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MODELING A CASE OF PARTICLE NUCLEATION IN THE MARINE BOUNDARY LAYER

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Abstract. A diagnostic modeling study is performed on a hypothesized case of particle nucleation in the marine boundary layer. A three-mode integral nucleation model is used and predicts particle concentrations in accord with observations when initialized with the appropriate field measurements. Further analysis of the data suggests the conditions favorable for nucleation at the surface were due to mixing of air at the top of the boundary layer down to the surface.

Introduction

It has long been realized that new particles are formed in the atmosphere from precursor gases, primarily sulfur gases [Junge, 1963]. This new particle formation, or nucleation, modulates the shape of the particle size distribution [Whitby, 1978] and, in remote oceanic air, may supply the majority of particles in the atmosphere. Indeed, this is the basis for recent interest in the relationship between marine sulfur gas emissions and cloud condensation nuclei [Charlson et al., 1987].

One interesting facet of this issue which must be addressed more fully is the conditions under which nucleation actually occurs in the troposphere. While most estimates of nucleation rates derived from sulfur budget or aerosol budget calculations are necessarily mean values, with an implicit assumption of spatial homogeneity [Charlson et al., 1987; Baker and Charlson, 1990], it is quite clear from the fundamental equations governing the nucleation of $H_2SO_4 - H_2O$ droplets – the most generally accepted atmospheric nucleation process – that the process is highly dependent on water vapor partial pressure, temperature and H_2SO_4 vapor pressure [Yue and Hamill, 1979; Seinfeld, 1986; Jaecker-Voirol and Mirabel, 1989]. Furthermore, the H_2SO_4 partial pressure is highly dependent on OH, SO_2, and aerosol surface area concentrations which are, in turn, dependent on still other variables. Quite clearly, nucleation in the atmosphere will be highly variable in space and time. Recent model calculations for the generic marine atmosphere using an integral nucleation model highlight this conclusion [Kreidenweiss et al., 1991].

A number of investigators have in fact found evidence of particle nucleation in the atmosphere under quite different conditions. For example, Shaw [1989] has reported observations supporting nucleation in arctic air with very low surface area of preexisting aerosol. Similar, but much more direct observations have been made by R. J. Ferek et al. (DiMethyl Sulfide in the Arctic Atmosphere, submitted to Journal of Atmospheric Chemistry, 1992) (herinafter referred to as Ferek et al., 1992). Certainly the low arctic air temperatures and relatively low accumulation mode number concentrations favor nucleation. For the same reasons, the observations of particle nucleation in the upper troposphere reported by A. D. Clarke (A Global survey of atmospheric nuclei in the midtroposphere: Their nature, concentration, evolution, submitted to Journal of Geophysical Research, 1992) (herinafter referred to as Clarke, 1992) are not unexpected. On the other hand, the concentrations of particle precursor gases under such conditions are generally low and nucleation is strongly dependent upon these concentrations [Hegg et al., 1990]. Hence surface areas must be very low indeed or, conversely, precursor gas concentrations anomalously high before nucleation should be expected. Examples of both scenarios can actually be found in the studies of Shaw [1989] and Ferek et al. (1992), respectively.

In the above examples of nucleation, the high precursor gas concentrations referred to in the discussion are, implicitly sulfur gases such as SO_2 and DMS which oxidize up to the H_2SO_4 necessary for binary nucleation. However, the nucleation process is indeed binary and high concentrations of OH or its precursors (e.g., H_2O, O_3, and UV light) will be equally effective in enhancing the potential for nucleation (since the H_2SO_4 source reaction is linear in both SO_2 and OH and OH, in turn, is linearly dependent on actinic flux, O_3, and H_2O). For example, Hoppel and his colleagues [cf. Hoppel et al., 1990] have presented evidence of particle nucleation in the marine boundary layer where neither temperature, nor aerosol surface areas are particularly low and sulfur precursor gas concentrations are not commonly very high. It is, presumably, the high relative humidity and periodically high UV light intensity, which results in high OH concentrations, that produce favorable conditions for nucleation. Hegg et al. [1990] have modeled the nucleation process for such conditions and find nucleation quite feasible, particularly in the high relative humidity fields near clouds. Indeed, Hegg [1991] has even hypothesized that nucleation can occur in marine clouds with low droplet number concentrations due to the enhanced UV flux in such clouds [Madronich, 1987].

In light of the above discussion, it is clear that the feasibility of nucleation as an explanation for observed high particle number concentrations must be assessed on a case-by-case basis, taking into account – either by measurement or modeling – all of the variables in the nucleation process. In this study, we make a model assessment of the novel "burst" in particle number concentrations observed in the marine boundary layer off the coast of Washington State. A full report and discussion of these data will be reported elsewhere (D. S. Covert et al., New particle formation in the marine boundary layer, submitted to Journal of Geophysical Research, 1992) (hereinafter referred to as Covert et al., 1992). We report here only those data relevant to our analysis.

