Nucleation in the equatorial Pacific during PEM-Tropics B: Enhanced boundary layer H$_2$SO$_4$ with no particle production


Abstract. During the second phase of the NASA Pacific Exploratory Mission to the Pacific Tropics (PEM-Tropics B), regions of unusually high concentrations of sulfuric acid vapor ranging from $10^4$ to $10^6$ molecules cm$^{-3}$ were detected near the ocean surface in equatorial regions between Hawaii and Tahiti. No 3-4 nm diameter nanoparticles were observed near the ocean surface where acid concentrations were highest; however, 3-4 nm particles were detected at higher elevations in regions near clouds. Calculations show that in some regions of high acid concentrations newly formed particles would be readily detected by our instruments and thus the lack of nanoparticles suggests that there was no nucleation. In contrast, in the previous PEM-Tropics A mission Clarke et al. [1998a] observed a large nucleation event in the equatorial marine boundary layer under similar temperatures, relative humidity, and sulfuric acid concentrations. Comparison between these two studies further demonstrates that some additional species or unknown process is necessary to significantly enhance nucleation in the remote marine troposphere and that this component is not always present at levels sufficient to sustain nucleation throughout the region, even at a low continuous rate. We speculate that if ammonia is one example of a critical nucleation precursor, tropospheric ternary nucleation (sulfuric acid/ammonia/water) under some conditions requires ammonia concentrations to be greater than typical background concentrations for particle production via this mechanism.

1. Background

Atmospheric gas phase reactions lead to the production of low volatility vapors. Formation of sulfuric acid (H$_2$SO$_4$) from sulfur dioxide oxidation (SO$_2$) is a well-known example. These products may either homogeneously nucleate to form new particles or condense onto existing particles. Nucleation leads to the production of large numbers of new fine particles whereas heterogeneous condensation increases the existing aerosol mass, thus the dominant processes will affect the ambient aerosol number distribution. Because aerosol light scattering properties depend on particle number and size, these processes can have global impacts ranging from agricultural productivity through regional haze [Chameides et al., 1999] to influencing climate by altering the terrestrial radiation balance [Charlson et al., 1987; Kiehl and Briegleb, 1993].

Recently, many studies have reported on observations of homogeneous nucleation events in the troposphere where large numbers of particles between 3 and 10 nm diameter were recorded [Birmili and Wiedensohler, 2000; Clarke et al., 1999; Harrison et al., 2000; Mäkelä et al., 1997; O'Dowd et al., 1998; Pirjola et al., 1998]. These measurements span a broad range of both geographical locations and ambient conditions under which nucleation was observed. Despite intensive research involving both measurements and modeling, a clear understanding of the particle formation mechanism has not been achieved.

Until recently, the predominant mechanism was thought to be binary sulfuric acid-water (H$_2$SO$_4$-H$_2$O) nucleation [Jaegker-Voirol and Mirabel, 1989]. However, more recent studies involving simultaneous measurements of H$_2$SO$_4$ vapor and nanoparticles (e.g., 3 to 10 nm diameter) have shown that in many cases current binary nucleation theory cannot explain the observations [Clarke et al., 1998a; Weber et al., 1995, 1996, 1997, 1998a, 1999b]. In these cases, nucleation events were correlated with H$_2$SO$_4$ concentrations, yet the H$_2$SO$_4$ concentration was often orders of magnitude too low, and in some cases nucleation did not appear to
be correlated with relative humidity (RH) [Weber et al., 1997, 1998a], in contrast to binary theory. Our recent analysis has suggested that nucleation observed near the surface at ground based sites or during low-altitude aircraft runs generally occur under conditions that are far from those necessary for binary nucleation. At higher altitudes, however, the conditions tend to approach those necessary for binary H$_2$SO$_4$-H$_2$O particle production [Weber et al., 1999b].

