al	15	$M_{\text{Al}} = 10^{-11.498}(N_{\text{Al}})^{0.776}$
	25	$M_{\text{Al}} = 10^{-10.925}(N_{\text{Al}})^{0.768}$
Si	15	$M_{\text{Si}} = 10^{-11.392}(N_{\text{Si}})^{0.768}$
	25	$M_{\text{Si}} = 10^{-10.821}(N_{\text{Si}})^{0.767}$

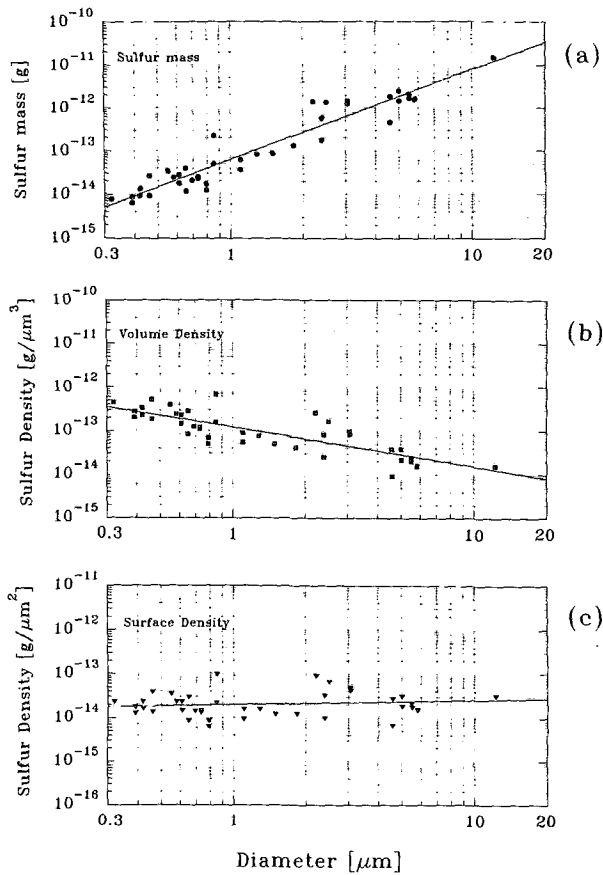


FIG. 2. (a) Mass of sulfur, (b) sulfur volume density, and (c) sulfur surface density, as functions of particle diameter, from measurements aboard a ship in the Mediterranean west of the coast of Israel at 1600 LT 18 November 1991.

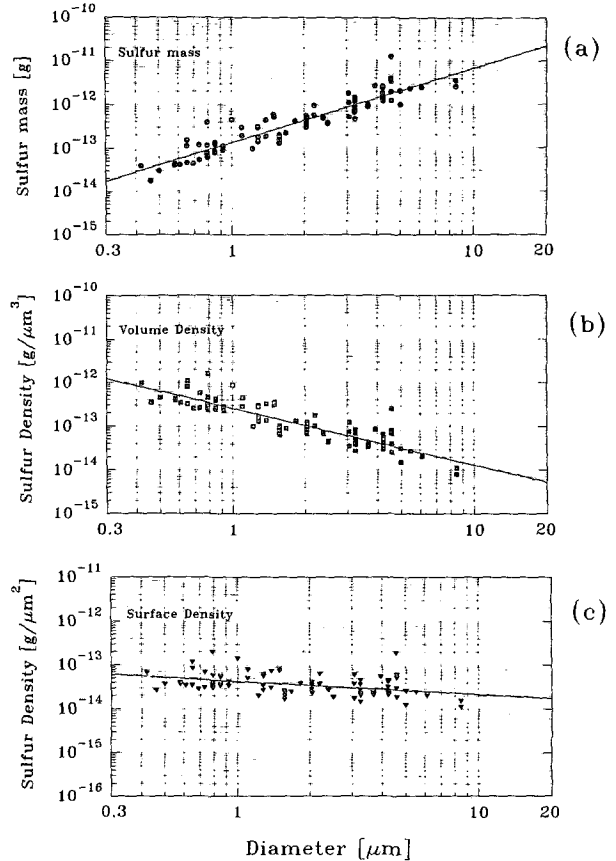


FIG. 3. The same as Fig. 2 but at 1600 LT 19 November 1991.

tal concentrations in the clouds over Israel should have been less than 0.01 L^{-1} at -10°C .

More questions regarding the continentality of the clouds over Israel were raised in the work of Levin et al. (1990). In their measurements the composition of the aerosols inside cloud drops near the bases of convective clouds was analyzed. They pointed out that the presence of sulfate and other chemicals in the drops depended on the origin of air mass trajectories, as analyzed by using 750-mb synoptic maps. Air masses coming to Israel directly from Europe (schematically shown in Fig. 1, trajectory A) contained less mineral dust with a higher fraction of sulfate particles. In contrast, drops in clouds whose air mass trajectories passed over North Africa (Fig. 1, trajectory C) contained sulfate but also more mineral dust particles. In fact, the sulfur mass in these latter trajectories was considerably higher than in clouds formed in a northwesterly flow. Based on these measurements it was suggested that these differences could have some significance for the microphysical development of the clouds.

In this paper the connection between the aerosol composition and the microstructure of the clouds is explored further.

TABLE 2. Averaged best-fit lines to the sulfur mass, sulfur volume density, and sulfur surface density as functions of particle diameter, as measured on board a ship on the Mediterranean Sea during winter, summer, and from a research airplane just below the bases of convective clouds over Israel.