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Observations

Ship Observations

As reported in the work by Covert et al. (1992), at approximately 1500 PST on April 22, 1991, the ultrafine condensation nucleus counter (UFCN) (detection limit = 3 nm) aboard the National Oceanic and Atmospheric Administration research vessel Discoverer registered a rapid increase in UFCN from a nominal baseline of 250 cm^{-3} to over 4000 cm^{-3} (see Figure 1a). Commencing just prior to this rise in UFCN, the total aerosol surface area, as determined by a differential mobility particle sizing system (DMPS), which measures the size distribution between 0.02 and 0.6 μm diameter, underwent a rapid fall which continued until shortly after the peak in UFCN was attained (see Figure 1c). Approximately 1 hour after the start of the rise in UFCN, the CN count at the ship also began to rise, achieving a peak ~5 hours after the start of the rise in UFCN (see Figure 1b).

Trends in several nonaerosol parameters are also of considerable interest. The relative humidity underwent a substantial drop (from 65 to 52%) followed by a sharp rise (from 52 to 67%) just prior to the rise of UFCN. Conversely, the surface temperature underwent a sharp fall (~1°C) preceded by a significant rise prior to the UFCN rise. Also of interest was a rise in SO_2 concentration prior to the rise in UFCN. The SO_2 concentration for several hours before the rise in UFCN was 25–30 pptv and rose to greater than 50 pptv about an hour prior to the UFCN rise.

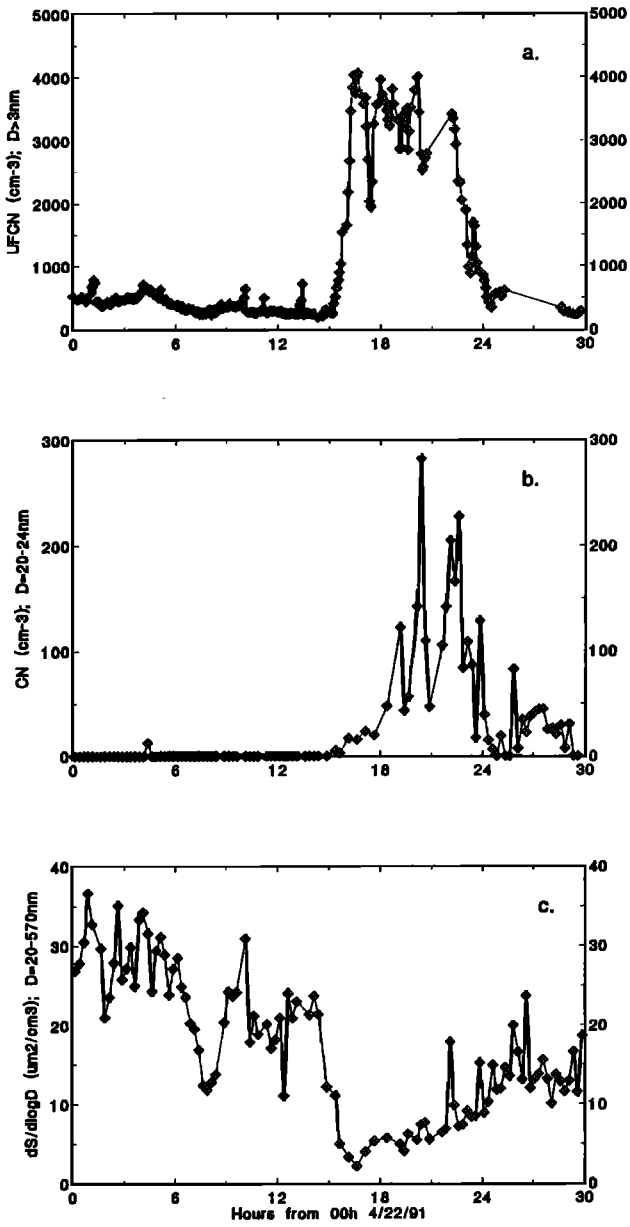

Fig. 1. Plots of the concentrations of (a) ultrafine CN, (b) CN, and (c) aerosol surface area as a function of time for April 22, 1991. Observations were taken from the R/V Discoverer.

