

Measurements of new particle formation and ultrafine particle growth rates at a clean continental site

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Abstract. Simultaneous measurements of aerosol particles and their expected gas phase precursors were made at Idaho Hill, Colorado, a remote continental site. This study used apparatus and techniques similar to those employed in an earlier study at the Mauna Loa Observatory, Hawaii [Weber *et al.*, 1995]. New particle formation, identified by the presence of ultrafine particles (nominally 3 to 4 nm diameter), was commonly observed in downslope (westerly) air and was correlated with high sulfuric acid (H_2SO_4) concentrations, low relative humidity and low particle surface area concentrations. The data point to H_2SO_4 as a principle nucleation precursor species with typical daytime concentrations between 10^6 and 10^7 molecules cm^{-3} . Particle production was observed at H_2SO_4 concentrations that are well below predicted values for binary nucleation of H_2O and H_2SO_4 , suggesting that another species participated. Particle growth rates were estimated from the data with two independent approaches and in both cases were ~ 5 to 10 times higher than can be explained by condensation of H_2SO_4 and its associated water. This suggests that species in addition to H_2SO_4 were also making large contributions to ultrafine particle growth. Finally, calculated steady-state H_2SO_4 concentrations were found to be in good agreement with measured values if the mass accommodation coefficient for H_2SO_4 on aerosol surfaces was assumed equal to ~ 1 .

Introduction

Tropospheric aerosol particles influence global climate by scattering radiation directly [Charlson *et al.*, 1991] and indirectly by altering the scattering characteristics of clouds [Twomey *et al.*, 1984]. Because both effects depend on particle size, processes which influence particle size distributions can influence climate. The formation of new particles from gas phase precursor species plays an important role in regulating aerosol populations; in the remote atmosphere it is thought to be the primary source for new particles. The growth rates of newly formed particles are also critical, since new particles must grow by orders of magnitude to influence Earth's radiation balance.

A field study at the Mauna Loa Observatory, Hawaii, provided insight into particle formation in the remote marine troposphere [Weber *et al.*, 1995]. At that site, evidence for particle formation was frequently observed in upslope (boundary

layer) air. This effort has been extended by measurements made at Idaho Hill, Colorado, a remote continental site. In this study, we focus on measurements made during periods of downslope (free tropospheric) air. The approach in both cases has been to examine atmospheric new particle formation by measuring the expected nucleation gas phase precursor species with simultaneous measurements of ultrafine (nominally 3 to 4 nm diameter) and fine (~ 15 nm to ~ 0.5 μm diameter) aerosols. Together, these two studies provide insight into atmospheric new particle formation and also permit comparison of particle production at two very different sites.

Due in part to the extent of Earth's oceans, marine aerosols are thought to have a significant influence on global climate [Charlson *et al.*, 1987]. These aerosols have received special attention in both modeling and atmospheric measurements. Currently, classic binary nucleation theory involving sulfuric acid and water ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) [Jaeger-Voirol and Mirabel, 1989] is used for predicting atmospheric particle formation rates. It has not been demonstrated, however, that remote tropospheric particles are formed by this mechanism. Measurements by various researchers have provided evidence of an insitu source for marine aerosols. Clarke [1993] observed evidence of particle production in the Pacific free troposphere, and modeling by Raes and coworkers [Raes, 1995; Raes and Van Dingenen, 1992] suggests that the free troposphere is the major source for marine cloud condensation nuclei (CCN). On Pacific Ocean cruises, Covert *et al.* [1996] consistently observed evidence of recent particle formation in regions of subsiding air masses but

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saw no evidence of new particle formation in the marine boundary layer itself. Evidence of particle production has also been detected in the outflow regions of precipitating marine cumulus clouds [Hegg *et al.*, 1990; Perry and Hobbs, 1994] and in clear marine boundary layer air [Hoppel *et al.*, 1994a]. A common feature to the marine sites where researchers have detected evidence of new particle formation was low aerosol surface area concentrations (typically less than $\sim 5 \mu\text{m}^2 \text{cm}^{-3}$).

Many of the phenomena observed for marine aerosols may also occur in clean continental air, although less attention has been given to these regions. Both gas phase species and aerosol concentrations are generally higher in continental than in marine environments. In addition, a greater variety of species, both natural and anthropogenic, may interact with aerosols, making continental regions more complex chemical systems. For example, vegetation-derived hydrocarbons may also contribute to particle formation [Lopez *et al.*, 1985] and growth. Based on measurements at a mountain site in Puerto Rico, Novakov and Penner [1993] speculated that the majority of particles less than 70 nm diameter were organic.

There is also evidence for new particle formation in clean continental air. A unique characteristic of these observations is a persistent diurnal variation in aerosol concentrations. This diurnal nature has been observed in a wide variety of continental settings and suggests a photochemical aerosol source [Koutsonogii and Jaenicke, 1994; Marti, 1990; Hogan, 1968; Bradbury and Meuron, 1938]. As with marine environments, there is evidence of particle formation in the continental free troposphere [Hofmann, 1993] and evidence of possible nucleation events in the vicinity of continental cumulus clouds [Radke and Hobbs, 1991].

This work reports on measurements made at Idaho Hill, Colorado, from September 5 to 29, 1993. Measurements representative of clean continental conditions are presented and compared to the earlier findings from the Mauna Loa Observatory.

Site

Idaho Hill is a remote continental site located on the eastern side of the Rocky Mountains ($39^{\circ}58'56''\text{N}$, $105^{\circ}34'32''\text{W}$), 9 km east of the continental divide and approximately 25 km west of Boulder. The site is situated just below the timber line at an average pressure elevation of 0.7 atm. (3070-m elevation). The local topography consists of generally higher elevations to the west and lower elevations to the east. The nearest populated areas (Boulder, Denver, etc.) are at lower elevations, east and southeast of the site. The western sector is sparsely populated, and the prevailing westerly (downslope) winds were associated with relatively clean, dry free tropospheric air. Upslope winds were typically from the SE, the direction of likely pollution sources. A more detailed description of the site is given by Olson *et al.* [1996].

Instrumentation

Pertinent gas phase species that were measured in this study include sulfur dioxide (SO_2), the hydroxyl radical (OH), sulfuric acid (H_2SO_4), and water (H_2O). In addition, alpha and beta pinene, which can also be aerosol precursors, were measured. An analysis of the role of the organic species in new particle formation is reported elsewhere [Marti *et al.*, 1996]. Here the focus is on the role of H_2SO_4 .

Concentrations of molecular gas phase OH and H_2SO_4 were measured to an absolute uncertainty of $\pm 35\%$ using a unique chemical ionization mass spectrometer [Eisele and Tanner, 1993; Tanner and Eisele, 1995]. The instrument's lower detection limit was approximately 10^4 molecules cm^{-3} . Sulfur dioxide was measured by pulsed fluorescence (Model 43S, Thermo Environmental Instruments Inc., Hopkington, Massachusetts). This instrument had a lower detection limit of ~ 100 pptv (parts per trillion by volume). For the latter part of the study (September 24-29) hourly SO_2 zeros were performed. This permitted correcting for a temperature-dependent systematic offset error observed with this instrument. The validity of the OH measurements made with this instrument were recently confirmed in a methods intercomparison study [Mount and Williams, 1996].