	Period of sampling	Average best-fit curve
Shipborne sampling	Summer (Jun 1991)	$M_s = 10^{-12.97} D^{1.798}$ $SD_s = 10^{-13.813} D^{-0.217}$ $VD_s = 10^{-13.276} D^{-1.217}$
	Winter (Nov 1991)	$M_s = 10^{-13.04} D^{1.618}$ $SD_s = 10^{-13.543} D^{-0.251}$ $VD_s = 10^{-12.765} D^{-1.208}$
Airborne sampling	Winter 1990 (Jan, Feb, Mar)	$M_s = 10^{-12.85} D^{2.183}$ $SD_s = 10^{-13.348} D^{0.18}$
	Winter 1991 (Jan)	$VD_s = 10^{-12.59} D^{-0.82}$

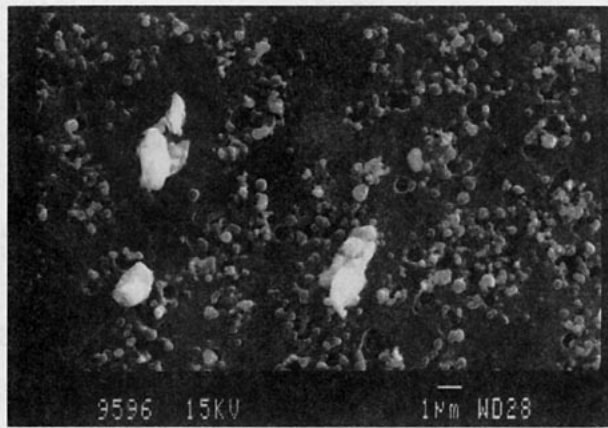


FIG. 4. A photomicrograph of a desert mineral dust with small sulfate particles on its surface, collected on polycarbonate membrane.

3. The measurements: Instrumentation and technique

Aerosol composition and size spectra have been measured sporadically during the last eight years on the top of Mount Meron (1100 m MSL) in the middle of the Galilee, Israel (during winter and spring of 1987/88), on a ship on the Mediterranean Sea (during early summer of 1990 and 1991 and during winter of 1991) and from airplanes below and inside convective clouds (during the winters of 1990/91, 1991/92, and 1994/95) in Israel.

The ground and shipborne measurements included standard meteorological parameters of temperature, humidity, and wind speed, as well as an analysis of the elemental composition of individual aerosol particles, collected on electron microscope grids placed in a cascade impactor. Each set of aerosol samples was composed of grids coated in a number of ways. One grid was coated with a thick layer of carbon in order to determine aerosol particle shape and identify whether the particles are coated with water. [Levin et al. (1990) pointed out that a thick water layer around the aerosol particle leaves a circular imprint on the grid.]

The sulfur content of individual particles was determined by a method previously described and calibrated (Levin et al. 1990; Pardess et al. 1992) using laboratory-generated aerosol particles of known sizes and composition, and a scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer. Recently, the calibration, in a modified form, has been extended to include other elements such as Na, Cl, Mg, K, Fe, and Si, which are found in some of our samples. A brief description of the calibration method is given in the appendix. Table 1 presents the calibration equations obtained for these elements.

Aerosol size was determined using an optical spectrometer PMS CSAS-100. A Cassella cascade impactor was used to enable a qualitative but easy classification

of the chemical composition based on size. Particle size was measured from the image of the particle on the grid as seen through the SEM. Since most large particles are not spherical, their size was determined by the diameter of the circumscribed sphere.

The procedure for the analysis was as follows: after the size of the particle was determined, the X-ray emission spectrum was measured for a set time (usually 100 s). The number of counts for S, Na, and the other elements was recorded as a function of particle size and then converted to mass, using the calibration equations from Table 1 [see Pardess et al. (1992) for more details].

The presence of S in the particles does not necessarily mean that the particles contain sulfate. Other less soluble compounds such as gypsum are known to exist in desert minerals (e.g., Levin and Lindberg 1979; Foner and Ganor 1992; and Ganor 1991). In order to better identify the compounds in the particles, aerosol samples have often been collected on grids coated with

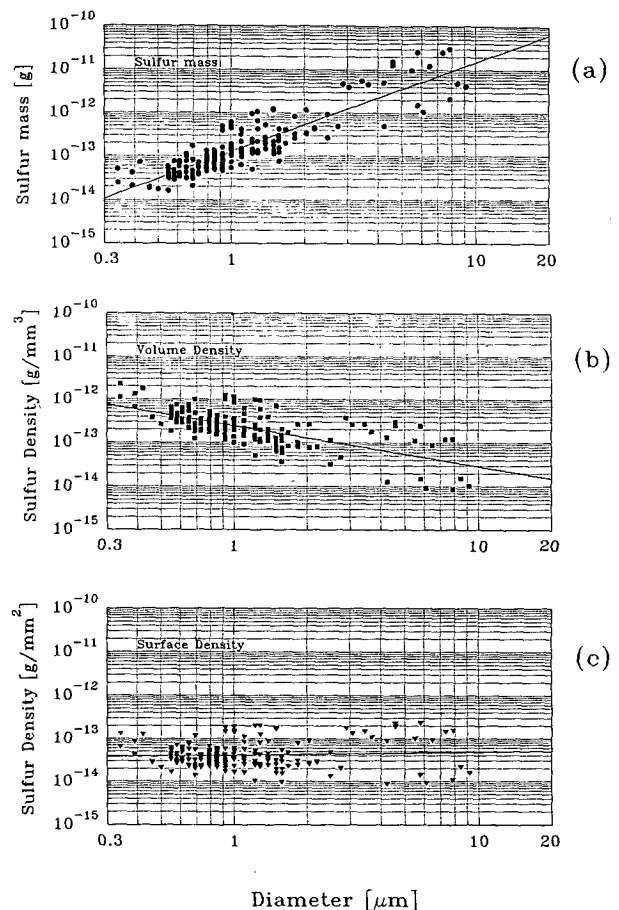


FIG. 5. (a) Mass of sulfur, (b) sulfur volume density, and (c) sulfur surface density, as functions of particle diameter, from airborne measurements below the bases of convective clouds over Israel on 15 March 1992.