Aircraft Observations

From roughly 1200 to 1500 PDT, the University of Washington's C-131A research aircraft was engaged in obtaining vertical profiles of SO_2, DMS, and CN concentrations over the Discoverer. These data are reported in the work by Ferek et al. (1992). Most relevant to the discussion here is the vertical profile of SO_2, shown in Figure 2. By comparison with the surface SO_2 data of Covert et al. (1992), it can be seen that the relatively high concentration of SO_2 seen at the surface prior to the UFCN rise was representative of the air aloft. Additional aircraft data allow a further refinement of this relationship. In Figure 3, the aircraft temperature and relative humidity profiles obtained concurrently with the SO_2 data are shown. In Figure 4, the liquid water and CN profiles obtained from the aircraft are also plotted. (Note that the CN counter employed on the aircraft is a modified GE CNC-1 and measures particles with diameters down to ~5 nm. It is therefore taken as equivalent to the UFCN counter used on board the Discoverer.) These show that the peak in SO_2 concentration at the surface prior to the UFCN rise was characteristic of air just above cloud top in the inversion capping the boundary layer. This suggests that a vertical mixing event may have contributed to the UFCN rise

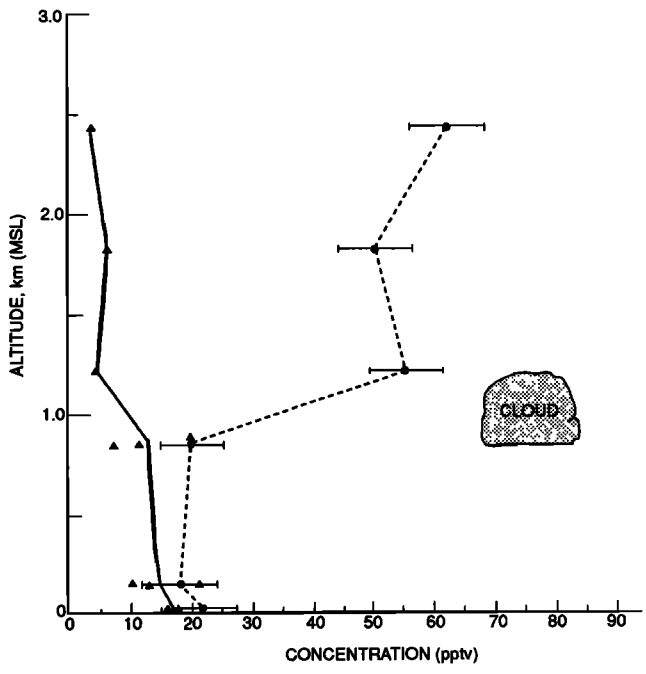

Fig. 2. Vertical profiles of the concentrations of SO_2 (dashed line) and DMS (solid line) measured between 1200 and 1500 PDT on April 22, 1991, by the University of Washington's C-131A research aircraft. The locale was over the R/V Discoverer [from Ferek et al., 1991b].

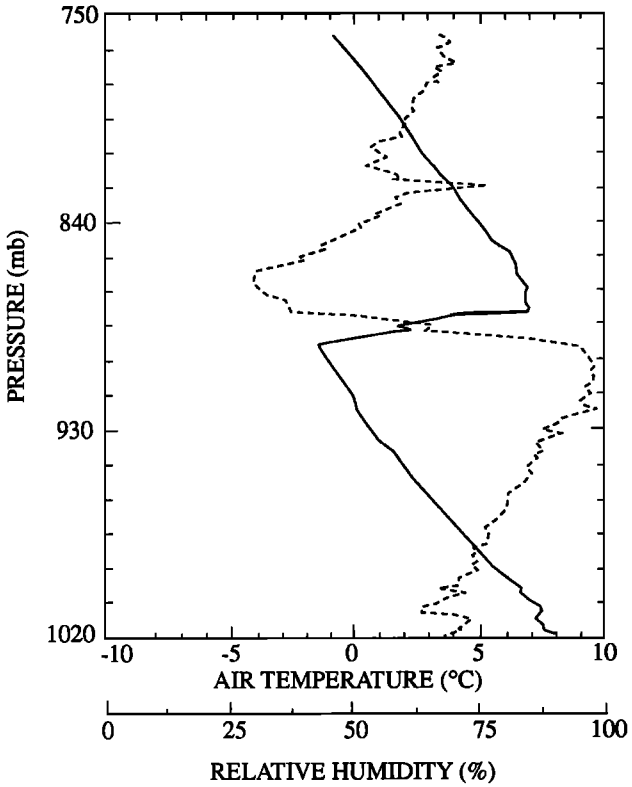

Fig. 3. Vertical profiles of temperature (solid line) and relative humidity (dashed line) obtained concurrently with the SO_2 and DMS profiles shown in Figure 2. For comparison with Figure 2, the 895-mbar level is at an altitude of 1 km and the 960-mbar level at 0.5 km.