The ultrafine aerosol is defined here as particles in the narrow size range from 2.7 nm, the lower detection limit of the ultrafine condensation particle counter (UCPC), to nominally 4 nm diameter. Measurements of the ultrafine aerosol concentration were made with the prototype of the TSI 3025 UCPC (TSI Incorporated, St. Paul, Minnesota) [Stolzenburg and McMurry, 1991]. Ultrafine particle concentrations were determined by measuring the UCPC photodetector pulse heights with a multi-channel analyzer (MCA) [Weber *et al.*, 1995]. This method of acquiring ultrafine particle size information is based on experimental work, which showed that, for particles smaller than ~ 15 nm, the final droplet size (pulse height), after growth in the UCPC condenser, is uniquely related to the initial particle size [Brockmann, 1981; Ahn and Liu, 1990; Stolzenburg, 1988; Saros *et al.*, 1996].

For this study, we diluted the sample aerosol prior to measuring the ultrafine concentration. Nevertheless, on rare occasions, significant particle coincidence (more than one particle in the UCPC optical scattering volume at a time) resulted in inaccurate sizing of the ultrafine aerosols. Based on laboratory experiments [Saros *et al.*, 1996], these episodes were identified by MCA dead times exceeding 15%, and the data were ignored. The UCPC sample flow rate was $0.5 \text{ cm}^3 \text{ s}^{-1}$, and the typical sampling period was 2.5 min. Considering only those uncertainties associated with Poisson counting statistics, these settings result in an uncertainty of $\pm 35\%$ for a measured ultrafine concentration of $0.1 \text{ particles cm}^{-3}$. Higher concentrations have lower uncertainties.

Because ultrafine particles of a given size produce a range of pulse heights, our method of measuring the ultrafine particle concentration does not count all particles in the ultrafine size range (i.e., ~ 3 to 4 nm diameter). This results in our underestimating the concentrations of these particles, typically by $\sim 50\%$. This shortcoming, however, is far outweighed by the measurement's high sensitivity for detecting ultrafine particle concentrations.

Aerosol size distributions covering diameters between 15 and ~ 500 nm were measured with a scanning mobility particle spectrometer [Wang and Flagan, 1990]. A complete scan through this size range was typically completed every 2.5 min. These data were inverted using the method of Hagen and Alofs [1983]; aerosol surface area concentrations were obtained by integrating over these distributions, assuming spherical particles. The concentrations of larger particles, $\sim 0.5 \mu\text{m}$ up to $9 \mu\text{m}$ diameter, were measured by other researchers at the site. These larger sizes contributed, at most, 3% to the total aerosol surface area concentration when downslope conditions prevailed.

However, when the wind was from the polluted sector (upslope), there were episodes when particles larger than 0.5 μm diameter made significant contributions to the total aerosol surface area.

Theory: Calculation of Particle Growth Rates

The data are used to calculate particle growth rates in a manner similar to that performed earlier with the Mauna Loa measurements [Weber *et al.*, 1995, 1997].

If particle growth is limited by condensation of H_2SO_4 vapor, the ultrafine particle growth rate is [Friedlander, 1977]

$$\frac{dD_p}{dt} = \frac{2\alpha v_1 (p_1 - p_d)}{(2\pi m k T)^{1/2}} \quad (1)$$

where α is the H_2SO_4 mass accommodation coefficient, T the temperature, k is Boltzmann's constant, and m and v_1 , the mass and volume respectively of the condensing vapor. The measured partial pressure of H_2SO_4 is p_1 , and the equilibrium partial pressure, p_d . We assume an accommodation coefficient of 1 and that evaporation of H_2SO_4 from the droplet is small compared to condensation (i.e., $p_d = 0.0$). We also assume that growth is from condensation of only hydrated H_2SO_4 molecules which are in equilibrium with the H_2O vapor phase at 10°C. The degree of hydration is calculated using the equilibrium data of Gmitro and Vermeulen [1963]. These assumptions provide an upper limit if growth is only by condensation of hydrated H_2SO_4 vapor. Actual growth rates could be higher if additional species were also involved, or if significant numbers of H_2SO_4 clusters also condense.

Results and Discussion

Aerosol Concentrations Versus Wind Direction

At Idaho Hill, measured ultrafine aerosol concentrations were found to depend strongly on wind direction. Figure 1 shows, as a function of angular wind direction, the concentration of particles greater than ~ 3 nm (all counts from the UCPC) and the ultrafine aerosol concentration. In contrast to the total aerosol concentrations (Figure 1a), which do not show a strong dependence on wind direction, high ultrafine concentrations were observed predominantly in downslope air (wind from western sector, Figure 1b). The narrow angular band where the highest ultrafine concentrations were recorded was the most common downslope wind direction. Total aerosol surface area was on average higher and more variable in upslope air. During the daytime between 600 and 1800 hours mountain standard time (MST), the period when significant photochemically derived new particle formation is expected, the mean and standard deviation of the aerosol surface area concentration were $85 \pm 57 \mu\text{m}^2 \text{cm}^{-3}$ for upslope air compared to $49 \pm 18 \mu\text{m}^2 \text{cm}^{-3}$ for downslope air. In this case the surface areas were calculated from particle size distributions spanning 15 nm to 9 μm diameter. The higher aerosol surface areas associated with upslope air were likely the result of anthropogenic sources to the east and are a possible cause for the low ultrafine aerosol concentrations when the wind was from this sector. Since the focus of this work is on particle formation and growth in the clean continental troposphere, only downslope data are analyzed further.

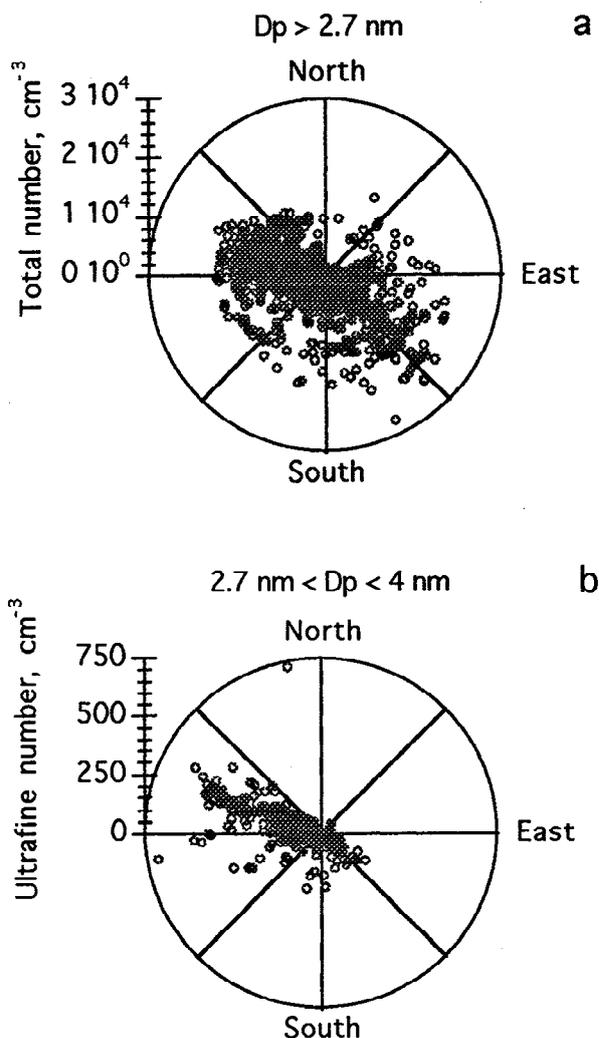


Figure 1. (a) Total aerosol number concentrations (diameters larger than 3 nm), and (b) ultrafine aerosol concentrations (diameters between nominally 3 nm and 4 nm), as a function of wind direction. The plot shows that high ultrafine aerosol concentrations were observed predominantly in air from the western sector (downslope).