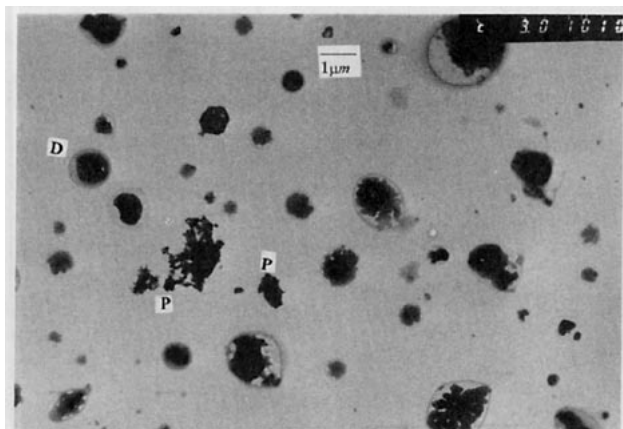


FIG. 6. A TEM photomicrograph of drops and aerosol particles collected on Mount Meron inside clouds. Note the coexistence of drops (D) and dry interstitial particles (P).

BaCl_2 . The reaction of sulfate-containing particles and BaCl_2 results in a chemical reaction that forms BaSO_4 , which could easily be identified under a transmission electron microscope (Mamane and de Pena 1978; Bigg et al. 1974). Because this method is very time consuming, we only used it on some of the samples to confirm that the particles contain sulfate. In most cases we simply assumed that the coexistence of Ca and S is an indication for the presence of gypsum.

The airborne measurements included cloud drop spectra using a PMS FSSP-100 probe. Ice crystals were identified using a PMS 2D-C probe. Aerosol samples were also collected by the airplane through a sampling tube extending out of the plane's boundary layer. A bend in the sampling tube inside the plane, which was necessary for collecting the particles, prevented us from correctly sampling particles greater than about $5 \mu\text{m}$.

Temperature was measured by a reverse flow thermometer. Since the Johnson-Williams hot-wire instrument malfunctioned on most of the flights reported here, the liquid water content (LWC) was calculated by integrating the measured drop spectra from the FSSP. Being aware that this method underestimates the LWC, we used it only for relative comparisons between clouds.

4. Results of measurements

a. Surface and airborne measurements outside the clouds

The few measurements that we conducted using the BaCl_2 method indicated that the S in most particles was in the form of sulfate. We arrived at this conclusion since most of the particles that contained S reacted with the Ba in the coating to form BaSO_4 . The presence of S in the particles could be divided into five categories: 1) S without any other identifiable elements, which are

assumed to be particles of ammonium sulfate, sulfuric acid, or ammonium bisulfate; 2) S associated with Na, Cl, and Mg, which are assumed to be of marine origin; 3) S associated with Ca (sometimes other elements were present also), suggesting the presence of gypsum; 4) S found together with Si, which implied interaction between soluble sulfate and desert minerals; and 5) S with Na, S with K, and S with Fe, which suggested that the particles are from some distant industrial sources.

Surface measurements taken west of the coast of Israel showed that the amount of sulfur in individual particles increases with particle size (e.g., Figs. 2a and 3a). This is an expected result because if the particles are made of sulfur, larger particles would contain larger masses of sulfate. However, sulfur density (the sulfur mass divided by the volume of the particle; Figs. 2b and 3b) decreases with increasing particle size. These graphs imply that many of the particles are of mixed composition, in which sulfate is only one of the components. The same dependence of sulfur on particle size was observed in all our surface measurements, and Figs. 2 and 3 are just typical examples. Table 2 represents the average best-fit curves to the data collected during early winter above the sea surface. For comparison, we also included in Table 2 the average best-fit curves from measurements taken during the summer (June) of 1991. Even though the coefficients of the best-fit curves are different, the general behavior is somewhat similar.

Using our calibration curves (Pardess et al. 1992 and Table 1), we observed that while most of the smaller particles ($<1 \mu\text{m}$) consist of sulfate alone, some of the larger particles consist of mixtures of sulfate and NaCl or mineral desert aerosols coated with sulfate (see Fig. 4). The surface density of sulfur, obtained by dividing the sulfur mass by the surface area of the particles (Figs. 2c and 3c), remains fairly constant with particle size. Thus, the mechanism responsible for sulfate deposition on desert particles depends more strongly on the surface area, or on D^2 , than on processes that have different dependence on size.

Measurements conducted below cloud base indicated that here too sulfate mass increases with particle size (Fig. 5a), volume density decreases with size (Fig. 5b), and surface density remains fairly constant (Fig. 5c). Many of these particles also contained NaCl or other soluble compounds. In contrast to S, whose surface density is independent of size, Si and other desert minerals have a constant value when the volume density is plotted against particle diameter. In Table 2 we also present the average best-fit curves to the sulfur data collected below the bases of convective clouds during the winters of 1990 and 1991.

Measurements carried out during airflow from the northwest, namely, directly from Europe, showed somewhat different particle compositions. The sulfate concentration was still very high, but particles of desert origin were more rare, even though not completely ab-

TABLE 3. Measurements of drop concentrations at cloud bases in Israel.

Date (cloud No.)	Altitude (ft)	Temperature (°C)	Max. drop conc. (cm ⁻³) with diameter 2–47 μm	Max. drop conc. (cm ⁻³) with diameter 20–47 μm
3 January 1990 (cloud D)	5000	4	70	2
3 January 1990 (cloud E)	5000	0	80	0.1
6 February 1990 (cloud A)	3000	5	100	0.4
6 February 1990 (cloud E)	3000	7	500	8
6 March 1990 (cloud A)	3500	5	500	10
6 March 1990 (cloud A)	3500	6.5	400	8
22 February 1995 (cloud A)	3000	3.5	170	0.3
22 February 1995 (cloud C)	3500	10	254	0.7
3 March 1995 (cloud A)	4000	3.8	291	2.7
3 March 1995 (cloud B)	4000	3.5	236	0.3
3 April 1995 (cloud A)	4000	4.7	560	1.5
3 April 1995 (cloud B)	3880	4.2	525	5.8
3 April 1995 (cloud D)	4400	3.6	557	7.9
3 April 1995 (cloud J)	5000	2	740	21
3 April 1995 (cloud M)	4800	3.9	638	130

sent. In addition, higher relative concentrations of other particles containing Na, Cl, and Mg were also present. Most particles were small, and only rarely have particles greater than 5 μm been observed.

b. Measurements in clouds

Our in-cloud measurements at the mountain station included the analysis of individual particles and cloud drops. In spite of the fact that these measurements did not include CCN spectra, they provided a way to identify the role of the aerosols in the formation of the cloud drops. Figure 6 is a photomicrograph of particles and drops collected at the base of a convective cloud. The aerosols and the drops were allowed to impact on an electron microscope grid with a heavy carbon coating (Levin et al. 1990). The analysis suggests that most cloud drops near cloud base contain sulfate. Larger drops often contain other salts such as NaCl, suggesting the presence of sea salt from marine origin. The most striking feature was the presence of dust particles together with sulfate in some of the larger drops, mostly in drops larger than about 10 μm.

