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New Particle Formation in the Marine Boundary Layer

DAVID S. COVERT

Departments of Environmental Health and Atmospheric Sciences, University of Washington, Seattle

VLADIMIR N. KAPUSTIN

Institute of Atmospheric Physics, Academy of Sciences, Moscow, Russia

PATRICIA K. QUINN AND TIMOTHY S. BATES

NOAA Pacific Marine Environmental Laboratory, Seattle, Washington

Aerosol measurements were made in the marine boundary layer along the coast of Washington State during the Pacific Stratus Sulfur Investigation. On April 22 the particle concentration increased to levels much higher than usual for the clean marine boundary layer. The total particulate number concentration greater than 3 nm diameter increased rapidly from about 250 cm^{-3} to 3200 cm^{-3}, remained near that level for 7 hours, and then decreased over the next 2 hours to less than 400 cm^{-3}. The change could not be attributed to either local or distant contamination. Immediately before the increase particulate surface area concentration dropped from 25 μm^2 cm^{-3} to less than 5 μm^2 cm^{-3}. The SO_2 concentration increased from about 20 pptv to 40–60 pptv just before the increase in particle concentration. While these measurements cannot distinguish between changes in number concentration caused by particle nucleation versus advection or vertical mixing, clearly there was recent or continuing particle production on a mesoscale in the air mass. Related aircraft measurements and model results support the hypothesis of new particle formation. These data provide evidence that at times high concentrations of new, ultrafine particles are formed at low SO_2 concentrations under marine conditions. This homogeneous nucleation, as opposed to heterogeneous condensation on existing particles, is strongly and inversely dependent on the concentration of existing particles.

INTRODUCTION

Particle production in the remote marine atmosphere is thought to be primarily the result of nucleation and condensation of vapors such as sulfuric acid and methanesulfonic acid [*Kreidenweis et al.*, 1991]. These compounds are formed through homogeneous gas-phase reactions of compounds including dimethylsulfide (DMS), SO_2, NO_x, and organics. While sulfuric acid, H_2SO_4, and methanesulfonic acid, MSA, are the major species involved in the nucleation, others such as NH_3 may contribute to the process. Although the general process is understood, the details of the chemical pathways, the physical and chemical processes and properties of the condensing species leading to particle formation are not well known. Setting the gas-phase reactions aside and just considering the dynamics of the two vapors (H_2SO_4 and MSA) and existing particles, the controlling parameters are the saturation vapor pressures (of H_2SO_4 and MSA as binary or higher component systems), water vapor pressure, temperature and existing particle concentration.

A major question that is addressed in the models and needs experimental testing is that of the partitioning of the condensed vapor between the processes of new particle production, initially at sub-nanometer sizes, and condensation onto existing particles at much larger sizes. For a given mass condensation rate of the vapor, the change in particle number concentration with time could be very large in the first case but would be zero in the second case [*Warren and Seinfeld*, 1985]. In the atmosphere there will always be a competition between these two processes depending on the existing particle size distribution. This partitioning is particularly important with respect to hypotheses regarding the links between gas-to-particle conversion, cloud condensation nuclei and cloud physics, and radiative transfer.

Existing data indicate that new particle production takes place in bursts under rather specific conditions to produce concentrations of 1000 to 10,000 particles per cubic centimeter in a limited time and volume of the atmosphere [*Shaw*, 1989; *Clarke*, 1991; *Hegg et al.*, 1990]. This would maintain a larger-scale, much lower average marine background aerosol particle number concentration of a few hundred per cubic centimeter. A discussion of the production of particles in clean air by nucleation of H_2SO_4 by *Shaw* [1989] presents the fundamental aerosol physics in a phenomenological and theoretical framework and in the context of observations. His results showed that maximum concentrations of 10,000 particles per cubic centimeter are possible over production times of 2 to 20 hours. Integral aerosol nucleation models [*Warren and Seinfeld*, 1985] incorporating a source and sink for the vapor phase and allowing competition between the processes of nucleation and condensation on existing aerosol have been applied to the conditions of the marine boundary layer. In these models, the vapor was described by its supersaturation and source or production rate. The aerosol was described by its integral number and mass concentration and consisted of one or more monodisperse modes. *Kreidenweis et al.* [1991] and *Kreidenweis and Seinfeld* [1988*a*,*b*] applied this model to the general case of the marine boundary layer and the nucleation and condensation of H_2SO_4 and MSA and tested its sensitivity to temperature, relative humidity and initial aerosol parameters. A range of steady state number concentrations from 10 to 10^4 particles cm^{-3} was predicted depending on the

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binary nucleation rate, the aerosol polydispersity and the vapor sticking coefficient. While the predicted range was large, the most likely value, in the range 50 to 600 cm^{-3}, is typical of those measured in the marine boundary layer and the upper limit is close to maximum observed values. A more specific application of the integral nucleation model was done for the marine boundary layer by *Hegg et al.* [1990] based on aircraft observation of gas and aerosol conditions. The model predicted profiles of aerosol concentration with pronounced layers corresponding to high relative humidity and low aerosol and droplet surface area. The modeled profiles matched measured profiles reasonably well and pointed out the sensitivity of nucleation to aerosol surface area and relative humidity. Laboratory studies of nucleation in smog chamber experiments for organic compounds and dimethyldisulfide (DMDS) have allowed the actual formation process to be followed with time [*Flagan et al.*, 1991]. Although the precursor concentrations were high compared to those in the marine environment, the results showed that nucleation occurs in successive bursts that are rapidly quenched by the increase of aerosol concentration.