Diurnal Variation of Species Concentrations at Idaho Hill

Analysis of all downslope flow data. In Figure 2 the concentrations of OH, SO_2 , H_2SO_4 , and ultrafine aerosol for periods of downslope flow are plotted as functions of the local time of day. Also included with each plot is the clear-sky ultraviolet solar intensity (wavelength range 290 to 385 nm). This can be interpreted as the envelope of UV solar intensity, since interference from clouds will result in attenuated values.

The rapid increase and subsequent decrease in OH concentrations corresponding with sunrise (600 MST) and sunset (1800 MST) shown in Figure 2a clearly indicate its photochemical source. Variations in OH concentrations likely result, in part, from variations in UV intensity. Similar observations of the diurnal variation of OH concentrations at the Mauna Loa Observatory are reported by Tanner and Eisele [1995]. Unlike OH, SO_2 had no diurnal pattern (Figure 2b).

Sulfuric acid is thought to be produced primarily by the reaction of OH and SO_2 (further evidence for this is provided in

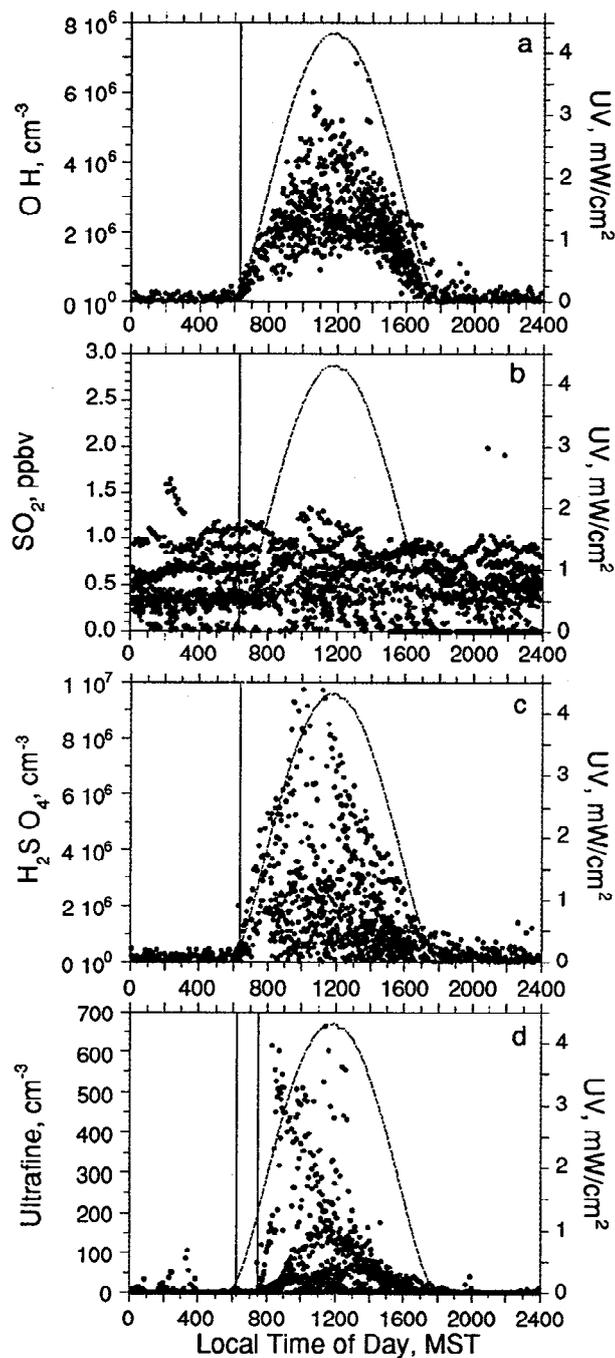


Figure 2. Recorded daily concentrations of (a) OH, (b) SO₂, (c) H₂SO₄, and (d) ultrafine particles. For all plots, only data during periods of downslope airflow are shown. Also plotted is the UV solar intensity on a clear day (September 26, 1993). Both OH and H₂SO₄ concentrations often increased from nighttime levels at sunrise. Ultrafine aerosol concentrations, however, never began to rise until over an hour later. This delay is used to estimate the growth rate of ultrafine particles.

the following section on predicted H₂SO₄ concentrations). The diurnal variation of OH is responsible for the rapid rise in H₂SO₄ levels observed at sunrise (Figure 2c). Note, there was practically no delay between the rise in OH and the earliest appearance of elevated H₂SO₄ concentrations at sunrise. Scatter in H₂SO₄ concentrations is probably from scatter in both the OH and SO₂, and also the variation in the aerosol surface area concentrations.

The ultrafine aerosol concentration also varied diurnally (Figure 2d). Unlike the H₂SO₄ concentration, which increased at sunrise (~0615 MST, Figure 2c), the concentration of ultrafine particles did not begin to increase significantly until approximately 0730 MST, more than 1 hour later. We interpret this delay as the time required for the precursor vapor, H₂SO₄ (~1 nm diameter), to grow to the ultrafine size range (~3 nm diameter). In a following section this delay is used to estimate ultrafine particle growth rates.

By late afternoon the ultrafine concentrations began to decline and were at background levels before sunrise of the next day. The median daytime ultrafine concentration was 48.2 cm⁻³ compared to 0.06 cm⁻³ during the night. These highly mobile ultrafine particles have short life spans, in part because of scavenging by existing aerosol surface. The median particle surface areas during day and night for downslope conditions were comparable; 42 and 48 μm² cm⁻³, respectively. If there are no sources, and growth out of the ultrafine size range is ignored (i.e., precursor vapor concentrations are low, such as at nighttime), and the primary sink for the ultrafine aerosol is scavenging by preexisting particles, the characteristic lifetime (e -folding time; τ) for a 3-nm particle is