Often, on the same EM grids, wet aerosols (inside drops) and dry particles were observed. They were distinguished from each other by the round imprint around

the wet particles, as seen in Fig. 6. The dry particles were always made of mineral dust, and they are believed to be interstitial particles made of nonhygroscopic materials.

We also conducted airborne measurements using our Aerocommander research airplane. Table 3 presents a summary of the maximum total concentrations of drops measured near cloud base. To illustrate the width of the distributions, the concentrations of the drops larger than 20 μm is shown. Figure 7 represents an example of cloud drop spectra measured during a flight on 6 March 1990 in a cloud that was part of a postfrontal system. The measurements were conducted at an altitude of 5000 ft, about 200 m above the base of what appeared to be a developing convective cloud. No precipitation was observed during the measurement. Figure 7 represents a pass through the cloud lasting about 60 s (each size distribution is for 1 s or a distance of about 70 m). Two definite cells are seen in the data, with one showing relatively wide drop size spectra with some drops larger than 20–30 μm. Drop concentrations in this instance were about 250–400 cm⁻³. In contrast to previous reports (Gagin 1975), the spectra suggest that these clouds are of a mixed nature, partly continental and partly maritime. They contain higher

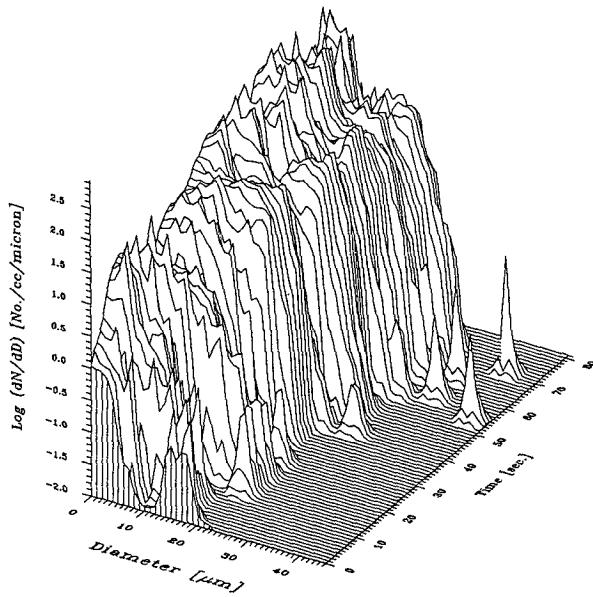


FIG. 7. Cloud drop spectra as measured during a flight near cloud base on 6 March 1990.

concentrations than are normally found in maritime clouds, but their wide spectra with few relatively large drops take them out of the continental category.

On the other hand, there were some in-cloud measurements that showed different spectra. For example, Fig. 8 represents the drop size spectra measured on 6 February 1990 at 3000 ft about 100–200 m above the base of a convective cloud. The figure represents a slice of about 50 s through the cloud. Again we see two distinct cells, both exhibiting narrow drop spectra, with drops seldom exceeding $18 \mu\text{m}$. Even though the widths of the spectra resemble continental clouds, the maximum drop concentrations were lower (about 420 cm^{-3}) than those normally reported for continental clouds.

These types of measurements continued during our 1995 winter experiment, where we carried out a number of in-cloud penetrations with our newly installed research aircraft (*Dash-7*), using the same equipment as on the *Aerocommander*. The relevant data is also listed in Table 3. We see that in most cases drops larger than $20 \mu\text{m}$ are present in concentrations of between 0.1 and 20 cm^{-3} , while the maximum total concentrations varied between about 70 and 700 cm^{-3} , with most cases below 500 cm^{-3} .

Preliminary measurements of ice crystal concentrations were also conducted, using the PMS 2D-C probe. This probe measures particles up to a size of about $800 \mu\text{m}$. The measurements were carried out in developing convective clouds in regions where the temperature was lower than -5°C and was most often near the -10°C level. Most of the particles appeared to be small crystals, but some larger graupel particles were also

identified. Large drizzle drops were sometimes observed, but they were seen mostly in cases when some rain was reported. Table 4 summarizes the ice crystal concentrations and the temperatures in which they were measured. Maximum ice crystal concentrations (only crystals larger than $90 \mu\text{m}$ were counted in this analysis) varied from cloud to cloud from more than 100 L^{-1} to as low as a few per liter at temperatures of -10° to -13°C in the clouds. Even though the reported ice crystal measurements are from different clouds than those for which the drop spectra is reported, it is interesting to note the high concentrations, which are in contrast to those expected in purely continental clouds.

5. Discussion

a. The aerosol particles

Even though the presence of sulfate on the mineral dust is interesting and important, and is a common feature in semiarid regions, the mechanism by which the coating is formed is not fully understood. The measurements at the bases of the convective clouds at Mount Meron give us some clues about it. We found that most cloud drops contained sulfate, which is believed to be the CCN that formed them. It is highly improbable that the mineral dust particles found in some of the drops were collected by collision with the drops since at that early stage drops are too small to be efficient collectors. It seems reasonable to conclude, therefore, that the particles themselves were the CCN that formed the drops. In other words, the aerosols in the free atmosphere consisted of the same chemical composition found in the drops. This is further corroborated by the results shown in Figs. 2, 3, and 5.