While most of the model results deal only with binary nucleation (H_2SO_4 and H_2O) it is clear that in the atmosphere higher order nucleation processes are probable. The presence of MSA or NH_3 will reduce the vapor concentration of H_2SO_4 necessary for the onset of nucleation. All of the models point out that one of the crucial parameters is the concentration of existing particles which are able to quench new particle production by providing a sink for the condensible vapor. This sink is proportional to particle surface area in the free molecular regime ($D_p << 2\lambda$, where λ = molecular mean free path, ~60 nm) and proportional to particle diameter in the continuum regime ($D_p >> 2\lambda$). *Warren and Seinfeld* [1985] showed that the number of particles produced is reduced by more than an order of magnitude if 4% of the total is present as existing "seed" particles at 10 nm diameter.

This paper will report a time series of measurements made from a ship in the marine boundary layer during which recent nucleation of particles and the dynamics of their ageing were observed. It is a presentation of a descriptive data set from 1 day and is used as a case study for the evidence of new particle formation and the conditions which supported this. The lack of a Lagrangian measurement platform and our inability to quantify advection precluded observation or description of the nucleation event directly from its beginning. A companion paper [*Hegg et al.*, 1992] presents measurements taken above and in the boundary layer near the ship and the theoretical results of an integral nucleation model using the observed data as input.

Consideration of theory and recent measurements indicates that monitoring of particles in the range less than about 10 nm in diameter is crucial to understanding new particle production. To simplify the discussion, we use the term "ultrafine" particles to refer to those particles in the decade of size less than 15 nm. This boundary is obviously arbitrary and was dictated by instrumental size sensitivity. This term supplements the "conventional but not too convenient" [*Sedunov*, 1974] terminology generally referring to the next three larger decades as nucleation mode (also condensation nuclei or Aitken particles, 10–100 nm), accumulation mode (or fine or large particles, 100–1000 nm) and the coarse mode (or large or giant particles >1000 nm), respectively.

EXPERIMENT

Cruise Description

Measurements were made aboard the NOAA ship *Discoverer* in the region extending from 30 to 280 km off the Washington State coast at 48.2 degrees north (Figure 1). The cruise, which occurred between April 15 and May 1, 1991, was part of the third Pacific Sulfur Stratus Investigation (PSI-3). PSI-3 was designed to define the role of marine biogenic sulfur emissions in the formation of nonsea-salt (NSS) sulfate aerosol particles and CCN, and to quantify the effects of these species on cloud albedo and climate. The program included ship, aircraft, satellite, and shore-based measurements to describe the biological, chemical, and physical oceanography, the atmospheric gas phase, condensed phase and cloud water chemistry, the aerosol size distribution, the cloud condensation nuclei population, cloud microphysics, cloud albedo, and meteorology.

Meteorological Data

Upper air wind, temperature, and humidity data were available twice per day from the National Weather Service's Quillayute Station located 30 km SSE of the land station at Cheeka Peak (Figure 1). Upper air temperature and humidity data were also available from radiosondes launched from the ship two or three times per day. Surface wind speed and direction, air temperature, humidity, and solar insolation data were recorded aboard ship. At the conclusion of the cruise, regional wind fields and isokinetic air mass back trajectories were calculated at the NOAA Air Resources Laboratory, Silver Spring, Maryland (nested grid model, R. Artz, personal communication, 1991). Cloud cover data from satellite photographs were provided by the Naval Postgraduate School, Monterey, California (P. Durkee, personal communication, 1991).

Trace Gas and Aerosol Measurements

The air sampling inlets were at the end of a 5-m vertical mast mounted on a van forward of the bridge of the ship. The mast extended 2 m above and 3 m forward of the ship's bridge and was 20 m above the sea surface. Trace gas and aerosol instrumentation was located in the laboratory van at the base of the mast. The SO_2 sampling, instrumentation and data have been previously described (E. S. Saltzman et al., Low-level atmospheric sulfur dioxide measurement using HPLC/fluorescence detection, submitted to *Journal of Atmospheric Chemistry*, 1992). Ozone was sampled through a 6 mm OD Teflon line extending to the top of the mast and measured with a Dasibi Model 1003-AH ultraviolet photometer [*Johnson et al.*, 1990]. Filter samples for chemical analysis of aerosols and gaseous sulfur dioxide were also collected from the top of the mast with a stacked sampling system consisting of a cyclone separator followed by a 1.0 μm pore size Teflon filter and four 47 mm Whatman 41 filters coated with K_2CO_3 [*Quinn and Bates*, 1989]. Details of the subsequent analysis by ion chromatography have been previously described [*Quinn et al.*, 1990]. A common inlet sample line (6 m of 15 mm ID polyethylene with a flow rate of 30 L/m) supplied all of the aerosol monitoring instrumentation in the van. From this larger flow a 4-mm-diameter 50-cm-long stainless steel sample line delivered air at a flow rate of 6 L/m to a common point between the instruments from which it was distributed by