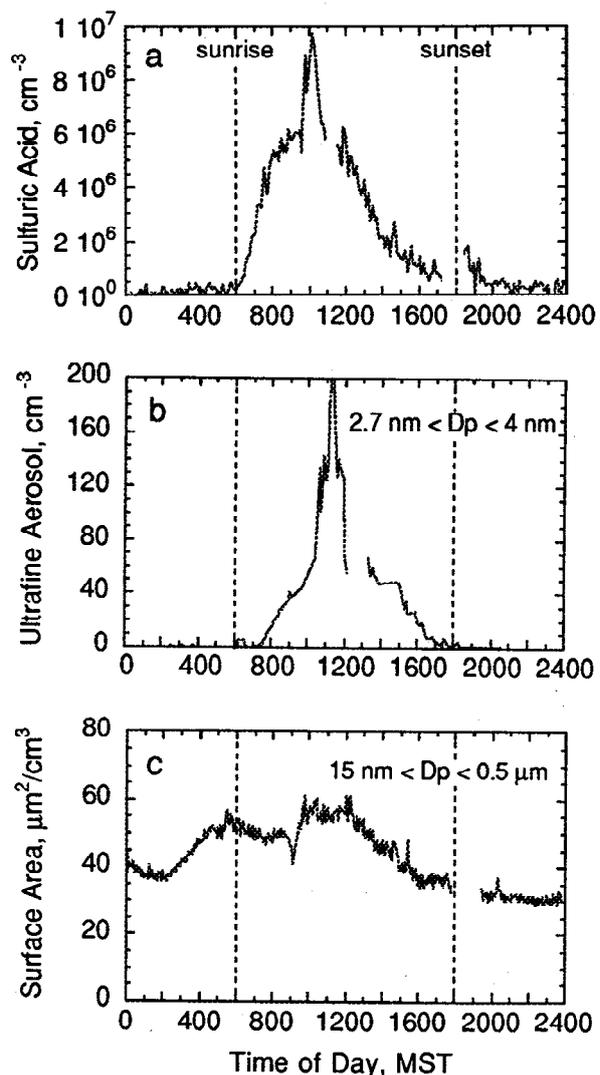


Figure 3. Measured (a) H₂SO₄, (b) ultrafine aerosol, and (c) aerosol surface area concentrations on September 21, 1993. On this day the airflow was downslope from 0000 to 1700 MST.

$$\tau = \frac{4\gamma}{\alpha c A} \quad (2)$$

The factor δ accounts for diffusional resistance to mass transfer that must be taken into account for preexisting particles that are of the order of or larger than the air mean free path. For the size distributions that we measured in this study, we found that $\delta=1.3\pm 0.2$. For the purpose of this discussion it is adequate to assume a fixed value of ~ 1.3 . The average thermal speed, \bar{c} , for a 3-nm hydrated H_2SO_4 particle of density 1.4 g cm^{-3} is $\sim 2 \times 10^3 \text{ cm s}^{-1}$ (assuming $T=10^\circ\text{C}$, relative humidity = 32%). The preexisting aerosol surface area concentration is A . If we assume the ultrafine particles are always captured when they collide with the larger preexisting particles (i.e., $\alpha=1$), the characteristic lifetime of a 3-nm particle at Idaho Hill was ~ 1.5 hours. Including growth out of the ultrafine size range will result in even smaller lifetimes. This short life span likely accounts for the observed decay in numbers of ultrafine particles by late afternoon and why ultrafine particle concentrations are near zero before sun rise.

A representative day. The H_2SO_4 , ultrafine particle, and particle surface area concentrations on September 21, 1993 are shown in Figure 3. Like most days at Idaho Hill, H_2SO_4 levels began to increase at ~ 0615 MST. The ultrafine particle concentration did not begin to rise above night-time levels until ~ 0730 MST, about 1.25 hours later. During the day, the H_2SO_4 and ultrafine aerosol concentrations tracked well; changes in ultra-

fine concentrations followed changes in H_2SO_4 concentrations. This general correlation between these species was observed on all but one of the sampling days at Idaho Hill. It was also commonly observed at Mauna Loa. The measurements suggest that at both sites, H_2SO_4 was a precursor of the ultrafine particles.

The measured fine aerosol size distributions for September 21 are shown in Figure 4. The data have been summarized by plotting the average distribution for three periods for which the distributions were fairly steady. From Figure 4a, the largest changes in the number distributions were for particles with diameters less than approximately 50 nm. The concentrations of larger particles were fairly steady. Note that the concentration of the smallest particles plotted, ~ 20 nm, did not significantly increase until approximately 1000 MST. Recall the ultrafine concentration (3 nm particles) increased much earlier, at ~ 0715 MST (see Figure 3). Again, this delay may be the time required for growth from ~ 3 nm to ~ 20 nm diameter.

Another noteworthy feature of the particle size distributions is that at some point during the day they had a slight bimodal shape. The minimum between the modes was at ~ 60 nm. This bimodal distribution for fine aerosols is a common feature of marine boundary layer particles where it is understood to result from aerosol processing by nonprecipitating marine clouds [Hoppel *et al.*, 1994b]. It was also a regular feature of the fine particle distributions recorded at Mauna Loa [Weber and McMurry, 1996]. Though such bimodality has not been commonly reported for continental aerosols, at Idaho Hill, it was observed at some time during the day for nearly one-half the sampling days.

Figure 4b shows the fine aerosol surface area distributions corresponding to the three average number distributions. Plotted in this manner, the area under the curve is the calculated aerosol surface area concentration.

In summary, our data suggest that ultrafine particles were produced by recent nucleation and that H_2SO_4 was a precursor species. The ultrafine particle concentrations varied diurnally due to the photochemical production of the precursor species and their short life spans. In the next section, the influence of parameters expected to affect the nucleation rate are studied by constructing scatterplots and calculating correlations between ultrafine concentrations and various parameters.

Correlations Between Ultrafine Concentrations and Measured Parameters

For all data free of local contamination and collected during downslope flow, the measured ultrafine concentrations are shown in Figure 5 as a function of the aerosol surface area, relative humidity, and H_2SO_4 concentration. These plots illustrate the recorded range of each parameter and give some indication of their influence on the ultrafine aerosol concentration and thus the extent of new particle formation. In all plots, an envelope roughly defining the maximum ultrafine concentration is indicated by a line. This shows qualitatively the influence of these parameters on ultrafine particle concentrations. Spearman rank correlation coefficients are also calculated to give a quantitative indication of association between ultrafine particle concentrations and the aerosol surface area, relative humidity, and H_2SO_4 concentrations. The Spearman rank correlation coefficient was used, since ultrafine particle concentrations are not expected to be linearly related to these parameters. Similar scatterplots for Mauna Loa data can be found in the work by Weber *et al.* [1995].

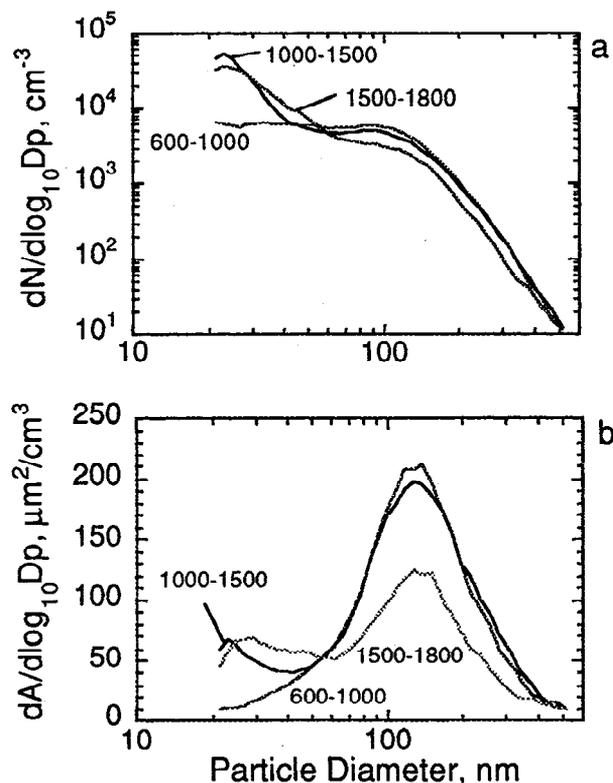


Figure 4. (a) Time averaged fine aerosol number and (b) surface area distributions for periods 600-1000, 1000-1500, and 1500-1800 MST on September 21, 1993. Increased concentrations of the smallest particles did not begin until ~ 1000 MST; concentrations of the higher mode were fairly steady. The fine aerosol also appears to be bimodal; similar (albeit more strikingly bimodal) distributions have been reported for remote marine aerosols.