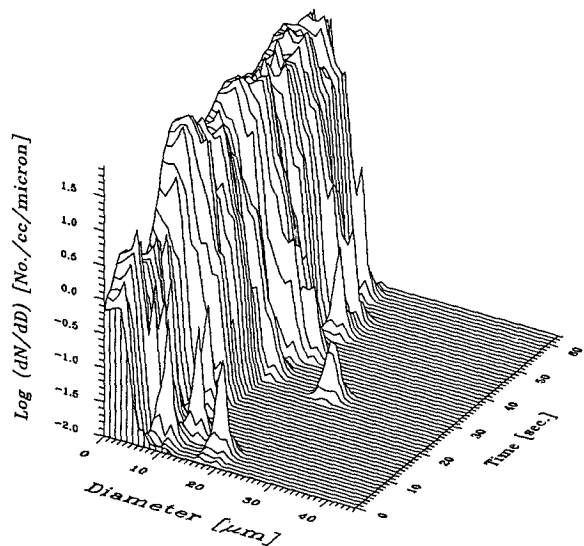


FIG. 8. Cloud drop spectra as measured during a flight near cloud base on 6 February 1990.

TABLE 4. Measurements of drops and ice crystal concentrations near cloud tops in Israel. Only crystals larger than $90 \mu\text{m}$ were counted.

Date (cloud No.)	Altitude (ft)	Temperature (°C)	Max. drop conc. (cm^{-3}) with diameter 2–47 μm	Max. ice crystal conc. (L^{-1})
3 January 1990 (cloud B)	13 500	-10	200	60
3 January 1990 (cloud C)	12 000	-6.5	450	50
1 February 1990 (cloud C)	14 000	-13	200	300
1 February 1990 (cloud D)	12 000	-10	400	100
6 February 1990 (cloud C)	12 000	-11	500	20
8 January 1990 (cloud A)	9500	-10	300	50

The above explanation also agrees with our measurements of pH of the cloud drops and the rain as measured on Mount Meron. As we reported before (Levin et al. 1990), small cloud drops were found to be mostly acidic, with pH as low as 2. The pH increased with drop size and drops as large as $8\text{--}10 \mu\text{m}$ had a pH of about 5 [see Fig. 9, which is based on the data of Levin et al. (1990)]. The increase in pH with drop size could be due to dilution following growth by condensation, but since the measurements were conducted near cloud base it is most probably a result of mixing acidic sulfate with more alkaline carbonates from desert dust.

It is interesting to point out that the low pH of the small drops indicates that the CCN were acidic and probably made of NH_4HSO_4 (ammonium bisulfate) or H_2SO_4 particles.

There are a number of possible sources for the sulfate-dust particles. They could originate from the soil

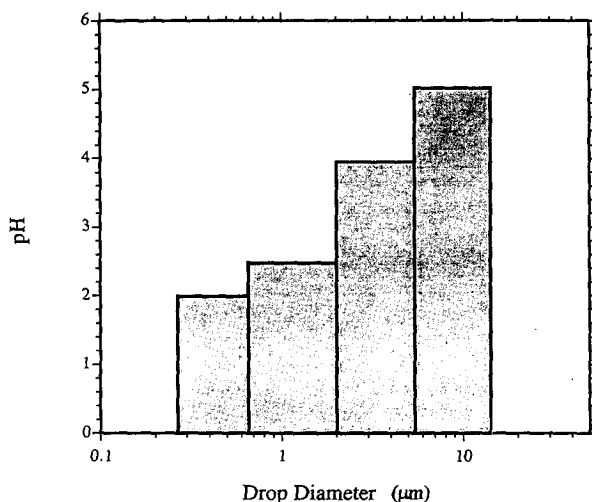


FIG. 9. The pH of cloud drops collected on Mount Meron [data taken from Levin et al. (1990)].

itself—for example, from dry lakes or from regions affected by rain with sulfate. These sources could not be completely ruled out, but it is difficult to see how they would produce sulfate coating on only a relatively few of the mineral dust particles in the air, as observed in our samples (e.g., Fig. 6).

Another possible mechanism is the coagulation of mineral dust particles with sulfate particles. Such interactions could occur if high concentrations of sulfate and sea salt particles in the atmosphere mix with air coming from the desert. Mixing of this type can happen when an air mass originating from Europe passes over the Mediterranean, circles around the low pressure region centered west of Cyprus, and then moves eastward over the southern portion of the sea and parts of North Africa. Desert dust originating from the latter also moves eastward on the same trajectory, bringing large quantities of dust to the Near East (Ganor 1991; Ganor and Mamane 1982; Prodi and Fea 1979). Even though the collision and sticking efficiencies are rather low, coagulation between two populations of particles is possible when the concentrations of both are high.

Deposition of sulfate on desert particles could take place by oxidation of SO_2 to SO_4 on the dry or slightly wetted surface of dust particles. Recent reports of measurements in the plumes of the Kuwait oil fires suggest that sulfate production increased dramatically in the presence of dust particles (P. V. Hobbs 1995, personal communication). The particle depicted in Fig. 4 is an example of something we believe could have been formed by coagulation of sulfate particles and desert dust or by oxidation on a dry mineral particle. This is so because electron micrographs sometimes reveal that the sulfate is present in a patchy form rather than in a uniform layer over the surface.