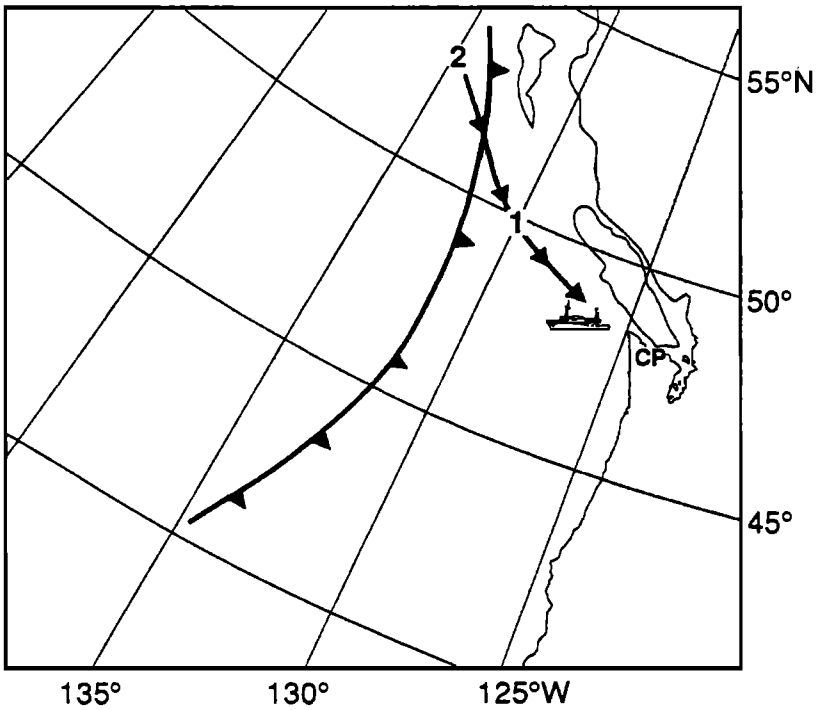

Fig. 1. Surface map of the region of the PSI-3 cruise experiment showing the location of the NOAA ship *Discoverer* at 1500 PDT on April 22, 1991, the location of the shore-based station (Cheeka Peak, CP), the location of a cold front to the west at that time, and an air mass trajectory. The air mass trajectory represents the horizontal motion of the air for the 2 days prior to arrival at the ship's location at 1500 PDT.

4-mm stainless steel tubing segments of 30 cm or less at flow rates of 1 to 3 L/m.

The total number concentration of particles greater than 3-nm diameter, $[N_t]$, was measured with an ultrafine particle counter (TSI model 3025, Thermo Systems Inc., St. Paul, Minnesota [*Stoltzenburg and McMurry*, 1991]). The number concentration of particles greater than 15 nm, $[N_{15}]$, was measured with another particle counter (TSI model 3760, *Keady et al.* [1986]; and *Zang and Liu* [1991]). These particle counters were operated according to the manufacturer's specifications. A diffusion drier (Permapure Inc., Falls River, New Jersey) was used on the inlet of the model 3760. The outputs were recorded by a data acquisition system every second and converted to 1-min averages for storage and subsequent analysis. In the terminology introduced above ultrafine particle concentration then becomes $([N_t]-[N_{15}])$. The lower size sensitivities of these instruments are not step functions at the specified values but rather have finite slopes. The specified lower limits are 50% counting efficiencies and particles down to a factor of two smaller are counted but with reduced efficiency.

The number size distribution, $d[N(D_p)]/d\log D_p$, was measured with a differential mobility analyzer (DMA). The DMA (TSI model 3071 [*Liu and Pui*, 1975]) was used to select narrow electrical mobility increments of the ambient particle distribution in a sequence of 17 steps covering the particle size range of 20-nm to 600-nm diameter (for singly charged particles). The number concentration in each of those increments was measured with a particle counter (TSI model 3760) operating at a flow of 1 L/m. The sequence of 17 steps was made over a period of 15 min or less. A minimum of 1000 particles was counted at each size increment for an uncertainty of ~3% based on one standard deviation and the assumption of Poisson counting statistics. The resulting number mobility distribution was inverted to a number size distribution using an algorithm similar to that provided by the manufacturer [*Keady et al.*, 1983]. The number concentration was corrected for the counting efficiency of the CNC [*Zang and Liu*, 1991] and diffusion losses in the DMA [*Reineking and Porstendorfer*, 1986]. A Boltzman-Fuchs equilibrium charge distribution was assumed to be present on the particles analyzed. A krypton-85 charge neutralizer (TSI model 3077) was used on the inlet of the DMA to produce an equilibrium charge distribution. The sample air passed through a diffusion drier to reduce the RH of the sample stream to less then 25% and subsequently through an impactor with a 50% cut-off diameter of 0.7 μm to eliminate large, multiply charged particles from the inlet flow to the DMA and to provide an upper boundary condition for the data inversion.