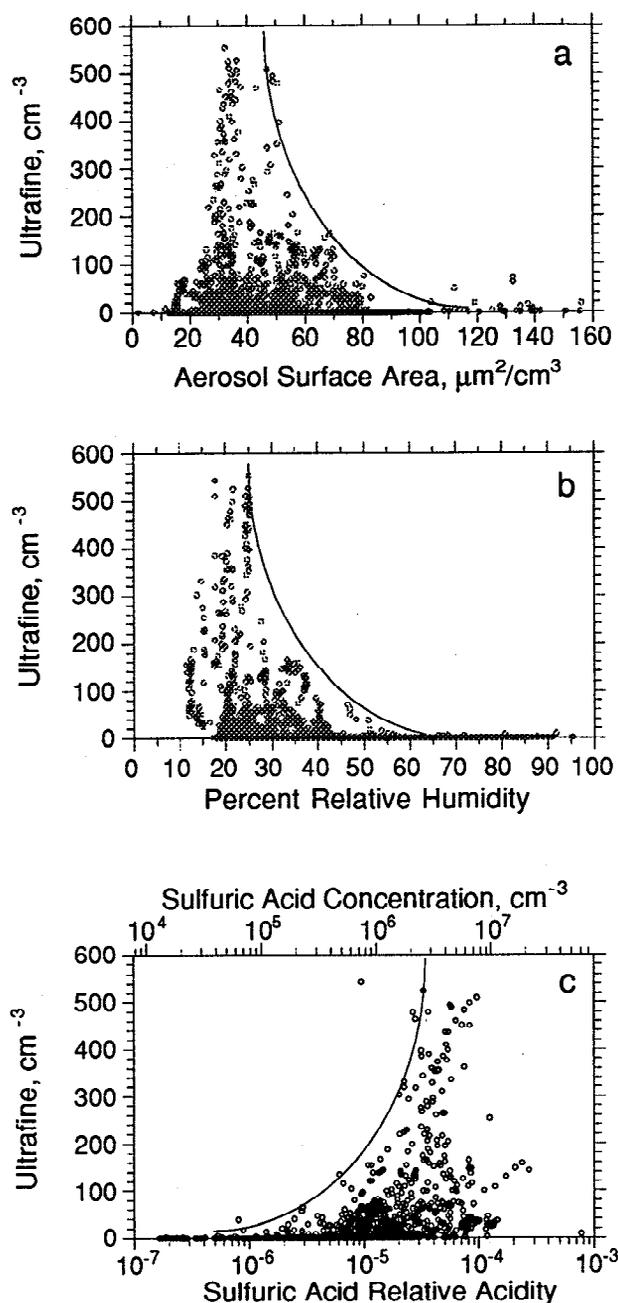


Figure 5. Scatterplots of the measured ultrafine concentration as a function of the (a) aerosol surface area, (b) the relative humidity, and (c) the H_2SO_4 relative acidity. In Figure 5c, the corresponding H_2SO_4 concentration is shown assuming a temperature of 10°C . All plots contain data for periods of only downslope airflow.

Ultrafine particle versus aerosol surface area concentrations. The effect of the aerosol surface area on ultrafine concentrations is shown in Figure 5a. Generally lower ultrafine concentrations were recorded during periods of high aerosol surface area concentrations. The envelope defining the maximum measured ultrafine concentration decreases with increasing surface area and the Spearman rank correlation coefficient was -0.26 . Note that "high" ultrafine aerosol concentrations were never detected at Idaho Hill during periods when the aerosol surface area was greater than $\sim 80 \mu\text{m}^2 \text{cm}^{-3}$.

Significant numbers of ultrafine particles were, however, recorded at surface areas up to this value. The observed decrease in ultrafine particle concentrations with increasing aerosol surface area is consistent with expectations. Concentrations of the nucleating species decrease due to heterogeneous condensation as preexisting aerosol concentrations increase; this leads to a reduction in particle production rates. Moreover, the likelihood that a freshly formed nucleus grows to a detectable size before it is scavenged by the preexisting aerosol also decreases with increasing aerosol surface area concentrations.

Scatterplots of Mauna Loa data [Weber *et al.*, 1995] show a similar envelope with the same general correlation between ultrafine and aerosol surface area concentrations, although the concentrations of both ultrafine particle and aerosol surface area were much lower at Mauna Loa. For example, high ultrafine concentrations were never observed at Mauna Loa during periods when the aerosol surface area was larger than $\sim 30 \mu\text{m}^2 \text{cm}^{-3}$. Different production rates of precursor species (i.e., differing SO_2 concentrations) at these two sites probably account for these observed differences.

Ultrafine particle concentration versus relative humidity. Ultrafine particle concentration and relative humidity were negatively correlated (-0.42 Spearman rank correlation coefficient). Evidence of significant particle formation, indicated by high ultrafine particle concentrations, was observed at relative humidities as low as 15% (Figure 5b). At both Idaho Hill and Mauna Loa there is no evidence that increases in relative humidity led to enhanced particle production, as would be expected if the ultrafine particles were formed by binary nucleation of H_2SO_4 and H_2O .

The observed negative correlation between ultrafine particle concentrations and relative humidity may be due to the observed positive correlation ($+0.30$) between aerosol surface area and relative humidity. This latter correlation could result from two differing influences. First, because the degree of sulfate particle hydration increases with relative humidity, the swelling of particles with increasing relative humidity leads to higher aerosol surface areas at higher humidities; this effect becomes significant as relative humidities increase beyond 85 to 90%, which is well in excess of values typically encountered in this study. Second, relative humidity at this site may have been an indicator of air mass origin; more pristine (lower particle surface area concentrations) downslope air from higher elevations would also likely be drier. In either case, the negative correlation between ultrafine particle concentration and relative humidity likely does not reflect the influence of water vapor concentration on atmospheric particle formation rates.

It is noteworthy that our observation of particle formation predominantly in dry downslope air (i.e., air originating from higher elevations) is similar to the marine observations of *Covert et al.* [1996]. They only observed high ultrafine particle concentrations (3 to 14 nm) in regions of subsiding air masses.