observed at the surface. It is important to note in this regard, however, that the concentrations of UFCN aloft ($\lesssim$900 cm^{-3}) are far from sufficient to produce the UFCN concentrations observed at the surface (~4000 cm^{-3}). For later reference, we also note that the measured accumulation mode dry surface area (by dry we mean unhydrated) was ~5 ± 1 μm^2 cm^{-3} in the inversion and ~4 ± 3 μm^2 cm^{-3} at the surface, i.e., essentially the same. Another possible explanation for the observed rise in UFCN at the ship is simply that there was horizontal advection of relatively high UFCN concentrations. However, the aircraft data show no evidence of horizontal variability in UFCN approaching anything like the large change in the UFCN shown in Figure 1. Thus the possibility of the increase in UFCN being due to in situ nucleation of new particles must be seriously considered.

The Nucleation Model

In previous studies [Hegg et al., 1990; Hegg, 1991], simple, integral nucleation models have been utilized to assess the viability of binary, homogeneous nucleation of sulfuric acid-water droplets as an explanation for observed variability in CN concentrations. We shall adopt the same approach in this analysis and attempt to replicate the observed time series of particle concentration and size distribution with an integral nucleation model.

The model employed is a refinement on the bimodal, integral nucleation model employed by Hegg [1990, 1991] which is, in turn, a modified version of the integral nucleation model of Kreidenweiss and Seinfeld [1988]. The basic idea of this model is that the particle size distribution, at least for purposes of estimating nucleation rates, can be parameterized in terms of its integral moments, for example, surface area. Thus the extent of nucleation can be predicted on the basis of a handful of simple equations: a parameterized nucleation rate based on laboratory studies of nucleation as a function of relative humidity, temperature, and H_2SO_4 partial pressure, an H_2SO_4 source term (SO_2 oxidation), a condensational sink term for H_2SO_4 condensing onto preexisting particle surface area, and conservation equations for particle number and mass, and H_2SO_4 and SO_2 concentrations. The model requires specification of initial values of SO_2, OH, H_2O, temperature, aerosol number concentration, and degree of polydispersion, and various microchemical parameters such as accommodation coefficients. For this study, an accommodation coefficient of 0.3 has been employed together with a parameterization of the nucleation rates of Jaecker-Voirol and Mirabel [1989], which take into account gas-phase hydration of H_2SO_4. The model sensitivity to these parameters is discussed in the work by Hegg et al. [1990]. The model has been expanded to encompass three modes: an initial accumulation, initial nucleation, and fresh nucleation mode. The initial accumulation and nuclei modes are used to represent the initial CN (as measured by the ship, i.e., particles with $d > 20$ nm) and UFCN concentrations, respectively. The fresh nucleation mode is initially zero and represents those particles nucleated in situ in the course of the simulation. This structure permits an assessment of the growth rate of the initial nucleation mode particles since the modal concentration will not change with time and changes in the modal mean diameter thus represent the influence of condensational growth alone.

While the above change from bimodal to trimodal structure is the only significant change in the parameterization of the model, the model is initialized and run in a somewhat different manner than was previously the case. In this instance, we are interested in the ability of the nucleation model to reproduce

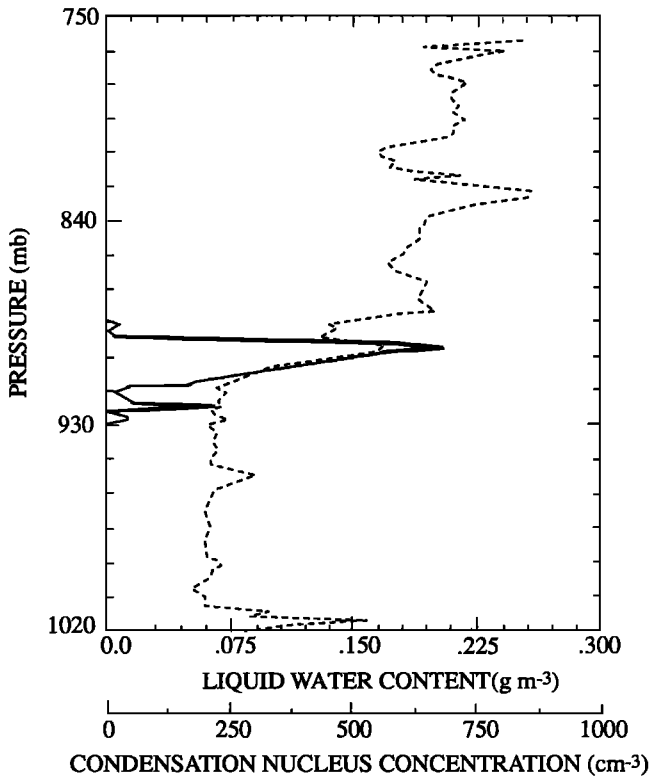

Fig. 4. Vertical profiles of aircraft CN – 5 nm lower size limit – (dashed line) and liquid water content (solid line) taken concurrently with the measurements shown in Figures 2 and 3.