The data were edited to eliminate periods of local contamination or instrument disruption according to the ship log entries and continuous meteorological and particle concentration data. The particle number size distributions were converted to surface, $[S]$, and volume distributions. Subsets of the distributions, e.g., $[N_{20-24}]$, number concentrations in narrow increments of size, were extracted and used as a single parameter to gauge the evolution of the size distribution. The parameter $([N_t]-[N_{15}])/[N_{15}]$ was also derived from the above data set. Following on the presentation of *Warren and Seinfeld* [1985], this ratio of ultrafine to Aitken nuclei particle concentration should be a good indicator of new particle production.

RESULTS

The time series plots of the aerosol parameters $[N_t]$, $([N_t]-[N_{15}])/[N_{15}]$, and $[S]$ for the entire cruise are shown in Figure 2. It can be seen in Figure 2*a* that there was one major period of high particle concentration during the afternoon of April 22 which lasted for about 7 hours. During this period the concentration was several times greater than during similar time intervals occurring before or after that. Several other increases or spikes in the record of total particle concentration in the time series, though perhaps significant, were of much shorter duration or lesser magnitude. To make potential new particle production events in the time record more clear, the parameter $([N_t]-[N_{15}])/[N_{15}]$ was calculated and plotted in Figure 2*b*. This record of the relative number of particles in the ultrafine size range exhibits much less variability and shows evidence for a second particle production event on April 24 that was not evident in the plot of $[N_t]$. The time series of particle surface area is plotted in Figure 2*c*. On two occasions $[S]$ decreased below 10 μm^2 cm^{-3} for more than 2 hours. Although there is no threshold of surface area or time that dictates conditions for new particle production, this time scale of 2 hours is predicted by model calculations to be appropriate for the initiation of particle production in the remote marine boundary layer, and on both of these occasions low $[S]$ was accompanied by high values of the parameter $([N_t]-[N_{15}])/[N_{15}]$. This report will focus on the first event and will discuss the atmospheric conditions which seem to have caused this particle production and the resulting aerosol dynamics which were observed.

The same three aerosol parameters, $[N_t]$, $([N_t]-[N_{15}])/[N_{15}]$, and $[S]$, are plotted in detail in Figures 3*a* through 3*c* for the 30-hour period subsequent to 0000 PDT on April 22. Prior to 1500 PDT, $[N_t]$ was relatively constant at 200 to 300 cm^{-3} (Figure 3*a*). After 1500 it increased over a period of 1 hour to a value of 3200 cm^{-3}, which was maintained (±25%) for a period of 7 hours. After 2300, $[N_t]$ decreased to about 500 cm^{-3} in a period of 2 hours. The number ratio, $([N_t]-[N_{15}])/[N_{15}]$, began to increase at 1400 from a value of 0.5 to 1.2 (Figure 3*b*) concurrent with the decrease in Aitken nuclei particle and surface concentration (Figure 3*c*). It