Ultrafine particle versus sulfuric acid concentrations. In Figure 5c the ultrafine particle concentration is plotted with respect to the H_2SO_4 relative acidity. Sulfuric acid relative acidity is the measured H_2SO_4 partial pressure divided by the saturation vapor pressure of pure H_2SO_4 at the measurement temperature [Ayers *et al.*, 1980]. Plotted in this way, the major influence of temperature on the tendency of H_2SO_4 and H_2O to nucleate is taken into account. A second abscissa showing H_2SO_4 concentrations is also shown. In principle, concentration and relative acidity cannot be shown on the same graph if

temperatures varied significantly. In this study the temperature did not vary widely; we used a characteristic value of 10°C when evaluating concentrations for this plot. From Figure 5c, it is evident that the measured ultrafine concentration and H₂SO₄ relative acidity were positively correlated (+0.67 Spearman rank correlation coefficient); higher ultrafine concentrations were detected at higher H₂SO₄ concentrations. The correlation between ultrafine particle and H₂SO₄ concentrations was slightly higher, +0.71. These results are consistent with expectations and our earlier observations [Weber *et al.*, 1995] that H₂SO₄ is a primary precursor species of the ultrafine particles generated by homogeneous nucleation.

At both sites, the H₂SO₄ concentrations typically ranged from approximately 10⁵ to 10⁷ cm⁻³, and significant ultrafine concentrations were recorded at unexpectedly low acidities (or H₂SO₄ concentrations). Figure 5c shows that at Idaho Hill, high ultrafine concentrations were detected at acidities less than 10⁻⁵, which is much too low for nucleation by H₂SO₄ and H₂O. Another major inconsistency with binary nucleation is found when comparing measurements at Mauna Loa and Idaho Hill. The maximum ultrafine particle concentrations at a given H₂SO₄ relative acidity were about an order of magnitude higher at Idaho Hill than at Mauna Loa, and relative humidities were much lower at Idaho Hill. This may indicate that species other than H₂SO₄ and H₂O (e.g., ammonia) also participated in particle formation. A conceptual framework for such a nucleation mechanism is discussed by Weber *et al.* [1996; Weber, 1995].

The observations of particle formation at extremely low relative humidities and acidities may indicate that nucleation actually occurred upwind of the site at a location where these parameters were much higher. During this study the sky was typically clear, making nucleation in the vicinity of clouds, as observed by Hegg *et al.* [1990], unlikely. There also is no evidence suggesting that H₂SO₄ concentrations were significantly higher upwind. The aerosol surface area, SO₂, and OH concentrations are expected to be reasonably spatially uniform, at least in ranges of the order of a few kilometers from the site. In a following section, we show that H₂SO₄ concentrations can be calculated from these parameters. Thus, in the vicinity of the site, daytime H₂SO₄ concentrations are expected to range from 10⁶ to 10⁷ cm⁻³. Moreover, daytime H₂SO₄ concentrations measured at Mauna Loa were also in this range, suggesting that these H₂SO₄ levels are typical for remote tropospheric locations where nucleation is observed. At these H₂SO₄ concentrations, according to classical nucleation theory, the only way to achieve H₂SO₄-H₂O nucleation is to reduce the temperature and/or increase the relative humidity, both of which may exist at higher elevations. Assuming a lapse rate of -6.5°C/km and constant water mixing ratio with altitude, using the mean temperature and relative humidity measured at the site to extrapolate to higher elevations, H₂SO₄-H₂O nucleation could be possible at H₂SO₄ concentrations of 10⁶ to 10⁷ molecules cm⁻³ at elevations of 3 to 4 km higher. At this elevation, we estimate that temperatures may be less than -10°C and relative humidities greater than 70%.

The possibility that particle formation observed during this study consistently occurred at elevations much higher than the sampling site by H₂SO₄-H₂O nucleation cannot be ruled out. However, we believe a more plausible explanation for particle formation at lower than expected H₂SO₄ and H₂O levels is that other species, like ammonia, also participated and permitted particle formation over a much broader concentration range of both H₂SO₄ and H₂O. We reached the same conclusions from the Mauna Loa measurements, where nucleation was observed at

similar H₂SO₄ levels. However, in that study, evidence for nucleation was recorded during upslope flow conditions.

In the following section we use our data to calculate ultrafine particle growth rates. Unlike observations of new particle formation, growth rates will not be significantly influenced by changes in temperature and relative humidity during advection. The analysis primarily depends on our arguments that H₂SO₄ concentrations are spatially uniform.

Ultrafine Particle Growth Rates

In this section, the data are used to estimate average growth rates of sub-3-nm particles. These rates are compared to growth by condensation of only hydrated H₂SO₄ vapor calculated using (1) and the measured H₂SO₄ concentration and relative humidity. Two approaches are used to estimate the growth rate of ultrafine particles. First, growth rates are inferred from the observed time lag between the rise in H₂SO₄ and ultrafine particle concentrations after sunrise. In the second approach, the observed effects of cluster scavenging by the preexisting aerosol surface area on ultrafine particle concentrations were used to estimate the ultrafine particle growth rate.

Growth rates inferred from the delay between H₂SO₄ and ultrafine particle concentrations at sunrise. As shown in Figure 3, the H₂SO₄ concentration began to increase at ~0615 MST on September 21, 1993, whereas the ultrafine concentration began to rise at ~0730 MST. Assuming this delay is the time required for a hydrated H₂SO₄ vapor molecule of diameter roughly 1 nm to reach our lower detection limit of ~3 nm, then the observed average growth rate was 2 nm in 1.25 hours, or ~1.6 nm h⁻¹. From the measurements of H₂SO₄ and H₂O concentrations between 0615 and 0730 MST, (1) predicts an average growth rate from condensing H₂SO₄ vapor and its associated water of ~0.2 nm h⁻¹, which is a factor of 8 below the observed growth rate. On this morning, if growth was solely due to condensation of H₂SO₄ vapor, the ultrafine particle concentration would not have begun to increase until approximately 1045 MST.

Recall that later in the morning of September 21 the concentrations of 20-nm particles did not increase until ~1000 MST (Figure 4a). The number of ultrafine particles (~3 nm) had increased about 2.5 hours earlier at 0730 MST. For 3-nm particles to reach 20 nm in 2.5 hours requires an average growth

Table 1. Comparison of Estimated Observed Growth Rates of Ultrafine Particles and Calculated Growth Rates Based on Measured H₂SO₄ and H₂O Vapor Concentrations Assuming That Growth is by Condensation of Hydrated H₂SO₄ Vapor

Day of September 1993	Observed Growth, nm/h	Calculated Growth, nm/h	Ratio of Observed to Calculated Growth Rates
6	1	0.1	10
10	1.3	0.2	9
11	1.1	0.1	12
12	1.3	0.1	12
15	2	0.1	10
21	1.6	0.2	8
23	1.3	0.1	12
24	1.1	0.09	12
26	0.5	0.04	13

rate of $\sim 7 \text{ nm h}^{-1}$. During this time the average growth rate by (1), based on measured H_2SO_4 concentrations, was $\sim 0.6 \text{ nm h}^{-1}$; the observed growth rate was roughly 11 times higher.

For other days, observed growth rates, based on the ultrafine concentration delay following sunrise, are compared in Table 1 with values calculated from (1). Results are shown for all days for which we had both H_2SO_4 and ultrafine aerosol concentrations in the morning. Note that growth rates of sub-3-nm particles were consistently 8 to 13 times higher than growth by condensation of only hydrated H_2SO_4 vapor.