the observed time variability of UFCN at a fixed point in space given the observed variability in such pertinent parameters as saturation ratios, temperatures, initial aerosol surface area, etc. at the same point. Hence, where possible, the critical variables for nucleation have been parameterized as smooth functions of time, either based on observations or theoretical considerations, for the time interval to be modeled. (On the basis of the variation in UFCN shown in Figure 1a, a time interval from 1324 to 1824 PDT has been selected for analysis.) For example, the water vapor saturation ratio (SATR), which is important for both the nucleation rate and the equilibrium aerosol surface area available for condensation, has been modeled as

$$SATR = C_1 t \sin(C_2 t) + C_3 \quad (1)$$

with $t = 0$ corresponding to 1324 PDT and the C_i fitted constants. Similarly, on the basis of direct observations of Eisle and Tanner [1991] at the same time of year in marine air, though somewhat lower latitude, the critical OH variance is parameterized as

$$OH = OH_0 \exp(-t/6600) \quad (2)$$

with $OH_0 = 1 \times 10^7$ molecules cm^{-3}.

However, several key parameters cannot be dealt with in this manner. Both SO_2 concentrations and aerosol particle surface area are internally calculated by the model and significantly influenced by the calculated nucleation rate. Thus, while they can be initially specified, they cannot be specified external to the model calculations as functions of time. We deal with observed variability in these parameters by conducting sensitivity studies.

One final variable is worth special note. The initial gaseous H_2SO_4 concentration employed was 2.8×10^7 molecules cm^{-3}, in accord with the direct measurements of Tanner and Eisle [1991] in marine air on the Washington Coast during early June of 1989. However, the model calculations have proven rather insensitive to the initial H_2SO_4 vapor pressure. Essentially, regardless of the initial concentration of H_2SO_4, it quickly builds up to ~10^7 molecules cm^{-3} for virtually all plausible combinations of OH, SO_2 and initial aerosol surface area in marine background air, i.e., the H_2SO_4 concentration is determined by a quickly established balance between the source and sink terms in the model. Hence the model is intrinsically consistent with the available observations of H_2SO_4 vapor for the given conditions.

Model Results

The first series of model runs were made with an initial SO_2 concentration of 27 pptv, a UFCN concentration of 257 cm^{-3} and a CN concentration of 10 cm^{-3}, all representative of surface conditions prior to ~1330 PDT (Covert et al., 1992). The diameters of the CN and UFCN, which are assumed to be monodisperse – in keeping with the constraints of the integral model – are selected to yield the measured surface areas (for example, the accumulation mode particles were given a mean diameter of ~0.6 μm for 10 μm^2 cm^{-3} surface area measurements). It is the integral surface area which is the key parameter in the model for nucleation. Plots of the predicted UFCN concentration as a function of time are shown in Figure 5. Curves are shown for both the lowest particle surface area observed prior to 1324 (10 μm^2 cm^{-3}) and the lowest seen for the entire day (2 μm^2 cm^{-3}). In neither case does the model predict sufficient nucleation to reproduce the observed rise in UFCN.

In the next series of simulations, an initial SO_2 concentration of 50 pptv was utilized. This concentration is similar to those observed by the aircraft at and above the boundary layer inversion, and at the surface itself between ~1330 and 1500 PDT (Covert et al., 1992). The results of these simulations are shown in Figure 6. Once again, for a