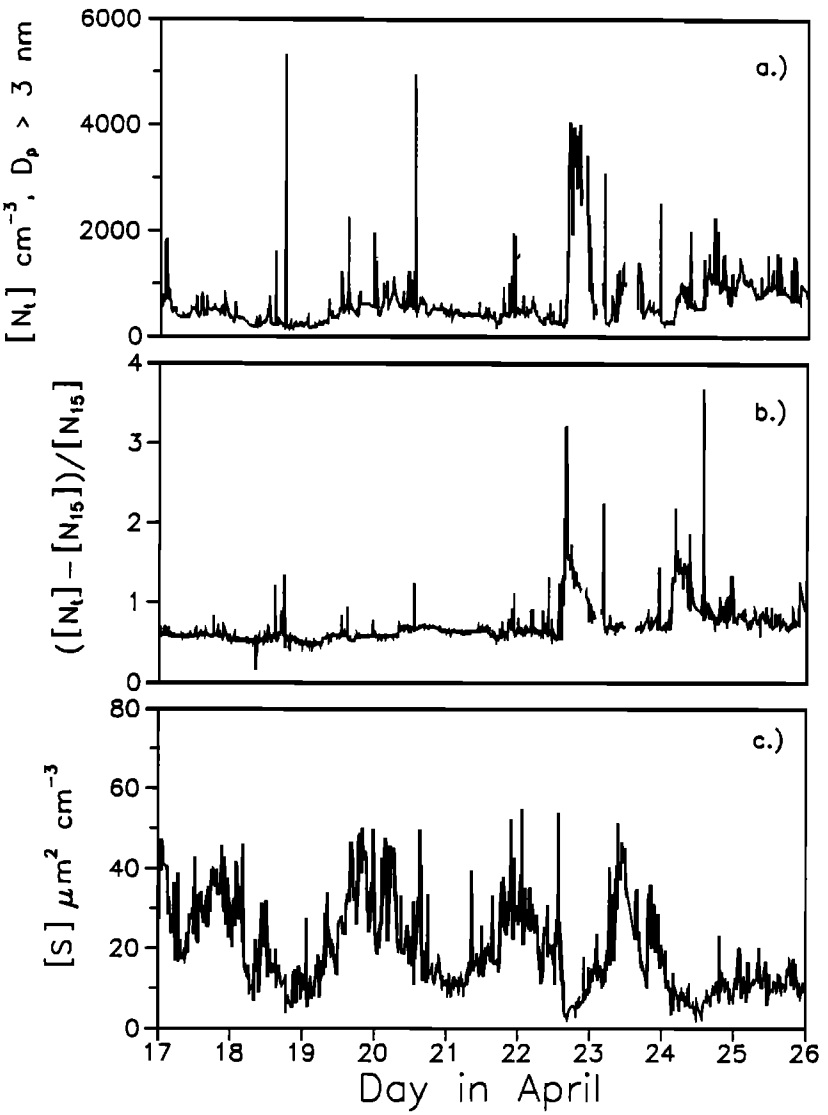

Fig. 2. Time series of aerosol parameters for the entire 1991, PSI-3 cruise. (*a*) Total particulate number concentration, $[N_t]$, for particles greater than 3-nm diameter, particles per cubic centimeter. (*b*) Ratio of ultrafine to Aitken nuclei, $([N_t]-[N_{15}])/[N_{15}]$; $[N_{15}]$ is the particle concentration greater than 15 nm. (*c*) Particulate surface area, $[S]$, for particles greater than 20 nm in diameter, square micrometers per cubic centimeter.