A variety of routes for new particle formation likely occur in the remote troposphere. A number of mechanisms have been proposed, although most still involve H$_2$SO$_4$ and water. For example, we have argued that a ternary mechanism of sulfuric acid, ammonia, and water (H$_2$SO$_4$-NH$_3$-H$_2$O) is a likely candidate. There is some ambient data supportive of a ternary mechanism [Weber et al., 1998a], and recent laboratory studies show that ammonia added to the H$_2$SO$_4$-H$_2$O binary system can significantly enhance nucleation rates [Ball et al., 1999], in agreement with recently developed ternary nucleation models [Coffman and Hegg, 1995; Korhonen et al., 1999]. In the Korhonen et al. [1999] model, NH$_3$ significantly enhances nucleation if concentrations are above 1 pptv, but the enhancement does not continue to increase with NH$_3$ concentration once 10 pptv is reached (at 25°C). Korhonen et al. [1999] also found that ternary nucleation is weakly dependant on RH for H$_2$SO$_4$ concentrations below 10$^3$ cm$^{-3}$, levels typically found in the troposphere. According to this model, background H$_2$SO$_4$ and NH$_3$ levels are sufficient throughout most of the troposphere during the daytime to support a continuous and ubiquitous production of new thermodynamically stable nuclei (TSN) [Kulmala et al., 2000]. It is argued that these nuclei are generally not detected since most don’t grow to the detection limits of current aerosol instruments (typically about 3 nm). Recent modeling studies suggest that it requires H$_2$SO$_4$ levels of about 6x10$^3$ cm$^{-3}$, sustained for a few hours, for newly formed particles in the marine boundary layer to reach a detectable size of 3 nm, if H$_2$SO$_4$ and H$_2$O are the only condensing species [Pirjola et al., 2000]. Thus particle growth and not homogeneous nucleation may limit the formation of atmospheric particles larger than a few nanometers in size.

Other mechanisms for particle production are possible. Nucleation of terpinoid species in forested regions has been proposed for some time [Went, 1960]. Particle production by H$_2$SO$_4$ chemi-ions has also been proposed. Models using this mechanism agree with ambient measurements [Yu and Turco, 2000], both in terms of enhanced nucleation rates and particle growth rates. These models have also tended to predict that nucleation is possible throughout the atmosphere and that a ubiquitous low production rate is possible [Turco et al., 1998]. Raes et al. [1997] has shown that a low ubiquitous production rate in the marine boundary layer, if it exists, could be an important source of tropospheric aerosols. Simulations of aerosol processes in the remote marine troposphere suggest that a continuous low production rate of 2x10$^3$ cm$^{-3}$ could sustain the observed marine aerosol size distribution and be a significant source of marine cloud condensation nuclei. Finally, nucleation due to mixing of air parcels of differing temperature and relative humidity is also a possible mechanism for new particle production [Easter and Peters, 1994; Nilsson and Kulmala, 1998, Nilsson et al., 2000].

One objective of the NASA PEM-Tropics B mission was to investigate nucleation mechanisms in the clean Pacific Basin region. A unique observation from this study was frequent encounters near the sea surface with regions containing unusually high H$_2$SO$_4$ concentrations, yet newly formed nanoparticles were only observed at higher altitudes. These observations can provide new insights into nucleation mechanisms since enhanced H$_2$SO$_4$ concentrations will lead to rapid growth of any newly formed particles making them readily detectable. Thus, in these regions, the influence of measurement limitations on nucleation studies is minimized. In the following, we investigate these regions for nucleation and compare the observations to binary and ternary nucleation models. Further analysis to explore other nucleation mechanisms, such as the role of ions, organic compounds, or fluctuating processes are not investigated in this paper.

2. Instrumentation

A suite of airborne measurements of various gases and aerosol physical properties were made from two aircraft during February through March of 1999. This paper focuses on measurements made from the NASA P-3 B research aircraft which operated between about 1.4 and 8 km altitude. During PEM-Tropics B the aircraft was stationed primarily at two sites for intensive studies in the central Pacific; Christmas Island and Tahiti.

A description of the instrumentation and an overview of the PEM Tropics B mission can be found in accompanying papers (JGR PEM T B special section). The instruments most pertinent to this study are the chemical ionization mass spectrometer (CIMS) [Eisele and Tanner, 1993] used to measure H$_2$SO$_4$ gas, and a custom Ultrahfine Condensation Particle Counter with pulse height analysis (PHA-UCPC) [Saros et al., 1996; Weber et al., 1998b] to measure concentrations of newly formed particles in the 3 to 4 nm size range. The PHA-UCPC technique allows for very sensitive measurements of 3-4 nm particle concentrations. This sensitivity is critical when striving to detect the presence or absence of a low particle production rate. It should be noted, however, that the measurement is not precise in an absolute sense due to large uncertainties in airborne nanoparticle sampling efficiencies [Weber et al., 1999a] and our
We estimate that reported 3-4 nm particle concentrations are underestimated by a factor ranging from 2 to 4.

In addition to the PHA-UCPC, two identical condensation nuclei (CN) counters (TSI 3010, Thermal Systems Inc., St. Paul, Minnesota) were deployed. These instruments have a lower size detection limit of about 10 nm. Sample-line heaters upstream of the CNCS were operated with a temperature difference of 22 °C to infer particle volatility.