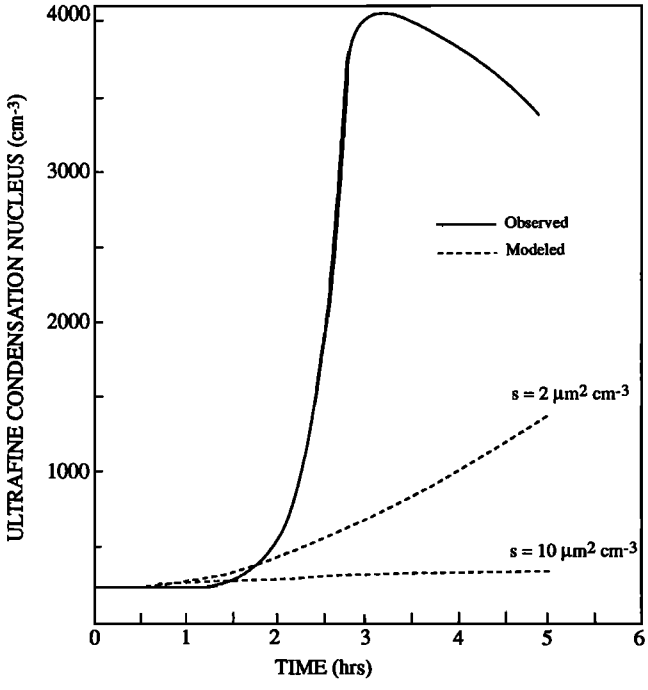

Fig. 5. Observed (solid line) and model predicted (dashed line) concentrations of UFCN for the April 22 case. The initial SO_2 concentration is 27 pptv. Time = 0 corresponds to 1324 PDT. The labels on the model curves are initial aerosol surface areas S.

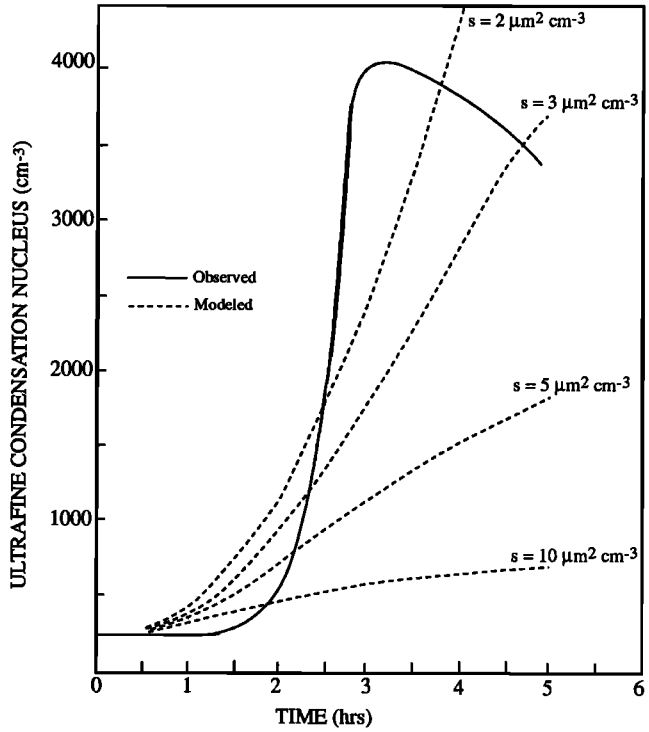

Fig. 6. As in Figure 5 except that the initial SO_2 concentration was 50 pptv.

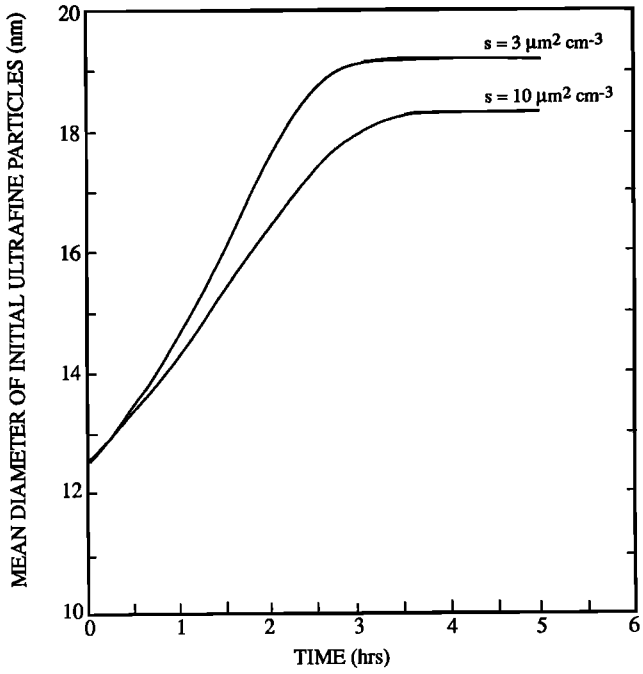

Fig. 7. Time variation in the size of the mean diameter of the initial nucleation mode particles for the April 22 case. The initial SO_2 concentration was 50 pptv. Time = 0 corresponds to 1324 PDT. The labels on the curves refer to initial aerosol surface areas S.

surface area of 10 μm^2 cm^{-3}, the results show that insufficient nucleation would occur to reproduce the observed UFCN curve. However, for the lower surface areas observed after 1330 PDT, the model predicts UFCN concentrations comparable to those actually observed and they are generated on roughly the right time scale. Thus the observed UFCN rise can be at least partially attributed to nucleation of H_2SO_4-H_2O droplets and the nucleation, in turn, is a consequence of both an increase in SO_2 and decrease in aerosol surface area which occurs at around 1330 PDT. On the other hand, the model does not predict quite so steep a rise in UFCN concentration as that observed. It is plausible to attribute this to the co-advection of UFCN from aloft simultaneously with the relatively high SO_2 and low total surface area of the aerosol. We shall discuss this point further in the next section.