Another mechanism, and in our view the most probable one, is related to the nucleation of drops on sulfate CCN and the subsequent collection of mineral dust particles. The process that we propose is that the desert particles that we sampled were collected by cloud drops

that had originally been nucleated by sulfate or other soluble particles. Additional amounts of sulfate could have been produced in the drops by oxidation of SO₂. Upon evaporation, particles of dust coated with soluble materials were left behind. Since generally most clouds evaporate and do not precipitate (see Pruppacher and Klett 1979), most aerosols that get incorporated into cloud drops are released after drop evaporation, producing mineral dust particles with a coating of sulfate. It is possible, therefore, that many of the aerosol particles we collected had this type of history. The above mechanism provides a consistent picture with the observation of the aerosol composition as well as with the fact that only a few of the mineral dust particles had this type of coating on them.

b. The potential of the giant mixed particles as CCN

We can check the ability of the desert particles, which are coated with a layer of sulfate, to be efficient CCN. To help us with this evaluation, we plotted the elemental mass of individual particles, collected below clouds, which contain Si together with some soluble compounds. Figure 10 presents the mass as a function of diameter of particles containing S + Si (representing particles with an insoluble core covered by sulfate) and S + Na + Cl + Si (representing particles containing insoluble core covered by a mixture of sea salt and sulfate). In the following calculation and for the sake of the discussion only, we will assume that the particles with insoluble core and sea salt coating have the same mass–diameter dependence as S + Si. In Fig. 10 all the particles containing Ca together with S were removed since they were probably gypsum, which is not as soluble as most other sulfate particles in the atmosphere. Taking the sulfur and the sea salt mass and assuming them to be only sulfate and NaCl, respectively, as shown in Fig. 10, one can evaluate the critical drop diameter and the corresponding critical supersaturation of the drops that would be formed on them. We assume that the core of the particles is made of insoluble material of radius r_u and that the coating is composed of sulfate and sodium chloride. We used Hanel's modified Köhler equation [as discussed in Pruppacher and Klett (1979), p. 146]. We see that

$$\frac{e_a}{e_{sat,w}} = 1 + \frac{A}{a} - \frac{B}{a^3 - r_u^3}, \quad (1)$$

where

$$A = \frac{2M_w\sigma_w/a}{R^*T\rho_w} \sim \frac{3.3 \times 10^{-5}}{T},$$

$$B = \frac{3nm_sM_w}{4\pi\rho_wM_s} \sim \frac{4.3nm_s}{M_s},$$

where a is drop radius, σ surface tension, R^* ideal gas constant, n number of ions into which a salt is disso-

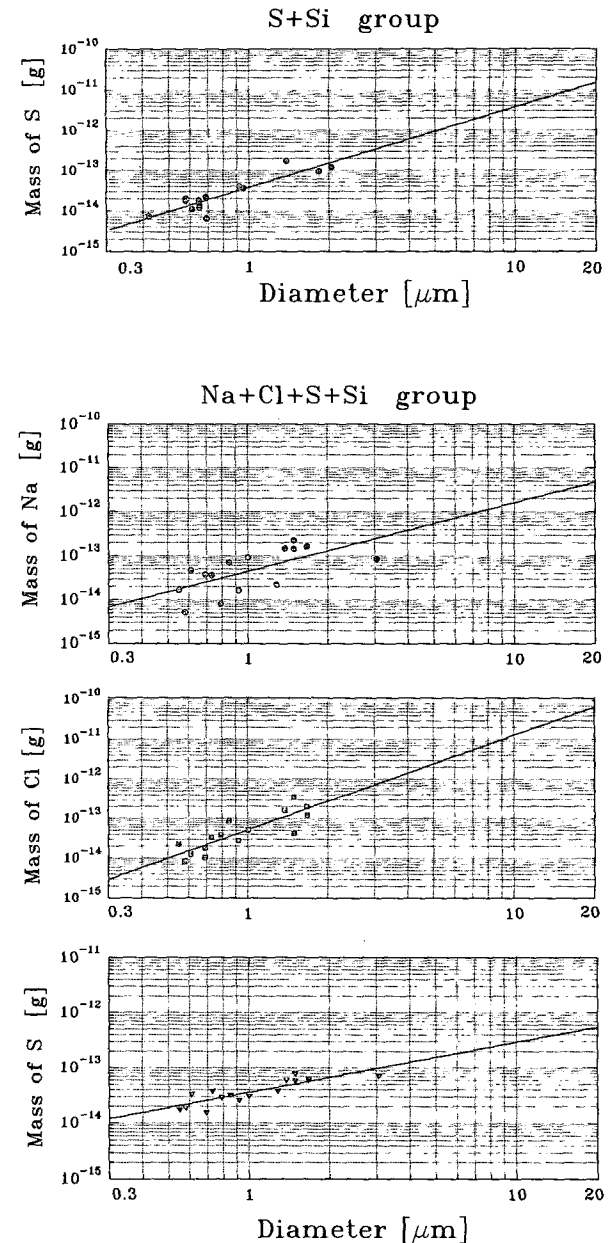


FIG. 10. The elemental mass as a function of diameter in individual particles collected below cloud base during the winters of 1990 and 1991. Only particles containing Si and other soluble material are plotted. All particles that were found to contain Ca together with S were removed from the data.

ciated in water, M_w molecular weight of water, M_s molecular weight of salt, m_s mass of salt, ρ_w density of water, e_a saturation vapor pressure over a solution drop of radius a , and $e_{sat,w}$ saturation vapor pressure with respect to a flat surface of pure water.

Assuming that the dry particle is composed of a spherical insoluble core and a shell of soluble material,

then the radius of the insoluble core can be expressed as

$$r_u = \frac{3D_N^3}{24} - \frac{3m_s}{4\pi\rho_s}, \quad (2)$$

where D_N is the diameter of the dry particle and ρ_s is the density of the soluble shell. Putting Eq. (2) into Eq. (1) using the values of D_N and m_s from Fig. 10, we can compute the critical supersaturation and the corresponding critical drop diameter.