Growth rates inferred from the effects of cluster scavenging. Insights about particle growth rates can also be obtained by investigating the relationship between ultrafine particle concentrations and aerosol surface area. The probability that a freshly nucleated particle will grow to our minimum detectable size ($\sim 3 \text{ nm}$) decreases with increasing particle surface area concentration. This probability also decreases with decreasing particle growth rates: lower growth rates lead to longer growth times during which losses to preexisting particles can occur.

The time-dependent concentration, N , of a population of uniformly sized particles that is growing by gas-to-particle conversion and is being scavenged by preexisting particles can approximately be expressed as

$$\frac{dN}{dt} \approx -\frac{N\bar{c}}{4} \frac{A}{\gamma} \quad (3)$$

where \bar{c} is the mean thermal speed of the particles and A is the surface area concentration of the preexisting particles. As was discussed above, we assume $\delta=1.3$. From kinetic theory, the mean thermal speed for spherical particles of diameter D_p and density ρ is

$$\bar{c}(D_p) = \left(\frac{48kT}{\pi^2 \rho D_p^3} \right)^{1/2} \quad (4)$$

where k is Boltzmann's constant and T is absolute temperature. As was discussed above in (1), condensational growth rates are independent of size if evaporation is negligible relative to condensation. Assuming that growth rates, dD_p/dt are also independent of time, the time-dependent size is

$$D_p(t) = D_{p1} + \frac{dD_p}{dt} t \quad (5)$$

where D_{p1} is the size of the freshly nucleated particle. Substituting (4) and (5) in (3) and solving for $N(D_{p2}(t))$ leads to the following result for the probability, P , that a particle will grow from D_{p1} to D_{p2} before it is scavenged by the preexisting aerosol:

$$P = \frac{N(D_{p2})}{N(D_{p1})} = \exp \left\{ -\frac{2(A/\gamma)}{\pi dD_p/dt} \left(\frac{3kT}{\rho} \right)^{1/2} \left(\frac{1}{\sqrt{D_{p1}}} - \frac{1}{\sqrt{D_{p2}}} \right) \right\} \quad (6)$$

Freshly nucleated particles probably consist of a few molecules. We will assume that $D_{p1} \equiv 1 \text{ nm}$; our discussion is not particularly sensitive to the assumed value. Furthermore, we assume that $D_{p2} = 3 \text{ nm}$, our minimum detectable size. It follows that

$$P = \frac{N(D_{p2})}{N(D_{p1})} = \exp \left\{ -6.8 \times 10^{-2} \frac{A}{dD_p/dt} \right\} \quad (7)$$

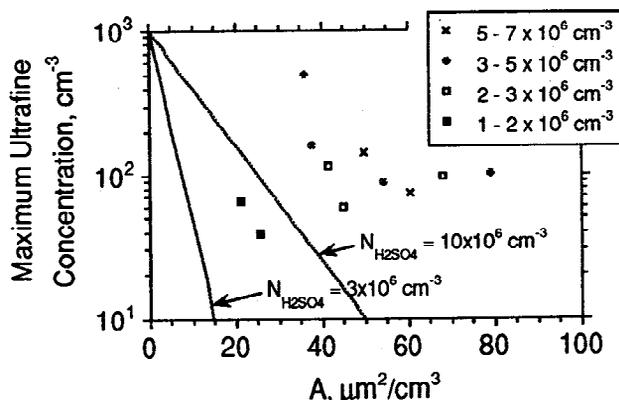


Figure 6. Maximum ultrafine particle concentration observed on individual days versus preexisting aerosol surface area concentrations on those days. The data are categorized by the H_2SO_4 concentrations that were measured about 1 hour prior to the peak ultrafine concentrations on the hypothesis that this was responsible for new particle production. The slopes of the solid lines (from (8)) show the expected sensitivity of ultrafine concentrations to aerosol surface area if growth rates are limited by H_2SO_4 condensation.

where A is in $\mu\text{m}^2 \text{ cm}^{-3}$, dD_p/dt is in nm h^{-1} , and a density of 1.4 g cm^{-3} was assumed. If growth is due solely to condensation of H_2SO_4 vapor, then from (1) and (7)

$$P = \frac{N(D_{p2})}{N(D_{p1})} = \exp \left\{ -9.2 \times 10^5 \frac{A}{N_{\text{H}_2\text{SO}_4}} \right\} \quad (8)$$

where $N_{\text{H}_2\text{SO}_4}$ is the concentration of gas phase H_2SO_4 in molecules cm^{-3} . An effective molecular weight of the condensing H_2SO_4 and its associated water, etc., of 200 was assumed.

Figure 6 shows the relationship between the peak ultrafine particle concentration measured on each day at Idaho Hill and the preexisting aerosol surface area concentration, A . Based on the hypothesis that particles are produced by a multicomponent nucleation process that involves H_2SO_4 , data are categorized by the peak H_2SO_4 concentration that was measured at or prior to (typically within 1 to 2 hours) the time that the peak in ultrafine concentrations was observed. We confine our attention to the peak daily ultrafine concentrations, since numerical calculations justify assuming steady state cluster size distributions that are dependent on the concentration of the nucleating vapor at this point [e.g., McMurry, 1983; Rao and McMurry, 1989]. Note that there is a general trend toward decreasing peak ultrafine concentrations with increasing aerosol surface areas and with decreasing H_2SO_4 concentrations, as expected.

Also shown in Figure 6 are two lines obtained from (8) assuming $N_{\text{H}_2\text{SO}_4} = 3 \times 10^6$ and $10 \times 10^6 \text{ cm}^{-3}$. Because we do not know how many particles are produced at a given H_2SO_4 concentration, for both curves, we arbitrarily set the number of particles formed when the aerosol surface area is zero to 10^3 cm^{-3} (i.e., $N(D_{p1})$ in (8) equals 10^3 cm^{-3}); our interest here is in comparing the slopes of these curves with trends in the data. Although there is too much scatter in the data to obtain accurate values for the log N versus A slopes, it appears that they are ~ 5 to 10 times smaller than predicted by (8). This suggests that growth rates are 5 to 10 times higher than can be explained by H_2SO_4 condensation. This is consistent with the results in Table 1 that were obtained independently, and further supports

our finding that a species in addition to H_2SO_4 is contributing to growth of freshly nucleated ultrafine particles. Our work [Marti *et al.*, 1996] showed no relationship between concentrations of ultrafine particles and of alpha or beta pinene (or estimates of their reaction products). This suggests that, at this site, terpenes played a minor role in new particle formation compared to sulfates. Terpenes, however, were found to be correlated with the aerosol surface area and volume concentrations. This may indicate that these species contributed to particle growth. If the high growth rates were from heterogeneous condensation of organics, a significant mass of the ultrafine particles would be organic.