Another prediction of the model which can be compared with observations is the rate of growth of the nucleation mode particles. Shown in Figure 7 is the time variation in the size of the mean diameter of the initial nucleation mode particles. It can be seen that, for the low initial aerosol surface areas which occur after ~1330, the ~250 cm^{-3} UFCN particles grow to ~19–20 nm diameter in ~ 3 hours. Turning to the observations shown in Figure 1a and 1b, we see that 200–300 cm^{-3} UFCN have reached the nominal 20-nm threshold of the shipboard CN counter ~4 hours after the UFCN are observed to rise, i.e., after in situ nucleation commences. Hence the model predicted growth of nucleation mode particles is in accord with the observations.

Discussion

Two questions arise in interpreting the observations presented above a in the work by Covert et al. (1992). First, can the observed rise in UFCN and later CN be attributed to in situ nucleation at the surface? Second, if nucleation is the explanation, what produced the conditions favorable for the observed "nucleation burst" at the surface and why did it occur there and not elsewhere? The first question has already been addressed in the presentation of model results. Nucleation does, in fact, appear to be a viable explanation for much of the observed increase in UFCN. However, vertical advection was invoked to rationalize the somewhat steeper than predicted rise in UFCN. This naturally leads to a consideration of the second question. If such vertical mixing is taking place, could this mixing itself plausibly produce the concurrent low aerosol surface area and high SO_2 observed prior to and during the nucleation event? We now consider this question in some detail.

It is well known that the cloud-topped boundary layer (CTBL) can entrain free tropospheric air from above the delineating temperature inversion and that this air, if only rarely, can reach the surface [Stull, 1988, p. 464]. Naturally, the boundary layer air must be unstable for such convective motion, both upward and downward, to be initiated. During the mixing event, however, the stability of the layer is uncertain because of the poor temporal resolution of the potential virtual temperature profiles derived from the sounding data shown in the work by Covert et al. (1992). The only sounding taken prior to the hypothesized entrainment event, at 1000 PDT, shows a mean gradient in θ_v from 0 to 300 m of -7.2×10^{-3} °K m^{-1} and one of -3.9×10^{-3} °K m^{-1} from 300 to 600 M. Hence the air was unstable over most of the boundary layer several hours prior to the hypothesized entrainment event. It is likely, though by no means certain, that this instability increased as the day progressed and surface heating continued. There was a 0.5 to 1°C rise in surface temperature lasting from 1200 to 1500 PDT. Certainly aircraft data taken over this time period, such as that shown in Figure 3, show a uniform potential temperature up to the boundary layer inversion, suggesting a well-mixed boundary layer.

Another methodology which can more directly assess the extent of mixing between the surface and air aloft is a conserved variable plot [Betts, 1985]. For this particular case, we have plotted total water substance mixing ratio (Q_T) against equivalent potential temperature (θ_e), the two variables being derived from the aircraft data shown in Figures 3 and 4. This plot is shown in Figure 8. The pattern shown suggests that the thermodynamics of the air is dominated by radiative cooling above the inversion and by mixing between the inversion and the surface below the inversion. Indeed, the lower leg of the plot forms a reasonably coherent mixing line [Betts, 1985; Stull, 1988]. Points falling along this line represent air which is a linear mix of air from both ends of the line and, furthermore, are present in amounts proportional to the distance of the points from the ends of the line. For example, a point which fell midway along the lower leg of the plot shown in Figure 8 would have equal proportions of air from the locales represented at either end of the mixing line, i.e., from the surface and the air in the inversion.

Values of Q_T and Q_e for the surface air sampled by the ship and derived from the data of Covert et al. (1992) are also plotted in Figure 8. It can be seen that prior to the rise in SO_2 and fall in aerosol surface area preceding nucleation, the air at the surface in fact originated at the surface. However, with the rise in SO_2 and fall in aerosol surface area associated with nucleation, a significantly higher proportion of the air at the surface originated aloft. Later, as SO_2 falls and aerosol surface area slowly rises, the surface air is once again mostly of surface origin. This analysis thus supports our hypothesis of a vertical mixing event as the root cause of the conditions favorable for the observed nucleation burst.