Both the CIMS and PHA-UCPC instruments were deployed on the NASA P-3 aircraft. No measurements of H$_2$SO$_4$ were made from the NASA DC 8, the other aircraft participating in the study. However, measurements of total CN were made on the DC 8 using two CN counters (a TSI 3025 and TSI 3760). With these two instruments, concentrations of all particles between roughly 3 and 15 nm can be calculated by difference.

Also pertinent to this study was the measurement of aerosol surface area concentration. This was determined by two techniques. In one approach the surface area was calculated from measured dry aerosol size distributions spanning the particle diameter range from 11 nm to about 4.5 μm. The size distributions of dried aerosol particles were measured inside the aircraft sampling through a shrouded nominally isokinetic inlet. Particles from 9 nm to 0.2 μm were measured using a differential mobility analyzer (DMA [Knutson and Whithy, 1975]), and from 0.2 to 3.5 μm diameter with a modified laser particle counter (PMS, LAS-X, Boulder, Colorado). At low altitudes in the marine boundary layer, aerosol surface areas were inferred from dry nephelometer aerosol backscattering measurements. Comparisons to optical particle counter measurements show that nephelometer backscatter is highly correlated with aerosol surface area (correlation coefficient of 0.91). However, it has been found that the nephelometer measurement suffers less from large particle losses than the DMA-OPC measurements, and thus provides a better measurement of total surface area near the ocean surface. In all cases wet aerosol surface areas are estimated based on an assumed growth of sea-salt particles. This will lead to an upper limit on the reported aerosol surface areas since aerosols composed of other species will generally absorb less water.

3. Theory

Atmospheric nucleation events are identified by the detection of the newly formed particles. Practically, this means measuring particles in the 3-4 or 3-10 nm range, depending on the instrumentation used. However, because current instrumentation can only detect particles down to about 3 nm, and newly formed particles composed of a few molecules can be about 1.0 nm diameter, these particles must grow to detectable sizes for a region of nucleation to be identified. Owing to their high mobility, these particles can have short life spans (on the order of hours). Thus the presence of large numbers of 3-4 or 3-10 nm particles is interpreted as resulting from a recent nucleation event, however, the lack of these particles in a region where nucleation is expected can result from different processes. Nucleation may not have occurred, or it may have occurred but most of the newly formed embryos did not grow sufficiently to be detected or were scavenged before they reached 3 nm. Scavenging can be significant in regions of high aerosol surface area concentrations and when growth rates are low. To determine the significance of scavenging during growth to detectable sizes, we compare an estimate of the average time for particle growth from 1 to 3 nm (time from formation to detection) to the characteristic time for these particles to be lost by scavenging. A more comprehensive approach would be to employ an aerosol model that accounts for all processes, as done by Pirjola et al. [2000]; however, that is not attempted here.

Growth times from condensing H$_2$SO$_4$ and H$_2$O are calculated under the assumption that growth is limited by the rate of H$_2$SO$_4$ condensation and that the droplet is in equilibrium with water vapor. The particle growth rate is determined by

$$ \frac{dD_p}{dt} = v_r \frac{[H_2SO_4]}{2} c_v, $$

where $v_r$ is the volume added to the particle by condensation of a H$_2$SO$_4$ molecule and the water absorbed to maintain equilibrium with the surrounding water vapor, and $c_v$ is the average thermal speed of a hydrated H$_2$SO$_4$ molecule. We are assuming a H$_2$SO$_4$ accommodation coefficient of 1 and ignore H$_2$SO$_4$ evaporation. If other species also condense, growth rates could be considerably faster. This has been found to be the case in a number of studies [ODowd et al., 1999; Weber et al., 1997, 1998a] where observed growth rates were higher by factors of 2 to 15.

As in earlier papers [Weber et al., 1997], characteristic scavenging times are estimated by

$$ \tau = \frac{4\delta}{c_A}, $$

where $\delta$ accounts for diffusional resistance to mass transfer when the preexisting particles are of the order of or larger than the air mean free path. From measured aerosol size distributions we estimate that $\delta$ is typically of the order of 1.3. We will assume a constant value of 1.3. In this case $c$ is the average thermal speed of the particle that is scavenged. We use 1.5 nm as the average diameter of a newly formed particle growing to detectable sizes and assume a constant RH and temperature of 85% and 25°C, respectively. This is reasonable since we are only seeking order of magnitude estimates of growth and scavenging rates. The total aerosol surface area
concentration is $A$. Note that scavenging results in an exponential time decay of newly formed particles where $\tau$ in equation (2) is one $e$-folding time. Thus, even if calculated scavenging times are near growth times, one would still expect to observe some newly formed particles. In the following analysis of ambient measurements, we interpret regions where no 3-4 nm particles were detected but where calculated growth times were of the order of or smaller than scavenging times to indicate that no new particle production had occurred since any particles formed should have reached detectable sizes.