Predicted H_2SO_4 Concentrations

If we assume that the only source of H_2SO_4 is the $\text{OH}\text{-SO}_2$ reaction, and that the primary removal mechanism is condensation on preexisting particles with an accommodation coefficient of 1.0, and that dry deposition is insignificant compared to these other rates, then the steady state H_2SO_4 concentration is

$$[\text{H}_2\text{SO}_4] = \frac{k[\text{OH}][\text{SO}_2]}{F} \quad (9)$$

where k is the rate constant for the $\text{SO}_2\text{-OH}$ reaction and $F[\text{H}_2\text{SO}_4]$ equals the rate of H_2SO_4 transport to preexisting particles. We take $k = 8.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [DeMore *et al.*, 1992; Gleason *et al.*, 1987; Wang *et al.*, 1988]. The loss factor, F , was obtained by integrating the transition regime expression of Fuchs and Sutugin [1970] across the measured aerosol size distribution. The steady state assumption and ignoring dry deposition are justified, since the characteristic time required to establish steady state between H_2SO_4 production and loss by particle scavenging is relatively short (10^2 to 10^3 s) and the characteristic time for dry deposition is roughly 10^4 s for a boundary layer thickness of 1 km and a typical dry deposition velocity of 3 cm s^{-1} [Schack *et al.*, 1985].

Sulfuric acid concentrations predicted with (9) are compared with measured values for July 24, 1992 (Mauna Loa), and September 21, 1993 (Idaho Hill), in Figure 7. These two days were selected because, unlike most days, the recorded SO_2 concentrations were sufficiently above the instrument's lower detection limit to provide confidence in the measured values. Median daytime H_2SO_4 production rates were 6×10^3 and $3 \times 10^4 \text{ cm}^3 \text{ s}^{-1}$ at Mauna Loa and Idaho Hill, respectively. Median fractional H_2SO_4 loss rates on these days were 5×10^{-4} and $6 \times 10^{-3} \text{ s}^{-1}$. Measured and calculated steady state concentrations are in very good agreement.

The loss factor, F , in (9) is an implicit function of the H_2SO_4 mass accommodation coefficient on aerosol particle surfaces. In our analysis we have assumed that the accommodation coefficient equals 1.0. Previous researchers have used values for mass accommodation coefficients ranging from about 0.3 to 0.04 [Hegg *et al.*, 1990; Raes and Van Dingenen, 1992; Raes, 1995]. These values would lead to increases in predicted steady-state H_2SO_4 concentrations by factors of ~ 3 to ~ 20 . We conclude that given the good agreement between measured and calculated values, the assumed value of 1.0 is in the right range.

In deriving equation (9) we also implicitly assumed that the equilibrium vapor pressure of H_2SO_4 above the aerosol particles is small relative to the measured H_2SO_4 concentrations. An estimate of the importance of evaporation can be obtained from the nighttime H_2SO_4 concentrations, which were in the range

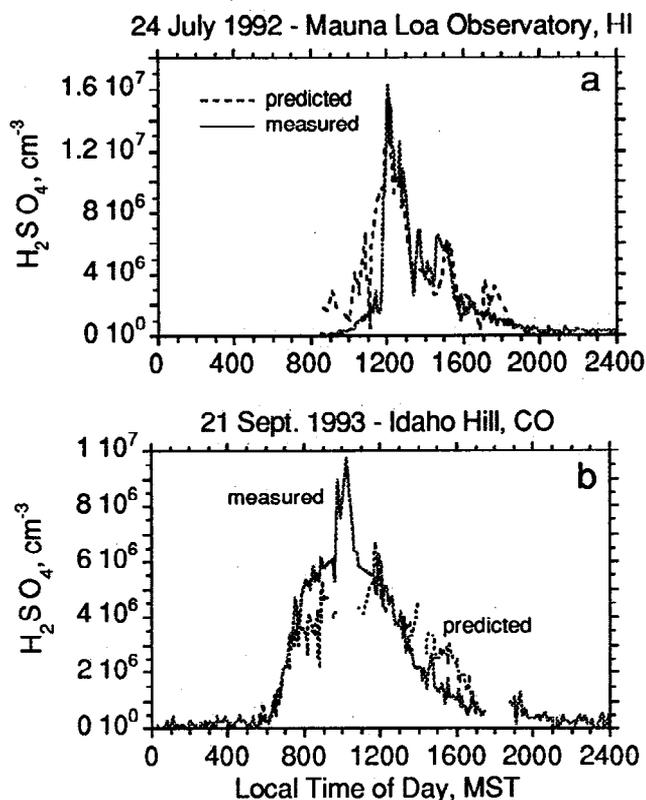


Figure 7. Comparison of the measured H_2SO_4 concentration and the predicted steady state concentration for July 24, 1992, at the Mauna Loa Observatory, Hawaii, and September 21, 1993, at Idaho Hill, Colorado. The predicted steady state H_2SO_4 concentration is determined from the balance between its production by the $\text{SO}_2\text{-OH}$ reaction and loss by aerosol particle scavenging.

$1 \times 10^5 \text{ cm}^{-3}$, or about 2% to 10% of daytime levels. Assuming that these concentrations are representative of daytime equilibrium concentrations, it follows that evaporation was a minor contributor to the observed daytime H_2SO_4 concentrations.

Conclusions

Measurements at a remote continental site indicate that elevated concentrations of ultrafine particles (nominally 3–4 nm diameter) resulted from recent new particle formation. The data point to H_2SO_4 as a precursor vapor of these newly formed particles.

The measured ultrafine particle concentration had a consistent diurnal pattern. There is evidence that this was due to the photochemical production of the precursor species (i.e., H_2SO_4 and possibly others) and the relatively short lifetime (less than ~ 1.5 hours) of the ultrafine particles. Although the H_2SO_4 concentration was observed to increase just after sunrise, elevated ultrafine particle concentrations were delayed by approximately 1 hour. Growth rates of ultrafine particles were estimated from this delay and found to be roughly 8 to 12 times higher than growth by condensation of hydrated H_2SO_4 vapor. By a completely different approach, ultrafine particle growth rates were estimated from the influence of cluster scavenging on ultrafine particle concentrations. With this method, we estimate that growth rates of ultrafine particles were roughly 5 to 10 times higher than growth by H_2SO_4 vapor.

New particle formation, indicated by high ultrafine concentrations, was common at Idaho Hill in downslope air and was observed during periods of low relative humidity (median relative humidity was 32%). Significant ultrafine concentrations were measured at H_2SO_4 relative acidities as low as 10^{-6} . These are water vapor and acidities for which classical H_2SO_4 - H_2O nucleation theory would predict practically no nucleation.

At both Mauna Loa and Idaho Hill, the two major factors influencing particle formation were found to be the H_2SO_4 and preexisting aerosol surface area concentration. Sulfuric acid appeared to be a primary precursor species of the ultrafine particles, and the highest ultrafine concentrations were recorded when the aerosol surface area was low (relative to typical surface area concentrations for that particular site). For a selected day at each site, the steady state H_2SO_4 concentration, calculated from the balance between H_2SO_4 photochemical production and H_2SO_4 scavenging by aerosol, agreed remarkably well with the measured values.

Compared to Mauna Loa, new particle formation was more vigorous at Idaho Hill, despite similar H_2SO_4 relative acidities at both locations and much lower relative humidities at Idaho Hill. We speculate that additional species, such as ammonia, may have also participated in new particle production and that higher levels of these species at the continental site enhance nucleation there. Participation of ammonia, however, is not expected to significantly enhance particle growth rates, although other species, such as organics, may. These species may not have been involved in new particle formation but could significantly enhance the growth rates of the newly formed particles and account for the high ultrafine particle growth rates observed at Idaho Hill.

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