Figure 11a shows the critical diameter of the drop as a function of dry particle diameter for ammonium sulfate coating on silicon core, for NaCl coating, and for a mixture of ammonium sulfate and NaCl. Figure 11b shows the supersaturation as a function of the dry particle diameter. From both graphs we see that with very low supersaturations the particles can reach their critical size. In fact, particles of mixed composition of sizes larger than $3 \mu\text{m}$ can produce drops of over $30 \mu\text{m}$, just as we observed in our cloud passes. Larger aerosols, say of about $10 \mu\text{m}$, can produce drops of 70 or $80 \mu\text{m}$. Since the aerosols could start growing below cloud base by absorbing water at a relative humidity of 70% or lower (Pruppacher and Klett 1979), the estimated time to reach drops of about $25 \mu\text{m}$ from $3 \mu\text{m}$ is about 30 s . Of course the time that it would take to reach drop sizes of 70 – $80 \mu\text{m}$ would be much longer, but the fact that the drops can be large even before reaching their critical size implies that they can participate in the collision coalescence process. In other words, they can collect other drops and grow even before reaching their critical size. Since the collision efficiencies of drops of about $40 \mu\text{m}$ is considerably greater than drops of less than $20 \mu\text{m}$, large drizzle drops can form very rapidly.

c. The effect of the large drops on ice formation

The high concentrations of the measured ice particles are also an indication of the mixed character of the clouds. As was mentioned before, in extreme continental clouds, ice crystal concentrations are expected to be low. In maritime clouds, on the other hand, much higher ice crystal densities have been reported (Rangno and Hobbs 1991; Hallett et al. 1978). The fact that the concentrations of ice found in the clouds over Israel (Table 4) were much higher than would have been predicted based on the IN activity spectrum (Gagin 1975) implies that either many of the clouds are not continental or there are other mechanisms that accelerate and enhance the ice formation.

The high concentrations of ice crystals could be attributed to the ice multiplication process suggested by Hallett and Mossop (1974). This is because some of the criteria required by their laboratory experiments, such as the presence of drops of sizes larger than $23 \mu\text{m}$, were definitely met. If we combine that with the observation of graupel (in some different clouds

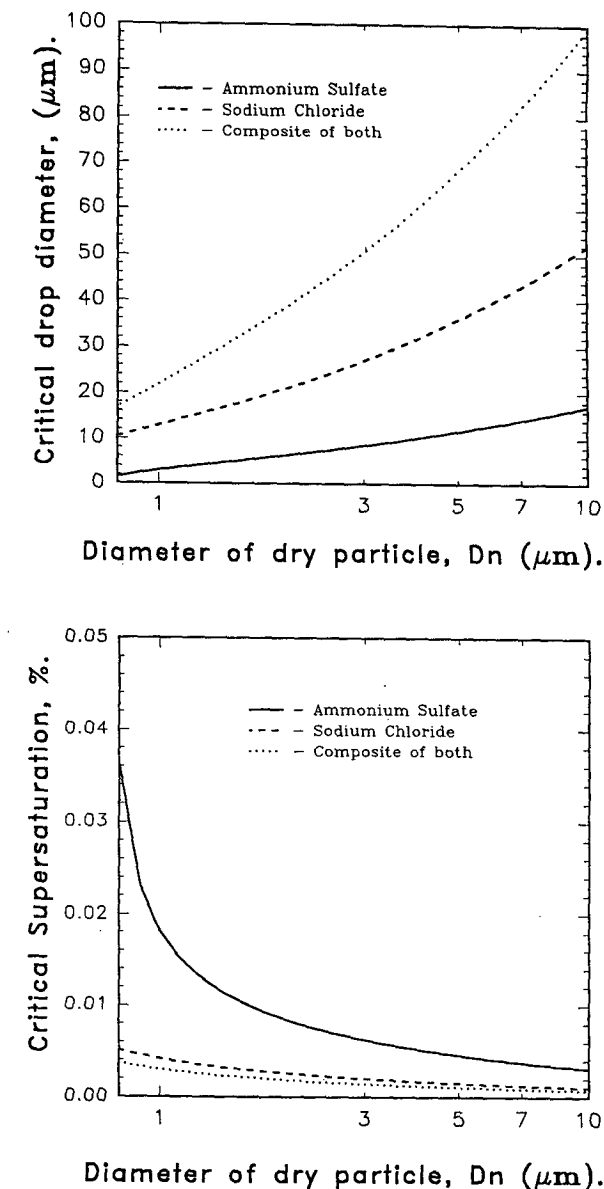


FIG. 11. (a) The critical drop diameter and (b) the critical supersaturation as functions of the dry particle diameter, as calculated using the measured mass of sulfate and NaCl shown in Fig. 10 and the formulation of Hanel (see Pruppacher and Klett 1979, p. 146).

though), this multiplication can definitely be operating. Recent work by Dong et al. (1992) points out that evaporating ice crystals could more easily break up and, therefore, enhance ice crystal concentrations. Many of the ice crystal measurements reported here were taken close to cloud top, suggesting that evaporation of ice crystals and their subsequent breakup could have taken place.

Another possible mechanism that could contribute to the observed high concentration of ice crystals and graupel particles is the enhancement of the production

of ice by the strong dependence of ice nucleation on supersaturation. Hussain and Saunders (1984) showed that ice nucleation depends exponentially on supersaturation. Even though their measurements covered only a limited range of temperatures and supersaturations, they showed that ice nuclei become activated at warmer temperatures when exposed to a high supersaturation. This is especially true when the supersaturation exceeds water saturation. Similar results were also reported by Gagin (1972) for larger drops. Rangno and Hobbs (1991) recently reported high concentrations of ice crystals where secondary ice crystal production was very unlikely. They concluded that ice must have been formed by a primary ice production mechanism such as exposure to high transient supersaturations. It is, therefore, conceivable that as drops grow by collection, their number concentration decreases, reducing the surface area and permitting the development of supersaturation. Such conditions may develop for short periods of time, but they occur because the excess water vapor, made available by the cooling of the rising air, does not have enough surface area on which to condense before more vapor becomes available (Reisin et al. 1992). During these times ice nucleation could rapidly proceed on existing IN, which otherwise, under normal supersaturations, would not be activated.

Furthermore, the probability of drop freezing increases with drop size, either due to immersion freezing or due to contact nucleation. Therefore, once these rapidly growing drops reach levels below the 0°C isotherm, they will be the first to freeze and form graupels, enhancing the concentration of ice and increasing the probability for secondary ice production.