4. Observations

4.1. Regions of Enhanced $H_2SO_4$ Concentration:

An Overview

In previous studies, we have found that in remote marine regions, $H_2SO_4$ concentrations typically ranged from mid $10^3$ to $10^4$ cm$^{-3}$, and that newly formed particles could be observed under certain conditions when $H_2SO_4$ was in this range. In this study, $H_2SO_4$ concentrations between $10^2$ to $10^3$ cm$^{-3}$ were frequently observed, yet little or no evidence for nucleation was detected in these regions. Highest acid concentrations were generally found near the ocean surface. This is shown in Figure 1a for data collected between latitudes of 21°N to 22°S, and longitudes of 194 to 220°W. The source of the unusually high acid concentrations is thought to be due, at least in part, to enhance biogenic production of DMS in this region. During the study this unique region was referred to as a sulfur pool. Change in sulfuric total relative acidity (RA) with altitude is shown in Figure 1b. Total relative acidity is the measured $H_2SO_4$ concentration (monoacid plus all hydrates) divided by the saturation concentration over a flat surface at the ambient temperature. We use the expression of Ayers et al. [1980] to calculate the $H_2SO_4$ saturation pressure. Note that the observed increase in relative acidity with altitude is due to its strong temperature dependence and that binary $H_2SO_4$-$H_2O$ nucleation is highly sensitive to relative acidity. Figure 1c shows that in this region, as is generally observed throughout marine regions, total ultrafine particle concentrations increased with altitude (referred to as ultrafine condensation nuclei, UCN, includes all particles larger than 3 nm). This increasing concentration with altitude has been interpreted as evidence that particle production occurs primarily in the free troposphere and that this region supplies new particles to the marine boundary layer [Clarke, 1992]. Here we have plotted UCN instead of 3-4 nm particle concentrations since this was a common measurement on both aircraft.

These data indicate a general negative correlation between $H_2SO_4$ and UCN concentrations and a positive correlation between relative acidity and UCN. The trends may result from $H_2SO_4$ production occurring near the ocean surface and new particle production primarily at higher altitudes, and

![Figure 1](image-url) Variation of (a) sulfuric acid, (b) sulfuric total relative acidity, and (c) ultrafine particle (all particles larger than 3 nm diameter) concentrations with altitude in the central equatorial Pacific (22°S to 21°N, and longitudes of 194 to 220°W). All concentrations are at ambient conditions. The data tend to support the view that $H_2SO_4$ is produced mainly near the ocean surface and particles are produced primarily at higher altitudes in regions of high relative acidity.
Figure 2. A specific case study comparing three measurement legs during Flight 13. The plots show the following: (a) The altitudes of the legs labeled as A, B, and C. (b) H₂SO₄ concentrations are highest at the ocean surface (Leg B) but H₂SO₄ relative acidity is highest at the higher altitudes due to colder temperatures. (c) Recently formed 3-4 nm particles were generally not found near the sea surface but at higher altitudes (Legs A and C). In Leg B the 3-4 nm particle concentrations and relative humidity rapidly increased together. These measurements were made in cloud detrainment fields suggesting nucleation was associated with the cloud outflow. (d) Aerosol surface area concentrations are highest at the surface and total UCN is lowest there.

is suggestive that nucleation depends more on relative acidity than the H₂SO₄ concentration. These observations are explored further by looking at a specific case study, Flight 13.

4.2. Flight 13: A Case Study

Flight 13 was based out of Tahiti. Here we focus on a 4-hour portion of the flight conducted in the vicinity of 8°S latitude and 216°W longitude. The altitude of the aircraft and recorded ambient temperature are shown in Figure 2a. During this period the aircraft made horizontal legs at various altitudes. Three legs of interest are identified in each plot in Figure 2. The first leg of interest (labeled A) was at an average altitude of ~5.5 km and occurred between 2100 and 2200 hours UTC (roughly 1130 to 1230 local Sun time, Sun reaches zenith at 1200). The aircraft then made a low-altitude run at about 0.3 km (leg B) between 2200 and 2230 UTC, and then a 7.5 km leg (C) from 2255 to 2355 UTC.