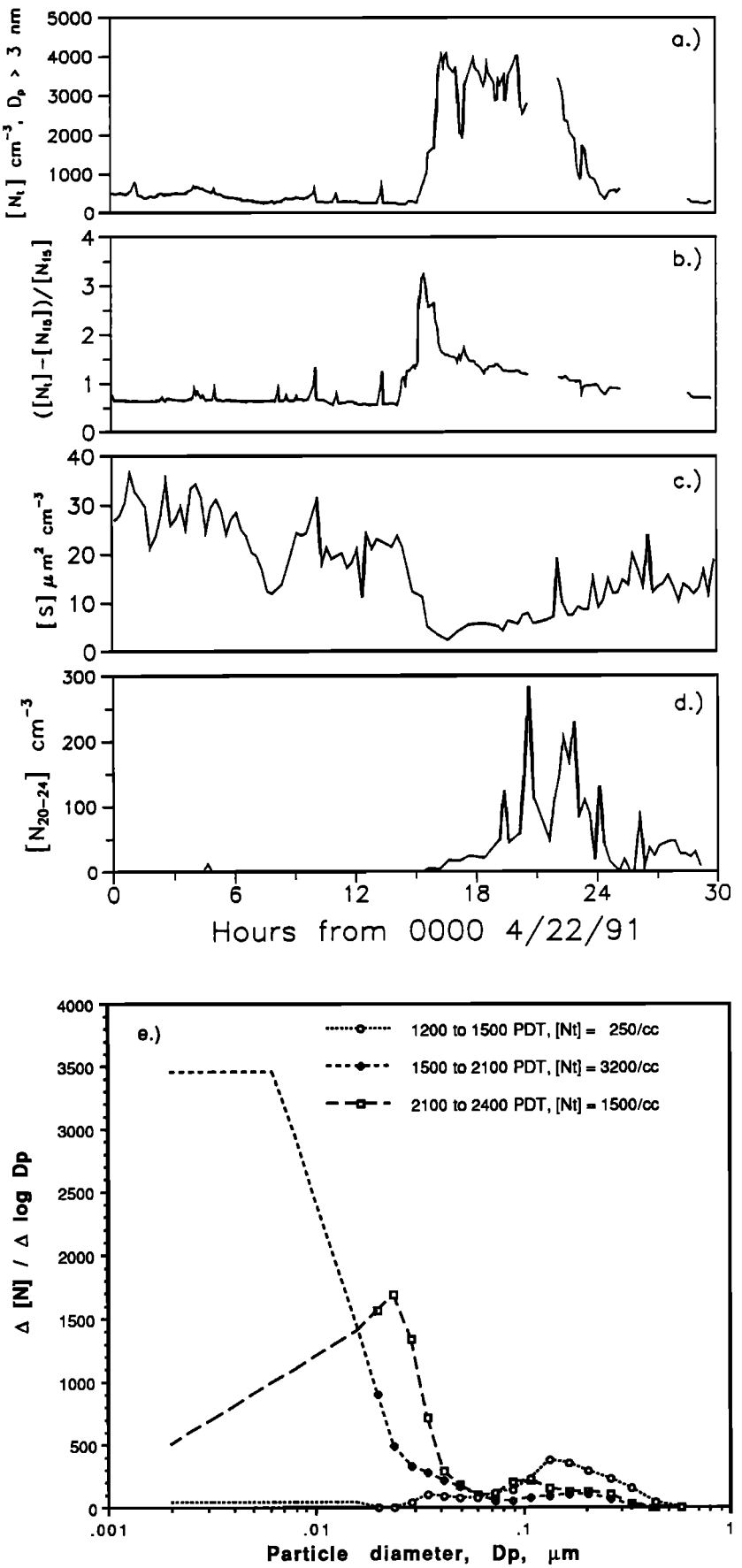

Fig. 3. Time series of aerosol parameters on April 22, 1991 of the PSI-3 cruise. (*a*) Total particulate number concentration, $[N_t]$, for particles greater than 3-nm diameter, particles per cubic centimeter. (*b*) Ratio of ultrafine to Aitken nuclei, $([N_t]-[N_{15}])/[N_{15}]$; $[N_{15}]$ is the particle concentration greater than 15 nm. (*c*) Particulate surface area, $[S]$, for particles greater than 20 nm in diameter, square micrometers per cubic centimeter. (*d*) Particulate number concentration in the diameter range 20–24 nm, $[N_{20-24}]$. (*e*) Number concentration size distributions before and during the nucleation event, $\Delta[N]/\Delta\log D_p$, particles per cubic centimeter.

increased further at the same time as the increase in $[N_t]$ to a value of 3.2, but began to decrease after 1600 as the particle size distribution shifted to a larger mean size. The aerosol surface area averaged around 22 μm^2 cm^{-3} before about 1400 PDT, dropped suddenly to less than 5 μm^2 cm^{-3} over a period of 2 hours and increased slowly over the next 7 hours to a value of 7 μm^2 cm^{-3}. The surface area, dominated by particles greater than about 80 nm, is clearly inversely related to the other two parameters, but the relationship is not necessarily causal as will be explained below.

The time series of particle concentration in the smallest channel of the DMA from 20 to 24 nm is presented in Figure 3*d*. This parameter is an indicator of the evolution of the ageing aerosol size distribution and its increase lags that of $[N_t]$ by several hours. Differential number size distribution measurements were limited to the range 20 to 600 nm and thus could not be used directly to quantify the increase in concentration or the evolution of the ultrafine aerosol resulting from the nucleation except in the negative sense that when the size distribution was closed at 20 nm, particle production had not occurred recently. However, using $[N_t]$ to define the integral particle number greater than 3 nm, the measured distributions were extrapolated to 3 nm. Averages were made for the periods prior to, during, and after the nucleation event, 1200 to 1500, 1500 to 2100, and 2100 to 2400 PDT, respectively (Figure 3*e*). Although the shapes of the curves below 20 nm are arbitrary, the integrals of the number distributions (areas under the curves) are accurate and defined by the $[N_t]$ measurements.

The meteorological data show that prior to and during the event the wind direction was backing from about 270 to 180° (true) while the wind speed decreased from 10 to 5 knots (5–2.5 m/s) (Figure 4*a*). The surface temperature was relatively constant at 8.3°C ± 0.4°C throughout the day (Figure 4*b*) and the surface relative humidity (RH) decreased from 75% early in the day to 55% by mid-day followed by a sudden increase to 60 to 65% just prior to 1500 hours. The several hour period of lower RH accompanied a 1° rise in temperature. The total solar radiation was fairly constant at 400 W/m^2 for the hour before and after the beginning of the event and decreased thereafter (Figure 4*c*). Evidence of broken cloud cover can be seen in the variability of the radiation data. The vertical temperature and RH profiles which were measured at 1000, 1640, and 1900 hours by radiosondes launched from the ship (Figure 4*d*) show that very similar conditions prevailed throughout the day with a 1200-m-deep marine boundary layer and a pronounced inversion above that level. Satellite pictures and aircraft observations indicate a scattered to broken cloud layer between 800- and 1200-m elevation and relatively uniform conditions in the horizontal plane. The boundary layer was conditionally unstable throughout part or all of that depth during the day allowing for the possibility of mixing from the top of the cloud layer.

A synoptic analysis of the meteorological situation over the NE Pacific shows a cold frontal zone (Figure 1) with associated clouds and precipitation between 135° and 130°W backed by strong westerly flow. Between 130°W and the coast there was split flow and generally WSW winds in the region of the ship (48°N, 127°W). Lower tropospheric wind field data, upper air data from Quillayute weather station and a coastal station at 400-m elevation, and surface wind data from the ship were all consistent with this picture and indicate relatively constant flow for the 36 hours prior to the event. Satellite photographs show the region of split flow to be evenly covered with broken marine stratus with tops at about 1200 m. Trajectory analysis from the nested grid model (NGM) shows 2-day transport to the ship's location from 135°W, 54°N, entirely over the North Pacific (Figure 1). The trajectory's closest approach to land was about 200 km which occurred along the Queen Charlotte Islands, British Columbia.

The O_3 concentration ranged from 25 to 35 ppbv on April 22, typical of the MBL at this latitude and time of year. A decrease from 33 to 27 ppbv occurred coincident with the increase in RH from 1400 to 1500 hours. SO_2 concentration averaged around 20 pptv during the day but there were at least two periods when the concentration increased to 40 to 60 pptv (E. S. Saltzman et al., submitted manuscript, 1992). One of these excursions occurred just prior to the observation of high particle concentration; the other occurred during the event at about 1800 PDT. This was after the maximum in solar radiation but during a 1-hour break in cloud cover and a local maximum in irradiance. DMS concentrations were high, 100–200 pptv, during the early morning and decreased to less than 10 pptv by mid-day (D. Cooper, personal communication, 1991).