In summary, the large mixed particles of sulfate and mineral dust produce large drops in the clouds, which grow fast by collecting the smaller drops. They then freeze and, potentially, also enhance ice crystal production through their influence on the development of supersaturation and secondary ice formation.

d. The connection to the clouds in the eastern Mediterranean

The results of our measurements suggest that the clouds over Israel do not always fit the classification of continental clouds. They are often of the mixed type, consisting of wide drop spectra with concentrations that are smaller than previously reported for continental clouds. Even for the cases in which the drop concentration is high, the number of drops larger than 20 μm is relatively high also. The nature of the clouds depends to a great extent on the aerosol composition, which in turn depends on the trajectory of the air. Most rain storms in the Middle East are in the form of cold winter fronts, which produce convective cloud bands. The recent classification by Singer et al. (1993) of the trajectories of rainstorms and their effect on the acidity of the rain on the northern coast of Israel could be adapted here as well.

Air coming from Europe (Fig. 1, trajectory A) contains anthropogenic aerosols in high concentrations. Most of the particles are sulfates in the form of $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , or NH_4HSO_4 . [Even though there are no reported measurements of DMS emissions from the eastern Mediterranean, it is safe to assume that some, though very few, could also come from DMS conversion to sulfate (Georgii 1978; Andreae and Raemdonck 1983).] Most of the sulfate particles are small ($<1 \mu\text{m}$) since they are produced by gas-to-particle conversion. Due to their effectiveness as CCN, these sulfate aerosols produce cloud drops of small sizes and narrow drop size distributions. Since these particles are found in high concentrations, it is reasonable to assume that the clouds they produce will have a more continental nature. But even here, the relatively few large particles composed of NaCl, other salts, and the small concentrations of mineral dust aerosols could modify the spectrum by introducing a tail with relatively large drops. The microphysical stability of these clouds depends, therefore, on the relative concentrations of these large drops. If there are only a few, say less than about 1 cm^{-3} , then the cloud is microphysically more stable where the collision-coalescence process is slow and where rain could be formed only through the formation and growth of ice. If, on the other hand, the cloud contains higher concentrations of large drops, the growth by collision-coalescence would become important, and the cloud would be identified as semicontinental.

In contrast, air trajectories that pass over the Mediterranean and also over parts of North Africa (Fig. 1, trajectory C) would contain similar, or even higher, concentrations of sulfate particles, but they also contain high concentrations of dust aerosols. A number of passes of these particles through clouds would result in the formation of large dust aerosols coated with sulfate, as was discussed above. These large CCN particles produce large drops and make the clouds microphysically unstable. Drizzle drops are rapidly formed and ice formation is enhanced, finally leading to effective rain production.

Of course, many storms take a path more like trajectory B in Fig. 1. In these cases a mixture of the two extreme conditions produced in trajectories A and C would result. The clouds will be more continental than in C but more unstable than in A.

e. Connection to cloud seeding in Israel

Based on the above observations, we could see that the basic hypothesis of the seedability of the Israeli clouds needs to be reevaluated. It is indeed possible that some of the clouds, namely the more continental ones, could be affected by IN seeding. Those clouds with semicontinental or somewhat maritime properties, however, would not benefit from the artificial introduction of IN. Since in the Israeli project seeding is

performed, assuming that all the clouds are strictly continental and without regard to the possible differences in the cloud microphysical properties, it is possible that some clouds are affected positively and rain is enhanced, while others are either not affected at all or could even be affected negatively.

6. Conclusions

The main conclusions of this paper are as follows.

1) Results of airborne and surface measurements suggest that, in contrast to general belief, water insoluble aerosol particles may strongly affect rain formation in clouds if they are coated with soluble materials.

2) Large insoluble particles coated with hygroscopic material, which form large drops, do not only accelerate growth by coalescence but also affect ice formation.

3) Clouds in semiarid regions, such as the eastern Mediterranean, are sometimes affected by such particles, making them more maritime with wider drops size spectra and higher concentrations of ice particles.

5) The semimarine properties of these clouds make them less suitable for rain enhancement by IN seeding.

6) Seeding with IN should be done only in those clouds that exhibit continental characteristics. These could be identified as those storms not affected by mineral dust particles.

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APPENDIX

Method of Calibration of Elemental Mass in Individual Particles

In Pardess et al. (1992) the method for calibrating the mass of sulfur S in individual particles was presented. In that study, particles containing S of known size and composition were used. In the present case the method was extended through the use of particles containing S and another element. Since S had been already evaluated, the mass of the other element can be estimated based on its known stoichiometric ratio to S.

For example, using Na_2SO_4 particles and knowing both the connection between the X-ray counts and the mass of S (from previous calibrations), and the known

ratio of Na to S in Na_2SO_4 , we calibrated the relationship between X-ray counts and the mass of Na.

Next, we used NaCl particles and calibrated the mass of Cl, knowing the mass of Na and the ratio of Na to Cl in the compound. Similarly, the calibration of the mass of Mg was obtained by using particles of MgSO_4 .

The calibration of Si was a little more involved. We first used particles of $\text{Fe}_2(\text{SO}_4)_3$ and then Fe_2SiO_4 . In this way we obtained the calibration for Fe as well as for Si. In a similar manner, calibration of K was obtained using K_2SO_4 , Ca through the use of CaSO_4 , and Al by the use of $\text{Al}_2(\text{SO}_4)_3$.

Table 1 presents the calibration curves where N_s , N_{Na} , etc. are, respectively, the normalized S and Na counts. By normalized we mean, as was the case in Pardess et al. (1992),

$$N_s = \frac{(n_s - B)A}{n_{\text{Co}}}$$

In this equation, n_s is the number of counts during Δt (100 s) under the S peak in the X-ray spectrum, and B is the number of counts in the background away from the S peak. The area scanned by the electron beam is represented by A , and n_{Co} is the number of X-ray counts obtained during the same time interval from a cobalt sample used as a reference for the calibration. The reason why Co was used for the reference is that its peak is found in a part of the spectrum far away from most other elements found in the samples.

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