The H₂SO₄ concentration and the H₂SO₄ total relative acidity is shown in Figure 2b where it is seen that the H₂SO₄ concentration is the highest near the surface on leg B with values ranging from about 2 to 5.5x10⁷ cm⁻³. For the mid-altitude leg A (5.5 km) the H₂SO₄ concentration was about 7x10⁷ cm⁻³, and at the highest altitude leg C (7.5 km) the H₂SO₄ concentration was the lowest at about 2x10⁷ cm⁻³. However, because it was much colder at the higher altitudes the relative acidity was higher there, ranging from about 10⁻⁷ (leg C), to about 5x10⁻⁴ (leg A), compared to 1x10⁻⁴ at the surface (leg B).

Although the H₂SO₄ concentrations are unusually high near the surface, Figure 2c shows that we detected practically no 3-4 nm particles in this region. It follows that no, or very few, new 3 nm particles were being produced under these conditions. However, we cannot yet exclude the possibility that smaller particles had been formed in this region but were not detected. This is explored later. At the mid-altitude leg (A), some 3-4 particles were detected. Comparing the ambient RH and 3-4 nm concentrations plotted in Figure 2c shows that most nanoparticles were observed in the region of highest RH, and that the sudden 3-4 nm particle concentration increase tracked with the jump in RH. During this part of the flight we were attempting to fly in regions of cloud outflow. We interpret the sudden jump in RH to over 80% at this altitude a result of entering a cloud detrainment region. Thus
Table 1. Measured Conditions and Calculated Scavenging and Growth Times of Newly Formed (1.5 nm) Particles in Regions Where H$_2$SO$_4$ Concentrations Were Greater Than 3x10$^7$ cm$^{-3}$ in Pacific Equatorial Regions During PEM-Tropics B (March 1999) $^a$

<table>
<thead>
<tr>
<th>Flight</th>
<th>H$_2$SO$_4$</th>
<th>RH, %</th>
<th>T, °C</th>
<th>Altitude, km</th>
<th>Surface Area, $\mu$m$^2$ cm$^{-3}$</th>
<th>3-4 nm</th>
<th>UCN, cm$^3$</th>
<th>Scavenging Time, min</th>
<th>Growth Time, min</th>
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<tr>
<td>6-A</td>
<td>4.0E+07</td>
<td>93</td>
<td>23</td>
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<td>87</td>
<td>0.00</td>
<td>595</td>
<td>14</td>
<td>22</td>
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<tr>
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<td>90</td>
<td>23</td>
<td>0.3</td>
<td>79</td>
<td>0.00</td>
<td>556</td>
<td>15</td>
<td>30</td>
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<tr>
<td>8</td>
<td>8.8E+07</td>
<td>81</td>
<td>20</td>
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<td>74</td>
<td>174</td>
<td>15</td>
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<tr>
<td>10-A</td>
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<td>50</td>
<td>12</td>
<td>2.4</td>
<td>10</td>
<td>0.03</td>
<td>366</td>
<td>127</td>
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<tr>
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<td>0</td>
<td>4.6</td>
<td>11</td>
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<td>428</td>
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<td>49</td>
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<tr>
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<td>13</td>
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<td>343</td>
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<tr>
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<td>69</td>
<td>27</td>
<td>0.2</td>
<td>119</td>
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<td>321</td>
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<td>36</td>
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<tr>
<td>PEM A</td>
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<td>25</td>
<td>&lt;1.3</td>
<td>4</td>
<td>1E+04</td>
<td>4E+04</td>
<td>296</td>
<td>15</td>
</tr>
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</table>

$^a$The data are conditions under which maximum H$_2$SO$_4$ concentrations were observed. The final row shows conditions under which a large nucleation event was observed during PEM-Tropics A (September 1996).

Observations of 3-4 nm particles in this region are consistent with many other studies suggesting particle production readily occurs in cloud outflow regions [Clarke et al., 1999, 1998b; Hegg et al., 1990; Perry and Hobbs, 1994; Weber et al., 1999b]. Throughout the highest altitude leg (C), 3-4 nm particles were also observed, but the concentrations were lower than leg A.