DISCUSSION

The formation rate of new particles by nucleation of H_2SO_4 or MSA vapors is sensitive to a change in one or more of the controlling physical and chemical parameters described earlier; particulate surface area, precursor gas or vapor concentrations, temperature and water vapor pressure. The H_2O vapor pressure and temperature changed relatively little during the entire day; $[S]$ and $[SO_2]$ varied by factors of 5 and 2, respectively, during the afternoon of April 22.

Beginning at 1430 the particulate surface area decreased from around 22 μm^2 cm^{-3} to less than 5 μm^2 cm^{-3} over a period of 2 hours. This decrease in surface area was a necessary condition for nucleation. According to the size distribution measurements, the decrease in particulate surface area was caused by the decrease in concentration of the particles in the 80- to 600-nm range. Either there was a very rapid sink for these particles or cleaner air was advected or mixed from aloft. Since particle coagulation processes are slow at these sizes and concentrations and there was no active area of precipitation within 24 hours or more upwind, the possibility of a rapid sink is excluded. The horizontal uniformity of the meteorological conditions as deduced from satellite data, aircraft observations, wind field and synoptic charts makes advection an unlikely cause for the change in particulate surface area. Especially the aircraft data show no evidence of horizontal variability in aerosol concentrations anything like those observed. Vertical mixing remains as a possibility and is supported by aircraft measurements aloft prior to 1500 on April 22 [*Hegg et al.*, 1992]. Conservative variable plots of equivalent potential temperature and total water mixing ratio for the boundary layer show evidence of mixing from cloud top levels where SO_2 was 50–60 pptv and $[N_t]$ was about 750/cm^3 and $[S]$ was 4 to 5 μm^2 cm^{-3} [*Hegg et al.*, 1992]. An additional cause of the decrease in surface area could have been a drop in sea salt particle concentration due to decreasing local wind speed over the time of the event.

An increase in ultrafine particle number followed the decrease in particulate surface area within a period of 30 min. The increase began as $[S]$ dropped below 10 μm^2 cm^{-3} and