Given the viability of a vertical mixing event as the precursor of favorable nucleation conditions at the surface, we must address the issue of why this mixing results in such marked nucleation at the surface rather than aloft where SO_2 is also high and dry aerosol surface area essentially the same as that at the surface. This can be simply explained in terms of the relative humidity and temperature profiles shown in Figure

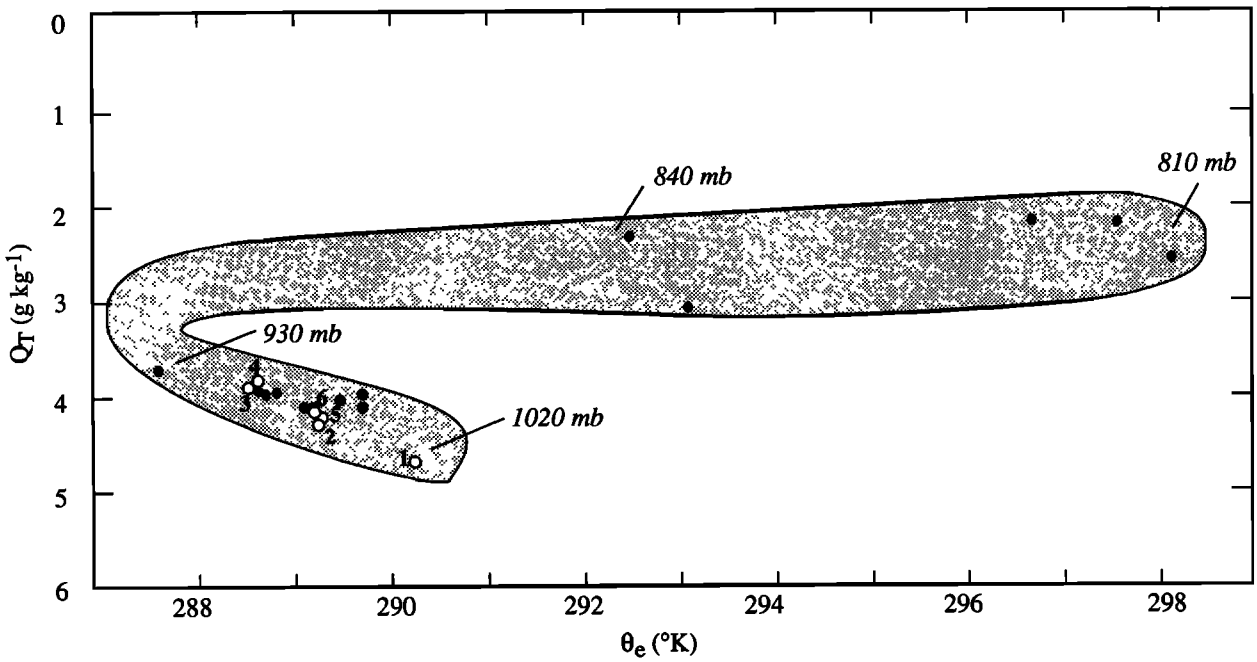

Fig. 8. Conserved variable plot of total water mixing ratio against equivalent potential temperature for the April 22 case. The solid circles are derived from the aircraft data shown in Figures 3 and 4. The open circles (o) are from observations on board the Discoverer as a function of time. The numbers correspond to the following PDT times: 1 = 0600, 2 = 0900, 3 = 1200, 4 = 1330, 5 = 1500, and 6 = 1630. Selected aircraft data points are also labeled with the pressure level at which the measurements were taken.

3. The relative humidity varies from 97.1% at 930 mbar (the lifting condensation level) to ~62% at the surface. Hence the actual hydrated aerosol surface area available for condensation of H_2SO_4 molecules is much larger aloft than at the surface, indeed, it is greater by 450%. In the cloud layer itself, of course, the presence of activated cloud drops raises the aerosol surface area still higher. As the air mixes downward and warms, the relative humidity and thus aerosol surface area fall below a nominal nucleation threshold near the surface. Of course, the warming will also decrease the nucleation rate but the effect is small given the modest ~3% change in absolute temperature. Furthermore, there is an ~9% increase in water vapor partial pressure to partially offset the impact of the warmer temperature on the nucleation rate.

Conclusion

The above analysis suggests that the peak in UFCN as a function of time, and the subsequent peak in CN observed by Covert et al. (1992), can be attributed to a burst of particle nucleation associated with relatively high SO_2 and low aerosol surface area. These favorable conditions for nucleation near the sea surface were plausibly attributable to a vertical mixing event which transported high SO_2 – low aerosol surface area air to the surface. Such mixing episodes may be expected on a periodic basis under commonly occurring conditions in the marine boundary layer [Stull, 1988]. This serves to emphasize the temporally, as well as spatially [Hegg et al., 1990] episodic nature of nucleation in the marine boundary layer. Furthermore, it suggests that a more detailed examination of the relationship between vertical mixing and nucleation near the surface in the marine boundary layer could prove fruitful.

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