The observed total UCN concentrations are generally consistent with the nanoparticle measurements. Total UCN and an estimate of the ambient (wet) aerosol surface area is shown in Figure 2d. Highest UCN number concentrations are found at the higher altitudes where the particle production was occurring. Highest aerosol surface area concentrations are found at the lowest altitudes being closer to the source where sea salt particle production occurs from ocean spray. Thus the measurements from this flight agree with the general trend shown in Figure 1. We find that in this region, H$_2$SO$_4$ is highest near the ocean surface and nanoparticle production occurs primarily at higher, midaltitudes, preferentially in the regions near cloud detrainment. Detailed investigations of nucleation events near clouds have been reported elsewhere [Hegg et al., 1990; Perry and Hobbs, 1994]. We do not pursue investigating that here, but instead focus on regions where H$_2$SO$_4$ concentrations were highest in search for nucleation in the remote marine boundary layer.

4.3. Nucleation in Regions of High H$_2$SO$_4$

The flight numbers, ambient conditions and various other measured parameters in regions of high H$_2$SO$_4$ concentrations encountered during PEM-Tropics B are summarized in Table 1. We have restricted our focus to events in which H$_2$SO$_4$ concentrations were greater than 3x10$^7$ cm$^{-3}$.

Table 1 shows that most regions of enhanced H$_2$SO$_4$ concentrations were found close to the surface where aerosol surface area concentrations were high (similar to leg B discussed in Figure 2). We did, however, encounter some regions where H$_2$SO$_4$ concentrations were over 3x10$^7$ cm$^{-3}$ and aerosol surface areas were fairly low (less than about 10 $\mu$m$^2$ cm$^{-3}$). These were typically located at altitudes from about 1 to 4 km, being separated from the sea surface source of larger salt particles. For example, on Flight 8 at about 1.1 km above the sea, H$_2$SO$_4$ concentrations reached 8.8x10$^7$ cm$^{-3}$, surface area concentrations were approximately 7 $\mu$m$^2$ cm$^{-3}$, 3-4 nm particle concentrations were 0.00 cm$^{-3}$, and total UCN 74 cm$^{-3}$. Approximately 3 regions similar to this were encountered during PEM T B. They are labeled Flights 8, 10-A, and 10-B in Table 1.
The absence of 3-4 nm particles in regions of high H$_2$SO$_4$ concentrations indicates that either nucleation had not occurred, or nucleation occurred but no new particles reached detectable sizes. To investigate these processes, we have estimated the time for particle growth to detectable sizes and the characteristic time for scavenging of a newly formed particle (e-folding time) using equations (1) and (2), respectively. These times are also shown in Table 1. If we assume that scavenging is the primary nanoparticle loss mechanism (i.e., ignore dry deposition and dilution, a good assumption for the time scales of interest here), the data in Table 1 shows that in the regions near the surface where aerosol surface areas are high, scavenging times can be on the order of, or smaller than the time for growth to detectable sizes. In these regions, losses of newly formed particles would be significant, making nucleation studies difficult. For example, for the events observed during Flight 16, the growth times are about 3 to 5 times longer than the scavenging times. In this case most of any newly formed particles are likely to be lost before detection. However, in regions where growth and scavenging times are similar (recall the scavenging time is an estimate for the time for a 63% decrease in concentration), and even more convincing, when scavenging times are significantly longer than growth times, most newly formed particles will grow to a detectable size. This is the case for the measurements labeled flights 8, 10-A, and 10-B in Table 1. In these cases, measurements of no 3-4 nm particles suggest that no nucleation had occurred. This would include the lack of any ubiquitous low-rate particle production mechanism contributing to the marine aerosol.

4.4. Comparison of PEM B Flights to PEM A Flight 19

In contrast to PEM-Tropics B, a large nucleation event was observed in the earlier NASA PEM-Tropics A mission. The conditions under which this nucleation event occurred are very similar to some of the PEM-Tropics B regions of high H$_2$SO$_4$ concentrations but under which no nucleation was observed.