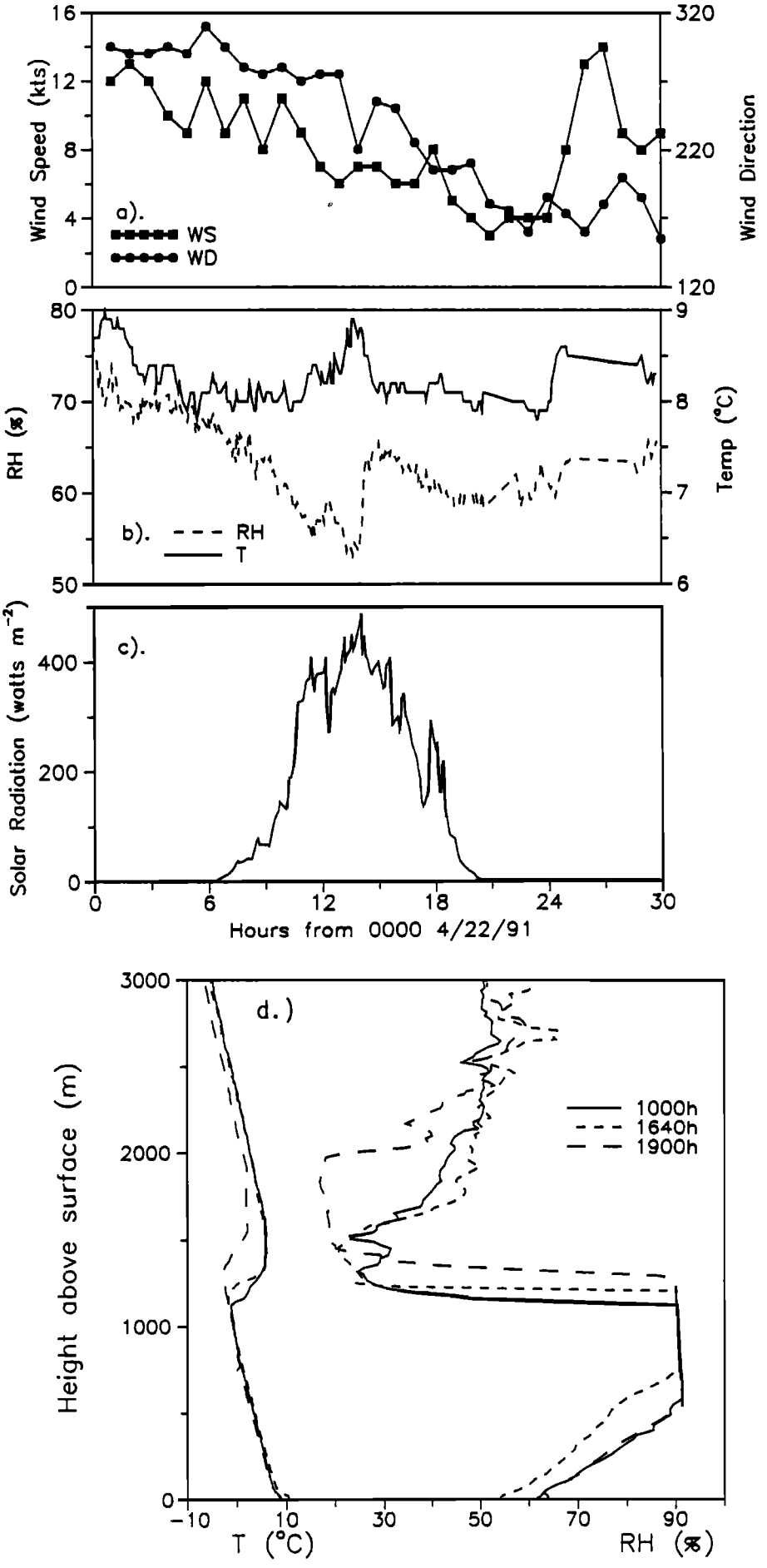

Fig. 4. Meteorological data collected by the *Discoverer* on April 22, 1991. (*a*) Wind speed and direction. (*b*) Surface temperature and relative humidity, RH. (*c*) Solar radiation. (*d*) Vertical profiles of temperature and RH.

became more pronounced when [S] decreased to <5 μm^2 cm^{-3}. The observed increase in $[N_t]$ from 250 to 4000 cm^{-3} in a period of an hour was more rapid than the production rate that can be predicted by nucleation theory and the observed atmospheric chemical composition, but it is easily within the range of theoretical predictions over a period of 3 hours [*Hegg et al.*, 1992]. Since our measurements follow the change in particulate concentration due to a production rate and motion across a spatial gradient, the observed change in concentration must be taken to represent the sum of these two differentials.

The particulate concentration in the size range 20 to 24 nm diameter ($[N_{20-24}]$) was initially less than 2 cm^{-3}. It did not increase significantly until 3 hours after the initial burst in $[N_t]$ and decreased rapidly from 2200 to 2400. Thus, most of the newly produced particles were less than 20 nm in diameter at the time when an increase in $[N_t]$ was first observed as would be expected for a newly nucleated size distribution. The number size distribution constructed from the DMA and $[N_t]$ measurements (Figure 3*e*) are consistent with this picture of the evolution of the distribution after the initial nucleation. Again, the coagulation process is not fast enough under these conditions to produce the observed increase in $[N_{20-24}]$ or subsequent decrease in either $[N_t]$ or $[N_{20-24}]$. According to theory, the number concentration should not increase or decrease appreciably due to coagulation under these conditions for times less than several days [e.g., *Shaw*, 1989]. The increase in $[N_{20-24}]$ may be due to heterogeneous condensation of the remaining H_2SO_4 vapor on the smaller, newly formed particles after the initial nucleation has peaked. The nucleation model of *Hegg et al.* [1992] supports such growth up to about 20 nm within a few hours. The rapid decrease in $[N_{20-24}]$ after 2200 must be due to further advection or mixing of clean air.

The sulfur dioxide concentration at the ship showed two excursions from the background level of 20 pptv measured prior to 1400 PDT to around 50 pptv which was similar to the level of SO_2 measured by the aircraft above the boundary layer [*Hegg et al.*, 1992]. An increase of this magnitude is adequate to increase the particle nucleation rate significantly.

CONCLUSION

Formation of new particles by nucleation is a variable and sporadic process rather than a continuous one. These intensive aerosol measurements in the marine boundary layer indicate that a local, mesoscale burst of new particle production in the size range less than 15 nm had occurred. This was caused by the physical and chemical conditions of the atmosphere involving both gas and condensed phase parameters as well as the atmospheric structure and the cloud and radiation fields. The controlling aerosol parameter was the surface area, as has been pointed out repeatedly by previous research, but never measured or quantified to the degree done in this case. Even at low concentrations of the precursor gas, SO_2, nucleation can occur if the particulate surface area is sufficiently low.

The parameter $([N_t]-[N_{15}])/[N_{15}]$ seemed to be useful for indicating occurrences of new particle production. While the differential size distribution or the ratio of its integral number to surface moments might be the more appropriate parameters to indicate nucleation, they are not so simple to interpret or to acquire instrumentally in real time.

The occurrence of short bursts of high concentration of particles in the marine boundary layer is not necessarily indicative of local contamination. Selection of data or control of sampling equipment by use of an upper bound on $[N_t]$ (or some subset thereof) may eliminate events of interest to the understanding of the marine background particle concentration and cloud condensation nucleus formation.

Based on these and previous results, the generally uniform background particle concentration observed in the marine boundary layer is not due to a continuous low source rate but rather to more sporadic high production rates distributed in space and time. This, coupled with mixing and the sink functions, produces the low, more uniform number concentration generally observed.

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T. S. Bates and P. K. Quinn, NOAA PMEL, 7600 Sand Point Way NE, Seattle, WA 98115.

D. S. Covert, Departments of Environmental Health and Atmospheric Sciences, University of Washington, Seattle, WA 98195.

V. N. Kapustin, Institute of Atmospheric Physics, Academy of Sciences, Moscow, Russia.

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