During the NASA Pacific Exploratory Mission A, conducted between August and September 1996, a large nucleation event was observed near the ocean surface about 300 km off the coast of Central America [Clarke et al., 1998a] (about 7°N 85°W). In this case, models have directly linked DMS sulfur production to the formation of new particles. Concentrations of newly formed particles (3-10 nm diameter) on the order of 10$^3$ cm$^{-3}$ were observed adjacent to a region scavenged by precipitation. Ambient conditions measured in this nucleation region are also included in Table 1. Comparisons show that the conditions under which nucleation was observed in PEM A are very similar in many respects to those recorded in PEM B in which there was no evidence for particle production. It is of particular interest to contrast the PEM B observations during Flights 6, 8, and 13-B (leg B in Figure 2) to the PEM A nucleation event. Note that the ambient conditions and altitude are very similar, as is the high H$_2$SO$_4$ concentration. (Relative acidities are also similar since ambient temperatures are similar.) The most striking difference between the events of PEM A and PEM B is the much lower aerosol surface area in PEM A. In the PEM A event the atmosphere was pristine, a result of precipitation scavenging of the marine boundary layer aerosol. However, note from Table 1 that Flight 8 had similar conditions to the PEM A nucleation event, including low surface area concentrations, but in this case nucleation was not observed (growth times were much shorter than scavenging times). Comparing relative acidities and humidities measured at the PEM A nucleation event to current binary nucleation models has shown that the production mechanism was likely not binary H$_2$SO$_4$-H$_2$O nucleation [Clarke et al., 1998a; Weber et al., 1999b]. Ternary nucleation has been proposed as a possible mechanism and recent modeling suggests that H$_2$SO$_4$ chemi-ion nucleation also tends to agree with the observations [Yu and Turco, 2001]. In a general sense, our comparison between PEM A and B missions agree with these findings since in both studies we encountered regions with nearly identical relative acidity and humidity (the primary parameters affecting binary nucleation) but two very different particle production rates. Thus some other parameter necessary for nucleation was absent or at insufficient levels to promote nucleation in the PEM B regions where high H$_2$SO$_4$ concentrations were recorded.

4.5. Comparison of Observations to Binary and Ternary Nucleation Predictions

In this section we compare observations to those necessary for the onset of binary H$_2$SO$_4$-H$_2$O nucleation and ternary H$_2$SO$_4$-NH$_3$-H$_2$O nucleation. This is done by plotting in Figure 3 the observed ambient relative acidity (RA) and relative humidity (RH), and comparing it to predictions of two binary models, [Jaecker-Voirol and Mirabel, 1989; Kulmala et al., 1998; Wilemski, 1984] and the ternary model of Korhonen et al. [1999]. In Figure 3 the model-predicted conditions necessary for a nucleation rate of 1 cm$^{-3}$ s$^{-1}$ is shown. Two binary models are plotted. The Kulmala et al. [1998] parameterization of the Wilemski [1984] model is likely the most accurate since it corrects for a thermodynamic inconsistency inherent with the Jaecker-Voirol and Mirabel [1989] model and is in fair agreement with recent laboratory measurements [Ball et al., 1999]. The Jaecker-Voirol and Mirabel [1989] model is included since it has been used extensively in the past to model marine boundary layer processes.

For the ternary comparison the relative acidity for two differing relative humidities and two differing NH$_3$ concentrations is plotted in Figure 3. Also plotted are the events from Flights 8, 10-A, and 10-B from Table 1 in which growth rates were
Figure 3. Comparison between observations and predictions from models for the onset of binary H$_2$SO$_4$-H$_2$O and ternary H$_2$SO$_4$-NH$_3$-H$_2$O nucleation (rate of 1 cm$^{-3}$ s$^{-1}$) [Jaeckel-Voiolet and Mirabel, 1989; Korhonen et al., 1999; Kulmala et al., 1998; Wilemski, 1984]. Evidence for nucleation was only observed for points identified as 13-A and 13-C (also shown in Figure 2), and the PEM A event. No nucleation was observed for the points labeled 8, 10-A, and 10-B since growth rates were sufficient to make any newly formed particles detectable (see corresponding growth and scavenging times in Table 1). The Wilemski/Kulmala model would never predict binary nucleation for the regions represented by the data points. The Jaeckel/Mirabel model would predict nucleation for the 13-A and 13-C, but none else, and if NH$_3$ concentrations were over roughly 10 pptv, the ternary model would predict nucleation for all (with the possible exception of 10-B where the model was not run at lower RH).

have occurred. We feel a definitive conclusion cannot be made given the uncertainty with binary nucleation models and the measurement limitations. However, the lower-altitude regions containing very high H$_2$SO$_4$ concentrations in PEM B Flights 8, 10-A, and 10-B, conditions were significantly further away from those necessary for binary nucleation. This is consistent with the observations of no nucleation in these regions.

Also shown in Figure 3 are predictions from the Korhonen et al. [1999] ternary model. This model predicts that if NH$_3$ concentrations were at least 10 pptv in the PEM B Flights 8 and 10-A, ternary nucleation should readily occur (i.e., the measured RA is higher than what the model predicts is necessary for ternary nucleation). Although not measured, typical background NH$_3$ concentrations are generally thought to be over 100 pptv [Warneck, 1988]. Thus the lack of nucleation in these regions appears to be inconsistent with this model, or ambient NH$_3$ concentrations are below 10 pptv.

The other data point in Figure 3 is the large nucleation event observed during PEM-Tropics A. As shown in earlier work [Clarke et al., 1998a; Weber et al., 1999b], this event is inconsistent with binary nucleation; however it is consistent with the ternary model if NH$_3$ concentrations were larger than 10 pptv. This figure also demonstrates the intriguing feature that although conditions were similar (RA and RH), a massive nucleation event was observed in PEM A but no nucleation was observed in PEM B (e.g., compare points labeled PEM A Event to 8 in Figure 3). Thus, under certain conditions significant nucleation can occur in the marine boundary layer, but it requires some yet to be determined additional critical parameter or process.

Assuming for the moment that ternary nucleation is the applicable mechanism, one possible explanation consistent with the observations is that ternary nucleation is more sensitive to NH$_3$ concentrations than what is predicted by the Korhonen et al. [1999] model, and that the NH$_3$ concentrations were much higher in the PEM A nucleation region than in the regions of PEM B. The latter is reasonable since the PEM A nucleation region was much closer to a continent, a known source for NH$_3$, and the region was influenced by a boundary layer westerly flow off the coast of Panama [Clarke et al., 1998a].

Overall, we could reconcile the observations by a ternary (or other) nucleation mechanism with the following attributes. Assuming that relative acidity and humidity are pertinent nucleation parameters, (i.e., H$_2$SO$_4$ and H$_2$O are involved) in regions approaching conditions necessary for binary nucleation, such as those observed near clouds (13-A and 13-C in Figure 3), nucleation could occur at slightly lower relative acidities through minor assistance from NH$_3$ (or other species or processes) and thus only low ambient NH$_3$ concentrations are required. This could explain nucleation observed at higher altitudes that approach conditions necessary
for binary nucleation but don’t agree exactly (i.e., 13-A and 13-C in Figure 3). In regions far from conditions for binary nucleation, ternary nucleation may only occur if NH₃ concentrations are substantially enhanced compared to background levels. Significantly enhanced NH₃ concentrations were used to explain the large nucleation events observed downwind of penguin rookeries on Macquarie Island during ACE 1 [Weber et al., 1998a].

It would follow then that under typical background marine situations, especially at lower altitudes, nucleation does not readily occur because the relative acidity is generally much too low and conditions are far from those necessary for binary nucleation. The implication of this is that there may not be a ubiquitous low rate of new particle production throughout the troposphere. This may not be true for continental regions where NH₃ concentrations can be significantly higher than marine areas [Warneck, 1988].

Alternatively and equally valid, nucleation in the PEM A event may have involved some other critical component, such as an organic species, or ions, and that this component was lacking in the regions where no nucleation was observed during PEM B. We also cannot exclude the possibility that some other aspect linked to the precipitation contributed to nucleation in that region, this includes mixing processes that may lead to enhancements in binary nucleation rates [Nilsson et al., 2000]. Clearly, a more complete suite of measurements, which includes NH₃ and ions, is required to make further progress in understanding atmospheric nucleation processes.

5. Conclusions

We have analyzed regions encountered during the PEM-Tropics B study where H₂SO₄ concentrations near the ocean surface were unusually high to gain insights into nucleation mechanisms. Generally, it was found that the presence of newly formed 3-4 nm particles was associated with regions of highest sulfuric relative acidity and were only detected at higher altitudes associated with cloud outflow fields and not near the ocean surface where H₂SO₄ concentrations were highest. In those regions where aerosol surface areas were low, newly formed particles in this high H₂SO₄ environment should rapidly grow to a detectable size, and thus the lack of any observed 3-4 nm particles in these regions suggests that nucleation had not occurred. Binary theory predicts that H₂SO₄ - H₂O nucleation should not occur in these regions; however, during the previous NASA PEM A mission, a large nucleation event was observed in the marine boundary layer under almost identical conditions as those observed in this study. A recently developed ternary model [Korhonen et al., 1999] predicts that if NH₃ concentrations were greater than 10 pptv, than nucleation should have occurred in both regions.

Although NH₃ was not measured, concentrations near the ocean surface are expected to be higher than this, making the observations inconsistent with the model.

One explanation consistent with the observations is that the ternary nucleation rate is more sensitive to NH₃ concentrations than models currently predict. An implication of these results is that we observed no evidence for ubiquitous particle production throughout the troposphere, as has been proposed by a number of nucleation models [Kulmala et al., 2000; Turco et al., 1998]. A clearer understanding of the processes leading to new particle formation in the atmosphere will require a more complete measurement suite of potential nucleation precursors.

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References


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